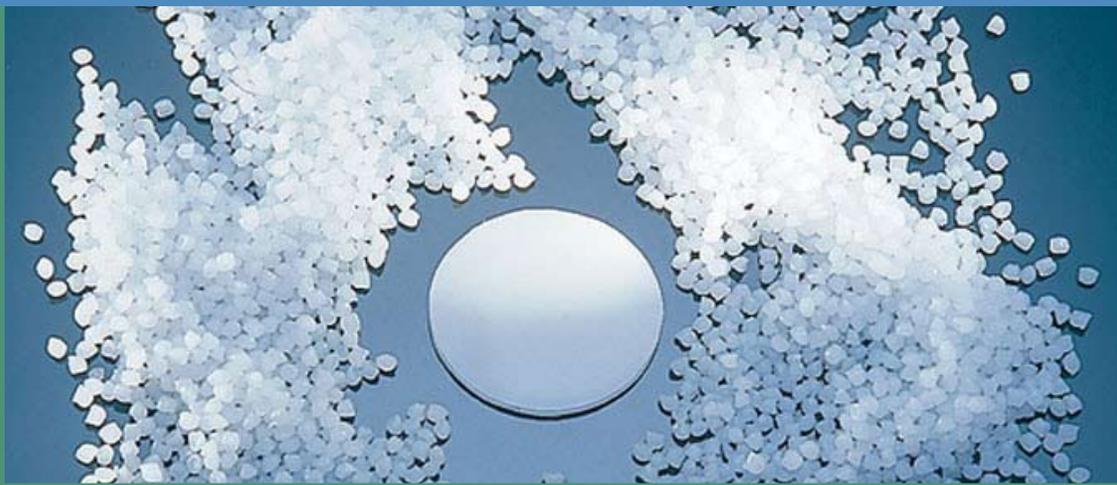


IR Spectroscopy of Polymers

N. A. Del Fanti

Translation and additional material by:
Kathryn Bradley, Dr. Michael Bradley, Federico Izzia,
and Dr. Jerry Workman



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Chapter 1 Introduction

Normal Mode Analysis

A molecule of “N” atoms has $3*N$ degrees of freedom, i.e. the possibility to make $3*N$ movements. Every atom can, in fact, move in the three directions of space (along the x axis, the y axis and the z axis). The infrared active movements are the **vibrations** that change the length and the angle of the bonds and the dipole. Therefore, of the $3*N$ total movements it is necessary to discount those movements that do not follow these conditions: the 3 translations of the molecule in the three directions of the space and the 3 spins of the molecule around the three Cartesian axes (i.e. 6 total movements). The vibrations of a **non-linear** molecule of N atoms will therefore number:

$$3*N-6$$

In the case of a **linear** molecule, the spin around its axis is not a movement, and it is therefore necessary to discount only the 3 translations and 2 spins (5 total). Thus the number of vibrations will be:

$$3*N-5$$

In the case of a hypothetical **linear polymer molecule of practically infinite length** for which the translation along the axis of the molecule is also not a practical movement, it is necessary to discount 2 translations and 2 spins (for a total of 4). Therefore the number of vibrations will be:

$$3*N-4$$

In a macromolecule where N has a value of millions, we would expect an exceptionally large number of vibrations. Fortunately, selection rules exist in which some **vibrations do not absorb a photon, and thus these vibrations do not result in an absorption band** (those in which there is not a variation of the dipole moment).

Moreover, simple operations of symmetry (spins with respect to a symmetrical axis or reflections with respect to a plane of symmetry) can transform one vibration into other. Since *a symmetry operation does not*

involve energy, these vibrations have the same energy and therefore the same frequency (*degenerate vibrations*). As a result of this symmetry, many of the $3 \cdot N - 4$ vibrations have the same frequency and a single band arises. Polymers, being formed from a monomeric unit that is repeated in space, are strongly affected by symmetry, and therefore many of the $3 \cdot N - 4$ vibrations will have the same frequency and will exhibit a single band. Therefore, the spectrum of a polymer fortunately will not consist of a million bands, but of a much more limited number.

In simpler terms, it can be said that *in a polymer, the number of bands will be determined by the formula $3 \cdot N - 4$, but N does not represent the number of atoms of the macromolecule, rather it is the number of atoms of the structural unit that is repeated.*

In amorphous polyethylene, the structural unit that repeats is a $-\text{CH}_2-$ group, and there will be $3 \cdot 3 - 4 = 5$ bands. But in the transplanar crystalline polyethylene (Figure 1-1),

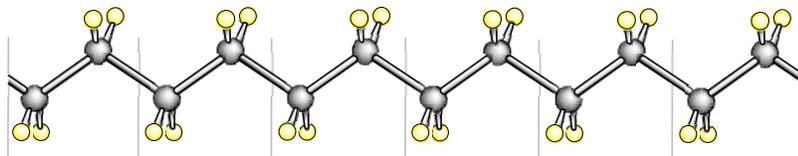
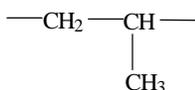


Figure 1-1.

the unit that is repeated in space is $-\text{[CH}_2\text{-CH}_2\text{]}-$, so there are $3 \cdot 6 - 4 = 14$ bands. In amorphous polypropylene, the unit that repeats is:



and so there are $3 \cdot 9 - 4 = 23$ bands. But in the structurally regular isotactic polypropylene, the macromolecule assumes a propeller shape (Figure 1-2),

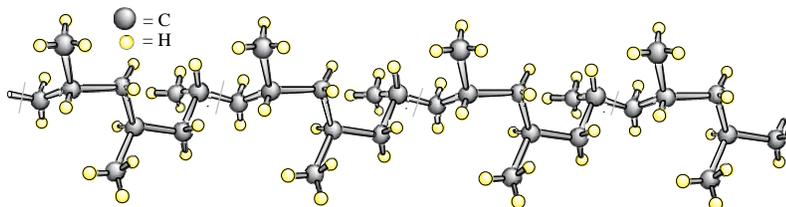
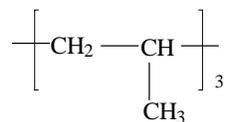


Figure 1-2.

and the structure that is repeated in space is:



and therefore $3 \times 28 - 4 = 77$ bands can appear.

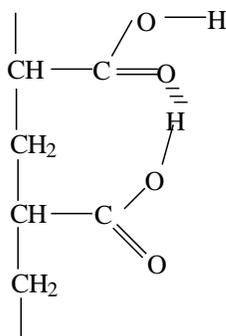
The infrared spectrum as presented thus far is diagnostic for molecular content. In the following chapters, distinctions will be seen to arise due to local order, crystallinity and other environmental influences. Later chapters will examine specific polymers and rubbers in detail, and will discuss sampling techniques, both classical and modern.

Chapter 2 Factors That Complicate the Infrared Spectrum of a Polymer

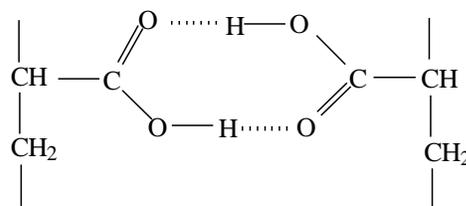
Hydrogen Bonding

The first factor that complicates the spectrum involves **intra- and intermolecular interactions**, where the macromolecule can interact with itself (intra-) or with a nearby macromolecule (inter-).

Besides the conformational interactions due to regularity and to crystallinity, which will be discussed later, the most common interaction that exhibits profound modifications to the spectra is the **hydrogen bond**. This bond generally establishes itself by a strong electrostatic tie between a mobile hydrogen (-O-H, -NH₂, -NH-) and an oxygen (-OH, C=O), and is therefore present in polymers that possess **alcohol** groups (i.e. polyvinyl alcohol), **carboxylic acid** groups (i.e. polyacrylic acid), **amide** groups (i.e. polyamides), **urethane** groups, etc.

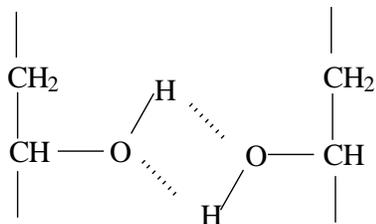


Intramolecular hydrogen bond

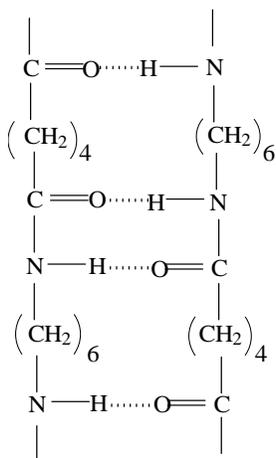


Intermolecular hydrogen bond

Polyacrylic acid



Polyvinyl alcohol



Nylon 6-6

In the last case, as an example, this leads to changes in the vibrations of the oxygen double bond.



Oxygen is attracted to the hydrogen, thereby lengthening the double bond, which as a consequence becomes weaker. This **decreases the frequency of absorption** (Figure 2-1) according to the relation:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{k \cdot \frac{m_1 + m_2}{m_1 m_2}}$$

where k is the force of the bond and m is the reduced mass.

There will be a wide variation in the distances between hydrogen bonding partners in a macromolecule, so there will be a range of weakening of the bond and therefore many possible shifts of the absorption. As a

consequence, the absorption band broadens considerably (Figure 2-1, Figure 2-2).

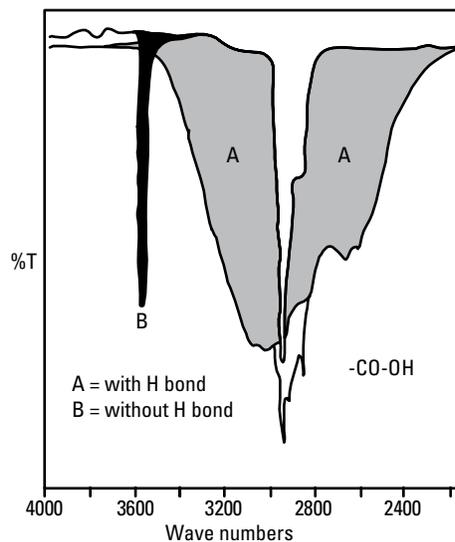


Figure 2-1. O-H Stretching

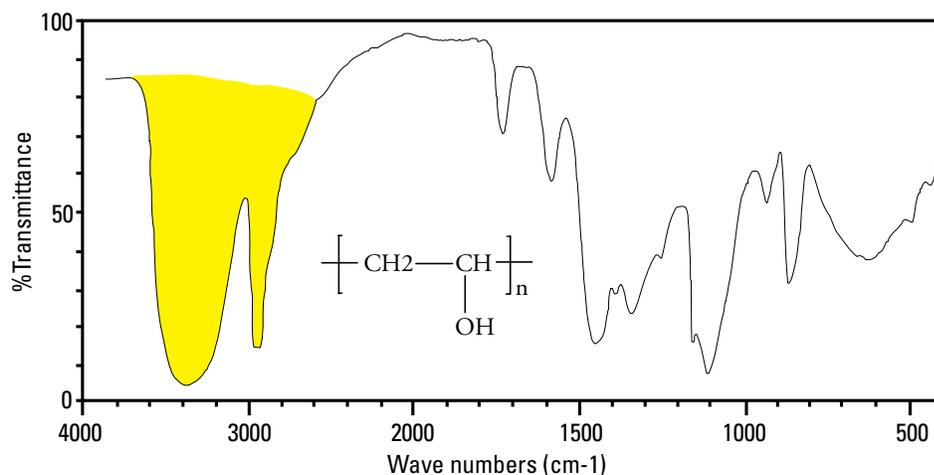


Figure 2-2. Polyvinyl Alcohol

The same things that are said for the stretching of the O-H are also true for the C=O and the N-H whose bands are as a result broadened, increased and lowered in frequency (Figure 2-3, Figure 2-4).

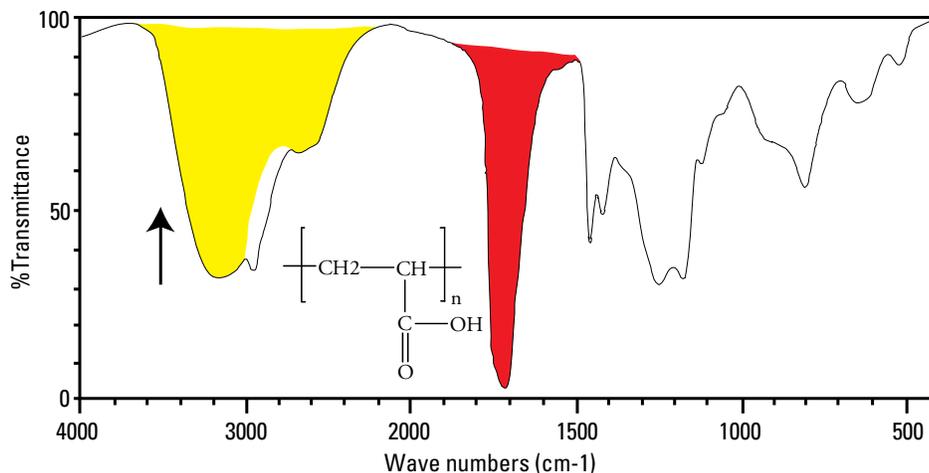


Figure 2-3. Polyacrylic Acid

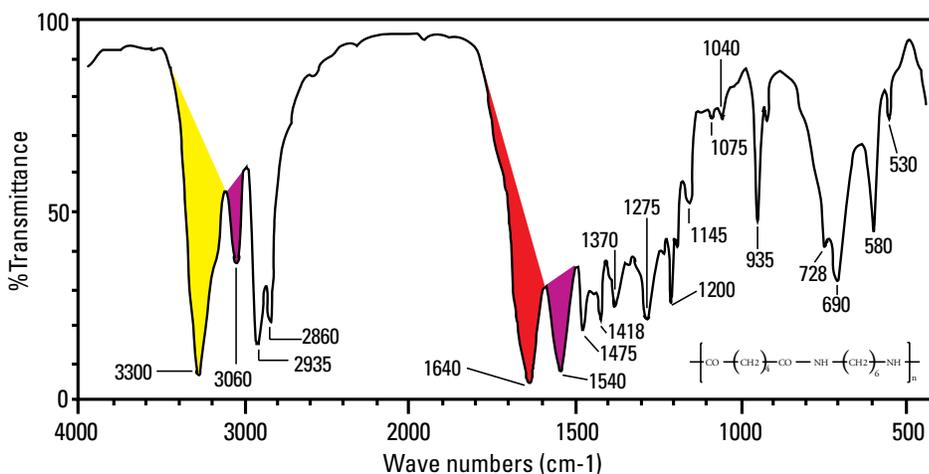
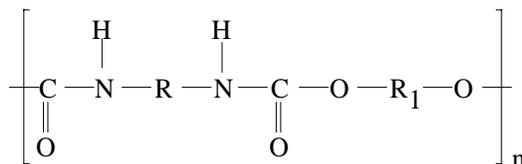


Figure 2-4. Nylon 6-6

A further complication is due to the fact that, besides the band broadening due to the hydrogen bonding, a band due to the functional groups not hydrogen bonded can also be present. As an example in polyurethanes (Figure 2-5),



the C=O results in bands both at 1735 cm⁻¹ (C=O not bonded) and at 1710 cm⁻¹ (C=O bonded).

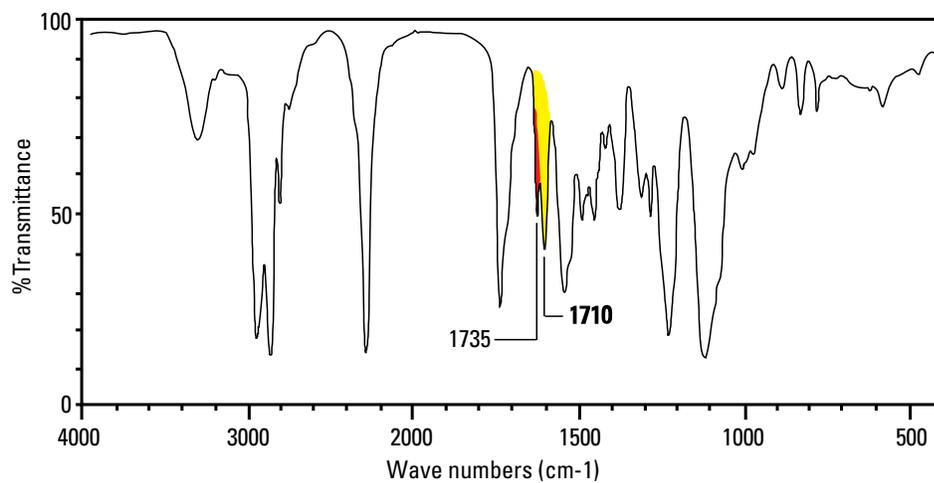


Figure 2-5.

Harmonics and Overtones

Another factor that complicates the infrared spectra, although in a lesser way, is the presence of **harmonic bands or overtones**.

The harmonics are due to the transition of the oscillator from the ground quantum state to the second or higher energy levels. These transitions occur at an energy *a little less than double* (first overtone) and *a little less than three times* (second overtone) the normal quantum transition, and thus **result in bands with wavenumbers a little less than double and a little less than triple the value of the fundamental band**.

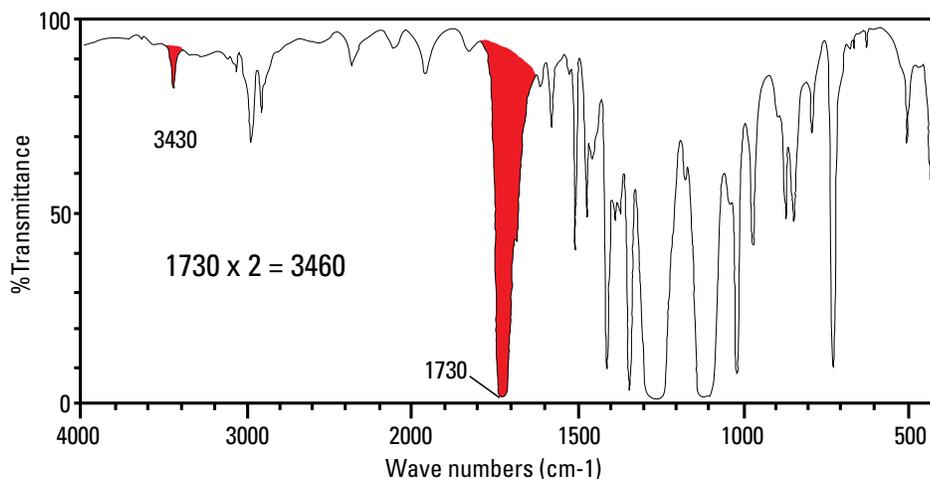


Figure 2-6. PET

The bands corresponding to overtones are of much lower intensity (and rarely appear), but they can cause errors in the analysis. For example the small band at about 3430 cm^{-1} that often appears in polyesters (Figure 2-6), could be interpreted as due to small amounts of OH groups or NH groups, and is instead the first harmonic of the band of C=O (1730 cm^{-1}). In fact, $1730 \times 2 = 3460$.

Another example is that of polyamides like nylon



in which, besides the band at about 3330 cm^{-1} due to stretching of the N-H of the secondary amide group, a smaller band at about 3050 cm^{-1} is observed that suggests the presence of smaller amounts of another group NH or NH_2 . In reality, it is the harmonic of the *amide II* band amide (about 1550 cm^{-1}). Thus, $1550 \times 2 = 3100$ (Figure 2-4).

Often harmonics are useful because they are much less intense than the main bands, which are often off scale.

The harmonic bands (about 2400 cm^{-1}) of the stretching (symm. and asymm.) of the CF_2 groups of polytetrafluoroethylene (Figure 2-7) are used instead of the main bands for measuring thickness in quantitative analyses (see the *Quantitative Analysis* section of this document). The same thing can be said of the harmonics of the stretching (symm. and asymm.) of CH_2 and CH_3 groups in the copolymer ethylene propylene.

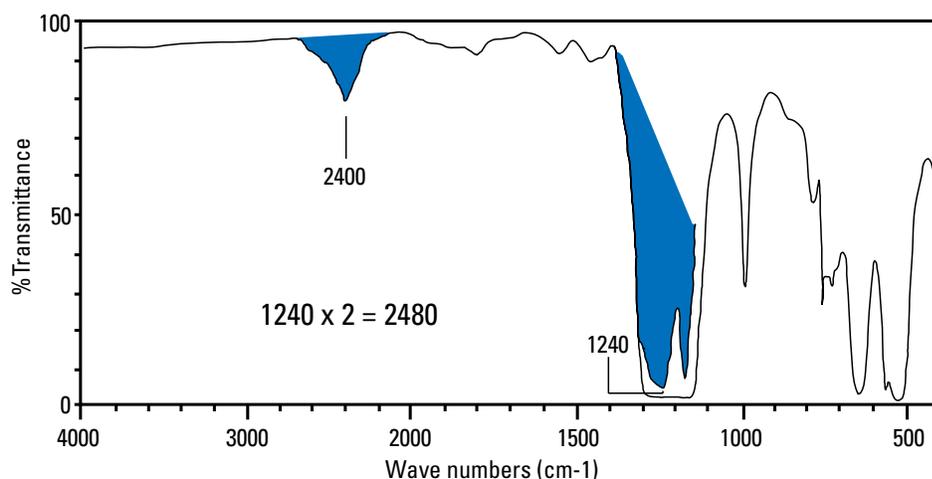


Figure 2-7. Perfluorate copolymer with a base of PTFE

The next few chapters now cover in detail how the infrared absorption bands of a polymer can be related to four key structural elements:

- Constitutional structure.
- Configurational structure.
- Conformational structure.
- Crystalline structure.

Chapter 3 Constitutional Structure

The constitution of a polymer is defined by the succession of atoms and the bonds in the macromolecule that define their position in space.

Consider the characteristics of the following constitution of the macromolecule:

- **Type of monomeric unit.** That is, the type of monomer that is repeated in the chain: ethylene, propylene, styrene, butadiene, etc.
- **Ramification and reticulation**
- **Amount and distribution of the monomeric units.** (When there are more than one: copolymers, terpolymers, etc.)
- **Type of ending groups**
- **Concatenation head-tail, head-head, tail-tail** (regioisomerism)
- **Modifications caused by environmental conditions** (molding, calendaring, etc), from aging or the action of atmospheric agents.

Part of the constitution can also be considered by:

- **The presence of various substances:** such as impurities (residual monomers, plasticizers, antioxidants, charges, colorants, etc.).

The bands due to the **constitution** therefore give us the chemical nature of the macromolecule. They are therefore analytically the more important bands.

This is for the molecule's own true chemical bonds, **not disassociated by melting or dissolution.**

Monomeric Units

A polymer is made from monomeric units that are repeated practically to infinity. Every type of monomeric unit will be characterized using characteristic bands that allow its identification. A monomeric unit is characterized from a head and a tail and can be represented as in Figure 3-1.



Figure 3-1. Monomer unit

Usually the monomeric units concatenate head to tail. A polymer constituted from a **single** monomeric unit that always repeats with concatenation **head-tail**, is called **constitutionally regular** (Figure 3-2).

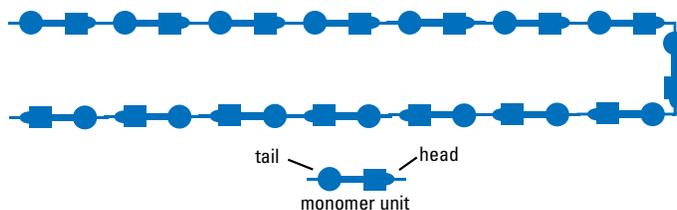


Figure 3-2. Constitutionally regular polymer

Ramification and Reticulation

At times the macromolecule loses its linearity and gives rise to lateral chains with a free ends (**ramification**) (Figure 3-3) or to lateral chains that join it to one or more other macromolecules (**reticulation**) (Figure 3-4).

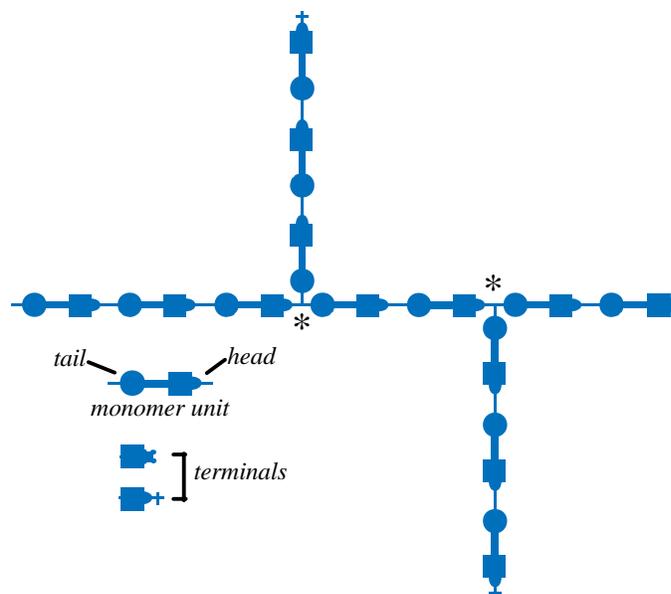


Figure 3-3. Ramified polymer

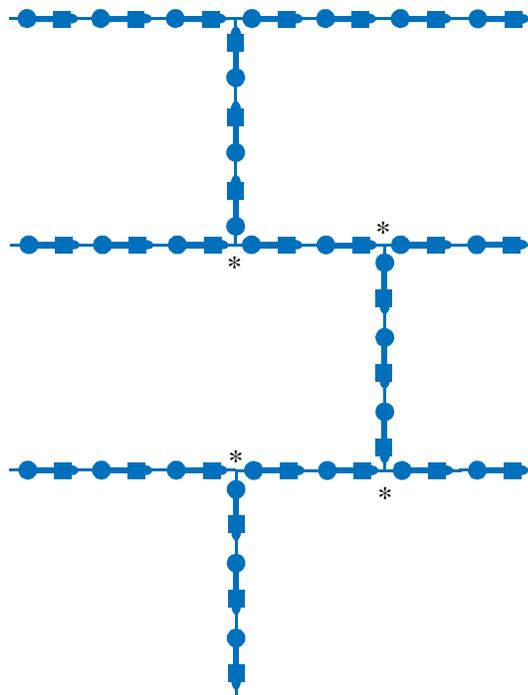
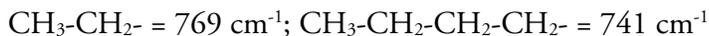


Figure 3-4. Reticulated polymer

The bands due to ramifications and reticulations are, in general, weak and are seen as single in particular cases.

As an example, in polyethylene the ramifications can be characterized from the presence of the $-\text{CH}_3$ group as evidenced by the weak band of $\delta_{\text{CH}_3}^s$ at about 1380 cm^{-1} .

Low density polyethylene (LDPE or HPPE) also contains ramifications constituted from ethyl and butyl groups individually, with, for the benefit of inventory, the weakest bands due to the various positions of σ_{CH_2} .



In order to see the ramification bands, it is necessary to operate with thick films, and frequently with a high number of spectral accumulations. It is also necessary to decide for sure if a polymer is not ramified in order to calculate the spectral difference and therefore to eliminate the background bands.

In the case of polyethylene, polymethylene can be used to obtain a reference for the polymerization of diazomethane (CH_2N_2).

To characterize reticulation with IR is possible, but much more difficult. It can only be seen in some cases with the support of other techniques (i.e. NMR) and with valid calibration sets.

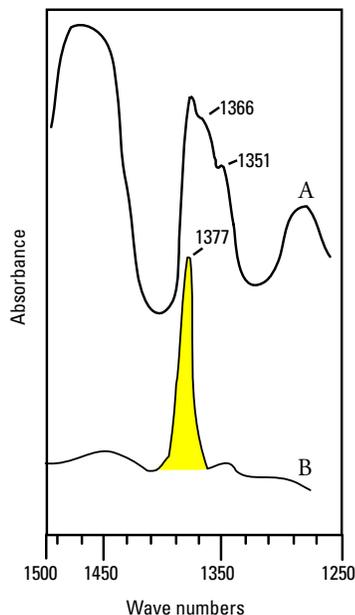


Figure 3-5. Determination of the methyl groups in polyethylene

Consider the spectrum of a film of polyethylene between 300 and 500 μ , as seen in Figure 3-5:

A = Spectrum of polyethylene

B = Spectrum with polymethylene removed.

The band at 1377 cm^{-1} is clear evidence of $\delta_{\text{CH}_3}^s$. These phenomena will also be discussed in the *Quantitative Analysis* section.

Distribution of the Monomeric Units

Random copolymer

The copolymer is a macromolecule in which two monomeric units are alternated in various ways. According to the distribution of these units, the copolymer can take several forms:

A random copolymer (Figure 3-6) is one in which the two monomeric units are distributed in a statistical way.

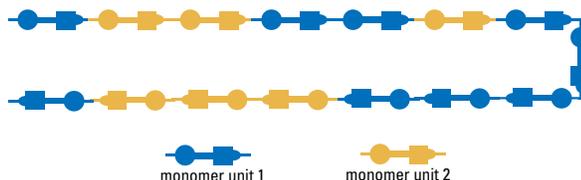


Figure 3-6. Random copolymer

The spectrum of this type of copolymer is, in general, *derived from the sum of the spectra of the two homopolymers*. For example, the spectrum of a random copolymer such as ethylene-propylene (Figure 3-9) is derived from the weighted sum of the spectra of the polyethylene (Figure 3-7) and of polypropylene (Figure 3-8). For this reason it is not possible to use mixtures of polypropylene and polyethylene as a sample for the quantitative determination of the relationship E/P in random copolymers.

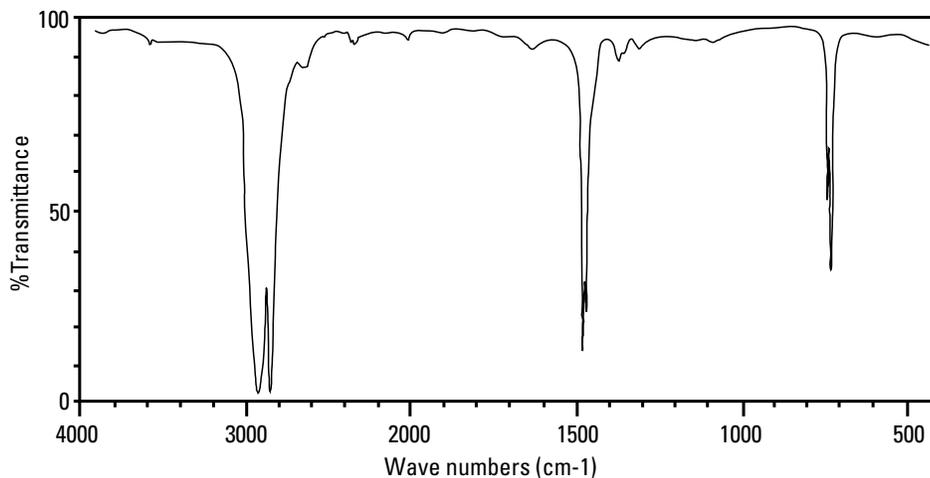


Figure 3-7. Polyethylene

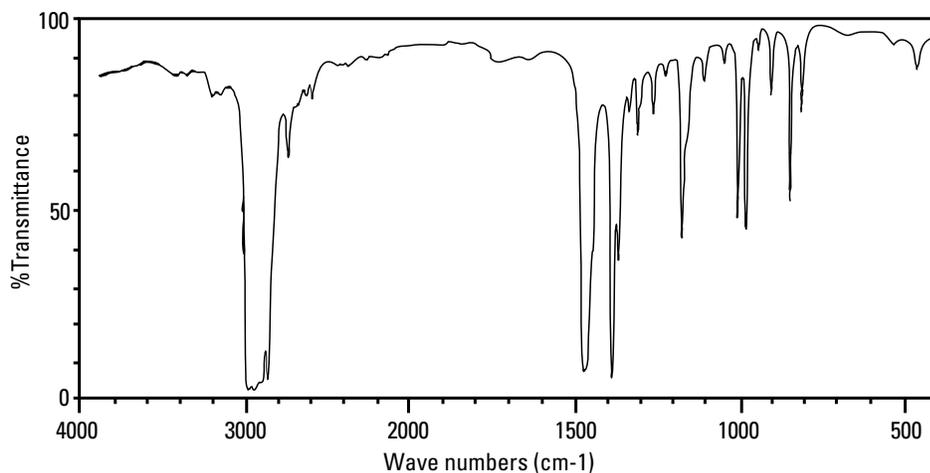


Figure 3-8. Polypropylene

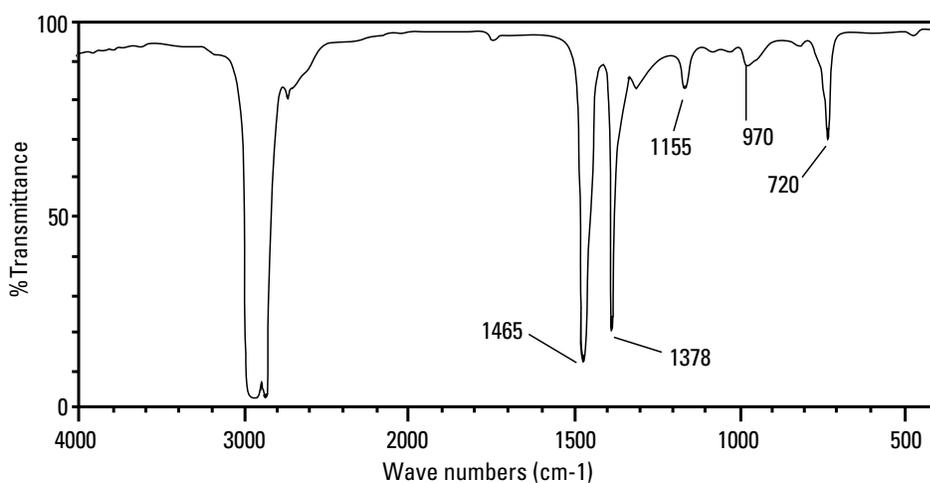


Figure 3-9. Ethylene propylene copolymer

In summary, the spectrum of a copolymer differs from that of the weighted sum of the homopolymers.

Block copolymer

A block copolymer is one in which the two unit monomers are distributed in rather long blocks (Figure 3-10)

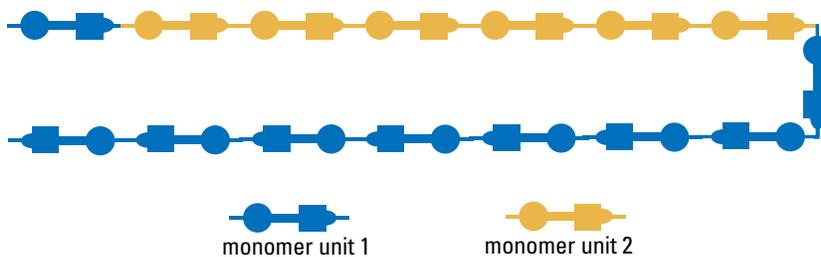


Figure 3-10. Block Copolymer

Grafted copolymer

A grafted copolymer consists of a second unit homopolymer that attaches at some points on the first macromolecule (Figure 3-11). The case of a block copolymer is that of a grafted copolymer.

The spectrum is practically identical to the weighted sum of the spectra of the two homopolymers. Also in this case, the use of the two homopolymers for the quantitative analysis of the monomeric relationship is not advised.

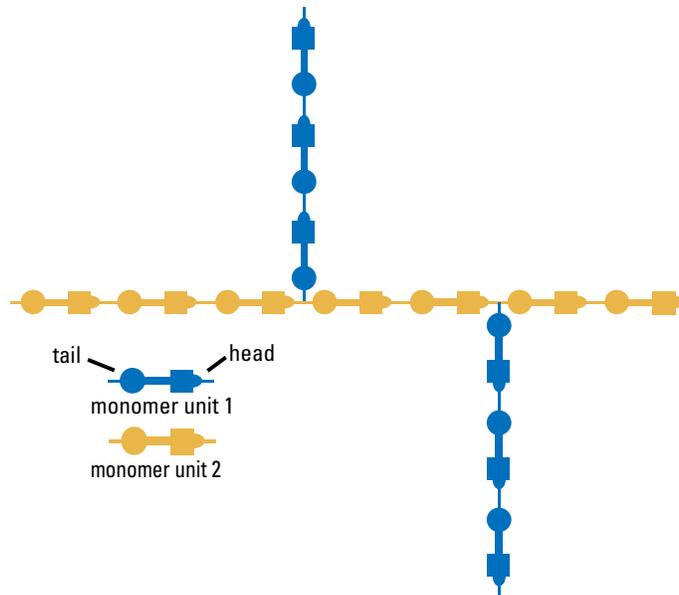
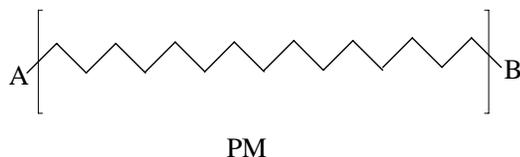


Figure 3-11. Grafted copolymer

Types of Terminal Groups

A macromolecule, having a very long length but not infinite length, will have on the extremities two groups that block the radical increase of the molecule and thus constitute the terminal groups. The identity of these groups is often predictable in how the polymerization was conducted (initiator, solvent, inhibitor, retardant, etc.). The percentage of their presence is a lot more important because it represents a way to determine the median molecular weight of the macromolecule.



Ideally, the concentration of A+B (in moles per 1000g) can be determined as follows.

In a polymer of molecular weight, PM, there are two end groups. The concentration of the terminal groups per 1000g of polymer will be given thus:

$$C_{A+B} = \frac{2}{PM} \cdot 1000 \text{ or } PM = \frac{2 \cdot 1000}{C_{A+B}}$$

From a known molar concentration of the terminal groups the molecular weight can be found. Infrared is one of the techniques commonly used for this type of determination. Since the PM is usually high and the bands of the terminal groups are extremely weak, it is necessary to run multiple scans and to collect a high number of accumulations, rather than to amplify the band. *It is useful to measure the polymer without the same type of terminal groups that are being analyzed in order to subtract the background.*

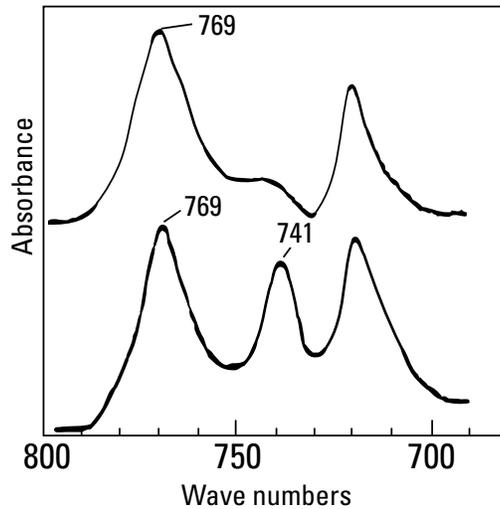


Figure 3-12.

The spectra of Figure 3-12 are those of two films of polyethylene of thickness 300μ from which the spectrum of **polymethylene** has been subtracted. In the known spectrum A the band at 769 cm^{-1} is attributable to a terminal ethyl group ($\text{CH}_3\text{-CH}_2\text{-}$). In spectrum B note the band of the terminal ethyl group, but also the terminal butyl group ($\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$) at 741 cm^{-1} .

The spectrum of Figure 3-13 is that of a film ($300\text{-}500\mu$) of a perfluorate copolymer with a base of PTFE. The PTFE base was subtracted out by an analogous copolymer with elementary fluorine to eliminate the non-fluorate terminal groups. In such a way it is possible to determine the percentage of the terminal group $\text{-CF}_2\text{-COOH}$.



Figure 3-13.

Modifications

The macromolecule can undergo modifications for various reasons.

- During manufacture (overheating and the eventual contact with air during shaping, machining, extrusion, etc.)
- During storage (action of atmospheric agents, action of oxone, etc.)
- During manipulation (the action of chemical agents, solvents, etc.)
- During sample preparation for infrared examination (too high of a temperature when shaping, oxidation during the shaping)

Those modifications due more to oxidation translate to the appearance of bands in the stretching zone of the hydroxyl and the carbonyl groups. The bands are often large and not resolved, and frequently a sole factor, like an *oxidation index* cannot be used to make the **relationship** between the **absorbance** and **that of one band of the polymer**.

To give an idea of the position of single absorptions, we recall the allocation of the absorption bands due to the oxidation of polyethylene.

$3555\text{ cm}^{-1} = \nu_{(\text{OH})}$ of $-\text{OOH}$; $3380\text{ cm}^{-1} = \nu_{(\text{OH})}$ of $-\text{OH}$

$1785\text{ cm}^{-1} = \nu_{(\text{C}=\text{O})}$ of $-\text{CO}-\text{OOH}$; $1763\text{ cm}^{-1} = \nu_{(\text{C}=\text{O})}$ of $-\text{CO}-\text{OOR}$

$1740\text{ cm}^{-1} = \nu_{(\text{C}=\text{O})}$ of $-\text{CO}-\text{OR}$; $1728\text{ cm}^{-1} = \nu_{(\text{C}=\text{O})}$ of $-\text{CHO}$

$1715\text{ cm}^{-1} = \nu_{(\text{C}=\text{O})}$ of $-\text{CO}-$; $1705\text{ cm}^{-1} = \nu_{(\text{C}=\text{O})}$ of $-\text{CO}-\text{OH}$

$1685\text{ cm}^{-1} = \nu_{(\text{C}=\text{O})}$ of $-\text{C}=\text{C}-\text{CO}-$

A polymer can also sustain breaks in the chain and therefore show increases, for example the terminal vinyl groups shown from ω_{H} of $-\text{CH}=\text{CH}_2$ at 908 cm^{-1} .

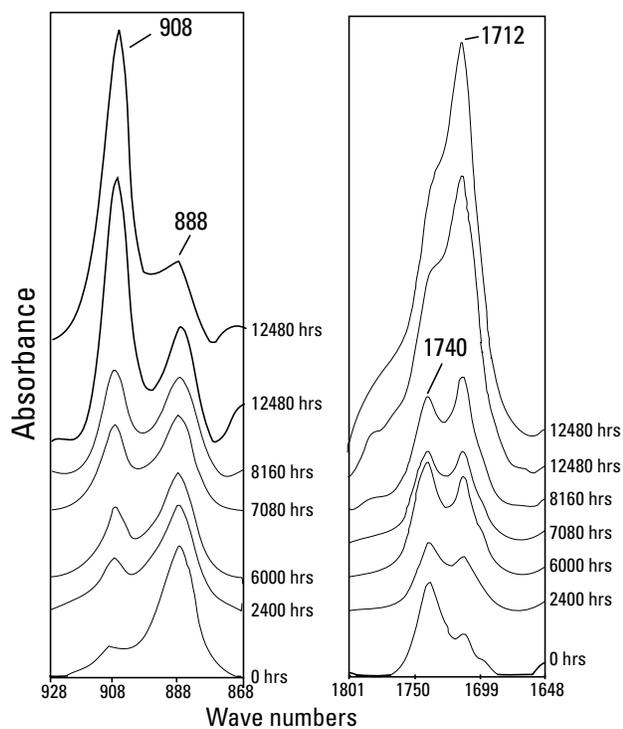


Figure 3-16.

In Figure 3-16 spectra of a film of polyethylene is shown after some hours of exposure to the sun (*Severini, Gallo, Ipsale, Del Fanti, Poly. Deg. and Stab.*, 17 (1987) 57-64). The increase in absorption due to vinyl (908 cm^{-1}) and ketone (1712 cm^{-1}) is clear. The bands at 888 cm^{-1} and 1740 cm^{-1} are respectively that of vinylidene and ester.

Presence of Various Substances

Infrared can also be used to identify residual materials in a polymer. These include (residual monomers, plasticizers, residual antioxidants, lubricants, surfactants, colorizers, fillers, etc.)

Once IR was the main technique used to determine **residual monomers**. Now residual monomers are determined nearly exclusively with chromatographic techniques. However, in some cases IR is still useful for this area. As an example, in the case of **nylon 6 (polycaprolactam)**, the residual monomer (caprolactam) can be easily determined with IR from the measure of the intensity of the bands at 868 cm^{-1} and 893 cm^{-1} .

Often the polymer contains introduced, known amounts of **additives** used to **improve the machinability**, to **increase the performance**, to **modify the properties**, etc. Sometimes these additives are present in small amounts, and their presence can be detected from the appearance of small bands in the hydroxyl or the NH area (as is the case of phenolic or aminic antioxidants or lubricants like amidic waxes) or in the CO area (phthalic ester plasticizers). But sometimes the absorptions are quite prevalent compared to the absorption of the real polymer.

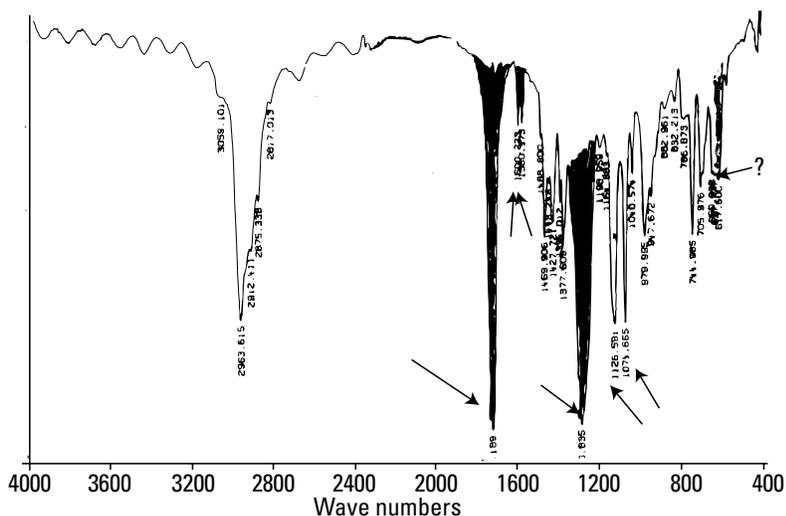


Figure 3-17.

In Figure 3-17, for example, the spectrum is shown of a commercial film of a polymer. The bands seem to indicate that the polyester is made up of phthalic acid. In truth, if we took the film, held in for some minutes in ethyl ether and then took a new spectrum after having dried it, the spectrum of Figure 3-18 is obtained. The bands of the phthalic ester, that seemed to indicate a polyester, are gone, and the obtained spectrum is that of classic PVC. In the previous spectrum, the PVC is hardly seen because of

the weak bands with questionable elements. Therefore, frequently in order to characterize the polymer, it is necessary to run simple extractions, thus providing more complete information, and making it possible to avoid making errors. Often the polymer contains pigments and inorganic additives. In this case, if it is possible, the polymer is extracted with an appropriate amount of solvent, and the spectrum of the polymer is run separately. If the polymer is insoluble, one resorts to the formation of ash, which will give a good idea of the types of additives employed. A more efficient method is to take the spectrum of the residual with thermogravimetric analysis in nitrogen.

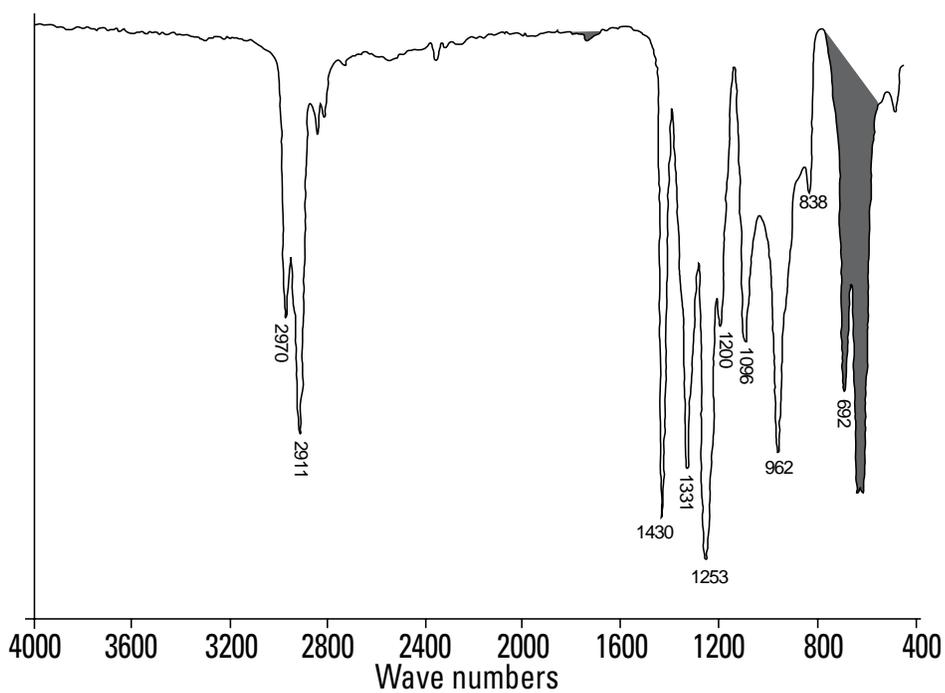


Figure 3-18.

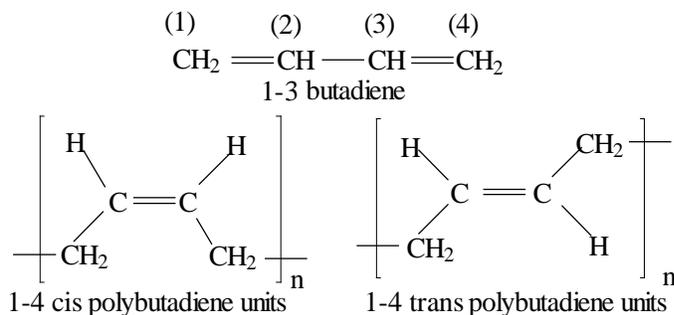
Chapter 4 Configurational Structure

This type of structure is related to the existence of cis- and trans- isomers with respect to a double bond (**geometric isomer**) or to the possibility of stereoisomers in monomeric units, which have an atom of asymmetric carbon (**optically active or optical isomer**). In this case, as in the constitutional structure, in order to change from one shape to the other, it is necessary to break a chemical bond, which means *the configurational bands do not change, or disappear, when the substance is melted or dissolved.*

Geometric Isomers

Identification when the monomeric unit contains a double bond.

As an example, butadiene can polymerize in position 1-4 giving origin to



That is, the two hydrogen atoms can be arranged on the same side of the double bond (cis) or apart from each other, on opposite sides of the bond (trans). These two types of double bonds can easily be distinguished from the strong bands due to the vibrations outside of the plane of the two hydrogens ($\omega_{\text{C-H}}$)

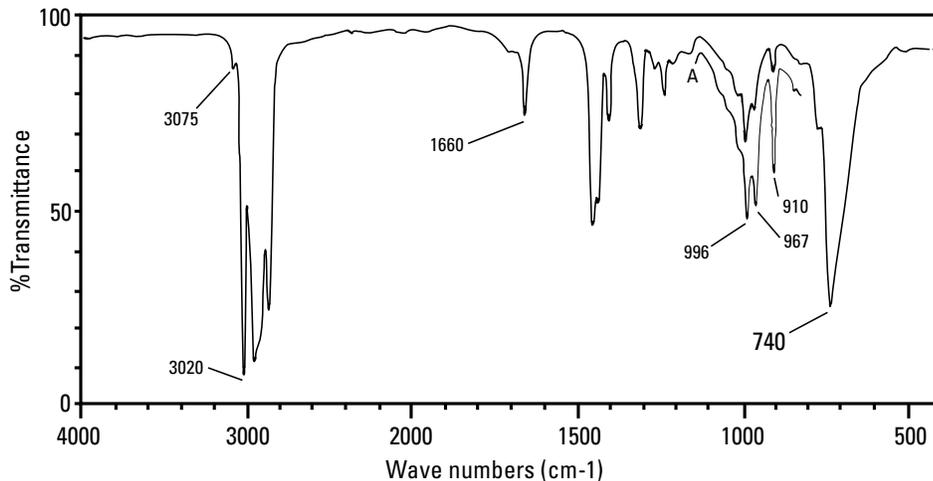


Figure 4-1. 1-4 cis Polybutadiene

1-4 cis $\rightarrow \omega_{CH} = 740 \text{ cm}^{-1}$

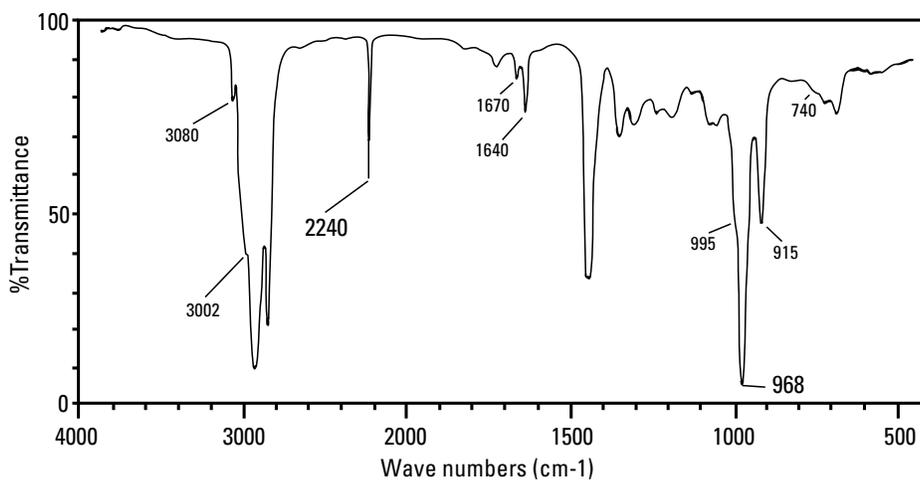
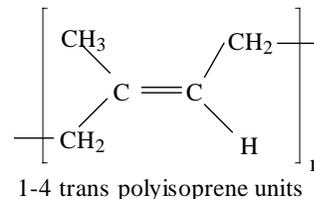
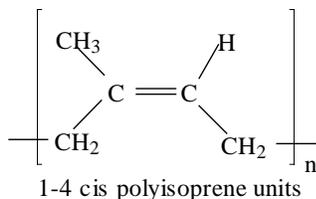
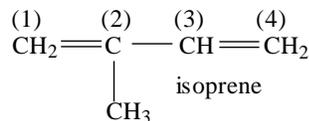


Figure 4-2. Nitrile rubber – (NBR) (low nitrile)

In Figure 4-2 the spectrum of nitrile rubber is shown in which butadiene units 1-4 (mostly of the trans type) are bonded to the acrylonitrile unit.

1-4 trans $\rightarrow \omega_{CH} = 968 \text{ cm}^{-1}$

Another example of cis-trans geometric isomers is isoprene, which can polymerize in position 1-4 giving



In this case we have:

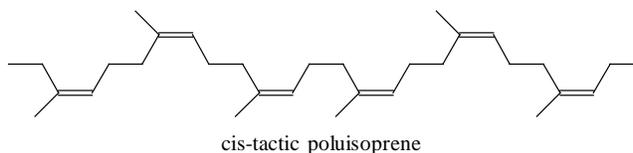
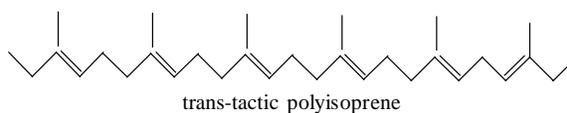
$$1-4 \text{ cis} \rightarrow \omega_{\text{CH}=\text{C}} = 833 \text{ cm}^{-1}$$

$$1-4 \text{ trans} \rightarrow \omega_{\text{CH}=\text{C}} = 843 \text{ cm}^{-1}$$

A polymer that is mostly 1-4 cis is present in nature as the latex of the *Hevea basiliensis* (natural rubber), while gutta-percha, present in nature as the latex of some Sapotaceae, has a mostly trans structure. More frequently, the cis and trans structures coexist in various proportions in the same macromolecule, and it is possible to determine their percentage constituency.

Stereoregular geometry

When the macromolecule contains **only** cis or trans units, it is said that it has **geometric stereoregularity**, and is called **cis-tactical** or **trans-tactical** respectively.



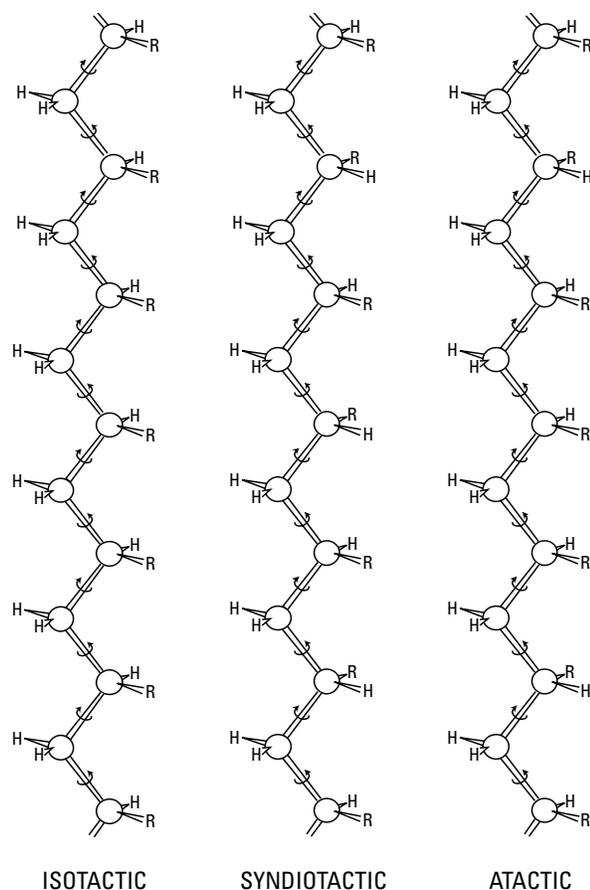


Figure 4-3.

What is more important to remember is that the tacticity, like pure geometric isomers (cis-trans), is due to proper chemical bonds. In order to change from one shape to another, it is necessary to *break bonds within the molecule*. Therefore an isotactic polymer always remains isotactic even if subjected to melting or dissolution in a solvent.

In geometric isomers (cis-trans), the two isomeric shapes are easily distinguished from each other. It is **not easy to distinguish the isotactic shape from that of the syndiotactic or atactic one**.

Consider the infrared spectrum of an isotactic polypylene sample manipulated by first hot pressing, then immediate cooling in liquid nitrogen.

The spectrum that is obtained is practically identical to that from atactic polypropylene. The *small* differences relate to the type of configuration (isotactic, syndiotactic, atactic) and *are difficult to see*.

In some cases, the spectrum appears to clearly show the differences between isotactic polypropylene and the syndiotactic and atactic versions. **However, the difference is not due to the various configurational structures, but due to the fact that the isotactic polymer stretches to assume a conformational structure different from that of the syndio and the atactic forms.**

Chapter 5 Conformational Structure

Until now we have represented polymers as straight and rigid chains. In reality, in the fused state, the macromolecules are movable and unexpected rotations around the C-C bond occur (Figure 5-1). This causes the molecule to get tangled in an unpredictable shapeless manner like a pile of spaghetti.

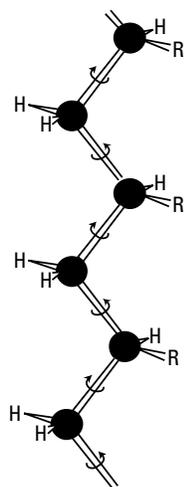


Figure 5-1.

The changes of the macromolecule brought about by free rotation around the simple C-C bonds leads to changes in the conformational structure.

Changes of conformational structure

Figure 5-2 is a schematic representation of the way three macromolecules can intertwine due to the random rotations around the C-C bonds.

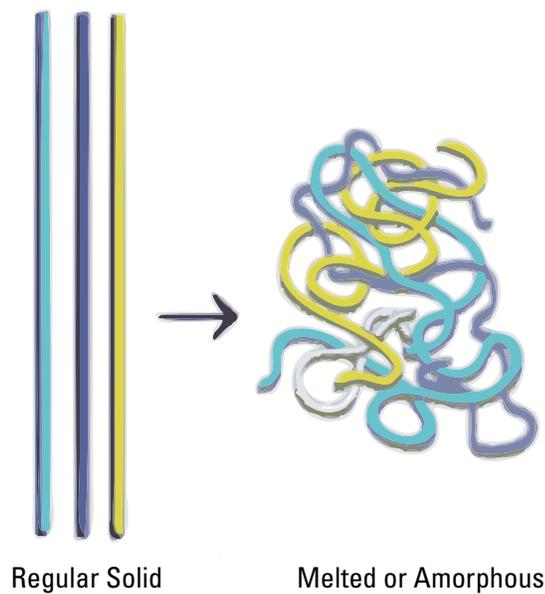


Figure 5-2.

Naturally, in spite of these changes, the macromolecules will maintain:

- their **constitutional structure**. Essentially, polypropylene will remain polypropylene, polybutadiene will remain polybutadiene, etc.
- their **configurational structure**. That is trans-polybutadiene will remain trans-polybutadiene and cis-polyisoprene will remain cis-polyisoprene. Also, isotactic polypropylene will remain isotactic, and atactic polypropylene will remain atactic.

Melting also does not change either the constitution or the configuration of the macromolecule. The constitutional and configurational spectral bands remain unchanged in the liquid state.

Isotactic and Atactic Polypropylene

Consider isotactic polypropylene. This polymer has **constitutional regularity** (*constructed only from monomeric units of propylene*) and **configurational regularity** (*constructed only of a single optical isomer*). If isotactic polypropylene is melted while maintaining constitutional regularity, the polymer will change due to free rotation around the C-C bonds to the amorphous shape outlined in Figure 5-2.

Suppose the melted polymer is now abruptly frozen in liquid nitrogen. This will freeze the polymer in the amorphous shape, and when it is returned to ambient temperature, the viscosity of the mass is such that the macromolecule maintains a shapeless and unpredictable conformational structure.

Consider the application of the same treatment to atactic polypropylene. This polymer has **constitutional regularity** (*constructed from only monomeric units of propylene*), but it **does not have configurational regularity** (*constructed from two optical isomer units that connect in a random pattern*). As before, the frozen polymer will be found in an amorphous tangled shape.

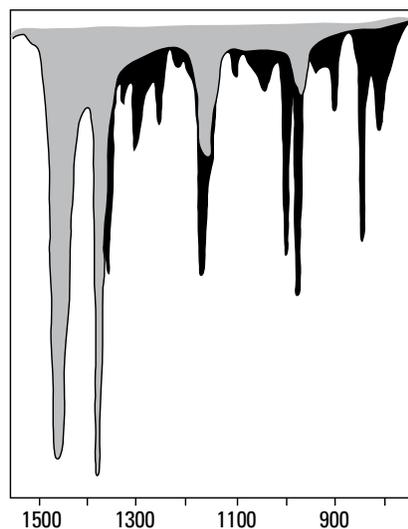


Figure 5-3.

The spectra of the two frozen films are practically identical and are shown in gray in Figure 5-3.

In fact, for the two polymers the constitutional structure is the same (polymers of propylene in which the propylene units are regularly concatenated head-tail). The absorptions will therefore be:

- those due to the CH₃ ($\nu_a=2955\text{ cm}^{-1}$, $\nu_s=2870\text{ cm}^{-1}$, $\delta_a=1450\text{ cm}^{-1}$, $\delta_s=1375\text{ cm}^{-1}$, $\nu_{C-C(CH_3)}=1150\text{ cm}^{-1}$)
- those due to CH₂, partially overlapped with the previous bands ($\nu_a=2920\text{ cm}^{-1}$, $\nu_s=2840\text{ cm}^{-1}$, $\delta_a=1435\text{ cm}^{-1}$, $\delta_s=1350\text{ cm}^{-1}$).

The bands are not significant enough for use in distinguishing the various types of configuration.

If instead, the two melted films are cooled *much more slowly*, the shapeless tangle of the macromolecules would still occur, but **according to the type of configuration, different behavior takes place.**

- **Atactic polypropylene.** A continuous free rotational movement around the simple C-C bond occurs with a consequent change of conformation. However, the macromolecule **does not find a preferred conformation**, and when cooled the viscosity increases, and a **disorganized random conformation** will be found in it.
- **Isotactic polypropylene.** Again in this case, a continuous free rotational movement around the simple C-C bond occurs with a consequent change of conformation. **The macromolecules then individually assume a conformation of minimal energy, also individually preferred**, and in this conformation the consequent increase in viscosity due to cooling is blocked. The conformation is a **regular helical structure** in which the repeating unit consists of 3 monomeric units (three monomeric units are necessary in order to repeat an identical spatial structure).

Therefore at the end of the treatment, the macromolecule assumes an **ordinary conformation**. Thus the macromolecules will give rise to **rigid spirals** dispersed in an unpredictable manner in space, as shown very schematically in Figure 5-4.

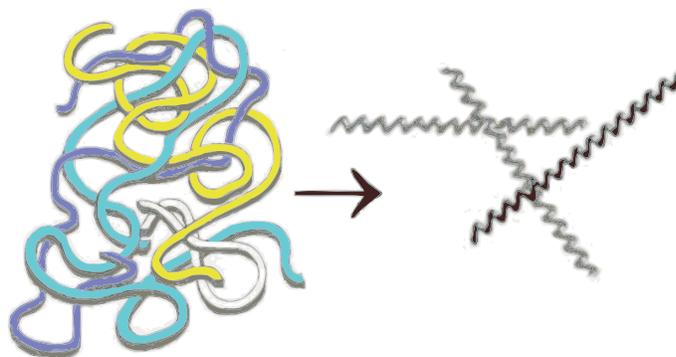


Figure 5-4.

The isotactic polypropylene spiral is represented in Figure 5-5.

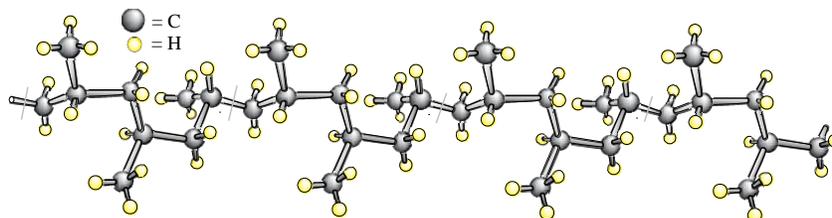


Figure 5-5.

If in this case, the methyl groups are taken as an example, these groups will not orient in a random way, like the melted *tangled shape*, but will be found in very predictable positions in space. A methyl is always seen in the same position as other methyls. Thus there are conditions for *vibrational interactions*. This means that the methyl groups will not vibrate independently one from each other, as in the melted case, but will have vibrations as a whole. For example, given $\delta_{\text{CH}_3}^s$, it will expand and contract all in phase (i.e. it will expand all at the same time and contract all at the same time). Or given $\delta_{\text{CH}_3}^a$, it will exhibit alternative phase (i.e. one expands while the next contracts). All of these concerted vibrations correspond to one absorption band.

The same thing can happen for many other CH_3 vibrations, between those of CH_2 , etc. *There will therefore be more bands than with the melted polymer.*

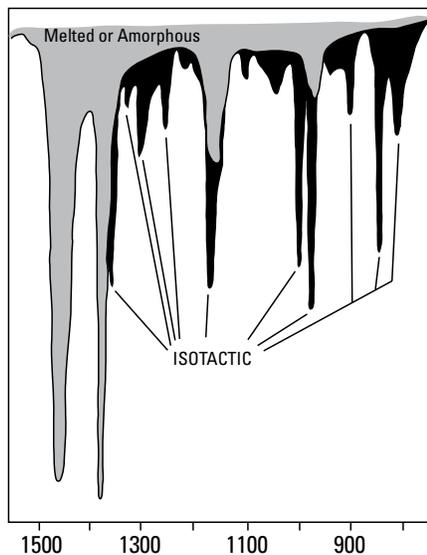


Figure 5-6.

The bands that then result are those shown in black in Figure 5-6, and are less intense than that of the melted state (the spectrum in gray.)

These new bands (1357, 1166, 998, 997, 841, 809 cm^{-1}) are bands of **conformational regularity**. They are generally *sharp bands*, and they have *the characteristic of disappearing due to melting and dissolution* in a solvent.

In fact, melting or dissolution destroys the conformational regularity (the macromolecule returns to a tangled up shape), and therefore there is no longer a presupposition for their existence. Often these bands are called *crystallinity bands*, even though the term is improper. In fact crystallinity demands regularity in the three dimensions of space, while in this case regularity is only along the axis of the chain. However, as will be shown, conformational regularity is often only a preceding step to crystallization.

To have conformational regularity, the macromolecule must have constitutional regularity and configurational regularity.

Polypropylene, to assume conformational regularity, will not be able to have many *defects of regular isomers*, for example, (i.e. it must have practically all head-tail concatenations), **otherwise it is not constitutionally regulated.**

Moreover, the optical configurations that follow will have to all be equal (isotactic), or to alternate regularly (syndiotactic), **otherwise they are not configurationally regulated.**

Polyisoprene, to assume a conformational regularity, must have configurational regularity. That is, it will have to be *transtactic* (gutta-percha) or *cistactic* (natural rubber). Natural rubber, in fact, can assume under tension a regular conformational structure, thus translating to the appearance of *crystallinity* bands.

Polyamides

The *bands of conformational regularity* are very useful in order to characterize the nature of the spectrum of a polymer. Besides the case of isotactic polypropylene we can cite the case of **polyamides** (nylon types).

Polyamides 6, 6-6, 11, 12, etc., have a very similar constitutional structure. In the melted or amorphous state it would be difficult to distinguish one spectrum from the other. The spectra for all is that of a secondary amide

___ $\nu_{\text{N-H}}$ = circa 3300 cm^{-1} *, Intense and sharp

___ $2\nu_{\text{C-N}}$ = $3080\text{-}3050 \text{ cm}^{-1}$, Weak and sharp

___ $\nu_{\text{C=O}}$ = $1640\text{-}1635 \text{ cm}^{-1}$, Intense and sharp

___ $\delta_{\text{N-H}}$ = $1560\text{-}1540 \text{ cm}^{-1}$, Intense and sharp

The spectra also presents a series of bands between 1400 cm^{-1} and 1040 cm^{-1} due to *conformational regularity or crystallinity*, such that Figure 5-7 can serve to distinguish one polyamide from the other .

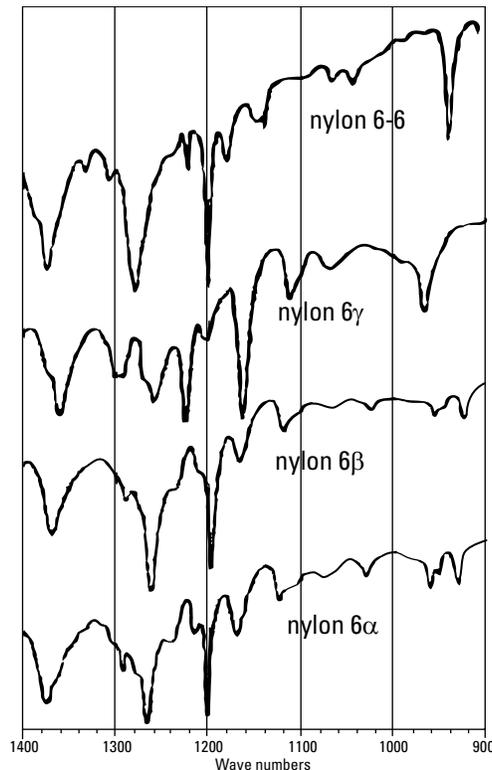


Figure 5-7.

Random Copolymer

And what of the copolymer as it behaves with regards to the bands of conformational regularity?

The most common random copolymer (Figure 5-8) has an **irregular distribution of the two monomeric units**, i.e. they do **not have constitutional regularity**, and thus they cannot have conformational regularity.

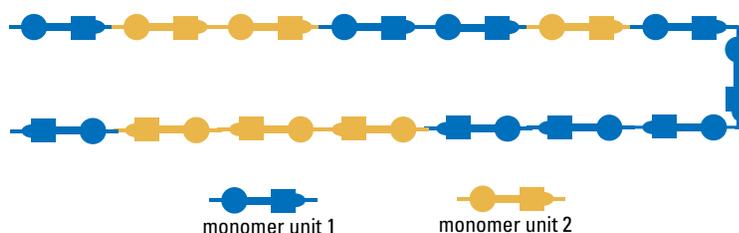


Figure 5-8. Random copolymer

Thus copolymers are always **amorphous**, and their molecules always have the tangled conformation of a melted polymer (Figure 5-9).

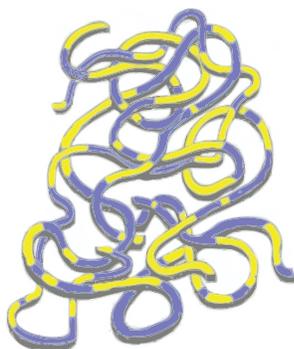


Figure 5-9.

Therefore random copolymers have spectra clearly different from that of two homopolymers.

In fact, besides having constitutional **bands associated with bonds between the two units** (bands that are not always identifiable) (Figure 5-10), they **lack all the conformational bands and crystallinity** of the two homopolymers.

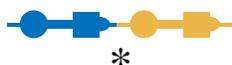


Figure 5-10.

The spectra of Figure 5-11 are those of polyethylene, polypropylene and ethylene-propylene rubber. In the latter, **the bands lack**, in fact, **all conformational regularity and crystallinity** present in the spectra of the single homopolymer.

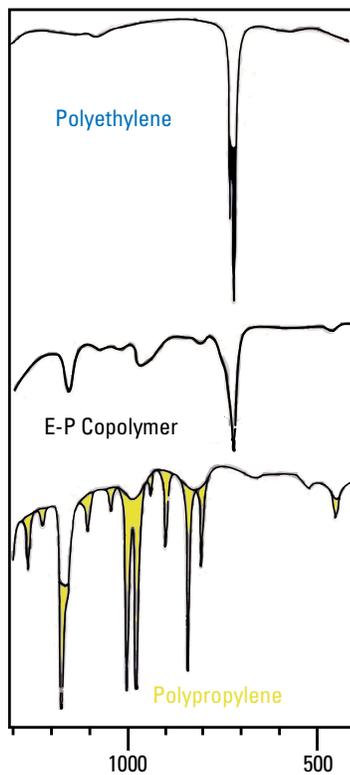


Figure 5-11.

Block Copolymer

In this instance (Figure 5-12) the length of the two unit sequences can be sufficient to insure that the blocks of two monomeric units assume an ordinary conformational structure, in which the macromolecule presents **rigid features with long ordered sequences** (Figure 5-13).

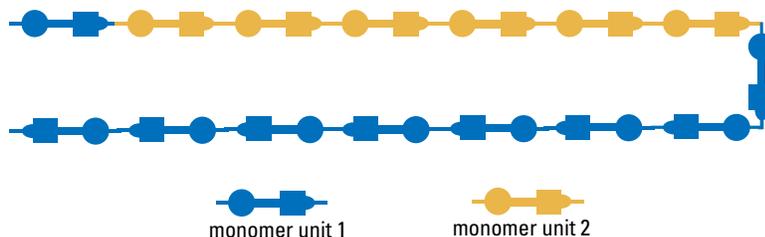


Figure 5-12. Block copolymer

Features such as short sequences distributed in a random manner are also present, so that it has an amorphous structure instead (not ordered).

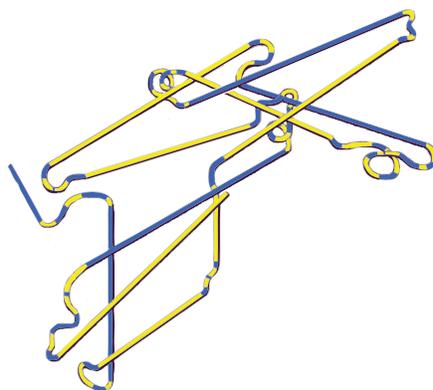


Figure 5-13.

In Fig. Figure 5-14, the spectra are presented of

- Polystyrene
- Polymethylmethacrylate
- Block copolymer Styrene MMA
- Random copolymer Styrene MMA

It is clearly shown that the spectrum of the block copolymer is practically equal to the sum of the spectra of the two homopolymers. The spectrum of the random copolymer is instead clearly different.

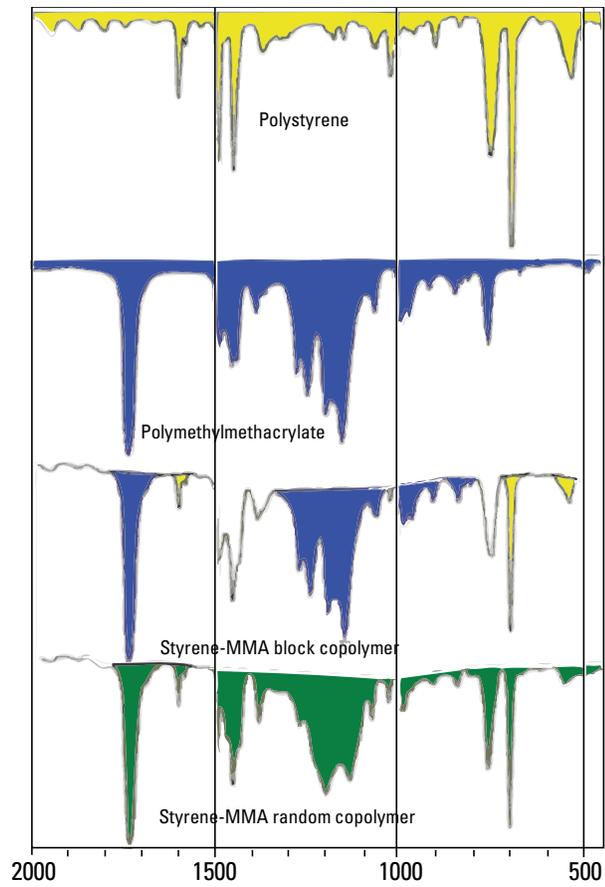


Figure 5-14.

Alternated Copolymer

There are many particular copolymers in which the two monomeric units regularly alternate.

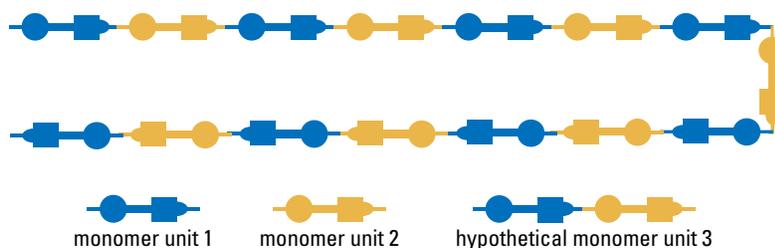
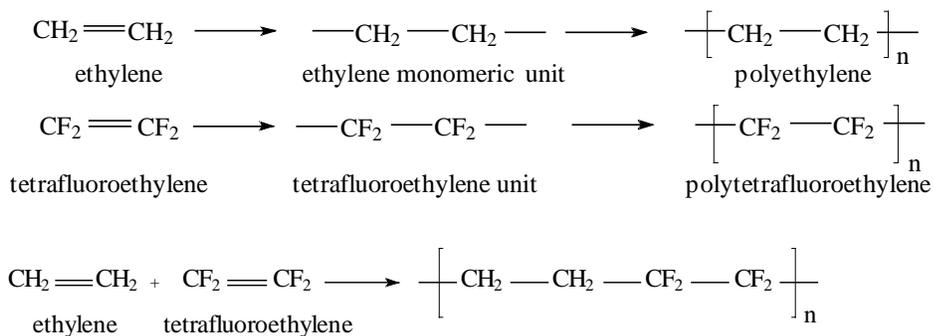


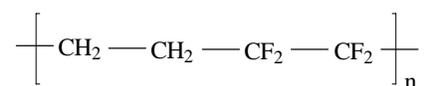
Figure 5-15. Alternated copolymer. A polymer of hypothetical monomeric unit 3 can be considered constitutionally regular.

In this case the spectrum is *quite different* from that of the two homopolymers. In fact the alternated copolymer is only called a copolymer because it is obtained by copolymerization of two monomers, but in fact it is a regular homopolymer of hypothetically 3 monomeric units (Figure 5-16, Figure 5-17, Figure 5-18).

As an example the alternated copolymer ethylene tetrafluoroethylene



is in fact a regular polymer of the monomeric unit



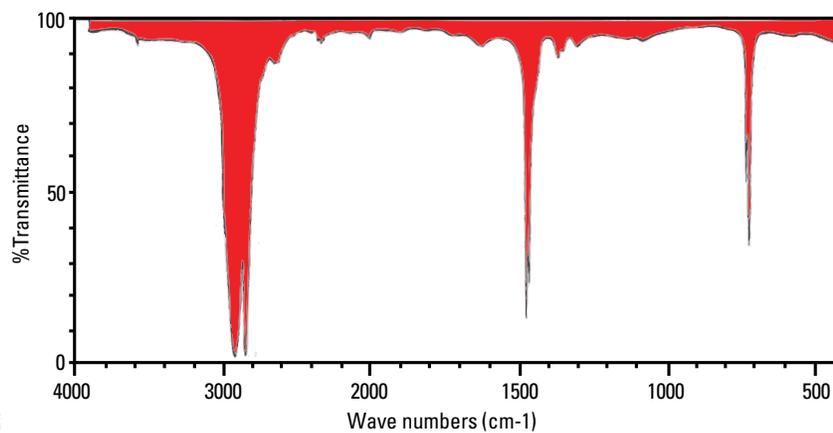


Figure 5-16. Polyethylene

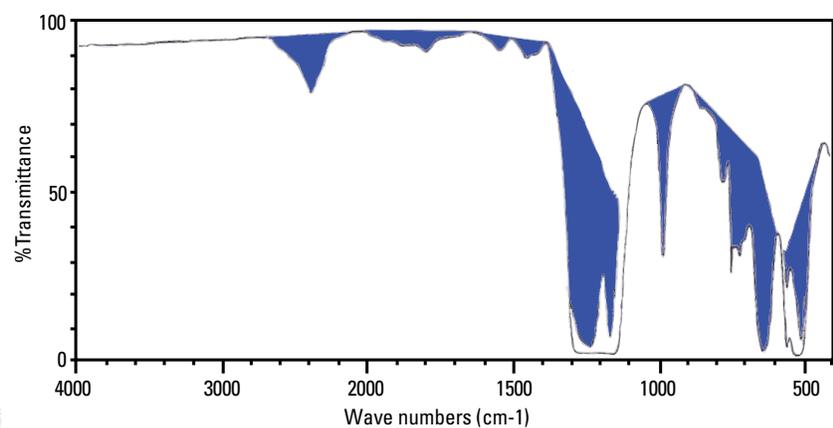


Figure 5-17. Polytetrafluoroethylene

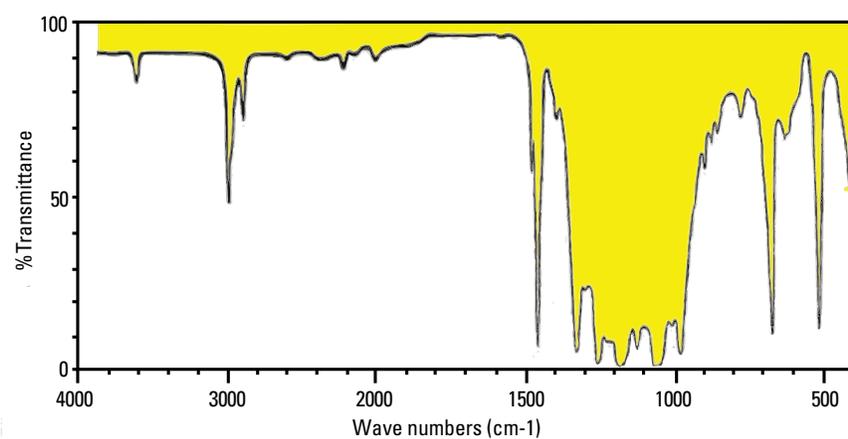


Figure 5-18. Ethylene – tetrafluoroethylene alternated copolymer

Chapter 6 Crystallinity

A **constitutionally regular** polymer (and therefore one also having constitutional regularity and configurational regularity) can achieve still greater regularity:

It can crystallize.

When we have a constitutionally regular (or nearly completely regular) polymer, the macromolecule presents rigid features in which the atomic groups assume spacial regularity (helical or planar zig-zag conformation).

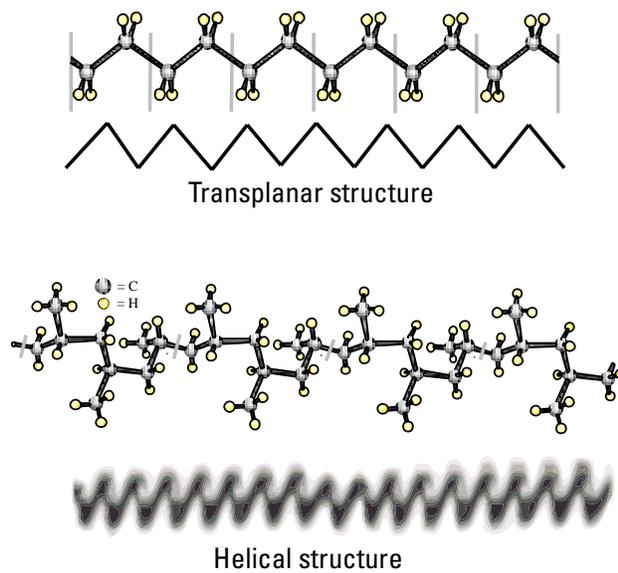


Figure 6-1.

For graphical simplicity we will represent the rigid structure of conformational regular macromolecules (planar zig-zag, helical) like a **rigid rod** and the non-regular structure (amorphous) like cord more or less tangled in a ball.



Figure 6-2.

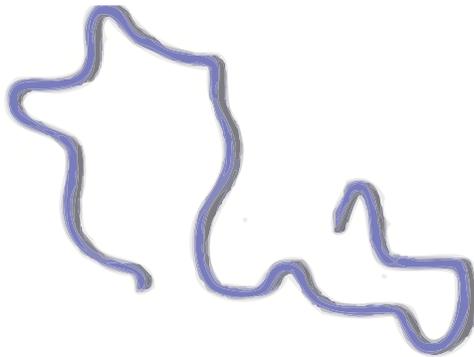


Figure 6-3.

A polymer with a conformational amorphous structure will therefore have the aspect of Figure 6-4, while one nearly completely regular will have the aspect of Figure 6-5.

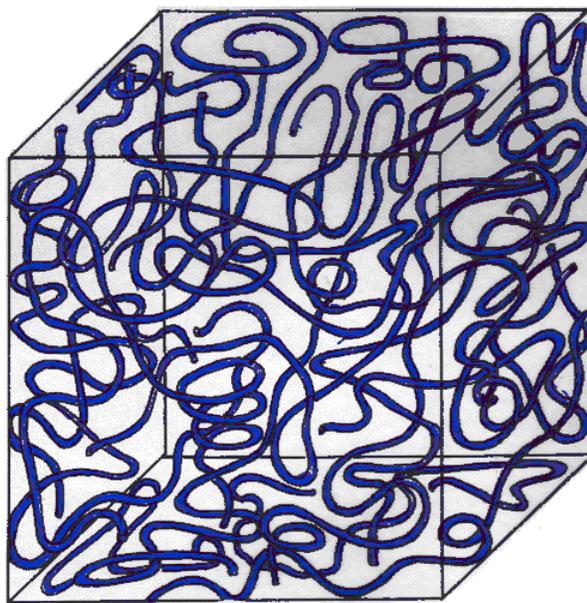


Figure 6-4. Amorphous polymer

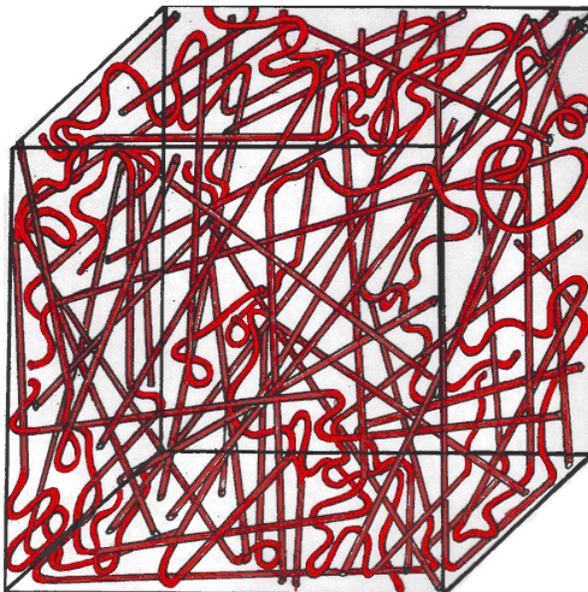


Figure 6-5. Ordinary conformational polymer with a little amorphous presence.

The polymer with **ordinary conformation** (Figure 6-5) will have **rigid chains ordered in a regular structure** (helical or planar). The regular features are singularly arranged irregularly in the three directions of space. The unordered polymer (Figure 6-4) will instead be a shapeless, amorphous tangle.

Often (spontaneously or from particular heat treatments) the chains with ordinary conformation stretch to join one to the others giving rise to a true and proper **crystalline lattice**.

These crystalline forms are thereby dispersed in a more or less disorganized manner in space (Figure 6-6).

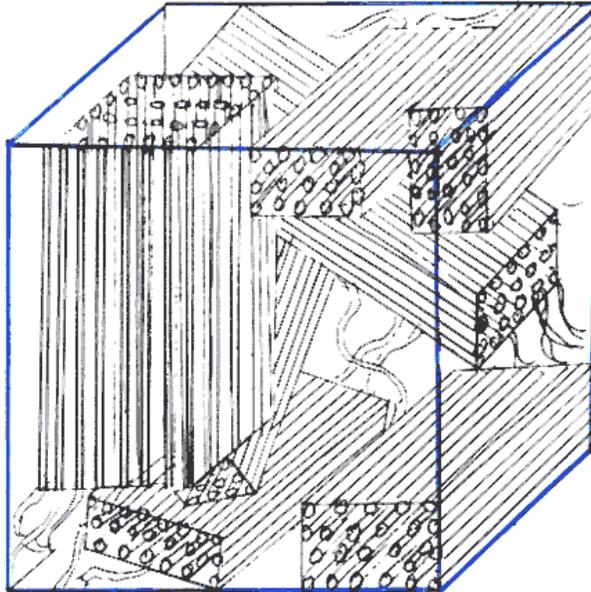


Figure 6-6. Crystalline polymer

Now the polymer is not only in ordered conformation, but it is **truly crystalline**.

What changes in an IR spectrum when the polymer crystallizes?

The chains with ordered conformation are at this moment arranged in a regular lattice, in which the chains, which before had vibrated independently from each other, can now have concerted movements (**inter-molecular vibrational interactions**). This is analogous to the determination of bands of conformational regularity, only in this case the result is an extension of the intra-molecular interaction.

A classic example of crystallinity is that of the rocking of the CH₂ of paraffin ($\rho_{\text{CH}_2} = 720\text{-}725 \text{ cm}^{-1}$) (Figure 6-7).

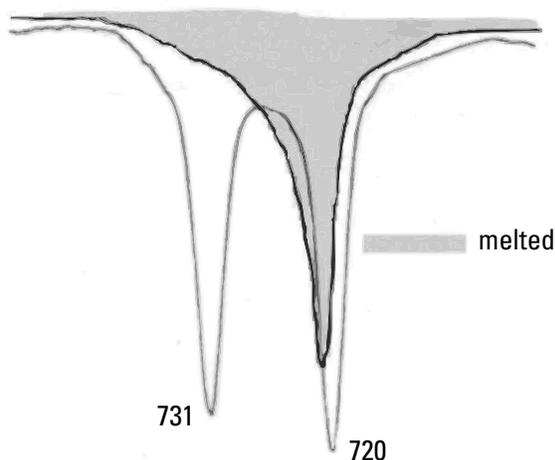


Figure 6-7.

In the melted state (ex: vegetable oil) note a rather increased band in this interval. In the solid state (fat, waxes, polyethylene...) note instead two sharp bands at 720 cm^{-1} and 731 cm^{-1} . **This split is due to crystallinity.**

The macromolecules in a polyethylene crystal are placed in a lattice that has four macromolecules at the intersections of a rectangular prism and a macromolecule in the center (Figure 6-8).

The CH_2 of the lateral chains always take the same position as the CH_2 of the central chain. The two types of CH_2 allows **inter-molecular** interactions that consist of two concerted movements:

- two rocking in phase $\rightarrow 720\text{ cm}^{-1}$
- two rocking out of phase $\rightarrow 731\text{ cm}^{-1}$

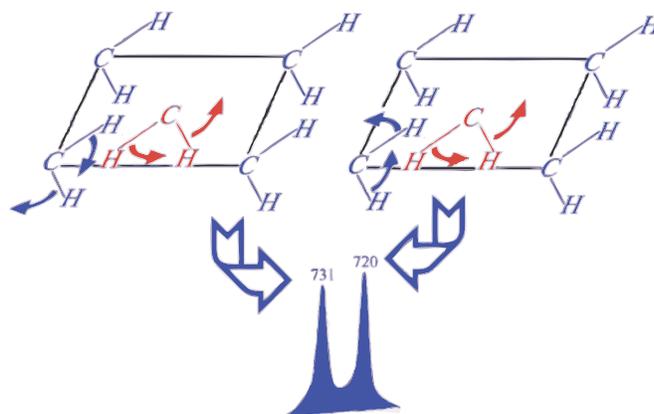


Figure 6-8.

It is not always easy to distinguish the **bands of crystallinity** from those of **conformational regularity**.

Both of these two types of bands have one thing in common: **decomposition by melting or dissolution in a solvent always gives sharp bands.**

It is therefore not important to know if a band is due to crystallinity or conformational regularity. This is also true because conformational regularity is the reason why the polymer crystallizes. In the literature, frequently the distinction is not made between the two types of bands, thus they are generally defined as **bands of crystallinity**.

The identity of a band as due to “crystallinity” (instead of a constitutional band due to a functional group, impurity, etc.) can be very important. Therefore it would be useful **in a IR polymer laboratory**, to be able to arrange a heating cell or ATR accessory. Such a cell allows running the spectrum at various temperatures. With this type of cell it is possible, without a shadow of doubt, to identify the bands of “crystallinity” in a spectrum. It allows for disassociation at a certain temperature (melting temperature) and the re-association by cooling. As we shall see later on, this type of cell can also serve other purposes.

Chapter 7 Orientation

Consider now a block of crystalline polymer compressed into a very thin film, while being slowly cooled. The individual crystals, once oriented in a disorganized fashion in all three directions of space, will now be arranged mostly in the X-Y directions of the film (Figure 7-1).

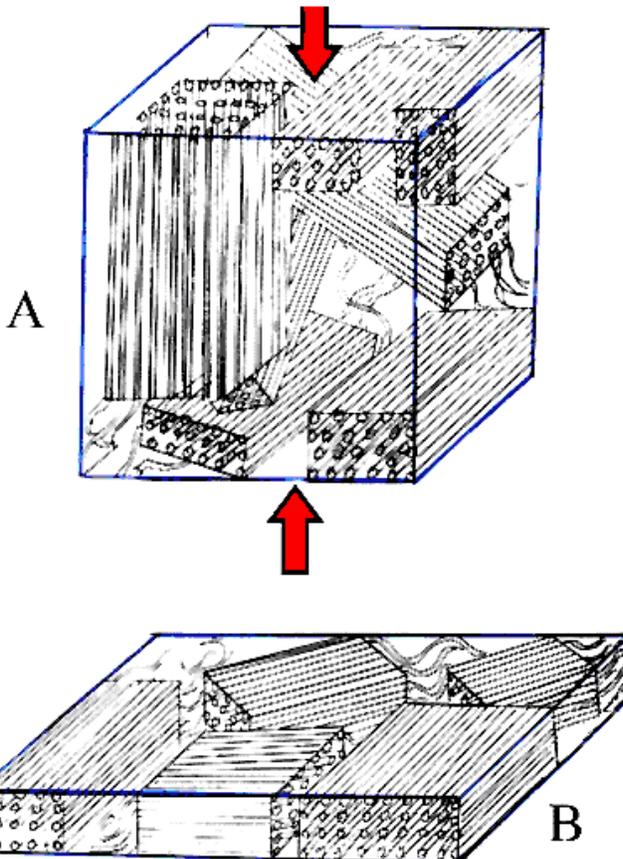


Figure 7-1. Pressing

If the film is rolled in one of two directions, note that in the beginning the film stretches without any great resistance. At a certain point, though, the resistance increases in a very noticeable way without warning, and, if continued, the film reaches the breaking point. During the first phase of lengthening, the crystals slide on each other and stretch to disperse in the direction of rolling, and continue in this process until all or nearly all of the

crystals are oriented in the rolling direction. This gives the film a particular mechanical resistance.

The process of rolling is commonly used in the industry in order to achieve the mechanical characteristics that it gives manufactured products (fibers, oriented films). Rolling also requires the analyst have a **technique** (beyond mechanical tests) that **successfully estimates the degree of orientation** of a polymer.

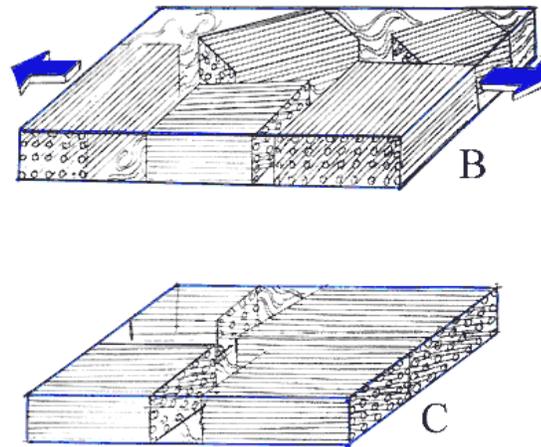


Figure 7-2. Ironing

IR is just such a valid technique.

This is true because the amount of **absorbance depends on the intensity of the dipole moment vector**. The mathematical relationship of this dependency is:

$$A \propto (\vec{E} \cdot \vec{\mu})^2 \propto (E \cdot \mu \cdot \cos\Theta)^2$$

In words, the absorbance is **proportional** to the square of the *scalar product* between the electric field vector, \vec{E} , and the dipolar moment vector, $\vec{\mu}$. The scalar product between the two vectors has as modulus the product of the two moduli for the cosine of the angle, $\mu\cos\Theta$, formed between the two vectors of direction $\vec{\mu}$ and \vec{E} (Figure 7-3).

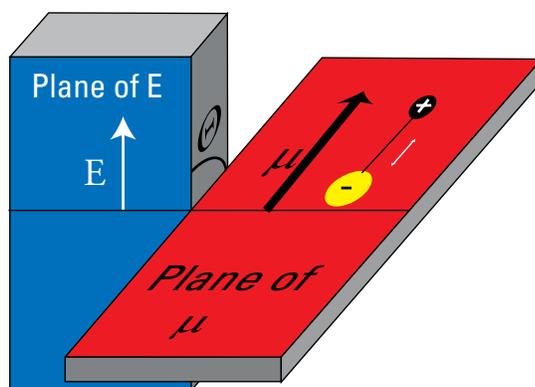


Figure 7-3.

From this relationship it is evident that the varied absorbance is due to the latter angle between the electric field vector of the infrared radiation and the dipole moment of the oscillating dipole.

If the angle $\Theta = 0$, that is if the two vectors are parallel, then $\cos\Theta = 1$ and the product therefore **reaches its maximum value** (the component $\bar{\mu}$ in the direction \bar{E} is equal to μ .)

If the angle, $\Theta = 90^\circ$, that is if the two vectors are perpendicular, then $\cos\Theta = 0$ and therefore $A = 0$ (the component $\bar{\mu}$ in the direction \bar{E} is equal to zero).

Usually, when a normal spectrum of a polymer is run **the value of Θ is not important**, for two reasons (Figure 7-4):

- **the light is not polarized**, for which \bar{E} can meet the oscillating dipole at all possible angles
- **the polymer is not oriented** and thus the molecules are arranged distributed in all directions, so that the oscillating dipole $\bar{\mu}$ can form with \bar{E} all possible angles.

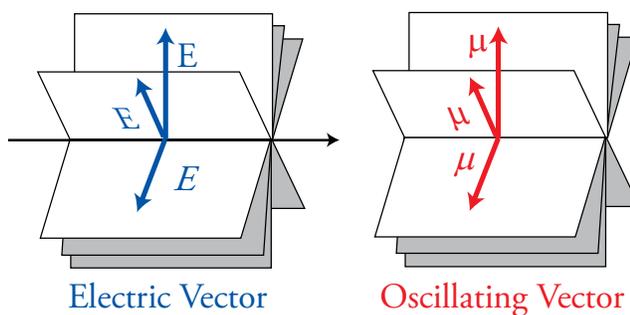


Figure 7-4.

However, even if polarized light is used, with a polymer that is not oriented (Figure 7-5) $\vec{\mu}$ can meet at all possible angles with \vec{E} .

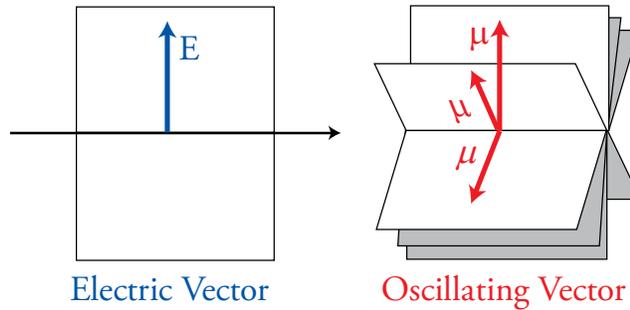


Figure 7-5.

This is also the case with an orientated polymer and light that is not polarized so that \vec{E} can meet with $\vec{\mu}$ at all possible angles (Figure 7-6).

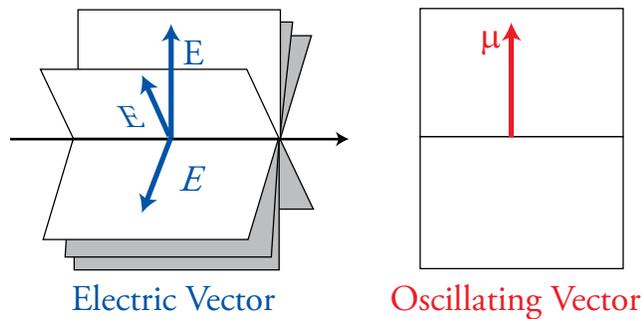


Figure 7-6.

Therefore, only when two conditions are met at the same time (Figure 7-7);

- the light is polarized;
- the molecules are oriented, such that they all only oscillate in a single plane;

does determination of the intensity of the band depend strongly on the value of the angle Θ .

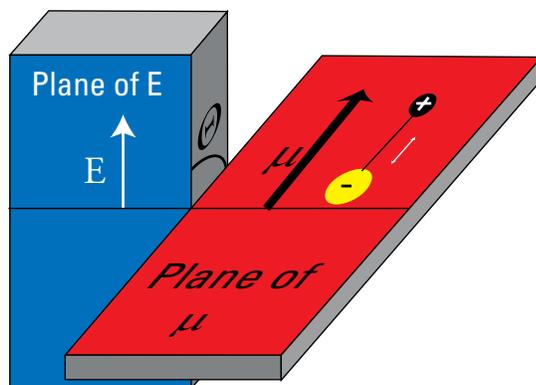


Figure 7-7.

The infrared spectra of compressed polymer films in polarized light has two uses:

- Assignment of infrared bands
- Control of the degree of orientation of a film during processing.

Allocation of Bands

An example is the assignment of the band at 638 cm^{-1} in the infrared spectrum of PTFE (polytetrafluoroethylene). The macromolecules of PTFE assume a conformational helical structure. If we compress the film, the chains will be dispersed in the direction of compression. The CF_2 groups are found perpendicular to the plane of the direction of compression (Figure 7-8).

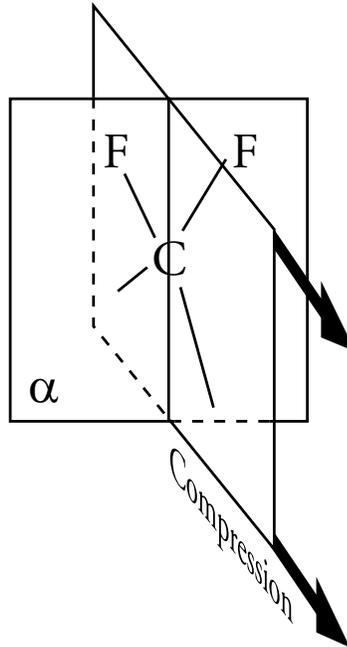


Figure 7-8.

The band at 638 cm^{-1} may be attributed through calculations to the wagging of the CF_2 , that is the concerted movement of the two atoms of F over and under the plane α .

The oscillating dipole relative to this movement is then directed in parallel with the direction of compression. If the assignment is right, spectra collected with light polarized in parallel with the direction of compression will give the maximum intensity of the band, while perpendicular light will show a minimum. This is in fact verified (Figure 7-9).

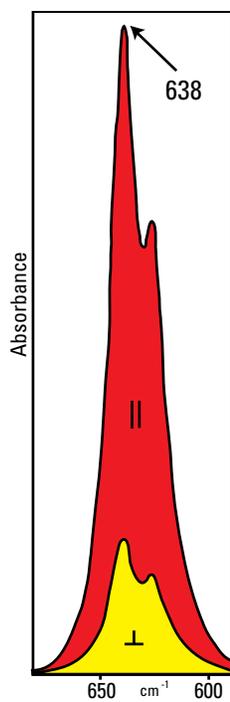


Figure 7-9.

The band obtained with light parallel to the direction of compression is much more intense. Rotation of the polarization by 90 degrees yields a band whose intensity is almost zero. That means that the dipole oscillates in the direction of compression.

Orientation of the Film

Orientation of the molecules can remarkably improve the mechanical characteristics of a film. Thus, it is very important in the industry to have a technique to estimate the degree of orientation or the orientability of a film.

For example waterproof PTFE tapes used in hydraulics must have a high degree of orientability. To determine the degree of orientation of a PTFE film, the absorbance (of the band at 638 cm^{-1}) is measured in **parallel** light first, and then in **perpendicular** light. The relationship of the two spectra, called a *dichroic relationship*, is determined according to the equation

$$R_{\text{dichroic}} = \frac{A_{\parallel}}{A_{\perp}}$$

In the case of PTFE the dichroic relationship varies from 1, when the film is not oriented, to 8, when the film is completely oriented. Thus the film examined in Figure 7-9 is nearly completely oriented.

Chapter 8 Sample Preparation

The information desired from infrared analysis of polymeric materials may be limited to the bulk material, or the user may require information about additives such as plasticizers. Different sample preparation techniques are available for optimizing the specific information obtained, or for allowing rapid analysis. This chapter will discuss classical and modern analysis techniques, and will cover the strengths and weaknesses.

A range of sampling techniques is available for the analysis of polymers. Transmission spectra can be obtained from preparation of thin films in solution or by compression. For some samples, it is desirable to examine only the surface, and still other samples need to be examined as a powder, solid, liquid or even as a flowing surface. Modern accessories allow data collection using attenuated total reflection, specular reflection or diffuse reflection that can address many of these sampling needs. Microscopy, especially micro ATR, is well suited to fibers and small particles. The selection of a specific method will be based upon the information required (bulk or trace?), the sample size (car bumper or single fiber), speed of analysis needed and skill of the operator.

Films

For many applications, it is necessary to obtain a thin film of sample.

Films in solution

1. The polymer is dissolved in a suitable solvent.
2. Some drops of the solution are smeared, as homogeneously as possible, on a disk of KBr.
3. The solvent is evaporated slowly.
4. Once the solvent is removed, a thin film remains adhered to the disk.
5. The disk is placed on the appropriate support and the spectrum taken.

Hot pressed films

1. The polymer is molded at the appropriate temperature (**a little above the melting point or softening point**), by placing a hundred milligrams of polymer between two sheets of aluminum.
2. In order to avoid damaging the delicate slabs of hot pressed sample, the polymer is broken up as much as possible. For similar reasons, before exerting pressure, the sample slabs must be warmed and then left for one or two minutes. This softens the polymer so that when pressure is applied, it is hard to ruin the slabs at this point.
3. The sample is cooled, and the aluminum sheets are detached. Normally these are detached easily enough. If not, the aluminum/polymer wafer is placed in 5% HCl or NaOH until all of the aluminum has dissolved. Instead of aluminum, thin sheets of PTFE can be used that do not adhere to the sample. Run the spectra of the film, placing it on the appropriate sample holder.
4. The spectrum of the film is then collected by placing the slab on the appropriate sample holder.

Advantages of films in solution

- Extremely thin films can be prepared by using very dilute solutions.
- There are no alterations of the sample due to the relatively high temperature experienced during compression.
- It is not necessary to have expensive equipment such as a hot press or a film-maker.

Disadvantages of films in solution

- It is not always possible to find an adequate solvent. The solvent must both dissolve the polymer and evaporate at a relatively low temperature.
- Elimination of the solvent is not always an easy enterprise. Frequently, low-boiling solvents also find it hard to leave the polymer.
- It is very easy for bubbles to form that damage the film.
- It takes a long time.

Advantages of hot pressed films

- It is much faster.

Disadvantages of hot pressed films

- It does not produce very thin films.
- It is necessary to have a hot press or other analogous accessory of a certain cost.
- The polymer can in some cases degrade from the effects of temperature or air.

Quality of the films

Films do not have to be punched or cooled. The presence of holes or bubbles alters the ratio of the bands. The more intense bands become proportionally less intense in regards to the weak bands.

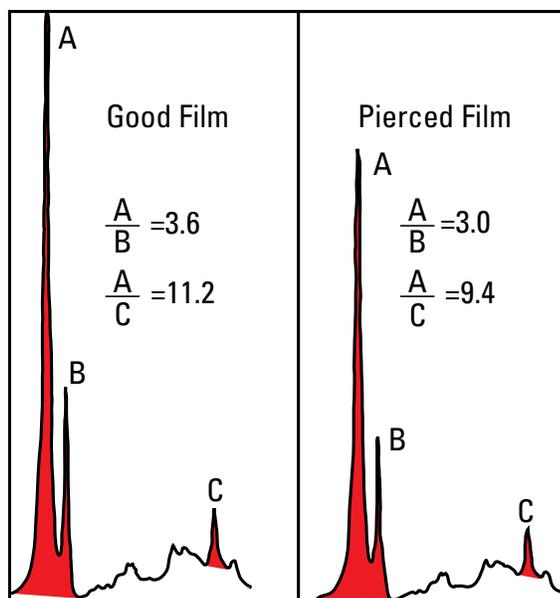


Figure 8-1.

Transmission Spectra

IR transmission spectra is obtained by passing infrared light through the sample. The sample can be prepared for transmission spectra by three general means.

Windows

Although there are a variety of transparent windows available for transmission spectra, KBr is the most commonly used. The selection of alternate window material depends on various experimental conditions such as the frequency range of interest, or the solubility of the material considering the solvent used in the sample.

A drop of fluid polymer or solution can be deposited on one window and covered with a second window. The resulting 'sandwich' is then pressed to obtain a capillary film of the solution. The spectrum can now be taken. In other situations the polymer solution is evaporated on the surface of the window before the spectrum is run.

Obtaining spectra via KBr windows is simple and fast, but presents some distinct disadvantages. KBr is hygroscopic and must be kept in a dry environment in order to preserve the transparency of the crystals. In addition, the windows can be quite fragile, and are prone to cracks.

Pellets

In this instance the solid sample is crushed and mixed with an IR transparent material (typically anhydrous KBr, although other materials can be used). The mixture is then formed into a pellet with a pellet press and analyzed.

This method is a traditional one, and can be quite useful. The disadvantages include the destruction of the sample and the fact that the technique does not lend itself to rapid analysis or automation. Some samples also do not form quality pellets.

Neat solid

Sometimes a sample lends itself well to be mounted in a sample holder and placed in the infrared beam without the means of windows or other sample preparations.

FT-IR Accessories

Accessories extend the usefulness of the FT-IR greatly for the analysis of polymeric materials. Most of the accessories exploit some reflection phenomena to speed the analysis by simplifying sample preparation. The transmission methods covered thus far tend to have higher sensitivity – the beam passes through the entire sample rather than reflecting off a portion of the sample – but many analyses will find the use of accessories highly beneficial. This is especially true when the identity of the bulk material is in question. Microscopy extends these capabilities to particles as small as 7 microns.

Specular reflection

This technique consists of running a reflectance spectrum of the polymer film deposited on a reflecting metal support. The radiation impacts the surface of the film, crosses it, reflects on the metallic surface and then passes through the sample a second time; the beam therefore doubly crosses the sample.

This technique is typically only used for the examination of thin polymer layers deposited on a reflecting layer (ex: manufactured sheets of steel and aluminum protected by a polymer layer). Several accessories from Thermo are designed for specular reflection, including the SpeculATR.

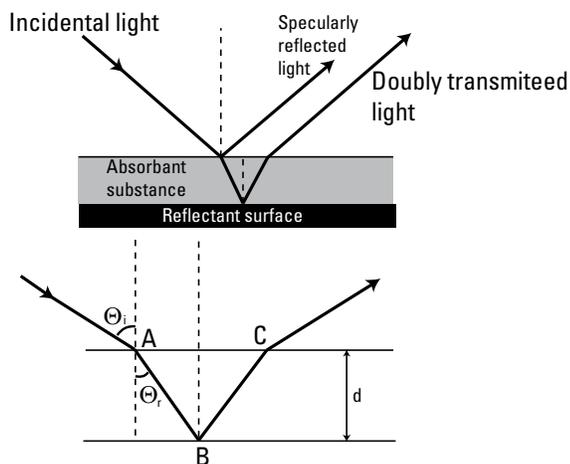


Figure 8-2.

As seen in Figure 8-2, some light that hits a sample and is partially reflected from the surface without penetrating the sample (specularly reflected light = I_r). Other light penetrates internally and is reflected by discontinuities of the sample that are near the surface, such as fillers, bubbles, microfissures, pigments, small superficial wrinkles. This represents diffuse reflection = I_d . Some of the light may cross the sample and pass through the other side (transmitted light = I_t).

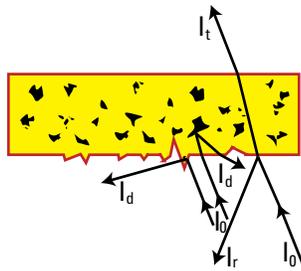


Figure 8-3.

In the case of a rubber loaded with carbon black, the diffuse reflection, caused by light that penetrates a certain distance in the sample, becomes totally absorbed by the carbon black. Therefore the only reflections are from specularly reflected light. The spectrum obtained with this type of reflection undergoes a distortion due to the *anomalous index of refraction* (Figure 8-4).

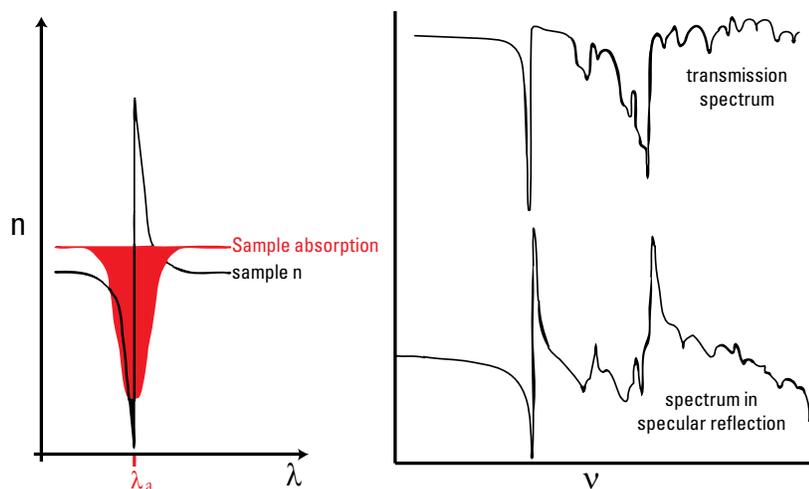


Figure 8-4. The reflection spectrum depends on a combination of the index of refraction and the coefficient of absorption. Since, the index of refraction introduces a discontinuous line (anomalous dispersion) near the maximum absorption, the resulting spectrum is considerably deformed.

The Kramers Kronig Transformation can be applied to correct the reflection spectrum. The KKT transforms the distorted reflection spectrum into a spectrum very similar to that of transmission.

The KKT (or OMNIC's Advanced ATR Correction) can also be used to effectively correct some ATR spectra when totally absorbing peaks are present. The use of Ge crystals can circumvent the absorption problem for most carbon black containing materials. The KKT can be used with some

success to correct spectra collected on other crystals. This is shown in Figure 8-5 and Figure 8-6. In ATR spectra, a component of light is always reflected specularly, since a portion of the IR beam reaches the sample at an angle outside the critical angle. There is also a component of reflected light due to the fact that, in the vicinity of an absorption band, the refractive index of the sample undergoes an abrupt change. The index can exceed that of the ATR crystal, and so the condition for internal reflection is not met. Part of the beam penetrates into the sample and a portion is reflected specularly. The penetrating portion becomes completely absorbed by the carbon black, while the reflected beam, even if weak, reaches the detector. Normally, the amount of this type of reflection is negligible in ATR and introduces modest distortions to the spectrum. In the case of rubber with carbon black, though, the specularly reflected light is the only light that reaches the detector. Instead of ATR, the spectrum is measuring Specular Reflection.

Before application of the Kramers Kronig Transform, the spectrum is absolutely un-interpretable (Figure 8-5).

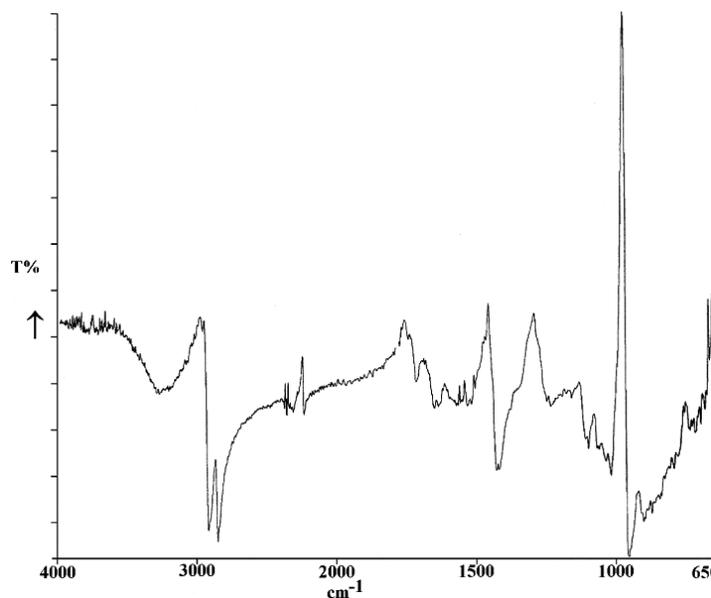


Figure 8-5. ATR of rubber with carbon black (before transformation)

After the transformation (Figure 8-6), intense bands of long paraffin chains are seen (2940, 2866 and 1450) due to paraffin lubricants migrating to the surface, but above all of the bands are clearly those of BN rubber (2233, 966, 913).

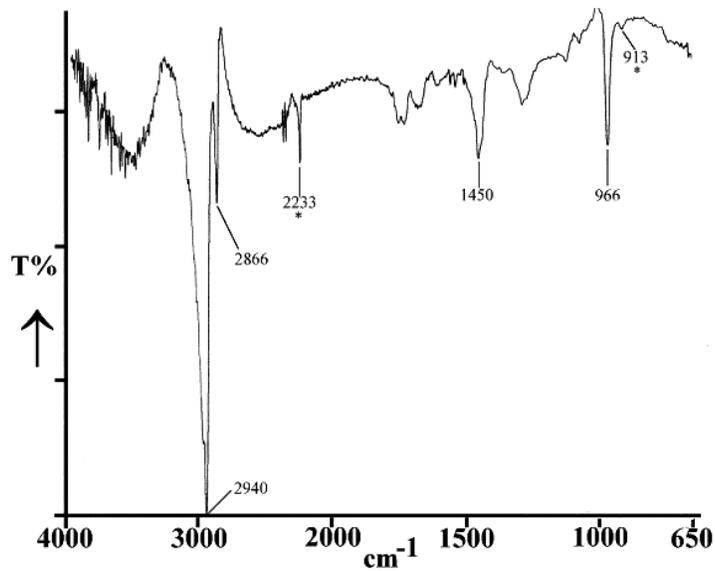


Figure 8-6. After transformation

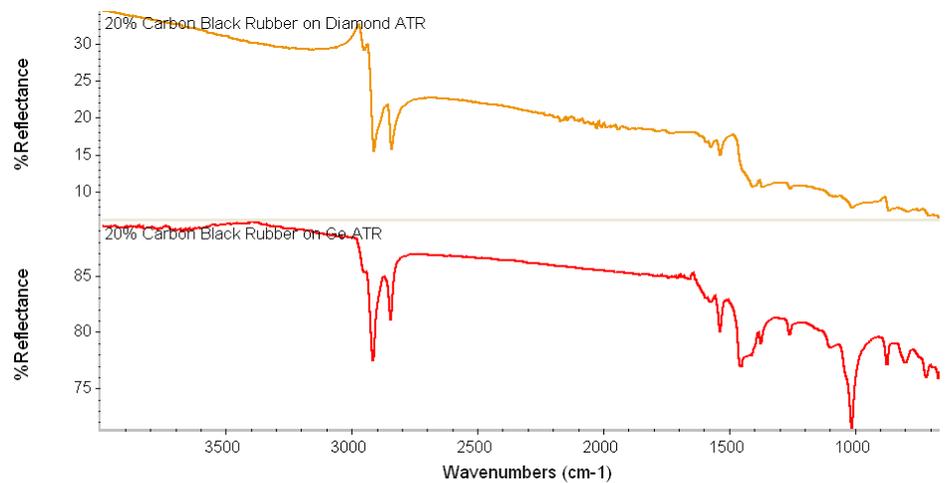


Figure 8-7. Comparison of carbon-black containing rubber spectra collected using Ge or diamond single-bounce ATR. Note the absence of the low frequency peaks in the diamond spectrum (due to the deeper penetration depth), while Ge has clearly defined peaks.

Oblique angle reflection (Grazing angle)

This accessory is analogous to the previous one with the two following modifications

- The angle of incidence is **nearly oblique** to the plane of the sample (80°).
- The incident infrared light is **polarized** with the vector \vec{E} parallel to the plane of incidence.

The SAGA accessory is a grazing angle accessory suited for this type of measurement. Ultra-thin films (down to a few microns) on reflective surfaces can be analyzed using the more sophisticated PM-IRRAS method; see Thermo for more details. With the SAGA or other grazing angle accessory, it is possible to examine layers of polymer of the order of 50-100 Å. The figure shows the spectrum of a monolayer of fluorate oil (polyhydroxypropylene perfluorate = Fomblin[®] of Ausimont) deposited on a metallic support. The inferior spectrum A is obtained with specular reflection using an angle of 45° and without the use of a polarizer. The resulting spectrum consists essentially of **only background noise**. Spectrum B, however, is obtained using the grazing angle accessory.

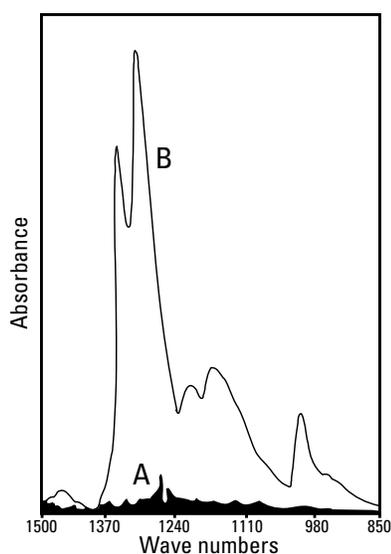


Figure 8-8.

**Attenuated total
reflectance (ATR)**

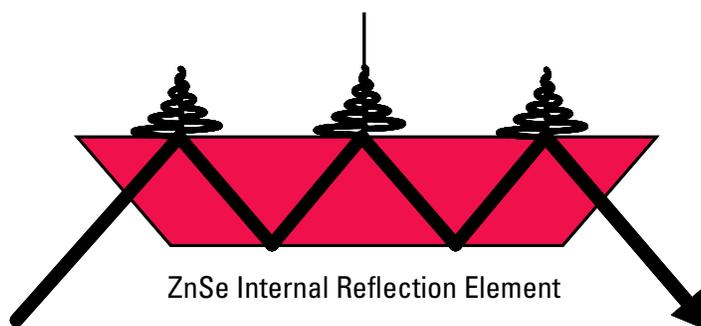


Figure 8-9. Multi-bounce ATR

In ATR, the infrared beam passes from a **high refractive index medium**, usually a crystal like ZnSe or Ge, to a lower refractive index medium (the substance). Since the angle of incidence is greater than the critical angle,

there is total internal reflection. A portion of the incident beam penetrates into the sample (up to 2 microns) – this is called the **evanescent wave**. Many ATR accessories exist, in both single-bounce and multi-bounce configurations. The depth to which the evanescent wave penetrates the sample is defined as being equal to

$$d_p = \frac{\lambda}{2\pi n_p \sqrt{\sin^2 \Theta_i - \frac{n_s^2}{n_p^2}}}$$

In actuality, this represents the depth for 1/e decrease in the evanescent wave, or about 1/3, so the actual depth of penetration is about three times more.

The ATR spectrum obtained differs from the transmission spectra in several ways. First, the **bands at longer wavelength** are relatively **more intense** since the depth of penetration increases with wavelength. Second, the index of refraction changes in the vicinity of a strong absorption. OMNIC provides an excellent advanced ATR correction based on the full functional difference between transmission and ATR, which allows many of the libraries built using ATR methods to be used.

Multi-bounce ATR is used heavily in the analysis of liquids, for reasons noted below. The multiple bounces effectively increase the path length of the accessory over the single-bounce tools (discussed in the next section). Heated accessories are available for melting studies also.

An experiment involving the use of an ATR accessory has several unique characteristics. The most critical for consideration here are:

- ATR is a **surface technique**. The depth of penetration for a ZnSe crystal is about 6 microns at 1000 cm⁻¹ and only about 1.9 microns for germanium (Ge). Therefore, the effects of substances on the surface (*separating agents, lubricating agents, soil...*) must be accounted for. In many cases, however, coatings are the target and ATR becomes the method of choice.
- The ATR crystals **absorb** and therefore may **limit the spectral range**. However, while Ge and ZnSe cut above about 650 cm⁻¹, the diamond Smart Orbit™ accessory can be used down to 100cm⁻¹. Diamond also has strong absorption bands between 1800 and 2700 cm⁻¹, so analysis of nitrile containing materials (strong peak around 2200 cm⁻¹) may not be optimal. Thus, the proper choice of crystal is important.

- The quality of an ATR spectrum depends in large part upon the intimacy of contact between the crystal and the sample. Pressure devices are used to make this contact happen. Thermoplastic polymers are **rigid**, and therefore a very smooth surface and high pressure is necessary to make sufficiently good contact with the crystal.

As already noted, ATR is a **surface technique**, and therefore it is a useful method for observing **differences between the surface and the bulk**.

Consider again the formula for the depth of penetration stated previously. An ATR accessory can, by varying the angle of incidence or by using crystals of various refraction indices, penetrate more or less deeply into the polymer. It can be used, as an example, for:

- Evidence of migration of additives to the surface.
- Evidence of oxidation or degradation that usually begin when materials are partially exposed to light or atmospheric agents.
- Examination of the interaction of polymers.

Single bounce ATR

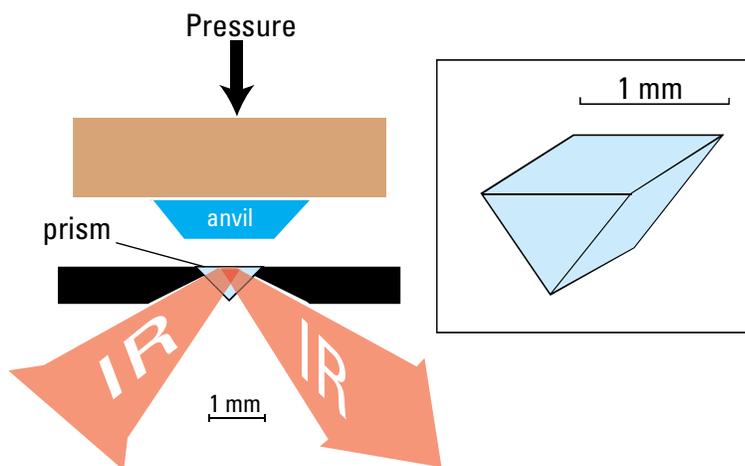


Figure 8-10.

Single-bounce (or single reflection) ATR accessories are now the most popular tool for sample analysis. The ease of sample preparation (almost none), and the versatility for liquids, solids, powders, gels, epoxies and many other samples has made this almost universally accepted. The accessory focuses the infrared light onto a small prism of diamond or other material (ZnSe, germanium, Si or AMTIR). Single bounce accessories have “sweet spots” for sample analysis varying from a few microns (in a microscope application) to a few mm². The versatility and low cost for the newest

generation of ATR devices has brought them into labs for bulk material analysis, inclusions, coatings, single fibers and many other samples.

The material spot is supported on the surface of the ATR crystal. An anvil is used to exert pressure on the sample, forcing good surface contact. The IR beam is directed onto the crystal with mirrors or lenses. Most of these accessories use a 45° angle.

Single-bounce ATR is useful when the sample amount is very low. Indeed, single crystals, residue from molds, and single fibers are routine samples.

As a particular application, carbon-black containing rubbers are very strongly absorbing. Even the thinnest films can be totally absorbing. The shallow depth of penetration given by the Ge crystals in a single bounce ATR application is beneficial. Diamond is considered the best general purpose crystal – it is easy to clean and maintain, and has a good depth of penetration – but it is not useful for black rubber. Thus, interchangeable crystals become a useful property.

It is important to **keep in mind that ATR is a surface examination**. However, powders and liquids, even flowing liquids, can be easily sampled using ATR.

Microscopy and micro-ATR

The FT-IR microscope has added a whole new dimension to spectroscopic analyses. With spatial resolutions down to 5-10 microns, and with ATR capabilities embedded in the scope, these tools allow many analyses to occur which were not previously possible.

FT-IR microscopes can function in transmission or reflection modes. In transmission mode, the IR radiation is directed through a sample holder using a condenser and an objective. Ultra-thin samples may be mounted directly under the objective, although total absorption is quite common. Films or microtomed sections can be laid on KBr windows (or other IR transparent materials).

The samples can also be contained within a compression cell. This both holds the sample and, through compression, thins the section to avoid total absorption. Simple compression cells using KBr or CaF₂ windows can flatten most materials. Harder polymers may require the use of a diamond compression cell. Typically, a small piece of KBr is placed in the compression cell for use as a transmission reference; otherwise, multiple reflections within the cell may cause “fringing” to appear, as a sine wave superimposed over the entire spectrum. Either of these is mounted directly under the objective.

In the reflection modes discussed next, the IR beam must travel through the objective in both directions. If the incoming beam is considered as a cylinder, then an internal mirror must be positioned in this cylinder to direct the reflected beam onto the detector. This cuts a fraction of the beam (up to 50%) from striking the sample, and also collects only a fraction of the reflected light (again, about 50%). Multiplying these two factors, reflection experiments in microscopes have about a 25% efficiency because of the need to place the mirror in the beam. Transmission experiments permit the passage of the full cylindrical beam through the sample, which accounts for their generally higher sensitivity.

Specular reflection is accomplished in a microscopy by placing the thin sample on a reflective slide (gold, silver and aluminum are common substrates). The IR beam travels through the film, bounces off the reflective surface, and then passes through the sample again. Functionally, this is identical to the accessory as discussed above.

Micro-ATR requires positioning of the sample precisely at the point where the ATR crystal will make contact. The crystal can be aligned using three set screws and a sample such as carbon black in which an impression can be left. The sample can then be positioned using the optical microscopy system (either video or direct viewing). A contact alert plate is used to prevent over-pressure application, and preview collection mode can serve to allow optimal contact results before data collection.

Micro-ATR is particularly useful for single fibers. The fiber can be placed on a glass slide and accurately positioned. The ATR crystal is then lowered onto the sample (or the sample raised to contact the crystal), and spectra collected.

Various ATR crystals are available for microscopy, including Si, Ge, ZnSe and diamond. A sharp Tip ATR can be used to penetrate into a sample, or to analyze circuit boards. The depth of penetration of the beam varies with ATR crystal shape and material.

Diamond compression cell

The diamond compression cell is based on two diamonds with parallel flat faces. The simplest cell uses three screws to compress samples between the diamonds. The pressure between the two diamonds is increased, more so because the surface of the crystals is minimal (approximately 1 mm²).

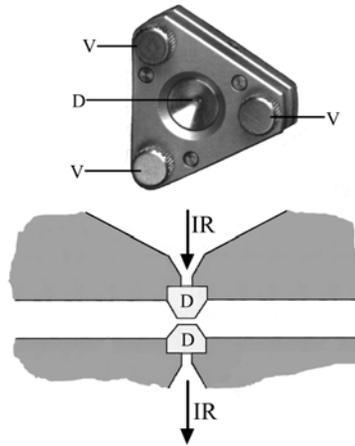


Figure 8-11.

Before closing the cell, a miniscule piece of a substance is introduced (1 mg or less). The diamond cell, with the substance crushed in the middle, is inserted into the beam of the spectrometer. The diamond is nearly transparent in the mid-IR spectral range, from which the spectrum of the substance is obtained. Diamond compression cells can also be used in transmission microscopy, so specks as small as 7 microns can be analyzed.

In comparison with ATR discussed above, there are some differences:

- The **whole polymer is analyzed**, and not just the surface.
- The full frequency range of the diamond is open. With the exception of the plasmon bands between about 1900 and 2400 cm⁻¹, diamond is generally open from the far-IR through the near-IR range.

Variable temperature cell

The variable temperature cell allows study of the bands of “crystallinity,” and in order to verify chemical modifications that take place with temperature (oxidations, degradation, reticulations, etc).

Various types of this accessory exist. Some use external baths, or thermoelectric heating. The simplest consists of a brass casing electrically heated via a temperature regulation system.

A film of the polymer is prepared and arranged between two disks of KBr, one of which is pierced. The sandwich is fitted with the appropriate metallic ring and is then tightened in the casing. Finally a thermocouple is introduced into the hole until it is in direct contact with the polymer. The thermocouple interfaces with the temperature regulation system. The sample chamber is inserted into the beam of the spectrometer.

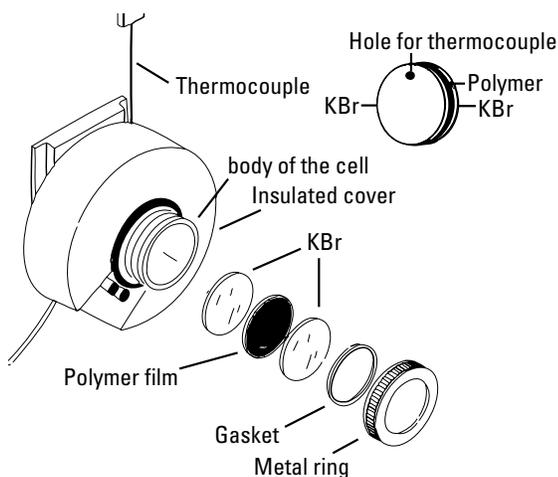


Figure 8-12.

The temperature is changed rapidly until close to the range of interest (melting or other transition). The sample is allowed to equilibrate, and the first spectrum is taken. The temperature is then elevated (or decreased), and another spectrum is taken when the system is stable. This continues through the transition.

ATR can also be done as a function of temperature. There are several variable temperature ATR accessories, including single and multi-bounce crystals. The temperature can vary from sub-ambient to over 200C depending upon design. DRIFTS environmental chambers are also available for high temperatures (up to 900C) and vacuum or elevated pressures.

Chapter 9 Thermoplastic Polymers

These polymers that have the characteristic of melting or softening in a certain temperature interval and then hardening when cooled. In contrast to what happens when rendering some thermosetting plastics, this operation is reversible, and the polymer can be melted again.

Thermoplastic polymers must have both a **melting point** and an **advanced vitreous transition point at ambient temperature**.

Polymers with a **vitreous transition lower than ambient temperature** are known as **rubbers**.

According to the way in which they have been synthesized, thermoplastic polymers are separated into polymers of **addition** and polymers of **condensation**.

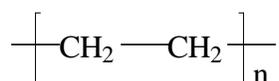
Spectra can be obtained from preparation of thin films in solution or by compression using many of the techniques discussed in the previous chapter.

Principal Thermoplastic Polymers

Polyethylene

Following is a list of the main thermoplastic polymers. For all of them, the formula, the principle uses, the melting point (M.P.) or the softening point (S.P.), and the main solvents are given. These last parameters are useful for sample preparation and some simple separations.

Two types of polyethylene exist: low density (LDPE) and high density (HDPE).



LDPE has a M.P. = 100-115°C.

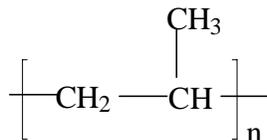
HPDE has a M.P. = 125-135°C.

Polyethylene does not dissolve in any cold solvent. At a temperature above 70°C it dissolves in aromatic hydrocarbons and chlorates.

LPDE is used for bags, toys, household articles, etc.

HPDE is used for packaging, pipes for building, film, fibers, etc.

Isotactic polypropylene

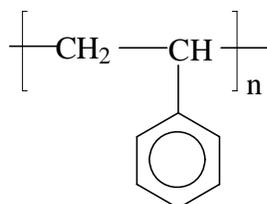


M.P. = 164-170 °C.

It dissolves in aromatic solvents and chlorates only at temperatures above 110°C.

It is used for household articles, technical articles, oriented film, fibers.

Polystyrene

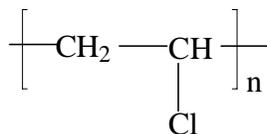


S.P. = 185°C.

It is dissolved easily in many organic solvents: acetone, methyl-ethyl-ketone, aromatic ethyl acetate, hydrocarbons and chlorates.

It is used for packings, household articles, household electrical fixtures, and furniture. In the form of expanded polystyrene, it is used in packings and insulation for buildings. Polystyrene is also used as a primary reference material in many infrared applications.

Polyvinylchloride or PVC

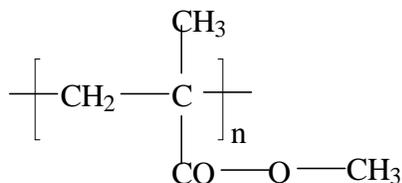


S.P. = 90-100 °C.

At ambient temperature it is a little soluble in most common organic solvents, but it dissolves very well in tetrahydrofuran.

It is used for film, plates, fixtures, pipes, imitation leather, pavement, covering cables, etc.

Polymethylmethacrylate

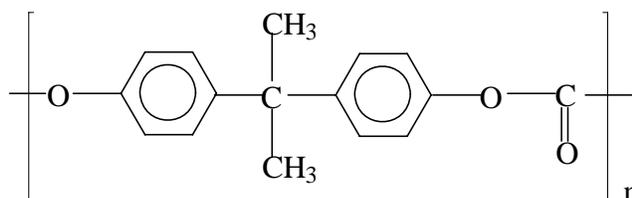


S.P. = 105-120 °C.

It is dissolved easily in acetone, methyl-ethyl-ketone, chloroform, and aromatic solvents.

Because of transparency, PMMA is employed in Plexiglas or Lucite, reflectors, luminous signs, ceiling lights, lenses, etc.

Polycarbonate



S.P. = 220-230 °C.

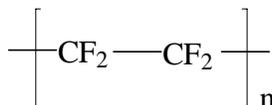
It is dissolved in chloroform, methylene chloride, dioxane, and dimethylformamide.

Due to transparency, resistance to abrasion and resistance to breaking, polycarbonate is employed in the electrical and electronics industry, in lighting (ceiling fixtures, reflectors), in the fabrication of eyeglasses, etc.

Other important thermoplastic polymers are polyamides, polyethylene terephthalates and polyacrylonitrile, especially with respect to synthetic fibers.

Polytetrafluoroethylene (PTFE)

This polymer that has the characteristics of a thermoplastic polymer, but PTFE doesn't melt and finally softens only at 325 °C.



No solvent exists.

Since PTFE doesn't melt and is not dissolved in some solvents, a diamond cell, ATR and micro-ATR must be used to run the IR spectrum. Especially for quantitative analysis, the fact that PTFE **sinters at high pressure** can be taken advantage of and used to prepare thin disks using a mortar and pestle without KBr.

IR is a technique utilized for the characterization of thermoplastic polymers. Remember that the spectra of polymers are reported in the appendix with the allocation of the main bands.

Chapter 10 Rubbers or Elastomers

The term rubber or elastomer denotes a polymer that, after having endured a treatment of vulcanization, assumes elastic characteristics. A material is elastic when, stressed with relatively modest force, it undergoes very great deformations, but it then returns quickly to the shape and dimensions it began with once the force has been removed. A polymer must possess certain characteristics to be able to be used like an elastomer.

- The macromolecule must consist of a **linear** chain, **without long ramifications**, and its molecular weight must be sufficiently high (200,000 - 1,500,000).
- Its T_g must be **much lower than ambient temperature** (or the temperature of use), and **it does not have to be crystalline**. In these conditions the polymer is found in the so-called gummy state. In this state the chain can assume all possible conformations, due to rotations around the simple bonds that join the atoms of the chain, and the polymer tends to assume a disorganized shape like a ball in such a way as represented very schematically in the following figure:

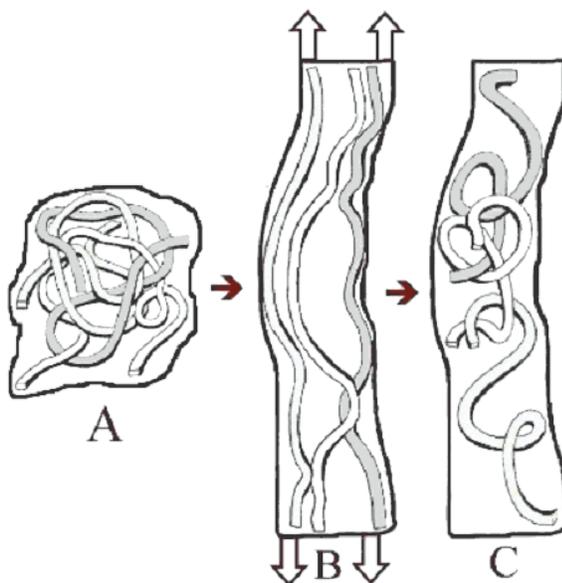
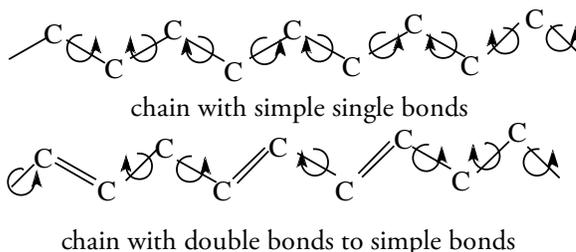


Figure 10-1. Behavior of a non-vulcanized elastomer with traction.

If the manufactured article is subjected to traction (B of the above figure), the macromolecules stretch to unroll themselves and disperse in the direction of stretching, more or less parallel to one another. Because this result can easily take place (essential for an elastomer), it is necessary that the ball is not tightened too much or too intertwined. Precisely because of this occurrence, it is necessary that the macromolecule have still other characteristics:

- There must be not be long ramifications present. These, in fact, would provoke such intertwining that unrolling of the macromolecules would offer relatively high resistance.
- The free spin around the simple bonds of atoms of the chain must exist, but it must be regulated in some way and limited so that the macromolecule can make a ball more easily, but not tightly. This result can be achieved in two ways:
 - a. Spacing out single bonds between atoms of the chain involved in double bonds.



Free spin is prevented around the double bonds, for which reason chain B will make a ball more easily than chain A, in which all the spins are possible. This is the case with all the unsaturated rubbers like polyisoprene, neoprene, etc.

- b. Inserting more or less cumbersome lateral groups in the macromolecule. These will hinder the spins around the single bonds for blocking reasons, rendering them less complete and therefore producing a little tighter ball. This is the case with **methyls** of ethylene-propylene rubbers and of butyl rubbers, the **ester** groups of acrylic rubbers, etc.
- Groups like those that have physical interactions with corresponding groups of a nearby macromolecule cannot be present (such as the hydrogen bond). This would prevent sliding of the macromolecules and

would favor their placement in a rigid lattice and make them, to some extent, crystalline. Thus alcoholic groups (- OH), carboxylic acid groups (- COOH), amidic groups (-CO-NH-), urethanic groups (-O-CO-NH-), etc. should not be present. Polymers and copolymers of polyvinyl alcohol, polymers and copolymers of acrylic acid, nylon types of polyamides or polyacrylamides, and polyurethanes cannot thus be used like elastomers (the polyurethanic rubbers are, in fact, very particular polyurethanes).

If the macromolecules have the aforesaid characteristics, then they assume a direction practically parallel to the direction of stress when under that stress. However, if the forces of stress are removed, and the manufactured article continues to maintain the deformed shape (C in the figure), without returning to the dimensions and the shape of the previous manufacture article: **it does not have elastic character**. The macromolecules, subject to Brownian motion, will tend to re-roll in a new way, leaving balls dispersed in the mass of the manufactured article, but maintaining a shape freed from stress.

In order to acquire an elastic behavior, the elastomer must be subject to the **process of vulcanization**.

Vulcanization

Vulcanization **welds** the macromolecules to each other at **some points** (see the following figure). The macromolecules will form a **net, or better, a three-dimensional lattice**.

The lengths of the chains between such welded spots are sufficiently long enough to still allow free spin and thus flexibility together. However, these chains are not completely free to slide in the direction of stress, and are very bound to the welding points. Therefore the lattice, when subjected to stress, offers a resistance to sliding. This resistance increases movement proportionally, thus behaving by itself like an elastic force. When the force of traction is eliminated, this elastic force acts to return the material to the shape and dimension it began with.

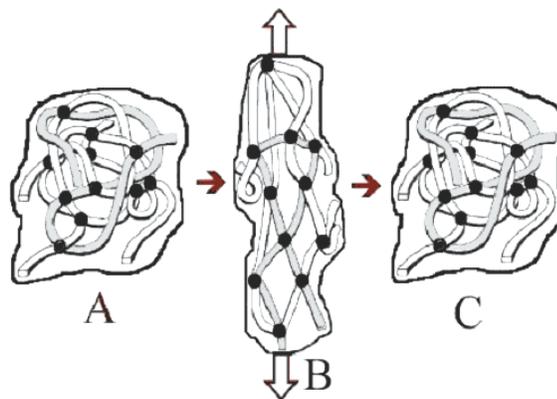


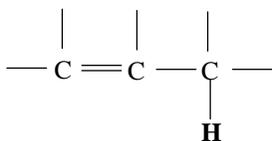
Figure 10-2. Behaviour of a vulcanized elastomer under traction

To be an elastomer the polymer must therefore also have another characteristic.

- **Reactive groups** that permit vulcanization **must be present** within the macromolecule. According to the type of these groups it is possible to have various types of vulcanization.

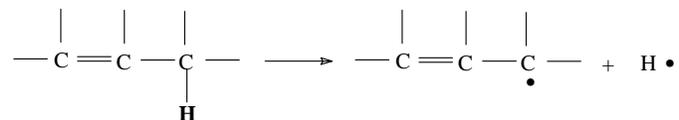
Vulcanization with sulfur

The most common method of vulcanization is that of treating the polymer in the presence **elemental sulfur**. Before this type of vulcanization can happen, it is necessary that **allylic hydrogens** are present in the macromolecule, that is, hydrogens positioned on a carbon atom adjacent to a double bond.

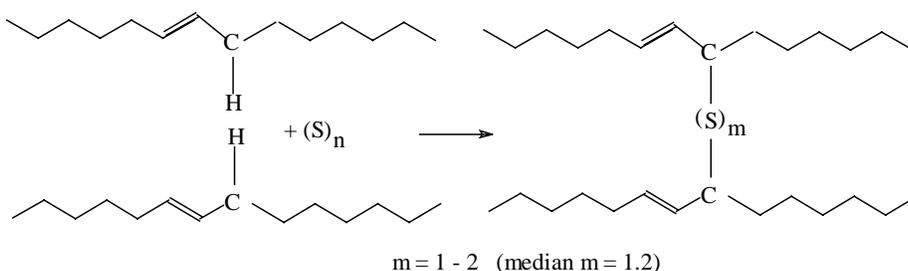


These hydrogen atoms are particularly mobile, detaching themselves to produce a very stable radical (**allylic radical**).

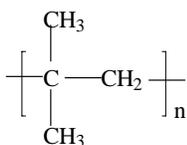
Because the radical is very stable, the preceding reaction tends to



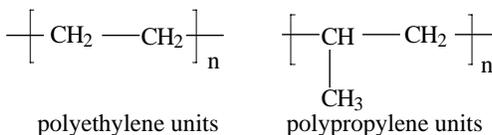
go to the right. Sulfur then reacts with the allylic hydrogens of two chains joining them with sulfur bridges.



In the case of an **elastomer that does not have lots of double bonds**, like polyisobutylene (butyl rubber)



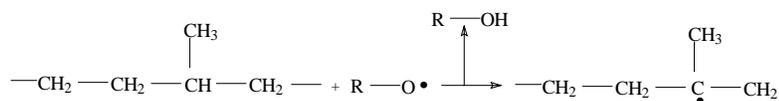
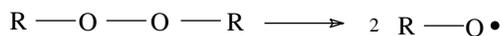
and ethylene-propylene rubbers (EPM) that contain ethylenic and propylenic units distributed statistically,



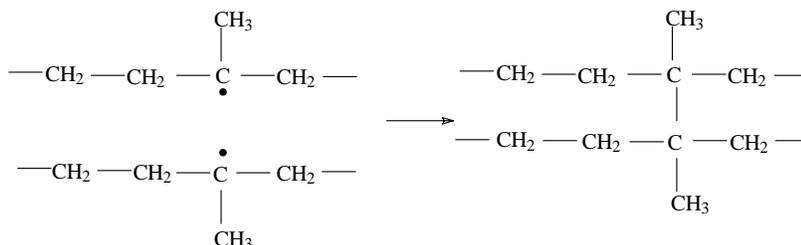
they are joined by adding a **small amount of diolefin** in the polymerization phase. This introduces double bonds into the polymer chain and thus the allylic hydrogens that will **allow sulfur vulcanization**. To polyisobutene is joined **isoprene**, obtaining butyl rubber; and to EPM is joined **ethylidenenorbornene** (or other diolefin) obtaining EPDM rubbers.

Vulcanization with peroxides

Vulcanization can also be carried out with means other than sulfur. As an example, saturated ethylene propylene rubbers (EPM) can vulcanize using peroxides that provoke the formation of C-C bridges. The mechanism is the following:



A radical polymer is formed and then is coupled with another producing an inter-chain C-C bond.



Vulcanization for polyurethanic rubbers

The urethanic group (-O-CO-NH-) has strong hydrogen bonds. The **urethanic resin** which contains a great number of such groups, is extremely rigid, and the sliding of macromolecules under traction is not possible. **It cannot therefore be used as an elastomer.**

Urethanic rubbers are formed from a long and naturally flexible polyether or polyester part and from a very short and rigid part with **urethanic** and **preurethanic** groups (i.e. groups that form urethanes). These groups represent the vulcanization points (see also *thermoplastic rubbers*).

During vulcanization the preurethanic groups produce **irreversible urethanic bridges between chains** that constitute the vulcanization welding.



Spectra of Raw Rubber

It is necessary to distinguish between running the spectra of raw rubber (not vulcanized) and the spectra of vulcanized rubber.

Rubber can be introduced in various ways that demand different methods of sample preparation. ATR is especially useful as the sample preparation can be very minimal, and will be covered separately.

Depending upon the sample, it may be necessary to begin the spectroscopy with some sample preparation. These methods can be applied regardless of the ultimate method for spectral analysis.

Rubbers dissolved in a solvent, or solvent mixture, is a method generally used for products used as superficial coverings or as adhesives.

The sample preparation is, in this case, quite simple. As covered previously, simply make a film by evaporation of the solvent, after scattering some homogenous drops on a KBr disk. A good companion experiment involves depositing one drop on the KBr disk, and then covering it immediately with another KBr disk, pressing it to obtain a capillary film of the solution. Then, take the spectrum as quickly as possible. Comparison of the two spectra can help eliminate false peaks due to residual solvents.

Emulsion or aqueous dispersions are generally used for impregnation or adhesive products.

A film of the emulsion is dried down on a ZnSe or other non-water soluble disk, as previously discussed. However, it is sometimes easier to simply dry a film down on a sheet of clean glass, using an infrared lamp. The sheet can generally be removed from the glass after drying, and then run (handle carefully!). If the film is too thick, stretch it gently.

Dense liquids or semifluid pastes are generally used in castings, or as prepolymers for products with two components, sealing materials, etc.

A good spectrum can be obtained by crushing a drop of liquid or small amount of paste between two KBr disks (or CaF₂).

Solid products are present in bales, pellets, sheets, and powders.

Many times, solid products will require pre-treatment. The sample will contain, besides the elastomer, many additives that it may be necessary to separate, if possible. The usual additives are: mineral fillers, carbon black,

plasticizers, antioxidants, etc. Most of these materials are very easy to analyze via ATR, but the classical methods which remove these additives may be required in some cases.

1. Elimination of plasticizers and antioxidants.

The sample, crumbled as small as possible, is run through a Soxhlet extraction with methanol (2-5 g of crumbled sample with 100 ml of methanol for 10-15 hours). The extract is evaporated in a rotoevaporator to eliminate the greater part of the solvent. The residual slurry is transferred to the smallest possible beaker, and elimination of the solvent is completed under a nitrogen flow.

2. Elimination of fillers and of carbon black.

The residual of the extraction in step 1 is dessicated at low temperature eliminating the residual methanol. The powder is then placed in tetrahydrofuran for 10-15 hours. *The tetrahydrofuran must be freshly distilled to eliminate the antioxidant normally present in the mixture. Its presence would also result in a remarkable pollution of the spectrum of the extract. If the mixture is declared antioxidant free, it is also necessary to assess that it is not too old, because in that case it could be full of peroxides, that can be dangerous during dessication. After use it is a good idea to flush the head space of the bottle with nitrogen before closing it.* The soluble fraction in tetrahydrofuran is mostly constituted from elastomers. The residual part consists of carbon black and mineral fillers that will be examined separately. The soluble fraction is evaporated in a rotoevaporator until a small volume is left. The evaporation is then finished under a nitrogen flow in the smallest beaker possible.

Spectra of the elastomer phase.

The spectrum of the raw rubber, or the THF soluble phase from step 2 above, can now be run in several ways.

- Film from solvents.

Evaporation from solution in THF or other volatile solvent directly onto a disk of KBr. Potentially useful solvents are shown in **Table 10-1**.

- Melted film.

This method is useful when an elastomer does not dissolve or is dissolved with difficulty in volatile solvents. Essentially, with the vitreous transition below the ambient temperature, the polymer is too greatly wound up and

sticky to be molded like a thermoplastic polymer. The film preparation tool is illustrated in Figure 10-3

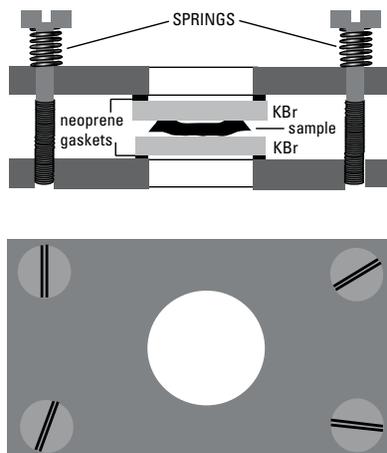


Figure 10-3.

A thin slice of rubber is placed in a sandwich between two disks of KBr. The sandwich is placed in the normal steel sample chamber for transmission examinations, modified by the insertion of four screws (see figure) that place tension on the sample. All of it is placed in a heater maintained at a temperature in excess of the softening point of the sample.

The sample then passes from the gummy state to a viscous fluid state, and, because of the screws, is crushed to form a thin film. It is cooled off slowly, and the spectrum is run.

- ATR
- Diamond cell.

The diamond cell, discussed above, is both rapid and convenient. A small piece of the sample is crushed under high pressure to form a thin film. The only drawback is when the sample contains nitriles of interest, which fall in the spectral range where the diamonds are strongly absorbing.

The method of comparing group frequencies like those for simple molecules can be used, and thus specialized spectral libraries coupled with rapid software searching capabilities are very useful for interpretation of the spectrum. In the appendix are the spectra of some rubbers with the assignments of the main bands.

Table 10-1 can be used to select the solvent to use in order to obtain the film following the above procedures. The letter S indicates the material is soluble in that solvent.

When two potential solvents are identified, it is generally better to choose the most volatile, as that will pose the least problems with residual solvents in the film. Wise choice of solvents can also be used to separate several components, as in the case of a mixture, where one is soluble and another not.

PVC, while not being an elastomer, has also been introduced in the table because it is employed a lot in rubber mixtures.

Table 10-1.

	ACR	BR	CSE	EPDM	ESR	ETR	EVA	FR1	FR2	FR3	FSR	HNBR	IR	NBR	NEO	NR	PBR	PVC	SBR	SIR	TIR	UES	UET
ACE	S	I						S	S		S		I	S	I	I		I	I				
BEN	S	S	S	S		S	S	I	I				S	S	S	S	S	I	S	S			
CLF	S				S	S	S	I	I														
DCB	S	S		S			S						S	S	S	S			S				
DCF	S												S			S					S		
DCM	S					S	S							S			S		S				
DIO		S		I											S				S				
DMF																						S	S
DMS																							
EAC	S									S													
HEX		S						I	I				S			S		I	I				
ISO		I						I	I				S			S		I					
MEK	S		S					S	S														
THF	S	S		S				I	I				S	S	S	S		S	S				

ACE	Acetone [CH ₃ -CO-CH ₃] B.P. 56°C	ISO	Isooctane [CH ₃ -C(CH ₃) ₂ -CH ₂ -CH(CH ₃)-CH ₃] B.P. 98-99°C	FR3	Fluorocarbon rubber VDF-Chlorotrifluoro ethylene	
BEN	Benzene [C ₆ H ₆] B.P. 80°C	MEK	Methylethylketone [CH ₃ -CO-C ₂ H ₅]	FSR	Fluorosilicon rubber	
CLF	Chloroform [CHCl ₃] B.P. 61°C	THF	Tetrahydrofuran B.P. 65-67°C	HNBR	Hydrogenated nitrilic rubber	
DCB	<i>o</i> -dichlorobenzene B.P. 180°C or <i>m</i> -dichlorobenzene B.P. 172-173°C	The raw rubbers are also indicated with acronyms:			IR	Synthetic polyisoprene
DCE	dichloroethane [Cl-CH ₂ -CH ₂ -Cl] B.P. 83°C	ACR	Acrylic rubbers	NBR	Nitrile rubber	
DCM	Dichloromethane or methylene chloride [CH ₂ Cl ₂] B.P. 40°C	BR	Butyl rubber	NEO	Neoprene	
DIO	dioxane B.P. 100-102°C	CSE	Polyethylene chlorosulfonate	NR	Natural rubber	
DMF	Dimethylformamide [H-CO-N(CH ₃) ₂] B.P. 153°C	EPDM	Ethylene-propylene	PBR	1,4 cis-Polybutadiene	
DMS	Dimethylsulfoxide [(CH ₃) ₂ SO] B.P. 189°C	ESR	Thermoplastic polyester	PVC	Polyvinylchloride	
EAC	Ethyl acetate [CH ₃ -CO-O-C ₂ H ₅] B.P. 77°C	ETR	Polyether	SBR	Butadiene-Styrene	
HEX	n-Hexane [CH ₃ -(CH ₂) ₄ -CH ₃] B.P. 69°C	EVA	Ethylene vinylacetate	SIR	Silicon rubber	
		FR1	Fluorocarbon rubber VDF-HFP	TIR	Polysulphide rubber	
		FR2	Fluorocarbon rubber VDF-HFP-TFE	UES	Polyurethane polyester thermoplastic rubber	
				UET	Polyurethane polyether thermoplastic rubber	

The data from the table can be taken advantage of in carrying out simple separations in the case of mixtures.

For example, a mixture of acrylic rubber (ACR), butyl rubber (BR) and butadiene-styrene rubber (SBR), can be treated with acetone (ACE). Only the acrylic rubber will dissolve. The mixture of BR - SBR will remain insoluble. The rest is then treated with hexane: rubber BR will dissolve and insoluble rubber SBR will remain.

Similarly, a mixture of EPDM and neoprene (NEO) can be dealt with by using dioxane. The neoprene dissolves and EPDM will remain insoluble.

Spectra of plasticizers and other additives

The methanol fraction from step 1 above can be run after eliminating the solvent. This is usually a liquid whose color ranges from yellowish to caramel, and it is often a little turbid. It consists mainly of plasticizers or a mixture of plasticizers, with a very minor amount of other additives (antioxidants, stabilizers, etc.). The spectrum of this residual is run by dipping a spatula into the dirty liquid. The drop is placed on a KBr disk, which is then sandwiched with a second disk and pressed lightly.

The spectrum that obtained is exactly that of the plasticizer mixture. The others additives normally are not looked at or can be determined intuitively with some difficulty by the presence of small bands that is odd for the plasticizer mixture. The spectra obtained must be compared with library spectra.

The spectra of the main types of plasticizers are also reported in the appendix.

Spectra of fillers

The residual extracted in tetrahydrofuran, after elimination of the THF, normally consists of **mineral fillers** or **carbon black**. In this case the solid material, if grindable, is placed in an agate mortar. If the material is gummy or hard, it means that insoluble elastomers in THF (for example, fluorocarbon rubbers) are also present in the mixture.

In the former case, the spectrum can be run using a KBr pellet to characterize the type of fillers.

In the latter case, using the information of Table 10-1, another solvent is chosen to dissolve the elastomer.

The fillers, especially carbon black, are not completely inert with respect to the rubber. During formation of the mixture, the mechanical energy

necessary for polymerization is sufficiently large to partially break the macromolecules. This results in the formation of radicals that can react with functional groups always present on carbon black, leading to strong cross-sectional bonds. Further, carbon black is extremely porous and has an enormous specific surface; the macromolecule is adsorbed by the carbon black which forms physical bonds of non-negligible force. The reason for not extracting the rubber from the fillers is that it takes a long time, and is not always complete.

Carbon black itself does not have specific infrared absorptions, and therefore IR is not very useful to confirm its presence. Unfortunately, carbon black absorbs strongly over the entire spectral range, and it affects the background in an abnormal way, often rendering the spectra of other components difficult to see. This is a major reason that Ge-based ATR is advisable.

Fortunately, in the case of carbon black/mineral filler mixtures, the spectra obtained permit determination of the inorganic substance without difficulty. This is because the inorganic bands are very intense, very simple and lie in an area in which the diffuse light (due to carbon black) is low.

Spectra of Vulcanized Rubber

Vulcanized rubber is not, spectroscopically speaking, much different from raw rubber. The small changes introduced by the little cross-sectional ties do not substantially modify the infrared spectrum. Thus we can expect that **raw and vulcanized rubber have practically the same infrared spectrum.**

However, the chemical bonds which led to the vulcanization, while being difficult to see in the IR spectrum, fundamentally modify the physical characteristics of the product.

The vulcanized product has the following particular characteristics:

- completely **insoluble** in all solvents
- **not meltable**
- **not fragile.**

The **first** characteristic prevents the running of the spectrum via evaporation from a solution and moreover renders it impossible to separate the rubber from carbon black.

The **second** characteristic does not allow the running of the spectrum by hot pressing a film. In fact, when raising the temperature, the features of the elastomer between welding points reaches a fluid state easily, but the macromolecules cannot slide with respect to each other, because they are prevented by the cross-sectional bonds of vulcanization.

The **third** characteristic does not allow the machining of the product and therefore renders the technique of running the spectrum by Nujol or a KBr pellet impossible.

Therefore the IR spectrum cannot be run with traditional techniques. By far the most common way to run these on a modern system involves the use of ATR technology, and spectral subtractions using pure component spectra. We briefly examine some of the more classical methods first

First, the manufactured product is cleared of all additives present, such as plasticizers and lubricants that would interfere heavily in successive treatments. The rubber, in the smallest pieces possible, is extracted with the solvent thought most opportune.

- **The extracted material**, once dried, can be used to **identify additives**, as already seen for raw rubbers.

- **The residual of the extraction** is desiccated until there is complete elimination of the solvent and is then subjected to treatments and the necessary techniques.

The most efficient method of extraction of the additives is generally as follows:

1. The rubber is shredded. The degree of shredding regulates the speed of the extraction. Milling is usually satisfactory, sometimes with material frozen in liquid nitrogen
2. The shredded rubber is extracted with the best solvent. A general procedure is to do a Soxhlet extraction for 24 hours with a chloroform-acetone azeotrope (68% - 32% by volume). The solute is desiccated and the spectrum is run to determine the additives, as already seen for raw rubbers. The insoluble part, containing the vulcanized rubber and the fillers, is vacuum desiccated at 60°C to eliminate all the impregnated solvent.
3. In an hour the product is ready for the treatment necessary to run the spectrum.

Spectra in o-dichlorobenzene

Vulcanized rubber is insoluble in all solvents because of the cross-sectional bonds caused by the vulcanization. These bonds, especially those due to sulfur vulcanization, can be routes for a prolonged permanence of the elevated boiling temperature of o-dichlorobenzene (179-182°C).

Approximately 1 g of finely subdivided sample separated from the additives is reheated with 50 milliliters of o-dichlorobenzene in a 250 milliliter flask. The final heating can last from 24 hours, in the case where chloroprene is present, to 2 or 3 days. The solution is cooled and the contents are moved to a beaker containing approximately 50 milliliters of toluene. The solution is decanted after stirring. If the vulcanized sample does not contain carbon black, the additives are deposited on the bottom. If they remain in suspension, and a centrifuge is available, it is a good idea to centrifuge the sample. The supernatant is used to run the IR spectrum by evaporation on a disk of KBr.

If the vulcanized sample contains carbon black, 10-20 g of diatomaceous earth is added to the beaker, churned, and filtered. The filtered solution is used to prepare a film on a disk of KBr.

To determine the **identity of the additives**, there are different ways to work, according to the absence or presence of carbon black.

- **With carbon black absent**, the residual fraction of the centrifugation (or the precipitate from decanting) is washed repeatedly with toluene and dried to eliminate the solvent. Then the spectrum is taken on a KBr pellet.
- **With carbon black present**, a part of the mixture is taken after adding toluene and before the introduction of diatomaceous earth. This mixture is still diluted equally with toluene. It is then filtered without worrying whether part of the coal passes through the filter. The residual of the filtration is washed several more times with toluene, and dried in warmth to eliminate the solvent. The KBr pellet method is then used. As has been previously stated for the additives of raw rubber, carbon black interferes only minimally.

There are advantages and disadvantages with the technique of solution in o-dichlorobenzene.

Advantages

- It does not require expensive equipment.
- The elimination of carbon black and additives allow consequent improvement of the quality of the spectrum.
- It allows identification of the additives.
- It also allows recognition of rubber mixtures.

Disadvantages

- It is a technique that demands much time and operation of a certain complexity.
- It is not *valid for all rubbers*, especially for *those not vulcanized with sulfur*.

Spectra of pyrolyzed liquids

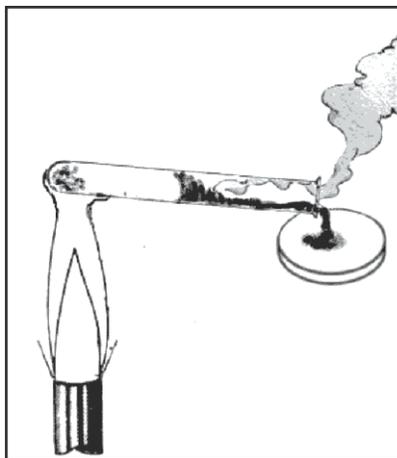


Figure 10-4.

0.2-0.5 g of sample separated from additives is placed in the bottom of a small glass test-tube (6-8 cm). If the presence of fluorocarbon rubber is suspected, it is a good idea to use a quartz test-tube to avoid formation of fluorosilicate. The bottom of the test-tube is placed in the warm part of a Bunsen flame. The test-tube is kept slightly tilted towards down as shown in the figure. At the open end of the test-tube, a disk of KBr is placed. The rubber will develop dense smoke (work in a hood). Some smoke escapes and some condenses on the cold end of the test-tube in the form of a dense liquid that drips on the KBr (one drop is enough). The drop is spread evenly on the window with a spatula with the help of a drop of acetone (or other solvent), and then evaporated under an IR lamp. If the liquid does not make it to the disk, the test-tube is removed from the flame, and a metallic spatula is used to attempt to get the liquid on the KBr or the walls are washed with acetone, and the solvent is evaporated on the disk.

The pyrolyzed liquid consists mostly of macromolecule fragments, and therefore its spectrum would not have to be much different from that of raw rubber. However, pyrolysis consists of a complex series of reaction chemistries for which the spectrum can also often be very different from that of the spectrum of raw rubber. Pyrolysis methods are very specific and allow an easy determination of the elastomer.

Spectra of pyrolyzed rubbers exist in the literature (*International Standard ISO 4650 - 1984 (E)*), but each lab is advised to take a reference set of samples subject to pyrolysis.

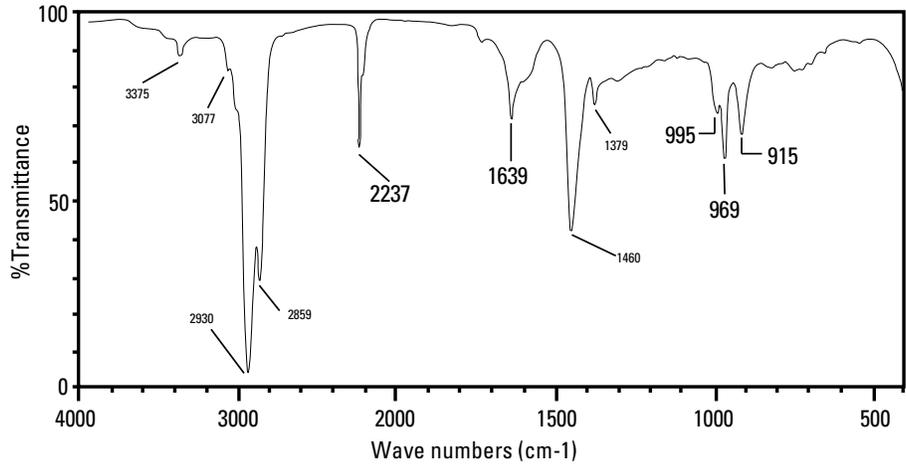


Figure 10-5. Spectrum of *pyrolyzed* nitrile rubber

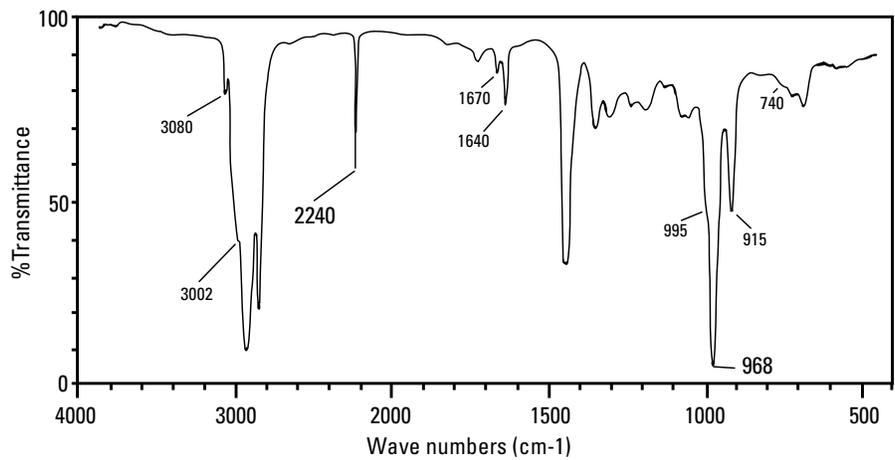


Figure 10-6. Spectrum of *crude* nitrile rubber

In this case the spectrum of the pyrolyzed sample is **similar** to that of raw rubber. The vinyl groups (995 and 915 cm⁻¹) are a lot larger. The band of trans 1-4 (969 cm⁻¹) is however more intense than that of the vinyl.

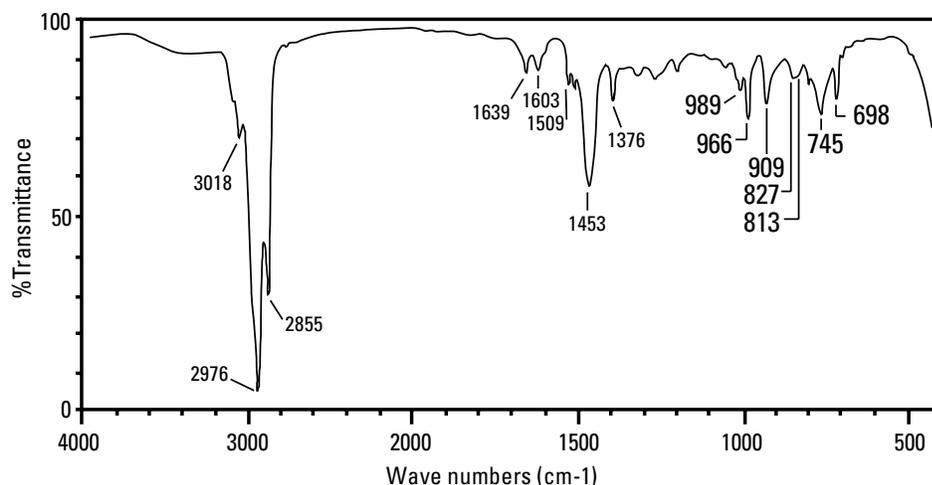


Figure 10-7. Spectrum of *pyrolyzed* polyethylene chlorosulfonate

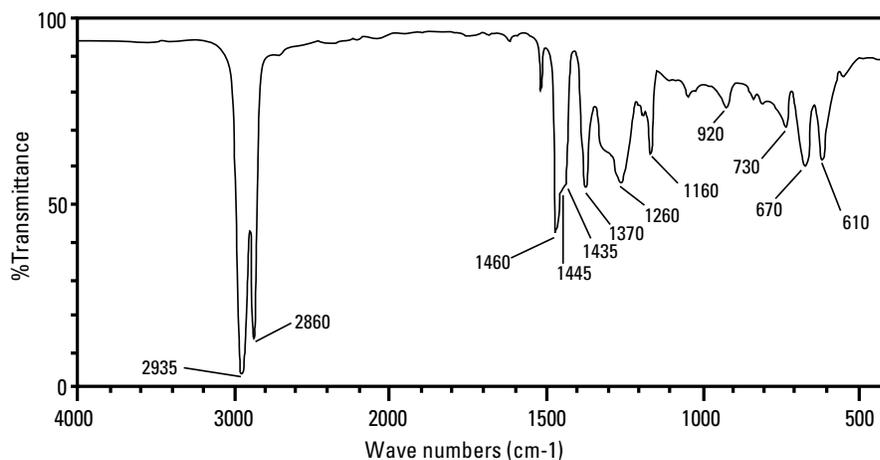


Figure 10-8. Spectrum of *crude* polyethylene chlorosulfonate

Here spectrum of pyrolyzed liquid is **completely different** from that of crude rubber largely because, during the pyrolysis, vapors of HCl and SO₂ are driven off, so there are no longer bands of the groups -SO₂- and -C-Cl (1370, 1260, 1160, 670, 610 cm⁻¹). However the spectrum of the pyrolyzed sample has a sufficiently characteristic spectrum.

There are advantages and the disadvantages to the pyrolysis technique:

Advantages

- It does not require expensive equipment.

- It is very fast.
- It permits the elimination of carbon black and additives.
- It is also valid for rubbers not vulcanized with sulfur.

Disadvantages

- It is a technique that it requires *work under a hood*.
- It is *not valid for a mixture* containing than one type of rubber, because during the pyrolysis, there is complex rearrangements of fragments from single rubbers.

ATR spectra

Rubbers are materials that, more than any other, are very well suited to being analyzed with ATR. Being elastic, they make very good contact with the crystal even with weak pressure.

There are advantages and the disadvantages of the ATR technique.

Advantages

- It is very fast and does not demand particular abilities.
- It is valid for all types of rubbers, vulcanized with sulfur or with other types of vulcanization.
- It is valid also for a mixture of rubbers.
- It is very versatile and has a high return on investment.
- With Ge ATR, high carbon black materials are easy to analyze. Diamond and other crystals are not useable for these, as the path length leaves too many totally absorbing bands.
- The spectral range can be wide open, depending upon the proper selection of crystal material.

Disadvantages

- ATR shows the effects of substances that migrate to the surface (lubricants) or those added to the surface like separating agents (talc).

Because ATR is a surface technique, it enhances these materials relative to the bulk. Samples should be cleaned or cut to reveal fresh surfaces.

Recent developments in ATR, including interchangeable crystals and high pressure devices, have greatly expanded the capabilities of this method. The speed of analysis in particular represents a huge gain over the classical methods. However, information about trace constituents (plasticizers, etc.) may still only be gotten after more extensive sample preparation, including the extraction steps discussed above. The final sample preparation, involving the KBr window, may be replaced with ATR analysis in many cases.

Specular reflection spectra

The specular reflection technique lends itself very well to the analysis of slabs, tapes, flat packings, etc.

Specular reflection is very useful in the analysis of slabs, tapes, flat packings, etc.

As noted in the chapter on Sample Preparation, in the case of carbon black, the only reflections from the sample are specularly reflected light, and it is necessary to apply the Kramers Kronig Transformation (or OMNIC's Advanced ATR Correction or use Ge crystals to obtain useful spectroscopic information.

Advantages

- It is very fast.
- It is also valid for a mixture of rubbers.

Disadvantages

- It cannot be used for mixtures without carbon black.
- An acceptable spectrum is not always obtained.

Diamond cell spectra

The diamond cell is an ideal accessory for the IR analysis of vulcanized rubber. However, samples containing high percentages of carbon black are not usable due to the strong absorption.

Advantages

- It is very fast.

- It requires a very small amount of sample.
- It permits the exploration of all of the spectral range.

Disadvantages

- The accessory is relatively expensive.
- It cannot be used in the presence of carbon black.

Single bounce ATR spectra

Single bounce ATR is also ideal for running vulcanized rubber spectra.

Advantages

- It is very fast.
- Using a Ge crystal, it is possible to obtain an excellent spectrum in the presence of large amounts of carbon black, as noted above.
- It requires *a very small amount* of sample.

Disadvantages

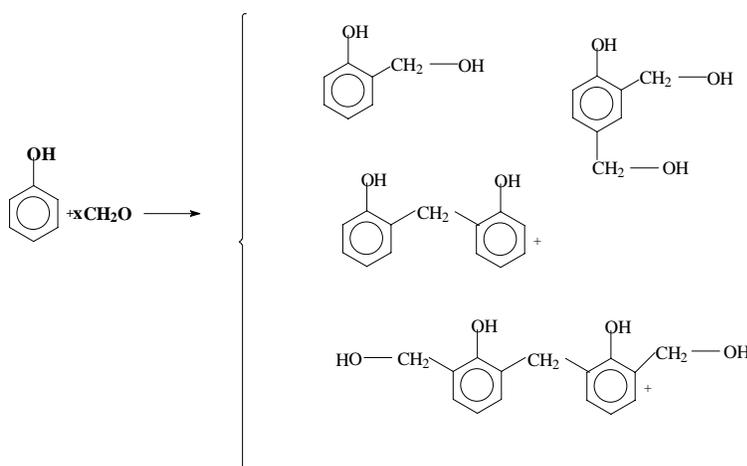
- It requires an upfront investment, albeit the rate of return on the investment is rapid due to increased productivity.
- With the exception of accessories like the Smart Orbit, most ATR crystals have limitations in spectral range.
- ATR is influenced by substances that migrate to the surface.

Chapter 11 Thermosetting Polymers

These are polymers whose lattice characteristics change when heated, yielding an irreversible three-dimensional lattice.

The most common thermosetting polymers, or more properly *thermosetting resins*, are **phenolic** resins, **ureic** resins and **melaminic** resins that are the products of reaction of formaldehyde with phenol, urea and melamine, respectively.

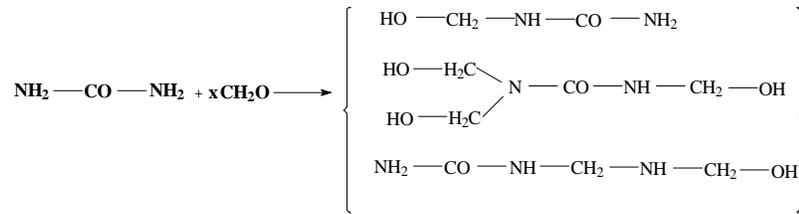
Before molding, the products are not truly proper polymers. They consist of simple molecules with a rather low molecular weight.



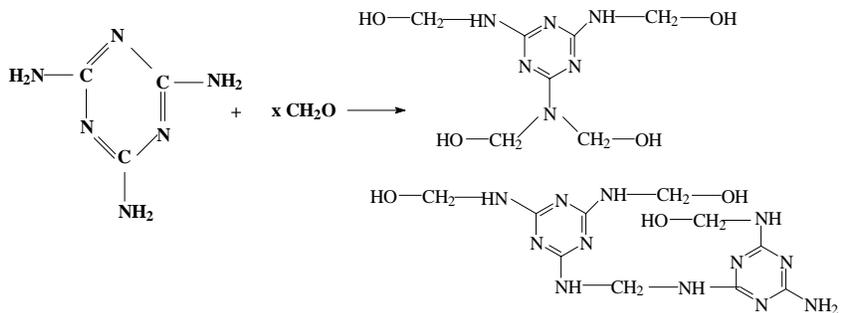
Phenol + formaldehyde = methylol- and methylene- phenol

The products containing mostly methylic groups are called industrial resols. They are not soluble in organic solvents and, in aqueous alkaline solution, are used to manufacture plywood and fiberboard panels, and molded materials.

Products rich in methylenic bridges are called industrial novolac. They are soluble in organic solvents and are used for varnishes.



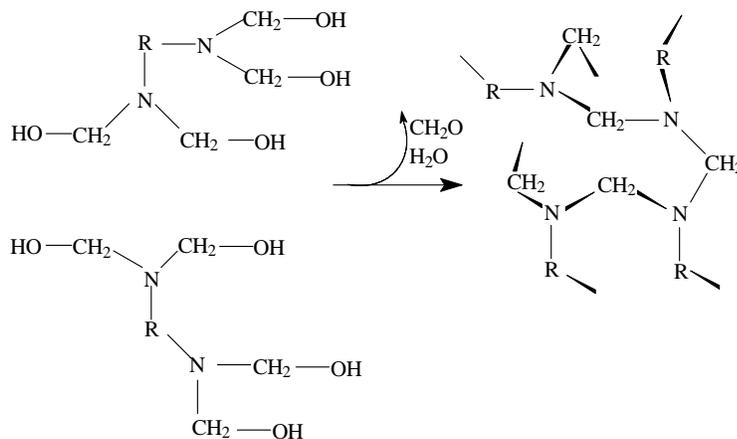
Urea + formaldehyde = methylol- and methylene- urea



Melamine + formaldehyde = methylol- and methylene- melamine

As you can see, the resulting small molecule does not have any obvious polymer features.

But when the product is molded in heat, the methylic groups react with formaldehyde by losing water. This leads to methylenic bonds in the three directions of space, which causes formation of a **spacially irreversible lattice** that is insoluble and un-meltable. Only at this point, can it be discussed as a polymer, even if it is a strange polymer, whose molecular weight is that of the entire manufactured product.



Before molding in heat, these products form very viscous aqueous solutions which for their colloidal aspect are called glues.

These glues are used in order to adhere thin layers of wood, which when warmed under pressure produces **plywood**.

When blended instead with wood flour or chips and then molded in heat, it produces **fiberboard panels**.

White or variously colored **paper sheets**, perhaps containing designs (ex: woodgrain), can be soaked with these glues. When deposited in layers and then molded with heating on top of fiberboard panels, these produce **enriched fiberboard** or **plastic laminates** like Formica[®]. Lower layers in the package of sheets are usually soaked with phenolic resin, the upper decorated ones with melaminic resin.

These glues are also added to wood dust, inorganic fillers and colored pigments; homogenized, dried at low temperature and milled. The **molded material** thus obtained is used, by means of hot pressing, to produce manufactured products like switches, camping plates, pre-fab furniture and bath accessories.

According to the type of product, the sample preparation for IR examination varies.

- For **glues**, a thin layer of material is spread on a KBr disk that is then dried at ambient temperature with a burst of air or dry nitrogen. The fact that the glue contains water is not an obstacle, since the quantity of water (50%) is so intermixed with the resin that it does not seriously attack the clarity of KBr.

Alternately, the product can be freeze-dried, so as to also prevent the reactions that can happen at ambient temperature, but that requires the acquisition of a freeze-dryer and takes longer.

- For **fiberboard panels**, the diamond cell or single-bounce ATR (with various types of crystals) are recommended. Some success with diffuse reflectance has been obtained after rough grinding of the sample.
- For **molded material**, ATR, KBr pellet preparation, and diffuse reflectance have been used.

- For the **enriched surface of the panels**, scraping of the surface with corundum which is then inserted into a diffuse reflectance accessory is useful. The scraped powder may also be run using a KBr pellet. This is also a sample for which ATR is an excellent choice
- For **molded materials**, the same techniques mentioned previously can be used.

IR spectra of thermosetting resins present in general very broad and complex bands, which are difficult to interpret. However, IR is practically the only usable technique that permits easy type recognition and gives good information on the fillers and pigments used. Several are noted in the schedules.

Phenolic resin (Schedule 17)

Ureic resin (Schedule 31)

Melaminic resin (Schedules 43 and 44)

Chapter 12 **Polymers That Set with Hardeners**

We have seen that thermosets harden with heat supplied during molding. But polymers also exist that harden (*i.e. produce a three-dimensional lattice*) by reacting with chemical compounds called **hardeners**.

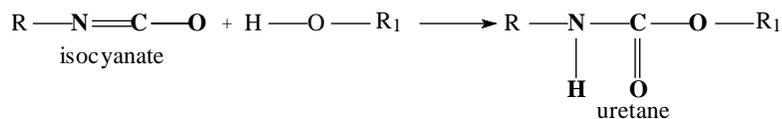
Among these polymers are noted:

- **Polyurethane resin** (Schedules 34, 35, 36, 37)
- **Epoxy resin** (Schedule 14)
- **Polyester resin**
- **Glycerophthalic or alkydic resin** (Schedule 27)
- **Silicon resin** (Schedules 45, 46)

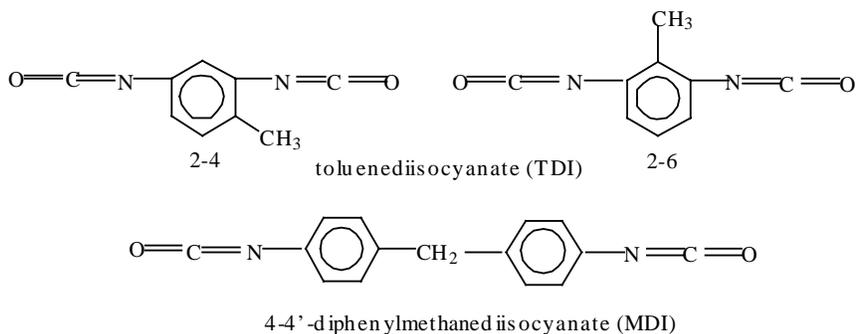
Urethanic Resins

These are polymers obtained by reaction of **diisocyanates** with **polyols**, i.e. compounds having 2 or more alcoholic groups.

The reaction of isocyanate with the alcoholic group yields the urethanic group



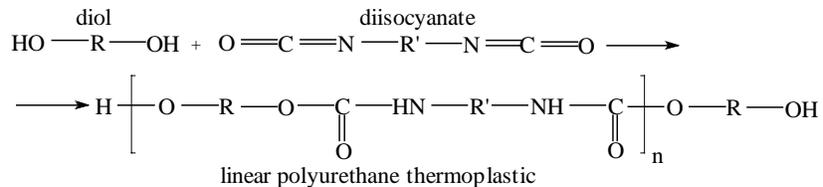
The diisocyanates used most are:



TDI is a diisocyanate mixture 2-4 and 2-6 toluene, and MDI is 4-4'-diphenylmethyl diisocyanate.

- **Thermoplastic polyurethanes**

If these diisocyanates are reacted with diol (HO-R-OH), **linear polyurethanes** are formed that have the characteristics of **thermoplastic polymers**, but fall in the category of the chemically hardened polymers.

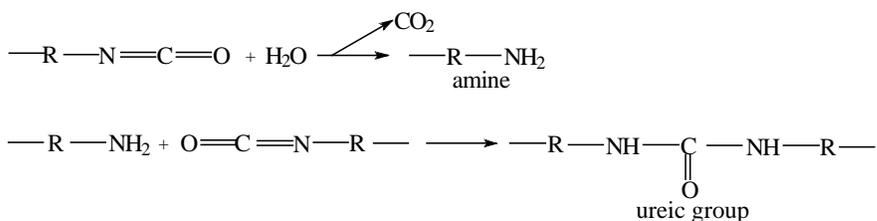


- **Expanded polyurethanes**

These are obtained by stirring the diisocyanates with **polyester or polyether prepolymers** containing free hydroxyl groups and with catalysts (amines and tin salts) and then adding water.

The isocyanic groups react with the hydroxyls developing the urethanic groups. The water also reacts with the isocyanic groups giving off CO_2 and forming aminic groups.

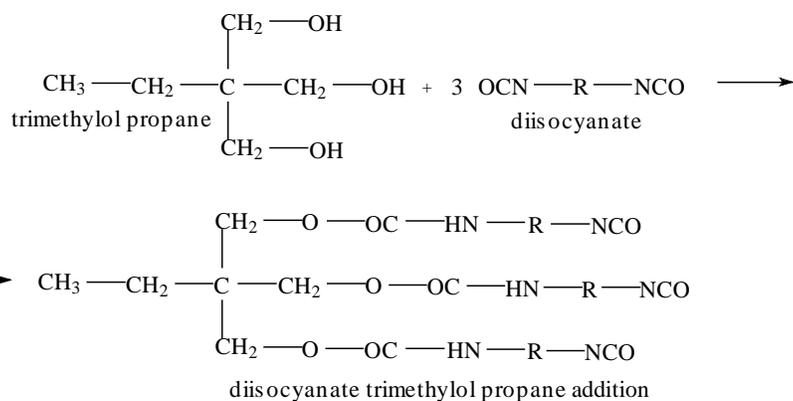
The CO_2 causes the expansion, while the aminic groups continue to react with the urethanic groups contributing to the formation of a lattice structure.



- **Glues and two part varnishes**

These materials consist of two components, one that contains isocyanic groups, and another that contains alcoholic groups and the amine based catalysts.

The compound containing isocyanic groups can be *an addition of trimethylolpropane* with three moles of diisocyanate, or a *urethanic prepolymer containing an excess of isocyanic groups*.



The compound containing hydroxyl can be a *polyol* or a *polyether* or *polyester prepolymer containing an excess of alcoholic groups*.

At the moment of usage, the two components are joined in a reaction between the isocyanic and the alcoholic groups producing cross-linked urethanic groups that form into a three-dimensional lattice.

- Polyurethanic rubbers (seen as rubbers and elastomers)

The sample preparation for IR examination depends upon the type of product.

To examine **expanded** products, ATR, single-bounce ATR or the diamond cell are recommended.

To examine the **prepolymers**, that normally have the consistency of viscous liquids or pastes, the transmission spectrum collected between two windows of KBr is a good method. ATR can also be used.

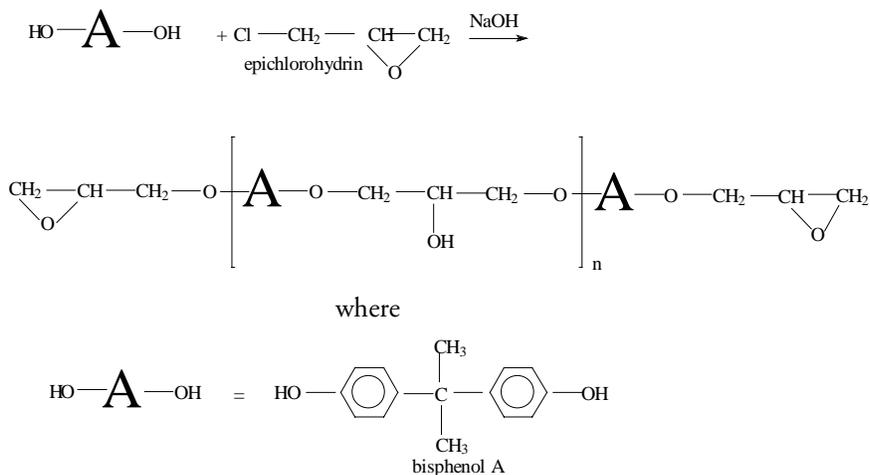
To examine **layers of varnish**, ATR, single-bounce ATR and the diamond cell are useful. Specular reflectance is also useful if the substrate is metallic or if a test coating can be placed on a metallic slide.

The IR spectra of polyurethanic resins contains information, first, about the nature of the resin. Additionally, the spectra provide information about the type of diisocyanate employed or at least can establish if it is aliphatic or aromatic. IR is also used:

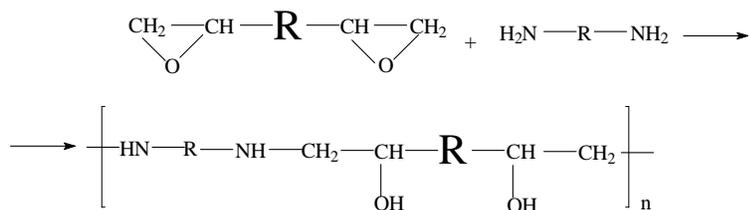
- To see if the prepolymer used is polyether or polyester.
- To detect the residual isocyanic groups and eventually to measure them.

Epoxy Resins

Some of the most common industrial resins are those that are obtained from bisphenol and epichlorohydrin. A prepolymer is obtained that contains ether and hydroxyl groups in the chain with two (or more) epoxy terminal groups. At the moment of usage, the prepolymer is stirred with compounds (hardeners) that react with the epoxy groups to provoke cross-linking and thus hardening.



The hardeners are constituted mostly from *diamine* that accordingly react with the epoxy groups as follows:



The secondary aminic groups subsequently react with the excess epoxy groups forming cross-linking ties.

Anhydrides and polycarboxylic acids also function as hardeners, creating cross-linked ester bridges.

Epoxy resins are used for adhesive and two part varnishes.

For infrared analysis, the sample preparations are similar to those noted previously for urethanic resin.

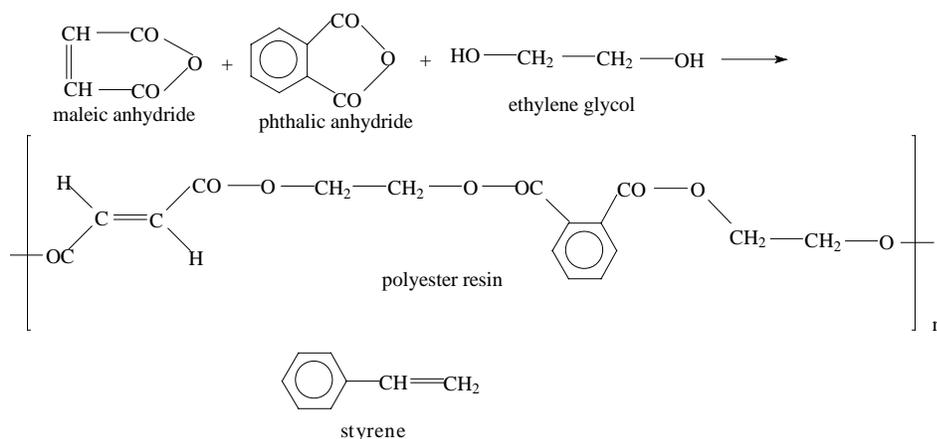
In the case of hardened products, IR spectra permit recognition of the nature of the resin. In the case of prepolymers or two member

compositions, it allows the characterization of the nature of the hardener and the concentration of the epoxy groups.

Polyester Resins

This is a general term used for *unsaturated polyester* resins obtained by the condensation of *maleic anhydride* and *phthalic anhydride* with a *glycol*. These are usually dissolved in a reactive monomer that is generally *styrene*.

The polyester resin can be mixed with fillers, pigments, glass fibers and, at the moment of the usage, the hardener consisting generally of *peroxides and Co salts*. This redox mixture induces a radical polymerization which also participates beyond the **double bonds of styrene to the double bonds of fumaric acid** (during condensation, maleic acid isomerizes to fumaric acid).



It then forms a compact three-dimensional mass in which the sequences of polystyrene are bonded irreversibly to the chain of the polyester.

Unsaturated polyester resins are used for varnishes and for fiberglass used in tanks, hulls of boats, auto body parts, etc.

Sample preparation for IR is done in the following way:

- **Non-reticulated polyester**

If fillers are present, dilute the sample with a solvent (ex: toluene) and centrifuge. The washed and dried solid part represents fillers, and the spectrum can be run using ATR or KBr pellet preparation. Diffuse reflection can also be used.

The spectrum of the liquid part is taken by making a film on a disk of KBr, or using a liquid ATR cell.

If fillers aren't present, the spectrum is quickly made by crushing a drop between two disks of KBr. The monomer reagent of the polyester can be observed in this manner. Frequently α -methyl styrene or methyl

methacrylate monomer is used rather than styrene. Then evaporate a drop on the disk of KBr and run the spectrum. In this way, the monomer reagent evaporates and the spectrum of the single polyester is obtained.

- **Reticulated polyester**

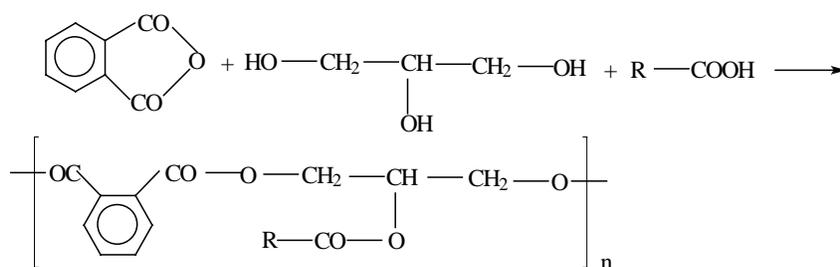
If the resulting varnish is deposited on a support, ATR is the best method. A diamond cell is useful if the sample is scraped or ground. If the support is metallic, specular reflection can provide excellent information also.

For **other types of manufactured products** the diamond cell or ATR are the best options.

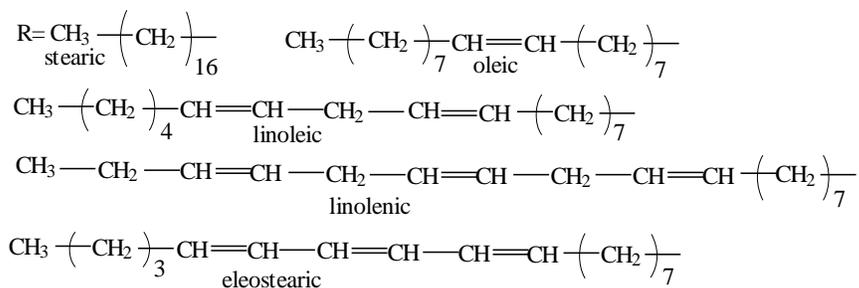
Glycerophthalic or Alkyd Resins

These resins are used for enamels and varnishes.

They are constituted substantially from polyesters obtained by condensation of phthalic anhydride with glycerin. A linear polyester is formed in which two of the three hydroxyls of the glycerin are engaged. The residual hydroxyl becomes esterified with fatty acids from the oils of wood, soya, dehydrated castor oil, tall oil, etc. These acids contain a remarkable fraction of unsaturated fatty acids (oleic, linoleic, linolenic, eleostearic). At times, the phthalic acid is replaced with saturated bicarboxylic acids (adipic, azelaic, sebacic). Glycerin is sometime replaced with trimethylolpropane or pentaerythrite.



R = radicals of fatty acids



The hardening action happens slowly in an oxygen atmospheric (which acts as the hardener). The conjugation and successive polymerization primarily consists of the formation of hydroperoxidic groups on the CH_2 close to the double bonds. These join between the molecules of fatty acids, forming a three-dimensional lattice with the glycerophthalic resin. In order to accelerate the slow dessication, Co salts of organic acids (naphthenic acids) are added.

Sample preparation proceeds as follows:

- Varnish or enamels

These consist of:

- a **solvent** (in general a *mixture of aromatic naphtha, turpentine essence, etc.*)
- **fillers and pigments**
- the **vehicle** (glycerophthalic resin).

The sample is first homogenized, and a portion is collected. This is diluted with an appropriate solvent (ex: aromatic hydrocarbon), and then centrifuged.

The liquid part contains *solvents* and the *glycerophthalic resin*. In order to characterize the solvents, the best technique is *gas chromatography*. To run the IR spectrum of the resin, deposit a film on a KBr window by evaporation of the solvent. The **spectrum of the resin** will reveal if the result is truly glycerolphthalic and if desiccated oils have been employed. To characterize the type of oil employed and the type of glycol, it is necessary to chemically treat the material using saponification and transesterification, and then resort to gas chromatography.

The spectrum can be taken of the washed and dried solid part using ATR, KBr pellet preparation, or diffuse reflectance.

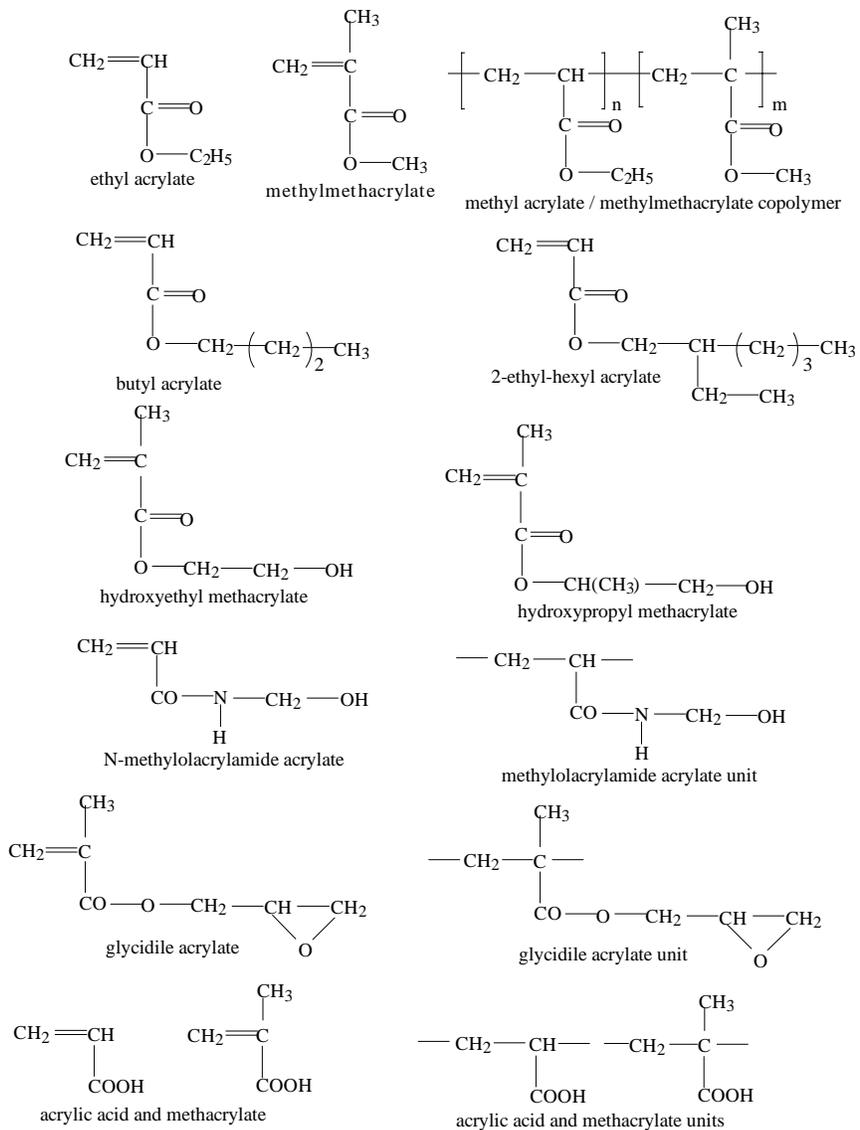
- Paint products

The simplest methods involve ATR or single-bounce ATR. If a very small chip can be detached with a razor blade, then the diamond cell works well. If the painted product is metallic, specular reflectance can also be tried.

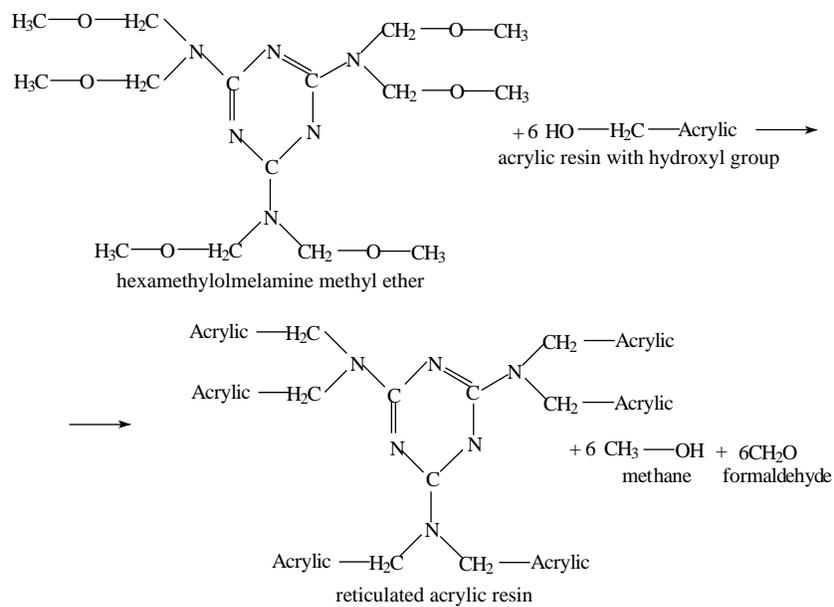
Acrylic Resins

Acrylic resins are mostly constituted from ethyl polyacrylate or its copolymer. Very commonly, this is methylmethacrylate, which increases the hardness, or acrylates of butyl and 2-ethyl-hexyl that instead increase flexibility. Acrylic resins do not contain unsaturations, so formation of the lattice structure requires modification of them with the introduction, in a polymerization phase, of a variable amount of 5 to 20% of functionalized monomer. Those used are:

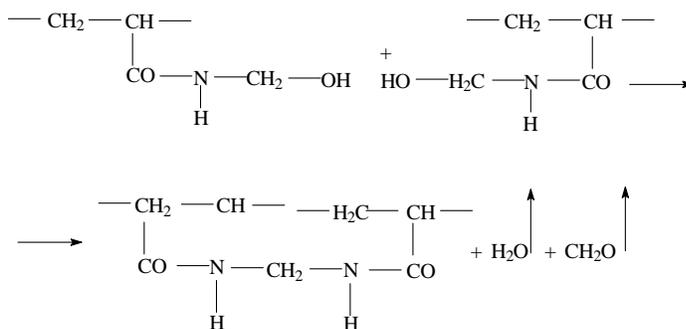
- hydroxyethyl and hydroxypropylene methacrylate to introduce hydroxylic functionality
- methylol-acrylamide acrylate
- glycidile methacrylate in order to introduce epoxy function
- acrylic acid or methacrylate to introduce the carboxylic acid function.



Resins with **hydroxyl functional groups** usually become hardened by adding melaminic resins and in particular by *hexamethyl melamine* or its *methyl ether*.



Resins with **acrylamide methylolate**, in presence of an acid catalyst, reticulate with heating at approximately 120°C.



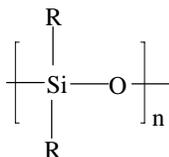
Resins with **epoxy groups** become reticulated with epoxy hardeners.

Resins with **carboxylic acid groups** become reticulated by treatment with epoxy resins.

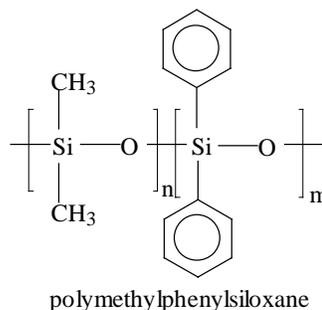
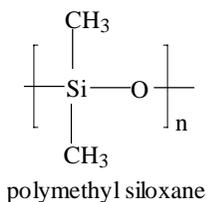
IR spectroscopy permits the characterization of the type of acrylic ester used.

Siliconic Resins

Siliconic resins are constituted from polyalkylsiloxane



where R consists mostly of methyl group (-CH₃). In some applications R can be in part replaced by a phenyl group.



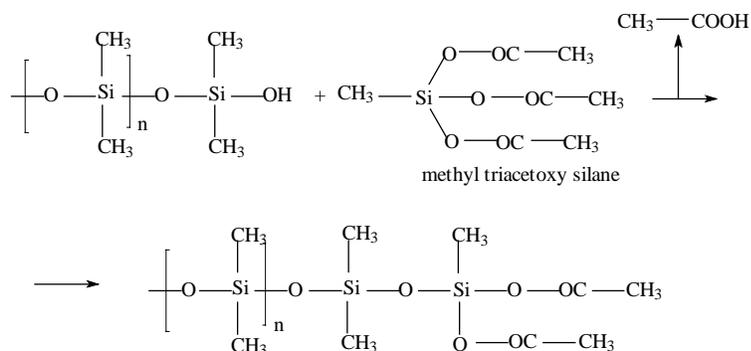
Applications are found, such as *fats and lubricating oils, rubbers, resins for adhesives and sealants, varnishes, impregnated waterproofing for wovens, etc.*

Spectra of fats and oils, used like high temperature lubricants, are run simply on a heated ATR or as a film between two windows of KBr.

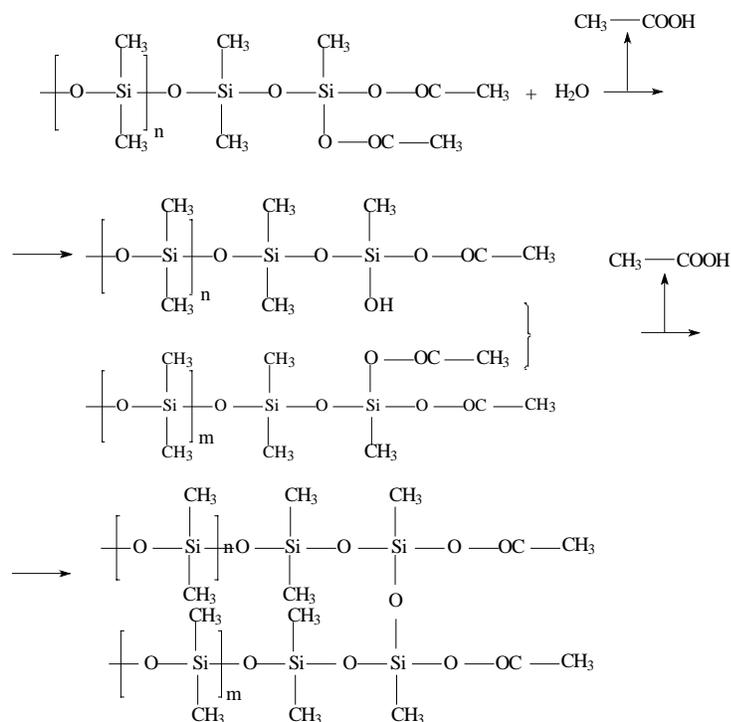
The spectroscopy of **rubbers** has already been discussed.

Resins for adhesives, sealants, varnishes, etc, become reticulated in several ways. Most commonly, they are made in a particular way for sealants and adhesives as follows:

In the macromolecule of polymethyl siloxane, two *acetoxy* groups are introduced making a terminal *silanol* (-Si-OH) with *methyl triacetoxysilane* and removing the acetic acid that is developed.



The product obtained is then kept out of contact with air until the moment of usage. With usage, it comes in contact with atmospheric humidity. First, the acetoxy groups react with H_2O liberating acetic acid (which goes away) and forming an extremely reactive *silanol* group. The latter immediately reacts with the *acetoxy* group of a nearby macromolecule, freeing acetic acid and forming a Si-O-Si bridge.



With more humidity, the mechanism repeats until all the acetoxy groups that have reacted forming numerous Si-O-Si bridges and therefore creating the product lattice.

Taking the spectra before the product forms the lattice is done quickly by forming a capillary film between two windows of KBr.

After the product lattice is created, the spectra can be run with a diamond cell, ATR or single-bounce ATR.

IR spectroscopy of product lattices permits confirmation of the siliconic nature and also the distinguishing between polymethylsiloxanes and polyphenylmethylsiloxanes.

In prepolymers and two part compounds, IR can be used to characterize the reactive groups and the nature of the hardeners.

Chapter 13 Woven Fibers

Woven fibers are polymeric materials, natural or synthetic, used for the production of thread and wovens.

Natural Fibers

These have been used since antiquity and have vegetable or animal origin.

Vegetable fibers are constituted from cellulose. The most important are:

- **Cotton** (spectrum 16) that is gained from the fruits of the *Gossypium hirsutum* and the *Gossypium barbadense* of the family of Malvaceae (length of the fiber is 10-40 millimeter; width 20 μ).
- **Linen** that is gained from stems of the *Linum usitatissimum* of the family of Linaceae (fiber length 12-26 millimeter; width 16 μ).
- **Hemp** that is gained from stems of the *Cannabis sativa* of the family of Cannabaceae (fiber length 7-60 millimeter; width 35 μ).
- **Jute** that it is gained stems of the *Corchorus capsularis* and of the *Corchorus olitorius* of the family of Tiliaceae (fiber length 10-32 millimeter; width 16-20 μ).

Animal fibers are constituted from *proteins*. The most important are:

- **Wool** that is gained from the fleece of sheep. It is constituted from a cheratinic type of protein (contains sulfur).(fiber length 40-350 millimeter; width 16-70 μ).

Other types of wool are:

Cashmere obtained from fleece of *Capra hircus blythi*

Mohair or angora obtained from fleece of *Capra hircus angorensis*

Camel hair obtained from the camel with two humps (*Camelus bactrianus*)

Alpaca obtained from the hair of alpaca (*Lama glama pacos*)

Vicuna obtained from the hair of vicuna (*Lama vicugna*)

- **Silk** (Schedule 33) that is obtained from the cocoon of the silkworm or silkworm larvae of the butterfly, the silkworm moth (*Bombyx mori*). It is constituted from two proteins: fibroin and sericin. During processing of the silk, the sericin becomes all or in part removed. (fiber length 700-1200 mm; width 13-16 μ)

The **sample preparation** for IR examination proceeds according to the type of manufactured product to be examined.

With **wovens and thread** use the following techniques:

- Diamond cell (better at high pressure)
- Micro ATR. The use of a microscope allows single fibers to be targeted, and the ATR crystals easily strike the fiber and give detailed information.
- Single-bounce ATR accessories. Use of viewing optics is optimal, for positioning the fibers.

With **single fibers**, the most outstanding technique uses the *infrared microscope*. The combination of optical and IR microscopy allows the complete characterization of the fiber: chemical nature (with IR), and morphology (with the optical microscope). This technique is particularly useful in the case of mixtures of several types of fibers.

Artificial Fibers

These fibers, of cellulosic nature (rayon and acetate), are obtained with opportune treatments on the cellulose of wood or the *linter* of cotton.

The ways to prepare the sample and carry out IR spectra are the same ones used for natural fibers. In the case of **cellulose acetate** (Schedule 26), one can turn to film from solution, taking advantage of the **solubility in various solvents** (acetone, chloroform, methylene chloride, glacial acetic acid).

Nitrocellulose (Schedule 42), obtained by partial nitration of the hydroxyl, **is not a woven fiber**, but a resin used for varnishes, called nitro. It is soluble in acetates and acetone. If the nitration is complete one obtains an explosive called nitrocellulose or *guncotton*.

Infrared provides good information about these fibers, but it may sometimes be difficult to differentiate between them.

In the case of cellulosic fiber, the *cellulosic nature* will certainly be assessed. Natural fibers, constituted from crystalline cellulose, can be difficult to distinguish from each other by means of their IR spectra. The weak absorption bands due to small amounts of minor components can be useful. With respect to cotton (pure cellulose), the spectrum of jute introduces two weak bands, for example, at 1600 cm^{-1} and 1505 cm^{-1} probably due to proteic substances, while that of linen introduces a weak band at 1740 cm^{-1} due to a small amount of compounds containing ester groups.

The difference between the spectrum of cotton and that of rayon is due only to the fact that, in cotton the cellulose has a crystallinity of approximately 75% and is practically all α -cellulose. In rayon, the crystallinity comes down to approximately 35% and is β -cellulose. However, these differences are very difficult to see, and it is necessary therefore to have experience in the field.

Also for **proteic fibers**, only the proteic nature can be assessed. It is not easy to distinguish the difference between wool and silk in the IR spectrum.

Much simpler instead is the determination of **cellulose acetate** (spectrum 26) that unequivocally introduces the bands of acetic ester.

$$\nu_{\text{C=O}} = 1745\text{ cm}^{-1}$$

$$\nu_{\text{C-O-C}} = 1230\text{ cm}^{-1}$$

Synthetic Fibers

These are polymers obtained from chemical compounds that are not comparable to natural polymers (cellulosic or proteic). The chemical nature of these polymers will be described shortly, as well as the melting points and the solubility in some solvents (parameters that can serve for sample preparation for IR examination).

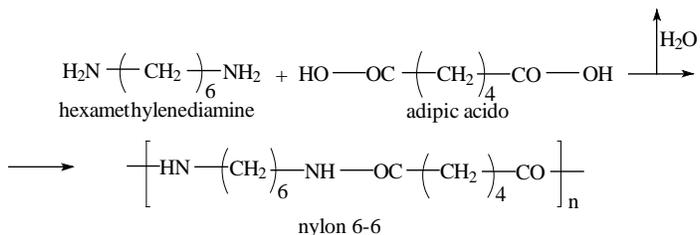
Polyamides

The polyamides (or nylon) are of two types:

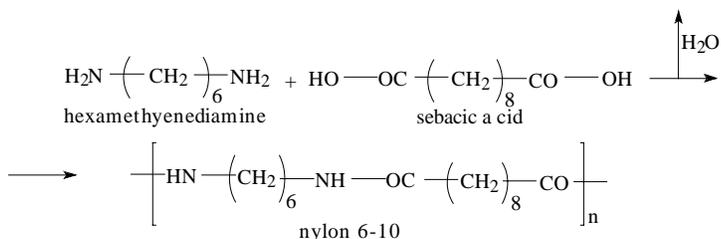
- Those indicated with two numbers (nylon 6-6, nylon 6-10).
- Those indicated with one number (nylon 6, nylon 11, nylon 12)

Polyamides indicated with two numbers are polymers of condensation between one diamine and bicarboxylic acid. The first number represents the number of carbon atoms of the diamine. The second number represents the number of carbon atoms of the acid.

For example, nylon 6-6 is the polymer of condensation between *hexamethylene diamine* and *adipic acid*,



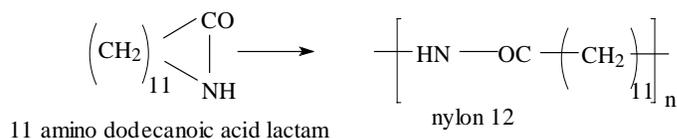
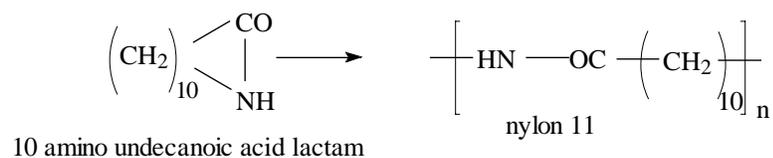
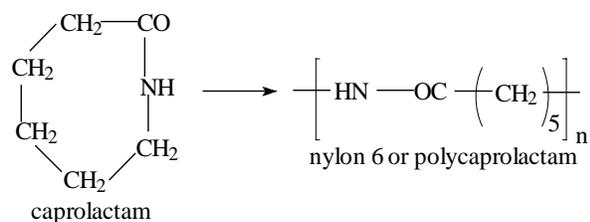
while nylon 6-10 is the polymer of condensation between *hexamethylene diamine* and *sebacic acid*.



Hexamethylene diamine has 6 C, adipic acid has 6 C → NYLON 6-6

Hexamethylene diamine has 6 C, sebacic acid has 10 C → NYLON 6-10

Polyamides indicated with one number are polymers of addition of a lactam (i.e. cyclical amide). The number represents the number of carbon atoms of the lactam.



Characteristics useful for sample preparation are given for the main types of nylon.

- NYLON 6-6

Chemical nature: polyamide condensation of hexamethylene diamine and adipic acid (see above discussion)

Solvents: formic acid, glacial acetic acid, meta-cresol, trifluoroethanol

Melting point = 250°C

- NYLON 6

Chemical nature: polyamide of addition of polycaprolactam (see above discussion)

Solvents: formic acid, glacial acetic acid, meta-cresol, trifluoroethanol

Melting point = 225°C

- NYLON 11

Chemical nature: polyamide from polycondensation of ω -amino-undecanoic acid (see above discussion)

Solvents: dimethyl formamide, metacresol, trifluoroethanol. It is not dissolved cold in either formic acid or in glacial acetic acid.

Melting point = 189°C

- NYLON 12

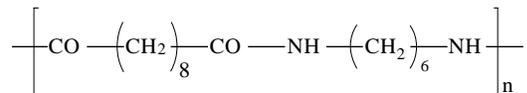
Chemical nature: polyamide from polycondensation of 11-amino-dodecanoic acid (see above discussion)

Solvents: m-cresol

Softening point = 175-180°C

- NYLON 6-10

Chemical nature: polyamide from polycondensation of hexamethylenediamine and suberic acid



Solvents: trichloroethanol, m-cresol, formic acid

Melting point = 240°C

The spectra of polyamides can be run in a number of ways:

- As a thin film obtained by evaporation of the solvent on a *disk of KBr*. The odd behavior of the solvent (formic acid, m-cresol, etc.) is not terrible.
- As a film obtained by hot pressing (over the melting of softening temperature).
- Using a *diamond cell* at high pressure.

- Using *micro ATR*. Again, this is an excellent analysis tool when samples are single fibers.
- Using a single-bounce *ATR* accessory, preferable with viewer.

To estimate the degree of orientation of the stretched film, proceed as described earlier.

The spectra of various polyamides are very similar to each other (Schedule 29). For this reason, it is very easy one to see if a fiber or woven material is made up of polyamides. It is more difficult to distinguish between one polyamide and another, but it is possible. For this purpose, it is necessary to neglect the main bands (common to all polyamides) and focus attention on the bands of smaller intensity that are found in the interval of 1400-900 cm^{-1} . These are crystallinity bands, and can be used to distinguish one type of nylon from the other (spectrum 29 bis). **In order to improve the possibility of succeeding with this type of investigation, it is advisable to increase the crystallinity of the polymer by means of an *annealing* operation.** Annealing involves maintaining the polymer film for some hours at the melting temperature and then very slowly cooling it (5 or 6 $^{\circ}\text{C}$ degrees per hour) to ambient temperature.

In contrast, it is nearly impossible to determine the polyamidic copolymer. In this case it is useful to resort to acid hydrolysis (boiling 20% HCl) and then to use chromatographic techniques and IR to identify the chlorides of amines, chlorides of amino acids, and bicarboxylic acids.

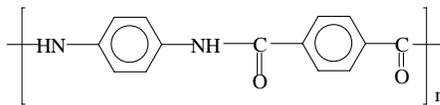
IR can serve to characterize, and if necessary, to determine concentration, of impurities and additives. For example, in nylon 6 it is possible to see and to quantify the residual monomer (caprolactam) based on the bands at 893 cm^{-1} and 868 cm^{-1} . It is also possible to see (and quantify) the aryl sulfonamides, used as plasticizers.

Aromatic polyaramides or polyamides

The two principle resins of this type are *KEVLAR*[®] (Du Pont) and *NOMEX*[®] (Du Pont).

- KEVLAR

KEVLAR is the product of condensation of p-phenylene diamine and terephthalic acid.



This fiber has exceptional thermal, mechanical and chemical characteristics. The material is actually a *liquid crystalline polymer*, where the alignment of the chains provides great material properties.

Melting point = 550°C

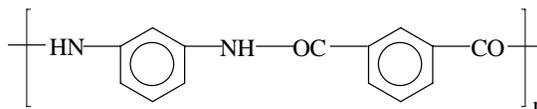
Solubility = insoluble in all solvents

KEVLAR is used in a generalized manner as a highly stiffened material of epoxy resins (or hardening resins) for parts used in aeronautics; for hulls of racing boats; in manufacture protective helmets; and, substituting asbestos, for brakes discs and clutches.

It is also employed for racing sails (as a cloth-like material) and in bulletproof vests (as a rigid material).

- NOMEX

NOMEX is the product of condensation of m-phenylene diamine and isophthalic acid.



This fiber also has exceptional thermal, mechanical and chemical characteristics.

Melting point = 375°C

Solubility = insoluble in all solvents

It is used for fireproof fabrics, such as cover-alls and gloves for race car drivers, as a replacement for asbestos.

Given their melting and solubility characteristics, it is nearly impossible to take the spectra of arylamides in the form of a film. The recommended sampling methods are

- the *diamond cell* at high pressure.

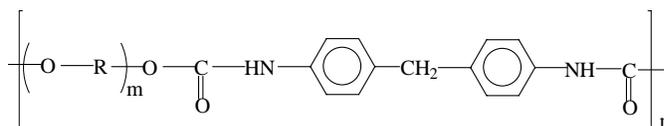
- single-bounce *ATR*, with Si, Ge or diamond.
- *micro ATR*, especially for small pieces.

The IR spectra (schedule 32) serve only to characterize the nature of the arylamide.

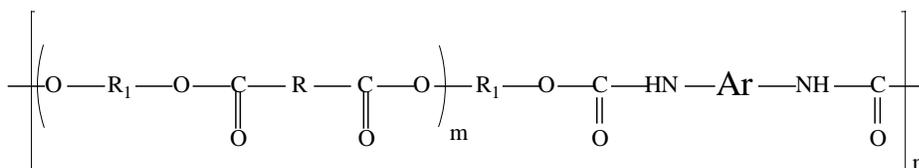
Polyurethanic elastomers

These are fibers used for the webbing of woven elastic.

Chemical nature: polyurethanes are obtained by treatment of polyalkylene glycol with diisocyanate (usually MDI)



or of a polyester terminated with hydroxyls with aromatic diisocyanate where Ar is usually MDI.



The polyether or polyester part is long and flexible, while the urethanic part is short and rigid, because of the strong hydrogen bonds that causes it to crystallize. The **melting temperature** of the urethanic part is approximately 200°C or greater. Above this temperature, the polymer flows and is formable. Under this temperature the urethanic parts become rigid and give origin to the points of physical vulcanization, conferring elasticity to the fiber. In general the result is then of *thermoelastomers*.

Solubility. In the case of thermoelastomers, those not vulcanized chemically, the best solvent is dimethylformamide.

For sample preparation, the characteristics of solubility and moldability could be taken advantage of in order to obtain a film. However, as for the arylamides, it is much more practical to use:

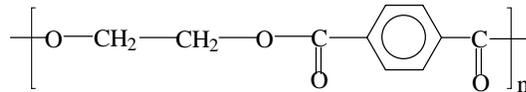
- the diamond cell.
- single-bounce *ATR*.

- ATR.

Infrared can easily confirm the polyurethanic nature. More in depth analysis allows some idea regarding the type of polyester and polyether used (schedules 36 and 37).

Polyester

Chemical nature: Polyesters are nearly exclusively constituted from polyethyleneterephthalate, that is from the product of polycondensation of ethylene glycol and terephthalic acid.



Melting point: 290°C

Softening temperature: 230-250°C

Solubility: It is dissolved in phenol, or chlorophenol, chloroacetic acid

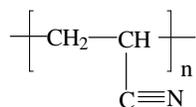
For sample preparation, the characteristics of solubility and moldability can be taken advantage of in order to obtain transparent films, but it is again much more practical to use

- the diamond cell.
- single-bounce ATR.
- ATR.

Beyond confirming the nature of the sample (spectrum 20), IR examination can serve to estimate the degree of crystallinity and orientation of the fiber.

Polyacrylic

Chemical nature: They are nearly exclusively constituted from polyacrylonitrile.

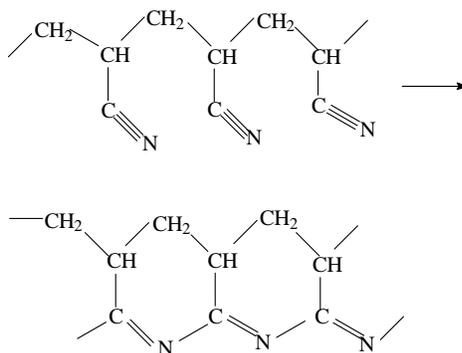


Melting point: 319°C (extrapolated). It partially decomposes before melting.

Softening temperature: 210-230°C

Solubility: It is dissolved in dimethylformamide and dimethylsulfoxide.

Heating polyacrylonitrile tends to degrade it due to polymerization of the triple bonds $C\equiv N$.



This reaction forms a series of conjugated double bonds $C=N$ that are chromophores responsible for the progressive yellowing → browning → blackening of the fiber.

Thus the preparation of the film by hot pressing is not advisable.

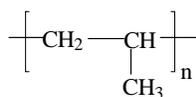
Instead the preparation of the film by evaporation from a solvent is possible. Once again, however, the most advisable techniques are:

- diamond cell.
- ATR.
- single-bounce ATR.

Besides confirming the nature of the material (schedule 38), IR examination can serve to estimate the degree of degradation of the fiber.

Polypropylene

Chemical nature: These materials are constituted from isotactic polypropylene.



Melting point: 160-170°C

Solubility: It is not dissolved in normal solvents.

The moldability characteristic can be taken advantage of in sample preparation to obtain transparent films, or the following techniques can be used:

- diamond cell.
- ATR.
- single-bounce ATR.

Beyond confirming the nature (spectrum 2), IR examination can serve to estimate the degree of crystallinity and orientation of the fiber.

Chapter 14 Quantitative Analysis

Beer-Lambert's Law

Even though infrared is an excellent qualitative technique, in the polymer field there is a certain use for the technique in more quantitative analyses.

This is true for two fundamental reasons:

- The technique is **very fast**.
- **It is not necessary that the polymer is soluble.**

In the Beer-Lambert relationship

$$A = k s C$$

four variables appear:

- Thickness, s
- Concentration, C
- Absorbance, A
- Absorption coefficient, k

We shall investigate each of these variables in more detail.

Thickness

Length is measured with units: μm , millimeter, or cm. The unit more commonly used is cm.

To measure thickness can seem somewhat simple, but instead in many cases it is not.

In the case of pure liquids and solutions, the problem is very simple: the pathlength is that of the cell. The thickness of an IR cell can vary from 0.006 cm (6 μm) to 1-2 cm, but generally it is in the order of 0.050-0.100 cm. The supplier of the cells also provides the thickness, but this can vary meaningfully in time due to loosening of screws, or corrosion of the delicate material of the windows. Thus it is necessary to measure the

thickness often. Measuring the thickness is done utilizing the interference fringe of an empty cell.

Quantitative analysis in solution, and therefore the use of a cell for liquids, is the advised practice every time that it is possible. However the use of a cell for liquids is a rare enough phenomenon in the quantitative analysis of polymers.

In fact, polymers liquid are very rare and are too viscous to be able to introduce them in the cell. Moreover it is difficult to find cells with a thin enough thickness to allow the bands of the polymer to register on the absorbance scale. As well, the spectra of polymers in solution are very rare.

In fact the solvent must **dissolve** the polymer and have **little absorption** in the measured zone.

For these two conditions to take place at the same time is not a very common event.

As we shall subsequently see, the use of a cell, and therefore analysis in solution, is instead common accepted practice for calculation of the coefficient by means of model compounds.

In the case of polymer films, the measure of the thickness cannot be made even with high precision micrometers. The microirregularities of the film distort the measurement, often in significant way.

The best method involves using a circular punch to make a small circle of film with a diameter 2.5 cm.

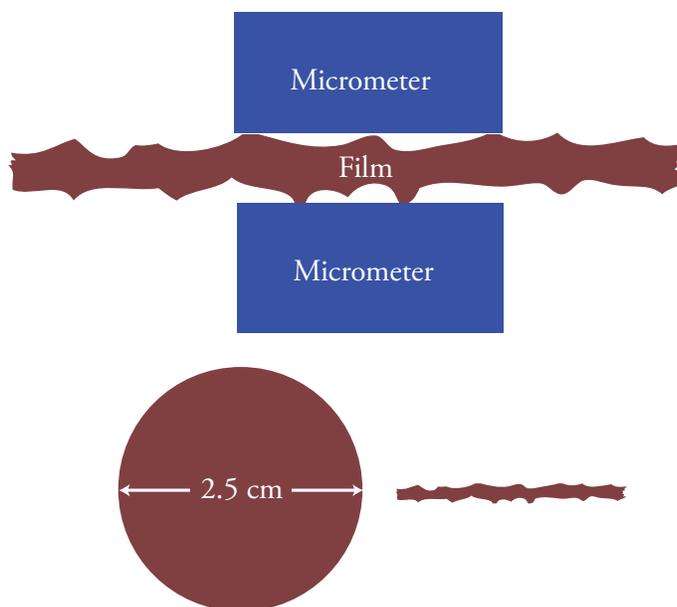


Figure 14-1.

The small circle, similar to a cylinder, is weighed with an analytical balance. Then the weight P (in grams) is divided by the surface S in cm^2 .

$$s = \frac{V}{S} = \frac{P}{S \cdot \delta} \quad s_p = s \cdot \delta = \frac{P}{S}$$

The relationship between P and S is not the thickness of the film, but the product of the thickness and the density, δ , of the polymer and a constant. Therefore s_p can be used in place of s in the Beer-Lambert law, as it is also proportional to the absorbance.

Concentration

Concentration, in the Beer-Lambert law, can be expressed in units of measure that we prefer. Normally in spectrophotometry it is used to express the concentration in two ways

$$C_{\text{Molar}} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$C\% = \frac{\text{grams of solute}}{100 \text{ ml solution}}$$

To make a usable solution for spectrophotometric measurement, there are two requirements necessary for the solvent:

- It must dissolve the solute well, without the suspended particles that remain.

- It must be sufficiently transparent in the measured range.

For ideal measurement the solvent would have to transmit an energy amount of at least 25% that of incident ($T=0.25$), through a thickness of 1 millimeter. Solvents that satisfy this requirement are those reported in Table 14-1.

Table 14-1. IR Solvents (having spectral intervals in which there is %T greater than or equal to 25 in 1mm cells)

Solvent	Formula	Spectral Intervals (cm^{-1})	
Carbon sulfide	CS_2	4000-2350	2100-1640
		1385-875	845-650
Dichloromethane	CH_2Cl_2	4000-3180	2900-2340
		2290-1500	1130-935
Chloroform	CHCl_3	4000-3100	2980-2450
		2380-1520	1410-1290
		1155-940	910-860
Carbon tetrachloride	CCl_4	4000-1610	1500-1270
		1200-1020	960-860
Tetrachloroethylene	$\text{Cl}_2\text{C}=\text{CCl}_2$	4000-1375	1340-1180
		1090-1015	

There are very few solvents, and between them, they are often toxic or dangerous and must therefore be used with appropriate precautions.

The modern spectrophotometer can work with far inferior transmittance values, and the window of transparency can be also very narrow as well: i.e. the solvent can greatly absorb in all of the spectral regions provided that it has a little transparency in the narrow range in which the measured band falls.

Removal of the solvent. The solvent is not always completely gone in the measured range. For example, in the figure below, the bands of the solvent, B and D, and, even in a minor amount, E, interfere in the determination of band of the solute, C, raising the absorbance.

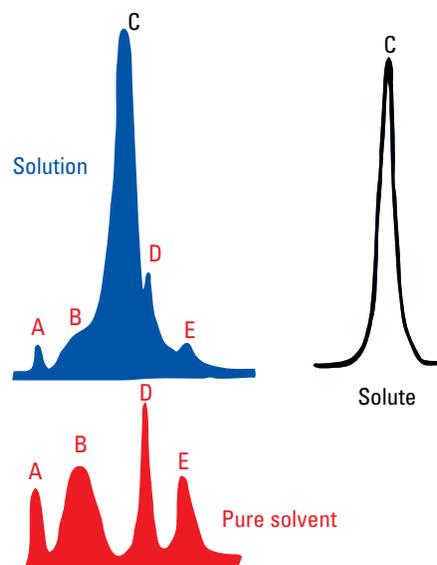


Figure 14-2.

If the concentration of the solute is very low, the spectrum of the solvent can be gotten directly, spectroscopically in the same cell.

If the concentration of the solute is high, it must be calculated differently. In fact if X is % concentration of the solute, $100-X$ will be the concentration of the solvent. Therefore if we subtract the pure solvent, subtract 100 instead of $100-X$, therefore obtaining a negative value of the absorbance measure of band C. In other words, there will be negative peaks corresponding to A, B and E. It is necessary then to choose a band of the solvent outside the measured range (for example, the band A) and carry out the spectral removal of the solvent by annulling this band. The other bands of the solvent (those comprised of B, D, and E) that interfere in the measurement will be annulled automatically.

The clean band of the solute is therefore obtained, from which we will measure the absorbance to determine its concentration.

Absorbance or optical density

The absorbance $\left(\log \frac{1}{T}\right)$, being a logarithm, is a pure number, and thus it does not have units of measure, and its value can go from 0 to ∞ .

In order to eliminate the influence of diffuse light and the influence of the nearby bands, always measure the absorbance with respect to a base line (net absorbance).

According to the base line AB (Figure 14-3), the absorbance of the band ν_1 is given from $A_3 - A_2$; while for the second base line CD, the absorbance is given from $A_3 - A_1$. The absorbance of the band ν_3 , with respect to the base line CD, will be given from $A_4 - A_1$.

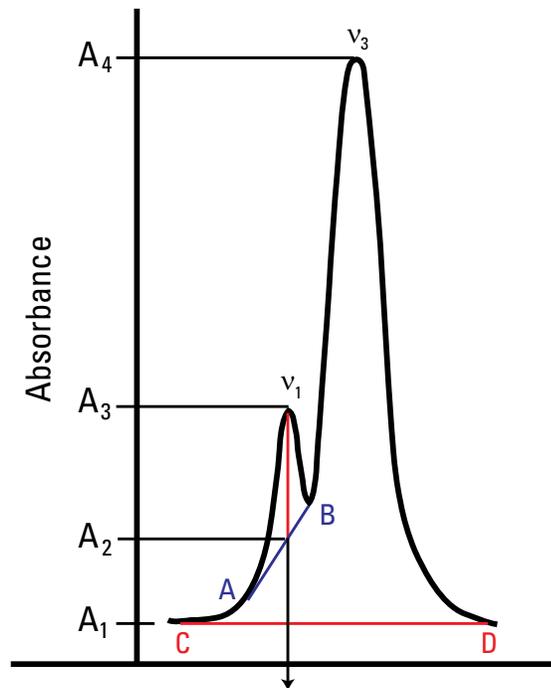


Figure 14-3.

Important:

- To have **significant results** in quantitative measurement, the value of absorbance must be

$$A \leq 0.8$$

- The base line can obviously be chosen at will (within certain limits) provided that we remember to always use the same one. If it is desired to change the base line, it is obviously necessary recalculate the coefficient of absorption with the new base line: that means changing the analytical method.

The choice of base line is left to good sense and experience. If, for example, our scope is to measure the small band on the flank of a more intense band (see previous Figure), it is more logical to use base line, AB, rather than

CD. In fact, with AB a great part of the influence of the more intense band is eliminated.

Absorption coefficient

The absorption coefficient depends on:

- the **units of measure** with which **concentration and thickness** are determined.
- the *characteristics of the oscillator* that lead to the absorption.

The unit of measure is

$$k = \frac{A}{C \cdot s}$$

Since A is a pure number, **the units of measure of k depend on the units of measure of C and s.**

In the literature there are two principle ways to express k:

- the molar coefficient of extinction

This is indicated by ϵ and is gotten when C is expressed in **moles/liter** and s in **cm**.

- E 1 percent 1 centimeter

This is indicated with $E_{1cm}^{1\%}$ and it is gotten when the C is expressed in **grams/100 ml** of solution and s in **cm**.

$$E_{1cm}^{1\%} = \epsilon \cdot \frac{10}{M} \quad \epsilon = E_{1cm}^{1\%} \cdot \frac{M}{10}$$

There are two simple expressions to give ϵ and $E_{1cm}^{1\%}$ and vice versa.

Nature of the oscillator

The absorption coefficient essentially **depends on how much the dipolar moment varies during oscillation**. If the variation is high, the value of k will be very high and vice versa. In particular if there is **not a variation of the dipolar moment, k is equal to 0**.

For example, in the butadiene acrylonitrile copolymer (Figure 14-4)

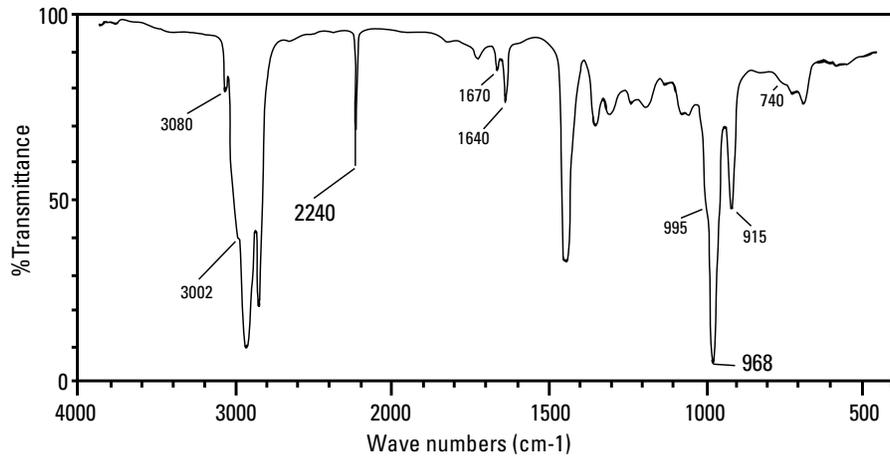
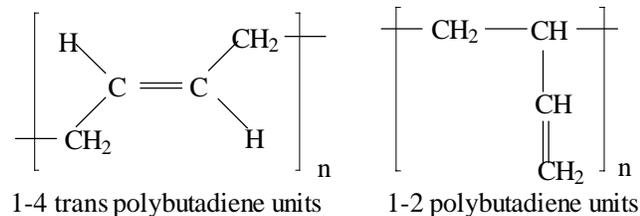


Figure 14-4. Nitrile rubber – (NBR) (low nitrile)

The butadiene units are present mostly in a 1-4 trans structure and with a small amount of 1-2 units.



If we look for the bands due to C=C stretching of the two units, it is observed that the band due to 1-4 trans units

$$\nu_{\text{C=C}} \text{ 1-4 trans} = 1670 \text{ cm}^{-1}$$

and is much weaker than the 1-2 units,

$$\nu_{\text{C=C}} \text{ 1-2} = 1640 \text{ cm}^{-1}$$

although the 1-4 trans units are by far the most prevalent.

This phenomenon is due to the fact that the 1-4 trans unit possesses a symmetrical center that is maintained during the oscillation, for which there is practically no variation of the dipolar moment and therefore absorption is practically equal to 0.

The vinyl $-\text{CH}=\text{CH}_2$ of 1-2 units is instead an asymmetric group (the right part is different from the left) for which there is a discrete variation of the

dipolar moment during the oscillation and thus there is a band of certain intensity.

The -C=O of a polyester is a very intense band, because the C=O dipole, caused by the strong electronegativity of oxygen with respect to carbon, is very strong. Still stronger are the bands of C-F stretching in PTFE (the F are the electronegative elements). There are many large bands that are crushed in the background.

As for the CH_2 stretching of vinylidene fluoride,

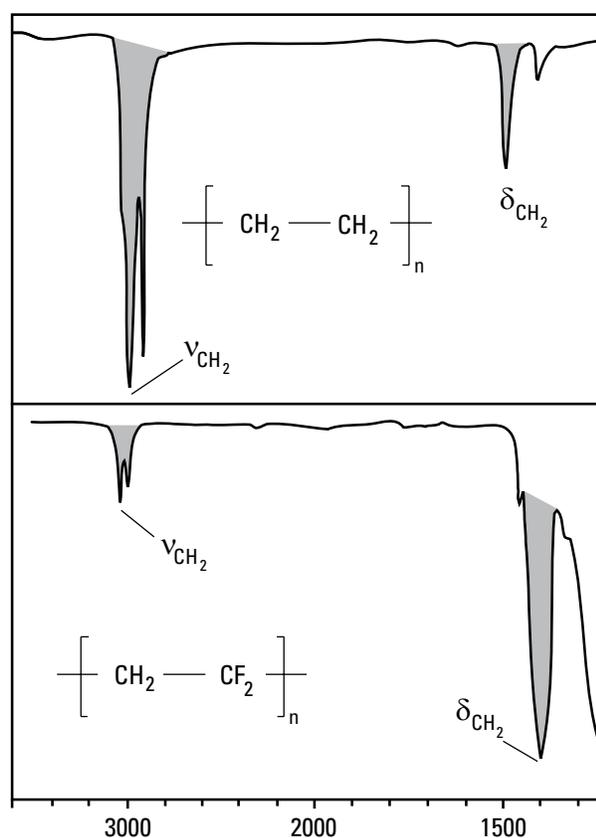
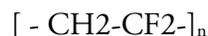


Figure 14-5.

there are many more weak bands than with polyethylene (see Figure 14-5) for the following reason:

The very electronegative fluorine attracts electrons from the carbon of the CH_2 and becomes slightly negative. For this reason the charge on the carbon becomes

much smaller than that of hydrogen, and therefore the C-H dipole is not very strong leading to weak bands.

Determining the absorption coefficient means putting a point to an analytical method in practice.

To determine k , proceed in the following way:

1. Procure a pure substance (for example, a **model compound** that contains a known quantity of functional groups for which we want to calculate the concentration) or a **homopolymer of monomeric units** that we want to determine, or a **copolymer** that contains a **known amount of the monomeric unit** that we want to determine.
2. A solvent is chosen that works well, that is, it must dissolve the substance well and be **transparent in the absorption range** of one of the vibration modes of the functional group or of the monomeric unit.
3. At least four standard solutions are prepared of the pure substance in the solvent. The **maximum concentration of these solutions** must be such that, with the thickness of the cell used, **the absorbance does not exceed value of 1 (better if it does not exceed 0.8)**.
4. Choose the cell for liquids -
 - The cell must have windows transparent in the chosen frequency.
 - The material of the cell must resist the action of the solvent.
 - The thickness of the cell must be such that the absorption of the solvent is not too high. Moreover the thickness must be such that at the maximum concentration, the absorbance does not exceed the value of 1 (better if it does not exceed 0.8)
5. Take the spectra of the solutions at the chosen frequency, and the contribution of the solvent is subtracted with the methods already seen.
6. The value of the absorbance of each of the standard solutions is read using the methods shown above.
7. A diagram is constructed (**linear calibration**) by recording on the **abscissas the concentrations of the functional group or of the**

monomeric unit to be determined, and on the **ordinates** the values of **relative absorbance**. A linear regression is constructed with the condition imposed that it pass through 0. **The slope of this straight line, uniform for the thickness of the cell in cm, is the absorption coefficient.**

- If the concentration has been expressed in moles/l the coefficient is that is the **molar coefficient of extinction**.
- If the concentration has been expressed in grams/100 ml the coefficient is $E_{1cm}^{1\%}$, that is **E 1 percent 1 centimeter**.

Table 14-2. Linear calibration

	C (grams/100ml)	Absorbance
1	0.4584	0.227
2	0.9221	0.458
3	1.3921	0.687
4	1.8276	0.921

Thickness of the cell = 0.0446 cm.

Slope of the straight line = 0.4995.

$$E_{1cm}^{1\%} = \frac{0.4995}{0.0446} = 11.2$$

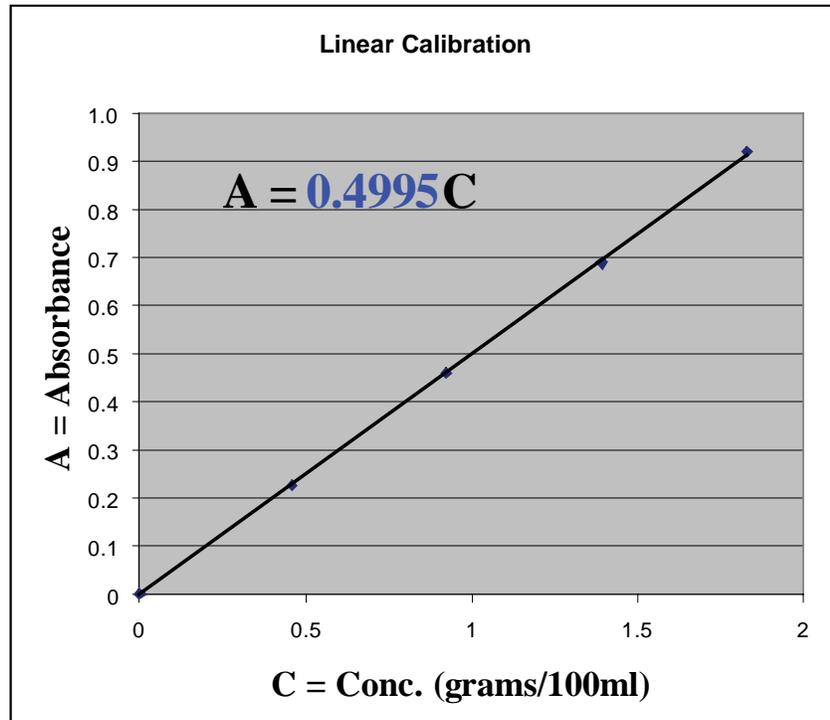


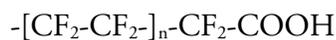
Figure 14-6. Linear calibration

Modern chemometrics programs, such as TQ Analyst, permit more sophisticated analyses to be performed. The statistical influence of impurities, process variability and material identification can be automated, and feedback can be used to actively control production processes. Mathematical models, such as partial least squares and principle component regression, may allow extraction of subtle details from a cloud of information. Databases of standard samples or of typical production samples can be built, and used to monitor quality and performance. A full discuss of chemometrics is beyond the scope of this book; contact Thermo for more information.

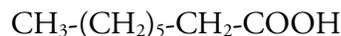
What are the model compounds?

The model compounds are **simple, soluble molecules**, if possible **similar to our polymer** and having **functional groups equal** to what we would want to determine in the polymer.

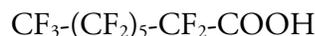
For example, if you want to determine the concentration of **terminal carboxylic** groups in the tetrafluoro ethylene copolymer,



you would not take certain model compounds like octanoic acid

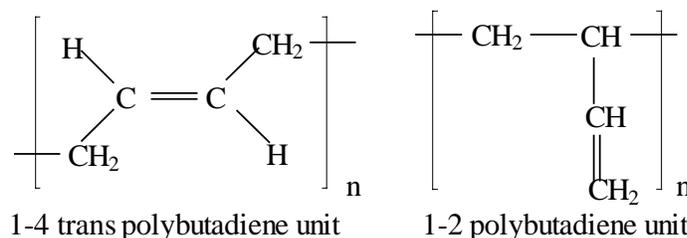


that is a completely different molecule and has a completely different carboxyl, but you would take perfluoro octanoic acid

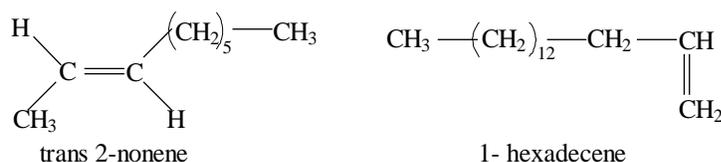


If you want to determine the content of 1-4 trans units and 1-2 units in a butadiene copolymer, use the bands

$$\omega_{\text{CH } 1-4 \text{ trans}} = 968 \text{ cm}^{-1} \text{ and } \omega_{\text{CH}_2 \text{ vinyl}} = 915 \text{ cm}^{-1}$$



As model compounds, one can use two hydrocarbons that have the same configurations, for example trans-2-nonene and hexadecene,



and calculate $E_{1\text{cm}}^{1\%}$ or ϵ of the bands at the two frequencies.

Instead of a compound model, often it is convenient to use a **low molecular weight fraction of the polymer in question**, that is soluble in a suitable solvent and that contains a significant quantity of the group you want to quantify. On this fraction the concentration of the group of interest is determined with another technique (NMR, elemental analysis, titration, etc.), and then this fraction can be used like a compound model.

In the copolymer example, one of the two **homopolymers** can be used as a compound model in certain cases.

As an example consider the case in which the content to be determined of VA in copolymer EVA contains VA above 30%. The coefficient is

determined using solutions of PVA in distilled cool tetrahydrofuran. (3 liters of tetrahydrofuran on 100g of caustic soda is boiled to reflux for 1 hour. It is distilled, eliminating the first 100 ml distilled.)

A cell of KBr with a thickness of 0.02 cm, and analytical bands, like that of C=O at about 1725 cm^{-1} , are used.

Analysis

Once $E_{1cm}^{1\%}$ or ϵ is calculated, it is possible to operate in two ways:

- Examination in solution
- Examination on film

Examination in solution

This technique must be used when the analytical band is influenced by crystallinity.

1. Prepare a solution of polymer in the same solvent in which the coefficient was determined.
2. Take the spectrum in a cell of appropriate thickness. The concentration of the polymer and the thickness of the cell must be such that the absorbance of the analytical band is less than 0.8-1, in this case as well.
3. Measure the net absorbance of the analytical band and apply the following formula:

$$C_{\%} = \frac{A}{E_{1cm}^{1\%}} \cdot \frac{100}{C_p}$$

where,

- A is the net absorbance of the analytical band.
- $E_{1cm}^{1\%}$ is the coefficient of absorption calculated via linear regression.
- C_p is the concentration of the polymer in question in the solution, expressed in g per 100 ml of solution.
- $C_{\%}$ results in the concentration of the unknown compound in the polymer, expressed in g for 100g of polymer.

If the following formula is used instead of $E_{1cm}^{1\%}$:

$$C_M = \frac{A}{\epsilon} \cdot \frac{1000}{C_p}$$

where:

- A and C_p have the same significance.

- E is the molar extinction coefficient.

C_M results in the concentration of the unknown compound in the polymer, expressed in moles per kg of polymer.

Analysis in solution is without doubt the **precisest**, even if it is longer and **complex**. However, it **requires** that the polymer in question is soluble in the same solvent, or a **very similar one chemically**, in which the **calibration curve has been carried out**.

Consider the case of the copolymer EVA (ethylene vinyl acetate) when the acetate content is above 30%. In this instance the copolymer is soluble in tetrahydrofuran.

As already stated, the calibration solutions are prepared using **polyvinylacetate** as a standard. The polymer in question is also dissolved in tetrahydrofuran. **However, it is obligatory to use this technique when the analytical band is influenced by crystallinity.**

Examination on film

Prepare a film by pressing the polymer in question. Punch a small circle of the film, about 2.5 cm in diameter. The circle, similar to a cylinder, is weighed with an analytical balance. The weight, P, (in grams) is divided by the surface area, S, in cm^2 ,

$$s_p = s \cdot \delta = \frac{P}{S}$$

to therefore *obtain the weighed thickness* that is the product of the thickness in cm multiplied by the density.

The absorbance of the band of interest is measured. From Beer's law

$$C = \frac{A}{s \cdot \epsilon}$$

where ϵ is the *molar coefficient of extinction*, the concentration will be expressed in *moles per liter* of polymer. If s_p is used instead, in reality we have

$$C = \frac{A}{s_p \cdot \epsilon} = \frac{A}{s \delta \cdot \epsilon}$$

and the concentration will be expressed in moles per kg of polymer.

If $E_{1cm}^{1\%}$ is used instead of ϵ , the concentration will be expressed in **grams per 100 grams** of polymer.

This type of analysis is used, for example, in the following cases:

- When the polymer is amorphous.
- When the analytical band is not influenced by crystallinity, but the polymer is crystalline.
- When the compound to be determined is in a very small amount with regards to the remainder (for example one of the two monomeric units of a copolymer). If the compound to be determined is in this instance one of the two monomeric units, the sequences of such a unit will be much too short to be able to crystallize (therefore we have the second case).
- When determining terminal groups or additives present in minimal amounts. In this case the concentration of such groups, or compounds, are so low as to advise against analysis in solution. In fact, in such a case we will have to use very concentrated solutions (and thus very viscous ones) and cells that are too highly thick for whatever type of solvent. Therefore, it is better to use a disk or film more frequently.

Quantitative analysis by band ratios

Consider the more common quantitative problem that it is faced in the field of the polymers: **the determination of the monomeric ratio in a random copolymer**, in which the analytical bands are not influenced by crystallinity. In this case the excellent quantitative method is that of **band ratios**.

Consider the copolymer AB (that is formed from monomer A and from the B monomer), and choose the analytical bands A (for monomer A) and B (for the B monomer) (see the following figure).

Procure a standard copolymer series of differing monomeric ratios, for example: A/B = 30/70; 45/55; 60/40; 70/30. The values can have been determined with another technique (NMR, elemental analysis, titrations, etc.).

In Figure 14-7 the spectrum of the 45/55 copolymer is shown..

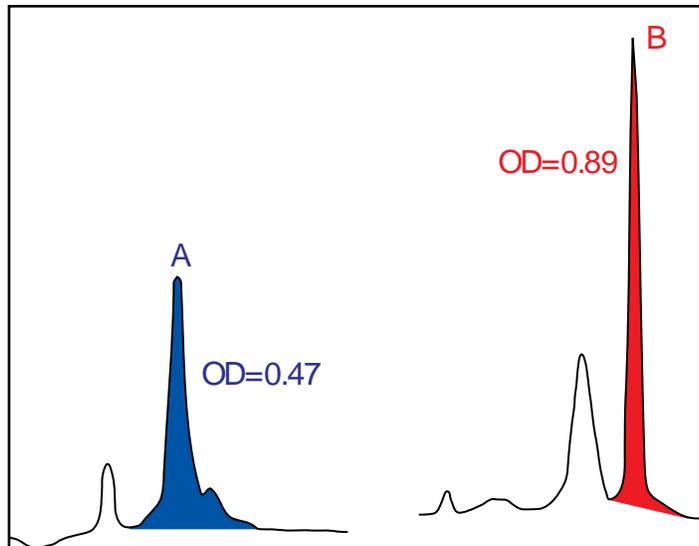


Figure 14-7. Copolymer AB (A=45, B=55)

From the Beer-Lambert law:

$$C_A = \frac{OD_A}{k_A \cdot s} \quad C_B = \frac{OD_B}{k_B \cdot s} \quad \text{from which} \quad \frac{C_A}{C_B} = \frac{k_B}{k_A} \cdot \frac{OD_A}{OD_B}$$

Notice that the relationship between the concentrations is proportional to the relative absorbance or the optical density (OD). The thickness does not factor any longer in the formula. Therefore an analogous law to Beer-Lambert can be written that does not factor in the thickness.

$$\frac{OD_A}{OD_B} = k_{AB} \cdot \frac{C_A}{C_B}$$

With this formula, if we have a copolymer of unknown composition, the ratio of OD_A to OD_B can be gained from the ratio C_A/C_B . For this it is necessary to calculate the k_{AB} , using linear regression with the copolymer standards that we have procured.

Table 14-3.

	% Monomer	C_A/C_B	DA	DB	D_A/D_B
1	30/70	0.428	0.222	0.791	0.278
2	45/55	0.818	0.470	0.895	0.525
3	60/40	1.500	0.463	0.477	0.970
4	70/30	2.333	0.600	0.401	1.495

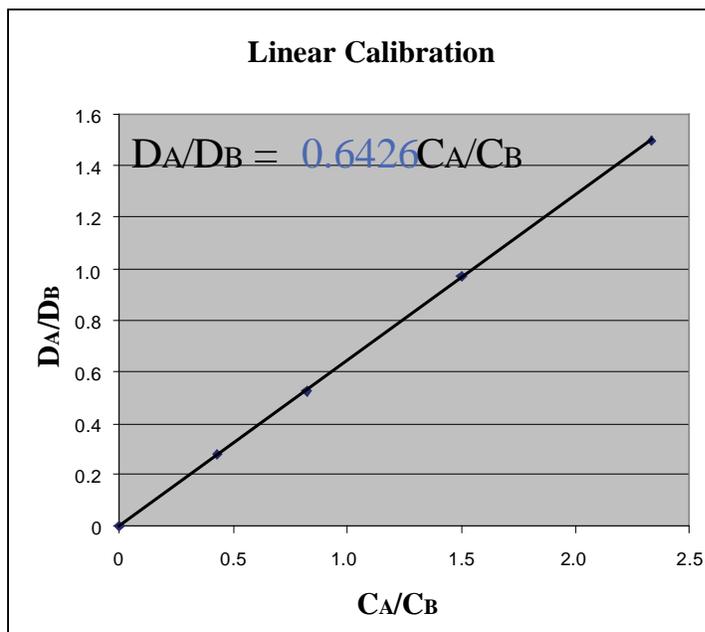


Figure 14-8. Linear calibration

The slope of the straight line is $k_{AB} = 0.6426$.

Then, if you have an unknown copolymer, measure the OD_A and OD_B and replace the values in equation 1. Suppose we found $OD_A = 0.728$ and $OD_B = 0.480$. We have

$$\frac{0.728}{0.480} = 0.6426 \cdot \frac{C_A}{C_B} \quad \text{from which} \quad \frac{C_A}{C_B} = 2.36$$

In the second part, we know that $C_A + C_B = 100$, for which the following is true:

$$\begin{cases} \frac{C_A}{C_B} = 2.36 \\ C_A + C_B = 100 \end{cases} \quad \begin{cases} C_A = 2.36 \cdot C_B \\ 2.36 \cdot C_B + C_B = 100 \end{cases}$$

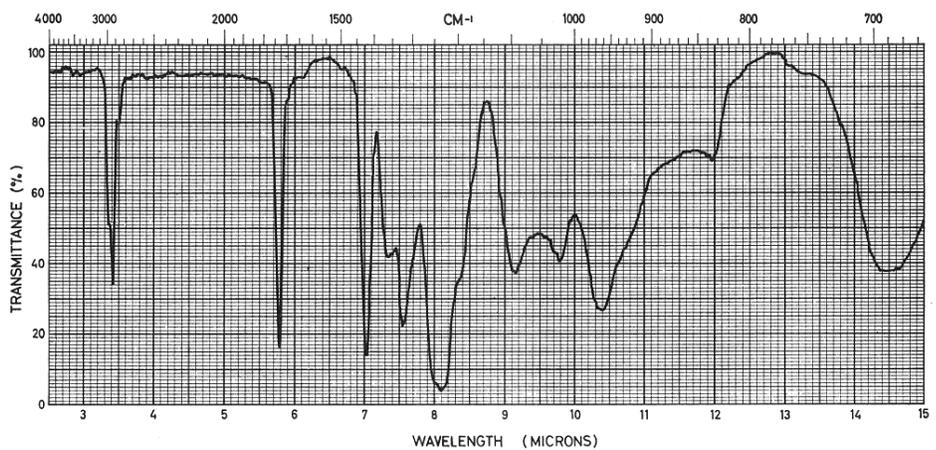
$$C_B = \frac{100}{2.36 + 1} = \frac{100}{3.36} = 29.8\% \quad C_A = 70.2\%$$

This type of approach to the quantitative problem is very convenient, because it allows one to make a quantitative analysis also with **film deposited on a disk of KBr** and also, with certain precautions, **with the technique of ATR**.

As much as the description above is a complete and rigorous method, often (at least for 90% of the cases) it is not necessary. A simplified and practical method will then be described.

Suppose that you have a recognized polymer like the vinyl acetate copolymer with vinyl chloride, but are still left with the question of the relationship between the two monomers. There are essentially two approaches to the problem.

- Obtain standard samples, run the spectra and compare the results to your sample.
- As an alternative, search the literature to see if a spectrum of the sort of copolymer with noted composition exists, even if it is in an old collection with linear spectra in microns, range limited to 15 μ (666 cm^{-1}) and intensities given in transmittance. For example, the spectra of Figure 14-9, taken from Haslam and Willis, of 95/5 of copolymer vinylchlorate/vinylacetate copolymer. It is not the best that can be found, but it is equally valuable.



*Spectrum 3.18. Vinyl chloride/vinyl acetate (95 : 5) copolymer
Film from ethylene dichloride solution*

Figure 14-9.

Choose analytical bands, such as $\nu_{\text{C=O}} = 5.78 \mu$ corresponding to the C=O stretching of acetate, and $\nu_{\text{C-Cl}} = 14.45 \mu$ of the C-Cl stretching of the vinyl chloride. Draw the base lines and calculate the net absorbance of the two bands. The band at 14.45 has a %T maximum of 37.5, and therefore

$$T_2 = 0.375 \text{ from } A_2 = \log \frac{1}{T} = \log \frac{1}{0.375} = 0.426$$

and $T_1 = 1$ $A_1 = 0$ at the **base** for which the net absorbance is

$$A_{14.45} = 0.426 .$$

The band at 5.78 has a %T **maximum** of 17 and therefore

$$T_2 = 17 \text{ from } A_2 = \log \frac{1}{T} = \log \frac{1}{0,17} = 0,769$$

and a %T to the **base** of 93 and therefore

$$T_1 = 0.93 \text{ from } A_1 = \log \frac{1}{T_1} = \log \frac{1}{0.93} = 0.031$$

and thus

$$A_{5.78} = A_2 - A_1 = 0.769 - 0.031 = 0.738 .$$

Then:

$$\frac{A_{14.45}}{A_{5.78}} = \frac{0.426}{0.738} = 0.577$$

For the other part of the equation it is reported that

$$\frac{C_{VCl}}{C_{VAc}} = \frac{95}{5} = 19$$

Then examine the spectrum of the unknown sample and read the values of net absorbance at the two wavelengths

$$A_{14.45} = 0.256 \quad A_{5.78} = 0.957$$

$$\frac{A_{14.45}}{A_{5.78}} = 0,267$$

Apply the simple proportion

$$0.577 : 19 = 0.267 : x$$

where x is the ratio $\frac{C_{VCl}}{C_{VAc}}$ of the unknown polymer,

$$x = \frac{C_{\text{VCl}}}{C_{\text{VAc}}} = 8.79$$

and applying the arrangement

$$\begin{cases} \frac{C_{\text{VCl}}}{C_{\text{VAc}}} = 8.79 \\ C_{\text{VCl}} + C_{\text{VAc}} = 100 \end{cases} \quad \begin{cases} C_{\text{VCl}} = 8.79 \cdot C_{\text{VAc}} \\ 8.79 \cdot C_{\text{VAc}} + C_{\text{VAc}} = 100 \end{cases}$$

$$C_{\text{VAc}} = \frac{100}{8.79 + 1} = \frac{100}{9.79} = 10.2\% \quad C_{\text{VCl}} = 89.8\%$$

The result is therefore a 90/10 copolymer. This type of analysis is sufficiently precise for the majority of cases, and is more frequently used.

In cases where the co-monomer is less than 5%, if you take the ratio between the intensity of the analytical band of the co-monomer and that of main monomer, in making the calibration curve, put on the abscissas, **the appropriate concentration instead of the value of the ratio**. In fact since the concentration of the main monomer is always near 100%, in the limits of analytical error it can be considered practically constant, and the curve is a straight line passing through the origin.

But be careful!!

If the content of the co-monomer is low, the large portion of the polymer is constituted from long blocks of homopolymers that can easy crystallize.

If in the spectrum of a copolymer, a band is successfully characterized whose intensity shows the effects of the contribution of the two monomeric units in a practically equal way, this can be considered proportional to the thickness of the film, for which, as in the previous case, **the appropriate concentration is put on the graph** instead of the value of the ratio. This is the case, for example, of the complex of bands (harmonic or combination) that appear in the interval, 4400-4000 cm^{-1} , in the ethylene propylene copolymer. If the ratio between the absorbance at 1150 cm^{-1} and that of one of the harmonics is plotted on a graph against the concentration of the polypropylene, one obtains a straight line passing through the origin. The band $\nu_{\text{C-C(CH}_3\text{)-C}} = 1155 \text{ cm}^{-1}$ is obviously proportional to the content of the polypropylene and is less sensitive to the distribution of the ethylenic and propylenic units. The harmonic bands and combinations are instead, in a monomeric interval ratio of sufficient width, proportional to the thickness of the film.

Appendix A Thermal Characteristics of Polymers

Heat treatment of polymers, like the rolling process described in the previous chapter, may alter the polymer. This is especially true if temperature drives the polymer through a **phase change**. This chapter briefly examines the different influences that temperature can have.

Melted state. The macromolecules are *mobile, subject to continuous movements*. Lowering the temperature of the melted substance such movements become more and more limited, eventually, below a certain temperature (the **melting temperature, or M.P.**), *crystallization can occur*. To crystallize, the macromolecule must be mostly regular (having constitutional, configurational and conformational regularity).

Crystalline state. Below the melting temperature, a polymer, even if only partially crystalline, is *hard, rigid and fragile* and often *opaque*. Some polymers are *not ever completely crystalline*, and usually do not have a single melting temperature, but a narrow *interval* of temperature.

Vitreous state. If the macromolecule is structurally irregular, it is *not able to crystallize*. In such a case, when lowering the temperature of the melted substance, the movements become more and more limited because of the increase in viscosity. During cooling, the polymer becomes *gummy*. Torsional movements are still possible, such as spins around the C-C bonds of portions of the macromolecule. Below a solidification temperature, the *vitreous transition* is made and the polymer passes into the *vitreous (glass-like) state*.

Softening point. This is a temperature over which the polymer passes from the gummy state to one *sufficiently fluid* to allow it to be worked (*molding, calendering, extrusion*).

Below the vitreous transition temperature (T_g), the polymer is *hard, rigid, fragile* and often *transparent*.

Over the vitreous transition temperature, the polymer is *gummy, soft and flexible*. Also a perfectly regular polymer can not crystallize and will pass to

the vitreous state if it is cooled rapidly so as to therefore not allow the formation of crystalline nuclei.

Appendix B Vibrational Glossary

Different types of vibrations:

Stretching

This is a variation of the **length** of the bond and is indicated with the symbol, ν , with a subscript that indicates the oscillating group.

Example: *stretching* of C=O $\rightarrow \nu_{\text{C=O}}$

If the group consists of 3 atoms, instead of 2, it can have two types of stretching: asymmetric and symmetric stretching.

In order to distinguish the two types of stretching, a superscript is introduced that is: “s” (for the symmetrical stretching) or “a” (for the asymmetrical stretching).

Examples: *symmetrical stretching* of CH₂ $\rightarrow \nu_{\text{CH}_2}^{\text{s}}$

(In this movement the two hydrogens go away from the C **at the same time** in the outward movement and approach **at the same time** in the return movement.)

asymmetric stretching of the CH₂ $\rightarrow \nu_{\text{CH}_2}^{\text{a}}$

(In this movement, while one hydrogen goes away, the other approaches)

symmetrical stretching of C-O-C $\rightarrow \nu_{\text{C-O-C}}^{\text{s}}$

(In this movement, the two carbon atoms go away from the O **at the same time** in the outward movement and approach **at the same time** in the return movement)

asymmetric stretching of C-O-C $\rightarrow \nu_{\text{C-O-C}}^{\text{a}}$

(In this movement, while one carbon goes away, the other approaches)

Bending

This is a variation of the **angle** of the bond that happens on the plane of the bond and is indicated with the symbol, δ , with a subscript that indicates the oscillating group.

Example: *bending* of $\text{CH}_2 \rightarrow \delta_{\text{CH}_2}$

If the group consists of 4 atoms, instead of 3, they can have two types of bending: symmetrical and asymmetrical bending.

Symmetrical bending is indicated by adding the superscript, s, and asymmetrical, the superscript, a.

Example: *symmetrical bending* of $\text{CH}_3 \rightarrow \delta_{\text{CH}_3}^s$

asymmetrical bending of $\text{CH}_3 \rightarrow \delta_{\text{CH}_3}^a$

In symmetrical bending (Figure B-1), the angle 4-1-3, the angle 4-1-2,

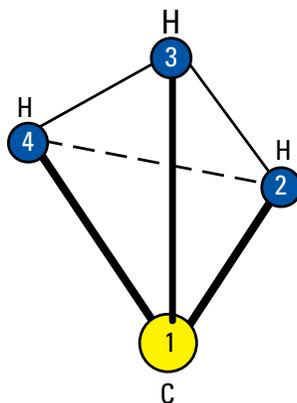


Figure B-1.

and the angle 3-1-2 are increased at the same time in the outward movement and are tightened at the same time in the return movement. This is a movement that simulates the opening and the closing of an umbrella. In fact, it is also called *umbrella* bending.

In asymmetrical bending, one of the three angles is tightened (in the outward movement), and the other two are increased; and vice versa in the return movement.

Rocking

This is a distortion of the bonds that is indicated with ρ with a subscript that indicates the oscillating group.

Example: *rocking* of $\text{CH}_2 \rightarrow \rho_{\text{CH}_2}$

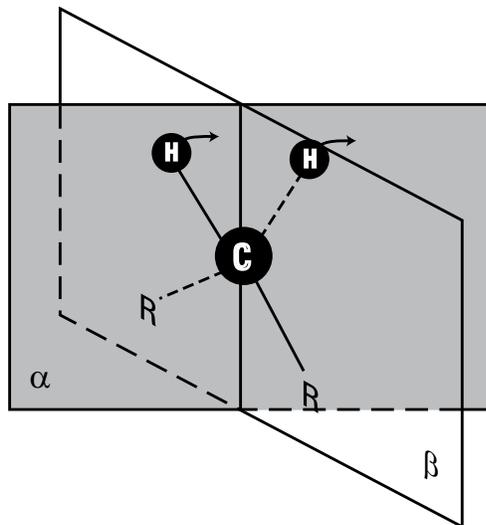


Figure B-2.

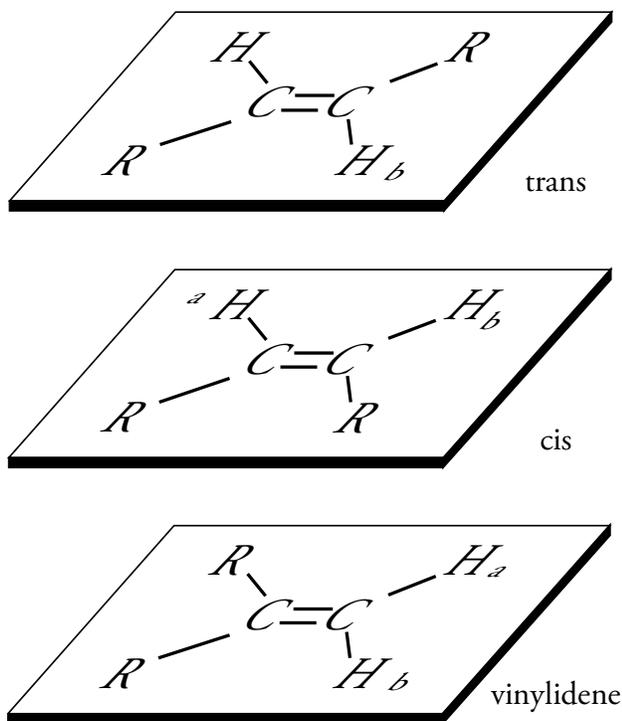
Rocking consists of a contemporary rotation, for a certain angle in the sense of time, of the two C-H bonds in the plane α (Figure B-2) and in counter-clockwise sense in the return movement.

Wagging

This is a distortion of the bonds that is indicated with ω with a subscript that indicates the oscillating group.

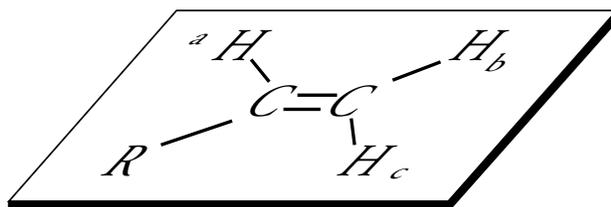
Example: *wagging* of $\text{CH}_2 \rightarrow \omega_{\text{CH}_2}$

The two atoms of H are moved at the same time above the plane α (Figure B-2) in the outward movement and under the plane in the return movement.

**Figure B-3.**

Another example of wagging is with the CH of a double bond (Figure B-3). In this case, the movement consists of the contemporary movement of two hydrogens *a* and *b* above the plane of the double bond; and under in the return movement.

In case where there is more than two atoms of hydrogen, like with vinyl, then two types of wagging (Figure B-4) can occur.

**Figure B-4.**

wagging of CH in trans $\rightarrow \omega_{\text{C-H}}^{\text{trans}}$

The movement consists in a contemporary movement of two hydrogens in *a* and *c* above the plane (and under the plane in the return movement).

wagging of CH in cis $\rightarrow \omega_{\text{C-H}}^{\text{cis}}$

The movement consists in a contemporary movement of two hydrogens in *a* and *b* above the plane (and under the plane in the return movement).

In the case of aromatic rings, the wagging of the C-H consists of the movement of hydrogen atoms over and under the plane of the aromatic ring. According to the substitution there will be:

5 adjacent hydrogens, mono-replaced in the aromatic $\rightarrow \omega_{5\text{Hadj}}$.

2 adjacent hydrogens replaced in para $\rightarrow \omega_{2\text{Hadj}}$.

and so like.

Twisting

This is a movement of torsion that is indicated with τ with a subscript that indicates the oscillating group.

Example: twisting of $\text{CH}_2 \rightarrow \tau_{\text{CH}_2}$

The two hydrogens of the CH_2 move one over and one under the plane (Figure B-2); and vice versa in the return movement.

Appendix C Mini-Schematic for Interpreting the Spectra of a Polymer

Point 1 Chlorine Test

This is an operation that may upset those looking for automated spectroscopic answers for every problem. However, this operation, although it can be defined as archaic, will be able to serve in order to prevent some blunders.

For this test, it is necessary to find an old Bunsen burner and equip it with a copper gas mantle.

The gas mantle is cleaned up by placing it on the oxidant flame of the burner; it is cooled; a small piece of the polymer in question is placed over it; and it is placed anew on the flame of the burner.

If the flame is an **intense** green – blue/green color, it means that organic chlorine is present thus a chlorinated polymer.

Go then to Schedules 9 and 10.

See also what is stated about the addition of various substances in the text. The inorganic chlorides do not interfere with the test and not even the fluoride polymers. If the flame is not green go on to Point 2.

Point 2 Absence of the Stretching Bands of Hydrocarbons

All polymers, with the exception of perfluorates, have CH, CH₂, or CH₃ groups that are evidenced in the IR by complex and **intense** bands in the 3000 - 2850 cm⁻¹ interval. Such a complex of bands, practically always present, is mostly of insufficient diagnostic importance. Instead it becomes of fundamental importance if this band is **not present**.

If the band is not present, or is weak, go to Schedules 11 and 12.

If it is present go on to Point 3.

Point 3 Intense Band in the Interval 1780 – 1730 cm^{-1}

Observe if a strong band is present in the interval 1780 – 1730 cm^{-1} .

If it is not present go on to point 4.

If it is present, watch also for a second band of average-high intensity in the 1530 – 1540 cm^{-1} interval.

If this second band is present, see the Schedules of the polymers containing urethane groups → Schedules 34, 35, 36 and 37.

If this second band is absent, see the Schedules of the polymers containing ester groups → Schedules 19 – 27.

If more detail is desired, go on to point 3.1.

3.1 Look for the bands between 1780 – 1730 and particularly in the 1780 – 1770 cm^{-1} interval.

In such a case the result is a polycarbonate **Schedule 28.**

If the band absorbs under 1770 pass to point 3.2.

3.2 Watch to see if a **second intense band** in the interval 1280 – 1260 cm^{-1} is present. If it is present, the result is a polymer that contains aromatic ester groups → **Schedules 20 and 27.**

If such band is absent go on to point 3.3.

3.3 Look for a second intense band present in the 1248 - 1230 cm^{-1} interval. If it is present, the result is a polymer containing acetic ester groups → **Schedules 24, 25 and 26.**

If such a band is absent, pass to point 3.4.

3.4 Look for a **second intense and complex band** in the interval 1210 – 1150 cm^{-1} . If it is present, the result is a polymer containing different ester groups (polyvinyl propionates, acrylates, methacrylates) → **Schedules 21, 22 and 23.**

Point 4 Watch for the presence of an **intense and increased band in the interval 1630 – 1660 cm⁻¹**.

If it is present, pass on to the Schedules of polymers containing amidic, proteic, and ureic groups → **Schedules 29 – 33**.

It is also possible that the features are of **nitrocellulose** → **Schedule 42**.

If the band is absent go on to point 5.

Point 5 Look for a **band present in the 2240 – 2290 cm⁻¹ interval**.

If present, the result is of acrylonitrile polymers → **Schedules 38 - 41** or urethanic prepolymers containing isocyanic groups → **Schedules 34 and 35**.

If it is absent pass to point 6.

Point 6 Watch to see if an **intense band in the interval 1690 – 1710 cm⁻¹ is present**.

If it is present pass to the Schedules of polymers containing carboxylic acid groups → **Schedule 18**.

If it is absent go to point 7.

Point 7 Watch for an **intense and increased band present in the 1550 - 1580 cm⁻¹ interval**.

If it is present, the result is of polymers containing carboxylic salt groups (sodium polyacrylates or polymethacrylates) → **Schedule 19** or melaminic resin → **Schedules 43 and 44**.

If it is absent it go on to point 8.

Point 8 Look to see if an **intense and increased band in the interval 1100 – 1250 cm⁻¹ is present**.

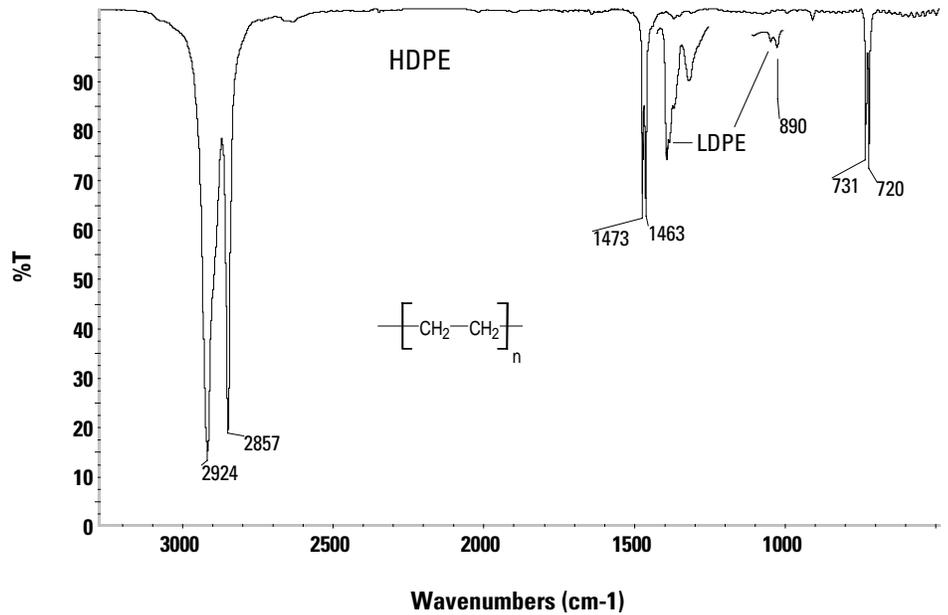
If it is present, the result is of polymers containing groups of various nature: alcoholic or ether → **Schedules 13 – 16**; phenolic **Schedule 17** or siliconic → **Schedules 45 and 46**.

If the result is **absent of hydrocarbon polymers** → **Schedules 1 – 8**.

Appendix C Mini-Schematic for Interpreting the Spectra of a Polymer

Appendix D Spectra of Polymers and Plasticizers

Schedule 1 Polyethylene



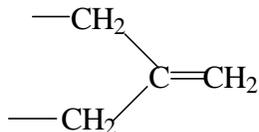
— $\nu_{\text{CH}_2}^a = 2924 \text{ cm}^{-1}$ - Very intense and sharp

— $\nu_{\text{CH}_2}^s = 2857 \text{ cm}^{-1}$ - Intense, sharp

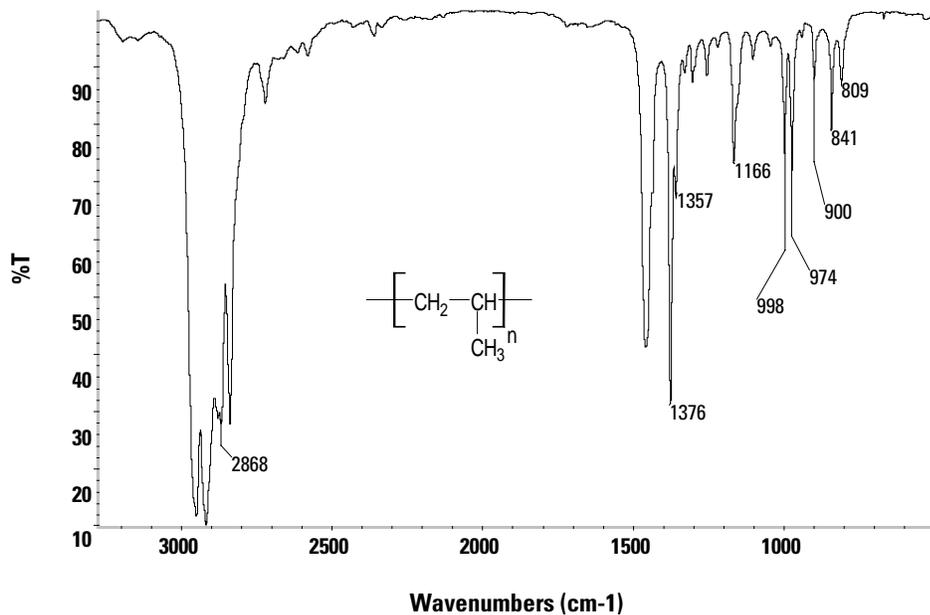
— $\delta_{\text{CH}_2} = 1473 \text{ cm}^{-1}$
— $\delta_{\text{CH}_2} = 1463 \text{ cm}^{-1}$ } - Intense. Doublet due to crystallinity.

— $\rho_{\text{CH}_2} = 731 \text{ cm}^{-1}$
— $\rho_{\text{CH}_2} = 720 \text{ cm}^{-1}$ } - Medium. Doublet due to crystallinity

In low density polyethylene (LDPE), the range around 1400 cm^{-1} is more intense and complex because of the presence of structural ramifications and a greater number of methyl terminal groups (see text). Weak bands also appear at 890 cm^{-1} due to ω_{CH_2} of the vinylidene groups.



Schedule 2 Isotactic Polypropylene



The bands of CH_2 and CH_3 are very intense, but overlapped between them.

$$\text{--- } \nu_{CH_3}^a = 2956 \text{ cm}^{-1}$$

$$\text{--- } \nu_{CH_2}^a = 2925 \text{ cm}^{-1}$$

$$\text{--- } \nu_{CH_3}^s = 2880 \text{ cm}^{-1}$$

$$\text{--- } \nu_{CH_2}^s = 2868 \text{ cm}^{-1}$$

$$\text{--- } \delta_{CH_3}^a = 1450 \text{ cm}^{-1} \text{ - Intense. Overlapping the following:}$$

$$\text{--- } \delta_{CH_2} = 1434 \text{ cm}^{-1}$$

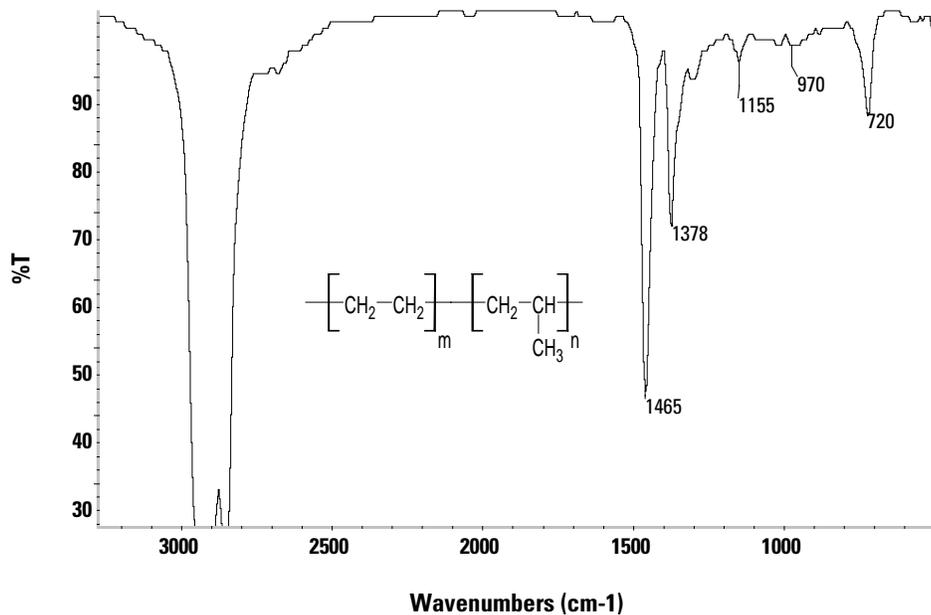
$$\text{--- } \delta_{CH_3}^s = 1376 \text{ cm}^{-1} \text{ - Intense, with a regularity band on the side (1357 cm}^{-1}\text{).}$$

There are also the following regularity bands:

$$1166 \text{ cm}^{-1}, 998 \text{ cm}^{-1}, 974 \text{ cm}^{-1}, 900 \text{ cm}^{-1}, 841 \text{ cm}^{-1}, 809 \text{ cm}^{-1}$$

These are of medium intensity or weak and very sharp.

Schedule 3 Ethylene Propylene Copolymer (EPM)



— $\delta_{\text{CH}_2} = 1465 \text{ cm}^{-1}$ - Very intense

— $\delta_{\text{CH}_3}^s = 1378 \text{ cm}^{-1}$ - Intense, sharp

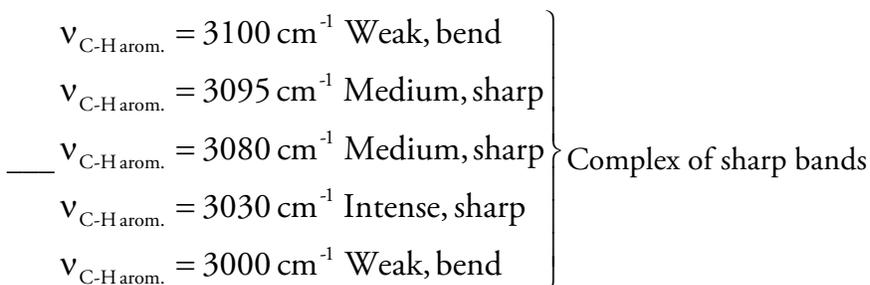
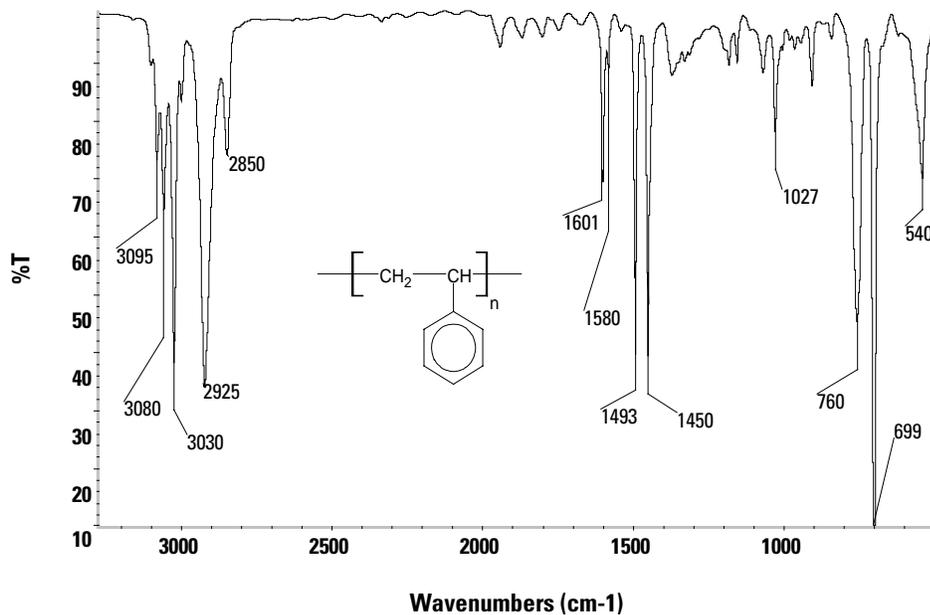
— $\nu_{\text{C-C}(\text{CH}_3)\text{-C}} = 1155 \text{ cm}^{-1}$ - Medium-weak

— $\rho_{\text{CH}_3} = 970 \text{ cm}^{-1}$ - Weak

— $\rho_{\text{CH}_2} = 720 \text{ cm}^{-1}$ - Medium

The presence of the double bond due to the polymerized presence of diene is not normally seen, thus the spectrum of EPDM is practically equal to that of EPM. Using very thick samples, it is only possible at times to find the presence of unsaturation.

Schedule 4 Polystyrene



$$\text{--- } \nu_{\text{CH}_2}^{\text{as}} = 2925 \text{ cm}^{-1} - \text{Intense, sharp}$$

$$\text{--- } \nu_{\text{CH}_2}^{\text{s}} = 2850 \text{ cm}^{-1} - \text{Medium, sharp}$$

$$\left. \begin{array}{l} \text{--- } \nu_{\text{ring}} = 1600.7 \text{ cm}^{-1} \text{ Medium, sharp} \\ \text{--- } \nu_{\text{ring}} = 1580 \text{ cm}^{-1} \text{ Weak, sharp} \end{array} \right\} \text{Doublet}$$

$$\text{--- } \nu_{\text{ring}} = 1492.7 \text{ cm}^{-1} - \text{Intense, sharp}$$

$$\text{--- } \delta_{\text{CH}_2} = 1450 \text{ cm}^{-1} - \text{Intense, sharp}$$

$$\text{--- } 1027 \text{ cm}^{-1} - \text{Weak, sharp}$$

$$\text{--- } \omega_{5\text{H adj.}}^1 = 760 \text{ cm}^{-1} - * \text{Very intense}$$

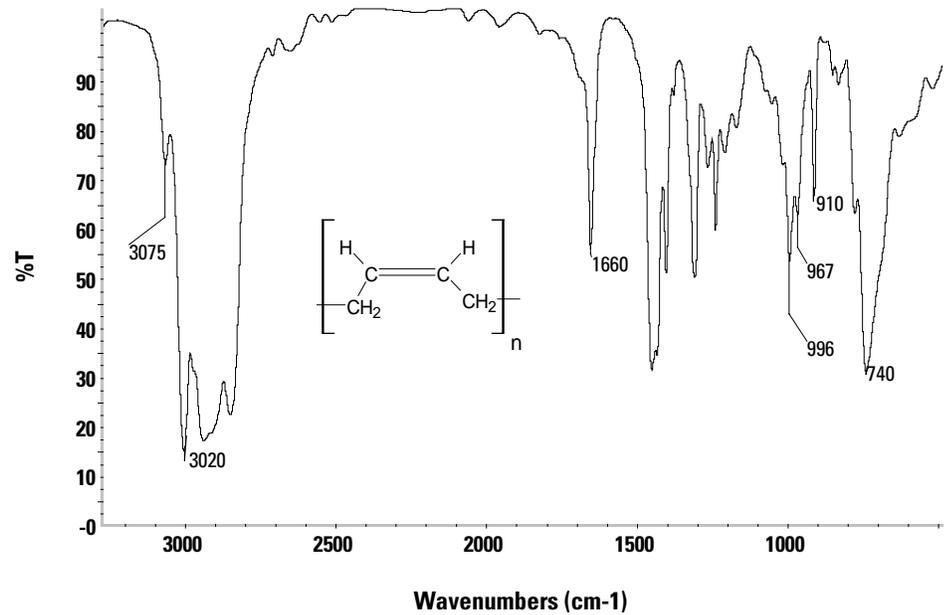
Appendix D Spectra of Polymers and Plasticizers

— $\omega_{5\text{Hadj.}}^2 = 699 \text{ cm}^{-1}$ - * Very intense

— 538-540 cm^{-1} – Intense, broad

Schedule 5

1-4 cis Polybutadiene



— $\nu_{\text{=CH}_2} = 3075 \text{ cm}^{-1}$ - Weak, sharp (due to 1-2 vinyl units)

— $\nu_{\text{=C-H}} = 3020 \text{ cm}^{-1}$ - Intense, sharp (due to the cis double bond)

— $\nu_{\text{C=C}} = 1660 \text{ cm}^{-1}$ - Medium sharp (due to the cis double bond)

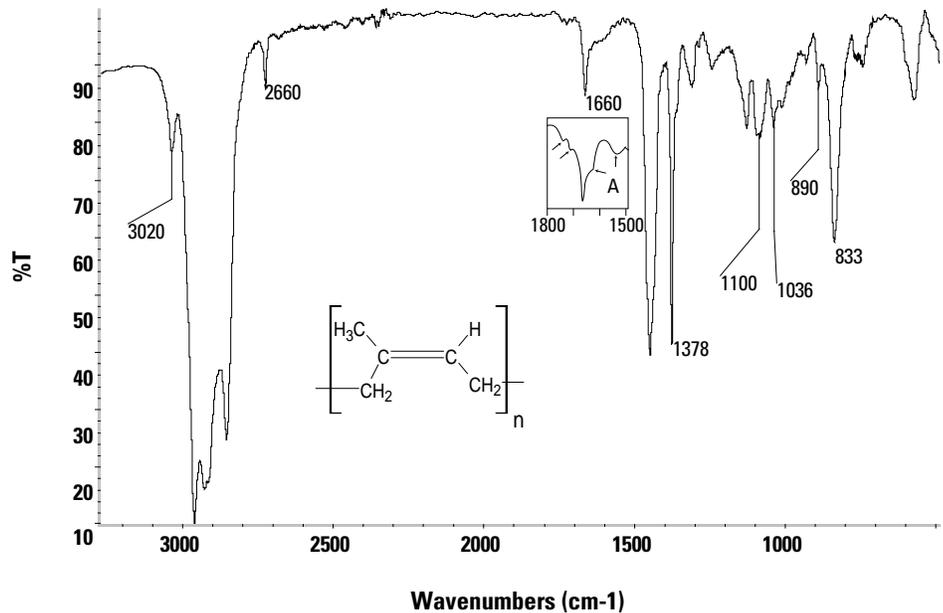
— $\omega_{\text{CH}}^{\text{trans}} = 996 \text{ cm}^{-1}$ - Weak (due to the 1-2 vinyl units)

— $\omega_{\text{CH}} = 967 \text{ cm}^{-1}$ - Weak (due to the trans double bond)

— $\omega_{\text{CH}_2} = 910 \text{ cm}^{-1}$ - Weak (due to the 1-2 vinyl units)

— $\omega_{\text{CH}} = 740 \text{ cm}^{-1}$ - * Intense, broad (due to the cis double bond)

Schedule 6 Natural Rubber – Polyisoprene



___ $\nu_{\text{C-H}} = 3020 \text{ cm}^{-1}$ - Weak, sharp

___ $2\delta_{\text{CH}_3}^s = 2660 \text{ cm}^{-1}$ - Weak, sharp

___ $\nu_{\text{C=C}} = 1660 \text{ cm}^{-1}$ - Weak, sharp

___ $\delta_{\text{CH}_3}^s = 1378 \text{ cm}^{-1}$ - Intense, sharp

___ 1100 cm^{-1} Medium

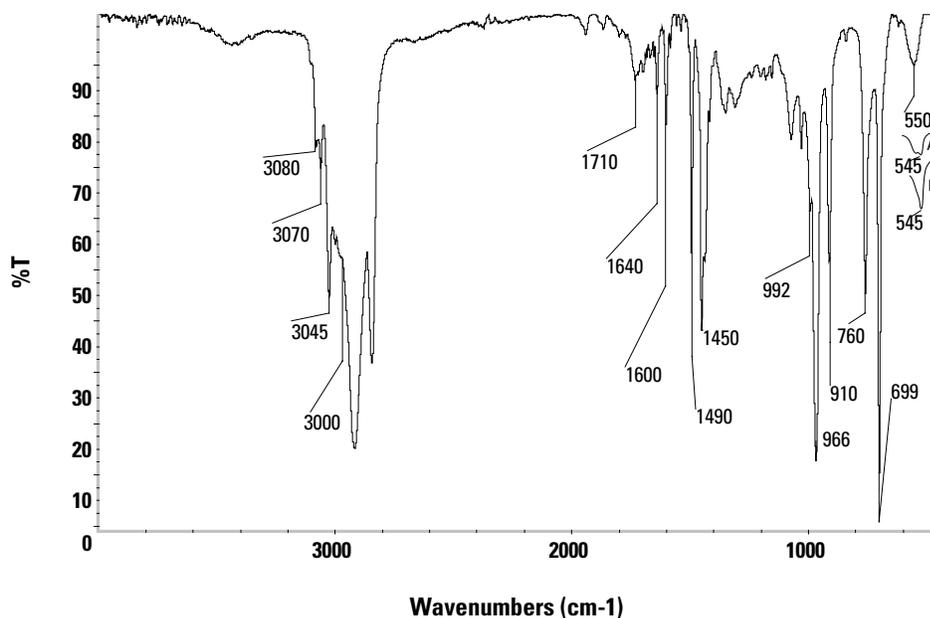
___ 1036 cm^{-1} Medium

___ 890 cm^{-1} Very weak, sharp

___ $\omega_{\text{=CH}} = 833 \text{ cm}^{-1}$ - * Intense

Weak absorptions are also present due to resins containing esters (1740 cm^{-1}), acids (1710 cm^{-1}) and at times proteins (1535 and 1630 cm^{-1}), as shown in inset A.

Schedule 7 Butadiene-Styrene Copolymer (Rubber SBR)



— $\nu_{\text{C-H arom. \& double bond}}$ $\left\{ \begin{array}{l} 3080 \text{ cm}^{-1} \\ 3070 \text{ cm}^{-1} \\ 3045 \text{ cm}^{-1} \\ 3000 \text{ cm}^{-1} \end{array} \right.$ Sharp, medium intense

— $\nu_{\text{CH}_2}^{\text{a}} = 2910 \text{ cm}^{-1}$ - Intense

— $\nu_{\text{CH}_2}^{\text{s}} = 2850 \text{ cm}^{-1}$ - Intense, sharp

— $\nu_{\text{C=O}} = 1690\text{-}1710 \text{ cm}^{-1}$ - Variable. Resinic acids or fatty acids derived from soaps are used like suspenders. They are nearly always present.

— $\nu_{\text{C=C vinyl}} = 1640 \text{ cm}^{-1}$ - Medium sharp

— ring vibrations $\left\{ \begin{array}{l} 1600 \text{ cm}^{-1} \text{ doublet} \\ 1490 \text{ cm}^{-1} \\ 1450 \text{ cm}^{-1} \end{array} \right.$ - Intense, sharp

— $\delta_{\text{CH}_2} = 1430 \text{ cm}^{-1}$ - Intense

— $\omega_{\text{CH vinyl}}^{\text{trans}} = 992 \text{ cm}^{-1}$ - * Sharp, medium

— $\omega_{\text{CH1-4 trans}} = 966 \text{ cm}^{-1}$ - * Very intense

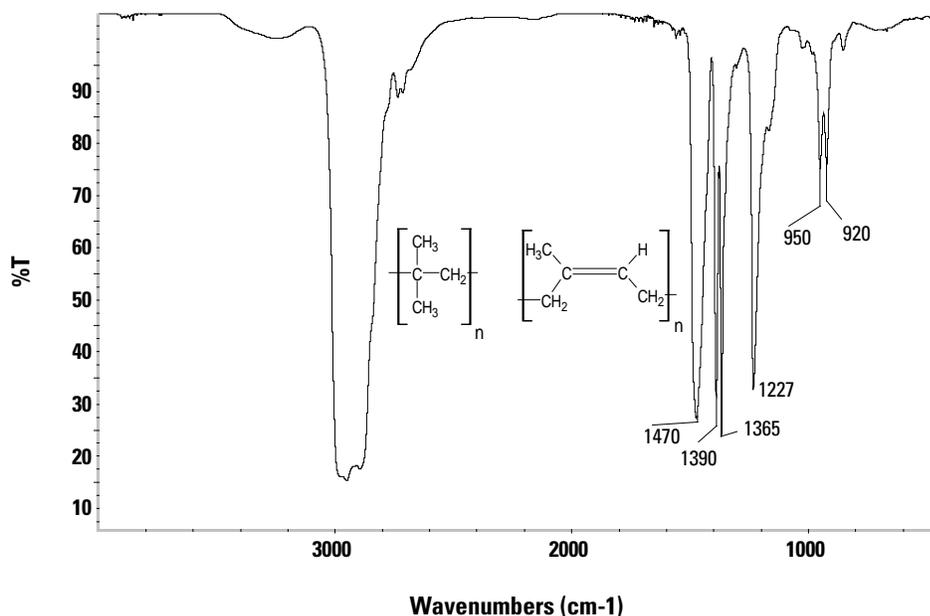
— $\omega_{\text{CH}_2 \text{ vinyl}} = 910 \text{ cm}^{-1}$ - * Sharp, intense

— $\omega_{5\text{H adj.}}^1 = 760 \text{ cm}^{-1}$ - * Intense. Monoreplaced aromatic ring. This band hides the ω_{CH} of the 1-4 cis double bond of butadiene, whose amount is very low.

— $\omega_{5\text{H adj.}}^2 = 699 \text{ cm}^{-1}$ - * Very intense. Monoreplaced aromatic ring.

— 550 cm^{-1} - * Weak, wide. The shape and position are tied to the length of the unit sequences $-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-$. The observation of this band is therefore the only possibility to distinguish SBR rubbers (in which the styrol is distributed in a statistical shape with the shortest sequences) from SBS (block thermoplastic rubbers) in which there are blocks of long sequence polystyrol alternated with blocks of polybutadiene. In this case (spectra A and B) the band develops a point at 545 cm^{-1} .

Schedule 8 Polyisobutylene (Butyl rubber)



— $\delta_{\text{CH}_2} = 1470 \text{ cm}^{-1}$ - Intense

— $\delta_{\text{CH}_3}^{\text{s in phase}} = 1390 \text{ cm}^{-1}$ - * Intense, sharp. With the following it constitutes the doublet typical of two methyls attached to the same carbon atom (vibrational interaction).

— $\delta_{\text{CH}_3}^{\text{s out of phase}} = 1365 \text{ cm}^{-1}$ - * More intense than the previous, sharp

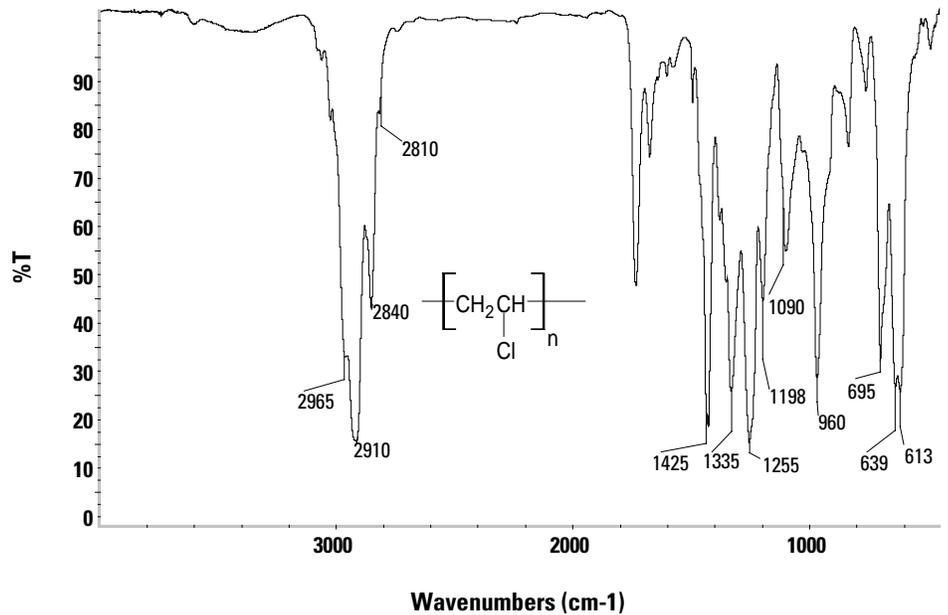
— $\nu_{-\text{C}-\text{C}(\text{CH}_3)_2-\text{C}} = 1227 \text{ cm}^{-1}$ - * Medium-intense

— $\rho_{\text{CH}_3}^{\text{in phase}} = 950 \text{ cm}^{-1}$ - * Weak (vibrational interaction with the following).

— $\rho_{\text{CH}_3}^{\text{out of phase}} = 920 \text{ cm}^{-1}$ - * Weak

It is not possible to characterize the presence of isoprenic units and not even the presence of bands attributable to modest amounts of halogens. Thus the spectra of butyl and chlorobutyl rubber are all identical to that of polyisobutylene. The weak bands between 1600 and 1500 cm⁻¹ can be of some usefulness because they indicate additives (fatty or resinic acid residue) often present in butyl rubber and generally absent in polyisobutylene. Halogen presence can be seen with elemental analysis or, more simply, with analysis in the flame of a copper gas mantle.

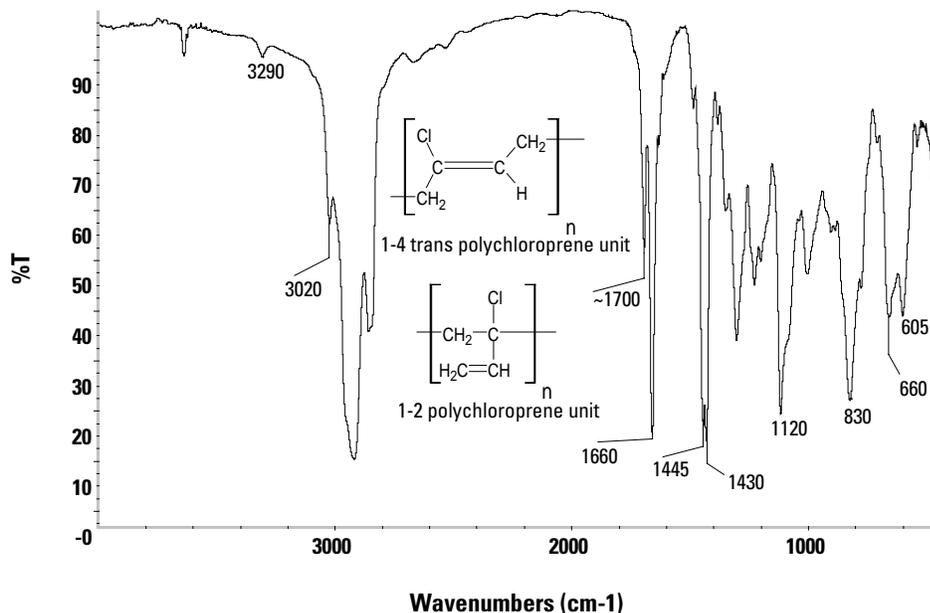
Schedule 9 Polyvinylchloride (PVC)



- ___ ν_{CH} 2965 cm^{-1} - Medium sharp
- ___ $\nu_{\text{CH}_2}^{\text{s}}$ 2910 cm^{-1} - Intense
- ___ $\nu_{\text{CH}_2}^{\text{s}}$ 2840 cm^{-1} - Weak, sharp. Due to different tactic units
- ___ 2810 cm^{-1} - Weak, sharp
- ___ δ_{CH_2} 1425 cm^{-1} - Intense, slightly split
- ___ $\delta_{\text{CH}} + \tau_{\text{CH}_2}$ 1335 cm^{-1} - Intense, wide, complex
- ___ δ_{CH} 1255 cm^{-1} - Very intense, broad
- ___ $\nu_{\text{C-C}}$ 1198 cm^{-1} - Medium
- ___ $\nu_{\text{C-C}}$ 1090 cm^{-1} - Intense, wide
- ___ $\nu_{\text{C-Cl}}$ $\left\{ \begin{array}{l} 695 \text{ cm}^{-1} \text{ medium} \\ 639 \text{ cm}^{-1} \text{ intense} \\ 613 \text{ cm}^{-1} \text{ intense} \end{array} \right.$

The multiple $\nu_{\text{C-Cl}}$ is due to the presence of various tacticity sequences and various head-head or head-tail concatenations.

Schedule 10 Polychloroprene (Neoprene)



— $2\nu_{C=C} = 2290 \text{ cm}^{-1}$ - Weak

— $\nu_{C-H \text{ of } C=CH} = 3020 \text{ cm}^{-1}$ - Weak, sharp

— $\nu_{C=O} = 1700 \text{ cm}^{-1}$ - Variable, at times absent. It is due to fatty or resinic acid residual derived from soaps used in the polymerization.

— $\nu_{C=C} = 1660 \text{ cm}^{-1}$ - * Very intense and sharp

— $\left\{ \begin{array}{l} \delta_{CH_2} = 1445 \text{ cm}^{-1} \\ \delta_{CH_2} = 1430 \text{ cm}^{-1} \end{array} \right.$ * Very intense and sharp. The first is due to CH₂

bonded to CH, and the second to CH₂ bonded to CCl.

— $\nu_{C-C-CCl} = 1120 \text{ cm}^{-1}$ - * Intense, complex

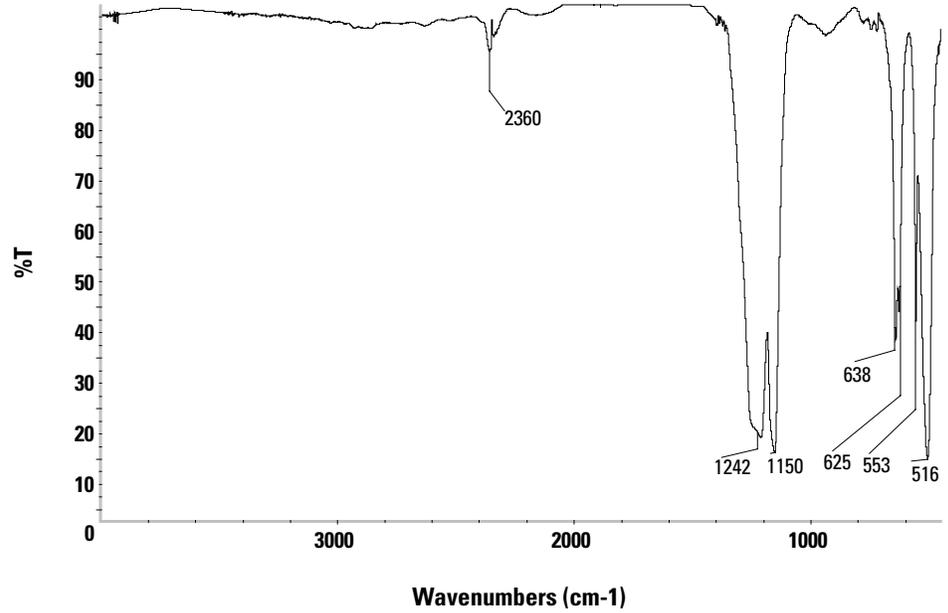
— $\omega_{C-H \text{ of } C=CH} = 830 \text{ cm}^{-1}$ - * Intense, complex

— $\nu_{C-Cl} \left\{ \begin{array}{l} 660 \text{ cm}^{-1} \\ 605 \text{ cm}^{-1} \end{array} \right.$ Weak

It is not easy to characterize the bands due to small amounts of other structures. Polychloroprene can crystallize with age, and that provokes the appearance of sharp bands that are diminished in the spectrum of the

amorphous form. The main bands of crystallinity are those at 782 and 952 cm^{-1} .

Schedule 11 Polytetrafluoroethylene (PTFE)



— $2\nu_{\text{CF}_2}^{\text{a}} + 2\nu_{\text{CF}_2}^{\text{s}} + (\nu_{\text{CF}_2}^{\text{a}} + \nu_{\text{CF}_2}^{\text{s}}) = 2360 \text{ cm}^{-1}$ - Medium bands, complex

— $\nu_{\text{CF}_2}^{\text{a}} = 1242 \text{ cm}^{-1}$ - Very intense

— $\nu_{\text{CF}_2}^{\text{s}} = 1150 \text{ cm}^{-1}$ - Very intense

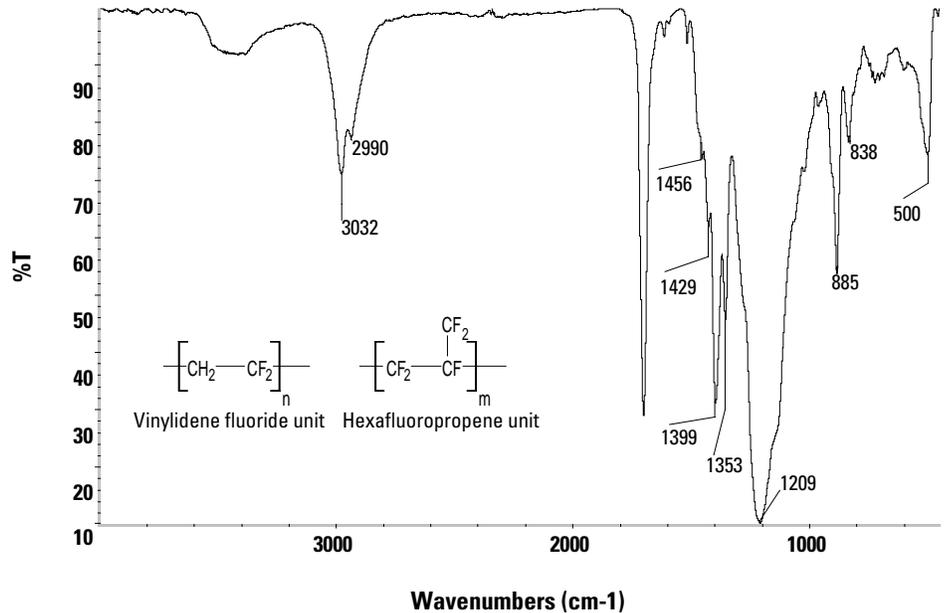
— $\omega_{\text{CF}_2} = 638 \text{ and } 625 \text{ cm}^{-1}$ - Intense

— $\delta_{\text{CF}_2} = 553 \text{ cm}^{-1}$ - Medium, intense

— $\rho_{\text{CH}_2} = 516 \text{ cm}^{-1}$ - Intense

Schedule 12

Vinylidene Fluoride – Hexafluoropropene Copolymer



— $\nu_{\text{CH}_2}^a = 3032 \text{ cm}^{-1}$ - * Weak. As already explained in the text, the presence of two fluorine atoms on the C adjacent to the CH_2 makes the C-H bond much shorter than normal, and therefore very strong, justifying the higher wave number value. In the other part, the presence of an electronegative element in α renders the C of the CH_2 much less negative in regards to the H. Thus the C-H dipole that results has a dipole moment that is much lower and therefore a much lower intensity.

— $\nu_{\text{CH}_2}^s = 2990 \text{ cm}^{-1}$ - * Weak. It is worth noting the observations made for the previous band.

$$\text{— } \delta_{\text{CH}_2 \text{ inverted units}} = \begin{cases} 1456 \text{ cm}^{-1} \\ 1429 \text{ cm}^{-1} \end{cases} \text{ Very weak.}$$

— $\delta_{\text{CH}_2 \text{ normal units}} = 1399 \text{ cm}^{-1}$ - * Intense, proportional to the VDF (vinylidene fluoride) content.

— $\delta_{\text{CH}_2 \text{ adjacent to hexafluoropropene}} = 1353 \text{ cm}^{-1}$ - * Medium, proportional to the content of hexafluoropropene.

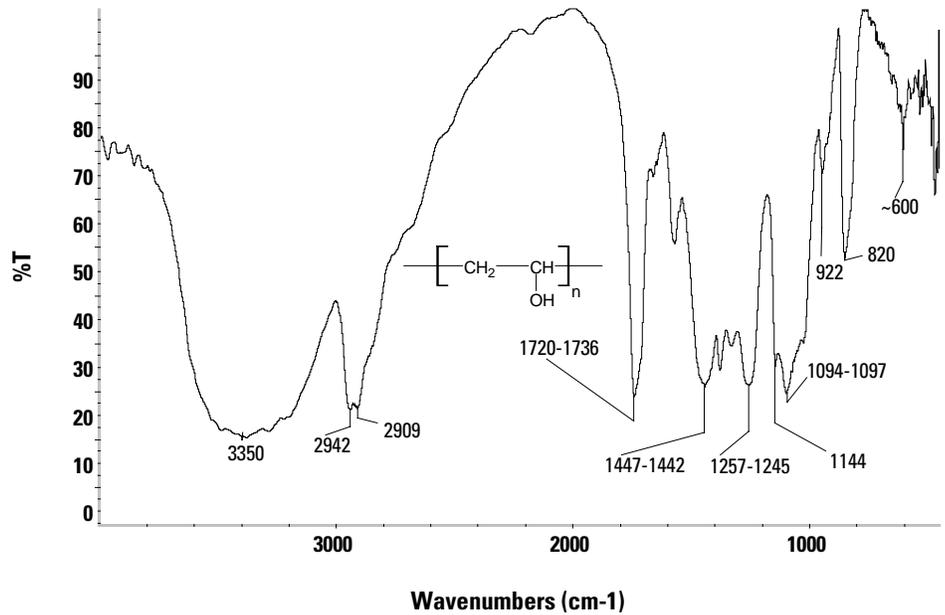
— $\nu_{\text{CF}_2} = 1209 \text{ cm}^{-1}$ - * Very intense, wide and complex

— 885 cm^{-1} - Medium, due to the amorphous sequences of VDF

___ 838 cm^{-1}

___ 500 cm^{-1}

Schedule 13 Polyvinyl Alcohol



___ $\nu_{\text{OH}} = 3350 \text{ cm}^{-1}$ - Intense, broad

___ $\nu_{\text{CH}_2}^{\text{a}} = 2942 \text{ cm}^{-1}$ - Intense, sharp

___ $\nu_{\text{CH}_2}^{\text{s}} = 2909 \text{ cm}^{-1}$ - Intense, sharp

___ $\nu_{\text{C=O}} = 1719\text{-}1736 \text{ cm}^{-1}$ - Variable. Due to non-hydrolyzed polyvinylacetate.

___ $\delta_{\text{O-H in the plane}} = 1447\text{-}1442 \text{ cm}^{-1}$ - Medium, broad, split

___ $\nu_{\text{C-O ester}} = 1257\text{-}1245 \text{ cm}^{-1}$ - Variable. Due to non-hydrolyzes polyvinylacetate.

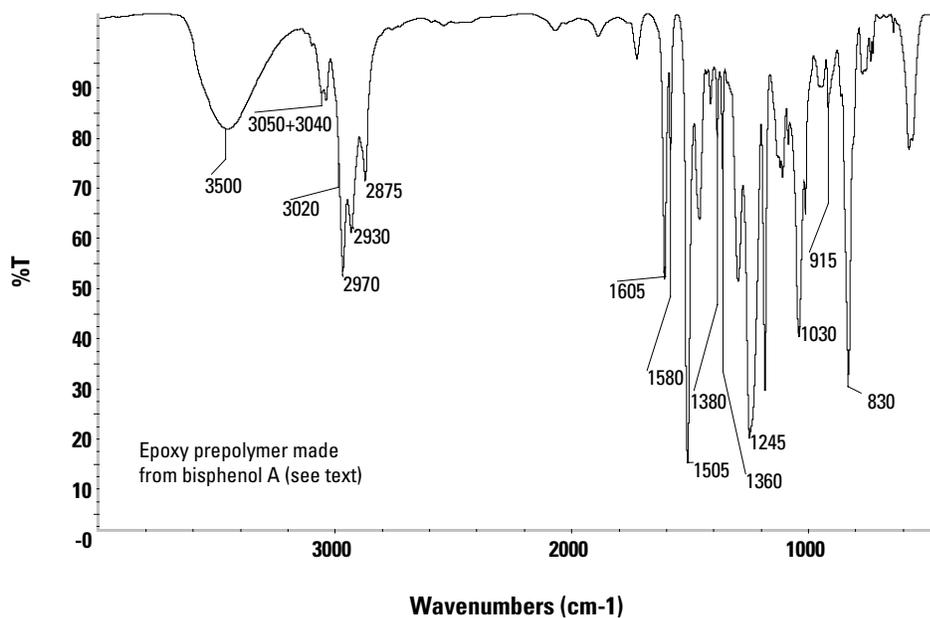
___ $\nu_{\text{C-O}} = 1094\text{-}1097 \text{ cm}^{-1}$ - Intense, complex, preceded by a sharp band at 1144 cm^{-1} (often only a bend) and continued from one at 1024 cm^{-1} (often only a bend).

___ 922 cm^{-1} - Weak, broad. Due to syndiotactic sequences.

___ 820 cm^{-1} - Medium, broad. Due to syndiotactic sequences.

___ $\delta_{\text{O-H out of the plane}} = \text{ca } 600 \text{ cm}^{-1}$ - Very wide

Schedule 14 Epoxy Resin



— $\nu_{\text{OH}} = 3500 \text{ cm}^{-1}$ - Weak, wide

— $\left\{ \begin{array}{l} \nu_{\text{CH arom.}} = 3050 \text{ cm}^{-1} \\ \nu_{\text{CH arom.}} = 3040 \text{ cm}^{-1} \end{array} \right.$ Weak, sharp

— $\nu_{\text{CH}_2 \text{ epoxy}}^{\text{a}} = 3020 \text{ cm}^{-1}$ - Bend

— $\nu_{\text{CH}_3}^{\text{a}} = 2970 \text{ cm}^{-1}$ - Medium, sharp

— $\nu_{\text{CH}_2 \text{ of } -\text{O}-\text{CH}_2-}^{\text{a}} = 2930 \text{ cm}^{-1}$ - Weak, sharp

— $\nu_{\text{CH}_2 \text{ of } -\text{O}-\text{CH}_2-}^{\text{s}} = 2875 \text{ cm}^{-1}$ - Weak, sharp

— $\left\{ \begin{array}{l} \nu_{1 \text{ of arom. ring}} = 1605 \text{ cm}^{-1} \\ \nu_{2 \text{ of arom. ring}} = 1580 \text{ cm}^{-1} \end{array} \right.$ Doublet of medium bands, sharp

— $\nu_{3 \text{ of arom. ring}} = 1505 \text{ cm}^{-1}$ - Intense, sharp

— $\delta_{\text{CH}_3 \text{ of isopropyl}}^{\text{s}} \left\{ \begin{array}{l} \delta_{\text{in phase}} = 1380 \text{ cm}^{-1} \\ \delta_{\text{out of phase}} = 1360 \text{ cm}^{-1} \end{array} \right.$ * Medium-weak, sharp

— $\nu_{\text{C-O-C of alkyl acrylic ether bond}}^{\text{a}} = 1245 \text{ cm}^{-1}$ - Very intense

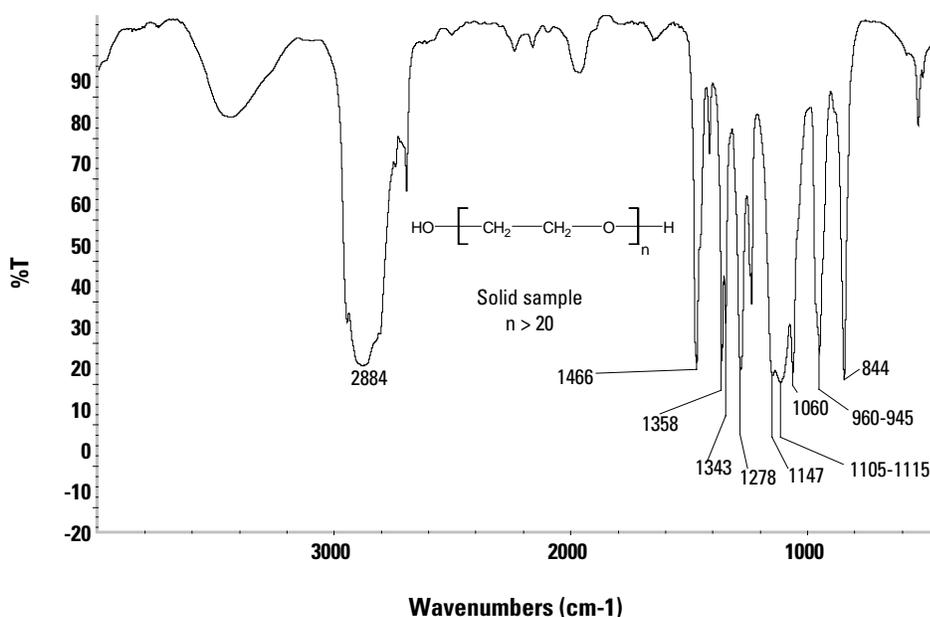
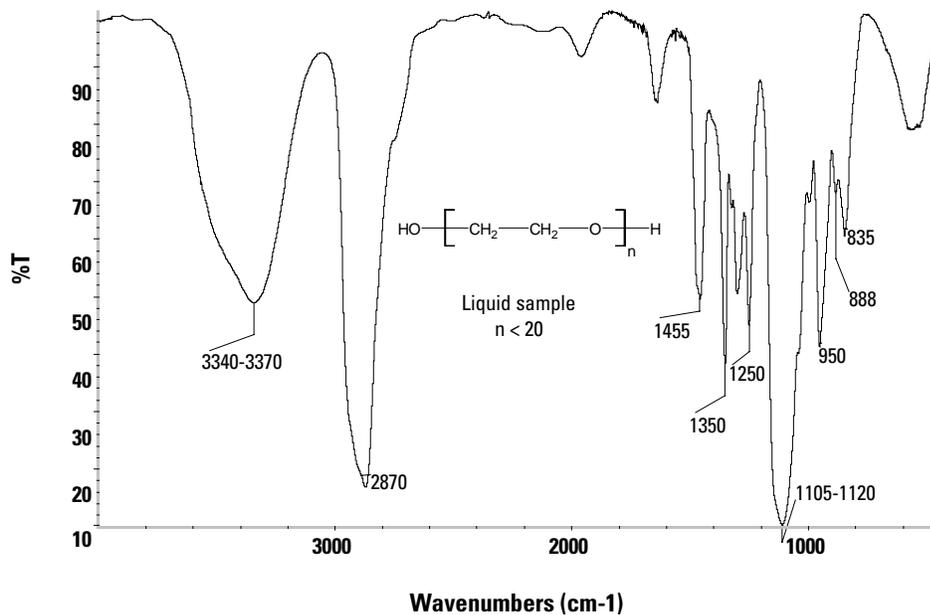
Appendix D Spectra of Polymers and Plasticizers

— $\nu_{\text{C-O-C of alkyl acrylic ether bond}}^{\text{s}} = 1030 \text{ cm}^{-1}$ - Very intense

— $\nu_{\text{epoxy ring}} = 915 \text{ cm}^{-1}$ - * Varies, sharp; its intensity depends on the number of terminal groups.

— $\omega_{2\text{H adj. aromatic}} = 830 \text{ cm}^{-1}$ - * Very intense. Characteristic of the para substitution.

Schedule 15 Polyethylene Glycol



If $n < 20$, the product is liquid; if $n > 20$, the product is crystalline. The spectrum of the solid product presents a greater number of bands with respect to the liquid. These bands, due to crystallinity, are sharpened and in the following are indicated by 'Cryst'.

— $\nu_{\text{OH}} = 3340-3370 \text{ cm}^{-1}$ - Variable, wide. It is very intense in liquid samples, that have a high number of terminal OH. In solids, it is very weak and often not visible.

$$\text{--- } \delta_{\text{CH}_2} = \begin{cases} 1466 \text{ cm}^{-1} \\ 1445 \text{ cm}^{-1} \end{cases} \text{ Doublet. The first band is very influenced by Cryst.}$$

In the solid it is very sharp and the most intense doublet.

--- $\omega_{\text{CH}_2} = 1350 \text{ cm}^{-1}$ - Medium. In solid samples, the band splits as follows:

$$\text{--- } \omega_{\text{CH}_2} = \begin{cases} 1358 \text{ cm}^{-1} \text{ in phase} \\ 1343 \text{ cm}^{-1} \text{ out of phase} \end{cases} \text{ Cryst.}$$

--- $\tau_{\text{CH}_2} = 1278 \text{ cm}^{-1}$ - Intense, sharp. Cryst.

--- 1147 cm^{-1} - Intense, sharp. Cryst.

--- $\nu_{\text{C-O-C}}^a = 1105\text{-}1120 \text{ cm}^{-1}$ - * Very intense and wide. In solids it is much sharper.

--- 1060 cm^{-1} - Intense, sharp. Cryst.

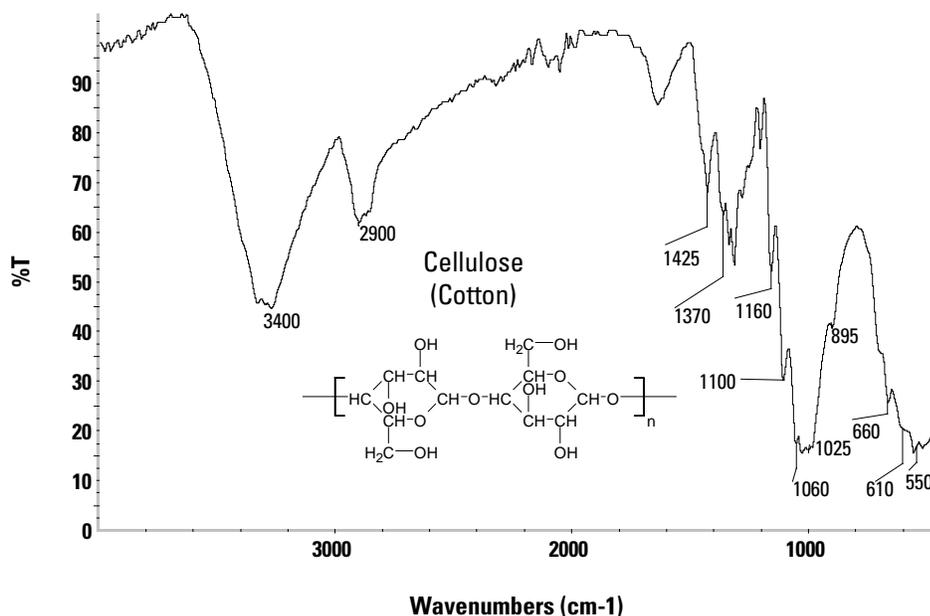
--- $\rho_{\text{CH}_2} = 950 \text{ cm}^{-1}$ - Medium-intense. In solid samples it splits as follows:

$$\text{--- } \rho_{\text{CH}_2} = \begin{cases} 960 \text{ cm}^{-1} \text{ out of phase} \\ 945 \text{ cm}^{-1} \end{cases} \text{ Medium-intense. Cryst. The first}$$

becomes more intense in samples at a more elevated M.P.

--- $\rho_{\text{CH}_2} = 844 \text{ cm}^{-1}$ in phase = 844 cm^{-1} in phase - Intense, sharp. Cryst.

Schedule 16 Cellulose



— ν_{OH} = 3400 cm^{-1} - Intense and wide

— $\nu_{\text{CH}_2 \text{ and CH}}$ = 2900 cm^{-1} - Medium, wide, complex

— δ_{CH_2} = 1425 cm^{-1} - Medium-weak, complex

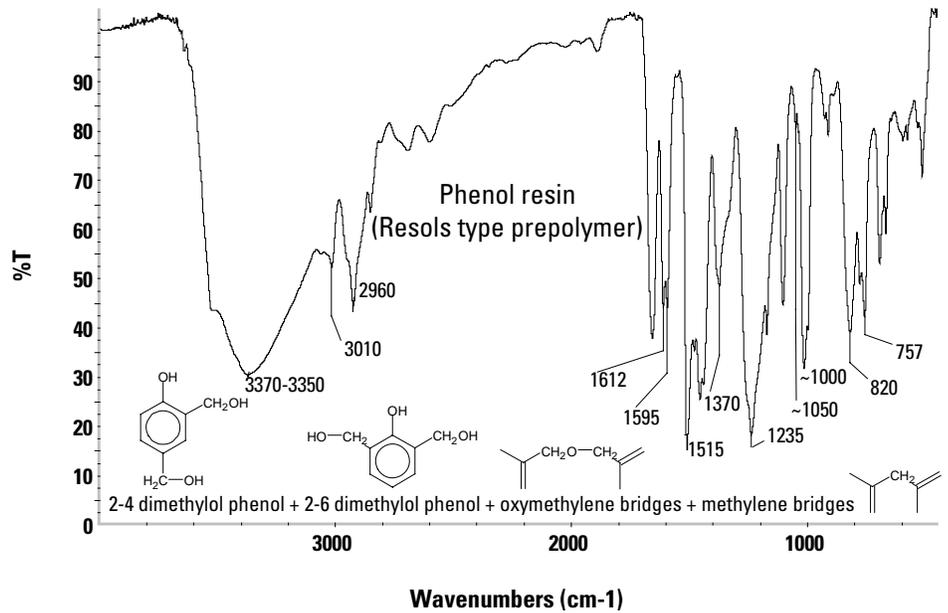
— $\delta_{\text{OH in the plane}}$ = 1370 cm^{-1} - Medium-weak, complex

— $\nu_{\text{C-O-C and C-O-H}}$ $\left\{ \begin{array}{l} 1160 \text{ cm}^{-1} \\ 1110 \text{ cm}^{-1} \\ 1060 \text{ cm}^{-1} \text{ Very intense, complex} \\ 1025 \text{ cm}^{-1} \\ 895 \text{ cm}^{-1} \end{array} \right.$

— $\delta_{\text{OH out of the plane}}$ = $\left\{ \begin{array}{l} 660 \text{ cm}^{-1} \\ 610 \text{ cm}^{-1} \text{ Intense, wide, complex} \\ 555 \text{ cm}^{-1} \end{array} \right.$

The multiple bands are due in great part to the presence of crystallinity bands. Cotton, in fact, is constituted from at least 70% crystalline α -cellulose.

Schedule 17 Phenolic Resin



— $\nu_{\text{OH of phenol and of CH}_2\text{-OH}} = 3370\text{-}3350 \text{ cm}^{-1}$ - Very intense, wide

— $\nu_{\text{C-H aromatic}} = 3010 \text{ cm}^{-1}$ - Weak

— $\nu_{\text{CH}_2} = 2960 \text{ cm}^{-1}$ - Medium, complex

— $\nu_{\text{arom. ring}}^1 = \begin{cases} 1612 \text{ cm}^{-1} \\ 1595 \text{ cm}^{-1} \end{cases}$ - Intense doublet, sharp

— $\nu_{\text{arom. ring}}^2 = 1515 \text{ cm}^{-1}$ - Intense, sharp

— $\delta_{\text{OH phenol}} = 1370 \text{ cm}^{-1}$ - Intense, wide

— $\nu_{\text{OH phenol}} = 1235 \text{ cm}^{-1}$ - Very intense, wide

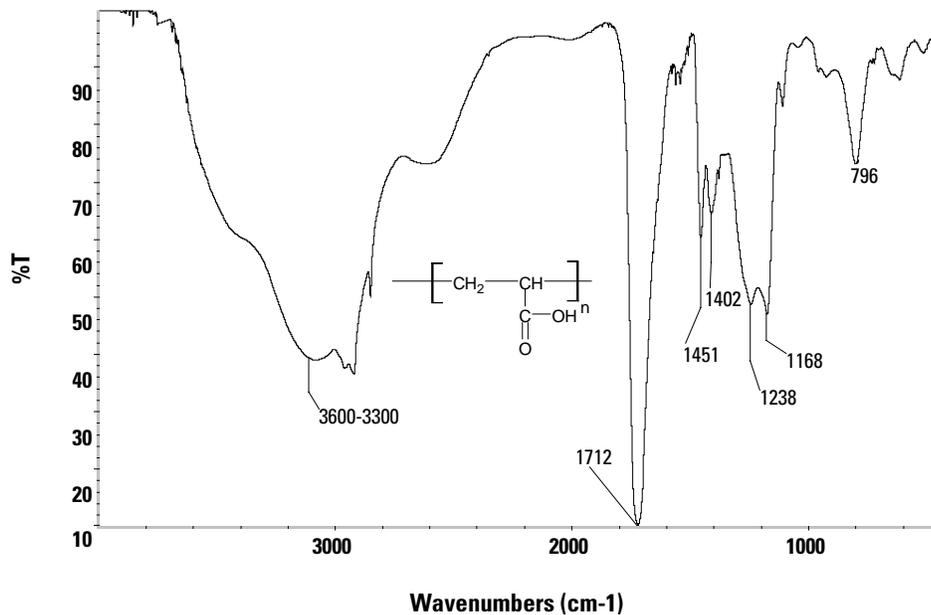
— $\nu_{\text{C-O-C oxymethylene bridge}} = \text{ca. } 1050 \text{ cm}^{-1}$ - Variable, complex. The intensity depends on the amount of oxymethylenic bridges present. It is absent in novolac.

— $\nu_{\text{C-O of the CH}_2\text{-OH group}} = \text{ca. } 1000 \text{ cm}^{-1}$ - Variable, complex. The intensity depends on the amount of $\text{CH}_2\text{-OH}$ groups present. It is absent in novolac.

— $\omega_{2\text{H adj. to the 2-4 phenol}} = 825 \text{ cm}^{-1}$ - Medium-intense

— $\delta_{\text{ring of 2-6 phenol}}^{\text{out of the plane}} = 756 \text{ cm}^{-1}$ - Medium, complex

Schedule 18 Polyacrylic Acid



— $\nu_{OH} = 3600-3300 \text{ cm}^{-1}$ - Intense and very wide. It nearly completely obscures the CH_2 stretching.

— $\nu_{C=O} = 1712 \text{ cm}^{-1}$ - Intense and wide

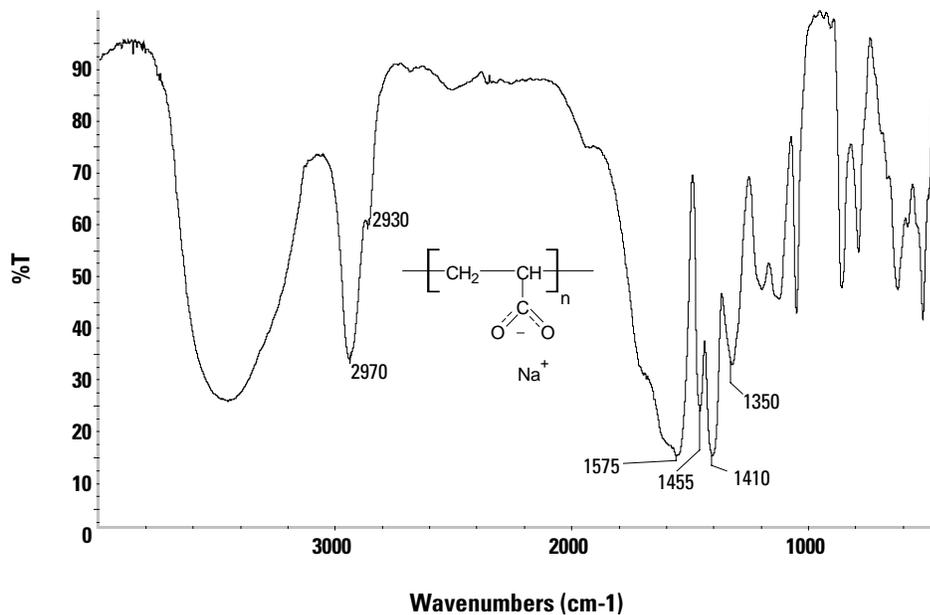
— $\delta_{CH_2} + \delta_{O-H \text{ in the plane}} + \nu_{C-O} = 1451 \text{ cm}^{-1}$ - Medium

— $\delta_{OH} + \nu_{C-O} = 1402 \text{ cm}^{-1}$ - Medium

— $\nu_{C-O} + \delta_{OH} = \begin{cases} 1238 \text{ cm}^{-1} \\ 1168 \text{ cm}^{-1} \end{cases}$ Intense and wide

— $\delta_{OH \text{ out of the plane}} = 796 \text{ cm}^{-1}$ - Medium, wide

Schedule 19 Disodium Polyacrylate



The bands between 3300 cm⁻¹ and 3100 cm⁻¹ are due to absorbed water and a non-salted (ionic) OH of COOH. The same thing is true for the bend between 1600 and 1700 cm⁻¹.

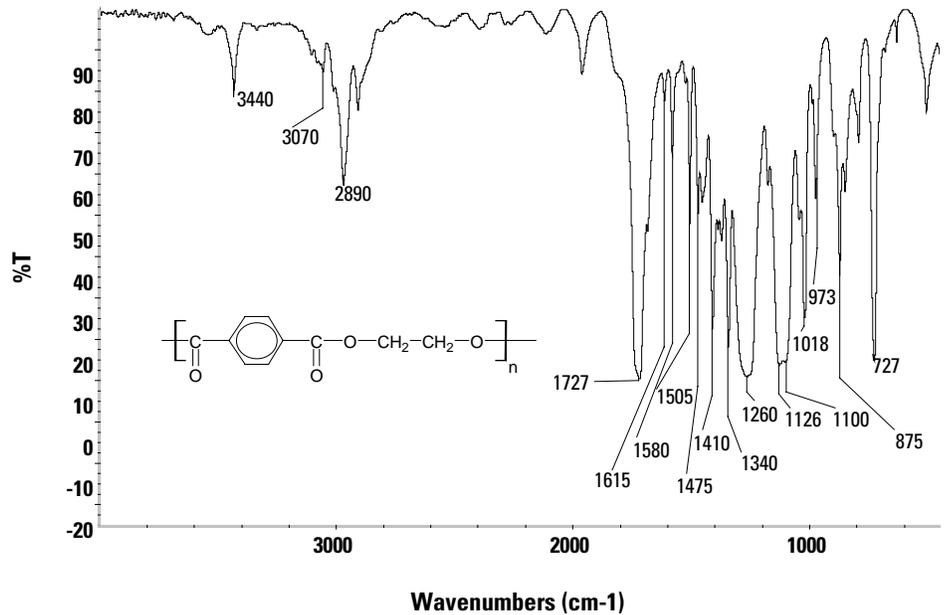
$$\text{--- } \nu_{\text{CH}_2}^{\text{a}} = 2970 \text{ cm}^{-1} - \text{Weak}$$

$$\text{--- } \nu_{\text{CH}_2}^{\text{s}} = 2930 \text{ cm}^{-1} - \text{Weak}$$

$$\text{--- } \nu_{\text{CO}}^{\text{a}} = 1575 \text{ cm}^{-1} - \text{Very intense}$$

$$\text{--- } \nu_{\text{C=O}}^{\text{s}} = \begin{cases} 1455 \text{ cm}^{-1} - \text{Medium} \\ 1410 \text{ cm}^{-1} - \text{Very intense} \\ 1350 \text{ cm}^{-1} - \text{Medium weak, broad} \end{cases} \quad \text{Hiding the } \delta_{\text{CH}_2}$$

Schedule 20 Polyethylene Terephthalate (PET)



___ $2\nu_{\text{C=O}} = 3440 \text{ cm}^{-1}$ - Very weak

___ $\nu_{\text{CH aromatic}} = 3070 \text{ cm}^{-1}$ - Weak, multiple

___ $\nu_{\text{CH}_2}^{\text{a}} = 2980 \text{ cm}^{-1}$ - Weak

___ $\nu_{\text{C=O}} = 1727 \text{ cm}^{-1}$ - Very intense, sharp

___ $\nu_{\text{ring}}^1 = \begin{cases} 1615 \text{ cm}^{-1} \\ 1580 \text{ cm}^{-1} \end{cases}$ - Weak, sharp

___ $\nu_{\text{ring}}^2 = 1505 \text{ cm}^{-1}$ - Weak, sharp

___ $\delta_{\text{CH}_2} = 1470 \text{ cm}^{-1}$ - Weak, sharp

___ 1410 cm^{-1} - Medium, sharp

___ $\omega_{\text{CH}_2} = 1340 \text{ cm}^{-1}$ - Medium, sharp

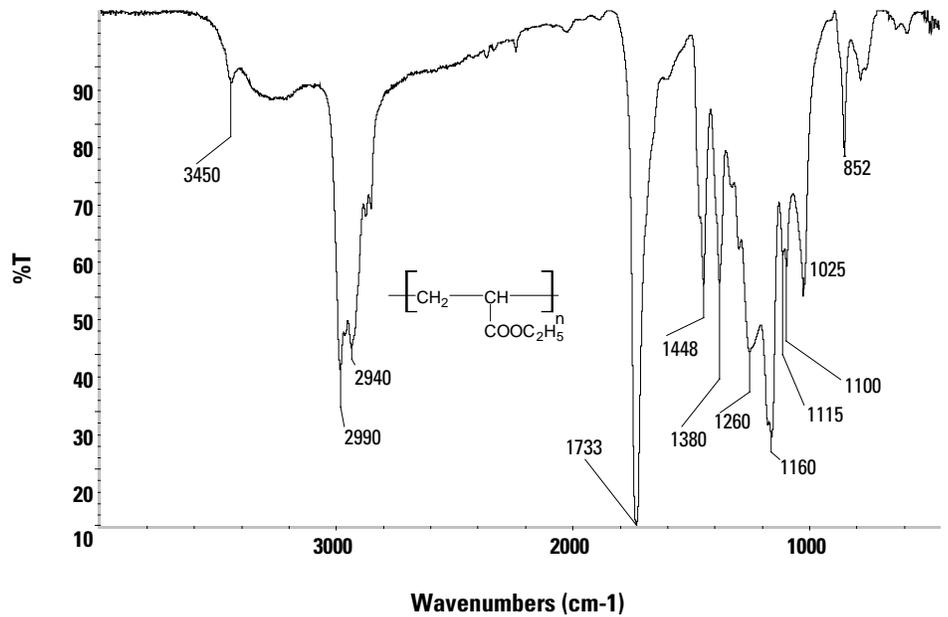
___ $\nu_{\text{C-O-C}}^{\text{a}} = 1270 \text{ cm}^{-1}$ - Very intense, wide

___ $\nu_{\text{C-O-C}}^{\text{s}} = \begin{cases} 1126 \text{ cm}^{-1} \\ 1100 \text{ cm}^{-1} \end{cases}$ - Intense doublet band, sharp

___ 1018 cm^{-1} and 973 cm^{-1} - Weak, sharp

___ $\omega_{2\text{Hadj.ring}} = 727 \text{ cm}^{-1}$ - Intense, sharp

Schedule 21 Diethyl Polyacrylate



___ $2\nu_{\text{C}=\text{O}} = 3450 \text{ cm}^{-1}$ - Weak

___ $\nu_{\text{CH}_3}^{\text{a}} + \nu_{\text{CH}_2}^{\text{a}} = 2990 \text{ cm}^{-1}$ - Medium, sharp, complex

___ $\nu_{\text{CH}_2}^{\text{s}} = 2940 \text{ cm}^{-1}$ - Weak

___ $\nu_{\text{C}=\text{O}} = 1733 \text{ cm}^{-1}$ - Very intense

___ $\delta_{\text{CH}_2} + \delta_{\text{CH}_3}^{\text{a}} = 1448 \text{ cm}^{-1}$ - * Medium, complex. This band, in shape and intensity, is extraordinarily similar to the following; it serves in order to recognize polyethylacrylate at a glance.

___ $\delta_{\text{CH}_3}^{\text{s}} = 1380 \text{ cm}^{-1}$ - * Medium, complex

___ 1300 cm^{-1} - Weak

___ $\nu_{\text{C}-\text{O}-\text{C}}^{\text{a}} = 1260 \text{ cm}^{-1}$ - Medium

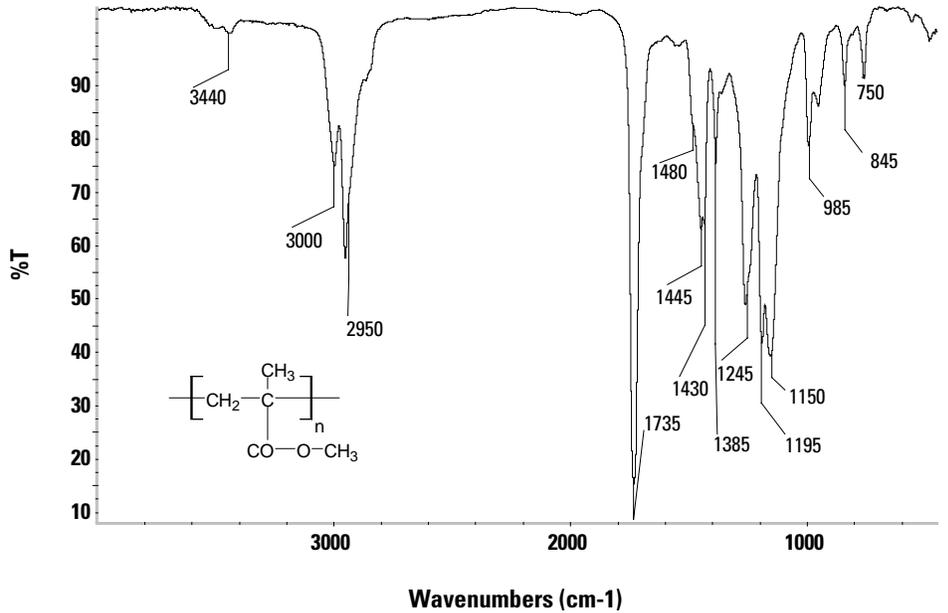
___ $\nu_{\text{C}-\text{O}-\text{C}}^{\text{s}} = 1175 \text{ and } 1160 \text{ cm}^{-1}$ - Intense

___ $1115 \text{ and } 1100 \text{ cm}^{-1}$ - *Medium

___ 1025 cm^{-1} - Medium

___852 cm⁻¹ - *Medium, sharp. This is the band that more than any other serves to identify polyethylacrylate alone as well as in mixtures or as a copolymer with other acrylates.

Schedule 22 Polymethylmethacrylate (PMMA)



$$\text{--- } 2\nu_{\text{C=O}} = 3440 \text{ cm}^{-1} - \text{Weak}$$

$$\text{--- } \nu_{\text{CH}_3 \text{ of O-CH}_3}^{\text{a}} = 3000 \text{ cm}^{-1} - \text{Medium, sharp}$$

$$\text{--- } \nu_{\text{CH}_2}^{\text{a}} + \nu_{\text{CH}_3}^{\text{a}} = 2950 \text{ cm}^{-1} - \text{Medium, sharp}$$

$$\text{--- } \nu_{\text{C=O}} = 1733 \text{ cm}^{-1} - \text{Very intense}$$

$$\text{--- } \delta_{\text{CH}_3 \text{ of O-CH}_3}^{\text{s}} + \delta_{\text{CH}_3 \text{ of O-CH}_3}^{\text{a}} + \delta_{\text{CH}_2} = \begin{cases} 1480 \text{ cm}^{-1} \\ 1445 \text{ cm}^{-1} - \text{Medium} \\ 1430 \text{ cm}^{-1} \end{cases}$$

$$\text{--- } \delta_{\text{CH}_3 \text{ of C-CH}_3}^{\text{s}} = 1385 \text{ cm}^{-1} - \text{Medium}$$

$$\text{--- } \nu_{\text{C-O-C}}^{\text{a}} = \begin{cases} 1275 \text{ cm}^{-1} \\ 1245 \text{ cm}^{-1} \end{cases} - \text{Intense}$$

$$\text{--- } \nu_{\text{C-O-C}}^{\text{s}} = \begin{cases} 1195 \text{ cm}^{-1} \\ 1150 \text{ cm}^{-1} \end{cases} - \text{Intense}$$

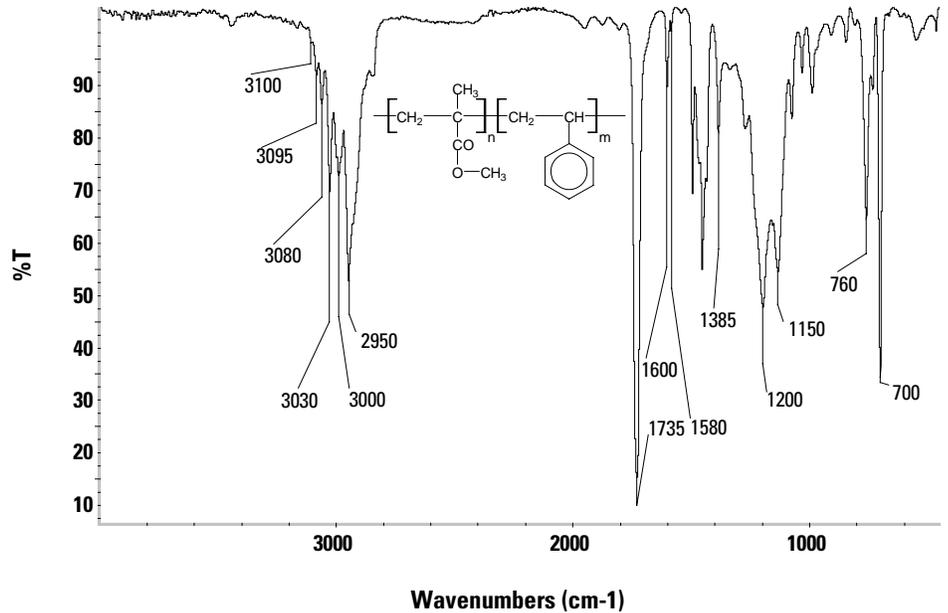
$$\text{--- } 985 \text{ cm}^{-1} - \text{Medium}$$

___ 845 cm^{-1} - Medium

___ $740\text{-}750\text{ cm}^{-1}$ - Medium. Characteristic of methacrylate; not present in acrylates.

Schedule 23

Methyl Methacrylate Styrene Copolymer



$$\text{--- } \nu_{\text{C-H aromatic}} = \begin{cases} 3100 \text{ cm}^{-1} \\ 3095 \text{ cm}^{-1} \\ 3080 \text{ cm}^{-1} \\ 3030 \text{ cm}^{-1} \end{cases} \text{ - Weak, sharp}$$

$$\text{--- } \nu_{\text{CH}_3 \text{ of O-CH}_3}^{\text{a}} = 3000 \text{ cm}^{-1} \text{ - Medium, sharp}$$

$$\text{--- } \nu_{\text{CH}_2}^{\text{a}} + \nu_{\text{CH}_3}^{\text{a}} = 2950 \text{ cm}^{-1} \text{ - Medium, sharp}$$

$$\text{--- } \nu_{\text{C=O}} = 1735 \text{ cm}^{-1} \text{ - Very intense}$$

$$\text{--- } \nu_{\text{ring}}^1 = \begin{cases} 1600 \text{ cm}^{-1} \\ 1580 \text{ cm}^{-1} \end{cases} \text{ - Weak doublet band, sharp}$$

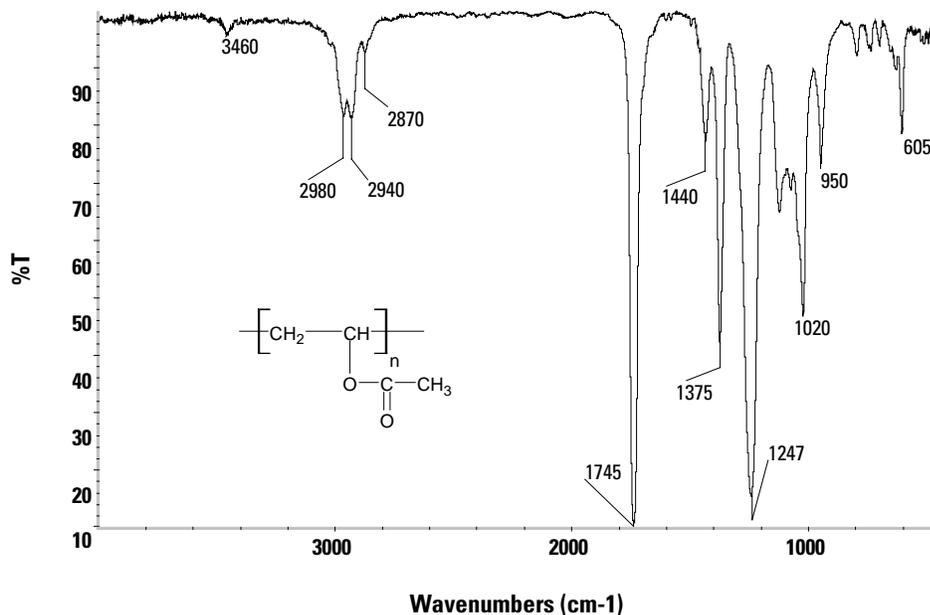
$$\text{--- } \delta_{\text{CH}_3 \text{ of C-CH}_3}^{\text{s}} = 1385 \text{ cm}^{-1} \text{ - Medium}$$

$$\text{--- } \nu_{\text{C-O-C}}^{\text{s}} = \begin{cases} 1200 \text{ cm}^{-1} \\ 1150 \text{ cm}^{-1} \end{cases} \text{ - Intense, complex}$$

$$\text{--- } \omega_{5\text{H adj.}}^1 = 760 \text{ cm}^{-1} \text{ - Intense}$$

$$\text{--- } \omega_{5\text{H adj.}}^2 = 699 \text{ cm}^{-1} \text{ - Intense}$$

Schedule 24 Polyvinylacetate



— $2\nu_{\text{C=O}} = 3466 \text{ cm}^{-1}$ - Very weak

— $\nu_{\text{CH}_3}^{\text{a}} = 2980 \text{ cm}^{-1}$ - Medium, sharp

— $\nu_{\text{CH}_2}^{\text{a}} = 1936 \text{ cm}^{-1}$ - Medium, partially overlapped by the previous band

— $\nu_{\text{CH}_2}^{\text{s}} = 2870 \text{ cm}^{-1}$ - Weak, sharp

— $\nu_{\text{C=O}} = 1745 \text{ cm}^{-1}$ - * Very intense

— $\delta_{\text{CH}_2} + \delta_{\text{CH}_3}^{\text{a}} = 1440 \text{ cm}^{-1}$ - Medium, complex

— $\delta_{\text{CH}_3}^{\text{s}} = 1375 \text{ cm}^{-1}$ - Intense, sharp

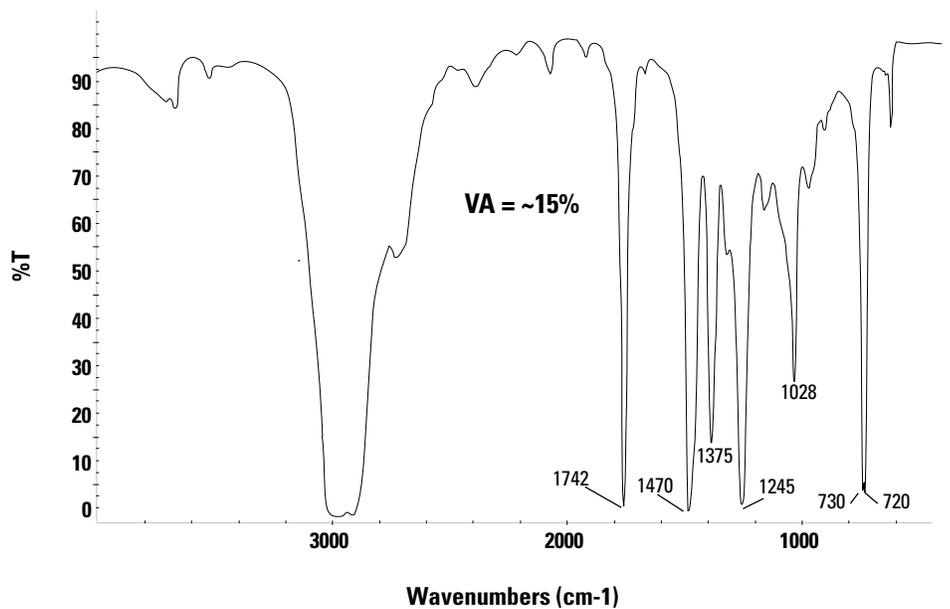
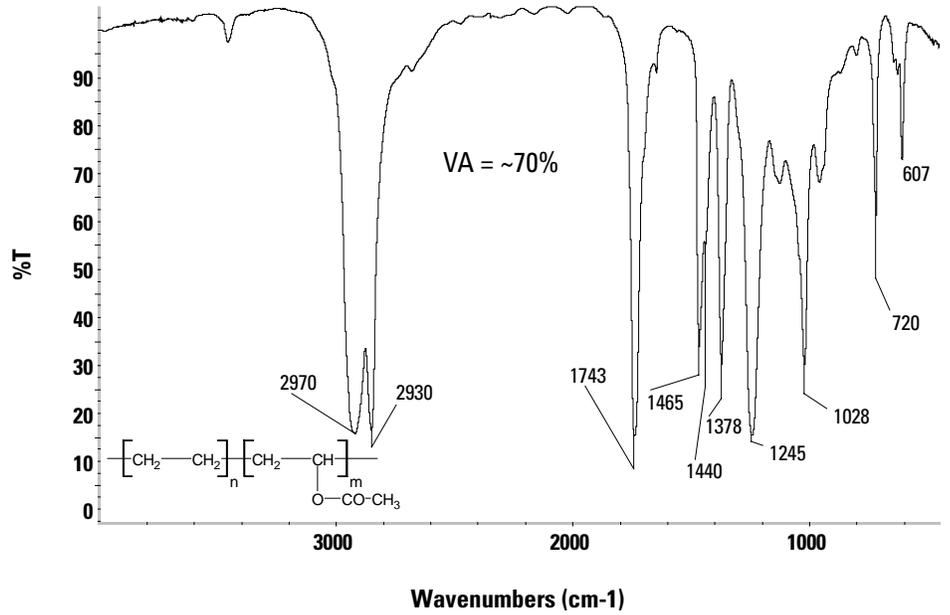
— $\nu_{\text{C-O-C}}^{\text{a}} = 1247 \text{ cm}^{-1}$ - * Very intense

— $\nu_{\text{C-O-C}}^{\text{s}} = 1020 \text{ cm}^{-1}$ - Intense, complex

— $\rho_{\text{CH}_3} = 950 \text{ cm}^{-1}$ - Medium

— $\delta_{\text{C-CO-O}} = 605 \text{ cm}^{-1}$ - Medium, sharp

Schedule 25 Ethylene-Vinylacetate Copolymer (EVA)



— $\nu_{\text{CH}_2 \text{ ethylene}}^a = 2970 \text{ cm}^{-1}$ - * Increases with increasing ethylene content

— $\nu_{\text{CH}_2 \text{ ethylene}}^s = 2930 \text{ cm}^{-1}$ - * Increases with increasing ethylene content

— $\nu_{\text{C=O}} = 1743 \text{ cm}^{-1}$

— $\delta_{\text{CH}_2 \text{ of the ethylene unit}} = 1465 \text{ cm}^{-1}$ - Increases with increasing ethylene content

— $\delta_{\text{CH}_2 \text{ of the vinylacetate unit}} = 1440 \text{ cm}^{-1}$ - Increases with increasing vinylacetate content

— $\delta_{\text{CH}_3}^s = 1378 \text{ cm}^{-1}$ - Medium, increases with increasing vinylacetate content

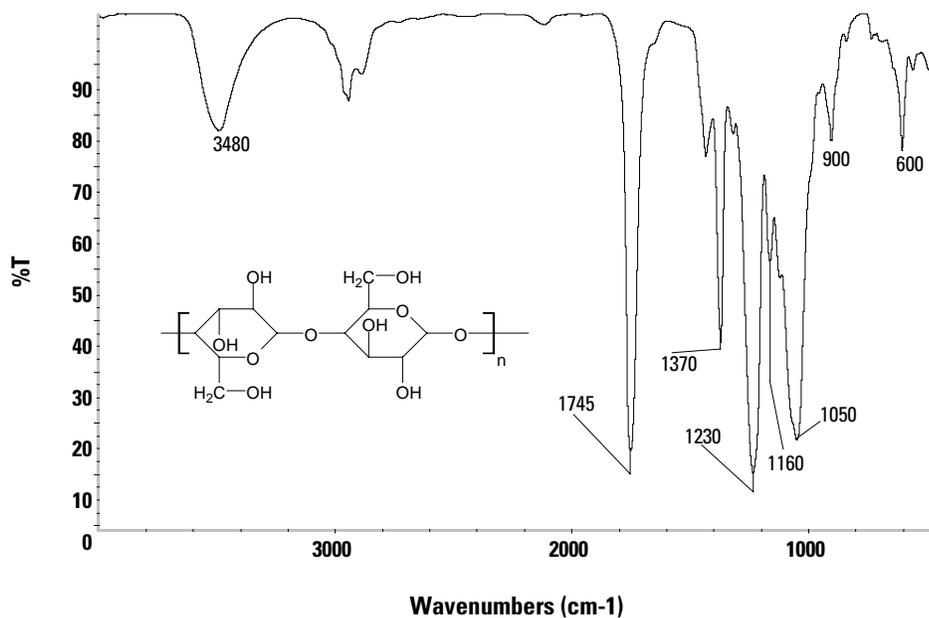
— $\nu_{\text{C-O-C}}^a = 1245 \text{ cm}^{-1}$ - * Very intense. It is characteristic of acetic esters.

— $\nu_{\text{C-O-C}}^s = 1028 \text{ cm}^{-1}$ - Increases with increasing vinylacetate content

— $\omega_{\text{CH}_2 \text{ ethylene sequence}} = 720 \text{ cm}^{-1}$ - * Increases with increasing ethylene content. When the ethylene content is very high, the band splits into a doublet indicating crystallinity (720 cm^{-1} and 730 cm^{-1})

— 607 cm^{-1} - Medium, related to units of vinylacetate.

Schedule 26 Cellulose Acetate



— $\nu_{\text{OH}} = 3480 \text{ cm}^{-1}$ - Wide, variable with the content of OH

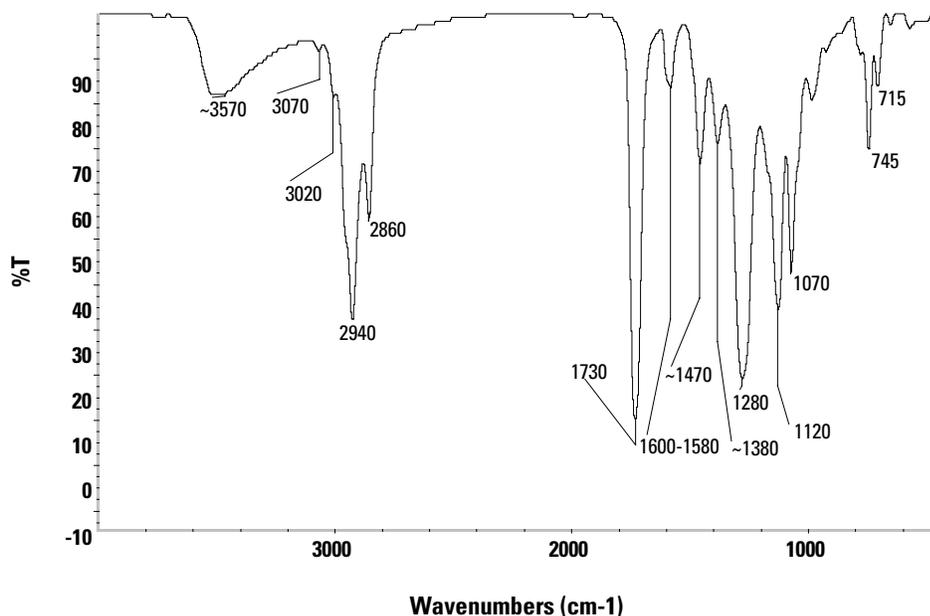
— $\nu_{\text{C=O}} = 1747 \text{ cm}^{-1}$ - Very intense

— $\delta_{\text{CH}_3}^s = 1370 \text{ cm}^{-1}$ - Intense

— $\nu_{\text{C-O-C of the acetate}}^a = 1230 \text{ cm}^{-1}$ - Very intense

— $\nu_{\text{C-O-C of the ether bond}}^a = 1050 \text{ cm}^{-1}$ - Very intense

Schedule 27 Glycerophthalic or Alkyd Resin



— ν_{OH} = ca. 3570 cm^{-1} - Medium, variable. It is due to the non-esterified residual hydroxyl.

— $\nu_{\text{C-H aromatic}}$ = 3070 cm^{-1} - Weak, complex

— $\nu_{\text{C-H of the double bond}}$ = 3020 cm^{-1} - Weak, almost a bend. It is due to the double bonds of esters of unsaturated acids.

— $\nu_{\text{CH}_2}^{\text{a}}$ = 2940 cm^{-1} - Very intense. It is due to the long sequences of CH_2 in esterified fatty acids.

— $\nu_{\text{CH}_2}^{\text{s}}$ = 2860 cm^{-1} - Intense

— $\nu_{\text{C=O of the phthalic ester}} + \nu_{\text{C=O of the fatty acid ester}}$ = 1730 cm^{-1} - Very intense

— $\nu_{\text{ring}}^{\text{1}}$ = $\begin{cases} 1600 \text{ cm}^{-1} \\ 1580 \text{ cm}^{-1} \end{cases}$ - Medium-weak doublet band of nearly equal

intensity. If the first band is much more intense than the second, it can be a matter of terephthalic esters instead of phthalic esters.

— δ_{CH_2} = ca. 1470 cm^{-1} - Medium, complex. Due to CH_2 chains of fatty esters.

___ $\delta_{\text{CH}_3}^s = 1380 \text{ cm}^{-1}$ - Medium. Due to CH_3 terminal groups on fatty ester chains.

___ $\nu_{\text{C-O-C of the aromatic ester}}^a = 1280 \text{ cm}^{-1}$ - * Very intense

___ $\nu_{\text{C-O-C of the aliphatic ester}}^a = \text{ca. } 1160 \text{ cm}^{-1}$ - A bend on the flank of the following:

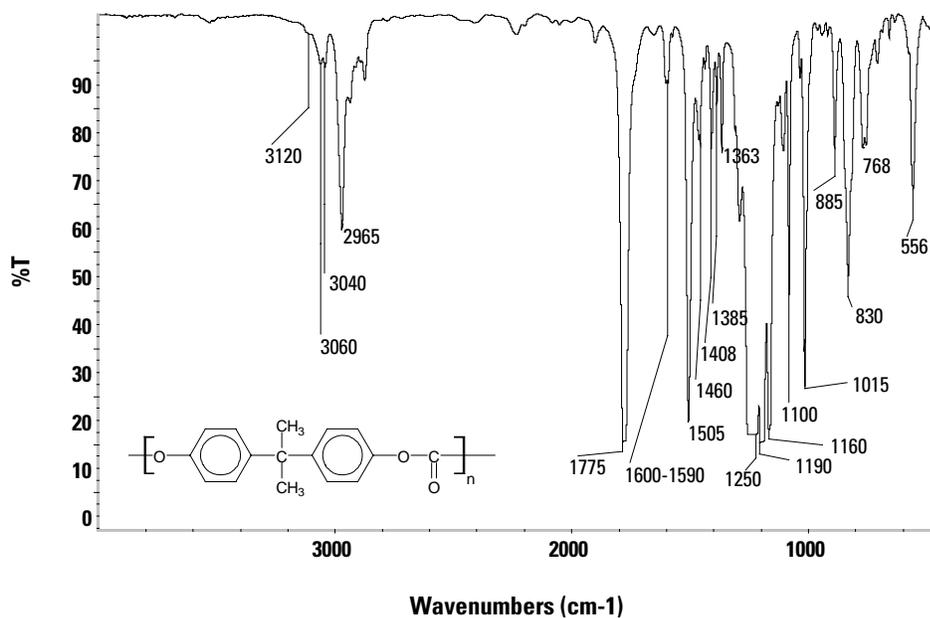
___ $\nu_{\text{C-O-C of the aromatic ester}}^s = 1120 \text{ cm}^{-1}$ - * Intense

___ 1070 cm^{-1} - Intense. Related to phthalic esters

___ $\omega_{4\text{H adj. aromatic ring}} = 745 \text{ cm}^{-1}$ - Medium-weak

___ 715 cm^{-1} - Variable. Related to phthalic esters.

Schedule 28 Polycarbonate



$$\text{--- } \nu_{\text{C-H arom.}} = \begin{cases} 3120 \text{ cm}^{-1} \\ 3060 \text{ cm}^{-1} - \text{Triplet, weak, partially overlapped} \\ 3040 \text{ cm}^{-1} \end{cases}$$

$$\text{--- } \nu_{\text{CH}_3}^{\text{a}} = 2965 \text{ cm}^{-1} - \text{Medium, sharp}$$

$$\text{--- } \nu_{\text{C=O}} = 1775 \text{ cm}^{-1} - \text{Very intense}$$

$$\left. \begin{array}{l} \nu_{\text{ring}}^1 = 1600 \text{ cm}^{-1} \\ \nu_{\text{ring}}^2 = 1590 \text{ cm}^{-1} \end{array} \right\} - \text{Medium-weak, doublet}$$

$$\text{--- } \nu_{\text{ring}}^3 = 1505 \text{ cm}^{-1} - \text{Intense, sharp}$$

$$\text{--- } \delta_{\text{CH}_3 \text{ out of phase}}^{\text{s}} = 1385 \text{ cm}^{-1} - \text{Medium, sharp}$$

$$\text{--- } \delta_{\text{CH}_3 \text{ in phase}}^{\text{s}} = 1363 \text{ cm}^{-1} - \text{Medium, sharp}$$

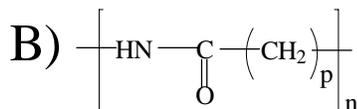
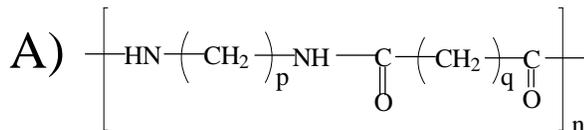
$$\text{--- } \nu_{\text{C-O-C}}^{\text{a}} = 1250 \text{ cm}^{-1} - \text{Very intense and wide}$$

$$\text{--- } \nu_{\text{C-O-C}}^{\text{s}} = 1190 \text{ cm}^{-1} - \text{Very intense and sharp}$$

$$\text{--- } \omega_{2\text{H adj. to the ring}} = 830 \text{ cm}^{-1} - \text{Intense. Para substitution.}$$

Schedule 29 Nylon types of Polyamides

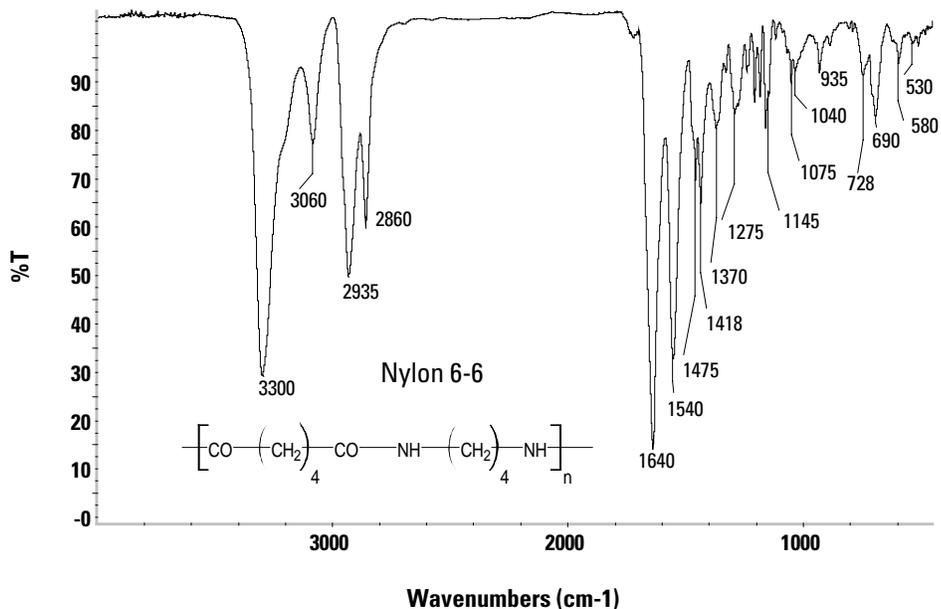
Two types of nylon exist.



The nylon of type A is produced by the condensation of diamine with bicarboxylic acid and is indicated with two numbers that represent the number of carbon atoms of the diamine and the acid (ex: Nylon 6-6).

The nylon of type B is produced by addition of a lactame (see text) and is indicated by a single number that represents the number of carbon atoms in the lactame (ex: Nylon 6).

The two types of polyamide have very similar spectra, so the spectrum of only Nylon 6-6 is shown.



— $\nu_{\text{N-H}} = \text{ca. } 3300 \text{ cm}^{-1}$ - * Intense and sharp. Common to all nylons.

— $2\nu_{\text{C-N}} = 3080\text{-}3050 \text{ cm}^{-1}$ - Weak and sharp. Common to all nylons.

— $\nu_{\text{C=O}} = 1640\text{-}1635 \text{ cm}^{-1}$ - * Intense and sharp. Common to all nylons.

— $\delta_{\text{N-H}} = 1560\text{-}1540 \text{ cm}^{-1}$ - * Intense and sharp. Common to all nylons.
It also varies in position with the type and the intensity of crystallinity.

— $\nu_{\text{C-N}} + \delta_{\text{N-H}} = 1275 \text{ cm}^{-1}$ - Medium, wide

— $\gamma_{\text{N-H}} = 690 \text{ cm}^{-1}$ - Intense, wide, complex

— $\gamma_{\text{CO}} = 580 \text{ cm}^{-1}$ - Intense, sharp

In order to distinguish one polyamide from another, it is very useful to consult the range between 1400 cm^{-1} and 900 cm^{-1} where many crystallinity bands lie. This range is also useful in order to see the changes in crystalline form (α , β , γ).

See the following figures.

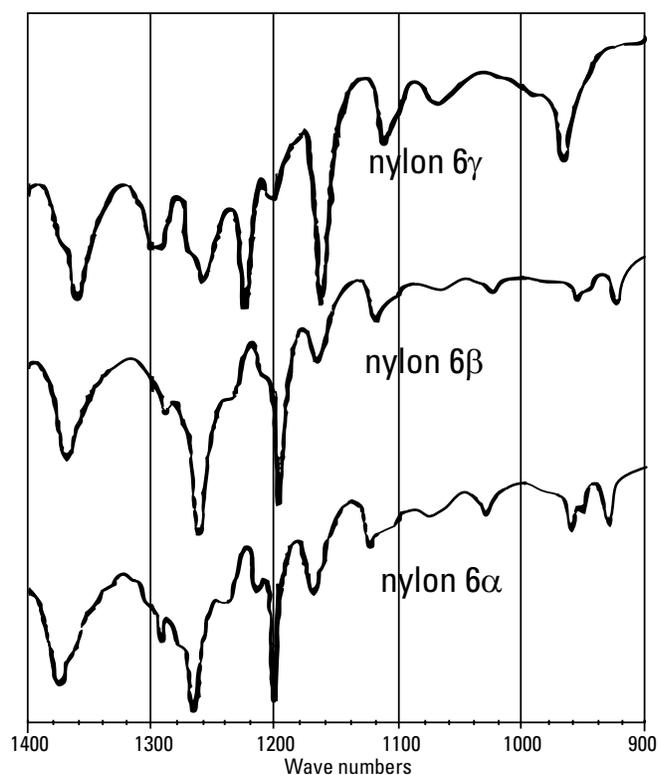


Figure C-1. Various crystalline forms of nylon 6.

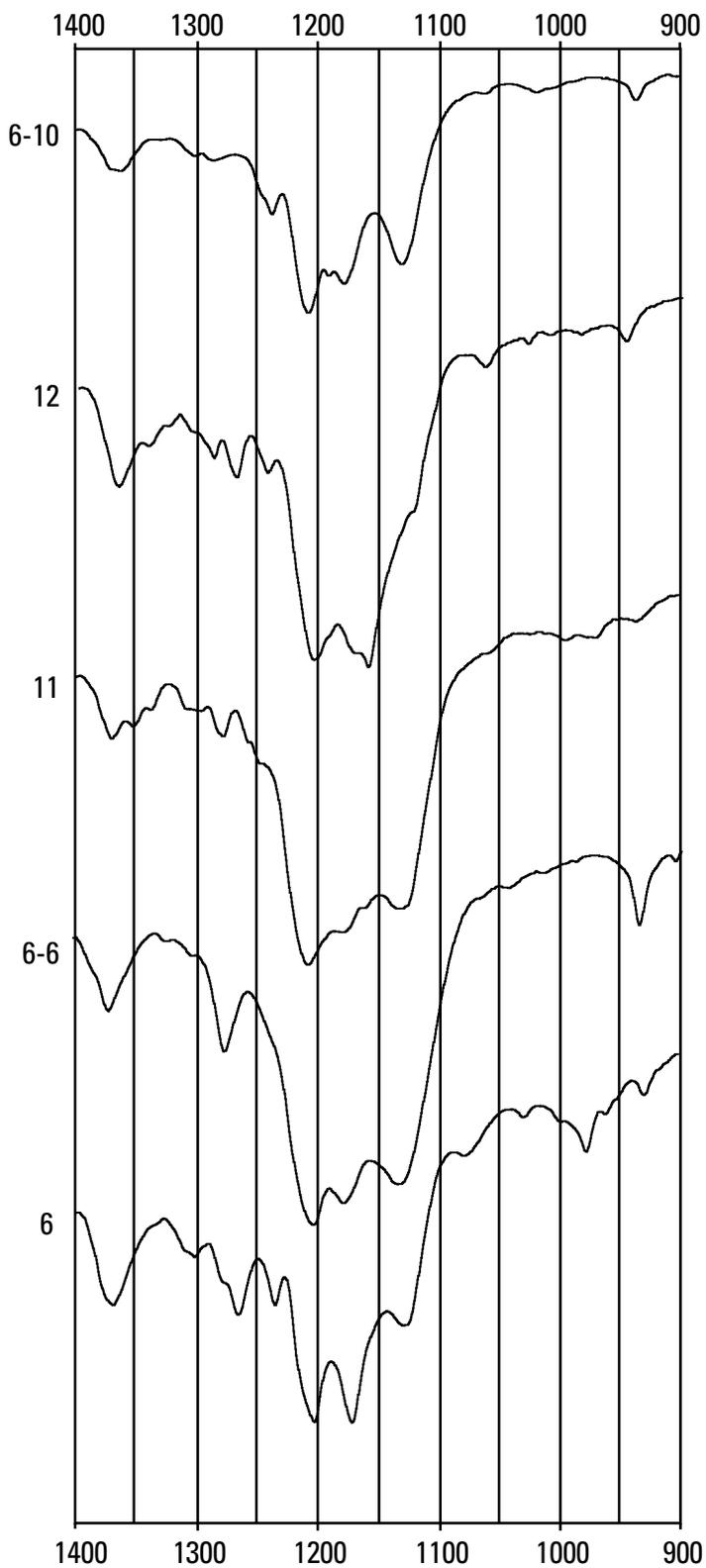
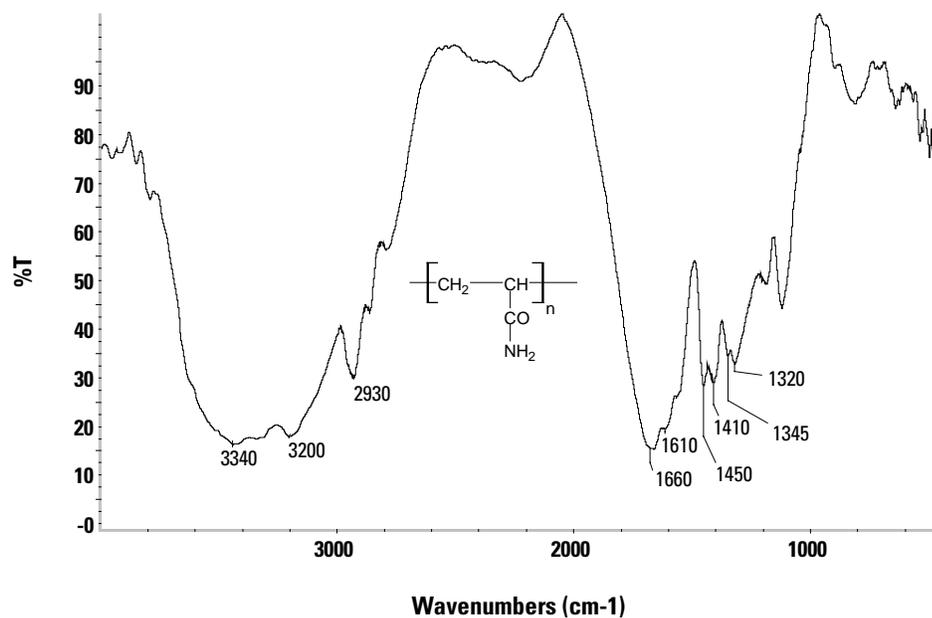


Figure C-2. Spectra of several types of nylon between 1400 and 1900 cm^{-1} .

Schedule 30 Polyacrylamide



— $\nu_{\text{N-H}}^{\text{a}}$ = ca. 3350 cm⁻¹ - Intense and wide

— $\nu_{\text{N-H}}^{\text{s}}$ = ca. 3200 cm⁻¹ - Intense and wide

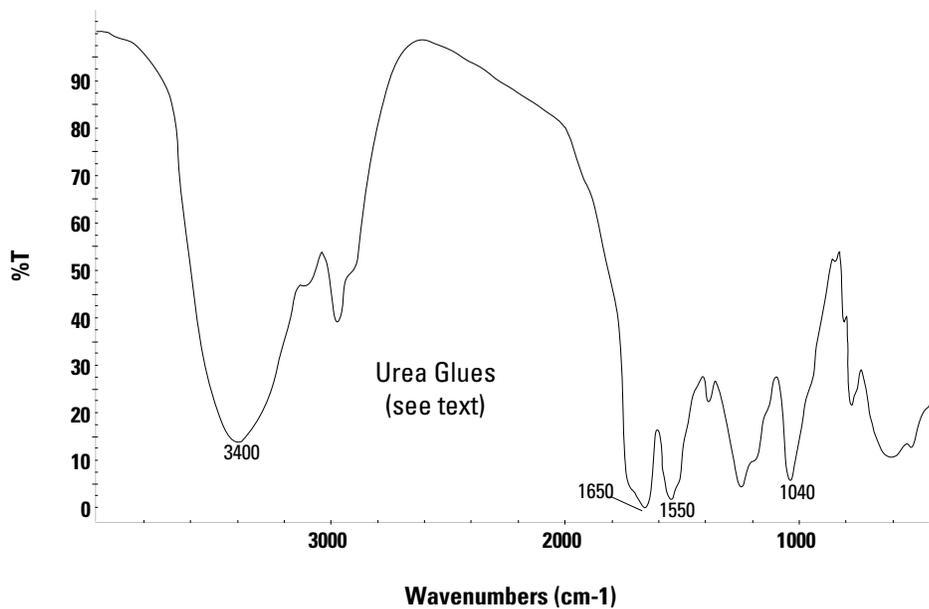
— $\nu_{\text{CH}_2}^{\text{a}}$ = 2930 cm⁻¹ - Medium-weak

— $\nu_{\text{C=O}}$ = 1660 cm⁻¹ - * "Amide I" Very intense

— $\delta_{\text{N-H}}$ = 1610 cm⁻¹ - * "Amide II" A bend on the tail of Amide I

— $\gamma_{\text{N-H}} + \gamma_{\text{CO}}$ = 500-700 cm⁻¹ - Intense, wide, complex

Schedule 31 Ureic Resin



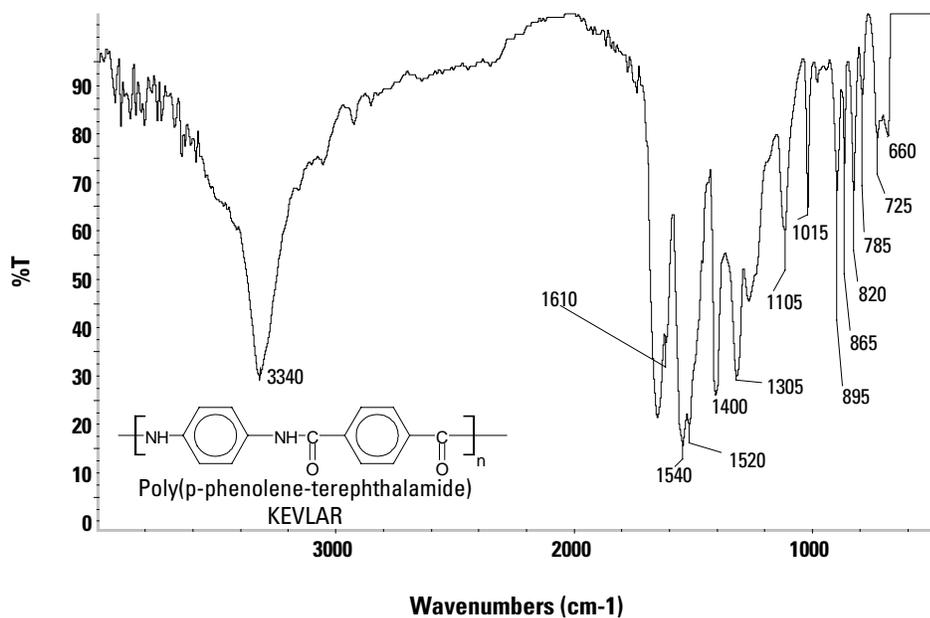
— $\nu_{\text{OH}} = 3300\text{-}3400 \text{ cm}^{-1}$ - Intense and very wide

— $\nu_{\text{C=O}} = \text{ca. } 1650 \text{ cm}^{-1}$ - Very intense and wide, partly overlapped by the following:

— $\delta_{\text{N-H}} = \text{ca. } 1550 \text{ cm}^{-1}$ - Very intense and wide

— $\nu_{\text{C-OH}} + \nu_{\text{N-C-N}}^{\text{s}} = 1050\text{-}1000 \text{ cm}^{-1}$ - Intense and wide

Schedule 32 Aromatic Polyamides (KEVLAR®)



— $\nu_{\text{N-H}} = 3340 \text{ cm}^{-1}$ - Medium, very wide, complex

— $\nu_{\text{C=O}} = 1645 \text{ cm}^{-1}$ - Very intense

— $\nu_{\text{ring}}^1 = 1610 \text{ cm}^{-1}$ - Bend

— $\delta_{\text{N-H}} = 1540 \text{ cm}^{-1}$ - Very intense

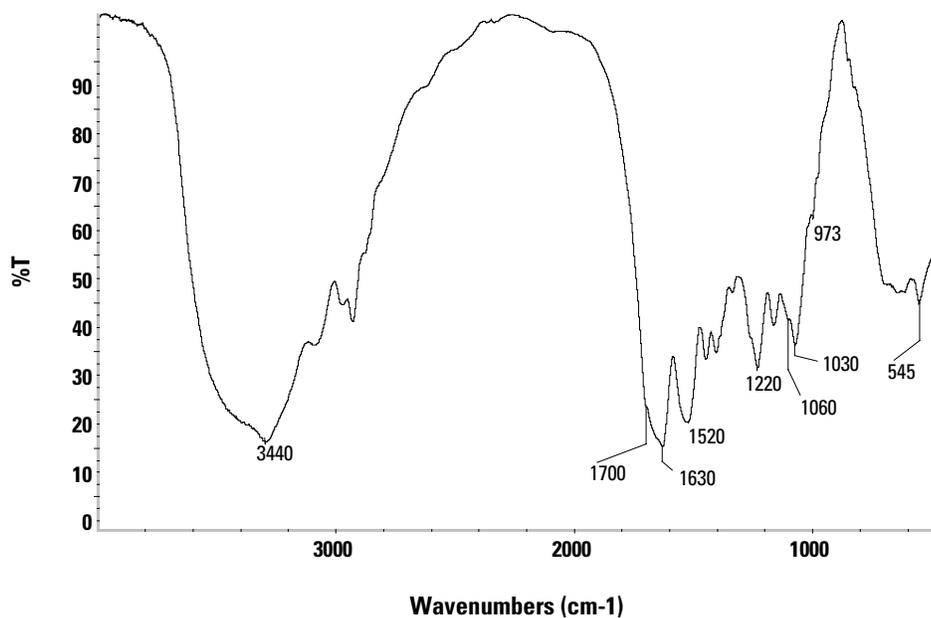
— $\nu_{\text{ring}}^2 = 1520 \text{ cm}^{-1}$ - Very intense

— $\omega_{2\text{Hadj.}} = 820 \text{ cm}^{-1}$ - Intense, sharp. Due to the paraphenylenediamine.

— $\omega_{2\text{Hadj.}} = 725 \text{ cm}^{-1}$ - Medium, sharp. Due to the terephthalic acid units.

— $\gamma_{\text{N-H}} = 660 \text{ cm}^{-1}$ - Medium-intense, wide

Schedule 33 Protein Polymers (Silk)

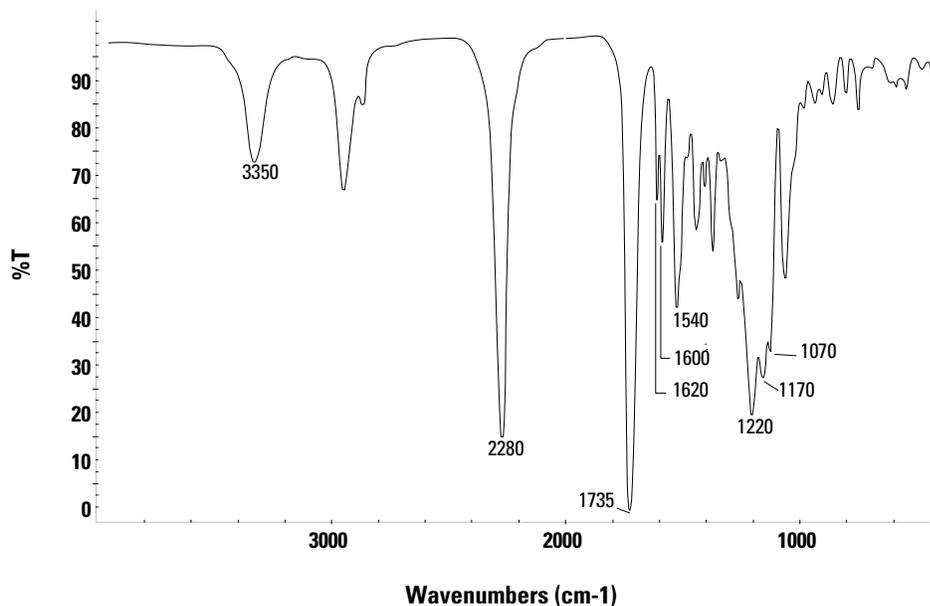


— $\nu_{\text{NH}} = 3440 \text{ cm}^{-1}$ - Very intense, wide

— $\nu_{\text{C=O}} = 1630 \text{ cm}^{-1}$ - Very intense, wide

— $\delta_{\text{N-H}} = 1520 \text{ cm}^{-1}$ - Very intense, wide

Schedule 34 Polyurethanes (Polyester-Urethanic Prepolymers)



— $\nu_{\text{N-H}} = 3350 \text{ cm}^{-1}$ - Medium

— $\nu_{\text{N=C=O}} = 2280 \text{ cm}^{-1}$ - Very intense

— $\nu_{\text{C=O ester}} = 1735 \text{ cm}^{-1}$ - Very intense; it hides the $\nu_{\text{C=O}}$ of the urethane.

— $\nu_{\text{ring}}^1 = \begin{cases} 1620 \text{ cm}^{-1} \\ 1600 \text{ cm}^{-1} \end{cases}$ - Medium doublet band, sharp

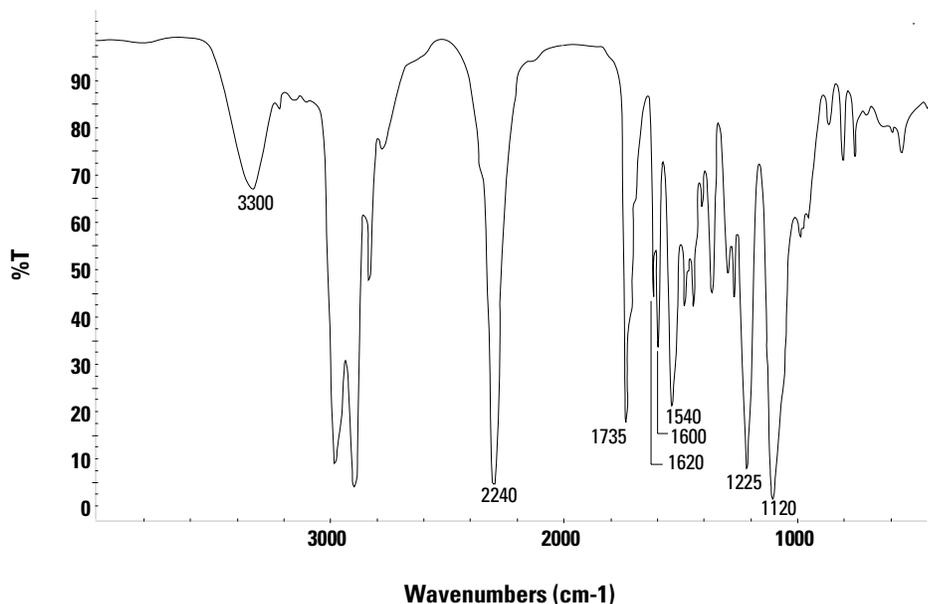
— $\delta_{\text{N-H}} + \nu_{\text{C-N}} = 1540 \text{ cm}^{-1}$ - Intense, complex

— $\nu_{\text{C-N}} + \nu_{\text{C-O urethanic}} = 1220 \text{ cm}^{-1}$ - Intense

— $\nu_{\text{C-O-C}}^a = 1170 \text{ cm}^{-1}$ - Intense, complex

— $\nu_{\text{C-O-C}}^s = 1070 \text{ cm}^{-1}$ - Intense, complex

Schedule 35 Polyurethanes (Polyether-Urethane Prepolymers)



— $\nu_{\text{N-H}} = 3300 \text{ cm}^{-1}$ - Medium, wide

— $\nu_{\text{N=C=O}} = 2240 \text{ cm}^{-1}$ - Very intense, sharp

— $\nu_{\text{C=O}} = 1735 \text{ cm}^{-1}$ - Intense, complex

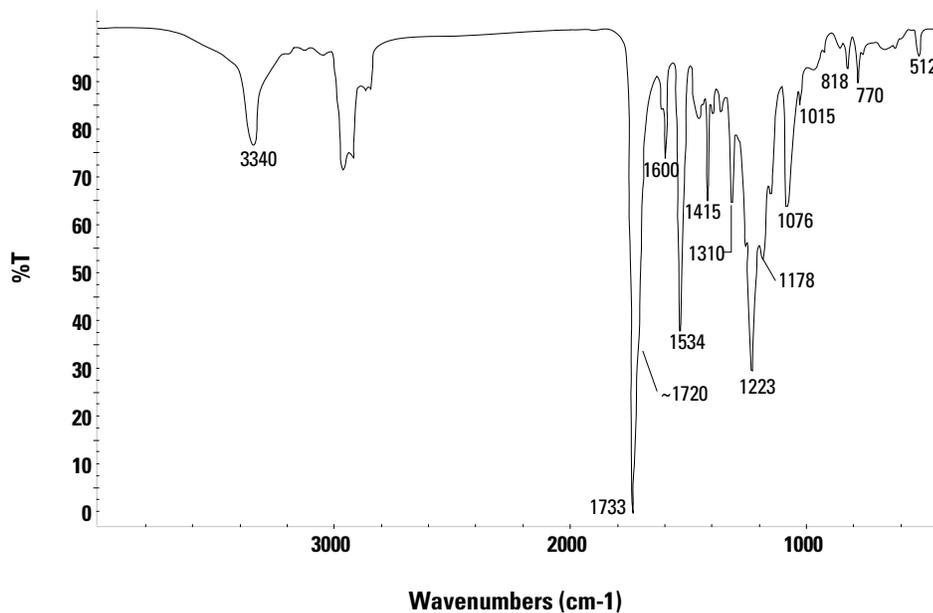
— $\nu_{\text{ring}}^1 = \begin{cases} 1620 \text{ cm}^{-1} \\ 1600 \text{ cm}^{-1} \end{cases}$ - Medium doublet band, sharp

— $\delta_{\text{NH}} + \nu_{\text{CN}} = 1540 \text{ cm}^{-1}$ - Intense, complex

— $\nu_{\text{C-N}} + \nu_{\text{C-O}} = 1225 \text{ cm}^{-1}$ - Intense, wide, complex

— $\nu_{\text{C-O-C}}^a = 1120 \text{ cm}^{-1}$ - Very intense, wide, complex

Schedule 36 Polyurethanes (Polyester-Urethane)



— $\nu_{\text{N-H}} = 3340 \text{ cm}^{-1}$ - Medium

— $\nu_{\text{C=O ester}} = 1733 \text{ cm}^{-1}$ - Very intense; it hides the $\nu_{\text{C=O}}$ of the urethane, that is suggested by the bend at about 1720 cm^{-1} .

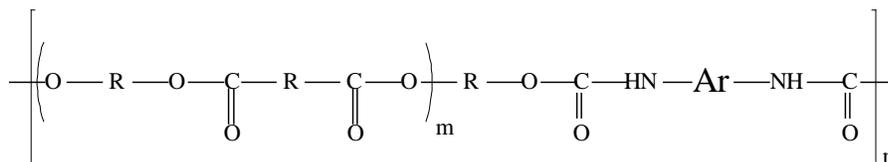
— $\nu_{\text{ring}}^1 = \begin{cases} 1620 \text{ cm}^{-1} \\ 1600 \text{ cm}^{-1} \end{cases}$ - Medium doublet band

— $\delta_{\text{N-H}} + \nu_{\text{C-N}} = 1534 \text{ cm}^{-1}$ - Intense, complex

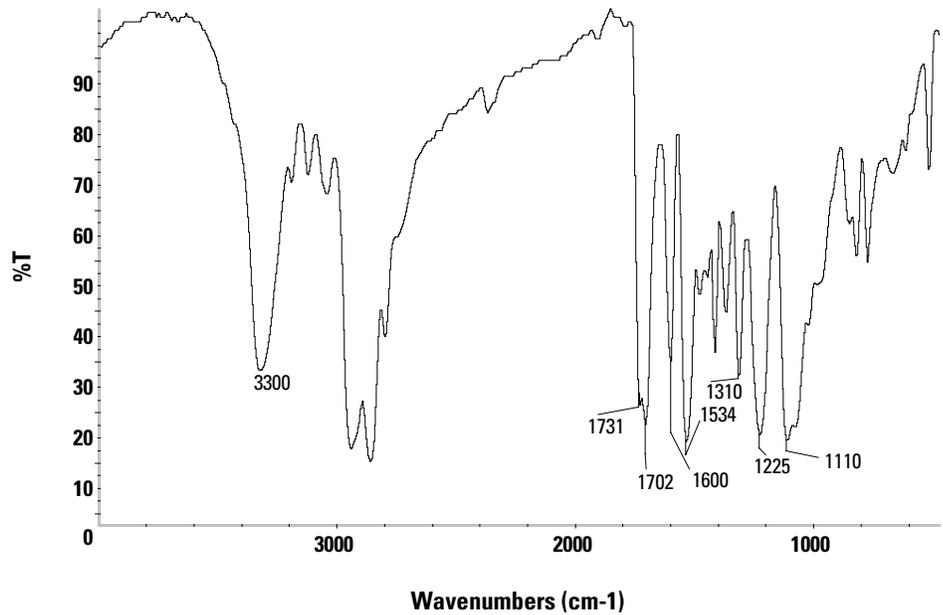
— $\nu_{\text{C-N}} + \nu_{\text{C-O urethanic}} = 1223 \text{ cm}^{-1}$ - Intense

— $\nu_{\text{C-O-C}}^a = 1178 \text{ cm}^{-1}$ - Intense, complex

— $\nu_{\text{C-O-C}}^s = 1076 \text{ cm}^{-1}$ - Intense, complex



Schedule 37 Polyurethanes (Polyester-Urethane)



— $\nu_{\text{N-H}} = 3327 \text{ cm}^{-1}$ - Medium, wide

— $\nu_{\text{C=O not bonded}} = 1731 \text{ cm}^{-1}$ - Medium, sharp

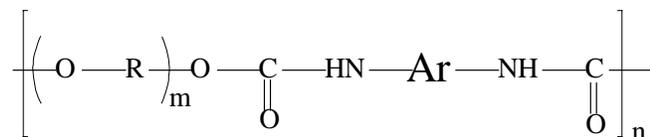
— $\nu_{\text{C=O with H bond}} = 1702 \text{ cm}^{-1}$ - Intense

— $\nu_{\text{ring}}^1 = 1600 \text{ cm}^{-1}$ - Medium, sharp, with a bend at about 1620 cm^{-1}

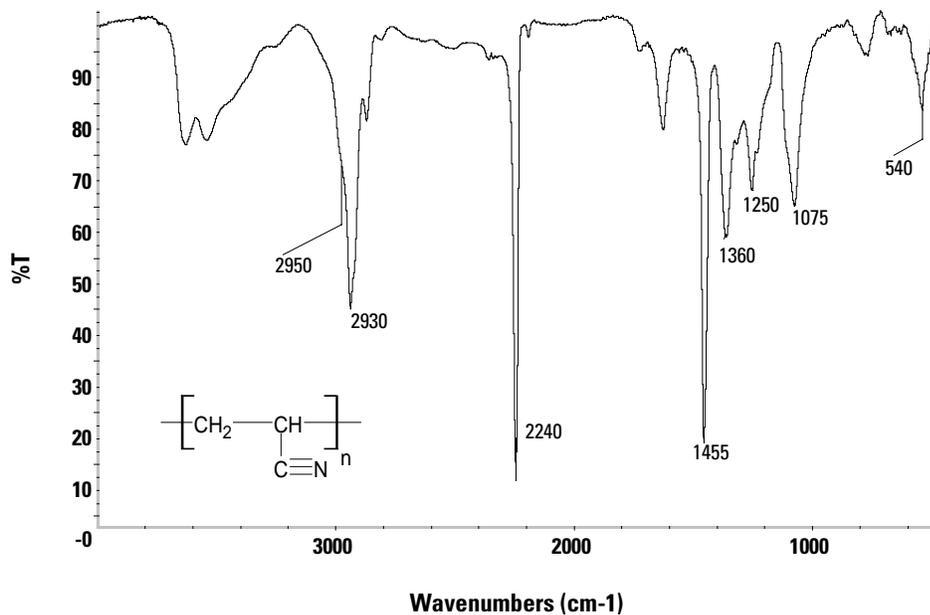
— $\delta_{\text{NH}} + \nu_{\text{CN}} = 1534 \text{ cm}^{-1}$ - Intense

— $\nu_{\text{C-N}} + \nu_{\text{C-O}} = 1225 \text{ cm}^{-1}$ - Very intense, wide, complex

— $\nu_{\text{C-O-C}}^a = 1110 \text{ cm}^{-1}$ - Very intense, wide, complex



Schedule 38 Polyacrylonitrile



— $\nu_{\text{CH}_2}^a = 2950 \text{ cm}^{-1}$ - Bend

— $\nu_{\text{C-H}} = 2930 \text{ cm}^{-1}$ - Intense

— $\nu_{\text{C}\equiv\text{N}} = 2240 \text{ cm}^{-1}$ - Very intense, sharp

— $\delta_{\text{CH}_2} = 1455 \text{ cm}^{-1}$ - Very intense

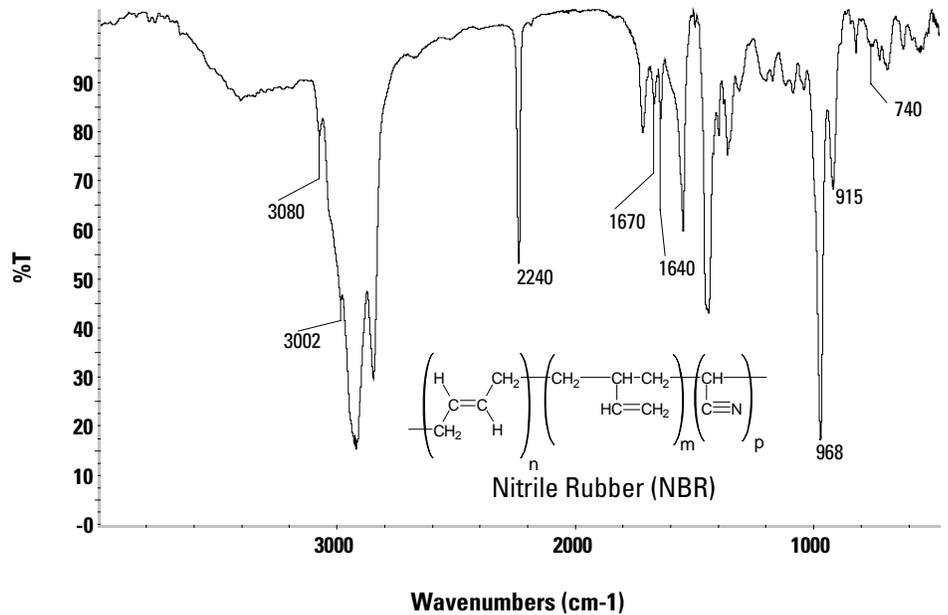
— $\delta_{\text{CH}} = 1360 \text{ cm}^{-1}$ - Medium-intense

— $\omega_{\text{CH}} + \omega_{\text{CH}_2} = 1250 \text{ cm}^{-1}$ - Medium, complex

— $\nu_{\text{C-C}}^s + \gamma_{\text{CH}_2} = 1075 \text{ cm}^{-1}$ - Medium-intense, wide, complex

— $\omega_{\text{C-C-CN}} = 540 \text{ cm}^{-1}$ - Medium-weak, wide, complex

Schedule 39 Butadiene Acrylonitrile Copolymer (NBR)



— $\nu_{=\text{CH}_2} = 3080 \text{ cm}^{-1}$ - Weak, sharp. Due to vinyl units.

— $\nu_{=\text{C-H}} = 3020 \text{ cm}^{-1}$ - Bend. Due to 1-4 trans double bond.

— $\nu_{\text{C}=\text{N}} = 2240 \text{ cm}^{-1}$ - * Sharp, medium intensity

— $\nu_{\text{C}=\text{C}} = 1670 \text{ cm}^{-1}$ - Sharp, weak. Due to 1-2 vinyl units of butadiene.

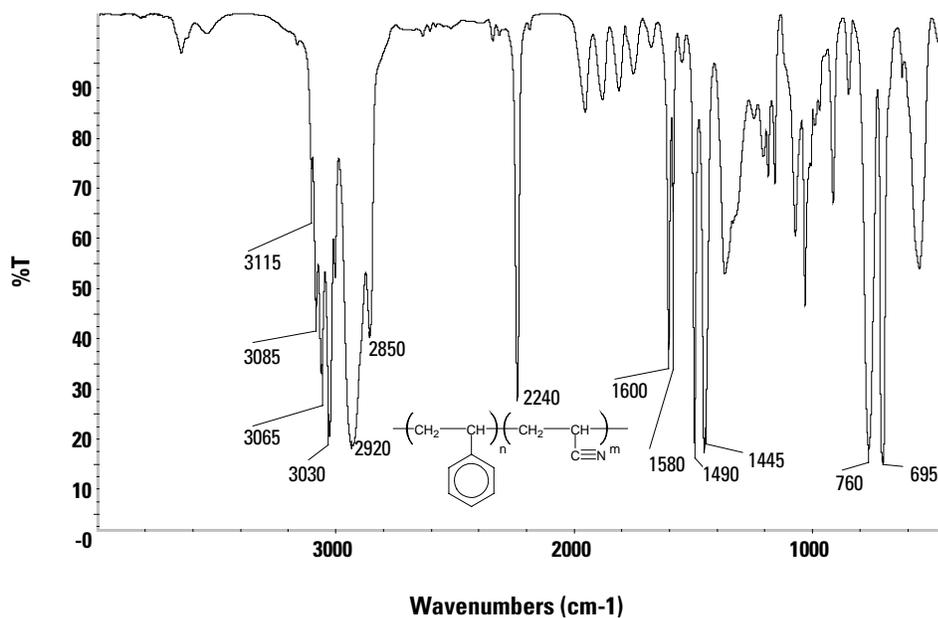
— $\nu_{\text{C}=\text{C}} = 1640 \text{ cm}^{-1}$ - Sharp, weak. Due to 1-4 trans units of butadiene.

— $\omega_{\text{CH vinyl}}^{\text{trans}} = 992 \text{ cm}^{-1}$ - Weak, bend. Due to 1-2 vinyl units of butadiene.

— $\omega_{\text{CH1-4 trans}} = 968 \text{ cm}^{-1}$ - * Intense. Due to 1-4 trans units of butadiene.

— $\omega_{\text{CH}_2 \text{ vinyl}} = 915 \text{ cm}^{-1}$ - * Medium. Due to 1-2 vinyl units of butadiene.

Schedule 40 Styrene-Acrylonitrile Copolymer



$$\text{--- } \nu_{\text{C-H aromatic}} = \begin{cases} 3115 \text{ cm}^{-1} \\ 3085 \text{ cm}^{-1} \\ 3065 \text{ cm}^{-1} \\ 3030 \text{ cm}^{-1} \end{cases} \text{ - Sharp quadruple band}$$

$$\text{--- } \nu_{\text{CH}_2}^{\text{a}} = 2920 \text{ cm}^{-1} \text{ - Intense, sharp}$$

$$\text{--- } \nu_{\text{CH}_2}^{\text{s}} = 2850 \text{ cm}^{-1} \text{ - Medium, sharp}$$

$$\text{--- } \nu_{\text{C}\equiv\text{N}} = 2240 \text{ cm}^{-1} \text{ - Medium, very sharp}$$

$$\text{--- } \nu_{\text{ring}}^1 = \begin{cases} 1600 \text{ cm}^{-1} \\ 1580 \text{ cm}^{-1} \end{cases} \text{ - Sharp doublet band}$$

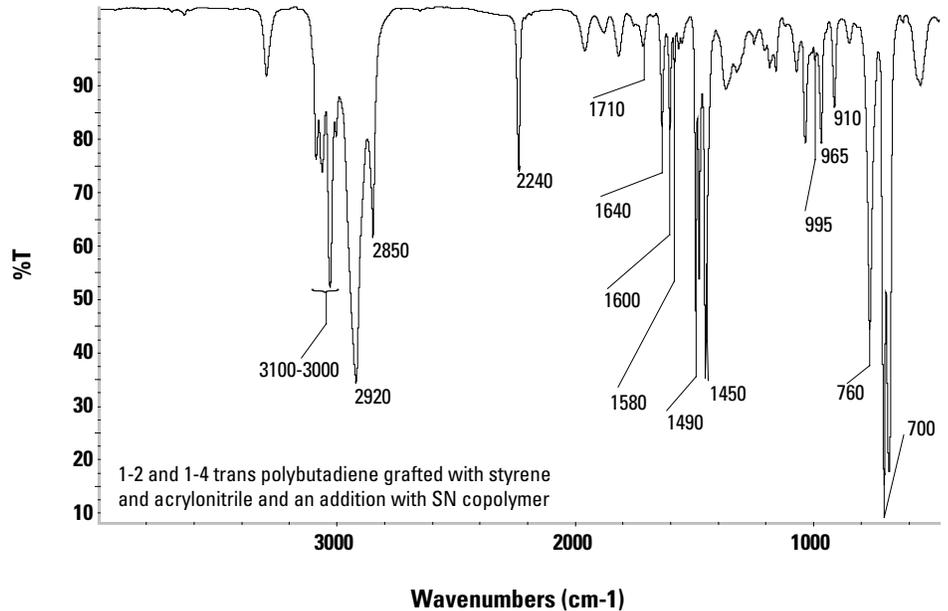
$$\text{--- } \nu_{\text{ring}}^2 = 1490 \text{ cm}^{-1} \text{ - Sharp, intense}$$

$$\text{--- } \delta_{\text{CH}_2} = 1445 \text{ cm}^{-1} \text{ - Intense}$$

$$\text{--- } \omega_{5\text{H adj.}}^1 = 760 \text{ cm}^{-1} \text{ - Very intense}$$

$$\text{--- } \omega_{5\text{H adj.}}^2 = 699 \text{ cm}^{-1} \text{ - Very intense}$$

Schedule 41 ABS Resin (Acrylonitrile- Butadiene-Styrene)



— $\nu_{\text{C-H aromatic and double bond}} = 3100\text{-}3000 \text{ cm}^{-1}$ - Multiple sharp bands

— $\nu_{\text{CH}_2}^{\text{a}} = 2920 \text{ cm}^{-1}$ - Very intense

— $\nu_{\text{CH}_2}^{\text{s}} = 2850 \text{ cm}^{-1}$ - Intense

— $\nu_{\text{C}\equiv\text{N}} = 2240 \text{ cm}^{-1}$ - Medium, very sharp

— $\nu_{\text{C}=\text{O}} = 1710 \text{ cm}^{-1}$ - Weak, due to resinic acid residual.

— $\nu_{\text{C}=\text{C of vinyl}} = 1640 \text{ cm}^{-1}$ - Weak, due to 1-2 units of butadiene

— $\nu_{\text{ring}}^1 = \begin{cases} 1600 \text{ cm}^{-1} \\ 1580 \text{ cm}^{-1} \end{cases}$ - Medium-weak, sharp

— $\nu_{\text{ring}}^2 = 1490 \text{ cm}^{-1}$ - Intense, sharp

— $\delta_{\text{CH}_2} + \nu_{\text{ring}}^3 = 1450 \text{ cm}^{-1}$ - Intense, sharp

— $\omega_{\text{CH vinyl}}^{\text{trans}} = 995 \text{ cm}^{-1}$ - Weak, sharp. Due to 1-2 units of butadiene.

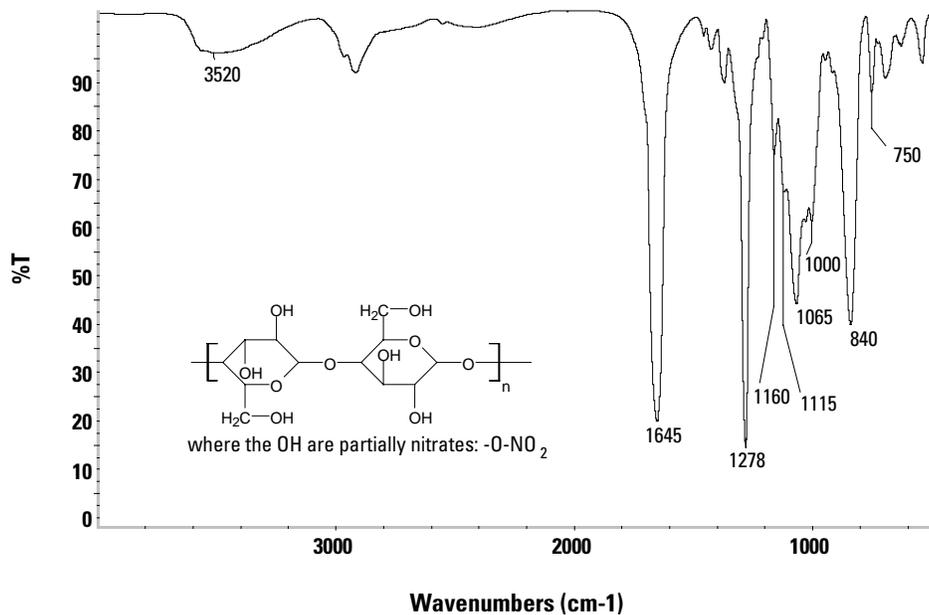
— $\omega_{\text{CH trans double bond}} = 965 \text{ cm}^{-1}$ - Intense. Related to the 1-4 units of butadiene.

— $\omega_{\text{CH}_2 \text{ vinyl}} = 910 \text{ cm}^{-1}$ - Medium-intense. Due to 1-2 units of butadiene.

— $\omega_{5\text{H adj.}}^1 = 760 \text{ cm}^{-1}$ - Intense. Related to the styrene units.

— $\omega_{5\text{H adj.}}^2 = 700 \text{ cm}^{-1}$ - Very intense. Related to the styrene units.

Schedule 42 Nitrocellulose



— $\nu_{O-H} = 3520 \text{ cm}^{-1}$ - Medium, wide

— $\nu_{NO_2}^a = 1645 \text{ cm}^{-1}$ - Very intense

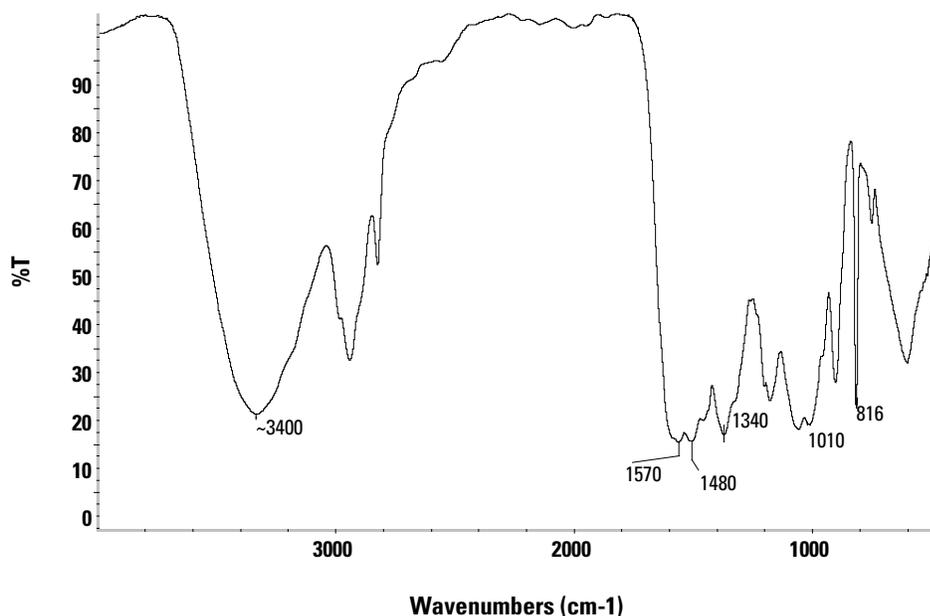
— $\nu_{NO_2}^s = 1278 \text{ cm}^{-1}$ - Very intense

— $\nu_{C-O-C} + \nu_{C-O-H} = \begin{cases} 1160 \text{ cm}^{-1} \\ 1115 \text{ cm}^{-1} \\ 1065 \text{ cm}^{-1} \\ 1000 \text{ cm}^{-1} \end{cases}$

— $\nu_{N-O} = 840 \text{ cm}^{-1}$ - Intense

— $\omega_{NO_2} = 750 \text{ cm}^{-1}$ - Medium-weak

Schedule 43 Melaminic Resin (Prepolymer)



— $\nu_{\text{O-H}} + \nu_{\text{N-H}} = \text{ca. } 3400 \text{ cm}^{-1}$ - Very intense, wide. It is essentially due to the methylol $\text{N-CH}_2\text{-OH}$. After molding the polymer the band diminishes remarkably in intensity depending on how much the methylol disappears. The residual band is due to the stretching of N-H .

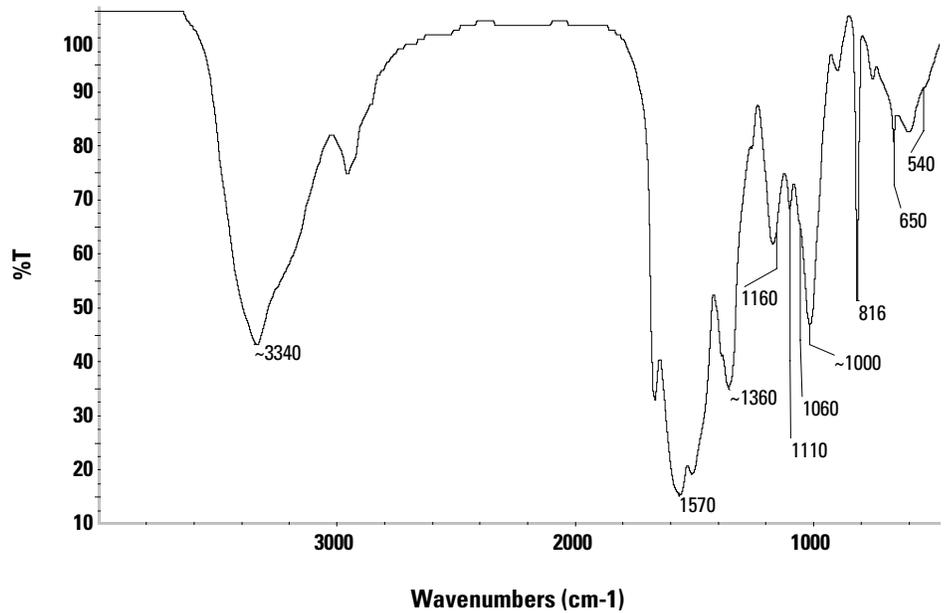
— $\nu_{\text{triazine ring}}^1 = \begin{cases} 1570 \text{ cm}^{-1} \\ 1480 \text{ cm}^{-1} \end{cases}$ - Very intense and wide. The attributes of the second band is uncertain.

— $\nu_{\text{triazine ring}}^2 = 1340 \text{ cm}^{-1}$ - Intense, wide, complex

— $\nu_{\text{C-O-H}} + \nu_{\text{C-O-C}} = \text{ca. } 1000 \text{ cm}^{-1}$ - Intense, wide, complex. It is essentially due to the methylol groups $\text{N-CH}_2\text{-OH}$. After molding the band diminishes remarkably in intensity depending on how much the methylol disappears.

— $\delta_{\text{triazine ring}}^{\text{out of the plane}} = 816 \text{ cm}^{-1}$ - Medium-intense, sharp. This is the most characteristic band of melaminic resin.

Schedule 44 Melaminic Resin (Molded manufactured product)



— $\nu_{\text{O-H}} + \nu_{\text{N-H}} = \text{ca. } 3400 \text{ cm}^{-1}$ - Very intense, wide. Since the methylol disassociates with hardening, this band would be low. The strong intensity is due to the hydroxyl of cellulose, added in the shape of paper or wood dust before molding.

— $\nu_{\text{ring}}^1 = 1570 \text{ cm}^{-1}$ - Very intense, wide, complex. The band at 1470 cm^{-1} , present in the prepolymer, becomes a bend.

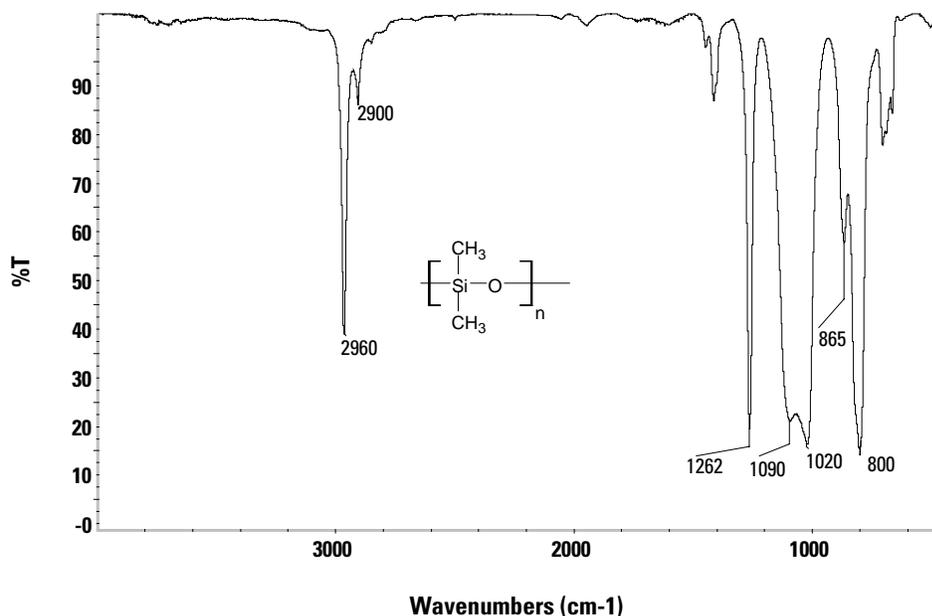
— $\nu_{\text{C-O-H}} + \nu_{\text{C-O-C}} = \begin{cases} 1160 \text{ cm}^{-1} \\ 1110 \text{ cm}^{-1} \\ 1060 \text{ cm}^{-1} \\ \sim 1000 \text{ cm}^{-1} \end{cases}$ - Intense. During molding, the methylol

(N-CH₂-OH) and the hydroxymethylene (N-CH₂-O-CH₂-N) bridges of melamine tend to disappear due to the formation of methylenic bridges (N-CH₂-N), for which this band would be the weakest. The shape and strong intensity confirm the presence of cellulosic material.

— $\delta_{\text{triazining}}^{\text{out of the plane}} = 816 \text{ cm}^{-1}$ - Medium-intense, sharp. It is the most characteristic band of melaminic resins, also when hardened.

The strong bands at 650, 540, and 420 cm⁻¹ do not belong to the melaminic resin, but are due to titanium dioxide added as a filler and colorant.

Schedule 45 Siliconic Resin (Polydimethylsiloxane)



— $\nu_{\text{CH}_2}^{\text{a}} = 2960\text{cm}^{-1}$ - Intense, sharp

— $\nu_{\text{CH}_2}^{\text{s}} = 2900\text{ cm}^{-1}$ - Weak, sharp

— $\delta_{\text{CH}_3}^{\text{s}} = 1262\text{ cm}^{-1}$ - * Intense, sharp

— $\nu_{\text{O-Si-O}}^{\text{a}} = \begin{cases} 1090\text{ cm}^{-1} \\ 1020\text{ cm}^{-1} \end{cases}$ - * Very intense and a very typical saddleback shape

— $\rho_{\text{CH}_3\text{-Si-CH}_3} = 865\text{ cm}^{-1}$ - Medium

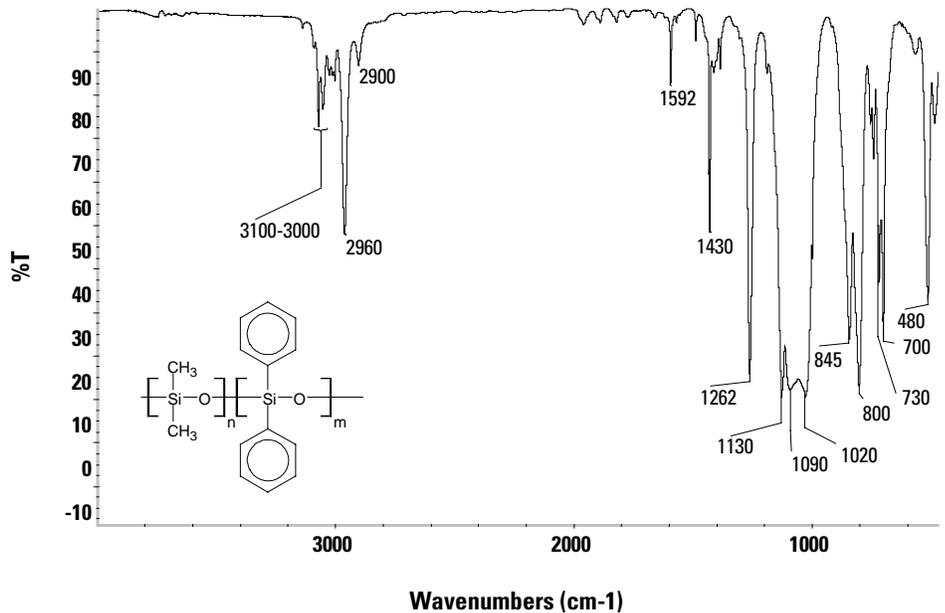
— $\nu_{\text{CH}_3\text{-Si-CH}_3}^{\text{a}} = 800\text{ cm}^{-1}$ - * Intense, rounded. The weak band at about 1410 cm^{-1} can be due to additives or the δ_{CH_2} of the vinyl: the characteristic bands of the vinyl double bond are looked at only if the vinyl content is very high:

— $\nu_{\text{vinyl C-H}} = 3060\text{ cm}^{-1}$ - Very weak and sharp

— $\nu_{\text{C=C}} = 1600\text{ cm}^{-1}$ - Very weak and sharp

The vibrational bands outside of the H plane in the vinyl group is hidden by the most intense band of O-Si-O stretching.

Schedule 46 Siliconic Resin (Polydimethyldiphenyl siloxane)



— $\nu_{\text{C-H arom. ring}} = 3100\text{-}3000 \text{ cm}^{-1}$ - Weak, sharp multiple bands

— $\nu_{\text{CH}_2}^{\text{a}} = 2960 \text{ cm}^{-1}$ - Intense, sharp

— $\nu_{\text{CH}_2}^{\text{s}} = 2900 \text{ cm}^{-1}$ - Weak, sharp

— $\nu_{\text{ring}}^1 = 1592 \text{ cm}^{-1}$ - Medium-weak, sharp

— $\nu_{\text{ring}}^2 = 1430 \text{ cm}^{-1}$ - Medium, sharp

— $\delta_{\text{CH}_3}^{\text{s}} = 1262 \text{ cm}^{-1}$ - Very intense, sharp

— $\nu_{\text{O-Si-O of Si(phenyl)}_2}^{\text{a}} = 1130 \text{ cm}^{-1}$ - Intense, sharp

— $\nu_{\text{O-Si-O of Si(CH}_3)_2}^{\text{a}} = \begin{cases} 1090 \text{ cm}^{-1} \\ 1020 \text{ cm}^{-1} \end{cases}$ - Very intense, wide and of a typical saddleback shape

— $\rho_{\text{CH}_3\text{-Si-CH}_3}^{\text{a}} = 845 \text{ cm}^{-1}$ - Intense, sharp

— $\nu_{\text{CH}_3\text{-Si-CH}_3}^{\text{a}} = 800 \text{ cm}^{-1}$ - Intense, rounded

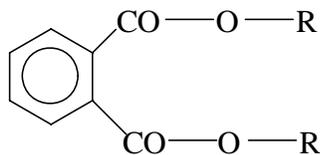
— $\omega_{5\text{H adjacent}} = 730 \text{ cm}^{-1}$ - Intense, sharp. Monosubstituted aromatic.

_____ $\delta_{\text{ring}}^{\text{out of the plane}} = 700 \text{ cm}^{-1}$ - Intense, sharp. Monosubstituted aromatic.

Appendix E **Spectra of Principle Plasticizers and Lubricants**

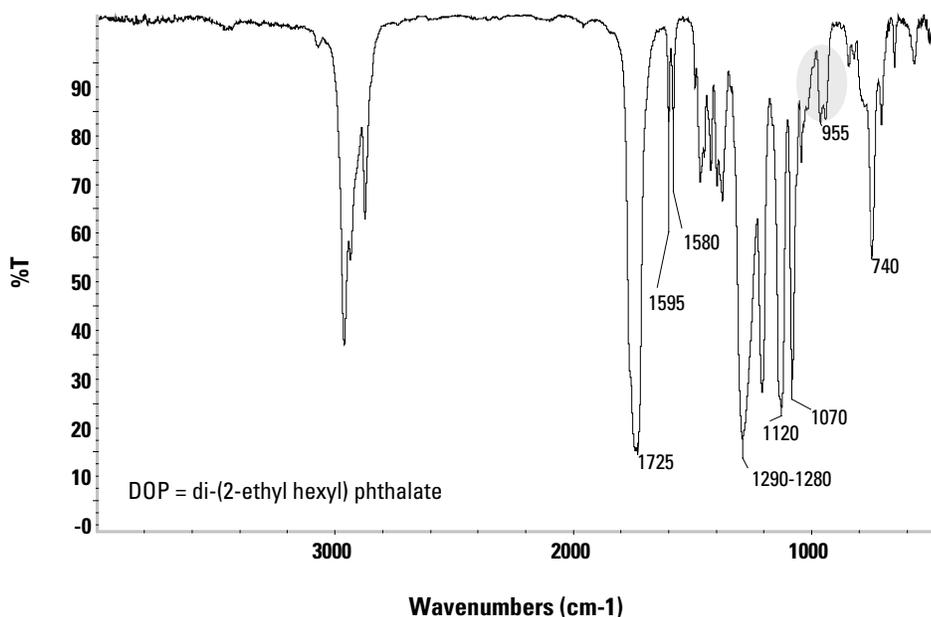
Plate 1 Phthalic Esters (Phthalates)

These are without doubt the most used plasticizers with the formula given as follows:



R can be methyl, ethyl, butyl, amyl, 2-ethyl hexyl [-CH₂-CH(C₂H₅)-(CH₂)₃-CH₃], cyclohexyl, etc. In the figure the spectrum of the dioctyl phthalate (DOP), or more accurately di(2-ethyl hexyl) phthalate, is shown.

This plasticizer is traditionally the most used in the polymer industry.



It is characterized by the following bands that are characteristic of all phthalates.

— $\nu_{\text{C=O}} = 1725 \text{ cm}^{-1}$ - Very intense

— $\begin{cases} \nu_{\text{ring}}^1 = 1595 \text{ cm}^{-1} \\ \nu_{\text{ring}}^2 = 1580 \text{ cm}^{-1} \end{cases}$ - Weak doublet band, sharp and of nearly equal intensity

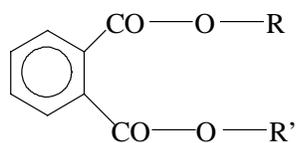
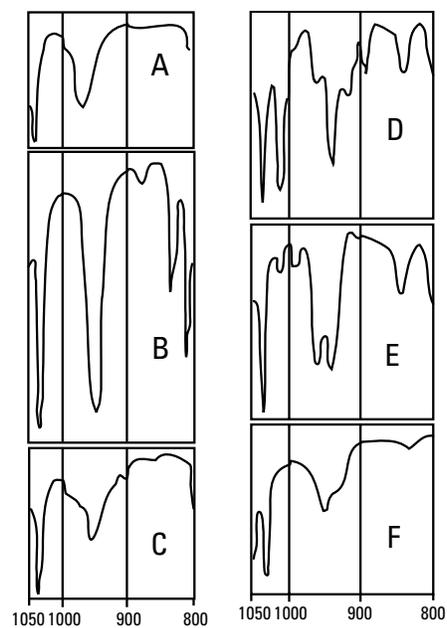
— $\nu_{\text{C-O-C}}^a = 1280\text{-}1290 \text{ cm}^{-1}$ - Very intense, split

— $\nu_{\text{C-O-C}}^s = 1120 \text{ cm}^{-1}$ - Intense

— 1070 cm^{-1} - Intense, sharp

— $\omega_{4\text{H adjacent}} = 740 \text{ cm}^{-1}$ - Medium, sharp

The shape and the position of the bands inside the gray circle distinguish one phthalate from the other.



A: $R=R'$ =isooctyl $-(\text{CH}_2)_5\text{-CH}(\text{CH}_3)_2$

B: $R=R'$ =methyl

C: $R=R'$ =octyl (2-ethyl hexyl) $-\text{CH}_2\text{-CH}(\text{C}_2\text{H}_5)\text{-(CH}_2)_3\text{-CH}_3$

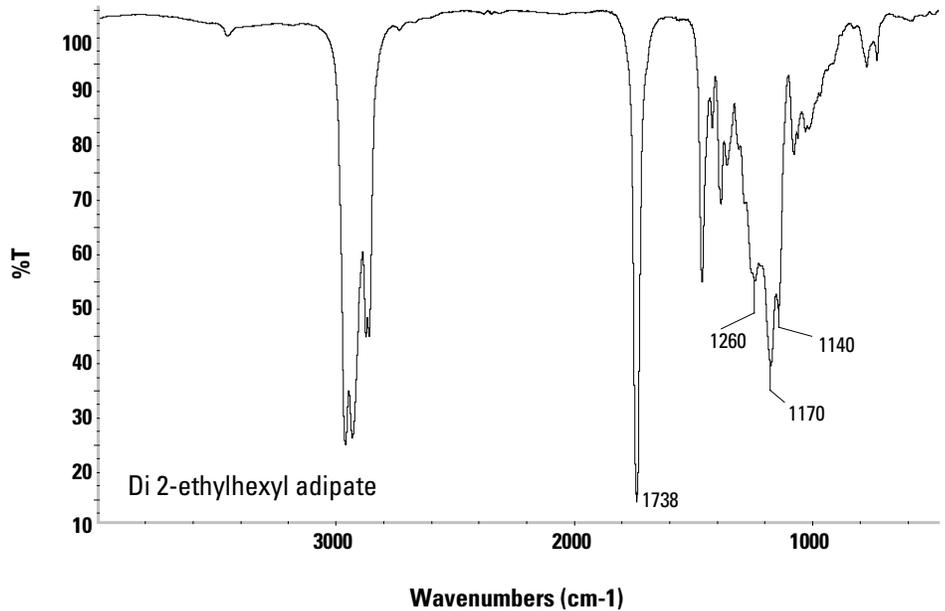
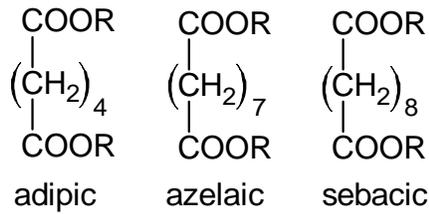
D: R =butyl R' =cyclohexyl

E: $R=R'$ =butyl

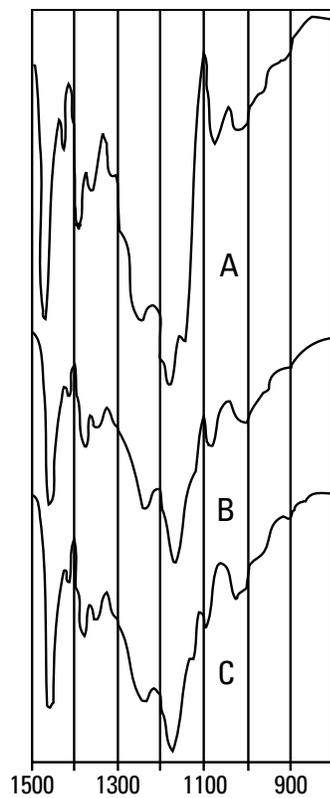
F: R =butyl R' =n decyl

Plate 2
Aliphatic
Bicarboxylic Acid
Esters

These substances are prevalently esters of adipic, sebacic, and azelaic acids.



The spectra of adipate (see Figure) is distinguished from the others by the characteristic shape of the complex band of asymmetric and symmetric C-O-C stretching, in which three bands are distinguished (1260 cm⁻¹, 1170 cm⁻¹, and 1140 cm⁻¹) whose relative intensities can vary but are always present. The other esters are not very individualistic (see Figure on the following page).

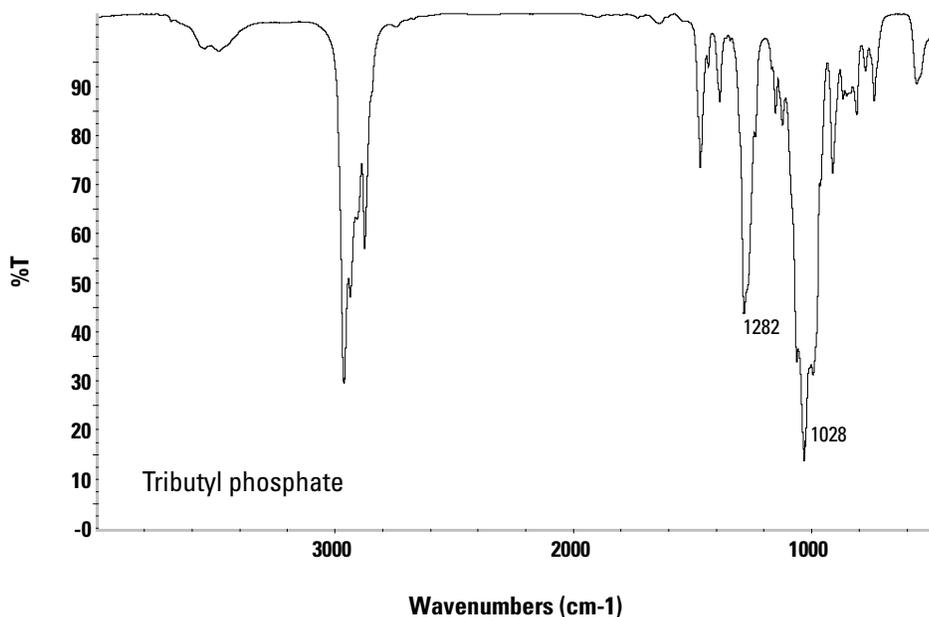
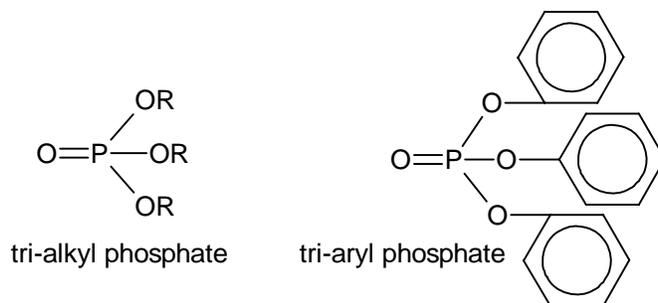


A = 2-Ethylhexyl adipate

B = 2-Ethylhexyl azelate

C = 2-Ethylhexyl sebacate

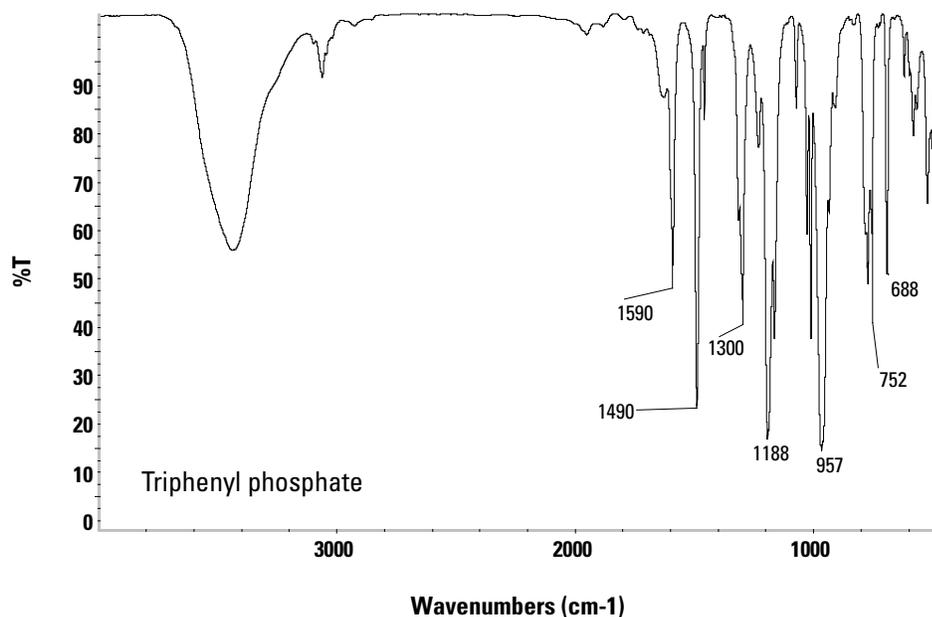
Plate 3 Phosphoric Acid Esters (Alkyl and Aryl Phosphates)



The spectra of alkyl phosphates are characterized by the following bands:

— $\nu_{P=O} = 1290-1260 \text{ cm}^{-1}$ - * Intense

— $\nu_{POC} = 1050-970 \text{ cm}^{-1}$ - * Very intense, complex



The spectra of aryl phosphates are characterized by the following bands:

___ ν_{ring1} = ca. 1590 cm^{-1} - Medium

___ ν_{ring2} = ca. 1500 cm^{-1} - * Intense. The strong intensity is due to the electronegative group on the ring.

___ $\nu_{\text{P=O}}$ = 1315-1290 cm^{-1} - * Intense

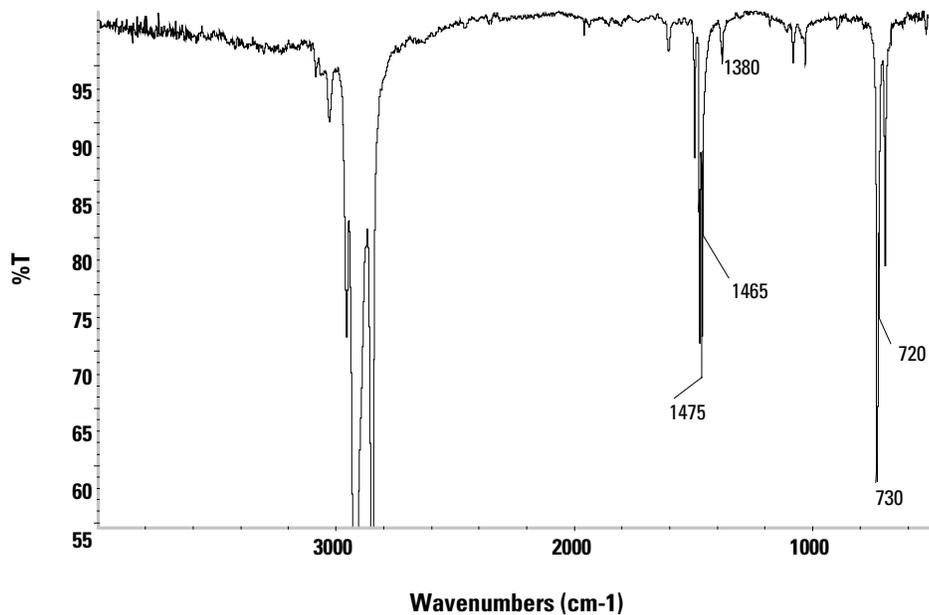
___ 1190 – 1140 cm^{-1} - * Very intense, complex

___ ν_{POC} = 1000-850 cm^{-1} - * Very intense, wide, complex

Plate 4 Paraffin Waxes

These linear paraffins have the general formula $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$.

The IR bands are due to the vibrations of the CH_2 present in very long sequences and organized in a crystalline lattice (see the following figure).



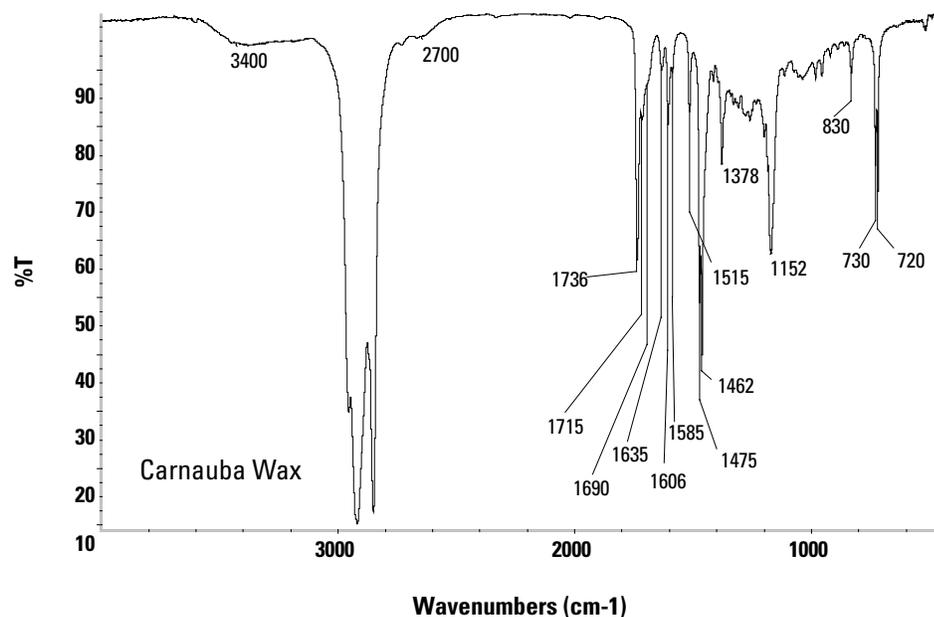
$$\text{--- } \delta_{\text{CH}_2} = \begin{cases} 1475 \text{ cm}^{-1} \\ 1465 \text{ cm}^{-1} \end{cases} \text{ - Split due to crystallinity. Very sharp doublet band.}$$

$$\text{--- } \delta_{\text{CH}_3}^s = 1380 \text{ cm}^{-1} \text{ - Due to the terminal CH}_3.$$

$$\text{--- } \omega_{\text{CH}_2} = \begin{cases} 730 \text{ cm}^{-1} \\ 720 \text{ cm}^{-1} \end{cases} \text{ - Split due to crystallinity. Very sharp doublet band.}$$

Plate 5 Vegetable or Animal Waxes

Vegetable waxes are produced from the leaves of many plants for the purpose of a protective film against excessive transpiration. The most commonly is carnauba wax, produced from the Brazil palm (*Copernicia cerifera*), whose spectrum is shown in the following figure. It is constituted from cerylic esters of cerotic acid [$\text{CH}_3-(\text{CH}_2)_{24}-\text{CO}-\text{O}-(\text{CH}_2)_{25}-\text{CH}_3$] and cerotic acid [$\text{CH}_3-(\text{CH}_2)_{24}-\text{COOH}$]. It also contains smaller amount of larger alkali and aromatic hydrocarbons.



— $\nu_{\text{OH}} = 3400 \text{ cm}^{-1}$ - Due to the hydroxyl alcohols and acids

— $\nu_{\text{OH}} = 2700 \text{ cm}^{-1}$ - Due to hydroxyl acids

— $\nu_{\text{C=O}} = 1736 \text{ cm}^{-1}$ - Due to ester groups

— $\nu_{\text{C=O}} = 1715 \text{ and } 1690 \text{ cm}^{-1}$ - Due to acid groups

— $\nu_{\text{aromatic ring}}^1 = \begin{cases} 1606 \text{ cm}^{-1} \\ 1585 \text{ cm}^{-1} \end{cases}$ - Due to aromatic hydrocarbons

— $\nu_{\text{aromatic ring}}^2 = 1515 \text{ cm}^{-1}$ - Due to aromatic hydrocarbons

— $\delta_{\text{CH}_2} = \begin{cases} 1475 \text{ cm}^{-1} \\ 1462 \text{ cm}^{-1} \end{cases}$ - Split because of crystallinity

— $\delta_{\text{CH}_3}^s = 1373 \text{ cm}^{-1}$

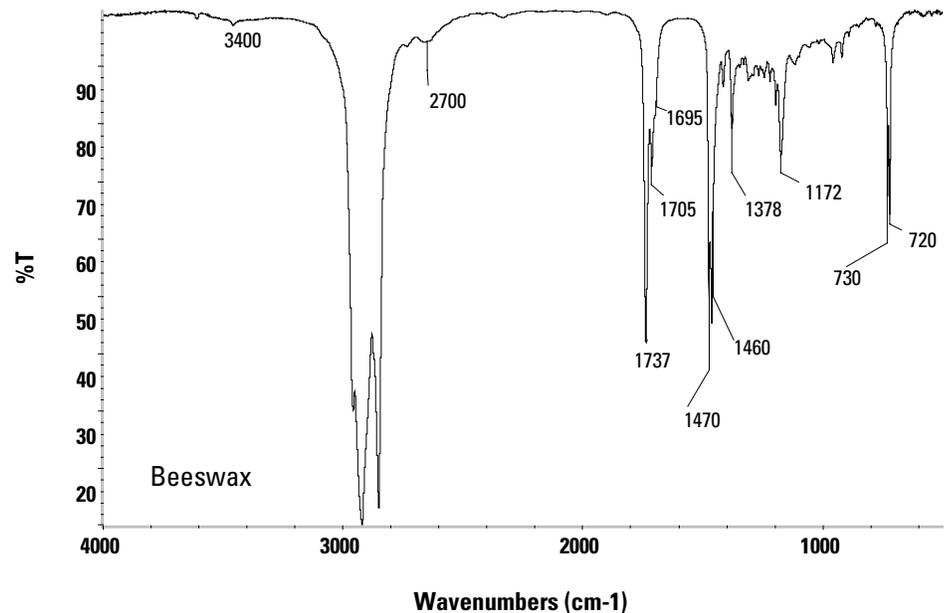
— $\nu_{\text{C-O-C}} = 1152 \text{ cm}^{-1}$ - Due to ester groups

— $\omega_{2\text{H adj.}} = 830 \text{ cm}^{-1}$ - Due to parasubstituted aromatic hydrocarbons

— $\omega_{\text{CH}_2} = \begin{cases} 730 \text{ cm}^{-1} \\ 720 \text{ cm}^{-1} \end{cases}$ - Split because of crystallinity

The band at 1635 cm^{-1} is not explicable, but taken together with the excessive intensity of the aromatic band at 1606 cm^{-1} , it could suggest the presence of amidic or proteic groups.

Animal waxes are produced from several bugs, and the most famous is the beeswax, that is constituted from approximately 70% of myricyl palmitate [$\text{CH}_3-(\text{CH}_2)_{14}-\text{CO}-\text{O}-(\text{CH}_2)_{30}-\text{CH}_3$], 10-14% of cerotic acid and paraffin hydrocarbons. Its IR spectrum is shown in the following figure:



— $\nu_{\text{OH}} = 1400-1700 \text{ cm}^{-1}$ - Wide and complex band, covered in part from the CH_2 stretching of the paraffins. It is due to the carboxylic acid groups binding with the hydrogen bond.

— $\nu_{\text{C=O}} = 1737 \text{ cm}^{-1}$ - Due to ester groups

— $\nu_{\text{C=O}} = 1705 \text{ and } 1695 \text{ cm}^{-1}$ - Due to acid groups

$$\text{— } \delta_{\text{CH}_2} = \begin{cases} 1470 \text{ cm}^{-1} \\ 1460 \text{ cm}^{-1} \end{cases} \text{ - Split because of crystallinity}$$

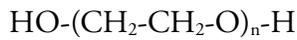
$$\text{— } \delta_{\text{CH}_3}^s = 1378 \text{ cm}^{-1}$$

$$\text{— } \nu_{\text{C-O-C}} = 1172 \text{ cm}^{-1} \text{ - Due to ester groups}$$

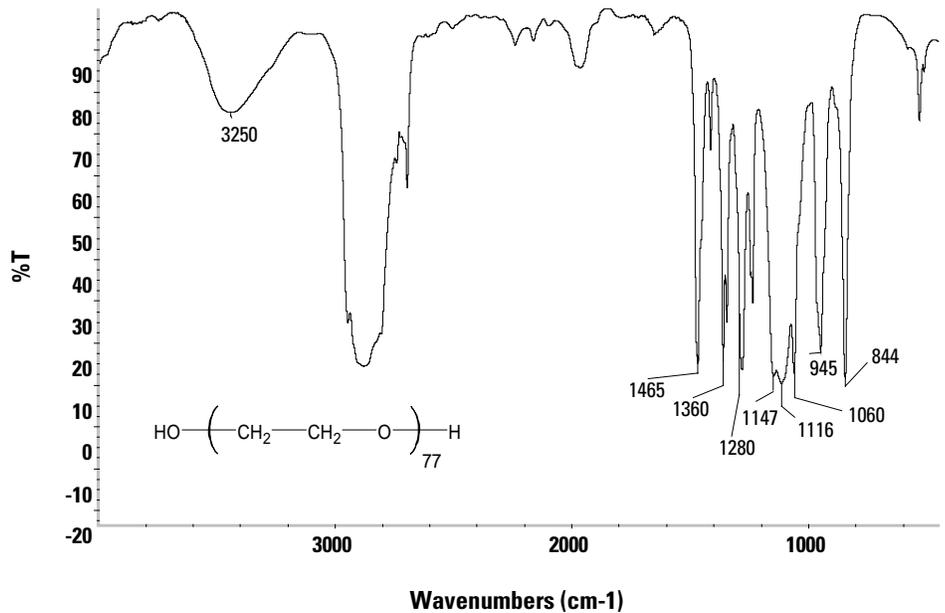
$$\text{— } \omega_{\text{CH}_2} = \begin{cases} 730 \text{ cm}^{-1} \\ 720 \text{ cm}^{-1} \end{cases} \text{ - Split caused by crystallinity}$$

Plate 6 Polyoxyethylenic Waxes

These waxes are constituted from polymers of ethylene oxide with a M.P. > 600 and have the general formula:



The IR spectrum is shown in the following figure:



— ν_{OH} = ca. 3250 cm^{-1} - Wide. Due to terminal OH, whose intensity depends on the M.P. of the wax.

— δ_{CH_2} = 1465 cm^{-1} - Sharp. The fact that the band is sharp is because of crystallinity.

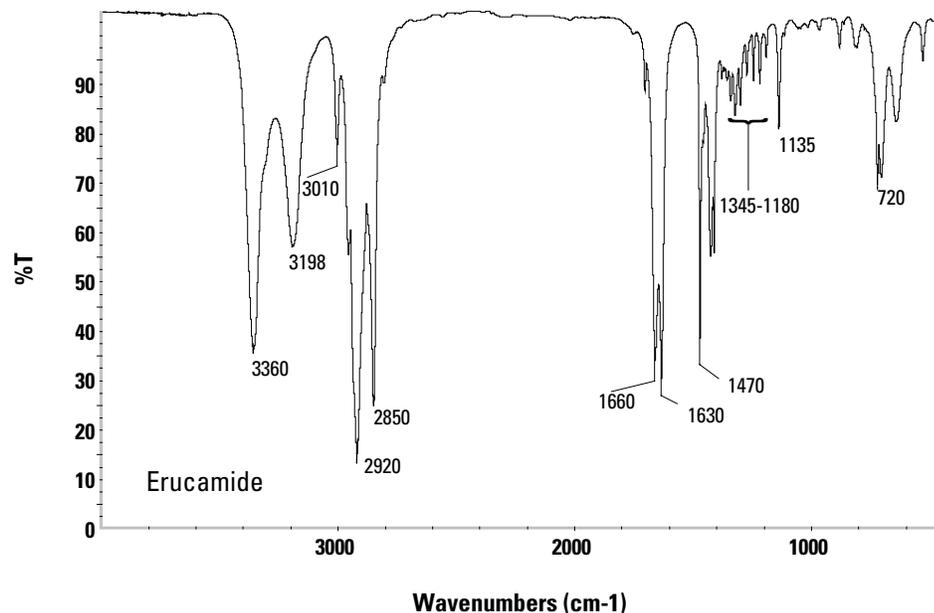
— $\nu_{\text{C-O-C}}$ = 1116 cm^{-1} - Very intense and sharp. In liquid samples, this band is very broad.

All other bands ($1360, 1280, 1147, 1060, 844 \text{ cm}^{-1}$) are essentially crystallinity bands, which disappear or reduce in intensity in liquid samples.

Plate 7 Amidic Waxes

Amidic waxes can be of two types: primary amides or secondary amides.

The most used primary amides are erucamide, oleamide, and stearamide. The spectra of erucamide is shown in the following figure:



— $\nu_{\text{NH}_2}^{\text{a}}$ = 3360 cm^{-1} - * Sharp, intense

— $\nu_{\text{NH}_2}^{\text{s}}$ = 3198 cm^{-1} - * Sharp, intense

— $\nu_{\text{C-H of the double bond}}$ = 3010 cm^{-1} - * Weak, sharp. It is obviously not present in stearamide.

— $\nu_{\text{C=O}}$ = 1660 cm^{-1} - * “Amide I” Intense, sharp. In stearamide the band is at 1645 cm^{-1} .

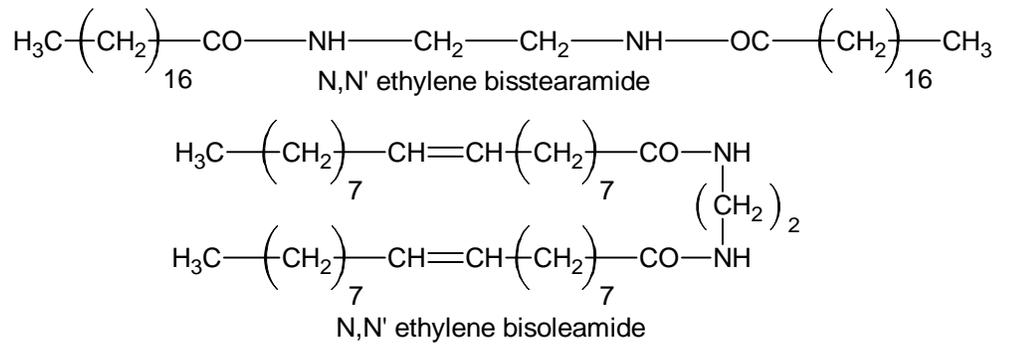
— δ_{NH_2} = 1630 cm^{-1} - * “Amide II” Intense, sharp. In stearamide the band is present as a bend on the flank of the previous band.

— δ_{CH_2} = 1470 cm^{-1} - Very sharp band caused by crystallinity

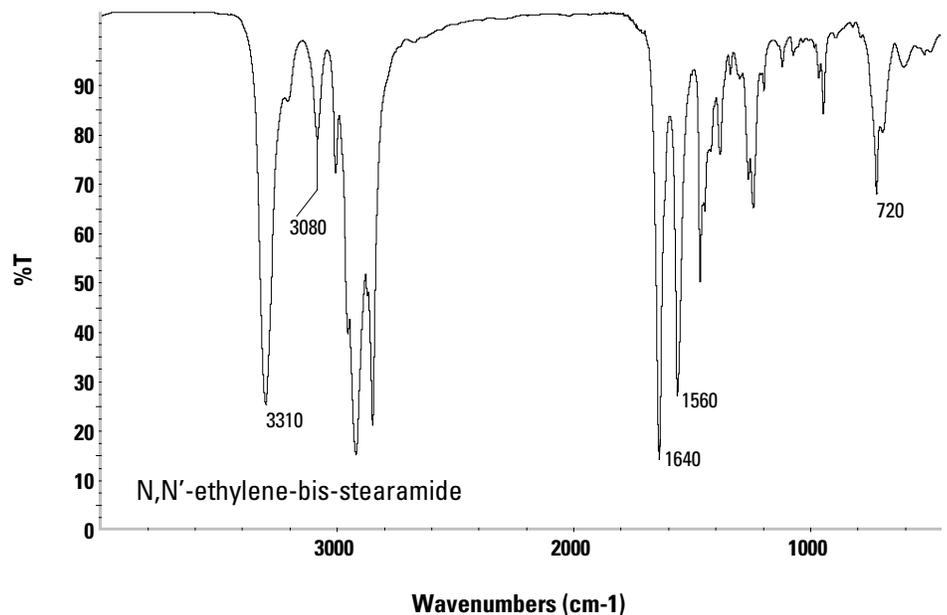
— 1345 – 1180 cm^{-1} - Series of weak and sharp bands. The number of these bands correlates to the number of CH_2 in the sequence. In erucamide, the number of such bands is $N=9$.

— $\nu_{\text{CH}_2} = 720 \text{ cm}^{-1}$ - This band, together with the one at 730 cm^{-1} , is overlapped by the wide amide bands due to O=C-N bending.

The most used secondary amides are N,N'-ethylene-bis-stearamide and N,N'-ethylene-bis-oleamide.



The spectrum of N,N'-ethylene-bis-stearamide is shown in the following figure:



— $\nu_{\text{N-H}} = 3310 \text{ cm}^{-1}$ - * Intense, sharp

— $2(\nu_{\text{C-N}} + \delta_{\text{N-H}}) = 3080 \text{ cm}^{-1}$ - * Weak, sharp

— $\nu_{\text{C=O}} = 1640 \text{ cm}^{-1}$ - * Intense, sharp

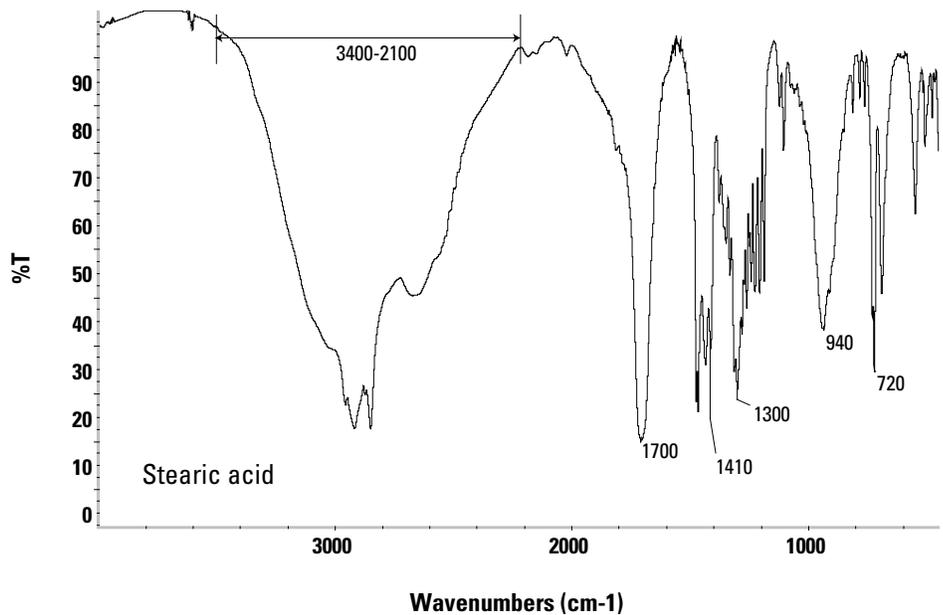
— $\nu_{\text{C-N}} + \delta_{\text{N-H}} = 1560 \text{ cm}^{-1}$ - * Intense, sharp

— $\omega_{\text{CH}_2} = 720 \text{ cm}^{-1}$ - Weak, sharp

In the spectrum of N,N'-ethylene-bis-oleamide, a band is present at 3010 cm^{-1} that is due to the presence of the double bond and analogous to that present in the spectrum of erucamide (see the figure).

Plate 8 Fatty Acids

These lubricants are usually fatty acid mixtures, improperly called stearine, that contain, among other things, stearic acid (prevalent) and palmitic acid. Stearic acid can also come from vulcanization enhancers, one of which is a stoichiometric mixture of stearic acid and zinc oxide. Another stearic acid source can be the hydrolysis of soaps used as lubricants (in particular zinc or calcium stearates), as stabilizers (barium, cadmium, or lead stearates) or as vulcanization enhancers (zinc stearate, instead of the stearic acid-zinc oxide mixture). The IR spectrum of stearic acid is shown in the following figure:



— $\nu_{\text{OH}} = 3400\text{-}2100 \text{ cm}^{-1}$ - * Extremely broad and complex band because of the strong hydrogen bond.

— $\nu_{\text{C=O}} = 1700 \text{ cm}^{-1}$ - * Very intense

— $\delta_{\text{O-H in the plane}} + \nu_{\text{C-O}} = 1410 \text{ cm}^{-1}$

— $\nu_{\text{C-O}} = 1410 \text{ cm}^{-1}$ - Intense

— $\delta_{\text{O-H out of the plane}} = 1300 \text{ cm}^{-1}$ - * Intense, broad

Frequently the separation of pure acid from the mixture of plasticizers and lubricants is not easy. In many cases an assumption can be made of its presence from the appearance of a bend or a weak band on the right flank of the C=O stretching of the phthalate. In order to confirm this hypothesis, the KBr window is exposed, covered with the plasticizer mixture, to vapors

of concentrated solution of ammonia. It is exposed for some minutes, and then the spectrum is taken. If the band that was suspected is truly that of a carboxylic acid, its disappearance will be noted. If the range is free, one looks for the appearance of a wide band around $1580\text{-}1530\text{ cm}^{-1}$.

In fact, the following salification reaction occurs.

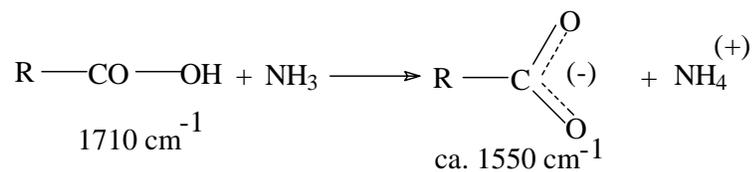
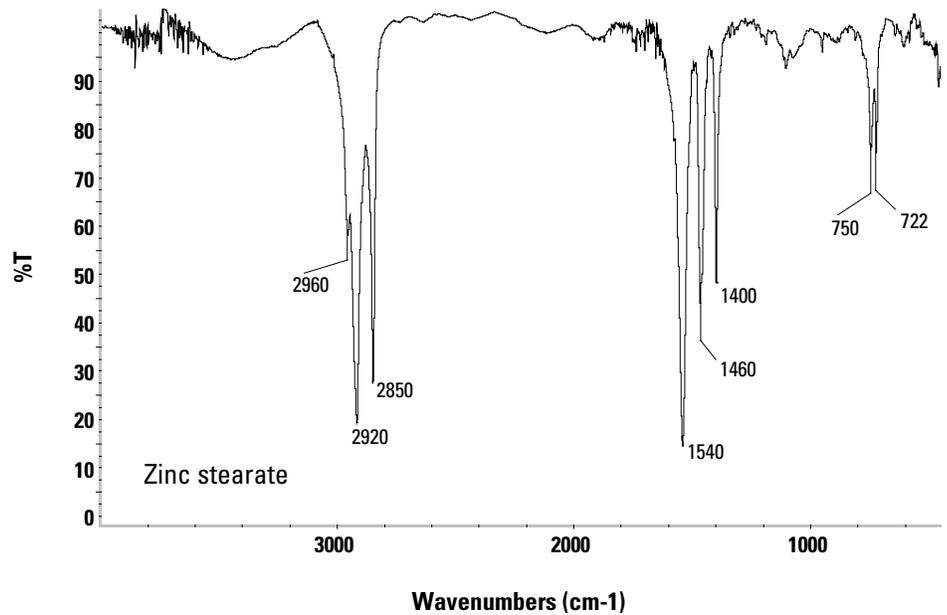


Plate 9 Soaps (Carboxylic acid salts)

Those soaps most used as lubricants are zinc stearate and stearates of Al, Mg, Ca and Ba.

The spectrum of zinc stearate is shown in the following figure:



$$\text{--- } \nu_{\text{CH}_3}^{\text{a}} = 2960 \text{ cm}^{-1}$$

$$\text{--- } \nu_{\text{CH}_2}^{\text{a}} = 2920 \text{ cm}^{-1}$$

$$\text{--- } \nu_{\text{CH}_2}^{\text{s}} = 2850 \text{ cm}^{-1}$$

$$\text{--- } \nu_{\text{C=O}}^{\text{a}} = 1540 \text{ cm}^{-1} - * \text{ Very intense}$$

$$\text{--- } \nu_{\text{C=O}}^{\text{sa}} = 1460 \text{ cm}^{-1} - \text{ Intense}$$

$$\text{--- } \delta_{\text{CH}_2} = 1400 \text{ cm}^{-1} -$$

$$\text{--- } \omega_{\text{CH}_2} = \begin{cases} 750 \text{ cm}^{-1} \\ 722 \text{ cm}^{-1} \end{cases}$$

The other stearates have the band due to asymmetric stretching of C=O in various locations:

Al = 1585 cm^{-1} ; Ca = 1575 and 1540 cm^{-1} ; Mg = 1580 cm^{-1} ; Ba = 1515 cm^{-1} .

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