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Simple Methods for Identification of Plastics

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1 Plastics and Their Characteristics

Plastics are high molecular weight (macromolecular or polymeric) organic substances that have usually been synthesized from low molecular weight compounds. They may also have been obtained by chemical modification of high molecular weight natural materials (especially cellulose). The raw materials are most often petroleum, natural gas, and coal. They can be reacted with air, water, or sodium chloride to prepare reactive monomers. The most important industrial synthetic processes for the preparation of plastics from monomers may be classified according to the mechanism of the formation reaction of the polymer, such as polymerization and condensation reactions. Since several chemically identical or similar plastics can be prepared in several different ways and from different raw materials, this classification has little meaning for the analysis of unknown plastics samples. On the other hand, in addition to chemical investigations, the appearance of a plastic as well as its behavior on heating yields useful information for its identification.

There are physical interactions between the individual macromolecules that constitute a plastic material, just as there are between the molecules of a low molecular weight compound. These physical interactions are responsible for cohesion and related properties such as strength, hardness, and softening behavior. Plastics that consist of linear threadlike molecules (several hundred nanometers (nm) long and a few tenths of a nanometer in diameter) (1 nm = 10^{-9} m = 10 Å = 10^{-6} mm), i.e., of macromolecules, that are not strongly crosslinked can usually be softened on heating. In many cases they melt. Thus, when a polymeric material is heated above a certain

temperature, the macromolecules which are more or less oriented with respect to each other at low temperatures can glide past each other to form a melt of relatively high viscosity. Depending on the degree of order of the macromolecule in the solid state, it is possible to distinguish between partly crystalline and (mostly disordered) amorphous plastics (see Figure 1.1). This degree of order also has an effect on the behavior of the plastic on heating and on its solubility.

Plastics that soften on heating and start to flow are called thermoplastics. On cooling, such plastics become solid again. This process can be repeated many times. There are several exceptions, as when the chemical stability (expressed in terms of the temperature at which chemical decomposition starts) is lower than the cohesion between the macromolecules due to interactions between the chains, in which case, on heating, the plastic undergoes chemical changes before it reaches its softening or melting point.
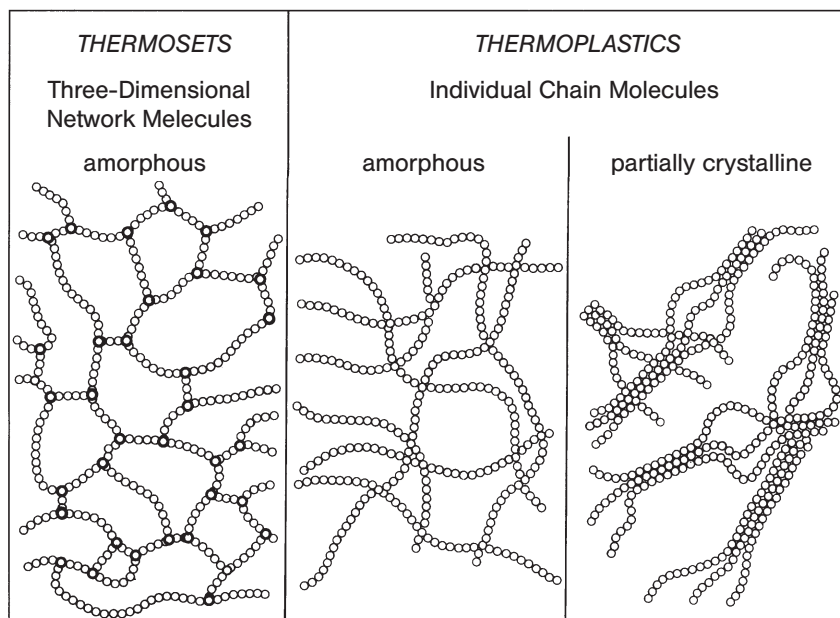

FIGURE 1.1 Schematic representation of the structure of plastics, showing the three major types of macromolecular arrangements. Approximately 1 000 000 times actual size and greatly simplified. (Crystallites can also occur as the result of chain folding.)

A further indication, with few exceptions, that macromolecules are linear or branched is their solubility in many liquids, such as organic solvents. This process also reduces the interaction between the macromolecules; solvent molecules insert themselves between the polymer chains.

In contrast to thermoplastic materials, there are the so-called thermosetting materials. These, after processing into their final state, are crosslinked macromolecules that can neither melt nor dissolve. For such products one generally starts with liquid or soluble raw materials of a rather low molecular weight. These may be crosslinked by heating with or without pressure or through chemical reactions with additives and concurrent molding conditions. The results are crosslinked (hardened) high molecular weight materials in three-dimensional networks. These giant molecules can be broken down into smaller and therefore meltable and soluble fragments only by chemical destruction of the crosslinks. This may occur at rather high temperatures or with certain chemical reagents. Thermosets often contain fillers that may strongly influence the appearance and properties of the products.

Finally, we may distinguish the elastomers by their physical appearance which is a rubberlike elastic material that usually consists of relatively weakly crosslinked macromolecules. Crosslinkages of natural or synthetic rubber are formed during the molding or vulcanization process. Because of their crosslinked nature, elastomers do not melt on heating until just below their decomposition temperature. In this sense they behave differently from many other elastic thermoplastic materials such as plasticized polyvinyl chloride (PVC). In contrast to the chemically crosslinked elastomers (rubber), e.g., by sulfur or peroxides, network formation in the so-called thermoplastic elastomers (TPE) occurs through physical interactions between the macromolecules. On heating, the physical interaction forces between the chain molecules decrease, so that these polymers can be thermoplastically shaped. On cooling, as the physical interaction between the molecules becomes stronger, the material again behaves like an elastomer.

Table 1.1 lists the most important characteristics of these three groups of polymeric materials. In addition to elasticity, behavior on heating, density, and solubility can be used to differentiate between these materials. However, it should be kept in mind that fillers, pigments, or reinforcing agents,

TABLE 1.1 Comparisons of Different Classes of Plastics

	Structure	Physical Appearance*	Density (g / cm³)	Behavior on Heating	Behavior on Treating with Solvents
Thermo-plastics	Linear or branched macro-molecules	**Partially crystalline:** flexible to horn-like; hazy, milky to opaque; only thin films are transparent	0.9 – 1.4 (except PTFE: 2 – 2.3)	Material softens; fusible and becomes clear on melting; often fibers can be drawn from the melt;	May swell; usually diffi-cult to dissolve in cold solvents, but usually readily dissolves on heat-ing the solvent, e. g., polyethylene in xylene
		Amorphous: colorless; clear and trans-parent without additives; hard to rubbery (e. g., on adding plasticizers)	0.9 – 1.9	heat-sealable (excep-tions exist)	Soluble (with few excep-tions) in certain organic solvents, usually after initial swelling
Thermosets (after pro-cessing)	(Usually) tightly crosslinked macromolecules	Hard; usually contain fillers and are opaque. Without fillers they are transparent	1.2 – 1.4; filled: 1.4 – 2.0	Remain hard and almost dimensionally stable until chemical decomposition sets in	Insoluble, do not swell or only slightly
Elasto-mers**	(Usually) lightly crosslinked macromolecules	Rubber-elastic and stretchable	0.8 – 1.3	Do not flow until close to temperature where chemical decomposi-tion occurs	Insoluble, but will often swell

* A rough measure for the hardness of a plastic is its behavior when scratched with a fingernail: hard plastics scratch the nail; hornlike plastics have about the same hardness; flexible or rubbery plastics can be scratched or dented with a fingernail.

** The behavior of thermoplastic elastomers is described on page 3.

4 Testing for Heteroatoms

The previously described simple screening tests are not always sufficient to identify an unknown plastic with certainty. In some cases the use of chemical reactions for identification purposes cannot be avoided. First, one tests for heteroatoms, those elements which are present in the plastic in addition to carbon and hydrogen, such as nitrogen, sulfur, chlorine, fluorine, silicon, and sometimes phosphorus. Unfortunately, there is no simple direct method for the certain identification of oxygen, so it is not possible to test for oxygen in a qualitative manner. The following reactions presuppose a certain amount of experimental skill and the necessary care.

For the qualitative determination of the elements nitrogen, sulfur, and chlorine, the *Lassaigne method* is usually used. Combine approximately 50 – 100 mg of a finely divided sample with a pea-sized piece of sodium or potassium in a pyrolysis tube. Heat this carefully in a Bunsen flame until the metal melts. (*Caution*: Wear safety glasses and keep the opening of the tube directed away from the eyes.) The sample must be free of water, which would react explosively with the metal. Sodium and potassium must be stored in oil or immersed in a similar inert hydrocarbon. When used, a small piece of the metal is held with tweezers and the required amount is cut off with a knife or a spatula onto a piece of filter paper. Then carefully blot it dry with the filter paper. Use it immediately and return the remainder to the oil-containing bottle. The remainder should not be destroyed by throwing it into water.

After heating, carefully place the red-glowing tube in a small beaker with approximately 10 m distilled water. The glass tube will shatter and the reac-

tion products will dissolve in the water. Unreacted metal will react with the water; therefore, carefully stir with a glass rod until no further reaction occurs. Then, filter the nearly colorless liquid or remove the liquid by careful pipetting from the glass splinters and carbonized residues. For the following tests, use approximately 1 – 2 ml of this original solution.

Nitrogen   Add a small amount (a spatula tip) of ferrous sulfate to a 1 – 2 ml sample of the original solution and boil it quickly. Let it cool and add a few drops of 1.5 % ferric chloride solution. After acidification with dilute hydrochloric acid, a precipitate of Berlin blue occurs. The presence of a small amount of nitrogen will result in a light green solution from which a precipitate then results, though only after standing for several hours. If the solution remains yellow, there is no nitrogen present.

Sulfur   The original solution is reacted with an approximately 1 % aqueous sodium nitroferricyanide solution. A deep violet color indicates sulfur. This reaction is very sensitive; to confirm, add a drop of the alkaline solution of the sample under investigation to a silver coin. If sulfur is present, a brown spot of silver sulfide will form. An alternative procedure is to acidify the original solution with acetic acid (test with litmus or pH paper) and then add several drops of aqueous 2 M lead acetate solution or test with lead acetate paper. A black precipitate of lead sulfide or darkening of the paper indicates sulfur.

The presence of sulfur in polysulfides, polysulfones, and in sulfur-vulcanized rubber can be demonstrated by the following somewhat uncertain test. The sample is heated in dry air (pyrolysis) and the gases formed during this process are bubbled through a dilute barium chloride solution. The presence of sulfur is indicated by a white precipitate of barium sulfate.

Chlorine   This is a general test for heavier halogens, but bromine and iodine almost never occur in plastics. Acidify a sample of the original solution with dilute nitric acid and add a small amount of silver nitrate solution (2 g in 100 ml distilled

water; keep the solution in the dark or in a brown flask). A white, flaky precipitate that dissolves again on the addition of an excess of ammonia indicates the presence of chlorine. A light yellow precipitate that is difficult to dissolve in ammonia indicates the presence of bromine. A yellow precipitate that is insoluble in ammonia is characteristic for iodine.

Fluorine   Acidify the original solution with dilute hydrochloric acid or acetic acid and then add a 1 N calcium chloride solution. A gel-like precipitate of calcium fluoride indicates the presence of fluorine (compare also below).

Phosphorus   On the addition of a solution of ammonium molybdate to a portion of the original solution that was acidified with nitric acid, one obtains a precipitate on heating for approximately 1 min. To prepare the molybdate solution, dissolve 30 g ammonium molybdate in approximately 60 ml hot water, cool, and add water to make 100 ml. Then add a thin stream of a solution of 10 g ammonium sulfate in 100 ml 55 % nitric acid (from 16 ml water and 84 ml concentrated nitric acid). Let it stand for 24 hr, remove the supernatant by suction or by decantation, and keep the solution well sealed in the dark.

Silicon   Mix approximately 30 – 50 mg of the plastic sample with 100 mg dry sodium carbonate and 10 mg sodium peroxide in a small platinum or nickel crucible (carefully). Melt it slowly over a flame. After cooling, dissolve the material in a few drops of water, bring it quickly to a boil, and neutralize or slightly acidify it with dilute nitric acid. Add 1 drop of molybdate solution (see phosphorus test), and then heat nearly to boiling. Cool the sample, add 1 drop of benzidine solution (50 mg benzidine dissolved in 10 ml 50 % acetic acid; add water to make 100 ml), and then add 1 drop of saturated aqueous sodium acetate solution. A blue color indicates silicon.

Other Identification Reactions

Halogens, especially chlorine and bromine, can be easily identified with the very sensitive *Beilstein test*. Heat the end of a copper wire in a Bunsen flame until the flame is colorless. After cooling, put a small amount of the substance to be examined on the wire and heat it at the edge of the colorless part of the flame. When the plastic burns, the presence of halogen can be inferred if the flame is colored green or blue-green.

Fluorine can be demonstrated by placing approximately 0.5 g of the plastic in a small test tube and pyrolyzing it in a Bunsen flame. After cooling, add a few milliliters of concentrated sulfuric acid. The presence of fluorine is indicated by a characteristic non-wettability of the wall of the test tube. (Make a comparison experiment with a sample of known fluorine content.)

From the results of the tests for heteroatoms, useful conclusions can be drawn:

Chlorine   occurs in plastics such as PVC, chlorinated polyethylene, and rubber hydrochloride. Some plasticizers also contain chlorine. Flame-proofing agents often contain chlorine or bromine.

Nitrogen   is found in polyamides, aminoplastics, cellulose nitrate, and in cellophane films treated with nitrogen-containing lacquers.

Sulfur   when found in rubber elastic materials, indicates vulcanized rubber, polysulfones, or polysulfides.

Phosphorus   is seldom found in plastics (with the exception of casein). However, it indicates the presence of phosphate plasticizers, stabilizers, or flame-proofing agents.

A compilation of the most important plastics containing heteroatoms is shown in Table 4.1.

TABLE 4.1 The Classification* of Plastics by Their Heteroatoms

Heteroatoms

—	O			Halogens	N, O	S, O	Si	N, S	N, S, P
	Cannot be saponified	*Can be saponified****							
		SN < 200	*SN > 200*						
Polyolefins	Polyvinyl alcohol	Natural resins	Polyvinyl-acetate and copolymers	Polyvinyl chloride	Polyamides	Polyalkyl-ene sulfide	Silicones	Thiourea conden-sates	Casein resins
Polystyrene	Polyvinyl ethers	Modified phenolic resins	polyacry-lates and polymeth-acrylates	Polyvinyl-idene chloride and copolymers	Polyure-thanes	Vulcanized rubber	Polysilo-xanes	Sulfamide conden-sates	
Polyiso-prene	Polyvinyl acetals		Polyesters	Polyfluoro-hydrocar-bons	Polyureas				
Butyl rubber	Polyglycols		Alkyd resins	Chlorinated rubber	Amino-plastics				
	Polyaldehydes		Cellulose esters	Rubber hydro-chloride	Polyacryloni-trile and copolymers				
	Phenolic resins				Polyvinyl-carbazole				
	Xylene resins				Polyvinyl-pyrrolidone				
	Cellulose								
	Cellulose ethers								

*   After W. Kupfer, *Z. analyt. Chem.* 192 (1963) p. 219.
** SN = Saponification number (amount of potassium hydroxide used in mg KOH per g of substance).

Polyethylene and polypropylene may also be differentiated by scratching the sample with your finger nail: whereas polyethylene will show scratch marks, polypropylene is scratch resistant.

6.2.2 Polystyrene

When polystyrene is heated in a dry test tube styrene monomer is formed, which is easily identified by its typical odor.

Polystyrene and most styrene-containing copolymers can be identified by placing a small sample in a small test tube, adding a few drops of fuming nitric acid, and evaporating the acid without having the polymer decompose. The residue is then heated over a small flame for approximately 1 min. Fasten the test tube with its open end tilted slightly down and covered with a piece of filter paper. Prepare the paper by drenching it in a concentrated solution of 2,6-dibromoquinone-4-chlorimide in ether and then drying it in air. On moistening with a drop of dilute ammonia, the paper turns blue if polystyrene is present. If the sample still contains some free nitric acid, the test is affected and the paper turns brown, which may conceal the blue color. This identification is also useful for styrene-butadiene copolymers as well as for ABS (acrylonitrile-butadiene-styrene copolymers). The presence of acrylonitrile can be confirmed by a test for nitrogen.

6.2.3 Polymethyl Methacrylate

Polymethyl methacrylate plays an important role among the acrylates as an injection molding material as well as a glasslike material. For its identification, 0.5 g sample is heated in a test tube with approximately 0.5 g dry sand. On depolymerization, monomeric methyl methacrylate is obtained. This is captured at the opening of the test tube on a glass fiber plug. The methyl methacrylate monomer may be distilled from one test tube into another through a bent piece of glass tubing passing through a rubber stopper (Figure 6.1). Heat a sample of the monomer with a small amount of concentrated nitric acid (density 1.4 g/cm^3) until a clear yellow solution is
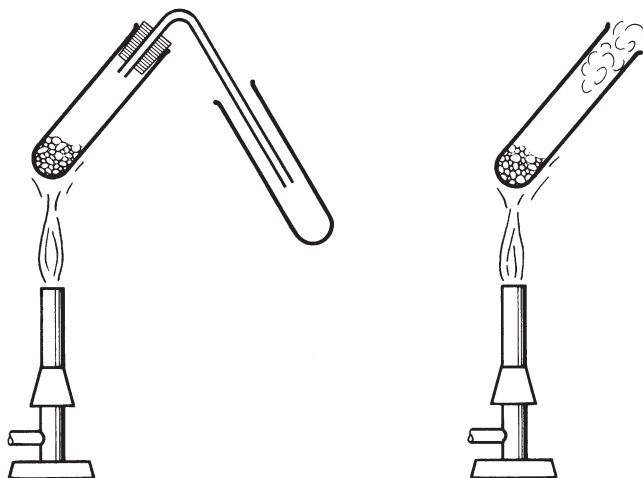
FIGURE 6.1 Depolymerization in a test tube.

obtained. After cooling, dilute with approximately half its volume of water, then add a 5 – 10 % sodium nitrite solution dropwise. Methyl methacrylate, which may be extracted with chloroform, is indicated by a blue-green color.

On pyrolysis, polyacrylates yield, in addition to monomeric esters, several strong-smelling decomposition products. The pyrolysates are either yellow or brown and acidic.

6.2.4 Polyacrylonitrile

Polyacrylonitrile is most often encountered as a fiber. It is also found in acrylonitrile-containing plastics copolymerized with styrene, butadiene, or methyl methacrylate. All such polymers contain nitrogen.

To identify acrylonitrile polymers, take a sample of the material and add a small amount of zinc dust and a few drops of 25 % sulfuric acid (1 ml concentrated sulfuric acid added to 3 ml water, slowly). Heat this mixture in a porcelain crucible. Cover the crucible with filter paper moistened with the following reagent solution: Dissolve 2.86 g copper acetate in 1.0 liter water. Then dissolve 14 g benzidine in 100 ml acetic acid, and to 67.5 ml of this

7.2.2 Natural Resins

In many cases, natural resins such as copal resins, amber, shellac, and colophonium, which were most widespread in the early period of plastics, differ widely in terms of their properties and chemical composition depending on their origins and production methods. Consequently, it is extremely difficult or even impossible to identify these materials by simple techniques. Instead, it would be advisable to conduct several laboratory tests. In the following, a few hints are given for a brief introduction. More detailed investigations may be based on the works of Thinius and Hummel, which mostly involve a higher test complexity.

As an initial laboratory test, the Liebermann-Storch-Morawski color reaction test outlined under Section 6.1.1 may be applied. The test is highly sensitive, but not very specific. Apart from the plastics mentioned under Section 6.1.1 above, the following products may be identified by their color reaction:

- **Colophonium:** violet changing to brown or olive
- **Manila and Congo copal; bitumen and pitch:**
  reddish brown or brown
- **Coumarone-indene resins:** orange or brown
  (often not clearly discernible)
- **Shellac:** no color reaction

For a similar laboratory test, dissolve powdery resins in acetic anhydride, either in a cold process or by heating. After cooling, cautiously add a drop of concentrated sulfuric acid and watch the color reaction.

TABLE 7.3 Color Reaction of Natural Resins after Addition of Sulfuric Acid

	Dissolved in acetic anhydride	After addition of sulfuric acid
Colophonium	Nearly colorless	Bluish violet
Copal	Nearly insoluble, turbid	Yellowish brown
Shellac	Lemon yellow, clear	Faintly yellow brown

To differentiate colophonium from copal, place a sample on a glass plate with an underlay of white paper, and dissolve the sample in a few droplets

of a freshly prepared mixture of acetic anhydride (15 parts by volume) and concentrated sulfuric acid (1 part by volume) (caution when mixing!). The color of colophonium will quickly change from violet to blue and greenish brown whereas copal turns yellowish red before it gets purple brown.

Amber, colophonium, copals, mastix, and shellac develop a beautifully blue color when in contact with ether mixed with ammonium molybdate (0.1 g in 5 ml concentrated sulfuric acid) and ammonia. Thinius reports a number of additional color reactions for the above natural resins, but these do not permit unambiguous identification in each case, especially since phenolic resins produce similar colors.

The flame test is a simple method to distinguish between amber and phenolic resins. Phenolic resins are flame-retardant and emit an odor of phenol and formaldehyde, whereas amber with its typical smell of resin is easily flammable and often ignites when in contact with a hot needle.

Shellac is the only natural resin of animal origin which still has retained significance as varnish resin and for coatings of pharmaceutical drugs and chocolate products. Around the mid-19th century, it was used for filled molding masses before it was processed into shellac records until about the middle of the 20th century.
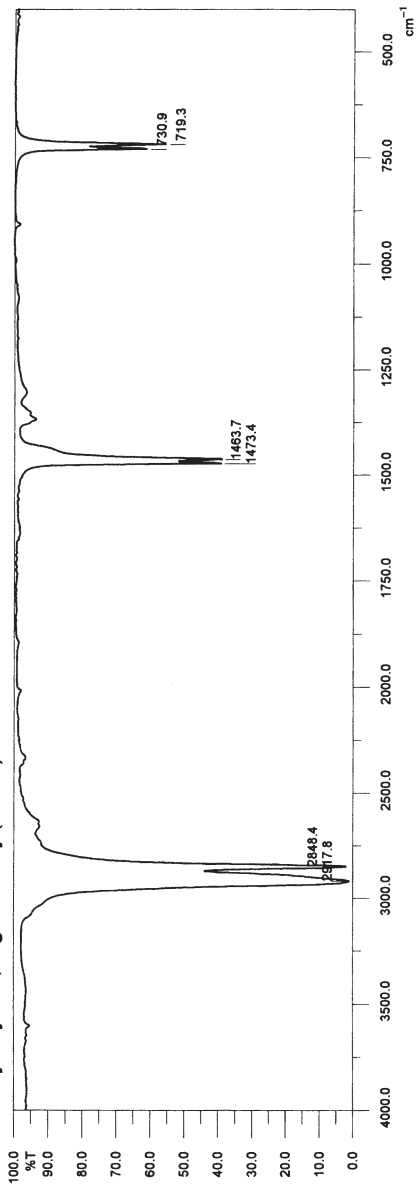
The shellac material that is not crosslinked characteristically dissolves in a 4 % borax solution. It may also be identified by a test for aleuritic acid as its main constituent as described by Hummel (Vol. 2, p. 427), which is a more complex technique.

When subjected to a burning test, shellac produces a yellowish orange flame with a blue core and develops an odor of sealing wax.

Because shellac articles are frequently not fully cured, finished products of this kind may be tested as follows: place a cut up sample of about 1 g in approximately 15 ml of boiling alcohol for a period of about one hour, and allow the sample to cool. Then boil down the extractive and test for shellac by adding diluted hydrochloric or acetic acid to the alcoholic extract in a test tube; then heat until the sample becomes clear. Upon addition of ammonia, shellac turns dark violet, and if it was chlorine-bleached, it turns brown.
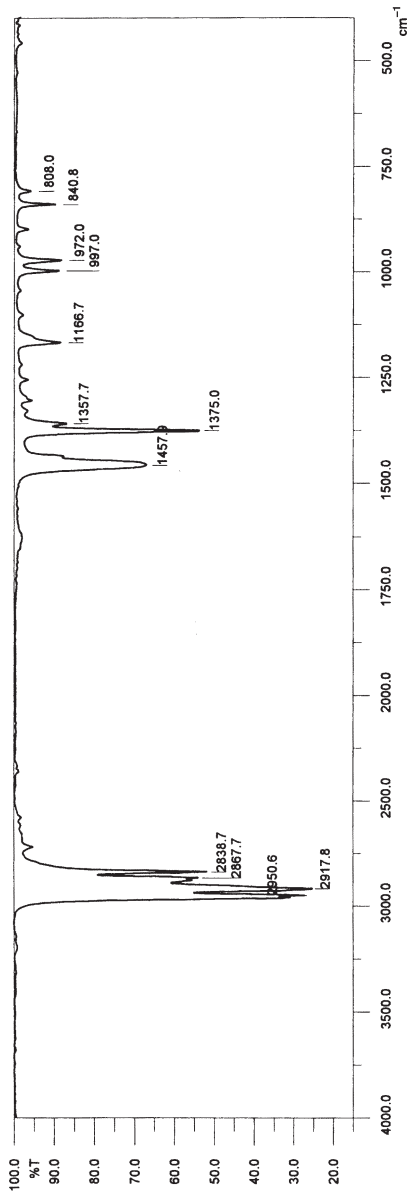
For additional literature refer to chapter 10.

Polyethylene, high density (HDPE)

1.

Polypropylene (PP)

2.