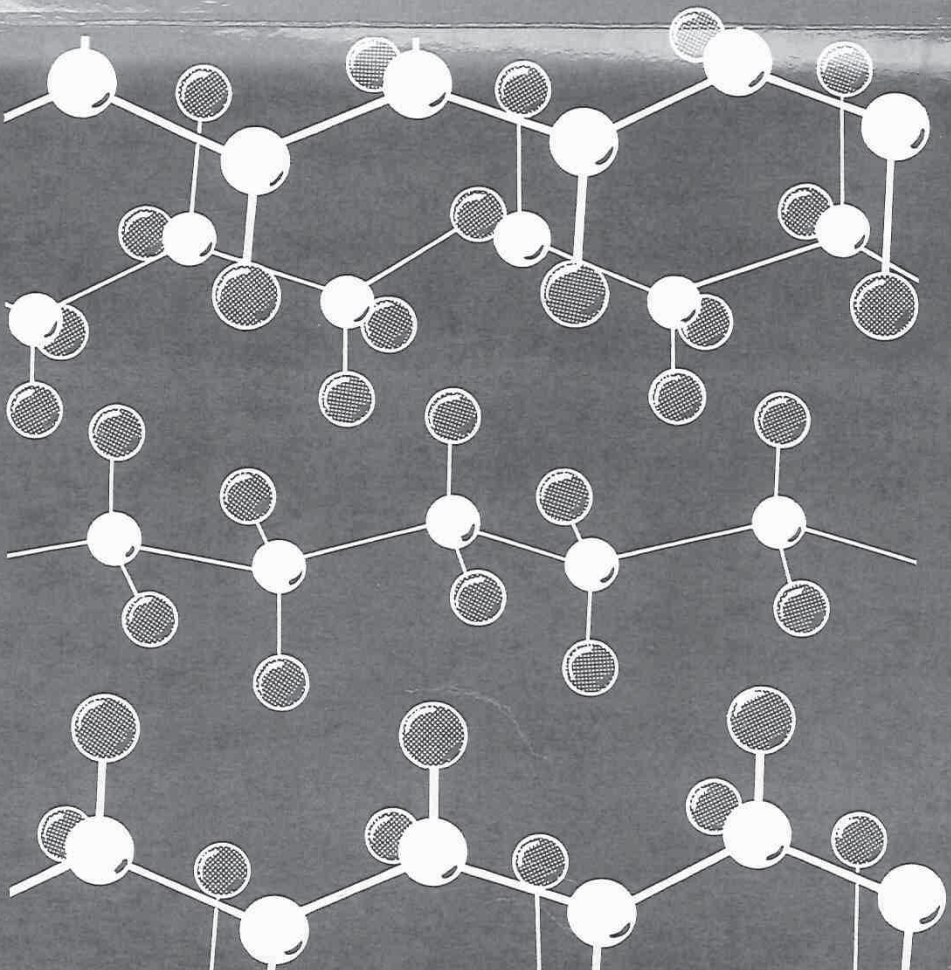


INTRODUCTION TO POLYMERS

Second edition

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Introduction to Polymers

Second Edition

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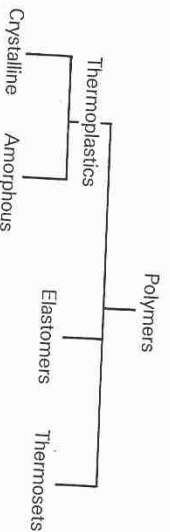


Fig. 1.2 Classification of polymers.

is named poly(ethylene-*stat*-propylene), and an ABA tri-block copolymer of styrene (A) and isoprene (B) is named polystyrene-*block*-polyisoprene-*block*-polystyrene. In certain cases, additional square brackets are required. For example, an alternating copolymer of styrene and maleic anhydride is named poly[styrene-*alt*-(maleic anhydride)].

1.2.4 Classification of polymers

The most common way of classifying polymers is outlined in Fig. 1.2 where they are first separated into three groups: *thermoplastics*, *elastomers* and *thermosets*. Thermoplastics are then further separated into those which are crystalline and those which are amorphous (i.e. non-crystalline). This method of classification has an advantage in comparison to others since it is based essentially upon the underlying molecular structure of the polymers.

Thermoplastics, often referred to just as plastics, are linear or branched polymers which can be melted upon the application of heat. They can be moulded (and remoulded) into virtually any shape using processing techniques such as injection moulding and extrusion, and now constitute by far the largest proportion of the polymers used in industry. Generally, thermoplastics do not crystallize easily upon cooling to the solid state because this requires considerable ordering of the highly coiled and entangled macromolecules present in the liquid state. Those which do crystallize invariably do not form perfectly crystalline materials but instead are *semi-crystalline* with both crystalline and amorphous regions. The crystalline phases of such polymers are characterized by their *melting temperature* (T_m). Many thermoplastics are, however, completely amorphous and incapable of crystallization, even upon annealing. Amorphous polymers (and amorphous phases of semi-crystalline polymers) are characterized by their *glass transition temperature* (T_g), the temperature at which they transform abruptly from the *glassy state* (hard) to the *rubbery state* (soft). This transition corresponds to the onset of chain motion; below T_g the polymer chains are unable to move and are 'frozen' in position. Both T_m and T_g increase with increasing chain stiffness and increasing forces of intermolecular attraction.

Elastomers are crosslinked rubber that can be stretched easily to high original dimensions) and which rapidly return to their original shape when the applied stress is released. The property is a reflection of their molecular structure of low crosslink density. The rubbery state is characterized by low modulus upon deformation but are prevented from permanent deformation by removal of the stress. The word rubber is often used for materials which are preferably should be used for describing crosslinked.

Thermosets normally are rigid materials which chain motion is greatly restricted. As for elastomers, they are intrinsically more difficult to melt upon the application of heat.

1.3 Molar mass and degree of polymerization

Many properties of polymers show a dependence on the molar mass of the polymer chains, so that it is essential to know the molar mass of a polymer. This normally is done by measuring the mass of a polymer sample which is simply the mass of 1 mole of polymer units of g mol^{-1} or kg mol^{-1} . The molar mass is a dimensionless quantity, but is not to be confused with the molecular mass, which is really a dimensionless quantity. It is really a dimensionless quantity, but is not to be confused with the molecular mass, which is really a dimensionless quantity. It is really a dimensionless quantity, but is not to be confused with the molecular mass, which is really a dimensionless quantity.

For network polymers the only way to determine the molar mass of the polymer chains existing between crosslinks is by measuring the molar mass of the network. The molar mass of a homopolymer (M_n), which is the average molar mass of the polymer chain, by the simple relation

$$M_n = xM_0$$

where M_0 is the molar mass of the repeating unit, x is the number of repeating units in the polymer chain, and M_n is the molar mass of the polymer chain.

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Elastomers are crosslinked rubbery polymers (i.e. rubbery networks) that can be stretched easily to high extensions (e.g. $3\times$ to $10\times$ their original dimensions) and which rapidly recover their original dimensions when the applied stress is released. This extremely important and useful property is a reflection of their molecular structure in which the network is of low crosslink density. The rubbery polymer chains become extended upon deformation but are prevented from permanent flow by the crosslinks, and driven by entropy, spring back to their original positions on removal of the stress. The word rubber, often used in place of elastomer, preferably should be used for describing rubbery polymers which are not crosslinked.

Thermosets normally are rigid materials and are network polymers in which chain motion is greatly restricted by a high degree of crosslinking. As for elastomers, they are intractable once formed and degrade rather than melt upon the application of heat.

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1.3 Molar mass and degree of polymerization

Many properties of polymers show a strong dependence upon the size of the polymer chains, so that it is essential to characterize their dimensions. This normally is done by measuring the *molar mass* (M) of a polymer which is simply the mass of 1 mole of the polymer and usually is quoted in units of g mol^{-1} or kg mol^{-1} . The term 'molecular weight' is still often used instead of molar mass, but is not preferred because it can be somewhat misleading. It is really a dimensionless quantity, the relative molecular mass, rather than the weight of an individual molecule which is of course a very small quantity (e.g. $\sim 10^{-19}$ – $\sim 10^{-18}$ g for most polymers). By multiplying the numerical value of molecular weight by the specific units g mol^{-1} it can be converted into the equivalent value of molar mass. For example, a molecular weight of 100 000 is equivalent to a molar mass of 100 kg mol^{-1} , 100 000 g mol^{-1} which in turn is equivalent to a molar mass of 100 kg mol^{-1} .

For network polymers the only meaningful molar mass is that of the polymer chains existing between junction points (i.e. *network chains*), since the molar mass of the network itself essentially is infinite.

The molar mass of a homopolymer is related to the *degree of polymerization* (x), which is the number of repeat units in the polymer chain, by the simple relation

$$M = xM_0 \quad (1.1)$$

where M_0 is the molar mass of the repeat unit. For copolymers the sum of the products xM_0 for each type of repeat unit is required to define the molar mass.

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seen. Similar structures have been seen in many glassy polymers and the nodules have been interpreted as domains of order. However, the presence of order has not been confirmed by X-ray diffraction which shows the structures to be random and some of the electron micrographic evidence has been criticized.

There are some polymers, such as poly(ethylene terephthalate) and isotactic polypropylene which normally crystallize rather slowly, that can be obtained in an apparently amorphous state by rapidly quenching the melt which does not allow sufficient time for crystals to develop by the normal processes of nucleation and growth. Crystallization can be induced by annealing the quenched polymer at an elevated temperature. The X-ray diffraction patterns which are obtained from the quenched polymer tend to be diffuse and ill-defined. This could be either because the samples are truly non-crystalline or due to the presence of very small and imperfect crystals. Crystallization is manifest during annealing by the diffraction patterns becoming more well defined. There must clearly be a certain amount of molecular rearrangement during annealing, but this cannot take place through large-scale molecular diffusion as the process occurs in the solid state. The mechanism of crystallization is therefore unclear and it is very difficult to decide whether the quenched polymers are truly amorphous or just contain very small crystals.

4.4.2 The glass transition

If the melt of a non-crystallizable polymer is cooled it becomes more viscous and flows less readily. If the temperature is reduced low enough it becomes rubbery and then as the temperature is reduced further it becomes a relatively hard and elastic polymer glass. The temperature at which the polymer undergoes the transformation from a rubber to a glass is known as the *glass transition temperature*, T_g . The ability to form glasses is not confined to non-crystallizable polymers. Any material which can be cooled sufficiently below its melting temperature without crystallizing will undergo a glass transition.

There is a dramatic change in the properties of a polymer at the glass transition temperature. For example, there is a sharp increase in the stiffness of an amorphous polymer when its temperature is reduced below T_g . This will be dealt with further in the section on mechanical properties (Section 5.2.6). There are also abrupt changes in other physical properties such as heat capacity and thermal expansion coefficient. One of the most widely used methods of demonstrating the glass transition and determining T_g is by measuring the specific volume of a polymer sample as a function of the temperature as shown in Fig. 4.31. In the regions above and below the glass transition temperature there is a linear variation in specific volume

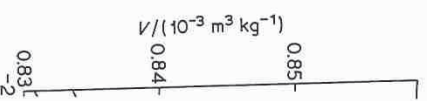


Fig. 4.31 Variation of specific volume with temperature showing the glass transition temperature T_g .

with temperature. The curve which shows the change in specific volume with temperature has a characteristic change in slope at the glass transition temperature T_g , at which the temperature is reduced low enough it becomes a relatively hard and elastic polymer glass. The temperature at which the polymer undergoes the transformation from a rubber to a glass is known as the *glass transition temperature*, T_g . The ability to form glasses is not confined to non-crystallizable polymers. Any material which can be cooled sufficiently below its melting temperature without crystallizing will undergo a glass transition.

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$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$