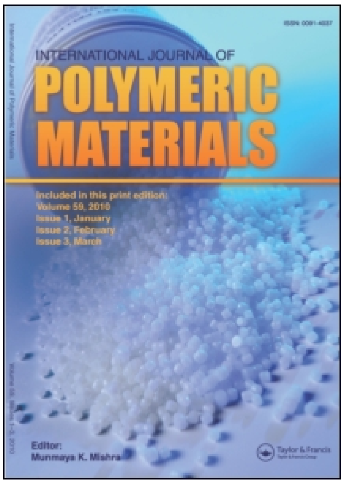

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Polymers as Materials

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To cite this Article Mark, H. F. and Pearce, E. M.(1976) 'Polymers as Materials', International Journal of Polymeric Materials, 5: 1, 5 — 42
To link to this Article: DOI: 10.1080/00914037608072387
URL: http://dx.doi.org/10.1080/00914037608072387

Intern. J. Polymeric Mater., 1976, Vol. 5, pp. 5–42

Printed in Reading, England

Polymers as Materials

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(*Received June, 1974*)

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1 INTRODUCTION

The chemistry and technology of polymers has developed rapidly during the last three decades; it concerns itself with materials consisting essentially of the elements C, H, N, and O, and being therefore conventionally classified as *organic* polymers. However, in many instances other elements such as B, Si, P, S, F, and Cl are present in certain proportions and have a more or less important influence on the ultimate properties of the products. Together with the large family of metallic compounds and ceramic systems, organic polymers represent useful and increasingly important engineering materials in the construction of buildings, vehicles, engines, applicanes, textiles, packaging, printing and writing materials, plastics, rubber goods and household articles of all kinds.

The rapid growth of these relatively new engineering materials in the recent past has been caused by several factors:

a) The basic raw materials for their production are readily available in large quantities and are, in general, inexpensive. Natural organic polymers such as cellulose (paper, textiles), proteins (wool, silk, leather), starch (food, adhesives), and rubber (tires and many other goods) are mainly available as products of farming and forestry activities, whereas the raw materials for the production of synthetic polymers are now essentially derived from coal, oil and gas. If needed, many of them could also be produced from yearly reproducing crops of cellulosic and proteinic materials.

The simplest building units are called *monomers*, some of which (ethylene, propylene, isobutylene, butadiene and styrene) are byproducts of the manufacturing of gasoline and luboils and consequently, are of low cost (three to ten cents per lb.), and are available in large quantities. Many others are simple derivatives of ethylene, benzene, formaldehyde, phenol urea and other basic organic chemicals; and range in cost from five cents to twenty-five cents at the most per lb., and they are also, in general, large industrial products. Thus the basic building units for organic polymers, as defined above, represent a large variety of compounds, are readily available, and are of low or moderate cost.

b) During the last decades, intense research activities in many laboratories have succeeded in elucidating the mechanism of those reactions which form long chain molecules from the above-mentioned basic units. They are called *polymerization reactions* and represent either typical chain reactions of highly exothermic character or step reactions in the course of which chains of systematically repeating units are formed. The results of this research have provided a sound fundamental understanding of the mechanism of these reactions and have permitted systematic engineering efforts which developed a number of relatively simple unit type processes permitting the translation of polymerization and polycondensation reactions into large scale industrial operations. Today several types of them (such as polymerization in the gas phase at high pressures, in solution, suspension, emulsion and even in the solid state) are well developed continuous standard procedures which allow rapid conversion of monomers into polymers rapidly, conveniently, and at low cost. In fact, in many cases, the actual conversion cost from monomer to polymer can be as low as three cents per lb., a condition which has greatly contributed to the rapid expansion of this field.

c) Thirty years ago there were only a few well developed processes and machines to convert organic polymers from the state of a latex, a molding powder or a granulate into such ultimate commercial products as fibers, bristles, films, plates, rods, tubes, bottles, cups, combs and other salable commodities. Today there are many continuous automatic, rapid, and inexpensive methods for spinning, casting, blow molding, injection and compression molding, stamping and vacuum forming which give each polymer with attractive properties an almost immediate chance of being converted into useful and marketable consumer goods. Obviously the existence of manifold applications and the availability of standardized and automated methods of converting a new polymer into many different products stimulated the synthesis and development of other new members of the organic polymer family.

d) The large number of available monomers and the even larger number of polymers and copolymers made from them has provided us with an almost continuous spectrum of composition and structure of organic macromolecules. On the other hand, the systematic exploration of their mechanical, optical, electrical and thermal behavior has provided us with an equally dense spectrum of characteristic practical properties, and their correlation has led to a relatively profound and dependable understanding of structure–property relationships. This has the great advantage that many new polymers or copolymers with desired and predetermined properties need not be looked for by the empirical, more or less random system of trial and error, but can be designed on paper; a realistic elimination of many possibilities can be effected before work is actually started in the laboratory. This approach has been so successful that, in many instances, one can speak of a *molecular engineering* approach in the synthesis and development of new polymeric materials.

All fundamental and applied efforts of monomer syntheses, polymerization techniques and manufacturing processes can eventually be condensed in a few guiding principles which represent, so to speak, the essence of our present understanding and know-how. Such principles are, of course, only qualitative generalizations and, in each individual case, have to be supplemented by quantitative considerations and numerical refinements, but they give a convenient and clarifying "helicopter view" of the present state of our knowledge and its practical applicability. As a consequence they are good working hypotheses or guide posts, if they are used with caution and with the realization of their character as approximations and illustrations.

In the following paragraphs we shall try to enumerate and discuss the most important principles of this type and to indicate the most prominent applications of them.

2 MOLECULAR WEIGHT

A factor of great importance in the synthesis and application of organic polymers is their molecular weight (compare Table I). The words macromolecule, giant molecule, high polymer or polymer indicate that the molecules of this class of compounds are large and hence consist of *many parts*. In fact, all existing experience indicates that many valuable and interesting properties of natural and synthetic polymers can only be obtained *if their molecular weight (MW) is sufficiently high*. Since many important materials consist of chain molecules with repeating units, one can also introduce the concept of the *degree of polymerization* (DP) which represents the *number of basic units* in a given macromolecule. In general, molecular weight and degree of

TABLE I

Relationship between molecular weight and mechanical properties of a polyethylene with 0.92 density

Molecular weight number average	14,000–18,000	20,000–22,000	26,000–28,000	30,000–32,000
Yield strength at 25° psi	1430	1490	1700	1720
Tensile strength at 25° psi	1430	1965	2965	3060
Ultimate elongation in %	305	550	580	625
Tear strength in psi	440	540	580	690
Abrasion volume loss (100 = butyl rubber)	85	50	40	30

polymerization are used interchangeably in the sense that they are related by the equation:

$$MW = DP \times (MW)_u \tag{1}$$

where $(MW)_u$ is the molecular weight of the repeating unit or monomer.

It has also been established that polymeric materials do *not* consist of strictly *identical* molecules, but always represent a *mixture* of *many species*, each of which has a different molecular weight or DP. The precise character of a given material is, therefore, indicated by a molecular weight *distribution function*, which can conveniently be expressed by a curve in which the frequency or percentage of each species is plotted against the molecular weight or the DP of this particular species. The narrower the distribution curve of a given polymer, the most *homogeneous* is the material. As a consequence of this polymolecularity of all synthetic polymers, one cannot simply speak of "a" molecular weight or of "a" DP, but must operate with an *average* molecular weight $\overline{MW}$ or an *average* degree of polymerization $\overline{DP}$.

Many tests have established the fact that all important mechanical properties, particularly tensile strength, elongation to break, impact strength and reversible elasticity definitely depend on the $\overline{MW}$ or $\overline{DP}$, in the sense that up to a certain, relatively low value no strength at all is developed. From then on, there is a steep rise of mechanical performance with $\overline{DP}$ until, at still larger molecular weights, the curve flattens out somewhat and one enters a domain of diminishing return of strength on further $\overline{DP}$ increments. Figure 1 shows the characteristic shape of this curve, which is typical for all polymers and differs for each individual material only in the numerical details. Each polymer has, for instance, a critical $\overline{DP}$ value $\overline{DP}_c$, below which it is essentially a friable powder, but the numerical value of $\overline{DP}_c$ is different for each polymer; polyamides start to develop strength at $\overline{DP}$'s as low as around 40, whereas cellulose needs values around 60, and many vinyl polymers need still higher values of 100 and more. The knee, K of the curve occurs at a $\overline{DP}$ of 150 for polyamides, 250 for cellulose and 400 for many vinyls. However, *all* polymers

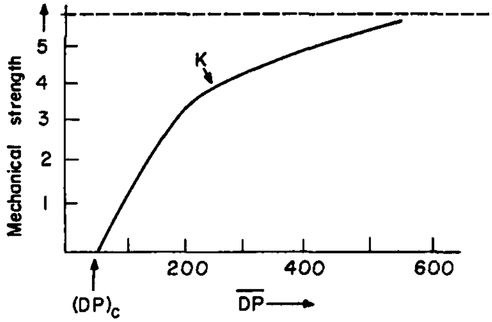


FIGURE 1 Mechanical strength as a function of degree of polymerization ($\overline{DP}$).

exhibit *no strength* below DP's of 30 and show small strength increments at $\overline{\text{DP}}$'s above 600. Even if there are still some gains in the higher molecular weight range of the curve, they are difficult to attain practically because very long chains produce high viscosities in the dissolved and molten state and become increasingly difficult and impractical to process. The characteristic shape of the curve in Figure 1 has the consequence that many practically useful polymers fall in the $\overline{\text{DP}}$'s range from 200 to 2000, which in general, corresponds to $\overline{\text{MW}}$'s from 20,000 to 200,000.

Evidently the curve in Figure 1 is of great interest and importance for anybody who wants to prepare and launch a new useful polymer. If he finds, at a certain point in his research, that the molecular weight of his present samples is around 5000, his attention and effort will be concentrated on changing the polymerization conditions in order to penetrate into a higher molecular weight range. If, on the other hand, he establishes that his present samples have molecular weights around 60,000, he will focus his interest on other factors, such as molecular weight distribution, branching, and the influence of reactive groups or stereoregulation, but not on a further increase of molecular weight or of chain length.

The curve of Figure 1 can be represented by an equation of the type:

$$\text{MS} = (\text{MS})_j - \frac{\text{A}}{\overline{\text{DP}}} \tag{2}$$

where:

(MS)$_j$ is the mechanical strength of infinitely long chains,

MS is the mechanical strength measured for a given $\overline{\text{DP}}$, and

A is a constant.

The parameters A and (MS)$_j$ are characteristic for any given polymer and are connected with $(\overline{\text{DP}})_c$, the critical DP, through:

$$(\overline{\text{DP}})_c = \frac{\text{A}}{(\text{MS})_j}.$$

Hence Eq. (2) may also be written as:

$$\mathrm{MS} = (\mathrm{MS})_j\, 1 - \frac{(\overline{\mathrm{DP}})_c}{\overline{\mathrm{DP}}} \tag{3}$$

It should be added that Eqs. (2) and (3) lose their significance when $\overline{\mathrm{DP}}$ becomes smaller than $(\overline{\mathrm{DP}})_c$. Furthermore, at least at this stage, they are only empirical, but it was shown by Flory and others that they can be rationalized by considering that the bonds along each individual chain are much stronger (chemical bonds) than those between chains (Van der Waals bonds). As a result, short chains slip easily along each other and offer little or no stress transferring action. This explains the existence and significance of $(\overline{\mathrm{DP}})_c$. On the other hand, if the chains become very long the accumulated resistance of many Van der Waals bonds against slippage becomes so great that eventually chemical bonds start to break. From this point on, further lengthening of the chains has only little influence on improved mechanical performance. By considering these arguments mathematically, it was not only possible to interpret the form of Eq. (3) rationally, but also to arrive at improved expressions which represent in greater detail the conditions for the mechanical failure of chain polymers.

Thus far, we have only discussed the influence of the length of the chain molecules; let us now pass to the consideration of other chain properties which are also important for the mechanical and thermal behaviour of polymeric systems.

3 CRYSTALLINITY

One of the first important notions of the basic properties of chain molecules was that they exhibit a tendency to form crystal like bundles or aggregates. If one uses the words "crystallite" or "crystallize" in connection with polymers, it must be understood that one wants to emphasize that certain volume elements of the polymeric system have reached a state of three dimensional order which, in *certain respects*, approaches the crystals of normal materials such as sugar, naphthalene, stearic acid or maleic anhydride. However, crystalline domains in a polymeric material do not have the regular shape of normal crystals; they are much smaller in size, contain many more imperfections, and are connected with the disordered, amorphous areas by through-going polymer chains, so that there are no sharp or distinct boundaries between the three dimensionally ordered (crystalline) and disordered (amorphous) parts of the system. Under certain conditions it is possible to obtain very small "single crystals" of linear macromolecules formed by chains which fold back on themselves in a regular manner and eventually produce highly ordered domains with distinct boundaries. These folded chain crystals and also those, in which extended chains form laterally ordered areas have sharp melting points, high densities, high moduli of rigidity, they resist dissolution and swelling, and are virtually impenetrable to diffusion of small molecules. They give relatively sharp X-ray and electron diffraction patterns and show characteristic absorption peak splitting in the infrared spectrum. In some instances (cellulose, polyvinyl alcohol and certain proteins), there are reasonably distinct boundaries between the crystalline and amorphous portions of a polymeric material, while in other cases (linear polyethylene, polyesters, polyacetals, etc.) it appears more appropriate to consider the entire system as crystalline, but with the understanding that flaws and imperfections (twisted or folded chains) are more or less uniformly spread out over its length and width and are responsible for the deviation of its behavior from that of a perfect crystal.

But whatever the best mental picture for an incomplete three-dimensional order may be in any special case, there can be no doubt that the tendency to crystallize plays a very important role in the thermal and mechanical behavior of polymers, and it will be useful to connect this tendency with the chemical composition and the structural details of the individual macromolecules. There are, of course, many factors contributing to such a complicated process as three-dimensional order and, in this paper, it will be appropriate to discuss only the most important ones. They seem to be the following:

a) Structural regularity of the chains, which can readily lead to the establishment of progressive periodicity.

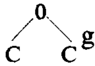
b) Free vibrational and rotational motions in the segments so that different conformations can be assumed without overcoming high energy barriers.

c) Presence of specific groups which produce strong lateral (intermolecular) bonds (Van der Waals bonds) and regular, periodic arrangement of such groups and;

d) Absence of bulky, irregularly spaced substituents which inhibit the chain segments from fitting into a crystal lattice and prevent the laterally bonding groups from approaching each other to the distance of best interaction.

Let us now analyze these factors, one after the other, and estimate how much each of them contributes to the crystallizability of a given material.

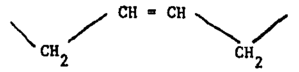
a) Structural regularity

The simplest polymer molecules are linear polyethylene and polyformaldehyde; their chains can readily assume a planar zig-zag conformation characterized by a sequence of trans-bonds and can therefore produce a very short identity period along their length. This characteristic evidently favors the establishment of lateral order, particularly if the macromolecules are oriented by stress or shear; in fact, both polymers are easily orientable and can attain very high degrees of crystallinity. The polyethylene chains are nonpolar, and all intermolecular attraction is due to dispersion forces; the rotation around the C—C bond is inhibited by an energy barrier of about 2.7 kg cal per mole of bonds. This limited flexibility and the dispersion forces between adjacent chains are responsible for the relatively high melting point and rigidity, and also for the low solubility of this material. In the case of polyformaldehyde the rotation about the C—0 bond is less inhibited than that about the C—C bond, but the dipole character of the  group produces polar forces between adjacent chains, which act over a longer range and are stronger than the dispersion forces in polyethylene. As a consequence, polyformaldehyde has a higher rigidity and a higher melting point than polyethylene, and is also less soluble.

If a substituent such as CH_3, Cl, or CN is attached to the chain of linear polyethylene in a 1,3 sequence, there exist two simple ways to establish regular geometric placement of the substituents along the length of the chain: the *isotactic* placement, in which all substituents (or at least a long row of them) have the *same* configurational position (either "d" or "l"), and the *syndiotactic* placement, in which there is a *regular alternation* between "d" and "l" over the entire molecule or at least over long stretches of it. Any deviation from these two cases or any mixture of them is called *atactic* and refers to more or less random geometric positions of the substituents along the length of the chain. Natta who first succeeded in preparing pure (or almost pure) representatives of these cases with polypropylene and other alpha olefinic polymers, has demonstrated that the *stereoregulated* or *stereospecific* species are rigid, crystallizable, high melting and relatively insoluble materials, whereas the *atactic* or *irregular* species are comparatively soft, low melting and easily soluble polymers which do not crystallize under any conditions. The spectacular influence of this structural regularity on crystallization and with it on most mechanical and thermal properties has been established by Natta and later by many investigators for numerous vinyl-, acrylic and allylic polymers, and has become an important principle in the designing and "tailoring" of new polymers, particularly since an appropriate choice of experimental conditions (such as catalyst, solvent, temperature, and additives) makes it possible to aim at a definite prevalence of one of the three steric structures.

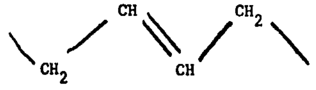
An equally important influence of structural regularity on ultimate properties has been discovered in the polymerization of conjugated dienes. If a butadiene molecule becomes the unit of a long chain, the following three structures are possible:

1,4 - cis



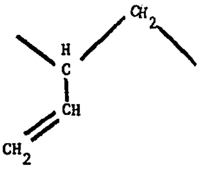
(I)

1,4 - trans



(II)

1,2



(III)

Through the use of appropriate initiators, solvents, temperatures and additives, Natta made it possible to synthesize each of these structures in almost pure form. Even though the same chemical monomer is used, the three different structural arrangements shown above produce dramatically different behavior.

(I) is a soft, easily soluble elastomer with a glass transition temperature, Tg, around —60°C and a high retractive force; it crystallizes on stretching over 200%, and the crystalline phase has a melting point around 20°C (Hevea Rubber belongs to this species if isoprene is the monomer instead of butadiene).

(II) is a hard, relatively insoluble polymer which crystallizes readily without mechanical deformation, has a melting point around 70°C and a glass temperature Tg of —20°C (Balata and guttapercha belong to this species if isoprene is the monomer instead of butadiene).

(III) exists in an isotactic, syndiotactic and atactic form, all of which have been prepared by Natta and his collaborators with the aid of Ziegler catalysts. The stereoregulated forms are rigid, crystalline, and relatively insoluble materials, while the atactic species are soft elastomers with slow and sluggish recovery characteristics.

Many other vinyl- and acrylic polymers have been obtained in atactic and stereoregulated forms, and in all cases the structural character has a pronounced influence on the ultimate properties, in the sense that regularity favors crystallizability and rigidity, high melting points, and resistance to dissolution.

Extensive work on copolymers of all kinds fully confirms the importance of structural regularity on crystallization tendency and, consequently, on properties. Those copolymers which are built by a regular alternation of their components A and B and which can be represented by:

—A B A B A B A B A B A B A B A B A B A B A B A B—

show a distinct tendency to crystallize, whereas the corresponding one-to-one copolymers with random geometric distribution of the two components along the length of the chain such as:

—A B B A A A B A B B A A B A B B B A A B A B B A A B—

are intrinsically amorphous and represent soft, soluble and low softening resinous materials.

b) Chain flexibility

The word *flexibility* in the context of linear macromolecules refers to the activation energies which are required to initiate vibrational and rotational motions around single bonds in a macromolecule, as a consequence of which different conformations of the chain can be assumed at moderate temperatures in relatively short times. Rigorous quantitative concepts and treatments of chain conformations have been worked out by several contributors and have been brought to perfection by Flory in a recent comprehensive and systematic treatise. The energy barriers which separate different individual conformations in organic molecules have been assiduously studied with many ordinary, low molecular weight organic compounds with the aid of specific heats, infrared absorption and magnetic resonance. The results have led to a rather complete knowledge of the stability of different conformational isomers and the rate with which the equilibrium between them is established. This information has been applied, with the necessary caution, to macromolecules and permits the following general conclusions:

1) Linear polymers which contain only or mainly single bonds between C and C, C and O or C and N allow rapid conformational changes; if they are regular, and/or if there exist considerable intermolecular forces, the materials are crystallizable, relatively high melting, rigid and relatively insoluble, whereas if they are irregularly built, they are amorphous, soft and rubbery materials.

2) Ether- and imine bonds or double bonds in the cis form reduce the energy barrier for rotation of the adjacent bonds and "soften" the chain in the sense that the polymers are less rigid, more rubbery, and more easily soluble than are the corresponding chains of consecutive carbon–carbon single bonds. This is particularly true if the "plasticizing" bonds are irregularly distributed along the length of the chains so that they inhibit crystallization, rather than favoring it.

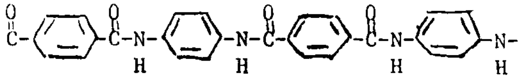
3) Cyclic structures in the backbone of a chain drastically inhibit conformational changes and lead to difficult or slow crystallization. This effect can go so far that, under most practical conditions, such polymers remain amorphous.

c) Groups which produce intermolecular attraction

If flexible chains with structural regularity are allowed to form aggregates or bundles, the stability of these supermolecular entities will depend on a firm cohesion between neighboring chains. It is obvious that *specific groups* which establish strong intermolecular bonds between such chains will favorably affect crystallization. This effect will be particularly pronounced if these groups are arranged along the macromolecules in regular distances so that they can get into each other's neighborhood without causing any valence strain in the chains themselves. In fact, it has been found that all groups which carry *dipoles, highly polarizable groups* or which permit the development of interchain *hydrogen bonds* favor crystallinity and, concomitantly, all the valuable properties which are a consequence of the presence of crystalline regions.

Thus, in polyvinylchloride and polyvinylidene chloride the C—Cl dipoles increase the lateral cohesive energy density of the system and, with it, the rigidity, softening temperature, and resistance to dissolution and swelling. This effect is enhanced in syndiotactic polyvinylchloride because of the spatial regularity of the C—Cl bonds. An example of the beneficial influence of polarizable groups can be found in polyethylene terephthalate, where the phenylene rings are polarized by the $C = 0$ dipoles, with the result that the lattice structure is firm and rigid. The consequence of interchain hydrogen bonding for crystallinity, rigidity, high melting and difficult solubility is very pronounced. Polyvinyl alcohol (PVA) with hydroxyl groups at every other carbon atom is a well known example. Even atactic (PVA) can establish frequent hydrogen bonds if they are first parallelized by stretch or shear, and the polymer is, therefore, a high melting, rigid fiber former. The syndiotactic PVA is even more rigid, higher softening and less soluble in water. Another case of strong lateral hydrogen bonding is provided by cellulose, where its effect is further enhanced by the rigidity of the gluco-pyranose rings in the beta-d-junction; as a consequence, cellulose is highly crystalline, infusible and insoluble (or soluble only with difficulty) and has an unusually high modulus of rigidity for an organic polymer. Perhaps the most striking effect of lateral hydrogen bonding between regularly spaced groups is demonstrated by the linear polyamides, where the —CO—NH— groups are responsible for the establishment of these bonds. Since these groups can be spaced at different distances by introducing paraffinic $—CH_2—$ chains of different lengths between them, it is possible to establish the fact that small and regular distances between successive amide groups along the chains lead to rigid, high melting and relatively insoluble types, whereas reduction of the lateral hydrogen bonding by large and/or irregular distances between the amide groups produces low melting and even rubbery types, which are easily soluble in many organic liquids.

A combination of pronounced chain rigidity with lateral hydrogen bonding would lead to polymers of the structure



which have, in fact, been prepared and which represent polyamides which are extremely rigid, high melting, and resistant to heat, dissolution and swelling.

d) Bulky substituents

The vibrational and rotational mobility of an intrinsically flexible chain can be inhibited by bulky substituents; the degree of stiffening depends on the size, shape, and mutual interaction of the substituents. Methyl-, carboxymethyl-, and phenyl groups have, in general, a noticeably inhibiting influence on the segmental mobility of linear macromolecules, as shown by the relatively high glass transition and heat distortion point of polymethylmethacrylate as compared with polymethylacrylate, or of polystyrene as compared with polyethylene. Larger aromatic groups have an even stronger influence, and polyvinyl naphthalene, -anthracene, and -carbazol are amorphous polymers of remarkably high heat distortion points and unusual rigidity; they are also difficultly soluble. In general, substituents from ethyl- to hexyl exhibit a softening influence, because they increase the average distance between the main chains and prevent their dipole groups from approaching close enough to each other for favorable interaction. The substituents in these cases are open chains with from two to six carbon atoms. They have, themselves, a considerable internal mobility, and they act as ingrown (or chemical) plasticizers rather than as stiffeners. Striking examples for this behavior are the polyacrylic- and methacrylic esters from ethyl to hexyl and the polyvinylesters from propionate to hexanoate, where rigidity, softening temperature and resistance to dissolution and swelling decrease as the number of carbon atoms in the chain of the substituent increases. If these chains become still longer (from twelve to eighteen carbon atoms) and remain unbranched (normal paraffinic alcohols or acids), a new phenomenon occurs: namely, the tendency of the side chains to form crystalline domains of their own, in which the side chains of neighboring macromolecules arrange themselves in bundles of ordered units with each other.

The result is as if one would push two brushes into each other and force their bristles to form tightly packed bundles with each other, which produces a firm and resilient system. In all these cases the softening range of the material is close to the melting point of the side chain crystallites. If the side chains are not homopolar, but contain polar or even hydrogen bonding groups, rather rigid, high softening, and solvent-resistant polymers are formed (as, for instance, in the case of polyphenylmethacrylamides or polytrichlorostyrene). Thus it can be seen that the proper choice of substituents in relation to their influence on crystallizability permits the preparation of a large variety of polymers, which in turn can be usefully applied to the synthesis of rubbery and fibrous materials.

4 MOLECULAR ENGINEERING OF ELASTOMERS

A particularly important class of polymeric compounds are the soft, tough, stretchable and resilient *elastomers*. They represent a combination of properties which cannot be matched by inorganic materials such as metals or ceramics. In fact, it is now recognized that rubber elasticity can only be exhibited by systems which consist of long, flexible chain molecules having weak intermolecular forces and being interconnected by primary valence bonds, at suitable intervals, so as to form a three-dimensional network with flexible connections between the tie points. In addition, it is also desirable if these connections show the ability to undergo reversible partial crystallization induced by stretching. In these terms the phenomenon of rubber elasticity, namely the ability to recover quickly and completely from imposed large strains, is ascribed to the uncoiling and recoiling of the long, flexible connections between the fix points. As for the phenomenon of partial crystallization on stretching, this has considerable bearing on the stress–strain curve and on the rupture and tear phenomena exhibited by the elastomer.

In order to treat rubber elasticity in a quantitative manner, it is necessary to define the statistical segment as that portion of the chain molecule which lies between tie points or cross links. Its mass is often referred to as the molecular weight between network junctions (M_n). It is obvious that the elastic behavior of the material is governed by the length of these segments. For instance, it can readily be seen that the force required to obtain a given extension will be an inverse function of this length, i.e., the force will increase with an increase in the number of cross links per unit volume of the elastomer.

a) Thermodynamic considerations

As in all molecular phenomena, rubber elasticity can be treated both by means of a thermodynamic and a kinetic approach. In either case, the network segment takes the place of the individual molecule, and an analogy may be drawn between it and the molecule in a gas or in a solution. The linear extension of such a chain can thus be compared to the volume compression of a gas. The flexibility of an elastic chain is due to the possibility of rotational movements around its single carbon–carbon bonds which permit the chain to be extended by uncoiling and, conversely, to retract by recoiling to its original conformation. The latter phenomenon, i.e., retraction, is caused by the kinetic energy of the chain atoms, whose transverse motions tend to force the extended chain to form a random coil.

The thermodynamic treatment of this phenomenon proposes that the unperturbed, randomly coiled network chain is in a state of highest probability of entropy, and that this entropy is decreased when the chain is extended by imposition of an outside force. In these terms rubber elasticity can be considered to be solely an entropy manifestation, unless the intermolecular forces between chains are large enough to introduce additional energy changes during extension and contraction, in close analogy to the behavior of a nonideal gas under the influence of Van der Waal forces.

This concept can be expressed by the equation:

$$F = (\partial E/\partial L)_{T,P} - T(\partial S/\partial L)_{T,P} \tag{4}$$

where

F is the external force of extension,
L is the length of the rubber specimen,
E is the internal energy,
S is the entropy, and
P and T are pressure and temperature, respectively.

Eq. (4) can also be written:

$$F = (\partial E/\partial L)_{T,P} + T(\partial S/\partial T)_{P,L} \tag{5}$$

and is readily seen to be analogous to the equation of state for a gas:

$$P = -(\partial E/\partial V)_T + T(\partial P/\partial T)_v. \tag{6}$$

In the absence of any intermolecular forces, the first term on the right side of Eqs. (5) and (6) vanishes and they simplify to the "ideal" expressions

$$P = T(\partial P/\partial T)_v \text{ and} \tag{7}$$

$$P = T(\partial F/\partial T)_{P,L}. \tag{8}$$

A study of the force–temperature relations yields the best information concerning the extent to which changes in the internal energy (E) and the entropy (S) contribute to the force of retraction. These relations have been investigated repeatedly, and it was found that, except at very low elongations, the force increases with increasing temperature. In other words, stretched rubber tends to react on heating, as would be expected from entropy considerations. Figure 2 represents the modulus of an elastomer as a function of temperature. The negative slopes at very low elongations are due to the imposition of the normal thermal expansion of the material, which predominates under these conditions. The elongation at which the two effects

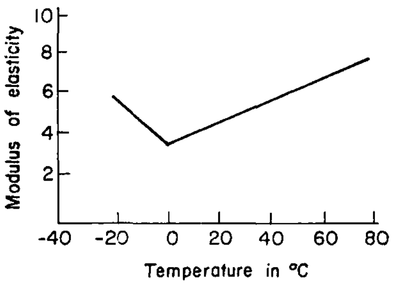


FIGURE 2 Modulus of elasticity of elastomers as a function of temperature.

balance is known as the *thermoelastic inversion* point; it occurs at about 10% elongation.

Using the extrapolation of the force–temperature plots to zero temperature, it is possible to obtain the appropriate values of $(\partial E/\partial L)_{T,P}$ and to appreciate the influence of the intermolecular forces. Experimentally, it has been found that the major contribution to the elastic force is due to the entropy change, with only a minor effect of the internal energy due to intermolecular forces. Hence the entropy theory or rubber-like elasticity appears to be well justified.

b) The kinetic approach

The relation between the applied force F and the extension α of a chain network can also be treated by means of kinetic considerations, where the extension is related to the restriction in possible spatial distributions of the freely rotating statistical chain segments, and this leads to the following equation for rubber elasticity:

$$F/A = NRT(\alpha - 1/\alpha^2), \tag{9}$$

where:

N = number of moles of network segments per unit volume,
A = original cross sectional area of the sample, and
α = ratio of extended length to original length.

Again, it can be seen that Eq. (9) is quite analogous to the equation of state for an ideal gas:

$$P = \frac{NRT}{V}$$

An attempt to obtain experimental verification of Eq. (9) has shown that there exist some deviations from the theory in the domain of low elongations. These deviations have to do with energy contributions. But there are much more serious discrepancies in the range of high elongation, such as 200% and more. This is shown in Figure 3, where a theoretical stress–strain curve of rubber is compared with an actually measured curve.

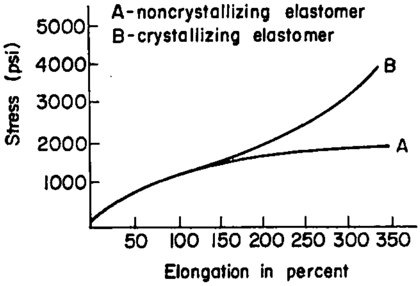


FIGURE 3 Stress–strain curve of two types of elastomers.

c) Influence of crystallization

The marked upward deviation from the theoretical force values of the stress–strain curve observed at higher elongations has been interpreted as a consequence of crystallization. Some elastomers (such as natural rubber, high *cis* polybutadiene, polyisobutylene and polychloroprene) which possess relatively regular chain structures exhibit the phenomenon of reversible, partial crystallization induced either by stretching or cooling. Hence, at sufficiently high elongations, some portions of the chains become parallelized and are in a favorable position to form crystallites. Of course, these crystalline domains are inextensible, and they cause a sharp rise in the stress–strain curve. It can be said that these rubbers, upon extension, produce "their own" reinforcing filler namely rubber crystallites. (See Figure 3.)

The occurrence of crystallization upon stretching of all sufficiently regular elastomers has been proven experimentally by the use of X-ray and electron diffraction and by IR absorption. While only diffuse halo patterns are obtained from stretched non-crystallizing, amorphous elastomers such as SBR and EPR, distinct diffraction spots are observed in the case of natural rubber or other crystallizing elastomers. It has also been found that the sharpness and intensity of the interference pattern are greatly increased at higher degrees of extension, because the crystalline areas become larger and more frequent.

Those elastomers which crystallize on stretching also generally crystallize on cooling in the unstretched state. They also exhibit the phenomenon of freezing and melting at the temperature at which the network segments lose sufficient kinetic energy to participate in the crystallization process. In view of the long-chain character of the rubber molecules, this process is imperfect and the material can be only partly crystalline at best, leading to melting or freezing points which are rather diffuse when compared to those of ordinary organic compounds. The phase transformations which a material such as natural rubber undergoes with changes in temperature can readily be demonstrated by the volume–temperature relations.

The imperfect crystallization process in elastomers is reflected in the sensitivity of the crystalline melting point to the conditions of crystallization. Thus the crystallites which are formed more rapidly, at lower temperatures, are also more imperfect and exhibit a lower melting point. This was strikingly demonstrated by the work of Roberts and Mandelkern as shown in Table II. Thus, by careful cooling at 14°C (and slow heating) the most accurate T_m value for natural rubber is found to be as high as 28–29°C.

Since the crystallites formed on stretching can also help to distribute the stresses to which a number of chains are subjected, they play an important role in rupture phenomena, such as tensile or tear strengths. It is not surprising, therefore, that those elastomers which show the ability to crystallize on stretching also exhibit high tensile strengths in the gum vulcanizates. On the other hand, those elastomers which cannot crystallize show relatively poor tensile strengths and require the use of reinforcing fillers, such as carbon black, in order to attain sufficient tenacities for practical use.

Table III shows a list of the physical properties of several important elastomers and Table IV adds to it the thermal properties of elastomers which have a stereoregular structure.

TABLE II

Effect of crystallization temperature on the melting point of natural rubber

Crystallization temperature, °C	Melting temperature, °C
−18	21.0–22.0
0	22.5–23.5
+ 8	22.5–23.0
+14	28.0–29.0

TABLE III

Physical properties of various elastomers

	300% modulus in psi	Tensile strength psi	Ultimate elong. in %	Hardness shore A
Nitrile rubber	500	4200	750	45
SBR	1300	4000	650	60
Chloroprene	600	2600	820	50
Hypalon	100% 1600	2400	190	90
Butyl rubber	1000	3000	620	55
Silicon rubber	300	800	300	50
Polybutadiene cis	500	2000	630	60
Polyisoprene cis	450	2200	620	55
EPM rubber	1200	1800	320	65
Hevea rubber	700	4400	780	50
Polyurethane types	600–3000	4000–6000	350–600	65–70

TABLE IV

Physical properties of a few stereoregulated elastomers

	T_m°C	T_g°C	Density
trans 1,4-polybutadiene I	75	—	1.02
trans 1,4-polybutadiene II	145	—	0.93
cis 1,4-polybutadiene	3	< -60	1.01
Isotactic 1,2-polybutadiene	128	—	0.96
Syndiotactic 1,2-polybutadiene	56	—	0.96
trans 1,4-polyisoprene	65	—	1.04
cis 1,4-polyisoprene	25	< -60	1.00

5 MOLECULAR ENGINEERING OF FIBER FORMERS

The manifold commercial, industrial and textile uses of fibers require an extremely wide variety of basic materials. In the domain of natural products we use such diverse substances as flax, cotton, silk, wool, rubber, metals, asbestos, and glass as fibers. The range of just *one* property, for example, *stiffness*, which is exhibited by commercial fibers of these materials is shown in Figure 4, which presents the initial stress–strain properties of fibrous materials derived from natural sources. One can see that the initial slope of the stress–strain curve traverses the range from rubber, with a modulus of only about 100 psi, to steel, with a modulus of 30 million psi.

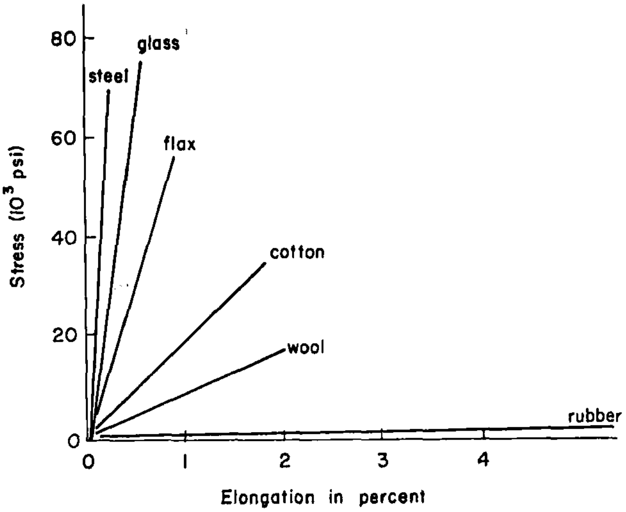


FIGURE 4 Moduli of fibers made from naturally occurring materials.

Synthetic materials presently in use or in development cover an even wider modulus range from Lycra to Thornel, that is, from about 50 psi to about 100 million psi. The lower limit is represented by the elastomeric spandex type fibers (compare Table V) which have pronounced rubber properties, and the upper by fibers which essentially have the structure of linearized graphite. All classical synthetic fibers (particularly rayon, cellulose acetate, the nylons, polyesters, vinyls, acrylics and polyolefins) fall between these extremes.

The *modulus of rigidity* is only one of many diverse properties which are important to the successful end use of a fiber. Technology can effect significant adjustments and changes of many fiber properties through mechanical or thermal treatment during or after the fiber manufacturing step. However, all these *physical* processes lead only up to certain limits; to obtain *really fundamental changes* in fiber properties, it is necessary to go back to chemistry and synthesize new polymers.

Table VI shows a few particularly important fiber properties, namely density, melting point, tensile strength in the conditioned and wet state, elongation to break and moisture absorption; they will be analyzed briefly in the light of the previous discussion in order to show how the general principles can be put to immediate practical application.

TABLE V

Physical properties of Lycra

Break tenacity in g/den	0.6–0.8
Break elongation in %	520–610
Refractive force at 50% elongation in g/den	0.03–0.04
Refractive force at 200% elongation in g/den	0.10–0.12
Tensile recovery from 50% elongation in %	94–96
Moisture regain in %	1.30
Melting point, °C	250
Stick point, °C	175

TABLE VI

Some properties of manmade fibres

Material	Density	T_m	TS_c	TS_w in % of TS_c	E_c	H_2 regain in
Rayon HM	1.52	—	3.5–4.0	55–65	10–15	8–10
6 nylon	1.14	215	4.5–5.0	90	20–25	3–4
66 nylon	1.14	260	4.5–5.0	90	20–25	3–4
Saran	1.70	210	1.2–1.7	95	20–30	—
Polyester	1.30	260	4.5–5.0	90	15–20	0.5
Polyacryl	1.30	—	3.5–4.0	95	20–25	0.5
Polypropylene	0.90	175	3.5–4.0	100	25–30	—

Let us consider the *melting point* first. All melting points, both those of polymers and of low molecular weight materials, depend on the ratio of the heat of fusion ΔH to the entropy of fusion ΔS:

$$T_m = \frac{\Delta H}{\Delta S} \tag{10}$$

Specifically, the melting point of a polymer is related to the strength and regularity of the sites of intermolecular attraction, which affects the heat of fusion, and also to the stiffness of the individual chains, which affects the entropy of fusion.

Figure 5 clearly demonstrates the effect of the intermolecular forces provided by hydrogen bonds in polyamides by plotting the melting point versus the concentration of amide groups per 100 Angstroms of extended chain length. The melting points are essentially a linear function of the amide group frequency; increase of heat of fusion is directly proportional to the frequency of hydrogen bonds being produced by the increase in amide concentration. One might expect the melting point to extrapolate to that of linear polyethylene at zero amide concentration, because in this case there are only relatively weak Van der Waals forces (which determine the heat of fusion of this polymer). But in reality, the extrapolated melting point is somewhat lower, an effect which could be caused by the higher conformational mobility of a —CH_2—CO—

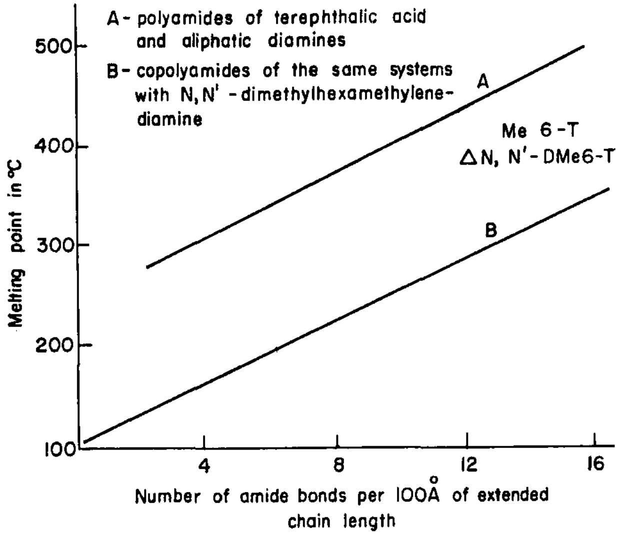


FIGURE 5 Melting points of polyamides as a function of frequency of —CO—NH— groups in the chain.

NH—CH_2— segment in comparison with a —CH_2—CH_2—CH_2—CH_2— segment in the event that the former is not hydrogen bonded.

The effect of chain stiffness is well known in the case of Terylene or Dacron, which are polyesters using terephthalic acid as a component resulting in the presence of paraphenylene units along the main chain. Since macromolecules of this type coil less flexibly in the amorphous state than their aliphatic counterparts, they have a lower entropy of fusion and, consequently, a higher melting point. In fact compounds based on ethylene glycol and sebacic acid are amorphous and soften at about 70°C, whereas polyesters made of ethylene glycol and terephthalic acid are crystalline and melt around 250°C. Thus the stiff paraphenylene ring in the main chain contributes a 180°C increase in melting point. The influence of chain stiffening on softening, melting, dissolving and swelling will be discussed in some more detail in the next paragraph.

The melting point of a polymer is also affected by the reduction of the regularity with which the monomer groups are spaced along the backbone chain, such as by random copolymerization. This is shown in Figure 6, where the melting points of random copolymers of 6–10/6–6 nylon are plotted against the composition of the material. The lowest melting point (190°C) is reached in the neighborhood of a 70/30 composition. Disturbing the regularity of the amide group spacings lowers the efficiency of hydrogen bonding, reduces ΔH

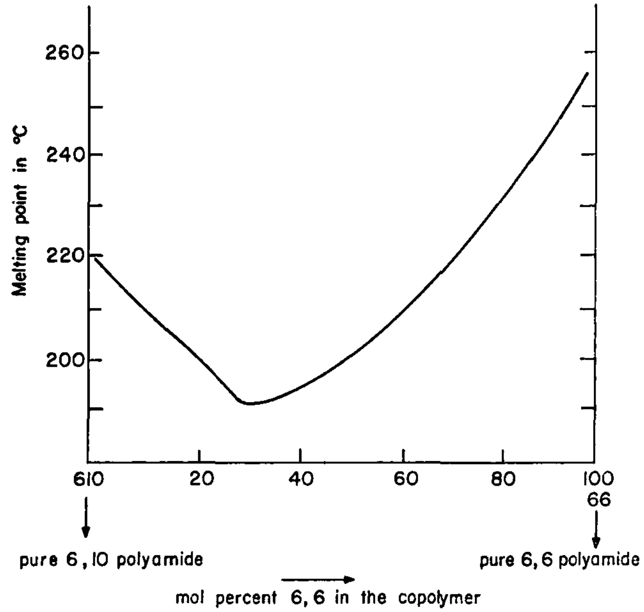


FIGURE 6 Effect of random copolymerization on melting point of polyamides.

in the basic melting point Eq. (10), and thereby lowers the temperature of fusion.

The melting point–composition diagram for the random copolymers made with a flexible and a stiff monomer unit shows very clearly the progressive softening effect due to the reduction in stiff segment content and in regularity. All factors which affect the melting point also affect the modulus, for much the same reasons, but there are also other contributing structural characteristics, namely orientation and degree of crystallinity. Thus the modulus of rigidity of a perfect 66 nylon or polyethylene terephthalate crystal with completely extended chains has been estimated to be in the range of several million psi. However, all available information on drawn commercial nylons and polyesters shows them to be not much more than 50% crystalline. This low degree of crystallinity and the presence of folded chains account for the fact that observed moduli are only a fraction of the theoretical value, since, at small deformations, the amorphous parts of the fiber and the folded chains yield under the load and cause elongation. Thus high fiber modulus requires rigid chain segments, regularly spaced crystallizable groups along the chains and a high orientation parallel to the fiber axis.

In the discussion of fiber modulus, we have limited ourselves to values referring to room temperature. Let us now consider how the modulus of rigidity of a fiber changes with temperature. Figure 7 shows the behavior

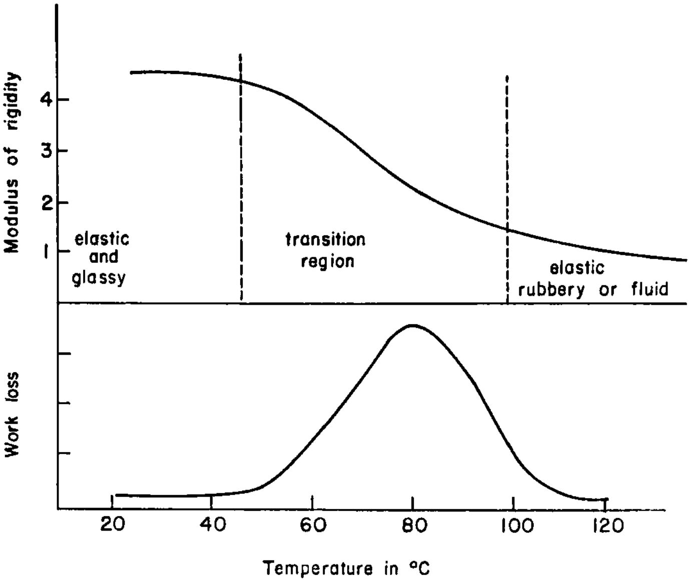


FIGURE 7 Dynamic modulus and work loss of polymers versus temperature.

characteristic of all polymers. Since the initial modulus is chiefly a property of the amorphous regions and folded chains in the test piece, its value is relatively high at low temperatures and does not show much change with temperature in this first part of the modulus–temperature curve. This low temperature region finds the amorphous domains of the polymer in the glassy state; and at relatively small deformations, the restoring force results from an increase in the energy of the bonds being deformed.

At the high temperature end of the curve, although the modulus is considerably reduced, it is again relatively temperature-independent. In this low modulus region, the amorphous portions and the folded chain areas of the sample are fluid, quite readily deformed, and the restoring force produced by extension results from the decrease in entropy of the uncoiled and unfolded polymer chains. At this end of the curve, the magnitude of the restoring force and of the modulus is proportional to the concentration of cross-links between polymer chains as well as to the amount of difficulty deformable crystalline region. The "cross-links" may be individual hydrogen bonds, covalent bonds, small crystallites or just chain entanglement. There is little hysteresis on cyclic loading of the test piece in either of these two regions and recovery from deformation is good in both.

However, in the intermediate range, which is known as the *glass* or *second order transition* region, the onset of sluggish responses in the partially melting amorphous regions results in a high hysteresis and in relatively poor recovery. The temperature of maximum work loss is close to the glass transition temperature T_g.

As the degree of crystallinity of a polymer is reduced, the curve tends to move to the left as well as to decrease in modulus level. If T_g is finally well below room temperature, the modulus becomes quite low, and, if the cross-linking efficiency through crystallites or through covalent cross-linking is adequate, we have an elastomer with rapid response to deformation and good recovery. Stress-sensitive cross-links such as hydrogen bonds do not lead to maximum recovery, because they rupture and eventually reform in new positions and, hence, contribute to poor recoveries. Without cross-links of any kind, we would just have a viscous liquid with no recovery.

It is not surprising that the same structural characteristics which influence the modulus of a polymer also affect the glass transition temperature, and it follows that, ideally, the glass transition temperature of a good fiber former should not be too close to the normal end use temperature. Table VIII illustrates the effects of changing structural polymer features by reducing crystallizability through disrupting chain regularity and reducing hydrogen bonding. A 50% substitution of N-alkylated 6–10 polyamide in regular 6–10 polymer and a 60% substitution of ethyleneglycolsebacate in polyethylene terephthalate produces a marked reduction in fiber modulus, reduces the glass transition temperature to below 20°C, and gives a typically elastomeric fiber for the polyamide and the polyester.

It is possible to improve the elastic properties of a fiber if, instead of preparing a random copolymer, one blends two homopolymers in the melt (for instance, polyethyleneglycol-terephthalate and polyethyleneglycol-sebacate in a 40/60 ratio) allowing a limited extent of ester interchange to occur. The result is a block copolymer (compare Table VII) which is also an elastomer, but which has a melting point about 50°C higher than that of the random copolymer (170°C versus 110°C).

Further improvements in properties of elastomeric fibers have been achieved in the block polymer framework by partly equilibrating relatively long chains (4000 molecular weight) or polyethylene glycol with polyethylene-glycolterephthalate. Here, because of the chemical inertness of the ether links with respect to interchange reactions, one obtains a substantial *weight percent* modification at a relatively small mole percent modification and melting point depression. Thus, with a 60 weight percent polyethylene-glycol modification, the melting point–elasticity relationship is even better than for the partially interchanged block copolymer; one observes substantial reduction in stress decay for the block copolymers as compared to the random copolymers. Long

TABLE VII

Comparison of the properties of a random copolymer with those of a block copolymer of the same chemical composition

Random copolymer made of 40% ethyleneglycol terephthalate and 60% ethyleneglycol sebacate:

M.P. = 120°C
Elongation to break = 300%
Modulus = 7000 psi

Block copolymer made of the same components in the same percentage:

M.P. = 170°C
Elongation to break = 200%
Modulus = 1000 psi

TABLE VIII

Reduction of regularity and hydrogen bonding lowers modulus and T_g and increases extensibility

	Properties at 25°C Modulus in 10^3 psi	Elongation to break in %	T_g in °C
610	280	25	~50
610/*N*-alkylated 610 (50/50)	6	400	~ 0
2GT/2G10 (40/60)	7	300	~ −20

discrete blocks of the terephthalic acid component are required in the chain to produce crystalline domains which act like cross-links and minimize creep under sustained stress.

Another interesting way to arrive at an elastomeric thread was recently pioneered by Rohm and Haas through their Anim 8 fiber. Instead of combining fiber and rubber properties in one and the same molecule through a segmented structure, there is here produced an intimate mixture of rubbery chains and of fibrous chains which are both prepared from an adequate modacrylic copolymer. These copolymers are coprecipitated, dissolved, cospun and finally cross-linked to obtain a three-dimensional network of chains some of which are rubbery whereas others are fiber forming. A carefully controlled balance of these two properties leads to an elastomeric fiber which may not have all the mechanical attributes of a spandex fiber but is, in any event, superior in its stability against hydrolysis, oxidation and discoloration.

In discussing structural conditions which influence modulus and melting point, we have been forced into considering factors which also govern elasticity and recovery from deformation. For a typically elastomeric fiber with high elongation and complete recovery from strain, such as "Lycra" we need certain segments with *low* modulus and a T_g *below* the use temperature. On the other hand, all important natural and synthetic apparel fibers are characterized by a balance of structural design to give much higher moduli and T_g values *above* normal end use temperatures.

Turning now to the factors which govern *tensile strength*, we already know that molecular weight is of prime importance. Most linear polymers with T_g above room temperature give high tensile strength if their molecular weight is above 10,000 and if the chains are well oriented parallel to the fiber axis. 66 nylon of molecular weight 18,000 can yield fibers having well above 100,000 psi tensile strength, and there are many other linear polymers which give similar values at normal temperatures. However, if tensile testing is done at a variety of temperatures or at varying rates of loading, other details of the polymer structure begin to show their influence.

Up to now we have mainly discussed the behavior of homopolymers, random copolymers, and block copolymers to show structure-property relationships. In block and random copolymers the chemical modification to the polymer is *in the chain*. Other types of copolymers can be made by creating free radical sites along the trunk polymer chain and initiating an addition polymerization in the presence of a desired monomer. The products of such an operation are *graft* copolymers in which the polymer backbone is unchanged and the chemical modification has the form of branches. High energy radiation, chemical free radical initiation, and even mechanical action of heat can be utilized to promote grafting processes. Grafts on preformed fibers may be uniformly distributed throughout the cross section of a fiber or may be confined to surface regions by using knowledge of the diffusion and solubility characteristics of various monomers in the substrate.

By proper selection of the modifying monomer in the light of its own polymer properties, it is possible to increase or decrease fiber modulus and recovery or to impart such properties as adhesivity, water absorption and increased dye receptivity. In grafting a monomer on a preformed fiber, the crystal structure of the backbone polymer remains essentially unaffected, as the acrylic acid graft on preformed 66 nylon fibers demonstrates.

The balance of some key fiber properties is altered by grafting 20% acrylic acid onto 66 nylon fibers and by converting the graft to the sodium or calcium salt of polyacrylic acid (Table IX). These properties are compared with those of a random copolymer of 66 and 6 nylon. It can readily be seen that:

1) A significant increase in moisture regain is obtained with the hydrophilic graft.

2) The static propensity as indicated by the log of the electrical resistance of a fabric is markedly reduced with the sodium salt of the graft.

3) Because of the highly swollen nature of the graft in water, the sodium salt of the graft also shows improved wet crease recovery.

4) The rate at which dyes are absorbed is considerably higher with the graft, as with the random copolymer, and

5) The divalent calcium ion produces ionic cross-links in the fiber, yielding a marked increase in fiber stick temperature and melting point.

In contrast, the random copolymer contributes improvement only in dye rate, but at a marked sacrifice in melting point.

The data presented and the examples chosen for illustrating characteristic behavior have been taken primarily from condensation polymers and their fibers, but the principles discussed and the conclusions drawn hold for fibers

TABLE IX

Property comparison of grafted fibers versus the ungrafted systems and random copolymers (66 nylon base)

Fiber	Moisture regain (%) (50% RH)	Static propensity (Log R)	Fiber stick temp. (°C)	Wet crease recovery (%)	Dye rate
66 nylon	2.5	13.3	240	70	normal
20% acrylic acid graft on 66 nylon (Na salt)	7.5	8	380	94	rapid
20% acrylic acid on 66 nylon (Ca salt)	5	13	420	70	normal
66/6 (80/20)	3.5	13	200	65	rapid

made from all classes of linear polymers. In vinyls and acrylics steric isomerism is important in governing intermolecular forces. Random, block or graft copolymerization affects them in a manner analogous to condensation polymers; chain stiffening is preferably carried out with the aid of side groups, since it is difficult to insert rings in the backbone chain of normal addition polymers.

6 MOLECULAR ENGINEERING OF POLYMERS FOR BUILDING CONSTRUCTION

There are many indications that the conventional, classical fields for the application of organic polymers are gradually getting amply supplied with various materials which compete with each other and do not offer any good prospect for substantial further expansion. These fields are essentially the industries of textiles, packaging materials, rubbers, plastics, coatings and adhesives, which together represent a very large volume of synthetic polymer consumption—more than 20 billion pounds or 10 million tons for the United States alone in 1970. The approaching saturation of these markets poses the question whether other large areas of industrial activity can be found which would be able to absorb substantial quantities of organic polymers if the properties and costs could be so adjusted that their systematic and large scale application would present a technical and economic advantage for these industries.

It appears that the construction of buildings of all kinds—small and large homes, office buildings, factories and laboratories—offers a very promising chance for the consumption of rather large quantities of many types of organic polymers if certain properties or (even better) certain combinations of properties could be conveniently built into these materials.

In order to get a rough estimate of the dimensions which are involved, it should be mentioned that the house and home building activities in the United States in 1970 amounted to a total investment of about 70 billion dollars, of which about 20% was spent for construction materials such as metals, concrete, bricks, glass and wood. If plastics are to be used in the building trade, they can serve as *structural* (load bearing) units or as *finishing* materials which service a building with water, air, gas and electricity, and provide for the finishing of floors, ceilings and walls. Until now, organic polymers have been used mainly in the finishing sector, as floor tiles, coatings, insulating foams, window and door frames and as roofing. About 20% of all plastics and coatings is already being used in these capacities, and it is probable that this volume will keep on expanding during the next years. The more important expansion, however, can be seen in the use of organic polymers as structural units, provided that certain improvements in properties can be effected.

Table X lists the most important demands for a structural polymer, states the present position of the art, and indicates the probable future outlook.

TABLE X
Key properties of polymers for building construction

Demanded property	Presently available materials	Outlook
Reasonable price	Improvement needed	Fair
Light weight	Excellent	Fair
Structural strength	In general satisfactory	Good
Fire proof	Needs improvement	Good
Long life time	Almost satisfactory	Very good
Easily transported	Excellent	Very good
Easily installed	Satisfactory	Very good
Easily repaired	Satisfactory	Very good
Corrosion resistant	Excellent	Very good
Moisture resistant	Satisfactory	Very good
Solvent resistant	Excellent	Very good

It is obvious that a successful invasion of this field cannot be brought about by the development of one single property—for instance, tensile strength—to an extravagantly high value, but that one must aim at a combination of *several properties* which make a polymeric material particularly valuable and attractive for this special use. For a pipe or tube, for instance, one will require rigidity, impact strength, resilience, abrasion resistance, impermeability to gases and resistance against temperatures up to about 150°C.

For the use as structural units in the building industry one may characterize a favorable compromise of properties about as follows:

a) High modulus of rigidity; if possible higher than 700,000 psi.

b) High softening or melting point; if possible higher than 500°C.

c) High tensile strength; if possible higher than 200,000 psi.

d) High elongation to break; if possible about 10%. Favorable values of (c) and (d) give a large requirement of energy to break or tear a piece of the material. This, in turn, manifests itself as a high impact strength and a high abrasion resistance.

e) High resistance to the action of solvents and swelling agents, even at elevated temperatures.

f) High resistance to deterioration through heat (flame-proofing), radiation, aggressive chemical reagents and micro-organisms.

Numerous profitable applications are bound to appear for any material with a low specific gravity and low cost, if a favorable combination of the above properties can be incorporated into it.

It will be useful, then, to recapitulate very briefly the different principles by which well balanced compromises of these properties have already been achieved. In a general and simplified sense, there are three main principles which have been very useful in the past and which should be good working hypotheses for future efforts:

a) crystallization,
b) cross-linking, and
c) the use of inflexible chain molecules.

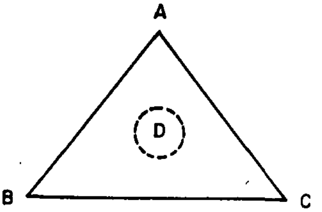
Let us therefore estimate the value of each of these principles for the present purpose and, at the end, consider how *combinations of them* could be used to arrive at improved products.

The principle of crystallization has already been discussed in some detail; it has long been known to be a very valuable property of linear, flexible macromolecules whenever one wants a good combination of thermal and mechanical properties. Even linear polyethylene, a completely non-polar material with weak interchain bonding, is rigid, relatively high melting (130°C), strong, tough, abrasion resistant and insoluble in anything at room temperature. All these qualities derive from its *strong tendency to crystallize*, which means, in this context, to form bundles or domains of high order. The same thing is true for isotactic polypropylene with a melting point of 170°C and for isotactic polystyrene, which melts around 230°C. If the macromolecules contain polar groups and are of regular architecture, even better combinations of mechanical and thermal properties can be materialized (as in polyvinyl alcohol, polyvinylidene chloride, polyoxymethylene and many aliphatic polyesters and polyamides such as polycaprolactam and 66 or 610 nylon.)

In all these cases we have intrinsically flexible chain molecules of regular architecture which have a distinct tendency to form crystalline domains of folded or extended chains. Inside these domains, a systematic accumulation of the interchain forces rigidifies and reinforces the entire structure to such an extent that the system becomes hard, high softening and insoluble.

Crystallization of linear flexible macromolecules is a phenomenon which has not only led to numerous practical applications, but has also stimulated a profound statistical analysis of these systems which permitted the rationalization of many empirical facts and provided for a rather satisfactory basic understanding of their behavior. (Figure 8).

It has long been known that a combination of the favorable properties enumerated previously can also be obtained in an entirely different manner, namely by the chemical *cross-linking* of long flexible chain molecules. Rubber is a convenient example. As one reduces the original segmental mobility of the individual chains by the establishment of localized but strong carbon–sulfur and sulfur–sulfur cross-links, the material becomes more rigid, higher



A Represents the principle of crystallizations
B Represents the principle of crosslinking
C Represents the principle of chain stiffening

FIGURE 8 Illustration of three principles which influence polymer properties.

softening and less soluble. If one continues to introduce more and more cross-links and, eventually, cyclic structures, their average distance along the flexible chains decreases, the system is progressively stiffened, and one finally winds up with hard rubber or Ebonite, a material which is rigid, has a high softening range, and is completely insoluble and unswellable. Considering cross-linking more in detail it appears that the following factors are of significance:

a) The *length of the cross-linking element* between the main chains, because very *short* cross-links (such as direct bonds between the carbon atoms of two chains, methylene (—CH_2—) bridges or —S— and —S—S—) create stiffness and high softening sooner than *longer* cross-links, as they have been established with the aid of diamines, diepoxides, diolefins, dialdehydes and diisocyanates. Apparently the relatively flexible chains of such cross-links permit the maintenance of some segmental mobility even if the tie-points are relatively close together, and they build up three-dimensional networks of remarkable resilience, toughness and recovery power.

b) The *chemical nature* of the cross-links is less connected with the mechanical and thermal effect which they produce, but is very important for their resistance to elevated temperatures and to chemical reagents. Thus —C—C— cross-links are very resistant to both influences, sulfide (—S—), disulfide (—S—S—) and ester (CO—O—) bonds are sensitive against heat and alkali, acetalic (—O—CH_2—O—) tie-points are sensitive to acids, and urethane type. (NH—CO—O—) bonds are cleaved by hydrolysis at elevated temperatures. Depending upon the nature of the base polymer, there is a rather wide choice of cross-linking agents available which often permit the production of a three-dimensional network with desired properties.

c) It should be added here that an effect similar to that of cross-linking can also be obtained by the incorporation of a *reinforcing filler* into a polymer. The word *reinforcing* refers to the fact that there is a very intimate contact between the filler and the chains of the polymer in molecular dimensions and that there exist strong adsorption forces which fix and immobilize the polymer chains at the surface of the filler particles.

Although, at first glance, the effect of cross-linking is very similar to that of crystallization, there are several important differences:

1) In a crystalline system the rigidity is the result of many, regularly spaced lateral bonds between the oriented chains; each of these bonds is weak, and the ultimate effect comes from their *large number* and their regularity. In a cross-linked system the bonds between the long flexible chains are *strictly localized*, and each of them is *strong*; in their entirety they are *randomly* arranged in the system. As a result crystallization is a *reversible* phenomenon, whereas cross-linking is *irreversible* and is the preferred technique for the production of thermoset resins.

2) Crystallization is a *physical* effect which takes place at different temperatures and is strongly influenced by physical processes such as orientation and swelling; cross-linking, on the other hand, is a *chemical* phenomenon which needs the presence of certain special reagents, is strongly accelerated by elevated temperatures, but is not very much influenced by orientation or swelling.

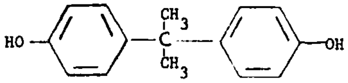
Many important projects which are hard, infusible and insoluble are made with the aid of cross-linking, such as resins of urea-, melamine- and phenol formaldehyde, epoxides, polyesters which use glycerol, trimethylol propane, or pentaerythritol as components, and resins which are hardened by the grafting of styrene on an unsaturated polyester backbone. While there are obvious and significant differences between the ways in which crystallization vs cross-linking acts, it is useful to have two different principles with which to attain a desirable combination of valuable properties. Even more encouraging is the fact that there exists a *third independent* principle, namely the use of *stiff linear chain* molecules.

Crystallization and cross-linking produce stiffness, *high softening temperature and difficult* solubility by the establishment of *firm* three dimensional connections between intrinsically *flexible chains*. However, this can also be attained by incorporating the stiffness in the *individual chains* and constructing them in such a manner that their segmental motion is intrinsically restricted; the hardening effect of bulky substituents has already been mentioned for polystyrene which is amorphous, has no cross-links, but is still a hard, relatively high softening (90°C) polymer. The absence of crystallinity results in a complete transparency, the absence of cross-linking in a reversible moldability and easy flow characteristics. Similar conditions prevail in the case of poly(methyl methacrylate), which is linear, amorphous, and has intrinsically flexible backbone chains which, however, are stiffened by the two substituents (CH_3 and $COOCH_3$) at every other carbon atom and, as a result, is a hard, brilliantly transparent, relatively high softening (95°C) thermoplastic polymer which has found many useful and valuable applications. The only weakness of both materials is their low resistance to swelling and dissolution. It seems that the bulky or polar substituents are capable of producing favorable mechanical and thermal effects which are connected with the over-all mobility and flexibility of the chain segments, but which cannot offer sufficient resistance to the penetration of the system by solvents or swelling agents, because this process is a strictly localized phenomenon and depends on the affinity of the substituents for the particular solvent molecules.

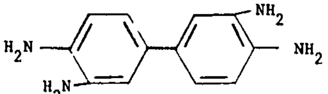
Similar effects are produced if the backbone chains themselves are rigid and if their substituents are so arranged that crystallization is prevented. Classical examples for such polymers are cellulose acetate and cellulose nitrate, where the glucosidic backbone chains represent a considerable *intrinsic stiffness*. The irregularly arranged acetyl- and nitrate groups of incompletely substituted samples *do not permit* the formation of a *crystalline order*. In fact, both materials are hard, transparent, high melting and amorphous *thermoplastic resins* which have been widely and successfully applied for many years; cellulose acetate is still rather sensitive to the action of solvents and swelling agents just like polystyrene and polymethylmethacrylate, whereas cellulose nitrate only dissolves in a few selected systems.

Recently the principle of using *intrinsically rigid* chains has been studied in more detail and has found several new and interesting embodiments. Based on rigid monomeric units, such as:

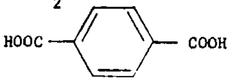
bisphenol —A



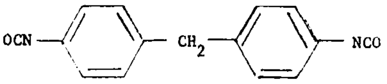
diaminobenzidine



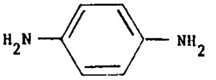
terephthalmic acid



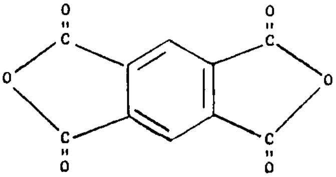
methylene bis phenylisocyanate



paraphenylene diamine

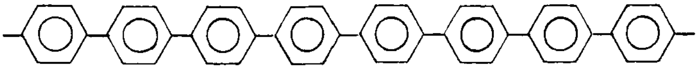


pyromellitic anhydride



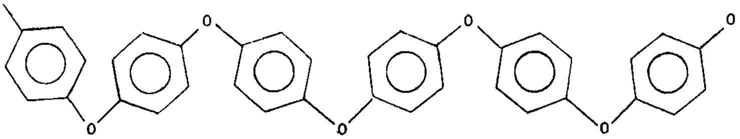
and others, a series of polymers have been synthesized which are substantially amorphous and uncross-linked, but represent very hard, high softening and solvent resistant materials. Earlier examples of this type are the polycarbonates and the linear epoxy resins, both of which are based on bisphenol —A; more recent representatives are the polybenzimidazoles, polyimides and polyphenyl oxazoles which exhibit unusually high resistance to softening, swelling, and decomposition. In fact, some of these newer materials can stand temperatures up to 500°C for long periods without softening and deterioration and are completely insoluble in all organic solvents up to 300°C.

Other rigid molecules which have been studied for possible application in the field of high temperature resistant materials are based on other aromatic chains such as polyphenylene,



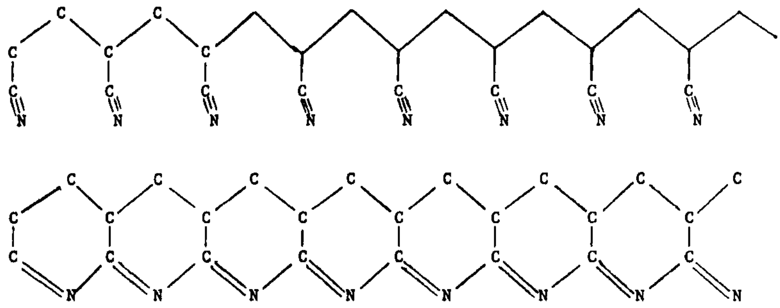
which cannot fold even at rather high temperatures, because rotation about the carbon–carbon single bond between the para-combined phenylene rings can only lead to different angles between the planes of consecutive rings, but not to a kink or bend in the main chain. In fact, representatives of this species are rigid, high melting, possess a pronounced tendency to crystallize, and are highly insoluble. This combination of valuable properties has not yet been fully brought to fruition because of the presently known polyphenylenes are only relatively short chains, and the higher molecular weight species are very intractable.

Para-polyphenylene oxide and polyphenylene sulfide are other cases which show the chain stiffening action of a para-phenylene unit.

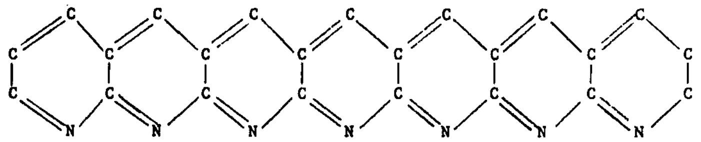


Rotation about the bonds between an ether oxygen atom and the adjacent carbon atoms of the rings does change the plane of the angle between two units and thus leads to bends and kinks in the chain, but the rotational freedom is noticeably inhibited by the presence of the aromatic rings on each side of the oxygen or sulfur atom. As a consequence, it has been found that chains of this type represent high melting, rigid and relatively insoluble materials.

Another interesting way to arrive at chains made up of condensed rings is the synthesis of so-called ladder polymers. The first case of such a structure was prepared by exposing polyacrylonitrile to elevated temperatures, which causes the formation of rows of condensed six rings by an electron pair displacement:



which involves stiffening, insolubility and discoloration. Further heating leads to evolution of H_2 and to aromatization



whereby a black, completely infusible and insoluble material is obtained which, in its structure, corresponds to a linear graphite in which one carbon atom of every ring has been replaced by nitrogen.

The formation of ladder polymers by progressive carbonization has the disadvantage that one has no control over the progress of the reaction and, as a consequence, knows nothing about the length of the "ladderized" sections of the chains. There are, however, numerous methods in a state of progressive development which allow the synthesis of ladder polymers with much more control of their structure.

A number of high temperature resistant organic polymers which are at various stages of commercializations are shown in Table XI. Properties of some of these materials are indicated in Table XII and indicate high melting ranges, glass transition temperatures, and moduli. In some cases, like Kevlar, very high tensile strengths as well as low thermal shrinkage are obtained.

These examples clearly show that there are many possibilities for the formation of long stiff chains and that, in all cases, the properties of the resulting materials confirm expectations.

The existence of *three different* and *independent* ways to establish favorable compromises of valuable properties stimulates the attempt to explore *combinations* of these principles and to see whether such combinations might lead to even better results. To get a convenient survey of these combinations,

TABLE XI

High temperature resistant organic polymers

Trade Name	Composition	Company
Eimac 221	*p*-Polyphenylene	Varian, Inc. San Carlos, Calif.
Poroc	*p*-Polyphenylene	Rocketdyne Los Angeles, Calif.
Doryl	Diphenyloxide	Westinghouse
PPO	Polyphenyleneoxide	General Electric
Noryl	PPO plus polystyrene	General Electric
Polymer 360	Polysulfone	3M Company
Parylene N	Poly-*p*-xylxylene	Union Carbide
Parylene C	Poly-*p*-xylxylene	Union Carbide
Kapton	Completely condensed polyimide	duPont
Vespel	Precursor of Kapton	duPont
AI	Polyimide polymer	Amoco
AI 220	Polyimide Lacquer	Anaconda
Amanim	Polyimide	Westinghouse
Imidite	Polybenzimidazole	Narmco, Calif. (Whittaker Corp.)
(No name yet)	Polybenzimidazole	Celanese
Ryton	Polyphenylenesulfides	Phillips
(No name yet)	Polybenzoximidazoles	Monsanto
XPI-MB	Polyimide	Amer. Cyanamid
XPI-182	Polyimide	Amer. Cyanamid
Nomex	Aromatic polyamide from *m*-phenylene diamine and isophthalic acid	duPont
Kevlar	Aromatic polyamide from *p*-phenylene diamine and terephthalic acid	duPont

TABLE XII

Some approximate data on fibers made of aromatic polyamides and related polymers

	Nomex	Kevlar	Kermel	Enka-therm	PBI	Carbon fiber
Melting range, °C	450	530	500	> 550	> 550	> 2000
Glass transition, °C	300	330	330	> 330	> 330	> 1000
Modulus, g/den	200	1000	200	250	250	up to 5000
Tensile strength, g/den	4–6	up to 25	4–6	4–6	4–6	up to 50
Elongation, %	20–25	1.5–2.5	20–25	15–20	15–20	< 1.0
Shrinkage at 160°C, %	4–6	< 1.0		< 2	< 2	zero

let us consider a triangle (compare Figure 8) in which the three principles of crystallization (A), cross-linking (B), and chain stiffening (C) are represented by the three corners A, B, and C.

The corner A is populated by a large number of crystallizable, thermoplastic polymers with flexible chains which have proved to be particularly successful as fiber and film formers and for the techniques of injection molding, blow molding and extrusion. Representative materials are polyethylene, polypropylene, polyoxymethylene, polyvinylalcohol, polyvinylchloride, polyvinylidene chloride, and such polyamides as 6 and 66 nylon.

In the corner B are located the typical thermosetting resins, highly cross-linked systems such as hard rubbers, urea-, melamine-, and phenolformaldehyde condensates, highly reticulated polyesters, polyepoxides, and polyurethanes.

Finally corner C is representative of the amorphous or almost amorphous, thermoplastic resins with relatively high chain rigidity and high softening range. At the low end of this scale are those which derive their chain stiffness from bulky substituents e.g. polystyrene, polymethylmethacrylate, and polystyrene derivatives; more recently, the stiffness has been put into the chain itself e.g. in polycarbonates, linear polyepoxides, aromatic polyethers, polyesters and polyamides. Finally, the point C is particularly characteristic for the addition and condensation polymers of high aromatic chain character.

One can now pose the question whether a combination of *two* principles has helped to arrive at products with more attractive and valuable properties. Let us therefore explore the *sides* of the triangle in Figure 8.

In fact, the line from A to C accommodates several interesting fiber and film formers. One of them is polyethylene glycol terephthalate (Terylene or Dacron), in which the para-phenylenic units of the acid introduce enough chain stiffening to bring the melting point of this polymer up to about 260°C, which is as high as the melting point of 66 nylon, even though a polyester has no *lateral hydrogen bonding* available to stiffen its solid crystalline phase. Thus chain stiffening cooperates with crystallization to produce attractive properties without bringing either of these two principles to an extremely high value. Cellulose is another case in which excellent fiber and film forming properties are produced by a combination of chain stiffening and crystallinity; these two effects together give a polymer which is extremely rigid, does not melt at all, and is soluble only in a very small number of particularly potent liquid systems. The presence of substantially rigid chains has the favorable consequence that high tensile strength and high softening characteristics become apparent even at relatively low degrees of crystallinity, which places cellulose somewhere in the middle of the line connecting A and C. Many of the recent spectacular improvements of cellulosic filaments are founded on a capitalization of the dual origin of its fiber forming potential. Another example of a beneficial combination of A and C is cellulose triacetate, in which the capacity to crystallize superimposes several favorable properties on the normal cellulose acetate—particularly insolubility in many organic liquids and heat settability through additional crystallization.

All those rubbers which are slightly or moderately cross-linked and which crystallize on stretching progressively are situated on the side A–B; examples are natural rubber, high cis polybutadiene and polyisoprene, Butyl rubber and Neoprene. Depending upon the degree of cross-linking, they are more or less close to B.

Until now we have considered systems of *one component*, namely a specific polymer or copolymer; in the technology of elastomers it is, however, customary to produce stiffening and temperature resistance by the addition of a hard, finely divided *solid filler* such as carbon black, silica or alumina. Such addition of a crystalline or pseudocrystalline reinforcing filler is a kind of quasi-crystallization of the system, in the sense that the flexible chains of the original polymeric matrix are restricted in their segmental mobility by the presence of the very small and hard particles of the filler, to the surface of which they are attached by strong adsorptive forces. Thus the presence of a reinforcing filler simulates and replaces crystallization and brings the system closer to point A.

The line from C to B has been populated with certain useful polymers in the attempt to increase rigidity, high softening and insolubility of stiff chain systems by additional cross-linking. There are several well known cases for the combination of these two principles, for example, the raising of the heat distortion point of acrylic- and methacrylic polymers by the incorporation of allylmethacrylate or ethyleneglycol dimethacrylate, and the "curing" of epoxy polymers which are based on such stiff chain elements as bisphenol and cyclic acetals of pentaerythritol. Currently, attempts are being made to improve the properties of the more recent systems consisting of aromatic chain segments by cautious cross-linking, and to move with these materials also from point C somewhat in the direction of point B. The principal reason for this approach is the improvement, for such systems, of resistance to dissolution and swelling at elevated temperatures.

The advantageous combination of two principles poses the question whether a proper combination of *all three of them* could lead to still further improvements in property compromises. At present, much exploratory work is being done in this field, and already certain interesting results have been obtained. One successful application of all three principles is the aftertreatment of cotton with certain cross-linking agents or the spinning of rayon in the presence of such agents. Cellulose has rigid chains which can be brought to a moderate degree of crystallinity and reactivity by the swelling of cotton or the appropriate spinning of rayon; the results are fibers of satisfactory strength, elongation, hand and dyeing characteristics, but of insufficient recovery power. The introduction of a cautiously controlled system of cross-links with the aid of bifunctional reagents leaves all other desirable properties essentially unchanged and improves the recovery power and wrinkle resistance. Similarly promising results have been obtained with mildly reticulated amorphous stiff chain systems of the epoxy and urethane type in which crystallization has been replaced by a reinforcing filler.

The combinations of all three principles are situated somewhere in the interior of the triangle around D, and one can expect that a thorough and systematic exploration of this area will lead to many new and interesting polymeric systems with properties superior to those which are at our disposal today.

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