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SCIENCE

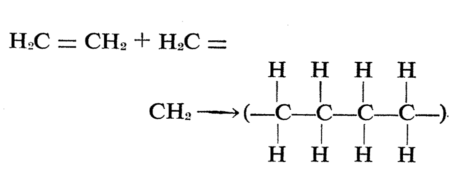
Cross-linking of Polymers by Radiation

Radiation has many effects on polymers; cross-linking is one that is useful as well as interesting.

George Adler

From both the technological and the biological point of view, possibly the most important class of organic materials is polymers. In the form of plastics, fibers, and rubber, polymers account for a large fraction of our industry. In the form of proteins, polysaccharides, and nucleic acids they lie at the basis of life itself. They are, indeed, ubiquitous.

The distinguishing characteristic of high polymers as a class is that they consist of very large molecules which are formed by the reaction of smaller molecules called monomers (see glossary). For example, polyethylene is made by linking together molecules of ethylene monomer into a large molecule in the following manner



$$H_2C = CH_2 + H_2C = CH_2 \longrightarrow (-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-)$$

Proteins are formed by linking together amino acids as the monomer units. Polysaccharides use sugar units such as, for example, glucose in starch. Conceptually, the simplest type of polymer consists of a long straight chain of monomer units. In most real cases, however, there is a tendency for some amount of chain branching to occur.

Polymers often engage in a process that is again important from both a biological and a technological viewpoint—the formation of cross-links. In this process two or more distinct polymer molecules are joined together by chemical bonds to form a single, larger molecule. In the limiting case the cross-links can bind the entire polymer mass together into a single network-like structure that is, in principle at least, a single, huge molecule.

The importance of cross-linking becomes evident when it is realized that, without it, rubber-like elasticity would not generally occur. In fact, cross-linking is the basis of vulcanization. On the biological side, the disulfide bonds which help give proteins their configuration are one example of cross-linking. On the whole, they determine a whole array of the physical and chemical properties of polymers.

Since polymers are ubiquitous and so important, it is not at all surprising that there has been a good deal of interest in the effect of radiation on these systems. It has long been known that ionizing radiation can break chemical bonds and that this often leads to degradation. Soon after this became known, it was demonstrated that cross-linking can occur as well. This opened up the possibility of enhancing the useful properties of many polymers, some of which are difficult to cross-link by conventional techniques. This, in turn, seemed to offer the hope of large-scale industrial use of radiation in this field. Unfortunately, this hope is still far from being realized, though it has led to a great deal of important and useful work. It is my purpose here to describe some of this work and to summarize briefly a few of the important concepts that have arisen in this field. Since there has been a large amount of work and this has been diversified, I cannot treat the subject in a complete or definitive manner in this article.

Production of Free Radicals and Mechanism of Cross-linking

If I am to describe radiation cross-linking adequately I must first say something about the production of reactive chemical sites on polymer molecules by radiation. It is not necessary to go into a great deal of detail. For the purposes of this discussion, the most important effect of the irradiation of organic matter is the excitation of a large number of molecules and the ejection of electrons from some, with resultant production of ionization. If the electrons are ejected with sufficient energy they will cause further excitation and ionization along their paths. In most organic systems, especially those of low dielectric constant, the electrons can be expected to recombine quickly with the ions, producing more excited molecules. This excitation energy can be degraded in various ways. The one that is of interest here is the rupture or dissociation of covalent chemical bonds. This leads to the formation of free radicals.

Polyethylene is structurally and conceptually the simplest of the organic polymers. In principle it is nothing more than a linear, long-chain, saturated hydrocarbon. For many processes it can serve as an adequate model

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for a large number of polymeric systems. For this reason, and because of its commercial importance, it is the polymer that has been most intensively studied. Therefore, I use it often in this article as a practical illustration.

For linear polyethylene some of the relevant bond-rupture processes are illustrated in Fig. 1. In process *a* the carbon-hydrogen bonds on two adjacent carbon atoms are broken; the result is a hydrogen molecule and a double bond. No free radical is formed. The polymer molecule is now inert as far as cross-linking is concerned, unless it is subjected to further irradiation. It need no longer concern us except insofar as the double bond affects the sensitivity of the molecule to cross-linking processes.

Process *b* is far more interesting. Here, a single carbon-hydrogen bond is broken and a hydrogen atom is removed. The polymer molecule now contains a carbon atom which possesses an unpaired electron. This is the alkyl free radical. The free hydrogen atom is chemically unstable and will abstract a hydrogen atom from some other molecule, generating another alkyl radical. Alternatively, it may add to any double bond which it encounters and again generate an alkyl radical.

The presence of odd unpaired electrons on free radicals makes the latter very reactive. They will react with any other free radicals. This reaction leads either to disproportionation or to the formation of a covalent bond between them. In the latter, more common event, the result is a cross-link. This is the process illustrated in Fig. 2*a*. For convenience, I call the alkyl free radicals type 1.

In the process illustrated in Fig. 1*c*, a carbon-carbon bond in the main polymer chain is broken. This also leads to the formation of two free radicals. These free radicals will recombine unless they are able to diffuse away from each other. If they do diffuse away, the molecule remains permanently broken. This can be considered a degradative step. In polyethylene and in polytetrafluoroethylene (Teflon), the two radicals formed in this manner are exactly the same. In other polymers, such as polyvinyl chloride, the two broken chain ends will be chemically different. Thus, two radicals of somewhat different reactivity may be formed. I call the radicals generated by carbon-carbon bond breakage type 2.

If the polymer molecule possesses side chains or branches, an additional reaction may be important. The points at which branching takes place are often somewhat more sensitive to radiation than the rest of the molecule. Carbon-carbon bond cleavage here results in both a type 1 and a type 2 radical. It is the reverse of the mechanism shown in Fig. 2*b*. If the side chain is short, this reaction produces hydrocarbons of low molecular weight.

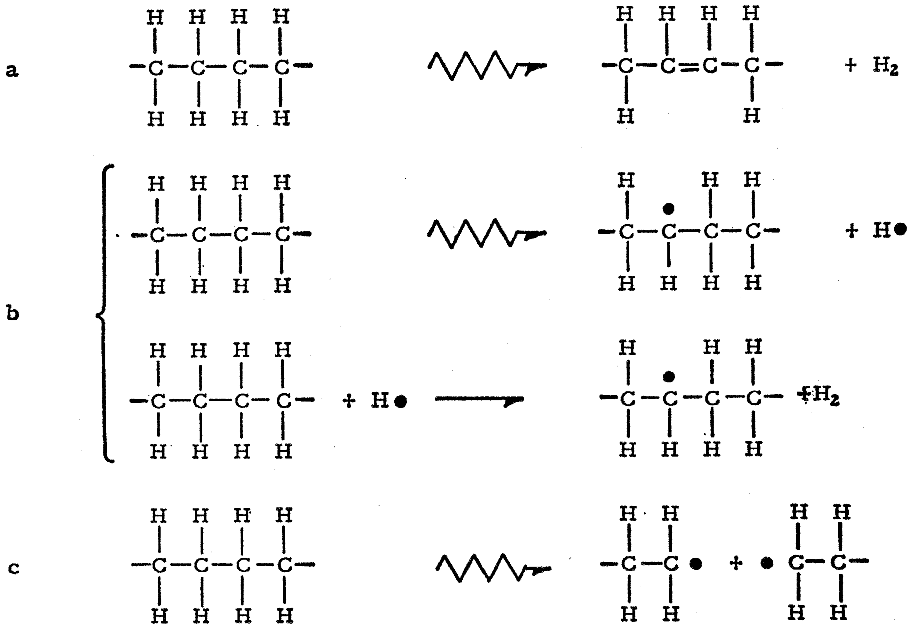


Fig. 1. Some of the bond-rupture processes in linear polyethylene. (*a*) Carbon-hydrogen bond rupture that leads to the formation of double bonds and hydrogen. (*b*) Carbon-hydrogen bond rupture that leads to the formation of radicals of type 1 and of hydrogen. (*c*) Carbon-carbon bond rupture that leads to chain scission and the formation of free radicals of type 2. In these diagrams the wavy arrow indicates radiation, the dot indicates the unpaired electron of a free radical.

As far as our story is concerned, there are several important ways in which a type 2 radical can react. It may react with its mate or with another radical of the same type to reform a polymer molecule like the original (Fig. 2*d*). It may combine with a type 1 radical in the so-called end-linking reaction illustrated in Fig. 2*b*. This produces a long side chain attached to the polymer molecule. The result of end-linking, like that of cross-linking, is an increase in molecular weight. It is not surprising, therefore, that some of the gross overall effects of these two processes are similar.

There is another reaction in which type 2 radicals can take part and which is analogous in its mechanism to the chain transfer step commonly encountered in ordinary polymerization reactions. Here the type 2 radical abstracts a hydrogen atom from a neighboring polymer molecule. The product is a type 1 radical and a shortened, now inert, polymer molecule. Unlike the other processes, this does not result in a decrease in the number of free radicals. This is illustrated in Fig. 2*c*.

Many polymer molecules, such as polyethylene, are flexible enough to double back on themselves and long enough to harbor more than one free radical. The free radicals can then react as if they were on an independent molecule. The cross-linking and end-linking reactions of Fig. 2, *a* and *b*, then result in closed loops or rings, but they do not lead to net increase in molecular weight or to the other effects commonly attributed to cross-linking.

The formation of cross-links in polymers raises a number of interesting mechanistic problems. For cross-link formation, an active radical on each of two molecules must approach each other and react. The difficulty is that the free radicals are attached to very large molecules imbedded in a very viscous medium. Even in the case of an amorphous polymer at a temperature above the glass transition temperature this is true. The diffusion of free radicals must, therefore, be considered a slow process at ambient temperatures, far too slow to account for the reported rapidity and extent of cross-link formation. Indeed, it has been shown by copolymer-grafting and electron-spin-resonance studies on polyethylene that a sizable fraction of the free radicals generated can persist for many months after irradiation (*1*). These radicals are normally considered a very reactive and short-lived chemical species. However, electron-spin-resonance studies have also indicated that a large proportion of the free radicals do disappear fairly rapidly (*2*). These are usually considered to be the alkyl or type 1 radicals which engage in cross-linking. Since the radicals can only react in pairs, some diffusion mechanism is presumably necessary.

As a solution to this problem, several variants of the mechanisms described, as well as some new ones, have been proposed. One is obvious from Fig. 1*b*. The hydrogen atom released in the first stage need only remove the second hydrogen atom from a neighboring molecule. This is especially likely to occur if the first atom is expelled with a large amount of kinetic energy. It will probably abstract the hydrogen atom on the first collision. The two radicals are now close to each other, and diffusion over large distances need not be involved. A mechanism of this pattern was first suggested for polyethylene by Miller, Lawton, and Balwit (*3*). It is interesting to note that a similar mechanism based on high kinetic energy or "hot" fragments has been postulated to explain the yields of "unscavengeable" hydrogen obtained in the radiolysis of saturated hydrocarbons (*4*).

Another suggestion is based on the well-known propensity of double bonds to take part in cross-linking reactions. The double bonds may be originally present in the polymer, or they may be the result of some previous radiation reaction, such as that of Fig. 1*a*. A reaction of the required type (*5*) is shown in Fig. 3*a*. This reaction can occur, for example, if the hydrogen generated in forming a type 1 radical adds to the double bond. The double bond now opens up and adds to the type 1 radical. This reaction is interesting in that it does not lead to the liberation of hydrogen.

Pearson (*6*) proposed another mechanism based on double bonds. In this one, a type 1 radical adds to one of the carbons of the double bond, which now opens up. The result is a cross-link and a free-radical site which is now on the other carbon of the double bond. This reaction does not reduce the number of free radicals. It was recently shown, however, that this is probably not a very important mechanism (*2*). At any rate, cross-linking is known to

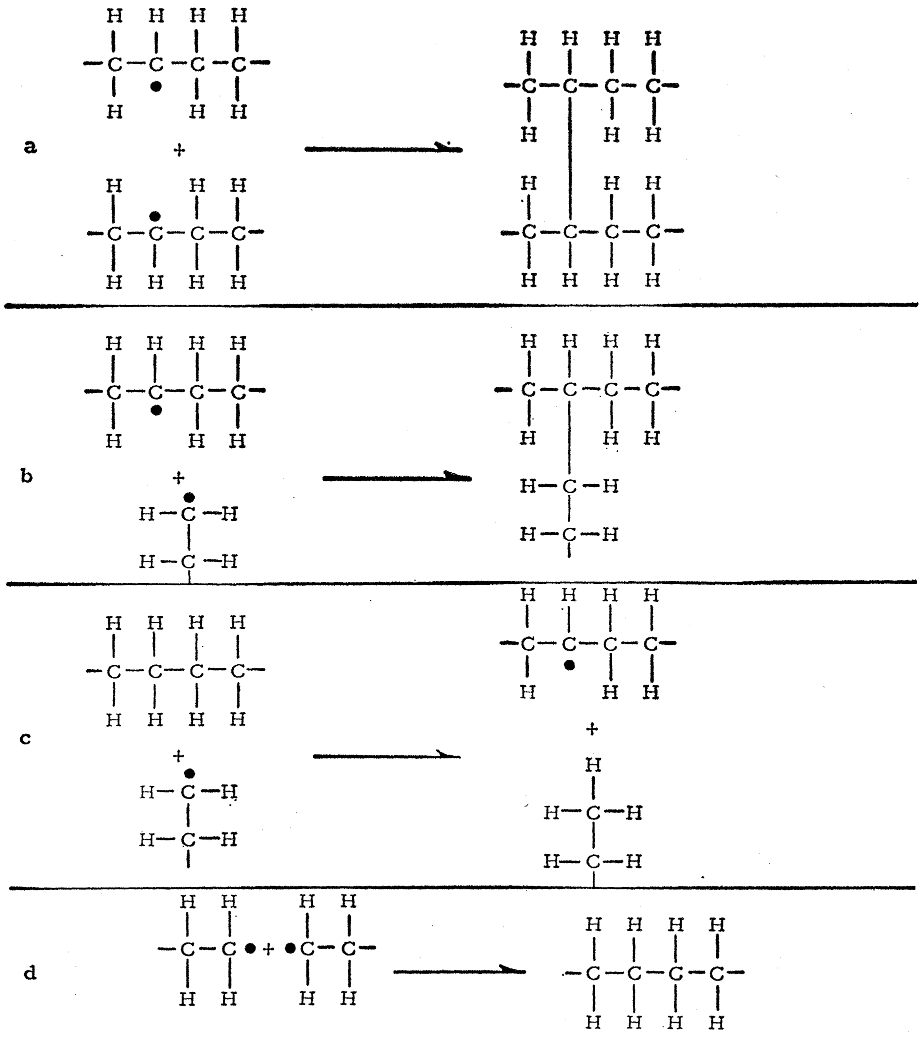


Fig. 2. A few of the pertinent radical processes which occur on polymer irradiation. (*a*) Recombination of two type-1 radicals to form a cross-link. (*b*) Recombination of a type-1 and a type-2 radical in the "end-linking" process to form a polymer chain branch. (*c*) Chain transfer; this can also involve type-1 radicals. (*d*) Recombination of two type-2 radicals to regenerate a molecule like the parent molecule. There is no attempt here to illustrate all the radical processes which occur in polyethylene or to imply that the ones shown occur to an equal extent. The purpose, rather, is to illustrate in simple fashion mechanisms assumed to occur in at least some polymers.

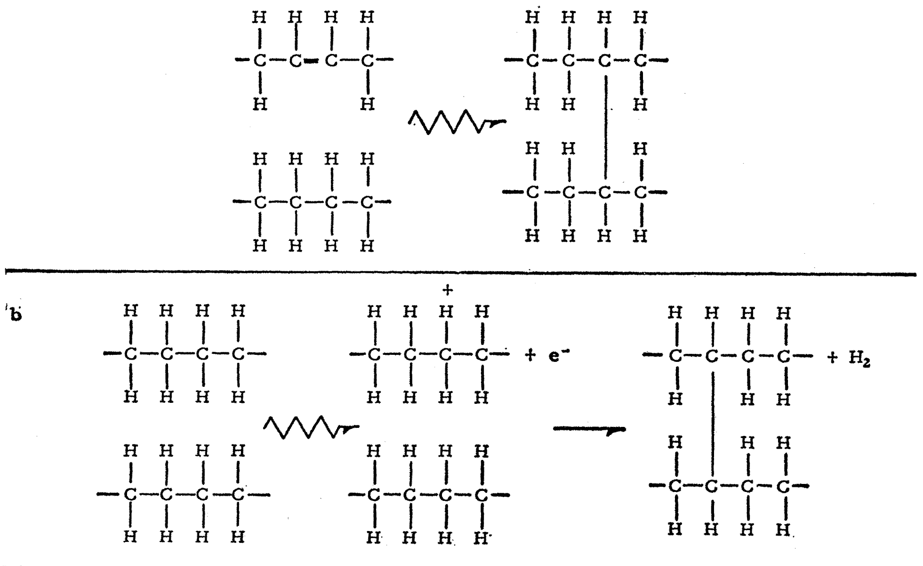


Fig. 3. Some addition mechanisms which have been invoked to explain cross-linking; e^- represents an electron.

occur in some polymers even when there are no double bonds present.

From time to time, ionic mechanisms have been proposed. An example of one is the ion-electron recombination reaction, such as the one shown in Fig. 3*b* (*7*). However, at present there is little evidence that these play an important role.

A most interesting proposal which helps explain the rapidity of free-radical decay and cross-linking was made in 1954 by Dole, Keeling, and Rose (*8*). They suggested that the free radical can migrate by a hydrogen transfer mechanism. This can occur in a two-step reaction in which an atom from a hydrogen molecule adds to a free radical. This leaves a free hydrogen atom. This hydrogen atom now abstracts another hydrogen atom from some other molecule. The second step is the same as the second step in the reaction illustrated in Fig. 1*b*. The hydrogen can come from the polymer, since this gas is almost always a product of the radiolysis of organic materials. It is suggestive that Dole and Cracco (*9*) have demonstrated hydrogen-deuterium exchange over irradiated polyethylene. They have also shown that the decay of free radicals is significantly more rapid in the presence of hydrogen than in its absence (*10*).

The mechanistic picture just outlined is supported by a good deal of evidence. First of all, cross-linking, chain scission, and the formation of hydrogen and other gas through radiolysis have been demonstrated for a number of polymers, including polyethylene (*11–13*). The presence of free radicals has been unequivocably demonstrated, by chemical means, such as the diffusion of monomers into irradiated polymers so as to produce graft copolymers (*1*), and by electron-spin-resonance spectroscopy. By the latter technique, some of the polymer radical structures have tentatively been identified (*14*). For example, part of the observed spectrum in polyethylene has been attributed to the alkyl or type 1 radical (*2, 15, 16*). The allyl $(-CH{=}CH-\dot{C}H-CH_2-)$ (*17*) and polyenyl $(-CH{=}CH-\dot{C}H-CH{=}CH-)$ (*16, 17*) radicals have presumably been identified; the latter appears after very high radiation doses, a finding that shows it is not generated in one step. This may also be true of the allyl. The role of these radicals is uncertain, but the allyl radical probably can also take part in cross-linking (*18*) even though it is more stable than the alkyl radical.

The actual processes as they occur in polymers are probably somewhat more complicated than the foregoing discussion indicates. This is probably true even for a polymer as simple as polyethylene. There are several reasons for this. First of all, commercial polyethylene is not strictly linear but always possesses a few side chains per molecule. In addition, there are a number of double bonds of varying type, originally present or formed during irradiation, and these show differences in reactivity. Thus, the vinyl and vinylidene groups disappear, while the trans-vinylene content increases at low radiation doses (*19*). The reactivity of the hydrogen atom that is on the carbon atom next to the double bond is greater than that of the others. Probably this accounts for the presence of the allyl free radical in polyethylene. Some polymers contain chemical groups which make them very sensitive to radiation, such as, for example, the sulfhydryl groups in proteins. In addition to cross-linking, polymers undergo degradation. In some, such as nucleic acids, chain splitting seems very likely to occur. These are complicating features. They amplify but do not greatly change the general validity of the cross-linking mechanisms described. It should be remembered that I have only concentrated on the simplest example of a complicated phenomenon.

Effect of Phase Structure on Cross-linking

According to one classification, polymers are divided into amorphous and crystalline structures. In the former the molecules are distributed and oriented in a random fashion, and they are usually coiled, if they are not too stiff. The polymer shows no long-range order and has a liquid-like structure. Above the glass transition temperature the segments of the molecule can show considerable thermal motion about their mean position. One can picture the molecules as something like writhing snakes. It is not difficult to see how, with such relative freedom of motion, cross-linking can take place.

In crystalline polymers the picture is different. In the common case—for example, commercial polyethylene—crystalline, well-ordered regions occur interspersed with amorphous polymer. The latter present no additional problems, but the crystalline regions require additional consideration. Here the molecules, or at least long segments of them, are precisely aligned, precisely positioned, and precisely oriented relative to each other. Long-range order exists. The presence of cross-links represents a serious disturbance in the regularity of the crystal lattice. The cross-links can be expected to interfere with crystallization. Thus it seems evident, from dielectric measurements on thermally cross-linked neoprene, that the links interfere with and reduce crystallization (*20*).

When a polymer such as polyethylene is irradiated at ambient temperature, the crystallites already exist before irradiation. Because of the relative immobility of the polymer chains and because of geometrical constraints of the crystal lattice, it can be expected that the cross-linking will be inefficient. On the other hand, because of this same low mobility, free radicals generated within the crystallites should show appreciably greater persistence than those formed in amorphous regions. In line with this prediction there is evidence that long-lived radicals are trapped in the crystalline regions (*1, 21*).

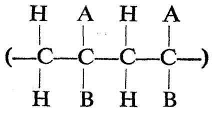
It has also been shown that irradiation sufficient to cause appreciable cross-linking at ambient temperature produces little change in crystallinity, as measured by birefringence (*22*), x-ray diffraction (*23*), or infrared techniques (*24*). This, as well as some work of Lawton *et al.* (*25*), suggests that cross-linking occurs mainly in the amorphous areas.

If polyethylene is irradiated at a temperature above its melting point and then cooled, there is a rapid loss of crystallinity. If the polyethylene is irradiated at lower temperatures, heated above its melting point, and then cooled, there is a similar loss of crystallinity (*22–24*). This shows that the radicals trapped in the polymer crystallites can, under some circumstances at least, eventually lead to cross-linking. At any rate, the usual techniques for measuring cross-linking, such as elastic modulus and gel determination, require that the crystalline polymers be heated above their melting point or swollen with solvent. Either treatment increases the mobility of the molecules sharply, and it is probable that a large fraction of the observed cross-linking occurs at the time of this increase. Considerable care must therefore be exercised in interpreting cross-linkage data from these polymers.

Cross-linking and end-linking may

be looked upon as mechanisms which increase the molecular weight. The chain scission of Fig. 1*c* suggests that processes leading to a decrease in molecular weight occur also. In most polymers both types of reaction take place simultaneously, with one or the other producing the major measurable effect. Which one this is depends upon the structure of the polymer.

In the case of vinyl polymers (those in which the monomer unit has a single terminal double bond), there is a rough rule by which we can predict which of the two mechanisms will produce the principal physical effect. The structure of these polymers can be written as follows:



$$(-\overset{H}{\underset{H}{C}}-\overset{A}{\underset{B}{C}}-\overset{H}{\underset{H}{C}}-\overset{A}{\underset{B}{C}}-)$$

In general, if either *A* or *B* is a hydrogen atom, cross-linking will predominate. If, on the other hand, neither is, the polymer will show an overall degradation. Thus, poly (methyl acrylate) and polystyrene cross-link upon irradiation, while polymethyl methacrylate and poly(α-methyl styrene) degrade. This has been explained by assuming that two bulky side groups substituted on the same carbon atom cause a certain amount of steric repulsion in the molecule and that the carbon-carbon bond in the main chain is thereby weakened (*11*). Wall (*26*) has shown that a reasonable correlation exists between cross-linking ability and heat of polymerization. If the heat of polymerization is high, this implies that the carbon-carbon bonds in the main chain are relatively strong and that cross-linking predominates. If the heat of polymerization is low, as in the case of polymers such as poly(α-methyl styrene), degradation results. Indeed, once the main polymer chain is split, these polymers often show an appreciable amount of degradation to monomers.

In applying the rule, it should be remembered that the two reactions often take place at the same time. In the case of polyethylene it has been estimated that the ratio of scission to cross-linking is about 0.35 (*27*), although, as Chapiro points out (*11*), this figure is probably a little high. It should also be borne in mind that the course of the reaction often depends on the reaction conditions. Although polystyrene is normally considered a cross-linking polymer, it degrades if irradiated in toluene (*28*) or chloroform (*29*). The presence of oxygen, especially, can make a profound difference. Thus, poly(vinyl alcohol) will cross-link if it is irradiated as a concentrated solution in deaerated water; if oxygen is present, it degrades (*30*). The structures of a few polymers are shown in Fig. 4, classified according to their predominant behavior in the radiation field.

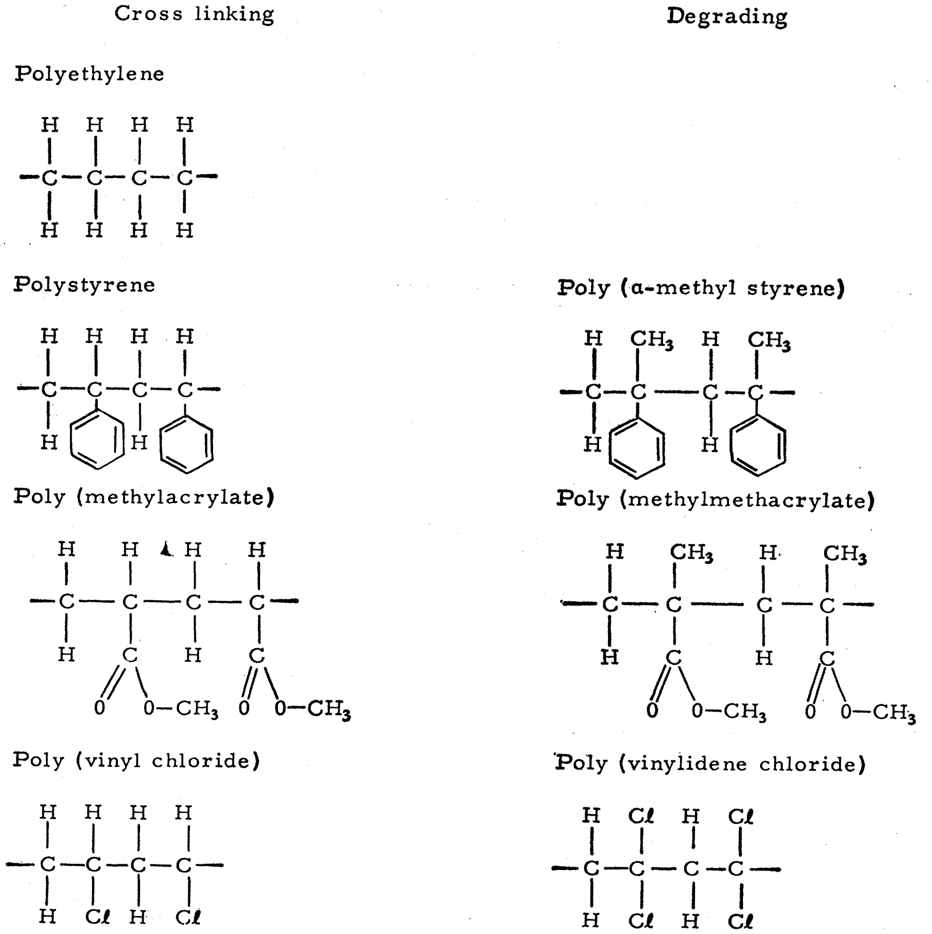


Fig. 4. Comparison of the structures of some cross-linking and degrading vinyl polymers.

Effects of Cross-linking, Elastic Modulus

As I stated earlier, a cross-link will bind two molecules into a single, larger one. There is no reason why one of the molecular segments branching from the cross-link cannot engage in the same process and bind a third molecule. In fact, the process can continue until the entire polymer mass is bound into a single network structure.

Network formation need involve only a relatively small number of cross-links. This can be seen from Fig. 5, which shows segments of four polymer molecules in an amorphous region being tied into a single structure by five covalent bonds. In principle, three strategically placed cross-links are all that are necessary.

It might be expected that tying the polymer into a network by a few covalent bonds in this fashion would have profound and easily observable physical effects, and this proves to be the case. Here, too, polyethylene provides an excellent example. Commercial, high-pressure polyethylene is a partially crystalline material. Above about 115° to 116°C, the polymer becomes mechanically weak enough to show viscous flow; in short, it melts. If the material is irradiated to a sufficiently high dose, and then heated, a new set of phenomena appear. The birefringence, for example, disappears at a somewhat lower temperature than previously (*22*), indicating that the crystallites melt and the polymer becomes amorphous more easily. However, the cross-links which have been formed prevent the molecules from gliding past each other. Instead of melting in the sense of becoming a flowing liquid, the material enters a rubbery state. It exhibits a readily measurable modulus of elasticity (Young's modulus) at temperatures far above those at which it would otherwise lose all semblance of a solid. The polyethylene will keep its form and show good thermal stability at temperatures up to and above 300°C (*11*) if heated in the absence of oxygen. There is also a reduction in stress and in heat cracking, cold flow, and related properties. This is not surprising if it is remembered that the cross-linking of rubber produces analogous changes.

Amorphous and not very densely cross-linked polymers tend to show rubber-like elasticity at temperatures above their glass transition temperatures. This is because there still is, on the average, a sizable length of polymer chain between cross-links and these chain sections have an appreciable amount of segmental motion. If the number of cross-links per unit volume of polymer becomes very high, the between-the-links chain length becomes small and the motion of the chain segments becomes much more restricted. In the limiting case, the material is hard, brittle, and infusible. The modulus of elasticity becomes very high, and the ability of the material to stretch when stressed becomes sharply limited. Classic examples of material of this type are Bakelite and hard rubber or ebonite.

This behavior has become the basis of a method of estimating the density of cross-linkage or, more strictly, the molecular weight between cross-links. In this test method, the polymer specimen is elongated a specific amount and the equilibrium stress is measured. The equation relating these quantities is as follows (*31*):

$$\tau = RT\,(1/\bar{v}M_c)\,(1 - 2\,M_c/M)\,(\alpha - \frac{1}{\alpha^2})$$

where τ is the tensile stress per unit initial cross-sectional area of the sample; R is the molar gas constant; T is the absolute temperature; $\bar{v}$ is the specific volume of the polymer; M_c is the average molecular weight between cross-links; M is the average molecular weight of the primary molecules; and α is the ratio of the extended length to the original length. This equation holds fairly well for values of α that are not very much greater than 2 and for cross-linkage densities that are not very high. This equation, or a variant of it, has sometimes been used in estimating the extent of cross-linking in irradiated polymers. It should be borne in mind that it is strictly valid only for amorphous polymers.

A polymer such as polyethylene must be heated above its crystalline melting point before this equation can be applied, and, as has been pointed out, an appreciable amount of cross-linking may occur during the heating. There is, in fact, no good way to determine the degree of cross-linking in crystalline polymers.

Interesting changes in solubility also occur when the polymer is cross-linked. In a good solvent the polymer molecules normally become solvated and

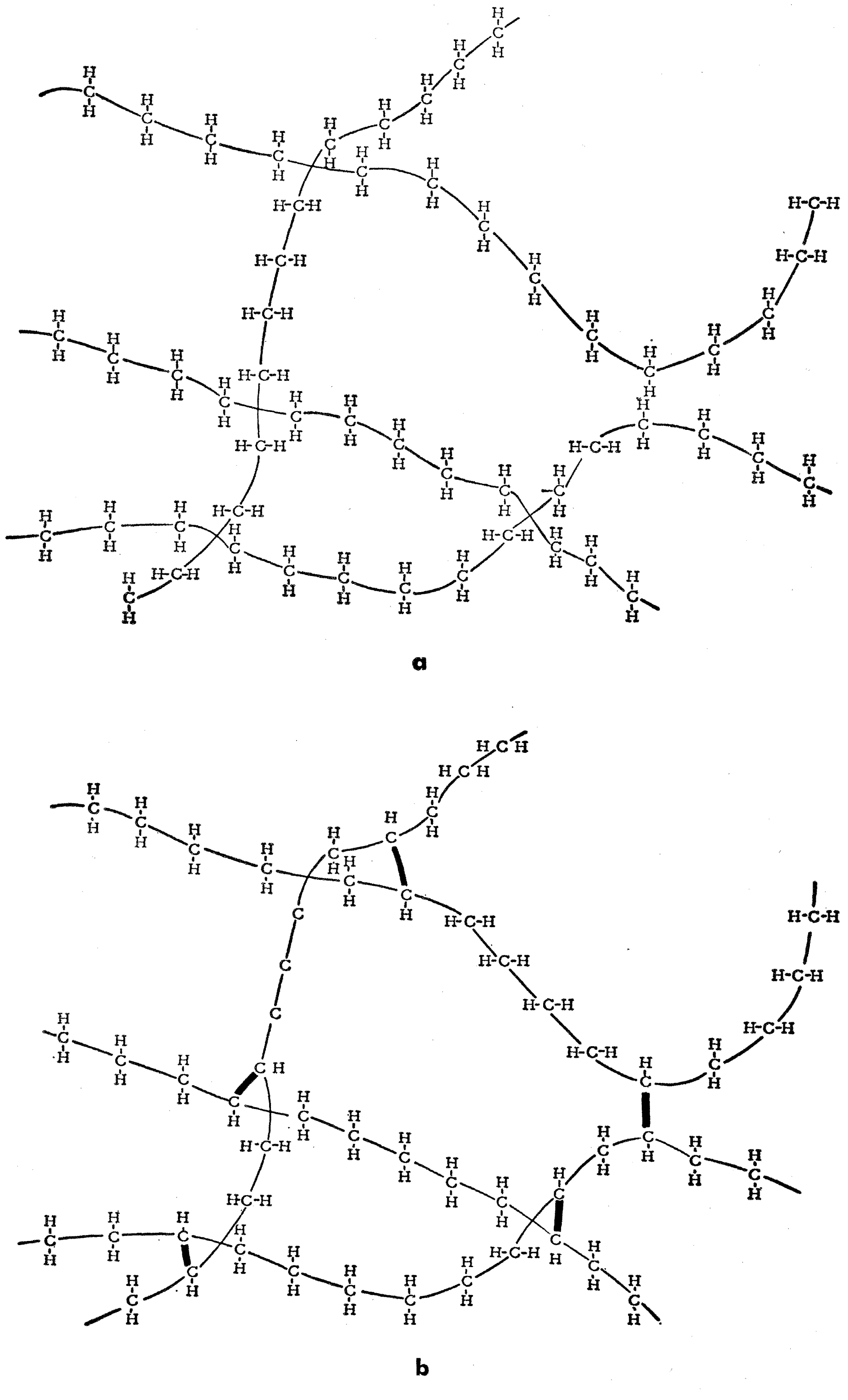


Fig. 5. Cross-linking in amorphous polyethylene. (*a*) Uncross-linked polymer; (*b*) cross-linked polymer. The heavy bars show the cross-links.

diffuse apart from each other. When the molecules are linked together into a network, this diffusion can no longer take place. The result is an insoluble gel swollen with solvent. The degree of swelling when the molecules are at equilibrium with the solvent is given by the following equation (*31*):

$$q_m^{5/3} = (\bar{v}M_C)\,(1-2\,M_C/M)\,(1/2-X_1)/v$$

where q_m is the ratio of the volume of swollen polymer to the volume of dry polymer; v is the molar volume of the solvent; and X_1 is a measure of the solvent-polymer interaction which is a constant for a given system and which can be determined from the behavior of the solution, as from the slope of the curve when the reduced osmotic pressure is plotted against concentration. The other symbols have the same meaning as in the earlier equation. The equation is valid only for good solvents and where cross-linkage density is low, so that the degree of swelling is high. The measurement of cross-linking on the basis of this equation again requires the destruction of crystallinity. The details of this treatment can be found in Flory's book (*31*), or in the classic paper by Flory and Rehner (*32*). What concern us here are the conditions for gel formation and the ways in which they are affected by the radiation process.

Let us suppose that a polymer is completely soluble in a given solvent, and let us assume that cross-links are progressively added at random. A stage is finally reached at which the gel just begins to form. On the basis of Flory's treatment it can be shown (*11*) that the critical condition for incipient gel formation is that there be, on the average, one cross-link for every two molecules of weight average molecular weight (see glossary). For the most probable molecular weight distribution, the weight average molecular weight is twice the number average molecular weight. The critical condition for gel formation is therefore one cross-link for every four molecules of number average molecular weight when the cross-links are randomly placed. If it is remembered that only three well-placed cross-links, for example, are needed to tie four molecules together and that most of the polymer is still soluble, it is evident that this is an entirely reasonable result. Also evident is the following relationship: the higher the molecular weight, the fewer the cross-links needed for gelation, provided chain scission is not too important. If chain scission occurs as well as cross-linking, more links are of course needed.

If both cross-linking and scission occur at random along the polymer chains, the radiation dose required to cause incipient gelation, R_g, is given, according to Charlesby (*33*), by

$$R_g = \frac{1}{(1/E_c - 1/2\,E_d)\,\overline{M}_w\,N}$$

where E_c and E_d are the total amount of energy absorbed by the polymer per cross-link and per chain scission, respectively; $\overline{M}_w$ is the initial weight average molecular weight; and N is Avogadro's number. Though this equation involves several assumptions and must be considered only approximately true for many cases, it does provide a means of estimating the relative rates of cross-linking and scission. It also leads to the result that, if we take the weight average molecular weight as a basis, no gelation will occur if the scission rate is more than two times the cross-linking rate.

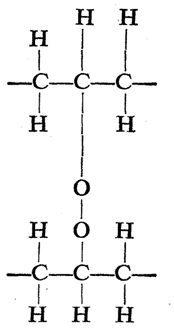
Effects of Oxygen

In much of the foregoing discussion the effect of oxygen has been ignored. Since oxygen reacts rapidly with free radicals it can alter the course of events considerably. Two biological examples of this are the effect of oxygen on irradiated ribonuclease (*34*) and the effect of oxygen on irradiated seeds (*35*). In the field of commercial polymers, polytetrafluoroethylene (Teflon) is a good example. It has been reported to be very sensitive to radiation degradation. Recently, Wall and Florin (*36*) reported that if oxygen is rigorously excluded from the system, the polymer can withstand considerably higher radiation levels than it can withstand if oxygen is present. It has also been shown that the presence of oxygen during the irradiation of polyethylene doubles the dose required for gelation (*37*).

The effects of oxygen are complex. Carbonyl and hydroxyl groups are usually found in polyethylene after irradiation in air (*38*). There is a degradation of mechanical properties (*8*). In general, oxidative effects occur with increased rapidity.

The effects of oxygen show a marked dependence on dose rate and on dimensions of the sample for many polymers. A waxy film tends to form on the surface of thick polyethylene samples subjected to high reactor doses in air (*39*). Polyethylene irradiated in air at high dose rates shows behavior similar to that of polyethylene irradiated in a vacuum. However, if the dose rate is low enough, the polymer is not completely cross-linked (*40*) even at high total doses. The reason for this seems to be that the diffusion of oxygen into polyethylene is relatively slow and, at high dose rates, the oxygen is consumed before it can diffuse very far.

Perhaps the most interesting result of irradiation of polymers in the presence of oxygen is the formation of organic peroxides and hydroperoxides. Organic peroxides probably have the following structure



and they form a sort of cross-link.

These are relatively labile chemical structures, and a moderate amount of heating can split them. This happens at a temperature of about 150°C for polyethylene (*40*). When the peroxy group splits, two free radicals are formed which are then capable of undergoing the normal free-radical reactions. For example, these radicals have been used to initiate the graft copolymerization of acrylonitrile onto peroxidized polypropylene (*41*) and the grafting of vinyl pyrrolidone onto peroxidized polymethyl methacrylate (*42*).

Other Forms of Cross-linking

Up until now I have limited the discussion almost entirely to the sort of cross-link that is formed by a single carbon-carbon molecule between two polymer chains. If we accept as a criterion for our consideration anything capable of binding a polymer into a network structure or into a swollen insoluble gel, other types of cross-linking are possible. For example, we can have short lengths of polymer chain tying the molecules together so that the cross-link has an H configuration. This length of chain may be of the same polymer type as the parent molecule, or it may possibly be of a different polymer type, as in the case of the graft-copolymers so easily formed by radiation. The cross-link may consist of one or two atoms, as in the case of the disulfide links in proteins and in sulfur vulcanized rubber. Or it may be a small molecule. This latter possibility led to the study of additives to promote the cross-linking of polymers in a radiation field. These additives are usually difunctional molecules, having at least two double bonds. Thus, by using 6.3 percent of N-phenyl maleimide, Vale and his associates have been able to increase the *G* value for cross-linking in natural rubber from 1.8 to 70 (*43*). Apparently, the proper additive can alter the overall direction of a radiation process. For example, polyisobutylene is a polymer that normally degrades rather than cross-links in a radiation field. Yet it has been reported that the use of 15 percent of allyl acrylate yielded a gel at a dose of approximately 1 megarad (*44*). This same additive has been reported to increase the efficiency of radiation cross-linking in polyethylene and polypropylene (*44*).

Finally, I shall mention a form of "cross-linking" that is not really cross-linking at all. The end-linking process of Fig. 2*b* leads to an increase in molecular weight. If a large enough fraction of the fragments which result from chain scission are involved in end-linking, gel formation may follow (*13*). A given amount of gel in an irradiated polymer can therefore be the result of this mechanism, as well as cross-linking. There are at present no experimental techniques which will distinguish between the two in a clearcut fashion, though true cross-linking is probably by far the more important process in most instances.

Conclusion

Cross-linking is a process of considerable commercial as well as biological importance. It gives useful properties to a wide variety of polymers; some, such as rubber, would be almost useless if it did not occur. The facilitation of cross-linking for commercial purposes, however, usually entails the use of heat or certain additives, or both. These agents sometimes alter certain of the properties of the polymer disadvantageously.

Radiation can bring about cross-linking without the use of heat or additives. In addition, it can do this in polymers in which it is difficult to bring about cross-linking by other means. Unfortunately, the *G* value for cross-linking, which is a measure of the process efficiency, is usually so low that relatively large radiation doses are needed. This makes the technique still economically unattractive. The use of certain types of additives sharply increases the *G* values in some instances, but these additives are in themselves relatively expensive. In addition, some of the materials in which cross-linking is produced by radiation seem to have poorer mechanical properties than equivalent materials in which it is produced chemically. Despite the production of a certain amount of polyethylene in which cross-linking has been brought about by radiation, we are still far from realizing the commercial promise of this process, though there seems to be some hope for the future. In a different sense, however, the large amount of work in this field has had a more fortunate issue. It has resulted in a better understanding of both polymers and radiation chemistry. Though the limitation of space has allowed me barely to hint at it, the gain in this respect has been huge and well worth the effort which has been, and continues to be, expended (*45*).

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Glossary

Cross-link. A link or connection between two polymer molecules. In general, it consists either of a valence bond between two polymer molecules or a group of atoms forming a chain segment which connects the two molecules by valence bonds.

Degree of polymerization. The number of monomer units that make up the average polymer molecule in a sample.

G *value.* The number of molecules which react, or the number of molecules of a reaction product which are produced, for every 100 electron volts of absorbed energy. This is a measure of the chemical yield and the efficiency of a radiation-induced reaction.

Gel fraction. The fraction of a polymer sample which cannot be dissolved without degradation although it may be swollen with the appropriate solvent.

Glass transition temperature. The temperature below which the thermal motion of the polymer chain segments becomes very small. The material enters a glassy, brittle state. It is a second-order transition.

Ionizing radiation. X-rays, gamma rays, and particle rays such as electrons and protons. Unless otherwise specified, the word *radiation*, as used in this article, means gamma or electron radiation. This is because these are the forms of radiation used in by far the greater part of the work. In general, gamma and electron radiation are not differentiated in this article. Since one of the effects of gamma radiation is the production of relatively energetic electrons in the substance being irradiated, the general effects of the two types of radiation are similar.

Megarad. One million rads.

Molecular weight. High polymers generally have a range or distribution of molecular weights. In molecular-weight determinations an average is arrived at. The statistical nature of this average is determined by the experimental technique used.

Monomer. (i) A small molecule which can enter a reaction to form a large polymer molecule. (ii) A segment of the polymer that corresponds to the monomer molecule. In the case of polyethylene this would be $—CH_2—CH_2—$, which corresponds to ethylene, $CH_2 = CH_2$.

Number average molecular weight. The average molecular weight defined by

$$\overline{M}_n = \sum_i Xi\,Mi = \frac{\Sigma Ni\,Mi}{\Sigma Ni}$$

where Xi is the mole fraction of species i, Ni is the number of moles of species i, and Mi is the molecular weight of species i. It corresponds to the arithmetic mean molecular weight and is usually determined from measurement of osmotic pressure.

Polymer. A molecule of high molecular weight which is formed from the reaction of a number of smaller molecules called monomers.

Rad. A radiation-energy absorption of 100 ergs per gram of sample. This is equivalent to 6.24×10^{13} electron volts per gram. A rad is the unit of absorbed dose.

Sol fraction. The fraction of a polymer sample which can be dissolved in the appropriate solvent.

Weight average molecular weight. The average molecular weight given by

$$\overline{M}_w = \sum_i Wi\,Mi = \frac{\Sigma Ni\,Mi^2}{\Sigma Ni\,Mi}$$

where Wi is the weight fraction of species i and the other symbols have the meanings given under *Number average molecular weight.* It is usually determined by light scattering in solution. If all the molecules have the same weight, then $\overline{M}_n = \overline{M}_w$. For the "most probable molecular weight distribution,"

$$\overline{M}_w = 2\,\overline{M}_n$$

Synthetic Elastomers

Development of synthetic materials is accelerated by stereospecific polymerization catalysts.

J. B. Campbell

A major impetus in the development and large-scale manufacture of synthetic elastomers was the shortage of natural rubber in World War II. The synthetic elastomers have proved to be more than substitutes and today constitute more than 75 percent of the total elastomer consumption in the United States. This replacement is due partially to economic factors but also to the wider range of desirable structures and properties available through synthesis. Preparative methods in elastomer chemistry have increased steadily in scope, with especially remarkable advances during the past 8 years. This development has been accompanied by physical studies that have led to better understanding of the basic structural features needed in elastomeric high polymers. Scientific effort in the field of synthetic elastomers continues to expand in academic, government, and industrial laboratories.

Structural Requirements

An elastomer is usually regarded as a solid material which can be grossly elongated or distorted and which rapidly recovers, to essentially the original dimensions, after removal of the stress. This property results from the introduction of restraining cross-links between linear chains of high molecular weight that otherwise have high mobility. It is desirable to consider separately the structural requirements of the linear chains and those of the final elastic network, in line with the actual technology in the utilization of elastomers; the "raw," linear polymer is formed in the desired shape by heat and pressure and then cross-linked or vulcanized to a three-dimensional network.

High internal mobility is essential in elastomeric polymers; this requirement precludes significant crystallinity in the unstretched chains, which may be visualized as existing in randomly coiled configurations of maximum entropy. The tendency of polymers to crystallize is enhanced by high regularity in structure and strong intermolecular forces resulting from polar groupings. While many crystalline high polymers become rubber-like at temperatures above the melting point, T_m, the common classes of elastomers are amorphous at ambient temperatures. As a consequence, elastomeric structures tend to be irregular and nonpolar, and hydrocarbon polymers predominate.

Similarly, the need for chain flexibility requires that the elastomer be above the glass temperature T_g. This is the temperature below which "segments" of chains in the amorphous high polymer no longer move as a whole but are restricted because of local intramolecular and intermolecular forces. Below this temperature, the elastomer becomes, physically, a hard, more or less brittle glass. This transformation is not a phase transition, as crystallization is, but may be compared to the solidification of a liquid to a glass (*1*). Properties such as the thermal expansion coefficient and heat capacity show abrupt changes in the region of T_g. Figure 1 is a typical plot of relative length against temperature for a neoprene synthetic elastomer which has a T_g of −48°C (*2*). No simple correlation of chemical structure and glass-transition temperatures can be made. In general, when the structural units have high rotational barriers, high van der Waals interactions, and bulky or polar substituents, the glass temperature of the polymer is high (*1, 3*). Molecular weight (beyond a minimum point) and cross-linking have no major effect on T_g.

A flexible polymer of high molecular weight must be cross-linked or vulcanized to prevent permanent flow and to obtain elastic recovery. In a typical elastomer containing a carbon-carbon "backbone," short cross-links are inserted randomly to give an average spacing of 400 to 800 chain carbon atoms between cross-links. The result is one "infinite" network in which the cross-linking structures constitute very little of the total mass. In Fig. 2, typical stress-strain curves (elongation and recovery) are shown for vulcanized and unvulcanized specimens of a neoprene synthetic elastomer in the "gum" state

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