RUBBER TECHNOLOGY

THIRD EDITION

Edited by

MAURICE MORTON

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Regents Professor Emeritus of Polymer Chemistry
The University of Akron
Akron, Ohio

Sponsored by the Rubber Division of the
AMERICAN CHEMICAL SOCIETY

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RUBBER TECHNOLOGY

To my wife
Lilian
for her patience
and encouragement

PREFACE

About ten years after the publication of the Second Edition (1973), it became apparent that it was time for an up-date of this book. This was especially true in this case, since the subject matter has traditionally dealt mainly with the structure, properties, and technology of the various elastomers used in industry, and these are bound to undergo significant changes over the period of a decade.

In revising the contents of this volume, it was thought best to keep the original format. Hence the first five chapters discuss the same general subject matter as before. The chapters dealing with natural rubber and the synthetic elastomers are up-dated, and an entirely new chapter has been added on the thermoplastic elastomers, which have, of course, grown tremendously in importance. Another innovation is the addition of a new chapter, ''Miscellaneous Elastomers,'' to take care of ''old'' elastomers, e.g., polysulfides, which have decreased somewhat in importance, as well as to introduce some of the newly-developed synthetic rubbers which have not yet reached high production levels.

The editor wishes to express his sincere appreciation to all the contributors, without whose close cooperation this task would have been impossible. He would especially like to acknowledge the invaluable assistance of Dr. Howard Stephens in the planning of this book, and for his suggestion of suitable authors. He would also like to express his sincere thanks to Connie Morrison, of the Rubber Division, ACS, for her painstaking efforts in carrying out the large volume of secretarial work involved in this type of publication.

MAURICE MORTON

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INTRODUCTION TO POLYMER SCIENCE

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Polymer science is concerned with the composition and properties of a large number of substances classed as "polymers," which include rubbers, plastics, and fibers. The meaning of the term "polymer" will become clear during the course of this chapter, but it does involve some understanding of basic chemistry. The science of chemistry concerns itself with the composition of matter and with the changes that it undergoes. To the layman, the methods and processes of chemistry appear quite baffling and difficult to comprehend. Yet these are essentially based on a simple, logical development of knowledge about the substances which comprise our physical world. Since this book is not intended exclusively for readers trained in chemistry, the subject of polymer chemistry will be developed from the type of first principles comprehensible to anyone.

ATOMS AND MOLECULES

In this "atomic" age, it is certainly common knowledge that the atom is the basic unit of all matter. There are as many different kinds of atoms as there are elementary substances, i.e., elements, and these number about 100. It is the myriads of combinations of these atoms which make possible the hundreds of thousands of different substances comprising our world. Just as in the case of the 100-odd elements it is the atom which is the smallest unit, so too in the case of all other substances (*chemical compounds*), it is the particular *group of atoms*, or *molecule*, which is the smallest possible unit. If the molecule of a compound substance is broken up, the substance ceases to exist and may be reduced to the elementary substances which comprise it. It is the various possible combinations of element atoms to form different molecules which is the basis of chemistry.

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Now, in this "nuclear" age, we hear much about "atomic fission" processes, in which atoms are split apart, with the accompaniment of considerable energy release. How then can an atom be split if it is supposedly a basic unit of matter? Well, we know today that atoms are not the indivisible particles they were originally believed to be. Instead, they, too, are made up of even smaller particles such as protons, electrons, neutrons, and others. The differences between atoms can be explained by the different numbers and arrangements of these subatomic particles.

The thing to remember, however, is that the different substances of our world make their appearance once atoms have been formed. This becomes obvious when we consider that all protons are the same, all neutrons are the same, and so on. There is no such thing as a "proton of iron" being different from a "proton of oxygen." However, an atom of iron is considerably different from an atom of oxygen. That is why the chemist is concerned mainly with the arrangement of atoms into molecules and considers the elemental atoms as the basic building blocks.

Valence

So far nothing has been said about the manner in which the subatomic particles are held together or what holds atoms together in molecules. Although this is not our immediate concern here, it should be understood that there are electromagnetic forces which hold all these particles together. Thus most of the subatomic particles carry either positive or negative electrical charges, which act as binding forces within the atoms as well as between different atoms. Because each atom contains a different number and arrangement of these charged particles, the forces acting between different atoms also are different. These forces, therefore, result in certain well-defined rules which govern the number and type of atoms which can combine with each other to form molecules. These rules are called the rules of *valence*, and refer to the "combining power" of the various atoms.

From the beginning of the nineteenth century, chemists have been carefully weighing, measuring, and speculating about the proportions in which the element substances combine to form compounds. Since they found that these proportions were always the same for the same substances, this was most easily explained by assuming combinations of fixed numbers of atoms of each element. This was the basis for Dalton's Atomic Theory, first proposed in 1803. In accordance with this hypothesis, an atom from the element hydrogen is never found to combine with more than one atom of any other kind. Hence, hydrogen has the lowest combining power, and is assigned a valence of 1. On the other hand, an atom of the element oxygen is found capable of combining with two atoms of hydrogen, hence can be said to have a valence of 2.

In this way, the kinds and numbers of atoms that make up a molecule of a given compound can be deduced and expressed as a *formula* for that compound. Thus the compound water, whose molecules are each found to contain 2 atoms of hydrogen and 1 atom of oxygen, is denoted by the formula H_2O, where the letters represent the kinds of atoms, and the numbers tell how many of each atom are present within one molecule. This formula could also be written as $H-O-H$ to show how 1 oxygen atom is bonded to 2 hydrogen atoms. In the case of the well-known gas, carbon dioxide, the molecule would be represented as CO_2, where the carbon atom would show a valence of 4, since it is capable of combining with 2 oxygen atoms (each of which has a valence of 2). This formula could also be written as $O=C=O$, which is known as a *structural formula*, since it shows exactly how the carbon and oxygen atoms are bonded. Such structural formulas must be written in a way which will satisfy the valence of all atoms involved.

MOLECULES AND MACROMOLECULES

We have seen how the chemist is concerned with the structure of the molecules which comprise the substances in our world. At this point it might be of interest to consider the actual size of these molecules. It is now known that a molecule of water, for instance, measures about ten billionths of an inch, that is, one million such molecules could be laid side-by-side to make up the thickness of the type used on this page. Putting it another way, one drop of water contains 1,500,000,000,000,000,000,000 molecules! Most ordinary substances have molecules of this approximate size. Thus the molecule of ordinary sugar, which has the rather impressive chemical formula $C_{12}H_{22}O_{11}$, is still only a few times larger than the water molecule.

Such substances as water, sugar, ammonia, gasoline, baking soda, and so forth, have relatively simple molecules, whose size is about the same as indicated above. However, when chemists turned their attention to the chemical structure of some of the "materials" like wood, leather, rubber, and so forth, they encountered some rather baffling questions. For instance, *cellulose* is the basic fibrous material which comprises wood, paper, cotton, linen, and other fibers. Chemists knew long ago that cellulose has the formula $C_6H_{10}O_5$, as shown by chemical analysis, yet their measurements did not indicate that the molecule of cellulose existed in the form shown by the formula. Instead, they found evidence that the cellulose molecule was unbelievably large. Hence they did not really believe that it was a molecule, but considered the true molecule to be $C_6H_{10}O_5$, and that hundreds of such molecules were bunched together in aggregates.

Rubber, like cellulose, was also classed as a *colloid*, i.e., a substance which contains large aggregates of molecules. Over 150 years ago, the formula for
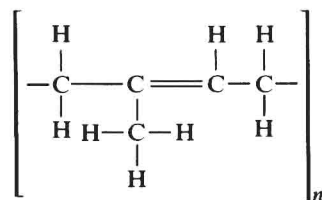
rubber was established as C_5H_8, but here again the evidence indicated that the molecule was much larger than shown by the formula. It was only as recently as the 1920's that Staudinger advanced the revolutionary idea that the rubber molecule was indeed a giant molecule, or *macromolecule*. Today, it is generally accepted that the class of materials which form the useful fibers, plastics, and rubbers are all composed of such macromolecules. Hence the formula for cellulose, if it is to represent one molecule, should more correctly be written as $(C_6H_{10}O_5)_{2000}$, while rubber should be represented as $(C_5H_8)_{20,000}$.

Such molecules are, of course, many thousands times larger than the molecules of ordinary chemical substances, hence the name "macromolecules." However, it should be remembered that even these giant molecules are far from visible in the best microscopes available. Thus the cellulose or rubber molecule may have a diameter several hundred times larger than that of a water or sugar molecule, but its size is still only several millionths of an inch! Even so, however, their relatively enormous dimensions, in comparison with ordinary molecules, give them the unusual properties observed in plastics, rubbers, and fibers.

POLYMERS AND MONOMERS

The molecular formula for rubber, $(C_5H_8)_{20,000}$, at first glance appears formidable indeed. There can obviously be a vast number of possible arrangements of 100,000 carbon atoms and 160,000 hydrogen atoms! To deduce the exact way in which they are arranged seems an impossible task. Yet it is not as difficult as it would seem. Fortunately—for the chemists—these huge molecules are generally composed of a large number of simple repeating units attached to each other in long chains. Thus the strucutral formula for the molecule of natural rubber may be represented by the simple unit C_5H_8 multiplied many thousand times. It is actually shown thus:

$$\left[\begin{array}{c} \overset{\displaystyle H}{\underset{\displaystyle H}{-C-}} \quad C = \overset{\displaystyle H}{\underset{\displaystyle H-C-H}{C}} - \overset{\displaystyle H}{\underset{\displaystyle H}{C}} - \\ \underset{\displaystyle H}{} \end{array} \right]_n$$

In the above structure, n represents a value of about 20,000, as stated previously. The arrangement of carbon and hydrogen atoms obeys the valence rules of 4 for carbon and 1 for hydrogen. The unattached bonds at each end of the unit are, of course, meant to show attachments to adjacent units.

Because these giant molecules consist of a large number of repeating units, they have been named *polymers*, from the Greek "poly" (many) and "meros"

(parts). The repeating unit shown above would, therefore, be called the *monomer*. It is actually very similar to a simple compound, known as isoprene, a low-boiling liquid. In 1860, Greville Williams first isolated this compound as a decomposition product obtained when rubber was heated at elevated temperatures, out of contact with air. The relationship between the monomer and polymer structures, in this case, is illustrated below.

monomer

polymer

isoprene

polyisoprene (natural rubber)
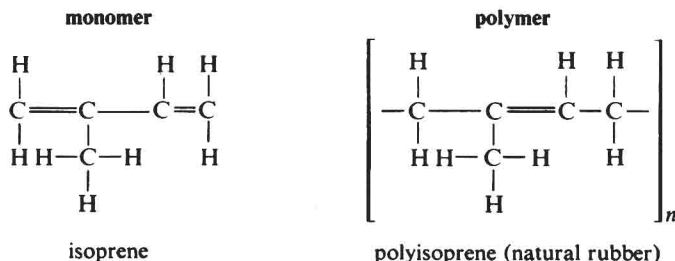
It can be seen here that the unit in the chain molecule corresponds exactly with the uncombined monomer molecule except for the necessary rearrangements of the bonds between the carbon atoms.

THE SYNTHESIS OF MACROMOLECULES

So far we have been discussing the macromolecules, or polymers, which occur ready-made in nature. Although the chemist may surmise, he cannot be entirely certain just how these large molecules are built up in nature. However, over the past half-century, chemists have become very proficient in producing synthetic polymers from a wide variety of possible monomers. It is from these processes that there have arisen all the new and varied synthetic rubbers that we know today.

In order to form a polymer molecule, it is, of course, necessary to find a way in which individual small molecules may join together in large numbers. This process is, for obvious reasons, called *polymerization*. There are a number of ways in which this process can be effected, but these can all be broadly classed under two main types of chemical reactions. One of these is known as *addition polymerization*, since it involves a simple addition of monomer molecules to each other, *without the loss of any atoms* from the original molecules. The other type is called *condensation polymerization*, since it involves a reaction between monomer molecules during the course of which a bond is established between the monomers, but some of the atoms present are lost in the form of a by-product compound. In this case, then, the polymer molecule is a *condensed* version of the original monomer molecules which reacted.

Addition Polymerization

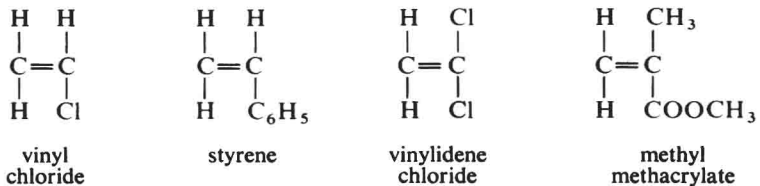The simplest example of addition polymerization is the formation of polyethylene from ethylene. This can be shown by means of the following molecular structures:
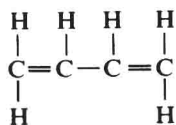
<div align="center">

monomer

$$
\begin{array}{cc}
H & H \\
| & | \\
C & = C \\
| & | \\
H & H
\end{array}
\qquad
\left[
\begin{array}{cc}
H & H \\
| & | \\
-C & -C- \\
| & | \\
H & H
\end{array}
\right]_n
$$

ethylene (gas)   polyethylene (flexible plastic)

</div>
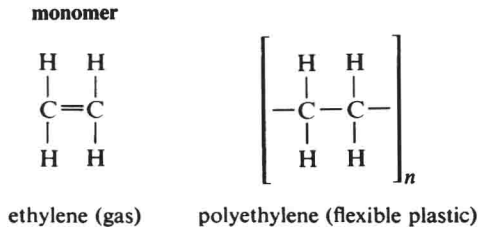
It can be noted that, in the ethylene molecule, after due regard is given to the requirements of valence, there is a ''double bond'' between the two carbon atoms. Furthermore, to cause polymerization, *one* of these two bonds must *open* and become available as *two bonds*, ready to unite with similarly available bonds from adjacent ethylene molecules. For this reason, ethylene is one of the compounds known as ''unsaturated,'' due to the presence of this extra bond between the carbon atoms, a bond which can be ''saturated'' by bonding to *two* other atoms, carbon or otherwise. This makes it possible for an ''unsaturated'' molecule to form a long-chain polymer molecule, as shown.

The well-known line of ''vinyl'' and ''acrylic'' polymers in the plastics and fibers field are all based on this activity of the carbon—carbon double bond. As a matter of fact, the term ''vinyl'' is a generic chemical name for this bond. The following monomers are the starting materials for the better-known polymers in this field, as the names will indicate.

<div align="center">

$$
\begin{array}{cc}
H & H \\
| & | \\
C & = C \\
| & | \\
H & Cl
\end{array}
\qquad
\begin{array}{cc}
H & H \\
| & | \\
C & = C \\
| & | \\
H & C_6H_5
\end{array}
\qquad
\begin{array}{cc}
H & Cl \\
| & | \\
C & = C \\
| & | \\
H & Cl
\end{array}
\qquad
\begin{array}{cc}
H & CH_3 \\
| & | \\
C & = C \\
| & | \\
H & COOCH_3
\end{array}
$$

vinyl   styrene   vinylidene   methyl
chloride   chloride   methacrylate

</div>

A somewhat more complex form of addition polymerization occurs with the unsaturated monomers of the ''diene'' type. These differ from the vinyl monomers in possessing *two* double bonds. An important and typical diene is *butadiene*, which forms the basis of the most important synthetic rubber today. The structures of the monomer and polymer are shown below.

$$
\begin{array}{cccc}
H & H & H & H \\
| & | & | & | \\
C=C & -C & =C \\
| & & & | \\
H & & & H
\end{array}
$$

Butadiene
(gas)

$$
\left[
\begin{array}{cccc}
H & H & H & H \\
| & | & | & | \\
-C & -C & =C & -C- \\
| & & & | \\
H & & & H
\end{array}
\right]_n
$$
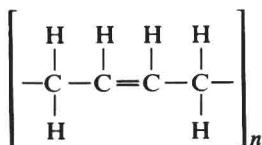
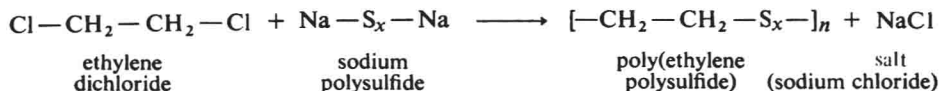Polybutadiene
(a rubbery solid)

The similarity between butadiene and isoprene is immediately apparent. Isoprene is actually the same as butadiene, except for the presence of a "methyl" group (CH_3) on one of the carbon atoms, instead of a hydrogen atom. As a matter of fact, isoprene has the chemical name 2-methyl butadiene.

It can be seen at once that when a diene is polymerized, the polymer obtained differs in one important respect from the vinyl polymers, viz., it still contains a *double bond* in each unit of the chain. This is a natural outcome of the fact that the monomer has *two double bonds* at the outset. The residual unsaturation in these polymers plays a very important role in the process of vulcanization, which will be discussed later. It is quite obvious, however, from the foregoing discussion, that the presence of these double bonds in the polymer makes it possible for the latter to react further with agents, like sulfur, which can add to these available double bonds, and actually form crosslinks between adjacent chain molecules.

Condensation Polymerization

Polymers made by a condensation reaction are not as important in the rubber field as the addition polymers discussed above. However, there are one or two types which are of some importance. One of these is the class of polymers known as polysulfide polymers, and bearing the trade name of Thiokol. This was one of the first synthetic rubbers developed in the United States, as an oil- and solvent-resistant elastomer. Various grades of this material are prepared using variations in starting materials, but the following will illustrate the process:

$$
Cl-CH_2-CH_2-Cl \; + \; Na-S_x-Na \; \longrightarrow \; [-CH_2-CH_2-S_x-]_n \; + \; NaCl
$$

ethylene   sodium   poly(ethylene   salt
dichloride   polysulfide   polysulfide)   (sodium chloride)

where $x = 2 - 4$.

The above equation shows that this polymerization proceeds by means of the reaction between the sodium (Na) atoms and the chlorine (Cl) atoms, which combine to form salt (NaCl). This results in a bond being formed between the sulfur and carbon atoms, and a long-chain molecule is thus formed. Here the

salt is the by-product of the condensation reaction and is not included in the polymer chain. In all such condensation reactions, provision must be made to remove such by-products in order to permit the reaction to proceed smoothly and to avoid contamination of the polymer. In the above case, the salt is conveniently removed by performing the reaction in the presence of water, which dissolves the salt but not the polymer.

THE PHYSICAL BEHAVIOR OF POLYMERS

Up to this point, we have discussed the basic principles involved in the synthesis and structure of polymers, and it would therefore be appropriate to consider in more detail the individual rubber polymers with which the technologist is concerned. However, before doing so it would seem highly desirable to consider the special features which make it possible for polymers to have their unique physical properties. We have seen how these macromolecules are composed of the same kinds of atoms as ordinary "chemicals," and are distinguished only by their enormous size. How does this difference in size convert a simple *chemical* into a strong, tough, durable *material*? That is indeed a question which scientists have been studying with a good deal of interest.

The most reasonable answer to the above question may be obtained by considering the two following aspects, viz., the type of forces which act on atoms and molecules in general and the structure and behavior of an individual polymer molecule.

Interatomic and Intermolecular Forces

We have already seen that there are electromagnetic forces operating between atoms, i.e., "valence" forces that bind atoms together. These forces, operating as they do at relatively short ranges, are very powerful indeed, so that a considerable amount of energy is required to break up a molecule of a compound. This is evident from the fact that high temperatures are usually necessary to decompose substances. The physical strength of interatomic bonds can best be exemplified by considering the basis for the strength of metals and minerals. It is generally agreed that such materials do not consist of molecules at all but contain a three-dimensional crystalline structure of atoms bonded to each other by the powerful valence forces mentioned above. Hence, to rupture the metal or mineral it is necessary to actually break these valence bonds, and this usually requires forces of many thousands of pounds per square inch.

On the other hand, a consideration of the forces operating *between molecules* soon shows that these are very much smaller than the interatomic forces. Hence it can be stated that those substances where atoms exist in small groupings, i.e., molecules, are either liquids or weak solids, since the intermolecular bonds are

very weak. It is well-known that the "states" of matter depend on the balance between the intermolecular forces and the heat energy of the molecules, as indicated by temperature. Thus heat tends to make atoms or molecules move faster, i.e., gives them a greater kinetic energy, while the intermolecular forces pull them closer together and tend to restrain their motions. This is the distinction between gases, where the intermolecular forces are far too weak to overcome the kinetic energy of the molecules, and liquids or solids, where the opposite is the case. There is a further distinction: between liquids, which flow because these forces are too weak to hold the molecules firmly in place, and true solids, where such molecules (or atoms) are held in a rigid pattern, i.e., crystals.

Structure and Behavior of Macromolecular Chains

In this regard, the behavior of macromolecules is further influenced by their long-chain character. Although the chemical formulas shown thus far for these molecules indicate that they are very long chains, they do not show that the chains are *flexible* by virtue of the ability of the chain carbon atoms, held together by single bonds, to *rotate* around their axis. Hence each macromolecular chain can be expected to be capable of twisting into various convolutions. Depending on the temperature, therefore, it could be expected that these chains would be in a constant twisting motion and that they would thus be badly entangled with each other. In such a disordered state, if the intermolecular (interchain) forces are not very strong, the polymer could be considered to be a *liquid*, but a very *viscous* liquid because of the long-chain, entangled state of the molecules. In fact, such a material would be so viscous as to have the appearance of a solid, i.e., an *elastic* solid or a rubber.

The reason for the "rubbery state" is, of course, that any deformation will tend to "straighten out," or uncoil, the entangled mass of contorted chains, and these will tend to coil up again when the restraining force is released. Thus the elastic retractive force is really due to the violent contortions of the long, flexible chains.

It should be remembered that the long-chain character of polymer molecules does not make it impossible for them to form crystals, just as small molecules do. However, as in the case of simple compounds, this crystallization will occur only if the intermolecular (interchain) forces are strong enough to overcome the kinetic energy of the contorting chains. This can happen in two ways, i.e., either the chain atoms, or groups of atoms, can exert very powerful attractive forces, and/or the chain sections can "fit together" so well that they can come close enough for the interchain forces to take over. The only real distinction between the crystalline, solid state of simple compounds and polymers is that the crystallization is much less complete in the case of the latter. Thus, whereas

sugar can be said to crystallize almost "perfectly," polyethylene is only a partly crystalline solid. This is because, as is obvious, it is very difficult, if not impossible, to form "perfect" crystals from a mass of entangled chains.

A large number of polymers exist as partly crystalline solids at normal temperatures, of which polyethylene is an excellent example. The reason this well-known, flexible plastic material is opaque is, in fact, due to the presence of very fine crystallites which refract and scatter light. These crystallites also "tie together" and restrict the motions of the polymer chains so that the latter lose their elastic character. Hence the material has only limited elasticity but retains its flexibility, as in the case of polyethylene and other flexible plastics.

The ability some macromolecular chains have of crystallizing under the right conditions plays a dominant role in the properties of two types of materials: *fibers* and *rubbers*. Thus, in the case of a fiber-forming polymer such as nylon, the polyamide chains can exert powerful attractive forces toward each other. Hence, when these chains are oriented, e.g., by cold drawing, the interchain forces are strong enough to cause the oriented chains to crystallize into elongated crystals containing bundles of rigid chains, i.e., *fibers*. These forces thus act to give the fibers very high strength, and the fiber "crystals" cannot be melted again even at temperatures high enough to cause chemical decomposition.

In the case of the rubbers, the macromolecular chains may or may not be capable of crystallizing on stretching, depending on their chemical structure and regularity. Thus natural rubber, which has a very regular chain structure, can undergo a high degree of crystallization on stretching and therefore becomes a "fiber" at high elongations. This results in a high tensile strength. However, the interchain forces which cause such strain-induced crystallization are not sufficiently powerful to maintain this fiber-like structure once the applied force is removed, so that the fiber-like crystals "melt" and the rubber chains retract to their normal configuration. This phenomenon of "temporary crystallization" therefore plays a very important role in controlling the mechanical properties of a rubber, especially strength, and these properties vary greatly depending on whether the polymer does or does not undergo crystallization on stretching.

It is important to note at this point that the ability of an elastomer to crystallize on stretching, advantageous for strength, also means that the elastomer will crystallize, at least partially, at some low temperature *without stretching*. This temperature is referred to as its *crystal melting point*, T_m, and is, of course, generally below room temperature; otherwise the rubber will crystallize on storage and harden considerably. As a matter of fact, this can sometime happen to natural rubber, whose T_m is just below normal ambient temperatures.

At lower temperatures, elastomers also exhibit another phenomenon, known as the "glass transition." This occurs regardless of whether or not the polymer is capable of crystallization, and results in a transformation of the elastomer