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Physics and the Behavior of High Polymers

By *Frank K. Schoenfeld*

A PHYSICIST is concerned with the properties of matter and the attendant energy fluxes, but so are many chemists, engineers, and applied mathematicians. Primarily, a physicist tries to discover the simplest, most general relationships to explain phenomena of scientific interest, but so do scientists in other fields.

It is really a way of thinking that distinguishes the physicist—a quantitative approach based on faith that there is an underlying concept; a unifying principle; an ultimate controlling factor. Since the fields of classical physics have been largely abandoned by the physicist, his habit of thinking is greatly missed in many of our industrial laboratories.

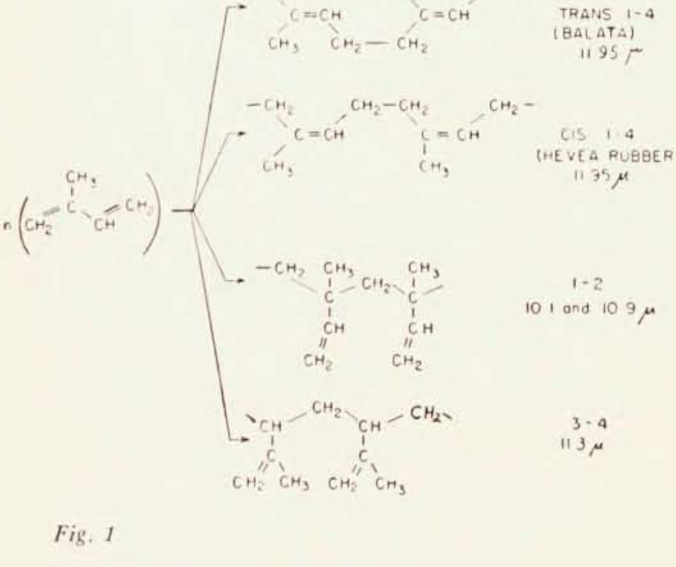

Fig. 1

Before I launch fully into my subject, I should like to address a brief, special appeal to physics educators. Show young people the fun, the beauty, the opportunities in the entire field of physics. Do this and we shall overcome our present lack of trained minds needed to improve and secure the future of those industries based on structural materials. The imaginations of young people of career-choosing ages are most likely to be stirred when you talk about the scientific areas that interest you. In my own case, I confess a special interest in the field of high polymers.

During the last decade there has converged on this group of man-made materials an array of scientific, engineering, and artistic talent as diverse as the technologies of materials polymers are replacing. In no other field has intelligent effort been rewarded with more striking or steadier advances.

Even the less informed layman is aware of synthetic rubbers, miracle fibers, plastics that replace leather or package his food. He is less aware that high polymers are the basic ingredient in new water-based paints, adhesives, glazing compounds, textile, paper, and leather finishes, medicinal and cosmetic aids. Still fewer realize that high polymers are invading the structural materials field, competing with lumber, glass, light metals, ceramics, and even iron and steel. High-polymer industries are among the fastest growing in the western world, and many scientists are deriving pleasure from intellectual achievements involved in developing these materials.

High polymers are made by chemists. The problems of creating such complex materials and then reproducing them are not small, but let us leave these problems entirely to the chemist.

High polymers are useful primarily for their impor-

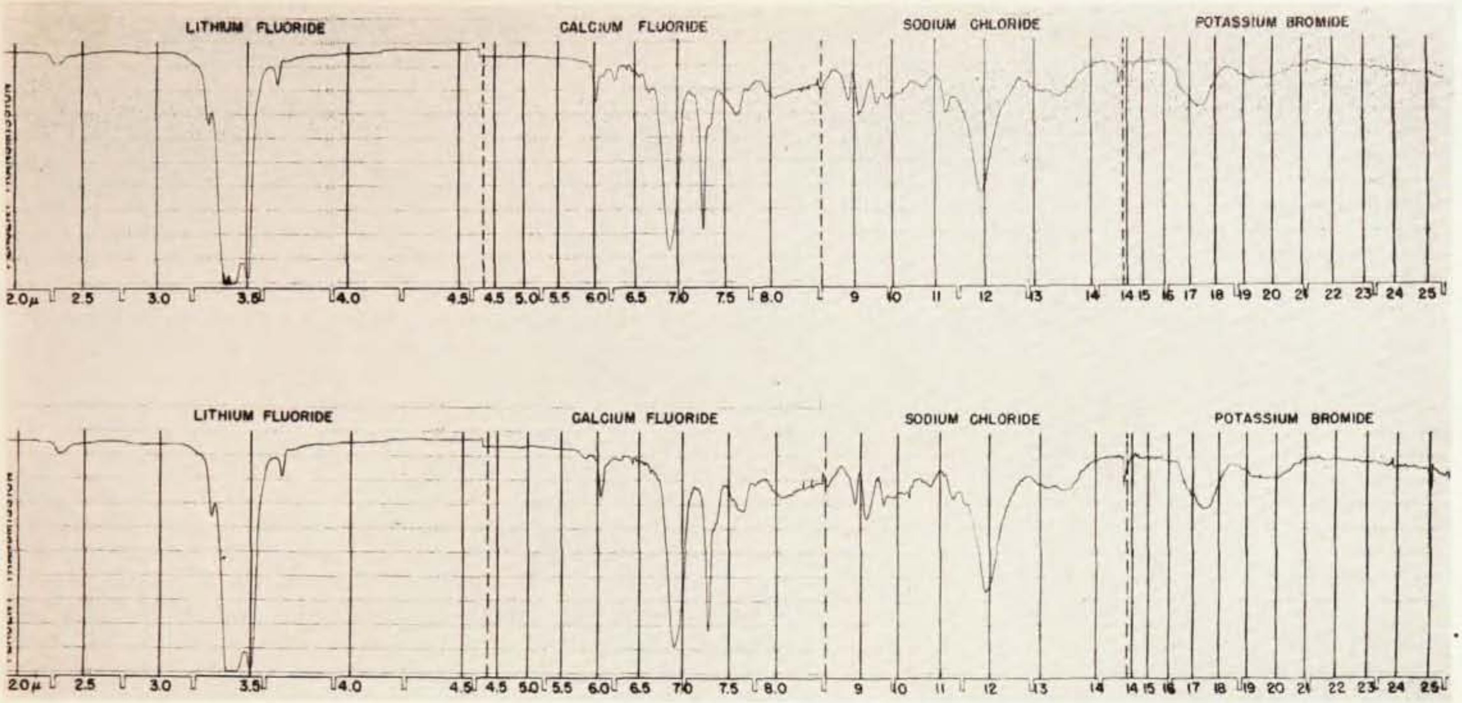

Fig. 2. Infrared absorption spectra, films on potassium bromide disks: (top) protected sample of Ameripol SN; (bottom) purified Hevea rubber.

tant physical properties; that is, for their strength, friction, rubberiness, electrical resistance, elasticity, transparency, and dimensional stability. What are the fundamental relationships between the chemical structures of polymers and their physical properties? Here is an area that might be called a branch of solid-state physics of challenging complexity.

In the natural occurring high polymers, or in the products of the chemists, thousands of atoms are linked in a more or less regular way to form gigantic molecules. Arrays of these molecules produce the rubbers, plastics, and fibers of commerce. Slight changes in molecular architecture make significant changes in physical properties and in commercial acceptance.

The polymer scientist has made some very important advances in clarifying the relationships between a polymer molecule's structure and how it will behave in a given environment. Let me illustrate with some polymers of the unsaturated hydrocarbon isoprene.

The four isomeric forms of polyisoprene are shown in Fig. 1. Since head-to-tail orientations must be considered because of the asymmetry of the isoprene molecule, there are eight possible arrangements that can occur in polymerized isoprene.

Here is a sample of cis 1,4 polyisoprene, the elastic polymer produced by the Hevea brasiliensis tree. It is the familiar rubber of commerce. Here is a strip of trans 1,4 polyisoprene, a hard resin produced by the Mimusops globosa tree. It is balata, most familar to you in the cover of your golf ball. Here is a mixture of polyisoprenes, a gunk produced by a member of the Homo sapiens family. These materials with such widely differing properties are chemically similar. They have the same empirical formula and roughly the same molecular weight. Their configuration in space differs.

Our friend Homo sapiens didn't compete too successfully in this illustration. However, within the past few years exciting discoveries have been made which greatly increase the importance of polymer structure studies. Catalysts have been found which force the monomer to take up a specific orientation within the molecule.

One of the most spectacular of these was the discovery in the B. F. Goodrich laboratory of how to make polymers which are identical to the natural rubber and natural balata molecules. It is hard to imagine a pinch of a chemical which can marshal the reactive forces so as to make most or all of the thousands of monomers add in such a regular manner.

But it does happen. Figs. 2 and 3 show both the infrared and the x-ray diffraction photographs of natural rubber and a synthetic rubber made by a directive catalyst. These should convince the physicist that nature has been duplicated.

To polymer people the resultant physical properties are even more convincing. We cannot tell the two rub-

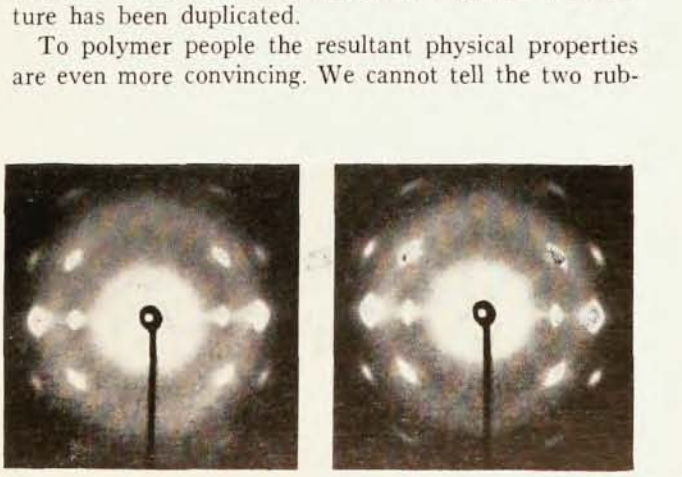

Fig. 3. X-ray diffraction patterns of Ameripol SN (left) and Hevea (right).

bers apart. This discovery was the long-sought goal in the field. Achievement of this goal was helped by the fact that we had a natural template for purposes of comparison. To do this detective job for a new polymer is more difficult. We have learned to do this with polyethylene, polymethylmethacrylate, and polybutadiene. There is much more to do.

Most of our common polymers are based upon carbon linkages of one kind or another. The properties of this carbon-to-carbon bond directly restrict the conditions under which we can use the polymeric product. For example, its stability at high temperature, or its chemical reactivity in oxidizing atmospheres is often limited. Hence, we would like to find other linkage systems that not only have some of the same polymer-forming properties, but have high-temperature stability. These bonds should not be affected or broken by thermal agitation. Today this need is one of the most pressing problems in developing improved materials for national defense hardware.

The physical behavior of high polymers is described by the laws of classical physics. From one point of view, the complete physics of the system is known, with application the only remaining problem. Physicists who take this point of view abandon the field to the physical chemist and engineer.

To those of us deep in the field, there is intellectual challenge for the best-trained physicists. We are troubled with many problems, not the least of which is that of controlling all the parameters which affect the absolute value of the physical constants with which we must deal.

These quantities, so important in use, are more dependent on temperature and time scales than other materials. The high polymer, when tested once, is not the same material in a second test. Admittedly, after a large number of tests or a large number of cycles of behavior, an equilibrium or quasi-equilibrium steady rate can be reached. Pause, or interrupt the steady cycles, and the next set of tests again will be different. This time-dependent phenomenon is intimately related on the molecular scale to what we know of the kinetic behavior of polymers.

The theory of the solid state of polymer materials has come a long way in the past decade, but it is still very rudimentary. By picturing the polymer network as a group of freely coiling, independent chains, it is possible to apply statistical mechanics and deduce the static properties of rubbers. The force of retraction is, then, essentially an entropy effect. This kinetic theory of elasticity has been a powerful tool for much research work, but is woefully inadequate to explain many situations.

In general, the freedom of rotation assumption is invalid; large deformations introduce internal energy changes; chain architecture is not simple. We still are waiting for the enterprising physicist who will be able to overcome the mathematical obstacles to a really useful description of the "solid-state" physics of polymers.

The physical properties of products can often be predicted if we know the physical properties of the materials that go into those products. Our polymeric materials fall into the class of partial mysteries. We don't know their properties sufficiently well. Products made from polymers, then, become those in which engineering and art of making products have advanced beyond the knowledge of the components used therein. The product leads the theory and science follows the art. A few examples might be considered.

Ours is an automobile economy. If we consider the tire as a toothless gear for transmitting high-torque couples, we are looking at a common object in an unusual way. We are looking at a pneumatic vessel with stressed skin construction of toroidal shape, that is anisotropic in every direction, yet still has its axis of symmetry. The mechanical properties of the tire are different in the radial, the tangential, and the circumferential sense. The tire has important elastic and stability problems and characteristics in each one of those dimensions.

The V-belt is a similar mechanism for transmitting torques as a toothless gear, but, of course, the mechanism of operation is different.

The fabrics we use represent another product in which art has led science. The geometry of the fiber, the shape of the yarn, the assembly of the fibers into yarns, the weave into the cloth, all change the properties of the fabric. The physics of the assembly is important. Cloths or fabrics having very different properties can be made from the same fiber merely by changing the nature or geometry of the assembly. Our problems that urgently need an understanding mind are multiplied when we combine the fabric with rubber.

I could continue to tell you about the many problems of material flow and heat transfer during the manufacture of consumer and industrial goods from high polymers. However, I hope by now that I have made clear that there is real scope for the competent physicist in the polymer industries.

In recent years much of the progress in the field of high polymers has stemmed from the stimulation of theoretical approaches. Now that the chemist can produce crystalline polymers, even more complex problems are presented. To make significant progress, we require scientists who are not content with empirical relationships or the mere lumping of unknown structural effects into a collective function. Rather, we require individuals dedicated to the tasks of unraveling the secrets of these mathematically useful parameters.

First as a polymer chemist and then as an administrator, I have followed closely the accomplishments of many workers in this field. I can only conclude that the science of high polymers offers to physicists problems as challenging to the intellect, as important to the material well-being of mankind as those in any other scientific field.

I am grateful to the Institute for the opportunity to discuss this problem and for providing this excellent forum for the discussion.