

Neutron scattering from polymers

The great difference in scattering power between a deuterated polymer and its hydrogenous counterpart allows one to determine the shapes and movements of polymers in solutions, melts, gels and crystals.

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Some years ago, one of our mentors expressed the desire to "color polymer molecules red" so that one could follow them in a solid and see how they arrange themselves and how they move among similar or different molecules. As we will see in this article, the excitement today over the application of small-angle neutron scattering to the study of polymers lies in the possibility of fulfilling his wish to understand the conformation and dynamics of polymer molecules.

The structural information we get from conventional light and x-ray scattering is a difficult-to-separate mixture of contributions from individual polymer molecules and from groups of polymer molecules. With the conventional techniques, we can find the single-molecule scattering function—the parameter that tells us the geometry of individual polymer molecules—only by studying the molecules in very dilute solution.

In 1972 this situation changed as small-angle neutron scattering brought us a convenient way of "coloring" a molecule or even part of a molecule. This labeling is made possible by the fact that the isotopes of an atom, particularly those of hydrogen, differ greatly in their abilities to scatter neutrons. The small-angle neutron-scattering technique is particularly useful in polymer science (figure 1) and biophysics (as Peter Moore discusses in

his article on page 62), because most polymer and biological molecules contain hydrogen. Substitution of hydrogen by deuterium is not a formidable task, and in principle does not change the chemical nature of a molecule significantly.

In addition to its role in this isotope-labeling technique, which allows us to focus on particular molecules in scattering experiments, neutron radiation offers other advantages. With thermal or cold neutrons, one can use time-of-flight, back-reflection or spin-echo techniques to determine the dynamic scattering function, or structure factor, $S(Q,t)$, which is a measure of how the configuration of the polymer or other molecule under investigation changes with time. Thermal or cold neutrons in the wavelength range of 5 Å to 15 Å transfer an amount of momentum Q that is convenient for studying polymers. The magnitude of the momentum transfer is $(4\pi/\lambda) \sin \theta/2$, where θ is the scattering angle and λ is the neutron wavelength. With a neutron wavelength of 10 Å, for example, Q^{-1} , which is the length of the "molecular probe," covers a range of 5 Å to 500 Å when the scattering angle θ ranges from 300 milliradians to 3 milliradians. The sizes of most polymer molecules lie within this range of probe sizes. Because small-angle experiments usually use neutrons of wavelengths longer than twice the spacing between the planes of atoms in most crystals, there is usually no interference due to diffraction or double diffraction from the sample. Also, because of the relatively large apertures used and the strong

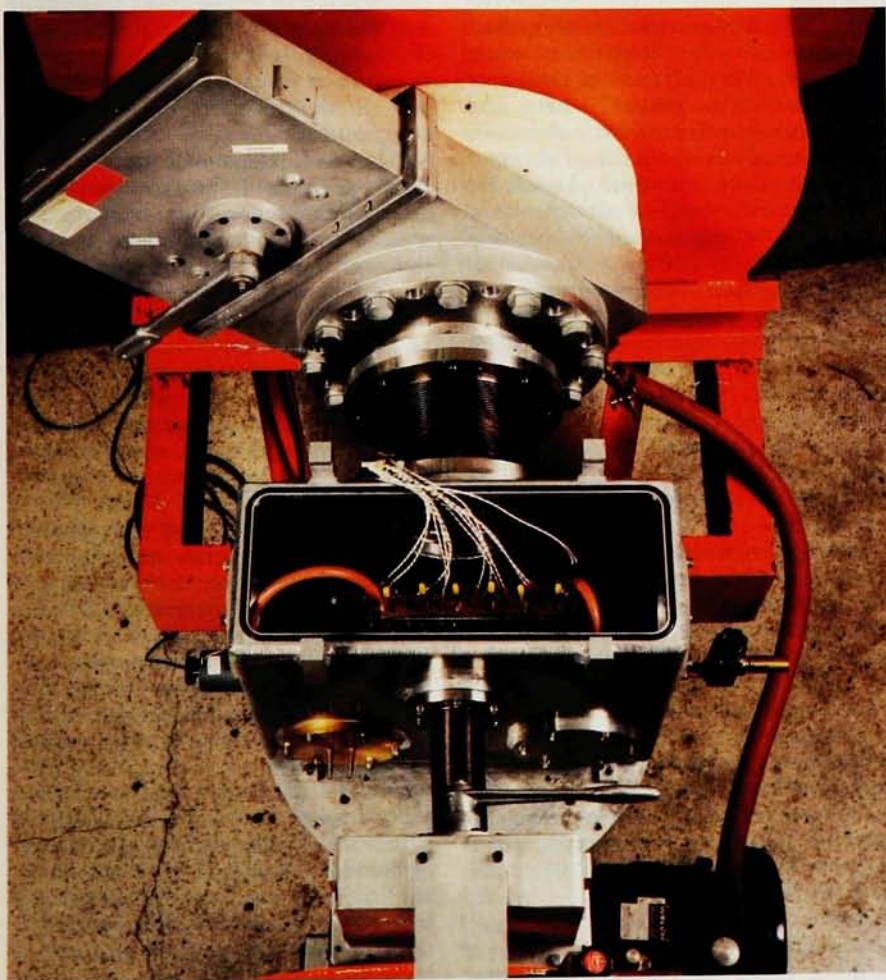
scattering of hydrogen and deuterium, interference due to dust and other contaminants is negligible.

Development of the technique

Historically, light or x-ray scattering was used to study isolated polymer molecules in dilute solution, so it was natural that polymer physicists looked at dilute polymer solutions in the early days of small-angle neutron-scattering experiments. Thus, in the early 1970s, Henri Benoit and his colleagues in a Strasbourg-Saclay-Collège de France collaboration, and Rudolf G. Kirste and his colleagues in a Jülich-Mainz collaboration, demonstrated that one can determine the radius of gyration R_g of polymer molecules in solution using small-angle neutron scattering. A molecule's radius of gyration is a good measure of its spatial extent.

Immediately after that, these groups began measuring polymer dimensions in the bulk by adding a very small fraction of deuterium-labeled polymers to regular hydrogenous polymer matrices. In a simple model, the polymer molecule is a series of connected segments laid out in a random-walk pattern, as indicated in the figure on page 79. (See also PHYSICS TODAY, November, page 48). According to this model, the straight-line distances between the ends of polymer molecules should follow a Gaussian distribution, and the radius of gyration of a molecule should be proportional to the square root of its molecular weight. By measuring the single-molecule structure factor, which Peter Debye had calculated based on this model, the Benoit and Kirste

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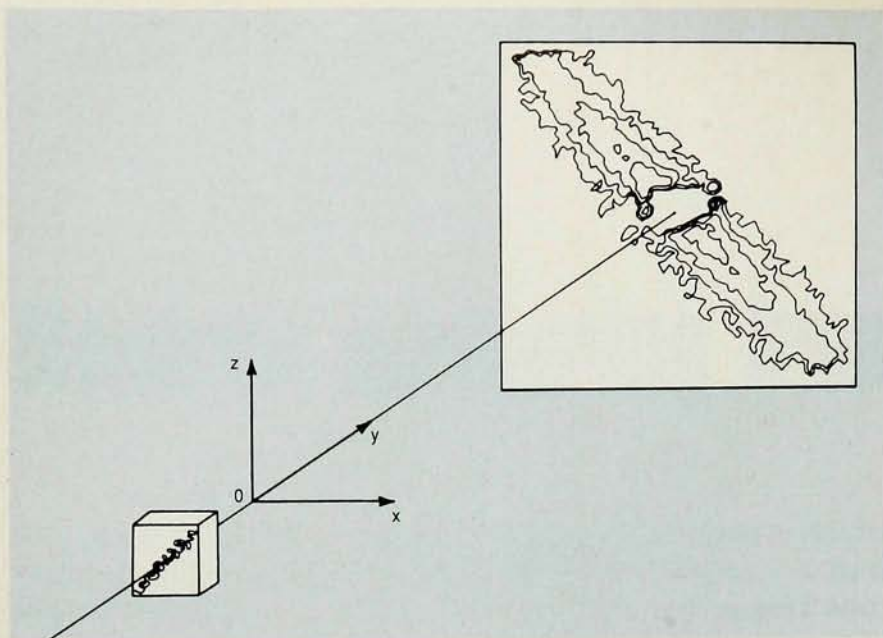
Chamber for holding polymer samples in a neutron beam at NBS small-angle neutron-scattering facility. This device holds six cells (the tubes with the yellow caps) containing polymer solutions. A computer moves the cells into the neutron beam and controls the temperature.

Figure 1

groups verified the Gaussian distribution of end-to-end lengths and the square-root relationship of radius of gyration and molecular weight. This confirmed Paul J. Flory's longstanding prediction that a polymer chain in the bulk amorphous state has the geometry of a random walk, or "Gaussian coil."

Scattering experiments measure the intensity of scattered neutrons as a function of the momentum transfer Q . For a given instrument, this intensity is directly proportional to the structure factor $S(Q)$. The structure factor is the Fourier transform of the function that describes the correlation of the spatial distributions of polymer molecules. The Fourier inverse of the structure factor gives information about the spatial distribution of polymer molecules.

Polymer scientists soon realized that they could measure the single-chain scattering function in solutions with a high concentration of deuterium-labeled polymers, despite considerable overlap and interpenetration of the labeled polymers, as long as the labeled polymers have the same size and distribution as the matrix polymers. At high polymer concentration, one can write the scattering function $S(Q)$ as the sum of two terms, one of which is the single-chain scattering function. The second term includes contributions from all of the chains in the system, regardless of their "labels." For homogeneous amorphous systems or solutions, this second term normally is small, and one can eliminate it by carrying out experiments at two different concentrations of labeled polymer. This high-concentration labeling method has made it



Geometry of a small-angle neutron-scattering experiment and an isointensity plot for scattering from a polystyrene sample oriented by elongation. The effective draw ratio is 4.2, with the elongation direction of the specimen at 45° in the x - z plane. Figure 2

possible to do many important experiments even at moderate-flux facilities.

Work on miscible multicomponent systems has also advanced. Through the use of linear response theory and the random phase approximation, theorists have calculated the scattering function for such systems. The approach of Pierre-Gilles deGennes for the simple case of two components A and B gives the following expression for the scattering function $S(Q)$:

$$1/S(Q) = 1/[\phi_A N_A S_A(Q)] + 1/[\phi_B N_B S_B(Q)] - 2\chi$$

Here ϕ , N and S are a polymer's volume fraction, degree of polymerization and single-chain scattering function, and χ is a measure of interaction between monomer A and monomer B. We will see later that this equation, or its equivalent as developed by others, plays an important role in the study of binary systems and block copolymer systems, especially in the area of critical fluctuations and phase separation.

Studies in dilute systems

Scientists have studied many aspects of polymers in dilute solutions by using one or a combination of the experimental techniques described above. Here we discuss three kinds of studies:

Chain dimension. Scattering experiments involving small momentum transfer show that the same Gaussian distribution as in the bulk state occurs for isolated chains at the θ temperature—the temperature at which the binary interaction between different monomers of a given polymer chain vanishes. Other neutron-scattering experiments involving momentum transfer have measured the effect of self-excluded volume on the shape of poly-

mer chains. Self-excluded volume is the volume not available to segments of a polymer chain because other segments of that chain already occupy the space. The self-excluded-volume effect is a collective effect that causes chain expansion. For polymers of relatively small molecular weight, where end effects become significant, physicists have labeled various parts of polymer chains to study the effect of excluded volume on individual monomer units as a function of the monomer's position along the chain and as a function of total chain length. The results are well described by perturbation theory.

Scaling. Polymer scientists have made many attempts to measure the temperature dependence of the excluded volume by studying the way the scattering function $S(Q)$ depends on the momentum transfer Q in the so-called intermediate- Q region. This region is defined by $l < Q^{-1} < R_g$, where l is the "statistical segment length," which can be viewed as the length of one step in the random-walk model of a polymer chain; the step length l is the length of a few monomers. Simplistically, the pairwise correlation function of monomers, which gives the probability that two monomers in a polymer chain are a given distance apart, can be approximated as the average number density of monomers n/r^3 , where n is the number of monomers in the polymer chain and r is the distance between the ends of the chain. Then

► for a Gaussian chain $r^2 \propto n$ and $S(Q) \propto Q^{-2}$

► for a chain with excluded volume $r^2 \propto n^{6/5}$ and $S(Q) \propto Q^{-5/3}$

► for a rod-like chain $r \propto n$ and $S(Q) \propto Q^{-1}$

► for a collapsed chain $r^{1/3} \propto n$ and $S(Q) \propto Q^{-3}$

One can easily obtain the Gaussian limit Q^{-2} by expanding the single-chain scattering function in terms of the product of momentum transfer Q and radius of gyration R_g and taking the limit in which the wavelength of the neutron probe is much less than the size of the molecule. This way of studying the Q dependence of scattering is used frequently, not only for problems in which the excluded volume depends on temperature and molecular weight, but also for problems in which the excluded volume depends on concentration. Such Q -dependence experiments are also used in crystallization and gelation problems.

In the high-momentum-transfer region where the probe length Q^{-1} is less than the statistical segment length l , the random-walk model of the polymer chain breaks down because the neutrons then probe the details of the chemical structure and the relationship between neighboring monomer units. Polymer scientists have calculated the detailed structure factor $S(Q)$ in this region by using a method known as the rotational isomeric state technique. This method takes into account the rotation of bonds, the lengths of bonds and the angles between bonds.

Selective labeling of polymers. Most early labeling studies used polymers in which all of the hydrogen atoms were replaced by deuterium. More recent studies have used polymers that are labeled either along a specific section of their contours or at a specific part of their component monomers. An exciting application of selective deuteration is to block copolymers. These are polymer molecules consisting of two or more chain parts composed of different monomer units. An example is the

two-block copolymer made up of styrene and isoprene monomers. Various groups have studied the effects of dissimilar blocks on the overall conformation of a single chain, and the nature of the ordering that might occur in concentrated solutions and in the bulk state. These studies often use the technique of contrast variation, in which a two-block copolymer with one deuterated block is dissolved in a solvent that is a mixture of hydrogenous and deuterated solvent molecules. By varying the fraction of solvent molecules that are deuterated, one can enhance or suppress each block's contribution to the total scattering as desired. Latex particles, which are a major ingredient of paint, have been partially deuterated and characterized with this technique.

Studies in dense systems

It is in the study of the conformation and viscoelastic properties of polymer molecules in semidilute, concentrated and bulk systems that small-angle neutron scattering has made its most important contributions. We will discuss five important examples.

Temperature and concentration scaling. The discovery that the problem of the self-avoiding walk and the problem of many mutually-avoiding chains are mathematically the same as the problem of magnetic systems (see *PHYSICS TODAY*, November, page 48) has led to an understanding of how the properties of polymer solutions scale with temperature and concentration.

One can visualize the physical picture qualitatively by the so-called "blob model." When we put more and more self-avoiding chains in a solution, eventually the sum of the volumes of all the polymer chains, measured as the vol-

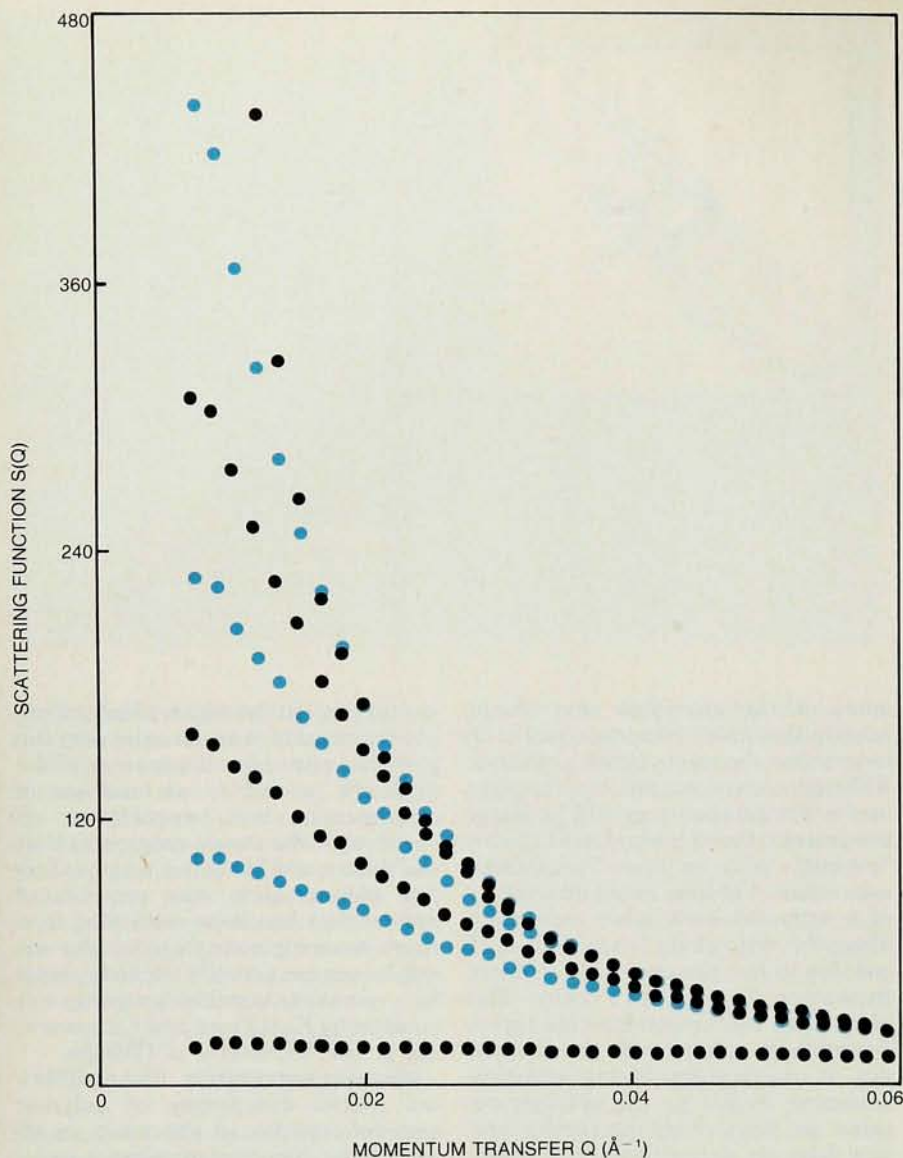
umes of the envelopes that would contain the chains, becomes equal to or larger than the total volume available. Although the concentration of the polymer in the solution may still be just a few percent, the coils may have to make "contact" with or even "penetrate" each other. The long-range interaction of a monomer with other monomers along the same chain is soon screened out due to the presence of monomers from other chains in the vicinity. The blob model uses a step-function representation to approximate this screening. It assumes that within a certain screening length ξ_C the polymer retains its single-chain properties and acts like an excluded-volume chain. The section of polymer chain within this screening length is called a "concentration blob." Beyond the screening length, the polymer molecule behaves like a Gaussian, or random-walk, chain.

Chain expansion due to self avoidance comes about less from monomers close to each other along a chain than from monomers farther apart on the chain. This leads to a competing "temperature blob" distance ξ_T , within which the chain behavior is Gaussian. This distance becomes longer as the temperature approaches the θ -point. Hence, at a given temperature and concentration, a polymer chain may exhibit Gaussian-like behavior at long distances (ξ above ξ_C) due to the concentration effect, excluded-volume behavior at intermediate distances (ξ between ξ_C and ξ_T) due to both concentration and temperature effects, and Gaussian behavior again at short distances (ξ below ξ_T but larger than l). Experimenters have looked at various systems to study the corresponding $Q^{-5/3}$ and Q^{-2} behavior of the scatter-

ing function in the region of intermediate momentum transfer, and also the predicted power-law dependence of the distances ξ_C and ξ_T as functions of concentration and temperature, respectively. We should emphasize that the "blob model" is only a very qualitative picture of a very complicated system that has been calculated in a much more rigorous fashion. For example, one can identify the blob length in a recent renormalization-group calculation by Karl Freed and his coworkers at the University of Chicago.

Dynamics and diffusion. The equilibrium spatial distribution of polymer segments mentioned above has an effect on the dynamics of polymer molecules and segments. The most important quantities in dynamics are the diffusion coefficient and its dependence on temperature and concentration. Unfortunately, the spin-echo technique, which offers the best possibility for studying polymer dynamics at small angles, does not yet have good enough frequency resolution or low enough momentum for studies of polymers with reasonably large molecular weight.

Still, spin-echo and back-reflection experiments using intermediate and high momentum transfer have shed some light on the way the dynamics of polymer chains depend on temperature and concentration. Experimenters have looked at the dynamic scattering factor $S(Q, t)$ and its initial decay rate $\Omega(Q)$, which is defined as the time rate of change of the log of the dynamic structure factor, for various polymer-solvent systems in the dilute and semidilute regions. Theorists predict that the dynamic structure factor obeys an unusual fractional power law: $S(Q, t)$ is proportional to $\exp(-t^{2/3})$ for systems



Scattering function at a sequence of temperatures for a deuterated polystyrene-polyvinylmethylether sample of weight ratio 60/40. From top to bottom, the curves represent data taken at the following centigrade temperatures: 160, 155, 150, 145, 135, 120 and 25. The polymer blend exhibits a lower critical solution temperature, below which the blend contains a single-component phase. The critical composition for this system is 30% by weight deuterated polystyrene. Away from this critical composition, the spatial extent of fluctuations in concentration, as extracted from the scattering-function curves, shows a divergence proportional to $(T/T_s - 1)^{-1/2}$ as the system approaches the spinodal temperature T_s of 166°C. Figure 3

with hydrodynamic interaction, and to $\exp(-t^{1/2})$ for systems without hydrodynamic interaction. Thus far, attempts to measure this behavior at large t have lacked sufficient accuracy and range to characterize the degree of hydrodynamic interaction between monomers. However, physicists in England and Germany have observed the effect of hydrodynamic screening in which the effect of a monomer's motion on other monomers is damped out by intervening monomers. They saw the hydrodynamic screening indirectly by doing spin-echo experiments at intermediate momentum transfer to observe the transition of the initial decay rate $\Omega(Q)$ from Q^3 behavior, which corresponds to a system with hydrodynamic interaction, to Q^4 behavior, which corresponds to a system without hydrodynamic interaction.

Experiments at large momentum transfer have detected local segmental motion in polymers in a few systems. The theoretical interpretation of the

results is very model-dependent at this time, but it is clear that high- Q neutron scattering is just beginning to make its contribution.

The diffusion coefficient of a polymer molecule with large molecular weight is difficult to obtain from the measured dynamic scattering factor $S(Q, t)$, which is equal to $\exp(-Q^2 D t)$ at small momentum transfer Q . At this time the most successful method involves stacking alternating deuterated and hydrogenous polymer layers and observing the scattering factor increase as a function of time as the molecules diffuse into each other at elevated temperature and produce scattering contrast within the layers.

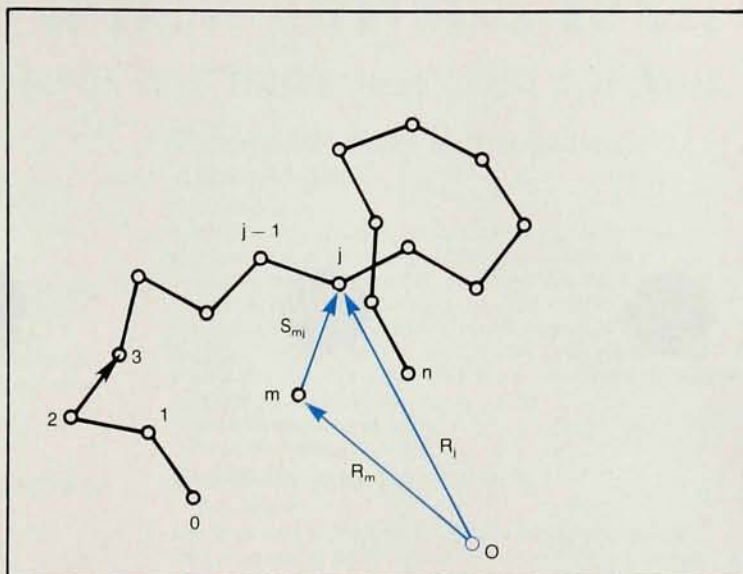
Gels, networks, amorphous polymers. Gels and rubbers, which are three-dimensional networks of polymer molecules, are important in polymer science as well as in biology. Vulcanized rubber, for example, consists of such networks in which molecules are linked together by chemical crosslinks. The

physical properties of the rubber depend upon the distribution of the crosslinking points.

It is common practice to determine the mean distance between such points by measuring the elastic modulus or the amount of swelling caused by solvents. Recent small-angle neutron-scattering experiments have given a detailed picture of both the disposition of the junction points and the deformation of polymer molecules upon macroscopic strain. Other small-angle neutron-scattering experiments have determined the inhomogeneity of the network upon swelling. The heterogeneity observed at small distances is evidently the result of a lower degree of swelling close to the crosslinking points, which restrict chain motion. Other recent small-angle neutron scattering measurements of technological importance include the characterization of epoxy resin, which forms the matrix of the increasingly used fiber-composite materials.

Figure 2 is a schematic representation of a small-angle neutron-scattering experiment on a sample of oriented polystyrene. The figure shows an iso-intensity contour plot from the sample, which was oriented by being extruded through a die at a temperature slightly above the glass transition temperature T_g , and immediately quenched to room temperature. The ratio of the length of the polymer sample after extrusion to the length before, called the effective draw ratio λ , is 4.2. The markedly anisotropic scattering pattern indicates that the polymer chains underwent an affine deformation in the draw direction—that is, it indicates that the molecular deformation was the same as

Polymer scattering model



In the schematic representation of a polymer molecule above, the center of mass m is located at the vector distance R_m from an arbitrary origin O . The j th monomer, which is located at R_j , has a scattering length of a_j . The scattering length is proportional to the square root of the scattering cross section. There are n monomers per polymer chain and p polymers in the system. With Q representing the momentum transfer upon neutron scattering, the density ρ of all the monomers in Fourier space is defined as

$$\begin{aligned}\rho &\equiv \sum_j a_j e^{iQR_j} \\ &= \sum_{m=1}^p e^{iQR_m} \sum_{j=1}^n a_j e^{iQS_{mj}} \\ &= \sum_{m=1}^p e^{iQR_m} \rho_s\end{aligned}$$

The Fourier-space density ρ_s is that of monomers from a single polymer.

the macroscopic deformation. Quantitatively speaking, in such a deformation $R_{\parallel} = R_0 \lambda$ and $R_{\perp} = R_0 \lambda^{-1/2}$. Here R_0 is the molecular end-to-end distance for the unstretched material; $R_{\parallel}$ and $R_{\perp}$ are the components of the polymer chain's end-to-end distance in the directions parallel and perpendicular to the draw. If the samples are heated above their glass transition temperatures, there is molecular contraction, and $R_{\parallel}$ and $R_{\perp}$ return to R_0 in a time characteristic of the molecular dynamics. A complete analysis of the scattering factor as a function of time serves to characterize the molecular dynamics over distances ranging from that of the entire polymer molecule to that of its individual monomer segments.

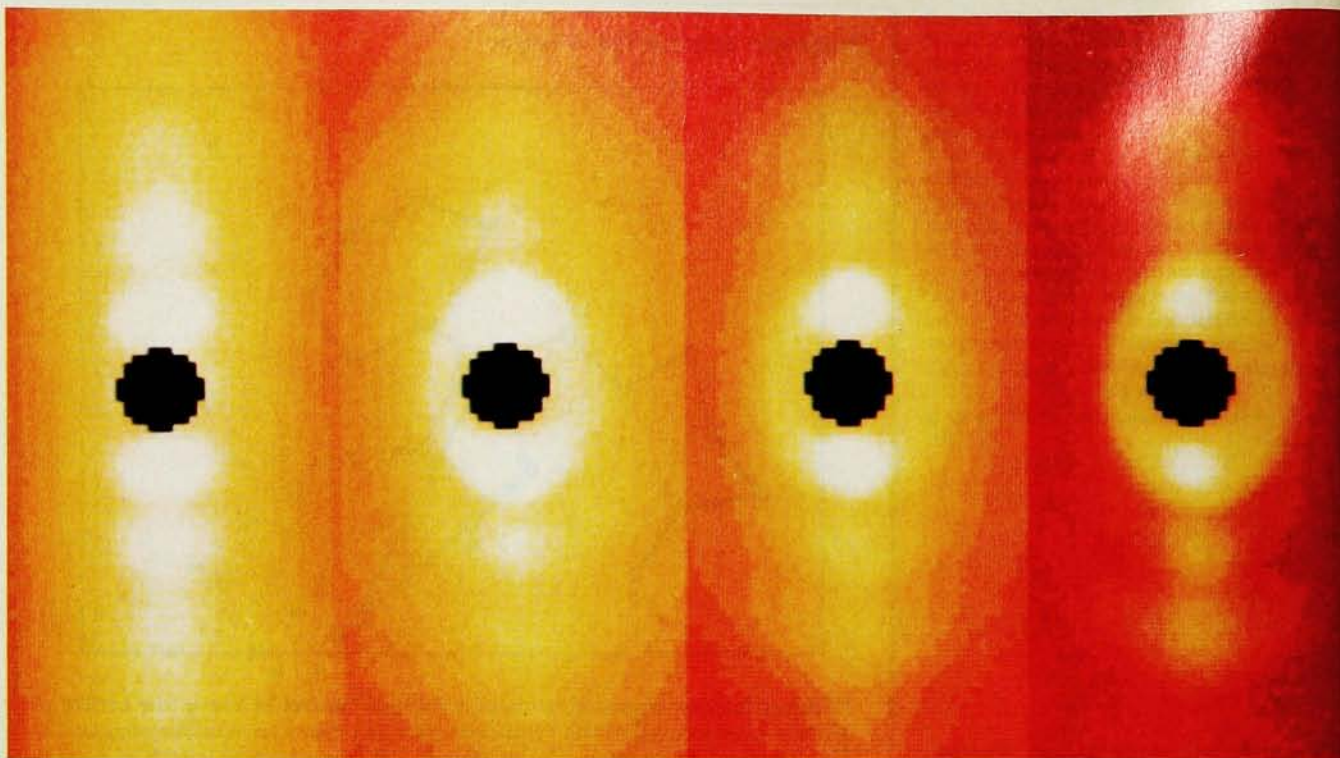
Rubber elasticity theory was originally based on what is now believed to be an oversimplified model of affine deformation of crosslinking points. Improvements in the model took into account fluctuations of the positions of the crosslinking points and the obvious constraint that chains cannot pass through each other during deformation. These considerations led to new predictions for the way the anisotropic scattering functions vary with elongation. Experimental tests of these predictions require the preparation of well-defined polymer networks in which a fraction of the chains are deuterated. The few experiments of this type performed to date have not had sufficient precision to give unambiguous results. Other experiments have monitored changes in the radius of gyration R_g and the scattering function $S(Q)$ as networks swell in solvent. The results disagree with existing theories, indicating a need for

refinements in models of swelling.

Phase-separated systems. Groups in the United States and Germany have used small-angle neutron scattering to measure the interaction between pairs of different monomer molecules in dilute and concentrated blends. Such studies are significant in view of the scientific importance of understanding critical phenomena and the increasing commercial interest in blends. The results from recent small-angle neutron-scattering measurements at low momentum transfer give many parameters that characterize blends of different polymers. The measurements and calculations tell us, for example, that in these blends the correlation length, which is the spatial extent of fluctuations in the concentrations of the individual components, diverges with temperature according to a power law (see figure 3); and the scattering function $S(Q)$, as Q approaches zero, diverges with an exponent -1 as the

system approaches the spinodal temperature. This is the temperature at which the system becomes unstable and starts to undergo phase separation everywhere simultaneously. The same small-angle neutron-scattering measurements yield the temperature and concentration dependence of the interaction between monomers in the blend. One needs this information to predict the rate of phase separation.

Block copolymers form another important class of phase-separated polymer systems. Block copolymers can form very regular macroscopic crystalline structures made up of microscopic spherical, cylindrical or lamellar phase-separated components. The scattering pattern in figure 4 is from a polystyrene-polyisoprene two-block copolymer system with lamellae of phase-separated polymers. Small-angle neutron scattering gives not only the spacing of the lamellae, but also the dimensions of a single deuterated block



Isointensity contour plots of neutrons scattering at small angles from polystyrene-polyisoprene two-block copolymers. The copolymers form almost perfect lamellae with double-layer spacing of 400 Å. In this picture, isointensity contours are mapped into a hot-body spectrum of colors. Experiments were carried out with the lamellae perpendicular to the incident beam for specimens with different ratios of deuterated polystyrene-polyisoprene to hydrogenous polystyrene-polyisoprene. From left to right, this ratio is 100-0, 50-50, 25-75 and 0-100. The contrast clearly varies with the different lamellae as well as the single-block structure factor.

Figure 4

in a two-block copolymer molecule. Neutron scattering experiments on two-block copolymer systems show that the component of the radius of gyration perpendicular to the lamella is extended while the parallel component is contracted relative to the radius of gyration of a single-component polymer in its bulk state. This indicates that the material has anisotropic molecular conformation and anisotropic macroscopic properties.

Crystalline polymers. The configuration of chains in crystalline polymers has been a subject of controversy. Polymer crystals are usually smaller than the polymer chain length, and the earlier "fringed micelle" model presumed that the excess polymer chain emerging from one crystal would go into another, serving as a "tie chain" to give the material mechanical integrity. The study of single polymer crystals grown from dilute solution, pioneered by Andrew Keller of Bristol, led to the realization that some polymer crystals are made up of folded chains, which are polymer molecules that zig-zag back and forth. Presumably, some of this chain-folding persists in polymers crystallized from the melt, and small-angle neutron scattering is playing an impor-

tant role in attempts to define the extent and regularity of such folding.

A complication in scattering experiments is that hydrogenous and deuterated polymers are really not thermodynamically equivalent. There is a difference of four degrees in the melting points of hydrogenous and deuterated polyethylene, for example. This leads to fractionation and segregation during crystallization, and affects the interpretation of small-angle neutron-scattering results. Researchers generally agree that, in spite of this problem and a certain degree of chain folding, the chains in polyethylene crystallized from the melt maintain their overall dimension or radius of gyration R_g .

The mechanical properties of polymers that consist of crystalline parts interconnected by amorphous chains depend on the number and nature of the tie chains. Small-angle neutron scattering may help to determine the number of tie chains that interconnect the crystals, and it may help to define the effects of parameters such as molecular weight and crystallization temperature on the number of tie chains. Such characterizations are useful in the development of fibers with very high strength. During manufacture,

these fibers undergo great elongation, which involves, in part, the "unfolding" and "recrystallization" of folded chain species.

Although neutron scattering is not the solution for all polymer problems, the technique has clearly opened up the opportunity to study many aspects of polymer systems for the first time. We believe that the technique will continue to make important contributions to polymer science, especially in studies of polymer dynamics and in measurements that require good time and momentum resolution.

Suggestions for further reading

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