Spectrometer used to gather information on the configuration of polymer molecules in the condensed phase. This small-angle neutron-scattering spectrometer is at the National Bureau of Standards, in Washington, D.C. The sample chamber is in the center, and the two-dimensional position-sensitive detector is at the far end of the left-hand tube. The neutron source, a reactor, is out of the photograph at the bottom right. Neutron spectrometry is one of a large number of modern experimental techniques used by polymer scientists. Figure 1

High-polymer physics

An account of this increasingly important science on the 40th anniversary of its APS division finds new discoveries stimulating activity in a vast array of topics.

Elio Passaglia, Martin Broadhurst, Edmund DiMarzio and Isaac Sanchez

The Division of High Polymer Physics of the American Physical Society was founded in 1944, spurred in large measure by the development of synthetic rubber during the Second World War. With the enormous postwar growth of the synthetic polymer industry, the field of polymer physics burgeoned—and along with it, the Division of High Polymer Physics. At the time of the March 1984 APS meeting, the division was an active, thriving community of 1001 members with a variety of scientific interests and activities. In this article, we will attempt to give the flavor of their work. We hope our account is sufficiently specific to be useful and interesting to polymer scientists, yet general enough to be intelligible and interesting to the general reader.

Like other areas of materials science and solid-state physics, polymer physics covers a vast array of topics. Without attempting to be all-inclusive, we can list the following areas in which research on the physics of polymers has traditionally centered:

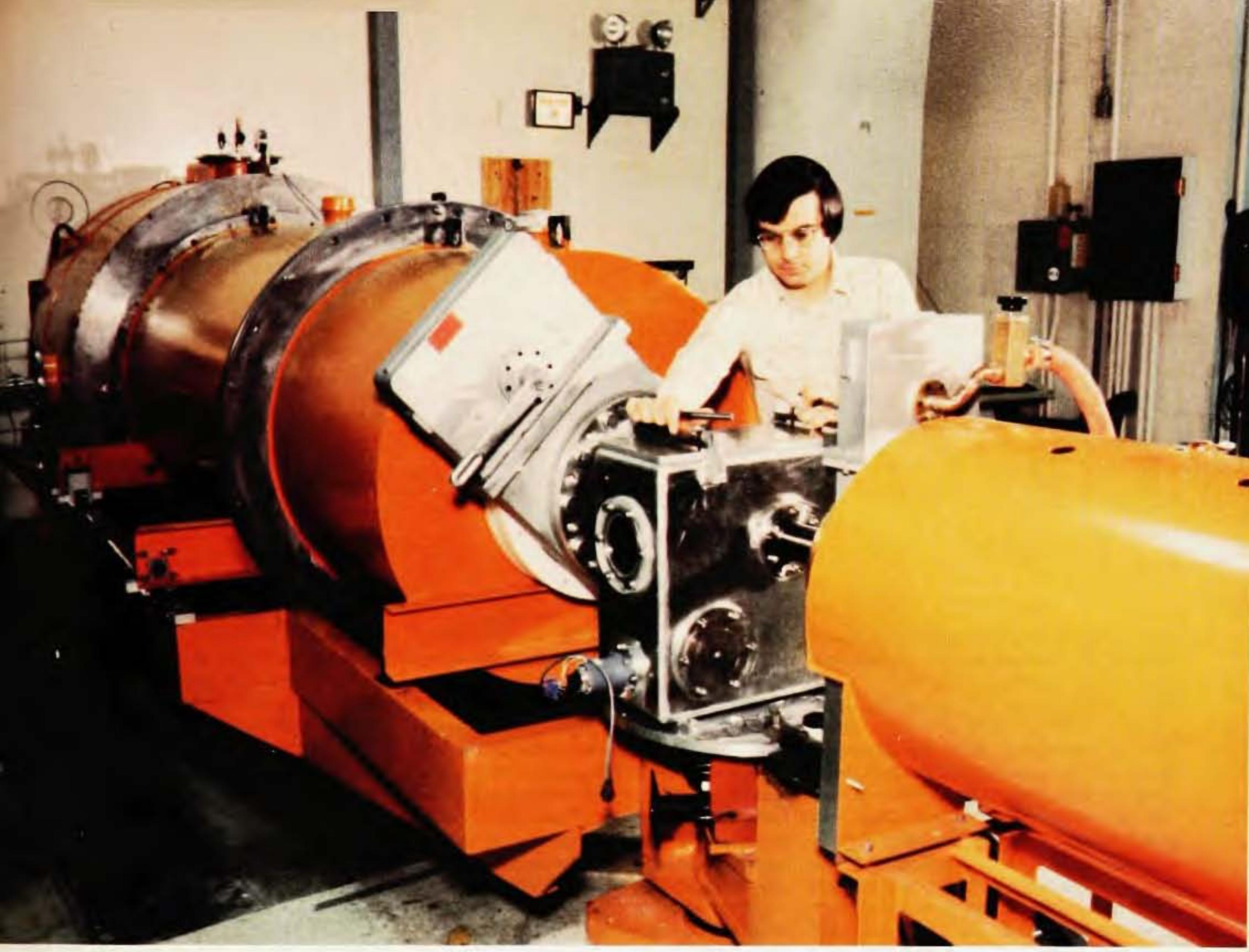
- Thermodynamic and transport properties in solutions and melts
- Chain conformation
- Viscoelastic properties of amorphous polymers: deformation, yielding, drawing and fracture
- Thermodynamics and relaxations in the glassy state
- Dielectric, mechanical and other relaxations in crystalline polymers
- Phenomena at interfaces
- Morphology of crystals and solid semicrystalline polymers
- Kinetics of phase changes, particularly crystallization
- Electrical and piezoelectric properties.

For this research, polymer scientists have taken advantage of a large number of modern experimental techniques, including dynamic light scattering, nuclear magnetic resonance, fluorescence spectroscopy, Raman and infrared spectroscopy, neutron spin-echo spectroscopy and small- and wide-angle neutron scattering (figure 1).

Polymers have a diversity of chemical structures and exhibit some unusual condensed phases, as figures 2 and 3 illustrate. There are homopolymers, chains of a single component; and copolymers, chains composed of two or more components arranged at random or grouped in "blocks." Polymers can be stereochemically regular or irregular. The chains can be linear or branched, and in the condensed phase, they can be crosslinked. In the solid state, polymers can be semicrystalline or glassy; in fact, some do not have the requisite stereoregularity to crystallize, and always form glasses. Polymers can form liquid crystals. They can exist as single species or as blends known as polymer alloys. Finally, polymers can exist in solution, permitting the study of isolated molecules and the effects of their overlap. Many hundreds of chemical structures have been synthesized, and many more continue to be. However, as we will see, many properties are independent of the chemical nature and depend only on the fact that polymers are very long chain-like molecules.

In this limited space, we can merely sample the work going on in polymer physics. Our principal criterion in choosing examples is that they illustrate new and potentially useful concepts and that they show the unity that exists between polymer physics and the other branches of physics. Thus we

Elio Passaglia, Martin Broadhurst, Edmund DiMarzio and Isaac Sanchez are members of the staff of the polymers division of the National Bureau of Standards.



will look at chain dimensions, solutions, molecular rheology, crystallization, glasses and electrical properties. This choice, ultimately, is personal and perhaps even biased, and we apologize to our friends and colleagues whose work had to be omitted. We include a list of suggestions for further reading where the references to the original work can be found.

Chain dimensions and solutions

In 1949, Paul J. Flory solved the "self-excluded volume" problem of a polymer chain in a mean-field approximation. Self-excluded volume is the volume not available to segments of a polymer chain because other segments of that chain already occupy the space. Flory found that, in the limit of high molecular weight, the radius of a flexible, linear chain of N monomer units varies as N^{ν}, where ν is $^3/_5$. The statistical model that mimics the behavior of a polymer chain in a good solvent is a self-avoiding random walk in three dimensions. (See PHYSICS TODAY, October, page 44.) After 1949, theorists made a considerable effort to improve upon Flory's calculation, but progress was relatively slow. A significant breakthrough came in 1972 when the French physicist Pierre-Gilles de Gennes made the remarkable observation that there is a correspondence between self-avoiding random walks and the phase-transition properties of the n-vector model of ferromagnetism for $n = 0$. (In the n-vector model, n denotes the number of degrees of freedom of electron spins; $n = 1$ corresponds to the usual Ising model.) This discovery made it possible to apply powerful scaling and renormalization-group methods to the problem.

The connection between self-avoiding random walks and the $n = 0$ vector model is made clear by examining the properties of a given component of the spin–spin correlation function $\langle S_i S_j \rangle$, which gives the relationship between the spins of electrons at lattice sites i and j. For $n = 0$, only the self-avoiding paths from i to j contribute to the correlation of spins S_i and S_j. Near the spin-system's critical temperature T_c (the temperature at which magnetism disappears), and in the absence of an external magnetic field,

$$\langle S_i S_j \rangle_{n=0} = \sum_N \exp(-N\epsilon)\ W_N(ij)$$

Here ϵ is defined as $(T_c - T)/T_c$ and $W_N(ij)$ is the number of self-avoiding walks of length N from spin i to spin j. Notice that the fundamental relationship between $W_N(ij)$ and $\langle S_i S_j \rangle$ is of the form of a (discrete) Laplace transform and that the walk length N and the temperature measure ϵ are reciprocal, or conjugate, variables. This reciprocity implies that if the correlation length of the magnetic domains varies as $\epsilon^{-\nu}$, then the correlation length or radius R of a self-avoiding random walk varies as N^{ν}. The most recent renormalization-group calculations on the n-vector model yield an exponent ν of 0.588 for $n = 0$. This value is in good agreement with Flory's original estimate of $^3/_5$, and the question of why the mean-field value is very nearly correct is still open.

In 1975, Jacques des Cloizeaux of Saclay, France, noted that the $n = 0$ vector model in the presence of an external magnetic field is related to a system of many mutually-avoiding, self-avoiding random walks on a lattice. One can then use this to simulate the properties of a semidilute polymer solution. The main result obtained by des Cloizeaux is that the osmotic pressure π in the semidilute regime is a universal function of the ratio of polymer concentration c to the concentration c^* at which polymer coils begin to interpenetrate:

$$\pi M/cRT \propto (c/c^*)^{1/(3\nu-1)}$$

In this expression, M is the molecular weight of the polymer molecules. Some very careful osmotic pressure measurements in 1981 by Ichiro Noda and coworkers at Nagoya University in Japan confirmed the validity of this universal scaling law for polymers of high molecular weight in good solvents. For the term ν in the exponent, they obtained 0.585, which is very close to the calculated renormalization group value of 0.588. However, as early as 1949, researchers in Canada had noted that in the semidilute range, the osmotic pressure term $\pi M/cRT$ varies not as c, as all classical theories predict, but as $c^{1.27}$, which implies that ν is 0.60.

A very important concept for understanding semidilute solutions is the screening of self-excluded volume. Sam F. Edwards of Cambridge University proposed the idea in 1965 that self-excluded volume in a polymer chain is diminished when the polymer concentration is high enough for polymer coils to interpenetrate. One can define a screening length that decreases with increasing concentration. In undiluted polymer, it becomes about the size of a monomer unit, and there is complete screening of self-excluded volume. In this case the exponent ν is $\frac{1}{2}$, and the polymer chains should behave as ideal random walks. Thus Edwards and, later, the French Strasbourg–Saclay–Collège de France collaboration quantified the imaginative insight of Flory, who suggested over 30 years ago that polymer chains would behave as simple Gaussian coils in the undiluted state. However, it was not until the 1970s that small-angle neutron-scattering experiments on bulk amorphous polymers confirmed Flory's intuition.

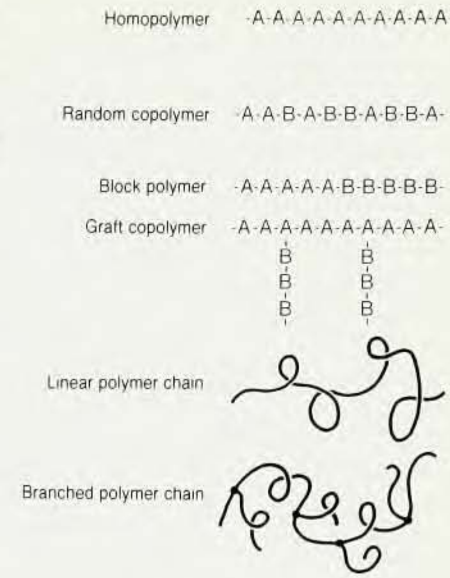
There is historical irony in this story of chain dimensions. Originally, Flory argued that polymer chains should behave as ideal random walks in the bulk polymer as well as in dilute solutions at the θ temperature—the temperature at which the second virial coefficient vanishes. This coefficient is that of the second term in a power series expansion of the osmotic pressure as a function of the concentration. When this coefficient vanishes, the expression for the osmotic pressure takes the form of the ideal gas law. The polymer community quickly adopted the attitude that ideal chain behavior did obtain at the θ temperature, but remained skeptical about the prediction of ideal random walks in the bulk until the aforementioned neutron scattering studies. Now the consensus is that polymers are configured more like ideal random walks in the bulk than they are at the θ temperature. The mutual repulsion that occurs in the relatively rare event that three monomers come together at the θ temperature causes deviations from ideal random behavior, and this leads to logarithmic corrections to the chain radius.

Phase transitions. Walter H. Stockmayer of Dartmouth College suggested as early as 1960 that individual polymer molecules might "collapse" from a coil configuration to a tight, globular structure, but this was not observed experimentally until the 1970s. Collapse transitions have now been observed in synthetic polymers and gels, as well as in biopolymers such as DNA. In ionic gels, experimenters have induced reversible volume changes of two orders of magnitude by varying the temperature, pH, ionic strength or electric field. These gels have a variety of potential applications, including artificial muscle and memory, and switching devices. Theory indicates that the collapse of an infinitely long polymer chain is a second-order phase transition, whereas gel collapse appears to be a first-order transition.

In recent years, Nobuhira Kuwahara, Motoza Kaneko and their coworkers at Hokkaido University in Japan have made high-precision measurements on coexisting polymer–solvent phases of polystyrene. These phases are polymer solutions of differing concentration, and they can coexist without becoming a homogeneous solution. The Hokkaido researchers find that the critical exponent β that characterizes the vanishing of the concentration difference between coexisting phases is 0.33, independent of the polymer's molecular weight. The most recent renormalization-group calculation of this exponent for the Ising model in three dimensions is 0.3265. Thus, even though the asymmetry in polymer and solvent molecular sizes may be of the order of 10^4 to 1, polymer–solvent critical behavior appears to be described by the same theory that describes a wide variety of other second-order phase transitions.

In the early 1960s, P. I. Freeman and John S. Rowlinson of the University of Manchester observed that nonpolar polymers dissolved in nonpolar solvents separate into phases of differing polymer concentration at elevated temperatures. The phase separation usually occurs at temperatures between 0.7 and 0.9 of the solvent's critical temperature. In many systems, phase separation occurs at both low and high temperatures, as schematically represented in figure 4. Such systems feature both an upper and a lower critical solution temperature.

High-temperature phase separation is relatively rare for low-molecular-weight solutions, but is quite common



Chemical structures of synthetic polymers. The A's and B's represent different chemical groups, or monomers. The two lower figures indicate that monomers can join to form linear or branched chains. Chains may contain as many as 10^5 monomer units. Figure 2

for polymer solutions. Thermodynamic arguments show that the heat of mixing must be negative near a lower critical solution temperature and that the phase separation is entropically driven. The question then arises: Why should a nonpolar polymer–solvent system exhibit a negative heat of mixing? The answer to this question began evolving in the 1960s and 1970s with the development of "equation of state" theories of solutions. These theories treat the solution as a compressible mixture and can qualitatively account for all the usual features of polymer–solvent phase diagrams. Negative heats of mixing are possible through negative volume changes, which become more probable at elevated temperatures. These molecular theories and subsequent thermodynamic arguments have made clear that the compressibility of a polymer solution or blend plays an important role in determining its phase behavior.

Molecular rheology

Because the extensibility of rubber is high as well as time-dependent, and because the flow of polymer solutions and melts is non-Newtonian, the mechanical behavior of polymers has been a rich field for experimentalists and a challenging one for theorists trying to predict behavior from the dynamics of polymer chains.

Theories that model the polymer chain as a collection of beads connected by entropic springs have been successful in predicting the viscoelastic behavior of polymers in dilute solutions. These "Rouse–Zimm" theories have also been successful in the regime in which the stress is a function of time but proportional to strain; that is, in the linear regime.

In concentrated solutions and melts, polymers are nonlinear in their stress–strain behavior, and on a molecular scale, the constraints on the movement of a molecule are highly anisotropic. A polymer molecule finds itself confined by its neighbors. Motion transverse to the path defined by the backbone of the molecule is very difficult because of this confinement, but motion along the contour of the chain is, in comparison, relatively easy. By Brownian motion, the chain snakes its way along the channel or "tube" formed by its neighbors. De Gennes coined the term "reptation" for this motion, and treated it analytically (PHYSICS TODAY, June 1983, page 33). He defined a diffusion constant D_{tube} for this motion, and showed that the average time for the disengagement is given by

$$\tau_d \simeq L^2/D_{\text{tube}} = N^3 a^2 \zeta / kT$$

Here L is the length of the tube, N the number of chain segments in the polymer, a the segment length and ζ the friction coefficient per segment. For polymers of high molecular weight, that is, for polymers with a large number N of segments, the disengagement time τ_d can be on the order of minutes.

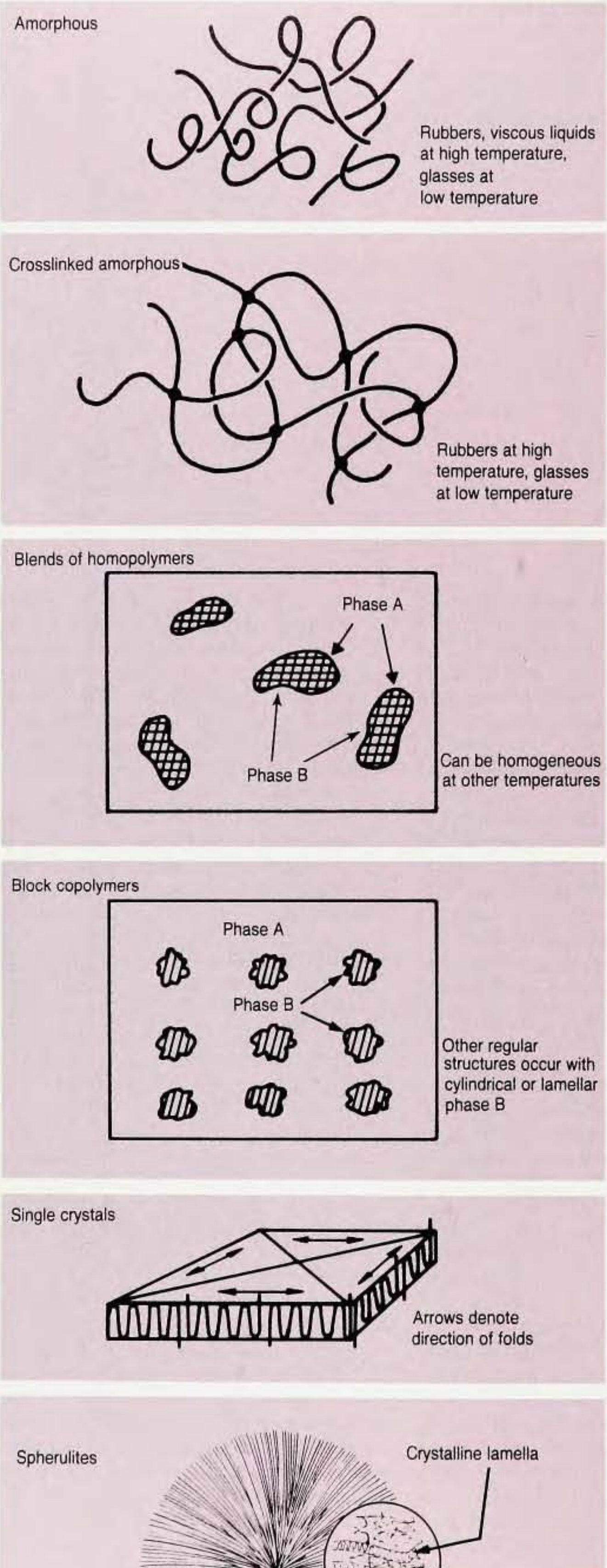
Masao Doi and Edwards used the reptation concept to construct a molecular theory for the mechanical behavior of concentrated polymer solutions and melts. Somewhat later, R. Byron Bird and Charles F. Curtiss (PHYSICS TODAY, January, page 36), using a quite different approach, but also using the reptation concept, developed a similar theory that gives the Doi–Edwards results as a special case.

In the Doi–Edwards theory, the imposition of an external deformation on the system "affinely" deforms the tube under consideration, as well as the chain within the tube. That is, the change in the shape of the tube is assumed to be similar to the change in shape of the system. Two processes then occur: First, the chain, modeled as a series of links, each of average length equal to the radius of the tube, comes into equilibrium with the deformed tube. This is a rapid process. Second, the chain disengages from the deformed tube with a time constant τ_d, the reptation time given above.

To calculate the stress from this and other models, one needs an expression for the spatial distribution of the segments of the chain—this is the crux of the problem—and one needs a means for calculating the stress tensor in terms of this distribution function. Doi and Edwards use a stress tensor from the theory of rubber elasticity, whereas Curtiss and Bird use a more general formulation, calculating specifically the intrachain, interchain and kinetic or momentum-transport contributions to the stress tensor. Curtiss and Bird use a general phase-space method for calculating the distribution function, and use a tensor friction coefficient so that the tension is permitted to vary from link to link. Despite these somewhat different approaches, the constitutive equations derived are remarkably the same.

The constitutive equation gives the stress as an integral over all past times of a product of a function of the relaxation times τ_d/n^2, where n is an integer, and a function of the applied deformation. In this constitutive equation, the behavior is factored into the product of a function of strain and a function of time. Phenomenological equations of this type are known to account for many aspects of nonlinear behavior.

Calculations, both by Doi and Edwards and by Curtiss and Bird, for a number of experimental situations show a rich variety of behavior. In some cases the calculations agree qual-



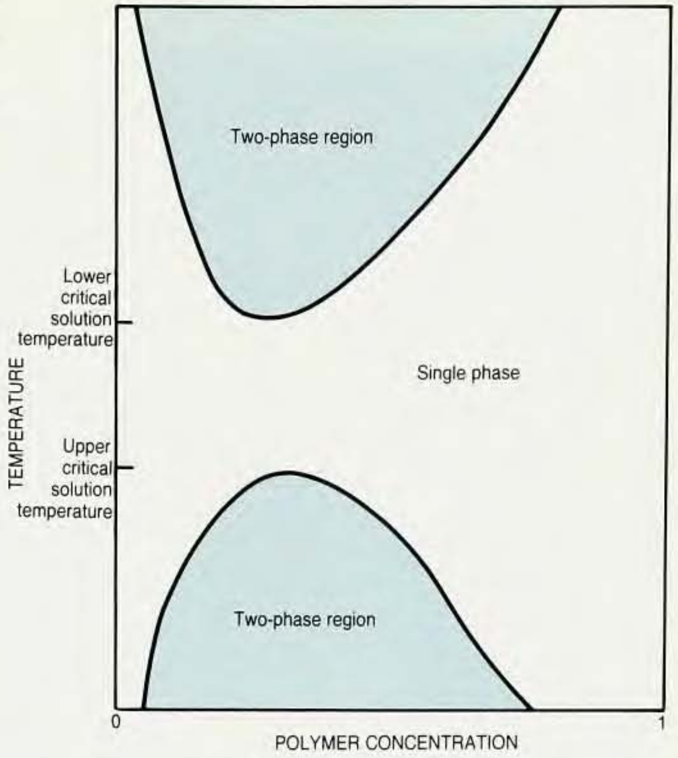
Condensed-state polymer structures. Polymers exhibit some unusual condensed phases. Crystalline polymers generally contain an amorphous component, and are termed "semicrystalline." The bottom diagram shows the dominant structure in undeformed semicrystalline polymers. Figure 3

itatively or semiquantitatively with experiment, but in other cases they do not. In particular, the exponent 3.4 in the well-established relationship between the viscosity η and the molecular weight N of heavy polymers—$\eta \propto N^{3.4}$—continues to be elusive. Several treatments, including calculations based on reptation, give a value of 3. Detailed consideration of the lifetime of the tube by Doi and others push the exponent higher, although no exact "3.4 law" has been derived. It is clear, however, that these theories are a major advance in polymer molecular mechanics and provide the impetus for a great deal of experimental and theoretical investigation.

Crystallization

In 1957, Andrew Keller rediscovered Keith H. Storks's 1938 finding that polymer crystals grow in the form of thin lamellae in which the chain molecules fold back and forth between two planes. This led to a veritable explosion of experimental and theoretical work. Experiments showed that the folding is quite regular, at least in crystals grown from solution. Theory as well as experiment indicated that, both from solution and from the melt, the crystals grow mainly by secondary nucleation—that is, nucleation of new layers on growing crystals. The nucleation event is seen as the deposition of a chain on the lateral edge of the lamellar crystal with subsequent folding back and forth between the two surfaces. The nucleus becomes of stable size, growth proceeds and a new strip of folded chains is added to the

Liquid–liquid phase diagram. This schematic diagram shows the phases of a polymer–solvent mixture that exhibits both an upper and a lower critical solution temperature. Figure 4



edge of the lamella. The equilibrium crystal is made up of polymer chains without folds; the thickness of such a crystal is then equal to the length of the polymer chains. Folding occurs because the thinner crystals that are the result of folding grow much more rapidly. The thickness is determined by kinetic factors. The subject is now mature, but there are some open questions concerning certain details.

One of these questions is the degree of regularity of chain-folding. While it is generally accepted that in dilute solution the folding is quite regular with one molecular chain forming a large number of adjacent folds, the situation in crystallization from the melt is not so clear. A new chain can begin adding to the end of the growing strip before the previous chain is fully deposited. This new chain may deposit a few folds and go off into another crystal, or fold onto subsequent layers of the growing crystal.

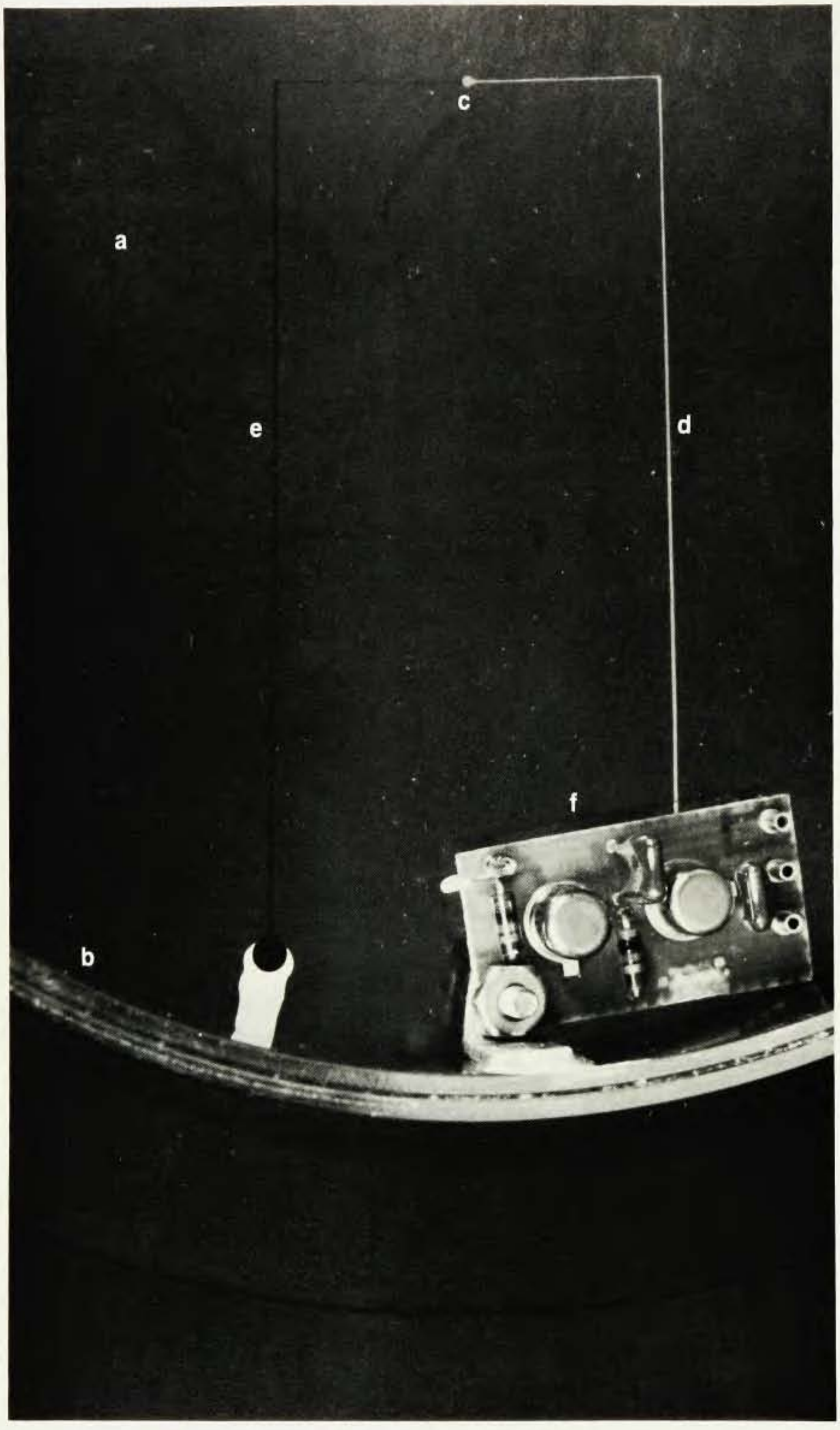
The quantity of interest is the extent of regular adjacent folding, or adjacent "reentry." Polymer scientists have studied this in recent years using neutron scattering. By mixing some fully deuterated polymer with its protonated analogue, one can measure the radius of gyration of individual chains by scattering. Model calculations for fully adjacent reentry and for various degrees of nonadjacent reentry give radii for comparison. For stereochemically regular polystyrene, the folding seems to be quite regular. For polyethylene, where one can make a solid solution of the deuterated species in the protonated polymer only by quenching, there appears to be a considerable degree of adjacent reentry. Further experiments and Monte Carlo calculations are clarifying reentry behavior.

There have been theoretical refinements as well. In their early forms, the nucleation theories calculated only the rate of growth of the strip on the edge of the lamellae. What is observed, however, is the growth of the edge in a direction normal to the strip. The effort to calculate this normal rate has led to the concept of regimes. In regime I, the rate of nucleation i of new strips is the controlling factor. In regime II, the rate of growth g of the strips is comparable to the rate i at which they nucleate, and the normal growth rate goes as $(ig)^{1/2}$. In regime III, the rate of nucleation i is so rapid that it is again the controlling factor. The temperature dependence of the normal growth rate in regime II is greatly different from that in regimes I and III, which have essentially the same temperature dependence. Theoretical problems remain in the transition regions between regimes, and in regime I, where the idealized theory predicts a normal growth rate that increases exponentially with time while a linearly increasing growth rate is observed.

Glassy polymers

Glassy amorphous polymers are a large and important class of polymeric materials. Glasses are formed by linear homopolymers such as polystyrene and polymethylmethacrylate, cross-linked materials such as epoxies and rubbers, and copolymers and polymer blends. A crucial point is that glass phases of polymers can theoretically exist at equilibrium. Not all materials are necessarily crystalline in their lowest-temperature equilibrium phase. In fact, even when that phase is crystalline, a polymer glass can exist in a metastable state because the crystalline phase is hard to initiate. (Large undercoolings—that is, coolings far below the melting point—are needed to initiate the crystalline phase because the size of the polymer crystal nucleus is large, and high viscosities make the coordinated motion that is necessary to form this nucleus difficult.) When glass-forming polymers are cooled as slowly as possible, they display what appears to be a finite discontinuity in the second derivatives of the free energy. In other words, they display a second-order phase transition in the Ehrenfest sense. The glass transition temperature T_g is defined as the temperature of this transition.

Using a lattice model and a mean-field approximation, Julian H. Gibbs and DiMarzio calculated the configurational entropy of a polymer liquid. They found that at a finite temperature ture T_2, the configurational entropy approaches zero and the liquid undergoes a second-order phase transition. Gibbs and Gerold Adam identified this configurational entropy as the underlying cause of the rapid increase of the viscosity on cooling. The experimentally observed glass transition temperature T_g, whose value depends on the time scale of the experiment, is larger than the calculated temperature T_2, but should correlate strongly with T_2. This correlation has found remarkable



Hydrophone. The piezoelectric polymer device shown here was developed by the National Bureau of Standards and the Food and Drug Administration for detailed calibration and spatial characterization of the ultrasonic fields generated by diagnostic ultrasonic equipment. A 25-micron-thick film of polyvinylide fluoride (**a**) is held taught by a pair of close-fitting hoops (**b**). The 0.5-mm-diameter piezoelectrically active area (**c**) of the hydrophone is connected to vapor-deposited leads, one on the top surface (**d**) and one on the bottom surface (**e**) of the film. The leads are separated to minimize capacitive loading of the signal. An amplifier (**f**) provides a low-impedance signal for processing. The close impedance match of the polymer to water makes it virtually invisible to the ultrasonic waves and thus nonperturbing of the sound field being measured. Figure 5

experimental confirmation. The dependence of the glass transition temperature T_g on parameters such as chain length, crosslinking, plasticizer concentration, pressure and copolymer composition mimics the dependence calculated for the temperature T_2.

In spite of the success of the theory, there is concern that the result that the configurational entropy goes to zero or to a limiting small value at the temperature T_2 is an artifact of the mean-field calculation. It is indeed a surprising result that the configurational entropy is expected to approach zero at a temperature above zero. In 1976, Manfred Gordon and his coworkers at the University of Strathclyde in Scotland noted that in the limit of infinite chain length and no vacancies, Gibbs's and DiMarzio's problem of calculating the entropy associated with the configuration of polymers degenerates into the classical problem of determining the number of distinct configurations of a "Hamilton walk" on a lattice. A Hamilton walk visits every point of the lattice exactly once, and the problem of the number of distinct walks has analytical solutions on certain types of two-dimensional lattices. In 1981, P. D. Gujrati and Martin Goldstein of Yeshiva University obtained lower bounds for the entropy of a two-dimensional Hamilton walk as a function of the fraction of bonds in the chain about which there have been rotations; these bonds are in high-energy states. They found that when this fraction is greater than zero, the entropy is nonzero, which suggests that the temperature $T_2 = 0$. However, their result does not rule out the possibility that the temperature coefficient of the entropy could still be discontinuous at a finite temperature T_2. Thus the question of the existence of a nonzero T_2 awaits a first-principles calculation.

A related unsolved problem is to prove rigorously that amorphous materials—not only crystals—can be stable as the lowest temperature equilibrium phase. It is known to be possible to prove this in two dimensions using nonperiodic tiling theory, provided that the tiles are of two or more different shapes. What we need is a similar proof when there is only one shape.

Spurred in part by a number of new experimental techniques, an understanding of the dynamics of glasses is slowly evolving. Dielectric and mechanical relaxation phenomena in glasses generally exhibit slower than exponential decay in the form of a "Kohlrausch–William–Watts" distribution: $\exp[-(t/\tau_0)^\alpha]$, where $0<\alpha<1$. Theorists have proposed random-walk and quantum mechanical explanations of this distribution.

Electrical properties

Most polymers are insulators, and their most common traditional use for electrical purposes has been insulation for capacitors, wire and cable. Beginning in the late 1960s, several findings stimulated renewed industrial and academic interest in the electrical properties of polymers beyond their use as insulators. Recently recognized properties of polymers include piezoelectricity, pyroelectricity, ferroelectricity, nonlinear optical behavior, photoconductivity, ionic conductivity and conductivity like that in metals and semiconductors. These discoveries are so new that their commercialization is still rudimentary.

In 1977, researchers at the University of Pennsylvania reported that the normally insulating polymer polyacetylene, $(CH)_n$, can be doped to vary its conductivity from 10^{-13} to 10^3 $ohm^{-1}\,cm^{-1}$. The conductivity is thought to depend on overlapping electron pi orbitals, which form extended conduction and valence bands. The dopants remove charges from the normally filled valence bands, or add charges to the normally empty conduction bands. A goal of this research is to find polymer–dopant combinations that improve thermodynamic and environmental stability. Two polymers to attract interest recently are electrochemically polymerized polypyrroles, which a group at IBM first studied extensively, and polythiophenes. Both of these polymers show more stability than polyacetylene.

Theoretical research on conducting polymers has centered on the physics of defects in the polymer backbone. These defects may be uncharged radicals with spins ½ or radical–charge pairs called bipolarons. In *trans*-polyacetylene, the defects form freely mobile boundaries that are solitons. Whether the theory of solitons is appropriate to explain the observed conduction over the entire range of dopant concentrations is a matter of debate. In *cis*-polyacetylene and in aromatic chains, the motion of defects involves chain states of various energies, which hinder defect mobility. So far, there is only one example of an intrinsically conducting polymer having an electronic structure with a partially filled shell. Interest in this polymer, $(SN)_n$ was revived in 1973 by researchers at Temple University, and experiments at IBM showed the material to be superconducting below 0.3 K. A complete description of electronic conductivity in polymers is still evolving.

A report in 1969 that polyvinylidene fluoride, $(CF_2\text{–}CH_2)_n$, shows significant piezoelectricity stimulated widespread research. Infrared measurements at RCA and IBM, and x-ray studies at Sandia Laboratories, showed that the polar beta phase of this polymer undergoes crystallographic reorientation under the influence of an electric field; x-ray studies at the National Bureau of Standards showed that large electric fields convert the nonpolar alpha crystal phase to a polar phase. Japanese workers developed a series of copolymers of vinylidene fluoride with trifluoroethylene having ferroelectric to paraelectric transitions below their melting points. Polyvinylidene fluoride's piezoelectricity, which arises when an applied stress changes the thickness of the material, is called "secondary piezoelectricity" because the dipole moment remains constant in the process. A large fraction of the piezoelectric activity in copolymers, on the other hand, is "primary," being accounted for by changes in dipole moment with temperature.

The stress and temperature sensitivities of these polymers are comparable to those of nonpolymeric transducer materials, and they have the added properties of low dielectric constants, flexibility, toughness and ease of fabrication in small thicknesses and large areas. The polymers have relatively low electromechanical coupling coefficients at ultrasonic frequencies, but this is partially offset by a broad frequency response, and medical and naval hydrophone and imaging transducers, such as the one shown in figure 5, are very promising. Other commercial possibilities include uses in radiation and heat sensors, intrusion detectors, gas-flow meters, microphones, speakers, headsets and room light controllers.

In the 40 years since the founding of the Division of High Polymer Physics, polymer physics has evolved into a thriving and exciting scientific field. We hope that the few research problems that we have discussed here help convey a sense of this excitement and illustrate the broad interdisciplinary nature of polymer physics.

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