TWO DECADES OF HIGH-POLYMER PHYSICS

a survey and forecast

By W. F. Busse

The twentieth anniversary of the founding of the Division of High-Polymer Physics of the American Physical Society is an appropriate time to review the progress of polymer physics over the last two decades, and to re-evaluate the hopes of the founders and the present need for the Division. The continuing need for our Division perhaps is best shown by the fact that each of the last two meetings have set new records for the number of papers presented. Much of this progress is due to the officers who have contributed so much of their time and effort to the Division. Those who served in the first decade were recognized in an earlier review.[1] The officers of the last decade are shown in the accompanying table. We are indebted to

Year	Chairman	Vice-Chairman
1954	J. D. Ferry	R. S. Marvin
1955	R. S. Marvin	T. G. Fox
1956	T. G. Fox	A. M. Bueche
1957-58	A. M. Bueche	R. Simha
1958-59	E. R. Fitzgerald	B. H. Zimm
1959-60	H. Leaderman	W. P. Slichter
1960-61	W. P. Slichter	John Rehner, Jr.
1961-62	H. Markovitz	J. H. Gibbs
1962-63	J. H. Gibbs	T. W. DeWitt
1963-64	T. W. DeWitt	R. S. Stein
1944-64	W. James Lyons (Secretary)	

all these men for their work to keep the Division running, and thus promote the progress of polymer physics.

Many others whose names are not mentioned here have also helped the Division. Among these is Elio Passaglio, the chairman of the Program Committee that arranged for the present most successful meeting.

W. F. Busse, physicist and chemist in the Plastics Department of E. I. duPont de Nemours and Co. in Wilmington, Del., was one of the organizers of the APS High-Polymer Physics Division. He served in 1946 as the Division's second chairman. This article is based on a talk presented at the March 1964 meeting of the American Physical Society in Philadelphia.

One man stands out in this list of officers. He is James Lyons, who has been our secretary for two decades. He has gone far beyond the call of duty in working for the Division, and he deserves our special thanks.

The rapid growth of polymer physics made it tempting to limit this review of technical progress to the last decade. However, while time dims the memory of some events, it puts others in a new perspective. Today, for example, some of the principles or philosophy back of our actions in founding the Division can be formulated more clearly than was possible when we were in the midst of the process. So, at the sacrifice of some technical discussions, we will discuss just a few of the reasons for having our Division, and the relation of our field to other branches of physics. We will then review some of the developments in polymer physics over the last two decades, and make a few fearless forecasts of things to come.

The field of high-polymer physics

The field of high-polymer physics had a pattern of development that is common to all the sciences.[2] It started with a primitive stage of gathering and organizing data that goes far back in the history of our race.

The second stage involved developing more sophisticated theories and models to fit these facts. Great physicists of the last century—Maxwell, Kelvin, Boltzmann, Joule, and others—were active in this phase of polymer science. But, after these men died, the theoretical developments in this field lagged. It may have been because of the competition of new and more fashionable fields that were just starting their data-gathering stages, such as x rays, radioactivity, and spectroscopy, or to the great new theoretical developments of relativity and the quantum theory.

The next stage of scientific development included the testing and modification of the initial theories to fit new facts. This phase of polymer science took a big spurt shortly before our Division was started. Staudinger and others had proved that polymers were long-chain, flexible, chemical molecules, and not just physical aggregates like soap micelles. This concept led to the recognition that it was the physical shapes, rather than the chemical structure, of macromolecules that made possible rubber elasticity. The kinetic theory of elasticity was then developed,[3] and the physics of polymers again was on the move.

But there was still some skepticism about polymers being a worthy field of physical research. In some quarters it was believed that the only worthwhile fundamental research problems in science were those that tested the predictions or extended the fringes of someone else's well-developed theory.[2] Although polymer science did not have these neat theories, it turned out, however, that in many cases the complexities of polymer structures were great enough to produce simple statistical regularities—just as the complexities of molecular motions in a gas led to simple gas laws.

In any case, physicists in industry have to deal with some of these complexities, whether they can be organized into theories or not. Industrial processes also involve large numbers of experiments covering wide ranges of parameters. Hence, this field offers a fruitful source of data for those who like to organize such facts into theories. Where successful, the results of these efforts are not only intellectually satisfying, but also economically profitable. It must be admitted, however, that sometimes it is as hard to sell this viewpoint in industry as in academic circles.

The formation of the APS Division of High-Polymer Physics provided a nucleus about which people who were interested in polymer research could gather and be activated, as it were, for further reactions in their own laboratories. Other groups have also become active in this field. The Society of Rheology has always been concerned with one phase of polymer physics, and more recently the Polymer Division of the American Chemical Society has had many papers on the physics of polymers. This is all to the good, provided the contacts with physicists also remain strong. Somehow, Nature seems to be blind to the organizational fences we erect between physics and chemistry.

The developments I will summarize today were reported in many places besides our Division, and they were made in many countries throughout the world. They will be limited to three fields: (1) electrical properties, (2) viscoelastic properties, and (3) crystal structure and morphology.

We will not only discuss some of the progress over the last twenty years, but also point out some of the gaps in our knowledge, and some of the old, but still current ideas that may be supported more by folklore than by facts.

Electrical properties of polymers

The dielectric properties of natural and synthetic polymers have long been of great practical importance to the electrical industry. About the time our Division started, Debye's theory of dipole rotation was applied to solid polymers. This led to what was then a far-out suggestion of a relation between the ease of dipole rotation in polyvinyl chloride and its macroscopic hardness.[4a] Since then, correlations between dielectric and mechanical properties have been studied extensively until the time of the present meeting.[4b]

The empirical study of static generation and contact potentials also has remained active because of its industrial importance.[4c] However, our theories of electrification mechanisms leave much to be desired. The second world war stimulated an intensive search for polymers with low loss factors at all frequencies from 60~ to radar ranges.[5a] Polyethylene and polytetrafluoroethylene were outstanding in this regard.

Our current interest in space travel makes us concerned with the effects of high-energy electrons and other particles on polymers.[5b] Figure 1 shows an interesting type of dielectric breakdown that can be obtained when 2 MeV electrons bombard a half-inch-thick block of polymethylmethacrylate or polystyrene.[5c] The electrons can penetrate only about halfway through the sample, so they become trapped in a layer at the middle. When a grounded point is touched to the edge of this layer, the Lichtenberg type of discharge shown in the slide is obtained.

An understanding of this mechanism of dielectric breakdown is also of vital importance in im-

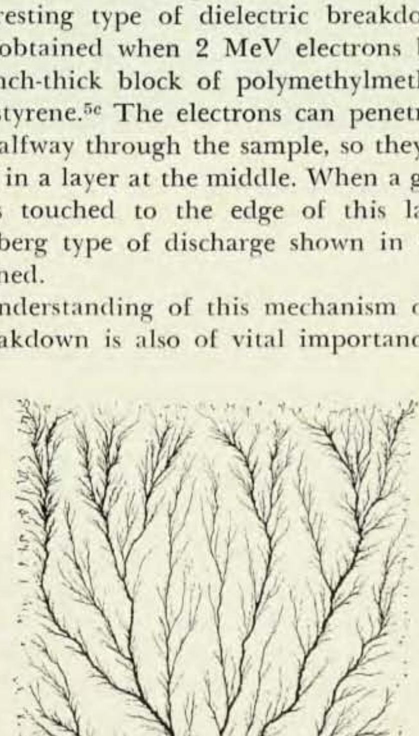

Fig. 1. Electrical discharge produced by electrons trapped between faces of a block of polymethyl methacrylate

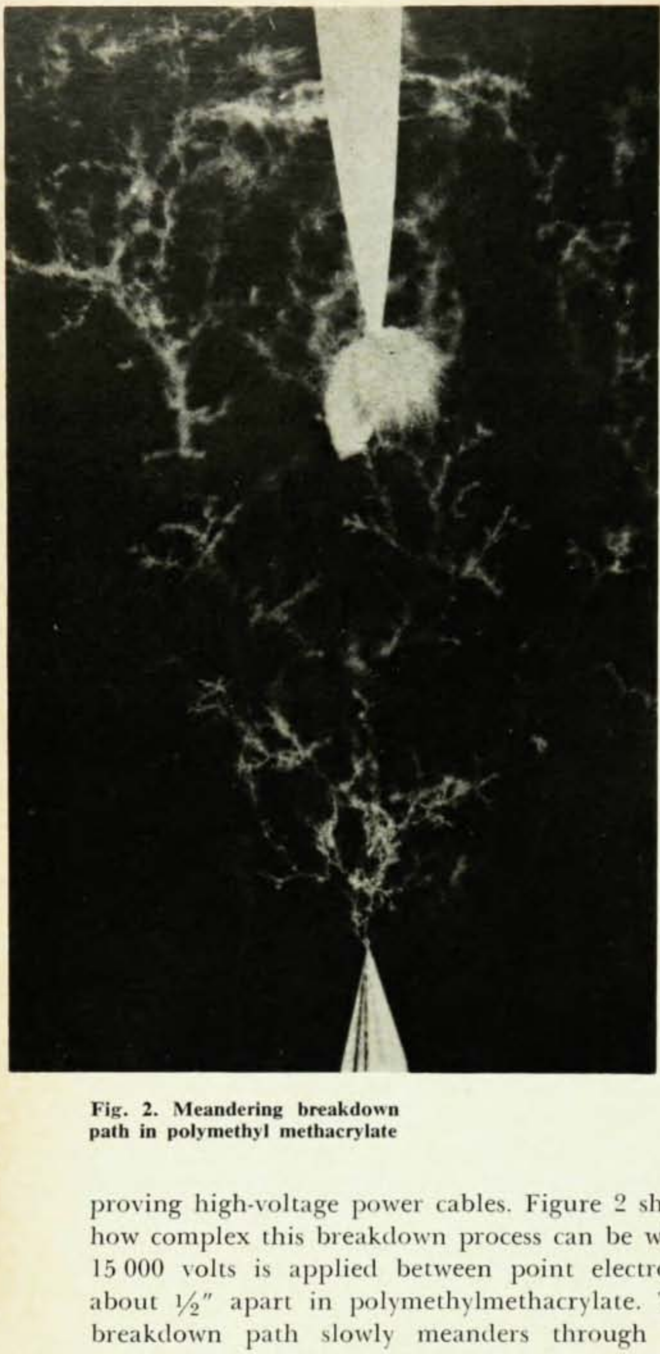

Fig. 2. Meandering breakdown path in polymethyl methacrylate

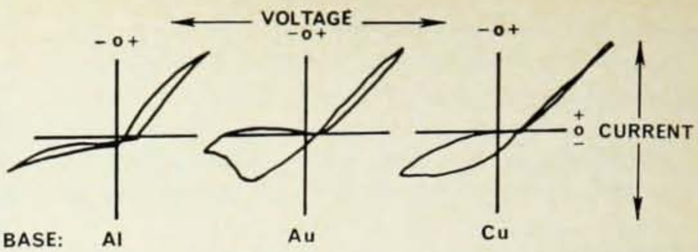

Fig. 3. Oscilloscope curves of triangular waves through ammonium salt of polymethacrylic acid. Point to plate electrodes

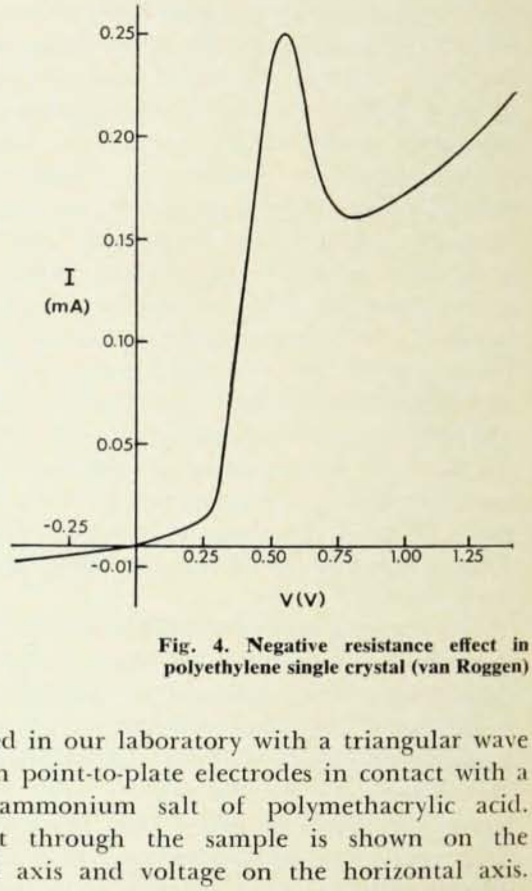

Fig. 4. Negative resistance effect in polyethylene single crystal (van Roggen)

proving high-voltage power cables. Figure 2 shows how complex this breakdown process can be when 15 000 volts is applied between point electrodes about ½″ apart in polymethylmethacrylate. The breakdown path slowly meanders through the sample over a period of hours with little reference to the over-all voltage gradient. This sample will still retain the 15 000-volt potential between the needle points.

E. J. McMahon, who took this picture, showed[6] that such discharges are initiated at voids at the electrode-polymer interface, and grow by an intermittent discharge mechanism. In the absence of voids at the electrode surface, polyethylene can withstand electrical stresses of well over 10 000 volts/mil, or 4×10^6 volts/cm.

Polymers may also have interesting semiconductor properties, as shown by the work of Pohl, Eley, and others.[7] Figure 3 shows oscilloscope traces of some unusual current-voltage relations obtained in our laboratory with a triangular wave between point-to-plate electrodes in contact with a moist ammonium salt of polymethacrylic acid. Current through the sample is shown on the vertical axis and voltage on the horizontal axis. The free polymethacrylic acid shows almost ohmic resistance and gives a straight line on this plot.

Polymer single crystals, like inorganic semiconductors, can also have a negative resistance. Figure 4, from van Roggen's data, shows negative resistance effects observed with single crystals of polyethylene.[8]

Polymers have also been prepared with extremely high dielectric constants, up to about 300 000, over the range from 50 to 50 000 cycles. This suggests a possible analogy to the inorganic ferroelectric materials.

The electrical properties of many biological polymers are of vital importance to us in many ways, from the electrical responses of our nerves, to the electromechanical responses of our muscles. These properties of polymers, like their negentropy that conveys genetic information, have had relatively little attention in our meetings. They will undoubtedly be discussed much more frequently in the next decade.

Viscoelastic properties

When our Division started in 1944, the macroscopic viscoelastic properties of solid polymers were receiving the most attention. The data were interpreted in terms of the spring and dash-pot models and the Boltzmann superposition principle. Leaderman had just suggested[9] the possibility of a relation between time and temperature in relaxation processes. This opened the door to the study of relaxation times over an astounding range—in some cases covering fifteen to twenty decades. These tools are still being used extensively, but with a better knowledge of their limitations. We are also developing more realistic models than springs and dash pots.

The early kinetic theory of elasticity has been refined and rechecked by many workers, and Mooney and Rivlin have extended the theory to calculate the behavior at large strains.[10a,b] New and unexpected results that do not fit our theories have also been found. These include the Weissenberg effect[10c] and other normal stress effects. Philippoff also found that the viscosity of polymers under oscillating deformations depends only on the frequency, and not on the amplitude of the deformation. This is contrary to the basic definition of viscosity. The explanation of these effects is still being debated.

Theories of dilute solutions have been studied from two viewpoints. One school believed that we must understand dilute solutions of polymers before we could begin to understand the behavior of more concentrated solutions or melts. But some feel that even a perfect understanding of dilute solutions would not enable us to understand polymer melts. Something new must be added.

Other people studied dilute solutions for more pragmatic reasons, namely that the available mathematical tools of continuum hydrodynamics and statistical mechanics were easiest to use, and most likely to work, with dilute solutions. It turns out that even for these systems, the mathematics get extremely complex and the final answers depend on the simplifying assumptions that are made.

Since 1944, the work of Debye, Kirkwood, Flory, Zimm, Rouse, and others[11] has given us several reasonably coherent theories of the effect of molecular weight on the intrinsic viscosity of dilute solutions. Stockmayer, Zimm, Kilb, and others also calculated the effect of branching on intrinsic viscosity. The accompanying table summarizes some of their results for the value of the exponent α in the viscosity equation:

$$[\eta]=kM^{\alpha}$$

α	Basic assumptions
1.0	Free draining model
0.5–1.0	Various amounts of hydrodynamic shielding and thermodynamic interaction
0.25	Much long chain branching
0.0	Cross linked to solid microgel particles

The calculated values of alpha range from 1.0 to 0, depending on the assumptions about hydrodynamic shielding or thermodynamic interactions, and the kind and amount of branching.

There is less agreement among theories as to the effect of shear rate on the viscosity of dilute solutions. Some theories predict a decrease in viscosity with increasing frequency of vibrations, or shear rate, while some other equally good theories predict no effect.

The experimental work of Mason and coworkers[12] on the motion of isolated particles in liquids under shear should be mentioned, as it is contributing to our understanding of the flow of dilute polymer solutions. They found that when suspensions of deformable drops or fibers flow through a tube, the particles tend to move to the axis. Long flexible particles also tend to coil up into tight bundles when the liquid is under shear.

New factors are present in the flow of polymer melts. The now well-known relation between polymer-melt viscosity and molecular weight shown in Fig. 5 was demonstrated by Flory and Fox[13] after our Division started. The critical MW, where the

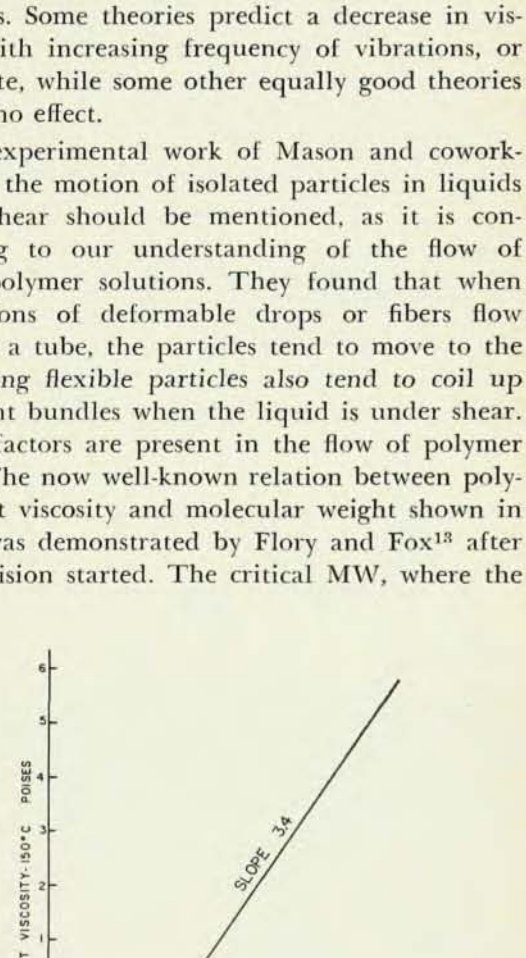

Fig. 5. Relation of molecular weight to melt viscosity

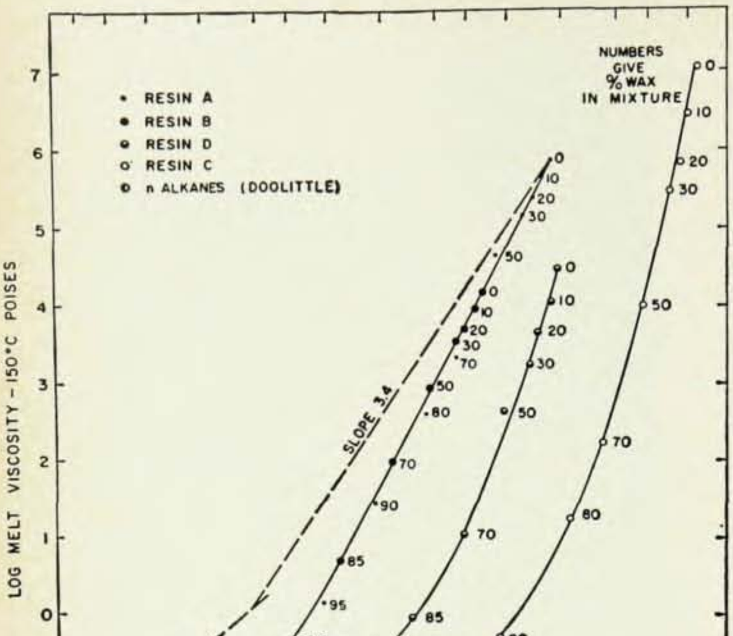

Fig. 6. Relation of melt viscosity to weight average molecular weights of polyethylene mixtures

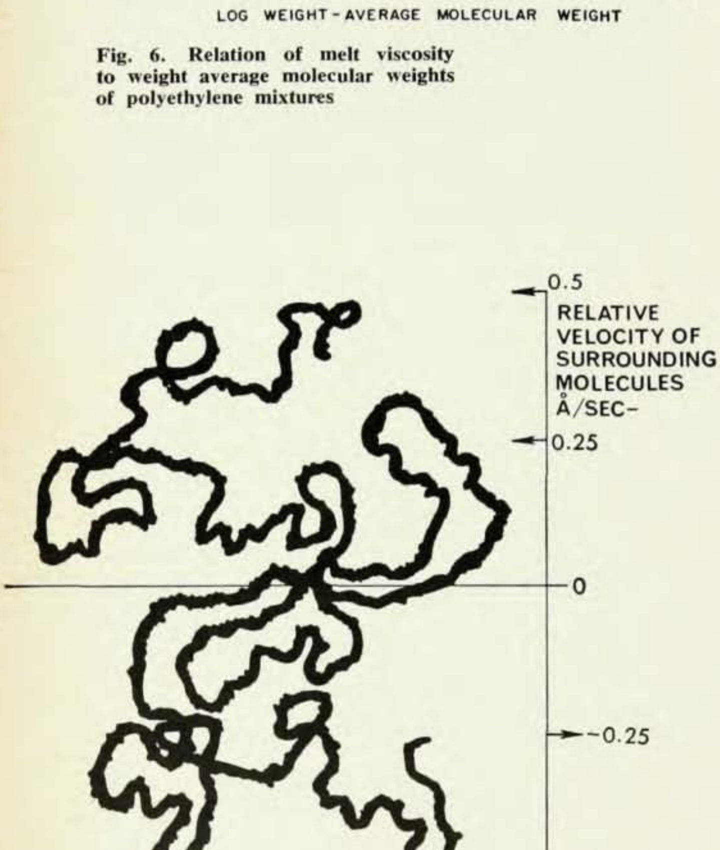

Fig. 7. Relative motion of random coil molecule and surrounding melt at shear rate of 10^{-3} sec^{-1}

lines change slope, is believed to be the place at which mechanical entanglements become important. Rouse, Bueche, and Eyring have attempted to derive this curve from theory.[14] None of these derivations are entirely satisfactory in accounting for all the properties of melts.

For example, melts are nearly Newtonian below, and are non-Newtonian above, this critical MW. Also, when a sample contains a range of molecular weights, the weight average molecular weight is generally assumed to determine the viscosity. Figure 6 shows that things are not quite so simple.[15] Here linear and branched molecules of polyethylene were mixed with low-molecular-weight polymer (paraffin wax). When the log melt viscosity is plotted against the calculated log weight average molecular weight, we see large discrepancies from the curve for sharp fractions. If the viscosity data are plotted against a viscosity average MW of the mixture, the curves all lie close to the curve of 3.4 slope (above M_c). Recent work on mixtures of polystyrene fractions[16a] and polypropylene mixtures[16b] also shows the melt viscosity to be determined by the viscosity average molecular weight. Better theories of melt viscosity are needed to account for these results.

It is worth noting that some of the concepts of the continuum hydrodynamics that are useful in dilute solution theories lose their meaning for the shear of polymer melts. The "streamline flow of a continuum" is one of these.

The Newtonian range of some high polymers is at shear rates below 10^{-3} sec^{-1}. If these molecules have a molecular weight of 10^6, their random coil diameter will be of the order of 10^3Å, as roughly illustrated in Fig. 7. If the center of the coil has the same average velocity as the surrounding molecules, the upper and lower ends of the coil will move past the surrounding molecules at an average rate of $\pm$ 0.5Å/sec. This rate is about one-tenth the thickness of a polyethylene chain per sec, and is much less than the Brownian motion of the end of a chain. Thus, the idea of a streamline flow in a continuum is quite artificial for polymer melts. Also, the rate of rotation of the random coils would be very small—about once every 100 minutes at this shear rate.

The concept of an "average friction factor" per unit chain length is useful for mathematical calculations, but it is a misleading model for understanding the physical mechanism of melt flow.

We know that the local viscosity around the segments of a polymer chain in a melt is comparable to the viscosity of a low-molecular-weight solvent.[17] If this were not true, a rubber band

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would not retract as rapidly as it does after it is stretched. We also know that the viscosity of a polyethylene solution in molten paraffin wax increases about 1000-fold on going from zero to ten percent concentration.[15]

It follows that *substantially all of the increase in viscosity with concentration must be due to the very high viscosity at the discrete entanglement points of the long chains.* It is hard to imagine the entangled molecules increasing the average friction factor by dragging second- and third-generation entanglements through the streamlined flow of surrounding molecules. A much more realistic picture has the entanglements figuratively acting as snubbing posts to multiply the relatively low viscosity of the chain segments.

We need theories that account more adequately for the change in the number of these snubbing posts with molecular weight, and for the rate at which tension can decrease with time because of slippage at these entanglements.

Various workers[18] have studied the rate of decrease in the elastic tension or birefringence in melts after sudden strain. However, they have often interpreted their results in terms of a very high average friction factor along the chains, or in terms of cross links having a limited life. Eyring's model[14c] of molecules "slaloming" around entanglements and Bueche's more recent proposals[19] and Mooney's model[20] are more realistic approaches, but still better models of stress relaxation and flow are needed.

The very complex mathematical problems involved in these more realistic theories may not be solved rigorously for some time. Meanwhile, we can draw some qualitative conclusions and predictions from this picture of entanglements as the major factor in the high viscosity of polymer melts.

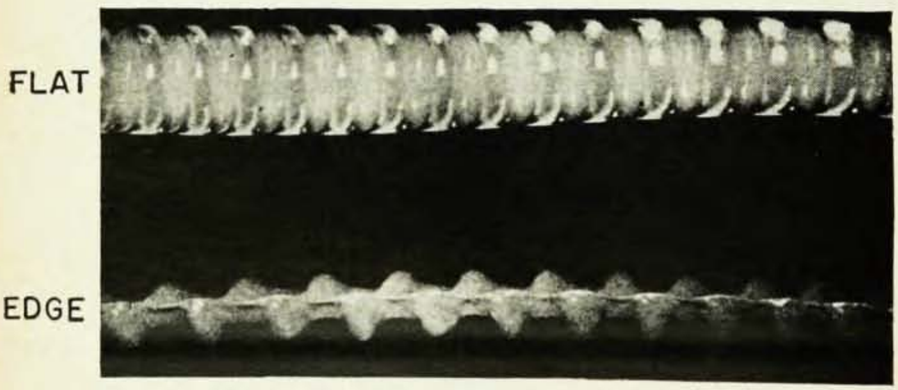
(a) The first conclusion, which is at least of some theoretical interest, is that a capillary viscometer should tend to fractionate polymer molecules with respect to molecular weight along the radius of the capillary. Near the wall, molecules of high molecular weight acquire relatively large amounts of free energy of elastic deformation, while very small molecules do not. Hence, there is a thermodynamic force that tends to increase the concentration of very small molecules at the wall, and of the larger molecules nearer the axis.

No measurements of such separations have been reported, to the author's knowledge, but this factor might play a part in the action of die lubricants. It may also cause some of the change in apparent viscosity with the ratio of the capillary length to diameter.

(b) A second conclusion from this molecular model of melt flow is that, at high shearing rates, the diffusion of the segments will no longer allow the single chains to "slalom" around the entanglements fast enough to keep up with the applied shear strains. Small groups of molecules may then become so tightly snarled that they will rotate as deformable clusters. This will reduce the energy required to shear the melt, and thus reduce the apparent viscosity.

Mooney, Bryce Maxwell, and others have provided considerable experimental evidence for this type of cluster flow in melts at higher shear rates.[21a,b] Lodge [21c] has also shown that fluctuating normal pressures develop in 2.0 percent solutions when they are sheared for long times at low rates, which strongly suggests a cluster type of flow.

If this entanglement mechanism is a major factor in generating non-Newtonian flow in melts, it is understandable why non-Newtonian flow is not predicted by good mathematical theories that



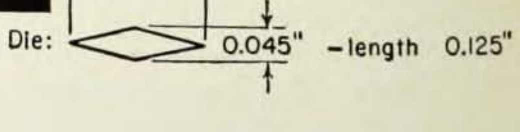


Fig. 8. Rhythmic flow of polyethylene through a rhombic orifice

consider only the deformation and flow of single molecules.

(c) A third deduction from this model suggests that a new type of resonance flow mechanism may occur at extremely high shear rates through orifices. This would result in various types of rhythmic distortions of the extrudates. Figure 8 shows one example of such flow through a rhombic orifice obtained by J. J. Christensen in our laboratory.

We know that the apparent viscosity decreases rapidly with the shear rate. The elastic energy increases with the shear rate, because of the distortion of the random coils. At some critical flow rate a further increase in rate will increase the stored elastic energy per unit volume more than it will increase the viscous loss. This could produce an elastic turbulence, analogous to the kinetic turbulence at the critical Reynolds number, where the kinetic energy is comparable to the viscous loss.

One pattern of this elastic turbulence is illustrated in Fig. 9 for the flow of a polymer through a slit die. The normal velocity profile will be somewhat as at 9 (a), with the elastic stress more or less parallel to the velocity profile. At a critical shear stress, the elastic stress and the applied stress will produce with very high shear rate and low viscosity in a layer near one wall, giving the velocity profile in 9 (b), and allowing the elastic stress on that side to relax. Then a layer of low viscosity will form on the other side as in 9 (c).

The flow will then oscillate between patterns b and c. Here the profiles approach one half of the velocity profile through a die twice as wide. Hence, the volume flow will approach twice that in a. So it is no wonder that, at high shear rates, Nature likes to produce irregular extrudates.

The low viscosity layer at the wall might appear operationally similar to slippage, as assumed by J. R. A. Pearson[22a] and others, but the oscillating behavior suggests another type of mechanism. The irregular motion of the melt at the entrance to the dies found by Tordella,[22b] and others also supports an oscillating flow mechanism.

Other resonance modes are possible, giving helical or irregular extrudates from round orifices. Lupton[23] has shown that elastic energy of compression can also produce the oscillating flow of a somewhat different type, that was first noted by Bagley.[24]

The enormous increase in viscosity and modulus of polymers at the glass temperature has aroused the interest of scientists for a century or more. In the last decade, Williams, Landel, and Ferry[25a] proposed their now well-known equation: $a_T = -C(T-T_G)/(C_2 + T-T_G)$. This empirically relates the time-temperature shift factor a_T to the glass temperature T_G. Subsequent work showed this shift can be related to the free volume over the range up to about 100° above the glass temperature. The relation of the transition temperatures to structures has been reviewed by Boyer.[25b]

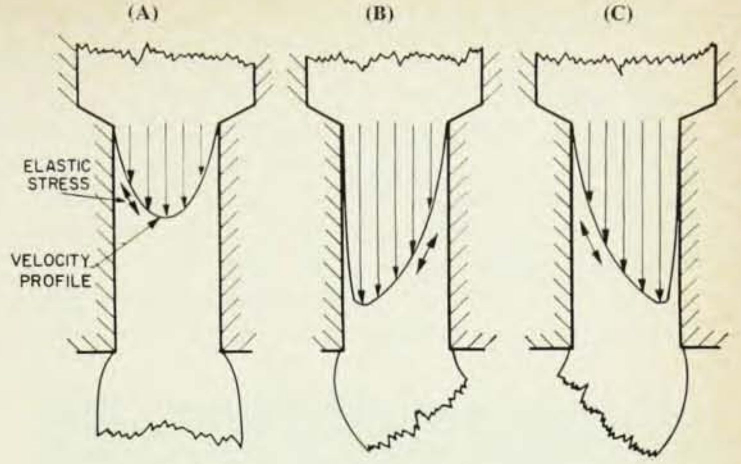


Fig. 9. Velocity profiles in laminar flow and in elastic turbulence. (A) Normal velocity profile; straight extrudate. (B) Low viscosity layer at left; bent extrudate. (C) Low viscosity layer at right; bent extrudate.

Work on the crazing, stress cracking, and fracture of amorphous and semicrystalline polymers shows their structure is not as simple as we once thought.[26] More data and theories are needed to account for the observed behavior.

Crystal structure and morphology

Today many different tools are being used to study the morphology of polymers, and our ideas of the morphology of polymer crystals are undergoing some revolutionary changes.

Infrared and x rays have long been used in this field. Since our Division was started, the tool of nuclear magnetic resonance has been discovered and used by many workers to study detailed molecular motions in polymers.[27] Its value is indicated by the number of papers on NMR studies at this meeting.

The use of optical light-scattering tests to measure the molecular weight of polymers was reported by Debye about twenty years ago.[28] More recently R. S. Stein has been using the scattering of polarized light to study the growth and structure of spherulites in solid polymers.[29]

It has been known for some forty years that fibers of cotton and ramie and stretched natural rubber were partially crystalline at room temperatures. Synthetic fibers, such as nylon, were known to be crystalline when they were first commercialized, some five years before our Division was organized.

A great many structural details of polymer crystals have been worked out by Bunn and others using x-ray and other techniques. Work of Hosemann et al. gave us new ways of interpreting the "amorphous" bands.

Recently, x-ray and NMR data have shown the details of changes in molecular motion in crystals of polytetrafluoroethylene at the 19° transition point.[30]

Because the calculated dimensions of the crystallites were much less than the length of the polymer molecules, the well-known fringed-micelle picture of the morphology of crystalline and amorphous regions was proposed about 30 years ago, and was almost universally accepted until very recently.

In 1957, three workers, P. H. Till in the United States, and soon after, A. Keller in England and E. W. Fischer in Germany,[30] revolutionized our views of the structure of polymer crystals and destroyed the fringed-micelle model. They showed that single crystals of polymers could be prepared from solution as thin platelets about 100Å thick. A typical electron-microscope picture of polyethylene is shown in Fig. 10. Figure 11 shows a crystal of polyoxymethylene, illustrating the screw axes of spiral growth. Electron diffraction patterns show the surprising result that the chain axes of the molecular are normal to the large dimension of the platelets.

Work of Geil, Reneker,[30] and others shows the polymer chains must be folded somewhat as shown in Fig. 12. These structures are now found in crystals from melts as well as from dilute solutions,

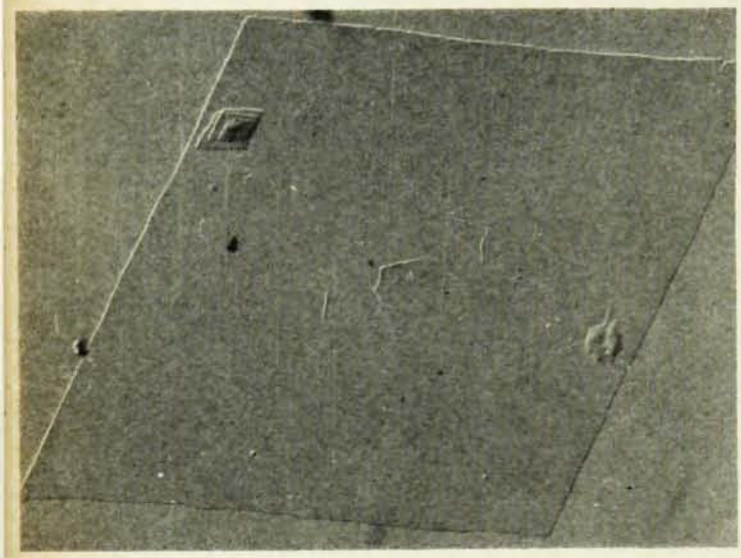


Fig. 10. Single crystals of polyethylene, above, as seen with an electron microscope

Fig. 11. The photomicrograph at right shows a crystal of polyoxymethylene growing with screw dislocations.

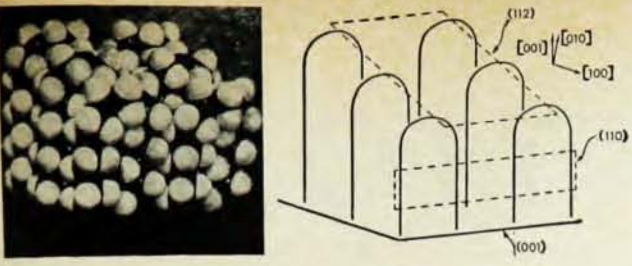


Fig. 12. Folding of polymer chains in laminar crystals

and they are accounting for some of the hitherto unexplained properties of spherulites.

While this concept was almost unthinkable just a few years ago, its importance is indicated by the fact that almost 30 percent of the papers at this meeting are concerned with these laminar crystals. The Ford Prize of the Division of High-Polymer Physics was given to A. Keller for his extensive work in this field.

With these new and challenging ideas in the field today, it would be most hazardous to speculate on where they will lead in the next decade. But it is safe to say that we will then have a far more detailed knowledge than now of the morphology of our polymers, and of the changes in structure during deformation. This will help us learn how to treat them to bring out their most useful properties.

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