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Reviews

Some Reflections on the Early Development of Polymer Dynamics: Viscoelasticity, Dielectric Dispersion, and Self-Diffusion

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ABSTRACT: Early events in the development of understanding the dynamics of configurational changes in macromolecules and their relation to physical properties (viscoelasticity, dielectric dispersion, and diffusion) are reviewed. The period covered is generally from 1930 (when polymers were first accepted as genuine molecules) to about 1970, though there are a few references to earlier and later contributions. Emphasis is given to early work that is less familiar to contemporary investigators and is seldom if ever cited in the current literature.

The year 1930 marked the turning of the tide in favor of the view that polymers were true molecules with normal covalent bonds, the evidence for which had been advanced vigorously and persistently by H. Staudinger and, with some differences in conclusions, by K. H. Meyer and H. Mark.[1] However, little was understood then about macromolecular configurations and in particular about configurational changes that could be related to observed physical properties. Some early stages in the development of understanding polymer dynamics from 1930 on are recalled in this review, with emphasis on lesser known events with which many contemporary investigators may be unfamiliar rather than topics that have been extensively reviewed in recent literature. The history reflects the writer's personal perspective and will inevitably slight some important contributions.

Staudinger first believed that a linear polymer such as polystyrene would have the configuration of an extended zigzag—a rigid rod—even in dilute solution. The alternative view, that rotation about chain backbone bonds would provide a variety of configurations with an average end-to-end separation much smaller than the contour length, was treated as early as 1932 by Henry Eyring;[2] the detailed statistics of random coils were calculated by Werner Kuhn[3] and others and the experimental evidence for bond rotation was summarized by H. Mark[4] in 1934.

The statistical basis of rubberlike elasticity is now so well understood that it is surprising to realize the puzzlement that existed at that time even though the experiments of J. P. Joule, interpreted by thermodynamic calculations of Lord Kelvin, had shown more than 70 years earlier that the retractive force of rubber was entropic.[5] The first quantitative connection between chain statistics and mechanical properties was a landmark paper by E. Guth and Mark[6] in 1934, in which the retractive force of an isolated molecule was calculated as a function of end-to-end separation. The calculation was extended by Kuhn[7] in 1936 to estimate the elastic modulus of macroscopic rubber, although it was not yet fully appreciated that equilibrium elasticity requires a *network* of flexible chains. In 1938, he recognized[8] that the molecular weight calculated from the statistical formula should represent that of a network strand rather than an original linear molecule. In the next few years, the theory of rubberlike elasticity reached essentially its present form, due largely to the calculations of F. T. Wall,[9] H. M. James and E. Guth,[10] P. J. Flory,[11] and L. R. G. Treloar.[12]

Time-Dependent Mechanical Properties

The statistical calculations of entropy differences implied that the molecular chains in a rubber must be changing their configurations very rapidly, even though the material, macroscopically, is a solid. However, there was very little mention of dynamics, in particular the question of time scale. Kuhn[13] in 1938 speculated that local ("micro-Brownian") motions should be very fast.

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Early evidence from experiments other than mechanical showed that local chain motions in rubber (Hevea), whether cross-linked or not, were rapid. Measurements in Kuhn's laboratory of translational diffusion of phenol[14] and azobenzene,[15] among others, in trace amounts through rubber provided diffusion coefficients on the order of 10^{-8} $cm^2\,s^{-1}$. This corresponded to a Stokes' law local viscosity on the order of 1 P, in contrast to an infinite macroscopic viscosity for vulcanized rubber. Also, a very early observation of NMR line width[16] in rubber showed a narrowing characteristic of a liquid rather than a solid.

A simple study at Notre Dame in 1944 of the kinetics of retraction of stretched Hevea rubber bands[17] showed that the relaxation times for configurational changes of network strands were in fact too short at room temperature to be measured by this kind of experiment. The progress of retraction at various points along a stretched band after release of one end was followed by a mechanical stylus and also high-speed photography. The midpoint of the band remained fully stretched until the released end had contracted to that point; a wave of contraction progressed along the band. Thus the process was governed by inertia rather than an internal friction related to rates of configurational changes. The only parameters involved were Young's modulus and the density. Retraction governed by internal friction would of course be uniform all along the length of the band.

Kuhn recognized[18] that the kinetics of configurational changes of random polymer coils would involve a broad spectrum of relaxation times and that these would eventually be related to macroscopic relaxation times observed in measurements of viscoelasticity. Because of the short time scale, dynamic experiments (with sinusoidally oscillating deformations) rather than transients (creep, stress relaxation) would be more useful to probe short-range configurational rearrangements.

Mechanical models (springs and dashpots) had been used to describe both dynamic and transient macroscopic viscoelasticity for several decades.[19-21] Electrical analogs[22] were also popular for a time because of a curious reversal of analogies. In the nineteenth century, exposition of electrical circuit theory could be facilitated by drawing parallels such as making a condenser correspond to a spring, a resistance to a viscosity, etc. But by 1920, electrical circuits were more familiar than mechanical models and were often considered as helpful crutches for understanding viscoelasticity. There were at least two different electromechanical analog schemes, with detailed rules for interconversion.[21-23]

Some mechanical models were drawn with complicated networks of springs and dashpots and even bizarre additions such as ratchets or chains in attempts to relate to molecular processes. However, *any* combination of springs and dashpots can be converted to either a generalized Maxwell–Wiechert or generalized Voigt–Kelvin array, corresponding, respectively, to the relaxation modulus or the creep compliance of linear viscoelasticity, and essentially only these two standard models survived. Rules for interconversions of models were discussed in detail by T. Alfrey[20] and others. The Maxwell model corresponds to a series of exponential terms in stress relaxation with relaxation times τ_k, or, for the complex elastic modulus in the frequency domain, a series of terms in $i\omega\tau_k(1 + i\omega\tau_k)^{-1}$ where ω is the radian frequency. Though this formulation was first used purely empirically with a few arbitrary τ_k's for rough data fitting, theories of dynamics eventually led to series of this form with the τ_k's specified by molecular parameters.

Even before good viscoelastic data had accumulated in significant amounts, it was recognized that a full description over wide ranges of time scale would require combining transient and oscillatory measurements either by interconversion of the complex elastic modulus (or compliance) with stress relaxation (or creep) or by representation with a relaxation spectrum or retardation spectrum. An early summary of the necessary interconversion formulations for linear viscoelasticity by T. Alfrey and P. Doty appeared in 1945.[24,25] An enormous volume of literature on this subject has evolved including both exact interrelationships and convenient approximation schemes, culminating in the 1989 monograph by N. W. Tschoegl.[21] (For practical purposes, of course, the different experiments are not necessarily equivalent. Compliance reveals long-time behavior more clearly than modulus, as first observed by Leaderman and Marvin[28] and recently emphasized by Plazek.[29] The complex modulus or compliance has the advantage over transient measurements of providing two numbers at each frequency, which, over a range of frequencies, have an interconnection that can and should be used to test the internal consistency of data.)

The interconversions were in some cases carefully tested. The first extensive, critical compilation which included not only different types of measurements but also a variety of experimental methods was the product of a cooperative program organized by R. S. Marvin at the National Bureau of Standards in 1949. A single batch of polyisobutylene was subjected to measurements of forced, free, and resonance vibrations, wave propagation, creep, and stress relaxation, in shear, elongation, and compression, by investigators in 27 different laboratories.[30] The effective ranges of time and frequency were extended by temperature superposition.[31] Most of the time scale (reduced to 25 °C) was covered by painstaking measurements at two laboratories: 0.3–3 × 10^6 s (stress relaxation) by A. V. Tobolsky at Princeton[33] and 5 × 10^{-8}–0.5 s (complex dynamic modulus) by E. R. Fitzgerald at Wisconsin.[34] Most of the other data agreed satisfactorily. Later, Tobolsky worked at lower temperatures and by superposition covered the entire range with stress relaxation, thereby checking with the dynamic data the interconversion with storage modulus as well as the validity of temperature superposition over an enormous range of time scale.[35] Marvin's compilation and analysis presented in 1953[30,36] provided perhaps the first complete experimental delineation of the terminal, plateau, transition or softening, and glassy zones of viscoelasticity together with complete relaxation and retardation spectra, though Tobolsky had covered most of the range with his master curves from stress relaxation.[37]

A quantitative relation between macroscopic viscoelasticity and molecular dynamics had remained elusive. Both Alfrey[38] and Kuhn[39] proposed that longer and longer relaxation times corresponded to rearrangements of longer and longer segments of random coils. From 1939 to 1950, Kuhn and his associates published a series of lengthy calculations of the forces on individual polymer molecules when stretched to different extents and at different rates, introducing the concept of the internal viscosity of a flexible chain[40] and describing the transition from entropy elasticity to energy storage by bond stretching as a carbon chain, for example, approaches its maximum extension to a planar zigzag conformation.[41] However, partly perhaps because extensive experimental results were not yet available to guide their concepts, their attempts to relate viscoelasticity to molecular motions failed to predict the magnitudes and frequency dependences for an undiluted amorphous polymer as exemplified in Marvin's compilation[30] or for the theoretically much simpler case of a linear polymer in dilute solution where the polymer molecules could be considered as isolated. The latter case was treated with striking success by P. E. Rouse, Jr., in 1952 with both theoretical[42] and experimental[43] results.

The somewhat unexpected fact that isolated random coils in very dilute solution could contribute to macroscopic viscoelasticity was first shown in 1948 by Baker, Mason, and Heiss[44] at Bell Laboratories with oscillatory measurements at 10^4–10^5 Hz on solutions of polystyrene and polyisobutylene at concentrations as low as 0.1%. This study was in part the motivation for an important but obscure paper[45] the following year by J. G. Kirkwood, who with J. Riseman had just completed their theory of the viscosity of dilute polymer solutions. He pointed out that Brownian motion would interact with hydrodynamic forces imposed on the polymer by the flowing solvent. Using a molecular model with fixed bond lengths and angles and rotation around successive bonds, which had earlier been applied to the steady-flow viscosity by Kramers,[46] he showed that the complex shear modulus could be formulated by a series of terms proportional to $i\omega\tau_k(1 + i\omega\tau_k)^{-1}$ with different relaxation times τ_k. However, the quantities appearing in the equations were inaccessible, and there was no way of comparing them with experiment.

In Rouse's well-known theory,[42] unlike Kirkwood's, no attmept was made to specify individual bond orientations; the coil was represented as a sequence of Gaussian submolecules within which configurational rearrangements are rapid compared with the time or frequency scale under consideration. (There was no mention of beads or springs.) By a transformation to normal coordinates, the complex shear modulus (or complex viscosity) was formulated as a series of terms corresponding to normal modes of motion with a frequency dependence $i\omega\tau_k(1 + i\omega\tau_k)^{-1}$ in which all magnitudes and relaxation times were specified by the molecular weight, concentration (low but finite), solvent viscosity, and two undetermined parameters: the arbitrary submolecule length and the friction coefficient per unit length. If the solution viscosity is known and high frequencies are avoided, these latter parameters cancel out and the components of the complex modulus are predicted as a function of frequency with no adjustable parameters whatever. To test the theory, Rouse also obtained some important experimental results that appear to have been forgotten. With K. Sittel, he devised an ingenious hollow torsion pendulum[47] for oscillatory measurements on very dilute solutions at audio frequencies. Combining this with the torsional piezoelectric crystals of Mason,[44] they measured the complex modulus of dilute solutions (concentration 0.1–0.3%) of fractionated polystyrene and polyisobutylene in good solvents and showed quantitative agreement with theory for different molecular weights, concentrations, and solvent viscosities, over a frequency range of 2.5 decades.[43,48]

In retrospect, the agreement should not have been quite exact, because of several shortcomings (neglect of hydrodynamic interaction, significant even in good solvents; some degree of polydispersity in polymer fractions; no extrapolation to infinite dilution). However, the molecular origin of viscoelasticity in dilute solution was clearly established. B. H. Zimm's reformulation of the problem,[49] more closely related to the earlier work of Kirkwood,[45] with a somewhat different model in which beads and springs are identified, provided for hydrodynamic interaction, which should be dominant in a Θ-solvent, and extended the application to birefringence and dielectric dispersion. For the case of no hydrodynamic interaction, the results agreed with those of Rouse. Subsequent modifications of the Zimm theory accounted for variable hydrodynamic interaction, branching, and block copolymer structure. Although measurements in 1962 at low concentrations down to 0.5% showed the necessity of including hydrodynamic interaction,[50] it was not until 1966 that data of Sakanishi and Tanaka[51] on very narrow distribution polymers in Θ-solvents were extrapolated to infinite dilution and shown to agree quantitatively with the Zimm theory (no adjustable parameters if the intrinsic viscosity is known). Large volumes of data became available for quantitative comparison with theory from 1970 on.[52]

At high frequencies, or in very high viscosity solvents, the Rouse and Zimm theories are of course expected to fail because motions within the submolecules cannot be ignored.[53] This subject, of much current interest,[54] is outside the scope of the present account.

It may be remarked that Staudinger's old concept of a rigid-rod macromolecule was finally confirmed for one megamacromolecule—tobacco mosaic virus—whose dilute-solution complex modulus, extrapolated to infinite dilution,[55] agreed with the frequency dependence for a rod calculated by Kirkwood and Auer,[56] with a single relaxation time.

F. Bueche,[57] a year after Rouse, developed a molecular theory for viscoelasticity of undiluted polymers and networks that was similar in some respects to Rouse's. However, it was based on a less detailed molecular model; the series of terms in $(1 + i\omega\tau_k)^{-1}$ describing the complex modulus (or exponential terms describing stress relaxation) was more complicated and inconsistent with Rouse's. Direct comparison with experiment was not made.

Rouse did not approve of applying his theory to concentrated solutions, undiluted linear polymers, or networks. However, others did not hesitate to try modifications. For an undiluted amorphous polymer, simple substitution of density for concentration provided approximate agreement in a limited frequency range with viscoelastic properties when the molecular weight was less than the critical value for manifestation of entanglements.[58,59] For a rubber network, analysis by M. Mooney of the normal modes for a chain anchored at both ends resulted in addition of one term with an infinite relaxation time, the appropriate molecular weight being the average value between cross-links, and provided qualitative agreement.[60,61] For a linear polymer of high molecular weight in the transition or softening zone, the modification corresponds to the network case with the appropriate molecular weight as the average value between entanglements.[58,59] Qualitative agreement with observed frequency dependence at the low-frequency end of the softening zone was sufficient to justify description of the slowest configurational mode of a linear molecule in a condensed environment, whether the ends were free or anchored, as the first Rouse mode, so that the longest relaxation time in this zone is often called the "Rouse time". However, at higher frequencies the frequency dependence in the softening zone of an undiluted polymer deviates from the Rouse prediction to an extent that varies considerably with its chemical nature—polystyrene and polyisobutylene contrasting sharply, for example, as discussed in 1956 by Tobolsky[63] and the writer.[64] The origin of these differences is still not clear.

Temperature Dependence of Dynamic Processes

The extensive tests of time–temperature superposition by Tobolsky and in Marvin's 1954 compilation have been mentioned, and of course this principle was used in processing many of the data referred to in the preceding paragraphs. The essential role of temperature in changing the time or frequency scale was recognized for dielectric dispersion as early as 1913 by K. W. Wagner.[65] The similarity in shape of logarithmic plots against time or frequency at different temperatures, for both mechanical and dielectric properties, was discussed in Leaderman's early monograph,[19] which cited some early experimental results[66] and stressed the necessary condition that *all* relaxation (or retardation) times depend on temperature identically. Tobolsky[67] was the first to construct composite curves that extended the effective time scale. For viscoelastic liquids, the writer[68] obtained the superposition shift factors from the measured temperature dependence of the steady-flow viscosity instead of empirically, without assuming any specific form of temperature dependence. The principle then emerged as a corollary of molecular theory as just described, which also justified the introduction of a minor temperature dependence of the magnitude of the modulus or compliance, as applied by Tobolsky[70] and the writer.[68,69]

At first, it was supposed that the temperature dependence of superposition shift factors would follow the Arrhenius relation and be described by an activation energy, and experiments over a moderate temperature range confirmed this expectation. Recognition of a very different relation over a broader range, with an apparent activation energy that increased sharply with decreasing temperature, spurred attempts to describe this analytically. Tobolsky[71] proposed a function of T/T_d, where T_d was near or equal to the glass transition temperature T_g, which described the temperature dependence within 20° of T_g. However, some old empirical equations for the steady-flow viscosity of supercooled liquids[72-74] would have implied $T - T_g$ as a more useful parameter than T/T_g. The WLF equation[75] described the shift factor (or the viscosity) as a function of $T - T_0$, where T_0 is any arbitrary reference temperature, over a range of roughly 100° above T_g; it was equivalent to the formulations of Fulcher[72] and Tammann and Hesse[73] for the temperature dependence of viscosity. The WLF equation was derived from the assumptions that the viscosity (or relaxation times) is an exponential function of the reciprocal fractional free volume[76] and the free volume is a linear function of temperature. Similar formulations in terms of free volume were later introduced for the dependence of relaxation times on concentration,[77] pressure,[78] and (low) molecular weight.[78] Measurements over wide ranges of confining pressure provided critical tests of time–pressure superposition and a more rigorous determination of free-volume parameters.[79] There is an extensive literature on modifications and improvements of free volume theory and various cases of minor or major departures from the applicability of time–temperature superposition where for a variety of reasons not all relaxation times depend identically on temperature or pressure. These developments are beyond the scope of this review.

Topological Restraints

Even before the statistical origin of rubberlike elasticity was understood, W. F. Busse[80] advanced the view that the retraction of rubber implied the presence of a network that in vulcanized rubber was held together by covalent bonds and in unvulcanized rubber by "entanglements". (He could not, however, explain the mechanism of energy storage and retraction.) After the statistical theory was established, L. R. G. Treloar[81] concluded from some simple but critical experiments that Busse was correct and he emphasized that the temporary network in an unvulcanized rubber must be held together by mechanical entanglement and not by van der Waals forces.

A. V. Tobolsky's precise measurements of stress relaxation of linear polymers identified the plateau modulus on the time scale where relaxation is very slow, which for high molecular weights was rather well-defined; he was apparently the first to use its value to estimate the molecular weight between entanglements by the standard relation for cross-linked rubbers.[82] The popular conception is that the primary evidence for entanglements (or, more generally, topological constraints) comes from the molecular weight dependence of steady-flow viscosity, but the existence of the plateau modulus was adduced at least as early and in the writer's opinion was more compelling.

The famous change in slope at a critical molecular weight, M_c, when viscosity is plotted logarithmically against molecular weight was observed by T. G. Fox and P. J. Flory[83] in an exhaustive series of measurements on dozens of fractionated polyisobutylenes and polystyrenes, from 1949 to 1951. They noted that below M_c the slope is not unity and the plot is not necessarily linear, a feature that is frequently neglected today. (It was later shown that this slope becomes unity if the effect of molecular ends on free volume is taken into account, an effect to which Fox and Flory also attributed certain anomalies in the temperature dependence of viscosity.) They determined the now well-known exponent of 3.4 but did not interpret its significance. (A similar exponent was noted by Tobolsky for the molecular weight dependence of the position of the terminal zone on the logarithmic time scale, a measure of the longest relaxation time.[84])

The change in slope at M_c was first interpreted qualitatively in 1952, with modifications in 1956, by F. Bueche,[85] with a model of entanglement coupling. He proposed that each linear molecule is coupled to a number of others and drags them along in its translational motions, each of them drags others, and so on, but with a certain slippage so the coupling decays with distance. With numerous simplifying assumptions, he obtained a logarithmic plot of viscosity versus molecular weight with an increase in slope to 3.5 at a molecular weight equivalent to an average of one coupling point per molecule. However, the rigor of the analysis has been questioned.[86] For a time there was some confusion about the relation between M_c derived from viscosity and the average molecular weight between entanglements, M_e, derived from the plateau modulus,[87] until the ratio $M_c/M_e \cong 2$ was clearly established experimentally.

The immense volume of subsequent work, especially the concept of reptation, undertaken to describe the nature of topological constraints and interpret their manifestation in viscosity, viscoelastic properties, and diffusion, is beyond the scope of this review.[86,88,89] Despite the natural reluctance to identify loci of constraint as entanglement points on a molecule of uniform chemical structure, all theories appear to involve a spatial scaling of some kind, which corresponds to the original concept of an entanglement spacing.

Dielectric Dispersion

A different physical manifestation of macromolecular configurational changes that was studied early is the frequency dependence of the complex dielectric constant. The existence of "anomalous dispersion", a decrease in dielectric constant with increasing frequency accompanied by energy absorption (dielectric loss), was noted by P. Drude[90] in 1897 for many simple liquids at frequencies on the order of 10^8–10^9 Hz. It was not until 1913 that P. Debye[91] first showed that this behavior could be explained by the presence of molecules with permanent electrical dipoles whose rotatory Brownian motion and perturbation thereof in response to an alternating electrical field are limited by frictional resistance. Debye's theory was developed subsequently and elegantly summarized in a book[92] in 1929. The frequency dependence of the real and imaginary (loss) components of the complex dielectric constant was characterized by a relaxation time whose magnitude could be calculated by modeling the polar molecule as a sphere rotating in a continuous medium with a specified viscosity. Comparison with experiments (e.g., those of S. Mizushima[93]) showed that, if the macroscopic viscosity of the liquid was chosen, the calculated molecular radius had the correct order of magnitude and the temperature dependence of the relaxation time paralleled that of the viscosity, despite the unrealistic model of a continuous medium. However, the calculated radius was sometimes implausibly small, especially in the case of a polar substance dissolved in a nonpolar liquid of high viscosity.[94]

The approximation of a continuous medium was better for a polar *macro*molecule dissolved in a liquid of low molecular weight, provided the polymer rotated as a rigid body. Early, somewhat fragmentary data on the globular proteins zein by J. Wyman[95] in 1931 and hemoglobin by J. Errera[96] in 1932 were fitted to the Debye theory[97] and provided molecular weights of the correct magnitude on the basis of a spherical model or even, if the dispersion could be separated into two components with different relaxation times, a model of an ellipsoid of revolution. More extensive and thorough data on several proteins in aqueous solution were obtained by J. L. Oncley[98] (who was able to handle solutions with some degree of conductance) and in alcohol–water solution by J. W. Williams.[99]

A flexible-chain polymer was of course quite a different matter. Measurements on dilute solutions of poly(ω-hydroxydecanoic acids) of different molecular weights up to 29 000 were made independently in 1937 by Williams[100] and Wyman.[101] Both showed that there was no frequency dependence in a range where it would be expected if the molecule rotated globally, and moreover the square of the average dipole moment was a linear function of the molecular weight, as expected for a random coil provided the dipoles are aligned parallel to the chain. Thus the individual polar groups were changing their orientations rapidly with only local correlations. Other examples of behavior in dilute solution accumulated gradually in subsequent years.

An attempt[102] to calculate the frequency dependence of the complex dielectric constant for a dilute solution of a polar macromolecule was made by J. G. Kirkwood and R. M. Fuoss in 1940, stimulated by Fuoss's experiments on solid polymers to be described below, even though the latter were far from dilute. Thus Kirkwood's dielectric dispersion theory antedated by nearly a decade his corresponding treatment of mechanical properties;[46] they were summarized in a general theory[103] in 1953, and two years later Hammerle and Kirkwood[104] extended the dielectric case to include hydrodynamic interaction. The shape of the frequency dependence of the dielectric loss[104] agreed rather well with some data on concentrated solutions of poly(vinyl acetate) by Funt and Mason[105] but predicted a dependence of the maximum-loss frequency on molecular weight that was not confirmed by later experimental work.[106] W. Kuhn subsequently attempted to formulate the distribution of dielectric relaxation times[107,108] but reached the erroneous conclusions that the result would not depend on whether the dipoles were parallel or perpendicular to the chain backbone and that the spectrum would be essentially a single relaxation time (corresponding to global rotation) unless the molecular weight was exceedingly high. Both the Kirkwood and Kuhn spectra were expressed as continuous functions, not series.

Finally, Zimm's normal-mode analysis[49] predicted the dielectric frequency dependence in the form of a series of terms similar to that for the complex elastic modulus except that only odd numbers of the index k appear and there is a weighting factor of $1/k^2$, which profoundly alters the shape of the spectrum. (The dielectric spectrum is more nearly analogous to the retardation spectrum of mechanical compliance than the mechanical relaxation spectrum.) Soon thereafter, van Beek and Hermans[109] treated a somewhat different model (free-draining hydrodynamics, plus internal viscosity) and predicted *two* loss peaks, of which one resembles Zimm's. Some time later Stockmayer and Baur[110] showed that the distribution of charges on the "beads" of the model can greatly affect the dielectric response and that Zimm's calculation corresponds to the case of dipoles rigidly oriented parallel to the chain backbone. For dipoles in perpendicular orientations or flexibly attached in side groups, an entirely different behavior is expected. Some early work on undiluted poly(propylene oxides) of low molecular weight[111] supported the normal-mode (Zimm) calculation, as have many more recent investigations beyond the scope of this review.

Some dielectric measurements on solid polymeric materials appeared early in the technical literature because of their use as insulators. A thorough study of the complex dielectric constant of natural rubber vulcanized with sulfur to different extents, by A. H. Scott[112] at the U.S. Bureau of Standards in 1933, was analyzed further by F. H. Müller.[113] The frequency dependence of both the real dielectric constant and the loss tangent was qualitatively similar to the prediction of the Debye theory though obviously broader than could be described by a single relaxation time.

However, basic investigation of dielectric properties of solid polymers can be said to have begun with R. M. Fuoss at the General Electric Co., who from 1937 to 1942 published a long series of papers.[114] In his meticulous experiments he avoided effects of surface polarization, distinguished between dielectric loss and conductance, and furnished exhaustive data for the complex dielectric constant of several polymers with carefully selected chemical structures, over wide ranges of frequency, temperature, plasticizer content (both polar and nonpolar diluents), and molecular weight. He identified two maxima in the frequency dependence of the dielectric loss of poly(vinyl chloride) and showed that the one observed at higher temperatures corresponded to a broad distribution of relaxation times with a relatively strong temperature dependence.[115] With added diluent, the relaxation times decreased and the distribution sharpened somewhat;[116] the relaxation times increased with molecular weight.[117] Subsequent work on polymers with flexible polar side groups showed somewhat sharper dispersions.[118] A monomeric polar diluent dissolved in a nonpolar polymer exhibited similar dielectric dispersion, though at higher frequencies than for the same polar group chemically attached to the polymer; it was concluded that configurational rearrangements of the macromolecules were required for rotation of the polar monomer.[117]

Large volumes of dielectric data on various polymers including plasticized mixtures were published by Würstlin and collaborators[119] from Badische Anilin- und Soda-fabrik (1948–1956) and by Reddish and collaborators[120] from Imperial Chemical Industries (1950–1954). The latter employed contour graphs and three-dimensional models to portray simultaneous frequency and temperature dependence of the real component of the dielectric constant and loss tangent, to identify clearly two different regions of dispersion with different temperature dependences as noted earlier by Fuoss. Deutsch, Hoff, and Reddish,[121] in an exhaustive study of poly(methyl methacrylate), were the first to denote these by the now popular designations α, β, etc., in the order of decreasing temperature or increasing frequency. They attributed the β dispersion to rotation of the ester side groups and identified it with a mechanical loss mechanism observed earlier in the viscoelastic glassy zone by Lethersich[122] and Schmieder and Wolf.[123] In subsequent studies by various investigators on many different polymers, dielectric and viscoelastic dispersions were compared, often simply by locating maxima in the respective loss tangents on the frequency scale. The dielectric α mechanism was identified with the transition or softening zone of viscoelasticity, and, with suitable normalization, temperature–frequency superposition could sometimes by applied over wide frequency ranges to determine the temperature dependence of the relaxation times. In two early detailed studies,[124,125] the dielectric and viscoelastic temperature shift factors were found to be identical (and later described by the WLF equation). For the β mechanism, unlike the α mechanism, temperature dependence could be described simply by an Arrhenius activation energy, which was found to be essentially the same for dielectric and viscoelastic in many cases.[126] Comparisons of the spectra of relaxation times and their magnitudes involve more complicated considerations, which are only recently being resolved.

Self-Diffusion of Probe Molecules

Another source of information for the kinetics of configurational changes in polymers is the diffusion of a probe ("penetrant") molecule, of monomeric or somewhat larger dimensions, through a polymer matrix. The early experiments of Kuhn and Grün, implying rapid molecular rearrangements in rubber to permit translatory movement of small organic molecules, have already been mentioned.[14,15]

Study of the diffusion of gases (*very* small probes) through natural rubber actually goes back to 1831 when J. K. Mitchell[127] measured the escape of air, hydrogen, and carbon dioxide from miniature balloons. T. Graham,[128] in the course of his extensive diffusion studies, measured the rate of permeation of various gases through rubber membranes in 1866. He recognized that its change with increasing temperature involved two opposing effects—diminishing solubility of the gas and increasing "softening" of the rubber, the latter predominating to give a net increase in permeation rate. H. A. Daynes[129] in 1920 expressed this quantitatively, showing that the permeability coefficient is proportional to the product of the solubility and the diffusion coefficient and that all three could be determined from a single experiment on permeation through a rubber film.[130,131] (With appropriate definitions the proportionality constant is unity.[132]) In subsequent years, various methods other than permeation for measuring diffusion coefficients were exploited and large amounts of data were accumulated, first on various small molecules in rubbers and then, with the advent of synthetic polymer films and their importance for packaging, in polymers of different chemical structures.[133]

Translatory diffusion of a probe molecule can be more clearly related to polymer dynamics if it is larger than a diatomic gas so that significant segmental rearrangements are required and if the self-diffusion coefficient of the penetrant can be evaluated. The self-diffusion coefficient at vanishing penetrant concentration can be identified with the mutual diffusion coefficient extrapolated to zero concentration as calculated from classical permeation (absorption–desorption) experiments by S. Prager and F. A. Long in 1951 for hydrocarbon vapors diffusing into polyisobutylene.[134,135] However, the self-diffusion coefficient can be better determined directly over a range of concentrations by use of radioactively tagged penetrants as introduced by Auerbach and Gehman[136,137] in 1954–1958 or measurements of pulsed gradient spin-echo NMR as introduced by Stejskal[138,139] in 1963–1965, and the majority of existing data have been obtained by these methods.

In Long's studies[134,140] over a range of temperatures, it was noted that the apparent activation energy for diffusion of moderately sized penetrants at vanishing penetrant concentration was similar to that for steady-flow viscosity of the polymer (at a specific temperature), with the suggestion that motion of polymer segments was rate-limiting, for example, by opening of holes. When viscoelastic data in the transition or softening zone became available shortly afterward, it could be shown that not only the temperature dependences but also the magnitudes of the friction encountered by motions of the penetrant and the polymer segments were closely related.[141] In comparing natural rubber[142] and polyisobutylene[143] at room temperature, for example, the diffusion coefficients of butanes and pentanes differ by 2 orders of magnitude (even though their glass transition temperatures are closely similar!), and the relaxation times for the first Rouse mode of the polymer differ by about the same factor. The translatory friction coefficient for penetrant motion and the monomeric friction coefficient for polymer segment motion were similar in magnitude. Later extensive studies with diffusion of radioactively tagged penetrants[142–144] (mostly *n*-hexadecane) showed in some cases approximate proportionality between the two friction factors for the same penetrant in several different polymers.

Spin-echo NMR was first applied in 1959 by McCall and collaborators[145] to measure self-diffusion in undiluted polymer of low molecular weight. Subsequently, they showed that in a solution the diffusion of both polymer and solvent could be detected.[146] With the introduction of pulsed-gradient spin-echo methods,[138,139] the self-diffusion coefficients of small diluent molecules (and of ternary probe molecules in trace amounts) could be determined over wide ranges of diluent concentration.[147] (More recent uses of various optical methods to provide similar information on diffusion are beyond the scope of this review.)

Most early studies of the temperature dependence of penetrant self-diffusion coefficients covered too narrow a temperature range to distinguish beteen the Arrhenius formulation (exponential in $1/T$) and a formulation of the WLF type, which could be related to free volume. Many comparisons of the apparent activation energy of penetrant diffusion with that for viscosity or viscoelastic relaxation times[148] confirmed the early observation[140] of close similarity but showed some systematic differences that have still not been clearly resolved. In only a few cases have free-volume parameters been determined from the temperature dependence. However, the dependence on diluent *concentration*, where the diluent is usually the penetrant itself, covering a wide range of polymer–diluent mixtures (excluding dilute soluions, of course) and many orders of magnitude of the diluent self-diffusion coefficient, was found to be described by free-volume theory[78] as formulated critically by Fujita.[148,149] This was first applied to radioactive tracer data[142] in 1960 and pulsed-gradient spin-echo NMR data[150] in 1967, and subsequently in numerous studies.[147,151]

Even when the self-diffusion of a penetrant molecule is determined by the segmental mobility of the polymer, the diffusion coefficient also depends on the penetrant's own size and shape, of course. For flexible linear penetrants, e.g., a series of normal paraffin molecules, early measurements quoted by Auerbach[137] suggested (at vanishing penetrant concentration) an inverse proportionality of the diffusion coefficient to the molecular weight, which was confirmed by further somewhat fragmentary data from radioactive tracers[143,153] and a thorough series of NMR measurements[147,154] on normal paraffins from C_8 to C_{36} in *cis*-polyisoprene. For more nearly rigid and/or bulky penetrants, the behavior was quite different. As early as 1947, F. Grün[15] showed that for a series of bulky benzene and naphthalene derivatives (e.g., 2,4-dihydroxy-1,1′-azonaphthalene dibenzoate) the diffusion constant in natural rubber decreased with increasing M much more sharply than inversely proportional. Much later studies by NMR revealed some specific effects of the molecular shape of rigid penetrants.[147]

Self-Diffusion of Polymer Molecules

Self-diffusion of polymer molecules, either in the presence of diluent or in undiluted polymer, is a more direct manifestation of configurational changes than diffusion of solvent or probe molecules but was more difficult to measure because the diffusion coefficients can be exceedingly small. In a pioneering study (1952), F. Bueche, W. M. Cashin, and P. Debye[155] used radioactively tagged poly(*n*-butyl acrylate) and polystyrene (plasticized with diethyl phthalate to increase the diffusion rate) to demonstrate that such measurements were feasible. They concluded that the product of the diffusion coefficient and viscosity was approximately independent of temperature, as expected. However, their conclusion that it was also independent of molecular weight (within rather large experimental scatter) for systems that should have been entangled does not agree with later work. In the first application (1959) of spin-echo NMR by McCall and collaborators,[146] as mentioned, diffusion coefficients were determined for polyethylenes with molecular weights on the order of 5000. There was then very little further work for about 2 decades, although two studies may be cited on diffusion in binary blends, a subject that has recently been very prominent. In 1968, Bueche[156] showed that radioactively tagged polystyrene diffused in polystyrene matrices of high molecular weight (M_m) with a diffusion coefficient independent of M_m. In 1971, Tanner[157] used pulsed-gradient spin-echo NMR to show similarly that in binary blends of high and low molecular weight poly(dimethylsiloxane) the self-diffusion of the latter was insensitive to the molecular weight of the former provided that the ratio of the two molecular weights was sufficiently high. These early observations have been extended by a large volume of recent work on self-diffusion employing NMR and other powerful experimental methods to test current theories of polymer dynamics.[88,158]

Other Manifestations of Polymer Dynamics

Various other less extensive experimental studies that reflected configurational changes in polymer systems were made in early years and were understood to some degree in molecular terms. These included flow birefringence,[159] oscillatory birefringence,[160,161] electrical birefringence,[162] fluorescence depolarization,[163] and NMR line width.[164] More recent investigations have greatly improved the success of these methods and have, of course, added new techniques of enormous power such as quasielastic light and neutron scattering, forced Rayleigh scattering, Rutherford back scattering, and time-resolved spectroscopy, which were undreamed of in the time period covered by this review.

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