Dielectric Relaxation in Polymer Solutions

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1 Introduction

A. Dielectric Relaxation.—When a molecular system is placed in an electric field, there is always the tendency for any electrically charged species to migrate along the field in the appropriate direction. If the charged species are completely mobile this results in the conductivity familiar in metals, electrolyte solutions, or semiconductors. However, if the charged entities can move only a certain distance, and then for some reason become localized, the net result is an electric polarization of the sample.

For example, charge carriers may migrate across a sample, but be unable to cross the boundary between the sample and the electrodes. Under these conditions the trapped charges collect at the surface, causing interfacial polarization of the sample. At the other extreme on a distance scale, electrons may migrate across the atoms in a molecule but not between molecules. Thus, each molecule in the field suffers a slight distortion of electron distribution, called electronic polarization (forming in the molecules an induced dipole moment). The addition of each molecular dipole along the direction of the field again causes a resultant polarization of the whole sample. A third example of a polarization process, and the one of interest in this review, occurs when the two opposite charges in a molecular dipole attempt to migrate in the field, thus applying a turning couple to the molecule. This tends to align the dipole in the field. Again the resultant effect is an electric polarization of the sample, called in this case 'orientation polarization'.

The migration of charges lowers the energy of the system in the field, and so is called 'relaxation', and the adjective 'dielectric' is added when polarization, due to localized charges, is involved.

It is evident that the formation of the polarization can take place only at a rate determined by the charge mobility. This is unimportant if the electric field changes slowly, but if the electric field is altered sufficiently rapidly (as with a high frequency alternating voltage or in the field of electromagnetic radiation) there is not time for an equilibrium polarization to be established. So a study of the frequency dependence of the macroscopic phenomena resulting from polarization can yield information on the charge carrier mobility. In the case of orientation polarization due to small fields, this mobility is the rate of Brownian rotational diffusion.

The theory of dielectric relaxation is available in several introductory reviews,[1—3] and here we are concerned with the principal features of orientation relaxation as illustrated in Figure 1:

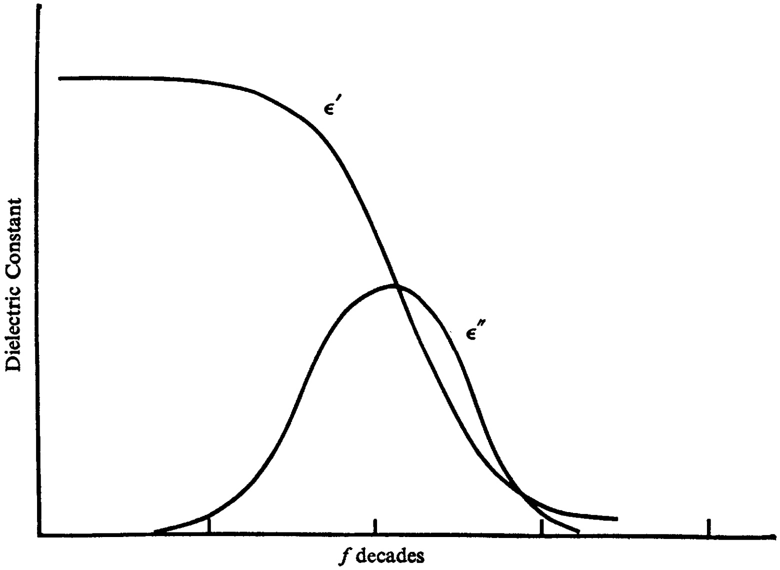

Figure 1 *Relationship between complex permittivity and frequency for ideal orientation polarization*

(*a*) As the frequency of the applied field is increased from below to above a possible frequency for dipole rotation, the macroscopic permittivity is complex and the real part, ϵ' (measured as electrical capacitance) decreases from a value characteristic of orientation polarization to one in the absence of orientation polarization.

(*b*) The imaginary part ϵ'' (measured as conductance, dielectric loss, or energy absorption) is zero when orientation can or cannot take place, but is a maximum when the frequencies of dipole rotation and electric field change are comparable.

(*c*) Both these macroscopic phenomena occur over a rather wide frequency range. Thus, for an ideal system in which the angular position and rate of rotation of any dipole are independent of those of its neighbours, and all rotations are described by a single rate, the width at half-height of the loss curve is 1.1 decades.

(*d*) The relationship between field frequency and dipole rotation rates in the ideal case is

$$2\pi f_{\max} \tau = \omega_{\max} \tau = 1$$

where $f_{\max}$ is the field frequency in Hz at which there is a point of inflexion in

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[1] Mansel Davies, *Quart. Rev.*, 1954, **8**, 250.
[2] Mansel Davies, 'Some Electrical and Optical Aspects of Molecular Behaviour', Pergamon, Oxford and London, 1965.
[3] C. P. Smyth, *Ann. Rev. Phys. Chem.*, 1966, **17**, 433.

the ϵ'-frequency relationship and a maximum in the ϵ''-frequency curve, ω_{max} is the same in radians per second, and τ is the rotational relaxation time. For our purposes, τ is defined simply as the time required for the extent of field-induced dipole alignment to drop to 1/e of its value upon removal of the field. This equation of a macroscopic relaxation time with a molecular rotation time is a considerable oversimplification and a more detailed relationship has been discussed by several authors.[4—6]

B. Molecular Motion in Polymers.—The technical significance of polymeric materials lies in their uses as plastics, rubbers, or fibres. Whether a particular polymer will behave as a glass, rubber, or leather, or whether it will be tough or brittle, is determined by the extent of molecular motion within the sample. Most polymers consist in whole, or in part, of linear backbone chains and the most significant mode of motion is the segmental 'worm-like' motion of these chains. Indeed, the major transition in solid polymers, the glass to rubber transition, is ascribed directly to the onset of large-scale segmental motion of this type.

This segmental motion, in its turn, has its origin in the total or partial rotation which may take place around individual covalent bonds in the backbone. Consequently, it is affected by both intramolecular phenomena (such as the steric hindrance of groups substituted close to the bond about which rotation occurs) and intermolecular phenomena (such as chain entanglement, crystallization on to a relatively close-packed lattice, or simply immobilization by strong intermolecular forces). Before a complete understanding of solid relaxation behaviour can be reached it is desirable to study separately the intra- and inter-molecular effects. Since gas-phase studies of such large molecules are impossible, the next best alternative is to study intramolecular effects in dilute solution, hoping to minimize inter-chain phenomena and to include sensibly the effect of polymer–solvent interactions.

In this review emphasis will be placed on those dielectric studies of polymer solutions which give clear information on the relationship between chemical structure and intramolecular rotational motion. This means that certain subjects (such as the detailed theories of polymer chain conformations or polarization phenomena due to ion-atmosphere migration) will not receive full coverage. In these cases the interested reader is referred to more detailed reviews[7—9] of the topic.

2 Modes of Motion of Dissolved Macromolecules

A. The Basic Rotational Movements.—From the viewpoint of dielectric activity,

[4] N. E. Hill, *Proc. Phys. Soc.*, 1954, **B67**, 149.

[5] R. Kubo, *J. Phys. Soc. Japan*, 1957, **12**, 570.

[6] R. H. Cole, *J. Chem. Phys.*, 1965, **42**, 637.

[7] L. De Brouckere and M. Mandel, *Adv. Chem. Phys.*, 1958, **1**, 77.

[8] W. H. Stockmayer, *Pure Appl. Chem.*, 1967, **15**, 539.

[9] H. Block and A. M. North, *Adv. Mol. Relaxation Processes*, 1970, **1**, 309.

an important mode of motion of a dissolved macromolecule is gross rotational movement of the whole molecule. In its simplest form this requires all segments of the molecule to move in unison, and so implies a clearly defined intersegmental geometry. This criterion exists in rod-like molecules (such as the helical form of certain polypeptides) where rotation may occur about the major or minor axes of the molecule. However, the molecular geometry need not be as perfectly defined as in an helix, and there is no difficulty in visualizing rotation of a random-coil molecule in which the segmental geometry remains fixed during the rotation. This is really introducing a time-dependent definition of molecular flexibility (or rigidity) in that we consider a molecule to be 'rigid' when the time required for changes in conformation by segmental rotation are greater than the time required for rotation of the whole molecule.

This is an interesting definition because it introduces a molecular-weight dependence. Brownian whole-molecule rotation will be very rapid for small molecules (or short chains) and very slow for large molecules (or long chains). Consequently, for a given chemical structure there must be, in principle, a molecular weight at which the times required for segmental rearrangement and whole-molecule rotation are comparable. Below this value the molecule will be defined as 'rigid', and above this value the chain will be defined as 'flexible'.

This leads us to the second important mode of motion, which is a rearrangement of the backbone geometry in chains defined (on the time- and molecular weight-dependent definition) as 'flexible'. A polar polymer molecule is considered to be made up of a large number of unit dipoles. In this form of motion reorientation of each unit dipole occurs almost independently of the motion of the other dipoles in the same chain.

The final intramolecular rotation of interest occurs when a dipole is contained in a side chain of the polymer molecule, and side-chain reorientation can take place independently of backbone motion.

Thus, the three basic motions discussed above can be considered simply as a reduction in size of the independently orienting moiety from the whole molecule, through sections of the chain, to substituent side-groups.

B. Processes other than Dipole Orientation.—Although this review is concerned primarily with the relaxation of orientation polarization, polymer solutions may exhibit a variety of different polarization phenomena which must be borne in mind. Of particular importance in this context are the charge-carrier phenomena exhibited by solutions of polyelectrolytes. It is assumed that effects due to polarization at electrodes can be eliminated, and that in a truly homogeneous solution there should be no Maxwell–Wagner–Sillars[10,11] interfacial polarization due to the large-scale migration of charge carriers across an occluded conducting phase. In this context we consider a separate 'phase' to contain many polymer molecules. However, ion migration can occur within the ion-atmosphere of a single dissolved polyelectrolyte molecule. This gives rise to a polarization which

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[10] K. W. Wagner, *Arch. Electrotechnol.*, 1914, **2**, 371.

[11] R W. Sillars, *J. Inst. Elec. Engineers* (*London*), 1937, **80**, 378.

is best treated by considering[12] each molecule as a conducting occlusion in a less-conducting matrix.

Polarization by means of a chemical reaction is always a distinct possibility. This is particularly the case if hydrogen-bond equilibria (involving differently polarized 'bonded' and 'non-bonded' states) are in existence.

C. The Normal Co-ordinate Analysis for 'Flexible' Chains.—It is necessary now to be more specific about the 'whole molecule' mode of motion for flexible chains. The problem lies in describing the rotational behaviour of a deformable body. This is usually done using a normal-co-ordinate analysis.[13–15] The important property of such an analysis is that motion in a many-particle elastic body can be described by a non-interacting set of differential equations which have, in principle, a definite solution.

Basically, the random coil is resolved into three unidimensional arrays of beads, each experiencing frictional drag with its environment, and each being connected to its neighbour by a volumeless Hookean spring. Each bead corresponds to a subunit of the chain sufficiently large that end-to-end separations within the units follow Gaussian statistics, and the connecting 'springiness' has its origin in the entropic nature of rubber elasticity. That is, stretching a random-walk chain reduces the number of possible conformations, and so increases the free energy of the stretched state. Recently, Tobolsky[16] has made an alternative suggestion in which the linear bead-spring arrays are replaced by damped torsional oscillators. However, the fundamental analysis remains unchanged.

When this elastic array of subunits is placed in some field (shear or elastic) which exerts a turning movement, the molecule is both rotated and distorted (Figure 2). The whole process gives rise to a basic 'breathing motion', together with overtone distortions in which the normal mode number corresponds to the number of nodes in the whole assembly. For the dielectric case[17] we are interested in the first normal mode (which, incidentally, is responsible for about half the polymer contribution to solution viscosity). The significance of the normal-co-ordinate model is that it allows calculation of the relaxation times for the various normal modes from expressions containing only solute concentration c, polymer molecular weight M, and zero-shear-rate viscosity coefficients (for solvent η_s, and solution η) as disposable parameters; see Table 1. In other words, as long as the subunits are sufficiently long to exhibit Gaussian behaviour there is no term in the expression for relaxation time, which is directly and obviously related to chemical structure. While this does give the analysis a very important generality, it also detracts from its usefulness in an attempt to correlate rate of molecular motion with chemical composition.

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[12] C. T. O'Konski, *J. Phys. Chem.*, 1960, **64**, 605.
[13] P. E. Rouse, *J. Chem. Phys.*, 1953, **21**, 1272.
[14] F. Bueche, *J. Chem. Phys.*, 1954, **22**, 603.
[15] B. H. Zimm, *J. Chem. Phys.*, 1956, **24**, 269.
[16] A. V. Tobolsky, *J. Polymer Sci., Part A-2, Polymer Phys.*, 1968, **6**, 1177.
[17] W. H. Stockmayer and M. E. Baur, *J. Amer. Chem. Soc.*, 1964, **86**, 3485.

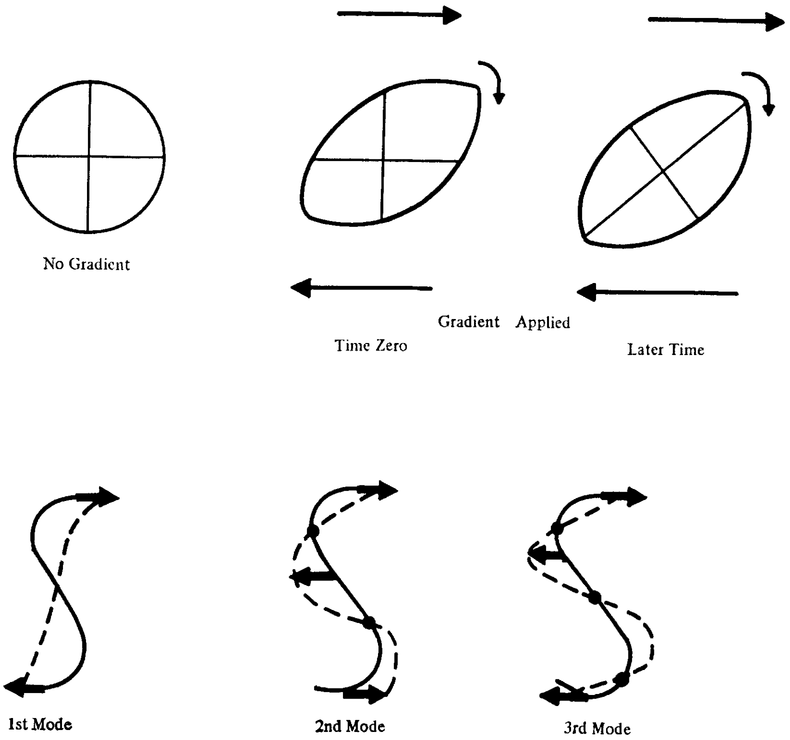


Figure 2 *Movement of a flexible coil in a turning field: zeroth and first two normal modes of motion*

Table 1 *Relaxation times for first normal modes of motion*

Polymer molecular model	*1st Mode relaxation time*
Flexible coil in which solvent movement is unhindered (free-draining coil)	$\dfrac{0.61\,(\eta - \eta_s)\,M}{cRT}$
Flexible coil within which solvent flow is impeded (non-free-draining coil)	$\dfrac{0.42\,(\eta - \eta_s)\,M}{cRT}$
Rigid rod of large length : diameter ratio	$\dfrac{1.25\,(\eta - \eta_s)\,M}{cRT}$

The normal mode, or 'whole molecule', analysis of molecular motion is relevant to a dielectric observation when a resultant displacement vector $\boldsymbol{d}_R$, of the molecule corresponds to the resultant dipole electric vector, μ_R. Thus, when the molecule is 'rigid' any molecular movement corresponds exactly with a movement of the total resultant dipole moment obtained by vector addition of all the individual unit dipoles. However, when the chain is flexible, and all the units in the chain are rotating with a considerable degree of independence, the displacement and electric dipole vectors correspond only when the dipoles are aligned parallel to, and unidirectional along, the chain contour; see Figure 3. This is a rather important restriction, because it implies that a dielectric relaxation rate observed for a flexible coil will be the rate of segmental (or side-group) rearrangement for all molecules except those with unidirectional parallel dipole components, when the observed rate will be that of the first normal mode of motion.

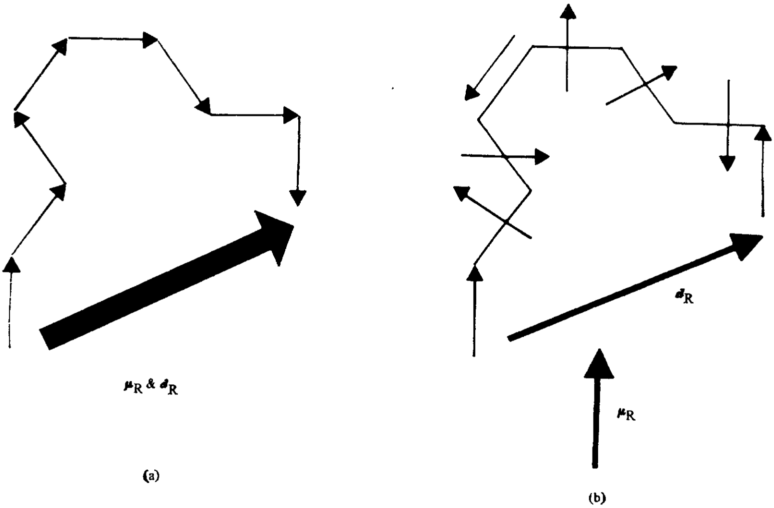


Figure 3 *Correlation of displacement and electric dipole vectors for unidirectional parallel dipole units,* (a); *but no correlation for random or perpendicular dipole units,* (b)

D. The Geometry of the Active Dipole.—The unit dipoles in a polymer molecule may be classified into three major types according to the relative geometry of the dipole moment and the backbone contour. Thus, we may have:

(*a*) the unit dipoles attached rigidly perpendicular to the chain backbone;

(*b*) the unit dipoles attached rigidly parallel to the chain backbone;

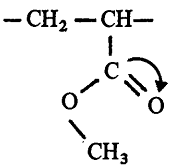
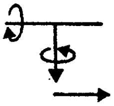
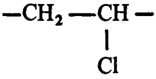
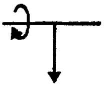
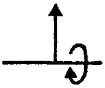
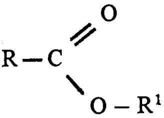
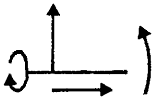
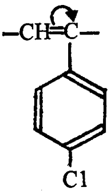
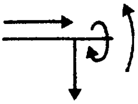
(*c*) the unit dipoles attached in a side group capable of movement independent of the chain backbone.

Of course any dipole moment fixed at an angle to the backbone contour may be resolved into parallel and perpendicular components, and so may be a combination of the above types. Some examples are given in Table 2.

3 Dielectric Relaxation of Rod-like Molecules

Considerable interest presently attaches to the study of rigid rod-like molecules in solution. A number of naturally occurring molecules such as proteins and

Table 2 *Dipole geometries in some common polymers*

Polymer	*Dipole geometry*	*Structure*	
Poly(methyl acrylate)	One component in flexible side-chain, one component rigid perpendicular		
Poly(vinyl chloride)	Rigid perpendicular	 $-CH_2-\underset{Cl}{CH}-$	
Poly(ethylene oxide)	Rigid perpendicular	$-CH_2-O-CH_2-$	
Polyester	Rigid perpendicular and parallel components		
Poly(*p*-chlorophenylacetylene)	Rigid perpendicular and parallel components		

nucleic acids fall into this category. Besides, for all long-chain polymers with finite energy barriers opposing segmental rotation, it must be possible to reduce the chain length to a size where the molecule is essentially rod-like. Conversely, any real rod must have a degree of flexibility, so that if the length can be increased sufficiently, a point must be reached when even slight curvature can build up to cause an overall coil-like conformation (Figure 4). Consequently, the only difference between molecules conventionally described as 'coils' and those con-

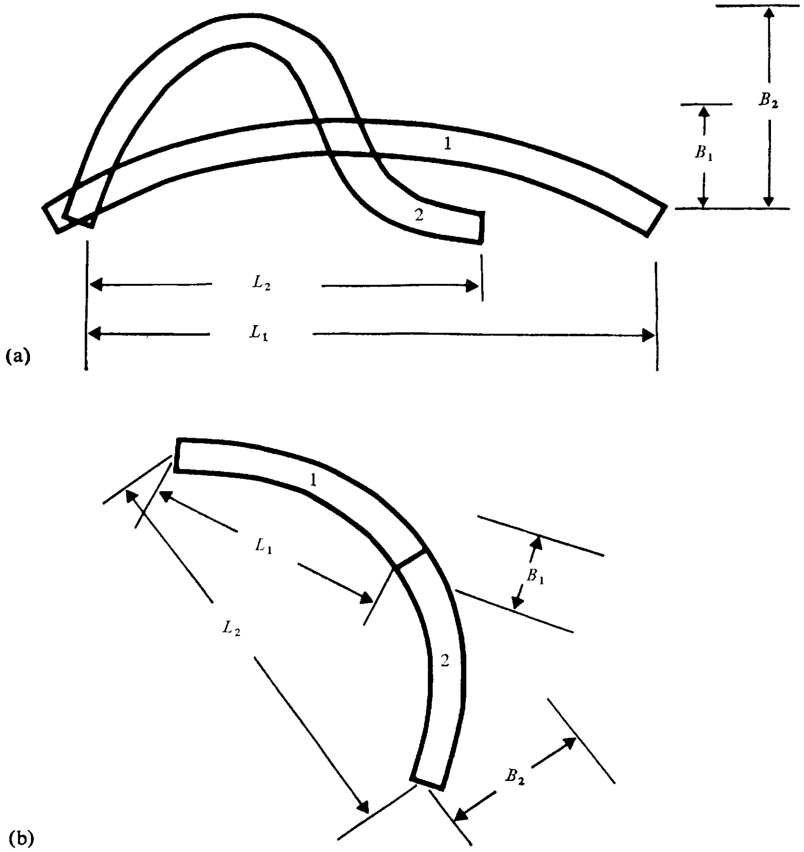


Figure 4 *Schematic picture of a 'bent rod' or 'truncated coil' molecule. L is the projection length along the major axis, and B is the* effective *'rod radius' or hydrodynamic minor radius of gyration;* (a) *shows the effect of increasing 'flexibility' for a given rod length and* (b) *shows the effect of increasing molecular weight for a given flexibility*

Table 3 *Form of certain polymers*

Polymer (*molecular weight* $\sim 10^5$)	*'Flexibility'*
Poly(methyl methacrylate)	Flexible coil
Poly(vinyl chloride)	Flexible coil
Cellulose esters	Stiff coil
Polysulphones	Stiff coil
Poly(n-butyl isocyanate) (molecular weight $< 10^4$)	Stiff rod
Poly(n-butyl isocyanate) (molecular weight $> 10^5$)	Stiff coil
Poly(γ-benzyl L-glutamate) (α-helix)	Stiff rod
DNA (molecular weight $< 10^5$)	Stiff rod
DNA (molecular weight $> 10^6$)	Stiff coil

ventionally described as 'rods' is the chain length, and hence length-to-diameter ratio, at some value of which the observed behaviour changes from 'coil-like' to 'rod-like'. Some examples are given in Table 3.

A. The Molecular Weight Dependence of the Dielectric Relaxation Time.—The rotational relaxation time of a rigid rod varies approximately as the cube of the rod length. Since the length of a rod-like polymer molecule varies linearly as the number of monomer units, the observed dielectric relaxation time associated with end-over-end rotation should vary approximately as the cube of the

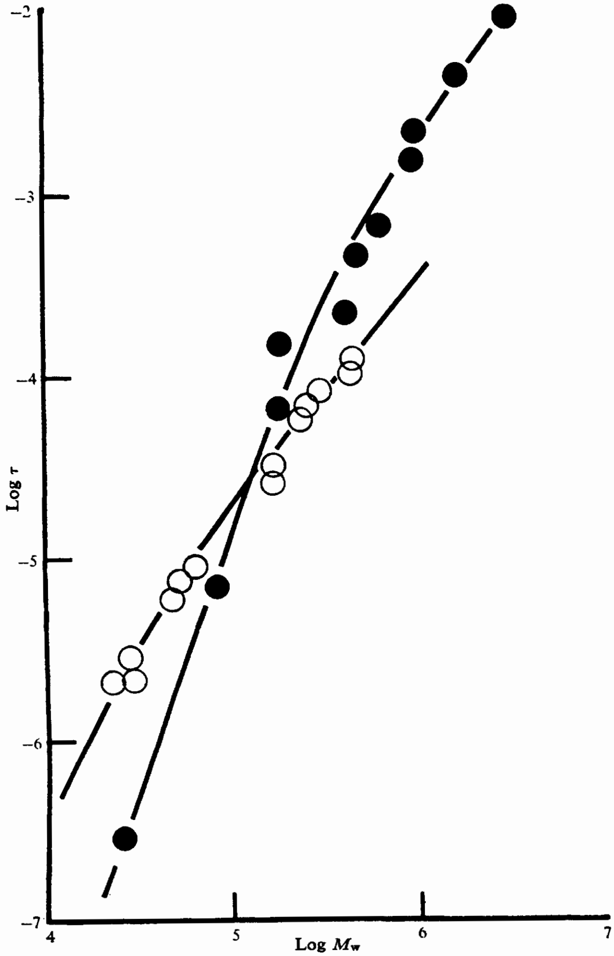


Figure 5 *Variation of relaxation time with weight-average molecular weight:* ○ *poly(γ-benzy-L-glutamate) (ref.* 19) *in benzene with ϵ-caprolactam as deaggregant or in* trans-*dichlorol ethylene with* NN-*dimethylformamide as deaggregant;* ● *poly(n-butyl isocyanate) in benzene*

molecular weight. Such a dependence has been observed[18] for dilute solutions of fractionated samples of poly(n-butyl isocyanate), of molecular weight below 10^5; see Figure 5. However, if curvature gives rise to coil-like behaviour, the radius of gyration varies as the square root of the degree of polymerization, and the dielectric relaxation time for rotation of the resultant vector varies as the three-halves power of molecular weight. Such behaviour is observed for poly(n-butyl isocyanate) when the molecular weight is above 10^5; see Figure 5.

An intermediate state of affairs seems to exist[19] in solutions of poly(γ-benzyl L-glutamate); see Figure 5. In the low-molecular-weight polymers studied the relaxation time varies approximately as the square of the molecular weight. It is not yet clear whether this is due to imperfections in the α-helix conferring a degree of curvature on the molecule (the effect is exaggerated by incorporation of the D-enantiomorph) or is a ramification of the molecular-weight distribution in the polymers studied.

B. Analysis of the End-over-end Relaxation Time.—Although dielectric observation of a rigid polymer does not give a measure of the effect of chemical structure on the rate of conformational changes, it is possible to obtain information on the overall molecular shape. In the case of a rod this will be the rod length and diameter. The analysis is carried out assuming an equation for the end-over-end relaxation time which has the form

$$\tau_{\text{e-o-e}} = \frac{\pi \eta n^3 L_0^3}{6kT[\ln(nL_0/B) - \gamma]} \qquad (1)$$

Here η is the solvent viscosity, n is the number of monomer units each of projection length L_0 along the rod, and B is the effective radius. γ is a term which accounts for end corrections. According to Broersma[20]

$$\gamma = 1.57 - 7[1/\ln(nL_0/B) - 0.28]^2$$

for perfect rods, or according to Perrin,[21] γ is 0.702 for prolate ellipsoids of revolution.

The problem in using equation (1) lies in determining whether or not it is permissible to assume $nL_0/B \gg 1$. This will be so for very long chains, but then these long chains will be beginning to exhibit curvature when different equations (or values of γ) must be used.

Many of the rod-like molecules which have been studied are biopolymers (such as deoxyribonucleic acid and ribonucleic acid) in which dipole orientation polarization is masked by ionic polarization phenomena. Despite these difficulties end-over-end relaxation times have been analysed for a number of polymers.

In the case of poly(γ-benzyl L-glutamate) dissolved in chloroform the disparity between an ideal Debye relaxation and the observed relaxation has been

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[18] A. J. Bur and D. E. Roberts, *J. Chem. Phys.*, 1969, **51**, 406.

[19] H. Block, E. F. Hayes, and A. M. North, *Trans. Faraday Soc.*, 1970, **66**, 1095.

[20] S. Broersma, *J. Chem. Phys.*, 1960, **32**, 1626.

[21] F. Perrin, *J. Phys. Radium*, 1934, **5**, 497.

used [along with the Burgers form of equation (1)] to estimate the molecular weight polydispersity. In addition, estimates of L_0 and B were more in accord with a 3_{10} helix than the standard α-helix. The problem in making such an assignment is that curvature of a helical molecule will result in the molecule functioning as a prolate ellipsoid of revolution and so yield large B values. Helix parameters estimated from these will always represent a lower pitch than is actually the case. The incorporation of γ-benzyl D-glutamate into the chain decreases the stability of the helix and so affects the relaxation behaviour. It has been suggested[19] that the helix dimensions are essentially unaltered up to a mole fraction of the D-enantiomorph of 0.1, but above this the helix is disrupted and larger B/L_0 ratios result.

Much the same is found[22] in the case of poly(n-butyl isocyanate). The monomer projection length along the rod is somewhat less than 1 Å and the rod diameter is between 5 and 10 Å, suggesting that the molecule exists as a loose imperfect helix, and not as the tight helix described for the crystalline state. Increasing temperature decreases the apparent L_0/B ratio. As can be seen from Figure 4a, the effect is interpreted as an increase in possible curvature.

The curvature causing these helices to depart from a perfect rod-like shape can be estimated from the molecular dipole moments. In this case the summation of the unit vectors depends on the chain 'persistence length', *i.e.* a measure of the distance in one direction over which the vector property of interest extends essentially unchanged. In rough qualitative terms this is the projection of the distance along a chain before curvature reverses the direction of our property of interest. For poly(γ-benzyl L-glutamate) in chloroform this distance is about 200 Å, and for poly(n-butyl isocyanate) it is about 220 Å. These molecules have, therefore, rather similar curvature in solution.

An interesting feature in the structure of these stiff chains is that the effective curvature seems to increase with molecular weight. The effect has been observed in both poly(n-butyl isocyanate)[22] and in DNA.[23] Presumably this is due to the greater torques exerted on the longer chains by thermal fluctuations of solvent.

It is not only polymers with a clearly defined helical structure that exhibit rod-like properties. In low-molecular-weight poly(*N*-vinylcarbazole) the restrictions on internal rotation are sufficiently large for the molecule to be rod-like in behaviour. An analysis[22] of the dielectric relaxation times for polymers of molecular weight less than 5 × 10^3 suggests that the overall shape of the molecule is rather as portrayed in Figure 4b, with a persistence length of *ca.* 250 Å.

4 The Change: Stiff Coil—Flexible Coil

In the preceding section we saw how increasing the molecular weight of a rod-like polymer brought it to a 'stiff-coil' geometry. As a result of this the molecular-weight dependence of the rotational relaxation time changed from a third to a three-halves power. Since for most polymers the end-to-end distances for a given molecular weight are rather similar (within the orders of magnitude under dis-

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[22] S. B. Dev, R. Y. Lochhead, and A. M. North, *Discuss. Faraday Soc.*, 1970, No. 49, 244.
[23] H. Eisenberg, *Discuss. Faraday Soc.*, 1970, No. 49, 286; *Biopolymers*, 1969, **8**, 545.

cussion), the dielectric relaxation times in a solvent of given viscosity should also be similar. This is illustrated in Figure 6, where the broken lines enclose a log frequency–log molecular weight band in which should lie the relaxation times for most stiff coils in a normal non-viscous solvent.

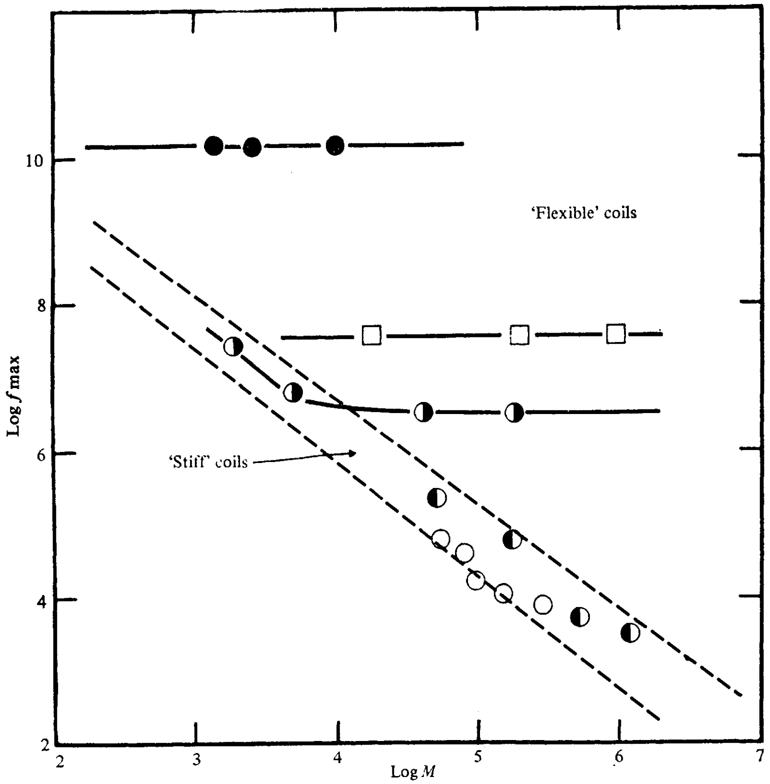

Figure 6 *Variation of relaxation frequency with molecular weight for dilute solutions in benzene or toluene at* 25 °C: □ *poly(methyl methacrylate);* ● *poly(ethylene oxide)* (*ref.* 8); ◑ *poly-* (N-*vinylcarbazole*) (*ref.* 24); ○ *poly(hexene* 1-*sulphone*) (*ref.* 25); ◐ *poly(*γ*-benzyl* L-*glutamate*) (*ref.* 19). *Broken lines bound 'universal line' for stiff coils*

A further increase in molecular weight must so increase the rotational relaxation time that segmental motion becomes the operative process for dielectric relaxation. When this occurs the dielectric relaxation time becomes independent of molecular weight. Such a situation has been observed[24] for poly(*N*-vinylcarbazole), and it can be seen from Figure 6 that the change occurs at a molecular weight of *ca.* 10^4. By the same token, the change should occur at molecular weights below 10^2 for the very 'flexible' poly(ethylene oxide) chain,[8] and above 10^6 for the very 'stiff' poly(hexene-1-sulphone)[25] and poly(γ-benzyl L-glutamate)[14]

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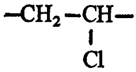
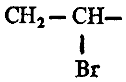
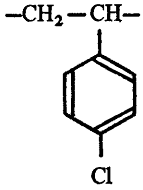
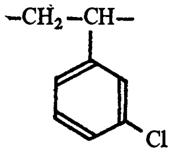
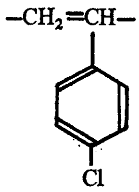
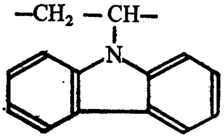
[24] A. M. North and P. J. Phillips, *Chem. Comm.*, 1968, 1340.

[25] T. W. Bates, K. J. Ivin, and G. Williams, *Trans. Faraday Soc.*, 1967, **63**, 1976.

Table 4 *Dielectric relaxation frequencies of some dissolved polymers with rigid perpendicular unit dipoles at* 25 °C

Polymer	*Solvent*	f_{max} (Hz)	$\Delta H^{\ddagger}$ (kJ mol^{-1})	*Ref.*
$-CH_2CH_2O-$	Benzene	1.5×10^{10}	10.3	26
 $-CH_2-\underset{Cl}{CH}-$	Tetrahydrofuran	2×10^{8}	9.2	29
 $CH_2-\underset{Br}{CH}-$	Cyclohexane	3×10^{7}	—	30
	Toluene	3×10^{7}	20.2	27
	Toluene	8×10^{7}	—	28
	Toluene	1×10^{10} (h.f. process)	6	27
	Toluene	9×10^{5}	42	24

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[26] M. Davies, G. Williams, and G. D. Loveluck, *Z. Elektrochem.*, 1960, **64**, 575.
[27] A. M. North and P. J. Phillips, *Trans. Faraday Soc.*, 1968, **64**, 3235.
[28] P. J. Phillips, Ph.D. Thesis, University of Liverpool, 1968.
[29] L. De Brouckere and R. van Nechel, *Bull. Soc. chim. belges*, 1952, **61**, 261, 452.
[30] M. Kryszewski and J. Marchal, *J. Polymer Sci.*, 1958, **29**, 103.

chains. By comparison, the change for poly(methyl methacrylate) should occur at molecular weights *ca.* 10^3. It is interesting that these values bear a distinct resemblance to the sizes of the 'equivalent freely rotating links' estimated from time-averaged observations such as light scattering or dipole moments.

5 Dielectric Relaxation of 'Flexible' Polymers

A. Polymers with a Rigid Perpendicular Unit Dipole.—One of the principal reasons for studying the dielectric relaxation of polymer solutions is to ascertain in some quantitative fashion how the chemical structure of a chain affects its flexibility. Intuitively, one might think that the larger, or more polar, a substituent on the chain, the greater would be the steric or electrostatic barriers to backbone rotation. That this is, indeed, part of the story can be seen from Table 4. In this Table are compared the relaxation frequencies and Arrhenius activation enthalpies for a variety of polymers dissolved in non-polar solvents at 25 °C. In general, the relaxation frequencies (a measure of the rate of backbone segmental motion) decrease with increasing size of substituent groups.

However, these results do present two rather strange features. In the first place the chlorophenyl-substituted chains do not fit neatly into the general scheme. Simple steric considerations would suggest that movement in *m*-chlorophenyl polymers should be more hindered than in *p*-chlorophenyl analogues. However, the dielectric observations imply exactly the reverse of this. Indeed, the glass transition temperatures[31] of the solid polymers also suggest that the *meta*-polymer chain is more flexible than the *para*-polymer. The reason is unclear but an explanation might be that steric hindrance due to the *m*-chlorine raises the energy of the most stable conformations of the chain unit, but does not proportionately raise the energy of some eclipsed state presenting a barrier to conformational change. Under these circumstances the activation energy for conformational change would be lowered and so the rate increased.

Even more surprising at first sight is the great speed of backbone rotation in the poly(*p*-chlorophenylacetylene) chain, which is ostensibly conjugated. In this case the steric hindrance of the substituents is less than in the saturated analogue, but is still sufficient that backbone and phenyl substituent cannot be coplanar. Under these circumstances rotation about a backbone single bond to destroy backbone planarity can be accompanied by rotation into conjugation of the phenyl side-group. Consequently, loss of resonance stabilization of the backbone is balanced by gain in the side group and the energy–angle profile is considerably flattened. That only a small energy is required to 'break' backbone conjugation in these polymers has been confirmed by measurement of a temperature dependence in the visible spectrum.[32]

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[31] K. R. Dunham, J. W. H. Faber, J. Vandenberghe, and W. H. Fowler, *J. Appl. Polymer Sci.*, 1963, **7**, 897.

[32] A. G. Hankin and A. M. North, *Trans. Faraday Soc.*, 1967, **63**, 1525.

The second strange feature in Table 4 is the magnitude of the activation enthalpies. For poly(ethylene oxide) and poly(vinyl chloride) these are only of the order of magnitude of the activation energy for viscous flow of solvent, and are no larger than the barrier to internal rotation in ethane! Even the chains with bulky substituents [such as poly(*p*-chlorostyrene] and poly(*N*-vinylcarbazole) have surprisingly low activation energies. The problem lies in ascertaining what exactly is the dipole orientation observed in the dielectric relaxation experiment. In general, the angular orientation imposed on each dipole by the field is about one radian, and so the backbone rotation observed may not involve crossing the highest energy barriers in the energy–angle profile.

However, measurements of the energetics of conformational changes in polystyrene solutions have also been made using acoustic techniques.[33] An activation enthalpy of 27.7 kJ mol^{-1} was found opposing the high-energy state to low-energy state transition, and this is not much higher than the dielectric activation energy observed for poly(*p*-chlorostyrene).

B. Polymers with a Unidirectional Parallel Unit Dipole.—In this class of polymers the resultant electric vector of the molecule coincides always with the end-to-end dimensional vector, and the dielectric observation is of the 'whole molecule' mode of motion. As mentioned in Section 2C, the dielectric relaxation time is that of the first normal mode of motion, and so is molecular-weight dependent. This means that in a chain of unknown flexibility it may be difficult to differentiate between whole-molecule rotation of a rigid entity (in which the unit dipoles are not necessarily unidirectional and parallel) and the normal mode of a perfectly flexible chain.

However, an unambiguous assignment can be made when a flexible chain contains both perpendicular and unidirectional parallel components. Under these circumstances the 'flexibility' is observed in the higher-frequency molecular-weight-independent relaxation of the perpendicular components, and the parallel components relax by the lower-frequency molecular-weight-dependent normal mode. Two such relaxation processes have been observed in poly(propylene oxide)[8] and in poly(*p*-substituted phenylacetylenes).[27]

In the case of atactic poly(propylene oxide) the measurements were made on undiluted low-molecular-weight liquid polymers rather than on solutions. The unidirectional parallel dipole component arises in the different polarizations of the $(CH_3)CH$—O and CH_2—O bonds. So long as the polymer is perfectly 'head-to-tail', this difference is unidirectional along the chain. The strengths of the two dipole components can be calculated from the magnitudes of the two relaxation processes (either in ϵ' or in ϵ'') and are 0.18 D and 1.0 D for the parallel and perpendicular components, respectively.

In the case of the poly(*p*-substituted phenylacetylenes) calculation of the dipole components was more difficult because the polymers were not of a sharp molecular-weight distribution and the two relaxation processes overlapped in

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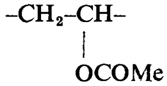
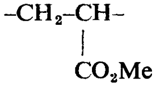
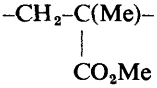
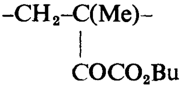
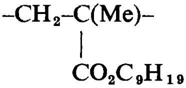
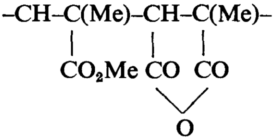
[33] H.-J. Bauer, M. Immendorfer, and H. Hassler, *Discuss. Faraday Soc.*, 1970, No. 49, 238.

the frequency plane. However, within an uncertainty of about 10% the parallel and perpendicular components are respectively 0.7 D and 1.4 D for poly(*p*-chlorophenylacetylene). In this case, the parallel component arises because of the different polarizations of the CH=CX and XC—CH bonds. The implication here is that conjugation in these systems is imperfect, the alternating double and single bonds retaining clear identities in the chain.

C. Acrylic Polymers: Backbone and Side-Group Motion.—The acrylic polymers are interesting because the unit dipole, residing primarily on the ester carbonyl group, can be resolved into parallel and perpendicular components. These differ in that rotation of the perpendicular component requires backbone rotation,

Table 5 *Dielectric relaxation frequencies of some acrylic-type polymers dissolved in toluene at* 25 °C

Polymer	f_{max} (Hz)	$\Delta H^{\ddagger}$ (kJ mol^{-1})
 $-CH_2-\underset{\underset{\displaystyle OCOMe}{\vert}}{CH}-$	2×10^9	18.5
 $-CH_2-\underset{\underset{\displaystyle CO_2Me}{\vert}}{CH}-$	1.8×10^9	23
 $-CH_2-\underset{\underset{\displaystyle CO_2Me}{\vert}}{C}(Me)-$	3.9×10^7	27
 $-CH_2-\underset{\underset{\displaystyle COCO_2Bu}{\vert}}{C}(Me)-$	3.4×10^7	27
 $-CH_2-\underset{\underset{\displaystyle CO_2C_9H_{19}}{\vert}}{C}(Me)-$	3.0×10^7	27
 (2% citraconic anhydride)	1.4×10^7	32

whereas rotation of the parallel component can take place by bond rotation in the side-group alone. Since the two components can relax by two different modes of motion, in principle two relaxation processes could be observed. However, all observations on polymer solutions detect only a single process. This is significant and means that rotations around the backbone and side-group covalent bonds neighbouring the carbonyl are co-operative in nature.

Consequently, the dielectric relaxation frequencies should be a measure of the steric constraints on backbone motion. An increase in the size, or number, of substituents on the backbone does, indeed, reduce the relaxation frequency, as can be seen in Table 5. Substitution of the α-hydrogen by methyl causes a fifty-fold decrease in the relaxation rate, and even quite small amounts of the hindered anhydride co-monomer bring about a further reduction. On the other hand, the dielectric process is relatively insensitive to the size of the alkyl group on the alcohol residue. This must be because the relatively small orientation of the carbonyl group in the electric field can be accommodated by partial rotation of the neighbouring bonds, and does not require movement of groups more than two or three atoms distant on the side-chain. This is in direct contrast to measurements of chain flexibility derived from the rate of diffusion-controlled reactions,[34] where large-scale movement of the whole chain unit is affected by ester group size.

D. The Distribution of Relaxation Times.—In many of the observations reported above, the relationship between complex dielectric constant and frequency does not follow the 'ideal' curves of Figure 1, but is broadened in the frequency plane. This is accommodated by postulating that the dipoles being observed exhibit a distribution of relaxation times. The observed data are then fitted to a semi-empirical relationship introducing a distribution parameter. This quantity is unity for the 'ideal' case, and decreases towards zero with increasing width of distribution. Some values of this parameter (calculated using the method of Davidson and Cole[35]) are illustrated for poly(methyl methacrylate) solutions in Table 6.

Table 6 *Distribution parameters for poly(methyl methacrylate) in toluene*

Concentration	*Temperature* (K)			
(wt %)	190	230	270	310
10	0.51	0.72	0.78	0.90
5	0.74	0.84	0.86	0.93
2	0.84	0.97	1.00	1.00

It can be seen that the distribution of relaxation times is broadened both by increasing the concentration and by reducing the temperature. However, at the

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[34] A. M. North and G. A. Reed, *J. Polymer Sci., Part A, Gen. Papers*, 1963, **1**, 1311.

[35] P. C. Scherer, D. W. Levi, and M. C. Hawkins, *J. Polymer Sci.*, 1957, **24**, 19.

highest dilutions and temperatures the relaxation becomes 'ideal'. The exact molecular origin of the distribution is still uncertain, although current explanations pursue the fact that movement of a unit dipole may not be completely independent of the movement of neighbouring dipoles. A correlation in angular position between neighbouring dipoles can affect the observed dipole moment per molecule, and the time dependence of this correlation may introduce the non-ideal relaxation behaviour.

It may be argued that the very presence of a limited number of covalent bonds between polymer unit dipoles must introduce some kind of dipole correlation and with it a broadening of the relaxation. However, the results of Table 6 show that this is not necessarily so for acrylic polymers, with four bonds between the two carbonyl groups.

In poly(vinyl halides) there are formally only two bonds between the chain-halogen dipoles. In the case of poly(vinyl bromide),[30] the distribution parameter is 0.94 at the highest temperatures and dilutions, so here too the dipole orientation conforms to almost 'ideal' behaviour. On the other hand, a distribution parameter as low as 0.7 has been quoted[29] for poly(vinyl chloride), although here measurements were made only at relatively high polymer concentrations.

6 Dielectric Relaxation in Solutions of 'Stiff-coil' Polymers

We have defined 'stiff' polymers as those chains for which segmental rearrangement is slower than some 'whole-molecule' modes of motion such as molecular rotation. Consequently, the dielectric relaxation frequency depends on molecular weight and gives little information on internal flexibility.

A. Random-coil Polymers, including Cellulose Derivatives.—Cellulose esters and ethers form the most widely studied class of stiff random-coil polymers. The monomer units in these polymers contain separate dipolar groups which have components parallel and perpendicular to the chain contour, as well as possessing a component located in the ester or ether side-chains. The expectation that these different components might relax by different modes of motion is borne out, and two dielectric relaxation regions are observed.[35]

The high-frequency process in cellulose acetate has been found[36] to be independent of molecular weight, with a relaxation frequency of *ca.* 10 MHz at room temperature. This is noticeably slower than in vinyl acetate, implying that in the cellulose derivatives the acetate side-groups are subjected to considerable steric hindrance or do not benefit from co-operative backbone movement. The distribution parameter is unity, suggesting that it is permissible to consider each acetate group as an independently orienting moiety.

A low-frequency molecular-weight-dependent relaxation has been observed in cellulose acetate,[36] ethyl cellulose,[35] and methyl cellulose.[37] In each case the relaxation frequency varies inversely as the molecular weight raised to a power

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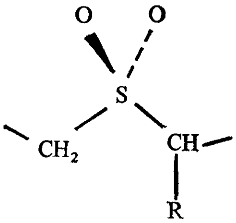
[36] A. Kheir, Ph.D. Thesis, University of Leiden, 1959.

[37] W. Kuhn and P. Moser, *J. Polymer Sci., Part A, Gen. Papers*, 1963, **1**, 151.

between 1.2 and 2.4. The observed[38] relaxation times for high molecular weights compare favourably with calculated times for non-free-draining random coils, whereas for lower molecular weights agreement is best with predictions for rod-like entities. Expressions relating relaxation frequency to molecular weight are given in Table 7.

Another class of polymers exhibiting a low-frequency molecular-weight-dependent relaxation are the poly(olefin sulphones). In this case no second high-frequency process is observed, as is expected when the dipole components are rigidly attached to the backbone chain.



The dielectric observations can be explained either if the chains are 'stiff' or if they are flexible with unidirectional parallel components and a structure in which the perpendicular components cancel. The former explanation is preferred,[39] although the fact that chain flexibility is so much lower than in vinyl polymers is somewhat surprising.

Table 7 *Molecular weight dependence of relaxation frequencies for stiff coils at* 25 °C

Polymer	*Solvent*	*Molecular weight*, M, *or degree of polymerization*, P, *related to relaxation frequency*, f_c. *Log* f_c =
Cellulose acetate	Dioxan	$14.9 - 2.4 \log M$
Ethyl cellulose	Dioxan	$5.5 - 1.9 \log P$
	Carbon tetrachloride	$4.2 - 1.2 \log P$
	Benzene	$4.8 - 1.4 \log P$
	Toluene	$5.2 - 1.6 \log P$
Poly(hexene 1-sulphone)	Benzene or toluene	$12.4 - 1.5 \log M$
Poly(2-methylpentene 1-sulphone)	Benzene	$14.9 - 2.0 \log M$

[38] P. C. Scherer, D. W. Levi, and M. C. Hawkins, *J. Polymer Sci.*, 1958, 31, 105.
[39] T. W. Bates, K. J. Ivin, and G. Williams, *Trans. Faraday Soc.*, 1967, 63, 1964.

7 Comparison with Other Measurements of Segmental Mobility

While dielectric relaxation is the method which has been most extensively used to study segmental mobility in a variety of polymer structures, complementary information can be gained from a variety of other experimental techniques.

A. The Rates of Diffusion-controlled Reactions.—A diffusion-controlled reaction is one in which the reaction rate is governed by the speed with which two reagents diffuse together, rather than by the probability of chemical reaction once they have come together. Obviously, in mobile liquid solutions only very reactive species will undergo reactions of this nature, but one such reaction is the mutual termination of two free radicals. In the case of dissolved macroradicals,[40] the rate of the reaction depends on the segmental mobility of the chain in the neighbourhood of the free radical unit.

The movement observed by measurement of these reaction rates differs from that observed by dielectric relaxation in that the kinetic study involves movement of several monomer units over a distance equivalent to several solvent molecules (or polymer chain segments), whereas the dielectric movement involves partial rotation with a relatively small amplitude of the unit dipole. Despite this difference, both rate processes show a similar variation with the backbone chain

Table 8 *Comparison of chain mobility measurements at* 25 °C

Polymer	*Dielectric relaxation frequency* (Hz)	*Radical–radical rate constant* ($\text{mol}^{-1}\ \text{s}^{-1}$)	*Fluorescence depolarization time* (ns)
Poly(ethylene oxide)	1.5×10^{10}	1.0×10^{8}	—
Poly(vinyl acetate)	2.0×10^{9}	2.0×10^{8}	—
Poly(methyl acrylate)	1.8×10^{9}	2.0×10^{8}	2.0
Poly(*p*-chlorostyrene)	3.0×10^{7}	7.7×10^{7}	—
Polystyrene	—	2.5×10^{7}	4.4
Poly(methyl methacrylate)	3.9×10^{7}	1.6×10^{7}	4.0
Polyacrylamide	—	1.2×10^{7}	4.0
Poly(butyl methacrylate)	3.5×10^{7}	2.5×10^{6}	4.0
Poly(nonyl methacrylate)	3.0×10^{7}	1.3×10^{6}	—
Poly(methyl methacrylate) (citraconic anhydride)	1.4×10^{7}	3.8×10^{6}	—
Poly(*N*-vinyl carbazole)	9.0×10^{5}	2.5×10^{5}	—

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[40] A. M. North, in 'Structure and Mechanism in Vinyl Polymerisation', ed. T. Tsuruta and K. F. O'Driscoll, Marcel Dekker, New York, 1969, ch. 4.

structure (Table 8). The similarity disappears, however, when alterations are made to the structure of side-chains some atoms removed from the backbone. Thus, the orientation polarization of the carbonyl dipole in three alkyl methacrylates is little affected by the nature of the alkyl group, whereas the diffusion-controlled reaction rate is reduced for large groups.

B. Fluorescence Depolarization.—Another method used in studying molecular rotation processes is the technique of fluorescence depolarization.[41] A fluorescent molecule or group is excited with plane-polarized radiation, and the extent of depolarization in the resulting fluorescence is a measure of the random rotation which has occurred during the lifetime of the excited state. An independent measurement of excited-state lifetime then permits evaluation of the rotational rate, usually as a rotational relaxation time.

In polymer studies a fluorescent dye molecule is either complexed to the chain or attached to one end by a radical transfer reaction during polymerization. The strength of the technique is the great sensitivity of fluorescence measurements, which allows study of a single group in a large chain. In principle, the fluorescent group could be situated in the middle or at the end of a chain, so allowing a comparison of mobility in different parts of the chain. In practice this has not yet been achieved. Indeed, in studies to date dye molecules such as fluorescein have been attached to chains either through several atoms (as in the reaction of fluorescein isothiocyanate with hydroxyl-ended chains) or through some indeterminate linkage. As a result, it is not certain how far rotation of the dye moiety truly reflects chain mobility, or whether the experiment merely detects completely independent rotation of the dye group.

Of those few polymers which have been studied by both techniques (all with a dyestuff ostensibly on the chain end), only poly(methyl acrylate) would be expected to have a rotational time markedly less than the others. As can be seen from Table 8, there is very little influence of chain structure on the rotational relaxation time. However, it still remains to be proved whether or not this is a true reflection of the mobility at the ends of polymer chains.

C. Ultrasonic Relaxation.—A study of the absorption of ultrasound by a system of molecules capable of existing in two states can, in principle, yield the energy difference between the states and the interchange frequency. The technique is particularly useful in examining the energetics of molecules which can exist as two rotational isomers. In the case of polymer chains it is assumed that rotation of each segment can be described as such a two-state isomerization.

At the present time the technique has been applied successfully only to solutions of polystyrene.[42] A relaxation is observed at about 10 MHz which is only slightly slower than would have been expected from dielectric measurements

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[41] G. Weber, in 'Fluorescence and Phosphorescence Analysis', ed. D. M. Hercules, Interscience, New York, 1966, ch. 8.

[42] H.-J. Bauer and H. Hassler, *Kolloid-Z.*, 1969, **230**, 194.

on poly(p-chlorostyrene). The activation energy (measured from the upper state) for the process is 28 kJ mol^{-1}, again rather similar to the values encountered in dielectric studies. Indeed, the general agreement between the two techniques is most encouraging, and it is to be expected that further ultrasonic measurements on polymer solutions will be made in the near future.

8 Comparison with Other Measurements of Molecular Rotation

A number of techniques are available for the study of molecular rotational diffusion coefficients. Among these are pseudo-steady-state techniques such as the measurement of flow birefringence and electrical birefringence (Kerr effect), as well as dynamic electro-optic techniques in which birefringence or Rayleigh light scattering are measured in non-stationary electric fields. The steady-state techniques yield, generally, a rotational diffusion coefficient. This can be related to a relaxation time; for example, when the molecule is a rigid rod, $\tau_{\text{e-o-e}}$ is $D/6$, where D is the rotational diffusion coefficient.

When rotational relaxation times obtained from these techniques agree with those measured for a dielectric process, it is tempting to ascribe the dielectric phenomenon to a rotational relaxation. Indeed, the two techniques have been combined in an analysis of bovine serum albumin,[43] yielding 0.23 and 0.11 μs as relaxation times for rotation about minor and major axes, respectively.

However, agreement between dielectric and electro-optic studies is not a totally unambiguous proof that the dielectric process being observed is molecular rotation. For example, the evidence in the case of poly(sodium methacrylate) is that an ionic conductance mechanism is responsible for the observed dielectric behaviour, yet the relaxation time is similar to that obtained from birefringence measurements. These birefringence studies, being most easily made on anisometric molecules, have been applied mainly to biopolymers, and have recently been reviewed by O'Konski.[44]

In the case of poly(hexyl isocyanate) it is possible to compare dielectric[45] and electro-optic light scattering[46] studies. Both techniques suggest that the molecule exists as a somewhat imperfect (slightly bent) rod or highly prolate ellipsoid of revolution. The principle dipole moment of the molecule lies along the major axis, and agreement is obtained in the end-over-end rotational relaxation time for a given molecular weight.

Although the optical techniques are most useful for rigid molecules, it is possible to measure the normal mode relaxation times for flexible molecules using the technique of viscoelastic relaxation.[47] A comparison[48] of dielectric and viscoelastic relaxation then aids the assignment of a particular mode of motion to the dielectric process. For example, dielectric relaxation in solutions

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[43] P. Moser, P. G. Squire, and C. T. O'Konski, *J. Phys. Chem.*, 1966, **70**, 744.

[44] C. T. O'Konski, *Encyclopaedia Polymer Sci. Technol.*, 1968, **9**, 551.

[45] R. Y. Lockhead and A. M. North, unpublished work.

[46] H. Plummer and B. R. Jennings, *European Polymer J.*, 1970, **6**, 171.

[47] J. Lamb and A. J. Matheson, *Proc. Roy. Soc.* (*London*), 1964, **A281**, 207

[48] A. M. North and P. J. Phillips, *Brit. Polymer J.*, 1969, **1**, 76.

of acrylic polymers occurs at frequencies a factor of 10^4 higher than viscoelastic relaxation, confirming the segmental nature of the former process. On the other hand, the viscoelastic and low-frequency dielectric relaxations coincide for the poly(*p*-substituted phenylacetylenes), providing evidence for the coincidence of the electric and displacement vectors.

9 Present and Future Trends in Research

Present trends in studies of dielectric relaxation in polymer solutions are moving towards an examination of the quantitative effects of detailed changes in chain structure. For example, the technique is being applied to regular head–head tail–tail polymers in order to ascertain whether the ease of backbone rotation (or the size of the rotating unit) is the same as in normal head–tail polymers. Similarly, the effect of increasing the separation between unit dipoles on dipole correlations and ease of movement is being studied in a quantitative way.

It is to be expected that as chains with different backbone units (perhaps incorporating hetero-atoms) are synthesized, the dielectric technique will continue to provide a relatively simple measurement of chain flexibility or stiffness. Of course, the hydrodynamic behaviour of stiff coils (or bent rods) will still be of interest.

The next year or so should see an increasing integration of other experimental techniques with dielectric studies. Although certain of these are very elegant and yield a considerable amount of information, often the apparatus is complex or expensive.

In this category fall two scattering techniques which are becoming available and which afford comparative evaluation of molecular and segmental rotational diffusion coefficients or relaxation times. One of these is an analysis of the frequency dependence of Rayleigh-scattered laser light. The major use of such studies lies in determining the translational diffusion coefficient of the dissolved macromolecule. However, under certain conditions (when the molecule is anisometric and observations are made at low scattering angles, preferably using polarized light) it is possible to measure the rotational diffusion coefficient and, hence, relaxation time.

The only polymer molecule which has been studied extensively by this[49] and a variety of techniques is tobacco mosaic virus. The general conclusion is that the molecule is rod-like with a rotational relaxation time of 1.7×10^{-2} s, in agreement with results of flow and electric birefringence studies.

As with dynamic electro-optic techniques, it is expected that in the future this method will be increasingly used to measure whole-molecule rotational processes, and so aid in the assignment of dielectric relaxation phenomena.

Another technique of growing importance which will almost certainly be applied to polymer solutions is neutron scattering. In principle, these studies should yield information on segmental diffusive processes complementary to the information obtained by dielectric and ultrasonic measurements.

The next few years, then, should see a rapid increase in quantitative knowledge relating chemical structure to chain rotational behaviour.

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[49] A. Wada, N. Suda, T. Tsuda, and K. Soda, *J. Chem. Phys.*, 1969, **50**, 31.