DIELECTRIC DISPERSION IN SOLUTIONS OF FLEXIBLE POLYMERS†

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INTRODUCTION

The dielectric properties of polar chain polymers have long[1,2] been of great interest to many workers. For solid materials, there is great practical justification for such interest in the sometimes very close relation between mechanical and electrical behaviour, as well as in direct applications to problems of electrical insulation. The study of dielectric constant and loss in dilute solutions has fewer technical applications, but offers information about molecular conformation under both equilibrium and dynamic conditions, and thus can be very useful in the characterization of macromolecular structure. As examples we may cite the classical work of Oncley[3] on globular proteins and the more recent studies of Wada[4] on synthetic helical polypeptides or of Yu, Bur and Fetters[5] on synthetic helical poly(isocyanates). These studies all deal with rigid ellipsoidal or rod-like macromolecules, while in the following pages we are concerned entirely with polar polymers in the randomly coiled state, in which there may of course be short chain segments assuming helical conformations, but no persistence of such special conformations over extended lengths. Although we stray from the narrow realm of dilute solutions on occasion, the emphasis is on the behaviour of macromolecules essentially isolated from each other by intervening solvent. Crystalline polymers or amorphous polymer systems with extensive mechanical chain entanglements will therefore not be discussed. Polyelectrolytes are also avoided.

It is well known that the mean square dipole moment of a polar macromolecule differs from the sum of squares of the individual bond moments through a factor which depends on the chain configuration and on the conformational statistics, thus affording one of the important methods for exploring these aspects of polymer structure[6,7]. We may not pause to discuss these equilibrium studies, but hasten to consider the dynamical behaviour, which also reveals the coupling effects of chain structure.

It may be recalled that the simple Debye[8] relation for the complex permittivity or dielectric "constant" ϵ^* under steady alternating field

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + (\epsilon_S - \epsilon_\infty) (1 + i\omega\tau)^{-1} \qquad (1)$$

(Eq. 1) obtains only if the orientations of all dipoles relax at exactly the same

rate by a random process, as described by the autocorrelation function

$$\langle \mu(t) \times \mu(0) \rangle = \langle \mu(0)^2 \rangle \exp(-t/\tau) \qquad (2)$$

(Eq. 2) for the dipole moment vector μ. In these equations ϵ_S and ϵ_∞ represent limiting low- and high-frequency dielectric constants, ω is the circular frequency of the applied field and τ is relaxation time[9]. Deviations from the Debye equation are frequent even in non-polymeric liquids[10], and physically are best explained by recognizing the orientational relaxation process to be too complicated[11, 12] to obey Eq. (2). For polymer systems, the deviations are on the average somewhat larger. As shown by Kirkwood and Fuoss[13], this is a natural consequence of chain connectivity, and the formal device of salvaging Eq. (1) by introducing a distribution of relaxation times acquires physical significance in this case. Some polymers have two or three distinct regions of dielectric dispersion, more or less widely separated from each other in frequency (at constant temperature) or temperature (at constant frequency). Each such region may itself comprise a band of relaxation times, yielding a broader curve than Eq. (1), but we shall not dwell on such details. Rather, we wish to examine the relation between the molecular structure of a polar chain polymer and the number and nature of its dielectric dispersion regions. For each such region, we ask for the dependence of its average relaxation time (adequately taken here as the reciprocal of the circular frequency ω_m at which ϵ'' achieves its maximum) on chain length and structure and on such variables of condition as temperature, concentration and nature of solvent.

Polar groups in the repeat units of a polymer chain may be classified geometrically into three types, as exemplified in *Table 1*. If the repeat unit

Table 1. Three types of dipolar groups in chain molecules: (A) Parallel to chain direction, (B) Rigidly attached to chain backbone but perpendicular to chain direction, (C) On flexible side chain

Examples	A	Types: B	C
Poly(vinyl halides) Poly-*p*-halostyrenes Poly(ethylene oxide)		×	
Poly(vinyl acetate) Poly(methyl methacrylate) Poly(*m*-halostyrenes)		×	×
Polyalanine Poly-β-propiolactone	×	×	
Cellulose acetate Poly-γ-benzylglutamate	×	×	×

cannot be chosen to have a plane of symmetry normal to the chain contour, it must have a dipole component *parallel* to the chain contour (Type A). For a sequence of n such units without reversal of directional sense, the dipole vector $\mu_n^{(A)}$ must correlate completely with the displacement vector r_n of the sequence, as sketched in *Figure 1*, and we have

$$\langle \mu_n^{(A)} \times r_n \rangle = \text{const.} \times \langle r_n^2 \rangle$$

for all conformations. The two important consequences of this correlation are: (1) the mean square dipole moment $\langle \mu_n^{(A)2} \rangle$ is subject to the same excluded volume effects as $\langle r_n^2 \rangle$; hence, if unreversed Type A sequences are long, the static dielectric increment per unit mass of polymer solute is an increasing function of molecular weight except under theta conditions; and (2) the relaxation behaviour of $\mu_n^{(A)}$ is identical to that of r_n, forcing intimate connections between dielectric and low-frequency viscoelastic relaxation if unreversed sequences are long. This second consequence is elaborated and cofirmed in the next section of this paper.
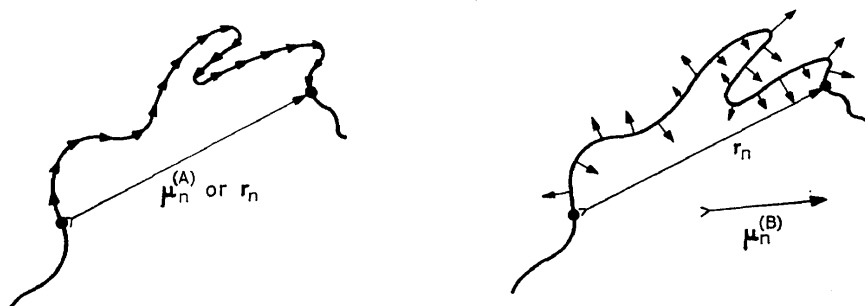

Figure 1. Schematic representation of chains with Type A and Type B dipoles. Correlation of dipole vector μ_n with displacement vector r_n occurs only in the former case.

The second kind of dipole component is like the first in being rigidly† attached to the chain backbone, but is *perpendicular* to the chain contour. For a sequence of n repeat units, there is no correlation between the vector sum of such Type B components and the displacement vector; we have $\langle \mu_n^{(B)} \times r_n \rangle = 0$. Physically this is easy to see, for a fixed displacement length r_n is compatible with many different values of $\mu_n^{(B)}$. We may therefore expect that: (1) the Type B contribution to the static dielectric increment shows negligible excluded volume effects; and (2) its relaxation will in general involve skeletal chain motions of smaller scale and shorter relaxation time than for Type A.

Finally, polar groups may be attached to side groups with one or more bonds permitting internal rotation. These will give a third type (C) of dipole component, whose relaxation behaviour need not directly implicate the chain backbone, as long ago pointed out by Tuckett[14]. In this article this kind of dipole will not be further considered.

PARALLEL DIPOLES

The behaviour of flexible chains bearing dipoles of Type A will now be illustrated by a well-documented example, that of atactic poly(propylene oxide) of low molecular weight[15,16]. Our own experiments[15] were all made with undiluted liquid polymers rather than on solutions, but the chains were short enough (the highest M_w being about 5×10^3) so that the effects of

† We mean that no bonds permitting internal rotation connect the polar group to the chain skeleton.

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mechanical entanglement could be neglected. This statement is supported by the fact that the viscosity of these liquid polymers is proportional to just the first power of molecular weight. Under such conditions[17], we may hope to apply without ambiguity existing theories of polymer Brownian motion.
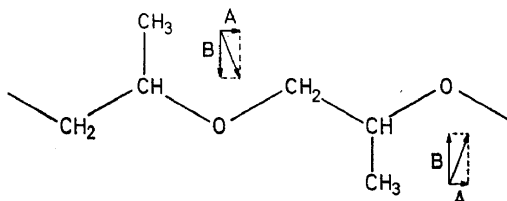

Figure 2. Head-to-tail poly(propylene oxide) chain, showing presence of both Type A and Type B dipole components in each repeat unit.

Since the polymers were commercial samples prepared by a non-stereo-specific base-catalyzed process, they have[18] an atactic, predominantly head-to-tail structure and a narrow molecular-weight distribution of the Poisson type[19,20]. It is seen from *Figure 2* that each repeat unit of the chain carries a small Type A dipole component.

The data for one sample with $M \cong 2 \times 10^3$ are shown in *Figure 3*, in
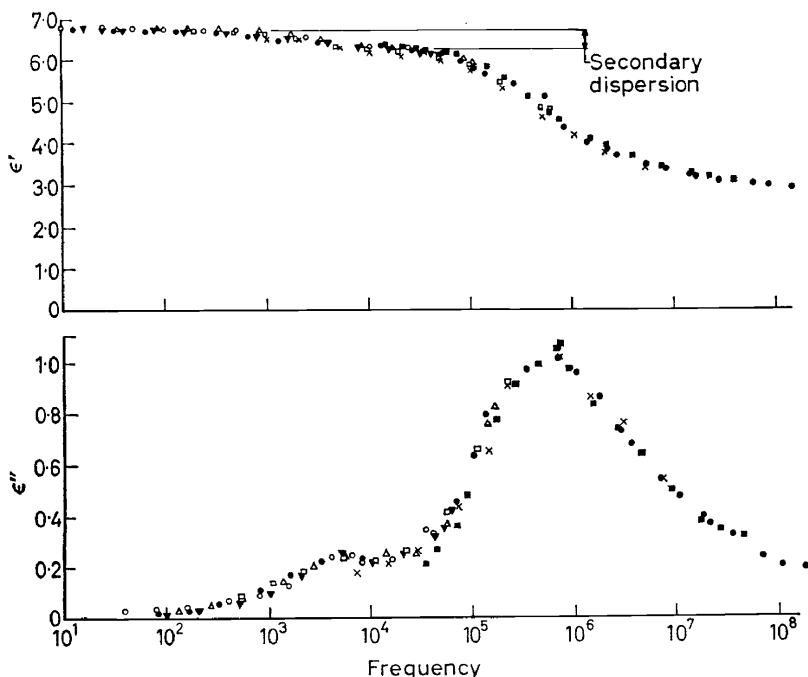

Figure 3. Reduced plots of dielectric constant ϵ' and loss factor ϵ'' at various temperatures against logarithm of frequency for an atactic poly(propylene oxide) with $M_w \cong 2 \times 10^3$ (data from ref. 15).

which results for a number of temperatures have been superposed by the well known reduction technique[17]. The small loss peak on the low-frequency of the big peak is clearly evident, perhaps especially so in the Cole–Cole plot of *Figure 4*. Experiments with propylene oxide polymers of other molecular
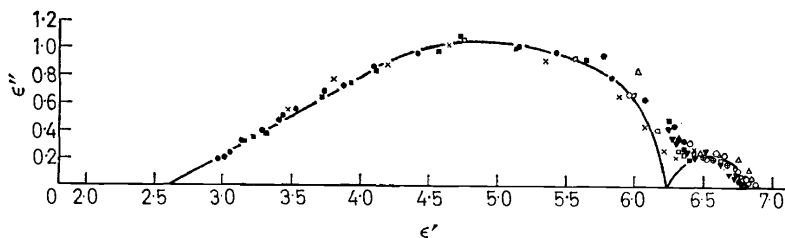
Figure 4. Reduced Cole–Cole plot of ϵ'' against ϵ' for the poly(propylene oxide) of *Figure 3* (ref. 15).

weights from 1×10^3 to about 5×10^3 show that the large peak is quite insensitive to chain length, but that the frequency of maximum loss for the small peak moves to lower values as the chain length is increased, varying about as $1/M^2$ over the range studied. Since the total dielectric polarization associated with this small dispersion region is also found to be independent of the nature or number of end groups, it must be an intrinsic property of the chain structure; and in view of the dependence of the relaxation time on chain length it can only be due to the Type A dipoles. So interpreted, it leads to a reasonable[69] Type A dipole moment component of 0·18 debye per repeat unit as compared to about 1·0 debye per unit for the perpendicular Type B component.

To discuss the chain motion in detail, it is useful to begin by recalling the well known normal-coordinate description[21, 22] of conformational diffusion. The symmetry of the first few (slowest) modes is indicated in *Figure 5*, where the arrows are placed at positions of maximum amplitude and the nodes fall between the arrows. The translational mode, $k = 0$, is electrically active only for ions. Mode 1 would clearly be active for chains bearing an unreversed sequence of Type A dipoles from one end to the other, since the electric field would tug the two chains ends in opposite directions. Indeed the ends move in opposite directions for all the odd-numbered modes, which would therefore all be dielectrically active to some extent for a chain of the type just mentioned. More generally, we observe that any specified arrangement of Type A dipoles responds to an alternating electric field by just those modes whose symmetry is congruent to that of the charge distribution along the chain contour.

The quantitative development of the above statements is straightforward. Since only the slow long-range diffusional modes of the chain are involved, it is adequate here to use the ball-and-spring model elaborated by Rouse[21], Zimm[22] and others. In this model, the chain is temporarily conceived to consist of an arbitrary large number N of Gaussian springs or "submolecules", connecting $N+1$ beads which serve as the centres of hydrodynamic interaction with the solvent. The resulting diffusion equation separates into independent parts, one for each normal coordinate in each spatial direction,
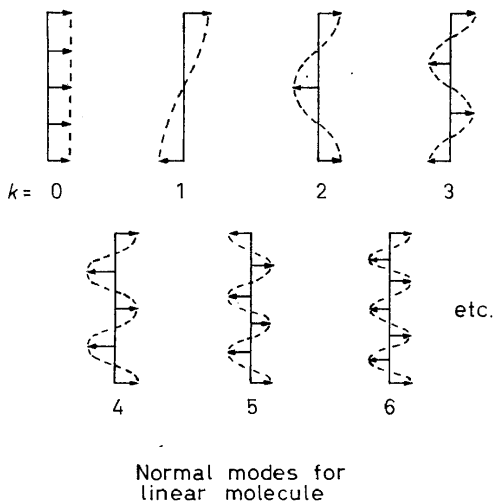
Normal modes for
linear molecule

Figure 5. Schematic representation of the normal coordinates for a linear polymer chain. The solid vertical lines represent the chain contour, which of course really follows a more or less randomly kinked space curve in any one conformation. The dashed lines indicate relative magnitudes of the displacements. Arrows are placed at positions of maximum amplitude.

provided that excluded volume effects between the beads are either ignored or approximated by a constant scale-factor, and further provided that the hydrodynamic interactions between the beads are either ignored[21] or represented by scalar averages[22]. If more realistic representations of excluded volume or hydrodynamic interactions are introduced, the normal coordinates are coupled and some form of perturbation theory is required for a complete treatment[23]. Very recently, Fixman has shown that field-theory operational techniques offer a powerful general method for coping with these more difficult mathematical problems[24].

Returning to Zimm's treatment, we find[25] that in dilute solution at a weight concentration c in a non-polar solvent the dielectric increment due to a polymer bearing Type A dipoles is described by the equations:

$$\Delta \epsilon^* - (\Delta \epsilon)_\infty = (4\pi N_A^2 c/27RTM) \, (\epsilon_0 + 2)^2 \, \langle \mu^2(\omega) \rangle \tag{3a}$$

$$\langle \mu^2(\omega) \rangle = \sum_{\text{modes } k} p_k^2/(1 + i\omega\tau_k') \tag{3b}$$

$$p_k = (Nb/k\pi) \sum_{\text{beads } j} e_j Q_{kj} \tag{3c}$$

$$Q_{kj} = (2/N)^{1/2} \cos \, (jk\pi/N) \tag{3d}$$

In these relations, N_A is the Avogadro number, RT thermal energy, M the polymer molecular weight, ϵ_0 the dielectric constant of the solvent, ω the circular frequency of the applied field, Nb^2 the mean square end-to-end distance for the entire chain and $e_0, e_1, \ldots, e_j, \ldots, e_N$ the assigned electric charges on the beads of the model. As given above, the result may appear to

depend on the number N of submolecules chosen, but this is not true if the sequences of Type A dipoles without reversal of direction are sufficiently long; for then we can replace the sum of Eq. (3c) by an integral, putting $j = sN$ and writing

$$p_{\mathrm{k}} = (2Nb^2)^{1/2} (k\pi)^{-1} \int_0^1 \cos (k\pi s)\, e\, (s)\, ds, \qquad (3c')$$

where $e(s)$ is an appropriately defined charge density along the chain contour, expressible in terms of the magnitude and disposition of the Type A dipoles. Relations (c) and (d) are not exact, for the true normal modes in the case of strong hydrodynamic interaction are not quite[26] the pure single trigonometric terms pictured in *Figure 5*; but the approximation is more than adequate for our purpose, and so we may say that the Fourier components of the charge distribution along the chain contour determine the activity of the low-frequency diffusional modes in the dielectric relaxation spectrum. For example, if we have an unreversed sequence of Type A dipoles down the entire chain, p_{k} vanishes for all even k modes, as required by the symmetry, and is inversely proportional to k for the odd modes. The first mode, $k = 1$, is therefore dominant, and this is (cf. *Figure 5*) largely a rotational diffusion.

The dielectric relaxation times τ_{k}' in dilute solutions are related to the intrinsic viscosity $[\eta]$ by Eqs. (4) and (5) which vary with the extent of hydrodynamic shielding:

$$\tau_{\mathrm{k}}' = 12\, M\, [\eta]\eta_0/\pi^2 R T k^2 \qquad \text{(dilute solution, free draining}[21]\text{)} \qquad (4)$$

$$\tau_{\mathrm{k}}' = 3\cdot42\, M\, [\eta]\eta_0/R T \lambda_{\mathrm{k}}' \qquad \text{(dilute solution, non-draining}[22]\text{)} \qquad (5)$$

where η_0 is the solvent viscosity and the λ_{k}' are numbers which have been tabulated[26, 23b] for low k and which become asymptotically equal to $\pi^2 k^{3/2}/2$ for large k. Equations for intermediate draining conditions are available if needed[27, 28]. For undiluted liquid polymers below the entanglement range, there is both theoretical argument[29] and experimental evidence[30] supporting the use of the free-draining model. This leads to Eq. (6)

$$\tau_{\mathrm{k}}' = 12\, M\eta/\pi^2 R T \rho k^2 \qquad \text{(undiluted polymer, free draining)} \qquad (6)$$

where η/ρ is the kinematic viscosity of the liquid polymer; while a similar manoeuvre for the non-draining limit would give Eq. (7), where $L^2 = Nb^2$.

$$\tau_{\mathrm{k}}' = 1\cdot61\, N_A\eta L^3/R T \lambda_{\mathrm{k}}' \qquad \text{(undiluted polymer, non-draining)} \qquad (7)$$

There is no good reason to expect Eq. (7) to succeed, and indeed the evidence favours the free draining formula (Eq. 6) for the undiluted poly(propylene oxides).

For polymers in which the rotational–diffusional mode ($k = 1$) should be dominant, the predicted relaxation time in dilute solution is similar for almost any model. Thus, Eqs. (4) and (5) yield Eqs. (8) and (9) respectively; but for a rigid impenetrable sphere of radius a, the Debye formula

$$\tau_1' = 1\cdot21\, M[\eta]\eta_0/R T \qquad \text{(free draining)} \qquad (8)$$

$$\tau_1' = 0\cdot85\, M[\eta]\eta_0/R T \qquad \text{(non-draining)} \qquad (9)$$

tively; but for a rigid impenetrable sphere of radius a, the Debye formula

gives Eq. (10) almost identical to Eq. (8). Factors not far from unity are

$$\tau_{rot} = 4\pi\eta_0 a^3/kT = 6\,M[\eta]\eta_0/5RT, \tag{10}$$

also found from other treatments of rotational diffusion, such as the wire-model results of Kuhn and Kuhn[31] or the calculations of Hearst[32] for a rigid spherical distribution of segments. Since the experimental precision of locating the frequency of maximum loss is not great, being subject to the effects of concentration and polydispersity, it is patent that the present theories are quite adequate to cope with the data for such polymers.

Returning now to poly(propylene oxide), we have first to remark that the polymers studied were produced by a process in which the chains actually grow in two directions, epoxide units adding to either hydroxyl end. Our chains therefore are best represented by the formula

$$H(-O-CHR-CH_2)_x-O-(CH_2-CHR-O)_yH,$$
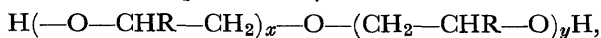
with $x \simeq y$. Thus there are two sequences of Type A dipoles pointing in opposite directions from a point near the middle of the chain contour; so the relevant modes (*Figure 5*) are numbered 2, 6, 10, 14, etc., with $k = 2$ as the dominant one. Baur's data for the sample of *Figure 3* are compared to this prediction in *Figure 6*, where it is seen that the Bueche formula, Eq. (6), is in excellent agreement with experiment, and even the less appropriate Eq. (7) gives the right order of magnitude.
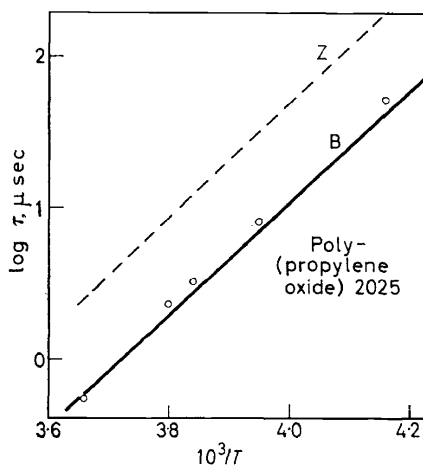
Figure 6. Arrhenius plot of relaxation times for small Type A dielectric dispersion peak in linear poly(propylene oxide) of molecular weight 2×10^3 (data from ref. 15). Solid line B, theoretical relaxation time ($k = 2$) according to free-draining formula, Eq. (6). Dashed line, non-draining formula, Eq. (7). Circles, experimental values.

Trifunctional star molecules, formed by initiating the propylene oxide polymerization with glycerol in basic medium, have been studied by

$$CH_2-O-(CH_2-CHR-O)_xH$$
$$|$$
$$CH-O-(CH_2-CHR-O)_yH$$
$$|$$
$$CH_2-O-(CH_2-CHR-O)_zH$$
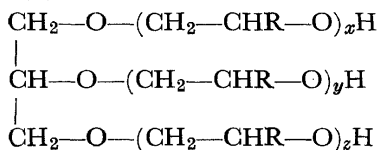
Burke[33], who again found a small low-frequency peak corresponding to a Type A dipole of 0·18 debye per propylene oxide unit. The active normal modes in this case are those for which the three ends move in opposition to the branch point, the principal one corresponding to the theoretical relaxation time[67, 68] (Eq. 11) for free-draining undiluted polymer. The experi-

$$\tau_2' = 12\ M\eta/7\pi^2 RT\rho \quad \text{(trifunctional star)} \quad (11)$$

mental data for one such polymer, with $M_w = 4·6 \times 10^3$, are shown as circles in *Figure 7*, and the curve is calculated from Eq. (11) with the measured
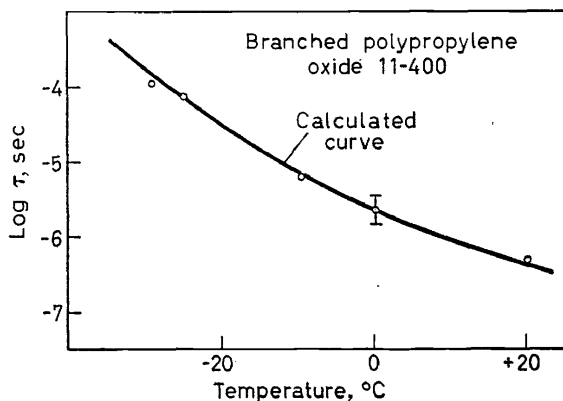

Figure 7. Relaxation times for small Type A dispersion peak in a trifunctional star polymer of propylene oxide with $M_w = 4·6 \times 10^3$. Solid curve, theoretical curve according to Eq. (11). Circles, experimental values (ref. 33).

values of M, η and ρ. The agreement is as good as for the linear polymer.

Loveluck and Cole[16] have confirmed Baur's results for poly(propylene oxide) and extended them to solutions in methylcyclohexane, and they have also observed a small Type A dispersion in poly(butene-1-oxide). Low-frequency dispersions strongly depending on molecular weight have also been reported in the past for cellulose esters and ethers[34, 35]. The authors did not offer a complete quantitative interpretation of their data, but in the case of ethyl cellulose, where the relevant viscosity and molecular weight data are available, the Zimm relation, Eq. (9), for τ_1' gives[36] a good account of the observed relaxation times. It seems safe to conclude that dielectric relaxation due to Type A dipoles is well understood, and that the existence of such a dipole in the repeat unit is a sufficient condition for a low-frequency dispersion with a molecular-weight-dependent relaxation time. But, as will later be seen, presence of Type A dipoles is not a *necessary* condition for such a dispersion.

One intriguing problem for further experimental study should be mentioned. If chain length or concentration are increased until mechanical entanglements become prevalent, the long-range modes will be inhibited and must eventually recede into the region of immeasurably low frequency. In fact, no trace of the small Type A peak is found in the data of Williams[37] for a poly(propylene oxide) of high molecular weight (M_w about 4×10^5).

With appropriate polymer systems, it should be possible to observe directly the effect of entanglements on $\tau_1{}'$ through the transition from unencumbered to strongly entangled chains.

PERPENDICULAR DIPOLES

Type B dipole components, rigidly attached perpendicular to the direction of the chain contour, present a much harder challenge to the theoretician than those of Type A. For flexible chains, the vector sum of a sequence of such dipoles does not correlate with the displacement length, so that the relevant modes of chain diffusion are usually short-range or local† modes which cannot be meaningfully described by the beads and springs of the Rouse–Zimm model except in a somewhat fictitious sense. Putting the matter in another way, we may say that the higher-frequency eigenfunctions and eingenvalues of the diffusion operator are not known or easily derivable for realistic models of the chain.

The first question to be asked about Type B dipoles is far from trivial, and in the past has not received a uniform reply in the literature: how does the mean relaxation time τ for dispersion of a chain with only Type B dipoles depend on the molecular weight M of the chain? In their pioneering theoretical study of the breadth of dielectric dispersions in polar polymers, Kirkwood and Fuoss[13] predicted that τ should be proportional to M for free-draining conditions. The calculation was later repeated by Hammerle and Kirkwood[38] with inclusion of hydrodynamic interactions between chain elements, which reduced the exponent of M to $\frac{1}{2}$ in the non-draining limit. The chain model employed in these papers is geometrically very realistic, but in the mathematical treatment of the diffusion problem it was necessary to resort to extensive premature averaging, a process which, in the authors' own words, introduces "approximations of unknown validity". Kuhn[39] treated a more elaborate dynamical model, providing for an internal viscosity; his result is essentially the same as that of Kirkwood and Fuoss when the internal viscosity is neglected. Two criticisms of Kuhn's work may be offered:

(1) He restricts his treatment to internal rotations about *only one chain bond at a time*. In other words, only certain rather large-scale chain motions are considered, and true local modes are excluded from the start.

(2) He asserts that the dielectric spectrum must have the same form for all flexible chains with rigidly attached dipoles, whether these are of Type A or of Type B. This assertion cannot be reconciled with the analysis we have presented above of dispersion due to dipoles of Type A.

Kuhn also emphasized that rotational diffusion always presents a possible mechanism of relaxation. The importance of this possibility will be seen later.

Some years after the above papers appeared, Bueche[40] pointed out that a true short-range mechanism must lead to a mean relaxation time independent of chain length. He made it clear that in such a case τ is inversely proportional to the frequency of passing from one stable local conformation to another, but he did not offer an expression of this frequency in terms of chain structure or properties. This is probably wise, as local mechanism for

† The adjective "local" is sometimes used in a more specialized and restricted sense in discussions of motion in solid polymers. See later in this article.

various chains may differ greatly. For example, a short section of chain between two coaxial bonds can move like a crankshaft[41], as has been examined in some detail for polyethylene by Schatzki[42]; while Reneker[43] has depicted a quite different kind of conformational defect which can travel easily along the polyethylene chain in its regular extended form; and doubtless there are other possibilities. It may also be recalled that VanBeek and Hermans[44] demonstrated a high-frequency dispersion for a Rouse chain (cf. previous section) carrying charges of alternating sign on the beads, $e_j = e_0(-1)^j$. The relaxation time is† close to the shortest time τ_N' permitted by the model, this being independent of chain length but proportional to the friction constant of a bead and to the mean square length of the subchain between adjacent beads. Of course such parameters cannot easily be related to local chain structure, but the calculation does serve again to confirm the idea that local-mode relaxation times need not depend on molecular weight.

The experimental evidence is now quite definite in indicating that the relaxation time for a pure Type B dispersion need not depend on molecular weight. To demonstrate this without ambiguity, we must not rely on data for poly(methyl methacrylate), poly(vinyl acetate) or other polar polymers which have both Type B and Type C dipole components, even though in these cases the range of molecular weights and the precision of the measurements may be specially high[45]. No doubt can remain for poly(vinyl bromide) in dioxane[46], poly(ethylene oxide) in benzene[47, 48], and poly(p-chlorostyrene) in benzene[48]. Some results for the last two systems are shown in *Figure 8*, which gives double-logarithmic plots of the frequency at maximum
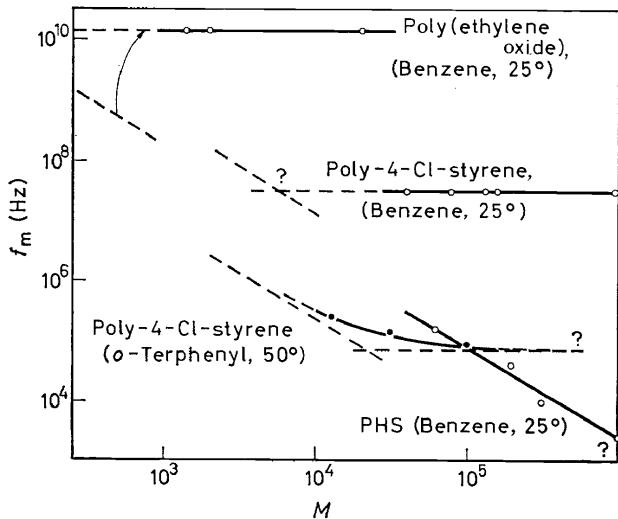

Figure 8. Double logarithmic plot of frequency of maximum loss, f_m, against molecular weight for several polymers with Type B dipoles. Data from refs. 48, 64 and 65. The abbreviation "PHS" stands for poly(hexene-1-sulphone).

† VanBeek and Hermans actually found *two* dispersions of equal strength, the second and slower one lying at τ_1'. But it is easily shown that the latter is actually due to the presence of a type A dipolar component in the charge distribution they used; if the charges on the two end beads are cut in half, the equilibrium polarization is also cut in half and the slow dispersion disappears!

loss $[f_m = 1/(2\pi\tau)]$ against weight-average molecular weight. It seems clear that truly local relaxation modes do exist.

Figure 8 also indicates that the speed of local relaxation processes is quite sensitive to chain structure, as the f_m values for poly(ethylene oxide) and poly(p-chlorostyrene) in the same solvent at the same temperature differ by a factor of about 500. Of course this is what we should expect if special alignments of bond axes or other special conformations are necessary for the relaxation to take place. It may also be conjectured that f_m should in general depend on the configuration and stereoregularity of the polymer, but the author is unaware of any experimental evidence on this question. The temperature coefficients of f_m are surprisingly low, to judge by the examples shown in *Table 2*. The very great kinetic flexibility of the polyoxyethylene chain is especially noteworthy[47].

Table 2. Dielectric relaxation in benzene or toluene solution

Polymer	Frequency (Hz) of maximum loss, 25°C	Activation energy (kcal/mole)
Poly(p-chlorostyrene)[48, 49]	3×10^8	4·8
Poly(p-fluorostyrene)[49]	4×10^8	4·8
Poly(ethylene oxide)[47, 48]	$1·5 \times 10^{10}$	2·5

Local relaxation processes in solution may also be observed by measurements of nuclear magnetic relaxation[50, 51]. In general, the information obtained complements rather than duplicates that from dielectric relaxation data, although a correspondence may occur in special cases. For example, McCall and Bovey[52] have found a longitudinal n.m.r. relaxation time T_1 of about 0·20 sec for the *para* ring-protons of polystyrene (free-radical type) in tetrachloroethylene solvent at 25°C. If we assume that the effects of non-aromatic protons are negligible, we may apply the standard theory[53] for a rigidly rotating frame, and thus obtain a rotational correlation time of about 6×10^{-9} sec. For poly(p-chlorostyrene) in benzene at 25°C the dielectric relaxation time corresponding to f_m is about 5×10^{-9} sec. The similarity of these two figures suggests that rotation of the aromatic ring about the axis of the *para* substituent bond is not a major process in the nuclear relaxation. For poly(ethylene oxide) we see at once that one of the most important processes for nuclear relaxation must be rotation about the CH_2—CH_2 bond, while for the dielectric problem the other chain bonds may play a larger role. Recent n.m.r. data for this polymer[54] support this statement, as the values of T_1 do not have a simple relation to the dielectric relaxation time; but the activation energies for the two phenomena are quite similar, being about 2·9 and 2·5 kcal/mole, respectively.

Concentration dependence of the relaxation times may be quite small for highly mobile chains at temperatures well above the glass-transition region. Thus, the observed values of τ for poly(ethylene oxides) increase by only about a decade in passing from dilute solution[47,48] to the undiluted liquid state[55]. In the case of poly(p-chlorostyrene), for which the glass temperature is about 110°C, dielectric relaxation at 25°C in toluene[41, 56] shows (*Figure 9*)

a greater variation with concentration. The curve drawn in the figure corresponds to an equation of the free-volume type (Eq. 12) where ϕ is the

$$f_{\mathrm{m}} = A \exp\left(-B/v_{\mathrm{f}}\right); \qquad v_{\mathrm{f}} = v_{\mathrm{f}}^0 - C\phi \tag{12}$$

volume fraction of polymer and A, B, C are constants. This type of equation has been successful in correlating translational diffusion measurements in polymer–solvent systems[57]. The constants used are of reasonable magnitude, but at present they cannot easily be predicted on *a priori* grounds. It may be observed that the relaxation frequency for the chlorostyrene polymer falls to very low values at a volume fraction between 0·7 and 0·8. This is about right for a polymer with a glass temperature of 110°C when undiluted. It is also consistent with data of Fuoss[58] on this polymer plasticized with biphenyl.

Students of dielectric dispersion in solid polymers will recall[59] that frequently two different dispersion regions can be identified as due to Type B
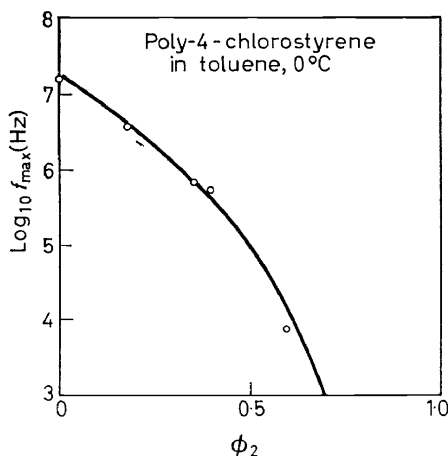

Figure 9. Effect of concentration on maximum loss frequency for poly(*p*-chlorostyrene) in toluene. Data from refs. 41 and 48. Solid curve, Eq. (12). Abscissa is volume fraction of polymer.

dipoles. Examples[60] are poly(chlorotrifluoroethylene) and polyvinyl halides. The slower relaxation (usually dubbed α) is much the larger in magnitude of polarization, and can be identified with the same mechanism that operates in dilute solution: passage from one local conformation to another over some sort of energy barrier. The smaller and faster β peak is found below the ordinary glass temperature ("Glass I" in McCrum's vocabulary[61]) and must represent highly damped torsional oscillations in the chain bonds but without passage over intramolecular barriers. In other words, the torsional vibrations of the chain, which in dilute solution would lie above the usual frequency range and would then be regarded as part of the so-called atomic or vibrational polarization, are so much slowed down by the medium that they appear as a loss region in the accessible frequency range. In solid-state language, the energy dissipation is due to phonon scattering by the anharmonic motions. The adjective "local" is sometimes restricted

to just this type of dispersion as distinct from the α-mechanism. The relevant force constants are of course composed of both intra- and intermolecular contributions, and in favourable instances it has been possible[60, 62] to estimate these and hence to predict the magnitudes of the associated polarizations. Formal treatments of the shape of the dispersions in such solid polymers have been offered[60, 63] but cannot be discussed here. The very interesting study by Work and Fujita[63] shows that delayed correlations between dipoles may broaden the dispersion and sometimes produce two distinct peaks. The application of this kind of model to experimental data may produce some reinterpretations.

We have purposely delayed until this point the discussion of some very recent measurements by Bates, Ivin and Williams[64] which demonstrate that our presentation as given so far is incomplete. They measured dielectric constant and loss in dilute solutions of several polysulphones, of which the results for poly-(hexene-1-sulphone), $[-CH_2CH(n\text{-}C_4H_9)SO_2-]_x$, in benzene may be presented as typical. Since the structure is known to be very strongly head-to-tail, there is certainly a Type A dipole component; and, since the initiator of polymerization was monofunctional, there is an unreversed sequence, leading to the prediction of a Type A dispersion at τ_1'. The measured dipole moments show a small excluded-volume effect, in confirmation of the Type A dipole, but they also make it clear that the major component must be of Type B, as would be expected from simple structural considerations. However, there is only a *single* somewhat asymmetric dispersion region for the entire polarization, centred at a frequency corresponding to $\tau \cong M[\eta]\eta_0/RT$. The curve and open circles marked PHS in *Figure 8* refer to this system. To explain this initially surprising result, we must recall with Kuhn[39] that rotational diffusion is always a possible path to dipole relaxation, as is indeed obvious for a perfectly rigid chain. In general, we may imagine an equivalent circuit in which the local modes for relaxation of Type B dipole orientation and the rotational diffusion mechanism are represented by two resistors in parallel. The observable relaxation time is then the harmonic mean of those for the two separate mechanisms, and of course in most situations one of these will be sufficiently faster than the other to dominate the behaviour. Since the rotational τ is proportional to $M[\eta]$, this process must become too slow for any flexible chain at sufficiently high M, and for most chains this will already come true at rather small molecular weights. The sloping dashed lines in *Figure 8* are those predicted from Eq. (9) for rotational–diffusion relaxation, and it is seen that for poly(ethylene oxide), which we recall as kinetically very flexible, the local mode is the faster process at all molecular weights above 10^3, while for the polymer of p-chlorostyrene in benzene we might encounter the cross-over range near $M \simeq 10^4$, where we have placed a question mark in the figure. For the sulphone, however, the cross-over must start only at molecular weights above 10^6, and the local mechanism cannot have a value of τ much smaller than one millisecond. Thus for this polymer both Type A and Type B polarization relaxes at τ_1' for molecular weights of a million or lower. Chain models suggest that rotation about the carbon–sulphur bonds may be very difficult, but that the carbon–carbon bond might be reasonably labile. But we recall that local relaxation requires two coaxial labile bonds

(or some other form of labile conformational defect), and this may be the crucial matter for the polysulphone chain.

Accurate experimental confirmation of the foregoing picture would require relaxation data for good fractions, preferably of pure Type B chains, over a range of molecular weights wide enough to span the entire transition region from rotational diffusion to local relaxation. To the author's knowledge, such data are not yet available, but some results of Davis[65] on three samples of poly(p-chlorostyrene) in the very viscous solvent o-terphenyl are at least suggestive and are displayed as the three filled circles in *Figure 8*. If our interpretation of these data is correct, a large participation of solvent in the local mechanism is also demonstrated, by comparison with the data for the same polymer in benzene. In the case of poly(ethylene oxide), a dependence of longitudinal n.m.r. relaxation time on M appears[53] at molecular weights below about 400, just at the expected value from *Figure 8*. The study of p-halostyrene polymers is being continued in our laboratory, in the hopes of supplying more adequate experimental evidence on this question.

Whether or not the preceding discussion of experimental results is correct, it would seem purely on conceptual grounds that a finite upper limit to the rate of local relaxation should be provided in formal theories of chain dynamics. The models of Rouse and Zimm cannot easily be extended in this way: the introduction of any physically meaningful "internal viscosity"† seems sure to produce serious mixing of the normal modes, perhaps rendering these far from convenient as a basis for perturbation[23] treatment. Further investigation is needed.

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† A damping term proportional to the time rate of change of the spring *vectors* does not alter the normal coordinates, and simply adds a constant term to each relaxation time, with[66] or without[44] the hydrodynamic interactions. But such a term effectively only adds to rotational, rather than local conformational, resistance.

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