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Equilibrium Polarization of Polar Polymers in a Matrix of Arbitrary Compliance

S. Havriliak, Jr.

Rohm and Haas Research Laboratories, P.O. Box 219, Bristol, Pennsylvania 19007.

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ABSTRACT: The assumptions underlying the computer-simulated motions by Mansfield and those by Perchak et al. are extended to the Onsager–Kirkwood theory of polar liquids to develop a model for polar polymers in a rigid environment. This extension is made by expanding the perturbed Hamiltonian of the system upon application of the electric field to include a strain energy term. The strain energy term arises because any finite orientation of polar groups in an electric field must also distort the system. The resulting distortion will cause the strain energy term to be finite because the equilibrium tensile compliance is not, in general, infinite for polymers as it is for polar liquids. Two cases are considered: The first one converges to the Onsager–Kirkwood results as the tensile compliance approaches infinity (i.e., strain energy is zero) and their reaction field is an adequate representation for long-range interactions. The second case assumes the tensile compliance to be finite, the point dipole to be located on a nonspherical molecular segment, and the reaction field not to be an adequate representation of long-range interactions. Under these assumptions, a Debye-like expression is obtained. However, unlike Debye's expression, a Curie point is not observed because the orientation process is inhibited by means of the finite strain energy.

Introduction

Mansfield[1] proposed a spring and dash pot model to represent intramolecular and intermolecular interactions in polymers and then calculated the loci of the dielectric relaxation process when represented in a complex plane for a range of model parameters. The significance of his calculation is that these complex plane loci are similar to those observed experimentally, a feature not obtained with any other polymer model. Most polymer chain models have molecular weight dependent shapes that are very narrow when compared to those observed experimentally. One interpretation of the dash pot connecting the polymer chain to the environment in Mansfield's model is that it represents the rigidity of the environment inhibiting the orientation process. More recently, Perchak et al.[2] computer-simulated the ring-flip motions (β-process) observed in the glass phase of polycarbonate. He found that a rigid lattice prevented the orientation process from taking place while flexible ones permitted them. It is the purpose of this work to generalize these inhibition mechanisms of the environment on the orientation process of polymer chains in the polar liquid theories on Onsager[3] and Kirkwood,[4] hereafter designated as O–K.[5]

O–K assumes polar liquids to be adequately represented by a collection of point dipoles in a microsphere that represents the local structure of a polar liquid. The medium outside this microsphere is considered to be adequately represented by the macroscopic dielectric constant, ϵ_0. When the electric field is turned on, the energy (Hamiltonian = $H^\circ(p,q)$) of the system is reduced (perturbation term to the Hamiltonian = $H'(p,q)$) by a reshuffling of the local structures to form a net dipole moment

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in the macrosphere. The reduction of the total energy of the system is equal to the scalar product of the induced moment of the macrosphere with the applied electric field. In the case of polar liquids, there is probably no reason to impose any further restrictions. In the case of polar polymers, any reshuffling of the dipoles in the macrosphere will probably distort the sphere and cause a strain energy term to arise because the equilibrium tensile compliance of the sphere is not infinite. The strain energy may offset the effects of the dipole energy term. In other words, any reshuffling of the point dipoles will probably cause a change in the shape of the macroscopic sphere, which in turn leads to a finite strain energy because the tensile compliance is never infinite. In the case of polar liquids, the equilibrium tensile compliance is probably always infinite.

The object of this work is to examine the effect of distortion energy on the polarization process. In the Results several cases are considered. a simple numerical case is examined to illustrate the magnitude of the energies involved. The approach is then generalized, and two cases are considered: O–K reaction field and the case of inconsequential electrostatic interactions. Finally, a numerical example of rigidity on relaxation time is considered.

Results

Numerical Example. The electrostatic energy (U_e)[6,7] of a sphere suspended in a vacuum and subjected to an electric field, E_o, is, for the case $\epsilon_o = 8$, $V = 100$ cm^3, and $E_o = 300$ V/cm or 1 esu

$$U_e = -\frac{(\epsilon_o - 1)}{(\epsilon_o + 2)}\frac{3V}{4\pi}E_o^{\,2} = -16.7 \text{ erg} \tag{1}$$

Consider the sphere to contain N ellipsoids with a major (2a) to minor (a) axis ratio of 2. The dipole moment, $\mu_o = 4$ D (computed from O–K's equation for the case of $g = 1$, room temperature, and $\epsilon_o = 8$), is along the major axis. The ellipsoids are regularly spaced on a lattice with an $N/2$ major axis and an $N/2$ minor axis pointing in the z direction. In other words, a two-site model is assumed for the ellipsoids in such a way that the dipole moment of the sphere is zero. This model, except for the dipole moments, is similar to the ring-flip mechanism of Perchak et al.[2] proposed for the β-process in polycarbonate. Consider a plane that contains 10^4 such sites perpendicular to the z direction. The average projection of the ellipsoids in the z direction is 1.5a. When the field is turned on (in the z direction), Frohlich[6] found that the fraction of ellipsoids that orient under these conditions is 10^{-4}. Computation of the average projection of the ellipsoids in the z direction is 1.5001a. The change in length/unit length due to the electric field, i.e., strain (Γ) is 6.6×10^{-5}. For most polymers the tensile compliance is in the range of 10^{-6}–10^{-10} cm^2/dyn. The strain energy under these conditions is given[8] by

$$U_s = \frac{1}{2}\Gamma\sigma V = \frac{\Gamma^2 V}{2D_o} \tag{2}$$

$$= 0.22 \text{ erg for } D_o = 10^{-6} \text{ cm}^2/\text{dyn} \tag{2A}$$

$$= 2200 \text{ erg for } D_o = 10^{-10} \text{ cm}^2/\text{dyn} \tag{2B}$$

The perturbation energy ($U_t = H'(p,q)$) of the system, when the field is turned on, is $U_t = U_d + U_s$. In the case of polar liquids, U_s is zero for any Γ because $D_o \rightarrow \infty$. In the case of polymers, D_o is usually finite. On the basis of the numerical example given above, when the asymmetry of the orienting segment is as low as 2 (one might expect considerably higher values in the case of polymers) and for the range of compliances that are usually observed in polymers, the strain energy can range from an insignificant fraction of the electrostatic energy to a fraction that dominates the entire process. The total energy of the system can never be positive, for if it were, the polarization process would cease because the driving force would vanish.

General Equation. The starting point of many dielectric theories that attempt to relate a point dipole moment, $\vec{\mu}_o$, to the macroscopic dielectric constant, ϵ_o, is a sphere of the dielectric medium under consideration suspended in a vacuum to which an electric field is applied. For the present case two macroscopic quantities are needed to represent the sphere, i.e., ϵ_o, the equilibrium dielectric constant, and D_o, the tensile compliance. We further assume that when the electric field, E_o, interacts with the sphere, a stress field (σ) is set up and is proportional to E_o; i.e., $\sigma = BE_o$. We assume that the sphere of volume V contains N units, each of which are characterized by two parameters. They are μ, the isolated dipole moment of the unit and γ, which represents the shape of the unit. We assume that the microscopic strain sums in the same way as the dipole moment does. In other words, the moment $\vec{M}$ of the sphere is the sum of individual moments, $\vec{\mu}_i$, and the strain of the sphere, $\vec{\Gamma}$, is the sum of the individual shape factors, $\vec{\gamma}_i$. The two quantities are specified for a given structural unit related through $\vec{\gamma} = \zeta\vec{\mu}$. In general, ζ is a tensor since there is no reason to assume the two vectors to be parallel, although for purposes of this study we will assume ζ to be a scalar.

The relationship between the moment induced in the sphere by the action of an electric field, E_o, is given by classical electrostatics to be[6,7]

$$\vec{M} = \frac{(\epsilon_o - 1)}{(\epsilon_o + 2)}\left(\frac{3V}{4\pi}\right)\vec{E}_o \tag{3}$$

where $\vec{M}$ is the moment of the sphere in vector notation. The electrostatic energy of the sphere is the scalar product of the field and the moment, viz., $-\vec{M}\cdot\vec{E}$. The combination of a finite stress at a finite strain described in the previous section leads to a strain energy term U_s. The total energy change (perturbation term in the Hamiltonian) caused by the action of the field on the sphere is given by

$$H'(q,E_o) = -\vec{M}\cdot\vec{E}_o + U_s \tag{4}$$

The perturbation term, $H'(q_o,E_o)$, is assumed to depend only on the positional coordinates, q, and the applied field, E_o.

The result of using this perturbation term in the total Hamiltonian of the system to calculate the average moment of the sphere results in the following relationship between the central point dipole, the moment of the sphere, and the dielectric constant.

$$\frac{\epsilon_o - 1}{\epsilon_o + 2}\frac{3V}{4\pi} = \frac{N}{3kT}\left\{1 + \frac{\zeta^2 V\langle\vec{\mu}\cdot\vec{M}\rangle_o}{6ND_okT}\right\}^{-1}\langle\vec{\mu}\cdot\vec{M}\rangle_o \tag{5}$$

In this equation the symbols V, N, and T have their usual significance while k is Boltzmann's constant. The broken brackets $\langle\ \rangle_o$ represent an equilibrium average of the scalar product of the central dipole moment, $\vec{\mu}_o$, with the moment of the sphere, $\vec{M}$.

If we define $\{\cdot\cdot\cdot\}$ to be

$$\{\cdot\cdot\cdot\} = \left\{1 + \frac{\zeta^2 V\langle\vec{\mu}\cdot\vec{M}\rangle_o}{6ND_okT}\right\}^{-1} \tag{6}$$

then the effects of various limiting values of ζ and D_o on eq 5 can be evaluated.

Case I. $\zeta \to 0$, i.e., symmetrical unit, finite D_o, so that $\{\cdots\} \to 1$ and

$$\frac{\epsilon_o - 1}{\epsilon_o + 2}\frac{3V}{4\pi} \to \frac{N}{3kT}\langle\vec{\mu}\cdot\vec{M}\rangle_o \tag{7}$$

Case II. $\zeta \to \infty$, i.e., needle shaped unit, finite D_o, so that $\{\cdots\} \to 0$ and

$$\epsilon_o \to 1 \tag{8}$$

Case III. $D_o \to 0$, i.e., rigid environment, $\zeta \neq 0$, so that $\{\cdots\} \to 0$ and

$$\epsilon_o \to 1 \tag{9}$$

Case IV. $D_o \to \infty$, i.e., flexible environment and $\zeta \neq 0$, so that $\{\cdots\} \to 1$ and

$$\frac{\epsilon_o - 1}{\epsilon_o + 2}\frac{3V}{4\pi} \to \frac{N}{3kT}\langle\vec{\mu}\cdot\vec{M}\rangle_o \tag{10}$$

These limit results suggest that eq 5 is well-behaved at the limits. For example, when $\{\cdots\} = 1$, eq 3 becomes the familiar polar liquid expression. On the other hand, when $\{\cdots\} = 0$, the equilibrium dielectric constant, $\epsilon_o = 1$, i.e., that of a vacuum and the material, behaves as if it were a nonpolar liquid.

Kirkwood's Approximation. The quantity $\langle\vec{\mu}\cdot\vec{M}\rangle_o$ can be evaluated using the arguments of O–K.[3,4] Briefly, the moment of the sphere, $\vec{M}$, is taken to be the sum of all moments μ_j, in the suspended sphere, i.e., $\vec{M} = \sum\vec{\mu}_j$. The sphere is divided into two concentric spheres, a microsphere containing all the local structural elements and a macrophage with dielectric constant ϵ_o. Electrostatic arguments (reaction field) are then used to evaluate the moment of the suspended sphere in terms of the moment of the local structure and its induced moment of the macrosphere. Application of their arguments leads to the following equation.

$$\epsilon_o - 1 = \frac{4\pi N}{3kTV}\left\{\frac{9\epsilon_o}{2\epsilon_o + 1}\right\}\left\{1 + \frac{9\zeta^2 V\epsilon_o\langle\vec{\mu}\cdot\vec{m}\rangle_o}{6ND_okT(2\epsilon_o + 1)(\epsilon_o + 2)}\right\}^{-1}\langle\vec{\mu}\cdot\vec{m}\rangle_o \tag{11}$$

If we define $\{\cdots\}$ as

$$\{\cdots\} = \left\{1 + \frac{9\zeta^2 V\epsilon_o\langle\vec{\mu}\cdot\vec{m}\rangle_o}{6ND_okT(2\epsilon_o + 1)(\epsilon_o + 2)}\right\}^{-1} \tag{12}$$

then the effects of matrix rigidity or (segment) shape factor on the dielectric constant can be examined. The results are listed below for the four limiting cases of the O–K approximation.

Case I. $\zeta \to 0$, i.e., symmetrical unit, finite D_o, so that $\{\cdots\} \to 1$ and

$$\epsilon_o - 1 \to \frac{4\pi N}{3kTV}\left\{\frac{9\epsilon_o}{2\epsilon_o 1}\right\}\langle\vec{\mu}\cdot\vec{m}\rangle_o \tag{13}$$

Case II. $\zeta \to \infty$, i.e., needle shaped unit, finite D_o, so that $\{\cdots\} \to 0$ and

$$\epsilon_o \to 1 \tag{14}$$

Case III. $D_o \to 0$, i.e., rigid environment, $\zeta \neq 0$, so that $\{\cdots\} \to 0$ and

$$\epsilon_o \to 1 \tag{15}$$

Case IV. $D_o \to \infty$, i.e., flexible environment and $\zeta \neq 0$, so that $\{\cdots\} \to 1$ and eq 11 becomes

$$\epsilon_o - 1 \to \frac{4\pi N}{3kTV}\left\{\frac{9\epsilon_o}{2\epsilon_o 1}\right\}\langle\vec{\mu}\cdot\vec{m}\rangle_o \tag{16}$$

In other words, cases I and IV lead to the Kirkwood expression while cases II and III lead to an equilibrium dielectric constant of 1 or that of a vacuum.

Inconsequential Electrostatic Interactions. An assumption basic to the O–K analysis states that the nature of the long-range coupling between the microsphere and the macrosphere is of electrostatic origin. This means that as the moment $\vec{m}$ in the microsphere is rotated, the moment induced in the macrosphere also rotates, assuming the rotation to proceed infinitesimally slowly so that the system always remains in equilibrium. As the moment $\vec{m}$ in the microsphere is made to vanish, the induced moment in the microsphere vanishes. Therefore, in the limit of a nonpolar polymer there is no correlation between the two spheres.

Let us now consider a microsphere in a nonpolar material such as polystyrene, in the limit of very high molecular weight. As the microsphere rotates slowly a disturbance will be set up at any arbitrary distance away from the microsphere, that is, proportional to the magnitude of the rotation. Such a disturbance has macroscopic dimensions and is assumed to give rise to orientation of polymer molecules in the macrosphere. In other words, a long-range nonelectrostatic correlation exists between the microsphere and the macrosphere.

The problem is how to evaluate $\langle\vec{\mu}\cdot\vec{M}\rangle_o$. Ideally, this would come from the statistical theories of polymers, but none are forthcoming that are independent of molecular weight. Though it is not possible to develop a statistical theory, it is possible to consider the O–K development as one limiting case and assume the other limiting case to consist of trivial (by comparison to steric factors) long-range electrostatic interactions. We can proceed along lines similar to those of McCrum, Read, and Williams[5] as follows:

$$\langle\vec{\mu}\cdot\vec{M}\rangle_o = \langle\vec{\mu}_i^{\,I}\cdot\vec{M}\rangle_o = \langle\vec{\mu}_i^{\,I}\cdot\{\vec{\mu}_i^{\,I} + \sum_{j\neq i}\mu_j^{\,I} + \sum_j\vec{\mu}_j^{\,II}\}\rangle_o \tag{17}$$

In this expression $\vec{\mu}_i^{\,I}$ is the ith unit on polymer molecule I and $\vec{\mu}_j^{\,I}$ represents the remaining units on molecule I, and $\vec{\mu}_j^{\,II}$ represents the units on all of the other polymer chains. Since all basic units are assumed to have the same dipole moment, we have

$$\frac{\epsilon_o - 1}{\epsilon_o + 2}\frac{3V}{4\pi} = \frac{N}{3kT}\left\{1 + \frac{\zeta^2 Vg_r\mu^2}{6D_oNkT}\right\}^{-1} g_r\mu^2 \tag{18}$$

The results for the four limiting cases discussed in the previous section are the same and will not be reproduced here.

Apparent Relaxation. Consider a case where the relaxation time of point dipoles in the system is much less than 10^{-7}. Then, in the experimental frequency range of 10^2–10^5 Hz, equilibrium dielectric constants will be measured. However, let us assume that γ^2/D_o is such that $\epsilon_o - 1$ is reduced in magnitude. Furthermore, the equilibrium compliance, D_o, is a function of time such that $D_o(t) = D_o\{1 - \exp(-t/\tau)\}$ where τ is the relaxation time somewhere in the experimental frequency range (10^2–10^5 Hz). This assumed relaxation process has a single relaxation time. The so-called equilibrium dielectric constant, $\epsilon_o(t)$, will have a value that is dependent upon the frequency of measurement, simply because $D_o(t)$ is time dependent. This time-dependent dielectric constant may be given by redefining ϵ_o to be $\epsilon_o(t)$ in eq 11. This sub-

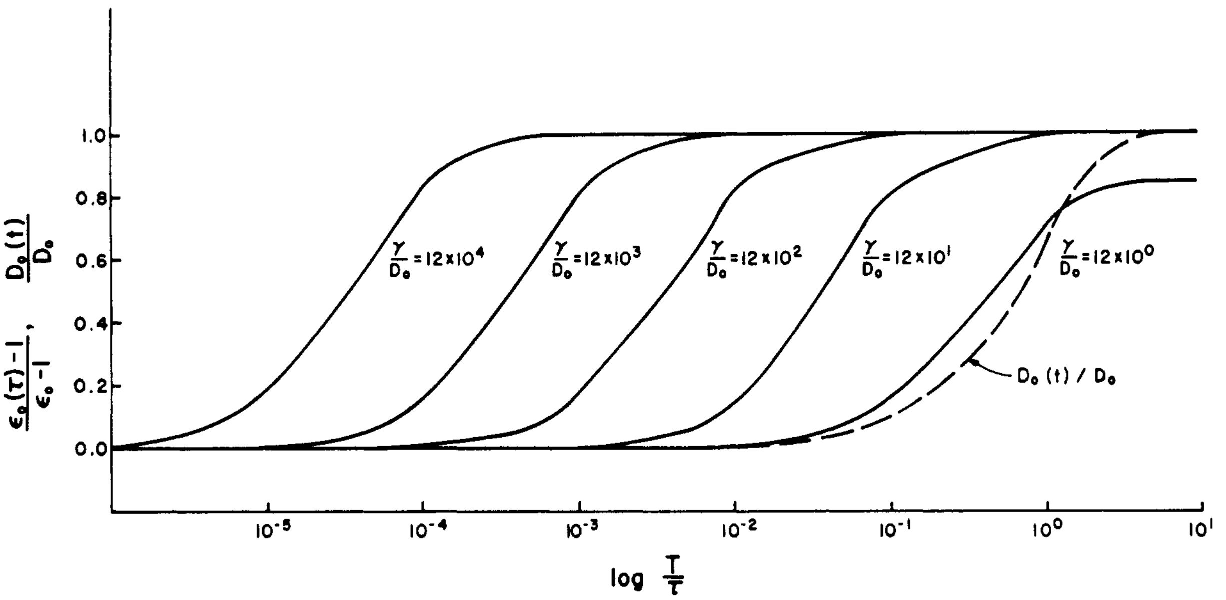

Figure 1. Equilibrium dielectric constant plotted against the effective dipole moment, $g\mu,^2$ for various values $(\gamma^2/D_0) \times 10^{11}$ dyn/cm^2.

stitution yields the following equation:

$$\epsilon_0(t) - 1 = \frac{4\pi N}{3kTV}\left\{\frac{9\epsilon_0(t)}{2\epsilon_0(t)+1}\right\} \times \left\{1 + \frac{9\zeta^2 V\epsilon_0(t)\langle\vec{\mu}\cdot\vec{m}\rangle_0}{6ND_0kT(2\epsilon_0(t)+1)(\epsilon_0(t)+2)}\right\}^{-1}\langle\vec{\mu}\cdot\vec{m}\rangle_0 \quad (19)$$

Numerical estimates can be made with a few simplifying assumptions such as $\epsilon_0(t) > 1$ and $\epsilon_0(t)D_1(t) \approx D(t)$ and finally scaling the results, i.e., $\{\epsilon_0(t) - 1\}/\{\epsilon_0 - 1\}$. In Figure 1 we have given the time dependence of fraction for a number of different values of $\gamma^2/D_0(t)$. In the first case, the value of $\gamma^2/D_0(t)$ was chosen such that part of the polarization process was partially "frozen out". In this case, the relaxation times are nearly the same; the dielectric process is the faster one by a factor of about 1.5. However, in the other cases $\gamma^2/D_0(t)$ was chosen to be much greater. Under these conditions, $\epsilon_0(t)$ comes to its equilibrium value (when $\gamma^2/D_0(t)$ is such that it no longer "freezes out" the process) much sooner, and its apparent relaxation time is much shorter. Clearly, from Figure 1, the relaxation time depends on the magnitude of D_0. This dependence can be seen be defining a relaxation time to be when $\epsilon_0(t)$ reaches a certain value $\epsilon_{0\tau}(t)$. This situation comes about when the quantity $D_0(t)$ reaches a specific value $D_{0\tau}(t)$ at which all other quantities have been assumed to be constant. For large values of D_0, this level will be reached in a short time so that $t/\tau < 1$. Making the substitution into the time dependence for $D_0(t)$, we have

$$D_0(t) = D_0 t/\tau \quad (20)$$

$$D_{0\tau}(t) = D_0 t_\tau/\tau \quad (21)$$

where t_τ implies a time that fixes $D_{0\tau}(t)$ for a given D_0. In other words, the apparent dielectric relaxation time will be a linear function of D_0.

Discussion

Limiting Cases. One of the most important results obtained in the previous section is that in the limiting case of polar liquids the O–K results are retained. Also important is that in the limiting case of immobilized dipoles the equilibrium dielectric constant approaches 1, i.e., that of a vacuum. In other words, the limiting cases are physically reasonable.

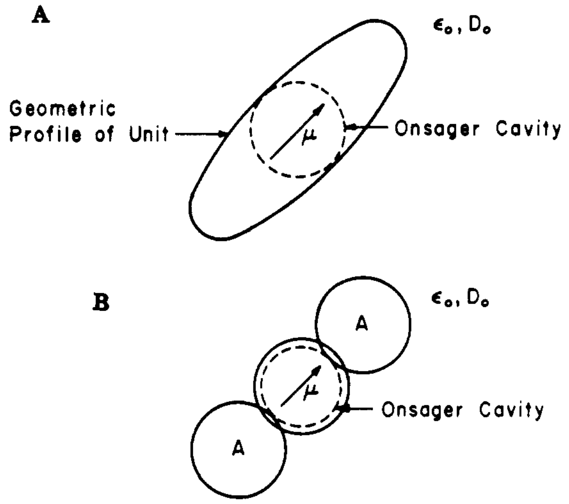

Figure 2. Elliptical unit immersed in its own medium. (A) The spherical cavity represented by the dashed line represents the Onsager cavity. (b) A spherical dipole in a cavity (dashed line) is rigidly connected to nonpolar spheres labeled A.

Onsager Model. The interaction of a point dipole with its environment is best seen from a consideration of the Onsager model. Consider the following schematic representation given in Figure 2A of a polar species. The shape of a polymer segment may be an ellipse (solid line in Figure 2A), but the point dipole is considered to be centered in the sphere. The material constants are ϵ_0 and D_0. In order for the dipole to orient, the ellipse must strain the environment surrounding the spherical cavity.

A more realistic model is the schematic representation given in Figure 2B. The proportion depicted in Figure 2B could be part of a polymer molecule or of some large molecule. The dashed line represents the Onsager cavity with a dipole moment of magnitude μ located at its center. Surrounding the Onsager cavity is a medium of dielectric constant, ϵ_0, and tensile compliance, D_0. Rigidly connected to the sphere-containing moment μ are two nonpolar spheres labeled A. When the field E_0 is turned on, the group μ tends to orient with respect to the applied field. To do so in this model, the sphere A must distort the medium, giving rise to a strain energy term. To evaluate the strain, the actual $\Delta l/l$ for the orienting species must be calculated.

Debye's Equation. Equation 18 is very similar to the Debye[9] equation. Furthermore, when the square brackets are taken to be unity, and g_r is set to 1, the Debye equation is obtained. However, the two differences just cited are quite important and in fact eliminate some of the original criticisms of the Debye theory. The one criticism is that short- and long-range correlations of the central dipole with its environment are neglected. In the present case the short- and long-range correlations are assumed to be structural rather than electrostatic in nature and are lumped into a geometric constant, g_r. The second criticism of the Debye equation is that it predicts an electrical Curie temperature. Equation 24 does not lead to an electrical Curie temperature for certain choices of the parameters. This point can be seen from the following variation of eq 18:

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\frac{3V}{4\pi} = N\left\{\frac{2D_0N}{6D_0NkT + Vg_r\gamma^2}\right\}g_r\mu^2 \tag{22}$$

When $6D_0NkT < Vg_r\gamma^2$, eq 34 becomes

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\frac{3V}{4\pi} = \frac{2D_0N^2}{V}\frac{\mu^2}{\gamma^2} \tag{23}$$

In other words, the polarizability, and hence the dielectric constant, are independent of temperature. Using the numerical constants in a previous section, the results are found to be quite reasonable and are given below:

For $D_0 = 10^{-6}$ dyn/cm^2

$$\frac{6D_0NkT}{Vg_r\gamma^2} = 2.49T$$

For $D_0 = 10^{-10}$ dyn/cm^2

$$\frac{6D_0NkT}{Vg_r\gamma^2} = 2.49 \times 10^{-4}T$$

In other words, for reasonably rigid systems with $\gamma \sim 2$, the polarizability, and hence ϵ_0, is independent of temperature.

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Polydispersity Effects on Dilute-Solution Dynamic Properties of Linear Homopolymers

R. L. Sammler,[†] C. J. T. Landry,[‡] G. R. Woltman, and J. L. Schrag[*]

Department of Chemistry and Rheology Research Center, University of Wisconsin, Madison, Wisconsin 53706.

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ABSTRACT: The bead–spring model of Zimm is generalized to predict the effects of molecular weight polydispersity in samples of linear homopolymers. The predictions agree quantitatively with the frequency dependence of the modified birefringence coefficient, S^*_Δ, measured for several polydisperse samples ($1.06 < \bar{M}_w/\bar{M}_n < 2.5$) of atactic polystyrene dissolved in Aroclor 1248. At low levels of polydispersity the effects are only seen in the low-frequency transition zone; at higher levels the effects are seen at all frequencies. Estimations of the number-, weight-, and z-average molecular weights from the frequency dependence of the intrinsic birefringence are possible after calibration with monodisperse standards. Consideration of sample polydispersity (and approximating S_e with S'_∞) leads to a 15% reduction in past estimates of the molecular weight of a Gaussian submolecule for polystyrene dissolved in Aroclor 1248 at 25.00 °C. The similarity between the frequency dependence of S^*_Δ for a sample of linear chains with a bimodal molecular weight distribution and that for a monodisperse sample of regular combs underscores the need to assess sample polydispersity when using dynamic properties to interpret long-chain structure.

I. Introduction

The frequency dependences of the modified intrinsic birefringence, $[S^*]_\Delta$, and complex viscoelasticity, $[\eta^*]_\Delta$, coefficients have been shown[1] to have excellent potential for characterization of long-chain structure in monodisperse samples of flexible homopolymers. This potential is often best realized when data are obtained under good solvating conditions, and recent[2] computations have established the interpretation of Gaussian bead–spring model (BSM) fit parameters obtained by fitting such non-Θ properties. Real samples of homopolymers are sel-

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[†] Current address: M. E. Pruitt Research Center, Dow Chemical Co., Midland, MI 48674.

[‡] Current address: Corporate Research Laboratories, Eastman Kodak Co., Rochester, NY 14650.

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