shown, however, that the direct measurement techniques of LS or LS–SEC yield precise, reproducible results.

A strong tendency toward formation of aggregates in solution was observed in the homopolymers with short spacers. This was not observed in the copolymers of similar spacer lengths, indicating a role of biphenyl–biphenyl interactions in this phenomenon as well.

An odd–even effect was observed in the measured exponent of the viscosity law as a function of the spacer length. This effect was also observed in the Flory χ values as a function of the spacer length.

The calculated end-to-end distances of the homopolymers and copolymers increased regularly with increasing spacer length, all being substantially greater than that of PMMA. This indicates that these polymers in solution are stiffer than PMMA and that the stiffness increases as the spacer length increases.

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Electric Field Induced Light Scattering from Polar Polymers

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ABSTRACT: A theory is presented for light scattering from a flexible polar polymer chain, in the presence of an electric field (EFLS). It is shown that the change in light scattering due to the applied electric field arises from two effects. First, the electric field deforms the polymer because the more polar configurations are energetically more favorable in the presence of the electric field. This fluctuation term is zero for rigid polymers. Second, the polymer orients in the field. It is also shown that the fluctuation and orientation terms can be separated by performing two experiments, where the applied field is normal and parallel, respectively, to the scattering vector. The general expressions that are derived in this paper for EFLS cannot be evaluated easily, for any polymer. However, in the small-angle scattering regime, the expressions for EFLS simplify so that they can be evaluated in the rotational isomeric state (RIS) scheme. EFLS promises to be a useful tool for characterizing semiflexible polymers and also complements other techniques (end-to-end distance, dipole moments, Kerr effect) for the characterization of polymers.

Introduction

The characterization of polymers by light scattering is a well-proven method from which we derive the structure factor, molecular weight, and solution second virial coefficient.[1] A closely related technique, electric field induced light scattering (EFLS),[2] has received less attention but is also potentially useful for polymer characterization. In the case of EFLS, we observe the change in light scattering intensity when a strong electric field E is applied across a medium. In the absence of an electric field we observe the isotropically averaged structure factor, which arises from the phase differences between different parts of a macromolecule. In the presence of a strong electric field, two additional effects occur; first, the polymer is oriented because of the interaction of the dipole moment with the electric field; second, in the case of flexible polymers, the shape is distorted by the electric field because the more polar conformations are energetically preferred. Thus, from an EFLS experiment, we can learn about polymer conformation and flexibility, and dipolar interactions with electrical fields.

EFLS is similar to two other nonlinear dielectric experiments; namely, the Kerr effect[3] and nonlinear dielectric effect (NLDE), or dielectric saturation.[4] The Kerr effect is the forward scattering of light in an electrical field which results in a change of refractive indices parallel and perpendicular to the applied field and gives information about polarizability, anisotropy, dipolar interactions, and polymer conformation. The NLDE is the change of the dielectric constant in a strong electrical field and gives information about polymer flexibility, conformation, and dipolar interaction.

Wippler, Benoit,[5,6] and, more recently, Jennings[2] have experimentally and theoretically studied EFLS and have

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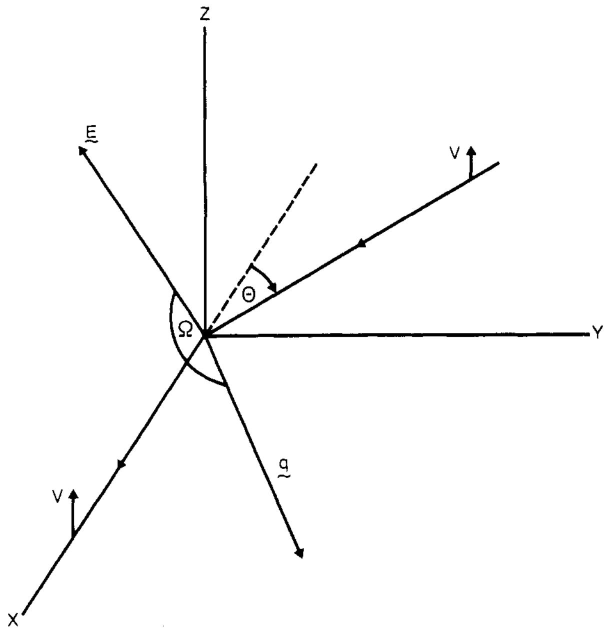

Figure 1. Scattering geometry and electric field in the laboratory coordinate system.

shown that it is sensitive to polymer shape, conformation, and degree of flexibility. However, all the theories to date have been for specific models; for example, rigid polymers which have rod or disk shapes or flexible polymers which obey Gaussian statistics.[6] In this paper, we derive a general theory for EFLS without recourse to specific models. The theory is applicable to single polymer chains, as obtained in dilute solution studies. This theory clearly shows the role of polymer flexibility, conformation, and dipolar interactions with electrical fields.

Theory

In this section, we derive the mathematical theory of EFLS. The first part deals with a specific scattering geometry where the applied field direction is normal to the scattering plane and vector. In the second part, we derive a general result for the applied field in an arbitrary direction relative to the scattering vector, and in the third part, we derive a result for small-angle scattering.

We assume that there are N polymer chains sufficiently apart that interpolymer interference scattering effects are negligible. Each polymer consists of n identical isotropically polarizable segments which act as scattering centers. The polymer has a total average polarizability α and dipole moment μ. Since the average polarizability is a scalar quantity, it will be independent of conformation; but the dipole moment, being a vector, will change with configuration τ. Consider the scattering geometry shown in Figure 1. The polarization of the incident and scattered radiation are along the z axis. It follows[1] that the scattered intensity, I, is equal to

$$I_{\mathrm{vv}} = N\alpha^2\langle P(q)\rangle_{E,\tau} \tag{1}$$

$$P(q) = \frac{1}{n^2}\sum_{i,j} e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \tag{2}$$

The summation extents over all polymer bonds i and j (1–n) and $i = -1^{1/2}$. In eq 2,

$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

is the magnitude of the scattering vector, and r_{ij} is the distance between the ith and jth scattering centers on the polymer chain; it is also a function of the polymer configuration τ. The angular brackets denote a double averaging, over all orientations of the vector $\mathbf{r}_{ij}$ in the applied field E and also over all internal configurations, τ, of the polymer. This is expressed by eq 3; $\hat{\mathbf{r}}_{ij}$ denotes a unit

$$\langle P(q)\rangle_{E,\tau} = \frac{\int P(q)e^{-U(E,\tau)/(kT)}\,d\tau\,d\hat{\mathbf{r}}_{ij}}{\int e^{-U(E,\tau)/(kT)}\,d\tau\,d\hat{\mathbf{r}}_{ij}} \tag{3}$$

vector along the vector $\hat{\mathbf{r}}_{ij}$ and the integration is over all orientations relative to the applied electric field. The total energy $U(E,\tau)$ of a polymer chain in a fixed configuration, τ, is the sum of the internal energy $U(\tau)$ and dipolar interaction with the electric field. Thus

$$U(E,\tau) = U(\tau) - \mu(\tau)\cdot\mathbf{E} \tag{4}$$

$\mathbf{E}$ is the internal electric field at the polymer chain and is different from the applied field F. Approximate relations exist between the two fields, such as the Lorentz or Onsager approximations.[7] To proceed further, eq 3 is expanded as a Taylor series in the applied field E and we neglect terms higher than E^2. Thus,

$$\langle P(q)\rangle_{\mathrm{E},\tau} = \langle P(q)\rangle_\tau + \frac{E^2}{2k^2T^2}\left[\left\langle P(q)\left(\frac{\partial U}{\partial E}\right)^2\right\rangle_\tau - \langle P(q)\rangle_\tau\left\langle\left(\frac{\partial U}{\partial E}\right)^2\right\rangle_\tau\right] \tag{5}$$

The first term is simply the structure factor of an isotropically oriented polymer in the absence of an electric field; thus[1]

$$\langle P(q)\rangle_\tau = \frac{1}{n^2}\sum_{i,j}\langle J_0(qr_{ij})\rangle_\tau \tag{6}$$

$J_0(x)$ denotes the zeroth-order spherical Bessel function $[J_0(x) = (\sin x)/x]$. The summation extends over all pairs of elements i and j of the polymer chain. This term is evaluated experimentally from a conventional light scattering experiment. The second term, which is proportional to E^2, is an additional term to the structure factor which arises from the interaction of the polar polymer chain with the electric field. The averages occurring on the right-hand side of eq 5 are now in the absence of the electric field (E = 0) and, therefore, all orientations are equally probable.

Therefore, it follows from eq 1, 5, and 6 that the change in light scattering intensity $\Delta I_{\mathrm{vv}}/E^2$ is

$$\frac{\Delta I_{\mathrm{vv}}}{E^2} = \frac{I_{\mathrm{vv}}(E) - I_{\mathrm{vv}}(E{=}0)}{E^2} = \frac{N\alpha^2}{2k^2T^2}\left[\left\langle P(q)\left(\frac{\partial U}{\partial F}\right)^2\right\rangle_\tau - \langle P(q)\rangle_\tau\left\langle\left(\frac{\partial U}{\partial E}\right)^2\right\rangle_\tau\right] \tag{7}$$

Equation 7 is now evaluated for a number of different geometries.

Case 1. Electric Field Normal to the Scattering Plane. Let the electric field be along the z axis (see Figure 1). From eq 4, we have

$$(\partial U/\partial E)^2 = ({}^{\mathrm{L}}\mu_z)^2 \tag{8}$$

where ${}^{\mathrm{L}}\mu_z$ denotes the z component of the dipole moment in the laboratory frame of reference. Since all orientations are equally probable, it follows that

$$\langle(\partial U/\partial E)^2\rangle_\tau = \tfrac{1}{3}\langle\mu^2\rangle_\tau \tag{9}$$

$\langle\mu^2\rangle$ denotes the mean-square dipole moment which can be obtained experimentally by measuring the dielectric constant of the polymer solution.

The evaluation of the orientational averages in the term $\langle P(q)\ (\partial U/\partial E)^2\rangle\tau$ is more difficult and we resort to a spherical rather than a Cartesian coordinate representation. We define the terms[1]

$$\mu_0^1 = \mu_z \qquad \mu_{\pm1}^1 = \frac{\pm1}{2^{1/2}}(\mu_x \pm i\mu_y) \tag{10}$$

In eq 10, $\mu^1_{0\pm1}$ is the spherical tensor representation of the Cartesian vectors $\mu_{x,y,z}$ and $i = -1^{1/2}$. Therefore

$$\mu_x = \frac{1}{2^{1/2}}(\mu_{+1}^1 - \mu_{-1}^1) \qquad \mu_y = \frac{-i}{2^{1/2}}(\mu_{+1}^1 + \mu_{-1}^1) \tag{11}$$

and eq 8 becomes

$$(\partial U/\partial E)^2 = ({}^{\mathrm{L}}\mu_0{}^1)^2 \tag{12}$$

As before, the superscript L denotes the laboratory coordinate system. The phase factor $e^{i\mathbf{q}\cdot\mathbf{r}_{ij}}$ in $P(q)$ is written as[8]

$$e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} = 4\pi\sum_{l,m} i^l J_l(qr_{ij})\,{}^{\mathrm{L}}Y^*_{l,m}(\hat{\mathbf{q}})\,{}^{\mathrm{L}}Y_{l,m}(\hat{\mathbf{r}}_{ij}) \tag{13}$$

${}^{\mathrm{L}}Y_{l,m}(\hat{\mathbf{r}}_{ij})$ denotes a sperical harmonic function in the laboratory coordinate system and a superscript star denotes its complex conjugate. $J_l(x)$ denotes the lth order spherical Bessel function. $\hat{\mathbf{q}}$ denotes a unit vector along the scattering vector $\mathbf{q}$.

Let another coordinate system be affixed to the body (B) of the polymer chain in a given fixed configuration, τ, such that the z axis points along the $\mathbf{r}_{ij}$ vector. The superscript B denotes the body coordinate system. The specification of x and y directions is not important in this problem. Let $D^l{}_{mn}$ denote the operator that transforms from the body (B) to the laboratory (L) coordinate system. It follows from the transformation theory of spherical tensors[1,8] that

$${}^{\mathrm{L}}\mu_0{}^1 = \sum_m {}^{\mathrm{B}}\mu_m^1 D_{m,0}^1 \tag{14}$$

Thus eq 12 becomes

$$(\partial U/\partial E)^2 = \sum_{m_1,m_2} {}^{\mathrm{B}}\mu_{m_1}^1\,{}^{\mathrm{B}}\mu_{m_2}^1 D_{m_1,0}^1 D_{m_2,0}^1 \tag{15}$$

Similarly, in eq 13

$${}^{\mathrm{L}}Y_{l,m}(\hat{\mathbf{r}}_{ij}) = \sum_{m'} {}^{\mathrm{B}}Y_{l,m'}(\hat{\mathbf{r}}_{ij}) D^l_{m',m} \tag{16}$$

But since $\hat{\mathbf{r}}_{ij}$ is along the z axis, it follows that

$${}^{\mathrm{B}}Y_{l,m'}(\hat{\mathbf{r}}_{ij}) = \left(\frac{2l+1}{4\pi}\right)^{1/2} \qquad m' = 0 \tag{17}$$

and eq 16 becomes

$${}^{\mathrm{L}}Y_{l,m}(\hat{\mathbf{r}}_{ij}) = \left(\frac{2l+1}{4\pi}\right)^{1/2} D^l_{0,m} \tag{18}$$

Thus, from eq 13, 15, and 18 we obtain

$$\left\langle P(q)\left(\frac{\partial U}{\partial E}\right)^2\right\rangle_\tau = \frac{(4\pi)^{1/2}}{n^2}\sum_{i,j}\sum_{\substack{l_3\\m_1,m_2,m_3}} i^{l_3}(2l_3 + 1)^{1/2}\,{}^{\mathrm{L}}Y^*_{l_3}(\hat{\mathbf{q}})\langle J_{l_3}(q\mathbf{r}_{ij})\,{}^{\mathrm{B}}\mu_{m_1}^1\,{}^{\mathrm{B}}\mu_{m_2}^1 D^{l_3}_{0,m_3} D^1_{m_1,0} D^1_{m_2,0}\rangle_\tau \tag{19}$$

In eq 19 the angular brackets denote averaging over all orientations of the vector $\mathbf{r}_{ij}$ and all internal configurations τ of the polymer. The averaging is done in two steps. First the vector $\mathbf{r}_{ij}$ is averaged over all directions. Thus

$$\langle D^1_{m_1,0} D^1_{m_2,0} D^{l_3}_{0,m_3}\rangle_\tau = \begin{pmatrix} 1 & 1 & l_3 \\ m_1 & m_2 & 0 \end{pmatrix}\begin{pmatrix} 1 & 1 & l_3 \\ 0 & 0 & m_3 \end{pmatrix} \tag{20}$$

From the symmetry properties[8] of the $3j$ symbols, it follows that $m_1 = -m_2$, $m_3 = 0$, and $l_3 = 0, 2$. Thus eq 19 becomes

$$\left\langle P(q)\left(\frac{\partial U}{\partial E}\right)^2\right\rangle_\tau = \frac{(4\pi)^{1/2}}{n^2}\sum_{i,j}\sum_{\substack{l_3=0,2\\m_1}} i^{l_3}(2l_3 + 1)^{1/2}\,{}^{\mathrm{L}}Y^*_{l_3,0}(\hat{\mathbf{q}}) \times \left\langle J_{l_3}(qr_{ij})\,{}^{\mathrm{B}}\mu_{m_1}^1\,{}^{\mathrm{B}}\mu_{-m_1}^1\right\rangle_\tau \begin{pmatrix} 1 & 1 & l_3 \\ m_1 & -m_1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 1 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \tag{21}$$

The angular brackets now denote averaging over all internal configurations. In the scattering geometry shown in Figure 1, the polar angles of the scattering vector $\hat{\mathbf{q}}$ are $\theta = 90°$ and $\phi = 90 - \theta/2$, where θ is the scattering angle. Thus

$${}^{\mathrm{L}}Y^*_{0,0}(\hat{\mathbf{q}}) = \frac{1}{(4\pi)^{1/2}} \qquad {}^{\mathrm{L}}Y^*_{2,0}(\hat{\mathbf{q}}) = -\frac{1}{2}\left(\frac{5}{4\pi}\right)^{1/2} \tag{22}$$

Using tabulated values of $3j$ symbols[8] and eq 22, eq 21 becomes

$$\left\langle P(q)\left(\frac{\partial U}{\partial E}\right)^2\right\rangle_\tau = \frac{1}{n^2}\sum_{i,j} \tfrac{1}{3}\langle J_0(qr_{ij})\mu^2\rangle_\tau + \tfrac{1}{2}\left\langle J_2(qr_{ij})\left({}^{\mathrm{B}}\mu_z{}^2 - \frac{\mu^2}{3}\right)\right\rangle_\tau \tag{23}$$

$J_2(x)$ is the second-order spherical Bessel function. ${}^{\mathrm{B}}\mu_z$ denotes the z component of the dipole moment in the coordinate system affixed to the polymer, i.e., the component of μ along r_{ij}. Thus

$${}^{\mathrm{B}}\mu_Z{}^2 = \frac{(\boldsymbol{\mu}\cdot\mathbf{r}_{ij})^2}{r_{ij}{}^2} = (\mu\cdot\hat{\mathbf{r}}_{ij})^2 \tag{24}$$

Combining the results of eq 1, 2, 5, 6, 8, 9, and 22–24, we arrive at the final result

$$\frac{\Delta I_{\mathrm{vv}}}{E^2} = \frac{N\alpha^2}{2k^2T^2}\left[\frac{1}{n^2}\sum_{i,j}\tfrac{1}{3}\langle J_0(qr_{ij})\mu^2\rangle_\tau - \tfrac{1}{3}\langle J_0(qr_{ij})\rangle_\tau\langle\mu^2\rangle_\tau + \tfrac{1}{2}\left\langle J_2(qr_{ij})\left(\frac{(\boldsymbol{\mu}\cdot\mathbf{r}_{ij})^2}{r^2_{ij}} - \frac{\mu^2}{3}\right)\right\rangle_\tau\right] \tag{25}$$

ΔI_{vv} is the difference in light scattering with the electric field on and off.

Case 2. Electric Field in an Arbitrary Direction to the Scattering Vector. Suppose we have the same scattering geometry as shown in Figure 1, but now the electric field is in an arbitrary direction. We generalize the derivation of the previous section. The energy of a polymer in a fixed configuration, τ, in an electric field is

$$U(E,\tau) = U(\tau) - (\mu_x\hat{e}_x + \mu_y\hat{e}_y + \mu_z\hat{e}_z)E \tag{26}$$

where $\hat{\mathbf{e}}$ denotes a unit vector in the direction of the electric field in the Cartesian coordinate system. Let $e^1_{\pm1}$ and e^1_0 be the spherical tensor representation of the unit vector $\hat{\mathbf{e}}$, following the definitions in eq 10 and 11. Thus

$$\partial U/\partial E = -\sum_m (-1)^m\,{}^{\mathrm{L}}\mu_m^1 e^1_{-m} \tag{27}$$

The spherical tensors $e_{\pm1,0}{}^1$ are related to the spherical harmonics by[8]

$$e^1_{-m} = \left(\frac{4\pi}{3}\right)^{1/2} Y_{1,-m}(\hat{\mathbf{e}}) \tag{28}$$

Therefore, from eq 27 and 28,

$$(\partial U/\partial E)^2 = \frac{4\pi}{3}\sum_{m_1,m_2}(-1)^{m_1+m_2}\,{}^{\mathrm{L}}\mu^1_{m_1}\,{}^{\mathrm{L}}\mu^1_{m_2} Y_{1,-m_1}(\hat{\mathbf{e}}) Y_{1,-m_2}(\hat{\mathbf{e}}) \tag{29}$$

After eq 29, the steps in the derivation are similar to case 1. ${}^{\mathrm{L}}\mu^1_m$ is transformed to the body coordinate system affixed to the polymer and we derive an equation similar to eq 19. After isotropic averaging and some manipulation, we arrive at

$$\langle P(q)(\partial U/\partial E)^2\rangle_\tau = \frac{1}{n^2}\sum_{i,j}{}^1\!/\!_3\langle J_0(qr_{ij})\mu^2\rangle_\tau - \left\langle J_2(qr_{ij})\left(\frac{(\mu\cdot\mathbf{r}_{ij})^2}{r_{ij}^2} - \frac{\mu^2}{3}\right)\right\rangle_\tau P_2(\cos\Omega) \quad (30)$$

where $P_2(x) = (3x^2 - 1)/2$ and Ω is the angle between the electric field E and the scattering vector $\mathbf{q}$. The final expression for the change in the intensity is

$$\frac{\Delta I_{vv}}{E^2} = \frac{N\alpha^2}{2k^2T^2}\left[\frac{1}{n^2}\sum_{i,j}{}^1\!/\!_3\langle J_0(qr_{ij})\mu^2\rangle_\tau - {}^1\!/\!_3\langle J_0(qr_{ij})\rangle_\tau\langle\mu^2\rangle_\tau - \left\langle J_2(qr_{ij})\left(\frac{(\mu\cdot\mathbf{r}_{ij})^2}{r_{ij}} - \frac{\mu^2}{3}\right)\right\rangle_\tau P_2(\cos\Omega)\right] \quad (31)$$

Note that when $\Omega = 90°$, we obtain the result of case 1, i.e., eq 25.

Case 3. Small-Angle Approximation. For a polymer chain which has many configurations accessible to it, eq 25 and 31 cannot be evaluated analytically, and one must resort to computer simulation of the many conformations accessible to a polymer chain. However, one can derive a simpler expression for EFLS in the small-angle scattering regime, so that $qr_{ij} \ll 1$. Consider eq 25 from case 1. Since

$$J_0(x) \simeq 1 - x^2/6 + \dots$$
$$J_2(x) \simeq x^2/15 + \dots \qquad x \ll 1 \quad (32)$$

It follows that eq 25 becomes

$$\frac{\Delta I_{vv}}{E^2} = \frac{N\alpha^2q^2}{2k^2T^2}\left[\frac{1}{n^2}\sum_{i,j}\frac{\langle r_{ij}^2\rangle_\tau\langle\mu^2\rangle_\tau}{18} - \frac{\langle r_{ij}^2\mu^2\rangle_\tau}{15} + \frac{\langle(\mu\cdot\mathbf{r}_{ij})^2\rangle_\tau}{30}\right] \quad (33)$$

The above expression contains averages of the second moment of the dipole moment μ and the distance vector $\mathbf{r}_{ij}$ and their products. The configurational averages in eq 33 can be evaluated exactly in the rotational isomeric state (RIS) approximation, as described by Flory.[9] For example, the second moment of the dipole moment is given by

$$\langle\mu^2\rangle = Z^{-1}JG_1{}^nJ^* \quad (34)$$

In eq 34, Z is the partition function, $G_1{}^n$ denotes a serial product of generator matrices for each bond in the chain (1–n), and Js are unit row and column vectors. The generator matrices contain information about the geometry, rotational states and their relative energies, and the dipole moments of the ith bond. The other moments occurring in eq 33 have not been reported in the literature but can be derived by using the procedures described in ref 9. Therefore, in the small-angle scattering approximation, we can derive expressions for EFLS which can be evaluated easily in the RIS approximation.

Calculations performed for second moments (dipole moments, end-to-end distance) and higher moments (Kerr effect, dielectric saturation)[3,4] reveal that these averages are sensitive to polymer structure, the relative energies of the rotamer states, tacticity, and comonomer composition, in the case of a copolymer. Thus, EFLS can be used to study the structure of polymers since it is also a function of configurational averages of a polymer chain.

Discussion

In this paper, we have derived an exact expression for EFLS from a polar polymer without any assumptions about the shape of the polymer. It can be used to perform exact numerical calculations and to compare with different models that have been derived previously.[2] The theory presented here assumes that the permanent dipole moment is the only interaction with the applied electrical field and neglects induced dipole contributions. This assumption is valid for polar flexible polymers, such as poly(vinyl chloride), and rigid rod polymers with large permanent moments.

The expressions derived in this paper, eq 25 and 31, show that EFLS arises from two effects. First, the electric field deforms the polymer chain because the more polar configurations are more energetically favored in the presence of the electric field. This gives rise to the fluctuation term in eq 25

$$A = \frac{N\alpha^2}{2k^2T^2}\left[\frac{1}{n^2}\sum_{i,j}{}^1\!/\!_3\langle J_0(qr_{ij})\mu^2\rangle_\tau - {}^1\!/\!_3\langle J_0(qr_{ij})\rangle_\tau\langle\mu^2\rangle_\tau\right] \quad (35)$$

The second effect is the orientation of the polymer in the electric field. This gives rise to the term

$$B = \frac{N\alpha^2}{2k^2T^2}\left[\frac{1}{n^2}\sum_{ij}\left\langle J_2(qr_{ij})\left(\frac{(\mu\cdot\mathbf{r}_{ij})^2}{r_{ij}^2} - \frac{\mu^2}{3}\right)\right\rangle_\tau\right] \quad (36)$$

The fluctuation term of eq 35 is equal to zero for a rigid polymer but is nonzero for a polymer that has some degree of flexibility. This term in EFLS can be used to characterize the degree of flexibility of polymers. Experimentally, the fluctuation term can be separated from the orientation term by doing EFLS in two geometries. When the electric field E is at 90° to the scattering vector $\mathbf{q}$,

$$\frac{\Delta I_{vv}(\Omega{=}90°)}{E^2} = A + B/2 \quad (37)$$

and when $\Omega = 0°$,

$$\frac{\Delta I_{vv}(\Omega{=}0°)}{E^2} = A - B \quad (38)$$

It follows from eq 37 and 38

$$B = \frac{2}{3}\left(\frac{\Delta I_{vv}(\Omega{=}90°)}{E^2} - \frac{\Delta I_{vv}(\Omega{=}0°)}{E^2}\right) \quad (39)$$

and

$$A = \frac{1}{3}\left(\frac{\Delta I_{vv}(\Omega{=}90°)}{E^2} + \frac{\Delta I_{vv}(\Omega{=}0°)}{E^2}\right) \quad (40)$$

Thus, from two EFLS experiments, we can delineate the fluctuation and orientation terms and gain information about polymer flexibility and conformation.

Since $A = 0$ for a rigid polymer, we can define the ratio R

$$R = \frac{\Delta I_{vv}(\Omega{=}0°)}{\Delta I_{vv}(\Omega{=}90°)} = -2 \quad (41)$$

The ratio R can be measured experimentally, and the deviation from $R = -2$ is also a measure of polymer flexibility. Jennings[2] has described experimental techniques for measuring EFLS in the two geometries, $\Omega = 0°$ and 90°.

Recently, there has been increased interest in heterocylic rigid-rod polymers, which form lyotropic liquid-crystal phases, and thermotropic liquid-crystal polymers consisting of mesogenic groups connected by flexible spacers.[10] According to present understanding, the degree of polymer flexibility plays a fundamental role in the formation and stability of various liquid-crystal phases. It is therefore important to characterize the degree of polymer flexibility by EFLS and other techniques.

Jennings[2] had alluded to a disadvantage of EFLS; namely, that the polymer size must be comparable to the wavelength of light. This can be overcome by using low-angle X-ray (LAXS) and neutron scattering (LANS) techniques in the presence of an electric field. The theory presented here would apply in the case of LAXS and LANS in an electric field, except that the polarizability α would be replaced by electron density and scattering length, respectively.

Conclusions

Electric field induced light scattering is a technique that is potentially useful in several areas of polymer characterization. By doing two EFLS experiments on the same polymer sample, one can separate out the two effects contributing to EFLS, namely, the fluctuation term which comes about from polymer flexibility and the orientation term. The first term is important for determining the degree of polymer flexibility and is useful for characterizing liquid-crystal polymers. For example, it can be used to distinguish between rods, disks, and semiflexible polymers. The second term will be sensitive to the details of polymer structure and can complement other methods for characterizing polymer, such as end-to-end distances, dipole moments, and Kerr effect. When EFLS is performed in the small-angle scattering regime, the theoretical expression for it can be evaluated exactly by using the RIS model.[9] In that case, there can be a simple direct comparison between experiment and theory.

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Dynamic Light Scattering Studies of Polymer Solutions. 6. Polyisoprenes in a Θ-Solvent, 1,4-Dioxane

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ABSTRACT: The dynamic properties of polyisoprenes in 1,4-dioxane at 34.7 °C (the Θ-temperature) have been studied by homodyne photon correlation spectroscopy. The infinite dilution characteristics, the translational diffusion coefficient D_0, and the effective decay rate (the first cumulant) $(\Gamma_e)_{c\to 0}$, have been analyzed as functions of the scattering vector $\boldsymbol{q}$. It has been found that isoprene chains in the unperturbed state are fairly well described by the *nondraining* Gaussian model with *nonpreaveraged* Oseen hydrodynamic interaction. However, it has been revealed that some 10% and some 20% differences of D_0 and $(\Gamma_e)_{c\to 0}$, respectively, exist between experiments and theories. The former difference might be explainable in terms of the *internal friction* of chains, which has recently been introduced by Fixman. The concentration dependence of the translational diffusion coefficient is also discussed in some detail.

Introduction

At the Θ-temperature where the excluded volume effect vanishes, dynamic light scattering by dilute polymer solutions provides precise information on the nature of the hydrodynamic interaction between chain segments. Experimental studies[1-3] so far made for an oridinary Θ-solution, polystyrene (PS) in cyclohexane, *trans*-decalin, and so on, have shown some puzzling results, for example, the superiority of the preaveraged (PA) form of the Oseen hydrodynamic interaction to the non-PA form and a 15% or 20% reduction of the translational diffusion coefficient D_0 from the Kirkwood value. These situations have been clearly summarized in the recent review of Stockmayer and Hammouda.[4] Similar results, though not very conclusive, have been obtained also for PS in benzene, a good solvent.[5]

We have recently studied[6] the dynamic behavior of polyisoprene (PIP) in cyclohexane and found that, in the good solvent, PIP chains are well described by the non-draining chain model with the non-PA Oseen tensor and with Domb–Gillis–Wilmers segment distribution. This result which is more reasonable as compared with the previous result for PS seems to be attributed to higher

Table I
Characteristics of Polyisoprenes in 1,4-Dioxane at 34.7 °C (Θ-Temperature)

			microstructure[b]		
polymer	$10^{-6}M_w$[a]	R_G, 10^{-6} cm	cis-1,4	trans-1,4	3,4
L-14	0.326	(1.91)[c]	73.3	21.9	4.8
L-12	0.568	2.53	67.0	25.3	7.7
L-11	2.44	(5.23)	84.1	11.9	4.0

[a] Measured in cyclohexane at 25 °C.[6] [b] Measured in $CDCl_3$ at 35 °C by using a 400-MHz ^1H NMR spectrometer.[6] [c] The values in parentheses were estimated from the empirical relation $R_G = 3.35 \times 10^{-9} M_w^{0.50}$ cm, which was obtained by analyzing the data of Hadjichristidis and Roovers[7] and ours.

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