Kerr Effect Studies of the Poly(oxyethylenes)

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ABSTRACT: Molar Kerr constants, $_{\mathrm{m}}K$, have been obtained for the first four oligomers of poly(oxyethylene) [POE $\equiv$ $CH_3(-O-CH_2-CH_2-)_xO-CH_3$], and for a higher molecular weight POE ($x = 91$) terminated with hydroxyl groups, from electric birefringence measurements performed in carbon tetrachloride solutions. In addition, the dipole moments of each of the POE's were measured in these solutions. The results are compared with average $\langle _{\mathrm{m}}K \rangle$ and mean square dipole moments, $\langle \mu^2 \rangle$, calculated for POE from its rotational isomeric state model through adoption of the valence optical scheme, which assumes bond polarizability tensor additivity. The bond polarizability tensors obtained from depolarized light-scattering studies performed on n-alkanes and POE, and the C–O and H–O bond dipole moments, were utilized in the calculations. Agreement between measured and calculated $_{\mathrm{m}}K$ is poor except for the sign of $_{\mathrm{m}}K$ and its dependence upon chain length. The calculated and measured $\langle \mu^2 \rangle$ are in good agreement including the dependence of $\langle \mu^2 \rangle$ upon chain length. Possible reasons for the disparity between the Kerr constants predicted and measured for POE are discussed.

Molar Kerr constants of polymers, as extracted from electrical birefringence measurements[1,2] performed on their dilute solutions, are potentially useful in an analysis of their conformational behavior.[3-6] The magnitude and sign of the birefringence produced in the solution by the externally applied field depend[3] only upon the dipole moment and the anisotropic polarizability tensor of the polymer solute if the solvent is isotropic.

The overall dipole moment and anisotropic polarizability tensor of the polymer chain are sums[3-5] of the moments and polarizability tensors, respectively, contributed by each bond constituting the chain, where each sum must clearly be averaged over all possible polymer chain conformations. If the bond moments and bond polarizabilities are known, then it should be possible to predict the observed birefringence provided the conformational characteristics of the polymer have been determined.

We present in this report results of electric birefringence measurements performed on the poly(oxyethylenes) [POE $\equiv$ $CH_3(-O-CH_2-CH_2-)_xO-CH_3$] with x = 1, 2, 3, 4, and 91 (hydroxyl termination) in carbon tetrachloride solutions. Because the conformational characteristics,[4,7,8] bond dipole moments,[4] and bond polarizability tensors[8] have been determined for the POE chain, we are able to calculate the expected birefringence and compare it to the observed. Also the calculated and observed dipole moments are obtained and compared.

Calculation of Kerr Constants

Kerr's law[9] describes the proportionality between the birefringence $\Delta\tilde{n}$ induced by and the square of the magnitude, E^2, of the applied electric field

$$\Delta\tilde{n}/\lambda = BE^2 \tag{1}$$

where λ is the vacuum wavelength and B is the Kerr constant. The molar Kerr constant $_{\mathrm{m}}K$ is then given by[1,2]

$$_{\mathrm{m}}K = \frac{6N_{\mathrm{A}}\lambda\tilde{n}B}{\rho(\tilde{n}^2 + 2)^2(\epsilon + 2)^2} \tag{2}$$

where $\tilde{n}$ and ϵ are the refractive index and the dielectric constant of the medium, ρ is the number density, and N_{A} is Avogadro's number.

Theoretically[3-5] the dipole moment μ and anisotropic polarizability tensor $\hat{\alpha}$ of a molecule can be related to $_{\mathrm{m}}K$ according to the relation

$$_{\mathrm{m}}K = \frac{2\pi}{135(kT)^2}[_{\mathrm{m}}K_{\mathrm{D}} + kT\,_{\mathrm{m}}K_{\mathrm{p}}] \tag{3}$$

where $_{\mathrm{m}}K_{\mathrm{D}}$ and $_{\mathrm{m}}K_{\mathrm{p}}$ are the dipole and polarizability contributions to $_{\mathrm{m}}K$.

$$_{\mathrm{m}}K_{\mathrm{D}} = \mu^{\mathrm{R}}\hat{\alpha}\mu^{\mathrm{C}} \tag{4}$$

$$_{\mathrm{m}}K_{\mathrm{p}} = (\hat{\alpha}^{\mathrm{R}}\hat{\alpha}'^{\mathrm{C}}) \tag{5}$$

where the superscripts R and C indicate row and column representation and the prime denotes static polarizability.

As mentioned in the introduction, both μ and $\hat{\alpha}$ for polymers consist of a sum of bond contributions which must be averaged over all possible chain conformations. To achieve the summation and appropriate averaging we adopt the rotational isomeric state (RIS) model[4,10] of polymers and the matrix multiplication techniques[4] developed to evaluate various conformationally dependent properties of the RIS chain.

For polymers this leads[4] to

$$_{\mathrm{m}}K_{\mathrm{D}} = \langle \mu^{\mathrm{R}}\hat{\alpha}\mu^{\mathrm{C}} \rangle = 2z^{-1}j^*\left(\prod_{i=1}^{n+1}\mathbf{Q}_i\right)j \tag{6}$$

and

$$_{\mathrm{m}}K_{\mathrm{p}} = \langle \hat{\alpha}^{\mathrm{R}}\hat{\alpha}'^{\mathrm{C}} \rangle = 2z^{-1}j^*\left(\prod_{i=1}^{n+1}\mathbf{P}_i\right)j \tag{7}$$

where z is the configurational partition function, $\mathbf{Q}$ and $\mathbf{P}$ are generator matrices of order $26\nu \times 26\nu$ and $11\nu \times 11\nu$, where ν is the number of rotational states allowed about each backbone bond ($\nu = 3$ for POE), j^* and j are the $1 \times (26 \text{ or } 11)\nu$ row and $(26 \text{ or } 11)\nu \times 1$ column vectors required to extract the appropriate terms from the product of generator matrices

$$\prod_{i=1}^{n+1}\mathbf{Q}_i \text{ and } \prod_{i=1}^{n+1}\mathbf{P}_i$$

and n is number of bonds in the chain. (For details of the matrix methods the reader is referred to ref 4). Each of the bond generator matrices is a function of chain geometry (backbone bond valence angles), the RIS model (location of rotational states and their probabilities), and bond polarizability tensors and dipole moments.

In utilizing the matrix methods to calculate $_{\mathrm{m}}K_{\mathrm{D}}$ and $_{\mathrm{m}}K_{\mathrm{p}}$ we are assuming the polarizability of the polymer chain to be the sum of bond polarizability tensors, each of which is independent of its conformation, or rotational state, averaged over all conformations of the chain. This assumption is called the valence optical scheme,[10] and its adoption is necessary to the present calculations even if its validity[10-13] has not as yet been fully determined.

Bond polarizability tensors, backbone bond valence angles, and the RIS model for POE determined[7] and used in the depolarized light-scattering studies of Patterson and Flory[8] are adopted here. Following Ishikawa and Nagai[5] the static bond polarizabilities $\hat{\alpha}'$ are assumed to be 1.1 times the optical polarizabilities $\hat{\alpha}$. Standard[4] moments of 0.99 and 1.70 D are used for the C–O and O–H bonds, respectively.

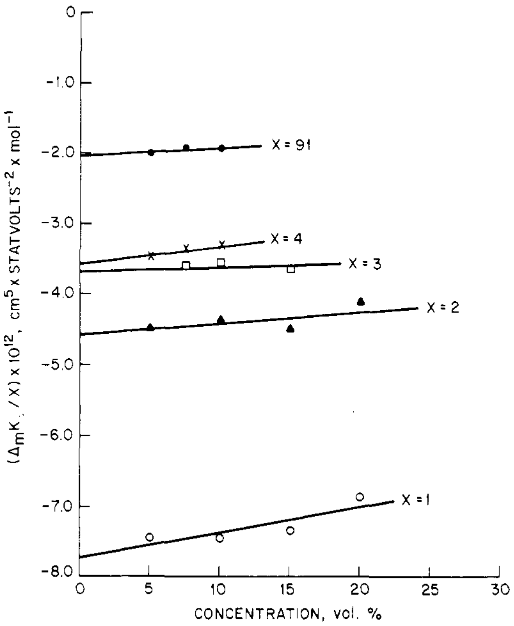

Figure 1. Incremental molar Kerr constants per repeat unit ($\Delta_m K/x$) measured for POE oligomers in CCl_4 solutions.

Measurement of Kerr Constants and Dipole Moments

The Kerr effect apparatus used here is similar to that previously described by Ingwall et al.[6] Differences include the use of a Babinet-Soleil compensator (1° 15′ wedge angle), a Spellman Model RHR30P10 power supply, and a Digitec Model 268 digital millivoltmeter and Spectra Physics Model 471 photodiode to detect the null point in the compensated laser beam. In addition, the Kerr cell itself was not jacketed for temperature control. Room temperature averaged 23 °C.

A WTW Model DM 01 dipolmeter was used to determine the dielectric constants of each POE solution as required by eq 2 to obtain ${}_mK$. The dipolmeter was equipped with a DFL 2 dielectric constant cell, and both are obtained from Kahl Scientific.

Densities were determined for the liquid POE oligomers with $x = 2, 3$, and 4 by weighing known volumes of each. Solution concentrations were then determined by pipetting known volumes of each oligomer into volumetric flasks and diluting with CCl_4. The hydroxyl terminated POE with $x = 91$ is a solid, hence its solutions were made by directly adding weighed amounts to volumetric flasks and diluting with CCl_4.

The refractive index $\tilde{n}$ of each POE solution was estimated from the known refractive indexes of CCl_4 and the first POE oligomer [$x = 1$ (1,2-dimethoxyethane)]. Volume fraction additivity of refractive indexes was assumed in evaluating each $\tilde{n}$. An indication of the accuracy of this procedure is the comparison between the calculated and measured (Abbe type precision refractometer from Bausch and Lomb Model 33-45-03-02) refractive indexes for a 10% by volume solution of 1,2-dimethoxyethane in CCl_4: $\tilde{n}^{20}{}_D$ (calcd) = 1.4521 and $\tilde{n}^{20}{}_D$ (exptl) = 1.4524.

To obtain[1,2,6] the molar Kerr constant of a solute dissolved in solution the incremental $\Delta_m K$ of the solution due to the solute is obtained from ${}_mK - {}_mK^0$, where ${}_mK$ and ${}_mK^0$ are calculated according to eq 2 from the observed Kerr constants B and B^0, number densities ρ and ρ^0, refractive indexes $\tilde{n}$ and $\tilde{n}^0$, and dielectric constants ϵ and ϵ^0 of the solution and solvent, respectively. $\Delta_m K$ is plotted as a function of concentration, and extrapolation to infinite dilution yields ${}_mK_s$ the molar Kerr constant of the solute, which is free of contributions due to solute-solute interactions.

Table I
Measured Molar Kerr Constants of POE at 23 °C in CCl_4

x	$({}_mK_s) \times 10^{12}$, cm^5 statvolts^{-2} mol^{-1}	$({}_mK_s/x) \times 10^{12}$, cm^5 statvolts^{-2} mol^{-1}
1	−7.7	−7.7
2	−9.2	−4.6
3	−11.1	−3.7
4	−14.4	−3.6
78[a,b]	−202.8	−2.6
91[a]	−182.0	−2.0

[a] Hydroxyl termination. [b] Measured in benzene at 25 °C by Aroney et al.[15]

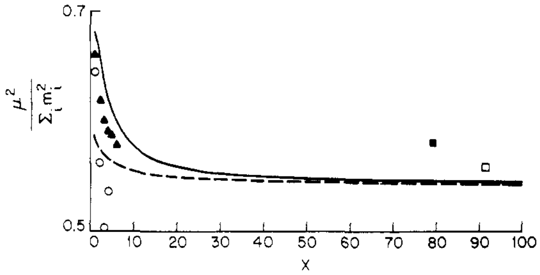

Figure 2. The ratio ($\mu^2/\Sigma_i m_i^2$) of the squared dipole moments of the POE oligomers divided by the sum of the squares of their bond moments plotted vs. chain length X. The open circles (○) correspond to the methoxyl terminated oligomers in CCl_4, as measured in the present study, the filled triangles (▲) are for the ethoxyl terminated oligomers measured[16] in benzene, and the open and filled squares (□, ■) correspond to the hydroxyl terminated oligomers measured in CCl_4 (present study) and benzene,[15] respectively. The solid and dashed curves are the calculated dipole moment ratios for the methoxyl and hydroxyl terminated POE, respectively.

Dielectric constant increments $\Delta\epsilon = \epsilon - \epsilon_0$ (ϵ_0 is the dielectric constant of CCl_4) measured for each solution are divided by the concentration and plotted against the concentration. The value of $\Delta\epsilon/c$ extrapolated to infinite dilution is proportional to μ^2, as treated in the procedure outlined by Smyth.[14]

Materials

Spectroquality CCl_4 and the second POE oligomer ($x = 2$) were obtained from Matheson Colman and Bell. POE oligomers with $x = 1, 3$, and 4 were Eastman samples, and the hydroxyl terminated POE with $x = 91$ was purchased from Polysciences. All solutes and solutions were dried over Linde 3 Å molecular sieves and filtered directly into the Kerr cell through 5 μ Millipore filters.

Experimental Results

The incremental molar Kerr constants $\Delta_m K$ of the POE oligomers in CCl_4 solution are presented in Figure 1, where, following division by x, a least-squares extrapolation to infinite dilution yields the ${}_mK_s$ per repeat unit for each oligomer listed in Table I. In Figure 2 the measured dipole moments μ^2 of each oligomer divided by the sum of the squares of the bond moments, m_i, are plotted as a function of chain length.

Calculated Results and Comparison with Experiment

In Figure 2 a comparison is made between measured and calculated dipole moments for both the methoxyl and hydroxyl terminated POE's. With the exception of the dipole moment of the third oligomer ($x = 3$) measured in the present study, the agreement between the calculated and measured dipole moments is good. The observed dependence upon chain length is very closely reproduced by the calculated dipole moments.

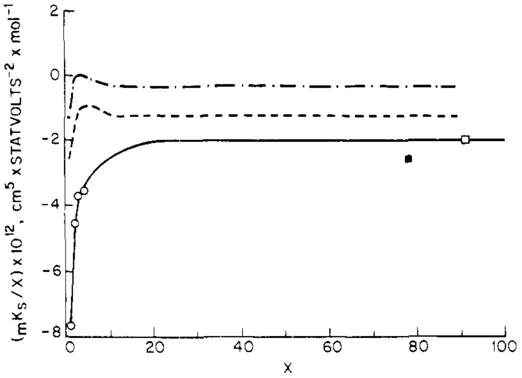

Figure 3. Molar Kerr constants per repeat unit $({}_mK_s/x)$ measured for POE oligomers and plotted as a function of chain length x. The symbols have the same meaning as in Figure 2. The (· - - ·) and (- - -) curves are the calculated molar Kerr constants including both ${}_mK_d$ and ${}_mK_p$ and only the dipolar term ${}_mK_D$, respectively.

A similar comparison between calculated and observed molar Kerr constants $({}_mK_s/x)$ is made in Figure 3. Here it is apparent that the calculated Kerr constants seriously underestimate the magnitude of those observed in the present study, although both experimental and calculated ${}_mK_s$ are negative. This behavior is similar to that observed by Ishikawa and Nagai[5] who compared molar Kerr constants calculated for hydroxyl terminated POE's to those measured by Aroney et al.[15] in benzene.

If the polarizability contribution ${}_mK_p$ to ${}_mK$ is neglected, leaving only the dipole contribution ${}_mK_D$ (see eq 3, 6, and 7), then the molar Kerr constants calculated for POE are in better agreement with the observed values. The opposite signs and similar magnitudes of ${}_mK_D$ and ${}_mK_p$ lead to small calculated ${}_mK$, which are much below those observed.

Despite the disparity in magnitudes, both the calculated and measured molar Kerr constants of POE show a similar dependence upon chain length. This is in contrast to the results reported by Aroney et al.[15] on the hydroxyl terminated POE's studied in benzene solutions. They found that $({}_mK_s/x)$ continues to decrease in magnitude with no sign of saturation (see Figures 2 and 3) for x as high as 153 repeat units, or 461 backbone bonds.

The failure of the data of Aroney et al.[15] to saturate, or reach an asymptote, was previously noted by Ishikawa and Nagai,[5] who attributed[3] this behavior to excluded volume effects. However, this interpretation is subject to considerable doubt for at least two reasons. According to the intrinsic viscosity $[\eta]$ molecular weight (M) relationship established for POE in benzene by Rossi and Cuniberti,[17] 25 °C (the temperature employed by Aroney et al.[15]) is the theta temperature for POE's with $M = 200$–8000 ($x \simeq 3$–177), as manifested by the relation $[\eta] = (1.29 \times 10^{-3})\ M^{0.5}$. It would appear that excluded volume expansion of POE, which would increase as the molecular weight is raised, should be negligible in benzene[18] at 25 °C and cannot explain the chain length dependence of the Aroney et al.[15] data.

In addition, there is reason to suspect that the molar Kerr constant of a polymer chain may be only moderately affected (moderate relative to other conformationally dependent properties such as the end-to-end distance of a polymer chain) by long-range excluded volume effects. Just as the mean-square dipole moments of polymer chains with the appropriate symmetry, such as POE, are uneffected[20–24] by excluded volume interactions so may be the dipolar contributions ${}_mK_D$ (see eq 4 and 6) to their molar Kerr constants. This expectation arrived at through reasoning by analogy, however, remains to be proven experimentally.

The polarizability contribution ${}_mK_p$ to the molar Kerr constant of a polymer chain is directly proportional[4] to its mean-square optical anisotropy $\langle \gamma^2 \rangle$ typically obtained in depolarized light-scattering studies.[8] Lemaire et al.[25] have recently calculated $\langle \gamma^2 \rangle$ for long (2000 bonds) polyethylene chains restricted to a tetrahedral lattice and obtained virtually identical results whether or not more than one polymer segment was permitted to simultaneously occupy the same lattice site. In other words, they found $\langle \gamma^2 \rangle$ (and hence ${}_mK_p$) to be independent of excluded volume effects.

Taken together it would appear reasonable to expect ${}_mK_s$ to be at the very least considerably less sensitive to excluded volume effects than are polymer chain dimensions. Consequently, we doubt that the pronounced chain length dependence of the molar Kerr constants measured for POE in benzene at 25 °C by Aroney et al.[15] has its origin in excluded volume effects, though at the present time we are unable to advance any reasonable alternative explantion. Due to solubility and drying difficulties encountered with hydroxyl terminated oligomers other than POE ($x = 91$), we were unable[26] to study the complete chain length dependence of ${}_mK_s$ for POE dissolved in CCl_4, i.e., data for $5 \leq x \leq 90$ and for $x \geq 92$ are absent.

Finally we wish to comment on the likely sources for the disparity observed between the calculated and measured molar Kerr constants of POE. The magnitudes of the experimental molar Kerr constants ${}_mK_s$ of the POE oligomers studied here are roughly 80–300% of that measured[28] for CCl_4 in benzene and extraploted to infinite dilution. According to eq 3, 4, and 5, the geometrically symmetric and isotropic CCl_4 molecules should not exhibit a Kerr effect at all.

Whichever factors, such as collision-induced anisotropy,[29] hyperpolarizability,[30,31] field-dependent polarizability tensors,[30–33] etc., cause the nonnegligible Kerr effect observed for CCl_4, they most likely also contribute to the molar Kerr constants of POE. Because the polarizability ${}_mK_p$ and dipole ${}_mK_D$ contributions to the Kerr effect (see eq 3, 4, and 5) substantially cancel each other in POE, it may be these higher order terms, which for polar molecules are usually overwhelmed by ${}_mK_p$ and ${}_mK_D$, that contribute most significantly in the case of POE and result in the disparity between the predicted and observed molar Kerr constants.

This would seem then to restrict the utility of Kerr effect studies, as applied to polymers,[34] to those with substantial dipole moments, or ${}_mK_D$, whose polarizability tensors, or ${}_mK_p$, do not, as in POE, oppose the dipole term, or to highly anisotropic polymers with symmetries that produce small dipole moments.

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Energy Transfer in Labeled Polymer Chains in Semidilute Solutions

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ABSTRACT: We discuss the possibility of using Förster resonance energy transfer between chromophores attached to a polymer chain as a monitor of the distribution function of the end-to-end distance in the semidilute regime.

Recently, Daoud et al.[1] have shown that in the semidilute region of polymer statistics there exists a characteristic length $\xi(\rho)$ defining the average distance between entanglement points at monomer concentration ρ. These authors give the average square end–end distance of a polymer as

$$\langle R^2 \rangle = N_\xi \xi^2 \quad (1)$$

and assume a Gaussian distribution for the end-to-end distance

$$f(R) = \left(\frac{3}{2\pi\langle R^2\rangle}\right)^{3/2} \exp\left(-\frac{3R^2}{2\langle R^2\rangle}\right) \quad (2)$$

where N_ξ is the number of segments of characteristic length ξ. Since N_ξ and ξ depend on concentration ($N_\xi \propto \rho^{5/4}$ and $\xi \propto \rho^{-3/4}$), the end–end distance (eq 1) is a function of the concentration

$$\langle R^2 \rangle = B^2 \rho^{-1/4} \quad (3)$$

Here B depends on the molecular weight of a polymer (M_w); in the following argument, we assume $B = 115$ for a polystyrene with $M_w = 114\,000$ g/mol (ρ in Å^{-3} and R in Å). The conjecture of Daoud et al.[1] has been formulated to apply to all intra-chain segment distances in the semidilute region. These authors have compared their theoretical predictions to experimental measurements of the radius of gyration R_G determined from Zimm plots. However, the predicted concentration dependence is not so pronounced for this quantity.

In this note, we discuss a possible experimental method to make a direct measurement of the polymer end–end distance by measurement of non-radiative energy-transfer processes. As discussed below, the energy-transfer parameters are expected to be sensitive to the theoretically predicted concentration dependence. For simplicity we explicitly consider the case in which the optical labels are placed on the chain ends; our arguments will apply with appropriate modification to labeling in the interior of the chain.

The Förster theory of resonance excitation energy transfer[2] states that the rate of transfer (probability of transfer per unit time) from an excited donor molecule, D*, to an unexcited acceptor molecule, A, depends on the inverse sixth power of the distance, R, between the two molecules

$$\gamma = \frac{1}{\tau_D}\left(\frac{R_0}{R}\right)^6 \quad (4)$$

Here τ_D is the mean lifetime of D* in the absence of the acceptor and R_0 is the "critical transfer distance" determined by the overlap of the fluorescence spectrum of D* and the absorption spectrum of A; the value of R_0 is 20–50 Å for a typical pair of chromophores. From eq 4, the light intensity, $I(t)$, of the fluorescence of the excited donor molecule t is given by

$$I_D(t) = \frac{n_D(0)}{\tau_D} \int f(R) \exp\left\{-\frac{t}{\tau_D} - \frac{t}{\tau_D}\left(\frac{R_0}{R}\right)^6\right\} d^3\mathbf{R} \quad (5)$$

where $n_D(0)$ is the number of donor molecules excited at $t = 0$ and $f(R)$ is a normalized distribution function of the donor–acceptor distance R [e.g., eq 2].

In eq 4 and 5, the assumption has been made that during the donor lifetime, the donor and acceptor dipoles take on all their possible orientations so that the angular part of γ can be replaced by its average. In addition, we make the assumption that the end-to-end distance of each polymer in the ensemble changes very little during the donor lifetime so that the average over initial static polymer conformations is important. If the characteristic time for appreciable relative motion of the chain ends becomes comparable to τ_D, then there will be dynamic contributions to the emission lifetime.