Macromolecules **1982,** *15,* 145–148

Kerr Effect and Dielectric Study of Poly(oxyethylene glycols)

G. Khanarian* and A. E. Tonelli

Bell Laboratories, Murray Hill, New Jersey 07974. *Received May 1, 1981*

ABSTRACT: We report the molar Kerr constants ${}_{\mathrm{m}}K$ and dipole moments squared $\langle \mu^2 \rangle$ of poly(oxyethylene glycols) $H(OC_2H_4)_xOH$ (POEG) (x = 2–317) and poly(oxyethylene dimethyl ethers) $CH_3(OC_2H_4)_xOCH_3$ (POEDE) (x = 1–4) in the isotropically polarizable solvents carbon tetrachloride, cyclohexane, and dioxane. Our data for ${}_{\mathrm{m}}K/x$ for POEG appear to reach an asymptotic value, unlike the data of Aroney et al. (*J. Chem. Soc.* **1960**, 2890) reported in the solvent benzene. Our ${}_{\mathrm{m}}K/x$ values for the oligomers of POEG are also considerably lower than those reported by Aroney et al. These differences are ascribed to specific solvation of the benzene molecules around the polymer. We also present calculations of ${}_{\mathrm{m}}K/x$ and $\langle \mu^2 \rangle / x$ based on the rotational isomeric state model of Flory, Mark, and their co-workers and find good agreement with the experimental results.

The Kerr effect of the poly(oxyethylene glycols) $H(OC_2H_4)_xOH$ (POEG) and the related molecules poly(oxyethylene dimethyl ethers) $CH_3(OC_2H_4)_xOCH_3$ (POEDE) have been studied experimentally and theoretically by several authors.[1-3] Aroney et al.[1] were the first to report molar Kerr constants ${}_{\mathrm{m}}K$ for POEG in the solvent benzene for x = 4–153 repeat units. A disconcerting feature of their results was that ${}_{\mathrm{m}}K/x$ did not reach an asymptotic value, even though their sample with highest molecular weight had 460 bonds along the backbone of the chain. Ishikawa and Nagai[2] presented calculations of ${}_{\mathrm{m}}K$ for POEG and POEDE based on the rotational isomeric state theory (RIS) and the optical valence scheme (bond additivity approximation, BAA). For POEG they found a large discrepancy between their calculated ${}_{\mathrm{m}}K$ values and those reported by Aroney et al. Kelly et al.[3] also reported ${}_{\mathrm{m}}K$ values for POEDE (x = 1–4, 91) in an isotropic solvent and presented calculations that were in only fair agreement with the experimental results. However their measurements were not extensive enough to see whether ${}_{\mathrm{m}}K/x$ had reached an asymptotic value. They speculated, as Ishikawa and Nagai had done previously, that the failure of the data of Aroney et al. to saturate was due to excluded volume effects. They discounted this possibility on the grounds that benzene at 25 °C was a Θ solvent and were unable to offer an alternative explanation.

Therefore two basic questions concerning the Kerr effect of POEG and POEDE remain unanswered, namely, the molecular weight dependence of ${}_{\mathrm{m}}K/x$ and the applicability of RIS theory and BAA to the calculation of their ${}_{\mathrm{m}}K$ values. In this paper we address these two questions by reporting ${}_{\mathrm{m}}K$ values for POEG (x = 2–317) in the isotropically polarizable solvents dioxane and carbon tetrachloride and for POEDE (x = 1–4) in cyclohexane. We also present calculations of ${}_{\mathrm{m}}K$ based on two approximations for the polarizability tensor of the repeat unit and show the dependence of ${}_{\mathrm{m}}K$ on the energetic and geometric parameters that enter into the calculations. We also present experimental and theoretical results for the corresponding dipole moments.

Experimental Methods and Results

The Kerr effect, dielectric, and refractive index apparatus used to make these measurements have been described before.[4] All chemicals were obtained from Aldrich Chemical Co. Dioxane was dried over type 4A molecular sieves. All other chemicals were used without further purification. The solution increments for the Kerr effect (δ), dielectric constant ($\alpha\epsilon_1$), density[23] (β), and refractive index (γ) were obtained from measurements of solutions whose weight fraction of solute was less than 3%. Careful extrapolation to infinite dilution was carried out to eliminate effects arising from solute–solute interactions. The temperature was kept constant at 25 °C, and the wavelength λ of the analyzing light beam used in the Kerr effect experiment was 6330 Å. The formulas of Le Fèvre and Le Fèvre[5] and Smith and Guggenheim[6] were used to calculate ${}_{\mathrm{m}}K$ and the dipole moments squared $\langle \mu^2 \rangle$. The results are shown in Table I.

Calculation of ${}_{\mathrm{m}}K$

Figure 1a shows the designation of bonds in POEG and POEDE used to calculate ${}_{\mathrm{m}}K$. In the RIS scheme[7] we require for each bond i the dipole moment μ_i, anisotropic polarizability tensor $\hat{\alpha}_i$, and the statistical weight matrix $\mathbf{U}_i$. The RIS model of Mark and Flory[8-10] has been used in these calculations. For the internal bonds a, b, and c (see Figure 1a) we have

$$\mathbf{U}_a = \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \sigma' & \sigma'\omega \\ 1 & \sigma'\omega & \sigma' \end{bmatrix} \qquad (1)$$

$$\mathbf{U}_b = \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \sigma' & 0 \\ 1 & 0 & \sigma' \end{bmatrix} \qquad (2)$$

$$\mathbf{U}_c = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \qquad (3)$$

σ', σ, and ω denote the Boltzmann factors $\exp(-E_{\sigma'}/RT)$, $\exp(-E_\sigma/RT)$, and $\exp(-E_\omega/RT)$, respectively, where $E_{\sigma'}$ and E_σ are the energy differences between the gauche and trans conformations about the C–O and C–C bonds, respectively, and E_ω accounts for second-order interactions. The U matrices for the terminal bonds 1, 2, 3, $n-1$, and n are given by Mark and Flory.[9]

Abe and Mark[10] have recently deduced "best" values for the energy parameters by examining dipole moments, end-to-end distances, and their temperature coefficients. They found that $E_{\sigma'}$ = 900–1300, E_σ = –400, and E_ω = 400 cal mol^{-1}. They also found that the gauche states about the C–C and C–O bonds were displaced by $\Delta\phi = 10°$ from the perfectly staggered positions ($\phi = \pm 120°$).

Now we consider the derivation of the dipole moment μ and the polarizability tensor $\hat{\alpha}$ for the repeat unit and the end groups of these polymers. A model compound for the end groups of POEG is methanol (see Figure 1b). The total dipole moment[11] (1.77×10^{-18} SC cm) (SC = statcoulomb) is the vector sum of the moments of the O–H and C–O bonds. From the dipole moment of dimethyl ether[12] (DME) (1.32×10^{-18} SC cm) we deduce that $10^{18}(\mu_{\mathrm{CO}}) = 1.15$ SC cm whence $10^{18}(\mu_{\mathrm{OH}}) = 1.78$ SC cm. We have assumed that the bond angles are 110° in these calculations.

Recently one of us[13] deduced from the Kerr effect of water in dioxane that the anisotropy of the O–H bond γ_{OH} is 0.43 Å^3. This agrees closely with the value derived by

0024-9297/82/2215-0145$01.25/0

Table I

Solution Increments for the Kerr Effect (δ), Dielectric Constant ($\alpha\epsilon_1$), Density (β), and Refractive Index (γ) for $H(OC_2H_4)_xOH$ and $CH_3(OC_2H_4)_xOCH_3$

						${}_{m}K/x$		$\langle\mu^2\rangle/x$	
x	solvent	δ	$\alpha\epsilon_1$	$10^2\beta^d$	$10^2\gamma$	this work	other work	this work	other work
					$H(OC_2H_4)_xOH$				
2	dioxane	3.2	6.25	7.97	2.18	0.69		2.63	3.62^d
									3.18^c
3	dioxane	1.3	5.60	9.19	2.13	−0.26		2.22	2.98^d
4	dioxane	5.85	4.90	8.11	2.30	2.5	21.7^b	1.88	2.64^d
									$1.95\ (x = 6)^e$
9	CCl_4	12.3	7.8		2.18	3.7	$10.3\ (x = 6)^b$	1.84	
13	CCl_4	8.77	7.00		3.16	2.6	$8.3\ (x = 18)^b$	1.62	$1.38\ (x = 18)^e$
22	CCl_4	3.26	5.8		3.44	0.59	$1.76\ (x = 34)^b$	1.31	
77	CCl_4	3.3	5.41		3.50	0.66	$-2.61\ (x = 78)^b$	1.20	$1.17\ (x = 79)^e$
							$-2.0\ (x = 91)^c$		$1.22\ (x = 98)^f$
154	CCl_4	−1.5	5.05		3.94	−1.14	$-4.76\ (x = 153)^b$	1.12	$1.15\ (x = 227)^e$
317	CCl_4	−1.3	5.46		3.70	−1.15		1.21	
					$CH_3(OC_2H_4)_xOCH_3$				
1	cyclohexane	−4.6	1.95		−4.20	−5.6	-7.7^c	2.24	2.59^g
2	cyclohexane	−5.2	2.14		−2.30	−4.7	-4.6^c	1.75	1.82^g
3	cyclohexane	−3.6	2.33		−1.43	−2.9	-3.7^c	1.66	1.58^g
4	cyclohexane	−4.1	2.47		−1.02	−3.2	-3.6^c	1.63	1.45^g

[a] ${}_{m}K \times 10^{-12}$ cm^7 SC^{-2} mol^{-1}; $\langle\mu^2\rangle \times 10^{-36}$ SC^2 cm^2; $\lambda = 6330$ Å; $T = 25$ °C. [b] From Aroney et al.;[1] measured in benzene. [c] From Kelly et al.;[3] measured in carbon tetrachloride. [d] From Uchida et al.[23] [e] From Marchal and Benoit.[24] [f] From Bak et al.[25] [g] From Kotera et al.[26]

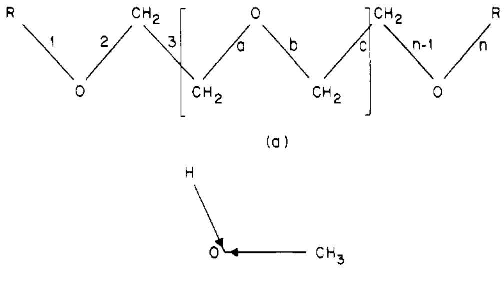

Figure 1. (a) Designation of bonds in POEG (R = H) and POEDE (R = CH_3). (b) Direction of bond moments in methanol.

Le Fèvre et al.[14] (0.46 Å^3). We may now deduce the anisotropy of the O–CH_3 group $\Gamma_{CO} = \gamma_{CO} - \gamma_{CH}$ from the Kerr effect of methanol, in the same manner that we recently deduced[4] the anisotropy of the C–Br bond from ethyl bromide. ${}_{m}K$ is given by

$$ {}_{m}K = \frac{2\pi N_A}{405}\left\{10\gamma^K + \frac{20\mu\beta^K}{3kT} + \frac{3\ \mathrm{tr}\ (\hat{\alpha}\hat{\alpha})}{kT} + \frac{3\mu^T\hat{\alpha}\mu}{k^2T^2}\right\} \tag{4} $$

γ^K and β^K are the second and first hyperpolarizabilities and the other symbols have their usual meanings. For methanol,[11,14,15] $10^{12}({}_{m}K) = -1.78$ cm^7 SC^{-2} mol^{-1}, $10^{30}\beta^K = -0.30$ cm^5 SC^{-1}, $10^{36}\gamma^K = 2.31$ cm^7 SC^{-2}, $10^{18}\mu = 1.77$ SC cm, $10^{18}\mu_{CO} = 1.15$ SC cm, $10^{18}\mu_{OH} = 1.78$ SC cm, and $\gamma_{OH} = 0.43$ Å^3. It follows that $\Gamma_{CO} = 0.66$ Å^3. This calculation has assumed that the polarizability of methanol is the sum of the segment polarizabilities consisting of the O–H and C–O bonds and is denoted approximation a. This value is slightly higher than that deduced by Patterson and Flory[16] (0.58 Å^3) and greater than the value of Le Fèvre et al. (0.43 Å^3). In our calculations we have assumed that $\hat{\alpha}_{CO} = 0.66\ \mathbf{F}$ Å^3 for all the C–O bonds in the polymer, where $\mathbf{F} = \mathrm{diag}\ (^2/_3, {}^1/_3, {}^1/_3)$.

Another way to derive the polarizability tensor of the H_3C–O group is to consider the Kerr effect of DME. For this molecule,[12,15] $10^{12}({}_{m}K) = -3.9$ cm^7 SC^{-2} mol^{-1}, $10^{18}\mu = 1.32$ SC cm, $10^{30}\beta^K = -0.574$ cm^5 SC^{-1}, and $10^{36}\gamma^K = 3.17$ cm^7 SC^{-2}. If BAA is assumed, $\hat{\alpha}_{DME}$ is given by

$$ \hat{\alpha} = {}^2/_3\Gamma_{CO}\begin{bmatrix} 3\cos^2\theta - 1 & 0 & 0 \\ 0 & 3\sin^2\theta - 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{5} $$

Here the xx term of $\hat{\alpha}_{DME}$ is along the dipole moment direction, the yy term is in the plane of the molecule, and the zz term is normal to the plane of the molecule. $\theta = 110°$ is the COC bond angle. When we substitute the relevant parameters and eq 5 into eq 4, we obtain a quadratic equation in Γ_{CO} for which there is no real solution. This means that BAA does not work for DME, and we may not partition the total polarizability of this molecule into two O–CH_3 segments. This was also found by Aroney et al.[12] Instead, in order to obtain the three principal components of $\hat{\alpha}_{DME}$, we require an additional equation which is obtained from light scattering,[18,19] namely, $\gamma^2 = {}^3/_2\ \mathrm{tr}\ (\hat{\alpha}\hat{\alpha})$. For DME $\gamma^2 = 1.432$ Å^6, and we deduce from eq 4 that $\hat{\alpha}_{DME} = \mathrm{diag}\ (-0.128, 0.746, -0.618)$ Å^3. This tensor is then transformed into the coordinate system of bond b of the repeat unit (see Figure 1a). This is denoted approximation b in this paper. The C–C bond anisotropy, Γ_{CC}, has been assumed to equal[20] 0.54 Å^3.

Matrix multiplication methods[7] were used to calculate ${}_{m}K$, using approximations a and b for the polarizability tensor and assuming that only the induced and permanent dipole terms contribute to the Kerr effect in eq 4. The static and dynamic polarizabilities were assumed to be equal in these calculations. From the ${}_{m}K$ of DME we estimate that the error introduced by neglecting the hyperpolarizability contribution is of the order of 20%.

Results and Discussion

In Table I we have compared our experimental data for ${}_{m}K/x$ of POEG with those of Aroney et al.[1] They differ in two important respects. First, for the shorter chains our values are significantly lower than their values. Second, for longer chains our ${}_{m}K/x$ reach an asymptotic value of -1.15×10^{-12} cm^7 SC^{-2} mol^{-1} while those of Aroney et al. do not appear to saturate. We propose a simple expla-

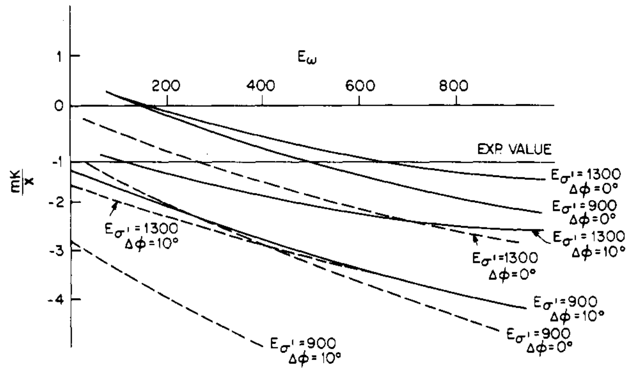

Figure 2. ${}_mK/x$ (x = 320) ($\times 10^{-12}$ cm^7 SC^{-2} mol^{-1}) vs. E_ω (cal mol^{-1}), with E_σ = −400 cal mol^{-1}. Full and dotted lines use approximation a and b, respectively, for the polarizability tensor of the repeat unit of the polymer.

nation for these differences. The repeat unit (DME) of POEG has a very low anisotropic tensor, diag (−0.128, 0.746, −0.618) Å^3, while that of the benzene molecule[21] is very large, diag (−2.49, 1.24, 1.24) Å^3. If there were specific solvation of the benzene molecules around the backbone of the polymer, then the effective polarizability of the repeat unit could easily change from the value it would have when it is surrounded by nearly isotropic molecules. That such changes in ${}_mK$ may occur has long been recognized from Kerr effect studies[21,22] on small rigid molecules.

The molecular weight independence of ${}_mK/x$ for POEG in carbon tetrachloride, which is not a Θ solvent at 25 °C, shows that ${}_mK$ together with $\langle\mu^2\rangle$ need not be studied in a Θ solvent in order to obtain a quantity unperturbed by excluded volume interactions. The only prerequisite is that the solvent consist of nearly isotropically polarizable molecules. To test this idea, we carried out a Kerr effect experiment on the high molecular weight samples of POEG in dioxane, which is also not a Θ solvent at 25 °C, and found that ${}_mK/x$ was again independent of x.

Our ${}_mK/x$ values for POEDE are in agreement with those reported by Kelly et al.[3], except for when x = 77, for which we obtain 0.66 $\times$ 10^{-12} cm^7 SC^{-2} mol^{-1} while they obtain −2 $\times$ 10^{-12} cm^7 SC^{-2} mol^{-1} for x = 91. The discrepancy between our two results arises from the extrapolation of the experimental data to infinite dilution. There is a fairly strong nonlinear dependence of the Kerr constant on the concentration of POEG, and it is necesary to extrapolate carefully to infinite dilution. Our more sensitive apparatus allowed us to work in the concentration range 1–5% w/w whereas Kelly et al. performed their experiments in the range 5–10% (w/w). Our $\langle\mu^2\rangle$ values for POEG are lower than those obtained by Uchida et al.[23] for the lower oligomers but are in good agreement with those of Marchal and Benoit.[24] Our values for $\langle\mu^2\rangle$ are in excellent agreement with literature values[25] for large x. Our dipole moments for POEDE are also in excellent agreement with those reported by Kotera et al.[26]

We now discuss the results of our calculations of ${}_mK/x$ for x = 320, when both experimentally and theoretically, ${}_mK/x$ has reached an asymptotic value. We carried out extensive calculations varying all the parameters and found that ${}_mK/x$ was least sensitive to changes in E_σ. We have therefore kept that value fixed at −400 cal mol^{-1} as found by Abe and Mark.[10] In Figure 2 we show ${}_mK/x$ (x = 320) as a function of E_ω for $E_{\sigma'}$ = 900 and 1300 cal mol^{-1}. These calculations were carried out for both approximations a and b for the polarizability tensor of the H$_2$COCH$_2$ group. We see that ${}_mK/x$ is fairly sensitive to $E_{\sigma'}$, E_ω, and $\Delta\phi$, and the two approximations of the polarizability tensor and that a number of different combinations of these parameters may reproduce the experimental result of −1.15 $\times$ 10^{-12} cm^7 SC^{-2} mol^{-1}.

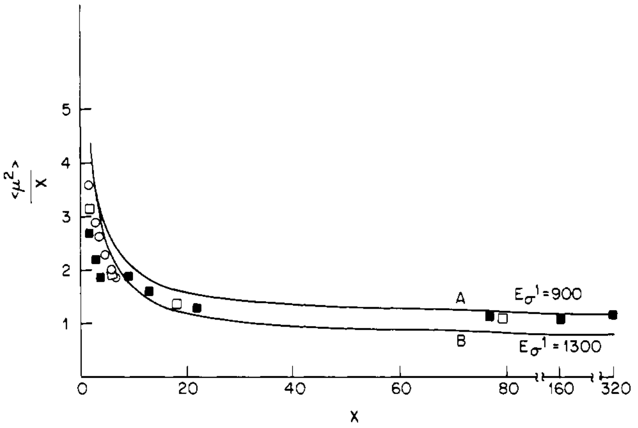

Figure 3. $\langle\mu^2\rangle/x$ ($\times 10^{-36}$ SC^2 cm^2) vs. x: curve A, $E_{\sigma'}$ = 900, E_ω = 0.0, E_σ = −400 cal mol^{-1}, $\Delta\phi$ = 0; curve B, $E_{\sigma'}$ = 1300, E_ω = 250, E_σ = −400 cal mol^{-1}, $\Delta\phi$ = 0°. Filled squares, this work; unfilled squares, ref 24; circles, ref 23.

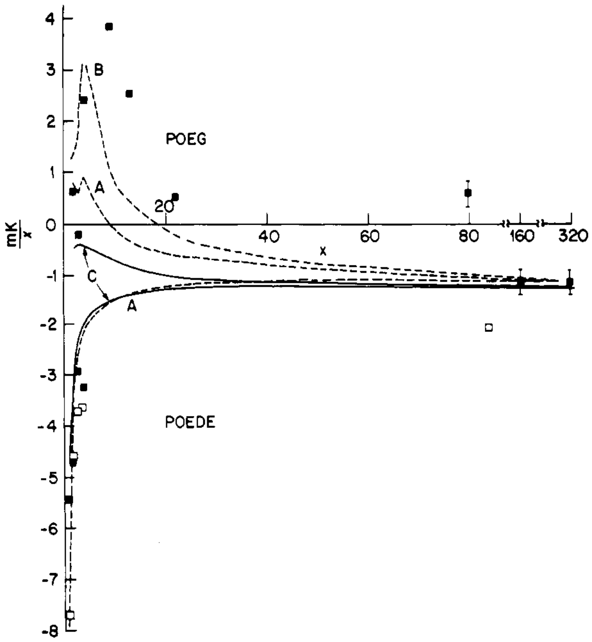

Figure 4. ${}_mK/x$ ($\times 10^{-12}$ cm^7 SC^{-2} mol^{-1}) vs. x for POEG and POEDE (full and dotted lines use approximation a and b, respectively, for the polarizability tensor of the repeat unit of the polymer): curve A, $E_{\sigma'}$ = 900, E_ω = 0.0, E_σ = −400 cal mol,$^{-1}$ $\Delta\phi$ = 0°; curve B, $E_{\sigma'}$ = 1300, E_ω = 250, E_σ = −400 cal mol,$^{-1}$ $\Delta\phi$ = 0°; curve C, $E_{\sigma'}$ = 900, E_ω = 0.0, E_σ = −400 cal mol,$^{-1}$ $\Delta\phi$ = 10°. Filled squares, this work; unfilled squares, ref 3.

In order to further discriminate between the different parameters, we carried out extensive calculations for $\langle\mu^2\rangle$. These indicated that $\langle\mu^2\rangle/x$ (x = 320) was most sensitive to $E_{\sigma'}$ and not very sensitive to E_ω and $\Delta\phi$. In Figure 3 we present our results for $E_{\sigma'}$ = 900 and 1300 cal mol^{-1}. Clearly, the dipole moment result favors the lower value of $E_{\sigma'}$, 900 cal mol^{-1}.

In Figure 4 we present the results of ${}_mK/x$ for all values of x for POEG and POEDE assuming that $E_{\sigma'}$ = 900 cal mol^{-1}. The other parameters used in these calculations were chosen from the results of Figure 2 in order to make ${}_mK/x$ (x = 320) consistent with the experimental value. We find that approximation a for the polarizability tensor gives good agreement for the short chains of POEDE but not for POEG. Approximation b gives very good agreement for POEDE and reproduces qualitatively the trend of the experimental values of the shorter chains of POEG.

Macromolecules 1982, 15, 148–154

If we use $E_{\sigma'} = 1300$ instead of 900 cal mol^{-1} (curve B, Figure 4), we obtain better agreement with the experimental data for POEG. However, then the calculated ${}_{\mathrm{m}}K$ values for POEDE (not shown here) are only in fair agreement with the experimental results.

These remaining small discrepancies should not be construed as a failure of the RIS and BAA schemes. Rather, one should bear in mind that the ${}_{\mathrm{m}}K/x$ values of POEG and POEDE are exceedingly small, being not very different from the ${}_{\mathrm{m}}K$ value of the solvent carbon tetrachloride (1.35×10^{-12} cm^7 SC^{-2} mol^{-1}). Therefore, given the approximations inherent in the RIS and BAA schemes and the smallness of the ${}_{\mathrm{m}}K$ values, we think that we have accounted reasonably well for the experimental results.

Conclusions

Our extensive data on POEG in isotropic solvents show that ${}_{\mathrm{m}}K/x$ reaches an asymptotic value, in contrast with the data of Aroney et al. which was measured in benzene. Such differences are attributed to specific solvation of the polymer with optically anisotropic benzene molecules. Our results, which were obtained in non-Θ solvent, show that ${}_{\mathrm{m}}K/x$ is independent of molecular weight and insensitive to excluded volume interactions. This makes ${}_{\mathrm{m}}K$ a particularly attractive quantity to characterize polymers, obviating the need for using Θ solvents.

We are also able to get good agreement between the calculated and experimental values of ${}_{\mathrm{m}}K/x$ for all x for both POEG and POEDE, using energetic parameters consistent with those derived by Flory, Mark, and their co-workers from other conformationally dependent properties.

References and Notes

(1) Aroney, M. J.; Le Fèvre, R. J. W.; Parkins, G. M. *J. Chem. Soc.* **1960**, 2890.
(2) Ishikawa, T.; Nagai, K. *Polym. J.* **1971**, *2*, 263.
(3) Kelly, K.; Patterson, G. D.; Tonelli, A. E. *Macromolecules* **1977**, *10*, 859.
(4) Khanarian, G.; Tonelli, A. E. *J. Chem. Phys.* **1981**, *75*, 5031.
(5) Le Fèvre, R. J. W.; Le Fèvre, C. G. In *Tech. Chem. (N.Y.)* **1972**, *1*, Chapter VI.
(6) Bottcher, C. J. F.; Bordewijk, P. "Theory of Electric Polarization"; Elsevier: Amsterdam, 1978; Vol. II, Chapter 14.
(7) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
(8) Mark, J. E.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1415.
(9) Mark, J. E.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 3702.
(10) Abe, A.; Mark, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6468.
(11) Le Fèvre, R. J. W.; Williams, A. J. *J. Chem. Soc.* **1960**, 108.
(12) Aroney, M. J.; Le Fèvre, R. J. W.; Saxby, J. *J. Chem. Soc.* **1962**, 2886.
(13) Khanarian, G.; Kent, L. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 495.
(14) Le Fèvre, C. G.; Le Fèvre, R. J. W.; Rao, B. P.; Williams, A. J. *J. Chem. Soc.* **1960**, 123.
(15) Ward, J. F.; Miller, C. K. *Phys. Rev. A* **1979**, *19*, 826.
(16) Patterson, G. D.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1111.
(17) Le Fèvre, R. J. W.; Sundaram, A.; Pierens, R. K. *J. Chem. Soc.* **1963**, 479.
(18) Bogaard, M. P.; Buckingham, A. D.; Pierens, R. K.; White, A. H. *J. Chem. Soc., Faraday Trans. 1* **1978**, 3008.
(19) Canselier, J. P.; Clement, C. *J. Chim. Phys.* **1978**, *75*, 880.
(20) Patterson, G. D.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1098.
(21) Aroney, M. J. *Angew. Chem.* **1977**, *10*, 663.
(22) Le Fèvre, R. J. W.; Radford, D. V.; Ritchie, G. L. D.; Stiles, P. J. *J. Chem. Soc. B* **1968**, 148.
(23) Uchida, T.; Kurita, Y.; Koizumi, N.; Kubo, M. *J. Polym. Sci.* **1956**, *21*, 313.
(24) Marchal, J.; Benoit, H. *J. Chim. Phys.* **1955**, *52*, 818.
(25) Bak, K.; Elefante, G.; Mark, J. E. *J. Phys. Chem.* **1967**, *71*, 4007.
(26) Kotera, A.; Suzuki, K.; Matsumura, K.; Nakano, T.; Oyama, T.; Kambayashi, R. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 797.

Monte Carlo Calculation of Hydrodynamic Properties of Freely Jointed, Freely Rotating, and Real Polymethylene Chains

José García de la Torre*

Departamento de Química Física, Facultad de Ciencias, Universidad de Murcia, Murcia, Spain

Agustín Jiménez

Departamento de Química Física, Facultad de Ciencias, Universidad de Extremadura, Badajoz, Spain

Juan J. Freire

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, Madrid-3, Spain. *Received May 20, 1981*

ABSTRACT: The hydrodynamic properties (translational and rotational coefficients and intrinsic viscosities) of freely jointed and freely rotating chains, as well as those of real polymethylene chains with excluded volume, are evaluated in this paper as functions of the chain length and the frictional radius of the repeating units. The properties are calculated as averages over samples of Monte Carlo generated chain conformations that are regarded as instantaneously rigid particles. The hydrodynamic treatment is a rigorous version of the Kirkwood–Riseman theory, which has been successfully applied earlier to rigid macromolecules. We consider also a typical approximate equation, namely, Kirkwood's formula for translational coefficients. Notwithstanding differences in model and procedure, our results for freely jointed chains are very close to those obtained in a recent paper by Zimm when the elements' frictional radius is given a well-established value. Furthermore, we analyze the effect of the chain constraints embodied in the freely rotating and polymethylene chains on the individual properties and compare the performance of Kirkwood's formula for each chain model. Some implications for long real chains are discussed.

Introduction

Over the past 30 years, the theory of the hydrodynamic properties of macromolecules in solution proposed by Kirkwood and Riseman[1,2] has been extensively used.[3] In its most rigorous form, such theory applies the Oseen–Burgers method to account for the hydrodynamic interactions between the frictional elements composing the macromolecular model. In practice, however, Kirkwood

0024-9297/82/2215-0148$01.25/0