Random-Coil Configurations of the Polyformals $[CH_2O(CH_2)_yO-]$. 1. Dipole Moments of Poly(1,3-dioxolane) $[CH_2O(CH_2)_2O-]$

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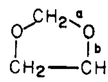
ABSTRACT: Mean-square dipole moments of poly(1,3-dioxolane) chains of repeat unit $[CH_2O(CH_2)_2O-]$ were determined as a function of temperature by means of dielectric constant measurements in the thermodynamically good solvent benzene. The experimental results were found to be in good agreement with theoretical results based on a rotational isomeric state model in which the required conformational energies of the chains were obtained from previous configurational analyses of polyoxymethylene and polyoxyethylene. The model assumes perfect alternation of oxymethylene units and oxyethylene units along the chain, rather than a more irregular distribution which could conceivably occur in the type of ring-opening polymerization used to prepare the polymer. The good agreement found between theory and experiment, therefore, is consistent with this regularly alternating structure. Although poly(1,3-dioxolane) can thus be considered an alternating copolymer of oxymethylene and oxyethylene units, its dipole moments and other configuration-dependent properties cannot in general be obtained by simply averaging the values of the same properties for the oxymethylene and oxyethylene homopolymers. The present analysis also indicates that poly(1,3-dioxolane), and a number of other polyformals, should have a relatively high degree of conformational randomness.

The polyethers are a class of macromolecules having C–O–C bonds in the chain backbone and are thus of a relatively polar nature. One of the most important and interesting types of polyether are the simple polyoxides, which have the repeat unit $[(CH_2)_yO-]$. A number of such polyoxide chains have been intensively investigated with regard to their configuration-dependent properties in the randomly coiled state, both from the experimental and theoretical points of view.[1-10] Another important class of polyethers, very similar in chemical structure to the polyoxides, are the polyformals $[CH_2O(CH_2)_yO-]$. As in the case of the polyoxides, the properties of these polymers vary markedly with the number of methylene groups in the repeat unit. The first member of the series, for example, is polyoxymethylene (POM, $y = 1$), which has been investigated to some extent[1,4] in studies of the polyoxide series, of which it is also a member. Unfortunately, there is relatively little experimental information[1,4,11-13] on chain configurations in this polymer, because of its high melting point (200 °C)[14] and its insolubility in most solvents. The second and fourth members of the polyformal series, however, have relatively low melting points, 55[15] and 24 °C,[16] respectively, and are readily soluble in a number of common organic solvents. These two polyformals are poly(1,3-dioxolane) (PXL) $[CH_2O(CH_2)_2O-]$ and poly(1,3-dioxepane) (PXP) $[CH_2O(CH_2)_4O-]$. Both polymers should be extremely useful for establishing and interpreting structure–property relationships for chain molecules in general.

The present investigation focuses on the dipole moments, and their temperature dependence, for the PXL chains. Of particular interest will be the molecular interpretation of these results in terms of rotational isomeric state theory,[1] and comparisons among results for various polyethers of related structure. The interpretation of the results of the present study should help elucidate the mechanism of the polymerization reaction used to prepare PXL. The polymerization involves the cationic ring opening of the monomer



Bond scissions which occur exclusively at a bonds or exclusively at b bonds would yield the same polymer $[CH_2O(CH_2)_2O-]$. If scissions occur at both types of bonds, however, the irregular sequences $-CH_2OCH_2O-$ and $-CH_2CH_2OCH_2CH_2O-$ would be introduced into the chains. The evidence at hand[15,17] indicates that little or no random bond scission of this type takes place; for example, no $-CH_2CH_2OCH_2CH_2O-$ sequences are found upon decomposition of the polymer.[17] Furthermore, PXL is highly crystalline, which also suggests the absence of significant amounts of such irregularities,[15] since CH_2 groups and O atoms are almost certainly too different in size and charge to participate in isomorphous replacements. In any case, it is obviously important to determine whether or not a model of the chain which assumes perfect structural regularity (alternation of CH_2O- and CH_2CH_2O- groups) will give theoretical results in good agreement with experiment. In addition, if PXL is indeed an alternating copolymer of oxymethylene and oxyethylene units, it would be of interest to establish the relationship between its dipole moments and those of its parent polyoxymethylene and polyoxyethylene homopolymers. Finally, it will be useful to compare the PXL chain with other polyether chains in regard to conformational randomness, as roughly gauged from the nature of the rotational preferences[3] within the repeat unit of the molecule.

Experimental Section

Materials. The monomer, 1,3-dioxolane (Fluka), was dried over calcium chloride and then distilled under vacuum while in contact with sodium metal. Tests with biphenyl demonstrated the absence of sodium impurities in the monomer. It was stored under vacuum in contact with calcium hydride. The solvent for the polymerization was methylene chloride (Merck); it was distilled from calcium hydride, and then stored in contact with it under vacuum. The polymerization catalyst was $(C_2H_5)_3OSbCl_6$, which had been synthetized by the Meerwein method.[18] It was washed

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Table I
Summary of Experimental Data and Results

sample	$10^{-3}M_\eta$	T, °C	$d(\epsilon - \epsilon_1)/dw$	$-d(n^2 - n_1^2)/dw^a$	$\langle\mu^2\rangle_0/nm^2$
A	12	20	1.01	0.094	0.160
		30	1.03	0.082	0.169
		40	1.06	0.073	0.181
		50	1.08	0.062	0.191
		60	1.11	0.052	0.204
B	16	20	1.04	0.094	0.164
		30	1.08	0.082	0.177
		40	1.11	0.073	0.189
		50	1.13	0.062	0.200
		60	1.16	0.052	0.213
C	42	20	1.13	0.094	0.177
		30	1.17	0.082	0.191
		40	1.18	0.073	0.200
		50	1.22	0.062	0.215
		60	1.24	0.052	0.227

^{a} The values were obtained on sample B and were assumed also to apply to samples A and C.

several times with ether and then dried and stored under vacuum. Reagent-grade chlorobenzene was used, as received, in the measurements of polymer solution viscosities (which were used to estimate molecular weights). The solvents used to calibrate the dielectric constant apparatus were benzene (Merck, 99.5% pure), toluene (Merck, 99.5% pure), and cyclohexane (Fisher, 99% pure); precise values of their dielectric constants are available in the literature.[19,20] The benzene was used as solvent for the PXL solutions. At 20 and 60 °C, its dielectric constant ϵ_1 is 2.2836 and 2.2036, respectively, and its density ρ_1 (as determined by pycnometry) is 0.8756 and 0.8503 g cm^{-3}, respectively. Its index of refraction n_1 at 546 mμ is essentially 1.500 over the temperature range of interest.

Preparation of the Polymer Samples. The polymerizations were carried out in evacuated sealed ampules, at either 0 or −15 °C.[21] The reaction was terminated with acetic anhydride and the polymer isolated by precipitation with methanol at low temperature. The polymer was then dissolved in benzene, the solution filtered, and the polymer reprecipitated. It was finally dried under vacuum at room temperature and freeze-dried twice to eliminate any remaining low molecular weight material. The polymer obtained from the first polymerization, carried out at 0 °C, was fractionated by dissolving it in chlorobenzene and then cooling the solution to precipitate the PXL fractions. The two fractions obtained in this way were designated samples A and B. Polymer obtained from a second polymerization, conducted at −15 °C, was studied unfractionated, and was designated sample C.

Viscometry. *Determination of the dipole moment ratios sought in the present investigation does not require the polymer molecular weights (see below).* They were, however, estimated from measurements of the intrinsic viscosity $[\eta]$ of each of the samples in chlorobenzene at 25 °C. The previously established relationship[22] used for this purpose was

$$[\eta] = 2.0 \times 10^{-3} M_w^{0.5} \qquad (1)$$

where M_w is the weight-average molecular weight.

Dielectric Constants and Refractive Indices. The dielectric constant measurements on the PXL solutions were carried out using a capacitance bridge (General Radio type 1620A)[5,8] at a frequency of 10 kHZ (at which the dielectric constant ϵ is to a good approximation the static value). A three-terminal cell was used,[5,8] and the apparatus was calibrated at each temperature of interest using benzene, toluene, and cyclohexane. Values of the index of refraction n of the solutions were obtained at 546 mμ using a Brice-Phoenix differential refractometer.

Results

The viscosity-average molecular weights obtained for the three samples are given in the second column of Table I. The dielectric constant measurements were conducted at 30, 40, 50, and 60 °C. Since it was difficult to obtain reproducible results at 20 °C, additional data were generally taken in the vicinity of 23 °C, and limited extrapolations were used to obtain the desired values at 20 °C. Typical results are shown in Figure 1. Dielectric constant differences and squared index of refraction differences were plotted against the weight fraction w of polymer in the solution, in order to obtain values of the derivatives $d(\epsilon - \epsilon_1)/dw$ and $d(n^2 - n_1^2)/dw$. Typical results are shown in Figure 2, and the complete set of values of the two derivatives are given in columns four and five of Table I. Values of the mean-square dipole moment $\langle\mu^2\rangle$ were then calculated from the equation of Guggenheim and Smith[23]

$$\langle\mu^2\rangle = \frac{27kTM}{4\pi N_A \rho_1(\epsilon_1 + 2)^2}\left[\frac{d(\epsilon - \epsilon_1)}{dw} - \frac{d(n^2 - n_1^2)}{dw}\right] \qquad (2)$$

in which k is the Boltzmann constant, T is the absolute temperature, and N_A is Avogadro's number. Because of the absence of excluded volume effects on the dipole moments of chains as symmetric as PXL,[24,25] the values of $\langle\mu^2\rangle$ thus obtained may be written as the "unperturbed" values $\langle\mu^2\rangle_0$.[1,24-26] These results are customarily expressed as the *dipole moment ratio* $\langle\mu^2\rangle_0/nm^2$, where n is the number of skeletal bonds (and is equal to $5M/M_0$, where M_0 = 74.08 g mol^{-1} is the molecular weight of the repeat

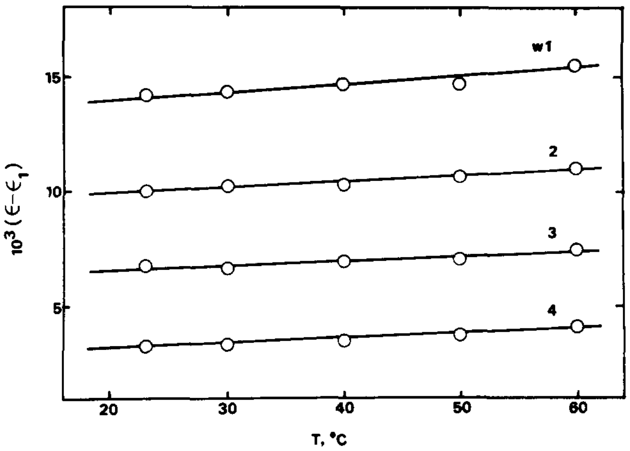

Figure 1. The dielectric constant increment shown as a function of temperature for poly(1,3-dioxolane) sample B in benzene. The values w1–4 of the weight fraction of polymer in the solutions were 13.3, 9.47, 6.41, and 3.11 × 10^{-3} respectively.

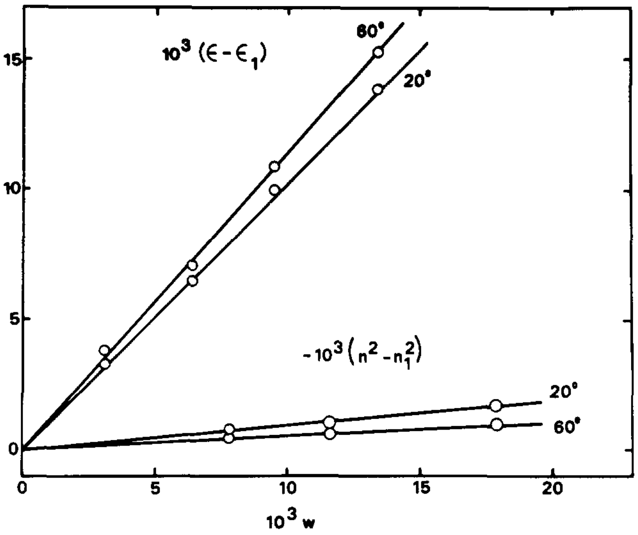

Figure 2. Typical data showing the concentration dependence of the increments in dielectric constant and squared index of refraction for PXL sample B at 20 and 60 °C.

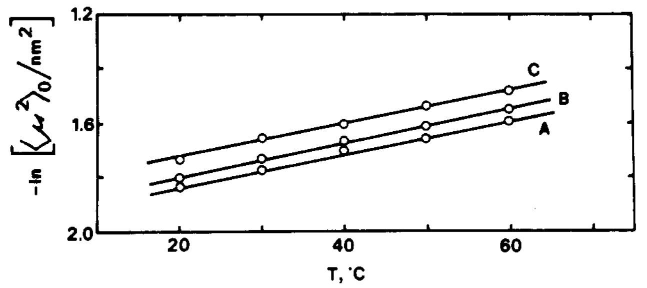

Figure 3. The temperature dependence of the natural logarithm of the dipole moment ratio for the three PXL samples.

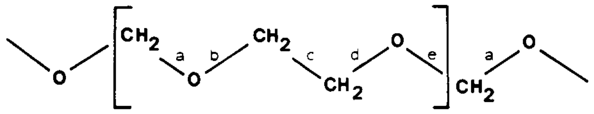

Figure 4. The PXL chain shown in the all-trans conformation, with brackets used to set off the repeat unit.

unit). The average m^2 of the skeletal bond moments was calculated from $m^2 = {}^1/_5(4m_{CO}{}^2 + m_{CC}{}^2)$, using $m_{CO} = 1.07$ D and $m_{CC} = 0.00$ D.[4,27] The values of the dipole moment ratio thus obtained are listed in the final column of Table I. The slight increase in the ratio with increase in molecular weight may simply be due to experimental errors. In any case, the results indicate that the dipole moment ratio of PXL is unusually[28] small, being 0.17 in the vicinity of 25 °C. Values of the temperature coefficient d ln $\langle\mu^2\rangle_0/\mathrm{d}T$ were obtained by plotting the natural logarithm of the dipole moment ratio against temperature. As shown in Figure 3, the three samples exhibited very nearly the same slope, which corresponds to d ln $\langle\mu^2\rangle_0/\mathrm{d}T = 6.0 \times 10^{-3}$ deg^{-1}. This is an unusually large value for the temperature coefficient of any configuration-dependent property.[1]

Comparison of Theory and Experiment

The rotational isomeric state model adopted for the PXL chain assumed perfect alternation between CH_2O– and CH_2CH_2O– units along the chain (see above), with rotational states located at 0° (trans, t), 120° (gauche positive, g^+), and −120° (gauche negative, g^-). The required energies of the intramolecular interactions occurring in PXL may be obtained from previous analyses of various polyoxides, primarily polyoxymethylene and polyoxyethylene,[4] as was pointed out by Andrews and Semlyen.[29] A brief summary of this information follows. Gauche states about skeletal bonds of type a and e in Figure 4 bring CH_2 groups and O atoms separated by three bonds into proximity; these states have an energy approximately 1.4 kcal mol^{-1} lower than the alternative trans states. Bonds of type b and d have gauche states approximately 0.9 kcal mol^{-1} higher in energy than the corresponding trans states, while bonds of type c have gauche states approximately 0.4 kcal mol^{-1} lower than the trans. The conformations $g^{\pm}g^{\mp}$ give rise to "pentane-type" interferences between groups and atoms separated by four bonds. In the case of bond pairs of the type ea, the interacting species are two CH_2 groups and their steric overlaps cause the complete exclusion of these conformations. For the other bond pairs in the repeat unit, the participating species are a CH_2 group and an O atom. Their interactions give rise to a repulsive energy of approximately 0.4 kcal mol^{-1}; these $g^{\pm}g^{\mp}$ conformations are thus somewhat suppressed, but by no means excluded.

The standard matrix multiplication methods[1] of rotational isomeric state theory were used to calculate values of the dipole moment ratio, at 25 °C, for PXL chains containing $n = 482$ skeletal bonds. Since the very strong preference for gauche states about bonds of type a and e is not at all understood in molecular terms,[1,4] the calculations were carried out as a function of this rotational state energy difference $[E(g^{\pm}) - E(t)]_{CH_2\cdots O}$. The results are shown in Figure 5. The dipole moment ratio is seen to decrease markedly with increase in the preference for such gauche states. This is due to the fact that $g^{\pm}g^{\pm}$ states in the bond pairs involved place pairs of bond dipoles in very nearly antiparallel orientations.[28] (The dependence of the dipole moment ratio on the gauche-trans energy difference for bonds of the type b and d is about one-seventh that shown in Figure 5. Its dependence on the other rotational state energy differences was even smaller and essentially of almost negligible importance.) Coincidence between theoretical and experimental values of the dipole moment ratio is seen to be achieved at a value of $[E(g^{\pm}) - E(t)]_{CH_2\cdots O}$ of approximately −1.2 kcal mol^{-1}, in good agreement with the value −1.4 kcal mol^{-1} obtained in the analyses of polyoxide chains.[1,4] The theoretical value of d ln $\langle\mu^2\rangle_0/\mathrm{d}T$ was calculated to be 6.1×10^{-3} deg^{-1}, in excellent agreement with the experimental value, 6.0×10^{-3} deg^{-1}.

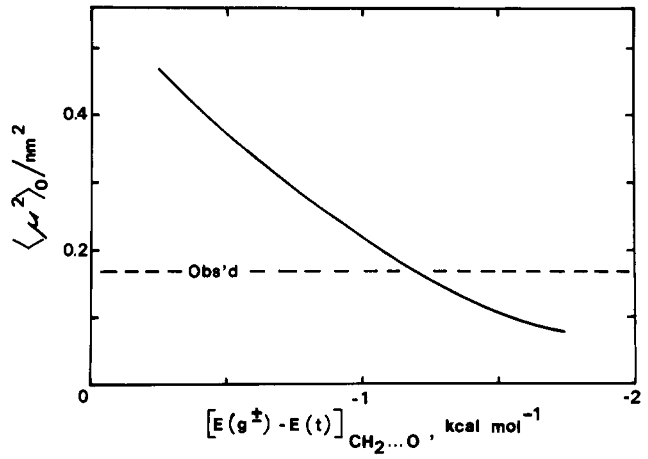

Figure 5. Results of rotational isomeric state calculations showing the dependence of the dipole moment ratio of PXL on the energy difference between gauche and trans states in which the interacting species are CH_2 groups and O atoms.

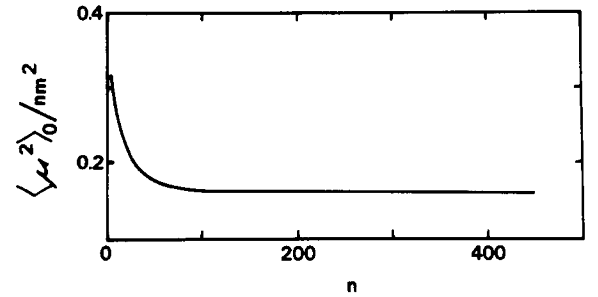

Figure 6. The dipole moment ratio of PXL at 25 °C shown as a function of the number of skeletal bonds in the chain.

In simplest molecular terms, the PXL chain has a very small dipole moment ratio largely because of its preference for gauche states of low dipole moment. Correspondingly, its dipole moment increases markedly with increase in temperature, primarily because of an increase in the number of alternative rotational states, of higher energy and larger dipole moment.

Figure 6 shows the calculated dependence of the dipole moment ratio, at 25 °C, on the number of skeletal bonds. As is generally found to be the case,[1,5,8,30] the dipole moment ratio reaches an asymptotic limit at relatively low chain length, well below the minimum value ($n \simeq 800$)

Table II
Dipole Moment Results on Polyoxymethylene, Polyoxyethylene, and Their Alternating Copolymer Poly(1,3-dioxolane)

	POM	POE	PXL
repeat unit	CH_2O-	$(CH_2)_2O$-	$CH_2O(CH_2)_2O$-
$\langle\mu^2\rangle_0/nm^2$	0.2[a]	0.52[b]	0.17
$10^3\ \mathrm{d}\ln\langle\mu^2\rangle_0/\mathrm{d}T$	6.0[c]	1.5[b]	6.0

[a] References 13 and 28. [b] References 1 and 5. [c] Measured on the oxymethylene dimer (ref 4 and 31); the polymer apparently also has a positive value of the temperature coefficient of $\langle\mu^2\rangle_0$ (ref 13), but its magnitude is not reliably known.

employed in the present investigation.

Discussion

As demonstrated in the preceding section, rotational isomeric state calculations give a very good account of the PXL dipole moments and their temperature dependence. Since the calculations were based on perfectly alternating sequences of CH_2O- and CH_2CH_2O- units along the chain, the good agreement between theory and experiment is consistent with this regular structure for PXL.

The theoretical analysis also indicates that the PXL conformation of minimum intramolecular energy has the rotational states [$g^{\pm}$,t,$g^{\pm}$,t,$g^{\pm}$] for bonds a–e in Figure 4. A very similar conformational sequence is adopted by the PXL chain in the most stable crystalline modification of the polymer.[15] Specifically, the crystalline state conformation has the rotational angles [−106,−7,117,86,−101°], in which the rotational states for bonds a–c and e are only moderately distorted from their symmetric locations at 0 or ±120°. The large discrepancy in the case of the bonds of type d is surprising, and may be due to intermolecular interactions within the crystalline lattice.

Since PXL can be considered a perfectly alternating copolymer of CH_2O- and CH_2CH_2O- units, it is informative to compare its configuration-dependent properties to those of its "parent" homopolymers, polyoxymethylene and polyoxyethylene. The comparisons for the dipole moment results[1,4,5,13,28,31] are given in Table II. For this particular property, PXL is seen to be much more similar to polyoxymethylene than it is to polyoxyethylene. This is presumably due to the very strong preference for gauche states in the oxymethylene-type sequences. In any case, the comparison once again demonstrates that it is not possible in general to predict the statistical properties of a copolymeric chain by simply averaging the values of the same property for the parent homopolymers.

Although the strong preference for gauche states is of paramount importance with regard to the dipole moments of PXL, other features may be of comparable importance in the case of other configuration-dependent properties. For example, the PXL chain is conformationally rather random in that two skeletal bonds of the repeat unit prefer trans states while the other three prefer gauche states. Although the magnitudes of the rotational state energy differences and the ordering of the conformational preferences within the repeat unit are obviously of importance, this type of analysis is sometimes useful in a qualitative sense.[3] In the case of PXL, for example, the fraction f_t of skeletal bonds in the repeat unit showing a preference for trans states is $^2/_5$. The closeness of this value to one-half suggests that PXL, like poly(trimethylene oxide),[3] should be a compact chain molecule, with relatively small unperturbed dimensions.[29] There are some preliminary estimates[32] of the dimensions of PXL which are in support of this conclusion. A number of the other polyformals [$CH_2O(CH_2)_yO$-], specifically those having $y = 4$–7, should also be relatively compact, judging from the fact that they also have values of this conformational preference parameter of $f_t = 0.5 \pm 0.1$.

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References and Notes

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969.
(2) G. D. Patterson and P. J. Flory, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1111 (1972).
(3) Y. Takahashi and J. E. Mark, *J. Am. Chem. Soc.*, **98**, 3756 (1976).
(4) A. Abe and J. E. Mark, *J. Am. Chem. Soc.*, **98**, 6468 (1976).
(5) E. Riande, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 2231 (1976).
(6) D. S. Chiu, Y. Takahashi, and J. E. Mark, *Polymer*, **17**, 670 (1976).
(7) J. E. Mark and D. S. Chiu, *J. Chem. Phys.*, **66**, 1901 (1977).
(8) E. Riande, *Makromol. Chem.*, **178**, 2001 (1977).
(9) K. M. Kelly, G. D. Patterson, and A. E. Tonelli, *Macromolecules*, **10**, 859 (1977).
(10) J. E. Mark, *J. Chem. Phys.*, **67**, 3300 (1977).
(11) V. Kokle and F. W. Billmeyer, Jr., *J. Polym. Sci., Part B*, **3**, 47 (1965).
(12) W. H. Stockmayer and L-L. Chan, *J. Polym. Sci., Part A-2*, **4**, 437 (1966).
(13) C. H. Porter, J. H. L. Lawler, and R. H. Boyd, *Macromolecules*, **3**, 308 (1970).
(14) K. F. Wissbrun, *J. Polym. Sci., Part A-2*, **4**, 827 (1966).
(15) S. Sasaki, Y. Takahashi, and H. Tadokoro, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 2363 (1972).
(16) S. Sasaki, Y. Takahashi, and H. Tadokoro, *Polym. J.*, **4**, 172 (1973).
(17) M. Okada, Y. Yamashita, and Y. Ishii, *Makromol. Chem.*, **80**, 196 (1964), and pertinent references cited therein.
(18) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939).
(19) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Vol. 1 and 2, Elsevier, Amsterdam, 1965.
(20) H. H. Landolt, "Landolt-Börnstein: Zahlenwerte and Funktionen aus Physics, Chemistry, Astronomy, Geophysics und Technology", Vol. II, Part 6, Springer, Berlin, 1959.
(21) Ye. L. Berman, Ye. B. Lyudvig, V. A. Ponomarenko, and S. S. Medvedev, *Polym. Sci. USSR (Engl. Transl.)*, **11**, 225 (1969).
(22) N. A. Pravikova, Ye. B. Berman, Ye. B. Lyudvig, and A. G. Davtyan, *Polym. Sci. USSR (Engl. Transl.)*, **12**, 658 (1970).
(23) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949); **47**, 573 (1951); J. W. Smith, *ibid.*, **46**, 394 (1950). As is commonly done, the equation assumes that ϵ_∞ can be approximated by n^2. In the case of PXL, the concentration dependence of ϵ is very much larger than that of n^2 and the error thus introduced should be relatively small.
(24) K. Nagai and T. Ishikawa, *Polym. J.*, **2**, 416 (1971); M. Doi, *ibid.*, **3**, 252 (1972).
(25) S. C. Liao and J. E. Mark, *J. Chem. Phys.*, **59**, 3825 (1973).
(26) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(27) A. L. McClellan, "Tables of Experimental Dipole Moments", Vol. I, W. H. Freeman, San Francisco, Calif., 1963; Vol. II, Rahara Enterprises, El Cerrito, Calif., 1974.
(28) J. E. Mark, *Acc. Chem. Res.*, **7**, 218 (1974).
(29) J. M. Andrews and J. A. Semlyen, *Polymer*, **13**, 142 (1972).
(30) J. E. Mark and J. H. Ko, *Macromolecules*, **8**, 874 (1975).
(31) T. Uchida, Y. Kurita, and M. Kubo, *J. Polym. Sci.*, **19**, 365 (1956).
(32) S. Gorin and L. Monnerie, *J. Chim. Phys. Phys.-Chim. Biol.*, **65**, 2084 (1968).