method should also be applicable to other polyelectrolyte–Cu(II) systems. The results no doubt help us to interpret the optical absorption data of the same systems less ambiguously.

Summary

The local structure of poly(Acr)– and poly(Glu)–Cu(II) macroions could be estimated in frozen solutions by the ESR method. The plausible structures of Cu(II)-residue complexes in poly(Acr)– and poly(Glu)–Cu(II) are summarized as follows. For poly(Acr)–Cu(II): (1) The Cu(II)–Acr complexes of species **1a**, **1c**, **1d**, **2a**, **2b**, and **2c** all involving either two, three, or four side-chain carboxylates are formed in the α' range of 0.4–1.0. (2) The complex species of **1b**, **1e**, and **2d** may be formed near $\alpha' = 1.0$ (in the pH range above 7). For poly(Glu)–Cu(II): (1) The Cu(II)–Glu complexes of species **1a**, **1c**, **1d**, **2b**, and **Nb** prevail in the coil region (α' 0.8–1.0 or pH 6–7), and in addition, the species **1b**, **1e**, **2d**, and **Nc** may also be present. (2) In the helix–coil transition region, the complexes of species **1a**, **1c**, **1d**, **2b**, **2c**, and **Nb** are predominant. The structure of species **Nb** seems to be compatible with the α-helical backbone at least in the R range 16–64. (3) In the helix–aggregate region (α' 0.2–0.3), the complexes of species **1a**, **1c**, **2a**, **2b**, and **Nb** are preferentially formed. The complexes of **1a**, **1c**, and **2a** may be formed between two or more helical strands.

References and Notes

(1) This is Macromolecules–Metal Ion Complexes. 7. For the previous paper of this series, see ref 24.
(2) Y. Moriguchi, *Bull. Chem. Soc. Jpn.*, **39**, 2656 (1966).
(3) H. Sigel and G. Blauer, *Helv. Chim. Acta.* **51**, 1246 (1968).
(4) A. Levitzki, I. Pecht, and A. Berger, *J. Am. Chem. Soc.*, **94**, 6844 (1972).
(5) M. Hatano and T. Nozawa, *Prog. Polym. Sci. Jpn.*, **4**, 223 (1972).
(6) A. L. Jacobson, *Biopolymers*, **1**, 269 (1963).
(7) N. Kono and A. Ikegami, *Biopolymers*, **4**, 823 (1966).
(8) O. Iwaki, K. Hikichi, M. Kaneko, S. Shimizu, and T. Maruyama, *Polym. J.*, **4**, 623 (1973).
(9) M. Hatano, T. Nozawa, S. Ikeda, and Y. Yamamoto, *Makromol. Chem.*, **141**, 1 (1971).
(10) T. Nozawa and M. Hatano, *Makromol. Chem.*, **141**, 21 (1971).
(11) A. Garnier and L. Tosi, *Biopolymers*, **14**, 2247 (1975).
(12) N. Hojo, K. Fukatsu, and T. Hayakawa, *Nippon Kagaku Zasshi*, **90**, 823 (1969).
(13) M. Kawai, T. Hayakawa, and N. Hojo, *Nippon Kagaku Zasshi*, **92**, 617 (1971).
(14) M. Palumbo, A. Cosani, M. Terbojevich, and E. Peggion, *J. Am. Chem. Soc.*, **99**, 939 (1977).
(15) M. Palumbo, A. Cosani, M. Terbojevich, and E. Peggion, *Macromolecules*, **10**, 813 (1977).
(16) K. Yamaoka and T. Masujima, *Bull. Chem. Soc. Jpn.*, **52**, 1819 (1979).
(17) A. L. Jacobson, *Biopolymers*, **2**, 207 (1964).
(18) H. Takesada, H. Yamazaki, and A. Wada, *Biopolymers*, **4**, 713 (1966).
(19) Y. Hibino and S. Sugai, *Rep. Prog. Polym. Phys. Jpn.*, **11**, 513 (1968).
(20) S. Inoue, K. Yamaoka, and M. Miura, *Bull. Chem. Soc. Jpn.*, **44**, 1443 (1971); **45**, 1314 (1972); *J. Sci. Hiroshima Univ. Ser. A*, **39**, 27 (1975).
(21) K. Yamaoka and T. Masujima, *Polym. J.*, in press.
(22) S. Yamashoji, H. Yoshida, and G. Kajimoto, *Yukagaku*, **25**, 128 (1976).
(23) J. A. Marinsky, *Coord. Chem. Rev.*, **19**, 125 (1976).
(24) K. Yamaoka and T. Masujima, *Bull. Chem. Soc. Jpn.*, **52**, 1286 (1979).
(25) T. Vänngård in "Biological Applications of Electron Spin Resonance", H. M. Swartz, J. R. Bolton, and D. C. Borg, Eds., Wiley, New York, 1972, pp 411–447.
(26) T. H. Crawford and J. O. Dalton, *Arch. Biochem. Biophys.*, **131**, 123 (1969).
(27) K.-E. Falk, H. C. Freeman, T. Jansson, B. G. Malmström, and T. Vänngård, *J. Am. Chem. Soc.*, **89**, 6071 (1967).
(28) G. F. Bryce, *J. Phys. Chem.*, **70**, 3549 (1966).
(29) K.-E. Falk, E. Ivanova, B. Roos, and T. Vänngård, *Inorg. Chem.*, **9**, 556 (1970).
(30) L. D. Rollmann and S. I. Chan, *J. Chem. Phys.*, **50**, 3416 (1969).
(31) J. Chen, M. Abkowitz, and J. H. Sharp, *J. Chem. Phys.*, **50**, 2237 (1969).
(32) A. Rockenbauer and P. Simon, *J. Magn. Reson.*, **18**, 320 (1975).
(33) J. S. Taylor and J. E. Coleman, *J. Biol. Chem.*, **248**, 749 (1973).
(34) D. I. Stock and C. W. Davies, *J. Chem. Soc.*, 1371 (1949).
(35) J. M. Peacock and J. C. James, *J. Chem. Soc.*, 2233 (1951).
(36) H. L. Riley, *J. Chem. Soc.*, 1642 (1930).
(37) F. A. Walker, H. Sigel, and D. B. McCormick, *Inorg. Chem.*, **11**, 2756 (1972).
(38) J. Peisach and W. E. Blumberg, *Arch. Biochem. Biophys.*, **165**, 691 (1974).
(39) A. M. Kotliar and H. Morawetz, *J. Am. Chem. Soc.*, **77**, 3692 (1955).
(40) H. P. Gregor, L. B. Luttinger, and E. M. Loeble, *J. Phys. Chem.*, **59**, 34 (1955).
(41) F. T. Wall and S. J. Gill, *J. Phys. Chem.*, **58**, 1128 (1954).
(42) J. C. Leyte, L. H. Zuiderwerg, and M. van Reisen, *J. Phys. Chem.*, **72**, 1127 (1968).
(43) T. D. Smith and A. E. Martell, *J. Am. Chem. Soc.*, **94**, 4123 (1972).
(44) D. S. Olander and A. Holtzer, *J. Am. Chem. Soc.*, **90**, 4549 (1968).
(45) R. Aasa and P. Aisen, *J. Biol. Chem.*, **243**, 2399 (1968).

Random-Coil Configurations of Polymeric Chains with Sulfur and Oxygen Atoms in Their Structure: Dipole Moments of Poly(1,3-dioxa-6-thiocane)

E. Riande* and J. Guzmán

Instituto de Plásticos y Caucho, Madrid-6, Spain. *Received May 25, 1979*

ABSTRACT: Dielectric measurements were carried out on solutions of poly(1,3-dioxa-6-thiocane) in benzene over the range of 20–60 °C. The dipole moment ratio of this chain has a value of 0.42 in the vicinity of 25 °C, which increases moderately with increasing temperature. Conformational energies arising from first-order interactions between sulfur and oxygen atoms were obtained by analysis of the dipole moments in terms of the rotational isomeric state theory of chain configurations. The present study indicates that intramolecular interactions involving S and O atoms have higher energy in gauche than in trans states, in agreement with the results found in previous studies on the configurational properties of poly(thiodiethylene) glycol.

The rapidly growing interest in elucidating structure–property relationships for polymeric systems has encouraged the study of the molecular configurations which is central to an understanding of the physical properties of any type of polymeric chains. The multitude of possible configurations, generated by different conformational sequences, gives a polymeric material the unique properties that set it off so distinctively from any low molecular

0024-9297/79/2212-1117$01.00/0

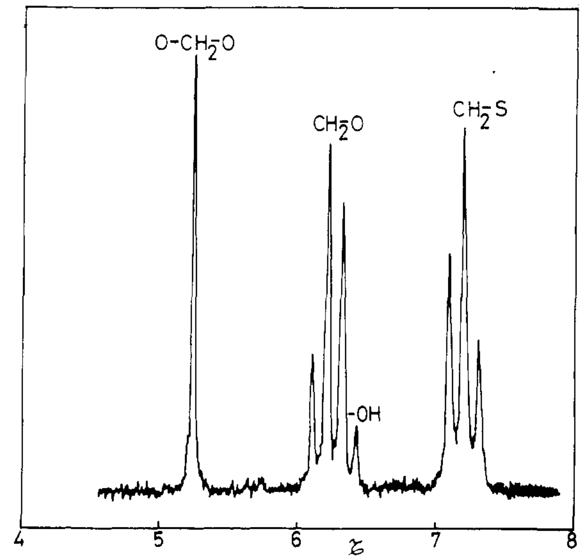

Figure 1. NMR spectrum of poly(1,3-dioxo-6-thiocane).

weight material.[1,2] The configuration-dependent properties most widely employed to characterize random-coil configurations of macromolecular chains include mean-square end-to-end distances $\langle r^2 \rangle$ and dipole moments $\langle \mu^2 \rangle$, as unperturbed by long-range interactions.[3,4] Both properties have been intensively used in conformational studies of linear polyoxides,[1,5-7] studies that have been extended to the polyformals,[8,9] another important class of polyethers very similar in chemical structure to the polyoxides.

In an earlier work,[10] the dipole moment ratio of poly(thiodiethylene glycol), an alternating copolymer of oxyethylene and thioethylene units, has been analyzed using the rotational isomeric state model. The results obtained indicate that the energy that comes from first-order interactions between sulfur and oxygen atoms is lower in trans than in gauche states. It would then be interesting to confirm this result, using other systems in which such interactions also occur. This circumstance has led to the present investigation which focuses on the statistical properties of poly(1,3-dioxa-6-thiocane) [$(CH_2)_2S(CH_2)_2O$-CH_2O-] (PTXL), a chain molecule that may be considered a regularly alternating terpolymer made up from oxymethylene, oxyethylene, and thioethylene units. Thus, the dipole moment ratio of the polymer has been measured, and the results have been compared with those calculated using the rotational isomeric state approximation.

Experimental Section

Preparation of the Samples. The polymer was obtained in condensation polymerization of thiodiethylene glycol with paraformaldehyde. The chemicals were reagent grade, and the polymerizations were carried out in nitrogen atmosphere in refluxing toluene and in the presence of *p*-toluenesulfonic acid (2%). Water was removed in a Dean-Stark distillation trap. The polymer was precipitated with *n*-hexane and washed several times with distilled water to eliminate the catalyst. Next, it was further purified by dissolution into chloroform, precipitation into *n*-hexane, and drying under vacuum. The polymer was liquid at room temperature.

Characterization of the Samples. Liquid-liquid fractional precipitations were carried out at room temperature, using chloroform as solvent and *n*-hexane as nonsolvent. Four fractions were obtained, the first and the third being the only fractions used for the dipole moment determinations. The first fraction was analyzed for carbon and hydrogen with the following results: found C, 44.94; H, 7.57; calcd from formula, C, 44.55; H, 7.50. The nuclear magnetic resonance spectrum, shown in Figure 1, was obtained by a Perkin-Elmer R-12 spectrometer at 60 MHz, using deutered chloroform as solvent and tetramethylsilane as reference.

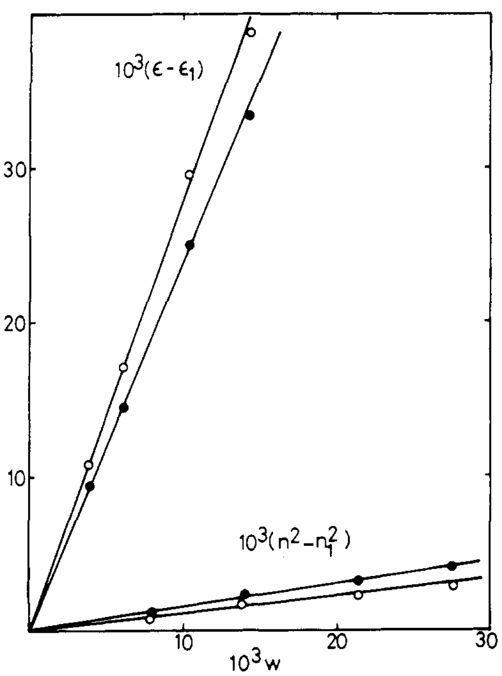

Figure 2. Concentration dependence of the increments in dielectric constant and squared index of refraction for PTXL A: sample at 20 (○) and 60 °C (●).

The spectrum clearly shows the purity and structure of the sample. Two triplets are observed at approximately τ 6.3 and 7.25 that correspond to the resonance of the adjacent protons to the ether and to the thioether groups, respectively, and a singlet that corresponds to the resonance of the acetal proton.

Number average molecular weights were determined using a Perkin-Elmer vapor pressure osmometer, which was calibrated with benzil. Since the synthesis of PTXL was carried out using mild conditions to prevent oxidations in the chains as well as dehydration between two hydroxyl groups that could alter the regular alternance of the units of the terpolymer, the molecular weight of the fractions was relatively low. The results for the two fractions used in this study are given in the second column of Table I.

Dielectric Constants and Refractive Indices. Dielectric constants of the solutions were measured by a capacitance bridge[6] operating at a fixed frequency of 10 kHz. The three-terminal dielectric cell[6] was calibrated at each temperature of interest, using benzene, cyclohexane, and toluene.[11,12] The refractive indices of the solutions were measured at 546 mμ, using a Brice-Phoenix differential refractometer.

Results and Discussion

Dielectric measurements were carried out on benzene solutions at 20, 30, 40, 50, and 60 °C. The dielectric constant and index of refraction for each PTXL solution were expressed relative to the corresponding values for the pure solvent, and the resulting quantities were plotted against the weight fraction w of polymer in the solution. As an example, plots of this kind are given in Figure 2. The slopes of the straight lines give values of the derivatives $d(\epsilon - \epsilon_1)/dw$ and $d(n^2 - n_1^2)/dw$. Values of the two derivatives at all of the temperatures are given in columns four and five of Table I. Mean-square dipole moments $\langle \mu^2 \rangle$ were calculated from the standard equation of Guggenheim[13] and Smith[14]

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

where k is the Boltzmann constant, ρ_1 is the density of the solvent, T is the absolute temperature, and N_A is Avogadro's number. The values of $\langle \mu^2 \rangle$ thus obtained for PTXL

Table I
Dielectric Results for Poly(1,3-dioxo-6-thiocane) Chains

sample	$10^{-3}M_n$	T, °C	$d(\epsilon - \epsilon_1)/dw$	$d(n^2 - n^2_1)/dw$	$\langle\mu^2\rangle_0/nm^2$
A	3	20	2.80	0.11	0.419
		30	2.70	0.12	0.425
		40	2.58	0.13	0.426
		50	2.48	0.14	0.429
		60	2.38	0.15	0.432
B	2.5	20	2.81	0.11	0.419
		30	2.71	0.12	0.425
		40	2.60	0.13	0.426
		50	2.48	0.14	0.429
		60	2.38	0.15	0.432

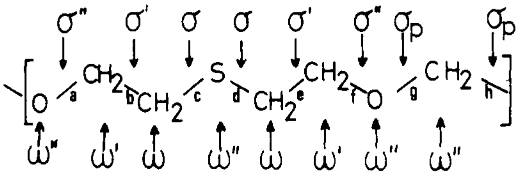

Figure 3. Section of the PTXL chain in the all-trans conformation.

chains coincide with the unperturbed values $\langle\mu^2\rangle_0$[1,15-17] and may be expressed in terms of the ratio $\langle\mu^2\rangle_0/nm^2$, where n is the number of skeletal bonds. The average of the skeletal bond moments was calculated using $m_{\text{C-O}} = 1.07$ D,[5,18] $m_{\text{C-S}} = 1.21$ D,[18,19] $m_{\text{C-C}} = 0.00$ D,[5,18] $m_{\text{H-O}} = 1.70$ D.[20] The values of the dipole moment ratio thus obtained are listed in the fifth column of Table I.

The theoretical calculations of the dipole moment ratio were made utilizing for the skeletal bond angles the following values: ∠CCS = 114°,[19] ∠CCO = ∠COC = 110°,[1] and ∠CSC = 100°.[19] It was also assumed that the rotational states are located, as first approximation, at 0° (trans, t), 120° (gauche positive, g^+), and −120° (gauche negative, g^-). The required energies of the intramolecular interactions occurring in PTXL may be obtained from earlier analysis on polyoxides,[1] polyformals,[8,9] and poly(thiodiethylene glycol).[10] A brief summary of this information follows. Gauche states about skeletal bonds such as a and f in Figure 3 have an energy approximately 900 cal mol^{-1} higher than the alternative trans states.[1,20] Raman and infrared spectra[21] of molecules with CH_2–S bonds in their structure such as ethyl methyl sulfide show that the gauche conformation is slightly more stable than the trans. According to literature,[21,22] a value of $E_\sigma = -0.1$ kcal mol^{-1} seems to be a reasonable choice for bonds c and d. Earlier studies on the statistical properties of poly(oxymethylene)[1,5] and polyformals[8,9] have shown that bonds of type g and h strongly prefer gauche states, the energy of these states being about 1.2 kcal mol^{-1} lower than that of the corresponding trans. Finally, gauche states about b and e bonds bring sulfur and oxygen atoms separated by three bonds into proximity. Although a qualitative analysis of the Raman spectra of 2-oxo-5-thiohexane[23] seems to suggest that the gauche conformation of these states is as stable as the trans, previous studies on the conformational properties of poly(thiodiethylene glycol) indicate that the energy of gauche states is higher than that of the alternative trans states, and its value lies in the vicinity of 400 cal mol^{-1}.[10] Pairs of gauche states of opposite sign $g^\pm g^\mp$ give rise to pentane type interferences between atoms and groups separated by four bonds. Complete exclusion of these conformations has been considered to occur in the case of bond pairs of type ah, cd, fg, and ha of Figure 3. For the bond pairs bc and de of the same figure, the participating species are a CH_2 group and an oxygen atom. Their interactions give rise to a repulsive energy of approximately 0.4 kcal mol^{-1}.[5,20] Interactions of this kind for bond pairs of the type ef and ab, where the participating species are a CH_2 group and an S atom, are somewhat more suppressed than in the above case but by no means excluded; a repulsive energy of about 1 kcal mol^{-1} was tentatively assigned to these $g^\pm g^\mp$ conformations.[10]

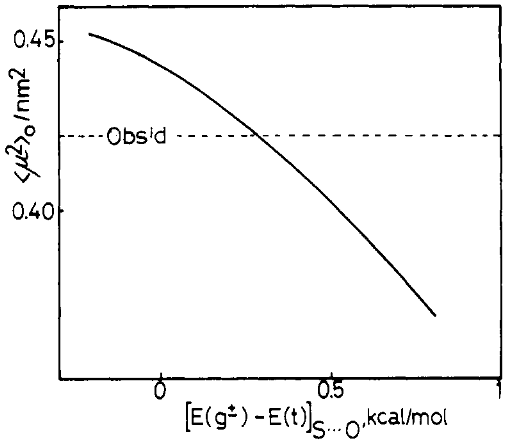

Figure 4. Theoretical dependence of the dipole moment ratio of PTXL on the energy difference between gauche and trans states in which the interacting species are S and O atoms.

The rotational isomeric state theory was used to calculate values of the dipole moment ratio at 25 °C for PTXL chains containing $n = 184$ bonds. The statistical weight parameters assigned to each of the states of each bond of the structural unit are represented in Figure 3. First-order parameters are indicated above the formula and second-order parameters below. The latter parameters are applied to the bond pair flanking the skeletal atom or group indicated. From the information given above it can be expected that the values of the conformational statistical weights are: $\sigma = 1.20$, $\sigma_p = 8$, $\sigma'' = 0.22$, $\omega = 0.56$, $\omega'' = 0$, and $\omega' = 0.20$. Moreover, since the information about the value of the energy associated with first-order interactions between S and O atoms is meager, the calculations were carried out as a function of the rotational state energy difference $E_{\sigma'} = [E(g^\pm) - E(t)]_{\text{S}\cdots\text{O}}$. In the calculations, the end groups were properly taken into account.

The dependence of the dipole moment ratio on $E_{\sigma'}$ is shown in Figure 4. It can be observed that this quantity is not so sensitive to the value of the energy associated to the first-order interactions between S and O atoms as it is in the case of poly(thiodiethylene glycol) (PTDG) chains. Actually, the coefficient $\partial \ln \langle\mu^2\rangle/\partial \ln \sigma'$ is only 0.14, sensibly lower than the value of 0.54 corresponding to this coefficient in PTDG.[10] The sensitivity of $E_{\sigma'}$ to the other conformational energies has also been studied. The theoretical analysis shows that the dipole moment ratio decreases with increase of $E_{\sigma'}$ and decrease of E_{σ_p}. Pairs of values of these conformational energies which reproduce the observed value of $\langle\mu^2\rangle/nm^2$ (0.42) are plotted in Figure 5. It can be observed that the value of $E_{\sigma'}$ is strongly dependent on the value chosen for the energy of the gauche states about the oxymethylenic bonds of the repeat unit. However, the sensitivity of $E_{\sigma'}$ to the set of conformational energies (E_σ, $E_{\sigma''}$, E_ω, and $E_{\omega'}$) is negligible in the present analysis, as can be observed in Figure 5, where pairs of values of $E_{\sigma'}$ and E_σ which reproduce the experimental results are plotted.

Taking for E_{σ_p} a value of −1.2 kcal mol^{-1},[8] we found agreement between theory and experiment for values of $E_{\sigma'}$ in the vicinity of 0.3 kcal mol^{-1}. The results seem to support earlier data[10] according to which rotations about skeletal bonds that give rise to first-order interactions

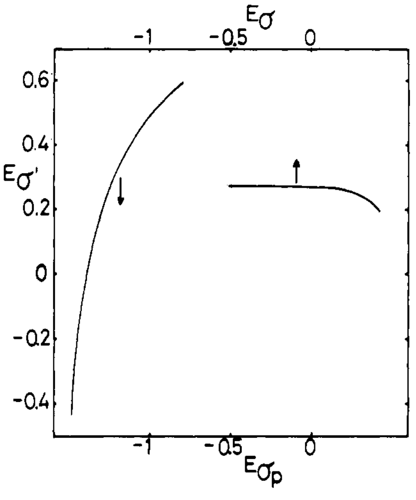

Figure 5. Pairs of conformational energies $E_{\sigma'}$ and E_{σ_p}, chosen so as to reproduce the observed value of $\langle\mu^2\rangle/nm^2$ (0.42). Pairs of values of $E_{\sigma'}$ and E_σ are also shown. The energies are given in kcal mol^{-1}.

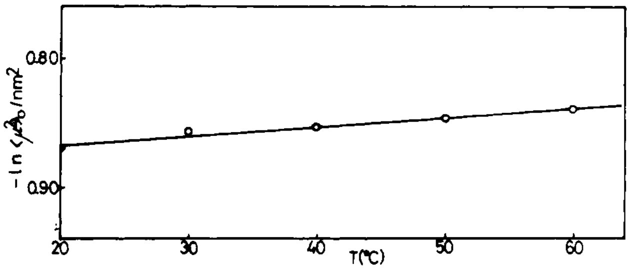

Figure 6. The temperature dependence of the natural logarithm of the dipole moment ratio for the PTXL samples.

between S and O atoms have gauche states of higher energy than the alternative trans states.

The theoretical value of the temperature coefficient d ln $\langle\mu^2\rangle/\mathrm{d}T$ was found to be 0.70 × 10^{-3} deg^{-1}, in qualitative agreement with the experimental value 1.5 × 10^{-3}, obtained from the plot of Figure 6. It should be stressed that d ln $\langle\mu^2\rangle/\mathrm{d}T$ is generally a small quantity which corresponds to changes of a few tenths of a percentage per degree. Consequently, it is difficult to determine with accuracy.

Consideration of PTXL to be a regular alternating terpolymer of formaldehyde, ethylene sulfide, and ethylene oxide can provide some information of interest by comparing its configuration-dependent properties with those of its parent homopolymers. The comparisons for the dipole moment ratio are given in Table II. Although the dipole moments of poly(ethylene sulfide) have not yet been measured, due to the insolubility of the polymer in most solvents, their values have been theoretically estimated by Abe,[19] who found that $\langle\mu^2\rangle_0/nm^2$ has a value in the vicinity of that of poly(oxyethylene). The value of the dipole moment ratio of PTXL coincides, therefore, with the average of the value of the same property for poly(oxymethylene), poly(ethylene sulfide), and poly(oxyethylene). However, this is not a general rule. For example, it can be seen in Table II that the value of the dipole moment ratio of poly(1,3-dioxolane), an alternating copolymer of oxymethylene and oxyethylene units, is vastly different from the average of the value of $\langle\mu^2\rangle_0/nm^2$ for poly(oxyethylene) and poly(oxymethylene). In the same way, if PTXL is considered to be an alternating copolymer of 1,3-dioxolane and ethylene sulfide, its dipole moment ratio is much more similar to that of poly(ethylene sulfide) than it is to that of poly(1,3-dioxolane). These comparisons show once more that the statistical properties of a terpolymer or of a copolymer cannot in general be obtained by simply averaging the values of the same property for the parent homopolymers.

Table II
Experimental Dipole Moment Results on Poly(oxymethylene), Poly(oxyethylene), Poly(1,3-dioxolane), and Poly(1,3-dioxa-6-thiocane)

polymer	repeat unit	$\langle\mu^2\rangle/nm^2$	10^3d ln $\langle\mu^2\rangle/\mathrm{d}T$
POM	CH_2O-	0.2[5]	6.0[5]
POE	$(CH_2)_2O$-	0.52[6]	1.5[6]
PES[a]	$(CH_2)_2S$-	0.49[19]	
PXL	$CH_2O(CH_2)_2O$-	0.17[8]	6.0[8]
PTXL	$(CH_2)_2S(CH_2)_2OCH_2O$-	0.42	0.70

[a] The dipole moment ratio of poly(ethylene sulfide) was theoretically calculated using the rotational isomeric state model (ref 19).

Acknowledgment. It is a pleasure to acknowledge the financial support provided by the Comisión Asesora de Investigación Científica y Técnica.

References and Notes

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969.
(2) J. E. Mark, *Macromolecules*, **11**, 627 (1978).
(3) J. E. Mark, *Acc. Chem. Res.*, **7**, 218 (1974).
(4) J. E. Mark in "Characterization of Materials in Research, Ceramics and Polymers", Syracuse University Press, Syracuse, N.Y., 1975.
(5) A. Abe and J. E. Mark, *J. Am. Chem. Soc.*, **88**, 6468 (1976).
(6) E. Riande, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 2231 (1976).
(7) E. Riande, *Makromol. Chem.*, **178**, 2001 (1977).
(8) E. Riande and J. E. Mark, *Macromolecules*, **11**, 956 (1978).
(9) E. Riande and J. E. Mark, *J. Polym. Sci., Part C*, in press.
(10) E. Riande and J. Guzmán, *Macromolecules*, in press.
(11) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Vol. 1 and 2, Elsevier, Amsterdam, 1965.
(12) H. H. Landolt, "Landolt-Börnstein: Zahlenwert und Funktionen aus Physics, Chemistry, Astronomy, Geophysics und Technology", Vol. II, Part 6, Springer, Berlin, 1959.
(13) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949); **47**, 573 (1951).
(14) J. W. Smith, *Trans. Faraday Soc.*, **46**, 394 (1950).
(15) K. Nagai and T. Ishikawa, *Polym. J.*, **2**, 416 (1971); M. Doi, *ibid.*, **3**, 252 (1972).
(16) S. C. Liao and J. E. Mark, *J. Chem. Phys.*, **59**, 3825 (1973).
(17) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(18) 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.
(19) A. Abe, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20**, 460 (1979).
(20) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 3702 (1966).
(21) N. Nogami, H. Sugeta, and T. Miyazawa, *Bull. Chem. Soc. Jpn.*, **48**, 3573(1975); *Chem. Lett.*, 147 (1975).
(22) M. Sakakibara, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 111 (1977).
(23) Y. Ogawa, M. Ohta, M. Sakakibara, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 650 (1977).