Dipole Moment of the Poly(thiocarbonate) of 2,2′-Bis(4-hydroxyphenyl)propane

Enrique Saiz,[†] María José Fabre,[‡] Ligia Gargallo,[§] Deodato Radić,[‡] and Irmina Hernández-Fuentes*,[‡]

Facultad de Ciencias, Universidad de Alcalá, Alcalá de Henares, Madrid, Spain, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain, and Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago, Chile.

Received December 1, 1988; Revised Manuscript Received February 13, 1989

ABSTRACT: The dipole moment of the poly(thiocarbonate) of 2,2′-bis(4-hydroxyphenyl)propane (PMTC) has been determined in 1,4-dioxane solution at 25 °C. The "effective" dipole moment of a sample having $\bar{M}_n = 7.0 \times 10^3$ (i.e. $x = 30$ repeating units) was found to be $\mu_{\text{eff}} = (\langle\mu^2\rangle/x)^{1/2} = 0.97$ D. Theoretical calculations were performed using the rotational isomeric state model with the scheme developed by other authors for polycarbonates. The calculated values of μ_{eff} are almost insensitive to the conformational parameters used in the calculations. Agreement between theoretical and experimental results is obtained, assuming that the end groups of the chains have dipole moments of ca. 1.5 D, which is roughly the dipole moment of the phenolic residues that the procedure of synthesis attaches to the polymeric chain.

Introduction

Poly(thiocarbonates) derived from Bisphenol A are a new family of amorphous polymers with an interesting perspective of practical applications. Many of the properties of poly(thiocarbonates) are quite similar to those of polycarbonates as may be expected from the structural simulitudes between both kinds of polymers. However, the substitution of an oxygen atom of the polycarbonate chains by sulfur in thiocarbonate also produces some interesting differences between these polymers. During the last years, the synthesis of some poly(thiocarbonates)[1,2] and many of their properties have been investigated. Thus, glass transition temperatures,[3] unperturbed dimensions,[4,5] partial specific volumes,[6] and specific refractive index increments[6] have been recently reported. However, the dipole moment of these polymers has not yet been studied from either an experimental or a theoretical point of view.

For these reasons, the aim of the present work is to measure the dipole moment of a thiocarbonate polymer, namely the poly(thiocarbonate) of 2,2′-bis(4-hydroxyphenyl)propane, and to compare the experimental value with the results calculated using the rotational isomeric states (RIS) model.

To our knowledge, no statistical model has yet been published for thiocarbonate chains. However, given the close similarity between carbonate and thiocarbonate molecules, it seems reasonable to use the same statistical model for both kinds of molecules. Unlike thiocarbonates, the carbonate chains have been studied for many years. Thus, the first RIS model for these molecules was formulated by Williams and Flory[7] more than 20 years ago and has been used either unchanged[8–10] or with some modifications[11–13] to calculate several properties of these polymers. The newest revised model that we know about was proposed by Hutnik and Suter[14] and incorporates structural and conformational data obtained with quantum chemical methods applied to several model compounds.[15–17]

In this paper, the statistical model developed by Hutnik and Suter for polycarbonates is applied to calculate the dipole moment of poly(thiocarbonates). A discussion is presented about the conditions in which agreement between theoretical and experimental values is obtained.

Experimental Section

(a) Materials. A sample of the poly(thiocarbonate) of 2,2′-bis(4-hydroxyphenyl)propane (PMTC), previously synthesized[6] by phase-transfer catalysis, was selected for the present work. Molecular weight ($\bar{M}_w = 9.4 \times 10^3$ g·mol^{-1}) and polydispersity ($r = \bar{M}_w/\bar{M}_n = 1.34$) were determined by size exclusion chromatography.

1,4-Dioxane used as solvent in refractometry, densimetry, and dielectric measurements was Carlo Erba of RPE quality. It had been dried over Merck 4-Å molecular sieves.

(b) Dielectric Measurements. The dielectric measurements were performed on a WTW Model DK 06 multidekameter, at a frequency of 2.0 MHz. The cell used was of silvered Pyrex glass and was calibrated at the working temperature, 25.00 ± 0.01 °C, using liquids with well-known dielectric constant (i.e., benzene, toluene, cyclohexane).[18] Polymer solutions in 1,4–dioxane were preserved over molecular sieves until the moment they were used. the concentration range of polymer solutions was $1 \times 10^{-3} < w_2 < 7 \times 10^{-3}$ (w_2 = polymer weight fraction). The same solutions were used for dielectric constant, refractometry, and densimetry measurements.

(c) Refractometry. The differences between the refractive index of solutions and pure solvent, Δn, were measured, at λ = 546 nm, in a Brice Phoenix 2000V differential refractometer, calibrated with aqueous solutions of KCl at 25.0 °C.

(d) Densimetry. An Anton Paar DMA 55 digital densimeter was used, with distilled water and air as calibrating substances. The temperature in the measuring cell was regulated to 25.00 ± 0.01 °C .

(e) Dipole Moment. The dipole moment per repeat unit, μ_{eff}, of PMTC has been determined by using the Halverstadt and Kumler equations[19] for the molar polarization, $[P]_2{}^0$, and molar refraction $[R]_2{}^0$, of the solute, both at infinite dilution

$$[P]_2{}^0 = \frac{3M_2 \upsilon_1}{(\epsilon_1 + 2)^2}\left(\frac{\partial\epsilon}{\partial w_2}\right)^0 + \frac{M_2(\epsilon_1 - 1)}{\epsilon_1 + 2}\left[\upsilon_1 + \left(\frac{\partial \upsilon}{\partial w_2}\right)^0\right]$$

$$[R]_2{}^0 = \frac{6M_2 \upsilon_1 n_1}{(n_1{}^2 + 2)^2}\left(\frac{\partial n}{\partial w_2}\right)^0 + \frac{M_2(n_1{}^2 - 1)}{n_1{}^2 + 2}\left[\upsilon_1 + \left(\frac{\partial \upsilon}{\partial w_2}\right)^0\right]$$

where υ and υ_1 are the specific volumes of solution and pure solvent, respectively, ϵ and ϵ_1 are their respective dielectric constant, n and n_1 are their refractive indices, M_2 is the molecular weight of the repeat unit, and the superscript zero means the magnitude extrapolated to infinite dilution. The molar orientation polarization of the solute at infinite dilution, $[P_0]_2{}^0$, was calculated as

$$[P_0]_2{}^0 = [P]_2{}^0 - 1.10[R]_2{}^0$$

where $[R]_2{}^0$ has been increased by 10% to include the approximate

---

[†] Universidad de Alcalá.

[‡] Universidad Complutense.

[§] Pontificia Universidad Católica de Chile.

0024-9297/89/2222-3660$01.50/0

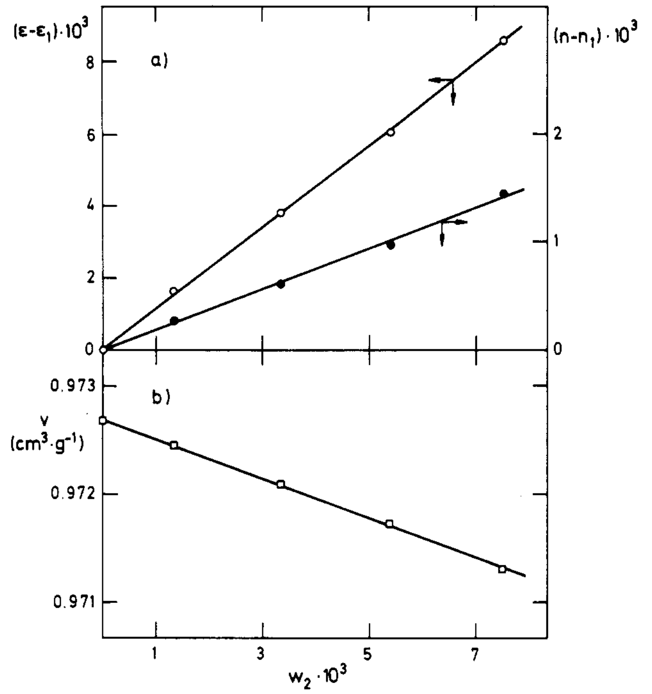

Figure 1. Dependence on weight fraction of polymer, w_2, of (a) dielectric constant (○) and refractive index (●) and (b) specific volume (□); for PMTC in 1,4-dioxane at 25 °C.

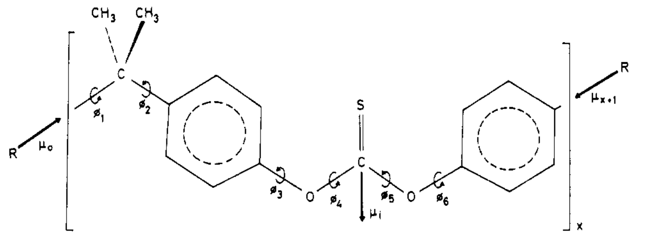

Figure 2. Segment of the PMTC chain shown in its all-trans (i.e. $\phi_i = 0$) conformation. Positive directions of dipole moments are indicated by the arrows. μ_i represents the dipole moment of each repeating unit while μ_0 and μ_{x+1} are the dipole moments of the end groups, which are represented by R.

atomic displacement polarization as in the case of dimethylcarbonate.[20]

And μ_{eff} was obtained according to the Debye method by

$$\mu_{\text{eff}}^2 = \frac{9kT}{4\pi N_A}[P_0]_2^0$$

where k is the Boltzmann constant, N_A is Avogadro's number, and T is the absolute temperature.

In the Figure 1 the measured dielectric constants, refractive index increments, and specific volumes of PMTC dioxane solutions are plotted against w_2. Good linearity is observed in all the cases.

The values of $(\partial\epsilon/\partial w_2)^0$, $(\partial n/\partial w_2)^0$, and $(\partial v/\partial w_2)^0$, determined as the slope of the corresponding plot by least-squares fit, are 1.130, 1.1885, and −0.1811 cm^3·g^{-1}, respectively. From these results, the experimental value of μ_{eff} for PMTC is 0.968 D.

Theoretical Analysis

In the present work, the model of Hutnik and Suter[14] was used for the thiocarbonate chains schematized in Figure 2. Table I summarizes the model that incorporates only one energetic parameter, namely E_γ governing the incidence of cis ($\phi = 180°$) versus trans ($\phi = 0°$) orientations on the O–C bonds of the thiocarbonate residue; however, cis–cis conformation of this group (i.e. $\phi_4 = \phi_5 = 180°$ in Figure 2) is forbidden due to severe steric repulsion between the two phenyl rings. A value of $E_\gamma \simeq 1.0$ kcal/mol was assigned in previous studies of carbonate groups;[14] we have used the same value for the thiocarbonate residue and checked afterward the sensitivity of the dipole moment of the chain to this parameter. The rotational states of all the other bonds of the chain (i.e. 1–3 and 6 on Figure 2) are displaced from their perfectly trans orientations by ca. $\Delta\phi \simeq 45°$; consequently, given the symmetry of the chain, four states located at $\pm\Delta\phi$ and $180 \pm \Delta\phi$ were allowed for each of those rotations. The values used for the bond angles (C^{Ph}–C–C^{Ph} = 109.8°, C^{Ph}–O–C = 117.7° and O–C–O = 105.8°) were also taken from ref 14.

Table I
Statistical Model[a] Used for Thiocarbonate Chains

bond no. (i)	ϕ_i	$\mathbf{u}_i$
1	$\Delta\phi$,[b] $180-\Delta\phi$, $180+\Delta\phi$, $360-\Delta\phi$	$\begin{vmatrix}1&1&1&1\\1&1&1&1\\1&1&1&1\\1&1&1&1\end{vmatrix}$
2	$\Delta\phi$, $180-\Delta\phi$, $180+\Delta\phi$, $360-\Delta\phi$	$\begin{vmatrix}1&0&1&0\\0&1&0&1\\1&0&1&0\\0&1&0&1\end{vmatrix}$
3	$\Delta\phi$, $180-\Delta\phi$, $180+\Delta\phi$, $360-\Delta\phi$	$\begin{vmatrix}1&1&1&1\\1&1&1&1\\1&1&1&1\\1&1&1&1\end{vmatrix}$
4	0, 180	$\begin{vmatrix}1&\gamma\\1&\gamma\\1&\gamma\\1&\gamma\end{vmatrix}$
5	0, 180	$\begin{vmatrix}1&\gamma\\1&0\end{vmatrix}$
6	$\Delta\phi$, $180-\Delta\phi$, $180+\Delta\phi$, $360-\Delta\phi$	$\begin{vmatrix}1&1&1&1\\1&1&1&1\end{vmatrix}$

[a] Taken from ref 14. [b] With ca. $\Delta\phi \simeq 45°$.

A dipole moment $\mu_i = 0.90$ D lying along the S═C bond was used for each repeating unit. The modulus of this vector is the experimental dipole moment of the dimethyl thiocarbonate (DMTC) in benzene solution.[21] Perhaps a better choice for μ_i would be the dipole moment of diphenyl thiocarbonate (DPTC), which is more similar to the repeating unit of the polymer; however, no experimental value of μ for DPTC was found in the literature. Moreover, in the case of carbonates, the dipole moments of dimethyl carbonate (DMC) and diphenyl carbonate (DPC) are identical;[9] in fact, dipole moments of DMC, DPC, and DMTC agree within the limit of experimental error. Therefore, it seems reasonable to assume that the difference between the dipole moments of DMTC and DPTC should be small.

The end groups of the chain are represented by R in Figure 2. They are supposed to have dipole moments μ_0 and μ_{i+1} with the directions indicated in the same figure (i.e. the R groups are more electronegative than the chain). In all the calculations, the moduli of these two vectors were assumed to be the same, so that if the chain was in the all-trans conformation and the valence angles were identical, μ_0 and μ_{i+1} would cancel each other out. However, with the actual values of the bond angles and in taking into account the flexibility of the chain, the effect of those two dipoles on the value of $\langle\mu^2\rangle_0$ for the whole chain is rather important, as will be shown below.

Standard methods of the matrix multiplication scheme[22,23] were employed to compute the mean-square dipole moment $\langle\mu^2\rangle_0$ of chains having different degrees of polymerization x. The values of $\langle\mu^2\rangle_0$ were converted into effective dipole moments $\mu_{\text{eff}} = [\langle\mu^2\rangle_0/x]^{1/2}$, which are the kind of results that will be shown in all the analyses.

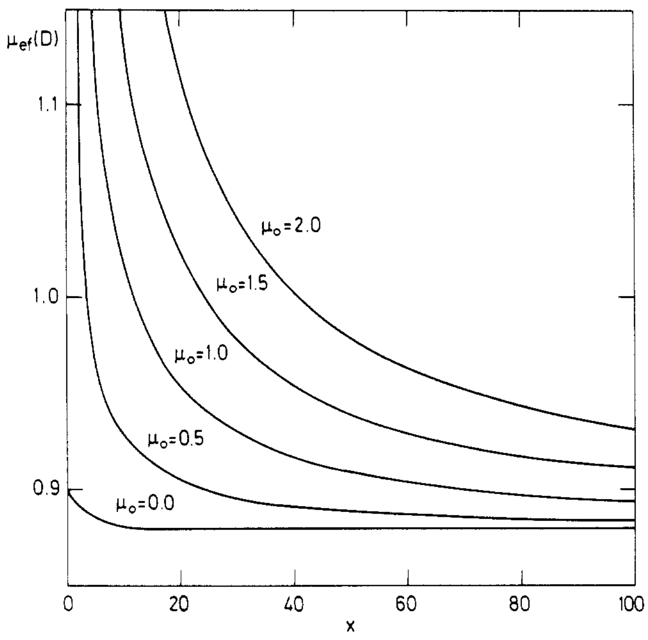

Figure 3. Effective dipole moments $\mu_{\text{eff}} = [\langle\mu^2\rangle_0/x]^{1/2}$ of the PMTC chain as function of the degree of polymerization x. Calculations were performed at 25 °C with $E_\gamma = 1.0$ kcal/mol and five different values of the dipole moments of the end groups, $|\mu_0| = |\mu_{x+1}| = 0, 0.5, 1.0, 1.5$, and 2.0 D.

Figure 3 shows the variation of μ_{eff} with x for five values of the dipole moments of the end groups. The calculations were performed at 25 °C with $E_\gamma = 1.0$ kcal/mol and the geometry summarized above. As Figure 3 indicates, when $\mu_0 = 0$, μ_{eff} reaches an asymptotic limit of ca. 0.88 D at very low values of x (ca. $x \simeq 10$). Moreover, the results of μ_{eff} are almost insensitive to the conformational parameters used on the calculation; thus, changes of 5° in the skeletal bond angles or 1 kcal/mol in E_γ modify the results of μ_{eff} by ca. 1–2%. The explanation of this behavior is straightforward: the dipole moment of the repeating unit is located in the thiocarbonate residue; therefore, the dipole moments of different units of the chain are separated by at least four skeletal bonds, which have high rotational freedom and consequently behave as if they were uncorrelated, so that the result for the whole chain is $\langle\mu^2\rangle_0 \simeq x\mu_i^2$ or, what is the same, $\mu_{\text{eff}} \simeq \mu_i$.

However, μ_{eff} is quite sensitive to the presence of dipole moments in the end groups, although obviously the effect of these groups becomes smaller as x grows larger. Thus, Figure 3 indicates that when $x = 10$ (i.e. short chains), μ_{eff} values increase by ca. 5, 16, 31, and 49% if the end groups have $|\mu_0| = |\mu_{x+1}| = 0.5, 1.0, 1.5$, and 2.0 D, respectively, while for $x = 100$, the same values of μ_0 and μ_{x+1} increase μ_{eff} by only ca. 0.5, 1.7, 3.5, and 5.9% respectively.

The polymer measured for the present work is relatively small (ca. $x \simeq 30$), and Figure 3 shows that the experimental result of $\mu_{\text{eff}} = 0.97$ D can be reproduced for this value of x by taking $|\mu_0| = |\mu_{x+1}| \simeq 1.3 - 1.7$ D, which is the dipole moment that can reasonably be expected if the end groups are phenolic residues as would be suggested by the method of synthesis used.[1]

We conclude that the dipole moment of the poly(thiocarbonate) of 2,2′-bis(4-hydroxyphenyl)propane can be reproduced with the same scheme used for polycarbonates assuming that the end groups have dipole moments of ca. 1.5 D. Under these circumstances, the end groups represent roughly 11% of the μ_{eff} of the whole chain for our sample, which has $x \simeq 30$.

Acknowledgment. This work has been supported by Grant No. 2953/83 from CAYCIT Ministerio de Educación y Ciencia, Spain, Dirección de Investigación (DIUC), Pontificia Universidad Católica de Chile, and Fondo Nacional de Ciencias, FONDECYT, Santiago, Chile.

Registry No. PMTC (copolymer), 120411-62-3; PMTC (SRU), 32200-44-5.

References and Notes

(1) Tagle, L. H.; Díaz, F. R.; Vega, J. C.; Alquinta, P. F. *Makromol. Chem.* **1985**, *186*, 915.
(2) Tagle, L. H.; Díaz, F. R.; Riveros, P. E. *Polym. J. (Tokyo)* **1986**, *18*, 501.
(3) Yazdani-Pedram, M.; Soto, E.; Tagle, L. H.; Díaz, F. R.; Gargallo, L.; Radić, D. *Thermochim. Acta* **1986**, *105*, 149.
(4) Gargallo, L.; Soto, E.; Díaz, F. R.; Tagle, L. H.; Radić, D. *Eur. Polym. J.* **1987**, *23*, 571.
(5) Gargallo, L.; Soto, E.; Tagle, L. H.; Radić, D. *J. Appl. Polym. Sci.* **1988**, *35*, 1103.
(6) Fabre, M. J.; Tagle, L. H; Gargallo, L.; Radić, D.; Hernández-Fuentes, I. *Eur. Polym. J.*, in press.
(7) Williams, A. D.; Flory, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 1945.
(8) Yoon, D. Y.; Flory, P. J. *Polym. Bull. (Berlin)* **1981**, *4*, 693.
(9) Erman, B.; Marvin, D. C.; Irvine, P. A.; Flory, P. J. *Macromolecules* **1982**, *15*, 664.
(10) Erman, B.; Wu, D.; Irvine, P. A.; Marvin, D. C.; Flory, P. J. *Macromolecules* **1982**, *15*, 670.
(11) Tonelli, A. E. *Macromolecules* **1972**, *5*, 558.
(12) Sundararajan, P. R. *Can. J. Chem.* **1985**, *63*, 103; *Macromolecules* **1987**, *20*, 1534.
(13) Laskowski, B. C.; Yoon, D. Y.; McLean, D.; Jaffe, R. L. *Macromolecules* **1988**, *21*, 1629.
(14) Hutnik, M.; Suter, U. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*(2), 293.
(15) Clark, D. T.; Munro, H. S. *Polym. Degrad. Stab.* **1982**, *4*, 83.
(16) Pérez, S.; Scaringe, R. P. *Macromolecules* **1987**, *20*, 68.
(17) Bicerano, J.; Clark, H. A. *Macromolecules* **1988**, *21*, 585; **1988**, *21*, 597.
(18) Petro, A. J.; Smith, G. P. *J. Am. Chem. Soc.* **1957**, *79*, 6142. Heston, W. M.; Smith, G. P. *J. Am. Chem. Soc.* **1950**, *72*, 99.
(19) Halverstadt, I. F.; Kumler, W. D. *J. Am. Chem. Soc.* **1942**, *64*, 2988.
(20) Yasumi, M. *J. Chem. Soc. Jpn.* **1939**, *60*, 1208.
(21) McClellan, A. L. *Tables of Experimental Dipole Moments*: Freeman: San Francisco, Vol. 1; 1963; Rahara: El Cerrito, CA 1974; Vol. 2.
(22) Flory, P. J. Statistical Mechanics of Chain Molecules; Interscience: New York, 1969.
(23) Flory, P. J. *Macromolecules* **1974**, *7*, 381.