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# Dipole Moment of Poly(thiocarbonates) with Chlorophenyl or Dichlorophenyl Side Groups

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ABSTRACT: The dipole moments of asymmetric poly(thiocarbonates) derived from Bisphenol A, having methyl and chlorophenyl or methyl and dichlorophenyl groups attached to the quaternary carbon, have been determined in benzene solution at 25 °C. Theoretical calculations were performed by using the statistical model developed by Sundararajan for methyl phenyl carbonate and the same procedure employed before for carbonate and thiocarbonate polymers having two methyl side groups. The polar side group in the repeating unit of the polymers studied here makes the dipole moment of the whole chain less sensitive to the end groups than in the case of dimethyl analogues. Good agreement between theoretical and experimental results can been obtained assuming that the direction of the dipole moment of the thiocarbonate group is opposite to that in carbonate residues. This assumption was confirmed by quantum mechanics calculations of the charge distribution in both carbonate and thiocarbonate groups.

## Introduction

In a previous paper[1] we have reported a conformational analysis of one poly(thiocarbonate) derived from Bisphenol A, the poly(thiocarbonate) of 2,2′-bis(4-hydroxyphenyl)propane (PMTC), based on the comparison between experimental and theoretical values of its dipole moment. The dipole moment of this polymer chain can be reproduced by using the rotational isomeric state (RIS) model with the scheme developed by Hutnik and Suter for poly(carbonates).[2]

Since most of the properties of poly(thiocarbonates) are strongly influenced by the structure of their side chains,[3-7] we thought that it would be interesting to study that influence in the case of the dipole moment for a series of poly(thiocarbonates) derived from Bisphenol A.[8]

The thiocarbonate was the only polar group on the repeating unit in all the cases studied up to now. Consequently, the dipole moment of each unit was always located along the C═S bond. In the present work, we wanted to analyze the effect that a second dipole moment in the repeating unit would have on the dipole of the whole chain. Thus, we have selected three different poly(thiocarbonates) in which one of the two substituents on the quaternary carbon is always a methyl group; however, they differ in the second substituent for which three polar groups, namely, 3-chlorophenyl, 4-chlorophenyl, and 3,4-dichlorophenyl, were chosen.

## Experimental Section

**(a) Materials.** Samples of poly(thiocarbonates) of 1,1′-bis(4-hydroxyphenyl)-1-(3-chlorophenyl)ethane (P3ClPhTC), 1,1′-bis(4-hydroxyphenyl)-1-(4-chlorophenyl)ethane (P4ClPhTC), and 1,1′-bis(4-hydroxyphenyl)-1-(3,4-dichlorophenyl)ethane (P34ClPhTC), previously synthesized[9] by phase-transfer catalysis, were selected for the present work.

Molecular weights ($\bar{M}_n$ = 5800 (P3ClPhTC), 5000 (P4ClPhTC), and 4500 (P34ClPhTC)) were determined by vapor pressure osmometry.

Benzene used as the solvent in refractometry, densimetry, and dielectric measurements was Carlo Erba of RPE quality. It was 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 a silvered Pyrex glass and was calibrated at the working temperature, 25.00 ± 0.01 °C, using liquids with a well-known dielectric constant (i.e., benzene, toluene, cyclohexane).[10] The concentration range of polymer solutions was $1 \times 10^{-3} \le w_2 \le 8 \times 10^{-3}$ ($w_2$ = polymer weight fraction). The same solutions were used for dielectric constant, refractometry, and densimetry measurements.

**(c) Refractometry.** The differences between the refractive indices of solutions and pure solvent, $\Delta n$, were measured, at $\lambda$ = 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 with distilled water and air as calibrating substances was used for the measurements. The temperature in the measuring cell was regulated to 25.00 ± 0.01 °C.

**(e) Dipole Moment.** The dipole moment per repeating unit, $\mu_{\rm eff}$, of the poly(thiocarbonates) was determined by using the Halverstadt and Kumler equations[11] for the molar polarization, $[P]_2^0$, and molar refraction, $[R]_2^0$, of the solute, both at infinite dilution

$$[P]_2^0 = M_2\left\{\frac{3v_1}{(\epsilon_1+2)^2}\left(\frac{\partial\epsilon}{\partial w_2}\right)^0 + \frac{\epsilon_1-1}{\epsilon_1+2}\left[v_1 + \left(\frac{\partial v}{\partial w_2}\right)^0\right]\right\}$$

$$[R]_2^0 = M_2\left\{\frac{6v_1n_1}{(n_1^2+2)^2}\left(\frac{\partial n}{\partial w_2}\right)^0 + \frac{n_1^2-1}{n_1^2+2}\left[v_1 + \left(\frac{\partial v}{\partial w_2}\right)^0\right]\right\}$$

where $M_2$ is the molecular weight of the repeating unit; $v$, $\epsilon$, and $n$ represent, respectively, the specific volume, dielectric constant, and refractive index of the solution while $v_1$, $\epsilon_1$, and $n_1$ indicate the same three magnitudes for the pure solvent. The zero superscript represents the value of 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 atomic displacement polarization as in the case of dimethyl carbonate.[12]

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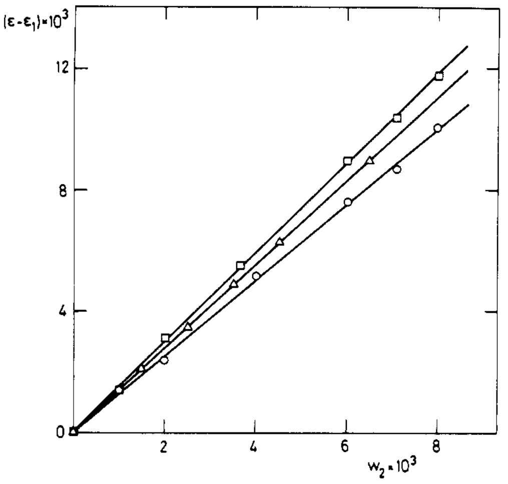

**Figure 1.** Dependence of the dielectric constants for P3ClPhTC (△), P4ClPhTC (○), and P34ClPhTC (□) on the weight fraction of polymer $w_2$, in benzene solutions at 25 °C.

The value of $\mu_{\mathrm{eff}}$ was obtained according to the Debye method by

$$\mu_{\mathrm{eff}}^2 = \frac{9kT}{4\pi N_{\mathrm{A}}}[\mathrm{P}_0]_2^0$$

where $k$, $N_{\mathrm{A}}$, and $T$ represent the Boltzmann constant, Avogadro's number, and the absolute temperature, respectively.

Figure 1 shows the dependence of the dielectric constant on polymer concentration for P3ClPhTC, P4ClPhTC, and P34ClPhTC in benzene at 25 °C. 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 plots by least-squares fitting, are summarized in Table I. Those results allowed the computation of $[\mathrm{P}]_2^0$, $[\mathrm{R}]_2^0$, and $\mu_{\mathrm{eff}}$, whose values are indicated in the last three columns of Table I.

## Theoretical Analysis

A sketch of the all-trans (i.e., $\phi = 0°$) conformation for the repeating units of the polymers investigated in this work is shown in Figure 2a while parts b–d of the same figure illustrate the relative orientation of the two side groups (i.e., one methyl group and a phenyl derivative) attached to each quaternary carbon.

The geometrical parameters and statistical model used in the present work for the polymer backbone are summarized in Table II. They differ from those previously employed in the analysis of both carbonate[2] and thiocarbonate[1] polymers having two methyl groups as substituents in the quaternary carbons only in the location of the rotational isomers of bonds 1 and 2 on the repeating unit. The values indicated in Table II were taken from the analysis of methyl phenyl carbonate reported by Sundararajan,[13] assuming that the differences between this polymer and the ones that we study, namely, the substitution of C=O by C=S bonds and the presence of chlorine atoms in the side groups of our polymers, have no effect on the conformational features of the chain backbone, including position and relative energy of rotational isomers and bond angles. Both assumptions have been used before,[1,14] and, at any rate, the incidence of these parameters on the dipole moments of the chains is almost negligible. Thus, the results shown below, which were computed in all cases with the rotational isomers indicated in Table II, differ by less than 4% from those obtained allowing symmetrical locations (i.e., $\phi = \pm 45°$; $180 \pm 45°$) for the rotational isomers of bonds 1 and 2. In a similar way, an increase in the bond angle OCO from the value $\theta_4 = 105.8°$ used throughout all the calculations to $\theta_4 = 110°$ modifies the results of $\mu_{\mathrm{eff}}$ by ca. 1%.

As in previous analyses,[1,2] cis conformations of C–O bonds (i.e., $\phi$ 180° over bonds 4 and 5 of the repeating unit) were supposed to have an energy of $E_\gamma \approx 1.0$ kcal mol$^{-1}$ higher than their alternative trans states (i.e., $\phi = 0°$).

Due to the presence of a chlorine atom in the meta position of the phenyl side groups on P3ClPhTC and P34ClPhTC, the angle $\chi$ that governs the rotation of the side group determines also the relative orientation of the two components to the dipole moment of the repeating units of these polymers. Two positions, $\chi = 0°$ and $\chi = 180°$, were allowed for this rotation; they are defined as the orientations in which the methyl group is, respectively, cis (as shown in Figure 2c,d) and trans with respect to the meta chlorine atom. These two orientations are close to the energy minima obtained in a full rotation over $\chi$; a better description of this rotation can be achieved by increasing the number of allowed states; however, the computation time increases noticeably with the number of orientations to be considered while the final values of $\mu_{\mathrm{eff}}$ are practically unchanged. A value $E_{\mathrm{c}}$ was assigned to the conformational energy of the $\chi = 0°$ orientation relative to $\chi = 180°$. Calculation of this energy using a standard Lennard-Jones potential[15] indicates a small preference for the cis conformation (i.e., $E_{\mathrm{c}} \approx -0.05$ to $-0.1$ kcal mol$^{-1}$) mainly due to attractive interactions between $\mathrm{CH_3}$ and Cl, which are placed at distances[13] of 5.10 and 6.45 Å, respectively, for $\chi = 0$ and 180°.

The conformational freedom $\chi$ was incorporated into the scheme of the calculation with a procedure employed before,[16] consisting of the use of the four-state scheme together with a random routine to decide which of the two allowed orientations of $\chi$ should be used for each unit, taking into account the fractions of those two orientations dictated by the conformational energy $E_{\mathrm{c}}$. All the results shown below are averages over 20 independently generated chains; standard errors of those averages amount to ca. 1–2%.

Two contributions were used for the dipole moment of the repeating unit (see Figure 2); $\mu_1$ represents the contributions of the thiocarbonate group for which a modulus of 0.9 D, corresponding to the experimental dipole moment of dimethyl thiocarbonate measured in benzene solutions,[1,17] was used; $\mu_2$ is the contribution of the side group and was taken to be 1.6 D for P4ClPhTC and P3ClPhTC and 2.2 D for P34ClPhTC, corresponding, respectively, to the experimental dipole moments measured in benzene solutions[17] for chlorobenzene and 1,2-dichlorobenzene. According to the method of synthesis used, it is reasonable to assume that the end groups of the chains are phenolic residues;[1,9] consequently, dipole moments $\mu_0 = \mu_{x+1} \approx 1.5$ D were used for these groups.

The dipole moment of the repeating unit, and therefore that of the whole chain, depends not only on the modulus of $\mu_1$ and $\mu_2$ contributions but on their relative orientation as well. In the case of chlorobenzene, the chlorine atom is the negative part of the dipole moment, which is represented in Figure 2 by an arrow pointing from negative to positive charges. The direction of $\mu_2$ within the side group is determined by the angle $\tau$ that it makes with the direction of the C–Ph bond. It can be seen in Figure 2 that $\tau = 0$, 60, and 30° respectively, for P4ClPhTC, P3ClPhTC, and P34ClPhTC. The dipole $\mu_1$ lies over the C=S bond, but it may, in principle, point either from S to C or vice versa depending on the relative polarity of the C=S and C–O bonds. In the case of the carbonate group, the C*=O* bond is more polar than the two C–O bonds,

**Table I**
**Total Molar Polarization, $[P]_2^0$, and Refraction, $[R]_2^0$, at Infinite Dilution and the Effective Dipole Moment, $\mu_{eff}$, of Poly(thiocarbonates) with Chlorophenyl or Dichlorophenyl Side Chains, in Benzene at 25 °C**

| polymer | $(\partial\epsilon/\partial w_2)^0$ | $(\partial n/\partial w_2)^0$ | $(\partial v/\partial w_2)^0$, $cm^3 \cdot g^{-1}$ | $[P]_2^0$, $cm^3 \cdot mol^{-1}$ | $[R]_2^0$, $cm^3 \cdot mol^{-1}$ | $\mu_{eff}$,[a] D |
|---|---|---|---|---|---|---|
| P3ClPhTC | 1.382 | 0.1446 | −0.4148 | 175.10 | 108.76 | 1.65 |
| P4ClPhTC | 1.245 | 0.1270 | −0.4181 | 165.30 | 104.72 | 1.57 |
| P34ClPhTC | 1.465 | 0.1289 | −0.4560 | 192.90 | 110.47 | 1.87 |

[a] Experimental error is estimated to be ca. 4%.

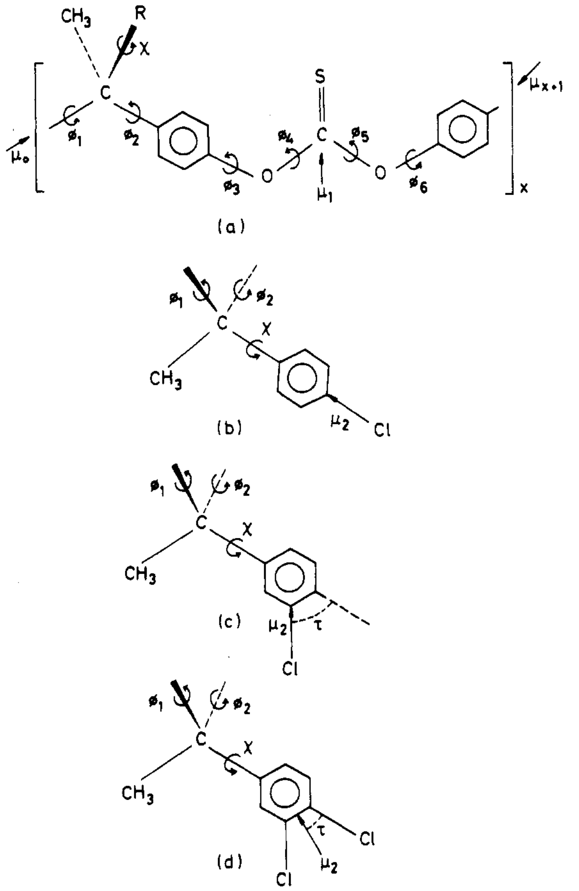

**Figure 2.** Sketches of the thiocarbonate chain shown in its all-trans (i.e., $\phi$ = 0°) conformation (a), and the side groups for P4ClPhTC (b), P3ClPhTC (c), and P34ClPhTC (d). Dipole moments $\mu_1$ for the thiocarbonate group, $\mu_2$ for the phenyl residue, and $\mu_0$ and $\mu_{x+1}$ for the end groups are represented by arrows pointing from negative to positive center of charges.

and therefore the dipole points from O* to C*; however, the situation could be different in the case of thiocarbonate due to the smaller electronegativity of the S atom as compared with O. In order to ascertain the direction of this dipole, we performed a quantum mechanics calculation of the charge distribution of both diphenyl carbonate and diphenyl thiocarbonate molecules using two semiempirical methods, namely, a standard MNDO and the AMPAC program[18] with an AM1[19] parametrization set. The results of both methods are almost identical; both give roughly the same dipole moment for carbonate as for thiocarbonate, in both cases smaller than the experimental value; but, whereas the dipole moment of the C*═O* bond on the carbonate is larger than the sum of the dipoles of the two C–O bonds so that the dipole moment of the whole group points from O* to C*, the opposite occurs in the case of thiocarbonate. All the results presented below[20] were computed with $\mu_1$ pointing from C to S, as indicated in Figure 2; some exploratory calculations performed with $\mu_1$ pointing in the opposite direction gave results that are ca. 20–30% higher than those reported below.

**Table II**
**Summary of Geometry and Statistical Model**

| bond *i* | $\theta_i$ | $\phi_i$ | | | | $U_i$ |
|---|---|---|---|---|---|---|
| 1 | 109.8 | 80 | 160 | 260 | 340 | $\begin{bmatrix}1&1&1&1\\1&1&1&1\\1&1&1&1\\1&1&1&1\end{bmatrix}$ |
| 2 | 180.0 | 20 | 100 | 200 | 280 | $\begin{bmatrix}1&0&1&0\\0&1&0&1\\1&0&1&0\\0&1&0&1\end{bmatrix}$ |
| 3 | 117.7 | 45 | 135 | 225 | 315 | $\begin{bmatrix}1&1&1&1\\1&1&1&1\\1&1&1&1\\1&1&1&1\end{bmatrix}$ |
| 4 | 105.8 | 0 | 180 | | | $\begin{bmatrix}1&\gamma\\1&\gamma\\1&\gamma\\1&\gamma\end{bmatrix}$ |
| 5 | 117.7 | 0 | 180 | | | $\begin{bmatrix}1&\gamma\\1&0\end{bmatrix}$ |
| 6 | 180.0 | 45 | 135 | 225 | 315 | $\begin{bmatrix}1&1&1&1\\1&1&1&1\end{bmatrix}$ |

The relative orientation of $\mu_1$ and $\mu_2$ for a given conformation of the repeating unit depends also on the configuration of the quaternary carbon, i.e., on whether the R group is placed above or below the plane of Figure 2. However, due to the rotations $\chi$, $\phi_2$, $\phi_3$, and $\phi_4$, the average is independent of that configuration. Consequently, the values of the averages computed for polymeric chains are independent of their tacticity.

The method of computation was the standard matrix multiplication scheme[21,22] that was used to calculate $\langle\mu^2\rangle$ for chains with the desired number of repeating units $x$. Values of $\langle\mu^2\rangle$ were then transformed into the "effective dipole per repeating unit" defined as $\mu_{eff} = (\langle\mu^2\rangle/x)^{1/2}$.

Values of $\mu_{eff}$ as function of $x$ computed with $\mu_0 = \mu_{x+1} = 1.5$ D for the dipole moments of the end groups are shown in Figure 3 for P4ClPhTC, P3ClPhTC, and P34ClPhTC together with the results reported in ref 1 for PMTC. The shape of the four curves given in Figure 3 is very similar, with only two noteworthy differences, namely, the polarity, which increases in the order PMTC, P4ClPhTC, P3ClPhTC, and P34ClPhTC, and the value of $x$ at which the asymptotic limit of $\mu_{eff}$ is reached, which is ca. 60–70 for PMTC and only ca. 20–25 in the other three cases. The reason for this behavior is that the variation of $\mu_{eff}$ with $x$ is mostly due to the effect of the end groups,[1] which is much smaller in the cases of P4ClPhTC, P3ClPhTC, or P34ClPhTC than in PMTC due to the larger polarity of their repeating units as compared with that of PMTC. Thus, for instance, taking chains with $x$ = 15 repeating units and changing the contributions of the end groups from 0 to 2 D, the values of $\mu_{eff}$ increase roughly by 4, 7, 1, and 40%, respectively, for P4ClPhTC, P3ClPhTC, P34ClPhTC, and PMTC. All the results reported below, including those of Figure 3,

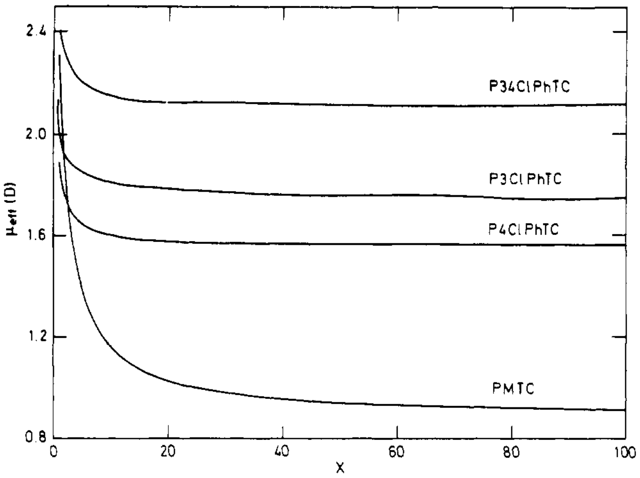

**Figure 3.** Effective dipole moment for P4ClPhTC, P3ClPhTC, P34ClPhTC, and PMTC chains as a function of the number of repeating units $x$. Values for PMTC were taken from ref 1. Computations were performed at 25 °C with $E_c = 0$, $E_\gamma = 1.0$ kcal mol$^{-1}$, and $\mu_0 = \mu_{x+1} = 1.5$ D. See the text for details.

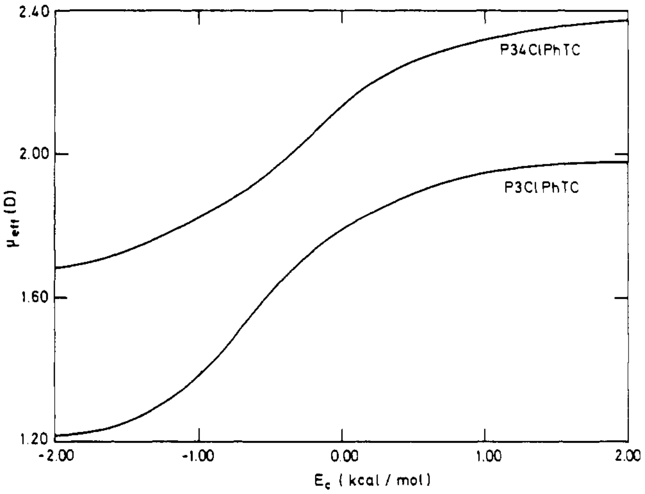

**Figure 4.** Effective dipole moment for P3ClPhTC and P34ClPhTC as function of the energy $E_c$ governing the relative incidence of $\chi = 0°$ versus $\chi = 180°$ orientations of the side groups. Computations were performed at 25 °C with $E_\gamma = 1.0$ kcal mol$^{-1}$ and $\mu_0 = \mu_{x+1} = 1.5$ D for chains having $x = 15$ repeating units. See the text for details.

were computed by using $\mu_0 = \mu_{x+1} = 1.5$ D for the end groups.

The sensitivity of $\mu_{eff}$ to the energy $E_\gamma$ governing the conformation of the thiocarbonate residue, although small, is larger than that in the case of PMTC. Specifically, a variation of 1 kcal mol$^{-1}$ in $E_\gamma$ changes $\mu_{eff}$ in ca. 14, 8, 8, and 2%, respectively, for P4ClPhTC, P3ClPhTC, P34ClPhTC, and PMTC. All the results presented in this work were obtained with $E_\gamma = 1.0$ kcal mol$^{-1}$.

As was indicated above, $\mu_{eff}$ for P3ClPhTC and P34ClPhTC depends also on the energy $E_c$ governing the orientation of the side group. This dependence is shown in Figure 4 for the case of short chains with $x = 15$ repeating units. As this figure indicates, the effect of $E_c$ is larger for P3ClPhTC than for P34ClPhTC due to the fact that the $\mu_2$ contribution departs more from the direction of the C–Ph bond (i.e., $\tau = 60$ and 30°, respectively, for P3ClPhTC and P34ClPhTC; see Figure 2) in the former than in the latter molecule. Consequently, the orientation of $\mu_2$ changes more with $\chi$ in the case of P3ClPhTC than in P34ClPhTC.

The comparison between the theoretical and experimental results of $\mu_{eff}$ is very good. Thus, taking the values computed with $x = 15$ to compare with the experimental values obtained for short chains in the Experimental Section, one finds $\mu_{eff} = 1.58$ D for P4ClPhTC, in excellent agreement with the experimental value of 1.57 D. In the cases of P3ClPhTC and P34ClPhTC, the results depend slightly on the value assigned to the conformational energy $E_c$ (see Figure 4); taking $E_c = -0.1$ kcal mol$^{-1}$, values of 1.75 and 2.05 D are obtained, respectively, for P3ClPhTC and P34ClPhTC, which are in good concordance with their respective experimental values of 1.65 and 1.87 D.

The dipole ratio $D_x = \langle\mu^2\rangle / x m_0^2 = \mu_{eff}^2 / m_0^2$ can be computed by identifying the dipole moment of the repeating unit $m_0^2$ with the sum of its contributions squared; i.e., $m_0^2 = 0.9^2$, $(0.9^2 + 1.6^2)$, $(0.9^2 + 1.6^2)$, and $(0.9^2 + 2.2^2)$, respectively, for PMTC, P3ClPhTC, P4ClPhTC, and P34ClPhTC. Values of this ratio computed at $x = 100$, when the effect of the dipoles $\mu_0$ and $\mu_{x+1}$ associated with end groups is negligible, are 1.0, 0.86, 0.72, and 0.76, respectively, for PMTC, P3ClPhTC, P4ClPhTC, and P34ClPhTC. Thus, values of $m_0^2$ for different units are uncorrelated in the case of PMTC, where they are separated by six rotating bonds, while there is a destructive correlation in the other three polymers, where the contributions are much closer along the chain. This partial cancellation of contributions is in part due to correlations between the dipoles within each repeating unit. Thus values of $D_x$ computed for a single unit ($x = 1$) taking $\mu_0 = \mu_{x+1} = 0$ are 1.0, 0.95, 0.93, and 0.94, respectively, for PMTC, P3ClPhTC, P4ClPhTC, and P34ClPhTC.

We can conclude that the statistical model used before for carbonate and thiocarbonate polymers having two methyl groups attached to the quaternary carbon can also be employed to calculate the dipole moments of thiocarbonates having chloro- or dichlorophenyl residues in one of the side groups. The presence of a second polar group in the repeating unit causes the dipole moment of the whole chain to be less sensitive to the end groups and, consequently, to reach an asymptotic limit for smaller values of $x$ than in the case of PMTC. However, despite the presence of this second polar group, $\mu_{eff}$ is not very sensitive to the conformational characteristics of the chain, due to the fact that the two contributions $\mu_1$ and $\mu_2$ are separated by four bonds having rotational freedom. The most important parameter is the direction of the dipole moment of the thiocarbonate group, which is opposite to that in carbonate residues; i.e., it points from S to C atoms.

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**Registry No.** (P3ClPhTC)($Cl_2C{=}S$) (copolymer), 133452-32-1; P3ClPhTC (SRU), 133451-80-6; (P4ClPhTC)($Cl_2C{=}S$) (copolymer), 133452-29-6; P4ClPhTC (SRU), 133451-78-2; (P34ClPhTC)($Cl_2C{=}S$) (copolymer), 133452-34-3; P34ClPhTC (SRU), 133451-82-8.