Dipole moment of poly(thiocarbonate)s derived from bisphenol A

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(Received 22 October 1990; revised 16 January 1991; accepted 16 January 1991)

The dipole moments of a series of poly(thiocarbonate)s derived from bisphenol A have been determined in 1,4-dioxane and benzene solutions at 298 K. The effect of the side chain structure of the polymer and the solvent on the dipole moment are analysed. A very small influence of the polymer structure on the dipole moment is observed.

(Keywords: poly(thiocarbonate)s; conformation; dielectric constant; dipole moment)

INTRODUCTION

Recently much attention has been focused on the solid state[1] and solution properties[2–5] of poly(thiocarbonate)s. A wide variety of poly(thiocarbonate)s with different lateral chains can be synthesized by phase transfer catalysis[6,7]. Most of the properties of these polymers have been analysed as a function of the side chain structure[1–5]. Studies relating to the dipole moment have not received the same attention, in spite of the conformational information that can be obtained from a knowledge of this.

In a previous paper[8], we reported the theoretical and experimental dipole moment of the poly(thiocarbonate) of 2,2′-bis(4-hydroxyphenyl)propane (PMTC). We compared the experimental value of the dipole moment with the theoretical results obtained using the rotational isomeric states model and the scheme developed by Hutnik and Suter[9] for polycarbonates, since there is a close similarity between carbonate and thiocarbonate molecules. Agreement between theoretical and experimental results was obtained, assuming that the end groups have dipole moments of approximately 1.5 D.

The aim of the present work is to analyse the influence of the side chain structure on the dipole moment of a series of poly(thiocarbonate)s derived from bisphenol A, the general structure of which is shown in *Scheme 1*.

This type of polymer, with no symmetry element, is sensitive to the specific solvent effects on chain conformations[10–14]. In principle, this should give rise to an excluded volume effect on the dipole moment of the polymer chain. For this reason the present study also includes the solvent dependence on dipole moments in 1,4-dioxane and benzene for some of the poly(thiocarbonate)s shown in *Scheme 1*.

EXPERIMENTAL

Polymers

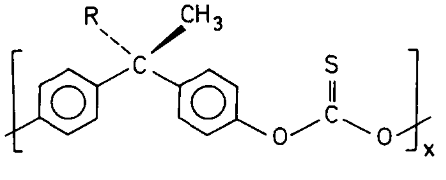
The polymers studied in this work were synthesized by phase transfer catalysis[6,7] and were fractionated and characterized[2,3] as described previously. Molecular weight and polydispersity of the samples were determined by size exclusion chromatography (s.e.c.). *Table 1* summarizes the molecular characteristics of the polymers studied.

Solvents

Benzene and 1,4-dioxane were used as solvents in refractometry, densimetry and dielectric measurements and were of RPE quality from Carlo Erba. They were dried over Merck 4 Å molecular sieves before use.

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,



R: $-H$; (PHTC)
$-CH_2-CH_3$; (PEtTC)
$-CH_2-CH(CH_3)_2$; (PiBuTC)
$-C_6H_5$; (PPhTC)

Scheme 1

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0032-3861/92/010194-04

Table 1 Molecular weight, polydispersity index, r, and degree of polymerization, x, of the poly(thiocarbonate)s studied

Polymer	$\bar{M}_w \times 10^{-3}$ (g mol^{-1})	$r = \bar{M}_w/\bar{M}_n$	x
PHTC	19.1	1.23	75
PEtTC	14.0	1.40	49
PiBuTC	40.0	1.24	128
PPhTC	93.0	2.07	280

298.00 ± 0.02 K, using liquids with known dielectric constants (i.e. benzene, toluene, cyclohexane)[15,16]. Polymer solutions in 1,4-dioxane were preserved over molecular sieves until immediately before they were used. The concentration range of polymer solutions was $1 \times 10^{-3} < w_2 < 8 \times 10^{-3}$ (w_2 = polymer weight fraction). The same solutions were used for dielectric constant, refractometry and densimetry measurements.

Refractometry

The differences between the refractive index of solutions and pure solvent, Δn, were measured at $\lambda = 546$ nm, in a Brice Phoenix 2000 V differential refractometer, calibrated with aqueous solutions of KCl at 298.0 K.

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 298.00 ± 0.01 K.

RESULTS

The dipole moment per repeat unit, μ_{eff}, of the poly(thiocarbonate)s has been determined using the Halverstadt and Kumler equations[17] for the molar polarization, $[P]_2^0$, and molar refraction, $[R]_2^0$, of the solute, both at infinite dilution:

$$[P]_2^0 = M_2\left\{\frac{3v_1}{(\varepsilon_1+2)^2}(\partial\varepsilon/\partial w_2)^0 + \frac{\varepsilon_1-1}{\varepsilon_1+2}[v_1+(\partial v/\partial w_2)^0]\right\}$$

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

where, for solution and pure solvent, respectively, v and v_1 are the specific volumes, ε and ε_1 are the dielectric constants and n and n_1 are the refractive indices, M_2 is the molecular weight of the repeat unit, and the superscript zero represents 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 dimethylcarbonate[18].

The value of μ_{eff} was obtained according to the Debye method:

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

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

In *Figure 1* the difference between the dielectric constant of polymer solutions and pure solvent, $\varepsilon - \varepsilon_1$, is plotted against the weight fraction of the polymer in the solution, w_2, for PHTC, PEtTC, PiBuTC and PPhTC in benzene at 298 K. *Figure 2* shows the same plot for

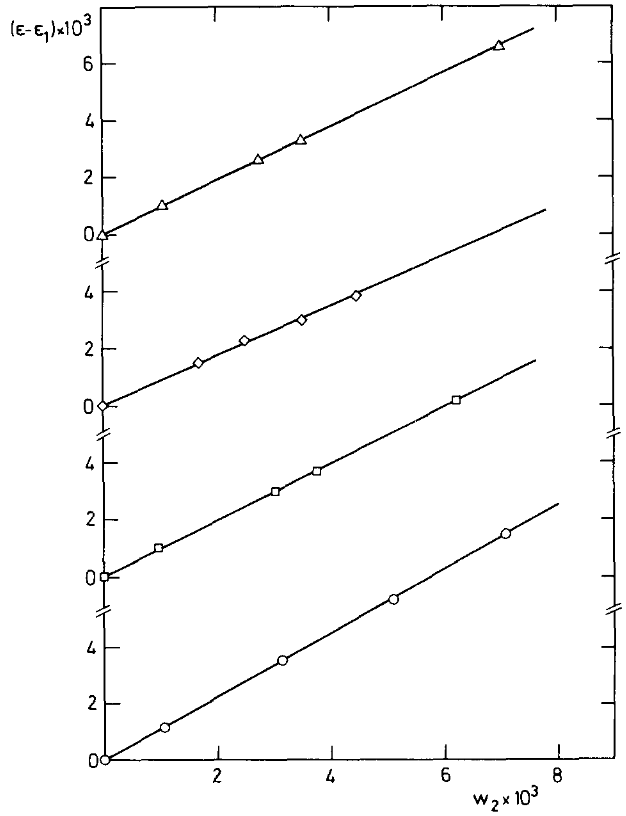

Figure 1 Dependence of dielectric constant on weight fraction of polymer, w_2, for PHTC (○), PEtTC (□), PiBuTC (◇) and PPhTC (△) in benzene at 298 K

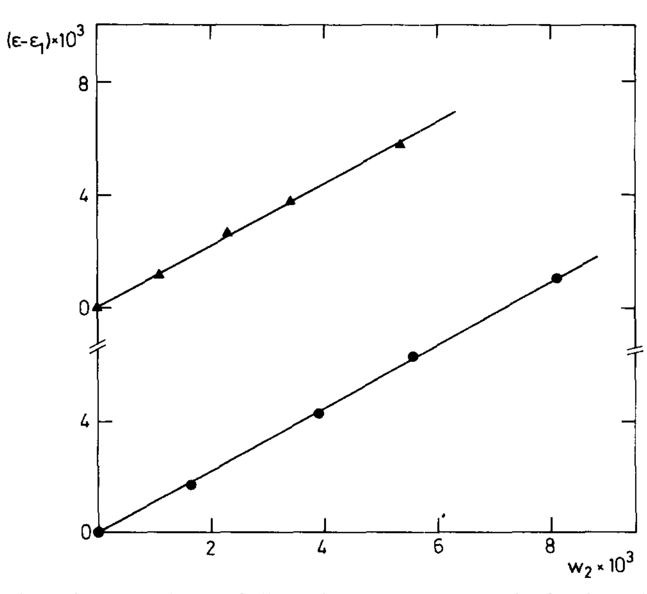

Figure 2 Dependence of dielectric constant on weight fraction of polymer, w_2, for PHTC (●) and PPhTC (▲) in 1,4-dioxane at 298 K

Table 2 Values of $(\partial\varepsilon/\partial w_2)^0$, $(\partial n/\partial w_2)^0$, $(\partial v/\partial w_2)^0$, molar polarization $[P]_2^0$ and refraction $[R]_2^0$, of solutions at infinite dilution, and effective dipole moment of poly(thiocarbonate)s at 298 K

Solvent[a]	Polymer	$(\partial\varepsilon/\partial w_2)^0$	$(\partial n/\partial w_2)^0$	$(\partial v/\partial w_2)^0$ ($cm^3 g^{-1}$)	$[P]_2^0$ ($cm^3 mol^{-1}$)	$[R]_2^0$ ($cm^3 mol^{-1}$)	μ_{eff} (D)
Bz	PHTC	1.129	0.1173	−0.3903	112.05	73.85	1.23
	PEtTC	0.987	0.1097	−0.3538	119.81	83.73	1.17
	PiBuTC	0.846	0.1029	−0.3102	127.40	94.77	1.06
	PPhTC	0.935	0.1202	−0.3680	135.39	98.49	1.15
Dx	PHTC	1.137	0.1885	−0.1706	136.67	101.02	1.11
	PPhTC	1.079	0.1901	−0.1811	91.94	66.20	1.12

[a] Bz = benzene; Dx = 1,4-dioxane

PHTC and PPhTC in 1,4-dioxane solution. Good linearity is observed in all cases.

From these results, the values of $(\partial\varepsilon/\partial w_2)^0$, $(\partial n/\partial w_2)^0$ and $(\partial v/\partial w_2)^0$ were determined as the slope of the corresponding plot by least-squares fit, for all the polymers in both solvents (see *Table 2*). The total molar polarization and refraction of the solute at infinite dilution and the experimental value of μ_{eff}, calculated according to the Halverstadt and Kumler method, are also included in *Table 2*.

DISCUSSION

The effective dipole moment of a macromolecule is a function of the degree of polymerization, x, for low molecular weights, reaching a constant value when this magnitude increases in the absence of excluded volume effect. On the other hand, for low molecular weights, μ_{eff} is drastically influenced by the end groups when these are polar. For these reasons, the effective dipole moment of the poly(thiocarbonate)s studied in each solvent have been corrected, taking into account the influence of molecular weight and end groups on the dipole moment. To this end, we have normalized the experimental μ_{eff} values at $x = 30$, in order to compare these results with those previously reported for other poly(thiocarbonate)s[8].

The end groups of poly(thiocarbonate)s are phenolic residues[6], which have a dipole moment of approximately 1.5 D.The dipole moment of the end groups ($\mu_0 = 1.5$ D) influences the dependence of x on μ_{eff}. Assuming that the degree of influence is the same for PMTC[8] as for the series of poly(thiocarbonate)s studied here, the experimental μ_{eff} value has been modified making use of the theoretical results for PMTC shown in Figure 3 of ref. 8. From the curve corresponding to 1.5 D in Figure 3 of ref. 8, the increment in μ_{eff} ($\Delta\mu_{eff}$) is obtained from the difference between the theoretical values of μ_{eff} at $x = 30$ and the x value for each poly(thiocarbonate) studied. *Table 3* summarizes the experimental μ_{eff}, the increment $\Delta\mu_{eff}$ and the corrected μ_{eff}^{cor}, for all the poly(thiocarbonate)s studied in benzene and in 1,4-dioxane at 298 K.

According to the results summarized in *Table 3*, a small influence of the side chain structure on the dipole moment can be observed. The maximum difference in μ_{eff} is 12% in benzene solution and 17% in 1,4-dioxane. Nevertheless it seems that a tendency to diminish μ_{eff} as the size of the alkyl side chain increases can be assumed. On the other hand, no solvent effect is observed.

Table 3 Values of the experimental effective dipole moment μ_{eff}, the increment in dipole moment $\Delta\mu_{eff}$ obtained from Figure 3 of ref. 8, and the corrected dipole moment μ_{eff}^{cor}, for PHTC, PEtTC, PiBuTC and PPhTC at 298 K

Solvent[a]	Polymer	μ_{eff} (D)	$\Delta\mu_{eff}$ (D)	μ_{eff}^{cor} (D)
Bz	PHTC	1.23	0.06	1.29
	PEtTC	1.17	0.04	1.21
	PiBuTC	1.06	0.08	1.14
	PPhTC	1.15	0.08	1.23
Dx	PHTC	1.11	0.06	1.17
	PMTC	0.97[b]	–	–
	PPhTC	1.12	0.08	1.20

[a] Bz = benzene; Dx = 1,4-dioxane
[b] Taken from ref. 8

ACKNOWLEDGEMENTS

Thanks are due to Dr Luis Hernán Tagle (Pontificia Universidad Católica de Chile) for the synthesis of the polymer samples. Thanks are also due to the Spanish Ministerio de Educación y Ciencia for financial help through a Cooperation Program between Universidad Complutense de Madrid and Pontificia Universidad Católica de Chile. D.R. and L.G. express their thanks to DIUC Universidad Católica de Chile and FONDECYT for partial financial support.

REFERENCES

1 Yazdani-Pedram, M., Soto, E., Tagle, L. H., Díaz, F. R., Gargallo, L. and Radic, D. *Thermochim. Acta* 1986, **105**, 149
2 Gargallo, L., Soto, E., Díaz, F. R., Tagle, L. H. and Radic, D. *Eur. Polym. J.* 1987, **23**, 571
3 Gargallo, L., Soto, E., Tagle, L. H. and Radic, D. *J. Appl. Polym. Sci.* 1988, **35**, 1103
4 Fabre, M. J., Tagle, L. H., Gargallo, L., Radic, D. and Hernández-Fuentes, I. *Eur. Polym. J.* 1989, **12**, 1315
5 Gargallo, L., Tagle, L. H. and Radic, D. *Br. Polym. J.* 1990, **22**, 227
6 Tagle, L. H., Díaz, F. R., Vega, J. C. and Alquinta, F. *Makromol. Chem.* 1985, **186**, 915
7 Tagle, L. H., Díaz, F. R. and Riveros, P. E. *Polym. J.* 1986, **18**, 501
8 Saiz, E., Fabre, M. J., Gargallo, L., Radic, D. and Hernández-Fuentes, I. *Macromolecules* 1989, **22**, 3660

9 Hutnik, M. and Suter, U. W. *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr.* 1987, **28** (2), 293

10 Roig, A. and Hernández-Fuentes, I. *An. Quim.* 1974, **70**, 668

11 Baysal, B. and Aras, L. *Macromolecules* 1985, **18**, 1693

12 Burshtein, L. L. and Stepanova, T. P. *Vysokomol. Soedin. Ser. A* 1969, **11**, 2885

13 Yamaguchi, N., Sato, M., Ogawa, E. and Shima, M. *Polymer* 1981, **22**, 1464

14 Baysal, B., Lowry, B. A., Yu, H. and Stockmayer, H. 'Dielectric Properties of Polymers', Plenum Press, New York, 1972

15 Petro, A. J. and Smith, G. P. *J. Am. Chem. Soc.* 1957, **79**, 6142

16 Heston, W. M. and Smith, G. P. *J. Am. Chem. Soc.* 1950, **72**, 99

17 Halverstadt, I. F. and Kumler, W. D. *J. Am. Chem. Soc.* 1942, **64**, 2988

18 Yasumi, M. *J. Chem. Soc. Jpn* 1939, **60**, 1208