Notes

Dipole Moment of Polycarbonates with Chlorophenyl or Dichlorophenyl Side Groups

Irmina Hernández-Fuentes,*,† Fernanda Rey-Stolle,† Luis Hernán Tagle,‡ and Enrique Saiz§

Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile, and Departamento de Química Física, Universidad de Alcalá, 28871 Alcalá de Henares, Madrid, Spain

Received November 13, 1991
Revised Manuscript Received February 3, 1992

Introduction

In a previous paper[1] we have reported a conformational analysis of asymmetric polythiocarbonates derived from Bisphenol A, having methyl and chlorophenyl or methyl and dichlorophenyl groups attached to the quaternary carbon, based on the comparison between experimental and theoretical values of their dipole moment. The dipole moment of these polymer chains can be reproduced using either the statistical model developed by Sundararajan for methyl phenyl carbonate[2] or the one developed by Hutnik and Suter for polycarbonates[3] which has been used before for thiocarbonate polymers having two methyl groups attached to the quaternary carbon.[4]

In the analysis of the dipole moments of thiocarbonates we had to assume that the dipole moments assigned to either carbonate or thiocarbonate groups are equal in magnitude but they had opposite direction; i.e., taking the direction of the dipole from negative to positive centers of charge, it points from oxygen to carbon in carbonates, while it goes from carbon to sulfur in thiocarbonates. This assumption was confirmed by quantum mechanics calculations of the charge distribution in both kinds of groups. However, we thought that it would be interesting to have some kind of experimental evidence for this difference in the dipole moments of these groups. With this aim, we selected for the present work the equivalent carbonate compounds of the thiocarbonates studied in the previous paper. We measured their experimental dipole moments and performed the theoretical analysis using the same procedures previously employed. The comparison between the results obtained for the two series of compounds allowed us to ascertain the direction of the dipole moment of these two groups.

Experimental Section

(a) Materials. Samples of polycarbonates of 1,1-bis(4-hydroxyphenyl)-1-(3-chlorophenyl)ethane (P3ClPhC), 1,1-bis(4-hydroxyphenyl)-1-(4-chlorophenyl)ethane (P4ClPhC), and 1,1-bis-(4-hydroxyphenyl)-1-(3,4-dichlorophenyl)ethane (P34ClPhC), previously synthesized[5] by phase-transfer catalysis, were selected for the present work. Figure 1 shows the structure of these

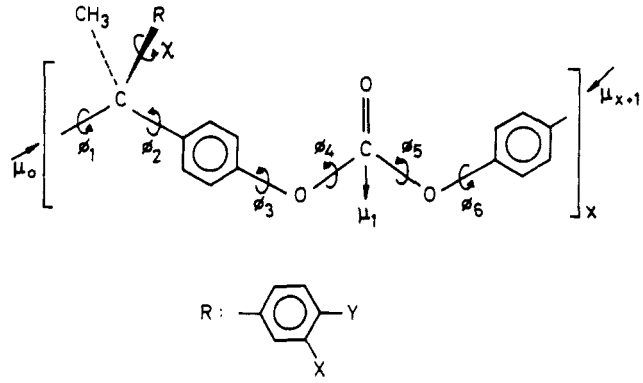

Figure 1. Sketches of the carbonate chain shown in its all-trans (i.e., $\phi = 0°$) conformation. R represents the polar side group, namely, 3-chlorophenyl in P3ClPhC (X = Cl; Y = H), 4-chlorophenyl in P4ClPhC (X = H; Y = Cl), or 3,4-dichlorophenyl in P34ClPhC (X = Cl; Y = Cl). Dipole moments μ_1 for the carbonate group, and μ_0 and μ_{x+1} for the end groups are represented by arrows pointing from negative to positive center of charges. The only difference between these compounds and their thiocarbonate counterparts is the reversal of the direction of μ_1 resulting from the replacement of C=O by C=S bonds (see Figure 2 of ref 1).

Table I
Experimental Values of $(\partial\epsilon/\partial w_2)°$, $(\partial n/\partial w_2)°$, $(\partial v/\partial w_2)°$, Total Molar Polarization $[P]_2°$, and Refraction $[R]_2°$ of Polycarbonates with Chlorophenyl or Dichlorophenyl Side Chains, in Benzene at 25 °C

polymer	$(\partial\epsilon/\partial w_2)°$	$(\partial n/\partial w_2)°$	$(\partial v/\partial w_2)°$, $cm^3 \cdot g^{-1}$	$[P]_2°$, $cm^3 \cdot mol^{-1}$	$[R]_2°$, $cm^3 \cdot mol^{-1}$
P3ClPhC	1.498	0.1009	−0.3989	176.74	96.89
P4ClPhC	1.402	0.1080	−0.4135	168.93	96.82
P34ClPhC	1.631	0.1056	−0.4472	198.23	101.98

polymers. Number-average molecular weights for P3ClPhC, P4ClPhC, and P34ClPhC, determined by size-exclusion chromatography, were 34 000 ($x = 97$), 31 000 ($x = 88$), and 28 000 ($x = 73$), respectively, where x is the number of repeating units. Benzene used as solvent in refractometry, densimetry, and dielectric measurements was Carlo Erba of RPE quality. It was dried over Merck 4-Å molecular sieves.

(b) Measurements. Dielectric constant, ϵ, refractive index, n, and specific volume, v, measurements were performed at 25 °C with the equipment already described in the previous paper.[1] The concentration range of polymer solutions was $1 \times 10^{-3} \leq w_2 \leq 6 \times 10^{-3}$ (w_2 = polymer weight fraction).

Results and Discussion

The experimental dipole moment per repeating unit, μ_{eff}, of the three polycarbonates was obtained according to the Debye method by using the Halverstadt and Kumler equations as was already described.[1]

Figure 2 shows the dependence of the dielectric constant on polymer concentration for P3ClPhC, P4ClPhC, and P34ClPhC in benzene solution at 25 °C.

The values of $(\partial\epsilon/\partial w_2)°$, $(\partial n/\partial w_2)°$, and $(\partial v/\partial w_2)°$ for the three polymers are summarized in Table I, together with the total molar polarization, $[P]_2°$, and refraction, $[R]_2°$, at infinite dilution. The corresponding values of the experimental effective dipole moments, μ_{eff}, are shown in the second column of Table II.

† Universidad Complutense.
‡ Pontificia Universidad Católica de Chile.
§ Universidad de Alcalá.

0024-9297/92/2225-3291$03.00/0

Table II
Comparison between the Effective Dipole Moments of Carbonate and Thiocarbonate Polymers

R side chain	μ(carbonates)/D			μ(thiocarbonates[a])/D			μ(carb)/μ(thio)	
	exptl	calc	exptl/calc	exptl	calc	exptl/calc	exptl	calc
3-chlorophenyl	1.75	1.88	0.93	1.65	1.75	0.94	1.06	1.07
4-chlorophenyl	1.85	1.89	0.98	1.57	1.58	0.99	1.18	1.20
3,4-dichlorophenyl	2.05	2.40	0.85	1.87	2.06	0.91	1.10	1.17

[a] From ref 1.

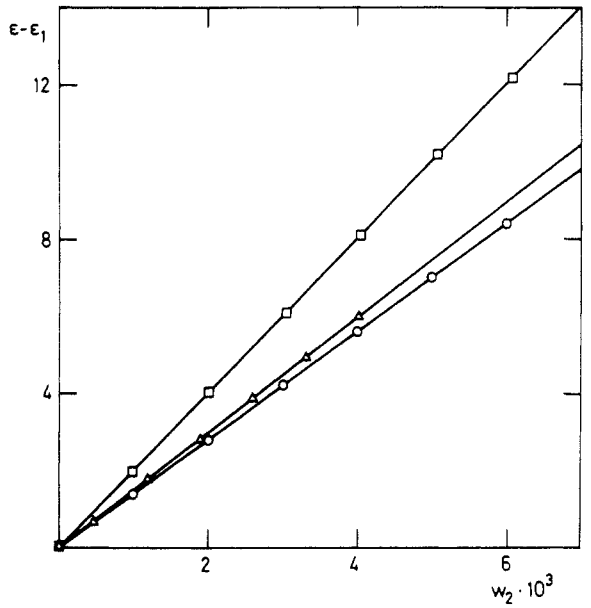

Figure 2. Dependence of the dielectric constant (ε) of benzene solutions of P3ClPhC (△), P4ClPhC (○), and P34ClPhC (□) on the weight fraction of polymer w_2. T = 25 °C. ϵ_1 = dielectric constant of the solvent.

Theoretical calculations were performed with the same procedures and exactly the same set of parameters used for the thiocarbonate polymers, with the only exception of the dipole moment of the carbonate groups which was taken to have the same magnitude as in thiocarbonates (0.9 D) but pointing from oxygen to carbon atoms.

The calculations were carried out for chains containing from x = 1 to x = 100 repeating units. As in the case of thiocarbonates, the values of μ_{eff} reach asymptotic limits for fairly small chains. For instance, differences between the values computed at x = 15 and x = 100 are ca. 2%. Theoretical values of μ_{eff} shown below for each carbonate polymer were obtained for chains having the number of repeating units indicated in the Experimental Section for that polymer.

Table II summarizes the results obtained in the present work for carbonates together with the values reported before for thiocarbonates. Columns four and seven of that table show the ratios between experimental and calculated values for both series of polymers, and they indicate that the agreement between theory and experiment is very similar for the two kinds of groups. The last two columns on the table show the ratios between the values obtained, both experimental and theoretical, for the two series, and they indicate that the dipole moments of carbonates are ca. 10–20% higher than those of thiocarbonates.

Since the only difference between the calculations performed for the two series of polymers is the direction of the dipole moment of carbonate and thiocarbonate groups, we conclude that our analysis supports the results of quantum mechanics calculations of charge distributions which indicate that the dipole moment points from oxygen to carbon in carbonates and from carbon to sulfur in thiocarbonates.

Acknowledgment. This work has been supported by DGICYT (Spain) under Grant No. PB89-0089.

References and Notes

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Registry No. P3ClPhC/$HOCO_2H$ (copolymer), 140201-97-4; P3ClPhC/$HOCO_2H$ (SRU), 133451-79-3; P4ClPhC/$HOCO_2H$ (copolymer), 140201-98-5; P4ClPhC/$HOCO_2H$ (SRU), 133451-77-1; P34ClPhC/$HOCO_2H$ (copolymer), 140201-99-6; P34ClPhC/$HOCO_2H$ (SRU), 133451-81-7.