The trends observed generally paralleled findings of other studies.

The need for low volatility and high electrical conductivity for solutions sampled with instrumentation used here imposes some significant limitations on systems amenable to EHMS analysis. However, recent improvements in the EH ion source design[33] have allowed sampling of aqueous solutions. Higher ion mobilities in water allow lower concentration for a given conductivity. This along with the solvent properties of water should greatly expand the range of systems amenable to EHMS analysis.

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Registry No. Poly(ethylene glycol) (SRU), 25322-68-3; $RbNO_3$, 13126-12-0; $LiNO_3$, 7790-69-4; $CsNO_3$, 7789-18-6; CsI, 7789-17-5; $NaNO_3$, 7631-99-4; KNO_3, 7757-79-1.

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Solution Dipole Moments of Atactic Poly(*p*-chlorostyrene) and Poly(*p*-bromostyrene) and Their Dependence on Temperature and Solvent

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ABSTRACT: Dipole moments of poly(*p*-chlorostyrene) (PPCS) and two samples of poly(*p*-bromostyrene) (PPBS) were extracted from dielectric and refractive index measurements performed on their dilute *p*-dioxane and carbon tetrachloride (CCl_4) solutions at temperatures of 20 and 50 °C. The mean-square dipole moments per repeat unit, $\langle\mu^2\rangle/x$, measured in *p*-dioxane at 20 and 50 °C were 2.11 and 2.46 D^2 for PPCS and 2.20–2.49 and 2.44–2.72 D^2 for the PPBS's. A 20% reduction in $\langle\mu^2\rangle/x$ was observed for PPCS in CCl_4, where 1.89 D^2 was obtained at 50 °C, while the dipole moments measured for one of the PPBS's in CCl_4, 2.12 and 2.54 D^2 at 20 and 50 °C, were nearly the same as those observed in *p*-dioxane. Dipole moments observed for PPCS and PPBS in both solvents increased as the temperature was raised, leading to $d \ln \langle\mu^2\rangle/dT \approx 0.005\ °C^{-1}$. These results are compared with previous dipole moment measurements performed on PPCS in a variety of solvents and with the dipole moments calculated by Saiz et al.[6] using a conformational model appropriate to polystyrene. ^{13}C-NMR spectroscopy was employed to determine the tacticity of the PPCS and PPBS samples used in this study, so that we could compare the observed dipole moments with those calculated for PPCS and PPBS chains of the appropriate stereoregularity.

Introduction

Among those physical properties of polymers measured in dilute solution, the dipole moments have often been used[1] to characterize the conformations and microstructures of polar homo- and copolymers. Unlike the dimensions of a polymer chain, the mean-square dipole moment, $\langle\mu^2\rangle$, can be measured over the entire range of chain length from monomer to high molecular weight polymer. In addition, long-range excluded volume interactions are not expected[2-5] to affect the dipole moments of polymers with no distinguishable direction along their chain contour. Only the dipole moments of polymers possessing dipole moment components parallel to the chain contour are expected to be sensitive to excluded volume effects. Thus,

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unlike the chain dimensions, polymer dipole moments measured in a variety of nonpolar solvents should be the same, eliminating the need to perform measurements in a Θ-solvent in order to compare with results calculated without consideration of excluded volume effects.

Saiz et al.[6] have compared the dipole moments measured for poly(p-chlorostyrene) (PPCS) to those calculated for PPCS using the conformational model derived by Yoon et al.[7] for polystyrene (PS). Attachment of a halogen substituent on the para position of the phenyl rings in PS should not affect the conformations available to the chain. The same conformational model should be appropriate for PS and its parahalogenated derivatives. Saiz et al.[6] found agreement between the dipole moments and their temperature dependence reported in the literature for PPCS and those calculated with the conformational model derived for PS.

More recently, however, Work[8] and his associates have reported measurements of $\langle\mu^2\rangle$ performed on PPCS in solutions using two different solvents and in undiluted bulk. It was found that the mean-square dipole moments per repeat unit, $\langle\mu^2\rangle/x$, are larger than those previously reported and they exhibit a positive temperature coefficient, in opposition to most previous measurements and the temperature dependence, d ln $\langle\mu^2\rangle/dT$, calculated by Saiz et al.[6] using the PS conformational model.

In the present study the dipole moments of two parahalogenated derivatives of PS, PPCS and poly(p-bromostyrene) (PPBS), were measured in two different nonpolar solvents that have very similar dielectric constants at temperatures of 20 and 50 °C. The stereoregularities of the PPCS and PPBS samples studied were determined by ^{13}C-NMR spectroscopy in order to facilitate comparison with the calculated dipole moments, which Saiz et al.[6] demonstrated to be sensitive to the stereosequence of the PPCS chains.

Experimental Methods

Dielectric constants were measured with a WTW Dipolmeter DMO1 using a water-jacketed dielectric cell DFL-1. A thermostatically controlled Bausch and Lomb Abbe-type refractometer was used to obtain refractive indices.

PPCS was obtained from Aldrich (no. 18,169-2, lot no. 08) and PPBS-I from Polysciences (no. 7030, lot no. 11299). A sample of PPBS-II, previously synthesized in our laboratory[9] from p-bromostyrene monomer, was also studied here, because the commercial PPBS-I was found to contain ca. 30% orthobrominated styrene units, apparently the result of polymerization of a mixture of p- and o-bromostyrene. A Pressure Chemical Co. sample of atactic polystyrene (lot no. 80317) was also used in our ^{13}C-NMR analysis.

Certified ACS grade p-dioxane and CCl_4 obtained from Fisher Scientific were used to prepare PPCS and PPBS solutions having solute weight fractions, W_2, between 0.5% and 3.0%. The dielectric constant ϵ and refractive index n for each polymer solution studied exhibited a linear dependence on concentration W_2 and were fitted to the following equations:

$$\epsilon = \epsilon_1(1 + \alpha W_2) \quad (1)$$

$$n = n_1(1 + \gamma W_2) \quad (2)$$

Subscripts 1 and 2 denote solvent and solute, respectively. α and γ are obtained by extrapolation of $\Delta\epsilon/W_2$ and $\Delta n/n_1W_2$, respectively, to infinite dilution.

Mean-square dipole moments $\langle\mu^2\rangle$ were obtained from the equation of Smith and Guggenheim[10]

$$\langle\mu^2\rangle = \frac{27kTM}{4\pi N_A d_1(\epsilon_1 + 2)^2}(\alpha\epsilon_1 - 2\gamma n_1^2) \quad (3)$$

where M is the molecular weight of the polymer solute, N_A is Avogadro's number, and d_1, ϵ_1, and n_1 are the density, dielectric constant, and refractive index, respectively, of the solvent. Solvent properties at T = 20 and 50 °C are presented in Table I.

Table I
Solvent Properties

property	CCl_4 T = 20 °C	CCl_4 T = 50 °C	p-dioxane T = 20 °C	p-dioxane T = 50 °C
d_1 [a]	1.59400	1.54520	1.03362	1.00000
ϵ_1 [a]	2.238	2.178	2.218	2.166
n_1 [b]	1.46060	1.44328	1.42295	1.40984

[a] Densities and dielectric constants were obtained from Timmermans.[11] [b] Refractive indices were measured in this study.

Table II
Dielectric and Refractive Index Increments and Mean-Square Dipole Moments per Repeat Unit for PPCS and PPBS in p-Dioxane and CCl_4

polymer	solvent	$\alpha\epsilon_1$ 20 °C	$\alpha\epsilon_1$ 50 °C	γ 20 °C	γ 50 °C	$\langle\mu^2\rangle/x$, D^2 20 °C	$\langle\mu^2\rangle/x$, D^2 50 °C
PPCS	p-dioxane	2.39	2.46	0.110	0.128	2.11	2.46
PPCS	CCl_4		2.93		0.146		1.89
PPBS-I	p-dioxane	1.90	1.91	0.102	0.118	2.20	2.49
PPBS-I	CCl_4	2.87	2.90	0.134	0.132	2.12	2.54
PPBS-II	p-dioxane	2.10	2.06	0.100	0.110	2.44	2.72

PS, PPCS, and PPBS-I 20 wt % solutions were made in 4:1 by volume mixtures of hexachlorobutadiene:p-dioxane-d_8 with a trace of hexamethyldisiloxane added as a reference. PPBS-II was dissolved at a concentration of 20 wt % in deuteriochloroform to which a trace of tetramethylsilane was added as a reference. The solution ^{13}C-NMR spectra of PS, PPCS, and PPBS-I were measured at 105 °C, while that of PPBS-II was observed at 40 °C, using a Varian XL-200 spectrometer operating at 50.3 MHz for ^{13}C. A 90° pulse was applied to the ^{13}C spins, and the free induction decay was acquired via continuous broad-band scalar decoupling of the protons. The FID's were stored in 32K computer locations using a spectral window of 8–10 kHz. Between 2000 and 12 000 FID's were signal-averaged to obtain each spectrum using a pulse sequence delay time of 5.0 s for PS, PPCS, and PPBS-I and 1.4 s for PPBS-II.

Results

Table II presents the dielectric and refractive index increments $\alpha\epsilon_1$ and γ (see eq 1 and 2) measured for PPCS and PPBS in p-dioxane and CCl_4. Mean-square dipole moments per repeat unit, $\langle\mu^2\rangle/x$, derived for PPCS and PPBS from eq 3 are also given in this table. The dipole moments for both polymers increase with increasing temperature and are characterized by d ln $\langle\mu^2\rangle/dT$ = 0.005 °C^{-1} (PPCS in p-dioxane), 0.004 °C^{-1} (PPBS in p-dioxane), and 0.006 °C^{-1} (PPBS in CCl_4).

^{13}C-NMR spectra at 50.3 MHz for PS, PPCS, and PPBS-II are shown in Figure 1.

Discussion

Recently, the resonances observed in the methylene and C_1 aromatic regions of the high-resolution ^{13}C-NMR spectra of atactic polystyrene have been assigned to the various stereosequences occurring along the chain. The assignments were made possible through the synthesis, separation, and ^{13}C-NMR study of the styrene diastereopentamers by Sato et al.[12] and the ^{13}C-NMR chemical shifts calculated via the γ-gauche method[13] by one of the present authors.[14]

Our previous study[9] of parabrominated styrene copolymers demonstrated that the backbone carbon resonances are insensitive to parabromination. Thus, by comparison of the methylene carbon portions of the ^{13}C-NMR spectra of PPCS, PPBS, and PS (see Figure 1a), coupled with a knowledge of the stereosequence assign-

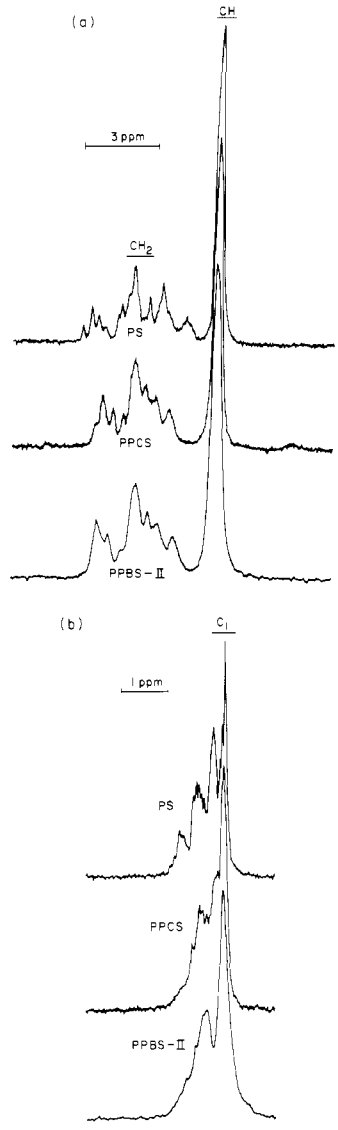

Figure 1. ^{13}C-NMR spectra of atactic PS, PPCS, and PPBS-II recorded at 50.3 MHz: (a) methylene carbon regions; (b) C_1 aromatic carbon regions.

ments in atactic PS, it is possible to estimate the tacticity of both parahalogenated polystyrenes. Such a comparison leads to the conclusion that the samples of PPCS and PPBS used in our dipole moment studies are both atactic and Bernoullian in structure with probabilities of meso dyads $P_m \approx 0.5$. This finding is further supported by a comparison of the C_1 aromatic resonances shown in Figure 1b.

Saiz et al.[6] calculate $\langle\mu^2\rangle/x = 2.0$ D^2 at 27 °C for PPCS chains with $P_m = 0.5$. This is in agreement with the value 2.11 D^2 we measure for PPCS ($P_m \approx 0.5$) in *p*-dioxane at $T = 20$ °C. Since the dipole moments[15] of *p*-chlorotoluene and *p*-bromotoluene are the same, dipole moments calculated and measured for PPCS and PPBS of the same tacticity should also coincide. At $T = 20$ °C we find $\langle\mu^2\rangle/x = 2.20$ D^2 (PPBS-I) and 2.44 D^2 (PPBS-II) in *p*-dioxane and 2.12 D^2 (PPBS-I) in CCl_4, which compare favorably with the values measured (2.11 D^2) and calculated (2.0 D^2) for PPCS.

Over the temperature range $T \approx 20$–60 °C Saiz et al.[6] calculate d ln $\langle\mu^2\rangle/dT = -0.001$ °C^{-1} for atactic ($P_m = 0.5$) PPCS chains. We find larger, positive temperature coefficients for the dipole moments of atactic PPCS and PPBS; d ln $\langle\mu^2\rangle/dT = 0.005$ °C^{-1} (PPCS in *p*-dioxane), 0.004 °C^{-1} (PPBS-I and PPBS-II in *p*-dioxane), and 0.006 °C^{-1} (PPBS-I in CCl_4). Consequently, dipole moments calculated by Saiz et al.[6] for atactic PPCS and PPBS using the conformational description of PS derived by Yoon et al.[7] agree in magnitude with those we measure for the same halogenated polystyrenes, but the calculated and observed temperature coefficients of the dipole moments are of opposite sign.

Table III
Experimental Dipole Moments of PPCS

T, °C	solvent	$\langle\mu^2\rangle/x$, D^2	reference
0	*p*-xylene	3.25	8
0	benzene	4.06	8
20	*p*-dioxane	2.11	present study
20	*p*-dioxane	2.20 (PPBS-I)	present study
20	*p*-dioxane	2.44 (PPBS-II)	present study
20	CCl_4	2.12 (PPBS-I)	present study
20	toluene	2.13	16
20	*p*-xylene	1.99	16
20	isopropylbenzene	1.54	16
25	benzene	2.55	17
25	CCl_4	2.00	17
25	benzene	1.93	18
50	*p*-dioxane	2.46	present study
50	*p*-dioxane	2.49 (PPBS-I)	present study
50	*p*-dioxane	2.72 (PPBS-II)	present study
50	CCl_4	1.89	present study
50	CCl_4	2.54 (PPBS-I)	present study
50	toluene	1.90	16
50	isopropylbenzene	1.42	16
50	benzene	2.02	18

As mentioned in the Experimental Methods section, the commercial PPBS sample (PPBS-I) was found to contain ca. 30% orthobrominated styrene units. We calculated dipole moments for random copolymers of *p*-bromo- and *o*-bromostyrene with 70% para- and 30% ortho-bromination. The conformational description derived by Yoon et al.[7] for PS was employed, and the calculations were performed as described in our study of styrene–*p*-bromostyrene copolymers.[9] We find $\langle\mu^2\rangle/x$ calculated for the 70:30 para:ortho copolymer to be 10–15% larger than for PPBS homopolymer, when each polymer is atactic ($P_m = 0.5$). The temperature coefficient of the dipole moment calculated for the 70:30 copolymer was negative, as calculated here for PPBS and by Saiz et al. for PPCS but about 50% smaller in magnitude. Keeping in mind the small differences in the dipole moments calculated for PPBS-I and PPBS-II, we treat the data obtained from both bromostyrene polymers as appropriate for PPBS.

In Table III we present the dipole moments measured for PPCS in solution by previous workers together with the values obtained in the present study. The dipole moment measurements lead to the following temperature coefficients d ln $\langle\mu^2\rangle/dT$: 0.004–0.006 °C^{-1} (present study), 0.009 °C^{-1} (Work et al.[8]), 0.002 °C^{-1} (Kotera et al.[18]), –0.005 °C^{-1} (Baysal et al.[17]), and –0.003 to –0.004 °C^{-1} (Burshtein and Stepanova[16]). In addition to the disagreement between the observed temperature dependencies of the dipole moments, there is considerable scatter in the reported magnitudes of $\langle\mu^2\rangle/x$ for PPCS. A portion of this scatter may in part be attributable[6] to differences in tacticity among the PPCS samples studied. Aside from the present study, all previous investigations did not characterize the stereosequence of the PPCS sample whose dipole moment was measured.

The most striking observation drawn from Table III is the apparent sensitivity of $\langle\mu^2\rangle/x$ for PPCS to the solvent in which the dipole moment measurements are performed. Values of $\langle\mu^2\rangle/x$ typically differ by ca. 20%, depending on the solvent.

Burshtein and Stepanova[16] noted that the dipole moment of PPCS increases as the quality of the solvent for PPCS increases, as manifested by increases in intrinsic viscosities and Huggins' constants. However, as pointed out by Burshtein and Stepanova,[16] the increase observed in $\langle\mu^2\rangle/x$ with increasing solvent quality, i.e., chain expansion as indicated by increasing intrinsic viscosity, is not a consequence of long-range excluded volume effects. As mentioned previously, the dipole moments of most polar polymers, including the parahalogenated polystyrenes, are expected[2-5] to be exclusively sensitive to short-range intramolecular interactions, or conformations, and not to excluded volume effects.

Hence, there may be specific, short-range solvent effects occurring in PS and its parahalogenated derivatives that affect the local backbone conformation. These specific solvent effects may also be the source of the disparity among the values reported for the temperature dependence of the dipole moments of PPCS.

Another possible manifestation of this conformational sensitivity to solvent is the solvent-dependent chemical shifts[14] observed in the ^{13}C-NMR spectra of PS. It has been demonstrated[13,14] that the ^{13}C-NMR chemical shifts observed for a given carbon type in each of the different stereosequences in PS are due to conformational differences among the stereosequences. Thus, it would appear that the observed solvent sensitivity of the backbone methylene and C_1 phenyl ring carbon chemical shifts, whose relative values depend on PS backbone conformation, may be due to differences in local backbone conformations produced by the same solvent–polymer interactions that affect the dipole moments of parachlorinated polystyrene.

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Registry No. Poly(p-chlorostyrene) (homopolymer), 24991-47-7; poly(p-bromostyrene) (homopolymer), 24936-50-3; poly(bromostyrene) (homopolymer), 39350-27-1.

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