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Mass Spectrometric Study of Interactions between Poly(ethylene glycols) and Alkali Metals in Solution

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ABSTRACT: Solution-phase ion–polymer interactions between poly(ethylene glycols) (PEG's) and alkali metal ions (in glycerol) were studied by electrohydrodynamic ionization mass spectrometry. Metal complexes of different oligomers (with degree of polymerization (n) as low as 4) were resolved. Mass spectral intensities of these complex ions supported the prediction of multiple-ion association by larger oligomers. The minimum n required for this multiple-ion association correlated positively with the size of the metal ion. In EH mass spectra of glycerol solutions containing PEG and more than one metal ion, preferential complexation by the PEG oligomers for one metal over another was observed. From the total spectral intensities of each metal complex, bulk selectivity of PEG for alkali metal ions was found to follow the order $K^+ > Cs^+ > Rb^+ > Na^+ > Li^+$ (1:0.94:0.79:0.46:0.08). These findings generally agreed with studies by other methods, although detection of lithium–PEG adducts has apparently not been previously reported in protic solvents.

Introduction

Interactions between metal ions and macromolecules play a fundamental role in many important phenomena, including selective transport of metal ions through membranes,[1] phase-transfer catalysis,[2] and biological enzyme systems.[3] To understand these interactions, properties such as the stoichiometry and structure of complexes formed, the site(s) of interaction, and the binding ability and selectivity of a given polymer for various metals have to be characterized. This study considers a way of probing two of these (the binding ability and selectivity), using a poly(ethylene glycol) model system in glycerol.

Linear poly(ethylene glycols) ($HO-(CH_2CH_2O)_n-H$, PEG's) of low molecular weight predominantly exist in a "zigzag" form, resulting in an open-coil extended conformation.[4] Chains longer than nine repeat units prefer the "meander" conformation, giving a more compact helical coil.[4] These chains form complexes with a variety of metals. The interactions between the polymer and metal ions are believed to involve the same kind of ion–dipole interactions observed in cyclic polyethers. In fact, proton,[5-7] carbon-13,[5,8] and sodium-23[9-11] magnetic resonance experiments have confirmed that the ethereal oxygens on the oxyethylene units of both PEG's and crown ethers are the sites of interaction with metal ions. Despite the similarity in their interaction mechanism, the complexing ability of noncyclic polyethers can differ markedly from that of their cyclic analogues. Yanagida et al.,[12] using a solvent extraction method, reported that the extracting ability of PEG is related to the number of repeating units on the chain. The extracting ability of low molecular weight PEG's ($n < 40$) for K^+ was smaller than that of

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18-crown-6 while larger PEG's could extract K$^+$ more efficiently than the cyclic ether. Ono et al.,[13] using conductometric measurements and nonlinear multiple regression computer analysis, reported that a minimum of 12–14 oxyethylene units separated adjacent charges (attached ions) on PEG complexes of K$^+$, Cs$^+$, and Rb$^+$. For the Na$^+$ complex, 28 oxyethylene units were reportedly required between charges.

Both conductometry and solvent extraction measure the average bulk behavior of the polymer and infer individual oligomer contributions; metal ion complexes of different oligomers are not resolved. While models calculating oligomer contributions from observed bulk behavior often provide useful estimates of species' distributions, they generally involve approximations and/or assumptions that can bias the results. These uncertainties could be partly relieved by examining monodisperse samples. However, use of such samples may distort or ignore the effect of one oligomer on another, and in any event, monodisperse samples are seldom available except for the smallest oligomers. The alternative approach of employing analytical methods that resolve oligomer contributions is made difficult because of the physical and spectroscopic similarity of adjacent oligomers. However, each oligomer has a characteristic mass separated from successive oligomers by the mass of the repeat unit. Thus, each oligomer–metal ion complex has a specific mass-to-charge ratio, suggesting that complexes of varying stoichiometry with different oligomers could be resolved by mass spectrometry. However, volatility constraints of most mass spectrometric techniques make them unsuitable for direct analysis of large molecules or solution systems.[14,15] Furthermore, the energy usually imparted to sample molecules during volatilization and/or ionization can greatly affect equilibria and/or cause fragmentation of molecular ions, impeding mixture analysis and characterization of labile molecules. While field desorption (FDMS) has been the most frequently successful technique for generating intact molecular ions of nonvolatile compounds, even FDMS spectra of polymers (including PEG's[16,17]) have been complicated by some fragmentation and/or time dependence due to "fractional distillation".

By contrast, electrohydrodynamic ionization mass spectrometry (EHMS)[18–22] has been shown to be particularly well suited for direct mixture analysis.[14,15] In EHMS, the formation of ions occurs in solution via electrolytic dissociation or by ion attachment. The ion attachment process is promoted by the addition of an inorganic salt (usually alkali salts), which also assists the ion emission process by increasing the conductivity of the solution. (To promote ion emission, solution conductivity on the order of $10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ is generally required.[21]) Volatile solvents increase the pressure in the ion source, resulting in ion scattering and/or electrical discharge between the emitter needle and counterelectrode. Thus, glycerol has been the solvent of choice for EHMS[21,22] because of its low volatility (vapor pressure = 3×10^{-4} torr at 20 °C) and its good solvent properties. Ions are extracted directly from solution by the action of an applied electrostatic field, imparting little or no excess internal energy to the sampled ions. Even samples predisposed to fragmentation (e.g., diquaternary ammonium salts, which are destabilized by intramolecular coulombic repulsions) are sampled intact.[23]

In spectra of glycerol solutions containing PEG and NaI, oligomers of PEG complexed with up to four sodium ions were resolved.[14,24] Retention of counterion(s) by the resulting multiply charged adducts was not observed. Such retention has been found to depend on the charge density of analytes and to correlate with expected ion pairing in solution.[25] When the charge centers are shielded by the complexing molecule (PEG[14,24] or a more conventional ligand, such as bipyridine[15,25]), counterion association may be less extensive than in field desorption or the various secondary ion mass spectrometric experiments. From the intensities of quasi-molecular (sodiated) oligomer ions, molecular weight distributions with accurate averages have been obtained.[14,24] The close agreement between molecular weight averages calculated from EH mass spectra and values obtained by conventional methods indicated that the spectra reflected oligomer abundances and therefore that sampling efficiencies were similar for structurally similar ions.

The work described here extends earlier experiments to compare the complexation of PEG with various alkali metal ions. The selectivity of the reaction and the relationship between the degree of polymerization (or chain length) of an oligomer and the number of ions it can complex are considered.

Experimental Section

Mass spectra were obtained with a double-focusing mass spectrometer (AEI MS902) equipped with an EH ion source described elsewhere.[21,26] Source emitter potential was varied from +4.5 to +8.5 kV (giving ions of roughly 4–8-kV energy[22,26]); lower potentials were used to improve instrument transmission of heavy ions. Source extractor potential was varied from −4 to −1.5 kV in order to maintain a potential difference between the emitter and extractor of about 7–9 kV. This resulted in a more or less constant electric field at the emission site and ensured the maintenance of acceptable emission current. Source collector potential was fixed at ground. For all spectra, exact emitter potential and spectrometer electric sector potential were empirically matched; thus only ions that had not undergone any metastable evaporative loss of solvating glycerol molecules prior to the electric sector were detected.[22] Spectrometer resolution of about 600 was employed. Typical ion emission current was 10^{-5}–10^{-6} A. The gain of the electron multiplier was on the order of 10^5–10^6. Sample consumption was on the order of a few microliters per hour.

$RbNO_3$ was prepared by dissolving RbCl (Alfa) in concentrated HNO_3 (Baker) and then evaporating to dryness. $LiNO_3$ (Baker), $NaNO_3$, KNO_3 (Mallinckrodt), $CsNO_3$ (A. D. Mackay), CsI (Alfa), and glycerol (Fisher) were reagent grade chemicals and were used as received. The PEG samples used were PEG 400, PEG 1000, and PEG 1540, for which average molecular weights were specified by the manufacturer (Baker) to be 380–420, 950–1050, and 1300–1600, respectively. These were also used as received.

In studies of the dependence of complexation on the degree of polymerization, samples containing PEG (~0.8 mol % PEG 1000 and ~0.08 mol % PEG 1540, where present) and supporting electrolyte (~5.0 mol % alkali salt) were prepared by dissolving in glycerol (100.0 mol %). The nitrates of Li, Na, K, and Rb were used. $CsNO_3$ was not soluble at 5.0 mol %; therefore, CsI was used instead. To study the selectivity of PEG for various alkali ions, a "mixed-loading" technique was employed. PEG 400 (1.0 mol %) was dissolved in glycerol (100.0 mol %) containing equal concentrations of two alkali salts. Solutions containing 3.0 mol % each of $NaNO_3$ and $LiNO_3$, $NaNO_3$ and KNO_3, or $NaNO_3$ and $RbNO_3$ were prepared. $CsNO_3$ was not soluble at this level. Thus, a solution containing 2.0 mol % each of $CsNO_3$ and $NaNO_3$ was used to compare the selectivity of PEG for these salts. All solutions were prepared by dissolving the polymer and salts with heating (~65 °C) and vigorous stirring overnight, while degassing[21,26] to $\leq 1 \times 10^{-2}$ torr. Positive-ion spectra were obtained. All data presented (except Figure 1) represent averages of three mass spectra.

Results and Discussion

In EH mass spectra of glycerol solutions containing PEG and alkali metals (M$^+$), ions of general formula $(\mathrm{PEG}_n + z\mathrm{M})^{z+}$ were detected. (z = number of cations complexed with the PEG n-mer.) Thus, if a given n-mer can interact

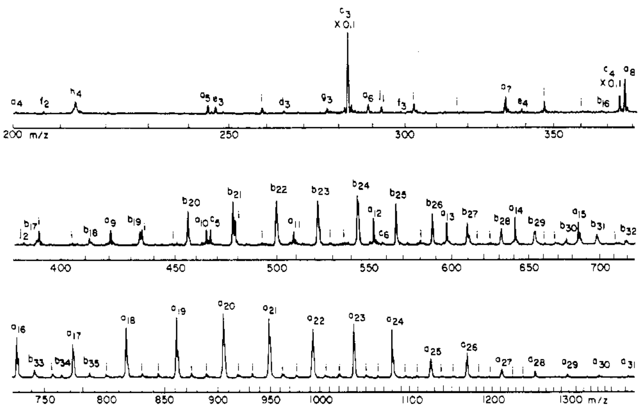

Figure 1. Trace from an oscillographic recording of the EHMS spectrum of a glycerol (G) solution containing PEG 1000 and $LiNO_3$. Peaks are labeled according to the following ion series (where n and m denote the degree of polymerization and number of solvent molecules in a detected cluster, respectively): $a_n = [PEG_n + Li]^+$; $b_n = [PEG_n + 2Li]^{2+}$; $c_m = [G_m + Li]^+$; $d_m = [G_m + Li - H_2O]^+$; $e_m = [G_m + Li - 2H_2O]^+$; $f_m = [G_m + Na]^+$ (impurities); $g_m = [G_m + H]^+$; $h_m = [G_m + Li]^+ \rightarrow [G_{m-1} + Li]^+$ (metastable ion); i = Li adducts of oligomers with intrachain impurities as observed in ref 14; $j_m = [G_m + PEG_4 + Li]^+$.

with one or more metal ions ($z \geq 1$), it will appear in the spectrum as a series of ions of mass-to-charge ratio $m/z = (44n + 18 + zA)/z$ (where A is the atomic weight of metal and other terms have been defined above) and intensity $I_{n,z}$. For ions detected, z was inferred from the spacing of ions due to successive oligomers (spaced at 44 m/z units for singly charged ions, 22 units for doubly charged ions, etc.). A typical EH mass spectrum of PEG–alkali metal (lithium) complexes is shown in Figure 1. Lithium complexes of PEG with n as low as 4 are observed. Similar results will be described below for the other metals. This contrasts with other reports[12,27] which suggested that $n > 6$ was needed for PEG to complex alkali metal ions in a protic solvent. Even in a nonprotic solvent, metal interactions with small PEG oligomers were observed to be very weak.[7] Detection of small oligomer adducts here may be attributable to the sensitivity of the mass spectrometric experiment and/or to the chemistry of the glycerol solvent.

The average charge of complexes of a given n-mer, $\bar{z}_n$, provides a measure of the ability of that n-mer to attach multiple metal ions. If an n-mer can attach only one ion, it will have $\bar{z}_n = 1$; otherwise, $\bar{z}_n > 1$. $\bar{z}_n$ can be estimated from spectral intensities using eq 1:

$$\bar{z}_n = \frac{\sum_z I_{n,z} z}{\sum_z I_{n,z}} \qquad (1)$$

Figure 2 shows the dependence of $\bar{z}_n$ on n for each of five alkali metals (Li^+, Na^+, K^+, Rb^+, and Cs^+). Two PEG samples (PEG 1540 and PEG 1000) were used to represent n from 4 to 40, except for Li^+, which evidently could not solubilize PEG 1540 (perhaps because of relatively weak complexation; see below). Therefore, only PEG 1000 was used with Li, covering the range from $n = 4$ to $n = 35$.

Strictly speaking, values for $I_{n,z}$ in eq 1 should reflect integration over all ions in the corresponding isotope cluster (including contributions from, for example, ^{13}C and ^{87}Rb, when present). However, over the mass range examined here, these ions were not all individually resolved. Therefore, the height of the base peak (or the maximum height of an unresolved isotope cluster) was used to estimate $I_{n,z}$ in calculating $\bar{z}_n$. Because only ions attributable to a single n-mer are involved in calculating a given $\bar{z}_n$, any error introduced by this approximation should be small, especially in view of the normalization by total n-mer intensity in the denominator of eq 1.

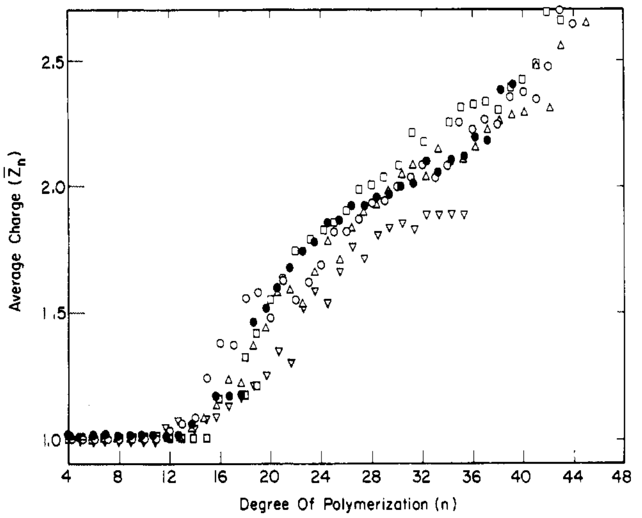

Figure 2. Variation of oligomer average charge ($\bar{z}_n$) with degree of polymerization (n) for adducts of five different alkali metals ((▽) Li^+; (○) Na^+; (△) K^+; (●) Rb^+; (□) Cs^+).

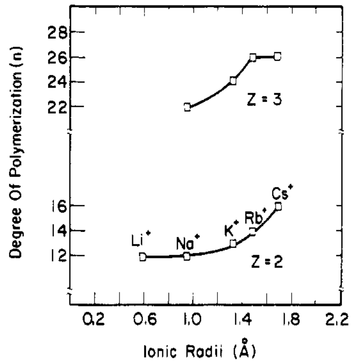

Figure 3. Minimum degree of polymerization (n) necessary for complexation of two ($z = 2$) or three ($z = 3$) ions of various size.

The general similarity of the curves in Figure 2 confirms that interactions between PEG and all metals are quite similar. The data for Li are particularly significant, because other workers[6,13] have been unable to detect Li–PEG complexes in protic solvents (although existence of such a complex in an aprotic solvent can be inferred from the data of ref 7). Again, success here may be due to the relative sensitivity of EHMS and/or to the fact that glycerol may not solvate lithium ions as well as other protic solvents used elsewhere. It is highly unlikely that the detected adducts are formed other than in solution (e.g., via gas-phase ion–molecule reactions), because ions formed elsewhere will not generally have the proper energy for passage through the electrostatic analyzer (energy filter) of the spectrometer.

Despite the general similarity of the curves in Figure 2, differences can be noted in the threshold value of n above which $\bar{z}_n$ first exceeds unity for each metal. This suggests variation (with metal) in the minimum number of repeat units required to allow chain interaction with more than one cation. Figure 3 relates the lowest n of PEG that formed detectable 2+ complexes to the ionic radii[28] of the metal substrates and indicates a positive correlation. (Because the intensity of multiply charged ions at threshold may be low, their initial contribution to $\bar{z}_n$ may be small and therefore the exact position of the threshold is not necessarily evident in Figure 2.) Also shown in Figure 3 is the lowest n value for which 3+ ions ($z = 3$)

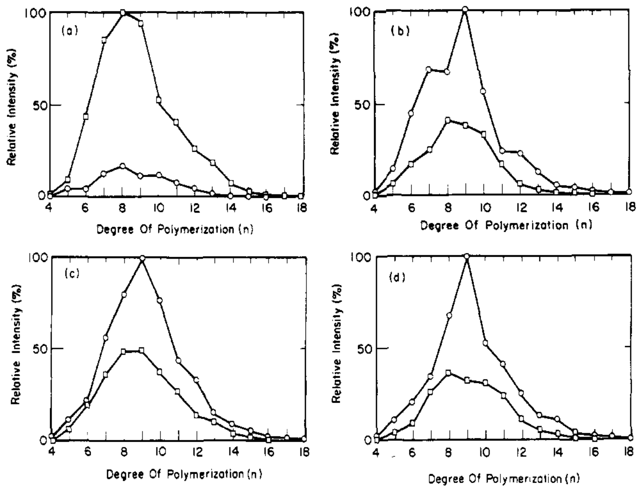

Figure 4. Relative abundance of PEG adducts sampled from solutions containing equimolar binary alkali metal mixtures. (□) $[PEG + Na]^+$ for all plots. (○): (a) $[PEG + Li]^+$; (b) $[PEG + K]^+$; (c) $[PEG + Rb]^+$; (d) $[PEG + Cs]^+$.

were observed with each metal. Positive correlation is again noted. These observations may suggest that the PEG chain spirals around the metal ions, requiring greater length for larger ions. Ono et al.[13] reached a similar conclusion, estimating that incorporated charges required 12.3, 13.2, and 14.5 repeat units for stabilization of two positive charges in K^+, Rb^+, and Cs^+ adducts, respectively (compared with 13, 14, and 16 found here). However, they reported that 28 repeat units were required to stabilize a complex incorporating two (relatively weakly bound) sodium ions. By contrast, Figure 3 shows multiple sodium attachment for $n \geq 12$, which is more consistent with the other metals.

To assess selectivity of various oligomers for different metals, a "mixed-loading" study was undertaken, in which mixtures of two alkali ions were allowed to equilibrate with PEG prior to obtaining spectra. Four equimolar binary mixtures of alkali ions, (Li^+/Na^+, K^+/Na^+, Rb^+/Na^+, and Cs^+/Na^+) were prepared and mixed with PEG 400 in glycerol. PEG 400 was used because it has relatively small oligomers (n = 4–18) with predominantly single-ion attachment. This allowed comparison of intrinsic complexation strengths without complication arising from multiple-ion attachment. (Oligomers able to complex more than one alkali ion are present in very low abundance in PEG 400.) Plots a–d of Figure 4 show the relative abundance of the two metal complexes for each oligomer in the four solutions. These data reveal the preference of each oligomer for various metals. In general, all oligomers show similar behavior in preferring one ion to another. For example, in Figure 4a, the Na^+ adduct is more intense than the corresponding one for Li^+, regardless of n. As a quantitative measure of this selectivity, a bulk selectivity ratio, $S(M_1/M_2)$, can be defined:

$$S(M_1/M_2) = \frac{\sum_n I_{n,M_1} / \sum_n I_{n,M_2}}{[M_1]_0/[M_2]_0} \qquad (2)$$

where $[M_1]_0$ and $[M_2]_0$ are initial concentrations of the alkali metal ions and I_{n,M_1} and I_{n,M_2} are intensities of n-mer adducts of metals M_1 and M_2, respectively. I_{n,M_1} and I_{n,M_2} were estimated from the intensities of the most abundant ion in each isotope cluster, corrected to include contributions from all isotopes (including ^{13}C and metals) by dividing by their relative natural abundances. This correction process was possible because in the m/z range of the oligomer ions of this sample, spectrometer resolution was adequate to resolve the peaks of the isotope clusters. Calculation of integrated intensity proved easier and more precise than attempting to measure intensities of several small peaks in each cluster.

Table I
Selectivity Ratios for EHMS Sampling of Metal Complexes of PEG 400

metal ion		
M_1	M_2	$S(M_1/M_2)$
Li^+	Na^+	0.17 ± 0.02
Na^+	K^+	0.46 ± 0.06
Na^+	Rb^+	0.58 ± 0.06
Na^+	Cs^+	0.49 ± 0.06

The S values of PEG 400 for the four pairs of alkali metal ions are tabulated in Table I. From these S values, the order of intrinsic selectivity was found to be $K^+ > Cs^+ > Rb^+ > Na^+ > Li^+$ in the ratios of 1:0.94:0.79:0.46:0.08. For comparison, the efficiency of extraction of these metal ions by PEG 1000 from water to dichloromethane was reported by Yanagida et al.[12] as $K^+ > Cs^+ > Na^+ > Li^+$ in ratios of 1:0.76:0.12:0.03. The good quantitative agreement is probably fortuitous, especially considering the different solvents involved, but the agreement in ranking is reasonable. On the other hand, Ono et al.[13] (using PEG 20000 and a conductometric method) reported the order of formation constants of PEG–alkali metal ion complexes as $Rb^+ > Cs^+ > K^+ > Na^+ > Li^+$ in ratios of 1.00:0.91:0.71:0.18:0.0. The higher molecular weight (longer chain) PEG's used in Ono's study may be more selective for larger ions, possibly accounting for the small difference in the order of selectivity. Unfortunately, the molecular weight range of Ono's sample exceeded both the range of the mass spectrometer used and the solubility limit in glycerol. Thus, the results cannot be directly compared. Nevertheless, the data clearly indicate that the EHMS spectra reflect the relative stability of the adducts in solution. The lithium adduct is clearly disfavored, although lithium is often the preferred cation for attachment in field ionization/field desorption experiments,[29-31] which are run without solvent.

As mentioned earlier, PEG–metal interactions are expected to parallel those of crown ethers. The relative formation constants (K_f) for crown ether–metal complexes in methanol determined by a titration calorimetric technique are $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$ (in the ratios 1.00:0.19:0.06:0.02:0.0).[32] Although the order is similar to that obtained here, the relative differences in K_f of these cyclic ether–metal complexes are generally greater than those in the intrinsic selectivity of PEG. This may reflect actual quantitative differences between crown ethers and the acyclic PEG's, or it may be due to experimental differences (e.g., solvent differences or mass spectral sampling effects). An EHMS study of crown ether selectivities has been undertaken and should clarify this point.

Conclusion

This study has clearly demonstrated the analytical applicability of EHMS for studies of solution-phase ion–polymer interactions. Metal complexes of different oligomers were resolved; the mass spectral intensities of these complex ions provided an estimate of the average number of ions complexed by each oligomer and the threshold for multiple-ion attachment. The results supported the prediction of multiple-ion association by larger oligomers. In the EH mass spectra, the selectivity of individual oligomers for different metal ions was also observed. From the total spectral intensities of each metal complex, bulk selectivity ratios of the polymer for the metal ions were calculated.

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 $d \ln \langle \mu^2 \rangle / dT \approx 0.005\ ^\circ C^{-1}$. 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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