Nonionic Polymer−Salt Interactions in Dilute Solution: The Poly(ethylene oxide)/$LiClO_4$/Methanol System

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Received December 11, 1995; Revised Manuscript Received January 30, 1996[⊗]

ABSTRACT: The interaction of lithium perchlorate with high molecular weight poly(ethylene oxide) (PEO) in dilute methanol solutions was studied using cloud point measurements, static and dynamic light scattering, and viscometry. For both good and poor solvent conditions, PEO/$LiClO_4$ complexes form in coil outer portions and charge−charge repulsions between these complexes swell the PEO coils and result in repulsive interactions between coils. A noteworthy consequence of this nonionic polymer → polyelectrolyte conversion is the “salting in” of PEO in methanol by $LiClO_4$.

Introduction

Recently, a new class of solid-state ionic materials having great potential for a variety of important applications has been developed.[1−4] These materials are “solid” polymer electrolytes, or “SPEs”, which consist of a molten polymer medium in which selected salts have been dissolved. The polymer of choice for SPEs is poly(ethylene oxide), PEO, a linear, highly flexible polyether. The most compelling interest in polymer electrolytes centers on their use in secondary (rechargeable) lithium batteries. In SPEs, salt cations complex with groups along polymer chain backbones and are subsequently transported through the polymer medium via long-ranged polymer motions. Although SPE polymer studies have mostly focused on short-ranged or “local” polymer behavior (complexation sites, structural relaxations, etc.), it is now appreciated that long-ranged or “global” polymer behavior, such as size-dependent motions associated with slow, collective relaxations in amorphous regions of the polymer medium, plays an important role in conductivity (ref 1, Wintersgill and Fontanella in ref 3).

To study the effects of polymer−salt complexing on global polymer behavior, a parallel study of such behavior for a selected polymer both in solution and in the melt was initiated. The system chosen for investigation was lithium perchlorate in poly(ethylene oxide), a system widely employed in SPE studies. The solvent chosen for the solution study was methanol, a solvent in which monovalent alkali metal cations generally,[5−8] and lithium salt cations in particular,[7,8] have been shown to complex with PEO backbone oxygens. Cloud point measurements, static and dynamic light scattering, and viscometry were used to investigate PEO−$LiClO_4$ interactions in methanol, and the results of this study are presented here. In particular, viscometry and light scattering were used to examine the effect of the complexation of $LiClO_4$ by PEO on overall PEO size in solution.

Aside from battery technology, understanding solvent−solute interactions generally is of fundamental interest and importance. For example, the controlled introduction of salts into solvents is used to study solvent properties. The structure and behavior of water has been extensively studied using this approach.[9] Alternatively, solute behavior, including that of binary nonionic polymer solutions, has been investigated via the controlled introduction of salts. Examples in which cosolutes have been used to study the behavior of nonionic polymers in solution include work on poly(vinylpyrrolidone), PVP, carried out by Molyneux and co-workers[10,11] and the work of Bailey and co-workers who studied the behavior of PEO both in water[12] and in methanol.[13] Understanding such behavior for PEO in particular is important because, aside from SPEs, PEO solutions enjoy an especially broad range of applications as well as providing a representative “model system” for investigating the behavior of linear, flexible nonionic polymers in solution.[14−19]

Experimental Section

The behavior of high molecular weight (838 000 MW, Pressure Chemical, Pittsburgh, PA, and 270 000 MW, Toyo Soda, Tokyo, Japan), narrow molecular weight distribution PEO in $LiClO_4$/MeOH solutions at 30 °C was investigated by determining solution coexistance curves, viscometry, static light scattering (SLS), and the dynamic light-scattering technique of photon correlation spectroscopy (PCS). As shown earlier,[20] methanol at 30 °C is a good solvent for PEO samples with the molecular weights and the range of PEO concentrations employed here.

The viscometry and PCS measurements were carried out as described in refs 21 and 22, respectively. SLS measurements were carried out as for binary solutions, although Zimm plot analyses of the resulting data required modification of the interpretation of the results as described below. Coexistance curves for PEO in MeOH and in $LiClO_4$/MeOH were determined by making solution cloud points measurements using the 670 nm output of a 1 mW diode laser (LX-100 laser pointer, Tandy, Forth Worth, TX) to monitor solution turbidity while varying solution temperature.

In both the SLS and PCS measurements, six 838 000 MW PEO concentrations in the range 0.2−2.0 mg/mL were used for each of five $LiClO_4$ concentrations: 0.0, 0.1, 0.3, 0.7, and 1.0 M. Viscosity measurements were made using 838 000 MW PEO concentrations between 0.5 and 5.5 mg/mL for the same salt concentrations employed in the light-scattering measurements. In addition, viscosities were measured for each salt solution without PEO. Cloud point measurements, both in methanol and in 0.1 M $LiClO_4$/MeOH solutions, were made using the 270 000 MW PEO with concentrations in the range 1.0−10.0 mg/mL for temperatures ranging from ambient to 10 °C. In all cases, individual solution concentrations were made up gravimetrically using spectrophotometric grade methanol (Burdick & Jackson, Muskegon, MI) and purified $LiClO_4$ (Microselect, Fluka, Buchs, Switzerland) which was oven-dried before use.

Results and Discussion

PEO phase separation from solution was first noticed serendipitously when an unscheduled overnight tem-

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

S0024-9297(95)01815-8 CCC: $12.00

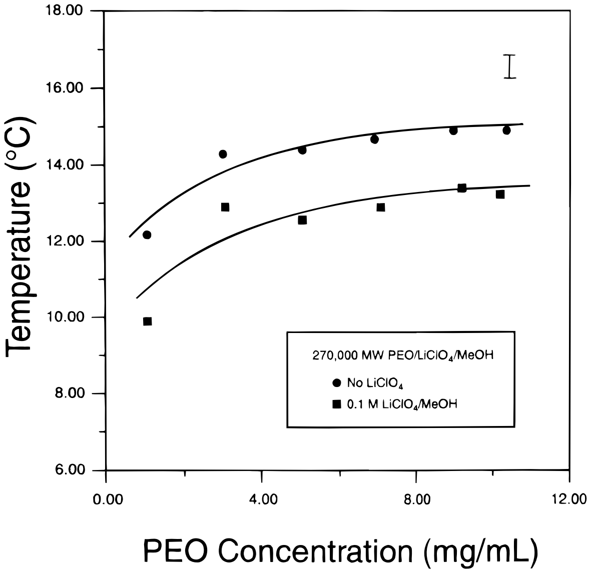

Figure 1. Coexistance curves for PEO in methanol with and without 0.10 M $LiClO_4$. The downward shift in the curve corresponds to the salting-in of PEO in methanol by $LiClO_4$ (the curves are only to guide the eye). The estimated uncertainty (error bar) for these measurements is ±0.3 °C.

perature drop caused PEO precipitation from MeOH—though PEO at the same concentration did not separate from several $LiClO_4$/MeOH solutions of varying salt concentration sitting alongside it. Cloud point measurements were made to chart the shift in this separation temperature due to the addition of the lowest salt concentration, 0.10 M $LiClO_4$, and the results are illustrated in the corresponding downward shift of the coexistence curves for PEO/MeOH solutions (Figure 1). This shift reveals a significant consequence of PEO–$LiClO_4$ interactions in methanol: $LiClO_4$ "salts PEO in". The mechanisms used to explain this "salting in" summarize the results of this study and are discussed below using the light-scattering and viscometry results. It is worth recalling that although for typical dilute solution concentrations, 270 000 MW PEO phase separates in methanol without salt around 14–15 °C (Figure 1), at 30 °C methanol is already a good solvent for PEO[20] of this molecular weight.

While the methods of data analysis employed in this study for the PCS and viscometry results were conventional,[21,22] Zimm plot analyses of static light-scattering data from dilute PEO/MeOH/$LiClO_4$ solutions were made employing a method developed by Yamakawa[23] for *three*-component solutions (components 1–3 are $LiClO_4$, PEO, and methanol, respectively). Because this method has certain unique features, a brief explanation of the method follows.

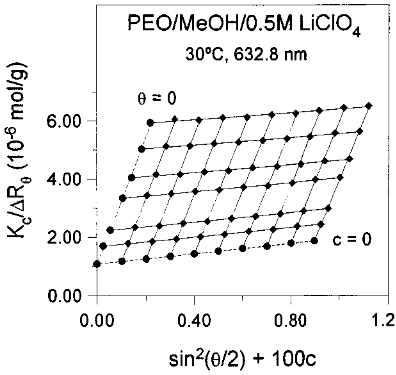

Figure 2. Typical Zimm plot for the PEO/methanol/$LiClO_4$ system illustrating binary solution form for this three-component system. From such plots, $\langle S^2(c_1)\rangle_z$ and $A_{2,22}(c_1)$ were determined (see text).

For ternary solutions, the form of the Zimm expression is identical with that for binary solutions,[23–25] so three-component Zimm plots are expected to be indistinguishable from binary solution plots—behavior confirmed in these measurements (Figure 2). The analysis does not require measurements made at constant solution chemical potential, and so does not require dialysis of polymer solutions, but relies instead on a prior knowledge of the true polymer molecular weight, M_2 (here, M_2 was determined earlier; see ref 22). Then the *true* value of the polymer *z*-averaged, mean-square radius of gyration, $\langle S^2(c_1)\rangle_z$ (or simply R_G^2), along with *apparent* values of the polymer weight-average molecular weight, $M_{2,ap}$, and the solution second-virial coefficient, $A_{2,ap}$, are extracted from SLS Zimm plots. The Zimm expression for these light-scattering data is

$$\frac{Kc_2}{R_\theta} = \frac{1}{M_{2,ap}}\left[1 + \frac{16\pi^2}{3\lambda'^2}\langle S^2(c_1)\rangle_z \sin^2(\theta/2)\right] + 2A_{2,ap}c_2 \tag{1}$$

with c_1 the salt concentration, c_2 the solution PEO concentration, and the other equation parameters having their conventional meanings, suitably modified for three-component systems.[23] Apparent values are related to true values via

$$M_2A_{2,22}(c_1) = M_{2,ap}A_{2,ap} \tag{2}$$

with $A_{2,22}$ the salt concentration-dependent PEO–PEO second-virial coefficient. Along with R_G, the length $\bar{S}$ for PEO coils in solution, which also depends on salt concentration, can be extracted from PEO–PEO second-virial coefficients using

$$\bar{S} = (3M_2^2A_{2,22}/16\pi N_A)^{1/3} \tag{3}$$

with N_A being Avogadro's number. $\bar{S}$ is a measure of the effective equilibrium range for PEO–PEO interactions in solution.[23,26] Note that although $LiClO_4$ dissociates readily in methanol,[14] charge neutrality for volumes with dimensions comparable to the wavelength of light is maintained in these solutions so that in light-scattering measurements, the solution is "seen" as a three-component system.[27]

Figure 3 summarizes the light-scattering results. Increases in both R_G and $\bar{S}$ with increasing salt concentration, corresponding to PEO coil swelling and the increase in the strength of repulsive PEO–PEO interactions in solution, respectively, are clearly evident in Figure 3. These increases occur even though PEO coils had already exhibited swelling and the repulsive interactions associated with good solvent behavior in the PEO/methanol system at 30 °C.[20]

In Figure 4, PCS measurement results illustrating the effect of increasing $LiClO_4$ concentration on isolated coil center-of-mass mutual diffusion coefficients are seen in the behavior of extrapolated, zero-concentration PEO diffusion coefficients. The behavior of corresponding isolated coil hydrodynamic radii, R_H, extracted from these intercept values via the Stokes–Einstein expression in the usual way,[28] is also illustrated in Figure 3.

The viscosity measurement results are presented in Figure 5 where PEO solution shear viscosity dependencies on PEO concentration are illustrated for each of

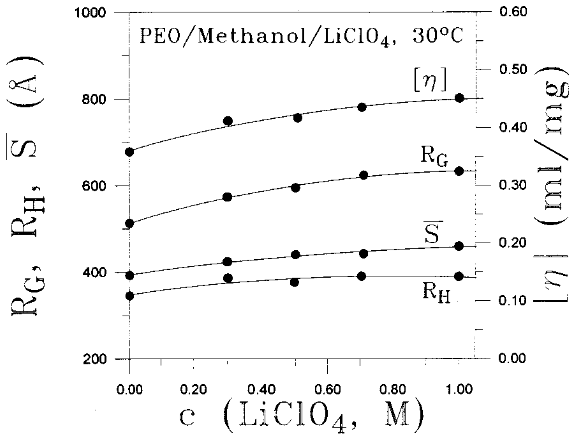

Figure 3. Plot illustrating the expansion of PEO coils in methanol with increasing $LiClO_4$ concentration—behavior associated with the salting-in of PEO in methanol by $LiClO_4$ (the curves are only to guide the eye). Estimated uncertainties for R_G, R_H, $\bar{S}$, and $[\eta]$ are 5%, 2%, 3%, and 1%, respectively.

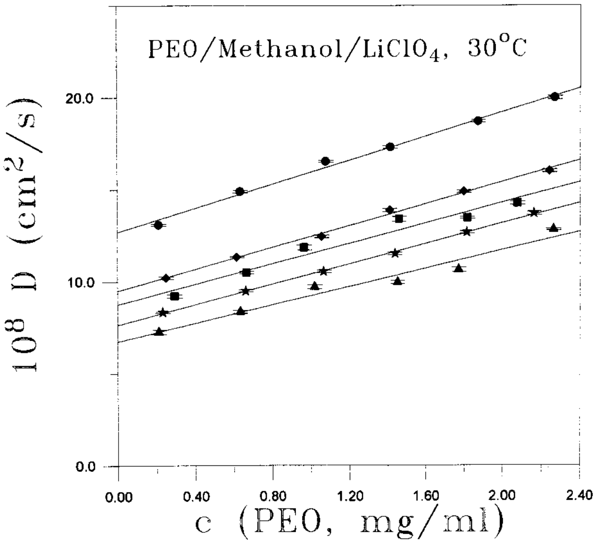

Figure 4. Dependence of PEO coil mutual diffusion coefficients on PEO and $LiClO_4$ concentrations. Intercept values correspond to isolated coil behavior for five $LiClO_4$ concentrations in the range 0.0–1.0 M (see symbol key, inset, Figure 5). Typically eight replicate measurements were made for each point, and error bars represent estimated errors of the mean for each set.

the five $LiClO_4$ concentrations. As for the $\bar{S}$ behavior, the increasing strength of PEO–PEO interactions with increasing salt concentration is evident here in the corresponding increasing upward curvature seen in these plots. To further assess PEO global behavior, i.e., size changes with increasing salt concentration, PEO intrinsic viscosities, $[\eta]$, a parameter proportional to the coil hydrodynamic volume in solution as $[\eta] \sim R_G^2 R_H$, were extracted from the data for each $LiClO_4$ concentration as described in earlier PEO/H_2O studies.[20] The increase in $[\eta]$ with increasing $LiClO_4$ concentration is also illustrated in Figure 3.

Measurements of the kind reported here cannot provide information about the nature of Li^+/PEO complexes formed in solution, per se. Nevertheless, they can provide important information about the distribution of these complexes along PEO chains. PEO is a sterically thin, highly flexible linear polymer. In solution, high molecular weight PEO is a very open structure: The volume of the chain itself represents <0.1% of the volume pervaded by the chain. Thus, methanol and Li^+ and ClO_4^- ions have access to PEO ether linkages all along the chain. The net effect of complex formation, including counterion screening, is one of repulsion between complexes. The results presented here suggest that complex formation is reduced in coil interiors, not because of restricted access to these areas—PEO coil interiors are quite open—but because it is energetically more costly to form repulsively interacting complexes in greater proximity in the more densely segmented regions of coil interiors. Recalling that R_H is a measure of coil size emphasizing the behavior of coil interiors while R_G primarily reflects the behavior of coil outer portions,[29] it is seen in Figure 3 that the relatively smaller increases in R_H with increasing salt concentration compared to those of R_G and $[\eta]$ are consistent with the premise that the complexation of Li^+ by PEO ether linkages occurs preferentially in PEO coil outer portions.

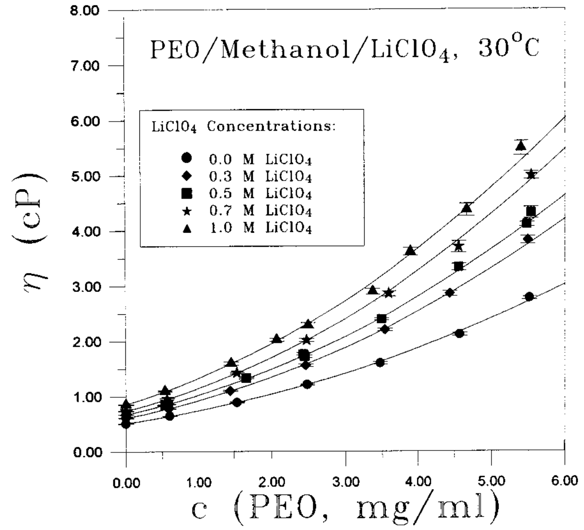

Figure 5. Dependence of PEO solution shear viscosities on PEO and $LiClO_4$ concentrations in solution. Typically five replicate measurements were made for each point, and error bars represent estimated errors of the mean for each set.

Intercoil behavior is consistent with the conclusion that complex–complex repulsive interactions in coil outer portions were mostly observed for intracoil behavior. First, increases in $\bar{S}$ with increasing salt concentration support this premise since $\bar{S}$ is a measure of the range of PEO–PEO interactions in solution under circumstances for which very little interpenetration between coils occurs. Second, PCS autocorrelation function-normalized second cumulants, which increase markedly with the association or aggregation of polymers in solution, remained small and comparable to salt-free values (≈0.05) upon the addition of $LiClO_4$, further demonstrating that PEO coils "kept their distance".

Thus, the study of PEO global behavior has provided important and useful information about the distribution of Li^+/EO complexes in PEO which complements earlier studies of local behavior both in PEO and in ethylene oxide oligomers (see below). For the most part, either discussion of this distribution has been absent altogether,[5,6,12,13] or it has been assumed that these complexes were distributed uniformly along the polymer chain.[7,8]

The behaviors of R_G, R_H, $[\eta]$, and $\bar{S}$ along with the results of earlier studies both confirm and extend the simple picture of the salting-in of nonionic polymers in salt solutions, which has evolved over the last 35 years or so. The complexing of Li^+ ions with PEO oxygens was demonstrated earlier,[7,8] and it was further shown that Li^+ binds weakly (compared to K^+ and Na^+, e.g.) to PEO.[7,8] The conversion of nonionic PEO in methanol to a weak polyelectrolyte via PEO−salt ion complexing was also recognized earlier.[13,5−8] Moreover, the open structure of PEO in solution and the accessibility of PEO ether linkages to salt and solvent means that the use of ethylene oxide oligomers to study ether linkage−salt complexing behavior is relevant to salt complexing with PEO. For example, the stability constant, $K_S \approx 10$, reported in the study[30] of Li^+ complexation with the ethylene oxide oligomer tetraglyme in methanol at 25 °C demonstrated that Li^+ binding to tetraglyme, as for PEO, is weak. Nonetheless, in the present study, the number of Li^+ ions bound to PEO may still be large because of the ranges of polymer and $LiClO_4$ concentrations employed;[31] the nominal value of the ratio of ethylene oxides to Li^+ ions, EO/Li^+, varied between 0.45 and 0.0045. The notion of significant binding of Li^+ to PEO is supported here by the observed increase in polymer size with increasing $LiClO_4$ concentration (Figure 3). Moreover, the effect of increasing salt concentration on the strength of PEO−PEO interactions, as seen in the behavior of $\bar{S}$, and on the nature of the distribution of Li^+/PEO oxygen complexes in PEO coils based on a comparison of the behaviors of R_G and R_H is now particularly evident.

Conclusions

In the PEO/methanol/$LiClO_4$ system, salting-in occurs as a consequence of intracoil expansion and enhanced coil−coil repulsion due to charge−charge repulsions between Li^+ cations complexed with PEO ether linkages. Charged complexes associated with this conversion from nonionic polymer to polyelectrolyte form preferentially in the outer portions of PEO coils.

The results presented here apply to nonionic polymers in salt solutions generally as long as repulsive interactions between charged salt ion/polymer complexes obtain, i.e., as long as the nonionic polymer → polyelectrolyte conversion occurs. Moreover, these results suggest that by use of appropriate salts, both the size and the interactions between PEO coils in solution can be controlled in order to modify solution properties in a desirable way. This would be useful, for example, in industrial processing solutions. Besides PEO, controlled modification of solution properties in this way should be possible for other nonionic polymer solutions as well.

Acknowledgment. The authors thank S. Grenda for helpful conversations about the solution properties of $LiClO_4$ and the US NSF (Division of Materials Research, DMR-9312075), the US DOE (Office of Basic Energy Sciences, DE-FG03-94ER14489/A001), and the Bigelow Foundation for support of this work.

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MA9518159