Chromatographic Investigation of the Structure, Crystallinity, and Complexation of a Conducting Polymer, $P(EO)_xLiCF_3SO_3$

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Inverse gas chromatography was used to investigate the physical properties and complexation reactions of two probe solutes, acetonitrile and benzene, in conducting polymers composed of mixtures of poly(ethylene oxide), PEO, and lithium triflate. The specific retention volumes of the probe solutes were measured from 15 to 200 °C for columns containing pure PEO, $P(EO)_{16}LiCF_3SO_3$, $P(EO)_8LiCF_3SO_3$, and $P(EO)_6LiCF_3SO_3$. *Benzene served as a nonspecific probe* to determine the degree of crystallinity of the polymer and polymer–salt complexes as a function of temperature. The van't Hoff plots for this probe showed two discontinuities at 68–70 and 130–170 °C corresponding to phase transitions caused by melting of the PEO crystalline material and the $P(EO)_xLiCF_3SO_3$ complex(es), respectively. At room temperature, the pure PEO and $P(EO)_xLiCF_3SO_3$ materials were all about 60–70% crystalline. In the range 70–130 °C, the 8:1 and 6:1 polymers were 20 and 30% crystalline, respectively. The transition temperature of the pure polymer was 70 °C, whereas the PEO in the polymer–salt mixtures "melted" at lower temperatures for 67–68 °C. The crystalline polymer–salt complexes melted in the range 130–175 °C. *The acetonitrile probe could complex with the lithium ion* in the conducting polymers. Thus the activity of Li^+ influenced the retention volume of this probe. At temperatures below 70 °C, the retention volumes of this probe were consistently higher for the polymer–salt columns than for the pure PEO. At intermediate temperatures, the order of retention was the same as observed for the benzene probe. However, at higher temperatures, >130 °C, the retention volume of acetonitrile *increased* linearly with the salt concentration.

Introduction

The potential applications of solid polymer electrolytes have sparked a great deal of research into the electrochemical properties of polymer–salt complexes. The most extensively studied complexes are high molecular weight poly(ethylene oxide), PEO, or poly(propylene oxide) containing lithium salts such as $LiCF_3SO_3$ or $LiClO_4$. The use of conducting polymers as electrolytes is especially valuable for microelectrodes that can function well at the intermediate conductivities observed with the semirigid polymer–salt matrices.

Unfortunately, the structural and physical characteristics of the polyether polymers and polymer–salt complexes, which can dramatically influence the electrochemical properties, are less than ideal in many ways. The polymers and polymer–salt complexes often are mixtures of crystalline and amorphous materials at room temperature; the heating and cooling curves often show a significant and sometimes irreversible hysteresis loop; the recrystallization kinetics are very slow; and the polymer–salt crystalline complexes often persist at temperatures far above the melting point for the crystals of pure polymer. The exact structure and crystallinity of the polymer and polymer–salt complexes at different compositions and temperatures are uncertain. In addition, it has been shown[1] that the charge-transport properties of conducting polymers are often significantly altered by the presence of a solvent vapor such as acetonitrile or dimethylformamide. Both the conductivity and ion-transport processes are significantly enhanced by the sorption of solvent vapors into the polymer electrolyte. The extent and speed of the enhancements are such that a microelectrode coated with a thin layer of conducting polymer has been used as a gas chromatographic detector.[1,2] However, again the exact mechanism of the detector response has not been determined.

Probably the most common polymeric electrolytes used to date are mixtures of PEO and $LiCF_3SO_3$. This polymer–salt complex has been studied by many investigators with a variety of physical and analytical techniques.[3-5] In the most recent investigation,[5] the authors proposed that two types of PEO–salt complexes exist with different stoichiometries, i.e., both the commonly accepted $P(EO)_7LiCF_3SO_3$ and a second form of crystalline complex $P(EO)_{3.5}LiCF_3SO_3$ were proposed at temperatures below the "melting" point of the complexes. Thus at the ambient conditions used for most electrochemical studies, the polymer phase is probably a complex mixture of crystalline and amorphous PEO, crystalline and amorphous $P(EO)_7LiCF_3SO_3$, and crystalline and amorphous $P(EO)_{3.5}LiCF_3SO_3$, and the exact stoichiometry and crystallinity will depend upon the formal composition, temperature, and prior history of the polymer. For the PEO polymers with high molecular weights, crystalline PEO does not exist at temperatures above 70 °C, whereas the crystalline complexes melt in the range 130–170 °C depending upon the composition. The exact phase diagram is very difficult to measure because of the complex stoichiometry, the very slow kinetics of crystallization, and the supercooling (hysteresis) effects observed with the PEO polymers of high molecular weight.

Inverse gas chromatography, IGC, is a unique additional physical tool used for the determination of the structure

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(1) Reed, R. A.; Geng, L.; Murray, R. W. *J. Electroanal. Chem.* **1986**, *208*, 185.

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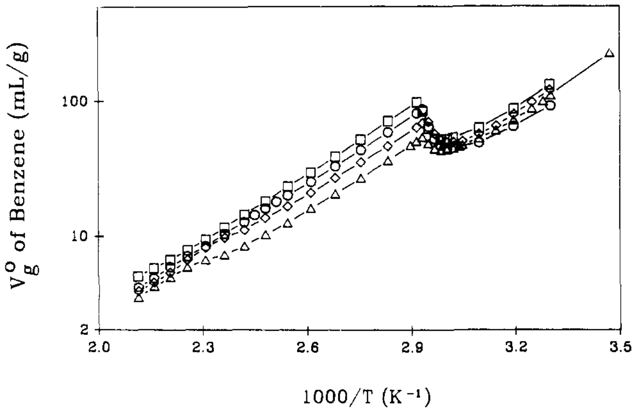

Figure 1. van't Hoff plot for benzene on PEO and P(EO)$_x$LiCF$_3$SO$_3$ columns: □, pure PEO; ◇, P(EO)$_8$LiCF$_3$SO$_3$; ○, P(EO)$_{16}$LiCF$_3$SO$_3$; △, P(EO)$_6$LiCF$_3$SO$_3$.

and crystallinity of polymers. In this technique, the polymer is used as the stationary phase and perturbed by molecular "probes" in the form of normal elution solutes. This method has been used extensively for the characterization of polymers and polymer mixtures;[6-13] however, the method has not yet been applied to the investigation of the recently developed conducting polymers. Nonspecific probes, i.e., solute probes that do not interact specifically with the polymer, can be used to investigate structure, crystallinity, and morphology, whereas specific probes can be used to study H bonding, complexation, and molecular interactions.

The current investigation using IGC was undertaken to study the structure and chemical characteristics of P(EO)LiCF$_3$SO$_3$ complexes with a variety of molecular probes over a range of temperature and composition.

Experimental Section

The poly(ethylene oxide) (600 000 daltons) and lithium trifluoromethanesulfonate (Aldrich) were used as received. The pure polymer or polymer–salt mixtures were coated on 60/80 Chromosorb G-AW-DMCS by evaporation of acetonitrile with subsequent drying in a vacuum oven. The exact liquid loadings were determined by burning (with a correction for the lithium oxide formed) and also by stripping in a Soxhlet extractor with acetonitrile. The analyses agreed within 2–3% (relative STD) in each case. The columns were $^1/_4$-in.-o.d. copper tubing approximately 2 m long containing 1–2 g of stationary liquid phase. The specific retention volumes were calculated on the basis of the weight of PEO, not P(EO)$_x$LiCF$_3$SO$_3$, in the column.

The probe solutes, benzene and acetonitrile, were injected as a gaseous mixture diluted with helium. Methane was added as the marker to measure the dead time for the columns. The injections were made with a gas sampling valve to obtain reproducible sample volumes. The gas chromatographs were Hewlett-Packard Models 5840 and 5890 with flame ionization detectors. The sample size was approximately 10–100 nmol of each component. Thus all of the solute probes were effectively at infinite dilution. Two columns of P(EO)$_{16}$LiCF$_3$SO$_3$ were prepared with different liquid loadings of 3 and 6% to test for liquid surface adsorption.

Results and Discussion

Crystallinity. Benzene is a nonspecific IGC probe that does not strongly interact with the PEO oxygens or Li$^+$ ions. The specific retention volumes of benzene as a function of temperature and polymer–salt formal composition are given in Table I, and the van't Hoff plots are shown in Figure 1 for temperatures from 30 to 200 °C. The retention volumes were measured on freshly prepared columns in an ascending temperatures sequence from 30 to 200 °C. Two nonlinear regions are evident in the plot. These are due to phase transitions involving a change in the crystallinity of the pure PEO (70 °C transition) and the crystalline P(EO)$_x$LiCF$_3$SO$_3$ complex (130–170 °C transition). These phase transitions at the same temperatures have been observed previously by differential scanning calorimetry.[5] *Reproducible phase transitions could be observed only for columns that were not heated above 170 °C.*

Table I. Specific Retention Volume of Benzene on PEO and P(EO)$_x$LiCF$_3$SO$_3$ Columns

	specific retention vol, mL/g of PEO			
temp, °C	PEO	P(EO)$_{16}$-LiCF$_3$SO$_3$[a]	P(EO)$_8$-LiCF$_3$SO$_3$	P(EO)$_6$-LiCF$_3$SO$_3$
15				224.5
30	130.7	91.3	119.8	108.8
32				98.6
35			97.0	86.9
40	86.6	64.2	78.7	71.2
45			64.9	60.1
50	62.6	48.6	56.2	52.2
55			49.8	46.8
56				45.6
58	53.0	44.4	49.1	44.1
60	51.7	44.3	49.2	43.1
62	51.3	46.4	51.1	42.8
64	52.0	51.7	56.6	43.7
66	61.7	63.7	69.2	47.8
68	83.4	85.8	67.8	53.3
70	97.3	80.6	63.3	49.8
72				46.5
80	70.3	58.2	45.8	35.8
90	51.4	43.0	34.9	26.6
100	38.3	32.5	26.6	20.3
110	29.4	25.0	20.7	15.9
120	23.0	19.8	16.4	12.4
125		17.8		
130	17.9	15.9	13.5	10.2
135		14.2		
140	14.4	12.7	11.1	8.48
150	11.6	10.4	9.76	7.30
160	9.43	8.46	8.23	6.69
170	7.90	7.11	6.68	5.91
180	6.70	5.92	5.38	4.96
190	5.79	4.89	4.53	4.21
200	5.04	4.17	3.89	3.48

[a] The subscript x in the formula P(EO)$_x$LiCF$_3$SO$_3$ represents the number of EO monomer units per Li$^+$ in the polymer–salt mixture, not the true stoichiometry of the crystalline complexes.

The degree of crystallinity as a function of temperature can be determined from the data for a nonspecific IGC probe by the method proposed by Guillet and Stein.[6] The method is based on the assumption that a linear extrapolation of the retention volume data from temperatures above a given transition temperature to temperatures below the transition temperature will provide an accurate measure of the retention volume of the probe at the lower temperatures *if the phase transition had not occurred*. Thus, the extrapolated retention volume is a measure of the amount of stationary phase that would be available without a phase transition, while the experimentally measured retention volume at the lower temperatures is proportional to the actual amount of stationary phase available to the IGC probe. The degree of crystallinity can be calculated from the difference between these two retention volumes. The results are shown in Figure 2 for

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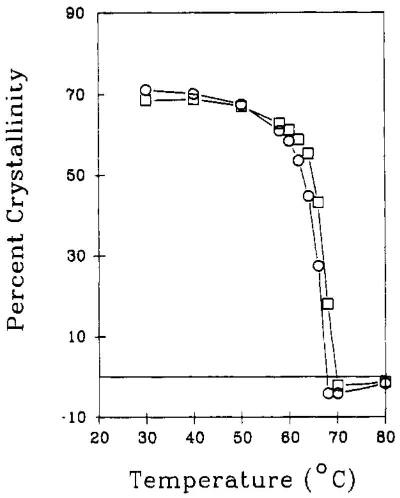

Figure 2. Percent crystallinity as a function of temperature: □, pure PEO; ○, $P(EO)_{16}LiCF_3SO_3$.

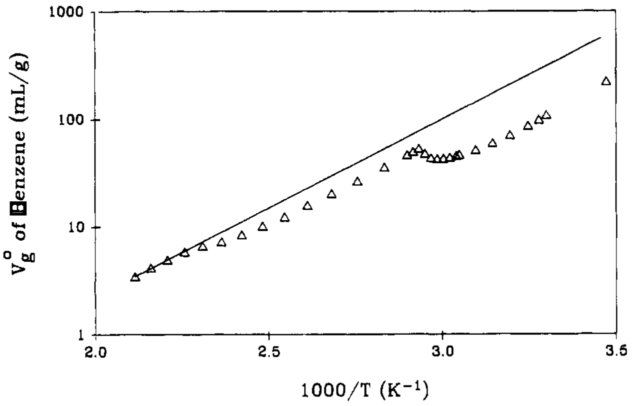

Figure 3. van't Hoff plot for benzene on $P(EO)_6LiCF_3SO_3$ column: △, $P(EO)_6LiCF_3SO_3$; —, extrapolated from 170 to 200 °C.

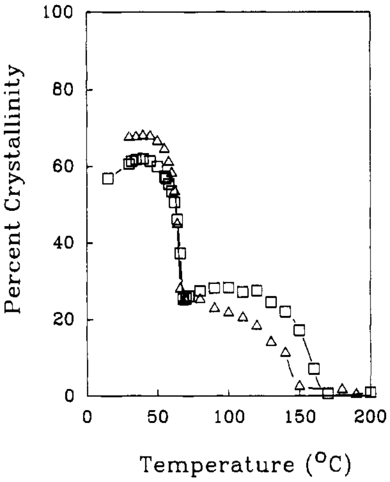

Figure 4. Percent crystallinity as a function of temperature: □, $P(EO)_8LiCF_3SO_3$; △, $P(EO)_6LiCF_3SO_3$.

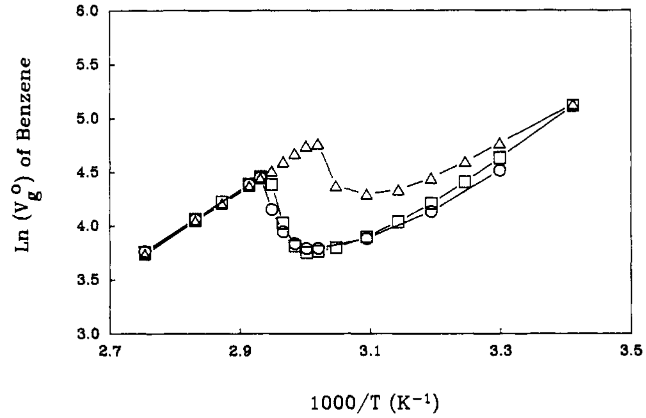

Figure 5. Heating and cooling cycles for benzene on $P(EO)_{16}LiCF_3SO_3$ column: ○, first heating cycle (30 → 100 °C); △, first cooling cycle (100 → 30 °C); □, second heating cycle (30 → 110 °C).

PEO and $P(EO)_{16}LiCF_3SO_3$. The calculations are based on the retention volumes measured at temperatures of less than 120 °C for the first heating cycle of freshly prepared columns. The results show that pure PEO and $P(EO)_{16}LiCF_3SO_3$ were approximately 70% crystalline at room temperature. This is somewhat higher than the commonly cited value of about 60%[4] determined from NMR studies. The transition temperature of the $P(EO)_{16}LiCF_3SO_3$ mixture (69 °C) was slightly lower than that of PEO (70 °C).

A high-temperature phase transition was observed at salt concentrations of 8:1 and 6:1. The van't Hoff plot for the $P(EO)_6LiCF_3SO_3$ column is shown in Figure 3. The straight line in the plot was calculated from a linear regression of the retention volume data at 170–200 °C. This illustrates the method for the calculation of percent crystallinity, i.e., the extrapolated line represents the values of the retention volumes that would be observed if no crystalline PEO or crystalline salt complexes formed at the lower temperatures. The calculated crystallinity for the $P(EO)_6LiCF_3SO_3$ and $P(EO)_8LiCF_3SO_3$ mixtures are shown in Figure 4. The uncertainty in the calculated crystallinity is highest at the lower temperatures because of the extensive extrapolation required; however, both mixtures were about 60–70% crystalline at room temperature. The most significant difference between the high and low salt concentration polymers is the degree of crystallinity in the temperature range from 70 to 150 °C. The $P(EO)_8LiCF_3SO_3$ material was about 20% crystalline and melted at 150 °C, whereas the $P(EO)_6LiCF_3SO_3$ mixture was closer to 30% crystalline and melted at 170 °C.

The apparent decrease in crystallinity at low temperatures in Figure 4 is an artifact caused by the linear extrapolation from 170 to 15 °C. This curvature has been observed previously and can be corrected by nonlinear extrapolation involving a correction for gas-phase imperfections.[9] The distortion, in this case, was not significant, and the calculated degree of crystallinity would be little affected, so no correction for gas-phase imperfections was applied.

In the temperature range 70–200 °C, where the PEO was completely amorphous or liquid and the salt complex was amorphous or partially crystalline, the retention volumes of benzene decreased with lithium concentration. This effect was due to the loss of PEO (available to the IGC probe) as $P(EO)_xLiCF_3SO_3$ crystals, at intermediate temperatures, or secondarily to the effect of Li^+ on the activity coefficient of benzene dissolved in the polymer, i.e., a "salting-out effect" at high temperatures.

Hysteresis Effects. A significant hysteresis effect was observed for all of the columns. In the temperature range 20–100 °C, the measured retention volumes were reproducible. Heating and cooling cycles for the $P(EO)_{16}LiCF_3SO_3$ column are shown in Figure 5. Supercooling was observed down to a temperature of 58–60 °C; however, the heating curve could be reproduced when the column was cooled overnight after a heating cycle. Thus, simple melting and recrystallization of PEO at

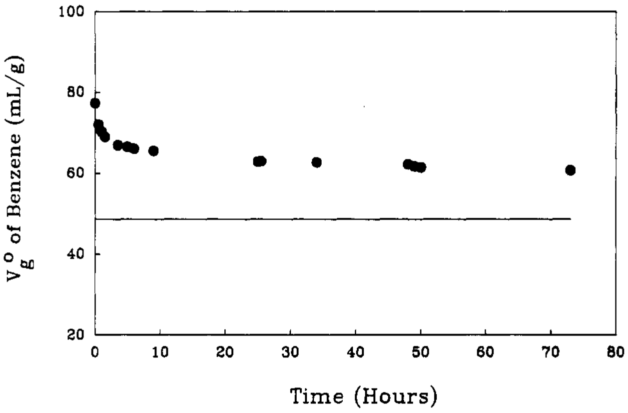

Figure 6. Recrystallization kinetics for $P(EO)_{16}LiCF_3SO_3$ at 50 °C: ●, retention volume of benzene on supercooled $P(EO)_{16}LiCF_3SO_3$; —, retention volume of benzene at equilibrium.

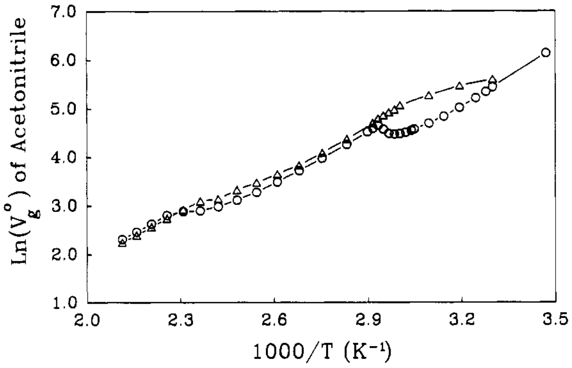

Figure 7. van't Hoff plots for $P(EO)_6LiCF_3SO_3$ column: ○, first heating cycle (30 → 200 °C); △, second heating cycle.

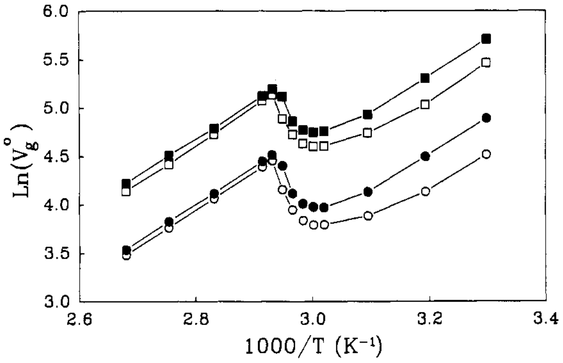

Figure 8. Effect of polymer liquid loading for $P(EO)_{16}LiCF_3SO_3$ columns: ○, benzene 6.30% loading; ●, benzene 2.35%; □, acetonitrile 6.30%; ■, acetonitrile 2.35%.

Table II. Specific Retention Volume of Acetonitrile on PEO and $P(EO)_xLiCF_3SO_3$ Columns

	specific retention vol, mL/g of PEO			
temp, °C	PEO	$P(EO)_{16}$-$LiCF_3SO_3$	$P(EO)_8$-$LiCF_3SO_3$	$P(EO)_6$-$LiCF_3SO_3$
15				460.5
30	215.4	235.7	251.7	230.5
32				209.3
35			204.6	183.7
40	140.9	153.1	165.9	150.4
45			137.3	126.0
50	100.7	114.4	118.1	109.1
55			103.9	96.6
56				94.4
58	84.1	99.9	100.6	90.9
60	82.0	99.4	100.4	88.4
62	80.8	102.6	103.4	87.6
64	82.0	112.7	113.0	88.7
66	96.3	132.5	134.7	96.5
68	128.7	169.8	130.5	104.9
70	147.7	159.9	121.7	97.9
72				91.5
80	103.1	113.0	87.6	70.7
90	74.0	82.7	65.5	53.2
100	53.8	62.8	51.5	41.1
110	39.6	49.3	40.9	32.6
120	30.4	40.1	33.3	26.3
125		36.3		
130	23.3	32.9	28.4	22.5
135		29.2		
140	18.2	26.0	25.0	19.7
150	14.3	20.8	22.9	18.1
160	11.6	16.8	19.4	17.9
170	9.44	13.8	15.9	16.5
180	7.81	11.4	13.3	13.8
190	5.78	9.52	11.1	11.8
200	5.04	8.06	9.63	10.1

moderate temperatures did not cause any irreversible changes in the chemical or physical characteristics of the polymer or polymer–salt complexes.

Although the process was reproducible, recrystallization of the PEO after melting was remarkably slow as shown in Figure 6, which is a plot of the measured retention volume of benzene as a function of time for a supercooled $P(EO)_{16}LiCF_3SO_3$ column. The column was heated to 100 °C and then cooled rapidly to 50 °C, and the retention volume of samples of benzene were measured at 50 °C for several hours. Clearly, the recrystallization process would take several days at 50 °C.

The retention volumes could not be reproduced at low temperatures once the column had been heated to 200 °C. Subsequent to heating the column to 200 °C, the phase transitions were shifted, obscured, or completely eliminated. This effect is illustrated in Figure 7 for the $P(EO)_6LiCF_3SO_3$ column. PEO has been shown[14] to be unstable to light, oxygen, and acidic metal ions. In this case, the diatomaceous earth solid support probably caused an irreversible decomposition, i.e., decrease in molecular weight, at the high temperatures which inhibited the formation of PEO microcrystals at the lower temperatures.

Surface Adsorption. Adsorption of poler IGC probes, such as water and *n*-propanol, at the gas–polymer interface has been observed[12] for a lower molecular weight PEO, e.g., Carbowax 20M. Similar effects have been found for benzene and toluene[8] and *n*-hexadecane[10] on polystyrene. To test for this phenomenon with benzene and acetonitrile probes, two $P(EO)_{16}LiCF_3SO_3$ columns were prepared with different liquid loadings of 2.35 and 6.30%. The van't Hoff plots for both IGC probes for these two columns are shown in Figure 8. The 2.35% loading column gave consistently higher retention volumes for both probes, although the differences were not large. This variation of the retention volume with polymer film thickness and liquid surface area has been observed previously,[8,10] and the usual correction is an extrapolation to infinite film thickness. However, the extrapolation is nonlinear,[8,10,12] and the exact cause of the dependence is not clear,[8] i.e., whether the increase in retention with thinner films is due to adsorption on the surface of the partially crystalline polymer or to the influence of the solid surface on the structure of the polymer spread as a thin film.[8] All of the columns used for the data reported in Tables I and II had approximately the same liquid loads (5–6%). Thus, because of the uncertainty of the correction procedure and the small effect of film thickness observed for the two $P(EO)_{16}LiCF_3SO_3$ columns, the retention volume data were not altered to eliminate

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[14] McGary, C. W. *J. Polym. Sci.* **1960**, *46*, 51.

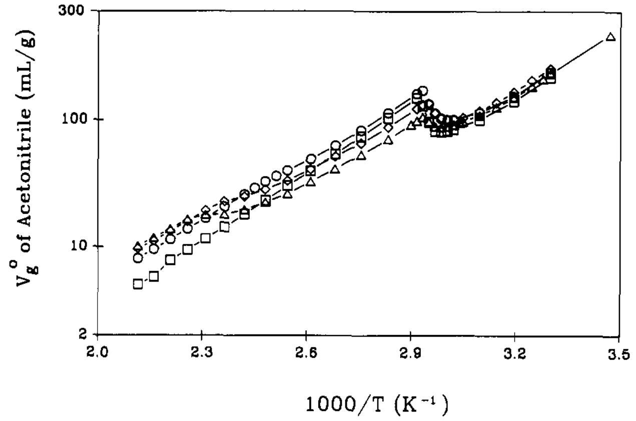

Figure 9. van't Hoff plots for acetonitrile (legend same as in Figure 1).

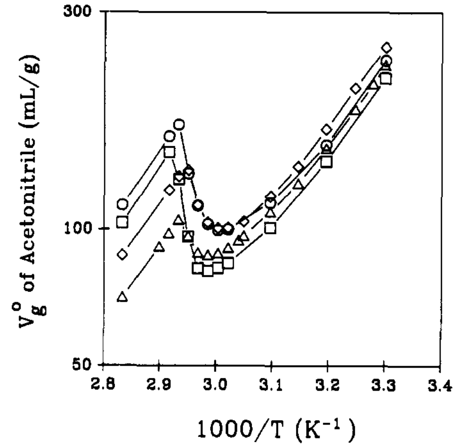

Figure 10. van't Hoff plots for acetonitrile at low temperatures (legend same as in Figure 1).

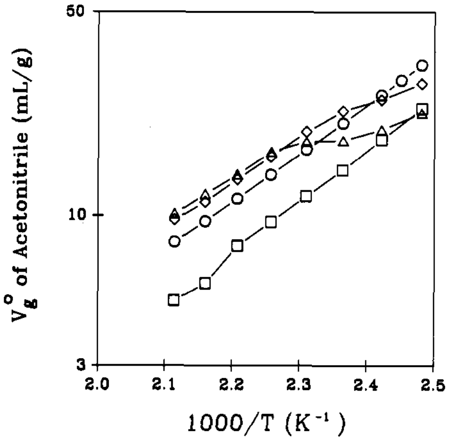

Figure 11. van't Hoff plots for acetonitrile at high temperatures (legend same as in Figure 1).

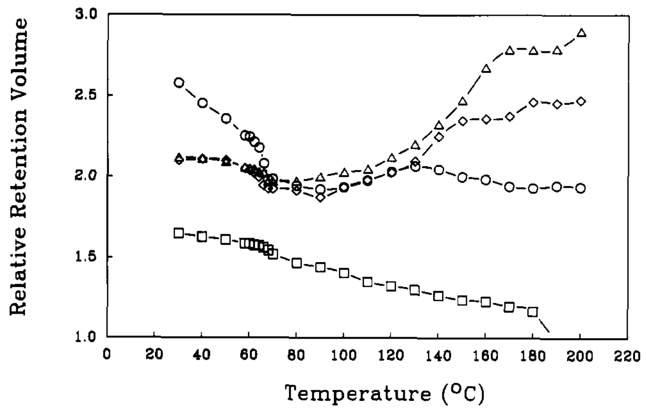

Figure 12. Relative retention volume of acetonitrile (legend same as in Figure 1).

the contribution from adsorption or structural effects.

Complexation. The results for a specific IGC probe, acetonitrile, were significantly different from the results obtained with the nonspecific probe. Acetonitrile is known to complex with Li^+ and would be expected to effectively interfere with the coordination between the Li^+ ion and the ether oxygens of the PEO. Electrochemical investigations[1] have shown that acetonitrile sorbed into $P(EO)_{16}LiCF_3SO_3$ polymers at temperatures up to 70 °C significantly increased the conductivity of the polymer as well as the diffusion coefficients of metal complexes dissolved in the polymer.

The specific retention volumes of acetonitrile on each of the polymer columns are given in Table II, and the van't Hoff plots are shown in Figure 9. Again, the same two nonlinear regions were observed; however, the effect of the $LiCF_3SO_3$ salt was pronounced, especially at temperatures higher than the melting point of the crystalline $P(EO)_xLiCF_3SO_3$ complexes and at temperatures below the melting point of crystalline PEO.

Figure 10 is a magnified portion of the van't Hoff plot for the lower temperatures. In contrast to the benzene data, in this case, the $LiCF_3SO_3$ salt caused an increase in the retention volume of the probe. However, the increase did not correlate with the formal concentration of the salt. At these temperatures, only about 30–40% of the polymer was amorphous and most of the Li^+ was locked in the crystalline domains and was unavailable to the IGC probe. The observed increase in retention of the probe caused by the $LiCF_3SO_3$ is probably due to the small amount of free Li^+ in the amorphous regions of the polymer. However, both the conductivity and metal complex diffusion coefficients are low at these temperatures,[15] indicating that the Li^+ is not mobile even in the amorphous regions of the material.

At intermediate temperatures (70–150 °C) the results for the acetonitrile probe were similar to the data observed for the benzene probe. This indicates that the Li^+ ions were not available to the acetonitrile probe, i.e., all of the metal ion was present as crystalline $P(EO)_xLiCF_3SO_3$ complexes. However, the ionic conductivity and metal ion diffusion coefficients were significantly higher at these temperatures than those measured at temperatures below 70 °C.[15]

At temperatures above the melting point of the crystalline $P(EO)_xLiCF_3SO_3$ complexes, the retention volumes again increased with formal salt concentration. A magnified van't Hoff plot for this temperature range is shown in Figure 11. The results indicate that the polymer is completely amorphous or liquid and that all of the Li^+ is available for complexation with acetonitrile.

The solute probes used in this investigation were chosen because they have approximately equal vapor pressures (at 25 °C, P°(benzene) = 95 Torr, P°(acetonitrile) = 92 Torr) but different chemical properties. However, even though the solutes had equivalent vapor pressures, the solubility of acetonitrile in the conducting polymers and pure PEO was greater than that of benzene. The relative retention, α, the ratio of the retention volume of acetonitrile to the retention volume of benzene, is a measure of the selectivity of the stationary phase for acetonitrile.

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(15) Geng, L.; Longmire, M. L.; Reed, R. A.; Parcher, J. F.; Barbour, C. J.; Murray, R. W. *Chem. Mater.* **1989**, *1*, 58.

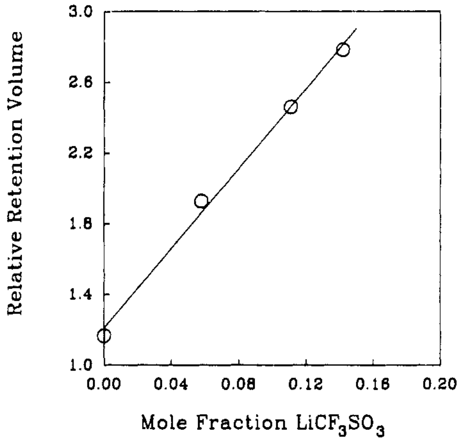

Figure 13. Relative retention volume of acetonitrile as a function of the concentration of LiCF$_3$SO$_3$ at 180 °C.

Because it is a relative parameter, the degree of crystallinity of the polymer should not affect the α value. The selectivity of the columns and the effect of the salt on this selectivity are illustrated in Figure 12.

Compared to pure PEO, all of the P(EO)$_x$LiCF$_3$SO$_3$ polymers show significant selectivity for acetonitrile, especially at high temperatures. Even at temperatures below 70 °C, where the polymer was only 60–70% crystalline, the presence of LiCF$_3$SO$_3$ enhanced the selectivity of the stationary phase for acetonitrile. The selectivity is relatively constant up to 130 °C, except for the abnormally high values for the 16:1 column. Above this temperature, the crystalline complexes were melted, and the selectivity increased with salt concentration as shown in Figure 13. If the acetonitrile formed a simple 1:1 association with Li$^+$, the retention volume of acetonitrile would increase linearly with [Li$^+$] and the slope of the plot should be proportional to the complex formation constant.[16] The complex formation constant calculated from the slope of the plot at 180 °C was 11.2 M^{-1}.

The effect of the sorption of the volatile solvents on the electrochemical response of P(EO)$_x$LiCF$_3$SO$_3$ has been studied for polymers containing several different soluble metal complexes.[15] It was shown that acetonitrile sorption increased both the conductivity of the polymer and the diffusion coefficients of the metal complexes at temperatures below the melting point of crystalline PEO. The acetonitrile appeared to have little or no effect at higher temperatures. The exact cause for the enhancement effect is uncertain, although the authors[15] proposed a "plasticization" effect caused by the interference of acetonitrile with the cross-linking function of the Li$^+$ allowing greater segmental mobility within the polymer. The effect of acetonitrile on the crystal structure of the P(EO)$_x$LiCF$_3$SO$_3$ complex has not been determined; however, the very fast plastization and relaxation processes observed[2] would seem to argue against any dissolution and recrystallization mechanism because the extremely slow kinetics observed for these processes.

Conclusions

The IGC results reported here confirm the DSC results reported previously[5] as far as the phase transitions observed at 68–70 °C for PEO and from 130 to 170 °C for P(EO)$_x$LiCF$_3$SO$_3$ complexes with the transition temperature increasing with salt concentration. However, the use of specific and nonspecific solute probes reveals more information than DSC investigations. The nonspecific probe, benzene, gave a reliable measure of the amount of amorphous liquid available, and hence the degree of crystallinity, in any of the P(EO)$_x$LiCF$_3$SO$_3$ mixtures as a function of temperature and composition. The IGC method for the determination of crystallinity is not as accurate as direct X-ray crystallographic methods; however, the technique is excellent for the rapid survey and comparison of a series of polymers or polymer–salt mixtures over a range of temperatures and pressures.

The specific probe, acetonitrile, was influenced by the degree of crystallinity but also by the availability of the particular component of the stationary phase that strongly interacts with the probe, in this case Li$^+$. The results indicate that the Li$^+$ ions are completely accessible to the acetonitrile probes at high temperatures, partially accessible at low temperatures, and apparently inaccessible at intermediate temperatures from 70 to 170 °C. This result is in apparent contradiction with the electrochemical results that indicate that Li$^+$ is immobile in the "conducting" polymer at low temperatures but readily transported through the media at temperatures greater than 50–70 °C.[15] No electrochemical studies of these particular systems have been carried out at the higher temperatures employed for the chromatographic investigation.

The 16:1 composition material is most useful for electrochemical applications because of the high conductivity of this particular polymer. The physical properties of the 16:1 mixture are very similar to those of pure PEO and quite different from the 8:1 or 6:1 materials. At this low concentration, there are apparently enough charge carriers to provide high conductivity but not enough to disturb the structure of the PEO polymer. However, the 16:1 polymer differs substantially from pure PEO in the selectivity toward acetonitrile, as shown in Figure 12. In terms of selectivity for acetonitrile, even a small amount of lithium enhances the solvent strength of the polymer significantly.

The combination of chromatographic and electrochemical methods provides an excellent method for the study of conducting polymers and other semirigid electrolytes. The use of different types of molecular probes in the IGC method and different sorbent vapors in the electrochemical methods provide complementary information concerning the chemical, physical, and structural properties of high molecular weight polymers which are difficult to study by classical methods.

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