Phase Diagram of the Poly(ethylene oxide):$Ca(CF_3SO_3)_2$ System

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Variable-temperature powder X-ray diffraction (VTXRD) and differential scanning calorimetry (DSC) have been used to determine the poly(ethylene oxide):$Ca(CF_3SO_3)_2$ phase diagram. A new crystalline complex with a stoichiometry corresponding to 6 ether oxygens/Ca^{2+} ion has been identified. The data show that this complex exhibits a phase transition at ~200 °C between a low temperature, α, and high temperature, β, polymorph; at higher temperature the β polymorph melts incongruently. At lower salt contents, precipitation of $Ca(CF_3SO_3)_2$ from the amorphous phase upon increasing the temperature is observed, indicating a negative entropy for the dissolution of the salt in the polymer. Finally, temperature dependent conductivities are presented for a range of compositions.

Introduction

Solid electrolytes may be formed by dissolving salts in high-molecular-weight coordinating polymers.[1] By addition of low-molecular-weight plasticizers, ionic conductivities at room temperature approaching that of liquid systems may be obtained. Even in the absence of plasticizers, films with a high conductivity can be prepared. In this paper we are concerned exclusively with solvent free systems. The archetypal polymer host for such electrolytes is poly(ethylene oxide) [PEO]. Whereas ionic conductivity is largely confined to amorphous polymer-salt phases, with hosts such as PEO both amorphous and crystalline phases generally form depending on the salt content and the temperature of the system. The fact that ionic conductivity and many other physical properties, e.g., relative permittivities, mechanical strength, etc., depend on the particular phase or combination of phases present means that to understand such properties and their variation with temperature and composition, it is essential to construct a phase diagram for the specific system under study. It is important however to appreciate that such diagrams frequently do not describe the system in true thermodynamic equilibrium. Since organic hosts such as PEO are stable only at moderate temperatures, all the phases must be formed at these low temperatures. The rate of formation of polymer-salt phases depends on the diffusion of long polymer chains, at low temperatures this can be a very slow process and hence kinetic rather than thermodynamic control may be significant. Strictly therefore, polymer-salt phase diagrams should be considered to be a convenient means of summarizing the reproducible behavior of the system as a function of composition and temperature.

To date, much of the interest in the field of polymer electrolytes has concentrated on systems containing lithium salts.[2,3] Rechargeable all-solid-state lithium batteries based on lithium ion conducting polymers are under intensive development in a number of industrial laboratories. Phase diagrams for several PEO:lithium salt systems have been determined as well as a number of other systems in which salts of monovalent cations have been dissolved in PEO.[4-6] Few detailed studies have been carried out of phase diagrams for PEO systems containing divalent cation salts although there is considerable interest in such systems.[7-10] As well as presenting the PEO:$Ca(CF_3SO_3)_2$ phase diagram and highlighting the fact that the phase relationships indicate a negative entropy for the dissolution of this salt in PEO, we also present conductivity measurements for this system as a function of composition and temperature.

Experimental Section

Preparation of Salt. $Ca(CF_3SO_3)_2$ was prepared by the slow addition of a 0.667 M aqueous solution of triflic acid (Aldrich) to an excess of $CaCO_3$ (BDH, 99%) suspended in distilled water. The mixture was stirred for 24 h and then vacuum filtered through a fine sinter. The bulk water was removed by rotary evaporation to yield the hydrate. By heating under vacuum at 180 °C for 24 h, the anhydrous salt was obtained. PEO (BDH, MW 5×10^6) was dried by heating under vacuum at 55 °C for 48 h.

Differential Scanning Calorimetry. Different polymer electrolyte compositions were prepared by the cryogrinding method.[11] The anhydrous salt was first finely ground in a mortar and pestle within a high-integrity MBraun glovebox filled with argon. The H_2O and O_2 contents of the box were each maintained below 1 pppm. The ground salt was then mixed with appropriate proportions of dry PEO and loaded into the chamber of a ball mill under argon. The sealed chamber was removed from the glove box and shaken for 20 min in liquid nitrogen. At this low temperature the polymer is brittle and fractures under the impact

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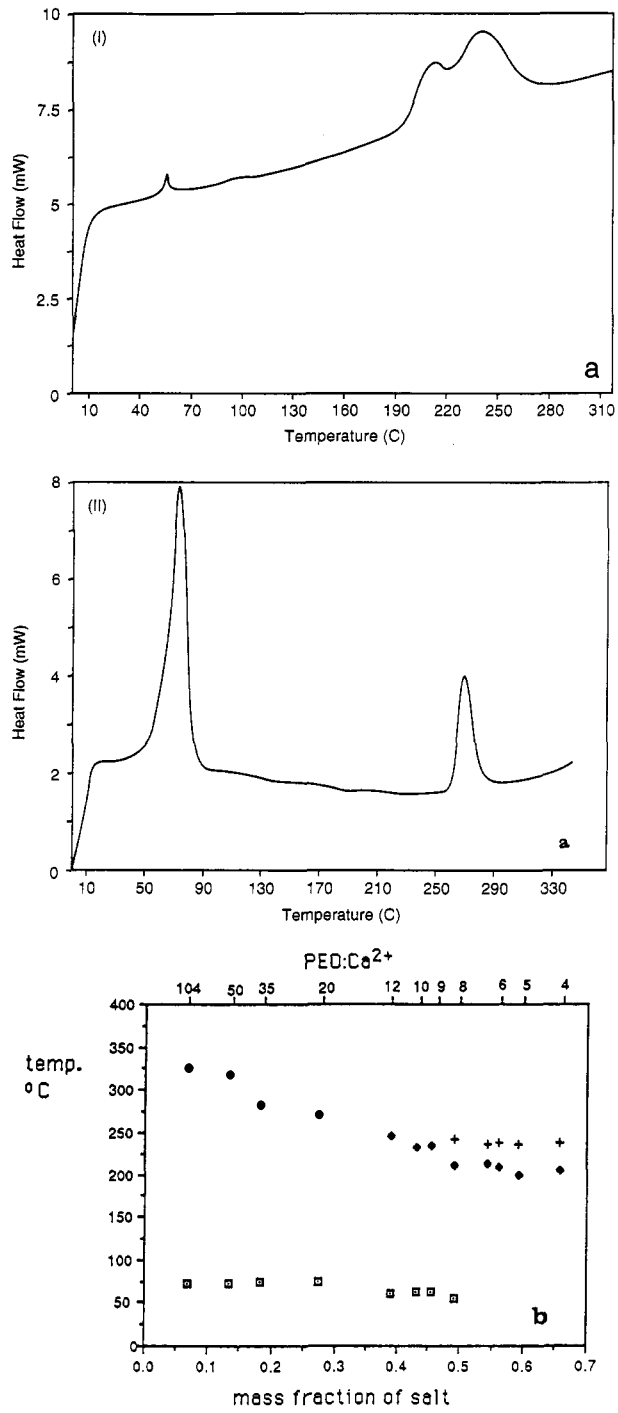

Figure 1. (a) DSC traces for (i) PEO_8:$Ca(CF_3SO_3)_2$ and (ii) PEO_{20}:$Ca(CF_3SO_3)_2$, both collected on the first heating cycle. (b) Plots of the endotherms from DSC measurements on the 1st heating cycle as a function of electrolyte composition; ⊡, ●, +, represent the first, second, and third endotherms, respectively.

of the ball bearings ensuring intimate mixing of the salt and polymer. After grinding, the mixture was allowed to stand for 2 h at room temperature before being transferred back into the glovebox.

A small sample (≈50 mg) was placed between two Teflon disks in a 13-mm die and pressed at 5×10^3 kg cm^{-2} for 30 s. The assembly was then heated between 130 and 150 °C for several hours in the absence of an applied pressure. Upon cooling to 60 °C, a pressure of 2×10^3 kg cm^{-2} was applied and the sample annealed at this temperature for 24 h before being allowed to slowly cool to room temperature. Typically, disks produced by this process were 0.1–0.4 mm thick.

DSC was performed on a Perkin-Elmer DSC 7. The hot-pressed polymer electrolyte films were sealed under argon in aluminium sample pans. The films were heated and cooled at 20 °C min^{-1}.

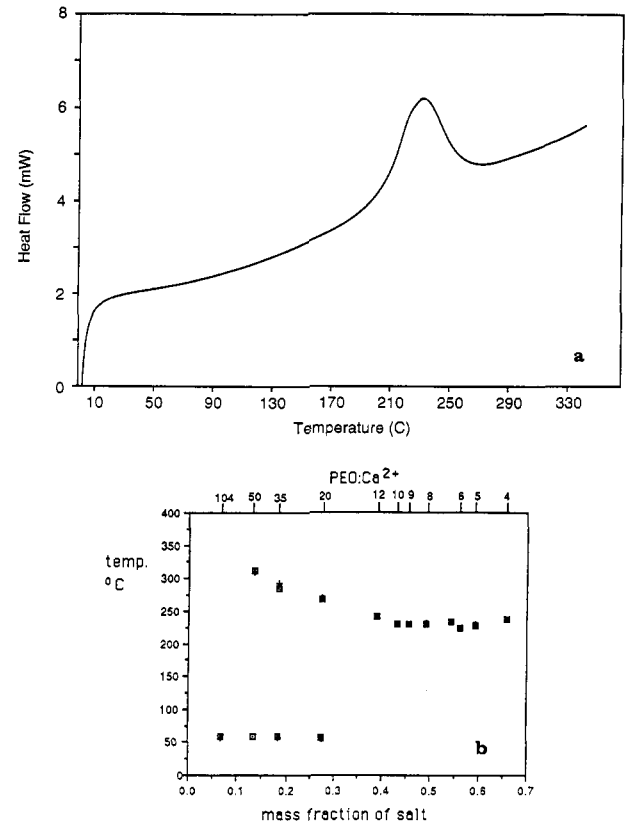

Figure 2. (a) DSC trace for PEO_8:$Ca(CF_3SO_3)_2$ on the second heating cycle. (b) Plots of the endotherms from DSC measurements on the second (⊡) and third (+) heating cycles as a function of electrolyte composition. Heating commenced as soon as the sample had cooled to 30 °C.

Table I. Powder X-ray Diffraction Data for the α Polymorph of the 6:1[a] Complex

			2θ (deg)				
h	k	l	obs	calc	delta	d(obs) (Å)	d(calc) (Å)
0	1	1	8.809	8.812	−0.0031	10.0297	10.0262
1	0	1	9.852	9.846	0.0063	8.9703	8.9761
1	1	0	10.954	10.939	0.0146	8.0704	8.0811
1	1	1	12.166	12.137	0.0293	7.2687	7.2863
0	2	0	14.161	14.186	−0.0253	6.2492	6.2381
0	2	1	15.127	15.133	−0.0060	5.8522	5.8499
2	0	0	16.672	16.703	−0.0302	5.3130	5.3034
1	2	1	17.288	17.297	−0.0089	5.1251	5.1225
1	2	2	19.584	19.570	0.0138	4.5292	4.5324
0	0	4	21.055	21.076	−0.0204	4.2159	4.2118
1	0	4	22.705	22.697	0.0084	3.9131	3.9145
1	2	3	22.893	22.879	0.0145	3.8814	3.8838
1	3	1	23.538	23.558	−0.0199	3.7765	3.7734
2	2	2	24.435	24.413	0.0226	3.6398	3.6431
3	1	1	26.709	26.713	−0.0037	3.3348	3.3344
0	2	5	30.145	30.119	0.0255	2.9622	2.9646
0	1	6	32.662	32.662	−0.0006	2.7394	2.7394
2	4	1	33.742	33.731	0.0108	2.6541	2.6549
0	3	5	34.237	34.222	0.0151	2.6169	2.6180

[a] The *hkl*'s listed are those used to refine the unit cell dimensions. Crystal system = orthorhombic. Lattice parameters: a = 10.607 Å, b = 12.476 Å, and c = 16.847 Å. Volume 2229.5 Å^3.

X-ray Diffraction. Sample preparation involved loading 0.5-mm Lindemann tubes (Pantak Ltd.) under argon with a cryoground mixture of dried PEO and $Ca(CF_3SO_3)_2$. The tubes were then sealed and heated between 130 and 150 °C for several hours to facilitate dissolution of the salt in the polymer. The samples were then cooled slowly to 60 °C and annealed at this temperature for a further 24 h.

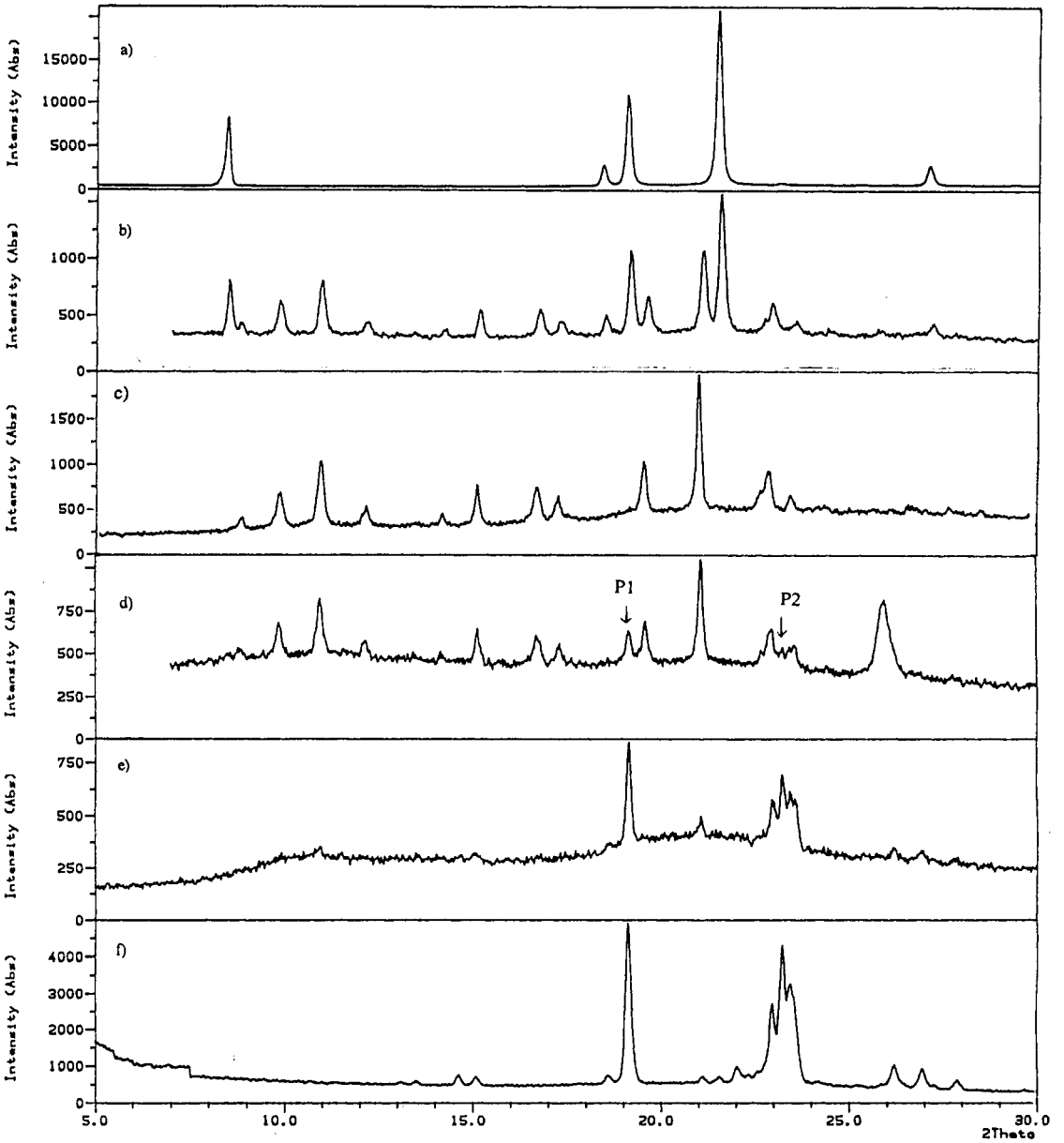

Figure 3. X-ray diffraction patterns for several compositions at ambient temperature: (a) $Ca(CF_3SO_3)_2$, (b) 4:1, (c) 6:1, (d) 8:1, (e) 9:1, (f) PEO. P1 and P2 in (d) indicate the positions of the most intense PEO peaks. The peak at 26° in (d) is associated with the graphite furnace.

Powder X-ray diffraction was carried out on a Stoe STADI/P high-resolution diffractometer fitted with a germanium monochromator and operating in transmission mode. Cu $K\alpha_1$ radiation was used throughout and the data collected using a small angle (6° in 2θ) linear position sensitive detector in steps of 0.02° in 2θ. The data collection was under the control of a Digital 3300 work station which was also used for data analysis. The system was equipped with a graphite furnace within which the samples, mounted in their capillaries, were heated. The furnace was fitted with an X-ray transparent window.

Conductivity Measurements. The polymer films were mounted between two stainless steel disk electrodes under a light spring pressure in a Teflon-bodied cell. The cell was located within an evacuable stainless steel chamber with electrical feedthroughs and a thermocouple. This permitted removal of the cell from the glovebox for the electrical measurements. The chamber was placed in a tube furnace controlled by a Eurotherm temperature programmer. The temperature could be maintained within ±1 °C. Ac impedance measurements were performed using a Schlumberger Solartron 1255 frequency response analyzer and 1286 electrochemical interface, both under the control of a Zenith microcomputer. Data were collected from 1 Hz to 100 kHz, and dc conductivities extracted from the complex impedance plots.

Results and Discussions

DSC Measurements. A survey of the literature indicates that no common practice has yet been adopted in the field of polymer electrolytes for reporting the temperatures of thermal events such as melting or crystallization. Strictly, onsets of thermal events most closely represent the temperatures of these events, however, in many cases there is extensive peak overlap making the extraction of onsets difficult. This is certainly the case for the PEO:$Ca(CF_3SO_3)_2$ system, and for this reason we report peak maxima in the paper. All of the thermal events observed on the first and subsequent heating cycles were endotherms. The DSC traces for two compositions, collected on the first heating cycle, are shown in Figure 1a and a plot representing the temperatures of the thermal events obtained from DSC on first heating polymer electrolytes with different compositions is shown in Figure 1b. The thermal event at ~60 °C may be associated with the melting of crystalline PEO. Events at higher tem-

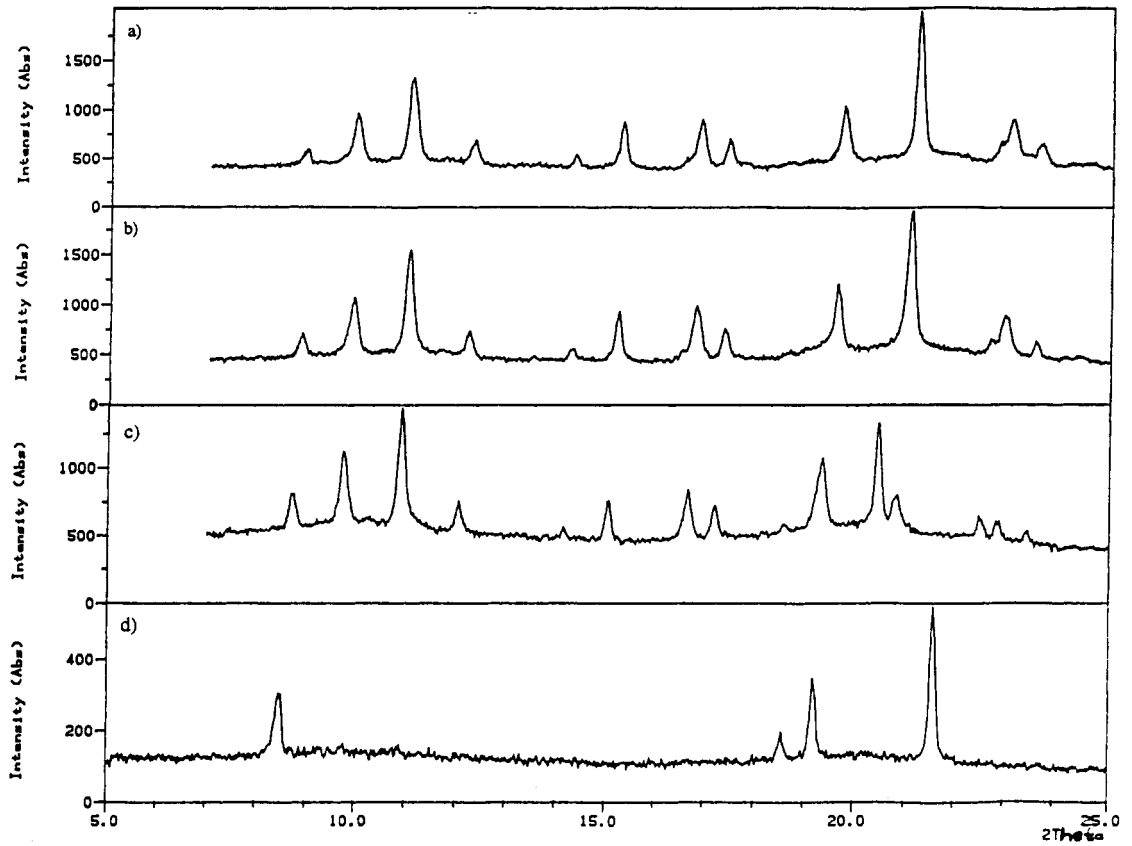

Figure 4. X-ray diffraction patterns for the 6:1 composition from 25 to 250 °C: (a) 25 °C, (b) 100 °C, (c) 201 °C, and (d) 250 °C. The samples were heated at 10 °C min^{-1} and equilibrated for at least 1 h at each temperature before data collection.

peratures may be divided into two composition ranges. For ether oxygen to Ca^{2+} ratios of 9:1 or more, only one transition is observed at high temperatures and the temperature of the transition increases with decreasing salt content in this range. In contrast two transitions are observed for ratios less than or equal to 8:1; neither of these exhibit a significant variation with composition. The two DSC traces in Figure 1a are typical of those observed above and below the 9:1 composition.

Transition temperatures for the second and third heating cycles are presented in Figure 2. PEO melting is only observed for ether oxygen to Ca^{2+} ratios greater than or equal to 20:1, whereas for the first heating cycle PEO melting occurred in all samples with ratios of 8:1 or greater. This difference reflects the slower kinetics of PEO crystallization as the salt concentration of the system is increased. The most striking difference between Figures 1 and 2 is the presence of only one transition at high temperatures regardless of salt content for the second and subsequent cycles. This behavior was observed reproducibly on subsequent samples.

Powder X-ray Diffraction. Although differential scanning calorimetry is an excellent technique with which to identify and locate the temperatures of thermal events, it does not directly reveal the nature of the processes involved. In contrast variable-temperature X-ray diffraction (VTXRD) is capable of following the appearance and disappearance of crystalline phases as a function of temperature and salt content and identifying such phases.[12] X-ray diffraction patterns have been collected as a function of both composition and temperature.

Beginning with the X-ray diffraction patterns at ambient temperature, these are presented in Figure 3. At an ether oxygen to Ca^{2+} ratio of ~6:1 a pure crystalline polymer: salt complex is obtained. There is no evidence of crystalline PEO or $Ca(CF_3SO_3)_2$ in the diffraction pattern for the 6:1 composition. The peaks associated with the new phase could be indexed on an orthorhombic unit cell with lattice parameters a = 10.607 Å, b = 12.476 Å, and c = 16.847 Å (Table I). Indexing was carried out using the program TREOR.[13] At lower salt concentrations the X-ray diffraction patterns indicate that the system is composed of a mixture of pure PEO and the 6:1 complex. At higher salt contents a two phase mixture is again obtained, consisting of the 6:1 complex and the pure $Ca(CF_3SO_3)_2$ salt.

Although VTXRD has been applied to the investigation of ceramic materials is has not, as far as we are aware, been used in the field of polymer electrolytes to determine phase diagrams. Perhaps the most interesting thermal behaviour is evident in X-rays of the 6:1 composition (Figure 4). Between 25 and 100 °C, there is little significant change in the powder pattern reflecting the absence of crystalline PEO; however, there is evidence of a change on raising the temperature to 201 °C. The major changes may be summarized as follows, two peaks are present in the range from 20 to 21° in 2θ, whereas only one is observed at lower temperatures and the peaks between 22.5 and 24° have changed in intensity. Apart from these changes and a general shift of the peaks to lower 2θ associated with thermal expansion, the rest of the pattern remains the same. The changes in the powder pattern between 100 and 210 °C are unlikely to be associated simply with the

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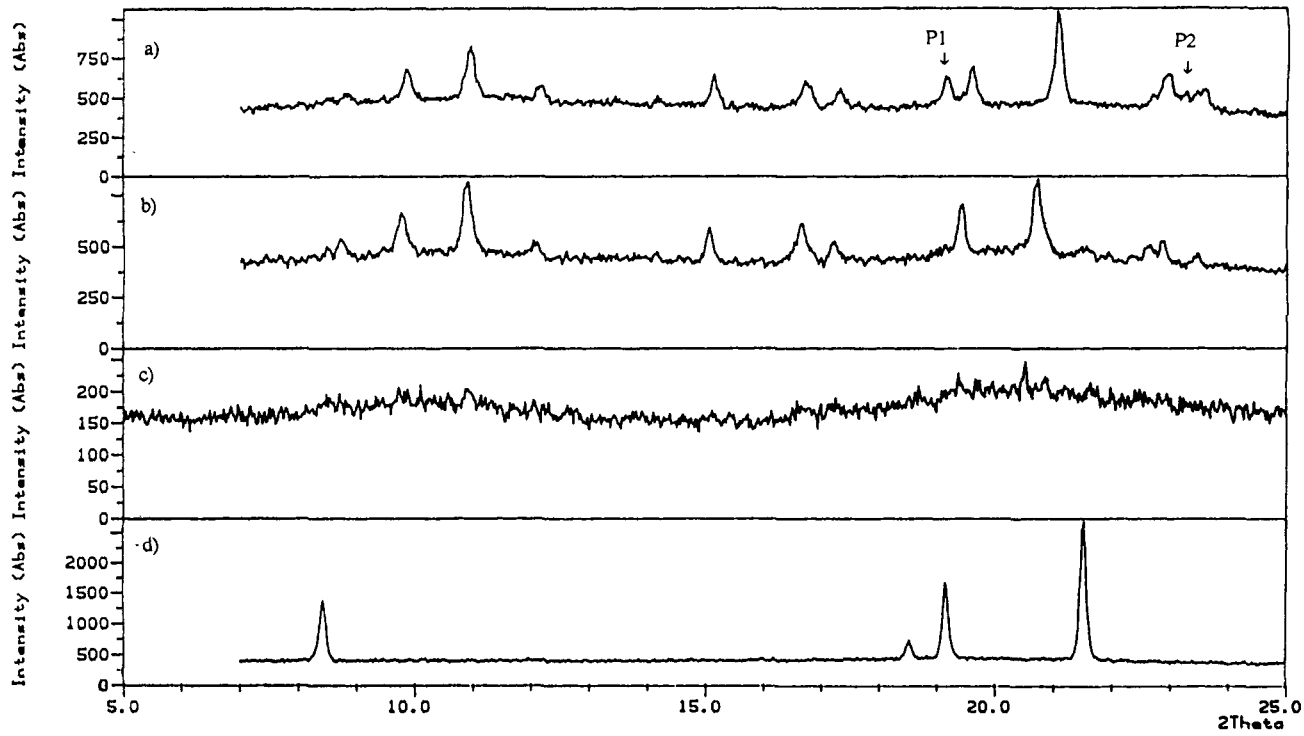

Figure 5. X-ray diffraction patterns for the 8:1 composition from 30 to 250 °C: (a) 30 °C; (b) 100 °C, (c) 204 °C, and (d) 250 °C. P1 and P2 in (a) indicate the most intense PEO peaks.

appearance of a second phase, due to decomposition, for example, since this would result in the appearance of additional peaks only; the changes are more consistent with a phase transition between two different polymorphic forms of the 6:1 complex. Although we cannot comment in detail on the nature of the structural change between the α and β polymorphs, it is likely to involve only a relatively minor displacement of atoms since the powder patterns for the two polymorphs are not radically different. Significant rotational disorder of the anions has been observed in the crystal structure of another polymer-salt complex, PEO_3:$NaClO_4$,[12] and it is possible that the phase transition observed in the case of PEO_6:$Ca(CF_3SO_3)_2$ is associated with the rotation of the triflate groups between two sites. At yet higher temperatures the complex disappears completely to be replaced by peaks corresponding to the $Ca(CF_3SO_3)_2$ salt (Figure 4d).

The two thermal events observed at high temperatures on the DSC for $Ca(CF_3SO_3)_2$ rich compositions (Figure 1) can now be explained. They are due to the $\alpha \rightarrow \beta$ transition followed at higher temperatures by incongruent melting of the β complex to liquid plus $Ca(CF_3SO_3)_2$ salt. Comparing Figures 1 and 2, the $\alpha \rightarrow \beta$ transition occurring on the first heating cycle is absent on subsequent cycles whereas the transformation of the β phase to liquid and salt is not. This implies that the $\beta \rightarrow \alpha$ transformation on cooling is slower than the formation of the β complex from salt plus liquid. X-ray diffraction patterns collected on cooling samples have shown that the $Ca(CF_3SO_3)_2$ salt does disappear rapidly.

The changes occurring in the XRD pattern with increasing temperature for the 8:1 composition are shown in Figure 5. At room temperature the mixture of PEO and the α polymorph of the 6:1 complex is clearly identified; the peaks associated with crystalline PEO are absent from the XRD at 100 °C, as expected. At 204 °C the 6:1 complex has melted completely to yield a single-phase all-amorphous material. No clear evidence for an $\alpha \rightarrow \beta$ transition was observed by X-ray diffraction. However, on raising the temperature from 100 to 204 °C the peaks associated with the complex are reduced in intensity as the complex continuously dissolves in the liquid phase. The more sensitive DSC technique does reveal an endotherm in a similar temperature region to that of the $\alpha \rightarrow \beta$ transition in the 6:1 composition. We therefore believe that at 8:1 the transition probably occurs before the complex dissolves completely. At lower salt contents, e.g., 9:1, there is no evidence of an $\alpha \rightarrow \beta$ transition in the DSC results. However, the most interesting feature of these VT results is revealed in the diffraction pattern collected at 250 °C, the featureless diffraction pattern observed at 204 °C is replaced by peaks corresponding to the $Ca(CF_3SO_3)_2$ salt. Therefore these diffraction results indicate clearly the precipitation of salt from the liquid polymer with an increase in temperature. This process is confirmed by examining the VTXRD results for the 20:1 composition (Figure 6), which again reveals the precipitation of $Ca(CF_3SO_3)_2$ from the liquid phase at elevated temperatures. This process accounts for the single high-temperature endotherm noted in all compositions with ether oxygen to Ca^{2+} ratios greater than or equal to 9:1. Considering now the thermodynamic implications of this result and recalling the Gibb's equation, $\Delta G = \Delta H - T\Delta S$, and then assuming that ΔH and ΔS for precipitation do not vary significantly with temperature, the appearance of the salt at high temperatures implies that ΔS for precipitation is positive. It further implies that both the enthalpy and entropy of dissolution of the $Ca(CF_3SO_3)_2$ in PEO are negative. Although a negative entropy of dissolution has been noted in the case of PPO [poly(propylene oxide)] systems there has been relatively little reliable evidence of such a phenomenon in the case of PEO.[14]

By combining the data from DSC and VTXRD measurements, it is possible to construct a phase diagram for

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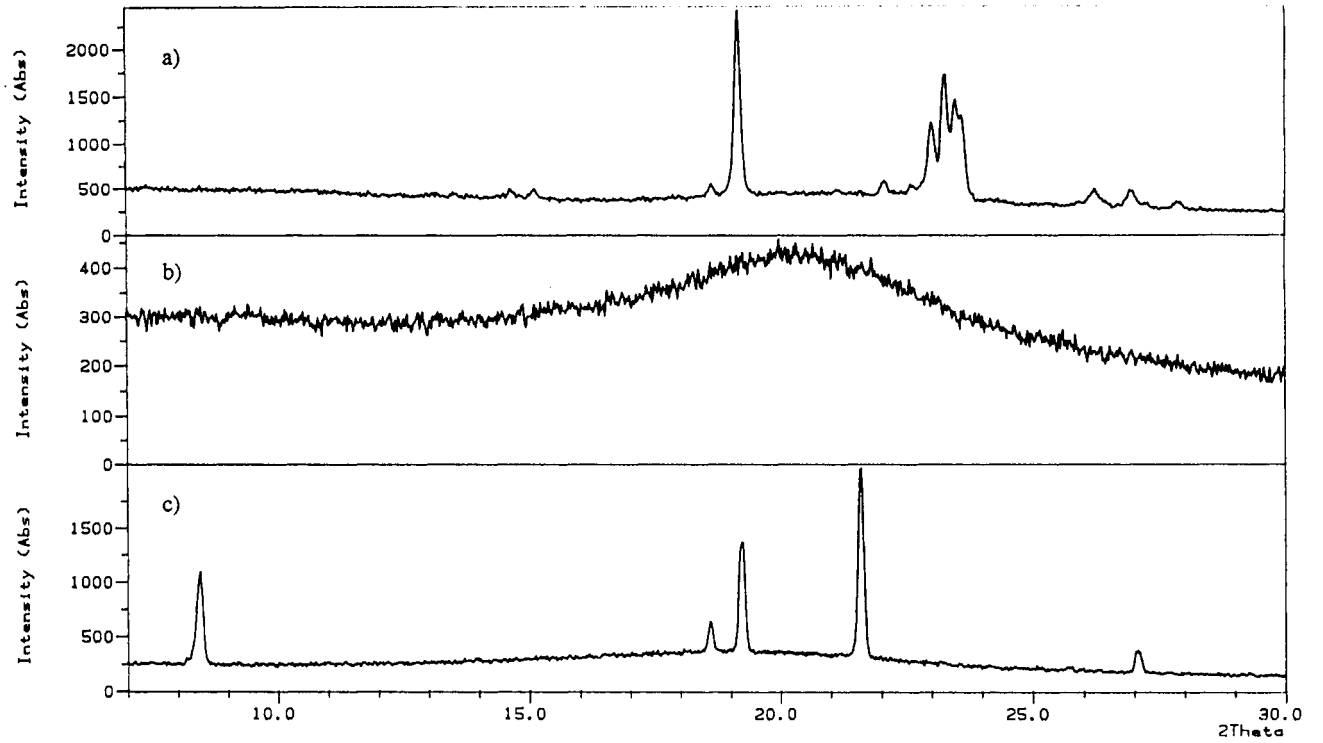

Figure 6. X-ray diffraction patterns for the 20:1 composition (a) 30 °C, (b) 100 °C, and (c) 300 °C.

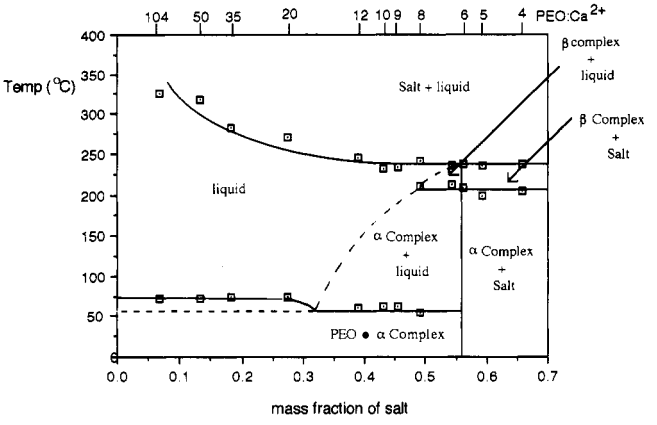

Figure 7. Phase diagram for the PEO:Ca(CF$_3$SO$_3$)$_2$ system.

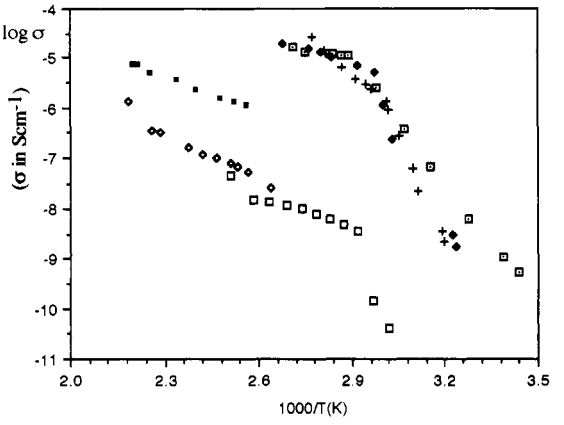

Figure 8. log σ vs^1 T for 50:1 (▣), 20:1 (◆), 12:1 (+), 6.5:1 (□), 5:1 (◇), PEO(□).

the PEO:Ca(CF$_3$SO$_3$)$_2$ system (Figure 7). The transition temperatures were in general taken from the peak maxima on the DSC traces whereas the nature of the phases present were obtained from the VTXRD results. The downward curvature for the precipitation of Ca(CF$_3$SO$_3$)$_2$ with increasing salt content is again consistent with a negative entropy of dissolution of Ca(CF$_3$SO$_3$) in PEO. Although both DSC and VTXRD data have been used, the diffraction data proved essential for the determination of this relatively complex phase diagram.

Conductivity Measurement. The temperature dependence of the conductivity for several compositions is presented in Figure 8. For all compositions the conductivity is enhanced compared with pure poly(ethylene oxide) although for the salt rich 5:1 material the enhancement is small. This is consistent with the phase diagram in Figure 7, which indicates that polymer films of this composition consist of complex and salt only. The conductivity of the system increases as the salt content decreases, down to the 12:1 composition; however, the conductivities of the three most dilute compositions, 50:1, 20:1, and 12:1, are similar. Their conductivities at high temperature are almost identical, and they all exhibit a sharp decrease in conductivity below ~60 °C. This decrease is associated with the loss of a liquid polymer phase as the system transforms to a mixture of crystalline PEO and the α polymorph of the 6:1 complex (Figure 7). The temperature-dependent conductivities of the PEO:Ca(CF$_3$SO$_3$)$_2$ films are clearly consistent with the phase diagram for this system.

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