Phase behaviour of poly(ethylene oxide)/poly(methyl methacrylate) blends containing alkali metal salts

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The effect of alkali metal salts on the phase behaviour of poly(methyl methacrylate) (PMMA)/poly(ethylene oxide) (PEO) blends was studied using d.s.c. Addition of lithium trifluoromethane sulfonate (LiT) to the normally miscible PEO/PMMA blends induced phase separation with the formation of a crystalline PEO phase, a crystalline PEO/salt complex phase and an amorphous PMMA phase. When potassium thiocyanate was used instead of LiT the mixture separated into two amorphous phases. Phase separation in these blends was not merely a result of the expected PEO/salt interaction, but also of the interaction of the salt with the PMMA. The evidence for this second interaction comes from an observed increase in the PMMA glass transition temperature with the addition of salt. Weak shifts in the carbonyl peaks in the i.r. spectra of the PMMA in the PMMA/salt mixtures suggest that the oxygen atom in the carbonyl interacts with the cation in the salt.

(Keywords: phase behaviour; blends; alkali metal salts)

INTRODUCTION

The ability to make multiphase polymer blends in which the minor phase is ionically or electronically conducting could yield polymeric materials with high electrical conductivities or dielectric constants. Keeping this in mind, previous work in this laboratory led to the development of a process whereby electric fields could be used to orient the minor phases of a multiphase polymer blend[1,2]. By controlling the orientation of the phases in this fashion the electrical properties of the blends may be optimized in a desired direction. Using this process, poly(ethylene oxide) (PEO)/polystyrene (PS) blends with oriented PEO phases have been produced. PEO was chosen to be the minor phase for two reasons: (1) it has a dielectric constant higher than that of PS, this is a prerequisite for observing any electric field induced changes in polymer blend morphology; and (2) under suitable conditions, by complexing alkali metal salts, PEO can transform itself into a solid-state ionic conductor[3].

This study cannot readily be extended to the poly(methyl methacrylate) (PMMA)/PEO system since in the composition range of interest in this study, PEO and PMMA form a miscible blend[4]. However, it seemed plausible that if the blends were made in the presence of the alkali metal salts, because of the favourable interactions between the salt and the PEO[3], a phase-separated system might result. In this paper we report the effects of two such alkali metal salts on the phase behaviour of PEO/PMMA blends. The blends that were studied had <25 wt% PEO, since we require the PEO to exist as the minor phase. Furthermore, above this value the PEO is known to crystallize out into a separate phase[4].

The discovery that PEO can form complexes with alkali metal salts introduced a new candidate to the field of solid-state electrolytes. Wright[5] found that when PEO and potassium thiocyanate (KSCN) were mixed, a crystalline complex phase was formed. This crystalline phase melted at a temperature $\sim 50°C$ higher than the pure PEO. X-ray diffraction experiments suggested that there was a contraction in the PEO helix upon complexation. The glass transition temperature (T_g) of the amorphous region also increased, suggesting that there is a decrease in the segmental mobility of the polymer chains due to the introduction of the salt. The phase behaviour of PEO/salt systems is fairly complicated. At least three phases coexist: (1) a pure PEO crystalline phase, (2) a crystalline PEO complex phase; and (3) an amorphous PEO complex phase. Zahurak *et al.*[6] have developed a phase diagram for the PEO/lithium trifluoromethane sulfonate ($LiCF_3SO_3$, from now on referred to as LiT) and the PEO/sodium tetrafluoroborate ($NaBF_4$) systems. They found thst if the oxygen:lithium ratio was around 4:1, all of the PEO crystalline phase existed as the complex. This suggests that about four ethylene oxide units are required to interact with one lithium ion.

EXPERIMENTAL

Materials

The weight average molecular weights of the PEO (Aldrich Chemical Company) and PMMA (Scientific Polymer Products) were 1.05×10^4 and 3.87×10^4,

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respectively, as determined by g.p.c. on a Waters unit interfaced with an NEC (IBM AT compatible) computer. A single linear g.p.c. column (Ultrastyragel, molecular weight range 2×10^3–4×10^6) was used and the peaks were detected by a Waters R40 differential refractometer. PMMA standards (Scientific Polymer Products) were used as molecular weight calibrants for both polymer samples. LiT and KSCN were the alkali metal salts used for PEO complexation. These were purchased from Aldrich Chemical Co. and were dried in a vacuum oven at ~50°C prior to being used.

Preparation of polymer blends

Polymer blending was carried out by solvent casting from 4% w/v (weight of polymer/volume of solvent) polymer solutions in acetonitrile (h.p.l.c. grade, from Aldrich Chemical Company) at room temperature. The samples were cast in aluminium dishes, then dried in a vacuum oven at ~80°C for ~2 h. Salt-containing solutions were made by dissolving the salt along with the two polymers in acetonitrile.

Differential scanning calorimetry

Thermal properties were studied using a Perkin Elmer DSC4 differential scanning calorimeter interfaced with an IBM AT computer in the laboratory of Professor C. I. Chung, Department of Materials Engineering, Rensselaer Polytechnic Institute. The thermal analysis software, called Thermal Analysis, resident on the hard drive of the computer was marketed by MC Squared, Inc. (now Laboratory Microsystems, Inc., Troy, NY). Samples, in the form of small discs, were punched out from solvent cast polymer films and placed in aluminium sample pans. All reported thermograms, unless specified otherwise, were collected at a heating rate of 10°C min^{-1}, after cooling from the maximum temperature to the minimum temperature at a cooling rate of 10°C min^{-1}. Temperature calibration was done using melting points of indium and dodecane. Heat capacity measurements were carried out using sapphire as a reference. Most of the d.s.c. scans started at around room temperature and were therefore carried out using ice water as the coolant and nitrogen gas as the purge gas. For d.s.c. scans which required cooling below room temperature, liquid nitrogen was used as the coolant and helium as the purge gas.

I.r. spectroscopy

Fourier-transform i.r. (*FT*i.r.) spectroscopy, in the frequency range 4000–500 cm^{-1}, was done on a Perkin Elmer PE-1850 spectrometer. This technique was used to study interactions of the carbonyl group on the PMMA with the alkali metal salt. PMMA and PMMA/LiT samples were in film form, cast from ~1.7% w/v solutions in acetonitrile.

RESULTS AND DISCUSSION

Effect of lithium triflate on PEO and PMMA homopolymers

As shown in the d.s.c. scan in *Figure 1A*, PEO homopolymer exhibits a melting peak at 62.4°C. A d.s.c. scan of this sample in the temperature range −100°C to +100°C (not shown) gave no evidence of a PEO glass transition (PEO T_gs are normally observed at around −60°C[7]). From the melting endotherm of the d.s.c. curve in *Figure 1A*, the molar heat of fusion (ΔH) of PEO was

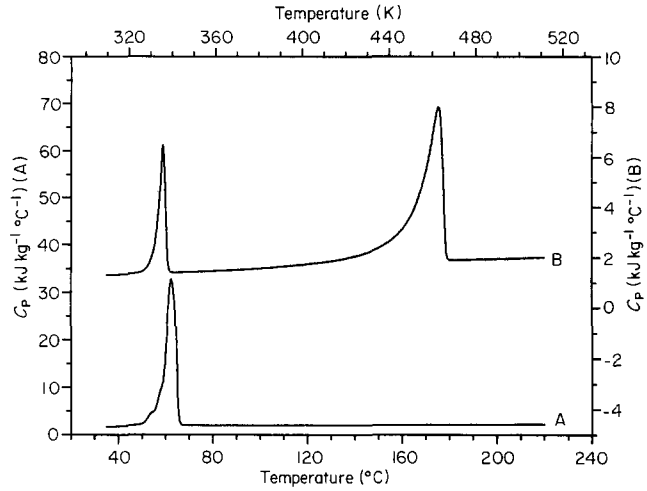

Figure 1 D.s.c. scans of (A) PEO homopolymer and (B) the PEO/LiT (O:Li = 4:1) system. Note that the C_p axis on the left-hand side of the plot corresponds to scan A and that on the right-hand side corresponds to scan B

calculated to be 7.6 kJ mol^{-1}. Using a value of 8.4 kJ mol^{-1} for the ΔH of 100% crystalline PEO[7,8], the sample was calculated to be ~91% crystalline. This high degree of crystallinity, which may be attributed to the low molecular weight of the PEO, explains the invisibility of a glass transition for this sample.

No attempt was made to obtain a d.s.c. trace of LiT since it is known that this salt has no thermal transitions in the temperature range of interest in this study[6]. *Figure 1B* shows the d.s.c. trace for a PEO/LiT with an oxygen to lithium (O:Li) ratio of 4:1. The two melting endotherms in this figure peak at 58.9 and 175°C. The 58.9°C endotherm corresponds to a pure crystalline PEO phase and the 175°C one to a crystalline PEO/LiT complex phase. A d.s.c. scan in the temperature range −100°C to +100°C (not shown) for this sample gave no evidence of a glass transition and hence indicates the virtual absence of an amorphous phase. In addition, from the ΔH of the 100% crystalline PEO[7,8], and the ΔH under the first endotherm (0.79 kJ mol^{-1}), we may calculate that ~10% of the PEO is in the uncomplexed crystalline state. The observation that some of the PEO is not complexed is consistent with the work of Zahurak *et al.*[6], who found that complete complexation of PEO only occurs if the O:Li ratio is ≤3.5:1. This ratio is believed to stem from the fact that PEO normally crystallizes as a 7/2 helix[9], and hence every turn of the helix contains 3.5 oxygens and can incorporate one lithium cation.

A d.s.c. scan for PMMA is shown in *Figure 2A*. As expected, it shows a single glass transition at 103°C, and no melting transition. The change in the specific heat capacity (ΔC_p) value for this PMMA sample at its T_g was measured to be ~30 J mol^{-1} K^{-1}. This value is in good agreement with the literature value[8] of 29.3 J mol^{-1} K^{-1} and confirms that the sample was completely amorphous.

The d.s.c. scans for five PMMA samples containing increasing amounts of LiT are shown in *Figures 2B–F*. The values of the T_gs in these scans are 124, 135, 148, 161 and 170°C, respectively. In general, increasing the salt concentration in the PMMA increased the T_g of the PMMA, indicating solubility and the possible presence of an interaction between the PMMA and the salt. For

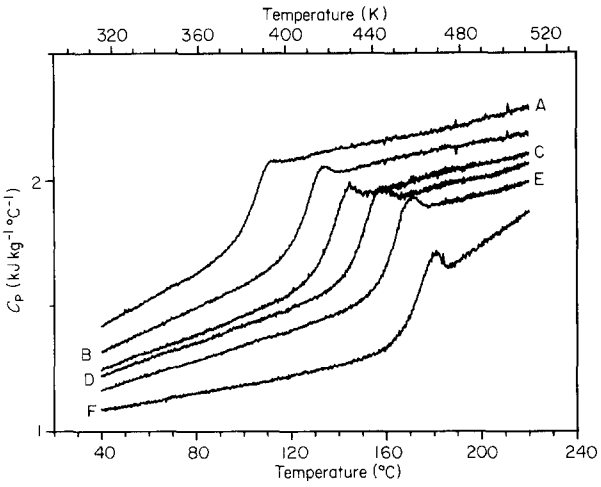

Figure 2 D.s.c. scans of (A) PMMA, (B) PMMA/LiT(8), (C) PMMA/LiT(14), (D) PMMA/LiT(22), (E) PMMA/LiT(30) and (F) PMMA/LiT(39). The numbers in parentheses indicate mole per cent of LiT. The glass transitions for the samples are: 103, 124, 135, 148, 161 and 170°C, respectively

concentrations up to 39 mol% LiT, the films that were formed were brittle and showed a progressive increase in T_g. The 49 mol% LiT film appeared hygroscopic suggesting that LiT may now be in excess. The d.s.c. scan for this film (not shown) indicated a T_g at ~150°C, about 20°C lower than the T_g of the 39 mol% film.

Another feature in the d.s.c. traces in *Figure 2* is worth mentioning. That is, the absolute values of C_p are consistently lowered by the addition of salt. This suggests that the C_p of LiT is much lower than that of PMMA. Alternatively, the lowering may be due to a decrease in mobility of the PMMA chains because of an increase in interactions with an increase in LiT composition. Observations of this nature have been reported for poly(*N*,*N*-dimethyl acrylamide)/poly(4-hydroxystyrene) hydrogen-bonded interpolymer complexes[10]. It is also of interest to note that the PMMA glass transitions develop a hysteresis peak (maximum in C_p) with increase in salt concentration. The origin of such peaks is complicated[11,12] and will not be discussed here.

The increase in the T_g of polymers with addition of salt has been observed by a number of research groups. Cowie and Martin[13] have seen increases in the T_g of poly(vinyl methyl ether) with the addition of lithium perchlorate and LiT. James *et al.*[14] have observed that with the addition of cobalt chloride to poly(propylene oxide) (PPO), the T_g may be elevated to ~140°C beyond that of the parent polymer. Both groups have reported that the elevation in T_g levels off beyond a certain salt concentration.

Two ion–dipole interactions between PMMA and salt are possible, either or both of which could lead to an increase in T_g of the PMMA. The first is an interaction between the cation and the PMMA carbonyl oxygen and the second, an interaction between the cation and the alkoxy oxygen. However, esters form resonance stabilized structures wherein the carbonyl oxygen acquires a negative charge and the alkoxy oxygen a positive charge[15]. The metal ion is therefore expected to prefer the carbonyl oxygen. Furthermore, in a resonance stabilized structure of the ester one would also expect an interaction between the alkoxy oxygen and the anion of the salt. Indeed, such oxygen/salt interactions are believed to occur in the PEO/alkali metal salt complexes[3] and also in the poly(vinyl methyl ether) complexes described by Cowie and Martin[13] and the PPO complexes described by James *et al.*[14]. Ion–dipole interactions have also been observed in mixtures of inorganic nitrate salts and a host of oxygen-containing polymers including poly(vinyl acetate), poly(vinyl alcohol), poly(methyl acrylate) and PMMA[16]. These systems show large shifts in T_g and large shifts in carbonyl and alkoxy group absorption frequencies in the i.r. spectrum.

The carbonyl stretching region of the *FT*i.r. spectrum of PMMA and two PMMA/LiT samples are shown in *Figures 3A–C*. This region of the i.r. spectrum was chosen on the assumption that the most likely interaction between PMMA and LiT would be an ion–dipole interaction between the LiT lithium and the carbonyl oxygen. Evidence for such an interaction, from i.r. spectra, is present in the literature[16]. The effect of complexation on the i.r. absorption characteristics of the alkoxy group of the PMMA could not be studied because that region of the spectrum is complicated by LiT absorptions. Minor differences between the carbonyl absorption peaks in the i.r. spectra of uncomplexed and complexed PMMA are visible in *Figure 3*. The pure PMMA carbonyl has a relatively narrow absorption peak centred around 1735 cm^{-1}. With the addition of 14 mol% LiT there is a broadening of the absorption band into the lower frequency region. This broadening may be due to the overlap of two peaks, one corresponding to free carbonyl and the other corresponding to complexed carbonyl. The appearance of two such peaks has been reported by Hannon and Wissbrun[16] for the PMMA/copper nitrate system. However, in their studies the two peaks were shifted by as much as 30 cm^{-1} and were hence distinct. In the i.r. spectrum of the PMMA with 30 mol% LiT the carbonyl peak appears to have shifted to the lower frequency side by ~10 cm^{-1} when compared to the corresponding peak in salt-free PMMA. This may be due to the reduction in the amount of free carbonyl with the increase in LiT composition. The difference in the magnitude of shifts between the current system and the PMMA/copper nitrate system[16] may reflect the difference between the strength of the interaction in the two. The shift towards lower frequencies suggests that the carbonyl bond order is decreasing. Such a decrease is expected to take place when the oxygen complexes a metal ion.

We attribute the additional peak near 1650 cm^{-1} that is observed in *Figure 3C* to water that is adsorbed by the LiT[17]. We have observed the same peak in the i.r.

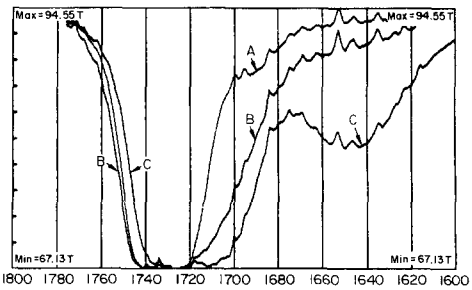

Figure 3 Carbonyl stretching region in the *FT*i.r. spectrum of (A) PMMA, (B) PMMA/LiT(14) and (C) PMMA/LiT(30)

spectrum of LiT that was dispersed in potassium bromide. The fact that this peak is not observed in *Figure 3B* suggests that the PMMA/LiT(14) sample was drier than the PMMA/LiT(30) sample. Although both samples were made under similar conditions, no attempt was made to monitor the adsorption of water by each sample. It is interesting to note that another recent study of the i.r. spectrum of PMMA/LiT mixtures by Mani *et al.*[18] has also shown a peak at 1650 cm^{-1}. However, the authors of that study have assigned this peak to a PMMA carbonyl whose absorption was shifted due to interaction with the lithium cation. This is rather an enormous shift for an interaction of the ion–dipole type[16]. Furthermore, Mani *et al.*[18] do not discuss the LiT spectrum which could also have contained this peak.

Effect of lithium triflate on PEO/PMMA blends

The d.s.c. scan in *Figure 4A* shows a single glass transition at 80.6°C measured for a 10% PEO/PMMA blend. No PEO T_g was found for this sample, indicating that the PEO and the PMMA were completely miscible in the amorphous state. This observation is consistent with those in the literature[4,19] which have shown that at low PEO compositions (<25% PEO) this blend exists as a single phase material. For the 20% PEO/PMMA blend, shown in *Figure 4C*, the glass transition was even lower and extended below the starting temperature (30°C), indicating that the PEO and the PMMA were still miscible in the amorphous state.

The d.s.c. scan for the 10% PEO/PMMA blend with LiT (O:Li=4:1), is shown in *Figure 4B*. This blend showed multiphase behaviour with two melting temperatures (T_m; one at 58.9°C and the other at 164°C) and one T_g (at 110°C). A d.s.c. scan of this sample in the temperature range −100°C to +100°C (not shown) did not yield any glass transitions and indicated the virtual absence of a PEO glassy phase. Since we know that the LiT interacts with both the PMMA and the PEO, it is not surprising that the addition of LiT to the 10% PEO/PMMA blend produced a phase-separated system, consisting of two crystalline phases and one amorphous phase. As expected there is a significant increase in the PMMA T_g (110°C) when compared with the T_g of the 10% PEO/PMMA blend (80.6°C) or even the T_g of homopolymer PMMA (103°C). While the formation of a PEO/LiT complex was also expected, it was initially surprising to observe the presence of an uncomplexed PEO phase in this system. From the enthalpy of fusion of the PEO (1.38 kJ mol^{-1} of PEO) in *Figure 4B* ~16% of the total PEO was calculated to exist as crystalline uncomplexed PEO. This suggests that apart from interacting with the two homopolymers separately the LiT also inhibits mixing of the two homopolymers. This may be because the LiT promotes the helical form of the PEO chain while the interaction of PEO with PMMA requires a planar zigzag conformation of the PEO. Ramana Rao *et al.*[20] have used vibrational spectroscopy to show that PEO exists in a planar zigzag conformation when blended with PMMA. Furthermore, they suggest that this new conformation may enable a weak dipole interaction between the PEO ether oxygens and the PMMA carbonyl carbon.

From the d.s.c. scan in *Figure 4D* it can be seen that the 20% PEO/PMMA blend with LiT (O:Li=4:1), behaves very much like the 10% PEO/PMMA/LiT system. Two T_ms (at 58.6 and 171°C) are visible as is one T_g (at 113°C), which is higher than the T_gs of the homopolymer PMMA and the 10% PEO/PMMA/LiT. Assuming that no amorphous PEO exists in this sample and using the enthalpy of fusion of the pure PEO (0.66 kJ mol^{-1} of PEO) in *Figure 4D*, the amount of uncomplexed PEO in this sample is estimated to be 7% of the total PEO present in the blend.

Effect of potassium thiocyanate on PEO/PMMA blends

Figure 5A shows a d.s.c. scan of KSCN. This scan indicates a large peak at ~177°C which can be attributed to the melting of KSCN. This scan also shows the existence of a small melting peak at ~141°C. The origin of this peak is not known to us.

All samples containing KSCN appeared to be hygroscopic. This is probably due to free KSCN resulting from the complexation of only part of the salt by the polymer and is confirmed by the d.s.c. scan of the PEO/KSCN (PEO oxygen:KSCN potassium=4:1) system in *Figure 5B*. This scan shows no indication of a PEO melting

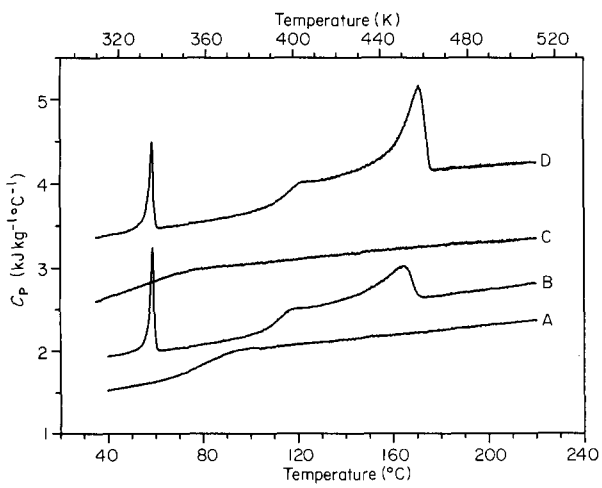

Figure 4 D.s.c. scans for (A) the 10% PEO/PMMA blend, (B) the 10% PEO/PMMA/LiT system (shifted up by 0.5 kJ kg^{-1} $°C^{-1}$), (C) the 20% PEO/PMMA blend (shifted up by 1.0 kJ kg^{-1} $°C^{-1}$) and (D) the 20% PEO/PMMA/LiT system (shifted up by 2.0 kJ kg^{-1} $°C^{-1}$)

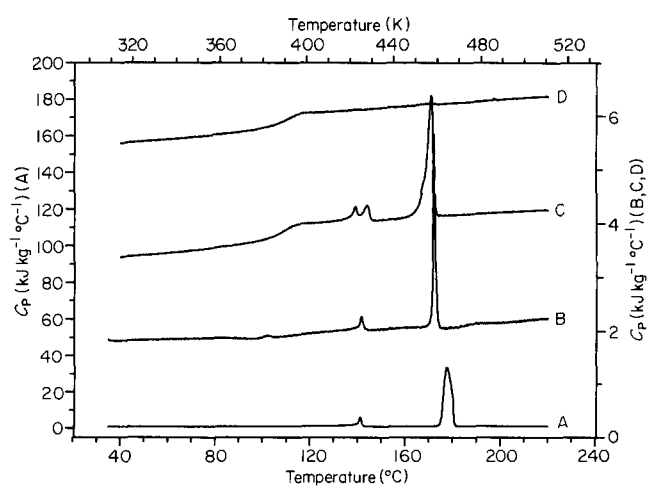

Figure 5 D.s.c. scans of (A) KSCN salt, (B) the PEO/KSCN system, (C) the PMMA/KSCN system (shifted up by 2 kJ kg^{-1} $°C^{-1}$ from B) and (D) the PEO/PMMA/KSCN system (shifted up by 4 kJ kg^{-1} $°C^{-1}$ from B). Note that the C_p axis on the left-hand side of the plot corresponds to scan A and that on the right-hand side corresponds to scans B, C and D

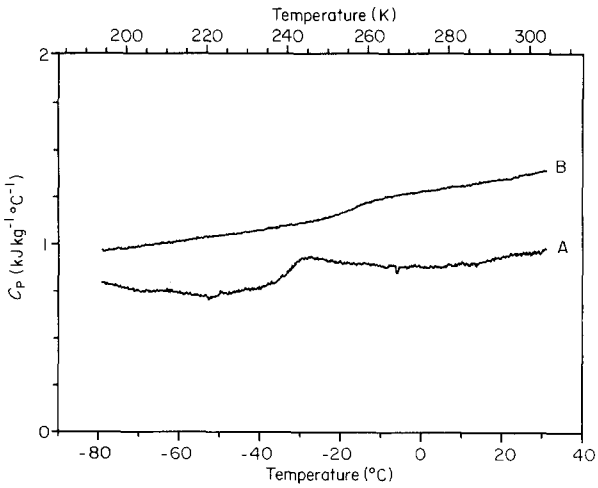

Figure 6 D.s.c. scans (in the low temperature range) of (A) the PEO/KSCN system and (B) the PEO/PMMA/KSCN system

peak. The uncomplexed crystalline PEO phase is hence absent in this sample. Two melting transitions at 142 and 172°C were observed. These transitions indicate the presence of free KSCN (cf. *Figure 5A*) and confirm that only part of the KSCN was complexed by PEO. The small peak at ~100°C indicates that very little PEO/KSCN complex exists in this system (the T_m of the crystalline PEO/KSCN complexes has been observed by Wright[5] at 100°C). Most of this PEO/KSCN complex appears to exist as an amorphous phase with a T_g of −34.2°C (*Figure 6A*). These observations may be attributed to the size of the potassium cation. Generally, the smaller alkali metal cations Li^+ and Na^+ readily form crystalline complexes, while the larger ones, such as Cs^+ and Rb^+, rarely do[21]. The helical structure that PEO prefers to adopt during crystallization is not favoured in the presence of larger cations[21].

Figure 5C shows the d.s.c. scan for the 7.7% KSCN/PMMA system. Three melting transitions (at 140, 144 and 171°C), the highest one corresponding to free KSCN, can be seen. The other two are believed to correspond to the impurity phase in the KSCN. There is also a PMMA T_g at 108°C, slightly higher than that of homopolymer PMMA. This indicates that some KSCN in the PMMA/KSCN system interacts with the PMMA, but a lot of it is left undissolved. The increase in T_g for this system is hence smaller than that observed for the PMMA/LiT system. The observation that the solubility of the potassium salt is less than that of the lithium salt was also made by Cowie *et al.*[13] for poly(vinyl methyl ether)/salt systems.

The d.s.c. scan for the 10% PEO/PMMA blend cast in the presence of KSCN (O:K = 4:1) is shown in *Figure 5D*. A slightly elevated PMMA glass transition, at 108°C, can again be seen. The low temperature d.s.c. data for the 10% PEO/PMMA/KSCN shown in *Figure 6B* indicates a second glass transition at −18.4°C, a temperature higher than the homopolymer PEO T_g of −60°C, thus indicating the existence of an amorphous PEO/KSCN complex as well as an amorphous PMMA/KSCN complex. Unlike the PEO/PMMA/LiT system, no crystalline phases were observed in this system. Both the glass transitions of this sample are above their respective homopolymer T_gs, indicating that the salt has partitioned between the amorphous phases of the two polymers. Judging from the larger increase in the PEO T_g (~40°C), when compared to the increase in PMMA T_g (~4°C), one may say that most of the salt resides in the amorphous PEO phase.

While both LiT and KSCN induce phase separation in PEO/PMMA blends, the nature of the phases formed in each case is different. A recent study by Floriańczyk *et al.*[22] on PEO/PMMA/alkali metal salt systems, with PEO as the major phase, has indicated that ionic conductivities of the order of 10^{-5} S cm^{-1} can be obtained in these samples. PMMA/salt interactions were not addressed in that study.

CONCLUSIONS

Lithium triflate is miscible with PMMA homopolymer up to ~40 mol%. Weak shifts in the PMMA carbonyl peaks in the i.r. spectrum of PMMA/LiT indicated that the lithium ion interacts with the carbonyl oxygen of the PMMA.

D.s.c. studies on the effects of alkali metal salts on the phase behaviour of polymer blends containing PEO have shown the following: addition of LiT to the normally miscible PEO/PMMA blend resulted in phase separation, with the formation of a crystalline PEO phase, an amorphous PMMA/LiT phase and a crystalline PEO/LiT complex phase; when KSCN was added to PEO/PMMA blends, two amorphous salt-containing phases, corresponding to PEO/KSCN and PMMA/KSCN, were formed.

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