

Thermal properties of poly(ethylene oxide)–poly(methyl methacrylate) blends and copolymers complexed with sodium thiocyanate

G. C. Eastmond* and P. Schofield†

Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

and P. Sakellariou‡

ICI Paints, Slough, Bucks, UK

(Revised 14 October 1996)

The phase behaviour of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) blends, a partially miscible system, and of PEO/PMMA block copolymers, all cast from acetonitrile, were determined in the presence of added NaSCN. The phase behaviour is dominated by the added salt, which forms an insoluble $P(\text{EO}_3 \cdot \text{NaSCN})$ complex and induces separation of PEO and PMMA in homopolymer blends. In block copolymers the PEO was either complexed with NaSCN or miscible with the PMMA block. Essentially the same phase diagram applies to the homopolymer blends and PEO-rich copolymer with added NaSCN and is identical to that previously found for mixtures of PEO and NaSCN cast from methanol. For the PMMA-rich copolymer the phase diagram is similar except that there is no evidence of PEO crystallinity, which is replaced by a miscible PEO/PMMA phase. Block copolymers in the presence of added salt were found to exhibit an additional endotherm ($\sim 280^\circ\text{C}$) which is attributed to a disorganization of the microphase-separated system at temperature above the melting point of the complex and is associated with a liquid–liquid phase separation. This process was found to be irreversible on cooling from the melt. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene oxide); poly(methyl methacrylate); sodium thiocyanate)

Introduction

Most pairs of chemically different polymers are immiscible because of the negligible entropy of mixing and the normally positive enthalpy of mixing. It is usually considered that miscibility requires the existence of a favourable interaction between the units of the dissimilar polymers¹. Poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) constitute a system with limited miscibility; the system is miscible over a limited range of compositions. Liberman *et al.*² determined that PEO/PMMA blends (PEO molecular weight up to 19 kg mol^{-1} , PMMA molecular weight 600 kg mol^{-1}) cast from chloroform and containing less than about 20 wt% PEO are miscible, but that blends containing more PEO phase separate to form a crystalline PEO phase. These observations indicate the existence of a specific interaction between PEO and PMMA. The magnitude of the interaction parameter has been estimated from melting-point depressions in the blends by application of the Nishi–Wang equation^{3,4}, and has been confirmed by small-angle neutron scattering⁵.

PEO forms complexes with salts of the alkali metals which involve interactions between the ether oxygens of PEO and the alkali-metal cation. Initially it was suggested that the PEO–cation complex has a stoichiometric ratio of four ethylene oxide (EO) repeat units per cation^{6,7}. Later Hibma⁸, using wide-

angle X-ray scattering, confirmed the 4/1 stoichiometry for K^+ and NH_4^+ ions, but found a 3/1 ratio for Na^+ and Li^+ ions.

Thermal stabilities for the PEO–alkali salt complexes depend on the EO/salt ratio, PEO molecular weight, polymer concentration, the solvent used in complex formation and thermal history. Melting points of the Na^+ and Li^+ complexes, for PEO molecular weights $> 10 \text{ kg mol}^{-1}$, are generally in the range $150\text{--}195^\circ\text{C}$. The most stable complexes of high-molecular-weight PEOs with LiCF_3SO_3 , NaI and NaSCN melt in the temperature range $190\text{--}195^\circ\text{C}$. Differential thermal analysis showed two distinct thermal transitions in the PEO–NaSCN system⁹. Robitaille *et al.*¹⁰ undertook a detailed study of the PEO/NaSCN system by differential scanning calorimetry (d.s.c.) and determined the complete phase diagram which defined the major features of the system (Figure 1). These workers identified the existence of a single crystalline complex, $P(\text{EO}_3 \cdot \text{NaSCN})$, with a melting point of 182°C and a PEO content of 62 wt%. With excess of PEO the complex forms a eutectic having a melting point of 58°C and PEO content of 93 wt%. Mixtures with less than 62 wt% PEO showed an incongruent melting point of the complex at 182°C and a melting endotherm at 309°C for the excess of NaSCN. Intermediate compositions, $62 \text{ wt}\% < \text{PEO} < 93 \text{ wt}\%$, showed a composition-dependent endotherm corresponding to dissolution of the complex into liquid PEO. These workers also concluded, from supplementary observations, that in the liquid phase the $P(\text{EO}_3 \cdot \text{NaSCN})$ converts into $P(\text{EO}_4 \cdot \text{NaSCN})$.

Being aware that the specific interactions in PEO/PMMA blends also probably involves the ether oxygens

* To whom correspondence should be addressed

† Present address: Department of Chemical Engineering, Cornell University, Ithaca, NY, USA

‡ International Paints, Felling, Northumberland, UK

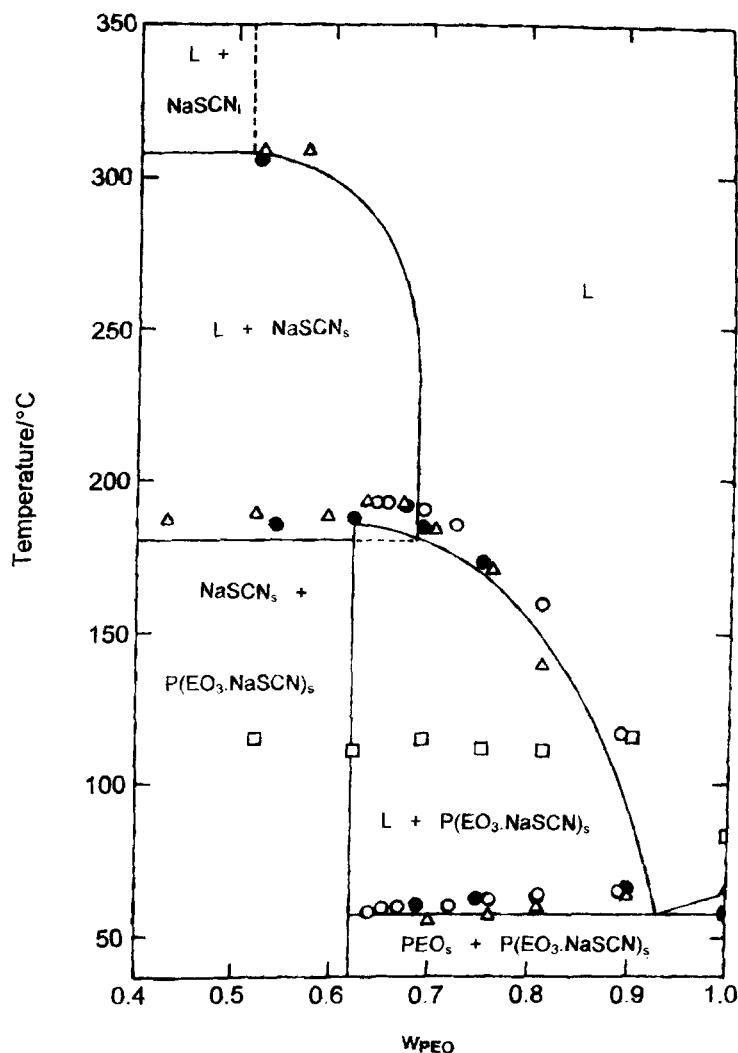


Figure 1 Transition temperatures from d.s.c. thermograms for PEO and blends of PEO and PMMA as functions of weight fraction of PEO. (Δ) Melting point for PEO plus NaSCN cast from methanol; (\circ) melting points for PEO plus NaSCN cast from acetonitrile; (\bullet) melting points for PEO with PMMA (PMMA:PEO, 4/1 w/w) plus NaSCN cast from acetonitrile; (\square) glass-transition temperatures for PEO with PMMA (PMMA/PEO, 4/1 w/w) plus NaSCN cast from acetonitrile. Solid lines represent the phase diagram for PEO/NaSCN adapted from ref. 10. Designation of phases are those identified in ref. 10

of the PEO¹¹, we undertook a research programme to investigate how addition of alkali-metal salts to PEO/PMMA blends would influence miscibility in those blends by the formation of PEO-cation interactions affecting the concentration of PEO-PMMA interactions. In the meantime, Venugopal *et al.*¹² reported on the effects of lithium methanesulfonate and KSCN on the phase behaviour of PEO/PMMA blends. In our current study we describe the effect of NaSCN on the miscibility in PEO/PMMA blends and also examine the influence of NaSCN on PEO/PMMA block copolymers. Phase diagrams for the systems were obtained by d.s.c. Our data are compared directly with the phase diagram reported by Robitaille *et al.*¹⁰, which forms the basis of *Figures 1* and *3*.

The synthesis of PEO/PMMA block copolymers has proved problematic in the past. Garg *et al.*¹³ reported a method for synthesizing the block copolymers by anionic polymerization; no molecular weight data were given to substantiate their results. However, the same group subsequently reported that the procedure did not produce linear block copolymers, but gave a

mixture of branched structures¹⁴, and subsequently reported additional difficulties associated with the low solubility of PEO in the tetrahydrofuran (THF), used as solvent for the synthesis, under conditions where MMA will polymerize¹⁵. Subsequently, and after our work has been completed, Wu and Piirma¹⁶ attempted to produce such copolymers by coupling terminally functionalized, oligomeric PMMA with PEO; the polymers had very low molecular weights and were unsuitable for our purposes. Consequently, we collaborated with the Liège group, which has been successful in developing control over anionic homopolymerization of MMA¹⁷ and in producing PEO/poly(butyl methacrylate) block copolymers by anionic polymerization¹⁸.

Experimental

Samples of PEO homopolymer ($M_n = 40 \text{ kg mol}^{-1}$), PEO/PMMA blends (PMMA, $M_n = 100 \text{ kg mol}^{-1}$) and PEO/PMMA block copolymers were prepared as thin films in the absence and presence of NaSCN. The samples were cast from homogeneous solutions in acetonitrile by allowing the solvent to evaporate

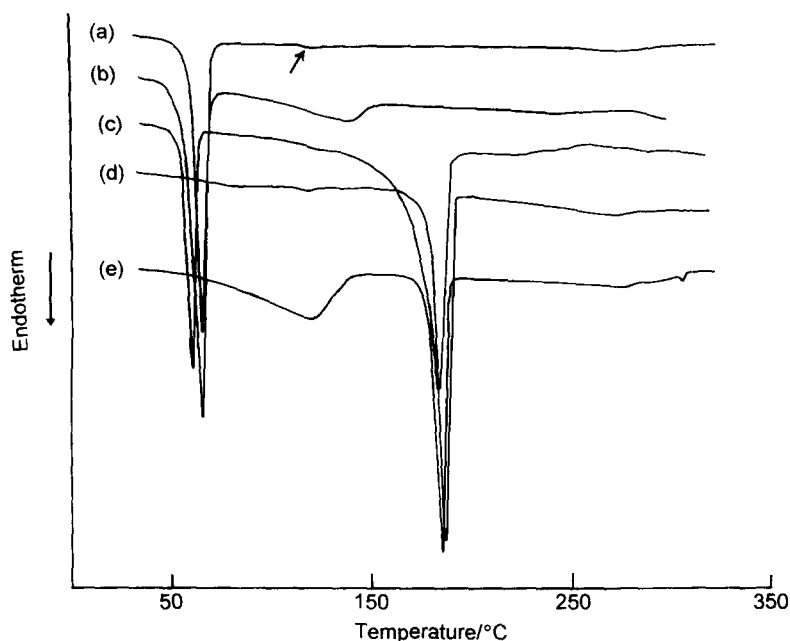


Figure 2 Thermograms for PEO/PMMA homopolymer blends in the presence of NaSCN: (a) EO:Na⁺ 16/1; (b) EO:Na⁺ 5.5/1; (c) EO:Na⁺ 4/1; (d) EO:Na⁺ 3/1; (e) EO:Na⁺ 2/1

slowly; some samples were cast from methanol. Films were subsequently dried from residual solvent by heating at 60°C under vacuum for several days and were stored in closed containers.

Thermal transitions were determined by d.s.c. using a Perkin-Elmer DSC912 (MCS66) by scanning from -50°C or 30 to 350°C at a scan rate of 20°C min⁻¹. The thermal transition behaviour, in several cases, was compared with observations made by heating samples on the hot stage of a polarizing microscope.

PEO/PMMA diblock copolymers were prepared by anionic polymerization in THF using diphenylmethyl potassium as initiator. Ethylene oxide was the first monomer polymerized and MMA was added to the living PEO. Molecular weights were determined by gel-permeation chromatography in THF and in *N,N*-dimethylformamide (DMF) calibrated with polystyrene standards. Gel-permeation chromatograms of the block copolymers, with THF as eluent, often showed two peaks, one due to copolymer and one to residual PEO homopolymer. The synthesis of well-defined PEO/PMMA block copolymers is more difficult than with other methacrylate monomer, such as *t*-butyl methacrylate; the system is more susceptible to chain termination, resulting in the presence of PEO homopolymer. Two copolymers were used in this study; details are given in Table 1. The overall compositions are those determined by ¹H n.m.r., rather than from the compositions determined from the monomers used. The number-average molecular weights quoted for PEO are those determined for samples extracted prior to addition of the MMA. Values of M_p are those of the peaks of the chromatograms for the copolymers. The peak was very narrow for copolymer-2, but somewhat broader for copolymer-1 when THF was the eluent; these values are probably close to the true values for the copolymer alone. Values of M_w are for total polymer. The use of DMF as eluent revealed that copolymer characterization is not simple; peaks were broader and consisted of more than one species, possibly due to graft copolymer

Table 1 Compositions and molecular weights of PEO-PMMA block copolymers

Sample	PEO content (wt%, by n.m.r.)	\bar{M}_n PEO (kg mol ⁻¹)	M_p (kg mol ⁻¹)	\bar{M}_w (kg mol ⁻¹)
Copolymer-1	25	13.3	52.7	49
Copolymer-2	80	32.6	71.2	57

formation. The synthesis and characterization of these polymers will be described in greater detail elsewhere¹⁹. The exact homopolymer contents are uncertain, but, based on the monomers used, the compositions determined by n.m.r. and copolymer peak molecular weights, the data suggest that in copolymer-1 less than 10% of PEO remains as homopolymer, but in copolymer-2 (which has about 50 wt% MMA) up to 75% of the initial PEO might remain as PEO homopolymer; this is probably an overestimate of the true PEO homopolymer content.

Results and discussion

Robitaille *et al.*¹⁰ determined the phase diagram for PEO and NaSCN from thermal transition temperatures of samples cast from methanol. In order to investigate the influence of NaSCN on the phase behaviour of PEO/PMMA blends it was necessary to identify a common solvent for all components; methanol is a precipitant for PMMA. The most suitable common solvent and that of choice was acetonitrile. We therefore redetermined the phase diagram for PEO and NaSCN mixtures cast from both acetonitrile and methanol prior to studying systems containing PMMA. Thermal transitions recorded are those determined on first heating to reflect the properties of as-cast materials and the phase diagram applicable to casting from solvent.

Complexes of PEO homopolymer with NaSCN. The phase diagram for mixtures of PEO and NaSCN is

shown in *Figure 1* in which transition temperatures determined by d.s.c. are plotted as functions of the weight fraction of PEO. Our data, for samples cast from methanol, are very similar to, and are superimposed on, the phase diagram taken from Robitaille *et al.*¹⁰; minor variations might reflect differences in thermal history and heating rates. These data confirm that our experimental procedures conform with those of Robitaille *et al.*¹⁰. The data for samples cast from acetonitrile, which gives colourless films, are essentially identical to those cast from methanol, indicating that the solvent does not have a major influence on the phase behaviour. Thus, the data points show, at high PEO contents (>60 wt% PEO, approximately), the melting of the eutectic of PEO and the P(EO₃.NaSCN) complex at about 60°C; in the absence of NaSCN, PEO melts at 66°C. The second thermal transition recorded, which corresponds to dissolution of the complex to give a homogeneous liquid phase at higher temperatures, varies with overall compositions as observed by Robitaille *et al.*¹⁰ who established that this transition is accompanied by formation of a P(EO₄.NaSCN) complex in the liquid state¹⁰. At higher NaSCN contents (PEO < 60 wt%, approximately), i.e. at NaSCN contents exceeding that required for P(EO₃.NaSCN), the major thermal transition is the incongruent melting of the P(EO₃.NaSCN) complex which, according to Robitaille *et al.*¹⁰, is accompanied by disproportionation into P(EO₄.NaSCN) and NaSCN. Melting of excess of NaSCN is seen at about 308°C; this melting point agrees with that of Robitaille *et al.*¹⁰ and is higher than that of 278°C reported elsewhere for NaSCN melting²⁰.

Complexes of PEO homopolymer with NaSCN in PEO/PMMA blends. Sodium thiocyanate was added to PEO/PMMA blends in homogeneous solution in acetonitrile in which the proportions of PEO and PMMA were varied. Precipitates formed were isolated and their thermograms exhibited a major thermal transition corresponding to melting of crystalline P(EO₃.NaSCN) (185–192°C). Precipitates from mixtures containing excess of PEO (EO:Na⁺ > 3:1) exhibited a crystal melting for the PEO/P(EO₃.NaSCN) eutectic (56–58°C). Similarly, precipitates from mixtures containing more PMMA than PEO also exhibited a glass-transition temperature of PMMA (109–110°C); this PMMA is thought to be adventitious to the precipitated complex. We found it impossible to determine reliable cloud points by adding NaSCN to PEO/PMMA blends in acetonitrile solution because of kinetic factors. Phase separation required addition of sufficient NaSCN to nucleate formation of a P(EO₃.NaSCN) phase which could start after standing for long periods. Precipitation then continued until at least a major portion of the NaSCN had precipitated as the P(EO₃.NaSCN) complex; reversible conditions could not be identified.

Figure 1 shows data for samples formed by the addition of NaSCN to PMMA/PEO blends rich in PMMA containing a constant proportion (80 wt%) of PMMA (based on PMMA plus PEO) and cast from acetonitrile. To allow data for different systems to be plotted on a common basis, i.e. in *Figures 1* and *2*, temperatures of thermal transitions, observable by d.s.c., are plotted as functions of w_{PEO} , the weight fraction of

PEO, expressed as

$$w_{\text{PEO}} = \frac{\text{mass}_{\text{PEO}}}{\text{mass}_{\text{PEO}} + \text{mass}_{\text{NaSCN}}}$$

That is, w_{PEO} is based on the amount of PEO and NaSCN irrespective of the presence or situation of any PMMA. In the absence of NaSCN, right-hand ordinate, the blend consists of crystalline PEO ($T_m = 58^\circ\text{C}$) and a miscible amorphous mixture of residual PEO with PMMA with a glass-transition temperature of 89°C (onset) or 94°C (mid-point); the crystal melting endotherm was very weak and the glass transition was dominant. Optical microscopy of the colourless samples showed loss of birefringence, due to PEO melting, at 60°C. The lower value of T_m for PEO in the presence of PMMA is consistent with a crystalline phase in contact with a homogeneous amorphous phase with which it is miscible on melting. The lower glass-transition temperature for PMMA, compared with that of the pure polymer (108°C) is consistent with miscibility of PMMA with the residual amorphous PEO. Other workers reported that, at the composition used here, PEO and PMMA are totally miscible. Liberman *et al.*² reported no crystallinity and a T_g of 64°C for samples cast from chloroform. Venugopal *et al.*¹² obtained similar results for polymers of lower molecular weight cast from acetonitrile. The small differences from previous work reported here probably reflect the sensitivity of the system, near to the phase boundary, to variations in molecular weight and casting solvents used; casting solvents are known to affect apparent miscibility in other systems. The higher T_g for the blend in this work is consistent with a little of the PEO crystallizing and increasing the PMMA content of the residual amorphous phase.

Addition of low concentrations of NaSCN (with respect to PEO), as low as EO:Na⁺ 16/1, had a marked effect on the thermal transition behaviour and a EO:Na⁺ ratio of 5.5/1 created a three-phase system. Optical microscopy showed the presence of birefringent crystalline regions and some non-birefringent regions present both between the crystalline regions and as spherical inclusions within crystalline areas. The temperatures of the thermal transitions observed by d.s.c. (*Figure 1*) are very similar to those obtained in the absence of PMMA with, additionally, T_g for PMMA. Thermograms for several samples are shown in *Figure 2*.

At the lowest EO:Na⁺ ratio of 16/1 there is a very strong low-temperature endotherm with a reproducible very small deflection above 100°C (arrowed), close to the normal T_g of PMMA (*Figure 2*). Values of T_m for the low-temperature melting endotherm in the presence of NaSCN (typically 62–66°C) were higher than for either pure PEO or for PEO in PEO/PMMA blends in the absence of NaSCN (~60°C) and were comparable with T_m for the PEO/P(EO₃.NaSCN) eutectic. With increasing NaSCN content the sharp melting endotherm decreases in relative magnitude and the small deflection above 100°C increases in size and resolves into a T_g for PMMA at about 110°C and a melting endotherm for dissolution/melting of the P(EO₃.NaSCN) complex. The observed glass-transition temperature for PMMA is raised by 2–5°C above that of normal PMMA; the relative heights of the peaks shown in *Figure 2* do not follow a simple trend because different vertical scales were used for individual thermograms. Energies

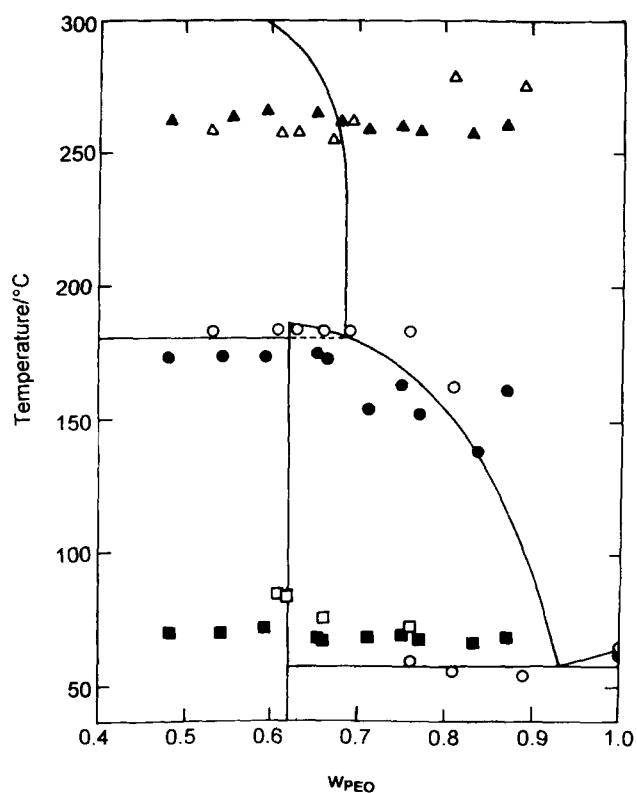


Figure 3 Transition temperatures from d.s.c. thermograms for PEO/PMMA block copolymers in the presence of NaSCN as functions of weight fraction of PEO for PEO plus NaSCN; PMMA/PEO ratio is constant. (●) Melting points and (■) glass-transition temperatures for samples containing copolymer-1; (○) melting points and (□) glass-transition temperatures for samples containing copolymer-2. Additional high-temperature endotherms for copolymer-1 (▲) and copolymer-2 (△) in the presence of NaSCN. Solid lines represent the phase diagram for PEO/NaSCN adapted from ref. 10

associated with the peaks at about 60°C in thermograms *Figures 2a, b* and *c* decrease with increasing NaSCN content and were 99.8, 79.8 and 21.7 J g⁻¹, respectively. Similarly, the energies associated with the endotherm at about 180°C increase with increasing NaSCN content and were, in *Figures 2c, d* and *e*, 63.3, 75.5 and 80.1 J g⁻¹, respectively. Thus, at relatively high PEO contents, where there is insufficient NaSCN to complex all the PEO, (i.e. at EO:NaSCN > 3/1) endotherms are observable by d.s.c. for both the melting of the PEO/P(EO₃.NaSCN) eutectic and dissolution/melting of the P(EO₃.NaSCN) complex (*Figures 2b* and *c*). When the NaSCN contents become sufficient to complex all the PEO (EO:NaSCN < 3/1) only the glass transition for PMMA and melting of the PEO/NaSCN complex are observable (*Figures 3d* and *e*). In the presence of excess of NaSCN (EO:NaSCN = 2/1) there was a very small endotherm at 305°C (*Figure 2e*) corresponding to melting of NaSCN. There were no other endotherms at high temperatures of about 260°C in any of these samples.

Under the polarizing microscope PEO melting was observed just below 60°C in samples containing 59 wt% or more PEO. Although samples with low NaSCN contents, e.g. 80 wt% PEO, did not show a thermal transition for P(EO₃.NaSCN) melting by d.s.c., some birefringence was seen to be lost between 140 and 167°C, consistent with melting of a small content of the complex. Liquid-like behaviour was observed in samples

above 100°C when, under the microscope, crystalline regions were seen to move through a fluid phase of molten PEO and liquid PMMA.

These several data together are consistent with even very low concentrations of NaSCN, far too small to produce significant proportions of the P(EO₃.NaSCN) complex, inducing segregation of the PMMA from its miscible blend with PEO. As the NaSCN content increases the crystalline PEO is converted into a crystalline P(EO₃.NaSCN) complex. The glass transition for PMMA becomes more apparent as the NaSCN content increases because the strength of the higher endotherm is less than that of the lower.

Venugopal *et al.*¹² observed a similar segregation of PEO and PMMA induced by lithium methanesulfonate (LiT). They also observed that in these circumstances the glass-transition temperature of PMMA was raised well above that of normal PMMA (up to 170°C), a much greater effect than observed in the current study. These workers attributed the increase in T_g to complexation of PMMA by LiT. This conclusion was supported by observing systematic shifts in T_g of PMMA on addition of the salt and changes in infra-red spectra. We note also that Cowie and Martin²¹ observed an increase in T_g on the addition of LiT or of NaClO₄ to poly(vinyl methyl ether). In contrast, Venugopal *et al.*¹² did not observe a similar segregation on adding KSCN to PEO/PMMA blends and proposed that complexing was weaker in the presence of larger cations. During the present study we added NaSCN to PEO/PMMA blends and, although the films became bright yellow, we did not observe a large increase in T_g and concluded that if such complexing does occur it is probably too weak to hinder molecular motions. In order to explain the sensitivity of the blend to added LiT, Venugopal *et al.*¹² also suggested that the salt changes the preferred conformation of the PEO chains from planar zig-zag (in the miscible blend) to helical (as in the crystalline state), thereby reducing its miscibility with PMMA. The corresponding high sensitivity to salt observed in this study, with a change from a largely miscible blend with a strong glass transition to largely crystalline PEO on addition of just a little NaSCN, suggests that a similar explanation might be applicable.

At high NaSCN contents (~50 wt%) the phase behaviour was essentially identical to that for PEO-NaSCN mixtures with, in addition, a separate PMMA phase. Optical microscopy of a sample with EO:Na⁺ 2/1, 52 wt% PEO, showed no loss of birefringence due to melting of PEO (consistent with all PEO being complexed) and the development of liquid-like behaviour between 80 and 140°C (consistent with the T_g of PMMA, the major component). Birefringence started to decrease at 167°C and decreased markedly by 186°C, with liquid fronts passing across the sample at 190°C. However, melting was not complete at this stage and a new crystalline texture developed, with the new birefringent crystals melting/dissolving between 240 and 270°C; there was no corresponding transition observable by d.s.c. This optical observation is consistent with an observation reported by Robitaille *et al.*¹⁰ who suggested that, at high NaSCN contents, melting of the P(EO₃.NaSCN) complex was accompanied by disproportionation to P(EO₄.NaSCN) and formation of crystalline NaSCN. We attribute the observed changes between 240 and 270°C to be due to dissolution of NaSCN so formed.

Effects of NaSCN on PEO/PMMA block copolymers. Proportions of NaSCN were added to acetonitrile solutions of the PEO/PMMA block copolymers identified in Table 1 and solvent was removed as for homopolymer blends. Transition temperatures from d.s.c. thermograms for the several samples are presented in Figure 3, superimposed on the phase diagram determined by Robitaille *et al.*¹⁰ as in Figure 1. Copolymer compositions are taken to be those determined by ¹H n.m.r. and includes PEO homopolymer impurity in copolymer-2, as discussed above.

Copolymer-1 (25 wt% PEO) had a similar overall composition to most of the PEO/PMMA homopolymer blends studied and provides direct comparison with those blends. The copolymer alone exhibited a weak double melting endotherm with peaks at 58 and 67°C, due to the presence of a crystalline PEO component; a weak endotherm is similar to that observed in the homopolymer blend and consistent with most of the PEO being miscible with PMMA. These peaks possibly overlie a glass transition for the PMMA block miscible with some of the PEO block as they were associated with a distinct shift in the baseline, characteristic of a glass transition; such baseline shifts were not associated with melting endotherms in other thermograms. This possible T_g corresponds well with that expected (~64°C) on the basis of the Fox equation, using a value of -73°C for the T_g of quenched PEO¹⁰.

Copolymer-2 (80 wt% PEO, including admixed PEO homopolymer) alone, dominated by a high PEO content, exhibited a distinct, large PEO melting endotherm at 65°C consistent with the limited miscibility in PEO/PMMA blends at high PEO contents. This melting transition was reversible on cooling to -50°C after heating to 200°C. No definite glass transition was observable for PMMA at this high PEO content. These observations are in general accord with earlier observations on miscibility in PEO/PMMA homopolymer blends².

Addition of NaSCN to copolymer-1 (75 wt% PMMA, Table 1), the PMMA-rich copolymer, produced pale pink, birefringent samples. All samples exhibited evidence of a glass transition for mixed PMMA/PEO regions at 65–70°C (mid-point), which coexisted with the P(EO₃.NaSCN) complex at all compositions investigated (Figure 3). There was, however, no observable PEO crystalline microphase. This observation is consistent with the reported miscibility of PEO and PMMA at low PEO contents and the low molecular weights of the blocks. An aspect of the behaviour of these samples, which contrasts with that of the homopolymer blends, is that small amounts of NaSCN did not cause segregation of PMMA from PEO in the copolymer. All the PEO appears to be either complexed with NaSCN or to be miscible with PMMA. In addition to these observations, the copolymer samples exhibited broad melting endotherms between 240 and 280°C, in marked contrast to the homopolymer blends which showed no such endotherm.

Thermal transition data were supplemented by optical microscopy. These samples did not show spherulitic structures, but a pattern of numerous tiny irregular crystals. Heating to 100°C produced some evidence of small liquid droplets, especially in systems dilute in NaSCN, consistent with passing through a T_g at about

65°C. At 150–160°C the birefringent pattern started to change and all birefringence was lost by 165 to 175°C in samples with EO:NaSCN stoichiometries greater than 3/1. At higher NaSCN contents, i.e. sufficient NaSCN to complex all the PEO as P(EO₃.NaSCN), in the same temperature range the birefringent pattern changed and the newly formed crystals melted between 215 and 225°C; the endotherm observed by d.s.c. corresponded to the changes in crystal texture and not to loss of birefringence of the complex. This behaviour was similar to that observed in samples of the homopolymer blends where loss of crystallinity was also not associated with a sharp endotherm, but dissolution of NaSCN formed on disproportionation of the complex. At higher temperatures, between 250 and 275°C, all samples showed evidence of a gradual liquid–liquid phase separation to give clear liquid films with inclusions of a separate liquid phase at 280–300°C. This phase separation correlates with the endotherms observed between 240 and 280°C.

Samples of copolymer-2 with NaSCN at a EO:NaSCN ratio less than 4/1 ($w_{PEO} < 0.69$) were bright yellow (samples with more PEO were colourless) and highly birefringent; none showed the pink colour of copolymer-1 samples. The difference in colour from copolymer-1 samples probably reflects the scale and organization of the microphases in the system as there was no evidence for new structures. At low concentrations of NaSCN, up to 13 wt% with respect to PEO, in the PEO-rich copolymer-2 (EO:Na⁺ > 8/1) there was a strong endotherm for the PEO/P(EO₃.NaSCN) eutectic, but no observable melting endotherm due to the P(EO₃.NaSCN) complex. Larger proportions of NaSCN brought about the appearance of a P(EO₃.NaSCN) melting endotherm. At a stoichiometric ratio of EO:Na⁺ 8/1 the P(EO₃.NaSCN) melting transition was at 169°C and was broad. At higher NaSCN contents the melting transition became narrow and shifted to the melting point of the complex in the homopolymer blends; the eutectic endotherm decreased in magnitude as that of the complex developed. There was no evidence of a glass transition corresponding to the presence of PMMA until the NaSCN content reached 24 wt% (EO:Na⁺ 6/1) when the P(EO₃.NaSCN) melting endotherm was narrow and a baseline shift probably corresponding to a PMMA T_g became apparent at the reduced temperature of 84°C due to miscibility with some PEO; it is possible that a small glass-transition at about 100°C could have been obscured by the broader melting endotherm at higher PEO contents. The glass transition became more prominent as the NaSCN content increased to 47 wt% (EO:Na⁺ 2.1/1). This glass transition, lower than that for pure PMMA, appears to be associated with PMMA plus a proportion of the PEO in the sample. As with samples of copolymer-1, all samples of copolymer-2 with added NaSCN, even low concentrations, exhibited a large broad endotherm at about 240–260°C. Apart from the presence of a separate crystalline PEO phase, attributable to partial miscibility of PMMA and PEO, the data were consistent with those from copolymer-1.

Optical microscopy provided information on the texture of the samples and supplemented the thermal transition data. Samples of copolymer-2 having EO:Na⁺ ratios 3.7/1 or greater ($w_{PEO} \geq 0.67$) exhibited large spherulite-like structures, but with no Maltese cross pattern. Between the major crystalline structures, in

some samples, there were spaces containing myriad small crystals and with a depleted zone at the boundaries of the main features. Under crossed polars, non-birefringent areas could also be identified within the large structures. On heating samples containing EO:NaSCN 3.7/1 ($w_{\text{PEO}} = 0.66$) and 8/1 ($w_{\text{PEO}} = 0.82$) a few liquid-like droplets appeared at about 60°C, due to melting of the eutectic, followed by other changes in contrast at 90–100°C, possibly due to an increase in liquid-like character on passing through the PEO/PMMA T_g ; this change was not observed in the sample with EO:Na⁺ 6/1 ($w_{\text{PEO}} = 0.76$). Further heating produced losses of birefringence consistent with the melting endotherms attributed to P(EO₃.NaSCN); samples with 81 (EO:Na⁺ 8/1), 76 (EO:Na⁺ 6/1), 66 (EO:Na⁺ 3.7/1) and 61 (EO:Na⁺ 2.9/1) wt% PEO lost birefringence by 179, 180, 180 and 183°C, respectively. Samples with 81 and 76 wt% PEO lost all birefringence at these temperatures, but those with 65 and 61 wt% PEO retained a new birefringent pattern of myriad small crystals which dissolved gradually on heating, without an equivalent observable endotherm, and disappeared totally by 250°C to form a single liquid phase. These observations parallel those with copolymer-1 and homopolymer blends. Between about 240 and 280°C that liquid phase in most samples underwent a liquid–liquid phase separation process, as observed with copolymer-1. These changes again appear to be associated with the broad endotherms observed by d.s.c., as discussed below. On cooling samples taken to 300°C, crystallization took place in both liquid phases and, on reheating, all birefringence was lost between 165 and 182°C, corresponding to crystallization and remelting of the P(EO₃.NaSCN) complex in both phases. The higher temperature endotherm was not reproduced; the process responsible for that endotherm was not reversible.

Thermal transition data for block copolymers were a little more scattered than for homopolymers, but superposition of data from Figures 1 and 3 show that, apart from two data points for copolymer-1, all data for P(EO₃.NaSCN) melting are essentially consistent with the phase diagram produced by Robitaille *et al.*¹⁰ for PEO and NaSCN in the absence of PMMA. Therefore, as with the homopolymer blends, PMMA has no

influence on the phase diagram for PEO and NaSCN with respect to complex formation, although in the presence of NaSCN the phase diagram for PEO/PMMA homopolymer blends is totally dominated by NaSCN, which causes segregation of PEO and PMMA. This segregation is not apparent in the block copolymers, certainly not in copolymer-1 where there was no melting endotherm observed at about 60°C.

The most prominent feature which appeared in the thermograms for PEO/PMMA block copolymers with added NaSCN, for both copolymers and at all compositions studied, and which was absent in all other samples, was an additional endotherm for a thermal transition in the temperature range 250–280°C. This endotherm was strong in all thermograms, especially in samples of copolymer-1, and was akin to a melting endotherm rather than a glass transition; example thermograms are shown in Figure 4. Associated energies, determined from the areas of the peaks, increased with increasing NaSCN contents from about 30–120 J g⁻¹ compared with 30–60 J g⁻¹ for melting of the complex in the copolymers. Peak temperatures from the several thermograms obtained are included in Figure 3. For samples containing copolymer-1 the peaks were sharp at high temperatures and did not extend above 300°C, but showed tails at low temperatures, to about 200°C; in some cases a small peak was observable at 240°C, approximately. For samples containing copolymer-2 the additional peaks were broader and extended from about 220–320°C. These peaks have no equivalent in the homopolymer mixtures, with or without PMMA, or in the pure copolymers.

Robitaille *et al.*¹⁰ established that the melting transition of the P(EO₃.NaSCN) complex at about 182°C was reversible if cooling rates from the melt were low, e.g. 5°C min⁻¹, but not at high cooling rates of 320°C min⁻¹. By cycling samples in the d.s.c., we also observed that the melting transition for the P(EO₃.NaSCN) complex in copolymers in the presence of NaSCN is similarly reversible if samples heated to about 220°C were cooled at 5°C min⁻¹, but not if cooled at 40°C min⁻¹. We made some additional observations on the reversibility of the high temperature transitions by d.s.c. and by optical microscopy. A sample of copolymer-2, with 23 wt% NaSCN, heated to only

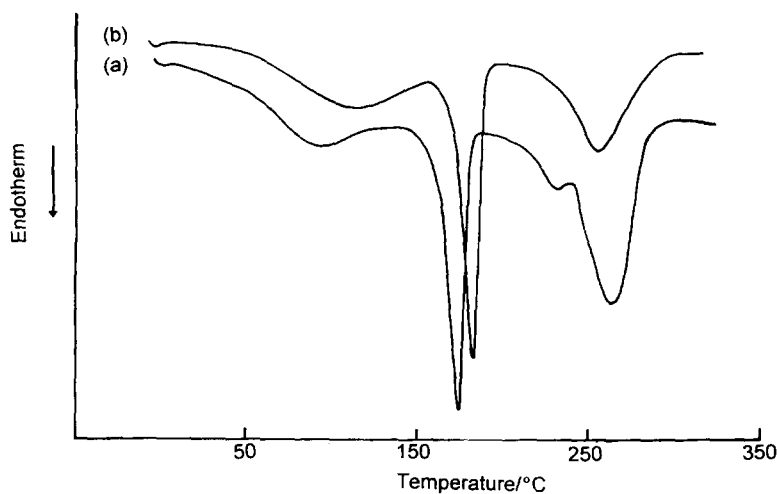


Figure 4 Thermograms for copolymers with added NaSCN: (a) copolymer-1; (b) copolymer-2

250°C, recrystallized on cooling and, on subsequent heating, lost birefringence at 180°C, commensurate with reversible P(EO₃.NaSCN) melting and recrystallization. However, samples of copolymer-2 with EO:Na⁺ = 2.9/1 heated to 217°C, to melt the P(EO₃.NaSCN) complex, and then cooled rapidly in the d.s.c. instrument to below 180°C developed birefringence which was not lost, as expected, at 180°C on subsequent heating, but was gradually lost between 220 and 260°C; no endotherm associated with this loss in birefringence was observed by d.s.c. That is, the endotherm at about 180°C is not reversible, by d.s.c., at higher cooling rates, but there is some form of recrystallization on rapid cooling. This effect may be associated with NaSCN formed on melting and disproportionation of the P(EO₃.NaSCN) complex and the lack of reforming this complex at high rates of cooling; these observations are consistent with those of Robitaille *et al.*¹⁰. We also determined that the broad high-temperature transition at about 270°C is not reversible. If samples which had undergone a liquid-liquid phase separation, as seen by optical microscopy, on heating to 300°C were cooled slowly no exotherms corresponding to a reversal of that transition were observed and, on re-heating, no endotherm for P(EO₃.NaSCN) melting was observed.

Although this high temperature endotherm occurs at the reported temperature for NaSCN melting, according to some published data²⁰ (but not according to Robitaille *et al.*¹⁰ or in this work), optical microscopy indicated that such a process was not the origin of this transition; as already discussed, NaSCN crystals formed by disproportionation of the P(EO₃.NaSCN) complex appear to dissolve gradually with no observable endotherm. There is also no evidence that the high temperature endotherm arises from a degradation process. On heating to 300°C, during d.s.c. analysis or under the optical microscope, samples discoloured slightly, but retained their initial form; samples of PEO-rich copolymer-2 fused. Under the optical microscope there was no evidence for evolution of volatiles or for material loss, except for one sample of copolymer-2, with only 11 wt% NaSCN, which emitted an acid odour on prolonged heating at 300°C in air on the microscope heating stage.

In an attempt to identify a possible mechanism for the process associated with the high-temperature endotherm, we relate the salient data to copolymer structure. From the foregoing it is clear that, in the presence of NaSCN, the copolymers (especially copolymer-1) consist of PMMA-rich regions (with a reduced T_g) and PEO/NaSCN-rich regions; copolymer-2 contains some crystalline PEO. Since the polymeric components (apart from PEO homopolymer impurity, which is negligible in copolymer-1) are constituents of block copolymers, we presume that these distinct regions are microphases (the PEO microphase in copolymer-2 samples is probably extended by homopolymer). The reversible melting endotherm for the P(EO₃.NaSCN) complex is essentially identical to that in simple PEO-NaSCN mixtures and we presume that this melting, and recrystallization, occurs within the microphase-separated system. The gradual loss of birefringence at higher temperatures in samples with high NaSCN contents, consistent with gradual dissolution of crystalline NaSCN, was not associated with an observable endotherm, in agreement with observations

and suggestions of Robitaille *et al.*¹⁰ for mixtures of NaSCN with PEO homopolymer. The strong, broad high-temperature endotherm was not associated with melting or dissolution of birefringent crystals, but required an increase in entropy. Optical microscopy suggests it occurs in the liquid state and is associated with a gradual liquid-liquid phase change. We therefore suggest that the reversible melting of the P(EO₃.NaSCN) complex seen at about 180°C does not involve total homogenization of the microphase-separated system, and we attribute the additional endotherm to a disordering process of the microphase-separated system at high temperatures. This proposal is consistent with reversible crystallization of the P(EO₃.NaSCN) complex in the microphase-separated system, after heating to 'low' temperatures and with slow cooling, but the absence of recrystallization from a disordered system produced by heating to higher temperatures where the microphase separation is destroyed. Complex formation in solution, during sample preparation, could force microphase separation in the copolymer whereas the corresponding process may not occur readily from the melt. The identities of the individual liquid phases produced above 250°C are unclear; in copolymer-2 it is possible that PEO homopolymer separates from the copolymer.

Conclusions

The phase diagram for PEO with added NaSCN and cast from methanol solution, previously reported by Robitaille *et al.*¹⁰, was confirmed for samples cast from methanol and was found to be equally applicable to samples cast from acetonitrile solutions. It was demonstrated that the sample phase diagram also applies to thermal transitions in blends of PMMA and PEO on addition of NaSCN, apart from small shifts in transition temperatures due to miscibility of components on melting.

NaSCN was found to complex so strongly with PEO in solution that it was not possible to observe any subtle influence of NaSCN on the phase diagram for PEO/PMMA blends. NaSCN totally dominates the phase behaviour of PEO with PMMA and reversible cloud points could not be determined.

Addition of NaSCN to miscible PEO/PMMA blends causes the PMMA to segregate from the blend, as Venugopal *et al.* found previously on addition of LiT to PEO/PMMA blends¹². We did not find strong evidence for complexing of NaSCN with PMMA, as was found with LiT by Venugopal *et al.*, although yellow colours were developed and there was a small increase in the T_g for PMMA.

Addition of NaSCN to PEO/PMMA block copolymers gave rise to phase diagrams virtually essentially identical to the homopolymer blends, as determined by the thermal transition behaviour for P(EO₃.NaSCN) melting, but in PMMA-rich copolymer PEO does not segregate and does not crystallize. However, an additional endotherm appears at high temperature (~280°C) in the thermograms for block copolymers in the presence of NaSCN, which is not associated with loss of crystallinity (birefringence), but was found to be associated with (or accompanied by) a liquid-liquid phase separation and its tentatively attributed to disruption of the PMMA and (PEO plus NaSCN) microphase-separated system at high temperatures.

Acknowledgements

The authors wish to acknowledge SERC and ICI Paints for financial support of one of us (P. Scofield) and Professor R. Jerome and Dr J. S. Wang (University of Liege, Belgium) for assistance with the synthesis of PEO/PMMA block copolymers.

References

1. Paul, D. R. and Newman, S., *Polymer Blends*. Academic Press, New York, 1978.
2. Liberman, S. A., Gomes, A. D. S. and Macchi, E. M., *J. Polym. Sci., Polym. Phys. Ed.*, 1984, **22**, 2809.
3. Cortazar, M. M., Calahorra, M. E. and Guzman, G. M., *Eur. Polym. J.*, 1982, **18**, 165.
4. Nishi, T. and Wang, T. T., *Macromolecules*, 1975, **8**, 909.
5. Ito, H., Russell, T. P. and Wignall, G. D., *Macromolecules*, 1987, **20**, 2213.
6. Fenton, D. E., Parker, J. M. and Wright, P. V., *Polymer*, 1973, **14**, 589.
7. Wright, P. V., *Br. Polym. J.*, 1975, **7**, 319.
8. Hibma, T., *Solid State Ionics*, 1983, **9/10**, 1101.
9. Lee, C. C. and Wright, P. V., *Polymer*, 1982, **23**, 681.
10. Robitaille, C., Marques, S., Boils, D. and Prud'homme, J., *Macromolecules*, 1987, **20**, 3023.
11. Ramana Rao, G., Castiglioni, C., Gussoni, M., Zerbi, G. and Martuscelli, E., *Polymer*, 1985, **26**, 811.
12. Venugopal, G., Krause, S. and Wnek, G. E., *Polymer*, 1993, **34**, 15, 3241.
13. Garg, D., Höring, S. and Ulbricht, J., *Makromol. Chem., Rapid Commun.*, 1984, **5**, 615.
14. Donth, E., Kretzschmar, H., Schulze, G., Garg, D., Höring, S. and Ulbricht, J., *Acta Polym.*, 1987, **38**, 260.
15. Reuter, H., Berlinova, I. V., Höring, S. and Ulbricht, J., *Eur. Polym. J.*, 1991, **27**, 673.
16. Wu, W. W. L. and Pürma, I., *Polym. Bull.*, 1993, **31**, 531.
17. Fayt, R., Forte, R., Jacobs, C., Ouhadi, T., Teysse, P. and Varshney, S. K., *Macromolecules*, 1987, **20**, 1442.
18. Wang, J., Varshney, S. K., Jerome, R. and Teyssie, P., *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 2251.
19. Eastmond, G. C., Schofield, P., Jerome, R. and Wang, J. S., (unpublished data).
20. West, R. C., ed., *Handbook of Chemistry and Physics*. CRC Press, Cleveland, OH, 1972, p. B-141.
21. Cowie, J. M. G. and Martin, A. C. S., *Polym. Bull.*, 1987, **17**, 115.