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UCST-type phase behaviour in poly(ethylene terephthalate-*co*-ethylene naphthalate)/ poly(ether imide)blends

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Miscibility between poly(ethylene terephthalate-*co*-ethylene naphthalate) (PTN) and poly(ether imide) (PEI) was investigated by the cloud point method with the aid of time-resolved light scattering analysis on crystallization and liquid–liquid phase separation. The system was found to exhibit upper critical solution temperature (*UCST*) type phase behaviour. The higher the ethylene naphthalate (N) content in PTN, the lower the *UCST* and the wider the single-phase region in the phase diagram. From the phase diagrams, the temperature dependence of the binary interaction parameters $\chi_{i/j}$ between constituent monomeric units (i,j =N, T and EI; T and EI being ethylene terephthalate and ether imide, respectively was estimated. $\chi_{T/N}$ was a positive but small quantity while $\chi_{N/EI}$ was negative, suggesting that the miscibility betwen PTN and PEI is mostly caused by an exothermic intermolecular interaction between N and EI units and that the repulsive intramolecular interaction between T and N in the copolymer plays a minor role. Based on the temperature dependence of $\chi_{i/j}$, a miscibility map (temperature–copolymer composition phase diagram) was established.

(Keywords: polymer blends; phase behaviour; miscibility)

INTRODUCTION

There has been much interest in miscible polymer blends in which one or both component polymers are random copolymers[1–4]. Such random copolymers are usually synthesized by free radical copolymerization. In contrast, copolymers synthesized by polycondensation are rarely used in studies on polymer blends even though many homo- and copolymer fibres and films are synthesized by the polycondensation reaction. Recently, it was found that the copolymer consisting of ethylene terephthalate and ethylene naphthalate units (PTN) was miscible with poly(ether imide) (PEI)[5]. In this paper, we investigate the phase diagram of PTN/PEI blends by cloud point method as a function of copolymer composition, and discuss the miscibility in terms of the temperature dependence of the interaction parameters $\chi_{i/j}$ between consituent monomeric units (i,j = T, N and EI, where T is ethylene terephthalate, N is ethylene naphthalate and EI is ether imide).

EXPERIMENTAL

PTN random copolymers used in this study were synthesized by polycondensation of dimethyl terephthalate, dimethyl naphthalate and excess ethylene glycol (*Figure 1*). Manganese acetate and Sb_2O_3 were used as catalysts. The reaction was carried out at 170–220°C for 3 h (ester exchange) and then at 285°C for 1 h under vacuum (0.1 mmHg) (polycondensation). The molecular weight was estimated by viscometry in a mixed solvent of phenol and tetrachloroethane (6:4 v/v) using:

$$[\eta] = 7.55 \times 10^{-4} M_n^{0.685} \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity and M_n is the number-average molecular weight[6]. The melting point and glass transition temperature (T_g) were measured using a Parkin–Elmer DSC-7 differential scanning calorimeter at a heating rate of 20 K min^{-1}.

PEI used in this study was a commercial product supplied by General Electric Co. (Ultem 1000, $M_n = 3 \times 10^4$, $T_g = 220$°C).

PTN and PEI were dissolved at 5 wt% of total polymer in a mixed solvent of phenol and tetrachloroethane (6:4 v/v). The solution was cast on a glass plate and the solvent was evaporated under a reduced atmosphere of 10 mmHg at room temperature for 1 day, followed by further drying at 80°C for 2 days. The thickness of the film specimen was ~ 20 μm.

The blend film thus obtained was inserted in a hot chamber kept at a constant temperature and annealing under a nitrogen atmosphere for 10 h[†]. When the film

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[†] Annealing for more than 10 h induced thermal degradation of PTN at high temperatures (> 300°C) and M_n decreased. The 10 h annealing was the upper limit for 'long annealing' to construct the phase diagram

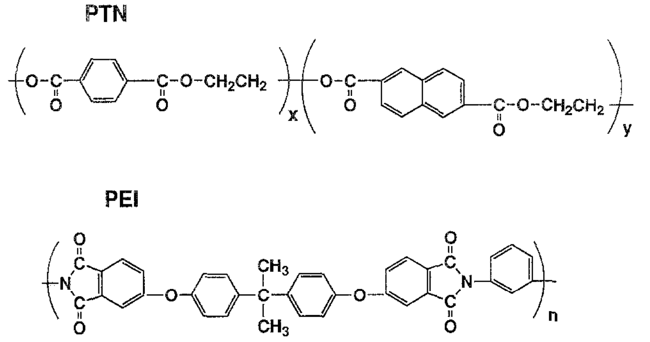

Figure 1 Chemical structure of PTN and PEI

became opaque and two-phase morphology was observed under an optical microscope, we judged that the blend was annealed in the two-phase region in the phase diagram. When the film was clear and any morphology was not seen under the microscope after annealing, we judged that the blend was in the single-phase region. These annealing experiments were repeated at various isothermal settings. Thus, we estimated the phase diagram by the cloud point method.

To verify the phase diagram, we carried out light scattering analysis on the kinetics of demixing and crystallization. The film was held at 305°C for 2 min and then the melt underwent a rapid quench to the crystallization (or phase separation) temperature by putting it in a hot-stage set in a light scattering photometer with a highly sensitive charge coupled device camera (Princeton Instruments, Inc.)[7]. Two optical alignments were used: (1) the *Hv* geometry in which the optical axis of the analyser was set perpendicular to that of the polarizer and (2) the *Vv* geometry with a parallel set of the two axes. Thus the time-resolved light scattering analysis of the two-rate processes was carried out at an isothermal setting.

To estimate the equilibrium melting point (T_m°) of the blends by the Hoffman–Weeks plot, the blend film was placed in the aluminium pan of the differential scanning calorimeter and isothermally crystallized for 16 h at various crystallization temperatures. The melting point of the crystallized specimen was measured by differential scanning calorimetry in the same way as mentioned above.

RESULTS AND DISCUSSION

Molecular charcteristics of the synthesized PTN are summarized in *Table 1*. Only polymer PTN10 was crystalline, the others being amorphous.

The solution-cast films of PTN10/PEI blends were opaque. By annealing above the melting point of PTN, the films lost optical anisotropy under the polarized optical microscope and no scattering intensity in the *Hv* configuration was detected. These results imply that the opacity was caused by crystallization of the PTN10-rich phase during the solvent evaporation process. The other solution-cast films of PTN/PEI blends with different copolymer compositions were optically clear. The films, with limited blend compositions, turned opaque with annealing above the T_g of PEI and two-phase morphology was observed under a microscope.

Table 1 Molecular characteristics of copolyesters

Code	N content (mol%)	T_g(°C)	T_m°(°C)^a	$M_n \times 10^{-4}$
PTN10	10	77.4	246.5	1.80
PTN15	15	80.4	–	2.40
PTN20	20	83.2	–	2.28
PTN25	25	83.3	–	2.32
PTN30	30	85.5	–	2.27

^{a}Estimated from the Hoffman–Weeks plot (see *Figure 5*)

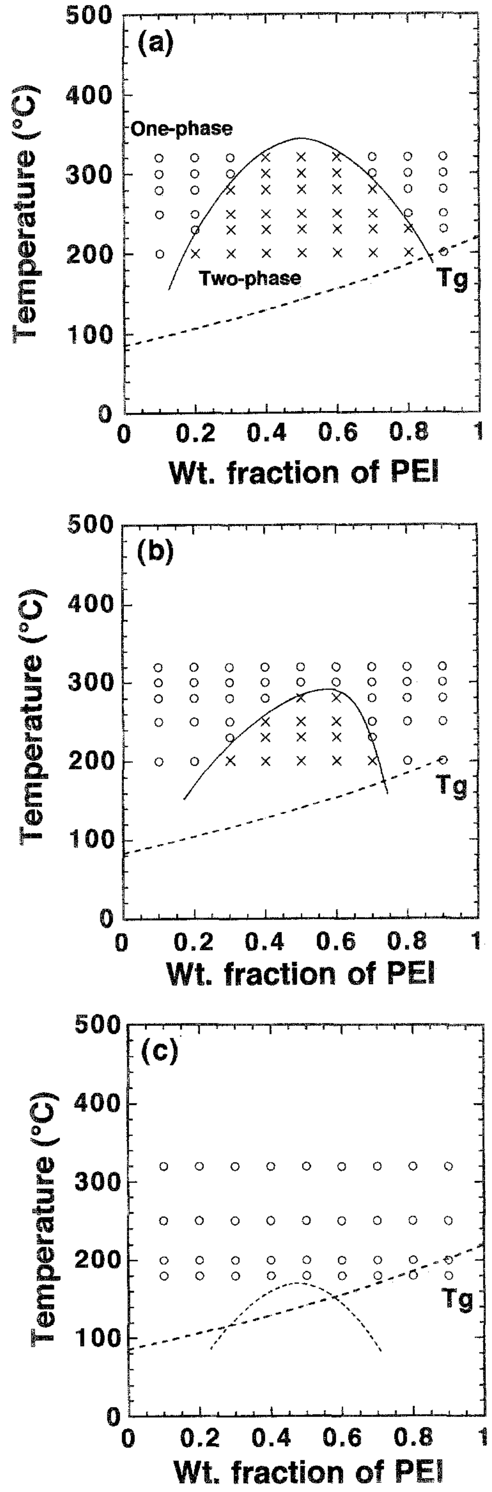

Figure 2 Phase diagrams of (a) PTN10/PEI, (b) PTN20/PEI and (c) PTN30/PEI. ×, Opaque film and two-phase morphology was observed under light microscope; ○, clear film after 10 h annealing. The broken line in (c) is a calculated binodal curve.

Typical phase diagrams are shown in *Figure 2*. Upper critical solution temperature (*UCST*) type phase behaviour can be seen, with the *UCST* decreasing with increasing ethylene naphthalate (N) content in the copolymer (*Figures 2a–c*). That is, the miscibility between PTN and PEI is enhanced with increasing N content in the copolymer. The T_g curve in *Figure 2* was calculated by the Fox equation[8]:

$$1/T_{g_b} = (w_A/T_{g_A}) + (w_B/T_{g_B}) \qquad (2)$$

where T_{g_b} is the T_g of the blend, w_i is the weight fraction of component i and T_{g_i} is the T_g of component i ($i = A$, B).

The thermodynamic description of the phase behaviour of copolymers as a function of copolymer composition is presented within the framework of the mean-field theory[2,3,9]. The interaction parameter of χ_{12} between PTN (polymer 1) and PEI (polymer 2) is given by:

$$\chi_{12} = \beta X_{N/EI} + (1-\beta)\chi_{T/EI} - \beta(1-\beta)\chi_{T/N} \qquad (3)$$

where β is the mole fraction of N in PTN and $\chi_{i/j}$ is the i–j binary segmental interaction parameter. One can estimate the values of $\chi_{i/j}$ when the values of χ_{12} are given for the blends of different β; at least for three systems (three equations for three unknown parameters). Since we have obtained the phase diagram, we can calculate the $\chi_{i/j}$ value as a function of temperature by assuming[10]:

$$\chi_{i/j} = A/T + BT + C \qquad (4)$$

where T is a temperature and A, B and C are constants. The first term on the right-hand side of equation (4) corresponds to the exchange energy contribution to the free energy of mixing and the second term to the so-called free volume contribution. In this equation, the composition dependence of $\chi_{i/j}$ is omitted. We selected the best set of parameters A, B and C to fit the calculated binodal curve to the phase diagram observed (*Figure 2* and other blends; PTN15/PEI and PTN25/PEI). The calculation program used was the 'Phase Diagram Module' (Biosym Technologies, Inc.)[11].

The calculated results are shown in *Figure 3*. $\chi_{N/EI}$ is shown to be negative, suggesting that poly(ethylene naphthalate) should be miscible with PEI. A positive but very small value of $\chi_{T/N}$ implies that poly(ethylene terephthalate) is not incompatible with poly(ethylene naphthalate) and the two polymers are expected to be miscible at high temperatures when the molecular weights are small. In any case, the results in *Figure 2* clearly show that the miscibility between PTN and PEI is mostly caused by the exothermic intermolecular interaction between N and EI units, and that the repulsive intramolecular interaction in PTN plays a minor role. Based on the temperature dependence of $\chi_{i/j}$, one can estimate the miscibility map: the temperature–copolymer composition phase diagram for a fixed blend composition. A typical result is shown by the straight line in *Figure 4*. Experimental results represented by open circles and crosses are nicely explained by the straight line.

Regarding the cloud point method, it must be remembered that PTN10 is a crystalline polymer so that the effect of crystallization should be taken into account when judging the PTN10/PEI blends to be single-phase or two-phase after annealng. In the PTN10/PEI blends the PTN10 did crystallize and the melting point T_m° was detected, as shown in *Figure 5* in terms of the Hoffman–Weeks plot[12].

When a 70/30 PTN10/PEI blend underwent a temperature drop from 305°C (above T_m° and the binodal temperature) to 155°C (below the binodal temperature),

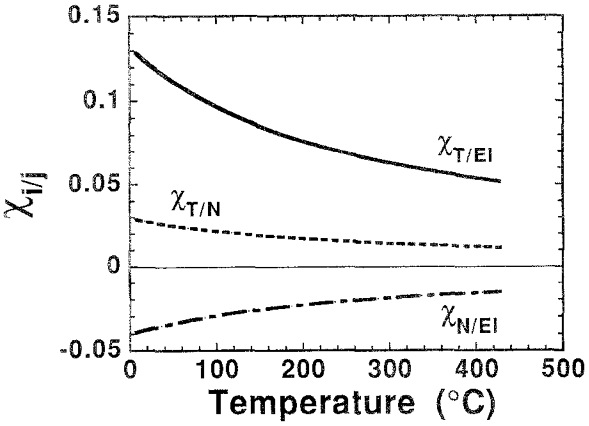

Figure 3 Temperature dependence of the binary interaction parameters $\chi_{i/j}$

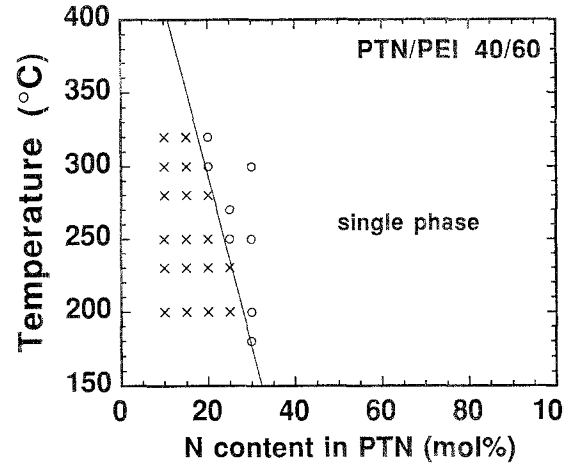

Figure 4 Miscibility map for 40/60 PTN/PEI blends

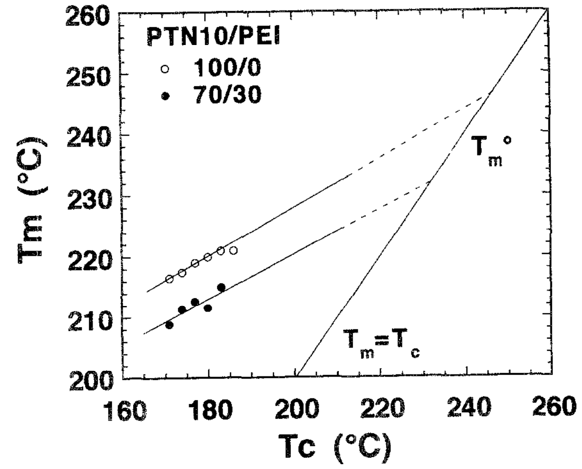

Figure 5 Hoffman–Weeks plots for neat PTN10 and 70/30 PTN10/PEI blend

the *Vv* scattered intensity immediately started to increase and the ring pattern characteristic to spinodal decomposition was seen; the *Hv* intensity remained at zero level until 1200 s, then started to increase and the four-leaf clover pattern appeared after 1350 s, suggesting the formation of spherulites. Under the light microscope a bicontinuous two-phase structure with periodic distance of $\sim 2\,\mu$m appeared at an early stage ($t < 1200$ s) and the periodic distance increased with time. *Figure 6* shows the time variation of the one-dimensional *Vv* scattering profile: a scattering peak appears and the peak angle shifts to smaller angles with time. This behaviour is quite typical for spinodal decomposition. *Figure 7* shows time variation of both *Vv* and *Hv* scattering intensities (I_{Vv} and I_{Hv} at two selected scattering angles (*Vv* and *Hv* scattering peaks appeared at $\theta = 12°$ and $\theta = 8°$ at $t = 1700$ s, respectively). One can see a large increase of I_{Vv}, suggesting the early stage of spinodal decomposition. One can also see a long time lag to the onset of *Hv* scattering. This implies that the concentration fluctuation starts immediatly after the temperature drop and, after a certain time lag, the fluctuation in optical anisotropy (i.e. the liquid–solid phase transition or crystallization) follows. That, is one can have a long enough time window for the cloud point method. Similar results were obtained for different blend compositions at a temperature range of 150–240°C. Based on such results, only for the crystalline/amorphous blend (PTN10/PEI) was the cloud point method carried out at a rather short time-scale of annealing (10–30 min).

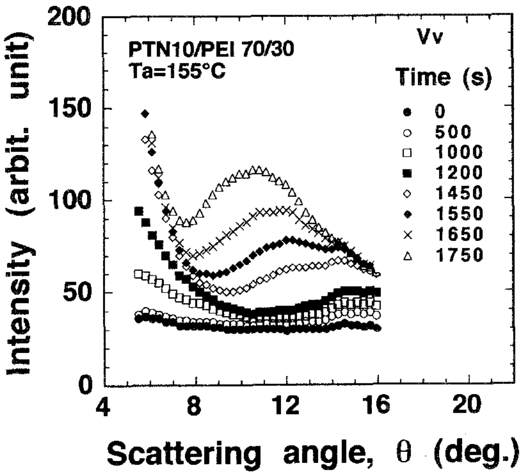

Figure 6 Change of *Vv* scattering profile with time after temperature drop from 305 to 155°C for 70/30 PTN10/PEI blend

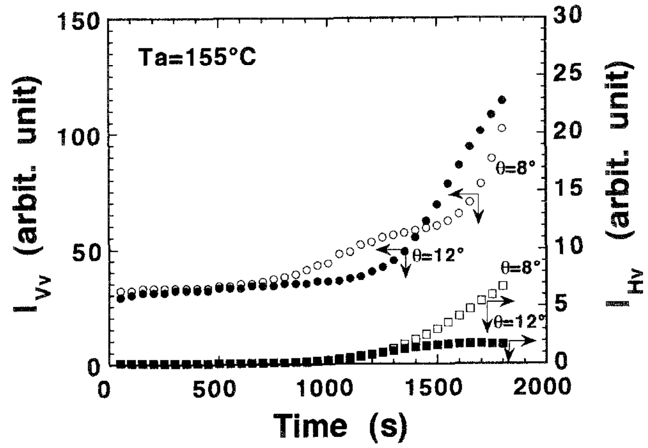

Figure 7 Time variation of the scattered light under *Vv* (I_{Vv}) and *Hv* (I_{Hv}; azimuthal angle = 45°) for 70/30 PTN10/PEI blend after temperature drop to 155°C from the melt (305°C), showing an immediate onset of spinodal decomposition after the temperature drop and a delayed onset of crystallization

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