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Experimental verification on upper critical solution temperature (UCST) behavior in blend of poly(2,6-dimethyl *p*-phenylene oxide) with poly(4-methyl styrene)

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Abstract

Rare upper critical solution temperature (UCST) behavior was found and experimentally demonstrated in the blend comprising poly(2,6-dimethyl *p*-phenylene oxide) with poly(4-methyl styrene) (PPO/P4MS). Complexity of phase behavior in the PPO/P4MS system has caused puzzling analyses in the past years. This study re-investigated and clarified past mis-interpretations related to this interesting blend system. This study concluded that the PPO/P4MS blend is an immiscible system at ambient, which, however, turns into a miscible phase with UCST behavior at higher temperatures. With the finding of UCST in the PPO/P4MS blend, a critical contribution of this work was to resolve the conflicting arguments that have gone on for a long time in determination and interpretation of the thermodynamic phase behavior of PPO/P4MS. Phase behavior with UCST in the PPO/P4MS blend system and its interpretation were supported with clear experimental evidence.

Keywords: Poly(4-methyl styrene); Poly(*p*-methyl styrene); Poly(2,6-dimethyl phenylene oxide)

1. Introduction

Polymer mixtures that are miscible at ambient temperature can usually exhibit phase separation at elevation temperatures, which is a phenomenon known as the lower critical solution temperature (LCST) phase behavior. On the other hand, polymer blends that are thermodynamically immiscible at lower (such as ambient) temperatures rarely become miscible at elevated temperatures, which, if does occur, is a behavior known as the UCST. Occurrence of UCST in polymer mixtures of high-molecular-weights constituents is generally rare, but it can be occasionally observed in some polymer blends. Examples are briefly mentioned here. Blends of different styrenic polymers have been an extensively studied subject. The phase behavior of blends comprising of polystyrene (PS) and poly(α-methyl styrene) (PαMS) has been widely investigated and reported [1–7]. Interestingly, PS and PαMS are immiscible at ambient temperature but can exhibit miscibility at elevated temperatures, which is known as upper critical solution temperature (UCST) behavior. Similarly, phase behavior in blends of different olefinic polymers has been studied. By utilizing a powerful technique of small-angle neutron scattering (SANS), Graessley et al. [8–10] have reported extensively on various interesting thermodynamics behaviors of miscibility with LCST or UCST phase separation, interactions in blends of polyolefins.

Miscibility in blends involving PS is occasionally seen. The most widely studied blends involving PS are probably those with some ether-containing polymers. The blend system of PS with poly(2,6-dimethyl-*p*-phenylene oxide) (PPO) is one of the most studied polyblends in this class, and its miscibility has been demonstrated since early time [11,12]. The PS/PPO blend system is known to be fully miscible with no observable LCST behavior (within the experimentally accessible temperatures). Another example of miscible blends comprising PS is given by the extensively studied PS/poly(vinyl methyl ether) (PVME) system [13,14]. PS/PVME, on the other hand, exhibit borderline miscibility with a quite low LCST just slightly above the blends' T_g. Other than these relatively few literature-documented examples, PS or other styrenic polymers are mostly immiscible with other polymers. Interestingly, the blends involving PS and other polymers can exhibit miscibility with or without an LCST or immiscibility with or without a UCST depending on the structures of the

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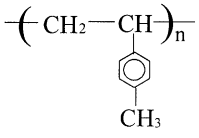
polymers with which PS is blended. On the other hand, alteration of the structure in PS can cause significant changes of phase behavior in a specific blend system, e.g. PPO/PS systems.

Following the discovery of interesting miscibility in PPO/PS blend in 1970, other blend systems of PPO with different styrenic polymers (such as modified PS) have also been investigated [15–17]. Attempts have also been made to understand the phase behavior in blends of PPO with a specific styrenic polymer, P4MS or P*x*MS, which differs from PS by an extra methyl group on the *para*-position (or *x*-position) of the pendant phenyl group [18–20]. However, studies on blends of PPO with P4MS have yielded ambiguous results and inconsistent interpretation, and contradictory conclusions of miscibility or immiscibility have been reached. Most as-cast blend samples (cast-film of ca. 100 μm) were slightly hazy/translucent with optically discernible phase domains for most intermediate compositions. Some were optically clear in a limited composition range. Apparently, separated domains existed in the blends. Morphology and/or possible existence of micro-domains in the blends were further examined using scanning electron microscopy. The objectives of this study were to resolve the phase behavior in blends comprising PPO and a styrenic polymer, P4MS, which differs from PS by an extra methyl group on the *para*-position of the pendant phenyl group.

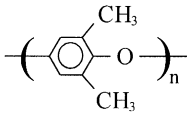
2. Experimental

Amorphous poly(2,6-dimethyl *p*-phenylene oxide) (PPO) was purchased from a specialty polymers supplier (Polysciences, Inc., USA), with an approximate $M_w = 50{,}000$ g/mol (Gel Permeation Chromatograph, GPC) and T_g= 207 °C. Poly(4-methyl styrene) (P4MS) was obtained from Scientific Polymers Product (SP2), Inc. (USA), with an approximate $M_w = 70{,}000$ g/mol (Gel Permeation Chromatograph, GPC) and $T_g = 106$ °C. The chemical structures of P4MS and PPO are as follows:

P(4MS):



PPO:



Blend samples in this study were prepared by solvent-mixing and solution-casting (chloroform) at constant temperatures (45 °C).

2.1. Apparatus

The glass transition temperatures were measured with a differential scanning calorimeter (Perkin–Elmer DSC-7) equipped with an intracooler and a computer for data acquisition/analysis. All T_g measurements were made at a scan rate of 20 °C/min, and the T_g values were taken as the onset of the transitions (the change of the specific heat) in the DSC thermograms. In addition, thermal treatments, annealing, quenching, etc. were performed inside the DSC cells.

An optical light microscope (Nikon Optiphot-2, POL) was used for observing phase transition upon temperature changes. The as-cast blends were spread as thin films on glass slides, dried properly in a temperature-controlled oven before they were examined using the optical microscope. For direct comparison, blend samples for optical examination were prepared using exactly the same solvents and casting temperature as those samples for thermal analysis. Preliminary blend morphology and cloud point measurement were examined using optical microscopy (OM) by placing the samples on a microscope heating stage, at approximately 2 °C/min from room temperature up to 300 °C. In addition, detailed phase homogeneity in the blends was examined using a scanning electron microscope (SEM, JEOL JXA-840).

3. Results and discussions

3.1. Phase behavior and thermal characterization

Morphology characterization using SEM was performed to reveal the scales of any possible heterogeneity. Heterogeneity of ultra-micro scales might exist in apparently clear-cast blends especially if the phase behavior borders on transition of immiscibility/miscibility (or de-mixing/mixing). The SEM characterization on the as-cast PPO/P4MS blends did reveal some discernible phase domains in most blend compositions. DSC was then performed to characterize the glass transitions in the blends, and T_g vs composition relationship was also investigated. Fig. 1(A) and (B) shows the DSC thermograms for 12 different compositions, which reveal two T_g's for most intermediate compositions of the blend system, as indicated in the curves. In addition, to more clearly illustrate detection of two T_g signals, the enlarged portions of DSC traces showing two T_g's are shown in Fig. 1(B). As the baseline stability/reproducibility was critical in assessing the correct T_g locations, DSC characterization was performed two or three times on several blend compositions and excellent reproducibility was found. Experience of thermal analysis and due care were used in assigning the T_g's on the DSC thermograms. By applying the conventional T_g criterion aided with the evidence of OM and SEM characterization, the PPO/P4MS blend is apparently an immiscible system at ambient temperature.

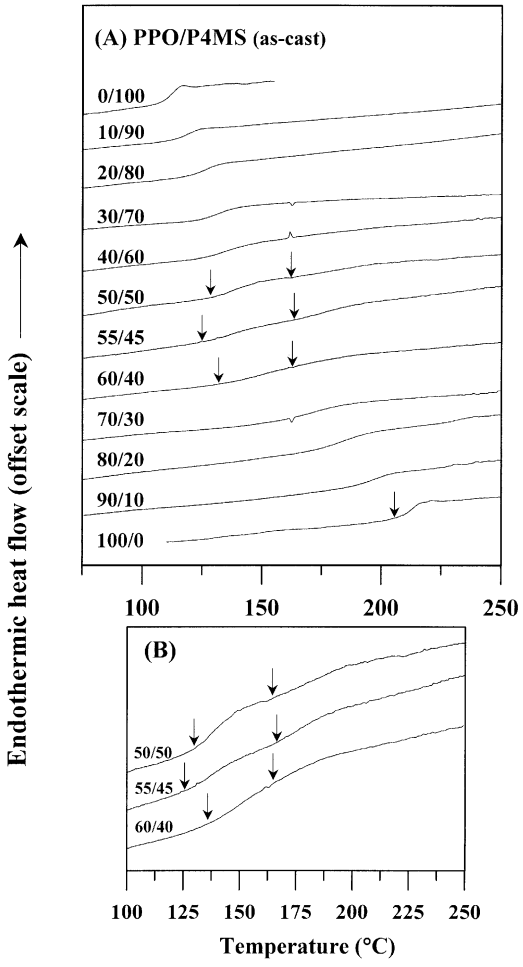


Fig. 1. (A) DSC thermograms for as-cast PPO/P4MS of 12 different blend compositions as indicated in the curves. (B) Enlarged portions of DSC traces showing two T_g's.

By summarizing the results of glass transition, OM, and DSC characterization, Fig. 2 shows the range of two phases for the PPO/P4MS blend. Although the range of blends showing two T_g's is limited to the intermediate compositions according to the DSC characterization, the OM and SEM characterizations did obviously reveal that except for the two extreme compositions near the two neat polymers, most compositions of the blend samples exhibited phase separation.

Interestingly, however, the phase morphology of PPO/P4MS changed evidently upon heating. The originally immiscible PPO/P4MS were heated slowly (ca. 2 °C/min) to higher temperatures for observing phase change using OM. At various higher temperatures, the initially immiscible blend samples were found to turn transparent and clear. Fig. 3 shows the result of 'homogenization temperature (or clarity point)' of the PPO/P4MS blend system as a function of composition. The figure shows a critical maximum point (UCST) at about 240 °C for the PPO/PS composition of 60/40 (weight ratio) thus estimated by heating the blend. The phase structure of the blends was originally immiscible but

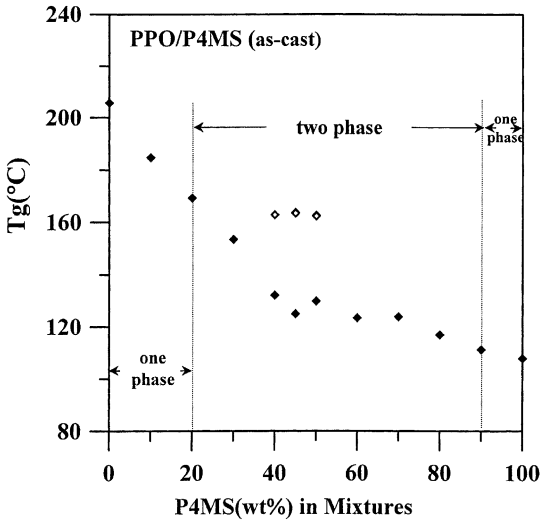


Fig. 2. T_g and composition range of two phases for the PPO/P4MS blend.

they could be brought to a miscible state at higher temperatures, which is a thermodynamic UCST behavior. Apparently, the thermodynamic driving force by heating the blends above the UCST temperatures allowed a kinetic process going from a 'de-mixing state' to a 'mixing one' (i.e. miscible).

Although UCST behavior in many polymer systems have been reported on heating/clarity [1–8], as also done in this study, certainly it may still be argued that cooling/turbidity, instead of heating/clarity, experiments are better estimate of UCST points for mixtures. However, experimental feasibility might be a factor in determining which of the schemes could be used. Experiments of cooling down from above UCST and observing phase reversibility were performed. However, owing to kinetic hindrance, it was found that the samples, upon cooling back from above UCST (clarity point) did not come back to original turbidity morphology

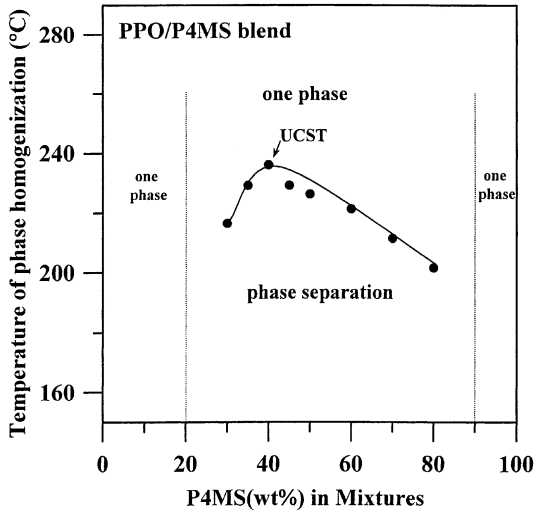


Fig. 3. UCST curve and homogenization (clarity-point) temperature of the PPO/P4MS blend system as a function of composition.

when observed by OM. The cooling scheme was controlled at very slow rates 1–2 °C/min on a microscopic hot stage, but the kinetic hindrance prohibited the long polymer chains from re-organizing into original phases within a reasonable experimental time frame. This situation is similar to many classical miscible blend systems showing irreversible LCST. Many miscible blends, upon heating above LCST, can readily turn to cloudiness (turbidity), but did not return back to miscibility clarity upon slowly cooling down. The lack of reversibility has been primarily attributed to kinetic hindrance of long polymer chains with high T_g's. This behavior has been observed in many classical miscible systems showing LCST. Generally speaking, if both blend constituents possess high T_g's (such as the current system of PPO and P4MS), phase reversibility is difficult to observe experimentally during cooling or heating due to kinetic restriction of chain mobility. On the other hand, if one of the constituents possesses low T_g's, such as PVME/PS system [13,14]. Upon heating of PVME/PS, LCST is observed; upon cooling slowly, the blend can be brought to original miscible state (i.e. reversible). Similarly, for polymer–solvent systems showing UCST, it is also easy to observe cooling/turbidity, because solvent is low-molecular weight and low T_g. On the other hand, miscible blends with high T_g's, such as poly(styrene-*co*-acrylonitrile)/poly(methyl methacrylate) (SAN/PMMA) [21] or polystyrene/poly(cyclohexyl methacrylate) [22], may show LCST phase separation upon heating but remained in the phase-separated state without coming back to original miscible state upon cooling (i.e. irreversible) down below LCST. It must be emphasized that the failure of observing reversible phase separation in OM did not mean that the UCST in PPO/P4MS system was not thermodynamically reversible. The cooled samples (stayed visually clear) were re-dissolved back to solvents, re-cast to films, then original phase-separate morphology was readily visible in OM. The solvent reduced the viscosity of the blend system and kinetically helped the morphology reversibility in shorter time frame. This indicates that as long as kinetic factors are favorable, the physical state was fully reversible and no chemical reactions took place during heating to above UCST. Furthermore, DSC thermal analysis was used to prove the reversible phase separation in the PPO/P4Ms system, which will be discussed in later figures.

Fig. 4 shows the OM evidence for the as-cast blends going from phase separation to one phase (i.e. clarity/homogeneous points) upon heating to above UCST temperatures (e.g. 260 °C) for three representative compositions of PPO/P4MS: (a) 50/50, (b) 40/60, and (c) 30/70. SEM was also performed on the as-cast vs heated/quenched PPO/P4MS blends. Fig. 5 shows the SEM evidence (fracture surfaces) in greater magnifications for the as-cast blends going from original phase separation to one phase upon heating above the UCST temperature (e.g. heated to 240–260 °C) for three representative compositions of PPO/P4MS: (a) 50/50, (b) 40/60, and (c) 30/70. The graphs are quite self-explanatory

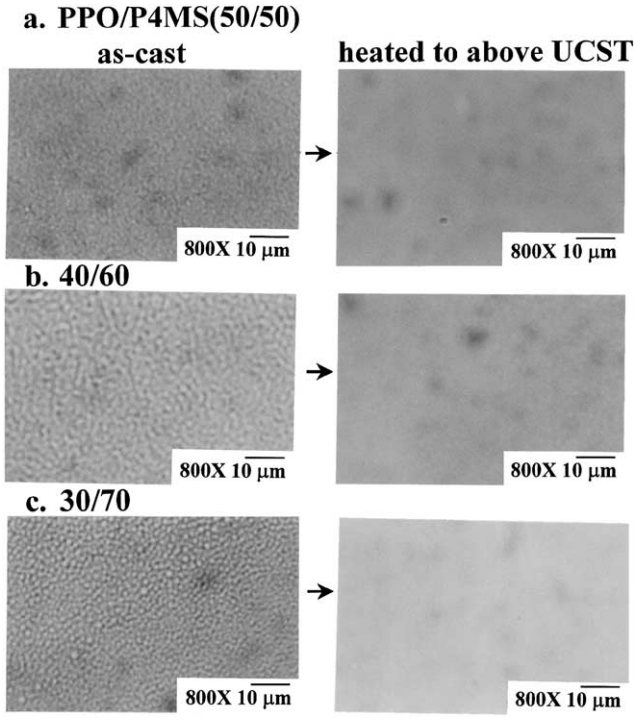


Fig. 4. OM graphs for the as-cast blends going from phase separation to one phase upon heating in PPO/P4MS: (a) 50/50, (b) 40/60, and (c) 30/70 (weight ratio).

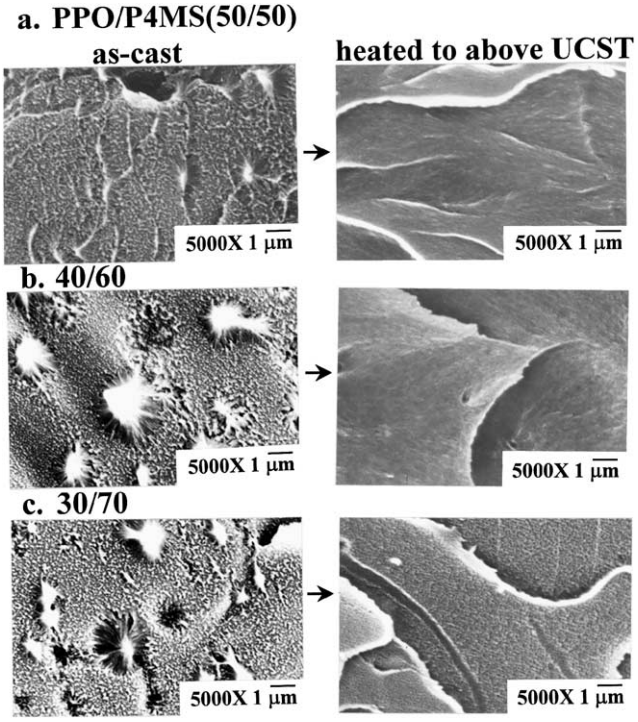


Fig. 5. SEM for the as-cast blends going from phase separation to one phase upon heating above UCST temperature for PPO/P4MS: (a) 50/50, (b) 40/60, and (c) 30/70.

in showing the phase separation regions. The white inter-connected webs and/or grainy particulate regions indicate separation of two phases. Distinct phase changes were found after heating above the UCST. Experimentally, it was observed that the blend samples were initially phase-separated but became homogeneous at higher temperatures as already shown in Fig. 3. The heat-homogenized blend samples remained clear and transparent and clear if quickly 'quenched' to ambient. However, when cooled slowly, the heat-homogenized transparent samples could return back to its original phase-separated morphology, which was characterized with cloudy appearance and optically visible domains.

However, it was necessary to prove that the initially phase-separated blends heated above the homogenization temperature indeed became one phase. The blend samples were heated to above the respective 'homogenization (clarity) temperature' (e.g. 260 °C) and quickly quenched to ambient to kinetically preserved its phase morphology. DSC characterization was then performed on the 'heated-and-quenched' samples. Technically the heating–quenching on the blends was performed inside the DSC cells. Fig. 6 shows the DSC thermograms (second scans after heating-quenching) for 12 different compositions, which reveal a single T_g for all of the blend compositions, as indicated in the curves. Although some of the intermediate composition showed slightly broadened (15–20 °C in breadth) glass transition, single T_g is apparent and composition-dependent on all samples. By applying the conventional T_g criterion, the heated/quenched PPO/P4MS blend was apparently locked into a miscible state, which, upon DSC characterization, revealed a composition-dependent single T_g.

Fig. 7 shows the T_g-composition dependence for the heated–quenched PPO/PS blend samples (kinetically

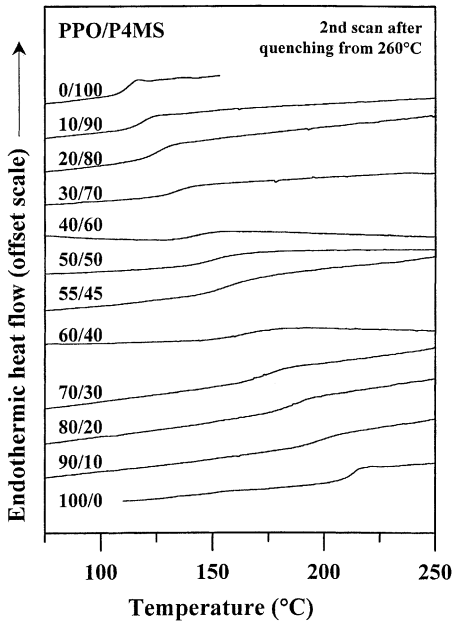


Fig. 6. DSC thermograms (second scans after heating–quenching) for 12 different compositions as indicated in the curves.

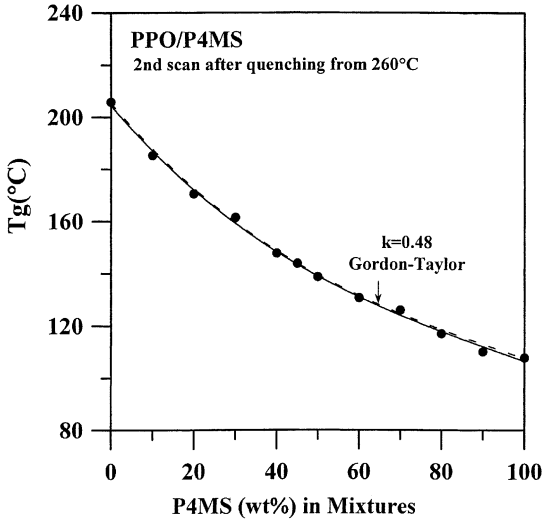


Fig. 7. T_g-composition relationship for the heated–quenched PPO/PS blend samples.

locked by quenching into a temporary miscible state). The T_g-composition dependence for the quenched blend was analyzed by fitting with the classical T_g model of Gordon–Taylor equation [23], i.e. $T_g = (\omega_1 T_{g1} + k\omega_2 T_{g2})/(\omega_1 + k\omega_2)$, where ω_i is the mass (weight) fraction of polymer component i, and k is a fitting parameter. A fitting parameter of $k = 0.48$ was obtained for this blend, suggesting reasonably good phase homogeneity. Thus, the phase behavior of the binary system is characterized with a UCST phenomenon. The heated–quenched blends were apparently locked into a miscible state, as revealed by the DSC result.

3.2. Reversible UCST transition

One may expect that if an UCST does exist in PPO/P4MS, it should be thermodynamically reversible. Above the homogenization temperatures (i.e. above the UCST curve), the originally immiscible blends were expected to turn a miscible homogeneous phase structure. By quenching, the homogeneous phase at above UCST could be preserved. If, however, the blends were heated above UCST but were cooled slowly, one may expect that the blend should go back to the original phase separation state. The blend samples of a few compositions were heated to various temperatures above the UCST, held to stabilize at the intended temperatures then they were quickly quenched to ambient to freeze the phase morphology. In comparison, a set of blend samples were heated to various temperatures above the UCST, held to stabilize at intended temperatures, but then slowly cooled (−2 °C/min) to allow kinetic accessible time for returning to the original equilibrium phase morphology. DSC was then performed on these samples to reveal the glass transitions in these samples. Fig. 8 shows DSC traces in direct comparison of: (a) the as-cast (phase-separated), (b) the UCST-homogenized/quenched,

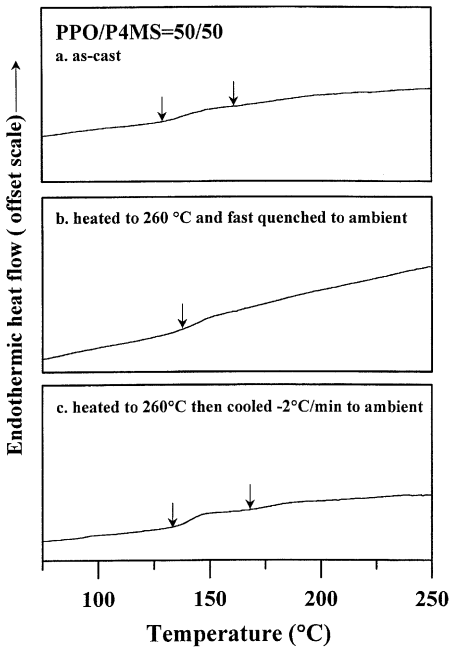


Fig. 8. Comparison of DSC traces for: (a) the as-cast (phase-separated), (b) heated/quenched, and (c) heated/slow-cooled PPO/P4MS (50/50) blend.

and (c) heated/slow-cooled PPO/P4MS (50/50) blend. The as-cast PPO/PS (50/50) blend exhibited two T_g's (Trace-a), as would be so expected for its two-phase morphology. In contrast, the heated PPO/PS blend was brought to its thermodynamic one-phase miscible state (above UCST) and upon quenching quickly it is kinetically locked into a pseudo-miscible homogeneous state. Upon DSC scan, the heated/quenched PPO/P4MS thus exhibited a single T_g (Trace-b). Additionally, it would be nice if DSC result could provide additional evidence that the UCST in the original immiscible PPO/P4MS blends is reversible when kinetically accessible time is allowed for the processes. Trace-c shows the DSC characterization result of two T_g's in the heated/slow-cooled PPO/P4MS (50/50) blend, proving that the homogeneous state at above UCST, if given sufficient time (cooling at -2 °C/min), could be returned back to its original immiscibility (as evidenced by two T_g's) below UCST. Even though the OM result earlier failed to reveal sufficiently large domains within the experimental time frames, the DSC result of two T_g's were indeed identified on the cooled blend samples, proving that the cooled blend already returned to phase separation. The thermodynamic equilibrium nature of UCST behavior, given kinetically sufficient time, in the PPO/P4MS system was evidently supported.

4. Conclusion

For the first time, the UCST behavior in PPO/P4MS blends was reported, and the complex phase behavior was re-investigated and clarified with no ambiguity. This study concluded that the PPO/P4MS blend is an immiscible system with UCST. This behavior in PPO/P4MS is quite different from the classical PPO/PS system that is miscible and remains miscible with no LCST at any experimentally accessible temperatures. The introduction of a methyl group into the pendant phenyl in PS apparently has caused an obvious significant alteration in the phase behavior. With the finding of UCST in the PPO/P4MS blend system, a more critical contribution of this work is to resolve the conflicting arguments that have gone on for quite a long time in determination of the thermodynamic phase behavior of PPO/P4MS [18–20]. Owing to the presence of UCST in PPO/P4MS, it was tricky in analysis. For example, if samples were prepared using melt lending at high temperatures and cooling at various rates to ambient, mis-interpretation might occur. A quenched blend samples of PPO/P4MS might be pronounced to be apparently 'miscible', while a slow-cooled sample might be concluded to be a phase separated (immiscible) system. In addition, more in-depth analysis and investigation of structural effects on LCST vs UCST behavior in blends are ongoing as future work.

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