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ORIGINAL CONTRIBUTION

Immiscibility with upper-critical solution temperature phase diagrams for poly(methyl methacrylate)/polyesters blends

Shu-Hsien Li · Eamor M. Woo

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Abstract Blend systems comprising poly(methyl methacrylate) (PMMA) and polyesters are classified as immiscible; however, this study has discovered that upper-critical solution temperature (UCST) behavior with partial miscibility is the more exact description for PMMA/polyester blend systems. Blends of PMMA with a series of polyesters, with structures varying in a range, were characterized in terms of phase behavior and dependence of the phase behavior on composition, temperature, and constituent's structure, and molecular weight. All PMMA/polyester blends are immiscible or only partially miscible in PMMA-rich compositions at room temperature; however, the blends can go through a phase change to miscibility at elevated temperatures. As the polyesters' structures are varied systematically (with CH_2/CO ratio from small to large), PMMA/polyester blends exhibit a trendy change in UCST phase behavior: from complete immiscibility, to complete immiscibility (in entire composition range) with UCST, then to partial miscibility (miscible in blends with PMMA contents greater than 70 wt%) with UCST, then finally back to complete immiscibility with no UCST. That is, no miscibility was found for blends of PMMA with all polyesters; however, UCST behavior, normally a rare occurrence in polymer blends, was found to be common in many of the PMMA/polyester blends investigated.

Keywords PMMA · Polyesters · UCST

Introduction

Miscible polymer blends at ambient temperature, upon heating to elevated temperatures, can exhibit a transition of phase behavior from original homogeneity (one phase) to phase separation, which is a phenomenon known as lower-critical solution temperature (LCST). Reversely, originally immiscible (or partially immiscible) blends at ambient temperature, upon heating to elevated temperatures, can exhibit a transition of phase behavior from original heterogeneity (phase separation) to homogeneity (one phase), which is a phenomenon known as upper-critical solution temperature (UCST). In the literature, there have been some demonstrated cases of UCST in polymer blends; however, the number is not too many, or at least, UCST is not often observed within the experimentally accessible temperature range (before thermal degradation). If a UCST exists at well above the degradation temperatures of polymers, then it would be beyond experimental approach to verify. Some polymer blends can indeed show UCST, especially in blends of two like polymers (with similar functional groups or structures). A few well-known examples of blends of two similar polymers showing UCST can be cited here. A widely studied blend system of polystyrene (PS) and poly(α-methyl styrene) (PαMS) is immiscible at ambient but exhibits a UCST phenomenon at elevated temperatures [1–7]. Note that PαMS differs from PS only in that the former has an extra α-methyl group (α-CH_3). The classical blend system of poly(2,6-dimethyl *p*-phenylene oxide) (PPO) with PS has been widely studied, and miscibility in this blend has been demonstrated. However, the blend of PPO and poly(4-methyl styrene) (P4MS), with an extra methyl at 4-position of pendant phenyl ring, is not miscible but shows a UCST behavior

S.-H. Li · E. M. Woo (✉)
Department of Chemical Engineering,
National Cheng Kung University,
Tainan 701-01, Taiwan
e-mail: emwoo@mail.ncku.edu.tw

[8]. Blend phase behavior is known to sensitively depend on structures of the constituent polymers in the blends.

In addition, UCST is also observed in a blend system of PS with P4MS [9]. The result of UCST in the PS/P4MS blend is quite comparable to the known UCST in the PS/PαMS blend, as the structure of P4MS (with a methyl in para-position of pendant phenyl) is an isomer to PαMS and differs from PαMS (with a methyl in α-position) only in the position of the methyl group. As P4MS and PαMS, two structural isomers, are formed into a mixture, the P4MS/PαMS blend is miscible but can become phase separated at higher temperatures with a LCST phenomenon [10], which is in distinct contrast to the phase behavior of immiscibility with UCST noted for both PS/PαMS and PS/P4MS blends. These examples demonstrate that blends of two like polymers, usually in the absence of any notable specific interactions, can exhibit various modes of phase behavior that sensitively responds to changes in the structures of the blend constituents. UCST is also seen in a crystalline/crystalline blend of poly(ε-caprolactone) (PCL) and poly(ethyl glycol) (PEG), as reported by Chuang et al. [11], who used time-resolved small-angle light scattering to monitor the kinetics of liquid–liquid phase separation in the blend of PCL/PEG (with UCST=115 °C for 60:40 composition). They have also concluded that competition between kinetics of crystallization vs phase separation determines the final morphology in the crystalline/crystalline blend of PCL/PEG.

Blends of poly(methyl methacrylate) (PMMA) with other polymers containing the same carbonyl group have been less studied. By introducing electron-withdrawing atoms to polymethacrylates, the polarity of the functional groups of the polymer chains is changed. Based on this concept, Goh et al. [12, 13] studied blends and miscibility based on chloro-, bromo-, or iodo-polymethacrylates. Blends such as poly(ethylene succinate) (PESu)/poly(3-chloropropyl methacrylate) (PCPMA), poly(ethylene adipate) (PEA)/PCPMA, PESu/poly(2-iodoethyl methacrylate) (PIEMA), and PEA/PIEMA are phase-separated systems; however, blends of poly(butylene adipate) (PBA)/PCPMA, PBA/PIEMA, PCL/PCPMA, and PCL/PIEMA are miscible systems [12, 13]. If PESu is substituted with another polyester of poly(2,2-dimethyl-1,3-propylene sebacate) (PDPS), then blends of PDPS with PCPMA, PIEMA, or PBEMA all become immiscible but can exhibit an UCST phenomenon of slightly different temperatures (near 105 °C) [12, 13]. The above cited examples are all related to blends of polyesters with modified polymethacrylates. However, phase behavior in blends of polyesters with unmodified polymethacrylates (i.e., without any substitution by chloro-, bromo-, etc.) have been rarely studied. A conventional notion in polymer blends was that it takes some specific interactions between two different functional groups to induce miscibility in long-chain polymers. This notion, however, is being modified gradually, as more and more demonstrated cases are brought up to demonstrate miscibility in blends of like polymers. For examples, miscible polyester/polyester blend systems can be illustrated with binary blends comprising any two of poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT) in a series of homologous aryl-polyesters [14–17]. It has been proven that any two of PET, PTT, and PBT can form miscible binary blends; furthermore, in addition to miscibility in binary blends, ternary blends comprising all three semicrystalline polyesters (i.e., PET, PTT, and PBT) are also miscible [17]. Certainly, the fact of these examples cannot be extended to say that it is easy to expect miscibility in blends of polymers of similar structures or functional groups. Usually, interactions in blends of like-polymers are weak, and a slight adjustment in structures of the constituent polymers can lead to dramatically different phase behavior. For examples, PET is miscible with PBT, but not miscible with poly(pentylene terephthalate) (PPT), although the functional group is identical in PBT and PPT.

Phase behavior of blends of PMMA with polyesters had been less studied because most of the blends were classified as immiscible blends, which were regarded as offering little interest. PMMA, with carbonyl in the pendant group, has not been regarded as a good candidate for forming miscible blends with polyesters with carbonyl in main chains. A literature survey reveals that blends of PMMA with aliphatic polyesters generally are not miscible. An extraordinary exception is the blend system of PMMA with semicrystalline poly(L-lactic acid) (PLLA). The miscibility of PMMA/PLLA blends, however, is reportedly conditional and is based on results of second-scan differential scanning calorimetry (DSC) on quenched amorphous blends. Peculiarly, as-cast semicrystalline PMMA/PLLA blends on first DSC scans exhibit two T_g's and an apparently phase-separated morphology [18–20]. Even more interestingly, without influence of crystallinity, amorphous poly(D,L-lactic acid) is miscible with amorphous PMMA [18–20]. By contrast, blends of PMMA with poly(β-hydroxy butyrate) (PHB) [21–23] or PCL [24], etc. have been traditionally classified in the literature as immiscible blends. Although PMMA/PHB is immiscible, poly(methyl acrylate) is miscible with PHB [29]. This fact suggests that a minor adjustment of structures of either of the constituents in a blend, a significant change in the phase behavior can result. In addition, the PMMA/PHB blends have been reported to present an UCST behavior [21–23]. The miscibility above UCST could be verified only with quenching (by liquid nitrogen) from the one-phase region. In this study, the fastest programmed cooling rate of the DSC (320 °C /min) was presumed to be sufficient to freeze the homogeneous melt phase only for the PMMA/PHB blends (80/20 and 90/10).

Generally, PMMA is not known to be miscible with any polyester, with the only exception cited above for the blend of PMMA/PLLA, whose phase behavior is peculiarly influenced by the crystallinity in PLLA. However, preliminary investigation in depth on blends of PMMA with other polyesters revealed interesting dependence of their phase behavior on composition and/or temperature, which has yet to be probed in greater details. By preparing and characterizing on blends of PMMA with a series of homologous polyesters whose structures varied in a range, the aim of this study was to analyze in greater details the phase behavior of PMMA/polyester blends and its dependence on composition, temperature, and structure of the constituent polymers. It is well established that the miscibility windows for the blend systems are known to depend on the (1) molecular weight of the constituent components [1, 3, 7, 27, 28], (2) polymers backbone chains characteristics [31, 32], (3) polymer polydispersity [33, 34], and (4) effect of end groups of polymers [7, 35, 36]. To compare the influence of chain structure of polyesters on the miscibility, the other effects should be avoided. The polyester sample used in this study have similar molecular weights and with similar molecular weight distributions. In addition, the molecular weights of polyesters are high enough, so the end groups are small fractions in comparison with the chain-chain backbones (concentration of end groups is less than 0.5 wt%), and its influence on miscibility could be neglected.

Experimental

Materials

Polyesters of various structures covering a wide range were purchased from Aldrich Chemical (USA), and Scientific Polymer Products (USA). For convenient references, the basic data, abbreviation, and names of the various polyesters used in this study are listed in Table 1. Molecular weights and polydispersity of the polyesters from suppliers were determined in-house using gel-permeation chromatography (Waters). PMMA was obtained from Aldrich Chemical, with a medium-weight-average molecular weight of M_w=15,000 g/mol and T_g(onset)=75.8 °C, which was also verified by in-house T_g measurement. For comparison, PMMA (Polysicences) of a higher weight-average molecular weight of M_w=100,000 g/mol and T_g (onset)=87 °C was also used, which was also verified by in-house T_g measurement (using DSC). For convenience of differentiation from the lower-M_w PMMA (15,000 g/mol), the higher-M_w PMMA with M_w=100,000 g/mol is designated as "PMMA-H." Note that the low T_g of both PMMA grades used in this study might be owing to some fractions of isotactic-PMMA (which has low T_g) present in the mostly atactic PMMA.

Sample preparation

Blend of PMMA and aliphatic polyester were prepared by solvent casting using $CHCl_3$ as a good mutual solvent. Both polymers with concentration of 4 g/100 mL in solvent were mixed in desired proportions, well stirred, and cast onto glass dishes at 45 °C. The solvent was evaporated for 24 h, and then the thin films were further dried in vacuum at 60 °C for 1 week.

Apparatus and procedures

A polarized-light microscope (Nikon Optiphot-2, POL), equipped with a digital camera and charge-coupled device (CCD), was used for characterizing optical homogeneity and/or crystalline morphology of the blends. A small quantity of the blend samples was transferred to between microglass slides, heated, and pressed into a thin film on a heating stage and examined using the optical microscope.

T_g transitions of the blend samples were measured with a differential scanning calorimeter (DSC-7, Perkin-Elmer) equipped with an intracooler for subambient temperature down to −65 °C. Before DSC runs, the temperature and heat of transition of the instrument were calibrated with indium and zinc standards. During thermal annealing or scanning, a continuous nitrogen flow in the DSC sample cell was maintained to ensure minimal sample degradation. For determining the T_g transition temperatures, a heating rate of 20 °C/min was used unless otherwise specified.

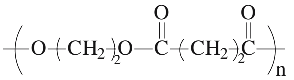
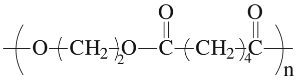
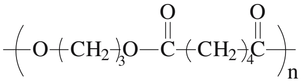
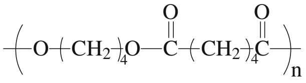
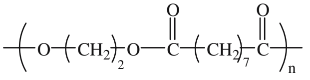
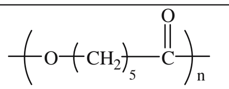
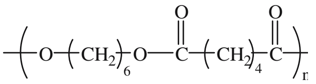
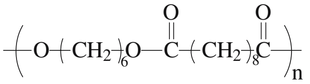
Blend samples were examined using a scanning electron microscope (Hitachi S-4100) for revealing possible submicron phase domains. Quenched samples (amorphous glassy solids) were used for Scanning electron microscopy (SEM) characterization because crystals, if present, might obscure observation of phase morphology of blends. The quenched film samples were fractured across thickness and coated with gold by vapor deposition using vacuum sputtering.

Results and discussion

Phase behavior at ambient vs elevated temperatures

Various PMMA/polyester blends of several compositions were examined for phase changes upon heating from ambient to 90 or 100 °C (near or above polyester's melting), then to elevated temperatures near 250 °C or higher up to thermal degradation. Phase behavior of the blends was found to be highly dependent on the structure of the polyester in the PMMA/polyester blends. Figure 1

Table 1 List of polyesters blended with PMMA

Aliphatic polyesters	Structures	(CH_2/CO) ratio	ρ (g/cm^3)	T_g (°C)	T_m (°C)	M_w[a] (g/mol)	PDI[a]
Poly(ethylene succinate), PESu	 $\left(-O-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-\right)_n$	2.0		-16	102	10,000	
Poly(ethylene adipate), PEA	 $\left(-O-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right)_n$	3.0	1.183	-52.7	45.4	12,000	1.42
Poly(1,3-trimethylene adipate), PTA	 $\left(-O-(CH_2)_3-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right)_n$	3.5	1.55	-69	38	3,800	1.41
Poly(1,4-butylene adipate), PBA	 $\left(-O-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right)_n$	4.0	1.019	-60	56-60	12,000	1.26
Poly(ethylene azelate), PEAz	 $\left(-O-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_7-\overset{O}{\overset{\|}{C}}-\right)_n$	4.5	1.183	-57.7	33.1	17,000	1.33
Poly(ε-caprolactone), PCL	 $\left(-O-(CH_2)_5-\overset{O}{\overset{\|}{C}}-\right)_n$	5.0	1.146	-70	60	20,000	1.35
Poly(1,6-hexamethylene adipate), PHA	 $\left(-O-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right)_n$	5.0	1.13	-65	56-65	15,000	1.32
Poly(1,6-hexamethylene sebacate), PHS	 $\left(-O-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-\right)_n$	7.0		-65	74	40,000	1.41

[a] Molecular weights of polyesters were determined by GPC.

shows optical microscopy (OM) graphs of (a) PMMA/PESu(CH_2/CO=2) blend, and (b) PMMA/PHS(CH_2/CO=7) blend. The OM clearly reveals two phases with binodal-mode spherical domains in the blend at ambient temperature (~25 °C) up to 90 or 100 °C. The originally immiscible blend was heated slowly (approx. 2 °C/min) to higher temperatures (up to 250 °C) for observing phase changes. Inset schemes show enlarged views of phase domains. The OM morphology remains phase separated; however, the domains become irregular with spinodal-mode characteristics. The PMMA/PESu blend is an immiscible blend and remains immiscible up to 250 °C, beyond which degradation of the samples would prevent further monitoring. Same behavior was found for the PMMA/PHS(CH_2/CO=7) blend, as illustrated for comparison in Graph-b for ambient temperature and 250 °C, respectively. The PMMA/PHS blend is similarly immiscible from ambient up to 250 °C. No UCST phase transition was observed up to degradation for either PMMA/PESu (CH_2/CO=2) or PMMA/PHS(CH_2/CO=7) blends.

However, for blends of PMMA with other various polyesters, such as PEA, PTA, or PBA, the phase morphology of the blends could change evidently upon heating to an elevated temperature, which depended on blend compositions. At higher temperatures, the initially immiscible blend samples were found to turn transparent and clear. OM result showed phase reversibility from immiscibility to phase homogeneity then back to immiscibility upon cooling/

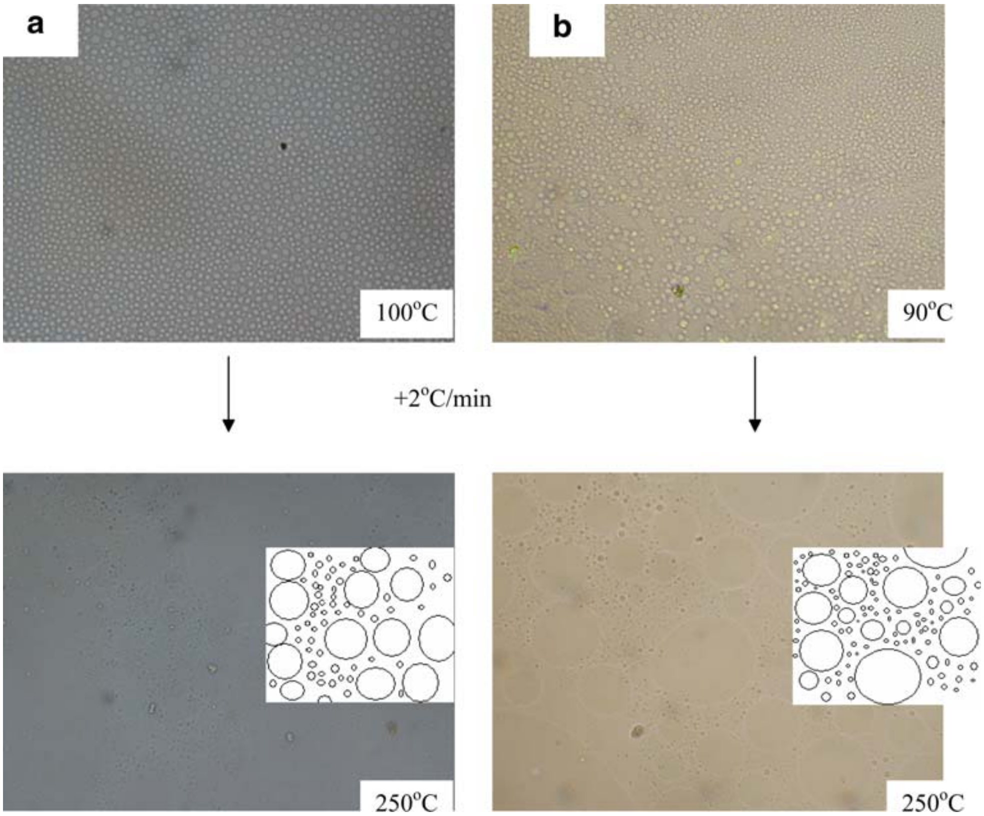


Fig. 1 OM result for immiscible **a** PMMA/PESu (50:50), and **b** PMMA/PHS (50:50) blend (approx. ×800). *Inset schemes* showing enlarged views. No UCST observed up to degradation

heating/cooling cycles imposed on the blends. Figure 2 shows result of "homogenization (or clarity) temperature" of PMMA/PEA blend (50:50 composition), whose phase change upon heating is graphically illustrated. The phase structure of the blends was originally immiscible, but 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 to above the UCST temperatures induced a process from a "de-mixing" state to a "mixing" one (i.e., miscible). Figure 3 shows clarity points, UCST, and phase boundary for the PMMA/PEA blends as a function of composition. In this figure, the "clarity point" (as opposed to "cloud point" in LCST blend systems) is defined as temperature at which the blend turns from phase separation to transparent appearance upon slowly heating (approx. 2 °C/min) from ambient temperature. This transition and the maximum temperature of the curve are noted as an UCST. The transition temperature varies with blend composition and displays a maximum (UCST=233 °C) for the 50:50 blend composition. For this blend system, the curve of clarity points with respect to composition is symmetrical.

Similarly, Figure 4 shows clarity points, UCST, and phase boundary for the PMMA/PTA blends as a function of composition. The blend system shows both compositional partial miscibility (for the blend compositions with PMMA contents greater than 70 wt%) and a UCST transition for the remaining blend compositions with PMMA contents less than 70 wt%. Within the composition range showing UCST behavior, the immiscibility-to-miscibility transition temperature again varies with blend composition and displays a maximum (UCST=116 °C) located at a PMMA/PTA blend composition near 70:30. By comparison, the UCST (116 °C) for this blend is much lower than the previous one (PMMA/PEA blend with UCST=223 °C). UCST seems to correlate with the structure of the polyester in the various PMMA/polyester blend systems investigated in this study, which will be discussed in the following section.

The structure of polyester was gradually changed by varying the CH_2/CO ratio, and phase behavior of blends of PMMA/polyester was similarly characterized. Figure 5 shows clarity points, UCST, and phase boundary for PMMA/PBA blends as a function of composition. Again, for the PMMA/PBA blend, the curve of clarity points with respect to composition is significantly asymmetrical. The UCST (145 °C) for this blend is slightly higher than the PMMA/PTA blend discussed in the previous figure. Similarly, phase behavior of the blend system shows both compositional partial miscibility (for blend compositions with PMMA contents greater than 70 wt%) and a UCST transition for the remaining blend compositions with PMMA contents less than 70 wt%.

An asymmetrical feature is apparently seen in the UCST diagrams for both PMMA/PTA and PMMA/PBA blends

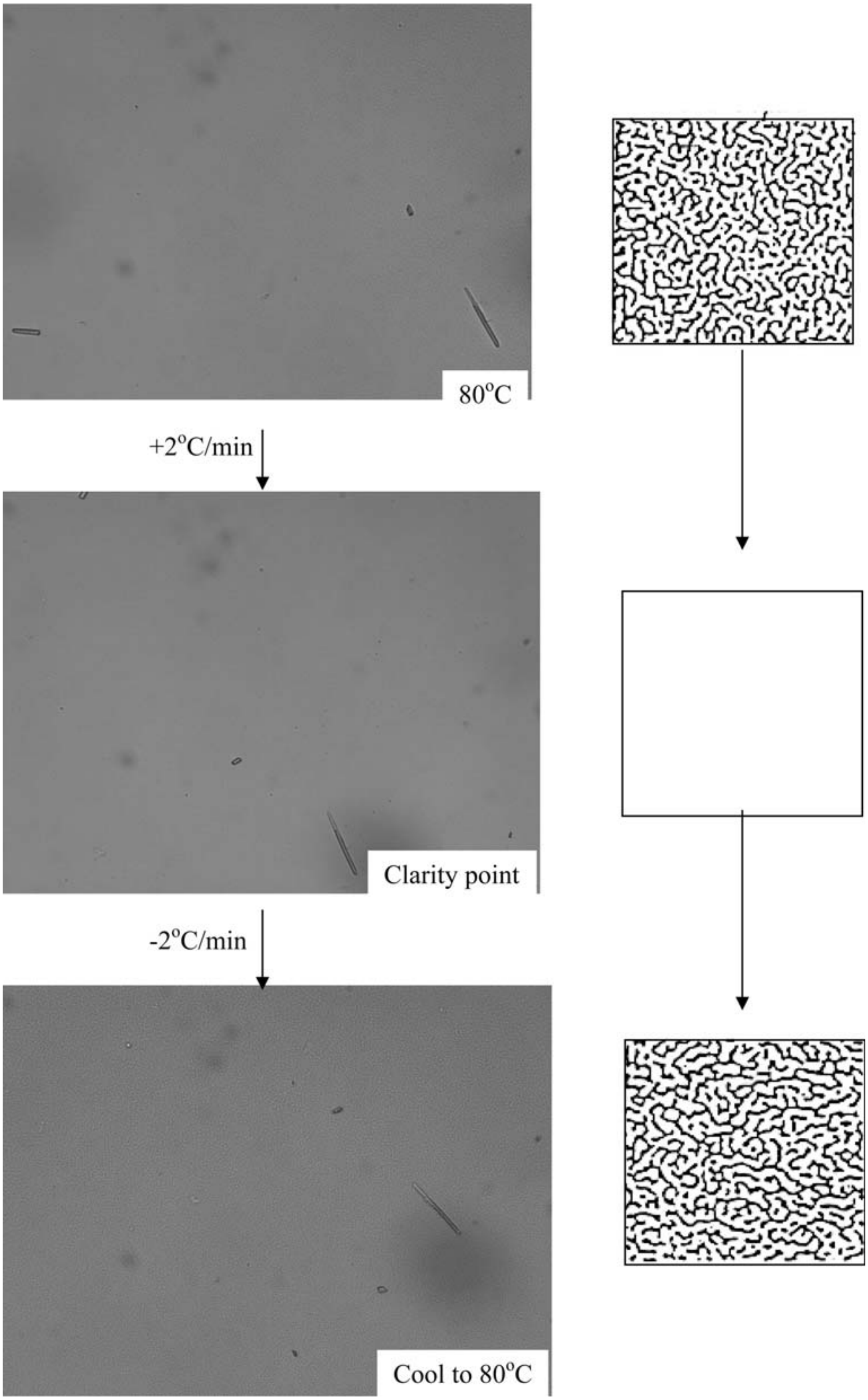


Fig. 2 OM result showing phase reversibility upon cooling→heating→cooling cycles for PMMA/PEA (50:50) blend (approx. ×800)

that the curve of clarity points with respect to blend composition is significantly skewing to the polyester-rich side. The skewing in Fig. 4 (PMMA/PTA) may be partially attributed to relatively lower M_w in PTA than that of PMMA, according to thermodynamic predictions using the Flory's theories [38–40]. However, the molecular weights of PBA and PMMA are roughly comparable, but significant skewing in the UCST diagram is also seen in Fig. 5, which

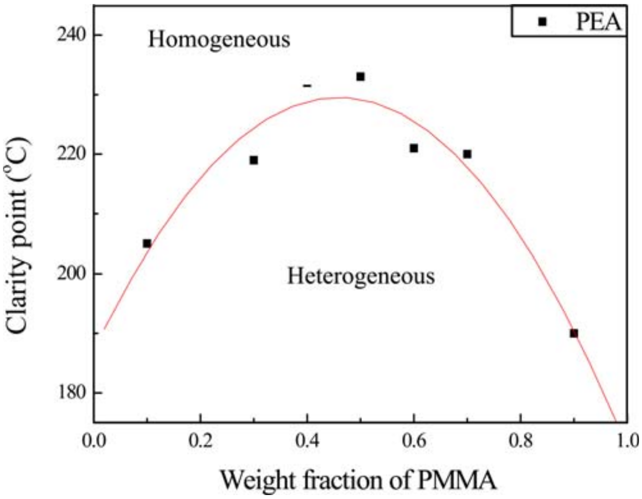


Fig. 3 Clarity points for PMMA/PEA blends as a function of composition

cannot be properly predicted by the molecular weight difference. Thus, low M_w of PTA may be a factor for the observed skewing in UCST of the PMMA/PTA blend, but one cannot preclude other possible factors leading to such phenomenon as the above two cases demonstrate that asymmetry in the UCST diagrams is also seen in blends of two polymers of comparable M_w.

Figure 6 shows clarity points and phase boundary for PMMA/PEAz ($CH_2/CO=4.5$) blends as a function of composition. For comparison of effects of solvent used for sample preparation, blends were cast with two different solvents: THF (filled circle) and $CHCl_3$ (open circle). Both yielded similar asymmetrical dependence of the clarity point on composition, differing slightly on the temperature values of the clarity points for blend compositions with PMMA contents less than 70 wt%. Both sample sets of the same blend system of PMMA/PEAz shows compositional partial miscibility for blend compositions with PMMA contents greater than 70 wt%.

For the evaluation of blend T_g, DSC analysis was performed. First, as-cast blends (before being heated to above UCST) were analyzed. Figure 7 shows DSC results for as-cast PMMA/PEAz blends of ten compositions. For most blends compositions, the figure clearly shows that two T_g's are seen, with lower T_{g1} at −60 to −50 °C and higher T_{g2} at 60–80 °C. As-cast PMMA/PEAz blends apparently are phase separated, with the two T_g's. Attempts for characterizing the phase behavior of the blends at above UCST were made. The PMMA/PEAz blends were heated above UCST and rapidly quenched (in DSC cells). Rapid quenching from above UCST was performed in attempt to preserve the phase state above UCST. Figure 8 shows DSC results for quenched PMMA/PEAz blends of ten compositions (quenched from above UCST). Nevertheless, the quenched blends' T_g's remain much the same as those in the previous figure for the as-cast blends. As it was not possible to directly characterize the T_g of the blends above UCST, rapid quenching from above UCST was usually used for preserving the state at UCST. The success of such manipulation, however, depends on the relative speed of quenching vs the rate of phase separation as the blends were cooled. Phase reversal from homogeneity to phase separation of the blends upon temperature lowering back to ambient might have taken place very quickly so that phase freezing upon quenching was made not likely. The PMMA/PEA and PMMA/PBA blends also exhibited such quick reversal from homogeneity back to phase separation upon quenching from above UCST to below UCST. The DSC results for other UCST blends, such as PMMA/PEA and PMMA/PBA blends, are similar to those shown in this figure for the PMMA/PEAz blend; for brevity, DSC traces are not shown. Similar behavior has also been reported in other UCST blend systems [7, 22]. Dilemma is faced in dealing with the T_g data of the rapid-quenched blend samples. On one hand, quenching was aimed to freeze the "above-UCST" state for T_g analysis by quenching. On the other hand, thermodynamic reversibility (back to phase separation upon cooling) and/or crystallinity(in polyesters)-induced phase separation might take place more rapidly than quenching. Similar experimental difficulty is also encountered by other investigators in previous reports in dealing with presumably UCST systems [7, 22].

The structure of the polyester in blends was again changed by varying the CH_2/CO ratio in polyester. Phase boundary of the blend of PMMA/PHA($CH_2/CO=5.0$) was similarly characterized. For comparison, the PMMA/PCL ($CH_2/CO=5.0$) blend was characterized as well. Figure 9 shows clarity point and phase boundary for two blend systems: PMMA/PHA and PMMA/PCL blends as functions of composition. Note that PHA and PCL are two polyesters of chemical isomers, with different structures in

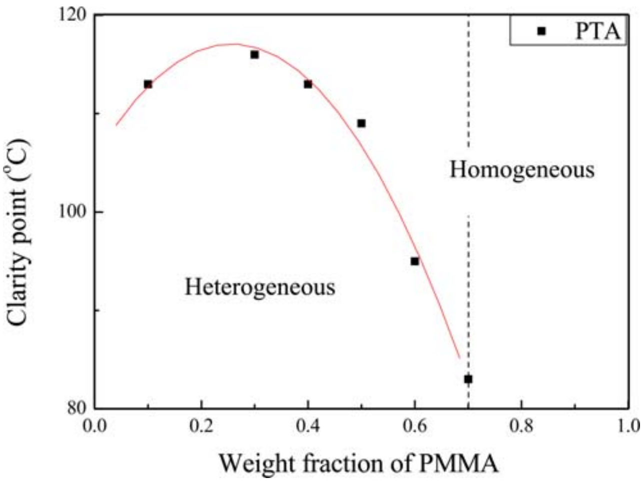


Fig. 4 Clarity points and phase boundary for PMMA/PTA blends as a function of composition

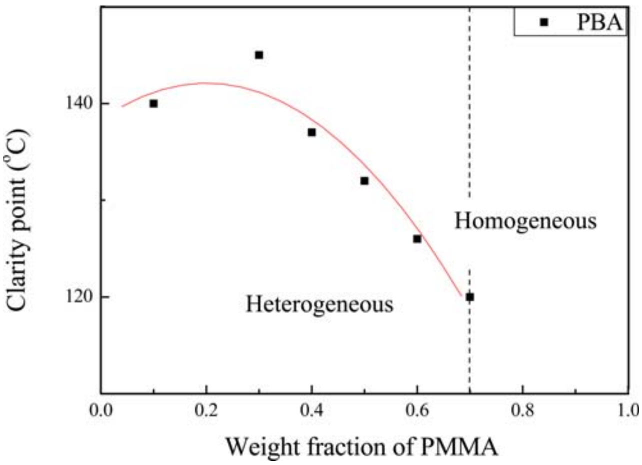


Fig. 5 Clarity points and phase boundary for PMMA/PBA blend as a function of composition

repeat units but identical $CH_2/CO=5$. Both blend systems show similar compositional partial miscibility for blend compositions with PMMA contents greater than 70 wt%; furthermore, both systems yield similar asymmetrical dependence of the clarity point on composition, for blend compositions of PMMA contents less than 70 wt%. The PMMA/PCL blend on average has higher UCST (or higher values of clarity points) than does the PMMA/PHA blend. The measured clarity points differ slightly between PMMA/PHA and PMMA/PCL, which is mainly attributed to effects of difference in the structures of these two polyesters. Other factors such as molecular weights or end groups may be influential too. The molecular weight of the polyester constituents may be partially responsible because PCL possesses a M_w of 20,000 g/mol, slightly higher than that of PHA.

In addition, similar skewing in UCST diagrams for the PMMA/PHA and PMMA/PCL blends is also present. Figure 9 shows that UCST for PMMA/PHA and PMMA/PCL are similarly skewing to the polyester-rich side. This is similar to the skewing in the UCST diagrams for the PMMA/PTA or PMMA/PBA blends; however, in both PMMA/PHA and PMMA/PCL blends, the polyester constituents of PHA and PCL have higher M_w's than does PMMA. Again, prediction by the Flory's theories on simple M_w effect would lead to an opposite result. Therefore, these experimental results on for the PMMA/polyesters blends may hint that the skewing in the observed UCST diagrams seems to be resulted by two working factors. The first factor may be due to asymmetrical interactions on the PMMA-rich side vs polyester-rich side leading to compositional partial miscibility. The first factor may originate from the enthalpic contribution. The second factor is the molecular effect originating from the entropic contribution, as earlier predicted by the Flory theories [38–40].

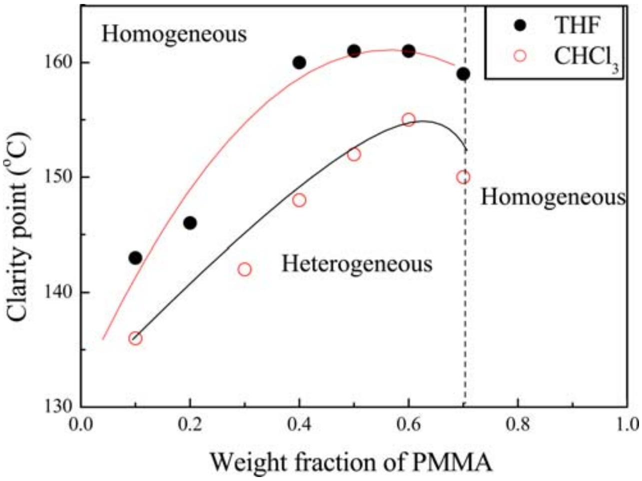


Fig. 6 Effect of solvents on clarity points and phase boundary for PMMA/PEAz blends. Blends cast with THF (*filled circles*) and $CHCl_3$ (*open circles*)

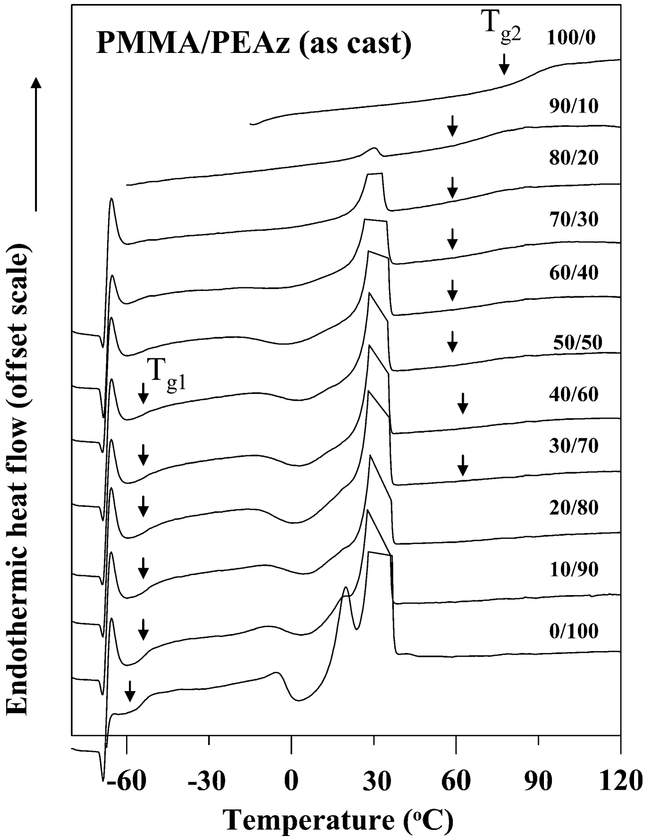


Fig. 7 DSC results for as-cast PMMA/PEAz blends of ten compositions

Phase morphology of the PMMA/polyester blend systems was characterized. Comparison was made between the as-cast vs UCST-quenched blends (i.e., quenched by liquid N_2 from the above-UCST state). Quite a few compositions were also characterized but not presented here for brevity owing to similar results; only a selected blend composition is presented and discussed here. SEM characterization (for larger magnification) was performed in a blend sample

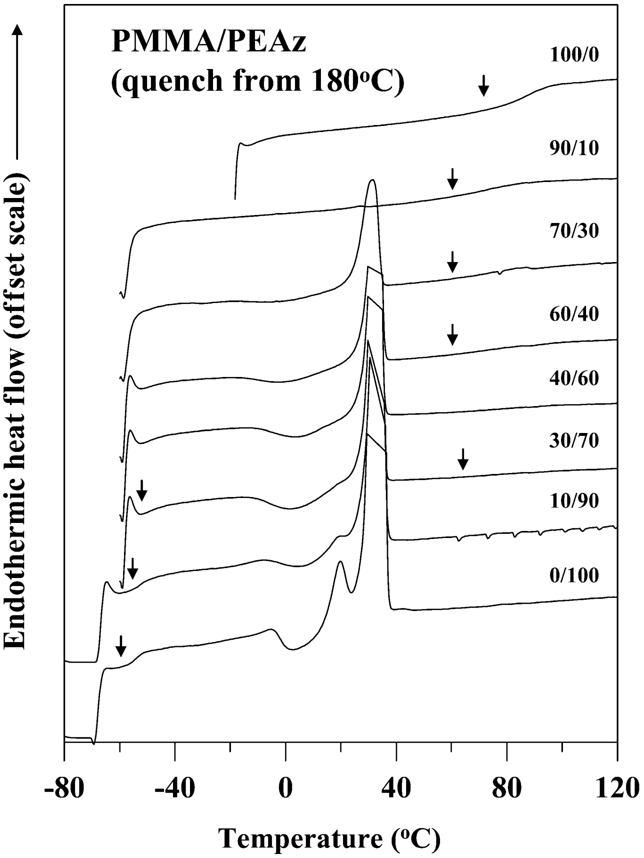


Fig. 8 DSC results for quenched PMMA/PEAz blends of ten compositions (quenched from above UCST)

below and above UCST. Figure 10 shows SEM micrographs for several blend systems: PMMA/PTA, PMMA/PEA, and PMMA/PCL (composition all fixed at 70:30 in weight ratio). As-cast blends (morphology at temperatures below UCST) show apparent phase domains. However, heating above UCST brought about a homogeneous morphology as shown in the figure. Note that SEM characterization could not be performed in situ at elevated temperatures; thus, samples were heated to above UCST and rapidly quenched to ambient to preserve/freeze the phase morphology at above UCST. The SEM graphs for the UCST-quenched blends are apparently homogeneous and free of discernible domains. One must be careful on possible interference by solvents on the blend systems prepared by solvent casting. That is to say, one should exclude the possibility of solvent drying caused phase separation in the as-cast blend, as subsequent heating on blends may bring the blends back to a homogeneous state and lead to erroneous interpretation on UCST [37]. In this study, a second set of samples of PMMA/polyester (PMMA/PCL, PMMA/PEA) of a few selected compositions were prepared using melting blending at ~120 °C, which is a temperature below the supposedly UCST but above polyester's T_m. The morphology results of melt-blended samples were identical to those by solvent blending/casting shown in this figure. For brevity, micrographs (above and below UCST) are not presented.

Dependence of blend phase behavior on polyester structure

Table 2 lists summary of phase behavior for PMMA/polyester blends. In this table, "complete immiscibility" means blends are immiscible within the entire composition range; "partial miscibility" means blends are miscible in part of composition range (in this case, blends with PMMA contents greater than 70 wt%) but immiscible in the rest of the range. "Immiscibility with no UCST" means the blends are immiscible within entire composition range; furthermore, upon heating, they show no transition into a homogeneous phase, up to 250 °C (experimentally accessible range). Beyond 250–300 °C, degradation rapidly took place; thus, any UCST, even if present, could not be experimentally verified.

With exception of the PMMA/PLLA blend whose phase behavior is already discussed in the literature, all PMMA/polyester blends investigated in this study are phase-separated and immiscible at room temperature. However, most PMMA/polyester blends, though immiscible at room temperature, show an interesting phenomenon of UCST behavior. For the blends showing a UCST transition, the measured value of UCST was found to vary with respect to the structure of the polyester in the blends. Certainly, complexity in such comparison may arise owing to effects contributed from factors such as molecular weights, polydispersity, and chain end polar groups, in addition to the (CH_2/C=O) backbone ratios, which are always present in determining this behavior. Other factors may also be influential to some extents. However, effects by factors such as M_w's, polydispersity, and chain ends are similar in influencing the phase behavior for all polyesters in the

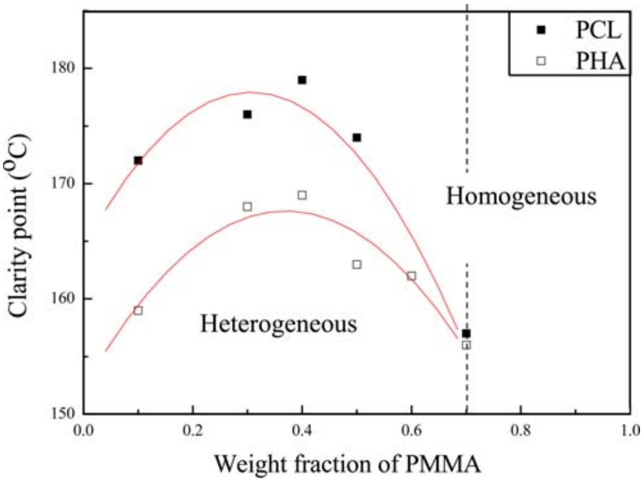


Fig. 9 Clarity point and phase boundary for PMMA/PHA and PMMA/PCL blends as a function of composition

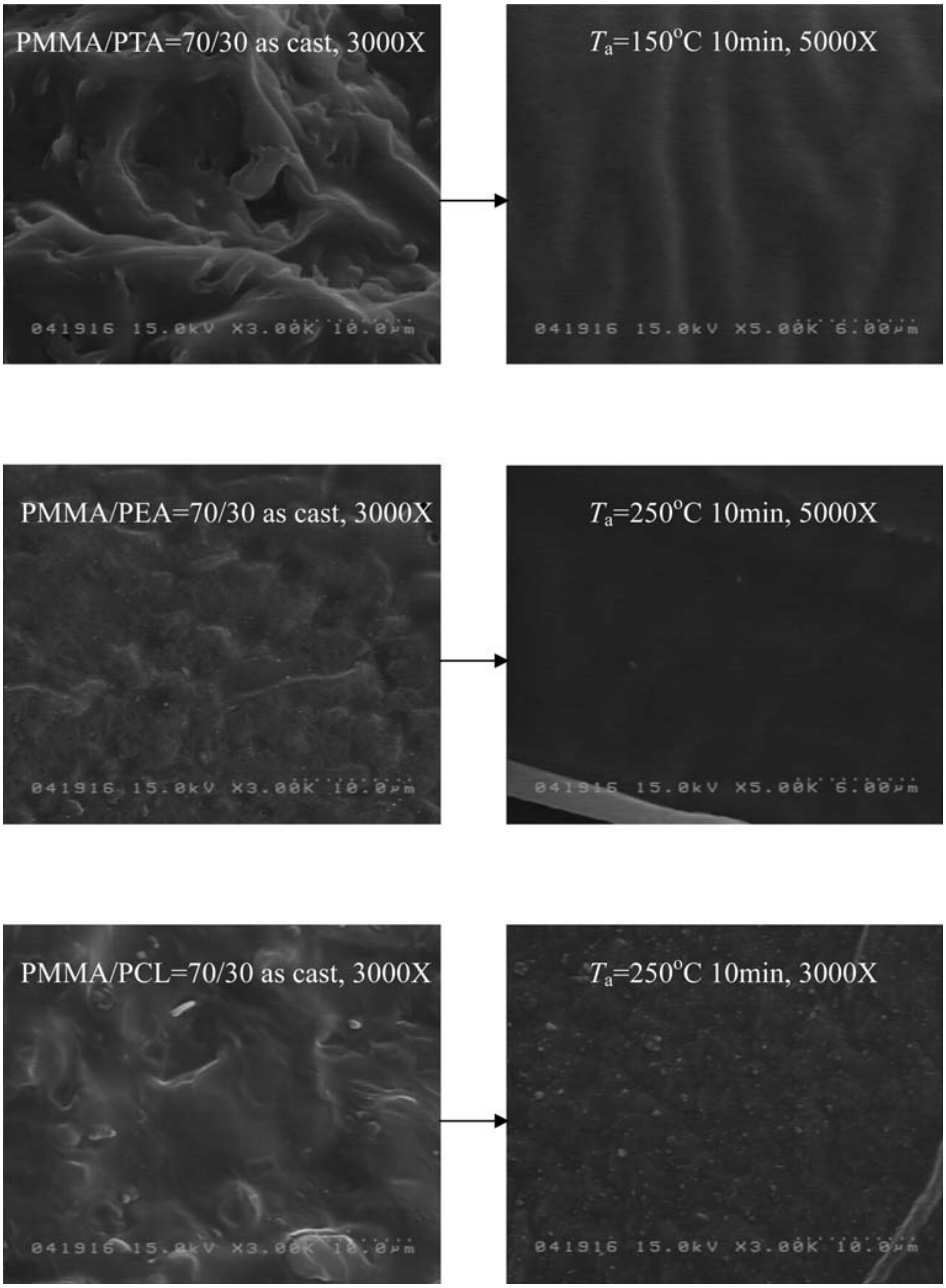


Fig. 10 SEM micrographs (*top to bottom*) of PMMA/PTA, PMMA/PEA, and PMMA/PCL (composition=70:30 weight ratio)

series of blends investigated. The only dominating factor, the difference in backbone as represented by averaging CH_2/CO ratio in polyester, plays a more critical role in determining the phase behavior of PMMA/polyester blends.

Thus, to simplify, one may exclude the factors of minor difference in M_w's, polydispersity, and chain ends. That is, polyesters are viewed as random copolymers comprising COO segments and CH_2 segments of various fractions. To show the variation trend of the blends' UCST with respect to the polyester constituent's structure, the values were plotted with respect to the polyester's structure. Figure 11 shows the values of UCST for various blends of PMMA/polyester as a function of the polyester structural parameter (CH_2/CO ratio). The trend of variation of UCST is such that, for blends of PMMA with the homologous polyesters (PEA, PTA, PBA, PEAz, PHA, PCL, respectively), the plot shows that a minimum (i.e., the lowest UCST value) is located near or at the blend system of PMMA/PBA(CH_2/CO=4.0). A more steep change in UCST values is seen in the range of the polyester's structural parameter of CH_2/CO, being low (from 2.0 to 3.5), but conversely, a less steep change in UCST values is seen in the range of polyester's structural parameter of CH_2/CO being higher (from 4.0 to 7.0). This is understandable as the polarity of

Table 2 Summary of phase behavior for PMMA/polyester blends

Blends blend system	phase behavior
PMMA/PESu	Immiscibility. No UCST up to 250 °C[a]
PMMA/PEA	Immiscibility with UCST=223 °C
PMMA/PTA	Partial miscibility with UCST=116 °C
PMMA/PBA	Partial miscibility with UCST=145 °C
PMMA/PEAz	Partial miscibility with UCST=155 °C
PMMA/PHA	Partial miscibility with UCST=169 °C
PMMA/PCL	Partial miscibility with UCST=179 °C
PMMA/PHS	Immiscibility. No UCST up to 250 °C

[a] Degradation at above 250–300 °C or higher prevented experimental observation of phase transition.

the polyesters tends to change more slowly with each additional methylene (or methyl) introduced as the CH_2/CO ratio in the main chain is already high. With either increase or decrease in the CH_2/CO ratio away from 4.0 in the polyester's structure, the value of UCST for the blends rapidly increases, eventually to an extent of above the thermal degradation point and no longer measurable experimentally. On the two extreme ends of polymer structures, PMMA/PES($CH_2/CO=2$) and PMMA/PHS ($CH_2/CO=7$) are immiscible at room temperature as well as elevated temperatures up to thermal degradation, which means UCST, if any, may be too high to be detected experimentally. The experimental data show that the PMMA/PTA($CH_2/CO=3.5$) blend seems to have the lowest UCST value; however, this point should not be regarded as the lowest one. After adjustment of its low M_w to a normal high of ~10,000 g/mol, the estimated UCST will be much higher as shown in the figure. For the PMMA/PEAz blend, UCST was found to vary slightly with respect to blending methods, where the upper bound is for the blend samples cast from THF and the lower bound for blend samples cast from $CHCl_3$. In the figure, one UCST data point for the blend of PMMA/PHB (with $CH_2/CO=3$) was taken from the literature [21–23] and replotted. In addition, the blend system of PMMA/PLLA($CH_2/CO=2$) [18–20], with peculiar phase behavior as discussed earlier, is the only exception to the variation trend of UCST in the PMMA/polyester blends with respect to the polyester backbone structure. Regardless of this only known exception, it seems surprising that UCST behavior is common in blends of two carbonyl-containing polymers of PMMA with polyesters.

In summary, solvent effects, M_w's, polydispersity, and chain ends in the constituent polymers can all affect phase behavior of blends. However, these factors have all been controlled in experimentally comparable scales in this study. To simplify, one may exclude the factors of minor difference in M_w's, polydispersity, and chain ends. That is, polyesters of similar MWs/chain ends, etc., are viewed as different random copolymers comprising COO segments and CH_2 segments of various relative fractions. The only dominating factor, difference in backbone as represented by averaging CH_2/CO ratio in polyester, plays a more critical role in determining the phase behavior of the PMMA/polyester blends.

Effect of M_w on UCST by model fitting

The polyesters used in PMMA/polyester blends are all of reasonably high M_w's (except for PTA). These polyester M_w's as used are high enough to represent the objectives of evaluating different backbones in polyesters. End groups in low-molecular-weight polyesters certainly might have some effects on phase behavior; but as exemplified, effects of end groups are quite limited. Slight deviation in results caused by the end groups was taken as inevitable experimental error within acceptable range. Aside from possible minor effects by the end groups, molecular weights of either of the two constituent polymers were expected to alter the values of UCST measured owing to entropic effect, which is quantitatively assessed as follows. Specifically, two blend systems were examined for effects of molecular weights: PMMA/PEA and PMMA/PBA blends. To explain the UCST behavior in the blends, a model based on binary interactions was constructed. The Flory–Huggins expression for the free energy of mixing of polymer mixtures is expressed [25, 26]:

$$\Delta G_{\mathrm{M}} = RT\left[\left(\frac{1}{V_1}\right)\phi_1 \ln \phi_1 + \left(\frac{1}{V_2}\right)\phi_2 \ln \phi_2\right] + B\phi_1\phi_2 \tag{1}$$

where V_1 and V_2 are the molar volumes of Polymer 1 and 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of the polymers. Expressed as a form depending on volume

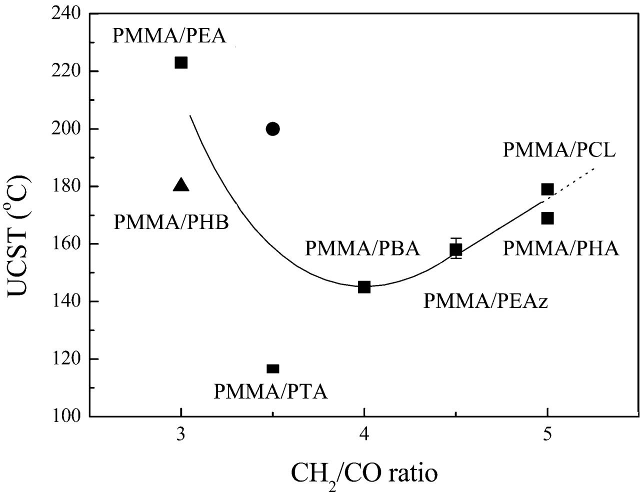
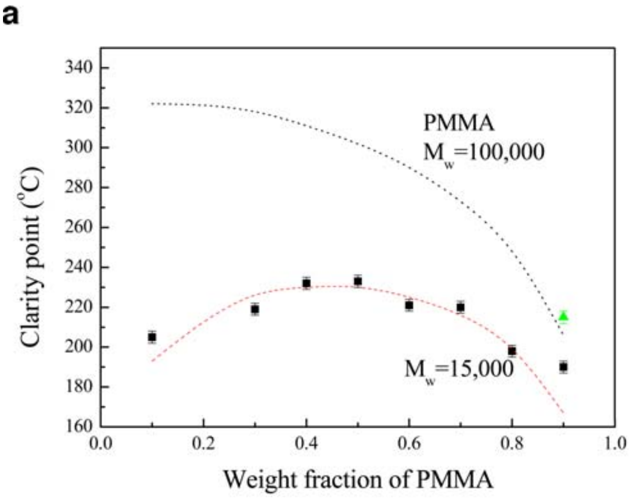


Fig. 11 Values of UCST for various blends of PMMA/polyester plotted as a function of polyester structural parameter (CH_2/CO ratio)



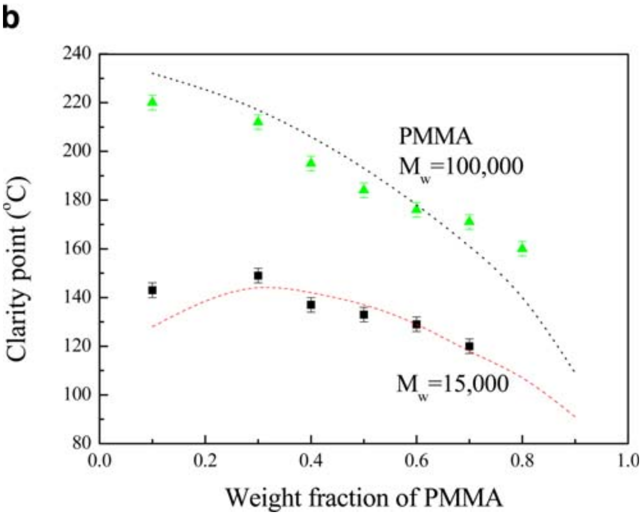


Fig. 12 Experimental vs calculated UCST phase diagrams for **a** PMMA/PEA and **b** PMMA/PBA blends. Comparisons shown for two different M_w's of PMMA

fraction and temperature, the interaction energy density (B) between two components can assume the following parametric from [27, 28]:

$$B = b_0 + b_1\phi_2 + b_2T \qquad (2)$$

This expression was assumed to be valid for the UCST blend systems (immiscible at ambient but miscible above UCST). The experimental data of the "clarity" points for the blend system of PMMA (M_w=15,000) blends were used for obtaining the model parameters (b_i) by using a nonlinear least-square fitting. The following expression for interactions between polymers was obtained:

$$B = 0.74850 - 0.010488\phi_2 - 0.0009343T \qquad (3)$$

$$\text{for PMMA } (M_w = 15,000)/\text{PEA}$$

$$B = 0.59084 + 0.11966\phi_2 - 0.0011464T \qquad (4)$$

$$\text{for PMMA } (M_w = 15,000)/\text{PBA}$$

The fitted parameters were then used to predict the phase behavior and UCST diagrams of the blends of high-molecular-weight PMMA (i.e., PMMA-H with M_w= 100,000 g/mol). The model based on the interaction energy would predict that UCST increases at increasingly higher molecular weights. Figure 12 shows the results of model prediction of phase diagrams for (a) PMMA/PEA vs PMMA-H/PEA and (b) PMMA/PBA vs PMMA-H/PBA blends, respectively, of the experimental UCST for PMMA blend and model-calculated UCST for PMMA-H blend. The curves in the figure are used for directly comparing the experimental vs predicted results. In the figures, symbols are the experimental data and dash lines are the calculations. The experimental result agrees well with the model prediction. The clarity points of PMMA-H/PEA blends were reported only for one composition of the PMMA-H/PEA blend (90:10) owing to concern of high-temperature (>250 °C) decomposition of PMMA. The figure shows that UCST for both blend systems increases with molecular weight of PMMA in the blends, which is also seen in other reported UCST blend systems [9, 10, 30]. In addition to effect of PMMA on blend's UCST behavior as noted, similarly, molecular weights of polyesters was expected to influence the temperature at which the PMMA/polyester blends turned from phase separation to a homogeneous-phase blend upon heating. Figure 13 shows the results of model prediction of phase diagrams for PMMA/PTA blends of two different PTA M_w's (3,800 vs 10,000 g/mol). In general, UCST of the blend systems increases with increase in the molecular weights of either constituents of PMMA or polyesters.

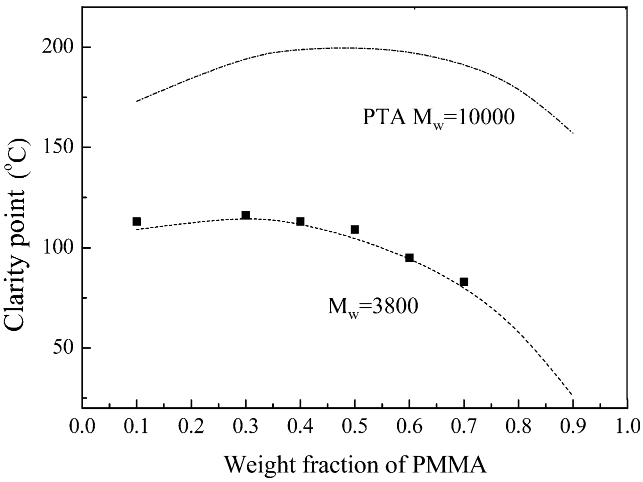


Fig. 13 Experimental vs calculated UCST phase diagrams for comparison of PMMA/PTA blends of two different M_w's of polyesters

Conclusion

Conventional notion that blend systems comprising PMMA and various polyesters are immiscible must be amended. This study has discovered that UCST behavior, superimposed on room-temperature immiscibility, is quite common for the PMMA/polyester blend systems. Blends of PMMA with a series of homologous polyesters, whose structures were varied in a range, were characterized in terms of phase behavior and dependence of the phase behavior on composition, temperature, and constituent's structure. UCST, i.e., behavior of immiscibility at ambient but turning to miscibility at elevated temperatures, is a quite often occurrence in blends of two polymers of similar structures or functional groups, as demonstrated by the blend systems of PMMA with a homologous polyesters.

As the polyesters' structures are varied systematically (with CH_2/CO ratio being from small to large), PMMA/polyester blends exhibit a stepwise change in phase behavior: from complete immiscibility, to complete immiscibility (in entire composition range) with UCST, then to partial miscibility (miscible only for blends with PMMA contents greater than 70 wt%) with UCST, then finally back to complete immiscibility with no UCST. The blend of PMMA/PTA ($CH_2/CO=3.5$) tends to have the lowest UCST. In the range of blend systems (with either partial miscibility or complete immiscibility at ambient) where UCST could be observed and recorded. As the polyester's structural parameter of CH_2/CO is varied from 2.0 to 3.5 then to 7.0, respectively, the values of UCST exhibit a systematic change from a high extreme of 223 °C to a minimum of 116 °C then back to another high of 179 °C. In summary, no miscibility was found for blends of PMMA with all polyesters; however, UCST behavior, normally a rare occurrence in polymer blends, was found to be common in many of the PMMA/polyester blends investigated. Furthermore, the values of UCST (maximum temperature of the clarity curve) are dependent on the polyester main-chain structures.

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