ELSEVIER

Polymer 40 (1999) 3803–3808

polymer

Phase structure and miscibility in blend of poly(4-methyl styrene) with poly(cyclohexyl methacrylate)

E.M. Woo*, Fan Hwei Jang

Department of Chemical Engineering, National Cheng Kung University, Tainan 701-01, Taiwan

Received 27 May 1998; received in revised form 30 July 1998; accepted 3 August 1998

Abstract

Thermal analysis, optical and scanning electron microscopy were performed to characterize solution-blended poly(4-methyl styrene) (P4MS)/poly(cyclohexyl methacrylate) (PCHMA) of full compositions. It is concluded that the true state of blend phase structure is miscibility with non-specific intermolecular interactions. To probe molecular interactions between the polymer pairs, FT-IR analysis was also used to assess possible evidence. The FT-IR results for the P4MS/PCHMA suggest that the intermolecular interactions between the pairs are likely non-specific and only comparable with those among the homopolymer molecules. Casting temperature did not seem to have any effect on the miscible phase structure of P4MS/PCHMA. Both optical microscopy and SEM characterization revealed that solution casting of P4MS/PCHMA at either temperature yielded equally homogeneous phase structure. The cloud point phenomenon is attributed to a thermodynamic lower critical solution temperature (LCST) but is kinetically irreversible at normally accessible time scales. The observed LCST could be made to be reversible in an appropriate environment where the molecules were given enough molecular mobility. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Blend; LCST; Miscibility

1. Introduction

Blends of polystyrene (PS) homopolymers or copolymers with other polymers were a focus of interest and extensively studied. The literature reports reveal that blends of polystyrene with ester-containing (main-chain carbonyl group) polymers or acrylic polymers (pendant carbonyl group) are mostly immiscible. For examples, blends of PS with poly(methyl methacrylate) (PMMA) are known to be immiscible and non compatible as reported in a paper by Shultz and Young [1], although manipulation of kinetic processes (e.g. freeze-drying, etc.) may result in a temporarily locked homogeneous phase structure showing an apparent single-T_g. This demonstrates that the phase stability in certain mixtures of PS can be unstable or kinetically dependent. In one of our earlier studies [2], we demonstrated partial miscibility and micro-heterogeneity domains of about 100–300 Å existing in some compositions of the ‘transparent’ blend of PS/poly(cyclohexyl methacrylate) (PCHMA) with an apparent single T_g, which was thought to be miscible in earlier reports by Friedrich et al. [3]. That is, although a single T_g is observed in the PS/PCHMA blend of all compositions, the phase structure contains sub-micron size heterogeneous domains for the PS-rich compositions, leading to a conclusion of partial miscibility with the PCHMA-rich compositions being completely miscible but the PS-rich compositions being only partially miscible. It was also further demonstrated that the partial miscibility in the blend of polystyrene with PCHMA, leads to an interesting phase behaviour with the resultant structure sensitively depending on temperature, solvent or composition.

Polymer miscibility in blends involving PS as one component has not been common. This is easy to understand as polystyrene (PS) does not possess any functional groups that are capable of interacting specifically with other polymer molecules. As a result, PS is not miscible with most other long-chain thermoplastic polymers. Two well-known exceptions of blends comprising PS and ether-containing polymers are known to be miscible. One is the blend system of PS with poly(1,4-dimethyl-*p*-phenylene oxide) (PPO), which is one of the most studied polyblends, and its miscibility was demonstrated since early time [4–6]. Another notable example of miscible blends comprising PS is given by the classical PS/poly(vinyl methyl ether) (PVME) system

---

* Corresponding author. Tel.: +886-6-275-7575 Ext. 62670; Fax: +886-6-234-4496; E-mail: emwoo@mail.ncku.edu.tw

PII: S0032-3861(98)00581-3

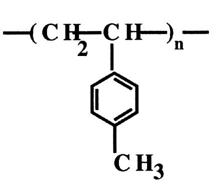
[7–9]. A recent study [10] revealed that the phase behaviour of the blend of semi-crystalline syndiotactic s-PS with PVME is as miscible as the a-PS/PVME blend. Unlike the miscibility in PS/PPO, which is well established in the literature, the miscibility in the PS/PVME system was more conditional owing to its peculiar T_g behaviour and significant broadening.

Partial miscibility was indicated for the PS/PCHMA blend. However, the demonstrated partial miscibility in PS/PCHMA suggests that a certain level of interactions may exist between PS and some carbonyl-containing polymers. Thus, the phase behaviour of the PS/PCHMA is just outside the borderline miscibility. A change in the structure of either polystyrene or PCHMA may result in the phase behaviour of such a blend going closer to or further away from miscibility. In this study, the structure of polystyrene was modified by introducing a methyl group onto the phenyl ring (para-substitution). Phase behaviour of such a blend comprising of PCHMA and the modified polystyrene was examined. As the T_g's of these two constituent polymers are close or almost the same, difficulty was expected in determining the true phase state. Relevant experiments other than thermal analysis were performed and results analysed with care. The true behaviour and its dependence on the structure of the constituent polymers is discussed.

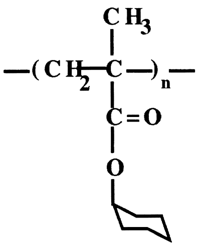
2. Experimental

2.1. Materials and sample preparation

As the methyl-substituted polystyrene is readily available from a specialty polymer supplier, laboratory synthesis was not needed. Poly(4-methyl styrene) (P4MS) was purchased from Scientific Polymers Product, Inc. (USA), with an approximate $M_w = 70{,}000\ \mathrm{g\ mol^{-1}}$ (Gel Permeation Chromatograph, GPC) and $T_g = 106°\mathrm{C}$. Poly(cyclohexyl methacrylate) (PCHMA) was also purchased from Scientific Polymers Product, Inc. (USA), with an approximate $M_w = 65\,000\ \mathrm{g\ mol^{-1}}$ (GPC) and a T_g of 110°C. Note that the T_g of these two polymers differ only slightly. The materials were free of additives and were used without further purification. The chemical structures of P4MS and PCHMA are shown as following:



P4MS



PCHMA

The blend samples in this study were prepared by solvent-casting at two different temperatures (20°C and 45°C, respectively). Tetrahydrofuran (THF) was used for blend preparation of all blend samples. Alternatively, for comparison of solvent effect on phase strucutre, dichloromethane (CH_2Cl_2) was also used for blending samples of some composition at ambient temperature. PCHMA and P4MS were first weighed respectively and dissolved into THF (or dichloromethane) with continuous stirring. Subsequently, the resulting polymer solution was poured into an aluminum mold kept at one of the two temperatures (20°C or 45°C). The solvent in the cast film samples was first vaporized under a hood at controlled temperature, followed by residual solvent removal in a vacuum oven for 48 h at 50°C–60°C. Subsequent vacuum degassing at an even higher temperature of 70°C–80°C was performed on the THF-cast samples for two more days to ensure removal of residual solvent.

2.2. Apparatus

2.2.1. Differential scanning calorimetry.

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 $\mathrm{min^{-1}}$ and the T_g values were taken as the onset of the transition (the change of the specific heat) in the d.s.c thermograms.

2.2.2. Optical microscopy.

A polarized-light microscope (Nikon Optiphot-2, POL) was used. 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 comparison, samples for optical examination were prepared using the same solvents and casting temperature as those in thermal analysis samples. Cloud point measurement of the blends was performed by placing the samples on a microscope heating stage (temperature-programmed), with a programmed heating rate of approximately 2°C $\mathrm{min^{-1}}$ from room temperature up to 300°C. Cloud point was registered as the initiation temperature at which separated domains were visible in samples using the maximum magnification of the optical microscope.

2.2.3. Scanning electron microscopy

Morphology (fracture surface) of blends was examined using a scanning electron microscope (SEM) (Model JEOL JXA-840). The THF solution-cast samples, prepared at room temperature and 45°C, were examined using SEM after preliminary optical microscopy characterization. The blend film samples for scanning electron microscopy were thick enough so that the fracture surface of the thickness (cross section) could be conveniently examined. The fractured blend samples were coated with gold by vapour deposition using a vacuum sputterer.

2.2.4. Infrared spectroscopy

Fourier-transform infrared spectroscopy (FT-IR., Nicolet

Magna-560) was used for investigating possible molecular interactions between the constituents. Spectra were obtained at 4 cm^{-1} resolution and averages of spectra were obtained from at least 64 scans in the standard wave number range of 400–4000 cm^{-1}. All the FT-IR samples were cast as thin films of proper thickness directly on KBr pellets kept at 45°C.

3. Results and discussion

3.1. Thermal behaviour and phase structure

The blend films of all compositions by THF casting (at either 20°C or 45°C) were crystal-clear and completely free of any haziness as observed using an optical microscope. D.s.c analysis was performed on the THF-cast (45°C) samples to reveal their thermal transition behaviour. It was expected that the thermal behaviour of blends samples cast at 20°C would be similar. Similarly, the blend samples cast with dichloromethane (at ambient temperature) exhibited an optically homogeneous phase structure when observed using an optical microscope at × 800.

With understanding that the T_g of the component polymers were almost the same (106°C and 110°C, respectively), d.s.c. analysis was proceeded with care. For a uniform thermal history, all thermograms are the results of second runs after quenching from above T_g. The d.s.c result revealed one apparent T_g in each of thermograms for the P4MS/PCHMA blends of different compositions. The T_g (on-set) is almost constant at 110°C, which is well expected because of the proximity of the component T_g. The thermal transitions for all blend compositions are reasonably sharp and not broadened with respect to compositions. Further, to enhance resolution of thermal transitions, physical aging (at 90°C for 30 min) was performed on the blend samples. D.s.c analysis was then performed on these aged samples in hope of leading to enhanced resolution by revealing multiple enthalpy relaxation peaks, if multiple transitions were indeed present. All d.s.c. curves of the aged samples exhibited one apparent enthalpy relaxation peak on top of each of the T_g transitions for each of the P4MS/PCHMA blends of five different compositions, as indicated in the curves. The T_g (on-set) is almost constant at 110°C, which is well expected because of the proximity of the component T_g. The thermal transitions for all blend compositions are reasonably sharp and not broadened at all. However, as the T_g of the two components (P4MS and PCHMA) do not differ much, neither the single T_g nor the lack of broadening may be used to suggest possible scales of molecular intermixing. Further evidence was needed.

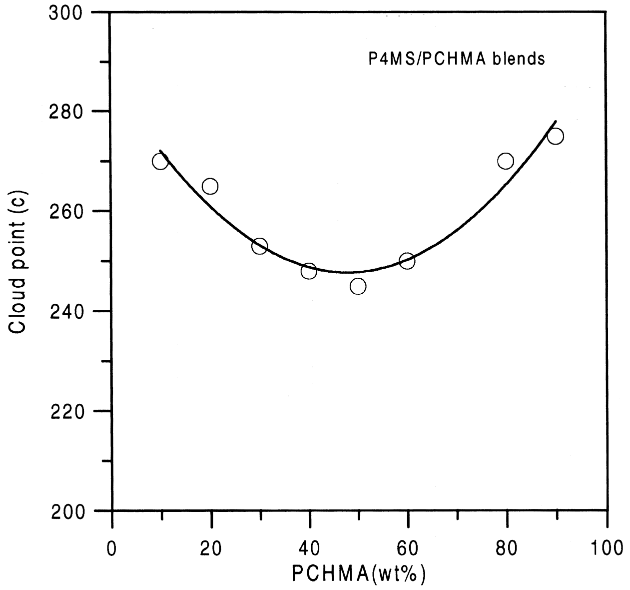


Fig. 1. Cloud point (initiation) of P4MS/PCHMA blend as a function of composition.

3.2. Microscopic network morphology

Although the proximity of the T_g of the constituent polymers hindered a more straightforward conclusion based on the thermal transitions, the morphology of these blends was carefully examined. Morphology characterization using SEM was performed to reveal the scales of any possible heterogeneity. For brevity, the micrographs are not shown here. The micro graphs revealed no discernible heterogeneity in the solution-cast P4MS/PCHMA blend samples in a wide composition range: 90/10, 10/90 and many intermediate compositions in between. Blends solution cast and prepared at the ambient temperature (20°C casting, THF) were also examined using SEM. Again, for brevity, micrographs of the ambient-cast P4MS/PCHMA blend samples are not shown. Apparently the samples cast at ambient temperature were found to be as homogeneous as those cast at 45°C.

3.3. Cloud point observation

The THF-cast (20°C or 45°C) blend samples were visually clear and free of any visibly heterogeneity domains. Changes of optical clarity of the blends with respect to temperature were inspected at step-wise elevating temperatures up to where degradation occurred (300°C) in order to monitor whether or not there existed a cloud-point transition. Fig. 1 shows the result of cloud point (initiation) of blend as a function of composition. The shape of the cloud point curve is quite symmetrical, with the cloud point transition for the 90/10 and 10/90 compositions occurring at about 270°C–280°C and the 50/50 composition showing a minimum cloud point of about 245°C. As the phase structure of the blend at below the cloud point was determined to be completely homogeneous and free of any micro heterogeneity, the occurrence of a cloud point phenomenon suggested a thermodynamic phase separation from original miscibility. The cloud point phenomenon observed in this blend system can be identified with its thermodynamic behaviour of LCST.

Fig. 2 shows the optical micrographs (× 800) revealing the size and distribution of the phase domains of the P4MS/PCHMA at above LCST for three different compositions: (A) 80/20; (B) 50/50; and (C) 40/60. Photos were taken after the samples were heated to 270°C–280°C for 5 min. The pattern of phase domain suggests a similar binodal decomposition upon heating to above LCST for all three compositions with different extents of phase separation. Samples of other compositions were also examined, which are not all shown in the figure for brevity. The phase domain size (2–3 μm) of 50/50 or 40/60 composition is apparently larger than that for the 80/20 composition (ca. 1 μm). As the 50/50 (or 40/60) composition had the lowest LCST (ca. 250°C), expectedly, thermal treatment at 270°C–280°C led to a greater extent of phase separation than the 80/20 composition, for example.

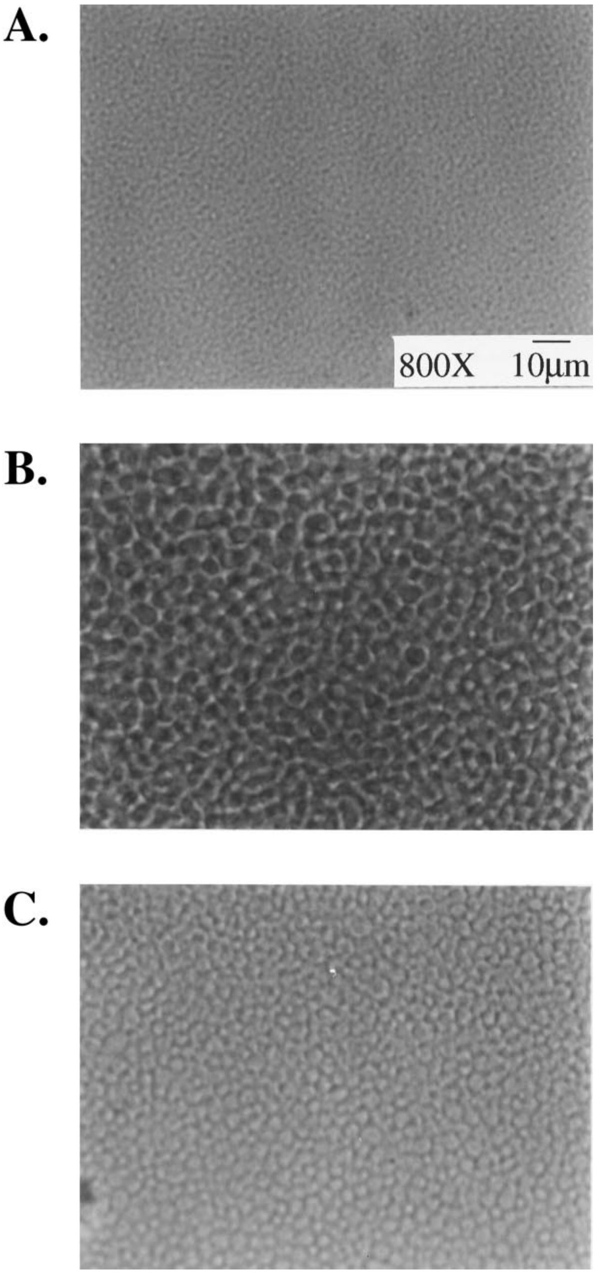


Fig. 2. Optical micrographs showing phase separation for the P4MS/PCHMA blend samples (at 275°C, 5 min.): (A) 80/20; (B) 50/50; and (C) 40/60.

3.4. Reversibility of LCST

In normally accessible time scales, the LCST phenomenon taking place in the P4MS/PCHMA blend upon raising the temperature was found to be irreversible upon lowering the temperature. This irreversibility was attributed to kinetic, but not thermodynamic factors, meaning that the LCST was irreversible in the experimentally obtainable time scales. This means that upon quenching (or cooling down slowly) from above the LCST temperatures to ambient, phase-separated structure remained. A true LCST should be thermodynamically reversible. To prove that this apparent irreversibility is kinetically driven (i.e. locked into a phase-separated structure), relevant experiments were performed.

A heating-induced phase separated blend sample (50/50 composition) was redissolved into THF and cast to prepare a regenerated blend, whose structure was again examined using SEM. Fig. 3 shows SEM results revealing that the phase structure of this recast blend (50/50) was as homogeneous as that of the original sample not subjected to LCST. This suggests that given enough molecular mobility in appropriate environments, the phase separation above LCST can be made to be reversible. This was uniquely demonstrated by recovery of a homogeneous phase by redissolving and recasting the phase-separtated polymer samples in a solvent. It further suggests that no chemical changes were involved in the phase separation process at above LCST.

3.5. Molecular interactions

Fig. 4 shows the spectra with the carbonyl (C=O) IR

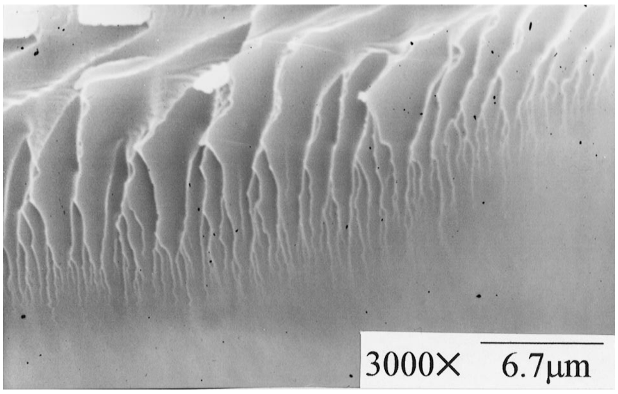


Fig. 3. SEM micrograph of the P4MS/PCHMA (50/50) blend that underwent phase separation at above LCST and were then redissolved and recast.

absorbance peak for the samples: (a) neat PCHMA and P4MS/PCHMA blend; (b) (20/80); (c) 50/50; and (d) 80/20 blend compositions. The absorption peak is seen to be located at approximately 1724.8 cm^{-1} for all compositions and the peak shift is negligible. The lack of peak shifting suggests that a relatively low level of specific interactions, if any, may be present between the two molecules. Additionally, the carbonyl group of PCHMA may not interact specifically with any specific sites of the P4MS molecule.

Absorption peaks other than the carbonyl were also examined. Fig. 5 shows the spectra in the wave number range where the absorbance peaks of ether group (1156 cm^{-1}) of PCHMA and aromatic C–H bending (near 813 cm^{-1}) of P4MS can be conveniently compared. Again, the ether (C–O–C) peak of PCHMA does not show significant shifting with respect to blend composition. For the extensively studied blend of PPO with PS, it was proposed that a likely site of mutual interaction is between the phenyl ring of PS with the ether of PPO. Similarly, Hsu et al. [11] conducted a spectroscopy study on PS-PVME blends prepared in compatible or non-compatible state and concluded that the vibrations most sensitive to change in molecular environment of compatibility are the C–H out-of-plane bending (at 700 cm^{-1}) in PS and C–O–CH_3 stretching (1100 cm^{-1}) of PVME. In this P4MS/PCHMA blend, the phenyl C–H bending of P4MS molecules is seen to shift slightly from 813 cm^{-1} for neat P4MS to 815 cm^{-1} for P4MS/PCHMA (20/80). The shifting, however, may not be significant and it can be viewed that the C–H bending absorbance peak stays at about the same wave number regardless of composition changes. The experimental IR result in this study shows that possible interactions between likely functional groups in P4MS and PCHMA are likely low or non-specific. The low level or non-specific interactions often typifies the molecular miscibility in blends comprising polystyrene type polymers. The FT-IR analysis suggests that relatively low intermolecular interactions, mostly non-specific, are present in the P4MS/PCHMA system. In general, the FT-IR results for the P4MS/PCHMA suggested that intermolecular interactions between the pairs are likely non-specific and at best only comparable with those among the homopolymer molecules.

4. Conclusion

Thermal analysis, optical and scanning electron microscopy were performed to characterize solvent-blended P4MS/PCHMA of full compositions. Further, to probe molecular interactions between the polymer pairs, FT-IR analysis was used to assess possible evidence. All blend samples cast at either ambient or high temperature were optically clear and appeared homogeneous. In addition, blend samples prepared using dichloromethane at ambient temperature also yielded a homogeneous phase structure. Both optical microscopy and SEM characterization revealed that P4MS/PCHMA blend prepared at either temperature yielded an equally homogeneous phase structure. It is concluded that the true state of blend phase structure is miscibility with non-specific intermolecular interactions. The phase stability is good as the miscibility of the P4MS/PCHMA blend does not seem to be influenced by different solvents or difference in casting temperature within a large range. This is in dramatic contrast with the phase behaviour of PS/PCHMA, which exhibits borderline partial miscibility

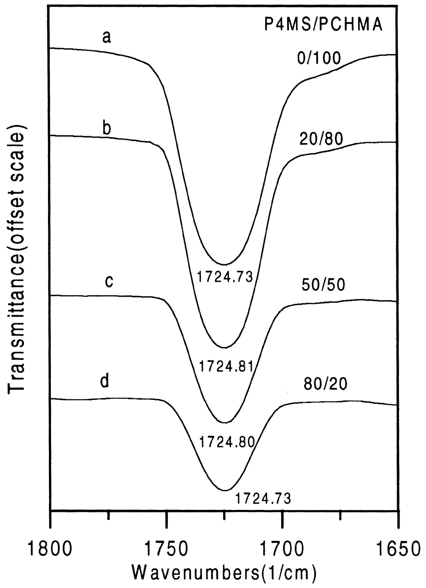


Fig. 4. Carbonyl absorbance peaks for: (a) neat PCHMA and P4MS/PCHMA; (b) 20/80; (c) 50/50; and (d) 80/20 compositions.

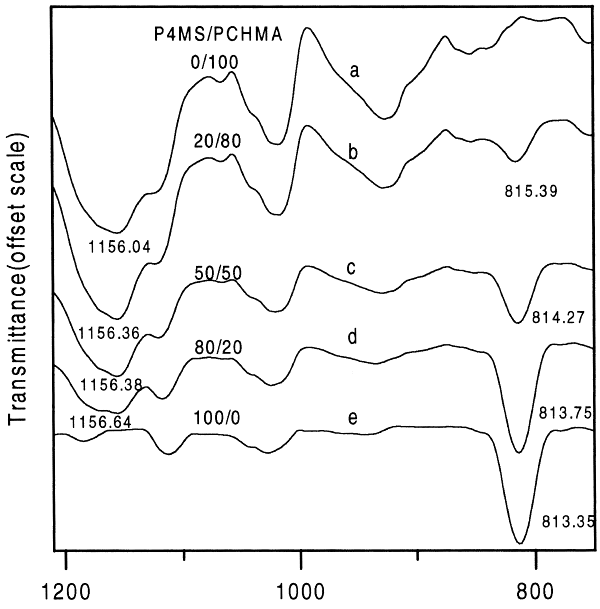


Fig. 5. IR absorbance peaks of the pendant ether group (in PCHMA) and aromatic C–H bending (in P4MS) of P4MS/PCHMA of several compositions, as indicated.

and whose phase structure is sensitively dependent on cast solvent or casting temperature [2].

Further, the LCST phenomenon is thermodynamically driven but the phase separation, once taking place, is kinetically irreversible in normally accessible time scales. This means that upon quenching (or cooling down slowly) from above the LCST temperatures to ambient, phase-separated structure remained. If the molecular chains were given enough mobility, e.g. by redissolving the phase-separated polymers into a solvent and recasting into a blend sample, phase separation above LCST could be made to be reversible by forming a homogeneous phase again. It further suggests that no chemical changes are involved in the phase separation process at above LCST and the phase separation induced by LCST is a reversible thermodynamic process. The FT-IR result for the P4MS/PCHMA suggests that the intermolecular interactions between the pairs are likely non-specific and only comparable with those among the homopolymer molecules.

Acknowledgements

Research grant was provided by National Science Council (#NSC 87-2216-E006-005). Instrument support of scanning electron microscopy by the NSC Regional Instrument Center (Tainan, Taiwan) is acknowledged.

References

[1] Shultz AR, Young AL. Macromolecules 1980;13:663.
[2] Jang FH, Woo EM. Polymer 1998;00:000. in press.
[3] Friedrich C, Schwarzwalder C, Riemann R-E. Polymer 1996;37:2499.
[4] Stoelting J, Karasz FE, MacKnight W. J Polym Eng Sci 1970;10:133.
[5] Shultz AR, Beach BM. Macromolecules 1974;7:902.
[6] Prest WM jr, Porter RS. J Polym Sci A 1972;2 (10):1639.
[7] Kwei TK, Nishi T, Roberts RF. Macromolecules 1974;7:667.
[8] Bank M, Leffingwell J, Thies C. Macromolecules 1971;4:43.
[9] Bank M, Leffingwell J, Thies C. J Polym Sci A 1972;2 (10):1097.
[10] Mandal TK, Woo EM. Polymer 1999; in press.
[11] Lu FJ, Benedetti E, Hsu SL. Macromolecules 1983;16:1525.