Miscibility of Poly(2-bromoethyl methacrylate) with Various Polymethacrylates

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ABSTRACT: The miscibility behavior of poly(2-bromoethyl methacrylate) (PBEMA) with various polymethacrylates was investigated by differential scanning calorimetry. PBEMA is only miscible with poly(tetrahydrofurfuryl methacrylate) (PTHFMA) and is immiscible with poly(methyl methacrylate), poly(ethyl methacrylate), poly(*n*-propyl methacrylate), poly(isopropyl methacrylate), poly(*n*-butyl methacrylate), and poly(cyclohexyl methacrylate). PBEMA/PTHFMA blends did not exhibit lower critical solution temperature (LCST) behavior and degraded before phase separation could be induced. In comparison, PBEMA has a more limited degree of miscibility with polymethacrylates than poly(2-chloroethyl methacrylate).

Introduction

The miscibility behavior of poly(vinyl chloride) (PVC) has been extensively studied. PVC is readily miscible with polymethacrylates[1,2] and polyesters.[3-6] However, similar studies on the miscibility behavior of poly(vinyl bromide) (PVB) are limited. Cousin and Prud'homme[7] studied the miscibility of PVC and PVB with a series of polyesters and found that PVB has a more limited miscibility as compared with PVC. Goh and co-workers[8,9] found that a polyester poly(neopentyl glycol adipate) is miscible with PVC but is immiscible with PVB. Karasz, MacKnight, and co-workers[10-14] studied the miscibility of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with halogenated polystyrene and they found that bromine has a better ability than chlorine to induce immiscibility in PPO/polystyrene blends.

We have recently found that chlorine-containing polymethacrylates such as poly(chloromethyl methacrylate) (PCMMA) and poly(2-chloroethyl methacrylate) (PCEMA) behave like PVC in forming miscible blends with several polymethacrylates.[15,16] PCMMA is miscible with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PnPMA), poly(isopropyl methacrylate) (PiPMA), and poly(tetrahydrofurfuryl methacrylate) (PTHFMA) but is immiscible with poly(*n*-butyl methacrylate) (PnBMA). The miscibility range of PCEMA is narrower, but it is still miscible with PMMA, PEMA, and PTHFMA. In this article, we report the miscibility of poly(2-bromoethyl methacrylate) (PBEMA) with various polymethacrylates. It will be shown that as compared with PCEMA, PBEMA has a very limited miscibility with the polymethacrylates.

Experimental Section

The monomer BEMA was obtained from Polysciences and purified by fractional distillation [72–73 °C (5.5 mmHg)]. BEMA was polymerized in 2-butanone at reflux temperature for 6 h with 0.25% by weight of azobisisobutyronitrile as initiator. The polymer was obtained by precipitation of the solution in excess methanol. The number-average and weight-average molecular weights of PBEMA determined by GPC were 25 000 and 37 000, respectively. The glass transition temperature (T_g) of PBEMA is 65 °C. The following commercially available polymethacrylates were used in the study: PMMA (Du Pont Elvacite 2010, M_w = 120 000, T_g = 100 °C), PEMA (Du Pont Elvacite 2042, M_w = 310 000, T_g = 65 °C), PnPMA (Scientific Polymer Products, M_w = 175 000, T_g = 45 °C), PiPMA (Scientific Polymer Products, $[\eta]$ = 0.33 dL/g in 2-butanone at 30 °C, T_g = 82 °C), PnBMA (Du Pont Elvacite 2044, M_w = 288 000, T_g = 20 °C), PTHFMA (Scientific Polymer Products, M_w = 240 000, T_g = 57 °C), and poly(cyclohexyl methacrylate) (PCHMA) (Scientific Polymer Products, M_w = 66 000, T_g = 95 °C).

Blends of PBEMA with various polymethacrylates were prepared by solution casting from tetrahydrofuran (THF). Solvent was allowed to evaporate slowly over a period of 1–2 days at room temperature. The cast films were then dried in vacuo at 90 °C for at least 3 days.

The glass transition temperatures (T_gs) of various samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20 °C/min. The T_g value was taken as the initial onset of the change of slope in the DSC curve. The reported T_g is the average value based on the second and subsequent runs.

All the miscible blends were examined for the existence of lower critical solution temperature (LCST) by using the method described previously.[15]

Results and Discussion

Blends of PBEMA with various polymethacrylates except PTHFMA were cloudy. Two distinct glass transitions were observed for blends of PBEMA with PMMA, PnPMA, PiPMA, PnBMA, and PCHMA. The T_g values of the blends are close to the respective component polymers. The results show that PBEMA is immiscible with these five polymethacrylates. Due to PBEMA and PEMA having same T_g values, conventional DSC measurements cannot be used to ascertain the miscibility of the blends. Nevertheless, the cloudy appearance of PBEMA/PEMA blends suggests that PBEMA is also immiscible with PEMA.

All the PBEMA/PTHFMA blends were transparent and remained so on heating to the maximum temperature allowed (300 °C) by the apparatus. The T_g values of PBEMA and PTHFMA are close to each other (ΔT_g = 8 °C). For a blend of two polymers with similar T_g values, the enthalpy recovery peak of an annealed blend can be used to ascertain its miscibility.[17,18] A single enthalpy recovery peak is indicative of a miscible blend. PBEMA, PTHFMA, and various PBEMA/PTHFMA blends were heated at 140 °C for 5 min to erase previous thermal history. The samples were then annealed at 45 °C for 10 days. The DSC curves of the annealed samples are shown in Figure 1. Each annealed blend showed a single enthalpy recovery peak, which moved progressively to a higher temperature with increasing PBEMA content. In contrast, a two-phase physical mixture of PBEMA and PTHFMA annealed under the same condition exhibited a shoulder and a peak as shown in Figure 1. Thus, the optical clarity and

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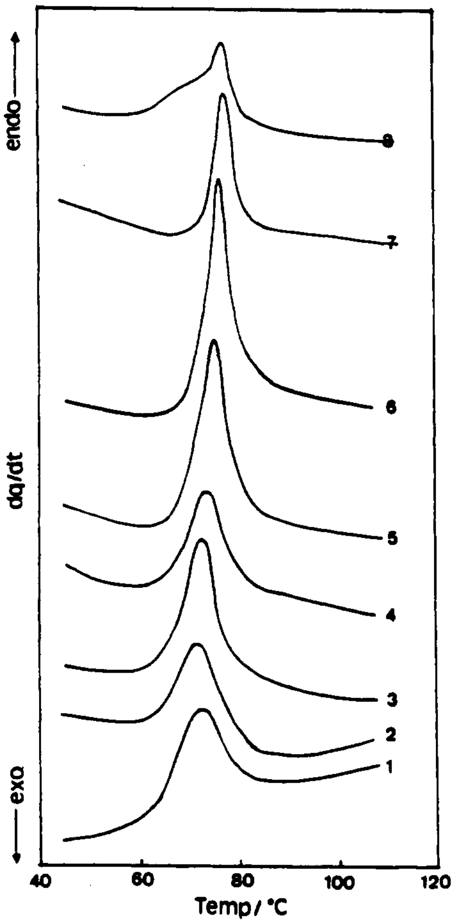

Figure 1. DSC curves for annealed PBEMA/PTHFMA blends. (1) 100% PTHFMA; (2) 90% PTHFMA; (3) 75% PTHFMA; (4) 50% PTHFMA; (5) 25% PTHFMA; (6) 10% PTHFMA; (7) 100% PBEMA; (8) physical mixture of PBEMA/PTHFMA.

existence of a single recovery peak in each blend show that PBEMA is miscible with PTHFMA.

It has been suggested that in PVC/polymethacrylate blends specific interactions occur between the carbonyl groups of the polymethacrylate and the α-hydrogens of PVC and also between the carbonyl groups and CCl groups.[2] Bromine is larger and less electronegative than chlorine. Therefore, the α-hydrogen in PBEMA is less acidic and the C–Br bond is less polar. As a result, PBEMA interacts less intensely with the polymethacrylates, resulting in a more limited miscibility as compared to PCEMA.

It is noted that PBEMA is miscible with PTHFMA but not with the other polymethacrylates. We have previously reported that PTHFMA is readily miscible with a large variety of polymers in spite of its big pendant groups.[15,16,19,20] The good miscibility of PTHFMA has been attributed to the presence of an additional interacting moiety, the ether oxygen atom, in the pendant tetrahydrofuran ring. The present work once again illustrates the good miscibility of PTHFMA.

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References and Notes

(1) Walsh, D. J.; McKeown, J. G. *Polymer* **1980**, *21*, 1330.
(2) Tremblay, C.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1857.
(3) Ziska, J. J.; Barlow, J. W.; Paul, D. R. *Polymer* **1981**, *22*, 918.
(4) Woo, E. M.; Barlow, J. W.; Paul, D. R. *Polymer* **1985**, *26*, 763.
(5) Riedl, B.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2565.
(6) Prud'homme, R. E. *Polym. Eng. Sci.* **1982**, *22*, 90.
(7) Cousin, P.; Prud'homme, R. E. *Eur. Polym. J.* **1982**, *18*, 957.
(8) Goh, S. H.; Paul, D. R.; Barlow, J. W. *J. Appl. Polym. Sci.* **1982**, *27*, 1091.
(9) Goh, S. H.; Siow, K. S.; Leong, Y. H. *Eur. Polym. J.* **1985**, *21*, 915.
(10) Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1978**, *11*, 150.
(11) Alexandrovich, A.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1977**, *18*, 1022.
(12) Ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(13) Vukovic, R.; Kuresevic, V.; Ryan, C. L.; Karasz, F. E.; MacKnight, W. J. *Thermochim. Acta* **1985**, *85*, 383.
(14) Vukovic, R.; Bogdanic, G.; Kuresevic, V.; Karasz, F. E.; MacKnight, W. J. *Eur. Polym. J.* **1988**, *24*, 123.
(15) Goh, S. H.; Lee, S. Y.; Siow, K. S.; Neo, M. K. *Polymer* **1990**, *31*, 1065.
(16) Neo, M. K.; Lee, S. Y.; Goh, S. H. *J. Appl. Polym. Sci.*, submitted.
(17) Bosma, M.; Ten Brinke, G.; Ellis, T. S. *Macromolecules* **1988**, *21*, 1465.
(18) Jorda, R.; Wilkes, G. L. *Polym. Bull.* **1988**, *20*, 479.
(19) Goh, S. H.; Siow, K. S. *J. Appl. Polym. Sci.* **1987**, *33*, 1849.
(20) Goh, S. H. *Polym. Bull.* **1987**, *17*, 221.

Registry No. PBEMA, 27136-26-1; PMMA, 9011-14-7; PEMA, 9003-42-3; PhPMA, 25609-74-9; PnBMA, 9003-63-8; PTHFMA, 25035-85-2; PCHMA, 25768-50-7; PiPMA, 26655-94-7.