Miscibility in Binary Blends of Poly(α-methylstyrene) and Poly(methyl methacrylate)

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Introduction

The ability to predict miscibility in polymer blends is not yet an exact science, although guidelines do exist which can provide reasonable approximations.[1,2] The majority of binary polymer mixtures tend to be phase-separated systems while most of those that can form one-phase blends show evidence of some form of specific intermolecular interaction which promotes the miscibility. There are also examples of binary miscible blends in which at least one of the components is a copolymer and where specific interactions are not obviously present or are very weak.[3] Finally there is a very small group comprising polymer pairs with similar chemical structures or with comparable cohesive energy densities that can form single-phase mixtures, e.g., the isomeric pair poly(methyl acrylate) and poly(vinyl acetate)[4] or the closely matched polystyrene/poly(α-methylstyrene)[5] where chain length can be a parameter controlling miscibility limits.

While a favorable interaction energy between the blend components is a major factor in determining the extent of mixing, the method of blend preparation can also determine, under certain conditions, whether a one-phase or a two-phase system is produced. This was highlighted originally in the work of Bank et al.,[6] who showed that the nature of polystyrene (PS)/poly(vinyl methyl ether) (PVME) blends was solvent dependent. They found that one-phase blends were obtained if films were cast from toluene solutions but that two-phase blends resulted when chlorinated alkanes were used as solvents. This behavior was later explained by Patterson and co-workers[7,8] from measurements of the ternary phase diagrams for PS, PVME, and either chloroform or trichloroethene. In both cases they found that an enclosed region of immiscibility existed covering a substantial part of the central region of the phase triangle. Thus, during the progressive removal of solvent to produce the binary polymer blend, the system phase-separated on entering this region and remained locked in a phase-separated state on reemerging because chain mobility was insufficient to allow remixing to take place. This gave a two-phase blend, forced into this state by the interactions with the solvent. The opposite situation may also arise; hence, freeze-drying samples may promote the formation of one-phase systems by locking the polymer pair into close segmental contact from which they cannot escape while solvent is removed.[9] The criterion for one-phase behavior normally used in these circumstances is the presence of a single glass transition temperature, T_g, in the blend.

We have recently encountered a system (that we did not expect to be one phase) in which the method of blend preparation played an important role in determining the homogeneity of the blend. It was observed that one-phase blends of poly(α-methylstyrene) and poly(methyl methacrylate) could be prepared that were stable up to an observed lower cloud point (LCP) temperature which was above the T_g of the blend. These observations are reported here.

Experimental Section

Polymer Samples. Poly(α-methylstyrene) (PαMS) was prepared, using standard procedures, by cationic polymerization at −75 °C using BF_3–etherate as the initiator. The nominal molecular weight was 2×10^5 (polystyrene equivalents) as measured by GPC. Two samples of poly(methyl methacrylate) (PMMA) were used, both of which were commercial products. One with a nominal molecular weight of 1.13×10^5 was used for the majority of measurements, and these were checked using a Polymer Labs standard PMMA with molecular weight = 5.9×10^5 and $M_w/M_n = 1.04$.

Glass Transition Temperature. The glass transition temperature, T_g, was measured by differential scanning calorimetry using a Perkin-Elmer DSC-4. The value of T_g was taken as the temperature of the onset of the base-line shift, characteristic of the glass transition, in the thermogram. The T_g values for the two components were PαMS = 182 °C and PMMA = 111 °C.

Blend Preparation. Weighed quantities of the polymer components were dissolved in a common solvent and then either cast as films or coprecipitated into petroleum ether. The solvents used were toluene, tetrahydrofuran (THF), and dichloromethane (DCM). Blends were also prepared by freeze-drying from benzene solutions. In all cases the samples were rigorously dried in a vacuum oven prior to use.

Results and Discussion

The criterion used to decide whether the binary blend had only one phase was taken to be the existence of a single T_g, which suggests that any segregated domain formation in the blend was less than 15 nm in diameter. This is an acceptable practical definition of miscibility. The blend characteristics for the various methods of preparation using 50/50 (wt %) mixtures are summarized in Table I. In all cases where the blends were prepared by casting films, two-phase systems were obtained, but coprecipitation from THF or DCM, or freeze-drying from benzene solution, resulted in miscible blends exhibiting a single T_g.

The stabilities of these one-phase blends were tested by searching for the LCP. This was accomplished by annealing the samples at a temperature T_1, above the T_g, for 5 min and then quenching the sample and measuring the T_g again by DSC. If this gave a single T_g, the procedure was repeated at a temperature $T_2 = T_1 + 5$ °C and so on until a temperature was reached at which phase separation occurred and the sample exhibited two T_g values characteristic of the individual components. A typical set of DSC curves illustrating this procedure is shown in Figure 1 for a PαMS/PMMA blend prepared by freeze-drying.

This approach was adopted for a wider range of blend compositions, prepared by coprecipitation from DCM, and the results are collected in Table II. The location of the LCP phase boundary is shown in Figure 2 and indicates that one-phase blends of PαMS and PMMA can be prepared that are stable up to ~187 °C, which is more than 40 °C above the T_g of the 50/50 blend. The glass transition is seen to occur over a temperature range of 10–20 °C, and this broadens as the LCP is approached as expected. The stability of a 50/50 blend was also tested by annealing the sample for 24 h at 160 °C, approximately 20 °C above the T_g, but the sample remained in one phase with one T_g.

In light of previous experience one has to ask the following question: Are one-phase blends of PαMS and PMMA mixtures to be expected?

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Table I
Phase Characteristics for 50/50 (wt %) Blends of Poly(α-methylstyrene) and Poly(methyl methacrylate) Prepared by Various Methods

solvent	preparation method	blend	T_g, °C	LCP, °C
toluene	film cast	two phase	110 + 170	
toluene	coprecipitation	two phase	110 + 170	
THF	film cast	two phase	110 + 170	
THF	coprecipitation	one phase	131	185
DCM	film cast	two phase	116 + 170	
DCM	coprecipitation	one phase	145	189
benzene	freeze-dried	one phase	138	183
MEK[11]	coprecipitation	two phase	111 + 178	

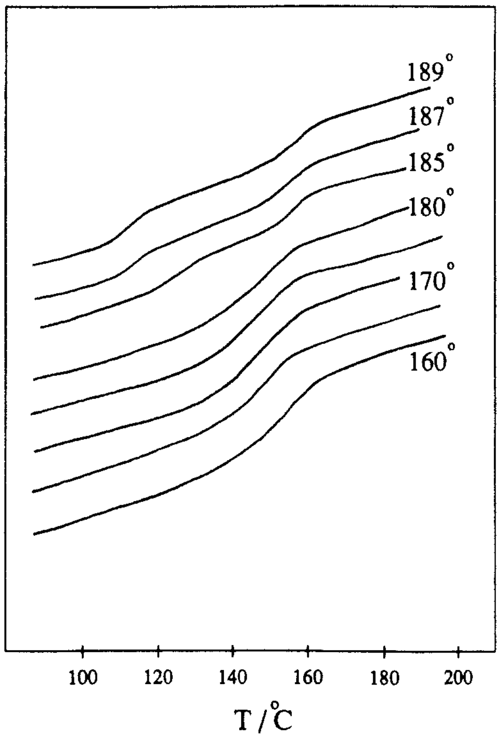

Figure 1. Dsc thermograms for 50/50 (wt %) blends of poly(α-methylstyrene)/poly(methyl methacrylate) prepared by freeze-drying from benzene solutions. The thermograms were run at 5 K intervals initially and then at 2 K intervals.

Table II
Glass Transition Temperatures and Lower Cloud Point Temperatures for Blends of (PαMS/PMMA) Coprecipitated from DCM

PαMS, wt %	T_g, °C	LCP, °C
18	121	198
33	133	187
50	145	189
68	161	194
81	167	202

PS and PMMA tend to form phase-separated systems both in the form of a block copolymer and also as blends, although Shultz and Young[9] found that they could prepare one-phase blends by freeze-drying. These were stable for short periods but tended to phase separate after annealing. Kuhn et al.[10] studied PαMS/PMMA blends, but while clear films could be obtained, they were uncertain as to whether these were miscible or not. Kotaka et al.,[11] working on the corresponding block copolymers, observed that the PαMS blocks were more compatible with PMMA than was PS, but scanning electron microscopic examination of the films showed that the system was two-phase as indicated by the presence of domains of PMMA measuring approximately 50–200 nm in diameter.[12] Our own work[13] on the miscibility of PMMA with poly(α-methylstyrene-*stat*-acrylonitrile) has demonstrated that one-phase blends defined by a so-called "miscibility window" are present but that a two-phase blend of PαMS with PMMA is obtained when prepared by coprecipitation from methyl ethyl ketone (MEK). A segmental interaction parameter was estimated, from the phase boundaries of this system, to be $\chi_{\text{MS-MMA}} = 0.015$,[14] which suggests that while this pair are not too alike, limited miscibility at molecular weights of less than 15 000 might be expected on the basis of a Krause analysis.[1]

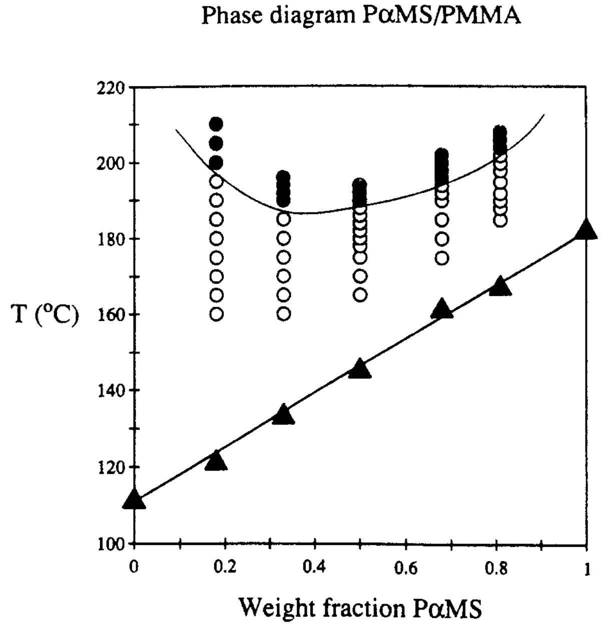

Figure 2. Phase diagram and glass transition temperatures for poly(α-methylstyrene)/poly(methyl methacrylate) blends prepared by coprecipitation from dichloromethane solutions. The LCP boundary was established as the boundary between the one-phase and two-phase blends as determined from DSC measurements: one-phase blends (○), two-phase blends (●), glass transition temperatures of the blends (▲).

Table III
Solubility Parameters (δ) for PαMS and PMMA Calculated from Various Group Additivity Methods, Compared with an Experimental Measurement (All in Units of $(\text{cal/cm}^3)^{0.5}$)

polymer	Small[15]	Hoy[15]	Askadskii[17]	Coleman–Painter[2]	expt[16]
PMMA	9.0	9.1	9.29	9.00	9.5
PαMS	8.9	9.0	9.0	9.06	9.2
$\Delta\delta$	0.1	0.1	0.29	0.06	0.3

The latter is based on the use of solubility parameters to determine the interaction parameter χ_{ij}, where

$$\chi_{ij} = \frac{V_R}{RT}(\delta_i - \delta_j)^2 \tag{1}$$

and V_R is the segmental reference volume.

The critical value χ_c is related to the degrees of polymerization r_i and r_j by

$$\chi_c = 0.5\left(\frac{1}{r_i^{0.5}} + \frac{1}{r_j^{0.5}}\right)^2 \tag{2}$$

and a one-phase system is obtained when $\chi_{ij} < \chi_c$.

As there is nothing to suggest that specific interactions exist between this pair, a comparison of the solubility parameters can be made to determine how closely these match. Values of δ, calculated from various group additivity methods,[15] are listed in Table III together with experimental measurements of δ using the maximum intrinsic viscosity method.[16] The differences, $\Delta\delta$, vary from 0.06 to 0.3, reflecting the difficulties in arriving at precise values of δ for a polymer. This range would predict that one-phase blends could be obtained for samples with molecular weights as high as 3×10^5 ($\Delta\delta = 0.06$) down to 0.15×10^5 ($\Delta\delta = 0.3$); note that the latter value obtained from experiment corresponds to our experimental χ value estimated using a different approach.[14] The sample molecular weights used here fall within this range, but similar results can be obtained if a PMMA of 5.9×10^5 is used. Hence, in this case it appears possible to force the system to adopt one phase, by selecting an appropriate method of sample preparation, which is nevertheless inherently more stable than the corresponding PS/PMMA blend as our annealing experiment has demonstrated.

Finally, attempts were made to determine whether the one-phase or the two-phase blend was closest to the thermodynamic equilibrium state. The procedure used was to anneal the two-phase blend at 150, 160, and 180 °C for 24 h and to observe if further mixing occurred to form a one-phase system. There was no evidence of any movement toward formation of a one-phase blend, although this is a difficult system to work with as the temperature range between the T_g and the phase-separation boundary is not large and the viscosity of the mixture will be high. In order to try and reduce this effect, an alternative pathway was followed. A one-phase blend was heated to 220 °C (e.g., above the phase-separation boundary) for 10 min to allow phase separation to take place and then cooled to 160 °C and held there for 24 h. Again there was no evidence of the mutual dissolution of the two components. These observations suggest either that the transformation from a two-phase to a one-phase blend at these temperatures is kinetically unfavorable or that the one-phase blend is not in thermodynamic equilibrium and is largely an artifact of the method of preparation.

This latter suggestion would point to the existence of the lower cloud point curve as only being representative of the temperatures at which chain mobility becomes sufficiently large to allow phase separation of the two components, locked into their one-phase structure, to occur. However, this may not necessarily be the case. We have observed, in work reported elsewhere,[18] that if PαMS is modified by introducing several mole percent of a hydrogen-bond donor site, then one-phase blends with PMMA can be obtained, using all the methods of blend preparation described here. The LCP curves established for these blends lie in approximately similar temperature ranges.

Thus, while one-phase PαMS/PMMA blends may not be thermodynamically stable, except when the component chain lengths are short, indications are that this system is close to the boundary between miscibility and immiscibility.

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Registry No. PαMS (homopolymer), 25014-31-7; PMMA (homopolymer), 9011-14-7; THF, 109-99-9; DCM, 75-09-2; MEK, 78-93-3; C_6H_6, 71-43-2; $C_6H_5CH_3$, 108-88-3.