

Miscibility of Some Hydroxyl-Containing Polymers with Poly(Acetonyl Methacrylate), Poly(Tetrahydropyranyl-2-methacrylate), and Poly(Cyclohexyl Methacrylate)

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SYNOPSIS

Poly(tetrahydropyranyl-2-methacrylate) (PThPMA) was found to be miscible with poly(vinyl phenol) (PVPH), poly(hydroxy ether of bisphenol A) (Phenoxy), and poly(styrene-co-allyl alcohol) (PSAA). However, poly(cyclohexyl methacrylate) (PCHMA) is immiscible with all these three hydroxyl-containing polymers. Poly(acetonyl methacrylate) (PACMA) was found to be miscible with PVPH but immiscible with Phenoxy and PSAA. Miscible PThPMA-Phenoxy blends showed lower critical solution temperature behavior.

INTRODUCTION

The formation of miscible blends is not a common phenomenon. However, miscibility can be achieved if there are some specific intermolecular interactions such as, hydrogen-bonding, ion-dipole, dipole-dipole, π -bonding, or charge transfer interactions between the two component polymers.¹⁻¹⁰ In certain copolymer blends miscibility is achieved by intramolecular repulsion effects rather than favorable intermolecular interactions.¹¹⁻¹³

In our earlier papers we have reported that poly(acetonyl methacrylate) (PACMA), poly(tetrahydropyranyl-2-methacrylate) (PThPMA), and poly(cyclohexyl methacrylate) (PCHMA) are miscible with some chlorine-containing polymers.^{14,15} We have also studied the miscibility window of the blends of PThPMA¹⁶ and PCHMA¹⁷ with poly(styrene-co-acrylonitrile) (SAN) and poly(*p*-methylstyrene-co-acrylonitrile) (*p*MSAN). We have noted that the miscibility behavior of PThPMA is quite similar to that of PCHMA even though the former contains an extra ether oxygen atom in its pendent group. We have also noted that the additional carbonyl group in the pendent group of PACMA enhances its miscibility.^{18,19} For example,

while poly(*n*-propyl methacrylate) (PnPMA) and poly(isopropyl methacrylate) (PiPMA) are immiscible with PVDF, PACMA is miscible with PVDF. In this study we report the miscibility behavior of PACMA, PThPMA, and PCHMA with three hydroxyl-containing polymers, poly(vinyl phenol) (PVPH), poly(hydroxy ether of bisphenol A) (Phenoxy), and poly(styrene-co-allyl alcohol) (PSAA). It would be interesting to compare the miscibility behavior of the three polymethacrylates to that of poly(tetrahydrofurfuryl methacrylate) (PTHFMA), which is miscible with PVPH, Phenoxy, and PSAA.^{20,21}

EXPERIMENTAL

Acetonyl methacrylate (ACMA) was prepared following the procedure reported by Ueda et al.²² ACMA was then polymerized in 2-butanone (MEK) at reflux temperature for 6 h using 0.25 wt % of α, α' -azobis(isobutyronitrile) as initiator. The polymer was obtained by precipitation of the solution in excess of methanol. It was then dried *in vacuo* at 90°C for 48 h. The number-average (\bar{M}_n) and weight-average (\bar{M}_w) molecular weights (polystyrene equivalent) of PACMA as determined by gel permeation chromatography (GPC) are 37,000 and 53,000, respectively. Tetrahydropyranyl-2-methacrylate was obtained from Polysciences and purified by fractional distillation at 83°C/2 mmHg. PThPMA was

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prepared by solution polymerization as PACMA. The \bar{M}_n and \bar{M}_w of PTHPMA are 44,000 and 65,000, respectively. PVPH with $\bar{M}_w = 1500$ –7000 was obtained from Polysciences. Phenoxy with \bar{M}_w of 28,000 and PSAA with hydroxyl content of 5.4–6.0 wt % and \bar{M}_n of 1600 were obtained from Scientific Polymer Products.

Blends of PVPH were solution-cast from MEK. All the other blends were solution-cast from tetrahydrofuran. Solvent was allowed to evaporate at room temperature. The resulting films were further dried *in vacuo* at 90°C for 3 days.

Measurements of T_g were carried out on a Perkin-Elmer DSC-4 differential scanning calorimeter (DSC), using a heating rate of 20°C/min. The initial onset of the change of slope in the DSC plot was taken as T_g . The reported T_g value 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) behavior by the method described elsewhere.¹⁵

RESULTS

PACMA–PVPH Blends

PACMA was found to be miscible with PVPH. The miscibility is ascertained on the bases of the transparency of the blends and the occurrence of a single composition-dependent T_g in each blend. The T_g composition curve is shown in Figure 1. All the blends remained transparent upon heating to 300°C. It is known that poly(*n*-propyl methacrylate) (PnPMA) and poly(isopropyl methacrylate)

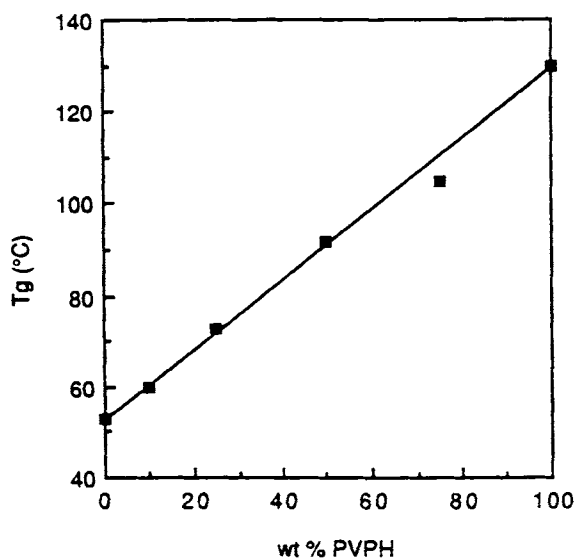


Figure 1 T_g composition curve for PACMA–PVPH blends.

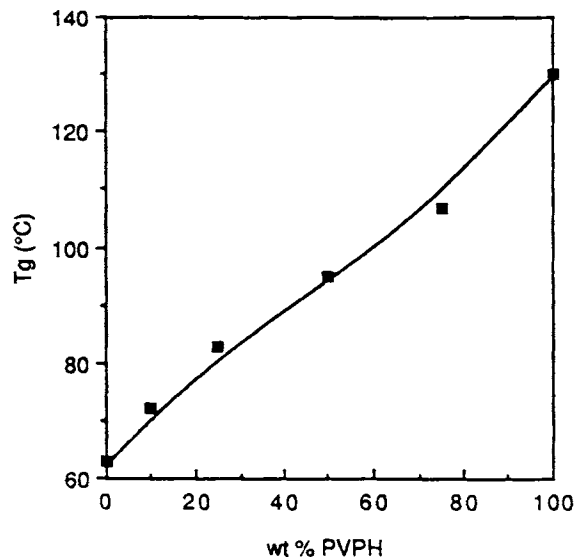


Figure 2 T_g composition curve for PTHPMA–PVPH blends.

(PiPMA) are also miscible with PVPH and the blends do not exhibit LCST behavior.²¹

PTHPMA–PVPH Blends

All the PTHPMA–PVPH blends were transparent, and each showed only one composition-dependent T_g . The T_g composition curve is shown in Figure 2. All the blends do not show LCST behavior. It is known that PTHFMA is also miscible with PVPH, and the blends do not show LCST behavior.²¹

PCHMA–PVPH Blends

All the blends were cloudy. DSC measurements revealed the existence of two glass transitions in each blend. The T_g composition curve is shown in Figure 3.

PACMA–Phenoxy Blend

All the PACMA–Phenoxy blends show optical cloudiness and two T_g 's, characteristic of an immiscible blends as shown in Figure 4. However, the lowering of the upper T_g values indicates the presence of PACMA in the Phenoxy-rich phase.

PTHPMA–Phenoxy Blends

All the blends were transparent and each blend showed a single composition-dependent T_g as shown in Figure 5, indicating its single-phase nature. All the blends showed LCST behavior upon heating, and the cloud point curve is shown in Figure 6. It is interesting to note that the phase separation induced by heating is reversible upon cooling. It is known

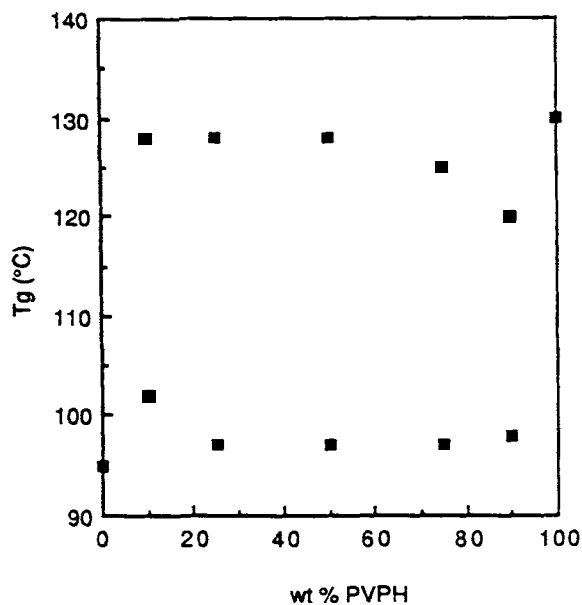


Figure 3 T_g composition curve for PCHMA-PVPH blends.

that the phase separation of many miscible blends is irreversible because of the low mobilities of the polymer chains.

PCHMA-Phenoxy Blends

The proximity of the T_g 's of PCHMA (95°C) and Phenoxy (90°C) precludes the use of conventional DSC measurements to ascertain the miscibility of the blends. However, all the blends were cloudy and remained so upon heating to 300°C. Therefore, the

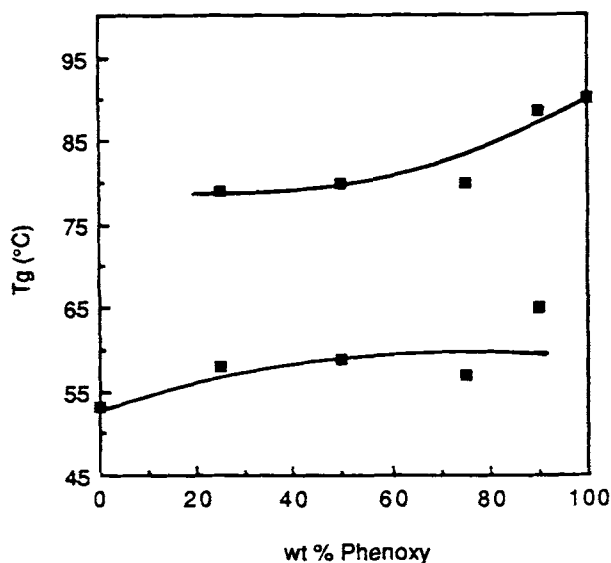


Figure 4 T_g composition curve for PACMA-Phenoxy blends.

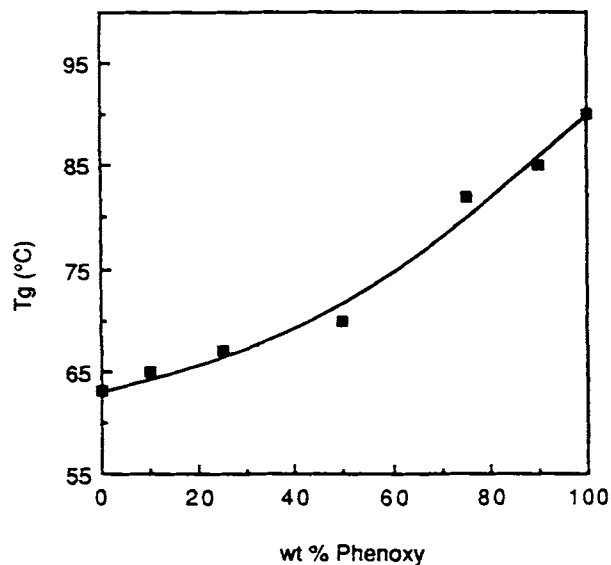


Figure 5 T_g composition curve for PTHPMA-Phenoxy blends.

PCHMA-Phenoxy blends were judged to be immiscible based on the opacity of the blends.

PACMA-PSAA Blends

All the blends were not homogeneous and cloudy. They remained so upon heating to 300°C. Because of the closeness of the T_g 's of PACMA (53°C) and PSAA (56°C), conventional DSC measurements cannot resolve the two T_g 's of a mixture of PACMA and PSAA. Nevertheless, the appearance of PACMA-PSAA blends suggests that PACMA is immiscible with PCHMA.

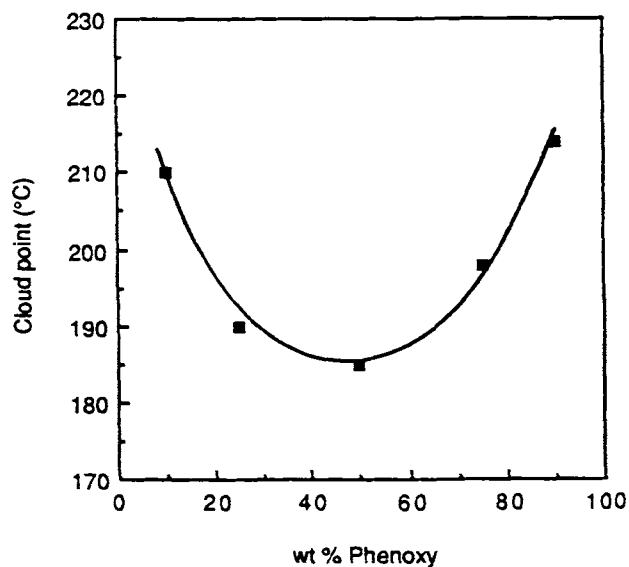


Figure 6 Cloud point curve for PTHPMA-Phenoxy blends.

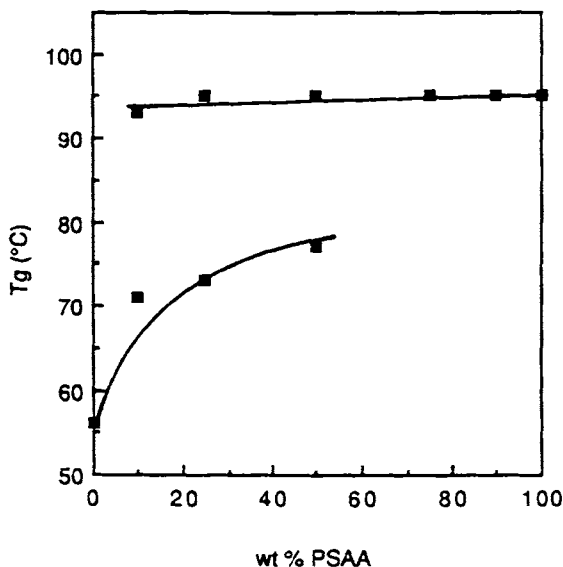


Figure 7 T_g composition curve for PCHMA-PSAA blends.

PTHPMA-PSAA Blends

The closeness of the T_g 's of PTHPMA (63°C) and PSAA precludes the use of conventional T_g measurement to ascertain the miscibility of the blends. Recently, annealing process has been successfully utilized to investigate the miscibility of blends containing two polymers with similar T_g values.²³⁻²⁵ Unfortunately, the enthalpy relaxation peaks of annealed PTHPMA and PSAA occur at about the same temperature, making it difficult to ascertain the miscibility of the annealed blends. However, all the blends were transparent and did not show LCST behavior even being heated to 300°C. The optical clarity of the blends can be taken to indicate miscibility. Although the refractive index of PTHPMA is not available, its value is expected to be close to that of PCHMA (1.5066)²⁶ based on the transparency of the immiscible PTHPMA-PCHMA blends.²⁷ This value is significantly smaller than that of PSAA (1.580).²⁰ The transparency, therefore, does not arise from the matching of refractive indices of PTHPMA and PSAA.

PCHMA-PSAA Blends

All the blends were cloudy. Blends containing 10, 25, and 50 wt % of PSAA show two T_g 's, character-

istic of an immiscible blend. On the other hand, only the upper glass transition was observed for the blends containing 75 and 90 wt % of PSAA. The lower ones were difficult to detect possibly due to the small amount of the PSAA-rich phase in the blends. The T_g composition curve is shown in Figure 7. PCHMA is immiscible with PSAA.

DISCUSSION

Table I summarizes the miscibility behavior of various blends. The miscibility behavior of PTHPMA with hydroxyl-containing polymers is similar to that of PTHFMA in which both polymers are miscible with PVPH, Phenoxy, and PSAA. On the other hand, PCHMA is immiscible with all the three hydroxyl-containing polymers.

Coleman et al.²⁸⁻³⁶ have used Fourier transform infrared spectroscopy (FTIR) to study a variety of blends involving strong hydrogen-bonding interactions. They have developed a theory to calculate the free energy of mixing, which is considered as a balance between unfavorable dispersion forces and favorable hydrogen-bonding interactions.^{34,35} If the contribution from the hydrogen-bonding term dominates, a miscible blend system is resulted.

Lower members of polyacrylates and polymethacrylates such as poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(methyl methacrylate) (PMMA), and poly(ethyl methacrylate) (PEMA) are miscible with PVPH.^{21,28,29} FTIR studies have shown that the carbonyl groups of the polyacrylates and polymethacrylates are hydrogen bonded to the hydroxyl groups of PVPH.^{28,29} Higher members of the polyacrylates and polymethacrylates are immiscible with PVPH, as there are fewer carbonyl groups per unit volume to undergo hydrogen bonding with PVPH. The immiscibility of PCHMA with PVPH also arises from the same effect. The fact that PTHFMA and PTHPMA but not PCHMA form miscible blends with hydroxyl-containing polymers indicates the importance of ether oxygen in achieving miscibility. Polymers containing ether oxygen atoms are miscible with other polymers. For example, poly(vinyl methyl ether) (PVME) is miscible with both PVPH³⁰ and Phenoxy.³¹ FTIR studies show the existence of hydrogen bonding between

Table I Miscibility Behavior of Blends of Hydroxyl-Containing Polymers

	PACMA	PTHPMA	PCHMA	PTHFMA
PVPH	Miscible	Miscible	Immiscible	Miscible ²¹
Phenoxy	Immiscible	Miscible	Immiscible	Miscible ²⁰
PSAA	Immiscible	Miscible	Immiscible	Miscible ²⁰

hydroxyl groups and the ether oxygen of PVME. In the present case, although the numbers of carbonyl groups per unit volume for PTHPMA and PTHFMA are about the same as that for PCHMA, the ether oxygen atoms provide additional sites for interaction with the hydroxyl groups of PVPH to form miscible blends.

The miscibility behavior of PACMA is rather interesting. One would expect the presence of an additional carbonyl group in the PACMA segment would be useful in forming favorable interaction with the hydroxyl group. Yet, PACMA is fully miscible with PVPH only, although the T_g values do indicate some degree of mixing between PACMA with Phenoxy and PSAA. Based on the frequency shift of the hydrogen-bonded hydroxyl band, Moskala and Coleman³⁰ concluded that poly(vinyl alkyl ether) interacts more strongly with PVPH than with Phenoxy. The present study also implies that PACMA interacts more strongly with PVPH than with Phenoxy such that PACMA is miscible with PVPH. Another interesting implication from the present study is that the interaction between ether oxygen and hydroxyl group is stronger than that between carbonyl group and hydroxyl group.

Note added in proof:

We have recently found that the monomeric tetrahydropyranyl-2-methacrylate used in the study is actually tetrahydropyranyl-2-methyl methacrylate. Therefore, the poly (tetrahydropyranyl-2-methacrylate) mentioned in the paper should be changed to poly(tetrahydropyranyl-2-methyl methacrylate). We thank Dr. W. R. Hertler for his advice on the identification of the monomer.

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