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Miscible blends of poly(N-vinyl pyrrolidone) with some hydroxyl-containing polymers

S.H. Goh and K.S. Siow

Department of Chemistry, National University of Singapore, Singapore 0511,
Republic of Singapore

Summary

Poly(N-vinyl pyrrolidone) (PVPr) forms miscible binary blends with poly(hydroxyethyl methacrylate), poly(hydroxypropyl methacrylate) and two styrene/allyl alcohol copolymers, as shown by their glass transition behavior. However, PVPr is immiscible with poly(ethyl methacrylate), poly(n-propyl methacrylate) and polystyrene. The results indicate the importance of hydroxyl groups in achieving miscibility.

Introduction

The blending of two dissimilar polymers usually results in the formation of an immiscible blend unless there are some specific interactions between them (1). These interactions include hydrogen-bonding, dipole-dipole and charge-transfer interactions. There are many examples of miscible polymer blends involving a carbonyl-containing polymer and a hydroxyl-containing polymer (2,3). The existence of hydrogen-bonding interactions between the carbonyl groups and hydroxyl groups has been confirmed by Fourier-transform infrared spectroscopy (2-4). The miscibility of a polymer can often be enhanced through specific interactions by incorporating suitable functional groups. For example, copolymerization of styrene with *p*-(hexafluoro-2-hydroxylpropyl)styrene gives polystyrene containing hydroxyl groups (2). While polystyrene is immiscible with poly(n-butyl methacrylate) (PnBMA), the incorporation of 1.8% of the hydroxyl moiety to polystyrene is sufficient to achieve miscibility with PnBMA.

There are several reports on the miscibility of poly(N-vinyl pyrrolidone) (PVPr). PVPr, a carbonyl-containing polymer, is miscible with hydroxyl-containing polymers such as poly(vinyl phenol) (4), poly(hydroxy ether of bisphenol-A) (5) and vinyl acetate/vinyl alcohol copolymers (6). PVPr is also miscible with poly(vinylidene fluoride) (7-10). In this communication, we report the miscibility of PVPr with some hydroxyl-containing polymers.

Experimental

The following commercial polymers were used: PVPr

(Scientific Polymer Products, Inc., M_w = 40,000), poly(hydroxyethyl methacrylate) (PHEMA) (Polysciences, Inc., M_w = 127,000), poly(hydroxypropyl methacrylate) (PHPMA) (Scientific Polymer Products, Inc., $[\eta]$ = 0.31 dL/g in tetrahydrofuran at 30°C), poly(ethyl methacrylate) (PEMA) (DuPont Elvacite 2042, M_w = 310,000), poly(n-propyl methacrylate) (PnPMA) (Scientific Polymer Products, M_w = 175,000) and polystyrene (PS) (BDH Chemicals, M_w = 150,000).

Two styrene/allyl alcohol (SAA) copolymers were obtained from Scientific Polymer Products, Inc. The one with a hydroxyl content of 5.4-6.0% is designated as SAAL; its M_w is 1,600. The other with a hydroxyl content of 7.3-8.0% is designated as SAAH; its M_w is 1,700.

Blends of PVPr with PHEMA and PHPMA were cast from dimethylformamide (DMF). The initial evaporation of DMF was done on a hot-plate maintained at 100°C. Other blends were cast from dichloromethane (DCM) at room temperature. Solution was placed in a desiccator with the lid slightly open to let DCM evaporate slowly. All the blends were then dried in vacuo at 90° for five days.

A Perkin-Elmer DSC-4 differential scanning calorimter was used to measure the glass transition temperatures (T_g) of various samples using a heating rate of 20°C/min. Since PVPr is hygroscopic, it may absorb moisture during storage. To remove moisture, the sample was first heated to 170°C and kept at that temperature of 5 min. The sample was then scanned several times to check the reproducibility of the T_g values. The initial onset of the change of slope in the DSC curve was taken as T_g.

The miscible blends were examined for the existence of lower critical solution temperature (LCST) behavior using the method described previously (11).

Results and Discussion

PVPr/PHEMA and PVPr/PHPMA blends

All the binary blends of PVPr with PHEMA and PHPMA were transparent and remained so upon heating to 300°C, the limit of the melting-point apparatus. The transparency of PVPr/PHEMA blends is likely a result of matching refractive indices of PVPr (n = 1.514 at 20°C) (12) and PHEMA (n = 1.515 at 20°C) (12). The miscibility of the blends was ascertained by T_g measurements. Each blend showed only one composition-dependent T_g. Therefore, PVPr is miscible with both PHEMA and PHPMA. Al-Issa and co-workers (12) have earlier reported that a PVPr/PHEMA (1:3) blend has a T_g value of 113°C which is in good agreement with our value of 116°C.The T_g-composition curves of the two blend systems are shown in Fig. 1. The T_gs of PVPr/PHEMA blends are a linear function of the composition of the blend, but the T_gs of PVPr/PHPMA blends show negative deviations from linear additivity rule. Both the curves can be described by the Gordon-Taylor equation (13)

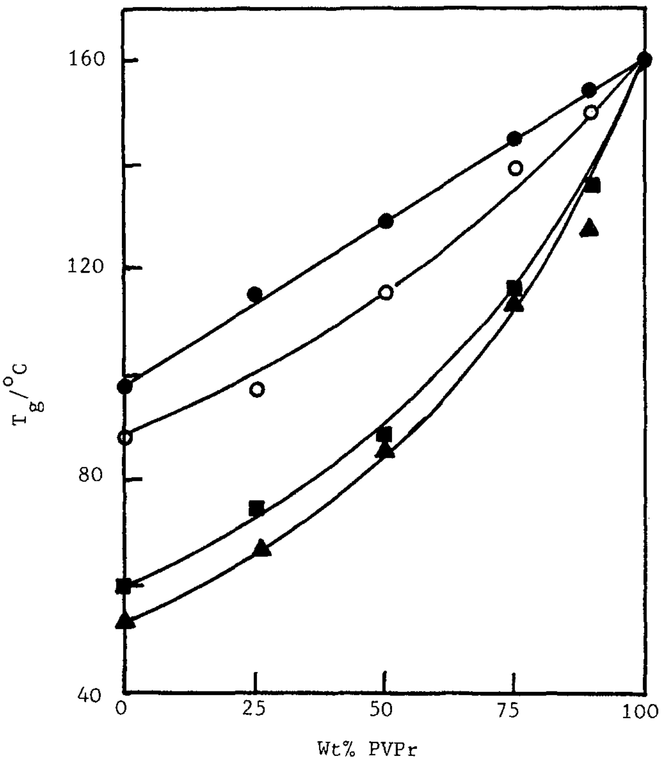

Fig. 1. T_g-composition curves of (●) PVPr/PHEMA, (○) PVPr/PHPMA, (■) PVPr/SAAL and (▲) PVPr/SAAH blends.

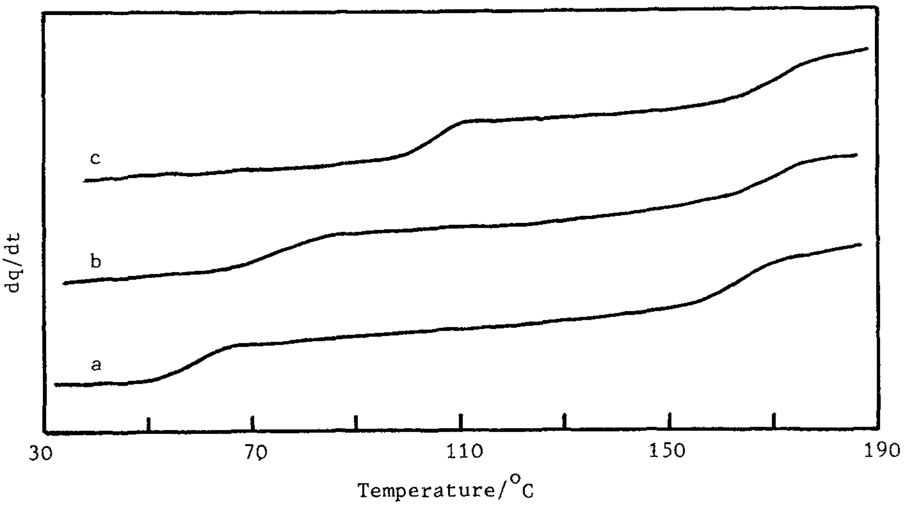

Fig. 2. DSC curves of 1:1 blends of (a) PVPr/PnPMA, (b) PVPr/PEMA and (c) PVPr/PS.

$$T_g(\text{blend}) = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)$$

where T_{gi} is the T_g of polymer i, w_i is the weight fraction of polymer i in the blend and k is an adjustable parameter. The linearlity of the T_g-composition curve for PVPr/PHEMA blends implies that k is unity. The curve for PVPr/PHPMA blends in Fig. 1 was drawn using a k value of 0.65.

The binary blends of PVPr with PEMA and with PnPMA showed gross phase separation. Fig. 2 shows the DSC curves of 1:1 blends of PVPr/PEMA and PVPr/PnPMA. The appearance of two T_g in each blend confirms the immiscibility of the blends. Therefore, while PVPr is immiscible with PEMA and with PnPMA, it is miscible with PHEMA and with PHPMA. This illustrates the importance of hydroxyl groups in achieving miscibility.

PVPr/SAA blends

Blends of PVPr with SAAL and SAAH were transparent and remained so upon heating to 300°C. Each of the blends showed one composition-dependent T_g. Therefore, PVPr is miscible with the two SAA copolymers. The T_g-composition curves of the two blends systems are also shown in Fig. 1. The two curves were drawn according to the Gordon-Taylor equation using a k value of 0.45 in both cases.

PVPr/PS blends were heterogeneous. The DSC curve of a PVPr/PS (1:1) blend reveals two glass transitions as shown in Fig. 2. Thus, PVPr is immiscible with PS. The results once again demonstrate the important role of the hydroxyl groups in achieving miscibility.

SAA is miscible with many polyesters (14-16) and the existence of hydrogen-bonding interaction in SAA/ polycaprolactone blends has been confirmed by Fourier-transform infrared spectroscopy (16). For PVPr/SAA blends, in addition to the hydrogen-bonding interaction, other factors may also contribute to the observed miscibility. Firstly, the combinatorial entropy of mixing favors the miscibility because of the low molecular weights of the SAA samples. Secondly, being a homopolymer/ copolymer blend, any repulsive intramolecular interaction between styrene and allyl alcohol segments also favors the formation of a miscible blend as suggested by the binary interaction model (17-19).

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