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Miscibility of poly(4-vinyl pyridine) with polysulfone and carboxylated polysulfone

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Summary

The miscibility of poly(4-vinyl pyridine) (P4Py) with polysulfone (PSf) and four carboxylated polysulfone samples (CPSf) was studied by differential scanning calorimetry. P4Py is immiscible with PSf but is miscible with CPSf having degrees of carboxylation of 0.43, 0.93, 1.38 and 1.93. In some cases, P4Py and CPSf form complexes with varying stoichiometries. A high degree of carboxylation of CPSf and a high CPSf content in the feed favor complexation.

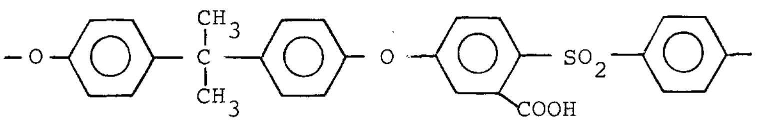
Introduction

Two dissimilar polymers are likely to be miscible with each other if there are some intermolecular interactions between them (1). Polymers containing proton-donating groups can be miscible with polymers containing proton-accepting groups. For example, poly(p-vinyl phenol) (PVPh), an acidic polymer, is miscible with a basic polymer poly(N-vinyl-2-pyrrolidone) (PVP) through hydrogen-bonding interactions (2). In certain cases where intermolecular interactions are particularly strong, polymer complexes are formed. Some recently reported polymer complexes include poly(methacrylic acid)/PVP (3), PVPh/poly(2-vinyl pyridine) (P2Py) (4), PVPh/poly(N,N-dimethylacrylamide) (PDMA) (5), PVPh/poly(ethyl oxazoline) (PEOx) (5), PEOx/poly(acrylic acid) (PAA) (6), PAA/poly(vinyl methyl ether) (7) and P2Py/poly(2-acrylamido-2-methylpropanesulfonic acid) (8) complexes. In some cases, the complex has a simple 1:1 stoichiometry, irrespective of feed composition (4,7). In other cases, the stoichiometry of the complex depends on the feed composition (5,6).

We have earlier reported the miscibility of polysulfone (PSf) and carboxylated polysulfone (CPSf) with PEOx (9) and PVP (10). PVP is miscible with PSf and CPSf. On the other hand, PEOx is immiscible with PSf and CPSf having a degree of carboxylation of 0.43, but is miscible with CPSf having degrees of carboxylation of 0.93 or more. In this communication, we report the miscibility of poly(4-vinyl pyridine) (P4Py) with PSf and CPSf. It will be shown that P4Py and CPSf can form polymer complexes, depending on the degree of carboxylation of CPSf and the feed composition.

Experimental

P4Py with a weight-average molecular weight of 60,000 was obtained from Polysciences, Inc.; PSf with a number-average molecular weight of 35,000 was obtained from Amoco Performance Products (Udel P-3500). PSf was carboxylated to various extents following the procedures by Guiver and co-workers (11). Four CPSf samples with degrees of carboxylation of 0.43, 0.93, 1.38 and 1.93 were used in this study. The value refers to the average number of carboxylic groups per repeating unit of PSf. In the following discussion, the number after CPSf denotes the degree of carboxylation. The repeating unit of CPSf1.00 is depicted as follows:



All the blends were prepared by solution casting from dimethylformamide (DMF). Initial removal of solvent was done on a hot plate at 90°C and the blends were further dried in vacuo at 100°C for 5 days. In some cases, the mixing of the DMF solutions of P4Py and CPSf resulted in the formation of gelatinous precipitates. The precipitates (i.e. the polymer complexes) were centrifuged, separated, washed with DMF and finally dried in vacuo at 100°C for 5 days. The supernatant liquids were similarly dried to obtain the blends. The compositions of complexes and blends were determined by elemental analysis for nitrogen.

The glass transition temperatures (T_g) of various samples were measured with a Perkin-Elmer DSC-2 differential scanning calorimeter using a heating rate of 20°C/min. Each sample was scanned between 50 and 240°C for several times and the sample was kept at 240°C for 10 min before cooling. The T_g was taken as the initial onset of the change of slope in the DSC curve.

Results and Discussion

All the P4Py/PSf blends were cloudy. DSC measurements revealed the existence of two T_gs in each blend, indicating the heterogeneous nature of the blends. The T_g-composition curve is shown in Fig. 1(a). The upper T_g values are substantially lower than that of PSf and the lower T_g values are higher than that of P4Py. Thus, the two polymers have a limited miscibility with each other.

All the P4Py/CPSf0.43 blends were clear. The single-phase nature of the blends was further confirmed by DSC measurements which showed a single T_g for each blend. The T_g-composition curve is shown in Fig. 1(b). Thus, the incorporation of carboxylic acid groups into PSf enhances its miscibility with P4Py.

P4Py/CPSf0.93 blends containing 10, 25, 50 and 75 wt% of CPSf were clear. DSC measurements also confirmed the single-phase nature of the blends. On the other hand, for a feed composition of 90 wt% of CPSf0.93, complexation occurred. The complex contains 27.7 wt% of CPSf0.93, which corresponds to an acid:base ratio of 1:1.94. The clear blend obtained from the supernatant liquid contains 85.1 wt% of CPSf0.93. Both the complex and the blend are single-phase materials as shown by their T_g behavior. The T_g-composition curve is shown in Fig. 1(c). The complex has a high T_g value. The high T_g values commonly observed for polymer complexes have been attributed to extensive hydrogen bondings in the complexes which act as physical crosslinks (5-7).

P4Py/CPSf1.38 blends containing 10, 25 and 50 wt% of CPSf1.38 were clear and judged to be miscible based on the single T_g criterion. However, complexation occurred when the feed contained 75 wt% of CPSf1.38. The complex contains 48.5 wt% of CPSf1.38, corresponding to an acid:base ratio of 1:3.7. Likewise, P4Py and CPSf1.38 formed complex when the feed contained 90 wt% of CPSf1.38. In this case, the CPSf content in the complex is 61.6 wt%, corresponding to an acid:base ratio of 1:2.2. Thus, the stoichiometry of the complex depends on the feed composition. The dependence of the stoichiometry of complex on feed composition has been observed for PVPh/PDMA (5), PVPh/PEOx (5) PVPh/PVP, and PEOx/PAA (6) complexes. However, there is no suitable explanation to account for the observation. The two clear blends obtained from the supernatant liquids contain 80.4 and 81.0 wt% CPSf1.38. The T_g-composition curve for this system is shown in Fig. 1(d).

CPSf1.93, the polysulfone with the highest degree of carboxylation, formed complexes with P4Py when the feed contained 50, 75 and 90 wt% of CPSf1.93. The CPSf contents of the three complexes are 44.0, 55.0 and 59.0 wt%, respectively. The corresponding acid:base ratios are 1:3.3, 1:2.1 and 1:1.8, respectively. As in the case of P4Py/CPSf1.38 system, the acid:base ratio of P4Py/CPSf1.93 complex increases with increasing CPSf content in the feed. The CPSf contents of the three blends obtained from the supernatant liquids are 61.1, 80.7 and 82.7 wt%, respectively. The T_g-composition curve is shown in Fig. 1(e).

The miscibility behavior of various blend systems is summarized in Table 1. Apparently, complexation between P4Py and CPSf is favored when the CPSf content in the feed and the degree of carboxylation of CPSf are high. It is of interest to note the effect of feed composition on complexation. It has been reported that PVPh forms complexes with PDMA in methanol when the feed contains 30, 50, 70 or 90 wt% of PVPh, but complex is not formed when the feed contains 10 wt% of PVPh (5). Complex formation generally exemplifies strong intermolecular interactions between two polymers. We have earlier reported that CPSf is miscible with PEOx and PVP, but complexation does not occur. Thus, the complexation between CPSf and P4Py may be taken to indicate that CPSf interacts more

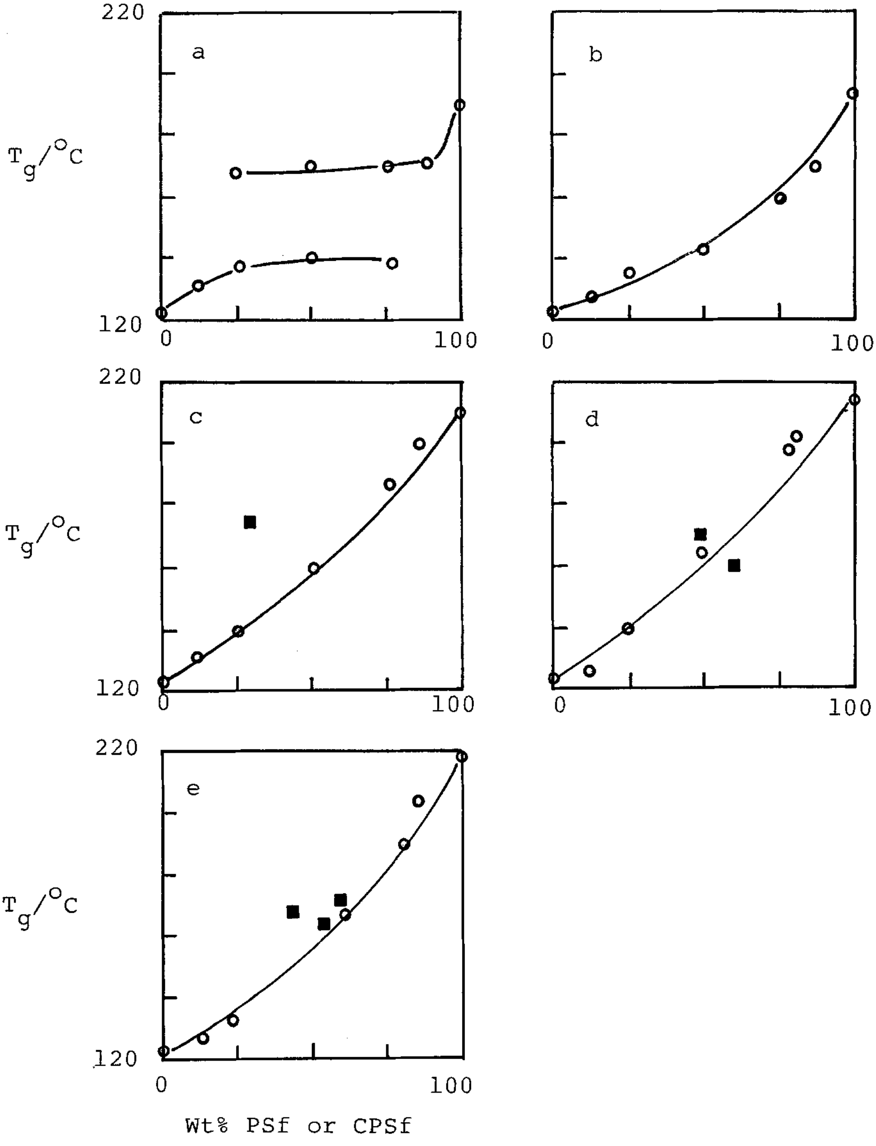


Fig. 1. T_g-composition curves of blends. (a) P4Py/PSf; (b) P4Py/CPSf0.43; (c) P4Py/CPSf0.93; (d) P4Py/CPSf1.38; (e) P4Py/CPSf1.93. (o) blend; (■) complex.

strongly with P4Py as compared with PEOx and PVP.

Table 1. Miscibility behavior of blends					
	Wt% of PSf or CPSf in feed				
	10	25	50	75	90
PSf	I	I	I	I	I
CPSf0.43	M	M	M	M	M
CPSf0.93	M	M	M	M	C
CPSf1.38	M	M	M	C	C
CPSf1.90	M	M	C	C	C
I: immiscible; M: miscible; C: complex formation					

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