Study of the compatibility of blends of polymers and copolymers containing styrene, 4-hydroxystyrene and 4-vinylpyridine

Marina Vivas de Meftahi* and Jean M. J. Fréchet*†‡
* *Department of Chemistry, University of Ottawa, Ottawa, Ontario, K1N 9B4, Canada,*
and † *Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York,*
14853-1301, USA
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Differential scanning calorimetry was used to show that poly(4-vinylpyridine) is incompatible with polystyrene but compatible with poly(4-hydroxystyrene) over the entire range of composition. Compatibility between poly(4-vinylpyridine) and styrene-rich copolymers is achieved by introducing into the copolymers reactive groups which are able to complex with poly(4-vinylpyridine) through hydrogen bonding. For example, it was found that poly(4-vinylpyridine) is compatible with a copoly(styrene-4-hydroxystyrene) containing 50 mol% of 4-hydroxystyrene units over the entire range of blend composition; however, if the styrene copolymer contains only 20–30 mol% of 4-hydroxystyrene units, compatibility is only achieved for blends which are rich in poly(4-vinylpyridine). Similarly, miscibility between poly(4-hydroxystyrene) and polystyrene, which are incompatible over the entire range of composition, is only achieved if polystyrene is modified by incorporation of large amounts of (4-vinylpyridine) units. Hence, compatibility is achieved for poly(4-hydroxystyrene) and a copoly(styrene-4-vinylpyridine) containing 50 mol% of 4-vinylpyridine units. But a similar copolymer containing only 20 mol% of 4-vinylpyridine does not form a compatible blend with poly(4-hydroxystyrene). These results confirm that for such dissimilar polymers compatibility can only be achieved through cumulative interactions of added functionalities.

(Keywords: poly(4-hydroxystyrene); poly(4-vinylpyridine); polystyrene; blend; compatibility; polymer–polymer interactions; hydrogen bonding)

INTRODUCTION

Our interest in functional polymers which can be used as speciality materials in a variety of applications from reagents[1] to photoresists[2] has led us to prepare a number of polymer systems containing a variety of reactive functional groups. Of particular interest are materials which contain pendant phenolic[3] or pyridine[4] groups. Though it is possible to prepare copolymers containing these functionalities, it would be desirable for some applications to blend more readily accessibly polymers or copolymers containing such reactive groups.

Polymer compatibility has been the topic of numerous recent studies. In general, thermodynamic considerations suggest that the blending of polymeric species, unlike that of low molecular weight materials, is a difficult task[5,6]. Thus it can be expected that unless strong interactions are present in the two polymers being mixed, the enthalpy of mixing will be positive or near zero while the entropy of mixing will only make a small or negligible contribution to the free energy of the process. Approaches to the blending of polymers have therefore focussed on systems where strong interactions of functional groups result in a negative enthalpy for the mixing process.

Such strong interactions resulting in the formation of compatible blends have been achieved in a variety of systems including, for example, those based on ionomeric species[7], donor–acceptor complexes[8], or hydrogen bonding[9]. The modification of polystyrene and poly(ethyl acrylate) through the respective introduction of as little as 5% of sulphonic acid and 4-vinylpyridine groups led to compatible blends[7,10] due to the formation of strong electrostatic interactions between the oppositely charged copolymers. In contrast, with weaker electron donor–acceptor interactions at least 25% functionalization with carbazoyl and 3,5-dinitrobenzoyl pendant groups was required to blend poly(2,6-dimethyl-1,4-phenylene oxide) with poly(epichlorohydrin)[8]. Finally, polymer miscibility studies based on hydrogen-bonding interactions have shown that improvements in compatibility are found for very small percentages of added reactive functionalities while full compatibilization of dissimilar polymers may require very large degrees of incorporation of hydrogen-bonding groups[9,11].

In this study we report on the compatibility of a variety of polymers and copolymers containing styrene, 4-hydroxystyrene and 4-vinylpyridine units.

EXPERIMENTAL

General

Infra-red spectra were recorded on a Nicolet 10-DX FT-IR spectrometer. N.m.r. data were obtained on a Varian XL 300 in $CDCl_3$ or d_6-DMSO; n.m.r. data are reported as δ values in ppm from TMS. D.s.c. measurements were performed on a Mettler DSC 20. Molecular weights were obtained by osmometry (Wescan membrane osmometer), g.p.c. (Waters 150 with five

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‡ To whom correspondence should be addressed

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microstyragel columns, polystyrene calibration) or viscometry as appropriate.

Preparation of poly(4-vinylpyridine)

Polymerization was carried out in 50% (w/w) toluene at 75°C and under nitrogen atmosphere for 7 h. AIBN was used as radical initiator and its concentration was 1% (w/w) with respect to the monomer. Once the polymerization was complete, the polymer was dissolved in methanol and precipitated into ethyl acetate. The filtered polymer was dried *in vacuo* first overnight at room temperature and then for 5 h at 50°C. The polymer has a viscosity average molecular weight $M_v = 46\,700$ as calculated from published data[14]. Its n.m.r. spectrum exhibits broad resonances centred at 1.47 (aliphatic 3H); 6.37 (aromatic 2H); 8.30 (aromatic 2H). The i.r. spectrum shows bands at 1596.2 cm^{-1} (C=N stretch in ring) and 1556.7 cm^{-1} (C=C stretch in ring).

Copoly(styrene-4-vinylpyridine)

Copolymers containing 20 and 50 mol% 4-vinylpyridine were prepared as described above. The copolymer containing 20 mol% 4-vinylpyridine was precipitated into methanol from a toluene solution, while the 1:1 copolymer was precipitated from THF into petroleum ether. The filtered copolymers were dried *in vacuo* first overnight at room temperature and then for 5 h at 50°C. The molecular sizes of the copolymers were estimated by g.p.c. using polystyrene calibration.

The n.m.r. spectra of both copolymers exhibit broad resonances centred at 1.44 (aliphatic backbone H); 6.30 (aromatic); 6.94 (aromatic) and 8.14 (aromatic). The n.m.r. integration data are in agreement with the expected compositions of the copolymers.

Preparation of copoly(styrene-4-hydroxystyrene)

In order to avoid the problems which plague polymerizations of 4-hydroxystyrene[15], copolymers containing 80, 70 and 50 mol% styrene were prepared in a two-step procedure involving first the copolymerization of styrene and 4-tert-butyloxycarbonyloxystyrene[3] followed by removal of the t-butyloxycarbonyl (BOC) groups by acidolysis.

Preparation of copoly(styrene-4-tert-butyloxycarbonyloxystyrene). The copolymers were prepared as described above using 80, 70 and 50 mol% styrene with 1% AIBN as initiator. After polymerization the copolymers were precipitated into methanol from a toluene solution. The white copolymers were dried under vacuum, first overnight at room temperature, and then for 5 h at 60°C. Molecular sizes were determined by g.p.c. measurements on the copolymers containing the t-BOC protecting groups. Previous data[3] on such polymers has shown that polystyrene calibration is directly applicable within a few per cent. Thus the copolymer containing 80% styrene had $M_n = 24\,000$, $M_w = 44\,000$; the copolymer containing 70% styrene had $M_n = 18\,700$, $M_w = 44\,500$ and the copolymer containing 50% styrene had $M_n = 23\,500$, $M_w = 45\,000$.

Their ^{1}H n.m.r. spectra included a sharp singlet at 1.48 (t-butyl) and broad resonances centred near 1.6 (aliphatic backbone), 6.4 and 6.9 (aromatic). The n.m.r. integration data are in agreement with the composition of the copolymers. The i.r. spectra showed a large carbonate C=O band at 1758 cm^{-1} and C–O bands at 1146.8 and 1277 cm^{-1}.

Removal of t-BOC protecting groups. In a typical reaction, about 4 g of the copolymers were dissolved in 20 ml of dichloromethane and 15 ml of trifluoroacetic acid were added. An evolution of gas was observed and the reaction mixture was stirred for 4 h. The copolymers were recovered by solvent evaporation and precipitation into petroleum ether from THF solution. The filtered copolymers were dried under vacuum for 5–6 h at 65°C. The n.m.r. spectra of these copoly(styrene-4-hydroxystyrene)s exhibit broad resonances centred near 1.5 (aliphatic backbone); 6.54 and 7.08 (aromatic) and 9.02 (OH group). The n.m.r. integration data are in agreement with the expected compositions. The i.r. spectra showed no remaining carbonate band at 1758 cm^{-1} and large new bands were seen at 3532 and 3400 cm^{-1} corresponding to free and hydrogen-bonded hydroxyl group, as well as C–O bands at 1170.9 and 1225 cm^{-1}.

Poly(4-hydroxystyrene) was obtained from Maruzen Oil Co. (resin PHM) and was purified by reprecipitation into water from a methanol solution. The polymer is dried under vacuum for 48 h at room temperature and then for 5 h at 50°C. Molecular size as measured by g.p.c. with polystyrene calibration indicates $M_n = 4400$ and $M_w = 9500$.

RESULTS AND DISCUSSION

Though we have prepared earlier high molecular weight poly(4-hydroxystyrene)[3] it appeared more useful to focus this study on commercially available poly(4-hydroxystyrene). As the materials which are available from Maruzen Oil Co. generally have fairly low molecular weights and broad molecular weight distributions, all the polymers and copolymers used in this study (*Figure 1*) also had relatively low molecular weights. Molecular weight data as well as glass transition temperatures (T_g) for the various polymers and copolymers are shown in *Table 1.*

In order to avoid the premature formation of hydrogen bonds which might interfere in the blend equilibration process solutions were made using a solvent which is able to interact with the hydrogen-bonding components of the mixtures, and then is removed gradually from the mixtures by a slow evaporation process during which equilibration is possible. Hence, the polymer blends were prepared by dissolving both components in pyridine, mixing their pyridine solutions in appropriate ratio, then

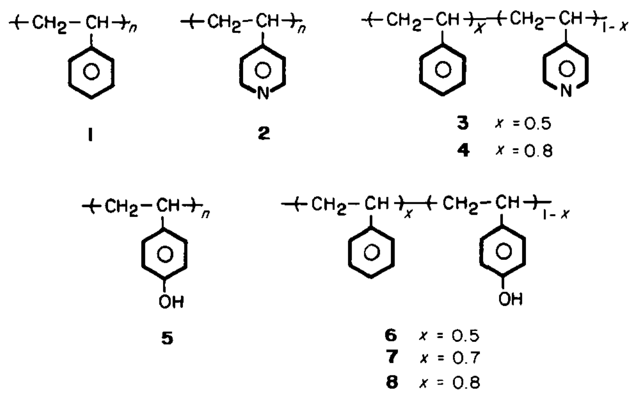

Figure 1 Stuctures of the various polymers and copolymers

Table 1 Composition and characteristics of the various polymers

	Composition (mol%)			G.p.c. molecular weight			
Polymer	Styrene	4-vinylpyridine	4-hydroxystyrene	M_n (10^{-3})	(M_w (10^{-3})	M_w/M_n	T_g (°C)[a]
1	100	–	–	4.0	31.4	7.9	88
2	–	100	–	–	46.7[b]		155
3	50	50	–	23.6	45.2	1.9	118
4	80	20	–	21.7	42.9	2.0	114
5	–	–	100	4.4	9.5	2.2	138
6	50	–	50	16.2	31.5	1.9	125
7	70	–	30	14.6	34.9	2.4	120
8	80	–	20	26.7	46.0	1.7	118

[a] Measured by d.s.c.

[b] Polymer **2** was insoluble in THF. The molecular weight was obtained by viscosity measurement using parameters given in ref. 14

Table 2 Glass transition temperatures of mixtures of polystyrene with poly(4-vinylpyridine) and various copoly(styrene-4-vinylpyridine), and of poly(4-vinylpyridine) with various copoly(styrene-4-vinylpyridine)s

Composition of blend			
Polymer mix	% weight ratio	T_{g_1} (°C)	T_{g_2} (°C)
1+**2**	26:74	92	149
1+**2**	50:50	90	147
1+**2**	77:23	88	148
1+**3**	50:50	70	104
1+**4**	50:50	84[a]	–
2+**3**	50:50	128	148
2+**4**	50:50	115	140

[a] A single T_g was observed for this blend

Table 3 Glass transition temperatures of mixtures of polystyrene with poly(4-hydroxystyrene) and various copoly(styrene-4-hydroxystyrene)s, and of mixtures of poly(4-hydroxystyrene) with various copoly(styrene-4-hydroxystyrene)s

Composition of blend			
Polymer mix	% weight ratio	T_{g_1} (°C)	T_{g_2} (°C)
1+**5**	64:36	86	138
1+**5**	57:43	83	127
1+**5**	23:77	85	119
1+**5**	15:85	83	130
1+**6**	50:50	73	122
1+**7**	50:50	78	106
5+**6**	50:50	126	146
5+**7**	50:50	118	145

Conditions for d.s.c. measurements: first scan from 35 to 220°C at 10°C min^{-1}, followed by slow cooling to room temperature (20–30 min) and a second scan from 35 to 250°C at 20°C min^{-1}. All experiments are done under nitrogen atmosphere

evaporating the pyridine solvent at atmospheric pressure until a dry film is obtained. Final solvent removal is then effected under vacuo. For d.s.c. measurements, samples weighing 5–10 mg were placed in standard aluminium pans and these were closed with a pierced lid. To reduce the possibility of solvent interference in the d.s.c. measurements, all blends were pre-heated in the d.s.c. cell under nitrogen to a temperature of 220 or 250°C at 10°C min^{-1} then cooled slowly prior to T_g measurements which were obtained using a rate of 20°C min^{-1}. In all cases T_g was taken as the mid-point of the heat capacity step-change in the glass transition measurement.

Blends based on polystyrene, poly(4-vinylpyridine) and various copoly(styrene-4-vinylpyridine)s

The results obtained in d.s.c. measurements on these polymer blends are reported in *Table 2*. These data show clearly distinct values for the components of the blend indicating that polystyrene **1** is incompatible with poly(4-vinylpyridine), **2**. However, in a 1:1 mix, polystyrene appears to be compatible with copolymer **4** which contains 80% styrene and 20% 4-vinylpyridine while incompatibility is again observed if the percentage of 4-vinylpyridine is increased to 50% as in structure **3**. Similarly, poly(4-vinylpyridine) does not form compatible blends with copoly(styrene 4-vinylpyridine) even in the case of copolymer **3** which contains 50% 4-vinylpyridine.

Blends based on polystyrene, poly(4-hydroxystyrene) and various copoly(styrene-4 hydroxystyrene)s

These blends were also prepared by mixing the appropriate pyridine solutions followed by solvent evaporation and drying. *Table 3* shows the results which were obtained. It is seen that polystyrene is incompatible with poly(4-hydroxystyrene). Moreover, polystyrene is incompatible with copolymers of styrene and 4-hydroxystyrene containing 50% and 30% of 4-hydroxystyrene. Likewise, poly(4-hydroxystyrene) did not show compatibility with copolymers of styrene and 4-hydroxystyrene containing 30% or even as much as 70% of 4-hydroxystyrene units.

Blends of poly(4-vinylpyridine) with poly(4-hydroxystyrene)

In view of the strong interaction between these two polymers which can form stable complexes, the method used in sample preparation is of particular importance. Both polymers, poly(4-vinylpyridine) and poly(4-hydroxystyrene), are soluble in methanol. When methanol solutions of these polymers are mixed, a 1:1 insoluble complex is formed regardless of the relative amounts of the individual polymers used. Any excess of either polymer remains in solution. Analytical data on the precipitated complexes after thorough washing with methanol always confirm that a 1:1 complex is formed. D.s.c. shows a single T_g at 210°C for the precipitated polymer complex. This value, which is significantly higher than that observed for each individual component of the mixture (155 and 138°C), indicates that strong interactions are resulting from significant hydrogen bonding between the two polymers amounting essentially to a form of thermally reversible crosslinking that significantly reduces the mobilities of individual chains in the compatible polymer blend. While the mixing of methanol solutions of the two polymers can only lead to 1:1 mixtures, the use of pyridine as solvent allows the

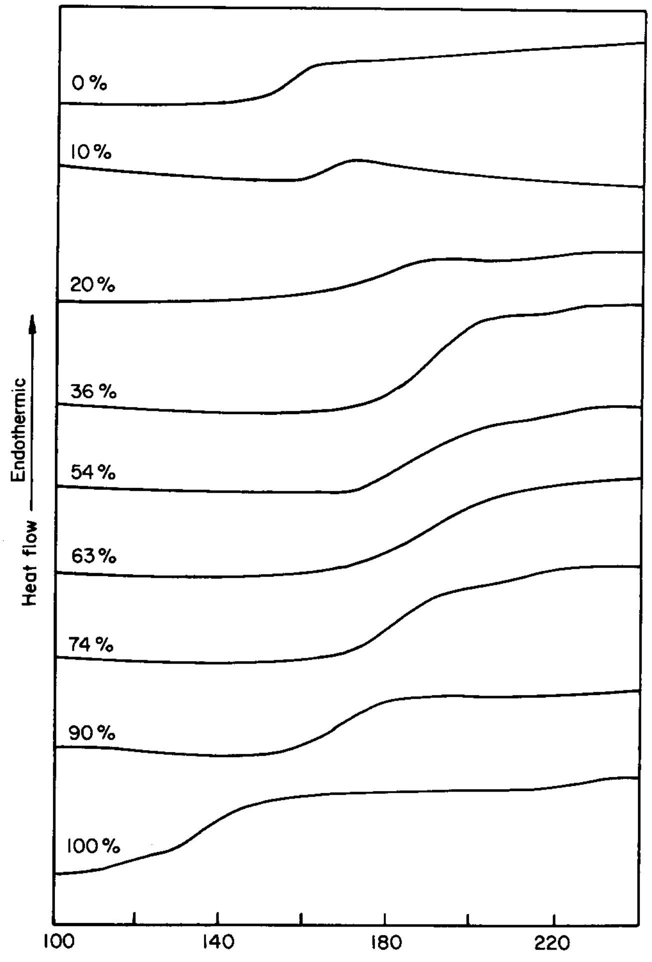

Figure 2 D.s.c. traces of blends of poly(4-vinylpyridine) **2** and poly(4-hydroxystyrene) **5**, at different compositions. The weight per cent of poly(4-hydroxystyrene) **5** is shown above the d.s.c. traces

preparation of compatible blends containing poly(4-vinylpyridine) and poly(4-hydroxystyrene) in any proportion. Sample preparation consists in the dissolution of both polymers in pyridine followed by mixing of solutions containing the desired proportions of each polymer; no precipitation is observed upon mixing and solvent evaporation leads to the desired blend. Pyridine is chosen as solvent as it can interact with poly(4-hydroxystyrene) thereby preventing polymer–polymer complex formation and precipitation when poly(4-vinylpyridine) is added. As the solvent is evaporated slowly, complexation of the polymers can occur by interaction of the reactive groups on both polymers leading to homogeneous films of the polymer blend. D.s.c. studies on the dry blends were carried out as described earlier with pre-heating to 220°C followed by slow cooling to room temperature prior to T_g determination at 20°C min^{-1}.

In all cases (*Figure 2*) a single T_g higher than that of either individual polymer was observed. *Figure 3* shows the change in T_g with composition of the homogeneous blend. The large positive deviation from the calculated weight-average values of T_g at different compositions appears to be proportional to the extent of mutual interactions between the two polymers. *Figure 3* shows clearly that maximum deviation and therefore highest T_g is obtained when blends with compositions approaching a 1:1 molar ratio are used.

Infra-red study. I.r. spectrometry has proven to be a very useful technique to follow specific interactions taking place between two polymers[12]. Films for *FT*i.r. spectrometry studies were prepared by casting them onto sodium chloride discs from 1% (w/v) pyridine solutions. When most of the solvent had evaporated, the samples were vacuum dried, first at room temperature for 24 h, and then for 5 h at 50°C to ensure complete removal of solvent. Films prepared under these conditions were thin enough to obey the Beer–Lambert law (thickness of films 2.0 μm). For poly(4-hydroxystyrene) a very broad absorption band is centred at 3360 cm^{-1} corresponding to the O–H stretch (self-hydrogen bonding). When hydrogen bonding takes place between poly(4-hydroxystyrene) and poly(4-vinylpyridine), the vibrational frequency for the O–H stretch occurs at a significantly lower vibrational frequency. We observed, for instance, that for the blend containing both polymers in 1:1 molar ratio this new O–H stretch is at *ca.* 3130 cm^{-1} (*Figure 4*). Similar results have been obtained in the study of hydrogen bonding for a phenol–pyridine complex[13].

Blends of poly(4-vinylpyridine) and various copoly(styrene-4-hydroxystyrene)s

Blends of poly(4-vinylpyridine) and copoly(styrene-4-hydroxystyrene) containing 50 mol% 4-hydroxystyrene were compatible over the entire composition range. Again T_g showed large positive deviations with respect to weight-average T_g (*Figure 5*). On the other hand, poly(4-vinylpyridine) was miscible with the styrene copolymer containing 30 mol% 4-hydroxystyrene units only for those mixtures which were rich in poly(4-vinylpyridine): a minimum of 60 wt% poly(4-vinylpyridine) was required to observe a single T_g for the blend while samples with lower amounts of poly(4-vinylpyridine) showed two T_g values (*Figure 6*). Similar results were obtained for a mixture of poly(4-vinylpyridine) and the styrene copolymer containing 20 mol% 4-hydroxystyrene. In this case however the compatibility range was even narrower: compatibility being only observed for those mixtures which contained at least 68 wt% poly(4-vinylpyridine) (*Figure 7*).

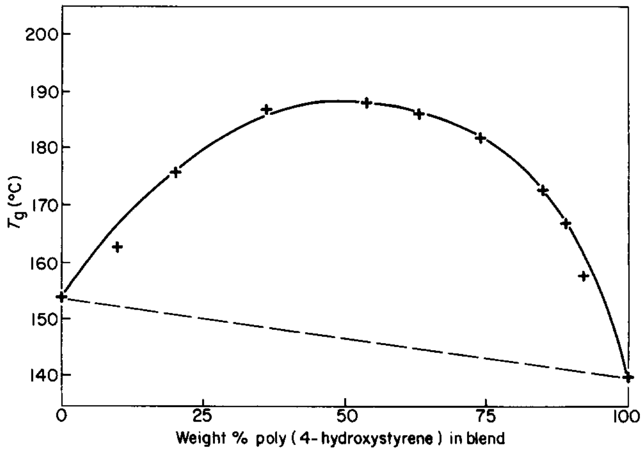

Figure 3 Glass transition temperatures of blends of poly(4-vinylpyridine) **2** and poly(4-hydroxystyrene) **5** *versus* weight per cent of poly(4-hydroxystyrene) **5**. The straight line is the weight average value of T_g as a function of composition

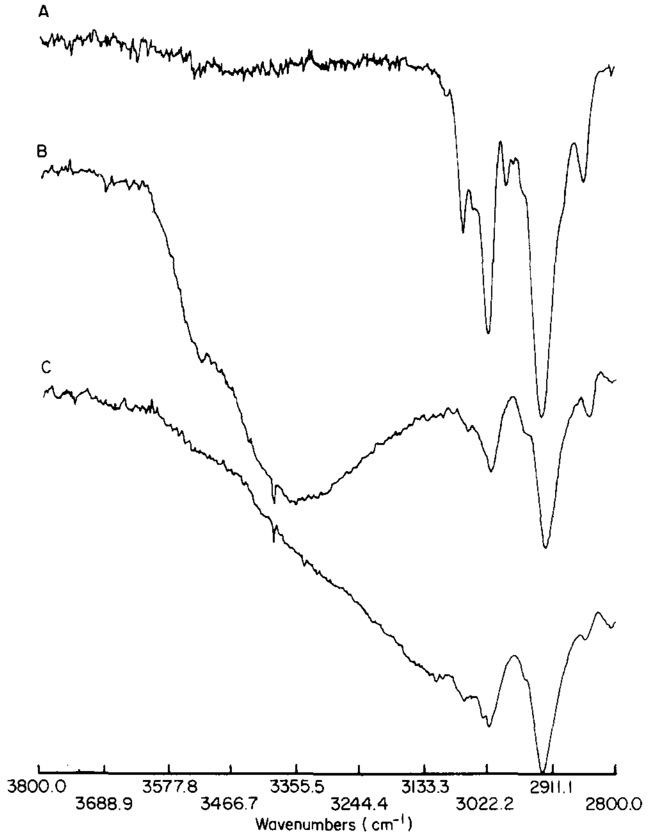

Figure 4 *FT*i.r. spectra from 3800 to 2800 cm^{-1} for films of: A, poly(4-vinylpyridine) **2**; B, poly(4-hydroxystyrene) **5**; C, blend containing both polymers in a 1:1 molar ratio

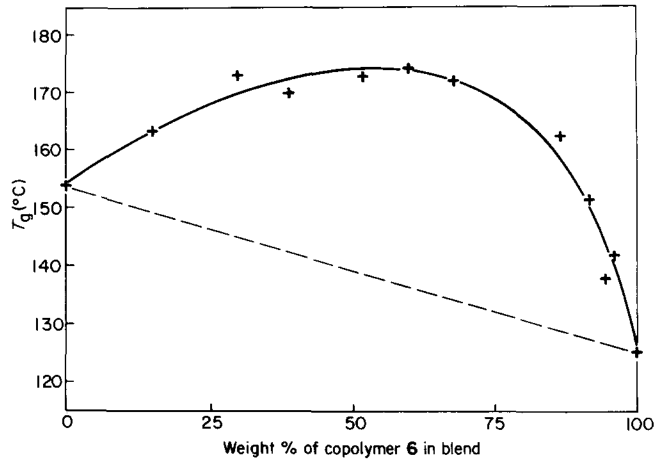

Figure 5 Glass transition temperatures of blends of poly(4-vinylpyridine) **2** and copoly(styrene-4-hydroxystyrene) **6** [50 mol% of each] *versus* weight per cent of copolymer **6** in the blend. The straight line is the weight average value of T_g as a function of composition

Blends of poly(4-hydroxystyrene) and various copoly(styrene-4-vinylpyridine)s

Poly(4-hydroxystyrene) was compatible with copoly(styrene-4-vinylpyridine) containing 50 mol% 4-vinylpyridine over the whole composition range (*Figure 8*), while blends of poly(4-hydroxystyrene) with a styrene copolymer containing 20 mol% 4-vinylpyridine showed neither a sharp single T_g nor two distinct separate ones (*Figure 9*). The results obtained from consideration of derivative curves of heat flow as a function of temperature were also difficult to evaluate as broad curves were obtained in all cases with two maxima clearly observed at certain compositions. However while we have shown earlier that compatible blends show T_g values with positive deviations from calculated data, the T_g values observed for these blends were never higher than the T_g values of the individual polymers, again suggesting incompatibility.

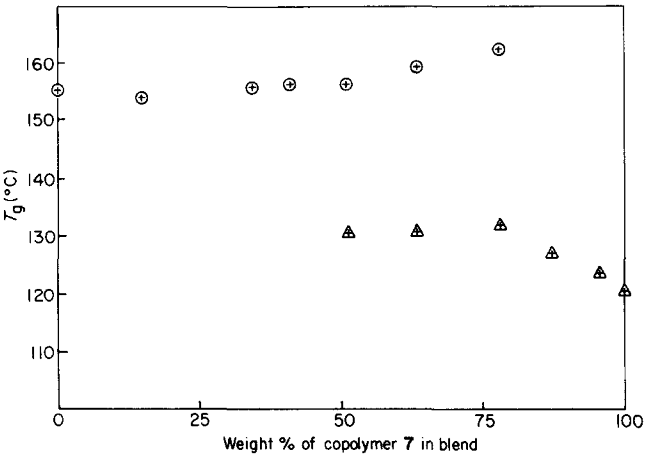

Figure 6 Glass transition temperatures of blends of poly(4-vinylpyridine) **2** and copoly(styrene-4-hydroxystyrene) **7** [70 mol% styrene] *versus* weight per cent of copolymer **7**

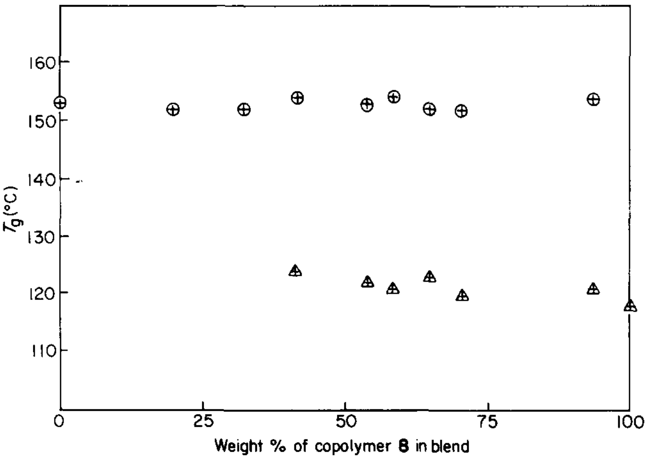

Figure 7 Glass transition temperatures of blends of poly(4-vinylpyridine) **2** and copoly(styrene-4-hydroxystyrene) **8** [80 mol% styrene] *versus* weight per cent of copolymer **8**

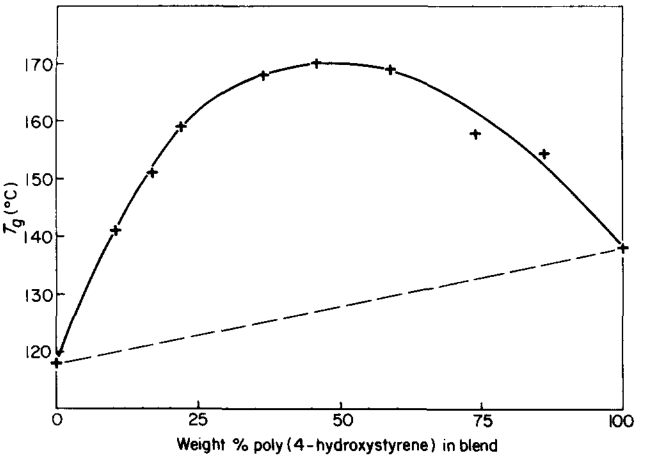

Figure 8 Glass transition temperatures of blends of poly(4-hydroxystyrene) **5** and copoly(styrene-4-vinylpyridine) **3** [50 mol% styrene] *versus* weight per cent of poly(4-hydroxystyrene) **5**

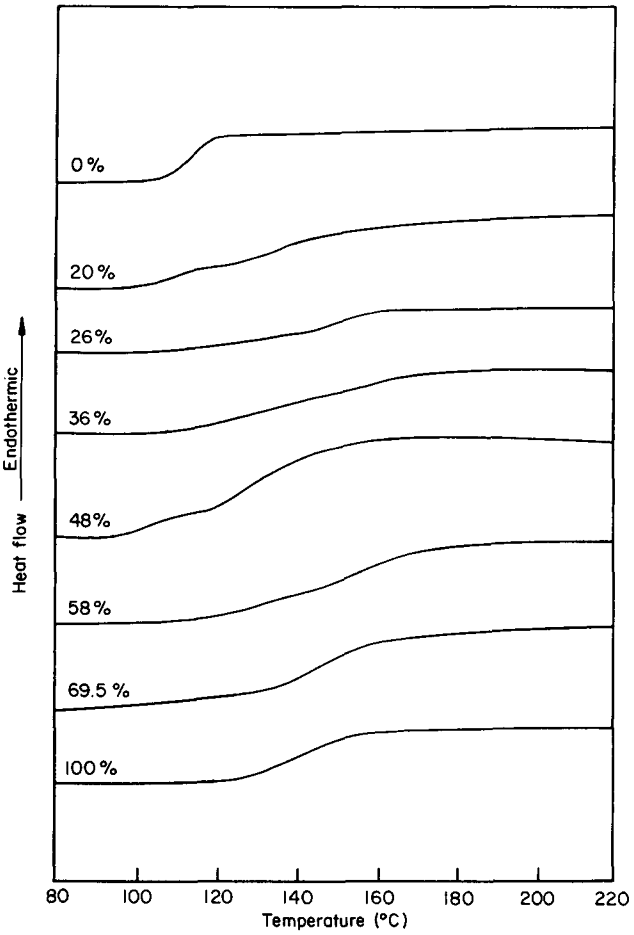

Figure 9 D.s.c. traces of blends of poly(4-hydroxystyrene) **5** and copoly(styrene-4-vinylpyridine) **4** at different compositions. The weight per cent of poly(4-hydroxystyrene) is shown above each d.s.c. trace

CONCLUSIONS

Poly(4-vinylpyridine) is shown to be miscible over the entire range of composition with poly(4-hydroxystyrene) and modified polystyrene containing 50 mol% of 4-hydroxystyrene. On the other hand, when it is blended with modified polystyrene containing 30 and 20 mol% of 4-hydroxystyrene, miscibility is observed only for those mixtures rich in poly(4-vinylpyridine). For blends of poly(4-vinylpyridine) and poly(4-hydroxystyrene) the maximum T_g deviation from calculated weight-average T_g values occurs for that blend which contains a stoichiometric ratio of interacting units. In contrast, for the system poly(4-vinylpyridine)–copoly(styrene-4-hydroxystyrene) containing 50 mol% 4-hydroxystyrene, maximum T_g deviation does not occur for a stoichiometric blend of interacting units. Instead a broad maximum in the curve percentage composition *versus* T_g for this system is seen for ratios of basic (pyridyl) units to acidic (phenol) units between 2 and 1.4. It appears that an excess of basic units is needed to attain the maximum interaction between both polymers; this is likely to be due to the fact that not all pyridine groups are able to complex with the phenolic units probably because of the presence of the intercalated styrene units.

Similarly, poly(4-hydroxystyrene) is shown to be miscible with a polystyrene copolymer containing 50 mol% of 4-vinylpyridine units. For this sytem, maximum T_g deviation is observed for blends containing a ratio of acidic to basic units of about 2. It is found that an excess of acidic units is required to achieve maximum interaction. Once again this is probably due to the inability of all phenolic units to complex. Finally, poly(4-hydroxystyrene) shows semicompatibility when blended with a modified polystyrene containing 20% of 4-vinylpyridine units. In order to compatibilize poly(4-vinylpyridine) or poly(4-hydroxystyrene) with polystyrene, a rather high percentage of complementary units (acidic or basic) must be incorporated into the polystyrene. Hydrogen-bonding interactions for the system pyridine: phenol are not strong enough to allow compatibilization with polystyrene containing a very low percentage of modification (5–10%).

This reflects the relatively low contribution of each phenol–pyridine pair to the compatibilization of the overall system. Compatibility for such dissimilar polymers is only achieved when the cumulative interactions between chains reach a threshold value.

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