Polymer Vol. 36 No. 17, pp. 3355–3358, 1995

0032-3861/95/$10.00 + 0.00

The compatibilization of methyl methacrylate–methacrylic acid copolymer and polystyrene through the functionalization of polystyrene

Nebahat Yurtseven and Leyla Aras*
Middle East Technical University, Department of Chemistry, 06531 Ankara, Turkey
(Received 19 July 1994; revised 7 February 1995)

The compatibility of ionomer/polymeric acid blends has been studied for polymer pairs consisting of sodium salts of sulfonated polystyrene and methyl methacrylate–methacrylic acid copolymer using dilute solution viscometry. The intrinsic viscosities of the blends, prepared in three different weight fractions (25, 50 and 75%) using the solution-blending technique, were measured in two solvents with different polarities: dioxane ($\epsilon = 2.24$) and tetrahydrofuran ($\epsilon = 7.26$). The degree of compatibility of the blends was characterized using the Δb parameter. Results show that the percentage sulfonation, temperature and polarity of the solvent all affect the miscibility.

(Keywords: blends; miscibility; Δb parameter)

INTRODUCTION

Polymer blends have become a very important subject for scientific investigation in recent years because of their growing commercial acceptance. The difficulty in forming miscible polymer blends is a result of the unfavourable thermodynamic conditions that normally occur because of the low entropies and positive heats of mixing. One method of overcoming this problem is to introduce specific interactions between the two polymers to be mixed. Recent work[1–7] has shown that it is possible to form miscible, partially miscible or immiscible but strongly interacting blends of ionized polymers, whereas blends of the unmodified polymers are immiscible, such as polystyrene (PS) and poly(methyl methacrylate) (PMMA). However, utilization of hydrogen bonding between dissimilar chains[8,9], formation of donor–acceptor complexes[10], and dipole–dipole[11], ion–dipole[12] and ion–ion[13] interactions have shown miscibility enhancement.

Although it is known (and confirmed by the present work) that blends of PS and PMMA are immiscible, when PMMA is copolymerized with methacrylic acid and PS is lightly sulfonated to produce some sodium ionomers, PS and PMMA are compatible to some extent. Some work on miscibility has been carried out using melt mixing, but in this work solution mixing and the effect of solvent polarity on miscibility have been studied.

The effect of temperature on the compatibility of PS/PMMA blends has been studied by Hong and Barns[14], and they found that the compatibility of equal weights of PS and PMMA in benzene decreased with increasing temperature. They also studied the effect of molecular weight on compatibility and found that the cloud point decreased with increasing molecular weight.

Because of its simplicity, viscometry is an attractive method for investigating the interactions of macromolecules in solution. Estimation of the compatibility of different pairs of polymers based on viscosity data for ternary polymer/polymer/solvent blends has been attempted by several authors[15–17]. Basically, dilute solution viscometry is based on the classical Huggin's equation[18], which expresses the specific viscosity η_{sp} for a single-solute solution as a function of the concentration c, i.e.

$$\eta_{sp} = [\eta]c + bc^2 \tag{1}$$

where $[\eta]$ is the intrinsic viscosity and b is related to the Huggin's coefficient k_H by

$$b = k_H[\eta]^2 \tag{2}$$

For non-electrolyte dilute solutions, a plot of η_{sp}/c vs. c should yield a straight line with intercept and gradient equal to $[\eta]$ and b, respectively. Theoretically, the parameter $[\eta]$ measures the effective hydrodynamic specific volume of an isolated polymer, whereas the quantity b reflects the level of interactions in solution.

When a ternary system containing a solvent (component 1) and two polymers (components 2 and 3) is used

$$c = c_2 + c_3 \tag{3}$$

$$[\eta] = w_2[\eta]_2 + w_3[\eta]_3 \tag{4}$$

$$b = w_2^2 b_{22} + w_3^2 b_{33} + 2w_2 w_3 b_{23} \tag{5}$$

where w is the normalized weight fraction of polymer and the subscripts refer to the component numbers.

---

* To whom correspondence should be addressed

Therefore, a measure of the intermolecular interactions is the arithmetic differential interaction parameter, defined as

$$\Delta b = b_{23} - (b_{22} + b_{33})/2 \qquad (6)$$

When $\Delta b > 0$ miscibility is signified, whereas when $\Delta b < 0$ phase separation is indicated. Therefore

$$\Delta b = (b - b')/2w_2w_3 \qquad (7)$$

where

$$b' = w_2b_{22} + w_3b_{33} \qquad (8)$$

The coefficients b_{22} and b_{33} are obtainable from solutions of polymers 2 and 3, respectively, as indicated by Chee[18].

In this work, the miscibility of sodium salts of sulfonated polystyrene and methyl methacrylate–methacrylic acid copolymer in dioxane and THF was studied. Miscibility was estimated from the Δb parameter calculated from viscosity measurements according to the method of Chee. The uncertainty in the calculation of the Δb values was approximately 0.001–0.007. To calculate b values for each system, a linear regression method was used. According to these results the '-*r*-' values for each system varied between 0.9969 and 0.9999, which is quite good for linear regression. The dielectric constants ϵ of the solutions were measured to check for their effect on compatibility. The results were supported by differential scanning calorimetry (d.s.c.) measurements.

EXPERIMENTAL

Anionic methyl methacrylate–methacrylic acid (MMA–MAA) copolymer with a molecular weight of 135 000 was obtained from Röhm Pharma with a ratio of carboxylate groups of 1 : 2 (i.e. 33.3% MAA). Samples of 1.7% and 2.6% NaSPS and PS were obtained from Exxon with approximate molecular weights of 300 000.

The polymer blends were prepared by the solution-blending method in three different weight fractions (25, 50 and 75%). Ionomer solutions of NaSPS and MMA–MAA copolymer were prepared in dioxane separately, then the blends were obtained by dropwise addition of the NaSPS solution to the MMA–MAA solution at room temperature. The blend samples were precipitated in deionized H_2O. Dioxane ($\epsilon = 2.24$) and tetrahydrofuran (THF) ($\epsilon = 7.26$) were obtained from Merck and used directly without further purification.

Viscosity measurements were obtained with an Ubbelohde viscometer in a constant temperature water bath at 20, 25 and 30°C.

Differential scanning calorimetry thermograms were obtained with a Perkin–Elmer DSC-4 using a heating rate of 20°C min^{-1}. The d.s.c. results for the PS/MMA–MAA blends were obtained at the National Physical Laboratory in London. The d.s.c. data presented are for the samples precipitated from dioxane into water.

For capacitance measurements a General Radio 1620-A capacitance measuring assembly was used.

RESULTS AND DISCUSSION

From *Table 1* it can be seen that all Δb values (calculated from *Figure 1*) for all of the blends are negative, indicating incompatibility. Moreover, the Δb values become more negative with increasing PS content. Since PS has no effective functional groups to interact with the MMA–MAA copolymer, chemical mixing is not possible and instead phase separation is observed. The medium is only available for the formation of hydrogen bonds among carboxylic acid groups, and this also hinders the mixing between the two copolymers. This fact is reflected in the last column of *Table 1*: the two T_g values for each blend confirm the incompatibility. For polymeric blends, it is well known that miscibility is

Table 1 Viscometric data for PS/MMA–MAA binary blends at 25°C in dioxane

MMA–MAA content (% w/w)	PS content (% w/w)	[η] (dl g^{-1})	b (dl^2 g^{-2})	Δb	ϵ	T_g (°C)
100	0	0.580 ± 0.001	0.111 ± 0.000		2.239	176
75	25	0.444 ± 0.001	0.140 ± 0.002	−0.082 ± 0.003	2.249	94, 158
50	50	0.561 ± 0.001	0.136 ± 0.001	−0.181 ± 0.002	2.247	91, 163
25	75	0.675 ± 0.001	0.114 ± 0.002	−0.448 ± 0.003	2.246	93, 168
0	100	0.675 ± 0.001	0.338 ± 0.000		2.244	100

Table 2 Compatibility data for NaSPS/MMA–MAA binary blends at 25°C in dioxane

MMA–MAA content (% w/w)	Na1.7SPS content (% w/w)	Na2.6SPS content (% w/w)	[η] (dl g^{-1})	b (dl^2 g^{-2})	Δb	ϵ	T_g (°C)
100	0		0.580 ± 0.001	0.111 ± 0.000		2.239	176
75	25		0.533 ± 0.001	0.196 ± 0.000	0.078 ± 0.000	2.250	172
50	50		0.497 ± 0.001	0.154 ± 0.002	−0.136 ± 0.004	2.246	108, 174
25	75		0.428 ± 0.001	0.353 ± 0.001	0.202 ± 0.003	2.261	111
0	100		0.424 ± 0.001	0.333 ± 0.000		2.230	113
75		25	0.285 ± 0.001	0.306 ± 0.002	0.394 ± 0.006	2.259	175
50		50	0.274 ± 0.001	0.071 ± 0.002	−0.272 ± 0.004	2.240	108, 172
25		75	0.300 ± 0.001	0.165 ± 0.002	−0.255 ± 0.007	2.255	111, 174
0		100	0.176 ± 0.001	0.302 ± 0.000		2.249	105

represented by a single T_g. *Table 1* also gives the dielectric constants (ϵ) of the solutions, and even though the ϵ values vary between 2.239 and 2.249, there is no significant effect on miscibility.

Effect of sodium ionomers on the compatibilization of NaSPS and MMA–MAA copolymers

Binary interactions between polymer segments can be effected by introducing some ionic groups into one of the copolymers. For this purpose, PS was sulfonated and then neutralized with sodium.

The degrees of sulfonation of PS were 1.7 and 2.6%, and in each sample the sulfonic acids were completely neutralized with sodium to obtain Na1.7SPS and Na2.6SPS. *Table 2* summarizes the viscometry and d.s.c. results for Na1.7SPS and Na2.6SPS with MMA–MAA copolymer in various ratios. For the 25% (w/w) NaSPS blends (both Na1.7SPS and Na2.6SPS), the d.s.c. results give only a single glass transition temperature. Positive Δb values are also obtained for these samples, indicating that these blends are compatible even though the degree of compatibility is different in each case. At 50% (w/w) MMA–MAA, two glass transitions are observed. The lower T_g values are even lower than the T_g values of the pure components Na1.7SPS (113°C) and Na2.6SPS (105°C). This may suggest that these samples are phase separated, with one phase being roughly an NaSPS/MMA–MAA blend and the second phase being essentially pure MMA–MAA copolymer[19].

As for the 25% (w/w) MMA–MAA blends, 75% (w/w) Na1.7SPS gives a single T_g and a positive Δb value, indicating compatibility, and 75% (w/w) Na2.6SPS gives two glass transitions and a negative Δb value, indicating phase separation. Again, the lower T_g (111°C) corresponds to an Na2.6SPS/MMA–MAA blend. When the lower T_g values of the 50 and 75% (w/w) Na2.6SPS blends are considered, a slightly higher Na2.6SPS content in the 75% (w/w) Na2.6SPS phase is suggested compared to the 50% blend, with the second phase being essentially pure MMA–MAA copolymer.

In *Figures 2* and *3* respectively, reduced viscosity vs. concentration data are plotted for the blends of Na1.7SPS and Na2.6SPS with MMA–MAA copolymer.

A variation in dielectric constants for mixed polymer solutions can be an indication of the development of a cluster morphology through the aggregation of ionomers, but this point needs further experimentation.

Effects of solvent polarity and temperature on polymer compatibility

Ionomer blends precipitated from dioxane into water were retested in THF for compatibility using viscometry, and the relevant data are summarized in *Table 3*. It is surprising that all Δb values are positive. In both dioxane (ϵ = 2.24) and THF (ϵ = 7.26), the intrinsic viscosities $[\eta]$ are larger for Na1.7SPS blends than Na2.6SPS blends. With the ionic aggregates behaving as physical cross-links[19] and NaSPS having strong ionic associations, these results seem reasonable. Because of its increased polarity, it can be proposed that ion–dipole interactions are more favoured in THF, and this may explain the difference in intrinsic viscosity values between the solvents.

Dobry and Boyer-Kawenoki[20] observed that temperature affects phase separation only slightly, but a higher temperature increases the rate of separation of the two phases. In contrast, Kern[21] did find evidence of temperature influences for the polymer pair PS/PMMA in *o*-xylene. At 25°C the PS/PMMA blend showed phase separation, but at 85°C it merged to form a single phase. The same blend in methoxybenzene separated into two phases at 85°C, even though there was only one phase at

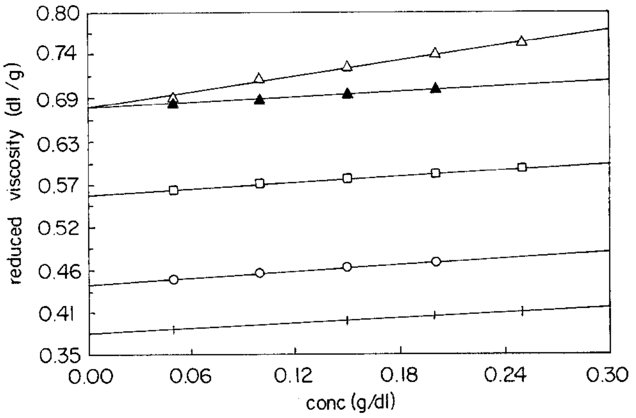

Figure 1 Reduced viscosity vs. concentration for MMA–MAA, PS and PS/MMA–MAA blends: (——) MMA–MAA; (△) PS; (○) 25% (w/w) PS; (□) 50% (w/w) PS; (▲) 75% (w/w) PS

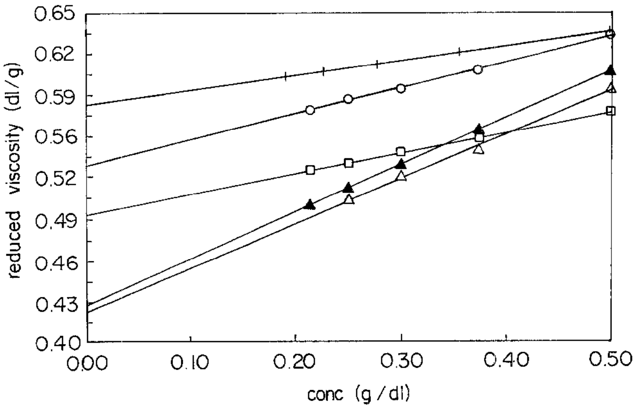

Figure 2 Reduced viscosity vs. concentration for MMA–MAA, Na1.7SPS and Na1.7SPS/MMA–MAA blends: (——) MMA–MAA; (△) Na1.7SPS; (○) 25% (w/w) Na1.7SPS; (□) 50% (w/w) Na1.7SPS; (▲) 75% (w/w) Na1.7SPS

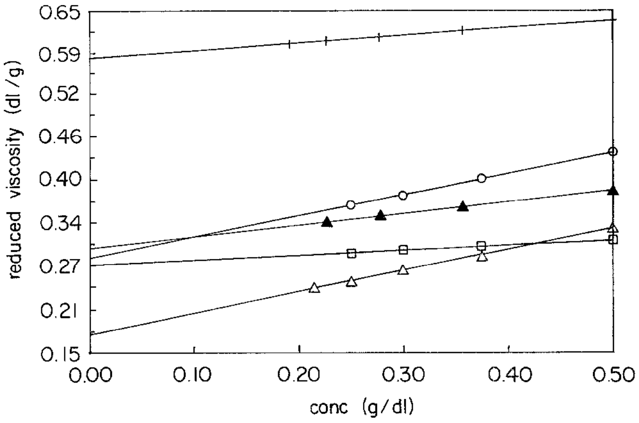

Figure 3 Reduced viscosity vs. concentration for MMA–MAA, Na2.6SPS and Na2.6SPS/MMA–MAA blends: (——) MMA–MAA; (△) Na2.6SPS; (○) 25% (w/w) Na2.6SPS; (□) 50% (w/w) Na2.6SPS; (▲) 75% (w/w) Na2.6SPS

Table 3 Effect of solvent polarity on Δb for NaSPS/MMA–MAA binary blends in THF

MMA–MAA content (% w/w)	Na1.7SPS content (% w/w)	Na2.6SPS content (% w/w)	$[\eta]$ (dl g^{-1})	Δb
75	25		0.319 ± 0.001	0.361 ± 0.003
50	50		0.409 ± 0.001	0.075 ± 0.004
25	75		0.485 ± 0.001	0.357 ± 0.006
75		25	0.293 ± 0.001	0.187 ± 0.002
50		50	0.366 ± 0.001	0.139 ± 0.006
25		75	0.302 ± 0.001	0.127 ± 0.004

Table 4 Effect of temperature on Δb for NaSPS/MMA–MAA binary blends in dioxane

Temperature (°C)	Na1.7SPS content (% w/w)	Na2.6SPS content (% w/w)	Δb
20	25		−0.252
20	50		−0.502
20	75		0.015
25	25		0.078
25	50		−0.136
25	75		0.202
30	25		0.515
30	50		0.056
30	75		0.270
20		25	0.028
20		50	−0.278
20		75	−0.247
25		25	0.394
25		50	−0.272
25		75	−0.238
30		25	0.422
30		50	−0.102
30		75	−0.085

25°C. Hong and Barns[14] found that the compatibility of equal weights of PS and PMMA in benzene decreased with increasing temperature.

In our experiments, the results of which are given in *Table 4*, both effects were observed. For Na1.7SPS blends, the compatibility increased at 30°C for all compositions, while only the 75% (w/w) blend at 20°C and the 25 and 75% (w/w) blends at 25°C were compatible.

Different behaviour for the Na2.6SPS blends was observed. For all three temperatures (20, 25 and 30°C), only the 25% (w/w) Na2.6SPS blend was compatible. An increase in ion content affected the compatibility, and phase separation was observed for mixtures containing 50 or 75% (w/w) Na2.6SPS.

CONCLUSION

It has been proposed by several researchers that PS and PMMA are incompatible; in this paper we have shown that these polymers are indeed incompatible even when MAA is copolymerized with MMA. On the other hand, the styrene-based sodium ionomers are compatible with MMA–MAA copolymer to some extent. The ionomers absorbed MMA–MAA up to different levels under various conditions. The factors affecting compatibility for this system are composition of the blend, ionomer content, temperature and solvent polarity.

It is difficult to generalize a set of conditions where compatibility can be expected, but a low sodium ion content and a highly polar solvent can be considered as favourable for compatibility. Except for Na1.7SPS at 30°C, all 50/50 mixtures are incompatible.

ACKNOWLEDGEMENT

This work was partially supported by the Middle East Technical University under research project AFP and the Turkish National Technical Research Council (TBAG-Ü/15-3). We express our appreciation to Dr M. J. Richardson for his cooperation in recording the d.s.c. thermograms at the National Physical Laboratory in London.

REFERENCES

1 Ruthowska, M. and Eisenberg, A. *Macromolecules* 1984, **17**, 821

2 Ruthowska, M. and Eisenberg, A. *J. Appl. Polym. Sci.* 1985, **30**, 3317

3 Beretta, C. A. and Weiss, R. A. in 'Proceedings of the 15th Meeting of the North American Thermal Analysis Society', Cincinnati, 1986, p. 148

4 Beretta, C. and Weiss, R. A. *Polym. Mater. Sci. Eng. Prepr.* 1987, **56**, 556

5 Simmons, A. and Eisenberg, A. *Polym. Prepr.* 1986, **27**, 341

6 Murali, R. and Eisenberg, A. *Polym. Prepr.* 1986, **27**, 343

7 Nathansohn, A. and Eisenberg, A. *Polym. Prepr.* 1986, **27**, 349

8 Djadaun, S., Goldberg, R. N. and Morawetz, H. *Macromolecules* 1977, **10**, 1015

9 Pearce, E. M., Kwei, T. K. and Min, B. Y. *J. Macromol. Sci., Chem. A* 1984, **21**, 1181

10 Pugh, C. and Percee, V. *Macromolecules* 1986, **17**, 1335

11 Prud'homme, R. E. *Polym. Eng. Sci.* 1982, **22**, 90

12 Hara, M. and Eisenberg, A. *Macromolecules* 1992, **17**, 1335

13 Smith, P. and Eisenberg, A. *J. Polym. Sci., Polym. Lett. Edn* 1983, **21**, 223

14 Hong, S. D. and Barns, C. M. *J. Appl. Polym. Sci.* 1971, **15**, 1995

15 Mikhailov, N. V. and Zelikman, S. G. *Kolloidn. Zh.* 1967, **19**, 465

16 Bohmer, B. and Florian, S. *Eur. Polym. J.* 1970, **6**, 471

17 Feldman, D. and Rusu, M. *Eur. Polym. J.* 1970, **6**, 627

18 Chee, K. K. *Eur. Polym. J.* 1990, **26**, 423

19 Tomita, H. and Register, R. A. *Macromolecules* 1993, **26**, 2796

20 Dobry, A. and Boyer-Kawenoki, F. *J. Polym. Sci.* 1947, **2**, 90

21 Kern, R. J. *J. Polym. Sci.* 1958, **33**, 524