Miscibility of Polymer Blends of Poly(styrene-*co*-4-hydroxystyrene) with Bisphenol-A Polycarbonate

GUANGXIAN LI,[1] J. M. G. COWIE,[2] V. ARRIGHI[2]

[1] Dept of Plastics Engineering, Sichuan Union University, Chengdu, Sichuan 610065, China

[2] Dept of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, United Kingdom

ABSTRACT: The miscibility of blends of bisphenol-A polycarbonate (BAPC) and tetramethyl bisphenol-A polycarbonate (TMPC) with copolymers of poly(styrene-*co*-4-hydroxystyrene) (PSHS) was studied in this work. It has been demonstrated that BAPC is miscible with PSHS over a region of approximately 45–75 mol % hydroxyl groups in the copolymer. TMPC has a wider miscible window than BAPC when blended with PSHS. The blend miscibility was considered to be driven by the intermolecular attractive interactions between the hydroxyl groups of the PSHS and the π electrons of the aromatic rings of both polycarbonates (PCs). As the FTIR measurements showed, after blending of BAPC with PSHS, there is no visible shift of the carbonyl band of BAPC at 1774 cm^{-1}, whereas the stretching frequency of the free hydroxyl groups of the copolymers at 3523 cm^{-1} disappeared. The large positive values of the segment interaction energy density parameter $B_{\text{st-HS}}$ calculated from the group contribution approach indicated that the intramolecular repulsive interaction may also have played a role in the promotion of the blend miscibility. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 639–646, 1999

Key words: bisphenol-A polycarbonate; poly(styrene-*co*-hydroxystyrene); blend miscibility

INTRODUCTION

Intermolecular attractive interactions and intramolecular repulsive interactions are two widely recognized mechanisms[1–8] that are currently considered to be favorable to producing a negative enthalpy of mixing in polymer blends to achieve miscibility. The former mechanism normally includes the action of so-called intermolecular-specific interactions, such as hydrogen-bonding,[1] ion-dipole,[7] and Lewis acid–base interactions,[8] and the driving force for the blend miscibility comes from the attraction between the functional groups from different molecular chains in the mixture. The latter usually requires that at least one of the components in the mixture should be a random copolymer, and the molecular origin of the blend miscibility lies on the repulsion between the dissimilar segments within the same molecular chains.[2–6] The majority of miscible blends observed so far may be well explained in terms of either of the two mechanisms.

It is not unreasonable, however, to be suspicious that under some circumstances the promoting power derived from one driving force alone might not be strong enough to overcome the dispersive resistance in the mixture and obtain a homogeneous single phase. For example, polybisphenol-A polycarbonate (BAPC) is immiscible with polystyrene (PS),[9] but their miscibility was

Table I   Characteristics of Polymer Properties Used in the Work

Polymer	Composition	M_w (g mol^{-1}) (before/after deprotection)	T_g (K)
BAPC	—	57,200	428
TMPC	—	50,000	465
PHS	—	30,000	430
PSHS20	20.0 mol % OH group	48,420	385
PSHS26	25.5 mol % OH group	46,800/43,700	385
PSHS44	43.5 mol % OH group	47,100/47,000	383
PSHS54	54.0 mol % OH group	55,500/44,800	383
PSHS63	62.5 mol % OH group	57,000	388
PSHS77	77.0 mol % OH group	60,300/44,600	389

improved remarkably[10] after incorporating certain amounts of acrylonitrile units into the styrene polymer chains; however, even then it was still an immiscible blend. Also, poly(4-hydroxystyrene) (PHS), which has a strong hydrogen-bonding tendency to act with other proton-acceptors,[11] was reported[12] to be immiscible with polyisobutyl methacrylate (PIBMA), but its copolymer with 40 mol % styrene units was miscible with PIBMA. Therefore, one may deduce that the possibility of obtaining the miscible blends should be enhanced if the intermolecular attractive and intramolecular repulsive interactions can exist in the same system and act in cooperation.

The miscibility of BAPC with various other polymers, including polyesters,[13–14] acrylic polymers,[15] and styrenic polymers,[9,10,16] has been studied extensively in the past, and it has been reported that BAPC was miscible with polyesters and acrylic polymers or copolymers, but immiscible with either PS or styrene-based copolymers, such as poly(styrene-co-acrylonitrile) (SAN) and poly(styrene-co-methyl methacrylate) SMMA.[9,10,17] Paul and coworkers studied a series of modified BAPC structures blended with PS or its copolymers.[18] They found that among these structures, where modification included ring substitution or substitution between two phenyls of BAPC with various polar connector groups or methyl groups, only the tetramethyl bisphenol-A polycarbonate (TMPC) was miscible with PS. Recently, Lu and Weiss reported[19] that BAPC was miscible with a slightly sulfonated PS (SPS) over a range of 10.1–11.3 mol % of sulfonation, and the driving force for the miscibility of the blend was attributed to the intramolecular repulsive interaction.

Following the strategy discussed previously, in this article, we studied the miscibility of BAPC and poly(styrene-co-4-hydroxystyrene) (PSHS). The introduction of the polar hydroxyl groups into the PS

molecular chains should generate a stronger intramolecular repulsive interaction and possibly initiate favorable intermolecular attractive interactions with appropriate sections of the BAPC as well. It is our expectation that under the action of the combination of the two forces the miscibility of the blends of BAPC with PS would be obtained.

EXPERIMENTAL

Polymers used in this study are listed in Table I. BAPC and TMPC were supplied by Aldrich, Gillingham, Dorset, UK and Bayer, Leverkusen, Germany, respectively; PHS was purchased from Polysciences, Inc., Warrington, PA, USA. Monomers, styrene, and 4-acetoxystyrene were treated to remove inhibitor and distilled prior to use. The copolymers PSHS were synthesized by copolymerization of 4-acetoxystyrene and styrene followed by hydrolysis of the acetoxy group. The copolymerization was carried out by free-radical solution polymerization at 338 K, with toluene as solvent and α,α'-azobisisobutyronitrile (AIBN) as initiator. The reactions were terminated by precipitation into petroleum ether (40–60°C) and the

Table II   Miscibility of Blends of BAPC with Copolymer PSHS

Blend (50 : 50 w/w)	Miscibility
BAPC/PSHS20	immiscible
BAPC/PSHS25	immiscible
BAPC/PSHS44	immiscible
BAPC/PSHS54	miscible
BAPC/PSHS63	miscible
BAPC/PSHS77	immiscible
BAPC/PHS	immiscible

Figure 1 FTIR spectrum of carbonyl bands of (1) BAPC, (2) BAPC/PSHS54 blend, (3) BAPC/PHS blend; blend ratio: 50 : 50 w/w.

fore and after the hydrolysis; the results are shown in Table I. It is clear that the hydrolysis reaction has no significant effect on the molecular size. The copolymer composition was determined by ^{1}H-NMR by using a 400-MHz machine.

All of the blends studied were prepared by co-dissolution of the relevant components at a 50 : 50 weight ratio into dioxane followed by coprecipitation into petroleum ether. The powder samples were then vacuum dried at 335 K for 48 h. The glass transition temperature (T_g) of all polymer samples and their blends were determined using a Perkin–Elmer DSC-4 differential scanning calorimeter at a heating rate of 20 K min^{-1}. Each sample was first heated at the rate of 20 K min^{-1} to a temperature 15–20 K above its T_g and kept at that temperature for a few minutes before quenching down to room temperature for normal measurement. Blend miscibility was judged using the criterion that a miscible blend exhibits a single T_g, whereas an immiscible one shows multiple T_gs corresponding to the glass transitions of the components. The FTIR spectra were measured on a Perkin–Elmer FTIR 1720 spectrometer at a resolution of 2 cm^{-1}. The samples were made by solution casting the blend onto a KBr disk; the melt-pressed samples were made by pressing the heated solution-precipitated blend powders under a hot-presser below 523 K.

resulting polymers purified twice by reprecipitation using THF as solvent, and then vacuum dried at 335 K for over 24 h. The composition drift is negligible because the reactivity ratios (0.88 : 1.18 for styrene : 4-acetoxystyrene[20,21]) are close to the values required for ideal copolymerization. The hydrolysis reaction was undertaken in 1,4-dioxane using hydrazine hydrate as hydrolytic agent.[20,21] The reaction was continued at room temperature for about 20 h and stopped by precipitation into petroleum ether. The deprotection of the acetoxy group was monitored by FTIR using the carbonyl group absorption at 1765 cm^{-1} that was present in the parent polymer. When this disappeared completely, strong broadbands were observed at 3600–3320 cm^{-1}, the stretching frequencies of free and self-associated hydroxyl groups. Gel permeation chromatography (GPC), with PS as the calibration standard, was used to measure the molecular weights of copolymers be-

Table III Carbonyl IR Frequencies of Carbonate Derivatives and Related Compounds[27]

Compounds	Frequency (cm^{-1})
$R-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'$	1741–1739
$R-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-Ar$	1787–1754
$Ar-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-Ar$	1819–1775
$Cl-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-R$	1780–1775
$R-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-Ar$	1784

R, R': aliphatic; Ar: phenyl.

Figure 2   FTIR spectrum of hydroxyl bands of (1) PHS, (2) PSH54, (3) PSHS20.

RESULTS AND DISCUSSION

The miscibility of BAPC blended with copolymers of PSHS containing different amounts of hydroxyl groups was studied and the results are listed in Table II. It can be seen that whereas BAPC is immiscible with either PS or PHS, which has the highest level of hydroxyl groups studied in this work, it is miscible with some samples of their copolymer PSHS. The miscible window is estimated to lie roughly within a region of 45–75 mol % hydroxyl groups in the copolymer.

As hydrogen-bonding is a quite common phenomenon in blends consisting of PHS and other proton-acceptor polymers, such as polyesters,[22] polyamides,[23] and polyacrylates,[24] the H-bonding-sensitive technique, FTIR, was used to inspect the possibility of H-bonding interactions between the carbonyl groups of BAPC and the hy-

droxyl groups of PSHS. Examination of the spectra in Figure 1 shows that no obvious band shift of the carbonyl of BAPC at $1774 \mathrm{~cm}^{-1}$ can be detected after blending with PSHS samples, which is a common feature associated with the presence of H-bonding. The melt-pressed samples were measured as well to exclude the possible influence of the solvent in the solution-casting method used in making the IR samples, as reported by others[11]; however, the result is the same and no carbonyl frequency shift was observed. This may not be an unusual example, as a similar phenomenon was reported by Lu and Weiss in their study of the blend of BAPC with SPS.[19] From the literature published so far, the miscibility of blends of BAPC with other polymers is mostly explained in terms of the interactions of the aromatic rings of BAPC with functional groups of other components.[13,16–18] There is no

Figure 3 FTIR spectrum of hydroxyl bands of (1) PSHS54, (2) PSHS54/BAPC blend (50 : 50 w/w), (3) PHS.

direct evidence to demonstrate the involvement of the carbonyl of BAPC in an interaction with other proton-donor polymers to form H-bonding.[19,25] The lower activity of carbonyl groups in BAPC may be caused by the conjugation of the ester groups with the aromatic rings of the BAPC, which would stiffen the carbonyl bond, resulting in the carbonyl band shift to a higher frequency.[26] The relationship between the conjugation bond strengthening and the corresponding band shift has been well established in the spectroscopy of simple organic compounds; some relevant data are shown in Table III for illustration.

Another region sensitive to hydrogen bonding is the stretching frequencies of hydroxyl groups at 3200–3600 cm^{-1}. Figure 2 shows that the intensity of the 3523 cm^{-1} band of the free hydroxyl groups[1,27] increases with increasing styrene content in the copolymer, an indication of the breakdown of the self-associated hydroxyl groups in the copolymer chains. After blending PSHS with BAPC, however, this band has almost disappeared (Fig. 3), compared with the homopolymer PHS, the hydroxyl groups of which are normally in a self-associated state, implying that there may be an intermolecular attractive interaction between the hydroxyl groups and the π electrons of the aromatic rings of BAPC, because the carbonyl groups are rather inert in this case. The H-bonding between the hydroxyl groups and the π electrons of aromatic rings are well recognized in the chemistry of carbonyl[28,29] and hydroxyl group[30] interactions. The association of phenol with an aromatic ring has been observed,[29] and it was found that for methyl-substituted benzenes,

Table IV   Miscibility of TMPC with PSHS

Blend (50 : 50 w/w)	Miscibility
TMPC/PSHS20 (immiscible with BAPC)	miscible
TMPC/PSHS44 (immiscible with BAPC)	miscible
TMPC/PSHS55	miscible
TMPC/PHS (immiscible with BAPC)	miscible

the H-bonding basicity with phenol protons increases regularly with the number of methyl groups substituted in the benzene ring.[30,31] Accordingly, then the TMPC, which has four ring-substituted methyl groups, should have a better chance than BAPC to form miscible blends with PSHS, as the electron-release character of the methyl groups would favor the interaction of the π electrons of the aromatic rings with the protons of the hydroxyl groups.

Table IV shows that TMPC is indeed miscible with those copolymers that were immiscible with BAPC, and even the blend of TMPC with homopolymer PHS is miscible, although the corresponding T_g

transition was not as sharp as those of the PSHS copolymer blends. The methyl groups substituted in the rings of TMPC also have an influence on the carbonyl bonds, as shown in Figure 4, where the carbonyl band of TMPC is slightly shifted to a lower frequency compared to that of BAPC, indicating the weakening of the carbonyl bond. This may be beneficial to the interaction between the carbonyl and the hydroxyl groups. Figure 5 is an IR spectrum of the blend TMPC/PHS at 20/80 w/w ratio. The observed shift of the carbonyl band to the lower frequency suggests the existence of H-bonding in the mixture; however, this interaction might not be very strong as it was not observed in the blend of 50/50 w/w ratio.

Because the relevant segment interaction energies of the blend of BAPC and PSHS are unknown at present, the solubility parameter method $B_{ij} = (\delta_i - \delta_j)^2$ was utilized[32] to estimate the three-segment interaction energies $B_{\mathrm{pc\text{-}st}}$, $B_{\mathrm{pc\text{-}HS}}$, and $B_{\mathrm{st\text{-}HS}}$. The corresponding solubility parameters used in the calculation were obtained through the group contribution approach.[33] The

Figure 4   FTIR spectrum of carbonyl bands of (1) BAPC, and (2) TMPC.

Figure 5 FTIR spectrum of carbonyl bands of (1) TMPC and (2) TMPC/PHS blend (20 : 80 w/w).

prediction of the blend-miscible window was made on the basis of the binary interaction model.[2–4] The results were listed in Table V.

The miscible window obtained according to the solution parameter method was very narrow, just between 58–59 mol % hydroxyl groups content in copolymers, located approximately in the middle of the miscible region of 45–75 mol % hydroxyl groups observed experimentally in this work. In view of the fact that the solubility parameter method normally does not take the intermolecular specific interactions (H-bonding) into consideration, this predicted miscible composition might be regarded as a measurement of the intramolecular repulsive interactions that bring the blend to be just on the boundary of forming the single phase. The contribution of the intermolecular attractive interactions to the blend miscibility should then be reflected in the wider

Table V   Calculated Segment Interaction Energies of Blends of BAPC and PSHS and the Predicted Miscible Regions Using the Binary Interaction Model

Source of the Data[34] for Group Contribution	$B_{pc\text{-}st}$	$B_{pc\text{-}HS}$	$B_{st\text{-}HS}$	Miscible Window (mol % OH)
Van Krevelan's	1.36	2.69	7.88	58–59
	0.61[a]	2.69	7.88	39.0–87.1
Hoy's	0.98	1.79	5.2	—
	0.61[a]	1.79	5.2	44.6–77.7

[a] Experimental data.[17]

miscible region observed for the copolymer hydroxyl group compositions. If we replace the value for $B_{\text{pc-st}}$ with the experimentally measured one $B_{\text{pc-st}}$ = 0.61[17] in the calculation, the predicted miscible window is 44.6–77.7 mol % hydroxyl groups (Table V), which is very close to the experimental results (estimated for 45–75 mol % hydroxyl groups).

CONCLUSION

This work demonstrates that the miscibility of the blends of BAPC with PS can be significantly improved by introducing a certain amount of polar hydroxyl groups into the styrene chains. BAPC is miscible with poly(styrene-*co*-4-hydroxystyrene) over a range of roughly 45–75 mol % hydroxyl groups in the copolymer. As TMPC is miscible with both PS and PHS, the blends of TMPC and PSHS show a much wider miscibility window than the corresponding BAPC blends. The driving force for the blend miscibility may originate from the combined actions of the intermolecular attractive forces, coming from the H-bonding between the hydroxyl groups and aromatic rings of BAPC, and the intramolecular repulsive forces resulting from the juxtaposition of the vinyl phenol and the styrene groups within the copolymer chains.

REFERENCES

1. Coleman, M. M.; Graf, J. F.; Painter, P. C. Specific Interactions and the Miscibility of Polymer Blends; Technomic Publishing: Lancaster, PA, 1991.
2. ten Brinke, G.; Karasz, F. E.; Macknight, W. J. Macromolecules 1983, 16, 1827.
3. Paul, D. R.; Barlow, J. W. Polymer 1984, 25, 487.
4. Cowie, J. M. G.; Reid, V. M. C.; McEwen, I. J. Polymer 1990, 31, 487.
5. Cowie, J. M. G.; Guangxian, Li; Ferguson, R.; McEwen, I. J. J Polym Sci, Polym Phys Ed 1992, 30, 1351.
6. Cowie, J. M. G.; Guangxian, Li; McEwen, I. J. Polymer 1994, 35, 5518.
7. Hara, M.; Eisenberg, A. Macromolecules 1984, 17, 1335.
8. Eisenberg, A.; Smith, P.; Zhou, Z.-L. Polym Eng Sci 1982, 22, 1117.
9. Kunori, T.; Geil, P. H. J Macromol Sci, Phys 1980, B18, 93.
10. Keitz, J. D.; Barlow, J. W.; Paul, D. R. J Appl Polym Sci 1984, 29, 3131.
11. Landry, C. J. L.; Massa, D. J.; Teegarden, D. M.; Landry, M. R.; Hendrichs, P. M.; Long, T. E. Macromolecules 1993, 26, 6299.
12. Prinos, J.; Panayiotou, C. Polymer 1995, 36, 1223.
13. Cruz, C. A.; Barlow, J. W.; Paul, D. R. Macromolecules 1979, 12, 726.
14. Fernandes, A. C.; Barlow, J. W.; Paul, D. R. Polymer 1986, 27, 1799.
15. Nishimoto, M.; Kesskkula, H.; Paul, D. R. Polymer 1991, 32, 1274.
16. Ziaee, S.; Paul, D. R. J Polym Sci, Polym Phys Ed 1997, 35, 489.
17. Kim, C. K.; Paul, D. R. Polymer 1992, 33, 4941.
18. Kim, C. K.; Paul, D. R. Macromolecules 1992, 25, 3097.
19. Lu, X.; Weiss, R. A. Macromolecules 1996, 29, 1216.
20. Ledwith, A. J. Polym Sci, Polym Chem 1974, 12, 2017.
21. Zhu, K. J.; Chen, S. F.; Ho, T.; Pearce, E. M.; Kwei, T. K. Macromolecules 1990, 23, 150.
22. Moskala, E. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. Macromolecules 1984, 17, 1671.
23. Landry, C. J. M.; Teegarden, D. M. Macromolecules 1991, 24, 4310.
24. Xu, Y.; Painter, P. C.; Coleman, M. M. Macromolecules 1992, 25, 7076.
25. (a) Ting, S. P.; Pearce, E. M.; Kwei, T. K. J Polym Sci, Polym Lett Ed 1980, 18, 201; (b) Akiyama, S.; Ishikawa, K.; Fujiish, H. Polymer 1991, 32, 1673.
26. Cothup, N. B.; Dalay, L. H. Introduction to IR and Raman Spectroscopy, 2nd ed.; Academic Press: New York, 1975; pp 278–295.
27. Xu, J.; Graf, J.; Painter, P. C.; Coleman, M. M. Polymer 1991, 32, 3102.
28. (a) Eicher, T. in The Chemistry of the Carbonyl Group; Patai, Saul, Ed.; Wiley: New York, 1966; (b) Kohnstam, G. and Williams, D. L. H. in The Chemistry of the Ether Lingkage; Patai, Saul, Ed.; Wiley: New York, 1967.
29. Bellamy, L. J. Advances in Infrared Group Frequencies; Methuen: London, 1968; p 241.
30. Yoshda, Z.; Osawa, E. J Am Chem Soc 1965, 87, 1467.
31. The Chemistry of the Hydroxyl Groups, Part 1; Patai, Saul, Ed.; Interscience: New York, 1971; p 327.
32. McMaster, L. P. Macromolecules 1973, 6, 760.
33. Van Krevelen, D. W. Properties of Polymers, 2nd ed.; Elsevier: New York, 1976, Chapter 7.