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Miscibility of styrene and *t*-butyl acrylate random copolymers and their ionomers with poly(2,6-dimethyl-1,4-phenylene oxide)

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Abstract

A series of poly(styrene-ran-*t*-butyl acrylate) (S-tBA) copolymers was prepared and characterized. The S-tBA copolymers containing less than ca. 23 mol% *t*-butyl acrylate were found to be miscible with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) at all composition ranges according to differential scanning calorimetry studies. The same S-tBA copolymer series was hydrolyzed and subsequently neutralized to produce potassium salts of poly(styrene-ran-acrylic acid). Miscibility of the ionic copolymers with PPO was found to reduce to below ca. 3 mol% of the ionic content. A qualitative X-ray analysis on the ionic blend indicated that the line of demarcation for incompatibility was related to the phenomenon of onset of ion-pair association. Interaction parameter for the above miscible blends was calculated using established semi-empirical relationships. The styrene and tBA moieties were found to have strong "repulsive" type interaction leading to an even more negative interaction parameter for the S-tBA/PPO blends at higher tBA contents. The combined favorable (S/PPO) and unfavorable (S/tBA) interaction, however, did not improve miscibility for the ionic polymer blends.

Keywords: Ion-containing polymers; Polymer blends; Random copolymers of styrene and *t*-butyl acrylate

1. Introduction

Polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) are known to produce miscible polymer blends at all composition ranges [1,2]. The origin of interaction responsible for the miscibility is unknown but has been suggested to be related to phenyl rings coupling [3]. Copolymers of styrene, however, were found to have both miscible and immiscible zones with PPO depending on the composition of the copolymer, the blend, as well as on the nature of the second component in the copolymer [4–7]. Using a mean field approach, miscibility between a homopolymer–copolymer pair has been suggested to promote not only by favorable "attractive" but also unfavorable "repulsive" segmental interaction [7,8].

Polymer blend in which one or more of its constituents are ion-containing have been the focus of a series of recent publications and reports [9–17]. Ionic polymer is interesting since the electrical interacting force is long range and the highly polarized ion-pairs may enhance miscibility. Increased compatibility for polymer pairs in which one or both polymers are ionomers have been explained according to specific interaction such as ion–ion, ion–dipole [9–13], ion-pair–ion-pair [14] or formation of acid–base complexes [15–17]. Recent experimental results indicated that miscibility also depends on the counter-ion type [9,10], ion concentration [13,14] and blend composition [9,10]. The ionic blends are expected to display improved mechanical properties due to formation of physical cross-linking sites from the aggregated ion-pairs. The same ionic moieties will also affect other physical properties such as their surface properties and melt flow behavior.

Enhancement of miscibility by ion–dipole interaction has been observed in otherwise immiscible systems in which one of the polymers has a polar backbone structure such as polyamide [9–11]. The effects of including ion moieties in known miscible blends such as PS/PPO and PMMA/PVF$_2$ have also been investigated [10,13]. At low ionic contents, miscibility was enhanced, but at higher ionic compositions, aggregation of the ion-pairs always results in phase desegregation of the polymer components. In order to study the

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Table 1
Composition analysis of copolymer samples (copolymerization of styrene and tBA is performed in toluene at 70°C using 0.4%, molar % of initiator in monomers, AIBN as initiator)

Sample name	Feed ratio Styrene:tBA (v:v)	Reaction time (h)	Molar composition from IR (%)	
			Styrene	tBA
S96	97.5:2.5	3	95.8	4.24
		6	95.8	4.24
S93	95:5	3	93.3	6.73
		4	93.3	6.67
		5	93.3	6.69
		6	93.5	6.53
S89	93.5:6.5	4	90.1	9.87
		8	89.4	10.6
S87	90:10	3	88.4	11.6
		4	89.2	10.8
		6	88.2	11.8
		8	86.6	13.4
S82	85:15	2	83.8	16.2
		4	85.3	14.7
		6	82.7	17.3
		8	82.0	18.0
S77	75.25	4	75.8	24.2
		8	76.6	23.4
S66	40:60	3	74.2	25.8
		4.5	65.9	34.1

relative magnitude of favorable and unfavorable interactions within a copolymer blend, miscibility for a series of acrylate-containing copolymers and PPO was compared to their ionic derivatives. A series of poly(styrene-ran-*t*-butyl acrylate) copolymers was prepared and characterized. The *t*-butyl acrylate group was subsequently hydrolyzed, and then neutralized to form potassium salt of the carboxylic acid. The miscibility of the unmodified copolymers with PPO was then compared to their ionic salts. The ion–dipole interaction in general is much stronger than the van de Waals type segmental interaction and was found to dominate miscibility behavior of the blend. The Flory–Huggins interaction parameter was calculated for the miscible blend from established semi-empirical equations [7,11]. The onset of phase separation in the ionic blend is related to the formation of ionic aggregates from a qualitative X-ray scattering analysis.

2. Experimental

2.1. Polymers synthesis

All chemicals and solvents used were AR grade unless specified otherwise. Styrene, *t*-butyl acrylate (Fluka, Switzerland) were purified and polymerized at different volume ratios using toluene as solvent and re-crystallized azobisisobutyronitirle (AIBN) as initiator according to procedures described previously [18]. In order to verify whether the copolymers obtained are random in nature, samples were withdrawn at constant time interval during polymerization for composition analysis using IR spectroscopy. All reactions were terminated at low conversion. The copolymers were then washed and re-precipitated using methanol and water. Molecular weight for the copolymers was determined by intrinsic viscosity measurement and gel permeation chromatograph.

Hydrolysis of the acrylate fraction in the copolymer series to acrylic acid was catalyzed by *p*-toluenesulfonic acid in toluene under reflux conditions for 24 h [18]. The acid copolymers collected by re-precipitation in ethanol were neutralized in a mix solvent of methanol and chloroform, 10 equivalents of potassium hydroxide after stirring for hours. The potassium salts of the poly(styrene-ran-acrylic acid) were then re-precipitated from *n*-heptane and underwent Soxhlet extraction by DI water for 1–2 days for the removal of excessive potassium ions.

The PPO (Aldrich, USA) was used “as received”. All polymer blends were prepared by dissolving the two components at various weight ratios (9/1, 7.5/2.5, 5/5, 2.5/7.5, 1/9) in chloroform and solvent cast on a glass plate. The thin films were then dried in vacuum at 45°C for days and stored in a desiccator before use.

Table 2
Molecular weight of copolymer samples (the number average molecular weight, M_n, and the weight average molecular weight, M_w, of the polymer samples are determined with respect to polystyrene standard in THF at 25°C. The viscosity average molecular weight, M_v, of the samples are calculated with respect to polystyrene in toluene at 25°C using $K = 34.5 \times 10^{-3}$ ml/g, $a = 0.62$)

Sample name	Molar composition (%)		Molecular weight		$\overline{M_w}/\overline{M_n}$	η (dl/g)	$\overline{M_v}$
	Styrene	tBA	$\overline{M_n}$	$\overline{M_w}$			
S96	95.8	4.19	43,700	64,100	1.48	0.2715	46,800
S93	93.47	6.53	115,000	168,000	1.47	0.4495	105,000
S89	89.4	10.6	45,200	68,200	1.51	0.3822	81,000
S87	86.6	13.4	115,000	164,000	1.42	0.4478	105,000
S82	82.0	18.0	113,000	166,000	1.47	0.4410	102,000
S77	76.6	23.4	78,700	119,000	1.52	0.4754	116,000
S66	65.9	34.1	57,000	81,900	1.44	0.3036	56,100
S57	57.2	42.8	68,200	99,700	1.40	0.3088	57,700

Table 3
Chemical composition of potassium salts (The molar composition of styrene and tBA is based on IR spectroscopy analysis, styrene 1601 cm^{-1}, tBA 1724 cm^{-1}. The molar percentage of acrylic acid is determined using titration method. The molar percentage of potassium acrylate is measured from flame atomic absorption spectrophotometry using Spectra AA-20 at 766.5 nm, 1 nm slit width and 5 mA lamp current.)

Sample name	Molar composition (%)			
	Styrene	*t*-Butyl acrylate	Acrylic acid	Potassium acrylate
K1S96	95.81	1.53	2.14	0.52
K2S93	93.47	2.60	1.97	1.96
K3S89	89.40	2.96	4.36	3.28
K7S87	86.60	5.66	0.85	6.89
K5S82	82.00	7.50	5.29	5.21
K16S77	76.60	4.06	2.88	16.46

2.2. Characterization

The molar composition of the neat copolymers was determined by IR spectroscopy (Hitachai 270-30 with data processor) using solvent cast thin films (styrene 1601 cm^{-1}, tBA 1724 cm^{-1}). The degree of hydrolysis was determined by IR spectroscopy from the acid and ester absorption peaks after Lorentzian correction (tBA 1724 cm^{-1}, acid 1703 cm^{-1}). The acid concentration of the hydrolyzed products was obtained by titration using 2 M potassium hydroxide (aq.) solution and an indicator. The potassium contents were determined by flame atomic absorption spectrophotometry (Spectra AA-20) at 766.5 nm using standard potassium ion solutions (KCl in HNO_3) for calibration. The difference between the number of acid groups and potassium ions gave the degree of neutralization. Intrinsic viscosity of the S-tBA copolymers was measured by an Ostwald viscometer in a constant temperature bath at 25°C using toluene as the solvent. The viscosity averaged molecular weight for the copolymers was calculated based on the Mark–Houwink equation using constants K (34.5×10^{-3} ml/g) and a (0.62) reported for PS at 25°C [19]. The molecular weight was also measured by gel permeation chromatography (Water Associates HPLC and Polymer Lab. PLgel 5 μm mixed column) calibrated with PS standards and using tetrahydrofuran as the mobile phase. Thermal analyses were effected on a thermogravimetric analyzer (Shimadzu DT-40/TG) at 5°C/min heating rate and a differential scanning calorimeter (Shimadzu DSC-50

Table 4
On-set degradation temperature of copolymer and its derivatives. The percentage indicated in the bracket is percentage weight loss of polymer

Name of neat copolymer	S96	S93	S89	S87	S82	S77
Copolymer	248°C (1.6%) 371°C (98.4%)	247°C (2.5%) 378°C (97.5%)	245°C (5.3%) 375°C (94.5%)	251°C (5.7%) 376°C (94.3%)	247°C (9.7%) 378°C (90.3%)	254°C (10.8%) 361°C (89.2%)
After hydrolysis	378°C (98%)	376°C (98%)	372°C (100%)	366°C (100%)	379°C (97%)	379°C (100%)
After K^+ salt formation	367°C (96.3%)	379°C (96.1%)	385°C (92.2%)	373°C (95.8%)	373°C (93.2%)	379°C (82.6%)

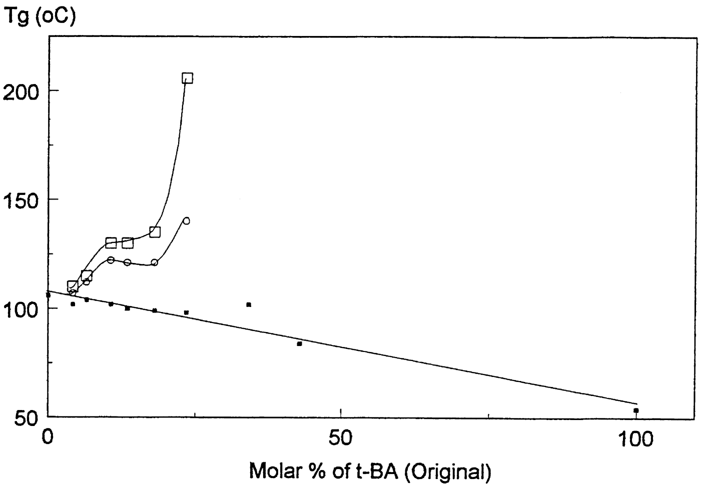


Fig. 1. Glass transition temperatures (mid-point) for the various copolymers. The *x*-axis is shown for the S-tBA copolymer series only. The T_gs for the acid and ionic copolymers were added to the figure only to indicate changes in T_g from their parent S-tBA copolymer. Solid squares are the S-tBA copolymers. Open circles are acid copolymers. Open squares are the potassium salt copolymers. The solid lines were drawn to indicate the overall trends only.

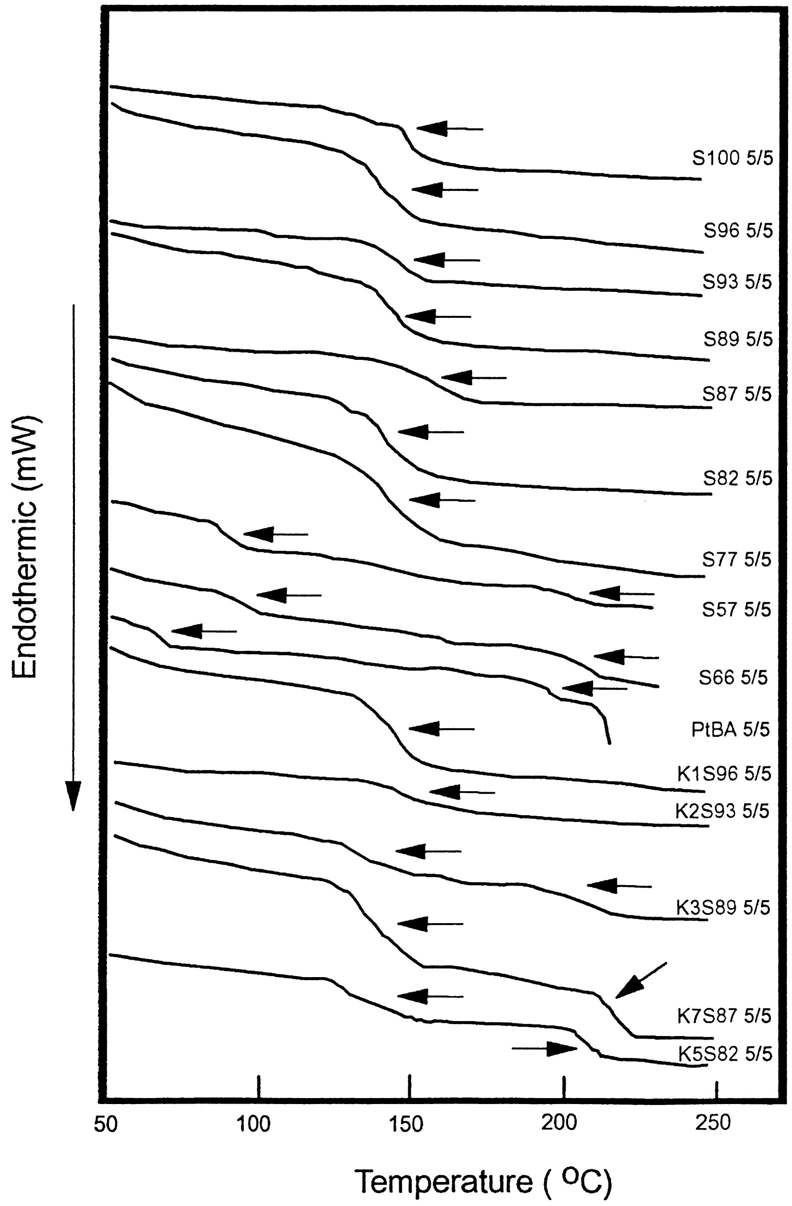


Fig. 2. DSC thermograms for the various copolymer blends. The arrows indicated the position of the glass transition regions and 5/5 represents a 50/50 wt% blend of the copolymers with PPO.

with LTC-50 cooling unit interfaced to a personal computer) at a scan rate of 20°C/min under nitrogen purge. TGA studies were performed from room temperature to 550°C. Thin films for DSC study were first annealed at 150 or 250°C for 30 min (depending on the degradation limit determined from TGA) and then cooled slowly to the next starting temperature (room temperature or −50°C). The temperature and heat of fusion readings from the DSC were calibrated using indium (T_m onset = 156.6°C and $\Delta H_f = 6.8$ cal/g). The glass transition temperatures (T_g) reported were the mid-point of a step-change in specific heat. Specific density of the S-tBA and K salt copolymer thin films was obtained from volume displacement method in a non-solvent (heptane, ethanol). Solvent cast blend films were also employed for X-ray scattering analysis using an X-ray diffractometer (Rigaku D/MAX-B system with rotaflex rotating anode X-ray generator and a wide angle goniometer using CuKα line at 1.54 Å) operated at 40 kV and 100 mA.

3. Results and discussion

The symbols used for the sytrene and *t*-butyl acrylate copolymers were S*XX*, where *XX* was mol% of the styrene moiety I in the copolymers. The copolymers were prepared by mixing different volume ratios of the two purified monomers and polymerized at 70°C using 0.04 mol% of

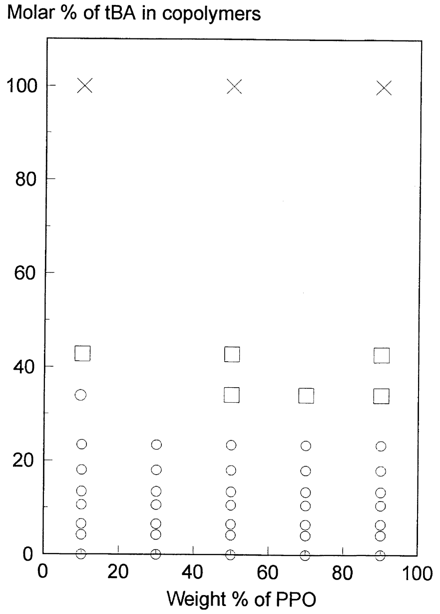


Fig. 3. Phase diagram for the miscibility of the S-tBA copolymers with PPO. The *y*-axis shows the composition of tBA in the copolymers and the *x*-axis shows the PPO wt% in the blends. Open circles indicate the blends were miscible. Open squares indicate partial miscibility. The crosses indicate immiscibility.

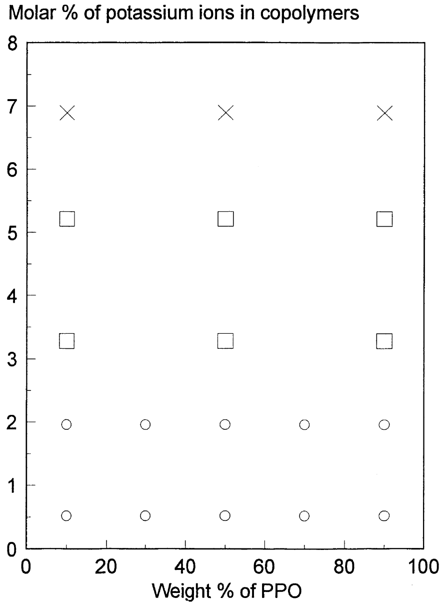


Fig. 4. Phase diagram for the miscibility of the K salt of the acid copolymers with PPO. The *y*-axis shows the composition of K ions in the hydrolyzed copolymers and the *x*-axis shows the PPO wt% in the blends. Open circles indicate the blends were miscible. Open squares indicate partial miscibility. The crosses indicate immiscibility.

recrystallized AIBN initiator under a nitrogen atmosphere. Table 1 listed the chemical composition of the copolymers obtained at different reaction times. The composition did not change significantly throughout the reaction period except at high tBA contents and it was assumed that the copolymers were indeed random. The chemical composition and molecular weight of the copolymers and their derivatives are presented in Table 2. The molecular weight of the copolymers ranged from 46,800 to 105,000 and the copolymers were polydisperse in M_w according to GPC measurements.

From an earlier report [18], hydrolysis of the ester group was incomplete and the yield ranged from 68 to 100 mol% depending on the molar tBA composition of the copolymers. The neutralization step, however, was also found to yield less than one potassium ion per carboxylic acid. The incomplete neutralization can be caused by loss of cations during the Soxhlet extraction process. In Table 3, the ionic copolymers are given the label K*Y*S*XX*, where K indicates a potassium salt and *Y* is the mol% of carboxylic potassium salt. The remaining composition $(100 - Y - XX)$ being tBA and acrylic acid.

Results from TGA studies are shown in Table 4. The S-tBA copolymers have two distinct degradation steps while the hydrolyzed and neutralized products have only one major weight loss step. The weight loss initially at ca. 250°C was related to the tBA contents and weight loss at 360°C was due to decomposition of the styrene moieties. All the ionic copolymers were found to have higher thermal stability than their parent copolymers and the weight loss was almost complete at their respective degradation temperatures. The glass transition temperatures (midpoint) measured for the various S-tBA copolymers and their parent homopolymers from DSC are shown in Fig. 1. The S-tBA copolymers shown a linear decreasing trends from 106°C for polystyrene to 54°C for poly(*t*-butyl acrylate). For comparison purpose only, the T_gs for both the acid and potassium salt neutralized copolymers were also shown in the same figure showing a huge increase in T_g from their parent S-tBA copolymers and were similar to an earlier report [20]. The deviation of the T_gs from the increasing trends could be related to their differences in overall molecular weight and ionic composition. The exact composition of the K salt neutralized and acid copolymers should be referred to in Table 3.

The "as received" PPO is semi-crystalline according to DSC measurements. The solvent cast blends, however, did not show any melting peak that was related to PPO crystallinity even after repeated heating and cooling cycles. The cast films were either transparent or opaque which could be an indication whether the blends were miscible or not. The miscibility of the blends was further evidenced by the detection of a single T_g in between those of the parent polymers. The upper limit for all DSC annealing studies was the degradation temperature of the tBA moiety, which was at approximately 250°C as determined from TGA. The DSC thermograms for some of the blends are shown in Fig. 2. The highest T_g found for the 50/50 blend of K7S85 or K5S82 with PPO was slightly higher than the T_g of pure PPO (ca. 210°C). The results were perplexing, but could

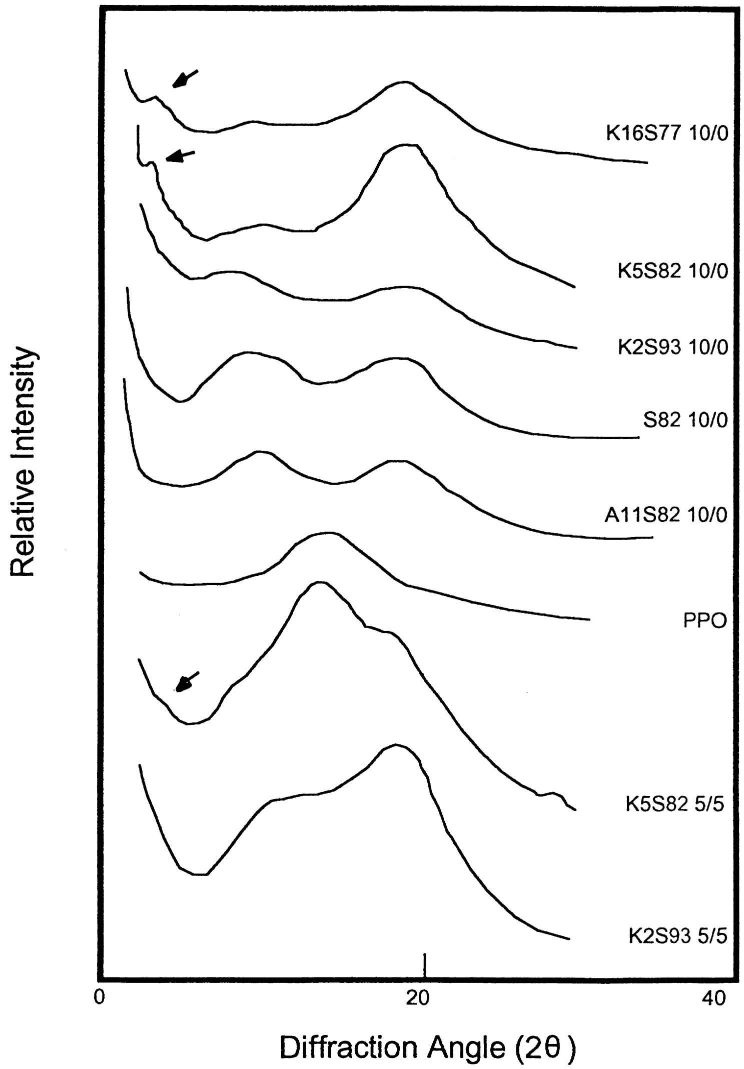


Fig. 5. X-ray diffraction patterns of the blend thin films. The curves were not normalized in order to emphasize the diffraction maximum at small angles ($2\theta < 5°$). The weight ratio at the end indicates whether it was a 50/50 wt% blend (5/5) or a pure copolymer (10/0). The arrows indicate the positions of the ionic peak.

be contributed to the anti-plasticizing nature of tBA or an indication of a strong repulsive interaction between tBA and PPO.

A phase diagram for the S-tBA copolymers with PPO at different tBA and weight compositions is constructed in Fig. 3. All poly(sytrene-r-*t*-butyl acrylate) copolymers containing 4.2–23 mol% tBA were found to be completely miscible with PPO in all composition ranges indicated by a single T_g lying in between those for the S-tBA copolymers and PPO homopolymers. At higher tBA contents, only partial miscibility is observed. The partial miscibility was manifested by two T_gs, one at about 200°C indicating a PPO-rich phase and one at temperature above the T_g of its parent copolymer indicating an S-tBA copolymer-rich phase. It is possible that the partial miscibility was caused by the lower M_w species because the M_w distribution of both components was rather broad. The blends were annealed at different temperatures (below the degradation limit) and no critical solubility temperature has been detected.

The miscibility behavior of the potassium salt of the acid copolymers and PPO was quite different from the neat copolymers. Only the ionic copolymers with 0.5–2 mol% potassium ions were found to be completely miscible with PPO. Those ionic copolymers with over 5.6 mol% potassium were found to be immiscible with PPO. Again, partial miscibility was observed at between 3 and 5 mol% K salt. The phase diagram for the ionic polymer blends is shown in Fig. 4. Annealing of the blends at different temperatures also did not result in any critical solubility temperature. The drastic shift in critical copolymer composition for miscibility could be due to a “long-range” electrical dipole–dipole interaction between the K ion-pairs dominant over the favorable “attractive” phenyl rings interaction. The onset

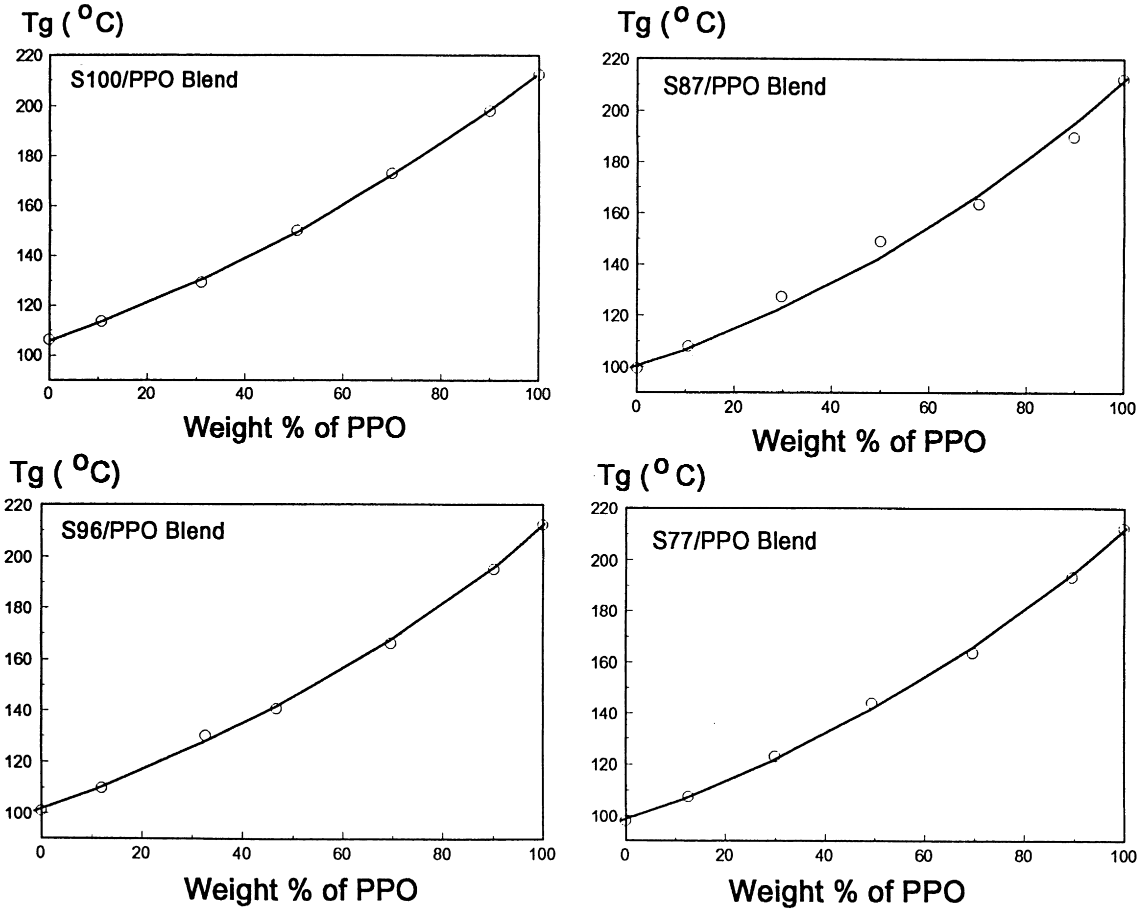


Fig. 6. (a–d) Fittings of the Lu–Weiss equation to the T_g for S-tBA and PPO miscible blends. Open circles indicate experimentally measured T_g for the miscible blends.

of phase separation at approx. 3–5% (molar) ion content coincided with results from a previous study for sodium salt of poly(styrene-methacrylic acid)/PPO blends and was suggested to be caused by the onset of clustering.[10,21] An X-ray scattering study (in Fig. 5) shows a diffraction maximum at the small angle region ($2\theta < 5°$) observed for the high ion-content copolymers and an immiscible ionic blend, and was an indication of formation of ionic clusters within the ionomers. The Bragg's spacing d for the diffraction maximum was approx. 24–30 Å according to Bragg's equation ($1/d = 2/\lambda \sin 2\theta/2$). The spacing d is related to the polymer molecular weight between ionic units (M) and has a scaling relationship of $d \sim M^a$ (where a is a scaling constant) [21]. The d values obtained for different ionomer blends were in the range 30–60 Å [9–12]. Several amorphous halos were also detected from the wide-angle X-ray diffraction study. The amorphous halo is related to the arrangement of the repeating unit structures at the atomic level. It is suggested that the amorphous halo detected at $2\theta = 9°$ was related to tBA, that at 15° related to PPO and that at 19° to styrene structures.

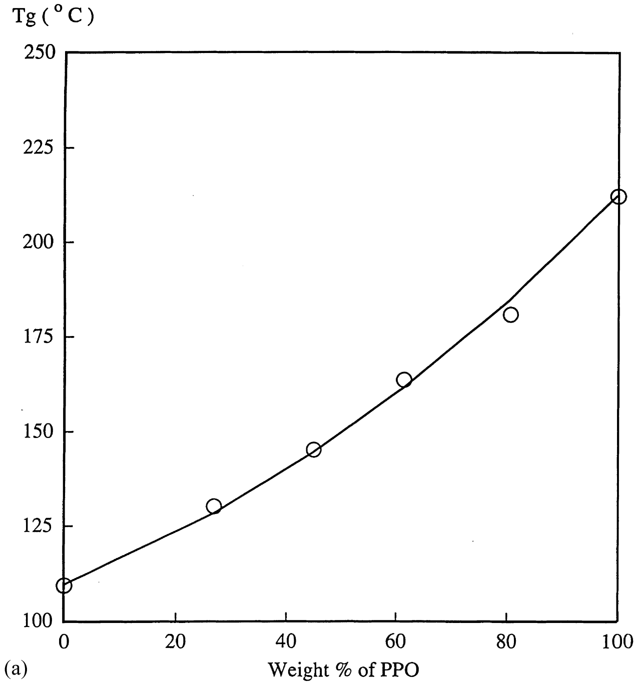
Lu and Weiss [11] have proposed a modified Fox–Flory-type equation of the following form:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} - \frac{A w_1 w_2}{(w_1 + k w_2)(w_1 + b w_1)(w_1 + c w_2)^2}$$

and

$$A = (\chi R(T_{g2} - T_{g1})c/M_1 \Delta C_{p1}),$$

where w_i, $T_{gi}\Delta C_{pi}$, M_i and ρ_i are, respectively, the weight fraction, glass transition temperature, the heat capacity change at T_g, molar mass and density for component i, and $k = \Delta C_{p2}/\Delta C_{p1}$, b is M_2/M_1 and c is ρ_2/ρ_1. The equation can be applied to the calculation of Flory–Huggins-type interaction parameter χ for an amorphous miscible blend. Fig. 6a–d show curve fitting of the above equation to the experimentally measured T_g for the miscible blends of the S-tBA copolymers and PPO. Fig. 7a and b show the same equation applied to the miscible blends of the potassium ionomer and PPO. The equation, in general, was shown to fit well with the experimental data. The interaction parameters



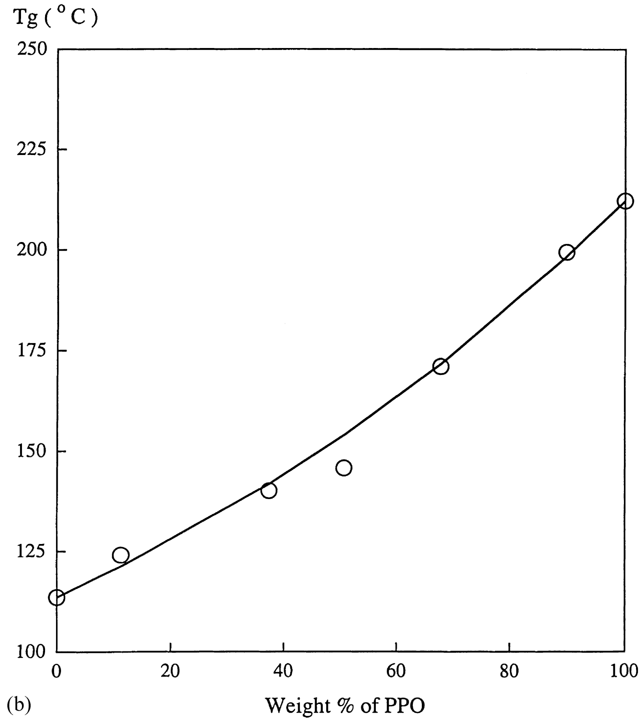


Fig. 7. Fittings of the Lu–Weiss equation to the T_g for K*Y*S*XX* ionomer and PPO miscible blends. Open circles indicate experimentally measured T_g for the miscible blends. (a) K1S96/PPO blends; (b) K2S93/PPO blends.

for the various miscible blends thus calculated are shown in Table 5. The negative χ value indicated that the blends were indeed thermodynamically favorably miscible and their magnitudes also suggested that the interaction was from medium to strong. At closer examination of the S-tBA copolymers/PPO blend series, it was found that the interaction parameter actually decreased with an increase in tBA compositions. As it was believed, the favorable interaction derived from phenyl ring coupling leading to a decrease in styrene contents should result in poorer compatibility. Therefore, one can assume that the increase in favorable interaction for the S-tBA/PPO pair with decreasing styrene

Table 5
Interaction parameter and *A* value of copolymers and PPO blends in the Lu–Weiss equation

Name of copolymer	A (K)	Average interaction parameter
S100	10.6	−0.40
S96	22.0	−0.71
S93	39.4	−1.23
S89	34.9	−1.09
S87	30.5	−1.02
S82	47.1	−1.43
S77	39.6	−1.19
K1S96	23.4	−0.81
K2S93	19.4	−0.67

contents (or higher t-BA contents) was due to the "repulsive" type segmental interaction between the S and tBA moieties.

In the derivation of a Flory–Huggins-type expression explaining a miscibility window found for a random copolymer $(A_xB_{1-x})_n$ and homopolymer $(C)_n$, ten Brinke and Karasz [7] suggested the following equation can be applied,

$$\chi_{\mathrm{blend}} = x\chi_{\mathrm{AC}} + (1-x)\chi_{\mathrm{BC}} - x(1-x)\chi_{\mathrm{AB}}$$

where x is the copolymer composition expressed in volume factions and χ_{AC}, χ_{BC} and χ_{AB} are segmental interaction parameters between the various components. From the miscibility data obtained for the S-tBA and PPO blends (for S96, S87 and S77), the segmental interactions calculated by a linear regression method were $\chi_{(\mathrm{S/PPO})} = -0.52$, $\chi_{(\mathrm{S/tBA})} = 9.28$ and $\chi_{(\mathrm{tBA/PPO})} = 3.73$. The segmental interaction thus calculated for S/PPO was the same order of magnitude compared to a previous study on a ternary blend of PPO/S/brominated-S or -PPO ($\chi_{(\mathrm{S/PPO})} = -0.986$). [4] The magnitude for the other two repulsive segmental interactions, however, were 1–2 orders larger than those previously reported.[1] Although one cannot confirm the absolute magnitude of the segmental interaction values, one can only suggest that any deviations might be related to the theoretical framework set for the above equation. The mean-field treated equation assumed that the polymers were monodispersed and with unlimited M_w, also the segmental interaction was composition independent and the free volume effects can be neglected. Other than the fact that the polymers used in this study were polydisperse and have limited M_w, the detection of heterogeneity in the blends at the repeating unit scale level was also evidenced by the coexistence of several amorphous halos relating to the individual components (S, tBA and PPO) according to the WAXS studies. One can therefore only conclude from the above equation that a relatively strong "repulsive" interaction existed between S/tBA and tBA/PPO segment pairs. The interaction parameters for the potassium ionomer/PPO blends increased slightly with an increase in the ion contents, indicating that the long-range ion-pair interaction tended to reduce compatibility for the ionic blends (see Table 5). However, due to incomplete hydrolysis and degree of neutralization, one cannot use the above relationship to calculate the individual segmental interaction for the ionic blends.

4. Conclusion

In this study, the miscibility of a series of S-tBA copolymers with PPO has been investigated. The transition from miscibility to immiscibility was in the range of above 23 mol% tBA contents. Once the same copolymer has been hydrolyzed and neutralized by potassium ions, the threshold composition for miscibility with PPO was reduced to ca. 3 mol% of the ionic contents. It is also evidenced that the immiscibility was incurred by the formation of ion-pair association or ionic cluster in the ionomer according to a qualitative X-ray scattering study. The interaction parameter for the various miscible blends has been calculated using a modified Fox–Flory-type equation. The negative interaction parameter calculated indicated that the blends are thermodynamically stable. A decrease in the magnitude of the interaction parameter with decreasing styrene contents suggested that "repulsive" type interaction within the S-tBA copolymer could be responsible for the improved compatibility of the S-tBA/PPO polymer pair even at higher tBA contents. The suggestion was concurred by using a copolymer equation to calculate the individual segmental interaction values, although the absolute magnitude cannot be confirmed.

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