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# Immiscibility in polystyrene/sulfonated polystyrene blends

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Miscibility in the binary system of deuterated polystyrene and lightly sulfonated polystyrene has been investigated. Small-angle neutron scattering was used to evaluate the physical state of deuterated polystyrene/polystyrene–1.67% sulfonic acid blends over a wide composition range. Scattering behaviour was found to agree with the Debye–Bueche theory indicating that the blends were phase-separated at all compositions. A large positive interaction between styrene and styrenesulfonic acid monomers is believed to be responsible for the observed immiscibility.

**(Keywords: miscibility; blends; sulfonated polystyrene)**

## INTRODUCTION

It is economically and environmentally advantageous to develop novel polymeric materials through blending of available polymers rather than through synthesis of new polymers. Most polymer pairs, however, are thermodynamically immiscible owing to the small mixing entropy of long-chain molecules. This immiscibility may result in coarse phase-separated blend morphologies. Traditionally, blend morphology control has been achieved through the addition of block copolymer compatibilizers, which segregate to the interfaces, thus improving the overall homogeneity of the mixture and under certain conditions also improving the interfacial strength. These copolymers have to be manufactured separately, typically at considerable cost, and thus many recent efforts have been redirected towards *in situ* compatibilization achieved by interaction of functional groups incorporated onto the blend components (see e.g. refs. 1). This 'reactive compatibilization' may be accomplished through various types of functional group interaction, including formation of covalent bonds, hydrogen bonding and ionic interaction, and potentially offers a simple and cost-efficient route to morphological control in immiscible blends.

Effective reactive compatibilization is dependent on the presence of strongly interacting functional groups. One such interaction, between sulfonic acid groups and various types of nitrogen-containing compounds, has been demonstrated to be particularly strong. For example, recent studies in ionic blends of poly(2-acrylamido-2-methylpropanesulfonic acid) and poly(vinylpyridine)s have shown that the interactions between pyridine groups and sulfonic acid groups are sufficient to cause an effective crosslinking in the blends, resulting in the formation of an insoluble polyelectrolyte complex for this case of fully functionalized components[2,3]. The identical ionic interaction has been exploited in copolymer–copolymer systems, where considerable enhancement in miscibility occurred in the systems poly(styrene-*co*-styrenesulfonic acid)/poly(ethyl acrylate-*co*-4-vinylpyridine)[4] and poly(styrene-*co*-styrenesulfonic acid)/poly(methyl methacrylate-*co*-4-vinylpyridine)[5] relative to the corresponding unfunctionalized homopolymer blends. Sulfonated polystyrenes have similarly been found to promote miscibility in polystyrene/polyamide systems through interactions of sulfonic acid and sulfonic acid salts with amide and amine nitrogens[6,7].

The above-mentioned studies have demonstrated that sulfonated polystyrenes have very strong interactions with nitrogen-containing compounds. In most cases the reactive blends formed have been mixed on the molecular scale, with morphology approaching that of a thermodynamically miscible system. Complete miscibility, however, is often not the desired result of compatibilization efforts. In many cases the goal is morphology control, i.e. the formation of a stable two-phase morphology wherein the size and/or dispersion of the second phase may be controlled. Sulfonated polystyrenes may be utilized to this end by adding them in dilute concentration to blend components, particularly to polystyrene. This approach requires that the functionalized copolymers be miscible with the homopolymer into which they are introduced.

The issue of miscibility in homopolymer/sulfonated copolymer blends has recently been addressed by Hsieh and Peiffer in the system polystyrene/poly(phenylene

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oxide) (PS/PPO)[8]. Blends of PS and PPO, which are miscible in all proportions, were found to exhibit miscibility gaps when one of the components was lightly sulfonated (as determined by thermal analysis). Blends of sodium-sulfonated PS/PPO were miscible over the entire composition range if the acid content did not exceed 2.6%, and miscible for blends in which the sulfonated polystyrene (PS–$SO_3H$) fraction did not exceed 60% for sulfonic acid contents of 4.2%. Similar behaviour was observed for sulfonated PPO/PS blends, where miscibility was observed in 50/50 blends in which the acid content did not exceed 1.9%. The favourable interaction between PS/PPO promotes miscibility in this system. Though this interaction is absent in blends of PS and PS–$SO_3H$, it does not seem unreasonable to speculate that some region of miscibility may exist in this system, particularly at low sulfonation levels and near the concentration extremes.

It is the purpose of this study to examine the compatibility of PS with its sulfonated copolymer counterpart. Other techniques for morphological studies, such as various microscopies, may not be suitable for the study of PS/PS–$SO_3H$ blends because of insufficient contrast between the phases, especially at the low sulfonation levels studied in this work. Small-angle neutron scattering (SANS) was used to determine the state of miscibility of this blend system. SANS is particularly suited to a study of PS and PS–$SO_3H$ because it discriminates among the blend components on the basis of isotopic labelling, rather than on changes in physical properties, which may be small between PS and lightly sulfonated PS.

## THEORETICAL BACKGROUND

The physical state of polymer blends may be determined from SANS experiments through analysis of the scattering function, which describes the relation between the scattered intensity and the scattering vector. The scattering function is, in general, distinctly different for one-phase and two-phase systems. In a miscible, binary system not too far from the critical point, scattering will arise as the result of fluctuations in local concentration[9]. For such a single-phase, binary, interacting system (miscible blend), the inverse of the total scattering may be represented by the sum of the inverse scattering of the individual components less an interaction term[9,10]:

$$\frac{1}{I(q)} = \frac{1}{\phi_1 N_1 D_1(q)} + \frac{1}{\phi_2 N_2 D_2(q)} - 2\chi \tag{1}$$

Here $\phi_i$ and $N_i$ are the volume fraction and degree of polymerization of component $i$, respectively; $q$ is the scattering vector defined as $q = (4\pi/\lambda)\sin\theta$, where $\lambda$ is the radiation wavelength and $\theta$ is the scattering angle; $\chi$ is the interaction parameter; and $D_i(q)$ is the Debye function for the $i$th chain, which may be represented, for small $q$, by the expansion of the Debye function, and takes the form[9]:

$$D_1(q) \simeq 1 - (R_{gi}^2/3)q^2 \tag{2}$$

where $R_{gi} = Nl_i^2/6$ is the radius of gyration of the coil and $l_i$ is the statistical segment length of chain $i$. On substitution and rearrangement, equation (1) may be rewritten in the Ornstein–Zernike form[10,11]:

$$I(q) = \frac{I(q=0)}{[1 + \xi^2(T,\phi)q^2]} \tag{3}$$

where $\xi(T,\phi)$ is the correlation length of the concentration fluctuations at temperature $T$ and composition $\phi$, and is related to the interaction parameter $\chi$, the blend composition $\phi$ and the degree of polymerization $N_i$ of the components. Equation (3) may be written in the form:

$$\frac{1}{I(q)} = \frac{1}{I(q=0)} + \frac{\xi^2(T,\phi)}{I(q=0)}q^2 \tag{4}$$

which demonstrates the linear relationship between $1/I(q)$ and $q^2$ for scattering from a single-phase system.

The expected relation between scattered intensity and scattering vector is considerably different for a phase-separated blend. The scattering from a two-phase system will arise due to differences in scattering length density between the two phases and from the length scale over which these fluctuations occur[12]. The scattering intensity from an isotropic substance is given by[12,13]:

$$I(q) = \kappa\phi_1\phi_2 \int_0^\infty \gamma(r) r^2 \frac{\sin(qr)}{qr}\,\mathrm{d}r \tag{5}$$

where $\gamma(r)$ is a two-point correlation function characterizing inhomogeneities separated by a distance $r$, and $\kappa$ is a constant related to the scattering contrast for the monomer species. The integral may be solved for a randomly dispersed, two-phase system with sharp interfaces by use of the correlation function given by Debye and Bueche[14]:

$$\gamma(r) = \mathrm{e}^{-r/a} \tag{6}$$

where $a$ is the correlation distance and is a measure of the size of inhomogeneities. The calculation results in the following form of the scattering intensity[12,13]:

$$I(q) = \frac{\kappa\phi_1\phi_2 a^3}{(1 + a^2q^2)^2} \tag{7}$$

for a randomly dispersed, two-phase system. Equation (7) may be represented in the form:

$$\frac{1}{[I(q)]^{1/2}} = \frac{1}{(\kappa\phi_1\phi_2 a^3)^{1/2}} + \frac{a^2}{(k\phi_1\phi_2 a^3)^{1/2}}q^2 \tag{8}$$

which indicates that a plot of $1/[I(q)]^{1/2}$ *versus* $q^2$ should be linear for scattering from a randomly dispersed, phase-separated blend.

## EXPERIMENTAL

Two narrow molecular-weight distribution, deuterated, linear polystyrenes (dPS) were obtained from Polymer Laboratories having $M_w = 188\,000$ and $M_w/M_n = 1.02$, and $M_w = 210\,000$ and $M_w/M_n = 1.02$. Sulfonated polystyrene (PS–$SO_3H$), provided by Exxon Research and Engineering Co., was produced from a commercial polystyrene having $M_w = 212\,000$ and $M_w/M_n = 2.36$ by sulfonating using the method of Makowski *et al.*[15] to an acid content of 1.67 mol% (PS-1.67 $SO_3H$). This sulfonation process is not believed to result in significant changes in molecular weight[16]. One blend of the 210 000 molecular weight dPS and PS-1.67$SO_3H$ was prepared in a 50/50 weight ratio. Blends of 188 000 molecular weight dPS and PS-1.67SO$_3$H were prepared in dPS/PS–SO$_3$H weight ratios of 5/95, 10/90, 90/10 and 95/5. All blends were prepared by solution casting from dilute tetrahydrofuran (THF), a common solvent, followed by drying under vacuum at 40°C for 4 h plus 4 h at 125°C. After drying, blends were compression moulded at $160 \pm 15$°C into discs nominally 14 mm in diameter and 0.5 mm thick suitable for the SANS apparatus. Typical times of 20–30 min at elevated temperature were used for compression moulding of discs, and it is during this step in the sample processing that the final physical state of the blend is believed to develop. The scattering experiments were performed on the 30 m SANS instrument at the Cold Neutron Research Facility of the National Institute of Standards and Technology, Gaithersburg, MD[17]. The scattering was recorded at 140°C, which is well above the glass transition temperature of blend components. The wavelength of incident neutrons used was 5 Å. Data were corrected for empty cell and background scattering and the intensity subsequently converted to absolute units using a secondary calibration standard.

## RESULTS AND DISCUSSION

The experimental scattering intensity of all PS-1.67SO$_3$H blends as a function of scattering vector is shown in *Figure 1*. The lower $q$ limit of the data range was approximately 0.004 Å$^{-1}$ corresponding to a real-space dimension of about 1570 Å.

*Figure 2* illustrates the experimental scattering from the 5/95 dPS/PS-1.67SO$_3$H blend in the $1/I(q)$ *versus* $q^2$ form. This blend is representative of the behaviour of the entire group of blends studied. The agreement between the experimentally measured small-angle neutron scattering in the dPS/PS–SO$_3$H system and the expected behaviour for scattering from a single-phase system is poor. In contrast, the agreement between the theory of scattering from two-phase structures and the

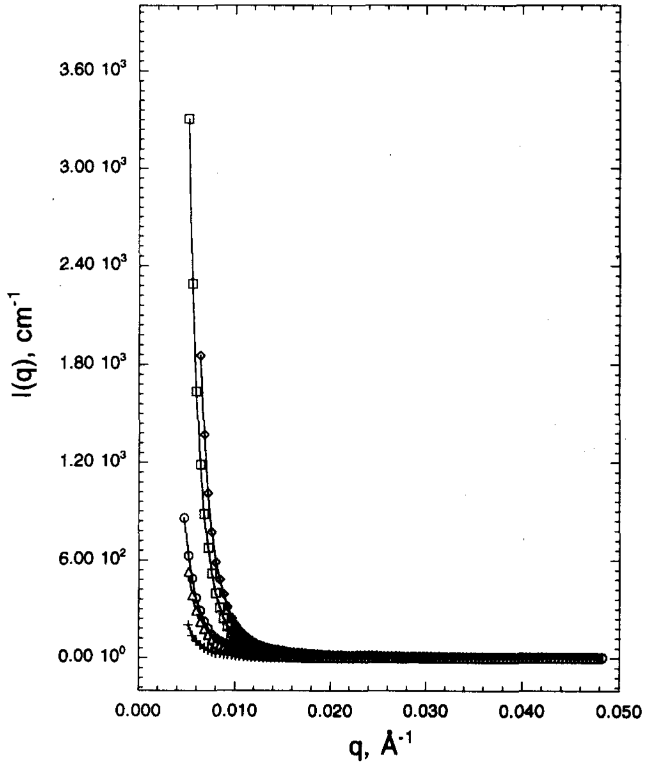

**Figure 1** Small-angle neutron scattering from dPS/PS-1.67SO$_3$H blends of various weight ratios: (○) 5/95; (□) 10/90; (◇) 50/50; (△) 90/10; (+) 95/5

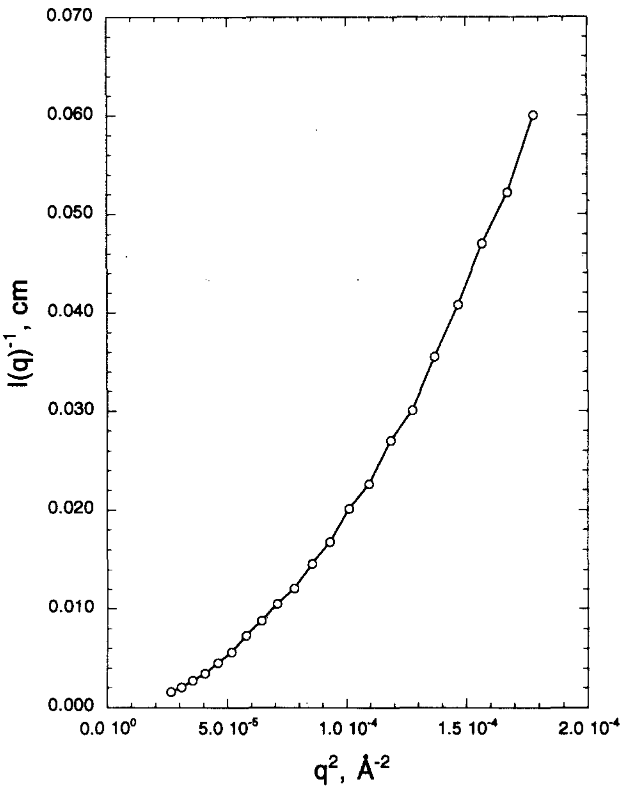

**Figure 2** Non-linear relationship between $I(q)^{-1}$ and $q^2$ in 5/95 dPS/PS-1.67SO$_3$H blends

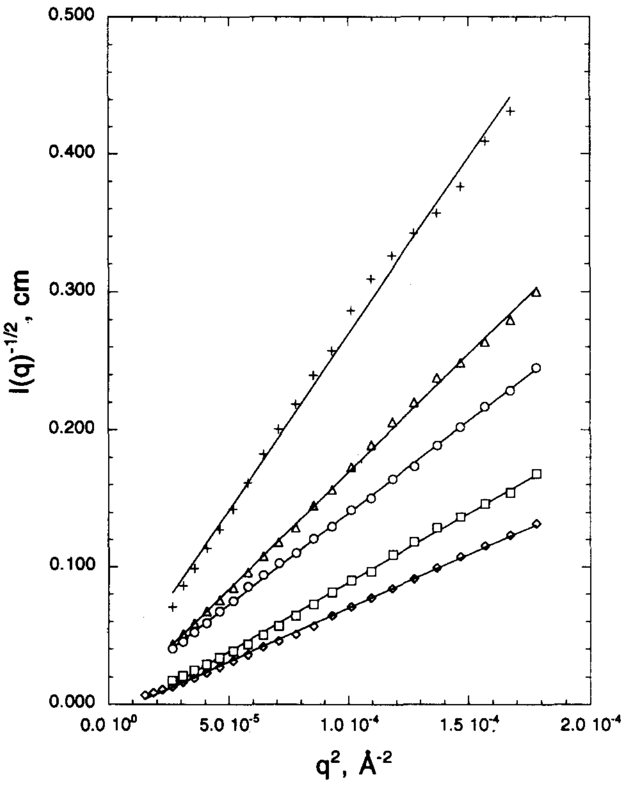

**Figure 3** Linear relationship between $I(q)^{-1/2}$ and $q^2$ in dPS/PS-1.67SO$_3$H blends of various weight ratios: (○) 5/95; (□) 10/90; (◇) 50/50; (△) 90/10; (+) 95/5

experimental results is excellent (*Figure 3*). A linear relation exists between $1/[I(q)]^{1/2}$ and $q^2$ for all of the blends studied. This result clearly indicates that the system dPS/PS–1.67SO$_3$H is immiscible over the concentration range investigated.

From equation (8) one can see that the square root of the slope-to-intercept ratio from the linearized plot should be equal to the correlation length, which as stated above is an indication of the average size of the inhomogeneities responsible for scattering. The curves of *Figure 3* were fitted with a linear regression to yield values for the slope and intercept. These are presented along with calculated values of the correlation length $a$ in *Table 1*. Owing to the small magnitude of the intercept, the calculation of $a$ is particularly sensitive to small errors in the intercept, and it was not possible to calculate meaningful values for all blends. The values that were obtained indicate that the correlation length is on the order of hundreds of ångströms or larger.

Though this scattering study determines unequivocally the phase-separated nature of dPS/PS–1.67SO$_3$H blends, these results are somewhat surprising. With such a low concentration of sulfonic acid groups, it was not intuitively obvious that the blends should exhibit phase separation at all, particularly near the concentration extremes. This behaviour indicates that the interaction parameter between styrene and styrenesulfonic acid is extremely large. It is possible to make a lower-bound estimate for this interaction parameter by invoking the classical Flory–Huggins theory of phase separation[18] along with a copolymer blend modification to the interaction parameter. For a blend of homopolymer A and copolymer $B_yC_{1-y}$ the total interaction parameter for the system may be represented by an effective blend interaction[19,20]:

$$\chi_{\text{blend}} = y\chi_{A/B} + (1-y)\chi_{A/C} - y(1-y)\chi_{B/C} \qquad (9)$$

which, for this system with $y = 0.0167$, reduces to:

$$\chi_{\text{blend}} = 0.0167\chi_{\text{dS/S-s}} + 0.9833\chi_{\text{dS/S}} - 0.01642\chi_{\text{S-s/S}} \qquad (10)$$

where the subscripts dS, S and S-s represent the deuterated styrene, styrene and styrenesulfonic acid monomers, respectively (see also refs. 21–24). In order to make a lower-bound estimate of the interaction parameter between styrene and styrenesulfonic acid, the assumptions $\chi_{\text{dS/S-s}} = \chi_{\text{S/S-s}}$ and $\chi_i \neq \chi_i(\phi)$ will be used. $\chi_{\text{dS/S}}$ may be estimated from the results given by Bates and Wignall[25] ($\chi_{\text{dS/S}} = 0.2T^{-1} - 2.9 \times 10^{-4}$) and takes the value of $1.94 \times 10^{-4}$ at 140°C. The criterion that the interaction parameter for this system ($\chi_{\text{blend}}$) must be larger than the value defining the single-phase stability limit (binodal):

$$\chi_{\text{blend}} \geqslant \chi_{\text{binodal}} \qquad (11)$$

**Table 1** Correlation length from linear regression for various dPS/PS–1.67SO$_3$H blends

| Blend | Correlation length, $a$ (Å) |
|---|---|
| 5/95 | 390 |
| 10/90 | 1040 |
| 50/50 | – |
| 90/10 | 510 |
| 95/5 | 430 |

is employed. The value of $\chi_{\text{binodal}}$ may be calculated for a blend of phases i and ii by setting the Flory–Huggins chemical potential ($\Delta\mu$) of species 1 (2) in phase i equal to the chemical potential of species 1 (2) in phase ii, and solving the resulting system of equations for $\chi$[26]:

$$\begin{aligned}\frac{\Delta\mu_1^{\text{i}}}{RT} &= \ln\phi_1^{\text{i}} + \left(1-\frac{N_1}{N_2}\right)\phi_2^{\text{i}} + N_1\chi_{12}(\phi_2^{\text{i}})^2\\ &= \frac{\Delta\mu_1^{\text{ii}}}{RT} = \ln\phi_1^{\text{ii}} + \left(1-\frac{N_1}{N_2}\right)\phi_2^{\text{ii}} + N_1\chi_{12}(\phi_2^{\text{ii}})^2 \qquad (12)\\ \frac{\Delta\mu_2^{\text{i}}}{RT} &= \ln\phi_2^{\text{i}} + \left(1-\frac{N_2}{N_1}\right)\phi_1^{\text{i}} + N_2\chi_{12}(\phi_1^{\text{i}})^2\\ &= \frac{\Delta\mu_2^{\text{ii}}}{RT} = \ln\phi_2^{\text{ii}} + \left(1-\frac{N_2}{N_1}\right)\phi_1^{\text{ii}} + N_2\chi_{12}(\phi_1^{\text{ii}})^2\end{aligned}$$

where

$$\phi_1^{\text{i}} + \phi_2^{\text{i}} = 1 \qquad \phi_1^{\text{ii}} + \phi_2^{\text{ii}} = 1 \qquad (13)$$

Equations (12) and (13) are readily solved by computer. For the most extreme case in this study, the 5/95 dPS/PS–1.67SO$_3$H blend:

$$\begin{aligned}\chi_{\text{binodal}} &= 1.758 \times 10^{-3}\\ \chi_{\text{blend}} &= 2.80 \times 10^{-4}\chi_{\text{S/S-s}} + 1.94 \times 10^{-4}\end{aligned} \qquad (14)$$

yielding:

$$\chi_{\text{S/S-s}} \geqslant 5.6 \qquad (15)$$

This value for $\chi_{\text{S/S-s}}$ is extremely large compared to typical values for polymer systems reported in the literature. This may not be surprising considering $\chi_{\text{S/S-s}}$ represents the interaction between an organic and an inorganic monomer and therefore should not necessarily be compared to previously measured interaction parameters in systems where both components are organic. It is noteworthy that for this example if $\chi_{\text{dS/S}}$, often considered negligibly small, is omitted the result is an error of approximately 12.4% during the calculation. Taking the broad molecular-weight distribution of the PS–SO$_3$H copolymer into consideration would result in a slightly decreased estimate for $\chi_{\text{S/S-s}}$ (refs. 10, 26), but in essence, the conclusions from this exercise remain the same. While this method may represent only a lower-bound estimate, it supports the experimental results, which indicate that the interaction between styrene and styrenesulfonic acid must be strong and positive, and prohibits miscibility in this system.

## CONCLUSIONS

Miscibility in the system dPS/PS–1.67SO$_3$H has been investigated through small-angle neutron scattering. The experimental scattering results were compared to the behaviour predicted by mean-field theory for scattering from one-phase blends and to the behaviour predicted by the Debye–Bueche relation for two-phase systems. Scattering from dPS/PS–1.67SO$_3$H blends exhibits the Debye–Bueche behaviour. The results indicate that the dPS/PS–1.67SO$_3$H blends are phase-separated and the polymer system is immiscible in the concentration region from 5% to 95% dPS.

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