Small-angle neutron scattering studies on the miscibility of deuterated polysulfone and modified polysulfone blends

H. Takeno[a,1], T. Hashimoto[a,*], M. Weber[b], H. Schuch[b], S. Koizumi[c]

[a]*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan*
[b]*BASF AG, Kunststofflaboratorium, B1, D-67056 Ludwigshafen, Germany*
[c]*Advanced Science Research Center, Japan Atomic Energy Research Institute Tokai, Ibaraki 319-11, Japan*

Abstract

Small-angle neutron scattering technique was used to study the effects of the microstructural change on the miscibility and the effective segmental interaction parameter (χ) of deuterated polysulfone (d-PSU) and protonated PSU (PSU) blends. For the studies of the end-group effects on the miscibility and the χ parameter, we prepared the three kinds of blends of d-PSU with PSU terminated with mostly Cl end-group (PSU–Cl), PSU terminated with mostly OH end-group (PSU–OH) and PSU terminated with phthalic anhydride group (PSU–PhAh). For the studies of copolymerization effects, we prepared a copolymer of a sulfone unit and a monomer unit with COOH group (DPA unit) (PSU–COOH). The χ parameters were estimated from the SANS profiles as a function of temperature for the blends of d-PSU with various modified PSUs and summarized in a figure in the text. Further, in the blends of d-PSU and PSU–PhAh, the χ parameter was found to be very sensitive to the molecular weight of PSU–PhAh: if the molecular weight of PSU–PhAh is small, the blend was shown to be phase-separated, i.e. the effect of the end-group of PhAh on the miscibility and the χ parameter was found to be very large. In the blend of d-PSU and PSU–COOH, the phase behavior was found to strongly depend upon the content of DPA unit included in PSU-COOH. The larger the content of DPA unit, the larger the χ parameter. If the content was larger than a critical value, the blend was found to phase-separate. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polysulfone; Blend; Small-angle neutron scattering

1. Introduction

Polysulfones (PSUs) are high-performance thermoplastics which have aromatic groups and sulfone groups (SO$_2$) in the backbone of the polymer chain. PSUs have characteristics of high temperature-resistance and excellent mechanical strength. However, to achieve better properties of polymer materials, blending a polymer with other polymers (polymer alloy) is generally a very useful technique, e.g. the mechanical properties may be improved. However, blending of PSU with other polymers is generally difficult because they are immiscible, which makes an application of it as polymer alloys difficult.

Reactive blending is a very useful technique for circumventing this difficulty and to compatibilize PSU with other polymers such as polyamides (PAs). The reactive blending of PSU and PA produces diblock or graft copolymers at the interfaces of two phases (e.g. PSU phase and PA phase) through a chemical reaction between end groups of PA and functional groups introduced into PSU. The block or graft copolymers thus produced behave as "surfactants", lowering the interfacial tension of the two coexisting phases and hence decreasing the size of macrophase-separated domains. Thus, they act as a "compatibilizer". For this reactive blending, it is necessary to attach a functional group to PSU. This modification of PSU is expected to largely change the miscibility against unmodified PSU, because the change in combinatorial entropy on mixing of polymer blends is remarkably small relative to that of mixtures of small molecules [1,2] and therefore, even a subtle change in the chemical structure of one component significantly affects the miscibility of polymer blends. In the reactive blending of PSU and PA, we blend the unmodified PSU with the modified PSU (m-PSU) and PA, i.e. we formulate a ternary mixture of unmodified PSU, m-PSU and PA. It is important to know the miscibility of

* Corresponding author. Tel.: +81-75-753-5604; fax: +81-785-753-4864.
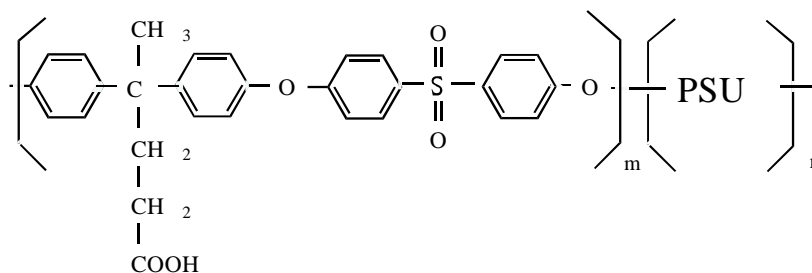*E-mail address:* hashimoto@alloy.polym.kyoto-u.ac.jp (T. Hashimoto)
[1] Present address: Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan.
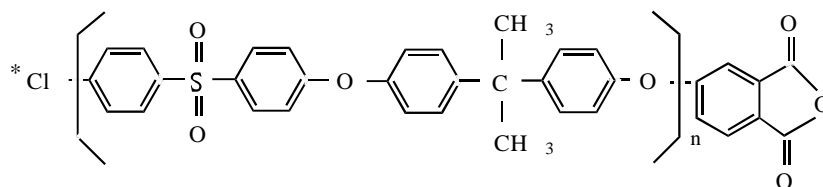
(a) PSU

X · ⟮ [phenyl]—S(=O)(=O)—[phenyl]—O—[phenyl]—C(CH₃)(CH₃)—[phenyl]—O ⟯ₙ · Y
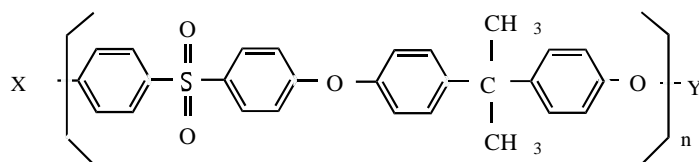
X,Y: Cl- or OH-group

(b) PSU-COOH (random copolymer of DPA
unit and sulfone unit)

· ⟮ [phenyl]—C(CH₃)(CH₂CH₂COOH)—[phenyl]—O—[phenyl]—S(=O)(=O)—[phenyl]—O ⟯ₘ ⟮ PSU ⟯ₙ

DPA unit

(c) PSU-PhAh

*Cl · ⟮ [phenyl]—S(=O)(=O)—[phenyl]—O—[phenyl]—C(CH₃)(CH₃)—[phenyl]—O ⟯ₙ · [phthalic anhydride]

* or   OH   group

Fig. 1. Chemical structures for (a) PSU, (b) PSU–COOH and (c) PSU–PhAh.

unmodified PSU and m-PSU, because it is expected to strongly affect the reaction efficiency between the m-PSU and PA: the efficiency depends on whether unmodified PSU and m-PSU are phase-separated or not.

In this study, we prepared two-types of m-PSUs, e.g. a random copolymer of sulfone unit and diphenoic acid [IUPAC-name: 4,4-Bis-(4-hydroxyphenyl)-valeric acid] unit (DPA unit) with COOH group, designated as PSU–COOH, and PSU end-capped with phthalic anhydride (PhAh) group, designated as PSU–PhAh. Both modified PSUs can react with PAs to form the graft or block copolymers at the interfaces of the phase-separated domains which act as a compatibilizer, creating finely dispersed

PSU-particles [3]. We report on the miscibility between the blends of d-PSU and their m-PSUs.

2. Experimental

2.1. Sample characteristics and sample preparation

Fig. 1 shows the chemical structures of PSU, PSU–COOH and PSU–PhAh. PSU has benzene rings and sulfone groups in the backbone with terminal Cl or OH groups. Three-kinds of PSUs were prepared; two of them have mostly Cl end-groups (PSU–Cl1 and PSU–Cl2), whereas

Table 1
Sample characteristics (T_g: glass transition temperature obtained by DSC measurements; N_w and N_w/N_n: weight-averaged degrees of polymerization N_w and heterogeneity indices for degree of polymerization; N_w/N_n, respectively, which were obtained by means of light scattering and GPC measurements)

Specimen	T_g (°C)	N_w	N_w/N_n	DPA (mol%)[a]	End group		
					PhAh%	OH%	Cl%[b]
d-PSU	180	41	4.07	–	0	3	97
PSU–C11	177	24	2.49	–	0	5	95
PSU–C12	174	32	2.60	–	0	3	97
PSU–OH	169	34	3.17	–	0	87	13
PSU–COOH1.6	–	33	2.88	1.6	–	–	–
PSU–COOH4.5	180	40	3.89	4.5	–	–	–
PSU–COOH6.0	174	22	2.64	6.0	–	–	–
PSU–PhAh1	182	43	3.70	–	42	40	18
PSU–PhAh2	186	177	7.19	–	42	8	50

[a] Content of DPA unit was obtained by ^{1}H NMR.
[b] The end-group was estimated by several methods such as titration, spectroscopy and elemental analysis.

one of them has mostly OH end-groups (PSU–OH). Their characteristics are shown in Table 1. PSU–COOH is a co-polymer of DPA units and sulfone units. In this study, we prepared three-kinds of PSU–COOHs with different contents of DPA unit as shown in Table 1. PSU–PhAh is terminated with PhAh group. However, not all the end-groups are PhAh, there are still Cl groups or OH groups left over (incomplete conversion). Two-kinds of PSU–PhAhs were prepared as shown in Table 1. Both PSU–PhAh1 and PSU–PhAh2 have 42% PhAh end-groups on average. However, as PSU–PhAh1 has a lower molecular weight than the PSU–PhAh2, the effect of end-group on the miscibility for the former is expected to be larger than that for the latter. Each of the above eight-kinds of PSUs or m-PSUs was blended with deuterated PSU (d-PSU) terminated mostly with Cl end-groups.

The blend samples were prepared by dissolving each polymer in dichloromethane. The solutions were mixed at room temperature and stirred for 30 min to prepare homogeneous solutions of the blends containing total amount of polymers by ca. 10 wt.%. The polymer blend solutions were then precipitated in methanol at room temperature. The precipitate was isolated by filtration, dried at 50°C in vacuo for 12 h, and then melt-pressed into films. The blend films obtained were sandwiched between copper plates for SANS (small-angle neutron scattering) measurements. All the blends prepared have a composition of 50/50 (wt.%/wt.%).

2.2. SANS

SANS measurements were performed with the SANS instrument (SANS-J) at the Japan Atomic Energy Research Institute in Tokai. Neutron beam with wavelength $\lambda = 6.5$ Å and $\Delta\lambda/\lambda = 0.13$ monochromatized with a velocity selector was used for the measurements. Neutron scattered intensity was detected by a two-dimensional detector, and circularly averaged scattered intensity was

obtained as a function of q, where q is a magnitude of the scattering vector given by $q = (4\pi/\lambda) \sin(\theta/2)$. λ and θ are the wavelength and the scattering angle in the medium, respectively. The scattered intensity obtained was corrected for the detector sensitivity, transmission, and the scattering from empty cell. The corrected intensity was further reduced to the absolute units (cm^{-1}) using water (H$_2$O) as a standard sample for calibration [4].

2.3. Scattering function in a single-phase state of polymer blends

The structure factor $S(q)$ of polymer blends with molecular weight polydispersity in the single phase state is given by

$$\frac{k_N}{S(q)} = \frac{1}{\phi_1 N_{n,1} v_1 P_{w,1}(q)} + \frac{1}{\phi_2 N_{n,2} v_2 P_{w,2}(q)} - \frac{2\chi}{v_0} \quad (1)$$

with

$$k_N = N_0 \left(\frac{a_1}{v_1} - \frac{a_2}{v_2} \right)^2 \quad (2)$$

according to the calculation based on random phase approximation (RPA) [5,6]. k_N and N_0 are contrast factor and Avogadro's number, respectively. a_i is the neutron scattering length for ith component ($i = 1$ or 2) with volume fractions ϕ_i, number-averaged degree of polymerization $N_{n,i}$ and molar volume of the segment v_i. v_0 is the reference volume defined by $v_0 = (\phi_1/v_1 + \phi_2/v_2)^{-1}$. $P_{w,i}(q)$ is a weight-averaged form factor of the single polymer chain for ith component. χ is the Flory–Huggins segmental interaction parameter between the two polymers comprising blends. This is an *effective* interaction parameter per segment. In the small q range, $P_{w,i}(q)$ is presented in the following form [6]

$$P_{w,i}(q) \approx \frac{N_{w,i}}{N_{n,i}} \left(1 - \frac{1}{3} \frac{N_{z,i}}{N_{n,i}} R_{g,n,i}^2 q^2 \right), \quad (3)$$

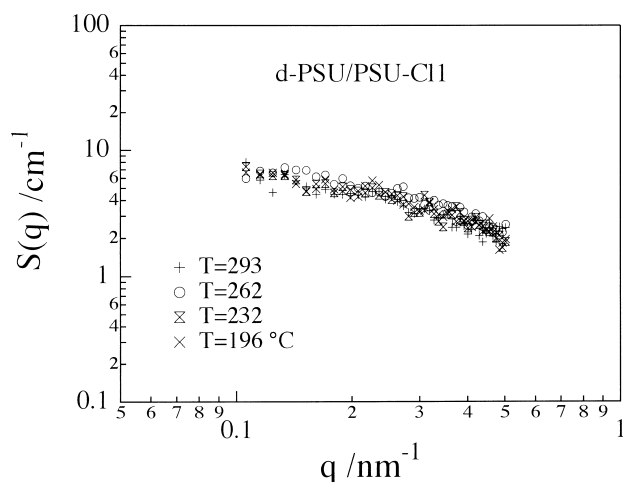where $N_{w,i}$ and $N_{z,i}$ are the weight- and z-averaged degrees of

Fig. 2. Temperature dependence of the scattering structure factor for d-PSU/PSU–Cl1.

polymerization for the ith component, respectively. $R_{g,n,i}^2$ is square of the number-averaged radius of gyration for the ith component. From Eqs. (1) and (3), $S(q)$ in the small q range is given in the Ornstein–Zernike (O–Z) form;

$$S(q)^{-1} = S(0)^{-1} + Aq^2, \tag{4}$$

$$S(0)^{-1} = \frac{1}{k_N}\left(\frac{1}{\phi_1 N_{w,1} v_1} + \frac{1}{\phi_2 N_{w,2} v_2} - \frac{2\chi}{v_0}\right). \tag{5}$$

We can estimate the parameter χ from the value of $S(0)^{-1}$ by using Eq. (5).

3. Results

Fig. 2 shows the neutron scattering profiles for the blend of d-PSU and PSU–Cl1 (d-PSU/PSU–Cl1; hereafter, we designate the blends of X and Y as X/Y) at various temperatures. The scattering profiles for d-PSU/PSU–Cl1 have almost no temperature dependence and a gradual q-dependence. Although we do not show the scattering profiles for d-PSU/PSU–Cl2 and d-PSU/PSU–OH here, they are very similar to that of d-PSU/PSU–Cl1, i.e. they are almost independent of the temperature and have a gradual q-dependence.

Fig. 3 shows the scattering profiles for (a) d-PSU/ PSU–PhAh1 and (b) d-PSU/ PSU–PhAh2 at various temperatures. Similarly to the scattering profile for d-PSU/ PSU–Cl1, both the scattering profiles are almost independent of temperature. However, the scattering profiles for d-PSU/ PSU–PhAh1 in the temperature range from 283 to 201°C have a slight upturn (an excess scattering) in the small q ($q < 0.14$ nm^{-1}), whereas such upturn is not observed in the scattering profile of d-PSU/PSU–PhAh2. As the upturn of the scattering profile for d-PSU/PSU– PhAh1 is weak and therefore not very obvious, we measured
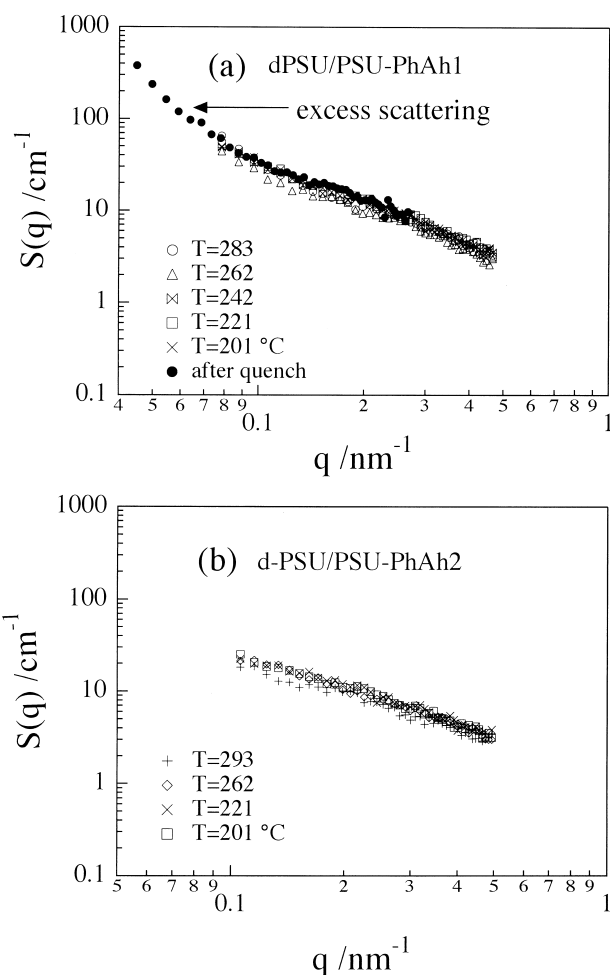

Fig. 3. Temperature dependence of the scattering structure factors for (a) d-PSU/PSU–PhAh1 and (b) d-PSU/PSU–PhAh2.

the scattering profile in the q range smaller than 0.08 nm^{-1}, i.e. the q range which was not covered by in situ measurements at temperatures from 283 to 201°C, on the blend sample vitrified by rapid quenching of the blend from 201°C to room temperature, which is lower than the glass transition temperature of the blend (182°C).[2] The scattering profile in the smaller q ($q < 0.08$ nm^{-1}) has more remarkable excess scattering than that in the larger q ($q > 0.08$ nm^{-1}) (see the data represented by filled circles in Fig. 3(a)).

Fig. 4 shows the scattering profiles for the three blends of d-PSU with PSU–COOH having contents of (a) 1.6 mol% DPA unit (d-PSU/PSU–COOH1.6), (b) 4.5 mol% DPA unit

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[2] The blend under consideration is phase-separating and hence the SANS profiles are time-dependent, especially at the small q range ($q < 0.08$ nm^{-1}) where the profiles are sensitive to the phase-separating domains. In contrast to the profile in the small q range, the profile at the large q range ($q > 0.08$ nm^{-1}) is less sensitive to the domains and hence to the time spent for the phase separation, because it depends on concentration fluctuations within the phase-separated domains [7]. Therefore, we measured the SANS profile (including the profile at $q < 0.08$ nm^{-1}) on the vitrified blend.
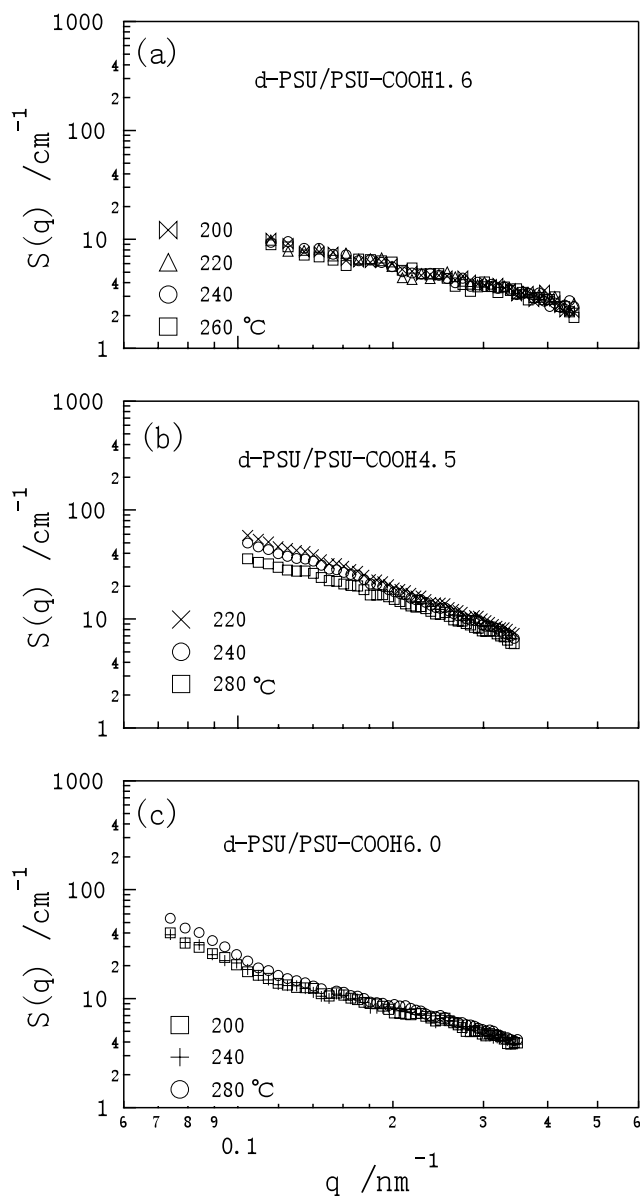
Fig. 4. Temperature dependence of the structure factors for (a) d-PSU/PSU–COOH1.6, (b) d-PSU/PSU–COOH4.5 and (c) d-PSU/PSU–COOH6.0.

(d-PSU/PSU–COOH4.5) and (c) 6.0 mol% DPA unit (d-PSU/PSU–COOH6.0). In Fig. 4(a), the scattering profiles for d-PSU/PSU–COOH1.6 hardly depend upon temperature. However, the scattering intensity for d-PSU/PSU–COOH4.5 increases with a decrease of temperature in the q range covered in this study (Fig. 4(b)). However, the scattering profile for d-PSU/PSU–COOH6.0 exhibits an upturn in the small q ($q \leq 0.15$ nm^{-1}) as shown in Fig. 4(c). In the high q ($q > 0.15$ nm^{-1}), the scattering intensity is almost independent of temperature, whereas the scattering intensity in the small q ($q \leq 0.15$ nm^{-1}) at 280°C is larger than those at 240 and 200°C.
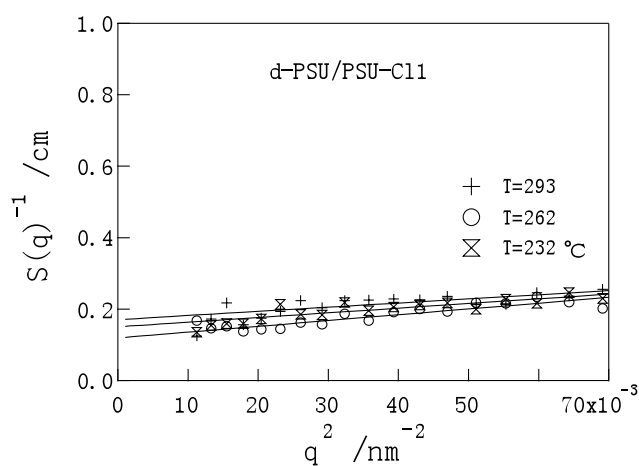

Fig. 5. O–Z plot for d-PSU/PSU–Cl1 at various temperatures.

4. Discussion

4.1. Miscibility and χ parameters for blends of d-PSU and various m-PSUs

Fig. 5 shows the O–Z plot [Eq. (4): $S(q)^{-1}$ vs q^2] for d-PSU/PSU–Cl1. The $S(q)^{-1}$ has a linear relation against q^2. This result indicates that d-PSU/PSU–Cl1 is in a single-phase state in the temperature range covered in this study. By using Eq. (5), we can estimate the χ parameter from the $S(0)^{-1}$ obtained by an extrapolation of the linear relation between $S(q)^{-1}$ and q^2 toward $q = 0$. The result is presented later in Fig. 9. Similarly, we obtained the χ parameter for d-PSU/PSU–Cl2 and d-PSU/PSU–OH at various temperatures from the $S(0)^{-1}$. We will discuss their χ parameters in Fig. 9 later.

Fig. 6 presents the O–Z plots for (a) d-PSU/PSU–PhAh1 and (b) d-PSU/PSU–PhAh2. In Fig. 6(a), $S(q)^{-1}$ for d-PSU/PSU–PhAh1 cannot be fitted well with the O–Z equation in the whole q range covered in this work. Though in the range of q^2 larger than $q^2 \approx 0.02$ nm^{-2}, $S(q)^{-1}$ linearly increases with q^2, $S(q)^{-1}$ deviates downward from the linear relation in the range of q^2 smaller than $q^2 \approx 0.02$ nm^{-2}. The straight line in Fig. 6(a) represents a linear fitting to the data at $q^2 > 0.02$ nm^{-2} and its extrapolation toward $q^2 < 0.02$ nm^{-2}. The value q^2, where $S(q)^{-1}$ deviates downward from the linear relation, corresponds to that of q where the scattering profiles start to exhibit the upturn, as shown in Fig. 3(a). The excess scattering in the small q range is considered to be caused by phase separation. As discussed earlier, in the small q range, we probably observed the scattering due to the phase-separated domains, which causes a larger scattering intensity compared with that in the single-phase state. However, in the high q, we observed the scattering from thermal concentration fluctuations inside the phase-separated domains and therefore, the relation between $S(q)^{-1}$ and q^2 is linear. In Fig. 6(b), the $S(q)^{-1}$ for d-PSU/PSU–PhAh2 has a linear relation against q^2
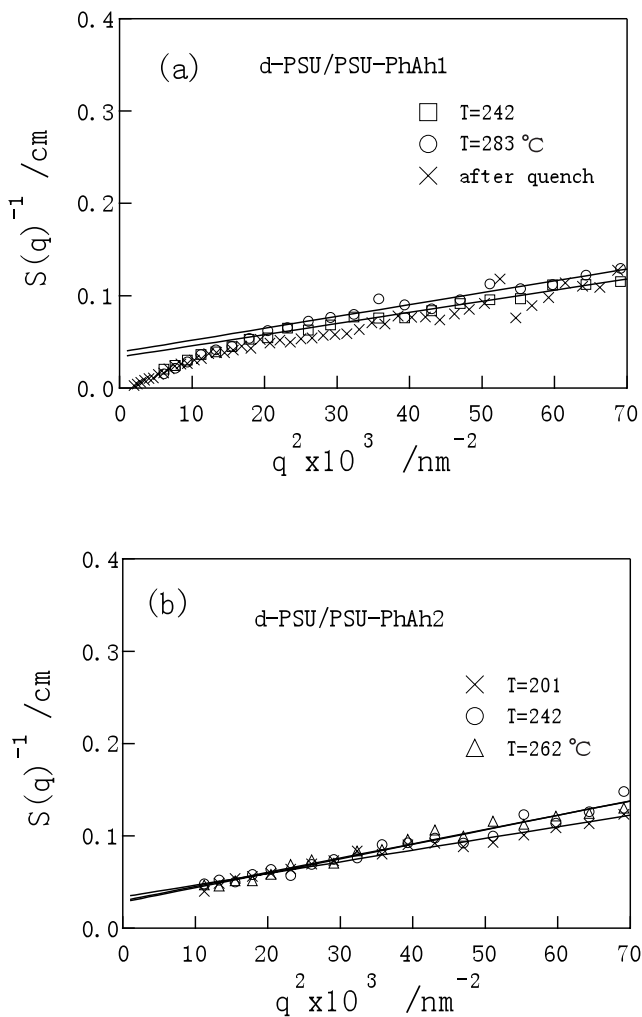
Fig. 6. O–Z plots for (a) d-PSU/PSU–PhAh1 and (b) d-PSU/PSU–PhAh2 at various temperatures.

Fig. 7. O–Z plots for (a) d-PSU/PSU–COOH1.6, (b) d-PSU/PSU–COOH4.5 and (c) d-PSU/PSU–COOH6.0 at various temperatures.

and deviation from the linear relation is not observed, indicating that d-PSU/PSU–PhAh2 is in the single-phase state in the temperature range covered in this study. The χ parameter obtained from the O–Z plot is presented later in Fig. 9 and will be discussed later.

Although both of PSU–PhAh1 and PSU–PhAh2 have 42% of end groups of PSU replaced by PhAh on average, our results show that d-PSU/PSU–PhAh1 is in the two-phase state in the temperature range covered in this study, whereas d-PSU/PSU–PhAh2 is in the single-phase state. This result is considered to be due to the fact that molecular-weight of PSU–PhAh1 is smaller than that of PSU–PhAh2. Namely, the former effectively has a larger effect of PhAh end-groups on the miscibility of d-PSU/PSU–PhAh than the latter. Thus, the effect of PhAh end-groups on the miscibility of d-PSU/PSU–PhAh is significant, and the effect largely depends on the molecular weight of PSU–PhAh or volume fraction of the end group. The mean-field analysis on interactions between end groups and those
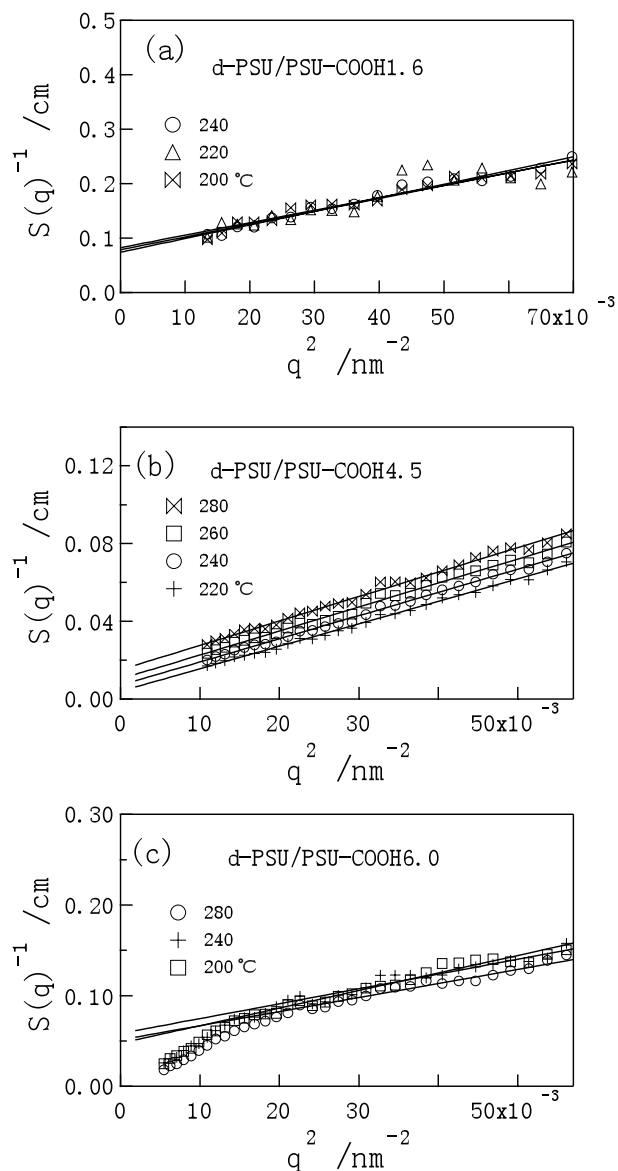
between end groups and middle groups will be presented in the following section.

As shown in Fig. 4, the scattering profiles for d-PSU/PSU–COOH1.6 have almost no temperature dependence, whereas the scattering intensity for d-PSU/PSU–COOH4.5 increased with decreasing temperature, which means that the concentration fluctuations increase with a decrease in temperature. Namely, the latter result indicates that d-PSU/PSU–COOH4.5 has a phase diagram characteristic of an upper critical solution temperature (UCST). However, for d-PSU/PSU–COOH6.0, the upturn of the scattering intensity in the small q ($q < 0.15\ \mathrm{nm}^{-1}$) was observed. This result is also considered to be caused by the fact that d-PSU/PSU–COOH6.0 is in the two-phase state as in the case of d-PSU/PSU–PhAh1. In order to
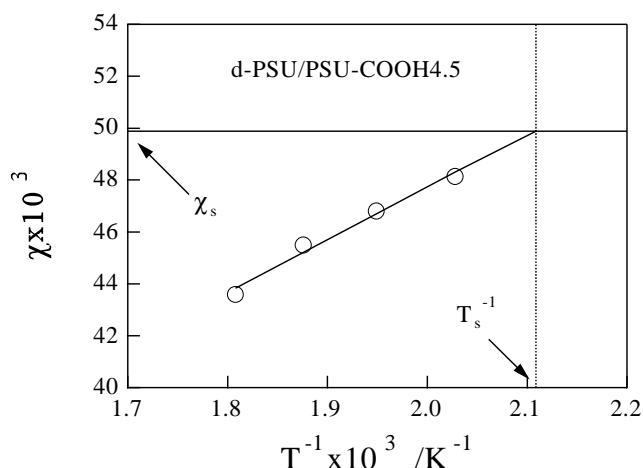
Fig. 8. Plot of the Flory–Huggins segmental interaction parameter χ for d-PSU/PSU–COOH4.5 against reciprocal absolute temperature.

confirm it, we present the O–Z plot in Fig. 7 for (a) d-PSU/PSU–COOH1.6, (b) d-PSU/PSU–COOH4.5 and (c) d-PSU/PSU–COOH6.0. As shown in Fig. 7(a), the relation between the $S(q)^{-1}$ and q^2 is linear and the $S(0)^{-1}$ obtained by extrapolation from the linear relation toward $q = 0$ is almost independent of temperature, which means that the χ parameter is independent of temperature as will be shown in Fig. 9 later. Thus, d-PSU/PSU–COOH1.6 is in the single-phase state in the temperature range covered in this work.

In Fig. 7(b) the relation between $S(q)^{-1}$ and q^2 for d-PSU/PSU–COOH4.5 is linear, similarly to that for d-PSU/PSU–COOH1.6, indicating that d-PSU/PSU–COOH4.5 is in the single-phase state. However, the temperature dependence of $S(q)^{-1}$ for d-PSU/PSU–COOH4.5 is different from that for d-PSU/PSU–COOH1.6. The $S(q)^{-1}$ at any q values covered in this work decreases with decreasing temperature, reflecting the UCST behavior. We estimated the χ parameter from the $S(0)^{-1}$ obtained by extrapolating the linear relation toward $q = 0$. In Fig. 8 we show the plot of the χ parameter against reciprocal absolute temperature T^{-1}. The χ parameter linearly increases with increase of T^{-1}, the temperature dependence of which is given by

$$\chi = 0.00708 + 20.3/T. \tag{6}$$

At spinodal point, $S(0)$ diverges, i.e. $S(0)^{-1}$ becomes zero. Therefore, by substituting zero for the left-hand side of Eq. (5), the value of χ at spinodal point, χ_s, is given in the following form in the context of the mean-field theory:

$$\chi_s = \frac{v_0}{2}\left(\frac{1}{\phi_1 N_{w,1} v_1} + \frac{1}{\phi_2 N_{w,2} v_2}\right). \tag{7}$$

Thus the value of χ_s can be calculated from the molecular parameters and compositions. By extrapolating the relation of Eq. (6) toward χ_s, we estimated mean-field spinodal temperature T_s of d-PSU/PSU–COOH4.5 was 201°C.

In Fig. 7(c), $S(q)^{-1}$ for d-PSU/PSU–COOH6.0 cannot be fitted well by Eq. (4) for the whole range of q covered in this work, whereas $S(q)^{-1}$ linearly increases with q^2 in the high q region ($q^2 \geq 0.021$ nm^{-2}), $S(q)^{-1}$ at $q^2 < 0.021$ nm^{-2} deviates downward from the linear behavior due to the same reason as that given in conjunction with the discussion of Fig. 6(a). The straight line in Fig. 7(c) was obtained by a linear fitting to the data in $q^2 > 0.021$ nm^{-2} and its extrapolation toward $q^2 < 0.021$ nm^{-2}. This behavior of $S(q)^{-1}$ is very similar to that of d-PSU/PSU–PhAh1. Namely, $S(q)^{-1}$ at $q^2 < 0.021$ nm^{-2} reflects the scattering due to the phase-separated domains, wheras $S(q)^{-1}$ at $q^2 \geq 0.021$ nm^{-2} is expected to originate from thermal concentration fluctuations inside the phase-separated domains. Thus, d-PSU/PSU–COOH6.0 is considered to be in the two-phase state.

Before discussing the interactions between d-PSU or PSU and the DPA units, let us first discuss the temperature dependence of the scattering profiles which show the upturn due to the phase-separated domains in the following two paragraphs.

As shown in Fig. 4(c) the scattering intensity at $q < 0.145$ nm^{-1} at $T = 280°C$ is larger than that at $q < 0.145$ nm^{-1} at $T = 240$ and $200°C$. This behavior is considered to be caused by the fact that these measurements were carried out in the cooling process and in the phase separation process. Namely, sizes of the phase separating domains at $T = 240$ and $200°C$ are larger than those at $280°C$, because the phase-separating domains grow with time during the measurements from 280 to $200°C$.

In the q scale covered by this SANS experiment, we often observe structures at the length scale smaller than that of the phase-separating domain, i.e. the q scale can be higher than the reciprocal of the phase-separating domain size. In such q scale, the scattering profile reflects a large-angle tail of the domain scattering. As the phase separated domains grow, the tail shifts toward smaller q, causing the scattered intensity at a given q (satisfying $q < 0.145$ nm^{-1}) decreases [7]. Consequently, the scattering intensity at 240 and 200°C is lower than that at 280°C. However, scattering intensities at $q > 0.145$ nm^{-1} at 280, 240, 200°C are almost the same. In this q scale, we observe the scattering due to thermal concentration fluctuations inside the phase-separated domains. In the time scale of our experiments the composition in each phase is predicted to attain an equilibrium one and not to change with time. Moreover the composition in each phase seems to be almost independent of temperature over the temperature range covered in this experiment.

We now discuss the interactions between d-PSU or PSU and the DPA units. We note that whereas d-PSU/PSU–COOH1.6 and d-PSU/PSU–COOH4.5 were in the single-phase state in the temperature range covered in this study, d-PSU/PSU–COOH6.0 was in the two-phase state. From the point of view of molecular weight,
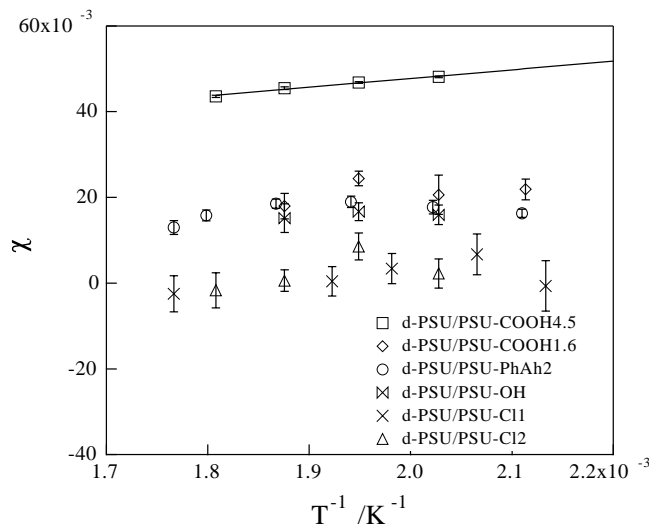
Fig. 9. Plot of the Flory–Huggins segmental interaction parameter χ for d-PSU/PSU–Cl1, d-PSU/PSU–Cl2, d-PSU/PSU–OH, d-PSU/PSU–PhAh2, d-PSU/PSU–COOH1.6 and d-PSU/PSU–COOH4.5, against reciprocal absolute temperature.

d-PSU/PSU–COOH6.0 tends to be more miscible than d-PSU/PSU–COOH1.6 and d-PSU/PSU–COOH4.5, because the molecular weight of PSU–COOH6.0 is smaller than those of PSU–COOH1.6 and PSU–COOH4.5. Therefore, the above result cannot be explained by effect of the molecular weight. Consequently, it should be primarily due to difference in content of DPA unit. Namely, because of a strong segregation effect of d-PSU or PSU against DPA unit, d-PSU/PSU–COOH6.0 with a larger content of DPA unit tends to segregate more than d-PSU/PSU–COOH1.6 and d-PSU/PSU–COOH4.5 having smaller contents of DPA unit. In the next section, we will discuss the interactions between d-PSU or PSU and DPA units in details.

In Fig. 9 we summarize the χ parameter for the blends investigated in this study. The χ parameters for d-PSU/PSU–Cl1 and d-PSU/PSU–Cl2 have almost no temperature dependence, reflecting that their scattering profiles do not change with temperature. The χ parameter for d-PSU/PSU–Cl1 has almost the same as that for d-PSU/PSU–Cl2 and is the smallest among the blends studied here. This result reveals that difference between molecular weight of PSU–Cl1 and that of PSU–Cl2 does not affect the χ parameter. The χ parameter for d-PSU/PSU–OH is slightly larger than

those for d-PSU/PSU–Cl1 and d-PSU/PSU–Cl2. Thus, even the difference between Cl end-groups and OH end-groups affect the miscibility of d-PSU and PSU blends, if the degree of polymerization of PSU is small. This again reveals the significance of the interactions between the end groups as discussed earlier and as will be discussed later in the next section.
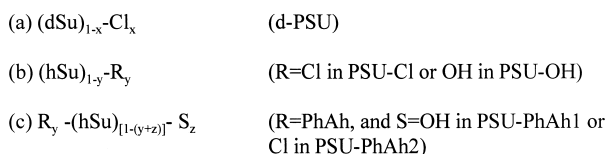
The χ parameter for d-PSU/PSU–PhAh2 hardly changes with temperature, in line with the blends of d-PSU/PSU–Cl1, d-PSU/PSU–Cl2 and d-PSU/PSU–OH. Further, the χ parameter for d-PSU/PSU–PhAh2 is slightly larger than those for d-PSU/PSU–Cl1, d-PSU/PSU–Cl2 and d-PSU/PSU–OH. Note that N_W of PSU–PhAh2 is much larger than those of PSU–Cl1, PSU–Cl2 and PSU–OH and therefore from the points of view of molecular weight, the effect of end-groups of PSU–PhAh2 on the miscibility is expected to be much smaller than those of PSU–Cl1, PSU–Cl2 and PSU–OH. Nevertheless, as the χ parameter for d-PSU/PSU–PhAh2 is larger than those for d-PSU/PSU–Cl1, d-PSU/PSU–Cl2 and d-PSU/PSU–OH, the effect of end-groups of PhAh groups on the net χ parameter is expected to be very large compared with that of end-groups of Cl and OH. This point will be discussed further in the next section.

The χ parameter for d-PSU/PSU–PhAh1 is much larger than that for d-PSU/PSU–PhAh2, because the former blend phase-separated in the same temperature range, as discussed earlier in conjunction with Fig. 3. The χ parameters for d-PSU/PSU–COOH1.6 and d-PSU/PSU–COOH4.5 are larger than those for d-PSU/PSU–Cl1, d-PSU/PSU–Cl2 and d-PSU/PSU–OH and d-PSU/PSU–PhAh2. Further, the χ parameters for d-PSU/PSU–COOH4.5 is much larger than that for d-PSU/PSU–COOH1.6, which means that the miscibility of d-PSU/PSU–COOH is largely affected by slight change in the content of DPA unit included in PSU–COOH.

4.2. Mean-field analysis on the effective χ parameter

In this section, we analyze the effective χ parameter for the blends of d-PSU with various m-PSUs on the basis of the mean-field approximation where the local composition is assumed to be spatially uniform (equal to the average composition). This assumption may not be rigorously true but may be good enough in the following qualitative discussion.

First, let us consider the end group effect on the effective χ parameters for d-PSU/PSU–Cl, d-PSU/PSU–OH and d-PSU/PSU–PhAh. For simplicity, we assume that both d-PSU and PSU–Cl have 100% Cl end groups, whereas PSU–OH has 100% OH end group. Further, as shown in Table 1, most of the end groups of PSU–PhAh1 are PhAh group or OH group, whereas PSU–PhAh2 has mostly PhAh end group or Cl end group, which may be a reasonable assumption (Table 1). Therefore, each polymer is expressed as shown in Scheme 1. d-PSU is comprised of deuterated

(a) $(dSu)_{1-x}$-Cl_x (d-PSU)

(b) $(hSu)_{1-y}$-R_y (R=Cl in PSU-Cl or OH in PSU-OH)

(c) R_y-$(hSu)_{[1-(y+z)]}$-S_z (R=PhAh, and S=OH in PSU-PhAh1 or Cl in PSU-PhAh2)

Scheme 1.

sulfone units (dSU) and Cl end group with the respective volume fractions being $(1 - x)$ and x (part a). PSU–Cl or PSU–OH is composed of sulfone unit (hSU) and end group R where R is equal to Cl for PSU–Cl or OH for PSU–OH with the respective volume fractions being $(1 - y)$ and y (part b). PSU–PhAh1 or PSU–PhAh2 is composed of end group R, end group S and the hSU unit with the respective volume fractions being y, z, and $[1 - (y + z)]$ where R is PhAh, and S is OH in PSU–PhAh1 or Cl in PSU–PhAh2 (part c).

In this case, the effective χ parameter for d-PSU/PSU–Cl, d-PSU/PSU–OH and d-PSU/PSU–PhAh is generally given by

$$\chi_{\mathrm{eff}} = xz\chi_{\mathrm{Cl-S}} + x\{1 - (y + z)\}\chi_{\mathrm{Cl-hSu}} + xy\chi_{\mathrm{Cl-R}}$$

$$+ (1 - x)z\chi_{\mathrm{S-dSu}} + (1 - x)\{1 - (y + z)\}\chi_{\mathrm{dSu-hSu}}$$

$$+ (1 - x)y\chi_{\mathrm{R-dSu}} - x(1 - x)\chi_{\mathrm{Cl-dSu}}$$

$$- z\{1 - (y + z)\}\chi_{\mathrm{S-hSu}} - yz\chi_{\mathrm{S-R}} - y\{1 - (y + z)\}\chi_{\mathrm{R-hSu}}, \tag{8}$$

where $z = 0$ in the case of d-PSU/PSU–Cl or d-PSU/PSU–OH. Subscript M–N denotes the χ parameter between M group and N group in Scheme 1.

For d-PSU/PSU–Cl or d-PSU/PSU–OH, the effective χ parameter, χ_{eff}, is given as follows by substituting $z = 0$ in Eq. (8),

$$\chi_{\mathrm{eff}} = x(1 - y)\chi_{\mathrm{Cl-hSu}} + xy\chi_{\mathrm{Cl-R}}$$

$$+ (1 - x)(1 - y)\chi_{\mathrm{dSu-hSu}} + (1 - x)y\chi_{\mathrm{R-dSu}}$$

$$- x(1 - x)\chi_{\mathrm{Cl-dSu}} - y(1 - y)\chi_{\mathrm{R-hSu}}, \tag{9}$$

Eq. (9) is arranged as follows:

$$\chi_{\mathrm{eff}} = x\{(1 - y)\chi_{\mathrm{Cl-hSu}} - (1 - x)\chi_{\mathrm{Cl-dSu}}\}$$

$$+ y\{(1 - x)\chi_{\mathrm{R-dSu}} - (1 - y)\chi_{\mathrm{R-hSu}}\}$$

$$+ (1 - x)(1 - y)\chi_{\mathrm{dSu-hSu}} + xy\chi_{\mathrm{Cl-R}}. \tag{10}$$

As the χ parameter between deuterated sulfone unit and protonated one, $\chi_{\mathrm{dSu-hSu}}$, is expected to be small [8–10], the third term is considered to be small, i.e. $\chi_{\mathrm{dSu-hSu}} \approx 0$.

In the case of d-PSU/PSU–Cl, as R = Cl, the fourth term is zero. Moreover, regardless of difference between degree of polymerization of PSU–Cl1 and that of PSU–Cl2, i.e. difference between $y = 0.00853$ and $y = 0.00667$, both the effective χ parameters for d-PSU/PSU–Cl1 and d-PSU/PSU–Cl2 were unchanged and small. Therefore, the difference between $\chi_{\mathrm{Cl-hSu}}$ and $\chi_{\mathrm{Cl-dSu}}$ also should be small. Thus, Eq. (10) leads to nearly zero for d-PSU/PSU–Cl.

In the case of d-PSU/PSU–OH, from the above consideration, as $\chi_{\mathrm{dSu-hSu}} \approx 0$, $\chi_{\mathrm{Cl-hSu}} \approx \chi_{\mathrm{Cl-dSu}}$ and $(1 - y) \cong (1 - x) \cong 1$. Moreover xy $\chi_{\mathrm{Cl-OH}} \cong 8.11 \times$

$7.66 \times 7 \times 10^{-8} \cong 4.35 \times 10^{-6}$,[3] the value of which is much smaller than the measured effective χ value shown in Fig. 9 (of the order of 10^{-2}). Thus we have $\chi_{\mathrm{Cl-OH}} \cong 0$. Therefore Eq. (10) is given as follows:

$$\chi_{\mathrm{eff}} \cong y\{\chi_{\mathrm{OH-dSu}} - \chi_{\mathrm{OH-hSu}}\}. \tag{11}$$

Thus, a small difference between $\chi_{\mathrm{OH-dSu}}$ and $\chi_{\mathrm{OH-hSu}}$ may cause the χ_{eff} for d-PSU/PSU–OH slightly larger than that for d-PSU/PSU–Cl.

We shall now consider the effective χ parameter for d-PSU/PSU–PhAh. Note in this case that y is larger than z, because of bulky PhAh group compared with Cl or OH group, although, in Table 1, mole percentage of PhAh group in the end group is almost the same as that of the S group. The miscibility of d-PSU/PSU–PhAh was dramatically affected by the volume fraction of PhAh group as shown in the previous section, indicating that the χ parameter between PhAh group and other group is very large. In this case, the isotope effect on the χ parameter may be negligible compared with the χ parameters between the PhAh group and the other group, i.e. $\chi_{\mathrm{S-dSu}} \approx \chi_{\mathrm{S-hSu}}, \chi_{\mathrm{dSu-PhAh}} \approx \chi_{\mathrm{hSu-PhAh}}, \chi_{\mathrm{Cl-hSu}} \approx \chi_{\mathrm{Cl-dSu}}$.

Further, as $\chi_{\mathrm{dSu-hSu}} \approx xz\chi_{\mathrm{Cl-S}} \approx 0$, as already discussed above, Eq. (8) is rewritten in the following form:

$$\chi_{\mathrm{eff}} = xy\chi_{\mathrm{Cl-PhAh}} - x(y + z - x)\chi_{\mathrm{Cl-hSu}}$$

$$+ z(y + z - x)\chi_{\mathrm{S-hSu}} + y(y + z - x)\chi_{\mathrm{hSu-PhAh}}$$

$$- yz\chi_{\mathrm{S-PhAh}}. \tag{12}$$

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[3] Spherical volume of Cl group per mole calculated from Van der Waals radius (0.180 nm) is 14.7 cm^3, the molar volume of PSU is 355.9 cm^3. If we assume that molar volume of OH group is equal to that of Cl group, x and y in part (a) of Scheme 1 is given as follows:

$x = 14.7 \times 2/\{(41/4.07) \times 355.9 + 14.7 \times 2\} = 0.00811$,

$y = 14.7 \times 2/\{(34/3.17) \times 355.9 + 14.7 \times 2\} = 0.00766$.

In this calculation, we used the number averaged degree of polymerization N_{n}, because the volume fraction of the end group with the volume v_e, f, is calculated as follows in taking polydispersity for the degree of polymerization into consideration:

$$f = 2\sum_i n_i v_e \Bigg/ \left[\sum_i n_i N_i v_m + 2\sum_i n_i v_e\right] = 2v_e\Bigg/\left[\frac{v_m \dfrac{\sum_i n_i N_i}{\sum_i n_i}} + 2v_e\right]$$

$$= 2v_e/[v_m N_{\mathrm{n}} + 2v_e],$$

where n_i is the number of the polymers with degree of polymerization N_i and with volume per segment v_m. The enthalpic contribution of the χ parameter (χ_{H}) calculated from solubility parameters of Cl group and OH group is ca. 0.07 at 280°C. The solubility parameters of Cl group and OH group were cited from the Polymer Hand Book (third edition). Hence, $xy \chi_{\mathrm{Cl-OH}}$ is very small and negligible compared with the measured effective χ value shown in Fig. 9.

As discussed in the previous section, as degree of polymerization of PSU–PhAh2 is larger than those of PSU–Cl1, PSU–Cl2 and PSU–OH, the end group effect on the effective χ parameter for the former with d-PSU is supposed to be smaller than that for the latter with d-PSU. Nevertheless, as shown in Fig. 9, the effective χ parameter for the former with d-PSU was larger than those for the latter with d-PSU. In the case of PSU–PhAh2, as S = Cl, Eq. (12) leads to

$$\chi_{\text{eff}} = (x - z)y\chi_{\text{Cl–PhAh}} - (x - z)(y + z - x)\chi_{\text{Cl–hSu}}$$
$$+ y(y + z - x)\chi_{\text{hSu–PhAh}}. \tag{13}$$

y is larger than x in terms of volume fraction because of bulky PhAh group.[4] Then, as $(x - z)$ and $(y + z - x)$ are positive, $\chi_{\text{Cl–PhAh}}$ or/and $\chi_{\text{hSu–PhAh}}$ should have very large values compared with the values of $\chi_{\text{Cl–hSu}}$ in order to cause the relatively large effective χ parameter for d-PSU/PSU–PhAh2 as shown in Fig. 9. It seems to be particularly reasonable that interactions between hSu and PhAh are largely repulsive because both of them are bulky. In the case when $\chi_{\text{Cl–PhAh}} \cong \chi_{\text{hSu–PhAh}} \gg \chi_{\text{Cl–hSu}}$, we obtain

$$\chi_{\text{eff}} \cong y^2\chi_{\text{hSu–PhAh}}. \tag{14}$$

As y is very small quantity, $\chi_{\text{hSu–PhAh}}$ is expected to have a very large positive value.

However, in the case of d-PSU/PSU–PhAh1, Eq. (12) leads to, by setting R and S equal to PhAh and OH groups, respectively,

$$\chi_{\text{eff}} = xy\chi_{\text{Cl–PhAh}} - x(y + z - x)\chi_{\text{Cl–hSu}}$$
$$+ z(y + z - x)\chi_{\text{OH–hSu}} + y(y + z - x)\chi_{\text{hSu–PhAh}}$$
$$- yz\chi_{\text{OH–PhAh}}. \tag{15}$$

As degree of polymerization of PSU–PhAh1 is smaller than that for PSU–PhAh2, y and z for the former are larger than those for the latter, respectively. As described above, if $\chi_{\text{Cl–PhAh}}$ or/and $\chi_{\text{hSu–PhAh}}$ have very large values, even the subtle change in y and z significantly affects the effective χ parameter for d-PSU/PSU–PhAh1 and consequently it may become much larger compared to that for d-PSU/PSU–PhAh2. This speculation seems to suitably explain our experimental results. Note that Eq. (15) reduces to Eq. (14) if $\chi_{\text{hSu–PhAh}} \cong \chi_{\text{Cl–PhAh}} \cong \chi_{\text{OH–PhAh}} \gg \chi_{\text{Cl–hSu}}$ and $\chi_{\text{OH–hSu}}$.

Finally, we shall consider the effective χ parameter for d-PSU/PSU–COOH. As we do not have any information about the end group of PSU–COOH, we neglect the effects of end group on the effective χ parameter. Even if we neglect the end group effects, we can interpret a series of results for d-PSU/PSU–COOH. We consider the following

scheme: d-PSU is comprised of only the dSu unit and PSU–COOH is composed of the hSu unit and the DPA unit with a volume fraction of $(1 - y')$ and y', respectively. In this case, the effective χ parameter for d-PSU/PSU–COOH is presented by

$$\chi_{\text{eff}} = y'\chi_{\text{DPA–dSu}} + (1 - y')\chi_{\text{dSu–hSu}} - y'(1 - y')\chi_{\text{DPA–hSu}}. \tag{16}$$

Under the approximation of $\chi_{\text{DPA–dSu}} \approx \chi_{\text{DPA–hSu}}$ and $\chi_{\text{dSu–hSu}} \approx 0$, the Eq. (16) is described as follows:

$$\chi_{\text{eff}} = y'^2\chi_{\text{DPA–hSu}}. \tag{17}$$

As shown in the previous section, the effective χ parameter and miscibility for d-PSU/PSU–COOH was very sensitive to the content y' of DPA unit in PSU–COOH. Therefore, it can be concluded that $\chi_{\text{DPA–hSu}}$ has a very large positive value, i.e. interactions between the DPA unit and the sulfone unit are largely repulsive.

The large repulsive interactions between the PhAh group and the hSu or dSu units or between the DPA units and the hSu or dSu units may suggest that the PhAh groups or the DPA groups may form aggregates even in the case when no macrophase separation is observed. If the DPA and/or PhAh groups formed aggregates, it would certainly affect the reactive blending of the PSU and PA. Hence this point is quite important and reserves future works.

5. Conclusion

We investigated the miscibility of blends of deuterated polysulfone (d-PSU) and modified polysulfones (m-PSUs) by means of small-angle neutron scattering. The d-PSU studied here has mostly Cl end-groups. The χ parameter for blends of d-PSU and PSU having mostly OH end-groups (PSU–OH) is slightly larger than that for blends of the d-PSU and PSU having mostly Cl end-groups (PSU–Cl). The miscibility of blends of d-PSU and the PSU end-capped with phthalic anhydride group (PSU–PhAh) largely depends on the degrees of the polymerization of PSU–PhAh. Moreover, the χ parameter for the blend of d-PSU and PSU–PhAh had almost no temperature dependence. As a repulsive interaction between PhAh groups and sulfone unit is so strong that d-PSU/PSU–PhAh1 studied in this work was phase-separated. The miscibility of blends of d-PSU and a random copolymer of sulfone unit and DPA unit (PSU–COOH) strongly depends on the content of DPA unit. The larger the content of DPA unit, the larger the χ parameter for the blend of d-PSU and PSU–COOH, whereas the χ parameter for the blend of d-PSU and PSU–COOH with a content of 1.6 mol% DPA unit had almost no temperature dependence, the χ parameter for the blend of d-PSU and PSU–COOH with a content of 4.5 mol% DPA unit showed a UCST type behavior. Further, the blend of d-PSU and PSU–COOH with a content of 6.0 mol% DPA unit was phase-separated in the temperature range covered in this work.

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[4] The molar volume of PhAh is 96.9 cm^3. The volume fraction of PhAh y is given by $y = 96.9/\{177/7.19 \times 355.9 + 96.9 + 14.7\} = 0.0109$, and $z = 14.7/\{177/7.19 \times 355.9 + 96.9 + 14.7\} = 0.00166$. As $x = 0.00811$, $(x - z)$, $(y + z - x) > 0$.

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