

# Quantifying the “Neutrality” of Good Solvents for Block Copolymers: Poly(styrene-*b*-isoprene) in Toluene, Benzene, and THF

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Received August 10, 1998

Revised Manuscript Received October 16, 1998

## Introduction

The phase behavior of block copolymer solutions is enjoying renewed interest.<sup>1–13</sup> For a given copolymer system, a particular solvent may be classified as neutral, slightly selective, or selective, according to whether it is (i) a good solvent for both blocks, (ii) good for one and marginal/poor for the other, or (iii) good for one and a nonsolvent for the other. The phase behavior is typically quite different among the three classes. In the case of a neutral solvent, it is unlikely that the two polymer–solvent interaction parameters ( $\chi$ ) are exactly the same, and the question naturally arises “how neutral is neutral?” In this Note we do not answer this particular question, but we do demonstrate a simple method for quantifying the small degree of selectivity that will generally exist for a copolymer in a solvent good for both blocks. The system in question is poly(styrene-*b*-isoprene) in the common good solvents toluene, benzene, and tetrahydrofuran (THF).

The method involves small-angle neutron scattering (SANS) measurements of the structure factor,  $S(q)$ , for a particular symmetric copolymer dissolved at a fixed concentration (in the ordered state) in protonated and deuterated versions of the same solvent.<sup>14</sup> If the solvent is perfectly neutral and distributes itself uniformly throughout the solution, the measured (coherent)  $S(q)$  must be identical between the two solutions. If the solvent collects preferentially at the interfaces between microdomains, to screen the unfavorable block–block contacts, this will result in a contribution to the second harmonic peak in  $S(q)$ , with an intensity that depends on the solvent scattering power. Such a slight solvent inhomogeneity is predicted by self-consistent mean-field theory (SCMF)<sup>3,15–17</sup> and has been demonstrated experimentally.<sup>14</sup> If the solvent exhibits a slight preference for one of the two microdomains, the solvent distribution will have a finite first harmonic component, and thus the intensity of the main peak,  $S(q^*)$ , will differ between the two solvents. Use of SCMF permits quantitative interpretation of this intensity difference in terms of differences between the two polymer–solvent  $\chi$  param-

eters. The detailed analysis of this method has been presented previously.<sup>14</sup>

## Experimental Section

**Samples and Solutions.** Two poly(styrene-*b*-isoprene) diblock copolymers were prepared by standard living anionic polymerization methods. One, designated SI(16-19), had  $M_{PS} = 1.6 \times 10^4$ ,  $M_{PI} = 1.9 \times 10^4$ ,  $M_w/M_n \leq 1.06$ , and an NMR-based composition (volume fraction)  $f_{PS} = 0.425 \pm 0.005$ , as previously described.<sup>18</sup> The other, designated SI(17-19), had  $M_{PS} = 1.7 \times 10^4$ ,  $M_{PI} = 1.9 \times 10^4$ ,  $M_w/M_n \leq 1.08$ , and  $f_{PS} = 0.457 \pm 0.005$  and was prepared following established procedures.<sup>19</sup> All solvents, protonated and perdeuterated, were obtained from Aldrich and used without further purification. Solutions were prepared gravimetrically by direct addition of polymer and solvent and contained in SANS cells fashioned from quartz disks as previously described.<sup>14</sup> The concentrations employed in this work were as follows: SI(17-19),  $\phi = 0.599$  in *h*-toluene and 0.602 in *d*-toluene; SI(17-19),  $\phi = 0.600$  in *h*-benzene and 0.600 in *d*-benzene; SI(16-19),  $\phi = 0.601$  in *d*-THF and 0.599 in *h*-THF, where the volume fractions  $\phi$  were calculated assuming densities of 1.05, 0.913, 0.867, 0.943, 0.874, 0.950, 0.889, and 0.985 g/mL for PS, PI, *h*-toluene, *d*-toluene, *h*-benzene, *d*-benzene, *h*-THF, and *d*-THF, respectively. Other solutions were prepared and examined, but introduction of the samples into the scattering cells generated a significant degree of lamellar orientation. Consequently, the scattering patterns did not exhibit isotropic rings on the area detector, and reliable peak intensity values could not be obtained.

**Measurements.** SANS measurements were performed on the 30 m Exxon/University of Minnesota/NIST (NG7) instrument at the National Institute of Standards and Technology in Gaithersburg, MD. Neutrons with  $\lambda = 6.0 \text{ \AA}$  and  $\Delta\lambda/\lambda = 0.10$  were incident on the sample, and the detector was placed 4 m behind the sample, to give a usable  $q$  range of ca. 0.01–0.09  $\text{\AA}^{-1}$ . Data were corrected for transmission, background, empty cell, and incoherent contributions and placed on an absolute basis by use of a silica standard (A1). Sample temperatures were maintained at 30 °C. As discussed previously, desmearing procedures did not provide more reliable peak intensity ratios and were thus not employed.<sup>14</sup>

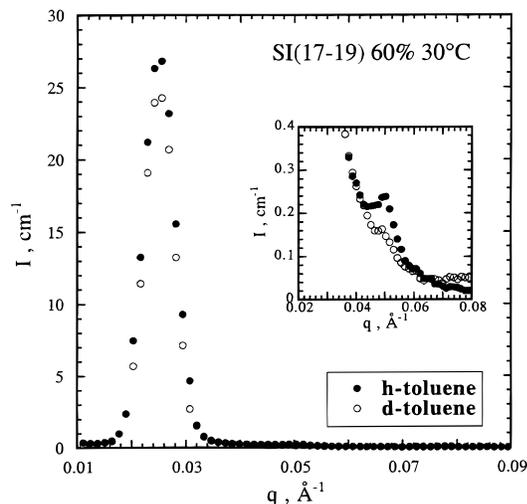
## Results and Discussion

The coherent  $S(q)$  from 60% solutions of SI(17-19) in *h*- and *d*-toluene are compared in Figure 1; the inset shows an expanded view of the second harmonic peak. The primary peak is larger in *h*-toluene, with the ratio of peak maxima  $I_h(q^*)/I_d(q^*) = 1.09$ . The second peak is also much more pronounced in the protonated solvent. The SCMF calculations of  $I_h(q^*)/I_d(q^*)$  for 60% solutions of SI(17-19) in toluene, benzene, and THF are shown in Figure 2, as a function of the polystyrene–solvent interaction parameter,  $\chi_{PS-S}$ . These calculations determine the amplitudes of the various harmonics in the concentration profiles of PS, PI, and solvent, with  $N$ ,  $\phi$ ,  $f$ , and the three binary interaction parameters as input. The values of  $N$ ,  $\phi$ , and  $f$  are determined from the polymer characteristics described above, with  $N$  calculated on the basis of a styrene segment reference volume. In this case  $\chi_{PI-S}$  has been fixed at 0.40, a typical value for a good solvent system and a literature value for toluene;<sup>20</sup>  $\chi_{PS-PI}$  is given by  $-0.0228 + (33/T)$ , utilizing a styrene monomer reference volume.<sup>1</sup> The calculation also requires the appropriate contrast factors, which are listed in Table 1. The curves all intersect

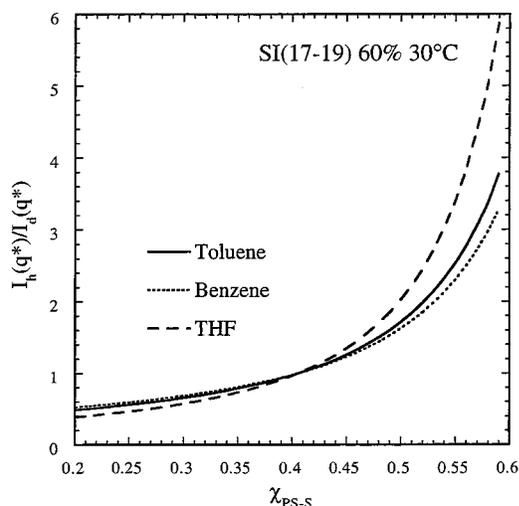
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**Figure 1.** Coherent scattered intensity for 60% solutions of SI(17-19) at 30 °C in *h*- and *d*-toluene. The inset shows an expansion of the second harmonic peak.



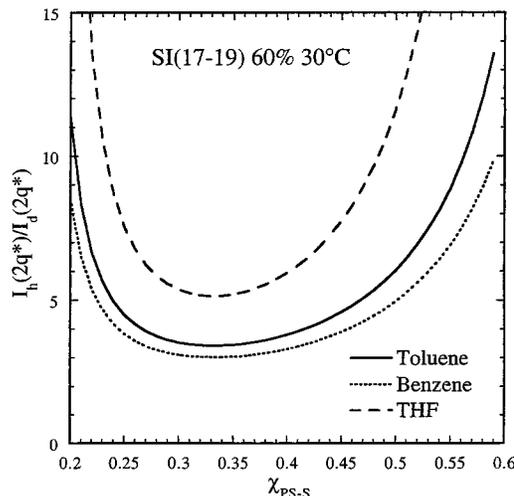
**Figure 2.** Computed intensity ratios for the main structure factor peak in protonated and deuterated toluene, benzene, and THF. The calculations are appropriate for a 60% solution of SI(17-19) at 30 °C, with  $\chi_{PI-S}$  fixed at 0.40.

**Table 1.** SANS Contrast Factors,  $(a_i - a)^2$ , in Units of  $\text{cm}^{-1}$ <sup>a</sup>

	PS	PI
PI	0.0216	0
<i>h</i> -toluene	0.00363	0.00753
<i>d</i> -toluene	0.298	0.480
<i>h</i> -benzene	0.000925	0.0136
<i>d</i> -benzene	0.267	0.440
<i>h</i> -THF	0.0249	0.000118
<i>d</i> -THF	0.402	0.610

<sup>a</sup> Based on a styrene monomer reference volume.

near  $I_h(q^*)/I_d(q^*) = 1$  for  $\chi_{PS-S} = 0.40$ , which would be required for a perfectly symmetric copolymer in a strictly neutral solvent. From Figure 2 it is possible to associate the measured  $I_h(q^*)/I_d(q^*)$  with a value of  $\chi_{PS-S}$ , which is relative to the reference  $\chi_{PI-S}$  of 0.40. Thus, for toluene the value of  $1.09 \pm 0.03$  implies  $\chi_{PS-S} \approx 0.43$ . One may thus conclude that toluene is a slightly better solvent for PI than PS, in agreement with our previous measurements on different SI copolymers.<sup>14</sup> A value of  $\chi_{PS-S}$  of 0.44 has been cited in the literature<sup>20</sup> and used in our previous work. This value would correspond to  $I_h(q^*)/I_d(q^*) = 1.18$ , which is not far from

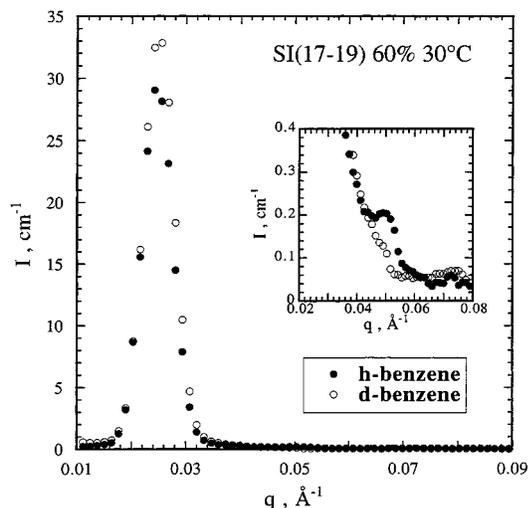


**Figure 3.** Computed intensity ratios for the second harmonic peak in protonated and deuterated toluene, benzene, and THF. The calculations are appropriate for a 60% solution of SI(17-19) at 30 °C, with  $\chi_{PI-S}$  fixed at 0.40.

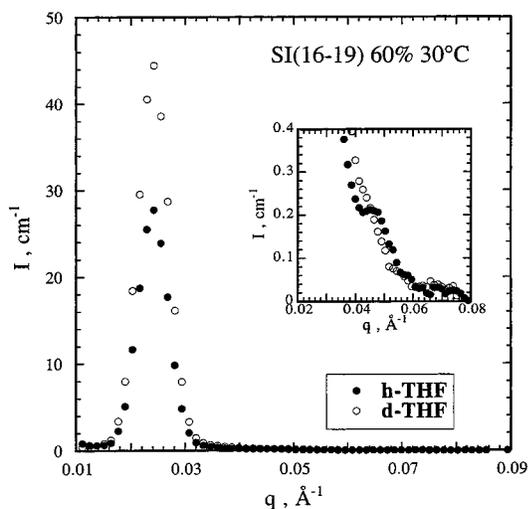
the experimental value, especially given the uncertainty due to the broadening of the primary peak. The second harmonic is distinctly larger in *h*-toluene, but as the peak is small and not completely resolved from the shoulder of the broadened primary peak, it is difficult to obtain a precise value of  $I_h(2q^*)/I_d(2q^*)$ . However, if one infers a background of ca.  $0.12 \text{ cm}^{-1}$  at  $0.05 \text{ \AA}^{-1}$ , then this ratio is about 3. The theoretical predictions for the second harmonic are shown in Figure 3. The curve for toluene never falls as low as 3, but for the inferred value of  $\chi_{PS-S}$ , the prediction is about 4, which is satisfactory given the experimental uncertainty. The curves in Figure 3 are not monotonic in  $\chi_{PS-S}$ , in contrast to Figure 2, and indicate a greater sensitivity to  $\chi_{PS-S}$ . However, although the ratio of the magnitudes of the second harmonic peaks in the two solvents may change greatly, it is always an experimental issue as to whether the two individual peaks will be large enough in absolute units to be well-defined. Furthermore, the calculations for  $I_h(2q^*)/I_d(2q^*)$  are quite sensitive to the exact value of  $f$ , especially in the vicinity of  $f = 0.50$ .

The scattering from a 60% solution of SI(17-19) in *h*- and *d*-benzene is shown in Figure 4. In this case the primary peak is larger in the deuterated solvent,  $I_h(q^*)/I_d(q^*) = 0.88 \pm 0.03$ , which from Figure 2 gives  $\chi_{PS-S} \approx 0.38$ . Again it should be emphasized that this value is relative to the value chosen for  $\chi_{PI-S}$ , and therefore it should not be ascribed any deeper significance, other than the conclusion that benzene is a slightly better solvent for polystyrene than polyisoprene. The second harmonic peak is larger in *h*-benzene, but it is so small in *d*-benzene (again relative to the background shoulder of the main peak) that reliable determination of the intensity ratio is precluded. However, from Figure 3  $\chi_{PS-S} = 0.38$  implies a second harmonic peak ratio of about 3, which is not inconsistent with the data.

Measurements on a 60% solution of SI(16-19) in *h*- and *d*-THF are shown in Figure 5. As with benzene, the main peak is larger in the deuterated solvent, with  $I_h(q^*)/I_d(q^*) = 0.62 \pm 0.02$ . Curves (not shown) similar to those in Figure 2, but calculated for the different copolymer (i.e., different  $N$  and  $f$ ), give  $\chi_{PS-S} = 0.32$ , relative to  $\chi_{PI-S} = 0.40$ . Thus, THF is a better solvent for polystyrene and is more selective than benzene. The



**Figure 4.** Coherent scattered intensity for 60% solutions of SI(17-19) at 30 °C in *h*- and *d*-benzene. The inset shows an expansion of the second harmonic peak.



**Figure 5.** Coherent scattered intensity for 60% solutions of SI(16-19) at 30 °C in *h*- and *d*-THF. The inset shows an expansion of the second harmonic peak.

second harmonic peak is clear in *h*-THF, but not in *d*-THF, so it is not possible to conclude anything from this peak except that  $I_h(2q^*)/I_d(2q^*) > 1$ , which is consistent with the calculations for all  $\chi_{PS-S}$ .

### Summary

Analysis of SANS measurements on matched pairs of SI copolymer solutions in *h*- and *d*-solvents, and comparison with SCMF calculations, indicates that toluene is very slightly selective toward polyisoprene,

whereas benzene and THF are better solvents for polystyrene. This slight selectivity is quantified by comparing the intensities of the main structure factor peak between *h*- and *d*-solvents. The results illustrate the simplicity of this method of assessing the relative solvent quality for a good solvent and a particular copolymer. However, the precision of the determination of particular  $\chi$  values depends on a variety of experimental factors (e.g., peak broadening, the accuracy of determining copolymer concentration, and composition) and the parametric sensitivity of the peak intensity ratios, which depend particularly on composition and the relevant contrast factors.

**Acknowledgment.** This work was supported by the National Science Foundation, through Award DMR-9528481 to T.P.L., and by the University of Minnesota Supercomputer Institute, through an allocation of computer time and through a Research Scholarship to C.H. We appreciate helpful suggestions from K. J. Hanley.

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MA981259T