

Effect of Sequence Distribution on Short-Range Ordering in Poly(ether sulfone) Copolymers

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ABSTRACT: Three kinds of poly(ether sulfone) copolymer samples, R50, B50, and A50, showing marked differences in tensile behavior because of different sequence distributions were investigated by radial distribution function (RDF) methods. The RDF patterns were not virtually identical and showed that the short-range order (0–14 Å) in the samples had been essentially affected by the sequence distribution. Most of the intramolecular distances in the copolymer were successfully resolved in the RDF pattern. However, there were only suggestions of broad peaks at $r = 5.5$ Å and $r = 11$ Å, attributable to intermolecular ordering, which indicated that little intermolecular order-

ing had occurred in either sample. The appearance of two peaks at about 5 Å periodic suggested the existence of more or less parallel chain segments in the copolymers. Therefore, substantial structural differences between the three copolymers were shown. The structural information revealed by these RDF results was in agreement with the tensile property changes caused by the sequence distribution. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 534–537, 2007

Key words: poly(ether sulfone); sequence distribution; short-range order

INTRODUCTION

Poly(aryl ether sulfone)s are high-performance engineering thermoplastics and have attracted much attention because of their excellent mechanical properties, solvent resistance, and high thermal stability. Different poly(aryl ether sulfone)s and their copolymers have been developed for some applications.^{1–3} Three kinds of poly(ether sulfone) copolymers with the same composition but different sequence distributions were obtained by different polymerization methods.⁴ The copolymers were obtained by incorporating the same amounts of poly(ether ether sulfone) (PEES) into the backbone of poly(ether sulfone) (PES). Studies of the tensile properties of the three copolymers revealed marked differences. In particular, the alternative copolymer (A50) was found to have higher yield strength than the random copolymer (R50) and the block copolymer (B50).

In the present study, the alignment of macromolecular chain segments in the three copolymers was examined by differential radial distribution function [$G(r)$] and double-body radial distribution function [$g(r)$] analyses of wide-angle X-ray scattering (WAXS) intensity. The study provided information leading

to a better understanding of polymer properties in molecular terms. It has been suggested that short-range ordering exists in poly(aryl ether sulfone)s, which would not give rise to sharp Bragg reflections if the ordered regions remained very small. The short-range order in "amorphous" materials can be characterized precisely by radial distribution function (RDF) methods,^{5–10} which have been derived from a careful analysis of the scattered diffraction pattern of the material. These techniques were used to examine the three copolymer samples in the present study.

EXPERIMENTAL

The 50 PES/50 PEES copolymers with different sequence distributions used in this study were synthesized by one-step and two-step reaction methods, using 4,4'-dichlorodiphenyl sulfone (DCDPS), 4,4'-dihydroxydiphenyl sulfone (DHDPS), and hydroquinone (HQ) in a sulfolane medium with a 30% solids content under a nitrogen atmosphere. The procedures for the synthetic routes have been described in detail previously.⁴ For each copolymer both amorphous samples approximately 1 mm thick were prepared. The amorphous samples were compression-molded at 280°C and rapidly quenched in ice water. Pertinent information on the preparation and properties of the three copolymer samples is given in Table I.

The X-ray scattering measurements were made on a Japan D/max-III. A diffractometer using monochrom-

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TABLE I
Some Properties of Copolymers R50, B50, and A50

Copolymer	Inherent viscosity (dL/g)	T_g (°C)	Randomness ^a	[HQ/DHDPS] ^a
R50	0.45	215.3	1.06	47.1/52.9
B50	0.41	216.1	0.22	51.4/48.6
A50	0.39	215.8	0	50.0/50.0

^a Values were measured by ¹³C-NMR in ref. 4.

atized Cu K α radiation (wavelength, $\lambda = 0.542 \text{ \AA}$) was adopted. The WAXS intensities for each sample were recorded by a step scanning procedure in the range of $4^\circ < 2\theta < 120^\circ$. Intensities for the lower scattering angles, that is, $2\theta < 4^\circ$, were obtained by extrapolating the experimental curve smoothly to zero at a zero scattering angle. Afterward, the raw intensity data were corrected for experimental factors, including background air scattering, absorption, polarization, and multiple scattering, according to standard methods.^{11–13} The corrected intensity data, $I_{e.u.}(s)$ were changed into interference intensity [$i(s)$], calculated using the equation:

$$i(s) = \left\{ I_{e.u.}(s) - \sum_m [f_m^2(s) + RC_m(s)] \right\} / f_e^2(s) \quad (1)$$

where $f_m(s)$ is the atomic fraction, $f_e(s)$ is the scattering factor, $C_m(s)$ is the Compton scattering of the s-type atom, $s = \sin \theta / \lambda$, and R is the normalization constant. The hypothetical chemical units of (C₄₂H_{2.8}S_{0.3}O₁) for three kinds of poly(ether sulfone) copolymers were assumed in the analysis based on the starting compositions of the copolymers.

The Fourier analysis of scattering intensities for a system containing several different types of atoms, in this case C, H, O, and S, were given by Waser and Scho-

maker,¹⁴ discussed by Pings and Waser,¹⁵ and applied by Longman and coworkers¹⁶ and Gupta and Yeh.¹⁷ Following this analysis, the $G(r)$ and $g(r)$ for each copolymer sample were derived according to the equations

$$G(r) = \sum_m K_m 4\pi r [\rho_m(r) - \rho_0] \\ = 32\pi r \int_0^\infty s i(s) \sin(4\pi r s) ds \quad (2)$$

$$g(r) = 1 + G(r)/4\pi r \rho_0 \quad (3)$$

where ρ_0 is the average electron density and $g(r)$ is the double-body distribution function.

The RDFs obtained were further smoothed beyond its second peak by multiplying a damping factor, $\exp(-7.5 s^2)$, by $i(s)$. Further information on proper construction of reliable RDFs was provided previously by examining all the available literature.¹⁸

RESULTS AND DISCUSSION

The corrected and normalized WAXS intensities for the quenched 50 PES/50 PEES copolymers are shown in Figure 1. Similar to most of the amorphous polymers, two peaks were present, at 18° and 43° , for three 50 PES/50 PEES copolymers. The WAXS patterns had no Bragg reflections, indicating the

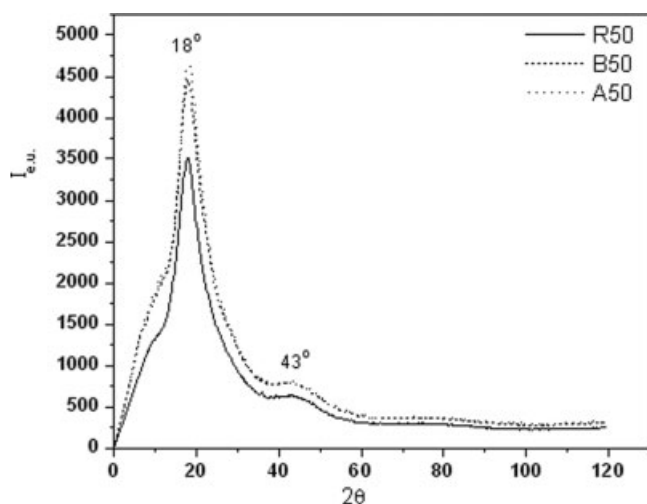


Figure 1 Corrected and normalized experimental WAXS data for quenched copolymers R50, B50, and A50.

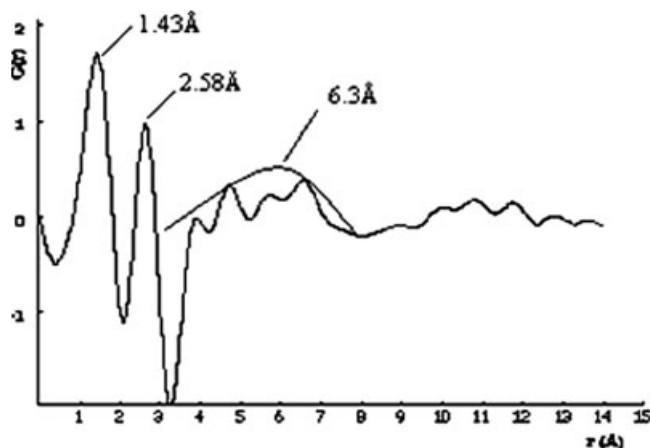


Figure 2 $G(r)$ curve for quenched copolymer R50.

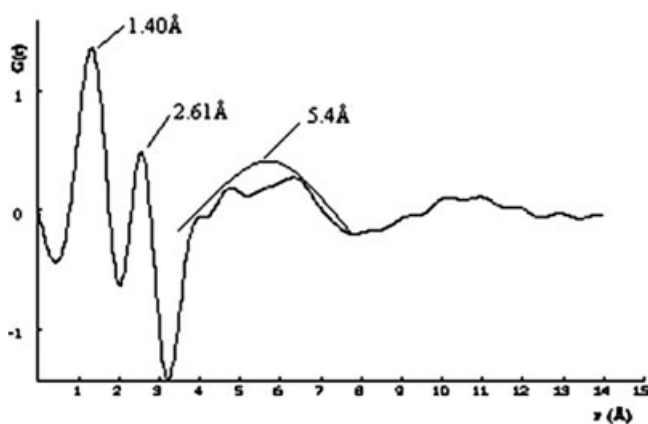


Figure 3 $G(r)$ Curve for quenched copolymer B50.

structure of the copolymer samples was noncrystalline. A comparison of the WAXS data of copolymer A50 with copolymers R50 and B50 shows that three polymers had very similar patterns in both peak intensity and position. For copolymers A50 and B50, the intensity of the principal peak at 18° was higher than that of copolymer R50 by approximately 20%. Another peak intensity at 43° was virtually unaffected by the sequence distribution.

The resultant $G(r)$ curves for the three copolymer samples are shown in Figures 2, 3, and 4. For copolymer A50, prominent sharp peaks at 1.4 and 2.6 Å and very weak peaks at 3.9–12.9 Å were observed. According to previous calculations of the intramolecular distances in the copolymer, the $G(r)$ curves for copolymers R50, B50, and A50 consisted of intramolecular peaks at approximately 1.4 and 2.6 Å and intermolecular peaks beyond the radial distance of about 4 Å. Three kinds of copolymers composed of C—C chains exhibited intramolecular mean interatomic distances of 1.4 and 2.6 Å. No attempt was made to attribute specific high-frequency peaks

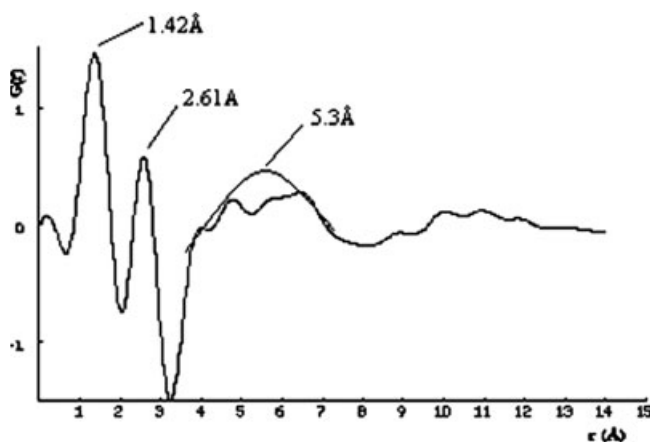


Figure 4 $G(r)$ Curve for quenched copolymer A50.

TABLE II
Description of Intermolecular RDF Peaks

Copolymer R50		Copolymer B50		Copolymer A50	
P (Å)	H	P (Å)	H	P (Å)	H
5.50	0.24	5.40	0.20	5.30	0.18
11.2	0.20	10.8	0.18	10.5	0.16

P, peak position; H, peak high.

occurring at values of $r > 4$ Å to specific interatomic distances mainly for two reasons. First, the largely random arrangement of the polymeric chains meant that the relative positions of any part of neighboring repeat units to each other was unknown, so that only an average disordered configuration could be assumed. Second, it was not possible to determine the relative abundance of any specific interatomic spacing or, indeed, to definitely confirm its presence, except by assuming all possible random configurations of the polymer chains within the steric limits of the structure. Thus, attempts to identify peaks in the RDF plot at values of $r > 4$ Å were not justified for the present copolymer samples. To ascertain the intermolecular structural changes caused by different macromolecular chain sequence distributions, the present study focused on examining the $G(r)$ curves beyond 4 Å. The positions and heights of two intermolecular $G(r)$ peaks are given in Table II for copolymers R50, B50, and A50. The results indicated that copolymers R50, B50, and A50 had similar local structures. In addition, the existence of local alignment of chain segments was suggested by the wide periodic $G(r)$ peaks between 5.5 and 11.5 Å. Two wide intermolecular peaks included a lot of intramolecular interatomic distances and reflected mainly intermolecular interatomic distance information. Furthermore, to compare the difference in short-range ordering for the three copolymers, we defined

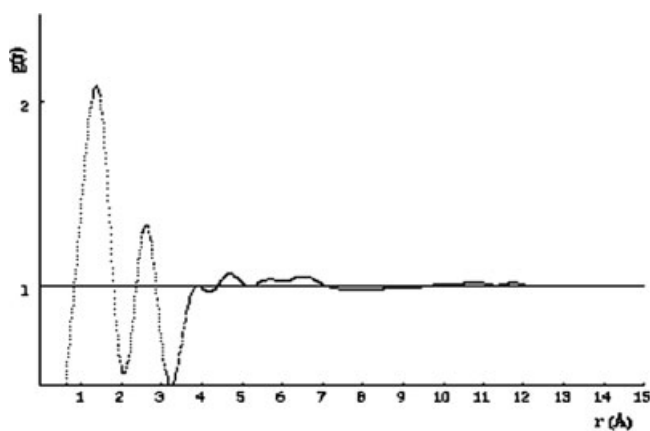


Figure 5 $g(r)$ Curve for quenched copolymer R50.

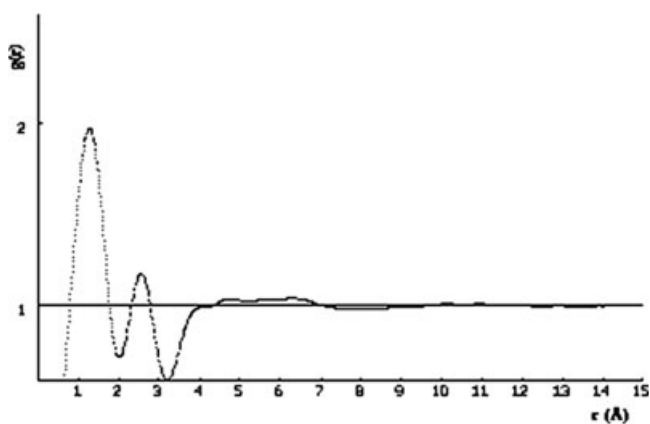


Figure 6 $g(r)$ Curve for quenched copolymer B50.

the first wide peak position as the intermolecular average distance (r_v).¹⁹ The short-range ordering of macromolecular chain segments could also be analyzed by the double-body distribution function [$g(r)$]. The $g(r)$ curves of three copolymers are listed in Figures 5–7. When the interatomic distance, r , increased gradually, the double-body correlation of interatomic distance approached zero for the three copolymers. In general, we defined the biggest r value of $g(r)$, 1 ± 0.02 , as the order region size (r_s).²⁰ At the same time, average atom displacement (σ) was used to denote an out-of-order material structure.²¹ A bigger σ value meant a greater out-of-order character of the molecular structure. The RDF descriptions of the three copolymers, shown in Table III, indicate that copolymer A50 had a lower intermolecular average distance and higher order region size than copolymers R50 and B50. Accordingly, copolymer R50 showed the least average atom displacement in the middle of the three copolymers. These structural changes explain the profound differences in melt viscosity, density, and tensile strength of the three copolymer samples with the same composition but different sequence distributions.

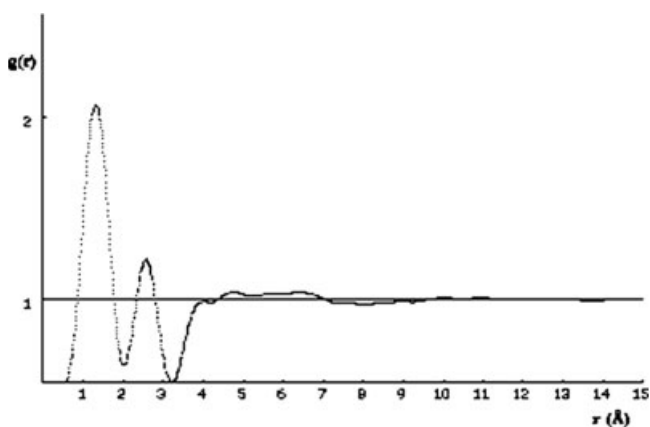


Figure 7 $g(r)$ Curve for quenched copolymer A50.

TABLE III
RDF Description of Copolymer Samples

Copolymer	ρ (g/cm ³)	Peak 1 (Å)	Peak 2 (Å)	σ (Å)	r_p (Å)	r_s (Å)
R50	1.368	1.43	2.58	0.277	6.3	7.4
B50	1.369	1.40	2.61	0.221	5.4	7.5
A50	1.371	1.42	2.61	0.205	5.3	7.8

CONCLUSIONS

This study of radial distribution functions showed that three kinds of 50 PES/50 PEES copolymers with different sequence distributions exist short-range ordering including intramolecular and intermolecular within 15 Å, and the short range structure of copolymer A50 has a smaller intermolecular average distance and a bigger order region size than copolymers R50 and B50. The structural information revealed by the RDF results are consistent with property changes resulting from varying the sequence distribution.

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