

# Investigation of Short Range Ordering in PES/PEES Alternative Copolymer by means of Radial Distribution Functions Derived from X-ray Diffraction

Xiao-Ming Zhou,<sup>1</sup> Zhen-Hua Jiang<sup>2</sup>

<sup>1</sup>Polymer Department, College of Material Science and Chemical Engineering, Tianjin University of Science and Technology, Tianjin 300457, China

<sup>2</sup>Polymer Department, College of Chemistry, Jilin University, Changchun 130023, China

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**ABSTRACT:** Two samples of poly(ether sulfone)/poly(ether ether sulfone) alternative copolymer, showing marked differences in tensile behavior due to different thermal histories, were investigated by radial distribution function (RDF) methods. The RDF patterns were virtually identical and showed that the short range order (0–14 Å) in the samples had been essentially unaffected by the annealing procedures. Two intramolecular distances in the polymer repeat unit 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, indicating that little intermolecular ordering had occurred in either sample. The appearance of two peaks at  $\sim 5$  Å periodic suggested the existence of more or

less parallel chain segments in the copolymers. Explanations of the different tensile properties of the two samples which assume a significant short range reordering on annealing are thus ruled out on the available evidence. A more highly annealed sample was examined to assess the sensitivity of the RDF method to short range intermolecular ordering. The RDF plot of this sample showed a marked periodicity peaking at intervals of  $\sim 5$  Å which was attributed to intermolecular ordering, thus confirming the above conclusion. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3746–3750, 2007

**Key words:** PES/PEES alternative copolymer; radial distribution function; short range order

## INTRODUCTION

In recent years, poly(ether sulfone) (PES) has been tailored to obtain optimum properties of toughness, strength, melt viscosity, and glass transition temperature by incorporating various substituents in its backbone. PES-type polymers have been known since 1962,<sup>1–4</sup> and PES copolymers have been developed for some applications. The main features of their synthesis, properties, and uses<sup>5,6</sup> have been set forth by others. Copolymers of PES and poly(ether ether sulfone) (PEES) units made either as blocks or as random materials show some improved properties.<sup>7</sup> In this article, PES/PEES alternative copolymer was firstly synthesized by two step reaction method. Studies of the tensile properties showed that a marked difference of the tensile strength on the thermal history of the sample was revealed. The structure of the material is amorphous both before and after annealing, when judged by the widely used criterion that the material does not give an X-ray

diffraction pattern comprising sharp Bragg reflections. It has been suggested<sup>8</sup> that short range reordering or crystallization might take place on annealing, 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 means of radial distribution function (RDF) methods,<sup>9</sup> derived from a careful analysis of the scattered diffraction pattern from the material. These techniques have been used to examine the two samples described earlier, and a more ordered specimen annealed at 200°C for 360 h. The latter sample was included to show that RDF techniques can reveal short range ordering in partially ordered polymers when the level of ordering remains comparatively low.

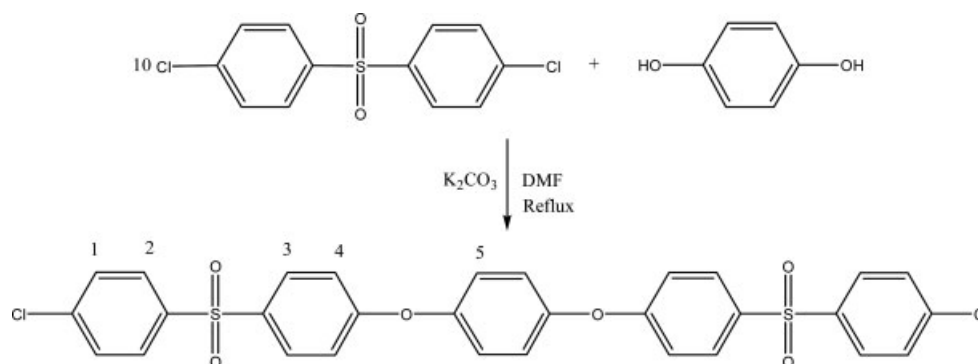
## EXPERIMENTAL

### Synthesis of PES/PEES alternative copolymer

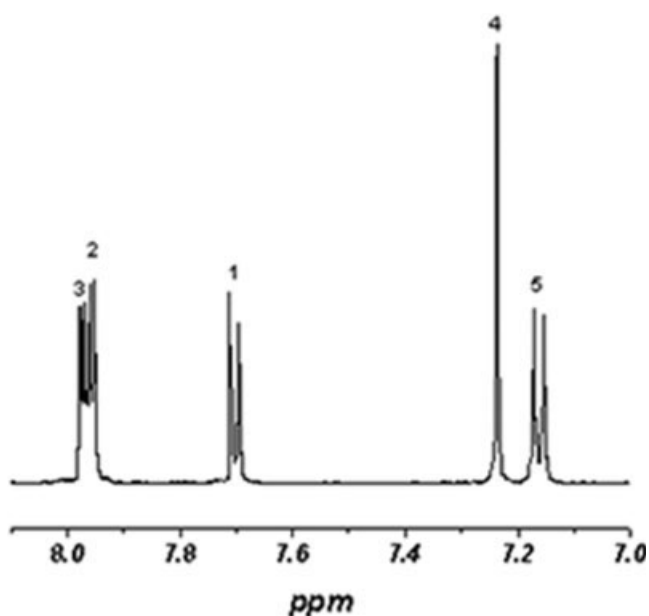
#### Preparation of PEES oligomer

First, chloro-terminated PEES oligomer was prepared from hydroquinone (HQ) and vast 4,4'-dichlorodiphenyl sulfone (DCDPS) with *N,N*-dimethylformamide (DMF, 99%) as solvent (reaction (1)).

Correspondence to: X.-M. Zhou (xiaomingzhou@tust.edu.cn).



Detailed synthesis process was described. The four-neck flask was charged with pure DCDPS (143.58 g, 0.5 mol), potassium carbonate (8.64 g, 0.06 mol), toluene (100 mL), and DMF (500 mL). Simultaneously, a solution of hydroquinone (5.62 g, 0.05 mol) in DMF (100 mL) was added in the flask, drop wise, under nitrogen to a refluxing suspension of potassium carbonate in DMF and toluene over 8 h, with continuous (Dean-Stark) removal of water as a toluene azeotrope. The toluene was then removed by distillation and the reaction continued for a further 12 h at 150°C. The mixture was cooled and poured into ethanol. After the mixture solution was heated, the resulting precipitates were collected by hot filtration, washed with water, and dried at 100°C for 24 h. The oligomer prepared as shown in scheme above was characterized by its melting point (mp = 253°C);  $^1\text{H-NMR}$  (DMSO- $d_6$ ) spectra (see Fig. 1):  $\delta\text{H}_1 = 7.712$  ppm,  $\delta\text{H}_2 = 7.964$  ppm,  $\delta\text{H}_3 = 7.974$  ppm,  $\delta\text{H}_4 = 7.164$  ppm,  $\delta\text{H}_5 = 7.236$  ppm. The yields for this oligomer were more than 70%.



**Figure 1**  $^1\text{H-NMR}$  spectra of oligomer recorded in DMSO- $d_6$ .

### Copolymerization

PES/PEES alternative copolymer was synthesized by the reaction of PEES oligomer with 4,4'-dihydroxydiphenyl sulfone (DHDPS) in sulfolane medium using KOH solution as the base under a nitrogen atmosphere. The inherent viscosity of PES/PEES alternative copolymer is 0.39 dL/g when measured in DMF at  $(25.0 \pm 0.1)^\circ\text{C}$  using an Ubbelohde viscometer. The glass transition temperature is 215°C when estimated by DSC using a Mettler Toledo DSC 821e. Copolymer powder was pressed at 280°C under a pressure of 10 MPa for 2 min, followed by quenching in an ice-water bath to obtain 1 mm thick amorphous sheets (sample A). Other two samples were named as sample B and sample C by subsequent annealing of the amorphous sample A in a vacuum oven. Pertinent information on the preparation and properties of the three copolymer samples is given in Table I.

### Measurement

The procedures employed for WAXS data collection and analysis have been described in detail elsewhere.<sup>10</sup> The X-ray scattering measurements were made on a Japan D/max-III A diffractometer using monochromatized Cu K $\alpha$  radiation (wavelength  $\lambda = 0.542 \text{ \AA}$ ). 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, i.e.,  $2\theta < 4^\circ$ , were obtained by extrapolating the experimental curve smoothly to zero at zero scattering angle. Afterwards, the raw intensity data were corrected for experimental factors, including background air scattering, absorption, polarization, and multiple scattering, according to standard methods.<sup>11–13</sup> The corrected intensity data,  $I_{e.u.}(s)$  were changed into interference intensity  $[i(s)]$ .  $i(s)$  was given using the equation:

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

where  $f_m(s)$  is the atomic fraction,  $f_e(s)$  the scattering factor, and  $C_m(s)$  the Compton scattering of the

TABLE I  
Description of the Preparation and Properties of the Copolymer Samples

Sample	A	B	C
Composition	50PES/50PEES	50PES/50PEES	50PES/50PEES
Thermal history	Quenched	Annealed 200°C, 72 h	Annealed 200°C, 360 h
Density (g/cm <sup>3</sup> )	1.356	1.361	1.375

s-type atom,  $s = \sin\theta/\lambda$ , and  $R$  is the normalization constant. The chemical units of (C<sub>4.2</sub>H<sub>2.8</sub>S<sub>0.3</sub>O<sub>1</sub>) for PES/PEES alternative copolymer were ascertained in the analysis based on the starting compositions of the copolymer. The Fourier analysis of scattering intensities for a system containing several different types of atoms, in this case C, H, O, and S, has been given by Waser and Schomaker,<sup>14</sup> discussed by Pings and Waser,<sup>15</sup> and applied by Wignall and Longman<sup>16</sup> and Gupta and Yeh.<sup>17</sup> Following this analysis, the differential RDF [ $G(r)$ ], for each alternative copolymer sample was derived according to the equations:

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

where  $\rho_0$  is the average electron density. The obtained RDF was further smoothed beyond its second peak by multiplying a damping factor,  $\exp(-7.5s^2)$ , by  $i(s)$ . Further discussions on proper construction of reliable RDF have been given previously by examining all the available literature information.<sup>18</sup>

## RESULTS AND DISCUSSION

The corrected and normalized WAXS intensities for the quenched sample A and the annealed sample B and C are shown in Figure 2. Similar to most of the amorphous polymers, two peaks are present at 18 and 43° for three PES/PEES alternative copolymer samples. The WAXS patterns comprise no Bragg reflections, indicating the structure of the copolymer samples is noncrystalline. A comparison of the WAXS data of copolymer sample A with copolymer sample B shows that two copolymer samples have very similar patterns in both peak intensity and position. For copolymer sample C, the intensity of the principal peak at 18° is higher than that of copolymer sample A and B by approximately 20%. Another peak intensity at 43° is virtually not affected by the thermal treatment for three copolymer samples.

The resultant  $G(r)$  curves for three copolymer samples are shown in Figures 3, 4, and 5, respectively. In general the peaks observed in the  $G(r)$  plot for a

polymer should be attributable either to intramolecular atomic distances dependent upon the repeat unit, or to intermolecular atomic distances determined by the short range order or packing of the chains. In the case of PES/PEES alternative copolymer, crystallization proceeds only very slowly over a restricted temperature range so that both samples A and B are unlikely to show any appreciable degree of intermolecular order, i.e., no extensive packing of the polymer chains into highly ordered regions, so that intermolecular spacings might be expected to remain ill defined. However, the intramolecular distances should be well defined at least for short distances,  $1 < r < 4$  Å. For copolymer sample A and B, prominent sharp peaks at 1.4 and 2.6 Å and very weak peaks at 3.9–12.9 Å are observed. According to previous calculations of the intramolecular distances in copolymer, the  $G(r)$  curves for copolymer sample A and B consist of intramolecular peaks at  $\sim 1.4$  and  $\sim 2.6$  Å and intermolecular peaks beyond the radial distance of  $\sim 4$  Å. No attempt has been made to attribute specific high frequency peaks occurring at values of  $r > 4$  Å to specific interatomic distances mainly for two reasons. Firstly, the largely random arrangement of the polymeric chains means that the relative position of any part of neighboring repeat units to each other is not known, so that only an

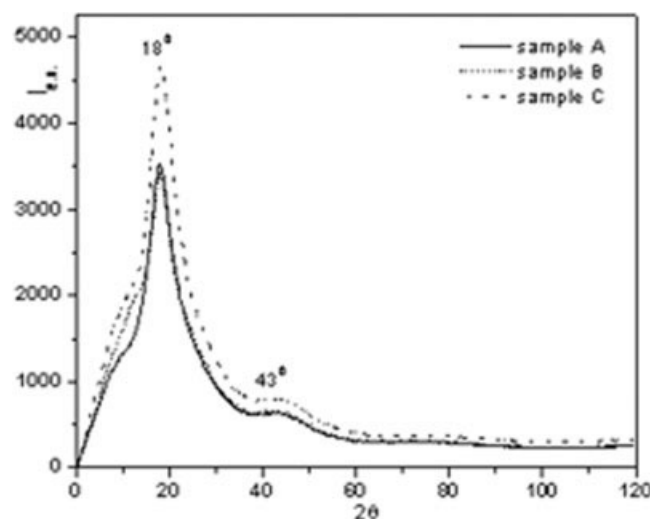


Figure 2 Corrected and normalized experimental WAXS data for samples A, B, and C.

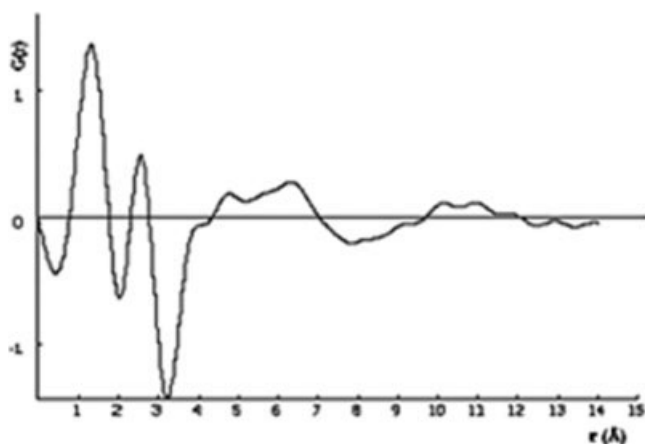


Figure 3  $G(r)$  curve versus  $r$  for sample A.

average disordered configuration could be assumed. Secondly, and resulting from this, it is apparent that a large number of possible interatomic distances exist, such that all observed RDF peaks could have interatomic spacings attributed to them. However, it is 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 copolymer chains within the steric limits of the structure. Thus attempts to identify peaks in the RDF plot at values of  $r > 4$  Å are not justified on the present samples. To ascertain the intermolecular structural changes caused by different thermal history, the present study is focused on examining the  $G(r)$  curves beyond 4 Å. It is apparent from Figures 3 and 4 that interchain ordering in samples A and B is present only vestigially as revealed by broad peaks at  $r = 5.5$  Å and  $r = 11$  Å upon which the intramolecular peaks are superimposed. These may be regarded as nearest neighbor chain interactions determined by the physical size of the polymer chains. It is apparent that there is no significant difference in the

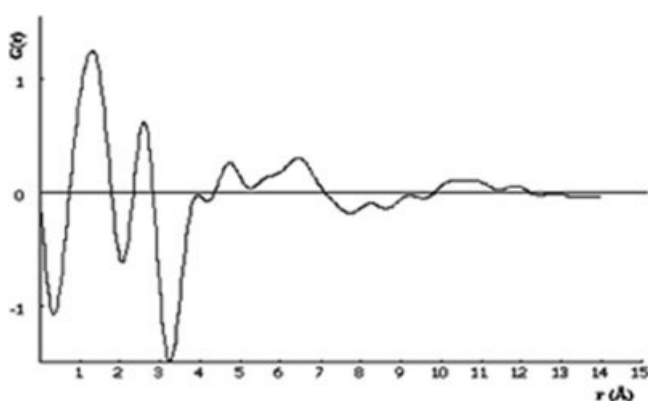


Figure 4  $G(r)$  curve versus  $r$  for sample B.

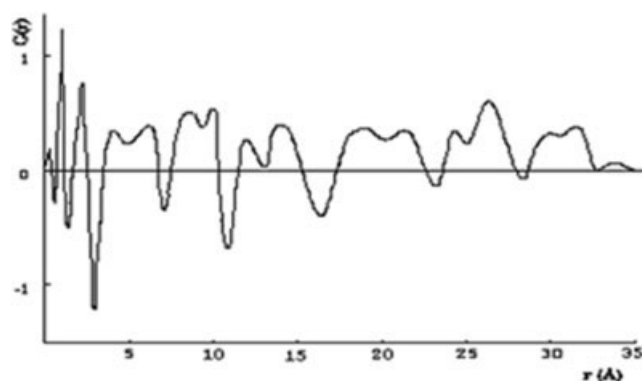


Figure 5  $G(r)$  curve versus  $r$  for sample C.

short range intermolecular order between samples A and B thus eliminating explanations of the change in tensile properties which assume such reordering. This is consistent with the very small difference in density between samples A and B.

The striking difference between A and B on the one hand (Figs. 3 and 4) and C on the other (Fig. 5) lies in the very marked long range order in the RDF with a period  $\sim 5$  Å. This apparently extends over distances of 30–35 Å but the correlation is not observed at greater distances. This is not unexpected, as packing faults occur even in well ordered regions in highly crystalline polymers. Since the order in sample C represents quite a low “crystallinity,” it is not surprising that intermolecular ordering is not detected at distances greater than  $\sim 35$  Å. However, the observed ordering is such that, it clearly demonstrates the sensitivity of the RDF technique to intermolecular ordering and reinforcing the conclusions concerning samples A and B.

## CONCLUSIONS

The  $G(r)$  results therefore suggest the presence of a short range molecular organization of  $\sim 15$  Å in the copolymer sample A and B, and the  $G(r)$  curve for sample A is found to be very similar to that for the sample B. The molecular alignment is markedly improved by annealing of the copolymer as shown by the appearance of prominent and additional periodic intermolecular peaks up to a much higher radial distance in the  $G(r)$  for the annealed sample C.

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