Effect of Sequence Distribution of PES/PEES Random, Block, and Alternative Copolymers on Excimer Formation in Solution

Xiao-Ming Zhou

Tianjin Economic-Technological Development Area, College of Material Science and Chemical Engineering, Tianjin University of Science and Technology, Tianjin 300457, People's Republic of China

Received 15 November 2006; accepted 20 May 2007
DOI 10.1002/app.26901

ABSTRACT: Three copolymers of poly(ether sulfone) and poly(ether ether sulfone) with the same composition but different sequence distribution were synthesized by three kinds of methods. Their molecular aggregation in dichloromethane was studied by fluorescence spectrophotometer and electron microscope. The experimental results revealed that the formation of intermolecular excimers in alternative copolymer (A50) dichloromethane solution were observed at a A50 concentration about 1.6×10^{-2} g/mL by the fluorescence analysis, but the formation of intermolecular excimers in dichloromethane were not found for random copolymer (R50) and block copolymer (B50). The electron micrograph of three copolymer films, heat-treated at 200°C for 7 days, presented a diffraction micrograph, which suggest that three copolymer molecular aggregation is changed from a randomly coiled amorphous phase to an ordered one, and the order structure of alternative copolymer (A50) was the most distinct in three copolymers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2263–2266, 2007

Key words: sequence distribution; fluorescence spectrophotometer; excimer

INTRODUCTION

Poly(ether sulfone)s (PESs) 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 sulfones) and PES-type copolymers have been developed for some applications.[1] The heat treatment of PES, an amorphous polymer, at an appropriate temperature below the glass transition temperature (T_g) changed the thermal and mechanical properties of the PES, as is different from that of general amorphous polymers.[2,3] From the structural viewpoint, it was supposed that the amorphous random arrangement of the molecular chains in the PES is changed to a certain ordered phase during the heat treatment. This assumption is satisfactory for the explanation of the various changes in the physical properties caused by the heat treatment.[4] For clarifying the existence of such an ordered phase, the conformation of the molecular chains in the PES dichloromethane solution was investigated by fluorescence spectra. The experimental results proved[5] that the intermolecular excimers in PES dichloromethane could be formed. In this paper, three copolymers of PES and poly(ether ether sulfone) (PEES) with the same composition but different sequence distribution were synthesized by different methods. Accordingly, we try to find the relationship between sequence distribution and excimer formation. The transmission electron microscopy as a assistant technique was adopted to study the effects of sequence distribution on the molecular aggregation for three kinds of copolymers.

EXPERIMENTAL

Copolymer Synthesis

PES/PEES random (R50), block (B50), and alternative (A50) copolymers with the molar ratio (50/50) were synthesized by one-step and two-step reaction methods, respectively, and the detailed procedures of the synthetic routes have been described previously.[6,7]

Measurement

The X-ray scattering measurements were made on a Japan D/max-IIIA diffractometer using monochromatized Cu Kα radiation (wavelength $\lambda = 0.542$ Å). The WAXS intensities for each sample were recorded by a step scanning procedure in the range of $4° < 2\theta < 120°$. The used fluorescence spectrophotometer was Hitachi F-4500 (Hitachi Co., Tokyo, Japan). The

---

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

Journal of Applied Polymer Science, Vol. 106, 2263–2266 (2007)

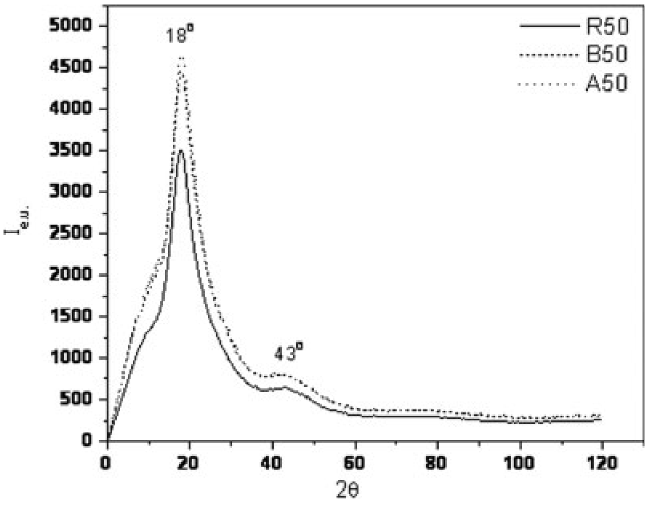

Figure 1 Corrected and normalized experimental WAXS data for quenched copolymer R50, B50, and A50.

scaning rate was 120 nm/min and response time was 2 s. The used transmission electron microscope was Hitachi model H-8100 (Hitachi Co.). The acceralation voltage was 200 kV.

Sample Preparation

Three PES/PEES random, block, and alternative copolymers dissolved in the dichloromethane at predetermined concentrations were used for the analysis. The samples for transmission electron microscopic investigations were obtained via solvent casting from 5 wt % dichloromethane solutions at 25°C. Thus-obtained bulk specimens were ultramicrotomed at −100°C with a diamond knife to sections of about 50 nm thickness using Reichert-Nissei Ultracut-S Ultramicrotome.

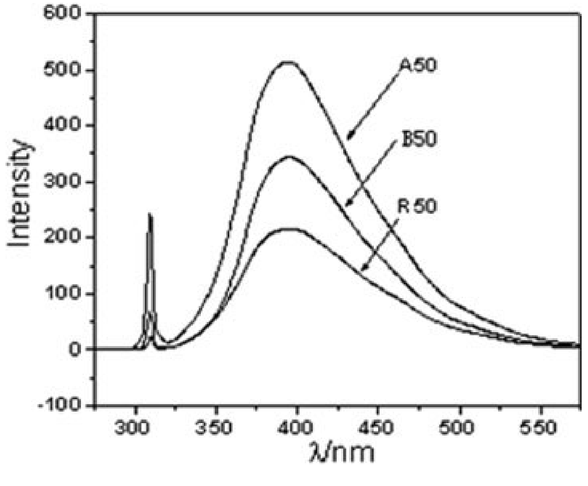

Figure 2 Fluorescence spectrum of the copolymers R50, A50, and B50 in dichloromethane solution (1.5×10^{-3} g/mL).

RESULTS AND DISCUSSION

The corrected and normalized WAXS intensities for the quenched copolymers R50, A50, and B50 are shown in Figure 1. The WAXS patterns comprise no Bragg reflections, indicating that the structure of the copolymer samples is noncrystalline.

Copolymers R50, A50, and B50 in dichloromethane with the lower concentration of 1.5×10^{-3} g/mL were measured by fluorescence spectrophotometer at room temperature, to examine whether an intermolecular excimer was formed in the copolymer solution. Figure 2 shows the obtained fluorescence spectra. The spectrum of the copolymer solution emitted only one band maximum at the wavelength λ of 395 nm. This band maximum was identified to correspond to monomers having a benzene ring in the fluorescence spectra. For the copolymer R50 and B50 in dichloromethane at the higher concentration, the fluorescence spectrum revealed that the emission intensity of monomer band maximum at λ of 395 nm first increased, and then began to decrease with the increase of the solution concentration. No other emission peak was found. Figures 3 and 4 shows the obtained fluorescence spectra. For copolymer A50 in dichloromethane at the higher concentration, the fluorescence spectrum revealed an anomalous emission at higher wavelength besides the monomer band maximum at λ of 395 nm described earlier. This suggests that an excimer was formed in the copolymer A50 solution. Generally, in case that an excimer is formed in a solution, the intensity of the monomer band maximum is more reduced with increase in the solution concentration. The fluorescence spectra of copolymer A50 in dichloromethane with the various concentrations were normalized with respect to the

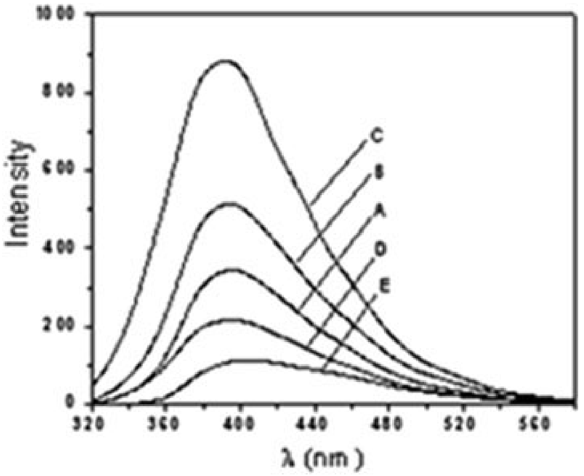

Figure 3 Fluorescence spectrum of the copolymer R50 with different solution concentrations. A: 1.6×10^{-3} g/mL, B: 7.8×10^{-3} g/mL, C: 1.6×10^{-2} g/mL, D: 2.8×10^{-2} g/mL, E: 3.5×10^{-2} g/mL.

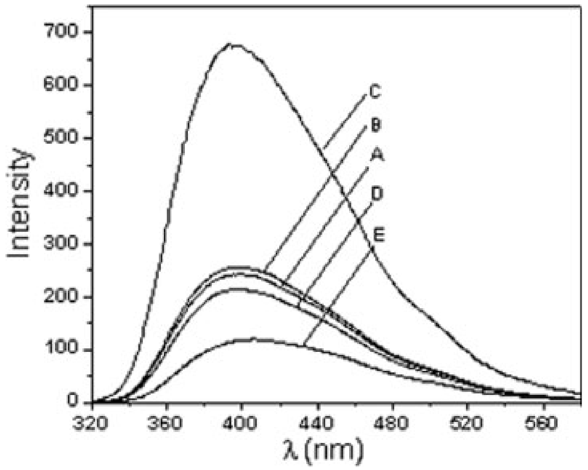

Figure 4 Fluorescence spectrum of the copolymer B50 with different solution concentrations. A: 1.2 × 10^{-3} g/mL, B: 2.8 × 10^{-3} g/mL, C: 1.8 × 10^{-2} g/mL, D: 3.2 × 10^{-2} g/mL, E: 4.8 × 10^{-2} g/mL.

intensity at 395 nm as shown in Figure 5. The fluorescence intensity of the monomer band is apparently reduced at above copolymer A50 concentration of 1.6 × 10^{-2} g/mL. The fluorescence intensity of the excimer band at 460 nm increases with the increase of concentrations of copolymer A50 solution. The band maximum is supposed to correspond to the structureless band, which is characteristic for excimers formed in certain polymers.[8–10] This implies that the formed excimer is an intermolecular one. Namely, chromophores (benzene ring) of copolymer A50 exist in the main chains which are relatively rigid. Accordingly, in normal conditions, there are less possibilities that two adjacent chromophores in the same molecule are so arranged in facial parallel that an excimer is formed as in polystyrene. However, for copolymer A50, with the increase of the solution concentration, two molecular chains gained on each other. It is suggested that the chromophores in the main chains arranged in facial parallel, so that intermolecular excimers were formed. But, the intermolecular excimers were not observed for copolymers R50 and B50 with higher concentration dichloromethane solution. This phenomenon could be due to the effect of different molecular chain sequence distribution.

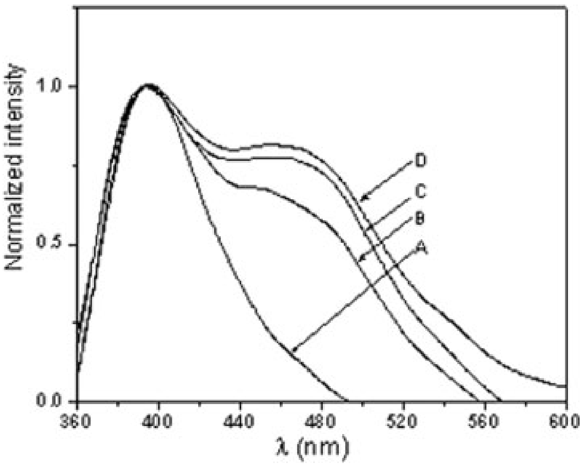

Figure 5 Fluorescence spectrum of the copolymer A50 with different solution concentrations. A: 1.8 × 10^{-3} g/mL, B: 1.6 × 10^{-2} g/mL, C: 2.3 × 10^{-2} g/mL, D: 3.1 × 10^{-2} g/mL.

As described earlier, in copolymer A50 molecular chains, the benzene rings of the main chains can gain on each other in parallel in higher concentration dichloromethane solution. Further, electron spectroscopy was applied to heat-treated copolymers R50, A50, and B50 in various conditions to investigate the possibilities that the molecular aggregation of the copolymers with different sequence distribution in a solid state is altered to an ordered phase under certain conditions. Figure 6 show the results. Figure 6(a,b) were the perspective and diffraction micrographs, respectively. Figure 6(A–C) showed the micrograph of heat-treated copolymer R50, B50, and A50 at 200°C for 7 days. The diffraction patterns of the heat-treated copolymer R50 and B50 had diffrac-

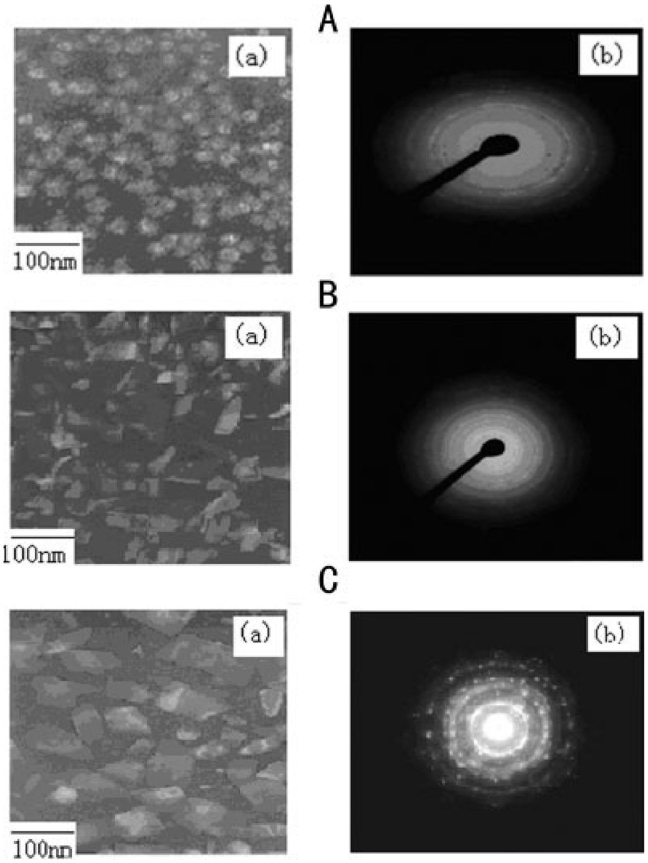

Figure 6 Diffraction pattern of the heat-treated copolymers at 200°C for 7 days. A: R50; B: B50; C: A50; (a) perspective pattern; (b) diffraction pattern.

tion ring, but which was not clear, if it implied formation of an ordered phase. But Figure 6(C) showed the micrograph of the heat-treated copolymer A50 at 200°C for 7 days, in which the diffraction pattern was more clear. This suggested that the heat-treated copolymer A50 at 200°C for 7 days had a molecular aggregation and formed an ordered phase, and the order structure of alternative copolymer was more distinct than random and block copolymers.

CONCLUSIONS

The molecular aggregation study of PES/PEES copolymers with the same compositions but different sequence distribution in dichloromethane solution showed that alternative copolymer A50 could form an intermolecular excimer, because alternative copolymer A50 had a more normalized chain than random and block copolymers. The observed changes in the electron micrographic diffraction patterns of the heat-treated copolymers R50, B50, and A50 suggested that three copolymer structure could all be altered to an ordered phase to some degree by heat treatment at high temperature, and the order structure of alternative copolymer A50 was more clear.

These experimental results obtained by fluorescence spectrophotometer and electron spectroscopy were consistent with radial distribution function methods[7] that were used to evaluate the short-range ordering of PES/PEES copolymers with the same composition but different sequence distribution.

References

1. Cinderey, M. B.; Rose, J. B.; Ger Offen 1978, 2803873.
2. Wu, Z.; Yokota, R.; Kochi, M.; Kambe, H. Kobunshi Ronbunshu 1981, 38, 601.
3. Wu, Z.; Yokota, R.; Kochi, M.; Kambe, H. J Soc Rheol Jpn 1981, 9, 59.
4. Wu, Z.; Wei, Q.; Chem J Chin Univ 1986, 7, 1046.
5. Wu, Z.; Zhang, L.; Wei, Q. Ryutoku Yosomiya 1988, 163, 115.
6. Zhou, X.-M.; Jiang, Z.-H. J Polym Sci Part B: Polym Phys 2005, 43, 1624.
7. Zhou, X.-M.; Gao, Z.-M.; Jiang, Z.-H. J Appl Polym Sci 2007, 103, 534.
8. Martin, T. J Chem Phys 1965, 43, 886.
9. Norman, S. Makromol Chem 1978, 179, 523.
10. Chiang, I. Y. Chin Sci 1981, 2, 133.