Studies on microdomain structure in segmented polyether polyurethaneureas by positron annihilation lifetime and small-angle X-ray scattering^{*}

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Abstract The microdomain structure of segmented polyether polyurethaneureas is investigated by means of positron annihilation lifetime spectroscopy, small-angle X-ray scattering and differential scanning calorimetry. The experimental results show that the decrease in the domain volume and free volume results from the increase in the hard segment (polyurethaneurea segment) contents as the number-average molecular weight $\overline{M_n}$ of the soft segments (polyethylene glycol segments) is the same, and that the increase in domain volume and free volume result from the increase in the $\overline{M_n}$ of the soft segments when the hard segment content is the same or nearly the same. These results demonstrate that positron annihilation lifetime spectroscopy is a sensitive technique to probe the microdomain structure in polymers. **Keywords** Positron annihilation, Small angle X-ray scattering, Segmented polyether polyure-

thaneurea, Domain structure, Glass transition temperature

1 Introduction

The advantages of associating a plastic electrolyte and a solid electrode were recognized as early as 1973.^[1] The polymeric solid ionic conductors have since generated widespread interest among both electrochemists and poly-The researches of polymeric mer scientists. solid ionic conductors, in which polyethylene oxide (PEO) is taken as the matrix, have been widely expanded since Armand et al. developed the complexes of PEO and alkali-metal salts in the end of 1970s. However, the PEObased solid ionic conductors have several disadvantages such as low conductivity at ambient temperature, low melting point, and bad mechanical properties. For this reason, Gu have developed a novel host polyet al. mer, poly(ethylene glycol) (PEG)-type segmented polyether polyurethaneurea (PEUU), which has a melting point of more than 180°C, the ionic conductivities of polymer film electrolytes formed by PEUU and LiClO₄ are $1\sim 2$ orders of magnitude higher than those of the PEO-based solid electrolytes at ambient temperature. The PEUU-LiClO₄ film electrolytes have good mechanical strength, high compli-

ance and better adherence to electrodes.^[2~4] Properties of polymeric solid electrolytes are strongly dependent on their molecular structure and aggregated structure. Poly(ethylene glycol)-type segmented polyether polyurethaneurcas (PEUU's) have typical two-phase microstructure, consisting of the PEG segment (soft segment) and polyurethaneurea segment (hard segment). At room temperature, the soft segment is in the rubbery state, whereas the hard segment is in the semicrystalline or crystalline state. Thus, the density difference between the soft segment phase and the hardsegment phase is large. There exists free volume in the soft-segment phase, and the hard segment exists as microdomain, so that the soft segment may be thought as a medium, while the hard segment as separated identical particles (the microdomains) in the medium.

Gyration radius R_g of the particles can be measured by using small-angle X-ray scattering (SAXS). According to the fundamental theory of SAXS^[5], we have

$$\lg \overline{I(h)} = -Kh^2 \tag{1}$$

$$h = (4\pi \sin\theta)/\lambda \tag{2}$$

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$$K = (R_{\rm g}^2 {\rm lg} e)/3 \tag{3}$$

In Eqs.(1), (2) and (3) $\overline{I(h)}$ is the scattering intensity of the X-rays, h is the amplitude of the SAXS, K is the slope of curve of $\lg \overline{I(h)}$ versus h^2 , θ is the X-ray scattering angle, and λ is the wavelength of the X-ray. The R_g can be determined by the relation of the Eq.(3)

$$R_{\rm g} = \sqrt{\frac{3K}{\lg e}} \tag{4}$$

where the $R_{\rm g}$ of the microdomains in the PEUU's may be obtained from the data of the SAXS.

It has been demonstrated that in the medium the longest component (τ_3) of the positron annihilation lifetime can be attributed to the decay of ortho-positronium (o-Ps) by pick-off annihilation in amorphous regions, that is, the τ_3 is the pick-off annihilation of the positronium in the free volume.^[6,7] Therefore, the positron annihilation lifetime (PAL) technique is a powerful tool to determine the change in the free volume in the polymer matrix.

In order to investigate the correlation between the structure of aggregation state and the ion-conducting behavior in the PEUU-LiClO₄ complexes, we studied the structure of aggregation state in the PEUU's by means of SAXS, positron annihilation lifetime (PAL) and differential scanning calorimetry (DSC) techniques. We here report the results on the character of microdomain structure in the PEUU's.

2 Experimental

PEUU's with the chemical structure shown in Fig.1 were synthesized from 4,4'methylenebis(phenylene isocyanate) (MDI). \mathbf{PEG} (number-average molecularweight $\overline{M_n}$ =600, 800, 1000 and 1540) and ethylenediamine (EDA). Full details were presented elsewhere.^[4] The samples for various measurements were prepared by casting a N,Ndimethylacetamide (DMA) solution of PEUU into polytetrafluoroethylene mold, followed by drying in a vaccum oven at 70°C for at least 4d to remove any traces of solvent.



Fig.1 Molecular structure of segmented polyether polyurethaneurea based on PEG



Fig.2 Typical Guinier-plot of the SAXS curves for the PEUU's



Fig.3 Typical positron annihilation lifetime spectrum in PEUU

SAXS curves were taken with a Model D/Max-ra Rigaku-Denki rotating-anode X-ray generator. The sample thickness was 0.3 mm. The SAXS intensity distribution was measured with Kratky camera in the 2θ region from 0.06° to 2.00°. The X-ray source was monochromatized to Cu K_{α} radiation with a Ni filter and a pulse-height analyzer. The scattering curve was corrected for air scattering. In order to eliminate slit smearing effects, an experimentally measured slit weighting function was used to desmear the data by the iterative method of Lake.^[8] The radius of gyration ($R_{\rm g}$) of microdomain was calculated by Guinier's method.^[6]

Positron annihilation lifetime measurements were made using a fast-fast coincidence circuitry positron lifetime spectrometer modified by ourselves from the fast-slow delayed coincidence positron lifetime spectrometer (CAN-BERRA) with a resolution time of 290ps. A ²²Na positron source of 740 kBq was sandwiched between two pieces of the PEUU sample (in disc form, 10 mm in diameter and 1 mm in thickness). This assembly was then put between two detectors. The total counts of each lifetime spectrum were up to 10^6 with good statistics. The lifetime spectra obtained were deconvoluted into a multi-exponential function by the IBM-PC/XT computer program Posifitextended. The actual resolution for the spectra was represented by two Gaussian functions in addition to the correction of the source. Every lifetime spectrum was carefully resolved into three components, of which each was characterized by a mean lifetime (i.e. lifetime τ_1, τ_2 and τ_3) and a probability per annihilation with that particular mean lifetime (i.e. intensity I_1 , I_2 and I_3).

Glass transition temperature $T_{\rm g}$ was determined by using a Perkin-Elmer DSC-II linked to a Perkin-Elmer thermal analysis data station. The experiments were carried out at a heating rate of 20°C/min under a He purge.^[3]

3 Results

Fig.2 shows a typical plot of $\lg \overline{I(h)}$ versus h^2 for the PEUU's. Fig.3 gives a typical lifetime spectrum for positrons annihilating in PEUU's.

The characterization of PEUU's and the experimental results are summarized in Table

1, where Δ is standard deviations. In polymers, the first lifetime τ_1 may be attributed to the free positron and para-positronium (p-Ps), the second lifetime τ_2 is a measure of the rate which positron decays by pick-off in the defect of crystalline region, the third lifetime τ_3 is associated with the rate which ortho-positron (o-Ps) decays by pick-off in the free volume.^[6,7,9] The intensities I_1 , I_2 and I_3 are the percentage of the number of the positron annihilations with lifetime τ_1 , τ_2 and τ_3 respectively, and $I_1 + I_2 + I_3 = 1$.

4 Discussion

From Table 1, one can see that when the $\overline{M_n}$ of the soft segments (PEG) is the same, with the increase in the hard segment contents in the PEUU's, the $T_{\rm g}$ will be higher, while the $R_{\rm g}$ of the domain and τ_3 (long lifetime) become smaller. These results indicate that the larger the hard segment contents, the larger the number of domains, but the smaller the domain volume, the greater the influence of the hard segments upon the soft segments, the more greatly the micro-Brown-movements of macromolecular segments (disordered zone) in between neighboring domains are impeded, and the smaller the free volume will become. Meanwhile as the short lifetime τ_1 and the middle lifetime τ_2 are nearly the same, the free electric density and the defect size all have no obvious changes. When the hard segment content is the same or nearly the same, increasing $\overline{M_n}$ of the PEG will lead to larger R_g and τ_3 , and less T_g , while the changes of τ_1 and τ_2 are not obvious. These phenomena also indicate that the number of the domains decreases, while the domain becomes larger, the influence of the hard segments on the soft segments decreases; the free volume of the disordered zone also decreases, but the free electric density and the defect size are nearly the same.

It is then concluded that the increases in $R_{\rm g}$ and in the free volume result from the increase in $\overline{M_n}$ of PEG, and that the decreases in $R_{\rm g}$ and in the free volume result from the increases in the hard segment contents, but the free electric density and the defect size are nearly the same under the mentioned conditions.

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| Number of samples | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|----------------------------|------------------------------------|--------|-------------|-------------|-------------|-------------|---------------|-------------|-------------|
| M _n of PEG | | 600 | 600 | 800 | 800 | 1000 | 1000 | 1540 | 1540 |
| Molar ratio of MDI/EDA/PEG | | 2/1/1 | 3/2/1 | 2/1/1 | 3/2/1 | 2/1/1 | 3/2/1 | 2/1/1 | 2.8/1.8/1 |
| Hard segment contents(wt%) | | 47 | 59 | 40 | 52 | 35 | 46 | 26 | 35 |
| $T_{r}/^{\circ}C$ | | -1.00 | +0.10 | -23.2 | -19.8 | -37.5 | -35.1 | -46.5 | -42.4 |
| $\frac{2g}{B_{\pi}}$ | | 6.5 | 6.0 | 7.3 | 6.7 | 7.6 | 7.1 | 8.3 | 7.9 |
| Lifetime $	au/\mathrm{ns}$ | $\frac{1}{\tau_1 + \Delta \tau_1}$ | 0.193 | 0.180 | 0.206 | 0.208 | 0.221 | 0.213 | 0.243 | 0.236 |
| | 11 ± -11 | +0.008 | ± 0.008 | ± 0.008 | ± 0.007 | ± 0.007 | ± 0.006 | ± 0.006 | ± 0.006 |
| | $\tau_2 + \Lambda \tau_2$ | 0.436 | 0.401 | 0.469 | 0.466 | 0.500 | 0.494 | 0.561 | 0.546 |
| | ·2 ± ± ·2 | +0.012 | +0.012 | ± 0.022 | ± 0.021 | ± 0.039 | ± 0.022 | ± 0.033 | ± 0.021 |
| | $\tau_2 + \Lambda \tau_2$ | 1.763 | 1.689 | 1.889 | 1.827 | 2.089 | 1.989 | 2.169 | 2.147 |
| | 13 ± ± 13 | +0.025 | ± 0.020 | ± 0.028 | ± 0.028 | ± 0.039 | ± 0.034 | ± 0.049 | ± 0.046 |
| | $I_1 + \Lambda I_1$ | 44.67 | 37.20 | 48.56 | 49.90 | 53.78 | 51.37 | 59.82 | 58.26 |
| Intensity I/% | 1 + 61 | +3.35 | +2.45 | ± 3.17 | ± 3.29 | ± 3.01 | ± 2.34 | ± 2.72 | ± 2.70 |
| | $I_0 \pm \Lambda I_0$ | 38 22 | 44.49 | 33.73 | 32.48 | 30.55 | 32.2 0 | 25.18 | 36.18 |
| | $12 \pm \Delta 12$ | +3.09 | +2.24 | +2.89 | ± 2.99 | ± 2.74 | ± 2.46 | ± 2.38 | ± 2.38 |
| | $I_{2} + \Lambda I_{2}$ | 17.11 | 18.31 | 17.71 | 17.62 | 15.67 | 16.43 | 15.00 | 15.57 |
| | 13 - 413 | +0.36 | +0.31 | ±0.38 | ± 0.40 | ± 0.36 | ± 0.37 | ± 0.44 | ± 0.42 |

Table 1 Sample characterization and experimental results

It is quite evident that positron annihilation lifetime spectroscopy is a valuable technique for the study of phase separation and microdomain structure in polymers.

References

- 1 Armand M B. In: van Gool W, ed. Fast iou transport in solids. N Y: North-Holland: 1973; p665
- 2 Gu Qing-Chao, Xu Wei-Zheng, Ye Wen-Wen et al. Chinese Journal of Polymer Science (English), 1991; 9:189
- 3 Xu Wei-Zheng, Gu Qing-Chao, Ye Wen-Wen et al. In: Chowdari B V R, Liu Q-G, Chen L-Q, eds. Recent advances in fast ion conduct-

ing materials and devices. Singapore: World Scientific, 1990; 313

- Gu Qing-Chao, Xu Wei-Zheng, Ye Wen-Wen et al. Functional Polymer (in Chinese), 1990; 3:265
- Guinier A, Furet G. Small-angle scattering of X-rays. New York: Wiley, 1955:126
- 6 Chuang S Y, Tao S J. J Appl Phys, 1973; 44:5171
- 7 Kluin J E, Yu Z, Vleeshouwers S et al. Macromolecules, 1993; 26:1853
- 8 Lake J A. Acta Crystallogr, 1967; 23:191
- 9 Wang Guang-Hou, Shen De-Xun, Lu Yong-Yi et al. Nuclear Instruments and Methods in Physics Research, 1986; B14:555