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Complementary SAXS and SANS for structural characteristics of a polyurethethane elastomer of low hard segment content

Ya-Sen Sun,[a] U-Ser Jeng,[a,*] Yu-San Huang,[a] Keng. S. Liang,[a] Tsang-Lang Lin,[b] Cheng-Si Tsao[c]

[a]*National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan*

[b]*Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30043, Taiwan*

[c] *Nuclear Fuel and Materials Division, Institute of Nuclear Energy Research, Longtan, Taiwan*

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Abstract

A polyurethane (PU) elastomer film based on segmented poly(tetramethylene oxide) (PTMO) has been studied using wide-angle X-ray scattering (WAXS), and small-angle X-ray and neutron scattering (SAXS and SANS). The broad WAXS peaks measured for the PU elastomer reveal a low crystallinity of the soft segments PTMO and no crystalline domains for the hard segments, methylene bis(4-isocynatobenzene) (MDI), at 20 °C. Whereas small angle scattering indicates the existence of hard-segment-rich aggregates. Using the contrast variation provided by the SANS and SAXS, we have extracted detailed structural information of the aggregates, including the shape, size, and the aggregation numbers. © 2001 Elsevier Science. All rights reserved

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1. Introduction

Polyurethane (PU) block copolymers belong to a class of thermoplastic elastomers with microstructures sensitive to chemical compositions of the soft and hard segments employed.[1,2] Due to the coexistence of multi-phases[3] and the slow dynamics of equilibrium phase,[4] the structures and thermal-mechanical properties of PU relate highly to the thermal and mechanical histories of the material.[5] The strong correlation between the microscopic structures and the technologically important macroscopic properties has made polyurethane attractive in academic as well as in commercial research. Numerous studies using various techniques, including DSC, WAXS,[2] SAXS,[1,2,5] FTIR, and NMR have been done. The majority of these studies focused on PU structures of a high hard segment content above ~30%, where continuous hard segment domains can be clearly identified and traced in structural transitions.[3,5,6]

On the other hand, PU elastomers of a low hard segment composition (less than 30%) are believed to have only discontinuous hard segment domains of a micellar nature[7] in the soft segment solvent-like matrix, especially when the sequence length of the hard segments is short.[5] In this report, we study the micellar structural characteristics of a segmented PU elastomer, of a low hard segment content and a short hard segment sequence length, using the contrast variation provided by SANS and SAXS.[8]

* Corresponding author. Tel.: +886-3-5742671; fax: +886-3-5728445; e-mail: tllin@mx.nthu.edu.tw ; usjeng@nsrrc.org.tw

2. Scattering model and SAXS/SANS contrast variation

Adapting the scattering formulism for aggregates in colloidal solutions,[8] we model the neutron or X-ray small angle scattering (SAS) intensity for the hard-segment-rich aggregates as

$$I(Q) = I_o P(Q) S(Q), \quad (1)$$

where $P(Q)$ is the normalized form factor with $P(0) = 1$, and $S(Q)$ the structure factor. The wave vector transfer $Q = 4\pi\sin(\theta/2)/\lambda$ is defined by the scattering angle θ and the wavelength λ of either neutrons or photons (X-rays). Whereas the zero-angle scattering

$$I_o = (C\text{-}C_o)N(b_h\text{-}V_{dry}\rho_s)^2 \quad (2)$$

depends on the concentration of the hard segment C, the critical concentration for aggregation C_o, the aggregation number of hard segment N, and the scattering contrast between the hard segment aggregates and the soft segment matrix of scattering-length-densities $\rho_h = b_h/V_{dry}$ and ρ_s, respectively. Here, b_h is the scattering length of the hard segment monomer of dry volume V_{dry}.

For rod-like aggregates, we use the form factor,

$$P(Q) = \int_0^1 \left| \frac{2J_1(v)}{v} \frac{\sin(w)}{w} \right|^2 d\mu \quad (3)$$

which integral takes into account the spatial orientations of right-circular cylinders of radius r and length L, with $v = Qr(1\text{-}\mu^2)^{1/2}$, $w = (1/2)QL\mu$, and the first order Bessel function J_1. For hard segment aggregates with no charge interactions, the structure factor derived from the Percus-Yevick model of hard sphere interactions may be appropriate.[8]

For a two-phase system containing hard segments and soft segments in a segmented PU film, I_o value in Eq. (1) changes with neutrons and X-rays due to the different scattering lengths b_h of the material. The scattering profile in Eq. (1) is irrelevant to the radiation quanta used. This contrast variation is equivalent to the hydrogen-deuteration substitution contrast method often used in SANS for polymers.[9] For the case of segmented PU, the scattering length densities estimated for a hard segment monomer of two MDI and a soft segment PTMO are $\rho_h \sim 13.3\times10^{-6}$ Å^{-2} and $\rho_s \sim 10.2\times10^{-6}$ Å^{-2} for X-rays, whereas $\rho_h \sim 2.84\times10^{-6}$ Å^{-2} and $\rho_s \sim 0.2\times10^{-6}$ Å^{-2} for neutrons. Here, we have used monomer volumes 710 Å^3 and 3510 Å^3 for the hard and soft segments, respectively, adapted from a previous study.[10] From the estimated contrast, SAXS intensity for the PU films studied is expected to be slightly higher than neutrons, provided that the hard segments form aggregates. Another aspect revealed from the above estimation is the nearly zero neutron scattering length density for the PTMO matrix, which makes neutrons virtually insensitive to the PTMO matrix as well as the density difference between the amorphous and crystalline domains of PTMO. In contrast, X-rays are much more sensitive to the same density difference due to the high absolute scattering length of the PTMO matrix for X-rays.

3. Experimental

Segmented poly(tetramethylene oxide)-based PU elastomer film of a thickness of 0.1 cm was prepared from the reaction of 1,4-butonediol (BD) with diisocyanated prepolymer, as detailed in a previous report.[11] The prepolymers were prepared from poly(tetramethylene oxide) glycol with two equivalents of methylene bis(4-isocynatobenzene), (MDI), at 60 °C under an ambient pressure of N_2. The number-average molecular weight, M_n, of PTMO is 2000, with a polydispersity of 2.25. The segmented PU elastomer thus synthesized contains 19.3 wt% hard segments, with each hard segment monomer consisting of two MDI and one BD extender.

SAXS measurement was performed at a sample temperature of 20 °C on the 8-m SAXS instrument at Tsing-Hua University. The monochromatic beam of 1.54 Å was collimated by three pinholes for a diameter of 1.0 mm. With a sample-to-detector distance of 2.8 m, the data collected by the 2-D detector covered a Q-range from 0.01 Å^{-1} to 0.2 Å^{-1}. The data were corrected for sample transmission, background, and detector sensitivity, and normalized to the scattering cross section per unit sample volume $I(Q)$ (the absolute intensity). On the other hand, SANS data were collected at 20 °C on the 8-meter SANS instrument at the National Institute of Standards and Technology (NIST). Pinholes of 2.5 cm and 1 cm diameters separated by 4.1 m were used to collimate the incident monochromatic beam of a wavelength dispersion of 25%. With a sample-to-detector distance of 3.6 m and two beam wavelength of 6 Å and 10 Å, data in the Q-range from 0.01Å^{-1} to 0.17Å^{-1} were collected. The SANS data collected by a two-dimensional detector were normalized to the absolute intensity using the same procedure as that used for the SAXS data.

For SANS, a high incoherent scattering background from the hydrogen atoms in the PU film, 0.76 cm^{-1} ($\lambda = 6$Å), is extrapolated from the high-Q data region of a featureless flat line. The incoherent scattering contribution subtracted from the SANS data is consistent with the value 0.74 cm^{-1} calculated according to an empirical formula of Jacrot.[12]

4. Result and Discussion

Fig. 1 shows the SAXS and SANS data for the segmented PU elastomer film. These two profiles are very similar in a wide Q range, except the sharp raising peak for SAXS in the Q region lower than 0.02 Å^{-1}. The result

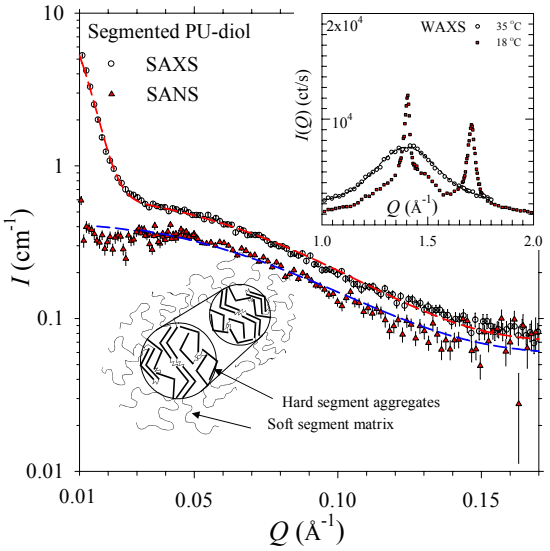

Fig. 1. The SANS and SAXS data for the segment PU film are fitted (dashed curves) using a rod form factor with a hard sphere structure factor. Based on the Guinier approximation,[8] we have included a term of $I_o\exp(-Q^2R_g^2)$ in the fitting process to take into account the scattering contribution (mainly in the low-Q region) by large PTMO crystalline domains, with a radius of gyration R_g ~ 140 Å. Inset demonstrates the WAXS profiles observed for the sample at 35 °C and 18 °C, resepectively. The cartoon illustrates a hard-segment-rich aggregate formed in the PTMO matrix.

indicates a general two-phase structure for the system[13] consisting of hard-segment-rich aggregates in the PTMO matrix. As to the low-Q sharp peak observed in the SAXS profile, we attribute it to the scattering from the partially crystalline PTMO domains of few hundreds angstroms estimated from the broad WAXS peak widths of PTMO chains (inset of Fig. 1). The PMTO crystalline domains are virtually invisible to neutrons due to the very low scattering contrast, as mentioned previously. In the following, we focus on the scattering from the hard segment aggregates.

Both the SANS and SAXS data in the region $Q \gtrsim 0.05$ Å^{-1} can be fitted adequately with the Kratky-Porod approximation for a rod-like shape.[8] Furthermore, distance distribution function $p(r)$ obtained from the SANS $I(Q)$ using the indirect Fourier transformation (IFT) for minimizing the data termination effects also indicates rod-like aggregates of a radius ~25 Å and a length ~60 Å.[14] Therefore, we adapt a cylinder form factor and a hard-sphere structural factor[8,9] in our model fitting for the detail structural information of the aggregates in the film. We integrate the SANS and SAXS data in a model fitting algorithm,[15] which helps in reducing the fitting parameters to five, including r and L for the cylindrical form factor, and C_o, N, and V_i for the scattering amplitude I_o. The $S(Q)$, depending on the volume fraction $\eta = (C\text{-}C_o)V/N$ and an effective sphere diameter σ approximated using $V_{agg} = \pi r^2 L = 4/3\pi(\sigma/2)^3$, adds no additional parameter in the fitting algorithm. We also take into account the data smearing effect of $I(Q)$ due to the beam divergence and the wavelength dispersion of the beam in the non-linear fitting process. The fitting result (dash curves in Fig. 1) demonstrates that the common rod structure parameters r = 20±2 Å, L = 50±5 Å, and V_{dry} = 710±30 Å^3 can largely satisfy both sets of data. In the fitting process, C_o and N are highly correlated, and cannot be determined with a single hard segment concentration. Nevertheless, we present the best-fitted C_o = 17.3 wt% (90% of hard segments in the PU) and N = 63. The high C_o value for the critical aggregation concentration of the hard segments in the PTMO matrix is generally consistent with the picture given previously that hard segments of short MDI sequence can dissolve in PU elastomer well up to ~30 %.[5,6,9] From the volume of the aggregate $V_{agg} = \pi r^2 L = NV_{dry} + MV_s$, with V_s = 3500 Å^3 for the volume of PTMO,[11] we can also deduce a PTMO association number M~7 for the hard-segment-rich aggregate.

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