

Structural Analysis of Three-Component Block Copolymers by Contrast-Variation Small-Angle Neutron Scattering with Dynamic Nuclear Spin Polarization

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1. Introduction

Small-angle neutron scattering (SANS) is one of the most effective tools for microphase separation analysis of block copolymers. Contrast variation neutron scattering (SANS), in particular, can be used to obtain partial scattering functions of specific components or between components by changing the deuteration ratio in the system and thus discussing the detailed nanostructure. Since the scattering length b_H of a hydrogen nucleus depends on its polarization P_H ($b_H = -0.374 + 1.456P_H$ (10^{-12} cm)), contrast variation experiments can be performed by controlling the hydrogen polarization rate. Experimentally, high polarization of hydrogen nuclei can be obtained by dynamical nuclear polarization (DNP), in which polarization is transferred from highly polarized electron spins (such as TEMPO radicals doped in the system) to hydrogen spins by microwave irradiation in a high magnetic field environment and at cryogenic temperatures. In this study, we used a block copolymer sample, poly(A)-*b*-poly(B-*ran*-C) in which one component is a deuterated random block, and a TEMPO radical was introduced into the matrix. Although a simple system, we will present the results of using DNP-SANS to analyze the microphase-separated structure of the block copolymer.

2. Experiment

Poly(deuterated styrene-*r*-bromo styrene)-*b*-poly(methyl acrylate) ((dPS-*r*PS)-*b*-PMA) (Br-dSMA) was synthesized by polymerizing d-styrene (ST) and styrene, and then tert-butyl acrylate by the ATRP method. TEMPO radicals were doped in the block copolymer film. The radical concentration was ca. 40 mM. Samples were slowly cast from a toluene solution over a week. Completely dried films were heat-treated at 140°C in a vacuum for 3 h. DNP-SANS experiments were performed at the beamline BL20 iMaterial at J-PARC Ibaraki Prefecture at 7T at a cryogenic temperature of 1.1K.

3. Result and Discussion

SANS measurements were performed for Br-dSMA in the range of hydrogen nuclear spin polarization from -42.1% to 37.6%. Figure 1 shows SANS profiles for different proton spin polarizations. The position ratio of q -values of the peaks is 1:2:3:4, indicating that a lamellar structure is formed, and the lattice spacing is 30.9 nm. The peak areas of the 2nd, 3rd, and 4th peaks relative to the 1st peak are shown in Figures 5-5. If BrSt is uniformly distributed within the BrPS domain, the SLD difference between the PMA and BrPS domains simply decreases with increasing P_H , so all peak areas decrease equally. In other words, the 2nd peak intensity relative to the 1st peak area is also constant regardless of the value of P_H . However, this is not the case, suggesting that BrSt is segregating within the BrPS domain.

To analyze the distribution state of BrPS in the BrPS domain, we considered the ABCB lamellar model, where the A domain is the PMA domain, the BC domain is the BrPS domain, 60 mol.% BrSt in the B domain and 20 mol.% BrSt in the C domain. The change in the form factor of the theoretical scattering curve is shown in Figure 2(a), assuming the presence of 60 mol.% BrSt in the B domain and 20 mol.% BrSt in the C domain. Figure 2(b) shows

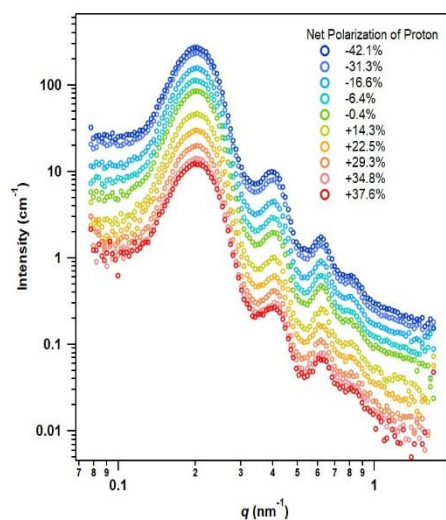


Figure 1. SANS profiles of Br-dSMA.

the P_H dependence of the scattering intensities of the 2nd, 3rd, and 4th peaks on the 1st peak intensity of the theoretical scattering curve. The P_H dependence of the SLD and SLD profile for each domain is shown in Figure 3, and Figure 2 shows that the 2nd peak intensity of the theoretical scattering curve decreases as the P_H value increases. This is the same trend as the experimental results, indicating that within the BrPS domain, BrSt is distributed more toward the interface with the PMA domain and less toward the interior. When 60 mol.% BrSt is present in the B domain and 20 mol.% BrSt is present in the C domain, the SLDs of the A domain (PMA domain) and the B domain coincide at a P_H of about 50% (Figure 2a). therefore, the polarizability dependence of the scattering intensity is expected to change significantly in the range of P_H lower than 50% and higher than 50% because the relationship between the SLDs is inverted. However, the sample used in this study had a low concentration of TEMPO radicals in the sample, which resulted in a polarization ratio of less than 50% for hydrogen nuclear spins. Therefore, the change in scattering intensity before and after the SLD matching point cannot be observed. If we could perform DNP-SANS measurements over a wide range of polarization, we would be able to make a detailed quantitative evaluation based on the changes in the scattering intensity and SLD profiles.

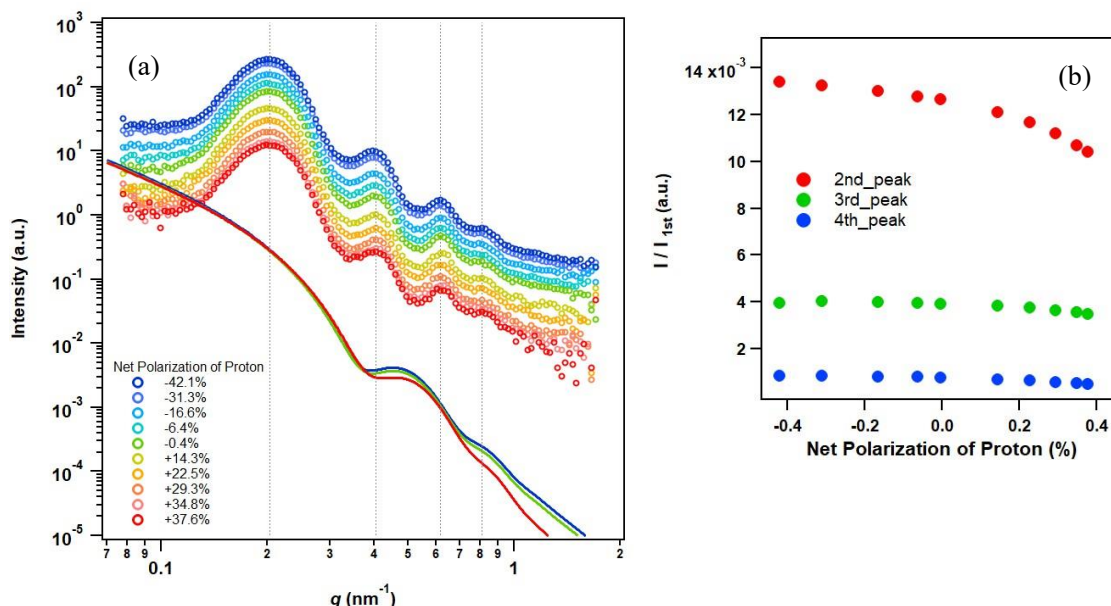


Figure 2. (a) DNP-SANS profiles and form factor calculated by ABCB Lamella Model. (b) Relative intensity of the calculated form factor corresponding to the 2nd peak, 3rd peak, and 4th peak.

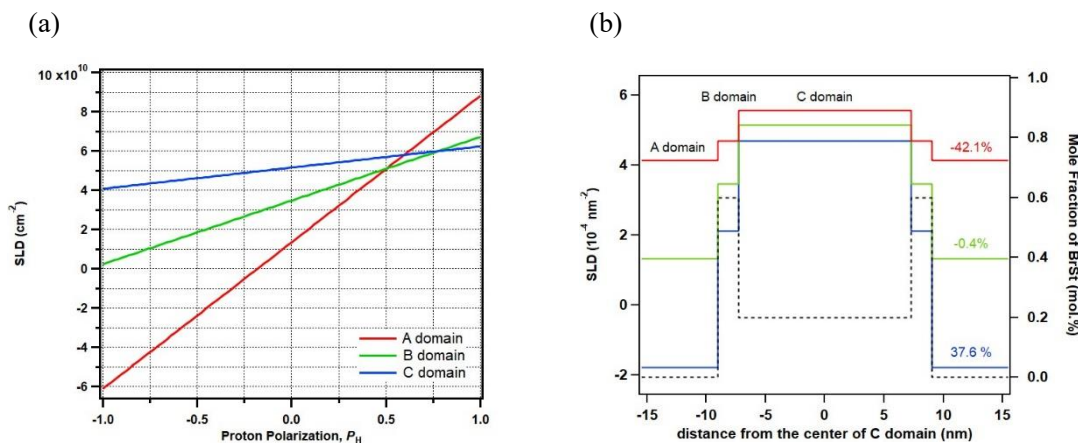


Figure 3. (a) SLD of A domain, B domain, and C domain as a function of proton spin polarization. (b) SLD profiles (solid lines) and distribution of BrSt (broken line).