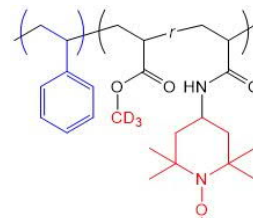


# Structure Analysis of Multi Components Polymer Alloy and Composite Utilizing of Contrast Variation by Dynamic Nuclear Polarization and Small Angle Neutron Scattering

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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 in which one component is a deuterated block, and a TEMPO radical is covalently introduced into the side chain (Figure 1). Although a simple system, we will present the results of using DNP-SANS to analyze the microphase-separated structure of the block copolymer.



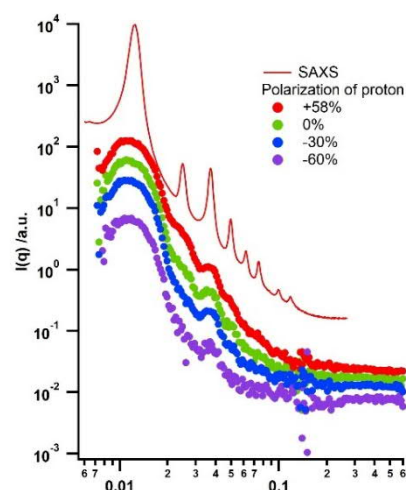
**Figure 1.** Chemical structure of the block copolymer.

## 2. Experiment

Deuterated polystyrene-*b*-polymethylacrylate (PS-*b*-dPMA) was synthesized by polymerizing styrene (ST) and tert-butyl acrylate by the ATRP method and completely replacing the PMA side chain of the resulting copolymer with ester exchange using deuterated methanol. In addition, a portion of the PMA side chain was replaced with TEMPO using 4-amino-TEMP. The radical concentration was 44 mM. The block copolymer has a molecular weight of PS of 37,100 dPMA of 38,800, and a volume fraction of PS of 53%. 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

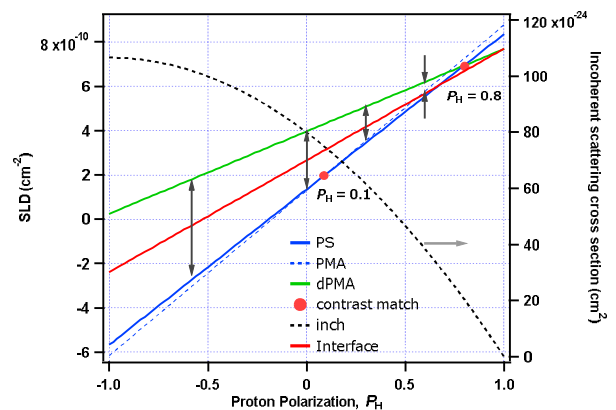
Figure 2 shows SANS profiles for different proton spin polarizations and SAXS profiles for comparison. The morphology is a lamellar structure, since the scattering peaks are observed at integer multiples. It can be seen that the scattering intensity increases as the polarizability changes toward the positive direction (actually, it is negatively polarized because the neutron polarizability  $P_N$  is negative). This is understood to be due to a decrease in the scattering length of styrene protons and an increase in the scattering length density difference between the PS and PMA domains (the scattering lengths of deuterium, oxygen, carbon, and nitrogen nuclei remain unchanged). The increase in the level of the wide-angle region is also due to the increase in an incoherent scattering of hydrogen nuclei.



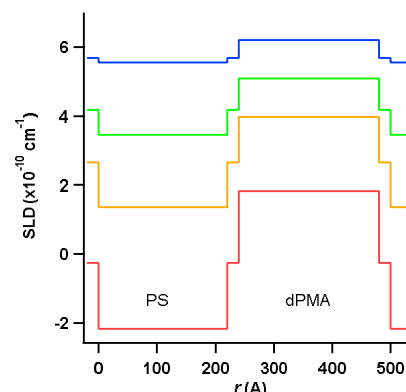
**Figure 2.** DNP SANS and SAXS profiles of PS-*b*-dPMA with TEMPO radicals. SAXS profile was shifted vertically to avoid overlapping.

The scattering intensity of the second-order peak (and fourth-order?) changed characteristically. If only the scattering lengths of the two-component domains changed, only the scattering intensity should change with polarization, and the profiles should change similarly. However, this is not the case, meaning the simple two-component model cannot explain the change. In order to explain the change in the scattering profile, it seems necessary to include, for example, the scattering length change in the mixed region at the interface. Therefore, the polarization dependence of the scattering length density (SLD) and incoherent scattering cross-section for the sample used in this study is shown in Figure 3. The green line represents the SLD of deuterated PMA, and the blue line represents the SLD of PS. The black dotted line represents the incoherent scattering cross-section due to hydrogen in the sample. For a simple two-phase system, only the scattering intensity decreases because the SLD contrast (indicated by the arrows) decreases with increasing polarization of the hydrogen nuclei, as mentioned earlier. The change in the scattering pattern is not simple because the shape of the profile is changing. On the other hand, for the incoherent scattering component, the polarizability dependence of the level (intensity) in the wide-angle side ( $2 < q < 6 \text{ \AA}^{-1}$ ) of Fig. 2 shows a perfect agreement with the dependence in Fig. 3. That is, the estimated error of the spin polarization is considered to be small. The major difference in the scattering profile is the change in the relative intensity of the secondary peak. This suggests that the SLD profile is not a simple two-component system. Therefore, we will focus on the SLD of the interfacial region. The interface region is usually a microdomain, and its effect is almost negligible in systems with large contrasts. However, we consider that there may be systems in which the contribution of SLD at the interface where the contrast between domains is slight must be considered. In the present study, we assume that the interface is a 1:1 mixing of the two components and that there is no volume change due to mixing, as shown by the red line in Figure 3. The phase-separated domain is divided into pure PS and PMA components, and the SLD profile is drawn assuming an interface thickness of 1 nm, taking the volume fraction into account. Based on this profile, we calculated the shape factor of scattering and estimated how the secondary peak intensity changes. The results are shown in Figure 5. Although the quantitative agreement with the experimental results is still insufficient, we confirmed that the decrease in the secondary peak intensity with increasing proton polarization could be reproduced.

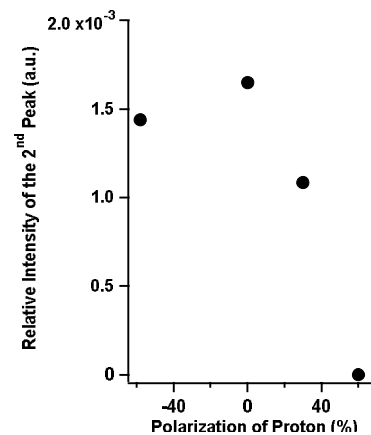
Since we have only given one solution in the structural analysis, further verification of the correctness of the model is needed. We will also discuss why the SANS profile obtained in this study is too broad compared to the SAXS scattering profile.



**Figure 3.** SLD and incoherent scattering cross section as a function of proton polarization of the sample.



**Figure 4.** SLD profiles assuming the interfacial thickness of 1 nm.



**Figure 5.** Relative intensity of the 2<sup>nd</sup> order peak calculated based on the SLD profiles given in Figure 3.