
Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Neutron Reflectivity from the Monolayer of SAN Random Copolymer

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Version of record first published: 24 Sep 2006

*Mol. Cryst. and Liq. Cryst.*, 2001, Vol. 371, pp. 211-214 



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The detailed structural aspects of the monolayer of SAN random copolymer with 22.6 wt% AN content at the air/water interface were investigated using neutron reflectivity(NR) technique. NR data at various surface pressures were analyzed to obtain the thickness, the density, and the concentration distribution. Well defined double-layered structure could fit the data.

Keywords: neutron reflectivity; segment density profiling; Langmuir monolayer; SAN random copolymer

## INTRODUCTION

Random copolymers with controlled hydrophilicity have been shown as a model material for the studies on the structures of the polymer monolayers.[1] Polyacrylonitrile does not form film at the air-water interface despite its polar C≡N groups attached along the hydrocarbon

chain, presumably because the three dimensional aggregate is rather formed due to the larger attractive force between the chain segments than the hydration force. Polystyrene that is moderately nonpolar polymer does not form Langmuir films by itself either. However it was recently observed in our laboratory that random copolymer (SAN) of styrene(S) and acrylonitrile(AN) could form stable monolayer at the air-water interface.[2] AN units which act as the hydrophilic part and S units which act as the hydrophobic part, are thought to balance the self interaction and the hydrophilicity on the water subphase. It could be confirmed by Brewster Angle Microscopy, surface pressure–area and surface potential–area isotherm studies. The scaling relationship between $\pi$ and monolayer concentration also showed that SAN on the water surface at the semidilute regime is close to the theta condition. The detailed segment density profiles was measured and analyzed in this study by NR which has been used to determine the detailed depth profiles with the depth resolution of less that 10 Å[3,4].

## MATERIALS AND EXPERIMENTS

SAN with 22.6wt% AN and deuterated S were synthesized by radical copolymerization reaction. Molecular weight was determined to be 180,000 by GPC using polystyrene as a standard. NR instrument located at National Institute of Standards and Technology, MD, USA (NG1 REFL) was used. The beam with the wavelength($\lambda$ ) of 0.47nm was used and $\Delta \lambda / \lambda$ value was 2.5%. SAN was spread on a mixture of 8.9% $D_2O$ and 91.1% $H_2O$ by weight which has a scattering length density of 0(null reflecting water). Measurements were made at three

surface pressures (4.5, 7.2, and 15.0mN/m) and the corresponding reflectivity data were shown in Figure 1.

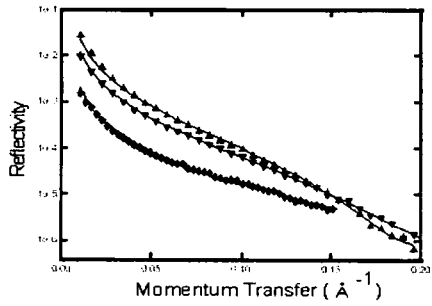


FIGURE 1. Neutron reflectivity as a function of momentum transfer at the surface pressures of 4.5 mN/m(▲), 7.2 mN/m(▼), and 15.0mN/m(◆).

## RESULTS AND DISCUSION

The scattering length density of a given layer is a weighted sum of the scattering length densities of S, AN, and the components with zero scattering length density (air and the null reflecting water). The optical matrix method was used to obtain the reflectivity as a function of momentum transfer (Q). Simplex method inside MATLAB program was used for fitting the data to the calculated values. The double-layered scattering length density profile could fit the experimental reflectivity profile well, whereas the one with a single layer could not generate the observed magnitudes and variation of NR values as a function of Q. By imposing the condition that the mass of S and AN is conserved in two layers and that the volume fraction of AN is richer in the layer next to water(lower layer) and that of S is richer in the layer

next to air(upper layer), the composition of each component could be calculated. The results are summarized in Figure 2. The total thicknesses of the layers, which increases with the surface pressure, were in good agreement with the predicted values using the separate observation obtained using surface pressure-area isotherm experiments[5].

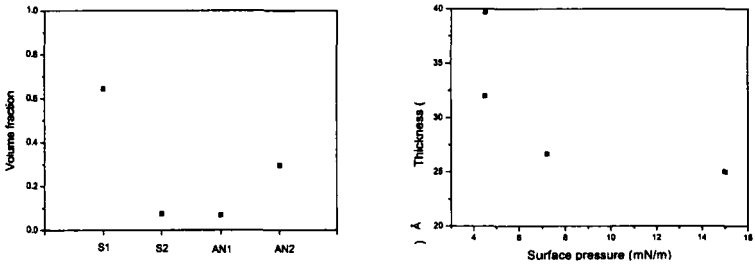


FIGURE 2. (a) Volume fraction of styrene in upper layer(S1), that of styrene in lower layer(S2), that of acrylonitrile in upper layer(AN1), and that of acrylonitrile in lower layer(AN2). (b) Total thickness of the monolayer as a function of surface pressure.

**ACKNOWLEDGEMENT**

This project was supported by Ministry of Science and Technology as a part of the Nuclear R & D Program made in the fiscal year of 1998.

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