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Small angle neutron scattering
study of the micelle structure of
amphiphilic block copolymers

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The amphiphilic block copolymers of vinyl ether were prepared by living cationic polymerization. The partially deuterated copolymers for SANS experiments were especially synthesized by introducing deuterated phenyl units in the hydrophobic chain. SANS measurements were performed for aqueous solutions of these copolymers by changing H₂O/D₂O ratios. The SANS profiles indicate that the micelles in the present system exhibit a core-shell structure and that the size and shape of micelles are largely dependent on the length of hydrophobic chain. The micelle of shorter hydrophobic chain was found to be nearly spherical, whereas the micelle of longer hydrophobic chain was confirmed to have an ellipsoidal shape.

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1. Introduction

The fundamental investigations on the structure and properties of micelles were so far concerned mainly with ionic surfactants such as soaps and detergents. In recent years, more interest has been focused on the micelles of nonionic surfactants from both scientific and industrial points of view. Amphiphilic block copolymers, which consist of hydrophilic and hydrophobic segments connected by a covalent linkage, are typical examples of polymeric nonionic surfactants [1-4]. Extensive efforts have recently been devoted to clarify the amphiphilic nature of these copolymers. However, little is known about the relationship between the structure of amphiphilic copolymers and their micellization behavior in solution. The purpose of the present work is to study the size and shape of micelles as a function of segment composition of the block copolymers by small angle neutron scattering (SANS) technique.

2. Experimental

The block copolymers of vinyl ethers were prepared by living cationic polymerization of 2-(acetoxymethyl)ethyl vinyl ether (AcOVE) and 2-(phenoxyethyl) vinyl ether (PhOVE). The block part of AcOVE in the resulted

copolymers was hydrolyzed to form hydrophilic segments as shown in the general formula of Fig. 1 [1]. The length of hydrophilic part, m , was fixed to 50 in order to obtain enough hydrophilicity. The length of hydrophobic part, n , was changed to 10 and 30. The block copolymers of shorter hydrophobic chain ($n = 10$) and longer hydrophobic chain ($n = 30$) will be referred to Polymer A and Polymer B, respectively. The partially deuterated copolymers for neutron scattering experiments were especially synthesized by introducing deuterated phenyl units in PhOVE of hydrophobic chain.

SANS measurements of Polymer A were performed with 30 m SANS facility of Oak Ridge National Laboratory, Tennessee [5]. The neutron wavelength was 4.75 Å with 6 % resolution and the data were obtained over the range of scattering vectors $3 \times 10^{-3} < Q < 3 \times 10^{-2}$ (Å⁻¹). SANS experiments of Polymer B were carried out with SANS-U spectrometer at JRR-3M in Japan Atomic Energy Research Institute, Tokai. The 7 Å incident neutron beam, taken from the cold neutron source and monochromatized by mechanical velocity selector, were used. The observed momentum transfer range was $2 \times 10^{-3} < Q < 2 \times 10^{-2}$ (Å⁻¹) and the wavelength resolution was 10 %.

Small angle X-ray scattering (SAXS)

measurements were performed by Kratky type camera of Rigaku Corporation which is equipped with Rotating anode X-ray generator and a position sensitive proportional counter. The details of SAXS instrument were described in the previous paper [6].

Results and Discussion

The results of SAXS experiments have suggested that the shape of the micelle formed from Polymer A is spherical and the micelle of Polymer B exhibits an anisotropic character. The radii of gyration of these micelles estimated from the initial slopes of Guinier plots of SAXS profiles are about 50 Å for Polymer A and about 80 Å for Polymer B, respectively [7]. An ellipsoidal sphere with a core-shell structure [8] has been proposed as a possible model for the micelle of Polymer B [7].

In order to estimate the shape and size of the micelles in further detail, SANS measurements were carried out by using the partially deuterated samples and the mixed solvent system of H₂O and D₂O. Fig. 2 shows SANS profiles of Polymer A and Polymer B in D₂O. The scattering intensity of Polymer A decreases gradually with an increase in q , whereas that of Polymer B drops steeply and then decreases slowly. These results indi-

cate that the micelle of Polymer A is spherical and that of Polymer B is anisotropic as suggested by SAXS measurements.

SANS experiments of Polymer A were performed in the solvents of various H_2O / D_2O ratios. For Polymer A, a spherical core-shell model was assumed as a micelle structure where a central core consists solely of partially deuterated hydrophobic segments and an outer shell is formed of hydrophilic segments swollen by the solvent. The scattering data from Polymer A were reasonably fitted with the geometric values that the diameter of core is about 35 Å and the thickness of shell is about 35 Å.

Fig. 3 represents typical examples of scattering patterns from Polymer B in different solvent systems. The minimum scattering intensity was observed at the (1:1) mixed ratio of H_2O and D_2O , although the contrast matching was not perfect. The fittings of the experimental profiles were performed under the assumptions that the micelle exhibits a core-shell structure as in the case of Polymer A and the shape of the micelle is an ellipsoidal sphere of anisotropic factor, μ . The shape and size of the micelle of Polymer B in aqueous solution estimated from the above-mentioned procedures are shown in Fig. 4. The salient feature of the micelle formed

is that the size of core part in the micelle are much smaller than the length of hydrophobic segments calculated as fully stretched chain. This indicates that the hydrophobic segments are compactly packed in the core part and the hydrophilic segments of shell part cover the surface of the core by forming a hairy corona. More details of the model and the data treatment will be given in a forthcoming paper.

4. Conclusion

The block copolymers of vinyl ethers consisting of hydrophilic and hydrophobic segments were demonstrated to form micelles in aqueous solution. The results of SAXS and SANS experiments indicate that the micelles in the present system exhibit a core-shell structure and that the shape and size of micelles are largely dependent on the length of hydrophobic segments. The copolymer with shorter hydrophobic segments tends to form a spherical micelle, whereas the copolymer with longer hydrophobic segments produces an ellipsoidal micelle. The estimated size of core part in the micelle is much smaller than the length of hydrophobic chain calculated as a fully stretched form, indicating that the hydrophobic segments of core part are compactly packed in the micelle.

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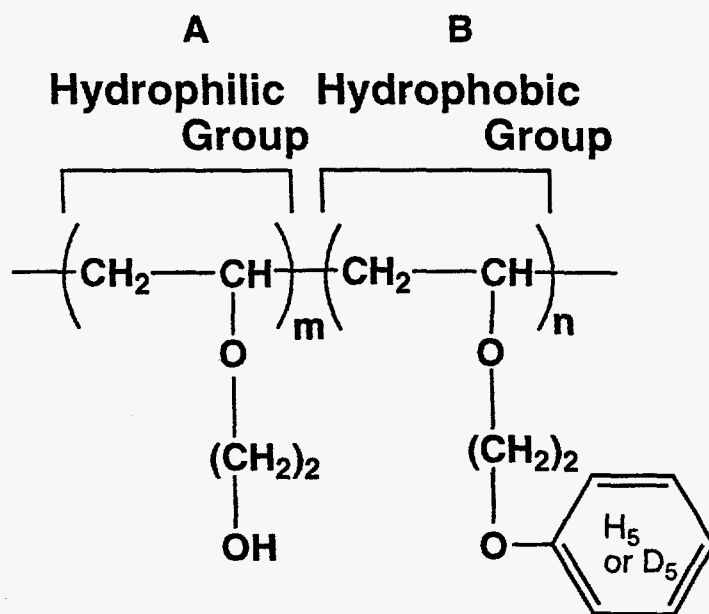
Figure Captions

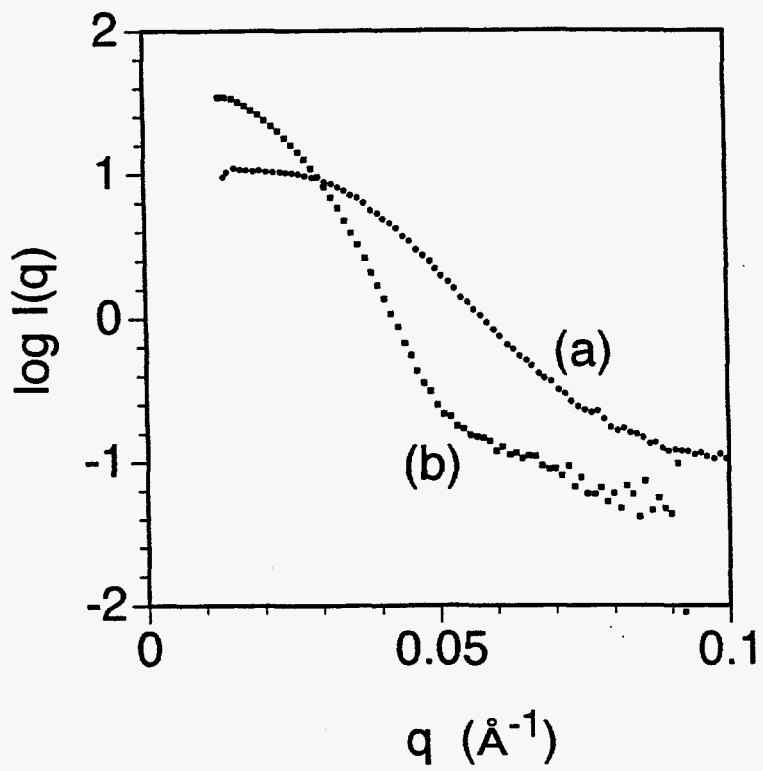
Fig. 1. General formula of amphiphilic block copolymer.

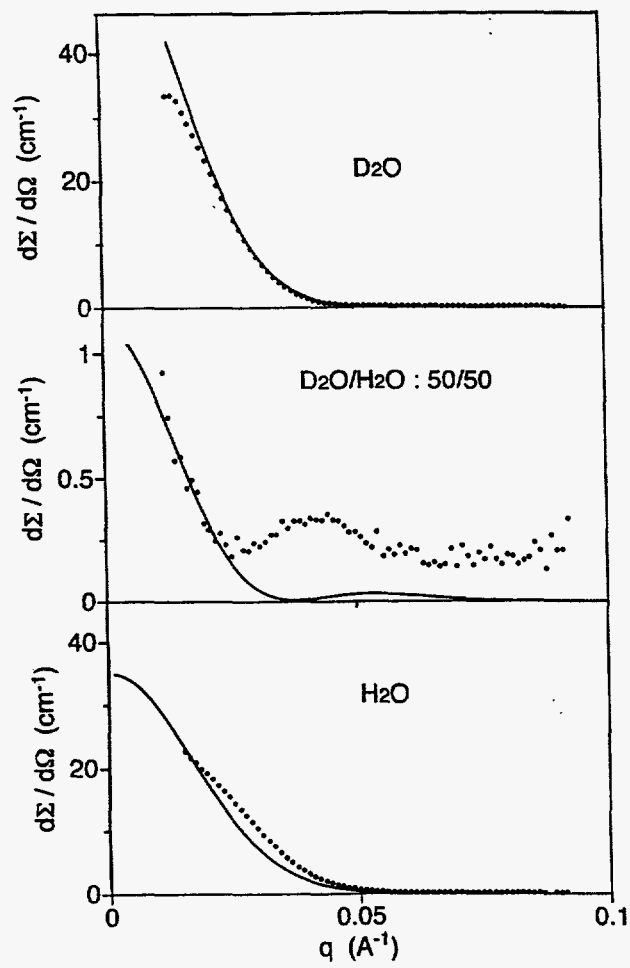
Fig. 2. SANS profiles of block copolymers in D_2O : (a) Polymer A;
(b) Polymer B.

Fig. 3. SANS profiles of Polymer B in different solvent systems.
The solid curves are drawn according to the core-shell
model calculations.

Fig. 4. Schematic representation of a possible micelle structure
of Polymer B in aqueous solution.







Yamacka et al., Fig. 3 (P3 A-13)

