

# Morphology Transition from Sphere to Rod by Confining the Polymer Chains in a Dilute Microemulsion System

Kaori Nakaya<sup>\*</sup>, Masayuki Imai<sup>\*</sup>, Shigeyuki Komura<sup>\*\*</sup>, and Naohito Urakami<sup>\*\*\*</sup>

<sup>\*</sup>*Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo, 112-0012, Japan*

<sup>\*\*</sup>*Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji-shi, Tokyo, 192-0397, Japan*

<sup>\*\*\*</sup>*Yamaguchi University, 1667-1 Yoshida, Yamaguchi-shi, Yamaguchi, 753-8512, Japan*

**Abstract.** In this study we investigated the morphology transition of microemulsion droplet induced by polymer confinement using a small angle neutron scattering (SANS) technique. By confining the polymer chain strongly the scattering profiles showed the following changes; 1) a characteristic scattering peak corresponding to the size of droplet shifts to the higher  $q$  side, and 2) the scattering intensity in the low  $q$  region increases considerably. These changes of the scattering profiles can be described by a rod (or sphero-cylinder) model. Thus, the strong confinement of polymer chains in droplets induces the morphological transition from spherical to rod-like droplet.

## INTRODUCTION

Microemulsion is a unique system in which water and oil coexist stably through a surfactant monolayer. It shows a variety of morphologies in membrane structure, such as globular (droplet), layered (lamellar) or network state (bicontinuous) depending on compositions or external fields. Recently an increasing interest is directed toward membrane-polymer system [1]. In the complex system of microemulsion and polymer, it is anticipated that it appears various phenomena based on a balance of energy and entropy, because each component has large internal degree of freedom. In the previous paper [2], we studied the static behavior of the membrane structure of a dilute microemulsion droplet confining a single polymer chain weakly. In this case the balance of entropy loss due to the polymer confinement and membrane elastic energy governs the droplet size. The purpose of this study is to clarify the morphology of the membrane confining polymer chains very strongly.

## EXPERIMENT

We used water-in-oil microemulsion droplets, which consisted of AOT, isooctane, and water. As a confined polymer it was adopted the water-soluble polymer, gelatin with the radius of gyration  $R_g=81\text{\AA}$ .

The radius of the droplet ( $R$ ) was controlled by changing the water to surfactant ratio ( $\omega_0$ ) and fixed at  $\omega_0=41.1$  in this study. The volume fraction of the dispersed phase that consists of water and AOT (and polymer) was fixed to 0.07. The static structure of the membrane was followed by the small angle neutron scattering (SANS) technique. The SANS measurements were performed using ISSP-SANS-U (Tokai) and KENS-SWAN (Tsukuba).

## RESULTS AND DISCUSSION

Figure 1 shows the SANS scattering profiles for water-in-oil microemulsion droplet with and without polymer in the film contrast condition. By confining the polymer chains strongly, the peak observed in the droplet without the polymers shifted to the higher  $q$  side, and the scattering intensity increased in low  $q$  region. The scattering profiles of droplet are described by form factor  $P(q)$  and structure factor  $S(q)$ . We fitted the experimental profiles with the spherical shell model [3] as  $P(q)$  and Percus-Yevic model as  $S(q)$ . The scattering profile of droplet without the polymers was fitted very well, which gives  $R=64\text{\AA}$ . Thus in this study we confined the polymer chain inside of a microemulsion droplet strongly. On the other hand, the scattering profile for microemulsion droplet + polymer system could not be described by the spherical model well. Then we adopted the rod (or sphero-cylinder)

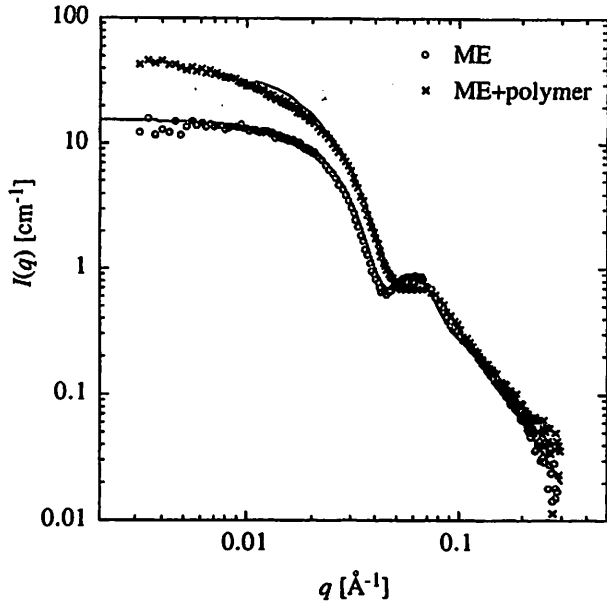


FIGURE 1. SANS profiles for the system of AOT-isooctane-water microemulsion droplet of  $\omega_0=41.1$  without (opened circle) and with (cross) gelatin at 30°C. The solid lines are curves fitted with the sphere and the rod model.

model;  $P(q)$  is approximated by the rotational ellipsoid and  $S(q)$  for the rod system was obtained from the Monte Carlo simulation. The scattering curve with polymer could be described well with the rod model. This result suggests that the morphological transition of membranes from sphere to rod is induced by strong confinement of the polymer chains. It was found that the radii of the minor axis and the major axis are about 45 and 360 Å, respectively. Using these parameters the number of the polymer chains was calculated to about 0.9 chains per rod-like droplet.

In order to elucidate this morphological change, we estimate the total free energy of each structure with three terms, the elastic energy of the membrane, the conformation entropy loss by the confinement of polymers, and the interaction between segments (excluded volume effect)

$$F_{tot} = F_{mem} + F_{conf} + F_{ex} \quad (1)$$

The elastic energy of a membrane is given by the Helfrich expression [4]

$$F_{mem} = \int [2\kappa(H - H_0)^2 + \bar{\kappa}K] dS \quad (2)$$

where  $\kappa$  is the bending modulus,  $\bar{\kappa}$  is the saddle-splay modulus,  $H$  is the mean curvature, and  $K$  is the Gaussian curvature. The free energy of the polymer

confinement can be estimated from the entropic confinement contribution [5] as

$$F_{conf} \sim T \left( \frac{R_F}{D} \right)^2 \quad (3)$$

where  $T$  is temperature and the free energy of the interaction between segments can be described as

$$F_{ex} = \nu \rho^2 V \quad (4)$$

where  $\nu$  is the excluded volume parameter,  $\rho$  is the density of segments, and  $V$  is volume of one droplet. On the basis of this concept, the total free energy of each structure was calculated. As the result, we found that the interaction between segments  $F_{ex}$  becomes dominant in the system, and stabilizes the rod shape compared with the spherical shape by confining polymer chains strongly.

## ACKNOWLEDGMENTS

This work was supported by Grant-in-Aid for Exploratory Research (No.13740252, 15740261) from the Ministry of Education, Sciences, and Culture of Japan. In addition, this work was done under the approval of the Neutron Scattering Program Advisory Committee, Japan. We are grateful to T. Kawakatsu and S.A. Safran for helpful discussions.

## REFERENCES

1. For example: (a) Lal, J., and Auvray, L., *J.Phys.II (France)* 4, 2119-2125 (1994), (b) Bellocq, A. M., *Langmuir* 14, 3730-3739 (1998).
2. Nakaya, K., and Imai, M., *J. Phys. Soc. of Japan* 70 Suppl. A, 338-340 (2001).
3. Grazielski, M., Langevin, D., and Farago, B., *Phys.Rev.E* 53, 3900-3919 (1996).
4. Helfrich, W., *Z.Naturforsch* 28c, 693-703 (1973).
5. de Gennes, P. G., *Scaling Concepts in Polymer Physics*, Cornell University Press, New York, 1979, pp.18-19.