# Morphology of Microemulsion Droplet Confining a Single Polymer Chain

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We have investigated morphological change of a microemulsion droplet induced by confinement of a polymer chain using a small angle neutron scattering (SANS) technique. The confinement induces two morphological changes, 1) increase of the mean droplet size and 2) increase of the droplet size polydispersity. The increase of mean droplet size can be described by a simple scaling concept on the basis of membrane rigidity and entropy loss of polymer chain by the confinement.

KEYWORDS: microemulsion, droplet, confinement of polymer, SANS, AOT

#### §1. Introduction

Microemulsions are thermodynamically stable structured fluids consisting of water, oil, and surfactants. By changing compositions or external fields, morphologies of the surfactant membrane show a variety of mesostructures having order of hundreds of angstroms, such as droplet (sphere), lamellar, and bicontinuous structures. Among these morphologies, water-in-oil droplets provide isolated meso-scale water region separated by continuous oil phase.

Recently behaviors of surfactant membrane confining polymer chains have received much attention. For example, the confinement of polymers between lyotropic lamellar structure brings change of elastic nature of the membrane.<sup>1)</sup> If we introduced water soluble polymers into the water-in-oil microemulsion droplet system, polymer chains can be confined in the spherical mesospace surrounded by the surfactant membrane. Lal and Auvray<sup>2</sup>) investigated perturbations of microemulsion droplets by confining poly(ethylene glycol) chains and observed increase of the droplet size distribution. Quellet et  $al^{(3)}$  and Hearing et  $al^{(4)}$  introduced concentrated associating polymer (gelatin) into dense microemulsion droplet system (isooctane/Aerosol OT/water) and found that the droplet system transforms to three dimensional network structure (formation of transparent stable gels). Thus the confined polymers affect behavior of surrounding membrane deeply.

In this study we introduced a single associating polymer chain into a microemulsion droplet, where the size of the droplet is comparable to the radius of gyration of the confined polymer chain and investigated morphology change of the surfactant membrane induced by the confinement using the SANS method.

#### §2. Experiments

In this experiment, we used water-in-oil microemulsion droplets consisting of isooctane, Aerosol-OT, and water. For the neutron scattering experiments, deuterated isooctane and deuterated water were mixed with corresponding hydrogenated components in order to adjust the scattering length densities. As confined polymers we used gelatin (type A, Bloom 300) having molecular weight of  $9.6 \times 10^4$ . The radius of gyration  $(R_g)$  of this gelatin was 81 Å which obtained by the SANS measurement.

We varied the droplet radius by changing the water to surfact ant ratio ( $\omega_0$ ) in the vicinity of the  $R_g$  of the gelatin. The volume fraction of droplets (water+AOT) was fixed to 7%. The microemulsion droplets confining polymer chains were made as follows: gelatin was allowed to swell in water at 60 °C and then mixed with solution of AOT in isooctane at 60 °C. After well-stirring, the samples were transferred to SANS cells and hold for 1 hour at 30 °C before SANS measurements.

The SANS measurements were performed using a SANS-U instrument of Institute for Solid state Physics, the University of Tokyo at JRR-3M reactor of Japan Atomic Energy Research Institute at Tokai.<sup>5)</sup> We used neutron wavelength of 7 Å with resolution  $\Delta\lambda/\lambda=0.1$ , which covers q (q: magnitude of scattering vector) range from 0.007 to 0.3 Å<sup>-1</sup>. All measurements were carried out at 30 °C. The obtained scattering patterns were corrected for the background scattering and incoherent scattering and then transferred to absolute intensity. All experiments were performed under the film contrast conditions where the scattering length density of water region matches with that of oil region.

### §3. Results and Discussions

First we show behavior of microemulsion droplets without polymers. In Fig. 1 we plot the scattering profile for  $\omega_0(=[H_2O]/[AOT])=57.6$ . The scattering profile shows a broad peak at q=0.04 Å<sup>-1</sup> and  $q^{-2}$  decay in  $q \ge 0.1$  Å<sup>-1</sup> region, which is typical behavior for microemulsion droplets under film contrast condition. The  $q^{-2}$ decay indicates sharp and smooth membrane interface of sphere droplets. The obtained scattering function can be described by a scattering function for spherical shell



Fig.1. SANS profiles for the system of AOT-isooctane water microemulsion droplet of  $\omega_0=57.6$  without (circle) and with(triangle) gelatin at 30 °C. The solid lines are curves fitted with the shell model.

model<sup>6)</sup> taking account of size polydispersity given by

$$I(q) = {}^{1}N \int_{0}^{\infty} f(r)P(q,r)dr$$
(3.1)

$$P(q) = 16\pi^2 (\rho_s - \rho_{oil})^2 \{R_2^3 f_0(qR_2) - AR_1^3 f_0(qR_1)\}^2 (3.2)$$
  
with

$$f_0 = (\sin x - x \cos x) / x^3 \tag{3.3}$$

$$A = (\rho_s - \rho_{water}) / (\rho_s - \rho_{oil})$$
(3.4)

where <sup>1</sup>N is the number density of droplets, P(q) is form factor, and  $\rho_s$ ,  $\rho_{oil}$ , and  $\rho_{water}$  are the scattering length density of surfactants, oil, and water, respectively. In the case of microemulsion droplets confining gelatin chains,  $\rho_{water}$  is replaced by  $\rho_{w/gel} = (1-a)\rho_{water} + a\rho_{gel}$ , where a is volume fraction of gelatin chains in the water pool and  $\rho_{gel}$  is scattering length density of gelatin. For the polydispersity function we adopted a Schultz distribution f(r) where  $r=(R_1+R_2)/2$ , and  $R_1$  and  $R_2$  are the inner and outer radii of the droplet shell. Here we assume the structure factor, S(q)=1 because we use the dilute system. The shell model well describes the observed profiles and as an example, the fitted curve is given as solid line in Fig. 1. From the fitting we extracted two parameters, mean radius of the droplet (R) and the polydispersity parameter p ( $p^2 = \langle R^2 \rangle / \langle R \rangle^2 - 1$ ). We obtained good linear relationship between R and  $\omega_0$ , and the samples with  $\omega_0 = 57.6, 65.4, \text{ and } 74.0 \text{ had } R = 78.0, 86.0, \text{ and }$ 98.0 Å respectively.

Before introducing a polymer chain into a droplet, we examined the interaction between the gelatin chain and the AOT membrane. Since the gelatin is a natural occurring polypeptide and the AOT is an anionic surfactant, it is considered that the gelatin chain strongly adsorbed at the interface due to the electrostatic interaction between the gelatin and AOT head group. The interactions between polymers and membrane have been well investigated using polymer containing lamellar systems. For nonadsorbing or weakly adsorbing polymers, the lamellar order and the membrane rigidity are little affected by the presence of the polymers, whereas for the strongly adsorbed polymers, these properties are significantly changed by the adsorption. Then we investigated effects of the gelatin on the structure and rigidity of lamellar membrane composed of AOT and H<sub>2</sub>O using the SANS technique.<sup>7)</sup> Scattering profiles of lamellar structure containing gelatin chains are measured as a function of gelatin concentration (0  $\sim 10 \text{ wt\%}$ ). The experimental profiles were fitted with a model scattering function for lyotropic lamellar systems proposed by Nallet  $et al.^{(8)}$  and we extracted three parameters, lamellar spacing, bilayer thickness, and Caillè parameter which is a measure of the membrane rigidity. The gelatin concentration dependence of the three parameters are fairly small compared with the prediction for strong adsorption case. Then we concluded that the gelatin chain is not strongly adsorbed at the interface and dissolved in the closed water pool.

Then we examined the microemulsion droplets confining a polymer chain system. The average number of polymer chain in a droplet  $(n_p)$  is calculated from the number of droplet and the number of gelatin chains in the system. In this study we prepared three samples  $\omega_0 = 57.6 \ (n_p = 0.82), \ 65.4 \ (0.88), \ and \ 74.0 \ (0.88).$  We plot the SANS profile for the droplet ( $\omega_0 = 57.6$  and  $n_p = 0.82$ ) with corresponding SANS profile without polymer in Fig. 1. The features of scattering profiles for the droplets confing a polymer chain are smearing of the characteristic peak of the droplet and asymptotic  $q^{-2}$  behavior in high q region. The latter indicates that the droplets are not deformed significantly and keep the spherical shape by the confinement. It should be noted that increase of scattering intensity in low q region is due to unmatch of the scattering length densities between inner water pool containing hydrogenated gelatin chain and outer oil matrix.

We fitted the experimental profiles with the shell model described above. The obtained R and p without gelatin and with gelatin are plotted as a function of  $\omega_0$  in Fig. 2. The R and p are increased by the confinement of a polymer chain. Taking account that the gelatin chain has  $R_q = 81$  Å the smaller droplets confine a polymer chain, the larger increase of the droplet size and polydispersity are observed. There are some candidates to explain the increase of the polydispersity; (1) inhomogeneous partition of polymer chains to the droplets, (2) polydispersity of the gelatin molecular weight, and (3)softening of membrane rigidity due to the polymer confinement.<sup>2)</sup> Unfortunately at present, we can not conclude which effect is responsible to the observed increase of the polydispersity. Here we focus our attention on the change of the mean droplet size.

In order to explain observed increase of the mean droplet size, we consider a simple scaling law describing free energy of droplet membrane confining a polymer chain. The droplet membrane with the spontaneous curvature  $H_0$  (or sphere radius  $R_0$ ) confines a polymer chain having Flory radius of chain  $R_F$ , resulting in the formation of sphere droplet having the radius of R. In this treatment we assume that the polymer adsorption at the



Fig.2. Changes of droplet radius (open) and poly-dispersity(closed) of microemulsion without(circle) and with(triangle) gelatin.

interface and electrostatic interaction are negligible. The total free energy of the system may be expressed by two terms, polymer confinement and membrane elasticity

$$F_{tot} = F_{conf} + F_{mem}.$$
 (3.5)

The free energy of the polymer confinement can be estimated from the entropic confinement contribution<sup>9)</sup> as

$$F_{conf} \sim T \left(\frac{R_F}{2R}\right)^{\frac{3}{3}}$$
 (3.6)

where T is temperature and the free energy of sphere membrane is given by the Helfrich expression<sup>10)</sup>

$$F_{mem} = \int [2\kappa (H - H_0)^2 + \overline{\kappa} K] dS \qquad (3.7)$$

where  $\kappa$  is the bending modulus,  $\overline{\kappa}$  is the saddle-splay modulus, H is mean curvature, and K is the Gaussian curvature. For simplicity we assume that the radius of droplet without polymer is  $R_0$ . Then we can express  $F_{tot}$  using three observable parameter,  $R_F$ , R, and  $R_0$  as follows

$$F_{tot} \sim T\left(\frac{R_F}{2R}\right)^{\frac{5}{3}} + 4\pi [2\kappa - 4\kappa \left(\frac{R}{R_0}\right) + 2\kappa \left(\frac{R}{R_0}\right)^2 + \overline{\kappa}]$$
(3.8)

Minimizing the total free energy against R gives a simple scaling law

$$\frac{R}{R_0} \sim \left(\frac{R_F}{R}\right)^{0.83} \tag{3.9}$$

In Fig. 3 we compared the experimental data with the scaling law, where we replaced  $R_F$  by  $R_g$  of the gelatin. Roughly speaking, the experimental data obeys this simple scaling law, although the data is limited in the narrow region. This is because that if we confine the polymer chains in a smaller droplet, large deformation of droplet is observed. This issue will be discussed forthcoming paper.



Fig.3. A log-log plot of  $R/R_0$  versus  $R_g/R$ . The slop represents the power law behabior  $(R/R_0) \sim (R_g/R)^{0.45}$ .

In this study we examined morphological changes of a microemulsion droplet when the droplet size is varied in the vicinity of the radius of gyration of a confined polymer chain. The confinement induces two morphological changes, (1)increase of polydispersity of the droplet size, and (2)increase of the mean droplet size. The latter behavior can be described by a simple scaling concept on the basis of membrane rigidity and entropy loss of polymer chain by the confinement. Thus the droplet size confining a polymer chain is governed by the balance of entropy loss due to the polymer confinement and membrane elastic energy.

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