Elasticity effects on domain coarsening of the lamellar-gyroid transition observed in a nonionic surfactant system

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The coarsening process of the gyroid phase of a nonionic surfactant system is investigated by time resolved small angle neutron scattering (SANS) and small angle neutron Laue diffraction techniques. The time evolution of SANS patterns shows anomalous coarsening of the gyroid domains. The observed Laue spot from a gyroid domain becomes elongated along the radial direction with the elapse of time and at a certain time the elongated spot is split into two spots. The results can be interpreted as follows. During the coarsening process, mismatch of the lattice orientation at the domain boundary brings strong stress to the gyroid domain, resulting in the distortion of the domain. The stored stress in the domain finally brings splitting of the gyroid domain. The elastic and fragile nature of the gyroid domains composed of the ''soft matter'' is responsible for the anomalous coarsening. [S1063-651X(99)04907-7]

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I. INTRODUCTION

Surfactant solutions and block copolymers show a variety of ordered mesophases. Typical examples are one dimensional cylinders, two dimensional lamellae, and gyroid structure having three dimensional bicontinuous cubic lattice with I_{a3d} symmetry. These ordered morphologies composed of amphiphilic molecules have large internal degrees of freedom and this ''soft'' nature brings unique features which are hardly observed in ''hard'' materials. From this point of view, the morphology transitions between these ordered phases have recently been investigated both experimentally [1–8] and theoretically [9–12]. Rançon and Charvolin [1] established epitaxial relations in the hexagonal-gyroid and lamellar-gyroid transitions of a nonionic surfactant-water system. Similar epitaxial relations have been observed in block copolymer systems [7,8]. Clerc *et al.* [2] investigated the kinetics of hexagonal-gyroid and lamellar-gyroid transitions in a nonionic surfactant system using a time resolved x-ray diffraction technique and found that the transitions proceed in a manner of nucleation and growth mechanism having a time constant of about 100 ms. On the basis of these experimental observations, Matsen [11] revealed the topography of the Landau free energy surface for the cylinder-gyroid transition and showed the cylinder-gyroid transition proceeded epitaxially by the nucleation and growth mechanism.

Recently we [5,6] have investigated the late stage of the hexagonal-gyroid and lamellar-gyroid transitions in a nonionic surfactant system using a time resolved small angle neutron scattering technique and found new features of the morphology transition. During the coarsening process of the gyroid domains, the scattering patterns show anomalous time evolution, i.e., the diffraction peaks from the gyroid domains irregularly vary their intensities with time. This behavior is quite different from the normal domain coarsening [13] such as metallurgical polycrystals and the soap froth systems in which the average domain size $\overline{R}(t)$ at time t obeys the power law of $\overline{R}(t) \sim t^{v}$ where v is the growth exponent. The purpose of this study is to make clear the origin of the anomalous domain coarsening observed in our previous study which may reflect the ''soft'' nature of complex fluids.

The coherent neutron scattering intensity from the ith domain having periodic lattice can be expressed by

$$I(\mathbf{Q},t) \propto n_i^2(t)\, \delta(\mathbf{Q}-\boldsymbol{\tau}_i(t))|F|^2, \tag{1}$$

where $\mathbf{Q}$ is the scattering vector, n_i is the number of unit cells in the ith domain, $\boldsymbol{\tau}_i$ is the reciprocal vector of the unit cell, and F is crystal structure factor. According to Eq. (1), the intensity fluctuation in the coarsening process should arise from the fluctuation of $n_i(t)$ or $\boldsymbol{\tau}_i(t)$. In order to distinguish these two effects, we employed a Laue technique. This technique releases the restriction $\delta(\mathbf{Q}-\boldsymbol{\tau}_i(t))$ and so enable us to follow the orientational fluctuation of the gyroid domain.

II. EXPERIMENT

A nonionic surfactant

$$C_{16}E_7\ (CH_3(CH_2)_{15}(OCH_2CH_2)_7OH)$$

was used as an amphiphilic molecule because the phase behaviors of the $C_{16}E_7/D_2O$ system have been investigated in detail [14]. $C_{16}E_7$ was purchased from Nikko Chemicals, Inc., and used without further purification and deuterium oxide purchased from ISOTEC, Inc. (99.9%) was used after

being degassed by bubbling of nitrogen to avoid oxidation of the ethylene oxide group of surfactant. The sample containing 55 wt % of $C_{16}E_7$ was sealed in a glass vial. For homogenization we annealed the sample for 3 hours at about 55 °C and then held it at room temperature for 21 hours. This annealing procedure was repeated for one week and the homogeneity of the sample was checked by a polarizing microscope observation. The sample in the vial was stirred just before being transferred to the small angle neutron scattering (SANS) cell.

SANS measurements were performed using the SANS-U instrument of the Institute for Solid State Physics, the University of Tokyo at JRR-3M of the Japan Atomic Energy Research Institute [15]. The SANS-U is installed at the end of a cold neutron guide (C-1). For the normal time resolved SANS measurements, we used a monochromatized cold neutron beam having wavelength of 7 Å with the resolution of 10% by a neutron velocity selector. The diameter of the irradiated neutron beam is 5 mm and the scattered neutrons are detected by a two dimensional position sensitive detector having $65\times65\,\mathrm{cm}^2$ (128×128 pixels) area. The sample to detector distance was 2 m, which covers the $Q(Q=4\pi\sin\theta/\lambda)$ range from 0.02 to 0.2 $\mathrm{Å}^{-1}$. The exposure time for the time resolved measurements is 10 min.

For the small angle neutron Laue diffraction (SANLD) experiment we used a ''white'' cold neutron beam obtained without the neutron velocity selector. This white beam has Maxwell distribution with characteristic wavelength of 4 Å. The incident white beam was attenuated to about $\frac{1}{50}$ because of its very high intensity. Other experimental conditions are the same as the normal SANS experiments and the exposure time for the time resolved measurements is 30 min. The obtained two dimensional (2D) scattering patterns were corrected using background scattering from the empty cell.

The 55 wt % $C_{16}E_7$-D_2O sample had hexagonal-gyroid and gyroid-lamellar transition temperatures at 41 and 47 °C, respectively. The sample was heated from 34 °C (hexagonal phase) to 56 °C (lamellar phase) and then annealed isothermally (±0.1 °C) for 100 min. After the isothermal annealing, the sample temperature was decreased to 46 °C (gyroid phase) and then we performed *in situ* time resolved SANS and SANLD measurements keeping the temperature constant at 46 °C. We repeated a series of these experiments to check the reproducibility.

III. RESULTS AND DISCUSSIONS

In the nonionic surfactant system, the morphology transitions take place by changing temperature. The scattering pattern of the gyroid phase transformed from the lamellar phase shows surprising time dependence as shown in Fig. 1. Figure 1 shows the time resolved SANS patterns in bird's eye view expressions. For each plot, the scale of the intensity axis is fixed. In the lamellar phase, the scattering pattern shows an isotropic Debye ring indicating randomly oriented polycrystalline state [Fig. 1(a)]. The peak position, $Q_{\max}$, is 0.105 $\mathrm{Å}^{-1}$ and this peak is attributed to lamellar spacing. When we decreased temperature to 46 °C, at the lamellar-gyroid transition temperature, the diffraction pattern changed to a speckle ring as shown in Fig. 1(b). The main peak around $Q=0.1\,\mathrm{Å}^{-1}$ corresponds to the (211) plane of gyroid lattice. We verified the lamellar-gyroid transition by the observation of the higher order reflections, especially the (220) reflection characteristic for the gyroid structure using small angle x-ray scattering measurements.

The obtained speckle ring patterns indicate randomly oriented polycrystalline state of the gyroid phase containing a small number of large domains. This speckle pattern is characteristic of the gyroid phase [16]. Such cellular systems are not in equilibrium and evolve toward their equilibrium states, decreasing their excess interface energy where coarsening of the domains takes place. However, in the case of the lamellar-gyroid transition, the coarsening process does not proceed straightaway. The diffraction peaks from the gyroid domains irregularly vary their intensity with time. The strong peak in the pattern does not always mean the formation of a stable large domain. With the elapse of time, formation and disappearance of strong peaks are observed repeatably on the ring. Thus the scattering patterns do not converge to the single crystal-like pattern but fluctuate in the polycrystalline state as shown in Fig. 1. As an example, the time dependence of the diffraction peak intensity marked by an arrow in Fig. 1(d) is shown in Fig. 2. This peak increases its intensity about four times from 550 to 800 min. After 800 min the peak intensity decreases with time. Surprisingly at 1000 min the intensity again increases greatly. After that the peak intensity decreases gradually with time. Other sharp peaks on the ring show similar time dependence.

There are two candidates to explain this anomalous peak intensity behavior, i.e., the orientational fluctuation and size fluctuation of the gyroid domains. In order to elucidate the origin of the anomalous behavior, we performed time resolved SANLD measurements for the late stage of lamellar-gyroid transition. In the lamellar phase consisting of polycrystalline domains, the SANLD pattern showed only a fairly diffuse ring. When we decreased the temperature to 46 °C (gyroid phase), the Laue spots from gyroid domains appeared. Figure 3 shows time evolution of the Laue patterns in two dimensional expression. The insets in Fig. 3 show the intensity profiles along the radial principle axis. In the initial stage, the Laue spot having circular shape appears and increases its intensity with time, indicating growth of the gyroid domain. However, after a waiting time, the spot becomes elongated along the radial direction, indicating deformation of the gyroid domain. With the elapse of time, the ellipticity of the spot [defined by $R=a/b$ where a and $b(a>b)$ are radii of two principal axes of the ellipsoidal spot] is increased as shown in Fig. 4 while the peak position remains unaltered. The time dependence of the ellipticity can be expressed by $R=\exp(0.0088t)$ where t is the nucleation time of the domain. We found that during the elongation process the radius of short principal axis b remains constant, suggesting that the R value is roughly proportional to the strain of the gyroid domain. Thus increases of R correspond to the increase of the strain of the gyroid domain with time.

It is interesting to compare the time dependence of the ellipticity with the integrated intensity of the spot. In Fig. 5 we plot the integrated intensity of the Laue spot in Fig. 3 as a function of time. While the spot keeps the circular shape ($R\sim1$) up to about 100 min, the integrated intensity increases very steeply. After the spot becomes elongated, however, the growth rate of the intensity decreases by a factor of

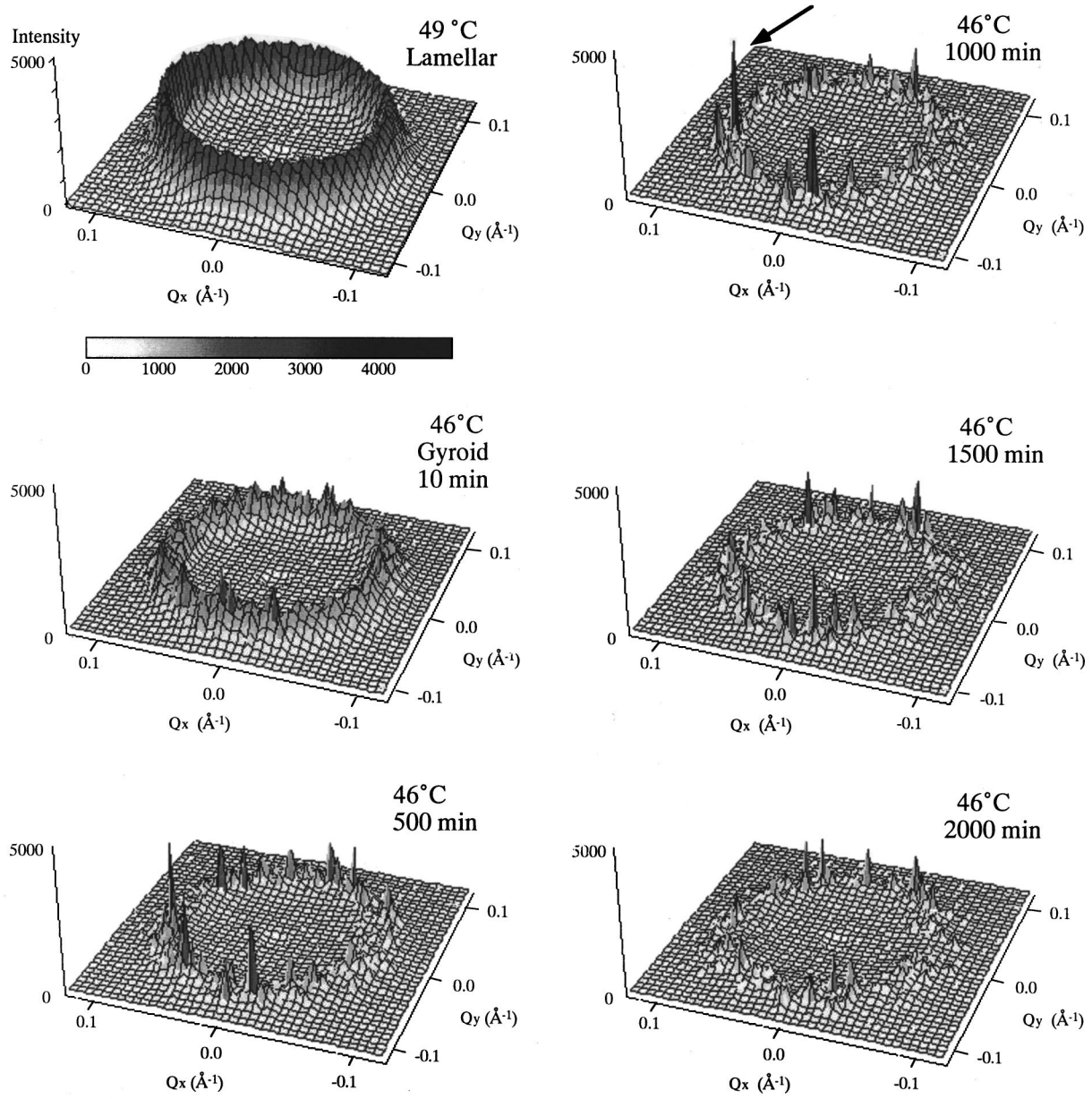

FIG. 1. Time resolved SANS patterns for cubic phase at 46 °C transformed from lamellar phase in two dimensional expression. The intensity and position of the peak marked by an arrow are plotted as a function of time in Figs. 2 and 5, respectively.

10 as shown in Fig. 5. This means that the coarsening of the gyroid domain is suppressed and that the domain begins to deform simultaneously. It is considered that the lamellar-gyroid transition proceeds by the nucleation and growth mechanism [2]. Then the gyroid domains should have the crystallographic misorientation at the domain wall. This misorientation at the boundary brings strong frustration to the gyroid lattice when the domain coarsening takes place, because at the boundary adjustment of the adjacent lattice is necessary to develop the domains. We considered that the adjustment slows down the growth of the domain and brings strong frustration to the domain, resulting in the deformation of the gyroid domain observed in SANLD measurements.

When the ellipticity reaches a critical value, i.e., about 2.5 in this case, the elongated diffraction spot splits into two peaks. This may be a result from the fact that the gyroid domain cannot withstand the bending deformation and so

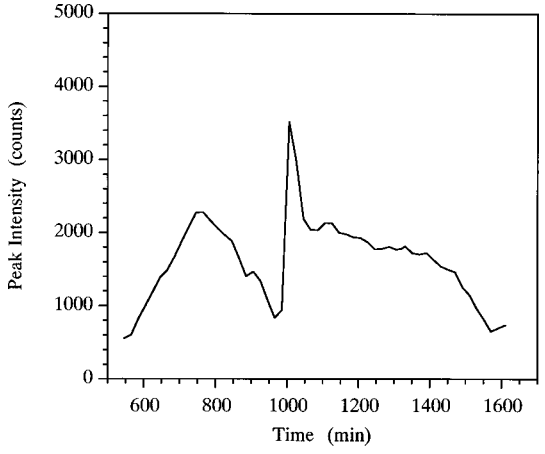

FIG. 2. Time dependence of the peak intensity marked by the arrow in Fig. 1.

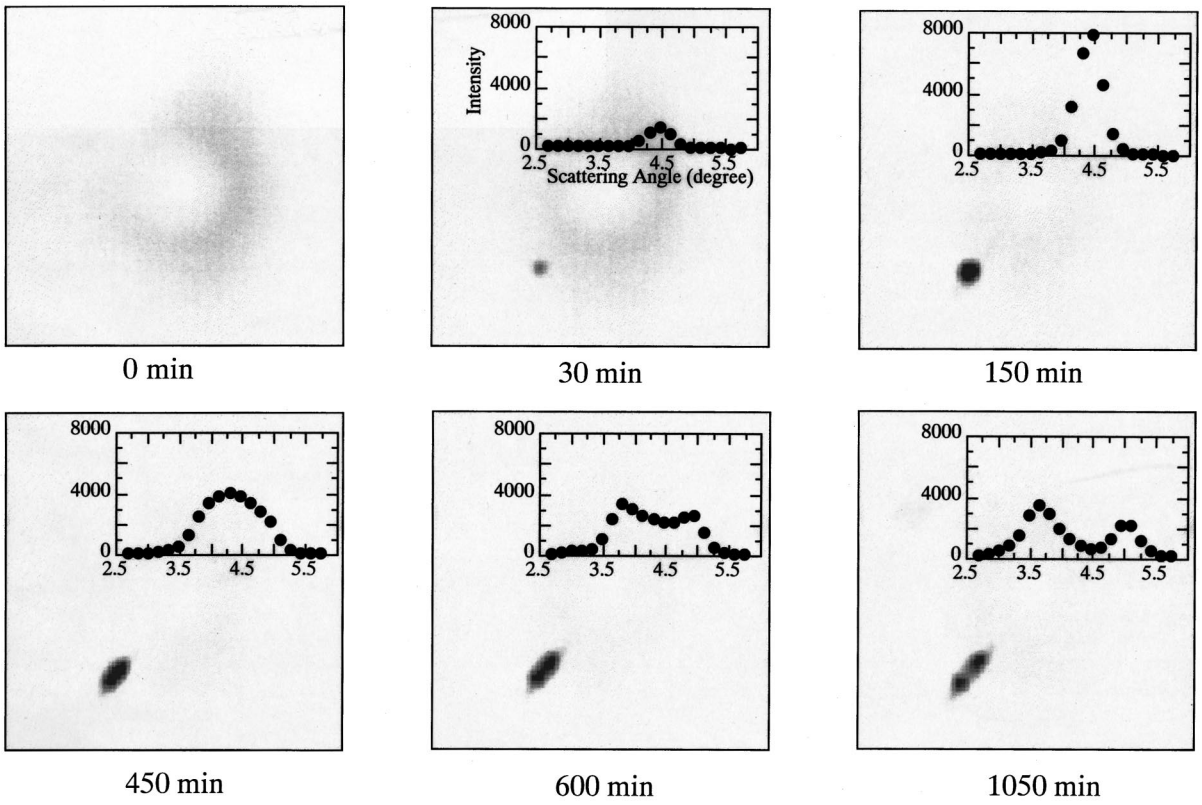

FIG. 3. Time resolved SANLD patterns for cubic phase at 46 °C transformed from lamellar phase in two dimensional expression. The insets show the intensity profiles along the radial principle axis.

splits into two domains. The positions of two separated peaks are almost symmetrical about the original peak position as shown in Fig. 4 and the spacing gradually increases with time. It should be noted that there is a scattering streak on the line between these two Bragg peaks, which indicates existence of a deformed interdomain structure. With the elapse of time, this streak decreases its intensity and finally we obtained two almost independent peaks having circular shape. This indicates formation of two independent gyroid domains. We schematically represent the model of the deformation and splitting process during the coarsening of the gyroid domain together with corresponding Laue patterns in Fig. 6. The growth of the gyroid domain is suppressed by the surrounding domains and then the elastic nature of the gyroid

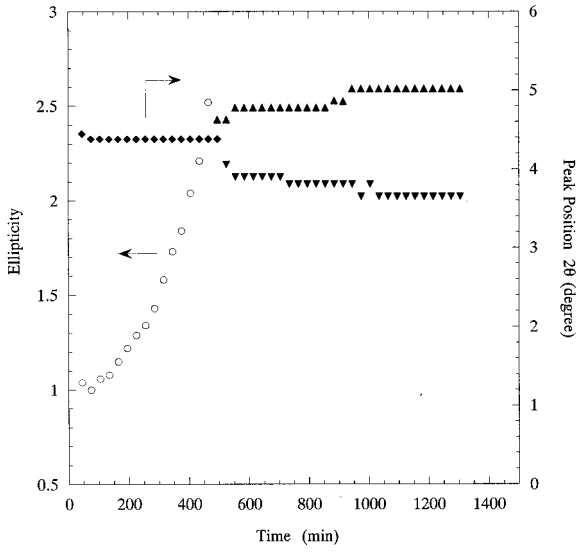

FIG. 4. Time dependence of the ellipticity and peak position of the Laue spots appearing in Fig. 3. Open circles denote the ellipticity and filled symbols (♦: before splitting and ▲, ▼: after splitting) denote the peak position.

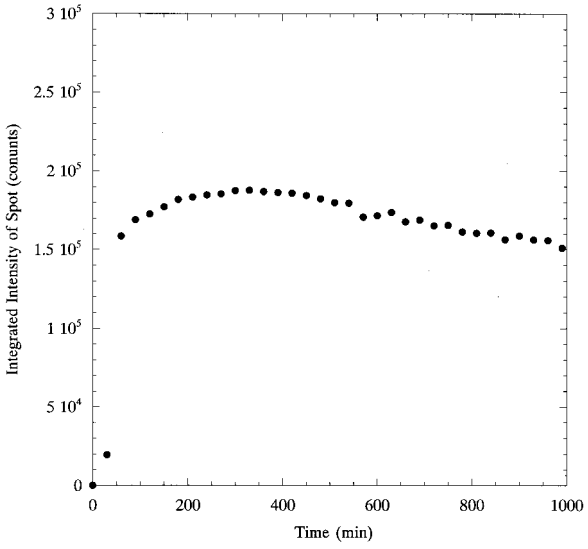

FIG. 5. Time dependence of integrated intensity of the Laue spot appearing in Fig. 3.

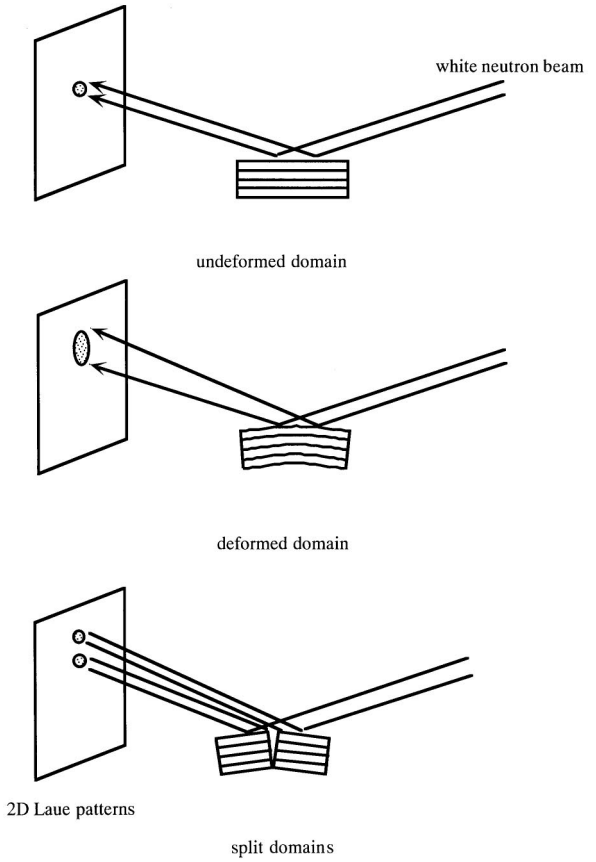

FIG. 6. Schematic representation of coarsening process of the gyroid domain with corresponding Laue patterns.

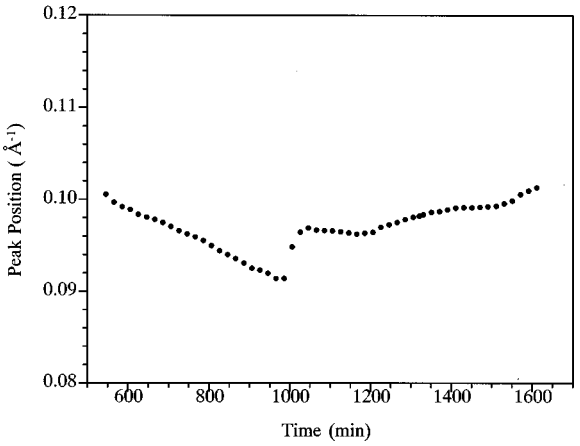

FIG. 7. Time dependence of the peak position marked by the arrow in Fig. 1.

domain brings the domain deformation. When the deformation reaches a critical value, however, the fragile nature brings splitting of the domain.

In the normal SANS measurements, we cannot observe these deformation and splitting processes of the gyroid domain because of the scattering condition expressed in Eq. (1) and the irregular time dependence of the diffraction peaks was observed. The orientational fluctuation due to the bending deformation is responsible to the observed time behavior of the SANS patterns. Here we should note the reason we observe only one spot in the SANLD patterns in spite of the fact that there should exist many gyroid domains in the irradiated volume. The Laue patterns in Fig. 3 are obtained from the polycrystalline gyroid phase. The small randomly oriented domains give high intensity background scattering and the diffraction peaks of definite number of large domains are embedded in the high background level. Thus one very large gyroid domain gives an outstanding spot in Fig. 3 although there are many domains having various sizes in the sample. In a logarithmic representation of the Laue patterns from the gyroid phase a large number of grains are visible (not shown).

We found another evidence of the deformation effects in the normal SANS profile. In Fig. 7 the position of the diffraction peak marked by an arrow in Fig. 1(d) is plotted as a function of time. From 550 to 1000 min, the peak position linearly shifts to lower Q side with time, indicating increase of the gyroid lattice spacing. The change of spacing is probably due to the deformation of the gyroid domain detected in the SANLD experiments. The reorganization of the gyroid lattice at the boundary brings strong stress to the gyroid domain. This deforms the domain and modified lattice spacing. This comes from the elastic nature of the gyroid domain composed of ''soft matter.''

At 1020 min, the peak position suddenly returns from 0.0915 to 0.098 $Å^{-1}$, corresponding to about 7% shrinkage of the lattice constant. At the same time, scattering intensity increases by a factor of about 5 (see Fig. 2). This abrupt behavior may correspond to the splitting of the gyroid domain indicated by the SANLD patterns. Thus the stored strain in the gyroid domain cannot keep the single domain and splitting into two domains occurs to release the lattice distortion. After the shrinkage, the peak position gradually shifts to high Q side. At 1600 min the peak position returns almost to the initial value, indicating the release of the strain in the gyroid domain. This behavior also corresponds to the formation of two independent circular spots shown in Fig. 3. The lattice distortion phenomena were generally observed for the sharp peaks on the Debye ring during the domain coarsening. Thus we demonstrate that the deformation and splitting of the gyroid domains take place in the coarsening process of the gyroid domain in the nonionic surfactant system and are responsible for the observed anomalous behavior in the time dependent SANS patterns.

The elasticity effects on the domain coarsening have been investigated from theoretical [17–20] and experimental [21–23] points of view. For the phase separating alloys, it is well known that the elastic field originating from the difference of the shear moduli between two phases leads to slowing down of the rate of coarsening and stop the domain growth in the extreme case. In this case the softer region wraps harder domains and then the coarsening slows down when the surface energy becomes less important in the domain growth. For the lamellar-gyroid transition of the surfactant system, the coarsening of gyroid domain is actually decelerated and is completely suppressed in the case of hexagonal-gyroid transition [5]. The mismatch of the lattice orientation at the domain boundary brings this suppression of the coarsening. It is known that the misorientation at the boundary brings so-called abnormal domain coarsening [24–26] in which a limited number of grains grow to anomalously large size and

coexisting small grains continue to grow normally until consumed by the very large domains. However, deformation and fracture of the growing domain during the abnormal coarsening have not been reported so far. Our experimental results clearly demonstrate that the anomalous coarsening of the gyroid domain coarsening is due to the elastic and fragile nature of the gyroid domain.

The most striking result is the splitting of the gyroid domain during the coarsening process. In the case of ''hard matter'' the elasticity does not bring the fracture of the domains but suppresses the domain growth [20,22]. However, in the case of the gyroid domain coarsening, the stored stress in the domain brings rearrangement of the gyroid network, resulting in the splitting of the domain because of the fragility of the surfactant network. The elasticity and fragility are a unique feature of ''soft matter'' that plays an important role in the morphology transition of the complex fluids.

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[1] Y. Rançon and J. Charvolin, J. Phys. Chem. **92**, 2646 (1988).
[2] M. Clerc, P. Laggner, A. M. Levelut, and G. Rapp, J. Phys. II **5**, 901 (1995).
[3] M. Clerc, A. M. Levelut, and J. F. Sadoc, J. Phys. II **1**, 1263 (1991).
[4] V. Luzzati, J. Phys. II **5**, 1649 (1995).
[5] M. Imai, T. Kato, and D. Schneider, J. Chem. Phys. **106**, 9362 (1997).
[6] M. Imai, T. Kato, and D. Schneider, J. Chem. Phys. **108**, 1710 (1998).
[7] D. A. Hajduk, R.-M. Ho, M. A. Hillmyer, F. S. Bates, and K. Almdal, J. Phys. Chem. B **102**, 1356 (1998).
[8] S. Sakurai, H. Umeda, C. Furukawa, H. Irie, S. Nomura, H. H. Lee, and J. K. Kim, J. Chem. Phys. **108**, 4333 (1998).
[9] S. Qi and Z.-G. Wang, Phys. Rev. E **55**, 1682 (1997).
[10] M. Laradji, A.-C. Shi, R. C. Desai, and J. Noolandi, Phys. Rev. Lett. **78**, 2577 (1997).
[11] M. W. Matsen, Phys. Rev. Lett. **80**, 4470 (1998).
[12] M. W. Matsen, J. Chem. Phys. **108**, 787 (1998).
[13] T. Okuzono and K. Kawasaki, Trends. Stat. Phys. **1**, 65 (1994).
[14] T. Kato, N. Taguchi, T. Terao, and T. Seimiya, Langmuir **11**, 4661 (1995).
[15] Y. Ito, M. Imai, and S. Takahashi, Physica B **213&214**, 889 (1995).
[16] D. A. Hajduk, H. Takenouchi, M. A. Hillmyer, F. S. Bates, M. E. Vigild, and K. Almdal, Macromolecules **31**, 3788 (1997).
[17] P. H. Leo, W. W. Mullins, R. F. Sekerka, and J. Viñals, Acta Metall. Mater. **38**, 1573 (1990).
[18] W. C. Johnson, T. A. Abinandanan, and P. W. Voorhees, Acta Metall. Mater. **38**, 1349 (1990).
[19] H. Nishimori and A. Onuki, Phys. Rev. B **42**, 980 (1990).
[20] A. Onuki and H. Nishimori, Phys. Rev. B **43**, 13 649 (1991).
[21] R. W. Carpenter, Acta Metall. **15**, 1567 (1967).
[22] T. Miyazaki and M. Doi, Mater. Sci. Eng., A **110**, 175 (1989).
[23] T. Miyazaki, M. Doi, and T. Kozakai, Solid State Phenom. **384**, 227 (1988).
[24] B. Ralph, Mater. Sci. Technol. **6**, 1139 (1990).
[25] A. D. Rollett, D. J. Srolovitz, and M. P. Anderson, Acta Metall. **37**, 1227 (1989).
[26] W. T. Read and W. Shockley, Phys. Rev. **78**, 275 (1950).