Effects of Domain Size on Viscosity of $\alpha$-Gel (\(\alpha\)-Form Hydrated Crystal) Prepared from Eco-friendly Cationic Surfactant

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Abstract: We determine the effects of the $\alpha$-gel ($\alpha$-form hydrated crystal) domain size on the viscosity of water-diluted $\alpha$-gels consisting of the N-[3-(dimethylamino)propyl]docosanamide (APA-22) L-lactic acid salt, 1-octadecanol (C\(_{18}\)OH), and water. A decrease in the C\(_{18}\)OH mole content results in increased domain size and viscosity of the water-diluted $\alpha$-gel system. Additionally, when a sample is prepared by slow cooling and/or at low stirring speed, the domain size and viscosity of the water-diluted $\alpha$-gel system increase. A similar increase in the domain size and viscosity of the $\alpha$-gel system is observed for annealed samples. The observed change in the $\alpha$-gel domain size is explained by the crystal growth theory.

Key words: $\alpha$-gel, $\alpha$-form hydrated crystal, domain, crystal growth, cationic surfactant, N-[3-(dimethylamino)propyl]docosanamide, hair conditioner

1 Introduction

Cationic surfactants are used in formulating hair conditioners. Adsorption of cationic surfactants on the hair surface leaves the hair feeling smooth\(^1\). However, cationic surfactants sometimes give a negative impression to consumers in the environmental and safety aspects. The $\alpha$-gel was found to increase with decreasing C\(_{18}\)OH mole content before dilution. Similar viscosity behavior was also confirmed at different dilutions. One of the key parameters affecting the viscosity is the balance between the amounts of water localized in different spaces\(^2\); one is the water incorporated between lamellar bilayers, and the other is the "excess" water being present between $\alpha$-gel domains. Nevertheless, the result of our previous study\(^3\) is still open for interpretation and cannot be explained by this consideration.

Herein, we put hypothesize that the dilution of the $\alpha$-gel phase changes the size and/or shape of the $\alpha$-gel domains. Yamaguchi and Noda\(^4\) reported that the shape and size of the $\alpha$-gel domains were affected by the mixing temperature of the system (made up of a mixture of octadecyltrimethylammonium chloride, 1-hexadecanol, and water). Spherical domains changed to flat lamellar domains when the mixing temperature was lower than the transition temperature (the $\alpha$-gel phase to a lamellar liquid-crystal phase transition temperature). Kawabata et al.\(^6-9\) conducted confocal laser scanning microscopy (CLSM) to confirm that the shape of the $\alpha$-gel domains depended on the length of the

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ethylene oxide unit (the nonionic polyoxyethylene-type surfactant) used in their experiments. When the length of the ethylene oxide unit was increased from 6 to 7, the morphology of the α-gel domains changed from “network” to “spherical vesicles”.

Herein, we examine the effects of the α-gel domain size and shape on the viscosity of the α-gel system. Experiments were conducted after diluting the α-gel phase with pure water. Conditioners are generally applied on wet hair, and the hair is subsequently rinsed with water. Therefore, it is important to study the dilution effects of hair conditioners on the α-gel viscosity.

2 Experimental Section

2.1 Materials

APA-22 (AMIDET® APA-22; purity before neutralization ≥ 97%) was supplied by Kao Chemicals Europe, S.L., and used as received. C18OH (KALCOL 8098; purity ≥ 98%) was obtained from Kao Corporation and used without further purification. L-lactic acid was purchased from Fujifilm Wako Chemical Corporation and used without further purification. 1,1’-Diocadecy-3,3,3’,3’-tetramethylindocarbocyanine perchlorate (DiI; purity ≥ 97%) was supplied by Sigma-Aldrich and used as received. Water used in this study was deionized using an ion exchange resin cartridge (Yamato CPC-S, 4L) and filtered through a membrane filter (pore size = 0.10 μm).

2.2 Sample preparation

2.2.1 Gel sample preparation

APA-22 and C18OH were mixed at 85°C. The mixture was then added to a water phase (temperature set at 62°C). The water phase contained equivalent amount of L-lactic acid to APA-22 (in mol) as a neutralizer. The mixture was stirred at 250 rpm for 10 min using a propeller and then cooled to room temperature while continuously stirring at 250 rpm or 50 rpm. The temperature during the cooling process was monitored (Supporting Information, Fig. S1). After degassing the mixture using a vacuum pump, the prepared gel samples were left in an incubator (set at a constant temperature of 30°C) for 2 weeks. The total concentration of APA-22 L-lactic acid and C18OH was fixed at 10 wt%, and the water concentration was set at 90 wt%. The gel samples were prepared at different mole ratios of APA-22 L-lactic acid and C18OH (APA-22 L-lactic acid: C18OH = 1:3, 1:3.5, 1:4, and 1:5).

2.2.2 Annealing

The prepared gel samples were annealed using an Espec SH-262 bench-top type temperature and humidity chamber. The temperature of each sample was decreased from 35°C to −35°C at a constant cooling rate of 0.32°C/min. The temperature was maintained at −35°C for 12 h. Following this, the temperature was increased from −35°C to 35°C at a constant heating rate of 1.1°C/min and maintained at 35°C for 6 h. The cycle was repeated 5 times.

2.2.3 Preparation of 5-fold diluted gel samples (dilution by water)

Pure water (20 g) was gradually added to each of the gel samples (5 g) with different APA-22 L-lactic acid:C18OH mole ratios while stirring (with a stirring rod). After degassing the samples using a vacuum pump, the diluted gel samples were left in an incubator (set at a constant temperature of 30°C) for 1 h.

For the particle size distribution measurement, the 5-fold diluted gel samples were further diluted by water (100-fold, in total 500-fold dilution) under slow mechanical stirring.

2.3 Characterization

CLSM was conducted using a Leica DM IRE2 microscope set at 30°C. The excitation wavelength was set at 549 nm, and the fluorescence wavelength was set at 565 nm.

The particle size distribution measurement was performed using a Horiba LA-950V2 system. The particle and dispersion medium refractive indices were set at 1.50 and 1.33, respectively.

Differential scanning calorimetry (DSC) was performed using a Hitachi DSC7000X instrument with sealed silver pans at a scan rate of 0.5°C/min and over the temperature range of 5°C–80°C. The results (shown in the “Results and Discussion” section) were obtained in the first temperature cycle.

Gel viscosity was measured using an Anton Paar MCR 301 rheometer with a CP-50 cone plate. The measurement was performed after setting each sample at 30°C. The shear rate was 0.001–1000 1/s.

Small- and wide-angle X-ray scattering (SAXS/WAXS) experiments were conducted using an Anton Paar SAXSees mc² instrument. The apparatus was operated at 40 kV and 50 mA using Cu-Kα X-rays. The X-ray irradiation time was fixed at 1 h. A blue imaging plate was used to collect the data. The raw scattering data consistently included a reduced primary intensity at scattering vector q = 0 because of the transmissive beam stop. The data were normalized to the same incident primary-beam intensity for the transmission calibration. The SAXS/WAXS measurements were carried out at 30°C. The lamellar d-spacing and intermolecular distance were calculated from the q values obtained from the SAXS/WAXS measurements (equation 1).

\[ d = 2\pi/q \] (1)
3 Results and Discussion

3.1 α-gel domain structure

Hair conditioners are usually used under 5- to 20-fold dilution by water. Herein, we report the results of the experiments conducted with 5-fold diluted samples. Figure 1 shows the CLSM images of the α-gel samples containing varying mole ratios of APA-22 L-lactic acid and C\textsubscript{18}OH. The images were recorded before (Fig. 1a) and after (Fig. 1b) the samples were diluted with water (5-fold dilution). We had previously reported that the α-gel consisting of APA-22 L-lactic acid and C\textsubscript{18}OH in the mole ratios of 1:3 to 1:5 (APA-22 L-lactic acid:C\textsubscript{18}OH) yielded two phases. One of the phases had a high amount of water incorporated between the lamellar bilayers, and the other phase contained excess water\textsuperscript{4}. DSC results did not confirm the phase separation of C\textsubscript{18}OH at these APA-22 L-lactic acid: C\textsubscript{18}OH mole ratios\textsuperscript{4}. In Fig. 1, the bright yellow parts indicate α-gel domains solubilizing the hydrophobic fluorescence dye (DiI) into their lamellar bilayers, while the dark black parts indicate the excess water present outside the α-gel domains. An individual α-gel domain structure was not clearly seen before dilution, particularly at the mole ratio = 1:3. This is reflective of the small amount of the excess water in these samples (25% or less, with respect to the total amount of water added to the samples), suggested in our previous paper\textsuperscript{4}. The presence of the dispersed α-gel domains (in the excess water phase) was confirmed after dilution by water. The domain sizes before and after dilution, at the mole ratio of 1:3, were larger than those at 1:5. The number of α-gel domain having uneven shape was larger at 1:3 (larger domain size) than at 1:5 (smaller domain size). We have discussed the effects of the domain size and shape on the viscosity of the α-gel in the subsequent parts of this manuscript.

Particle size distribution measurement confirmed the presence of different domain sizes after dilution. The 5-fold diluted α-gel samples were further diluted (under slow mechanical stirring) to produce 500-fold diluted α-gel samples, which were then used for determining the particle size distribution. We believe that the further dilution has no signifi-
and C18OH, at 85°C above their melting points, was added to aqueous L-lactic acid solution. The mixture was subsequently homogenized at 62°C. Next, the mixture was cooled to room temperature (below their melting points). These procedures can be referred to the crystal growth in the solid and the molten liquid; and Δμ denotes the interfacial free energy (γ) or the interfacial tension (ʣ). This equation predicts the growth of the α-gel system under study, i.e., the solid state was energetically more stable than the supercooled liquid state. We also observed that a decrease in the C18OH mole content resulted in a decrease in Δμ, resulting in higher Eγ. Hence, it can be inferred that crystal growth is preferred at low C18OH mole content, resulting in a larger crystallite size (domain size). The smallest Δμ at the mixing mole ratio = 1:3 further suggests the ease of the phase transition into the α-gel when compared with the samples having larger Δμ. In general, an α-gel can be prepared from mixtures of cat-ionic surfactants and long-chain alcohols at a mole ratio of 1:3 (surfactant:alcohol); in these systems, the surfactant and alcohol molecules are arranged within the lamellar bilayers without excess or deficiency of the long-chain alcohols [47]. Therefore, the appropriate amount of α-gel constituent molecules helps in achieving the lowest Δμ value (at a mole ratio of 1:3) when the degree of supercooling (ΔT = Tm − Tf) is the least. Figure 3 summarizes the relationship between the α-gel domain size (Fig. 2) and Δμ (Table 1) when the mole ratios of the constituents (APA-22 L-lactic acid:C18OH) are varied. A decreased C18OH mole content resulted in a decreased Δμ and an increased domain size (as per the crystal growth theory). Thus, the mechanism of crystal growth can explain the growth of the α-gel domains. The viscosity of the α-gel samples measured at a shear rate of 0.005 s⁻¹ after 5-fold dilution is shown in Fig. 3. We had previously reported that the viscosity of the α-gel samples after dilution decreased with increasing shear rate, indicating the shear thinning of the α-gel samples [4]. The viscosity increased when the domain size increased and the C18OH mole content decreased.

We had previously reported that an increased amount of the excess water outside the lamellar bilayers resulted in decreased viscosity [5]. In this study, however, the amount of the excess water remains almost unchanged at different mole ratios [4]. Hence, other factors should have a greater effect on the viscosity. Yamagata and Senna [13-16] reported that the α-gel morphology significantly affects the viscosity. The lamellar network structure yielded a higher viscosity than the multilamellar vesicular structure. We suggest that the larger α-gel domains give rise to higher friction in the

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**Table 1** ΔH, Tm, Tf, and Δμ values obtained from DSC measurements.

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<th>1:3.5</th>
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<td>2.3</td>
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Fig. 2 Size distribution of α-gel domains prepared at different mole ratios, measured after 500-fold dilution by water.
shear flow because of their uneven shape (Fig. 1) although dilution results in an increased domain-to-domain distance, leading to network collapse. In such cases, higher friction gives rise to higher viscosity, as observed at low C18OH mole content.

3.3 Effect of preparation method on α-gel domain size

We studied the effect of the rate of cooling and the stirring speed during the preparation of the α-gel on the α-gel domain size. As mentioned before, two cooling rates (normal and low cooling rates) and two stirring speeds (250 rpm and 50 rpm) were considered during the experiments at a given mole ratio (APA-22 L-lactic acid:C18OH = 1:4).

Figure 4 shows the size of the α-gel domains after 500-fold dilution. The low cooling rate or the low stirring speed resulted in increased domain size. Campos et al. reported that rapid crystallization yielded a large number of small crystallites of anhydrous milk fat and lard, while slow crystallization yielded a small number of large crystallites. Kaufmann et al. reported that the size of fat crystals in mixtures of milk fat and rapeseed oil increased with decreasing shear rate during the cooling process. Our results are consistent with previous reports. In other words, the low rate of cooling induces growth of the α-gel domains and slow mechanical stirring inhibits the fragmentation of the α-gel domains.

Furthermore, the viscosity of the prepared samples was measured. The flow curves for the dilute α-gel samples are shown in Fig. 5. The viscosity of the sample with a larger domain (formed by slow cooling or slow stirring) was found to be higher than that for the sample with a smaller domain. This is consistent with the result shown in Fig. 3. Thus, the α-gel samples with larger domains have higher viscosity after dilution.

3.4 Annealing effect

In general, annealing induces a transition from the metastable phase to a stable phase. For example, the binary mixture of dioctadecyldimethylammonium bromide and water showed a transition from the thermodynamically metastable gel phase to the stable core gel phase because of annealing at −20°C. We annealed the α-gel sample of APA-22 L-lactic acid:C18OH = 1:4. Figure 6 shows the SAXS and WAXS profiles of the α-gel sample before and after annealing. Repeated peaks with the q ratio of 1:2:3:4:5 were observed in the small-angle region of the annealed samples. These peaks were attributed to the lamellar structure of the α-gel. The number of repeated peaks increased after annealing. This suggests that annealing causes regular ar-
arrangement of the lamellar structure. In the wide-angle region, a sharp peak \( q \approx 15\text{–}16 \text{ nm} \) was detected both before and after sample annealing. Furthermore, no significant change was observed in the SAXS/WAXS profiles of the 5-times-annealed \( \alpha \)-gel samples (Fig. S2). In general, the \( \alpha \)-gel phase is a thermodynamically metastable state that transforms into the stable core gel phase\(^{19\text{–}22}\). However, the annealing results suggest the formation of a stable \( \alpha \)-gel in the system under study.

The \( \alpha \)-gel domain size (after dilution with water) of the annealed sample (Fig. 7) was also evaluated. Annealing resulted in an increased size of the \( \alpha \)-gel domains, suggesting the growth of the domains. This observation is consistent with the crystal growth theory. The viscosity of the annealed sample (after dilution with water) was significantly higher than that of the non-annealed sample (Fig. 8), indicating the larger domain size of the annealed sample.

### 4 Conclusion

The effects of the \( \alpha \)-gel domain size on the viscosity of the diluted \( \alpha \)-gel were studied in the system consisting of APA-22 L-lactic acid and \( \text{C}_{18}\text{OH} \). A decrease in the \( \text{C}_{18}\text{OH} \) mole content increases the domain size and viscosity of the diluted \( \alpha \)-gel system. A low rate of cooling and/or low stirring speed during the preparation of the \( \alpha \)-gel increased the domain size and viscosity of the diluted \( \alpha \)-gel system. Annealing increased the size of the \( \alpha \)-gel domains, leading to high viscosity. The observed change in the \( \alpha \)-gel domain size was rationalized by the crystal growth theory. We expect that controlling the viscosity of \( \alpha \)-gels, by adjusting the \( \alpha \)-gel domain size, will help in tuning the performance of the \( \alpha \)-gels in hair conditioners.

### Supporting Information

This material is available free of charge via the Internet at http://dx.doi.org/jos.69.10.5650/jos.ess20213

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