Micelle-Templated Mesophases of Phenol-Formaldehyde Polymer

Isamu Moriguchi,* Akemi Ozono, Kumiko Mikuriya, Yasutake Teraoka,* Shuichi Kagawa, and Masaya Kodama†
Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852-8521
†*Kyushu National Industrial Research Institute, Shuku-machi, Tosu, Saga 841-0052*

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Phenol-formaldehyde polymers and surfactant assembly was structuralized into lamella and disordered mesophases depending on the surfactant/phenol molar ratio at the synthesis.

Recently there has been intensive interest in the fabrication of nano- or meso-structured materials consisting of either organic or inorganic framework. In particular, the use of surfactant templates to control the structure of inorganic solids has proven very successful for tailor-making mesoporous materials such as MCM-41,[1] which open up new opportunities in catalysis and separation technology.[2] In case of the mesoporous silicate (MPS), a cylindrical micelle serves as a template for assembly and subsequent condensation of silicate ions to give a hexagonally arrayed surfactant/silicate composite mesophase which can be converted into MPS by a heat-treatment.[3,4]

We focused here on the control of mesophase structure of surfactant/organic polymer composite by the micelle-templated synthesis. There were some studies on the formation of ion-complexes between surfactant and ionic polymer, but the lamella phase was the predominant arrangement.[5] Although replication of zeolite using poly(acrylonitrile) and phenol-formaldehyde resin were studied to synthesize a mesophase of polymer,[6,7] there is no study on the synthesis of three-dimensional polymer-based mesophase by using micelle templates. The present study describes micelle-templated synthesis of phenol-formaldehyde (PF) polymer mesophase as the first example.

Figure 1 shows the strategy for the synthesis of mesophase of surfactant/PF polymer by taking the hexagonal arrangement as an example. PF polymer solutions were prepared by heating the mixture of phenol and 37% aqueous formaldehyde at 60-70 °C for 1 h with stirring under the presence of a small amount of HCl or NaOH as a catalyst. The molar ratio of mixture, phenol/formaldehyde/HCl (or NaOH), were 1/0.85/0.003 and 1/1.8/0.03 for HCl- and NaOH-catalyzed condensation reactions respectively. After adjusting pH of the obtained viscous polymer solutions to 11-12 by adding conc. aqueous NaOH, the solution was added dropwise into a vigorously stirred aqueous solution of cetyltrimethylammonium bromide (CTAB) with the final molar ratio of phenol/CTAB/water=1-6/1/852. The mixture was further stirred for 3 h at room temperature and the precipitates were filtered, washed with water and dried under vacuum. In the following, the complexes between CTAB and the polymers obtained via acid- and base-catalyzed condensation reactions are referred to as complex A(x) and complex B(x), respectively, where x is the molar ratio of [phenol]/[CTAB].

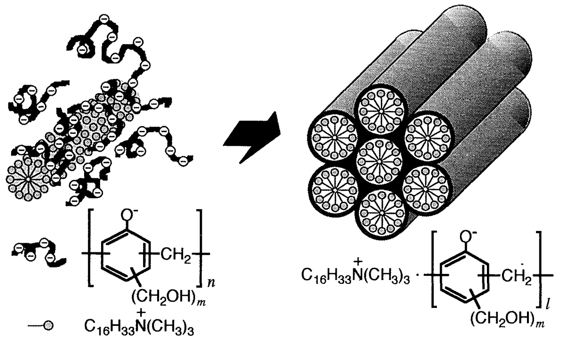

Figure 1. A strategy for the synthesis of micelle/polymer composite mesophase (hexagonal structure) by using a cylindrical micelle.

On IR measurements (Perkin Elmer 1650), all of complexes synthesized here showed CH_2 stretching bands at 2850, 2920 cm^{-1} due to a long alkyl chain of CTAB and C=C vibration bands of phenol around 1465, 1500 and 1600 cm^{-1}, indicating the formation of CTAB/PF polymer composites. The composition of complex A(3) and complex B(3) was determined by elementary analysis to be l=2.0, m=1.0[8a] and l=2.7, m=1.5[8b], respectively, if the complex was assumed to have the chemical formula shown in Figure 1. Thermogravimetric (TG) measurements (Seiko, TG-DTA 200) under a stream of N_2 gas showed that the complexes underwent thermal decomposition in two stages; the sharp weight loss at around 250 °C and gradual one above 500 °C. The weight losses at the first stage, 51% (complex A(3)) and 41% (complex B(3)), was ascribable to the elimination of cetyltrimethylammonium (CTA^+), because the observed values were in good agreement with the calculated from elementary analysis data; 48% for complex A(3) and 41% for complex B(3). The gradual weight loss above 500 °C, which was also observed with PF polymer alone, was ascribed to the carbonization of the polymer. The PF content in the complexes estimated by the TG weight losses tends to increase with increasing the [phenol]/[CTAB] ratio (x) at the synthesis.

Figure 2 shows X-ray diffraction (XRD) patterns of the complex A(x) with x=1, 1.5, 3 and 6 (Rigaku, RINT-2200 (CuKα)). As can be seen from Figure 2a, the complex A(1) showed two XRD peaks at 2θ/deg. = 3.55 (d/Å=24.8) and 6.90 (12.7), suggesting the formation of layered (lamella) phase. On transmission electron microscopy (TEM; JEOL, JEM-2010UHR) of the complex A(1), which was negatively stained by uranyl acetate to give a good contrast, a lamella phase with the periodicity of about 50 Å was observed as shown in Figure 3a. Since the molecular length of CTA^+ is 22-23 Å,[9] it is considered that the layered structure was composed of CTA^+ double layers (white layers in Figure 3a) and PF polymer layers in the CTA-hydrophilic interlayers (dark layers).[10] The two XRD peaks at d/Å=24.8 and 12.7 are reasonably assigned to 002 and 004 diffraction lines from the lamella phase.

When the x value became larger, XRD patterns were drastically changed. One broad XRD peaks centered at 2-3 deg. (34-35 Å) were observed for the complex A(1.5) (Figure 2b), and the XRD peak weakened at x=3 (Figure 2c) and almost disappeared at x=6 (Figure 2d). For MPS, the XRD pattern of MCM-41 type materials with the hexagonal arrangement of silicate/micelle complexes or mesopores is characterized by the

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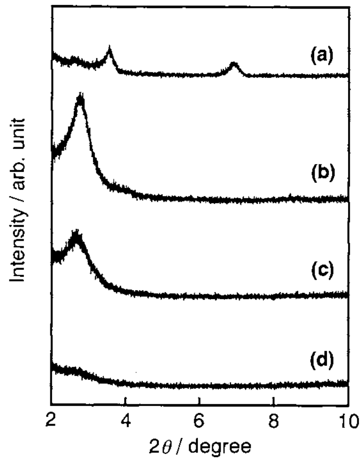

Figure 2. X-Ray diffraction patterns of complex A(x) with x=1 (a), x=1.5 (b), x=3 (c) and x=6 (d).

appearance of a sharp, strong peak at low angle (d_{100} reflection line) and three weaker peaks at higher angles (110, 200 and 210 reflection lines); the appearance of higher-order reflections depends on the degree of arrangement.[1,3] When the hexagonal arrangement is disordered or silicate/micelle complexes are irregularly merged in some extent, the so-called disordered mesophase is formed, which shows one broad XRD peak at low angle close to that of 100 reflection of the hexagonal phase.[11,12] The XRD patterns of complexes A(1.5) and A(3) resembled those of disordered MPS.[11,12] The TEM image of the complex A(3) (Figure 3b) was completely different from those of the lamella phase (Figure 3a) or the hexagonal phase reported for MPS but very similar to that of the disordered mesophase.[11] The isolated cylindrical micelles of the surfactant (white part) were observed in some parts, and the merged micelles in other places. Observed in the selected area marked with white circle was the nearly hexagonal arrangement of isolated micelles with the periodicity close to the d value from XRD (ca. 35 Å). It seems that the small size of the hexagonal domain is the reason for the appearance of broad single XRD line corresponding 100 reflection of hexagonal arrangement. The d value are actually close to those reported for CTA^+/silicate hexagonal phases. It was also found that the d value depended on the alkyl chain length of surfactants; for example, 29 Å for *n*-tetradecyltrimethylammonium bromide, 35 Å for CTAB as stated above, and 37 Å for *n*-octadecyltrimethylammonium bromide. These results strongly suggest that the disordered CTA^+/PF polymer is structuralized by the micelle-templating mechanism. The phase transition from the lamella (x=1, 1.5) to the disordered (x=3, 6) was also observed for B(x) complexes, though the critical value of the transition in the B(x) system is larger than that of the A(x). The lamella-disordered phase transition with increasing the PF content (x) might be explained by whether the amount of the polymer is sufficient for covering the micelle surface (disordered) or not (lamella).

When complexes A(3) and B(3) were heated under a stream of N_2 gas, the disordered mesostructure was kept upto 200 °C though the XRD peak intensity became weaker. The heating upto 300 °C, at which CTA^+ was eliminated, resulted in the disappearance of the XRD peak. This might indicate that micelles are necessary to keep the disordered mesophase under heating. On the other hand, the disordered mesophase was maintained in some extent even after the surfactant micelles were removed by the treatment which consisted of heating the complexes at 110 °C for 1 day and the subsequent washing with aqueous HCl solution (pH=4). This implies that there is possibility for synthesizing mesoporous PF framework if a mild condition for removing surfactant is adequately selected.

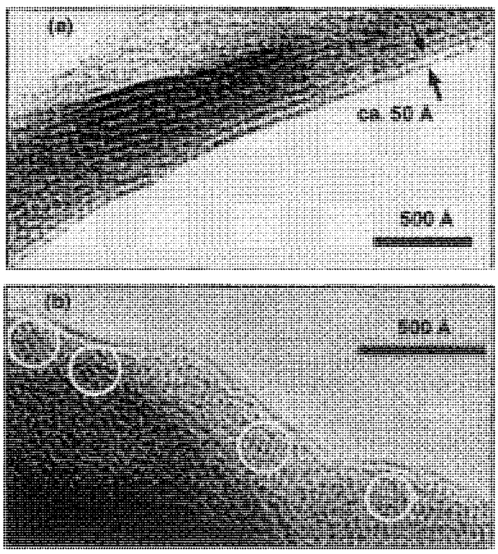

Figure 3. TEM images of complex A(x); (a) x=1, (b) x=3 .

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References and Notes

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, **359**, 710 (1992)
2 S. Biz and M. L. Occelli, *Catal. Rev., Sci. Eng.*, **40**, 329 (1998).
3 Q. Huo, D. I. Margolese, U. Ciesla, D. G. Gemuth, P. Feng, T. E. Goer, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schmth and G. D. Stuckey, *Chem. Mater.*, **6**, 1176 (1994).
4 Y. M. Setoguchi, Y. Teraoka, I. Moriguchi, S. Kagawa, N. Tomonaga, A. Yasutake and J. Izumi, *J. Porous Mater.*, **4**, 129 (1997).
5 C. K. Ober and G. Wegner, *Adv. Mater.*, **9**, 17 (1997).
6 C. G. Wu and T. Bein, *Science*, **266**, 1013 (1994).
7 S. A. Johnson, E. S. Brigham, P. J. Ollivier and T. E. Mallouk, *Chem. Mater.*, **9**, 2448 (1997).
8 a) Calcd. for l=2.0, m=1.0: C, 75.74; H 10.09; N 2.52%; (C/N=30.0). Found: C, 75.59; H, 10.09; N, 2.58%; (C/N=29.4).
9 b) Calcd. for l=2.7, m=1.5: C, 73.00; H, 9.22; N, 2.04%; (C/N=35.8). Found: C, 73.05; H, 9.79; N, 2.05%; (C/N=35.6).
10 C. Tanford, *J. Phys. Chem.*, **78**, 2469 (1974).
11 Since uranyl acetate is included preferentially in the hydrophilic region, the white and dark layers in Figure 3a correspond respectively to the hydrophobic CTA^+ double layers and hydrophilic ionic polymer layers.
12 P. T. Tanev and T. J. Pinnavaia, *Science*, **267**, 865 (1995).
13 R. Ryoo, J. M. Kim, C. H. Ko and C. H. Shin, *J. Phys. Chem.*, **100**, 17718 (1996).