Thermotropic Behavior of the Silica−Alkyltrimethylammonium Chloride Mesostructured Materials

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Received November 25, 1997. Revised Manuscript Received February 25, 1998

The characteristics of the thin films of silica−alkyltrimethylammonium chloride mesostructured materials have been investigated by means of the fluorescence of pyrene as well as the infrared spectra at variable temperatures. Pyrene molecules were incorporated in the hydrophobic part of the silica−surfactant mesostructured materials without aggregation even at a high loading amount. The temperature dependence of the luminescence of pyrene revealed that the microviscosity of the probe microenvironments decreased gradually with decreasing temperature. The infrared absorption bands of the mesostructured materials confirmed the thermotropic change in the state of the surfactant aggregates.

Introduction

The preparation of mesostructured silicates[1−4] and other metal oxides[5−12] using surfactant aggregates as structure-directing agents has attracted increasing interest for applications including catalysts[13] and hosts for inclusion compounds.[14,15] For their applications such as sensors and inclusion compounds, thin films would be an ideal morphology. Consequently, the preparation of supported and unsupported thin films of the silica−surfactant mesostructured materials has been reported so far.[16-26] Among possible approaches for the preparation of thin films, the modified sol−gel method, in which thin films are prepared by spin coating a precursor solution containing soluble silicates and quaternary ammonium surfactants on a solid substrate, is an attractive way since the transparent thin films with large areas can be conveniently obtained.[27−32]

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S0897-4756(97)00770-9 CCC: $15.00

Beside the mesoporous solids obtained after the removal of surfactants, the as-synthesized inorganic−surfactant mesostructured materials are materials to be studied since they can be regarded as a novel state of surfactant aggregates immobilized by ultrathin inorganic layers. The immobilized surfactant aggregates have been investigated in a wide range of scientifc fields including the synthesis of advanced materials.[33] Since the products have been obtained as continuous transparent films, the immobilization of organic photoactive species is a possible application. The physical state and the temperature dependence of the surfactant aggregate in the silica−surfactant mesostructured materials need to be clarified before their utilization. In this study, the thermotropic behavior of the silica−alkyltrimethylammonium chloride mesostructured materials have been investigated by means of the temperature dependences of the fluorescence spectrum of pyrene as well as the infrared spectrum.

The spectroscopic probe study has extensively been conducted in order to understand the nature of a wide variety of supramolecular systems.[34] Fluorescence of pyrene has been used as a probe for location and distribution in surfactant aggregates.[35] Relative intensity ratios of the first to the third monomer vibronic peak may reflect the polarity of the surroundings.[36] Ratios of excimer to monomer fluorescence intensities provide information on the proximity and the mobility of the probe molecules. In the preliminary communication, pyrene molecules have been successfully introduced into the thin films of the silica−hexadecyltrimethylammonium bromide mesostructured materials.[28] The location and proximity of the incorporated pyrene molecules in the composite materials have been discussed on the basis of the luminescence characteristics. Fourier transform infrared spectroscopy has previously been employed to understand the structural features of the change in the states of surfactants and lipids.[36−41]

Experimental Section

Materials. Tetramethoxysilane (abbreviated as TMOS) and alkyltrimethylammonium chlorides [$(C_nH_{2n+1})(CH_3)_3NCl$; abbreviated as C*n*TAC, where *n* denotes the carbon number in the alkyl chain] were obtained from Tokyo Kasei Industries Co. and used without further purification. Pyrene was used after recrystallization from ethanol.

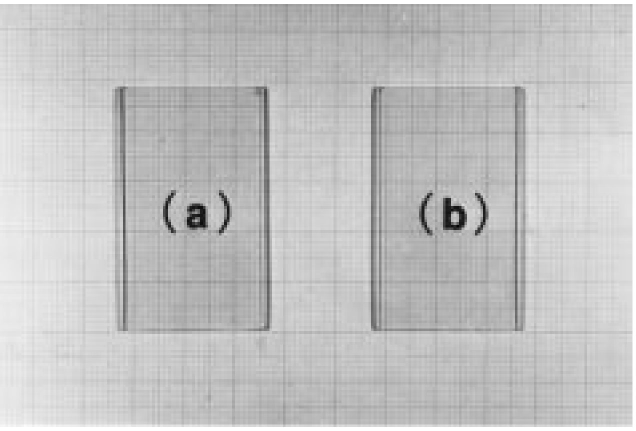

Figure 1. Photographs of the thin films of (a) the silica−C16TAC and (b) the silica−C16TAC−pyrene (the molar ratio of pyrene to C16TAC is 1/9) mesostructured materials coated on a glass substrate.

Sample Preparation. The thin films of the silica−surfactant mesostructured materials were prepared by the method described in the previous communications.[27,28] Tetramethoxysilane was partially hydrolyzed by a substoichiometric amount of water (the molar ratio of TMOS:H_2O was 1:2) under acidic conditions for 2 h at room temperature. Then an aqueous solution of hexadecyltrimethylammonium chloride (abbreviated as C16TAC; 0.50M) was added. After the mixture was stirred for a few minutes at room temperature, the homogeneous solution was spin coated on a quartz or glass substrate and dried in air. The molar ratio of TMOS:C16TAC was 4:1 in this study. For the incorporation of pyrene into the layered composites, pyrene was first solubilized into an aqueous solution of C16TAC. The molar ratios of pyrene to C16TAC varied from 1/100 to 1/9.

Characterization. X-ray diffraction was performed on a RINT 1100 diffractometer (Rigaku) using Mn-filtered Fe Kα radiation operating at 40 kV and 30 mA. The thicknesses of the films were determined with a surface profilometer (Kosaka Laboratory Co., SE 1700). Scanning electron micrographs were obtained on a Hitachi S-2840N scanning electron microscope. Luminescence spectra were recorded on a Hitachi F-4500 spectrofluorophotometer at the excitation wavelength of 340 nm. Infrared spectra of KBr disks were recorded on a Bio-Rad FTS-60 Fourier transform infrared spectrophotometer with the resolution of 2 cm^{-1}. A sample was set in a cryostat with optical windows (Oxford DN-1704), and the luminescence and the infrared spectra were recorded at constant temperatures from 80 to 320 K. After reaching each scheduled temperature, the sample was allowed to stand for several minutes prior to the measurements to establish the thermal equilibrium. To avoid the desorption of pyrene molecules from the composites at elevated temperatures, the sample temperature was kept as high as 320 K throughout this study.

Results and Discussion

As reported previously,[27,28] transparent thin films formed on the substrates by spin coating. The photographs of the films (the thicknesses of the films were ca. 0.8 mm) of the silica−C16TAC and the silica−C16TAC−pyrene composites on the glass substrates are shown in parts a and b of Figure 1, respectively. Scanning electron micrographs (not shown) revealed that the films are continuous in the millimeter length scale, and the incorporation of pyrene does not affect the surface morphology of the films.

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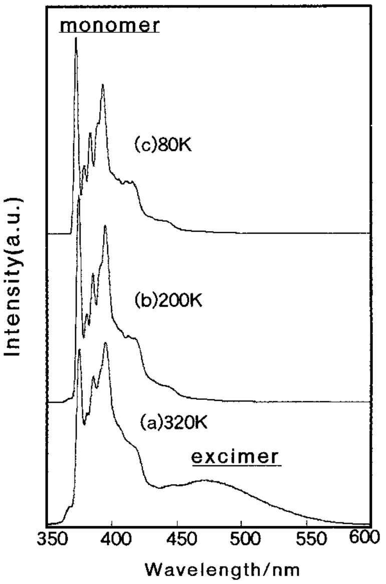

Figure 2. The emission spectra of the silica−C16TAC−pyrene (the molar ratio of pyrene to C16TAC is 1/9) composite film recorded at (a) 320, (b) 200, and (c) 80 K. Excitation wavelength was 340 nm.

The X-ray diffraction pattern of the silica−C16TAC film (the molar ratio of pyrene to C16TAC is 1/9) showed a very sharp diffraction peak with *d* spacing of ca. 3.6 nm along with a second-order reflection at ca. 6° ($d =$ 1.8 nm). A very sharp diffraction peak that shows the *d* spacing of ca. 3.7 nm was observed, and no diffraction peaks attributable to pyrene or C16TAC crystals were detected in the X-ray diffraction pattern of the silica−C16TAC−pyrene composite film. These observations indicate that the silica−C16TAC mesostructured materials containing pyrene formed on the substrates.

The films were transparent in the visible wavelength region. In the absorption spectra of the films of the silica−C16TAC−pyrene composites, the absorption bands due to $\pi-\pi^*$ transition of pyrene were observed at 340, 320, 310, 275, 265, 243, and 235 nm. The absorbance increased with the increased amount of pyrene. (The absorbances at 340 nm are 0.16 and 0.016 for the composites containing pyrene at the molar ratios of pyrene to C16TAC of 1/10 and 1/100, respectively.)

These observations are consistent with those observed for the previously reported silica−hexadecyltrimethylammonium bromide−pyrene system[29] and indicate that the added pyrene molecules have been quantitatively incorporated into the films which retain a periodic microstructure. The amounts of the added pyrene were as much as 1/9 (for pyrene/C16TAC) in this study, since the addition of larger amounts of pyrene caused the precipitation of pyrene during the reaction of a C16TAC micellar solution with the prehydrolyzed TMOS.

Figure 2a shows the fluorescence spectrum of the thin film of the silica−C16TAC−pyrene (the molar ratio of pyrene/C16TAC is 1/9) mesostructured material recorded at 320 K. When pyrene is forced into close proximity or in high concentration solution, an excited-state dimer (excimer) forms and the emission from the excimer is observed at around 475 nm in the fluorescence spectrum. The spectrum of the silica−C16TAC−pyrene (1/9) composite film showed excimer emission along with monomer emission. The excitation spectrum of the excimer emission (475 nm) was consistent with that of the monomer emission (monitored at 390 nm), suggesting that there were no significant ground-state interactions between the incorporated pyrene molecules. Although the amount of pyrene was high, the contribution of the excimer emission (at around 475 nm) was small for the present silica−C16TAC mesostructured material. Therefore, it was thought that the added pyrene molecules are solubilized molecularly in the silica−C16TAC nanocomposite and that the mobility of the pyrene molecules is restricted.

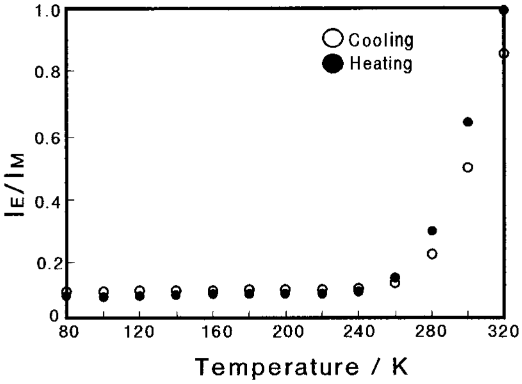

Figure 3. Temperature dependence of the relative intensity ratio of excimer to monomer emission observed for the silica−C16TAC−pyrene (the molar ratio of pyrene to C16TAC is 1/9) mesostructured material.

The fluorescence spectra of the silica−C16TAC−pyrene (the molar ratio of pyrene/C16TAC is 1/9) mesostructured material at lower temperatures (200 and 80 K) are also shown in Figure 2. (The intensity range of each spectrum was corrected for simplicity.) At lower temperatures, the intensity of excimer emission became negligible. Figure 3 shows the temperature dependence of the relative intensity ratios of excimer to monomer emission. There is a general tendency toward lower intensity ratios of excimer emission to monomer emission with decreasing temperature, indicating that the microviscosity of the probe microenvironment changed to suppress the excimer formation at lower temperatures. The excimer/monomer intensity ratio gradually decreased, indicating that the pyrene molecules were distributed homogeneously in the silica−C16TAC mesostructured materials and that the pyrene diffusion is suppressed more effectively with decreasing the temperature. The temperature dependence of the fluorescence of the embedded pyrene was thought to reflect the thermotropic change in the state of the surfactants in the silica−C16TAC mesostructured materials.

The phase transitions of lipid−water and surfactant−water systems have extensively been studied because of the chemical and biological importance.[42.43] The temperature dependence of the pyrene luminescence has been investigated for lipid−water systems.[44−47] As the temperature decreased, excimer/monomer intensities

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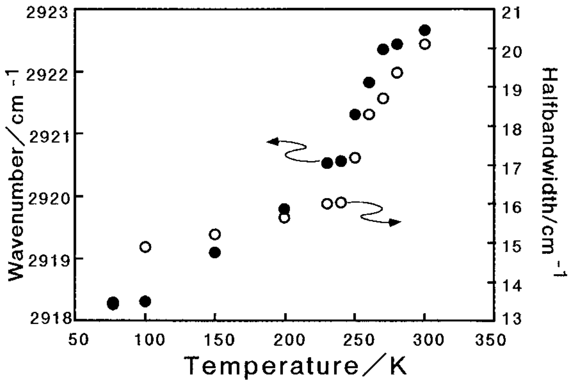

Figure 4. Temperature dependence of the wavenumber (filled circle) and half-bandwidth (open circle) of the antisymmetric CH_2 stretching band of C16TAC.

ratio decreased because the mobility of pyrene molecules in the lipid matrix was more restricted. Then a sharp increase of the excimer/monomer intensity ratio was observed when the temperature was further decreased, and this decrease was thought to indicate the phase transition temperature. Due to the lower solubility of pyrene in the crystalline lipid matrix, pyrene aggregates into small clusters embedded in the lipid matrix to give excimer emission below the crystal−liquid crystal−phase transition temperature.[44] No such discontinuity in the temperature dependence of the excimer/monomer intensity ratio was observed in the present system, indicating that the embedded pyrene molecules do not aggregate at low temperature.

To understand the thermotropic change in the states of the C16TAC aggregate in the silica−C16TAC mesostructured material, revealed by the temperature dependence of pyrene fluorescence, the infrared spectrum of the silica−C16TAC composite film was recorded at various temperatures. Fourier transform infrared spectroscopy has been used to study thermotropic phase transitions of lipid−water[37−39] and surfactant−water[40,41] systems, and information on alkyl chains has been revealed so far. The phase transition of the surfactant assemblies immobilized at solid surfaces has also been investigated by means of infrared spetroscopy.[48,49] Frequencies and bandwidths of the C−H stretching mode are often used to characterize the states of surfactants.

The infrared spectra of the silica−C16TAC composite films showed the strong bands at around 2920 and 2850 cm^{-1} , which are assigned to the antisymmetric and symmetric CH_2 stretching modes, respectively. Spectral changes with temperature are seen in this figure. The strong bands at 2923 and 2852 cm^{-1} shift to lower wavelength regions (2918 and 2849 cm^{-1}, respectively) on cooling. The wavenumber of the infrared absorption band has been determined by the center of gravity of each band. The temperature dependence of wavenumber and half-bandwidth of the symmetric CH_2 stretching band is shown in Figure 4. A similar temperature dependence has been observed for the antisymmetric CH_2 stretching band. The CH_2 stretching bands became narrower and the bands shifted to the lower frequency region with decreasing the temperature.

The change in wavenumber and bandwidth of the CH_2 stretching bands of the methylene chain is generally observed for the phase transition of amphiphilic compounds.[37−41] For alkyltrimethylammonium salts−water systems, there have been drastic changes in the plots of the temperature dependence of the frequency and the half-bandwidth, and the changes have been ascribed to the coagel−gel and gel−liquid crystalline transitions.[40,41] The increase in the wavenumber and the bandwidth of CH_2 stretching bands upon transition from a lower temperature phase to a higher temperature phase is partly due to the increase in the number of gauche conformers of methylene chains and partly due to the change in the density or packing state of methylene chains. A gradual change of frequency and half-bandwidth as a function of temperature observed in the present silica−C16TAC system indicates that no apparent phase transition occurred in the present system and that the gauche conformer increased with increasing the temperature.

The observed temperature dependence of the infrared spectrum correlates directly with the temperature dependence of excimer formation of pyrene. In a wide temperature range from 100 to 300 K, the C16TAC aggregate in the silica−C16TAC mesostructured material exhibits the change of its state from a more ordered crystalline phase to a less ordered (*liquid crystal like*) phase in which the solubilized pyrene molecules have greater mobility with increasing temperature.

Conclusion

The characteristics of the silica−alkyltrimethylammonium chloride mesostructured materials have been investigated by means of the fluorescence of pyrene as well as the infrared spectral changes at variable temperatures. The temperature dependence of the luminescence of pyrene revealed that the microviscosity of the probe microenvironments decreased gradually with decreasing temperature. The infrared absorption bands of the mesostructured materials confirmed the thermotropic change in the state of the surfactant. Since the immobilization of organic photoactive species is a possible application of the present thin films of the silica−surfactant mesostructured materials, the thermotropic behavior observed in the present study is an important characteristic of the silica−C*n*TAC mesostructured materials to control the functions and reactions of the immobilized guest species.

Acknowledgment. The authors are grateful to Dr. Hideki Kandori, Department of Biophysics, Kyoto University, for the IR measurements and valuable comments. This work was partially supported by a Grant-in-Aid for Scientific Research, from the Ministry of Education, Science, Culture and Sports of Japan. Waseda University also supported us financially as a Special Research Project.

CM970770I

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