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Preparation of Fibrous TiO_2 Material Using an Organogelator

Satoshi Kobayashi, Kenji Hanabusa,* Masahiro Suzuki, Mutsumi Kimura, and Hirofusa Shirai

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University,
Ueda, Nagano 386-8567

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A TiO_2 material with a fibrous structure was prepared using an organogelator, Z-L-Ile-$NHC_{18}H_{37}$, as a structure-forming agent for the sol-gel polymerization of titanium tetraisopropoxide, $Ti[OCH(CH_3)_2]_4$. Z-L-Ile-$NHC_{18}H_{37}$ is an excellent gelator that can harden metal alkoxide, mainly by forming intermolecular hydrogen-bonds. The gelling phenomenon is attributed to the formation of a three-dimensional network based on fibrous aggregates in organic fluids. When Z-L-Ile-$NHC_{18}H_{37}$ is used as a structure-forming agent for sol–gel polymerization, the unique structure of the fibrous TiO_2 material is created by the hydrogen-bonds between the fibrous gelator aggregates and oligomeric titanias in the sol–gel polymerization system.

Porous inorganic materials have received special attention because of their potential applications as sorption media,[1] molecular sieves,[2] and catalysts.[3] In particular, porous TiO_2 materials have great potential for possible applications to photovoltaic cells,[4] catalysts, and semiconductor devices.[5] In spite of their certainly defined utilities, the morphological control of porous inorganic materials is considerably difficult. The method most commonly used to produce inorganic materials is sol–gel polymerization through the hydrolysis and polycondensation of metal alkoxide precursors under acidic or basic conditions. Ordered arrangements of porous inorganic materials have been accomplished with the post-synthetic removal of various organic templates including surfactant self-assemblies,[7] liquid-crystalline molecules,[8] and block copolymers.[9] In such syntheses, the morphology is determined by the cooperative organization of inorganic and organic species into a three-dimensional mesostructure. Non-covalent bonds, i.e., electrostatic, hydrogen-bonding, and van der Waals interactions are used to achieve this cooperative organization.

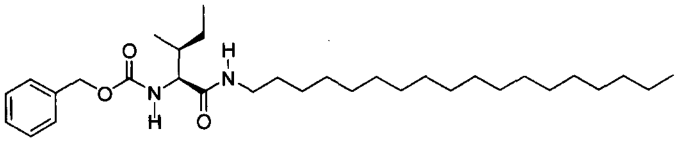
Recently, Ono and co-workers have reported on the preparation of unique porous silica with a hollow-fiber structure by using organogelators with the ionic charge density as a structure-forming agent.[10] Their study suggested that the electrostatic interaction between fibrous aggregates of the organogelator and the silica species is an important factor regarding the template effect. On the other hand, organogelators are low-molecular-weight compounds capable of gelling solvents at low concentrations.[11] This gelling phenomenon has been attributed to a three-dimensional network formed by fibrous aggregates in organic fluids. We have developed organogelators that can gelate organic fluids mainly through hydrogen-bonding interactions.[12] In particular, *N*-carbobenzyloxy-L-isoleucylaminooctadecane, which is referred to as Z-L-Ile-$NHC_{18}H_{37}$, is an excellent gelator that can harden a wide variety of organic fluids (Chart 1).[13] Since Z-L-Ile-$NHC_{18}H_{37}$ possesses amide and urethane segments, this gelator will form hydrogen-bonds with inorganic species.

We have already reported that a TiO_2 material with a fibrous structure was prepared by using Z-L-Ile-$NHC_{18}H_{37}$ as the structure-forming agent for a sol-gel polymerization of titanium tetraisopropoxide, $Ti[OCH(CH_3)_2]_4$.[14] In this paper, we report on the details of preparing TiO_2 and SiO_2 materials with a fibrous or a pleated structure using Z-L-Ile-$NHC_{18}H_{37}$.

Experimental

Gelation Test and Minimum Gel Concentration. The gelation testing procedure[13] was as follows. A weighed gelator was mixed with an organic liquid (2.0 mL) in a test tube with a screw cap (inside diameter 14 mm); the mixture was heated until the gelator dissolved. After the resulting solution was cooled to 25 °C for 2 h, the gelation was checked visually. When no fluid ran down the wall of the test tube upon inversion of the tube, we judged it to be a "gel". The minimum gel concentration (MGC), which is the minimum concentration of the gelator necessary for gelation at 25 °C, was used to evaluate the gel-forming ability.

Sol–Gel Polymerization and Calcination. The precursor



Z-L-Ile-$NHC_{18}H_{37}$

Chart 1.

solution of a typical sol–gel polymerization under an acidic condition comprised $Ti[OCH(CH_3)_2]_4$ (0.1 mL; 0.34 mmol), Z-L-Ile-$NHC_{18}H_{37}$ (17.5 mg; 0.034 mmol or 175 mg; 0.34 mmol), ethanol (1.5 mL), and 2 M HCl aqueous solution (5.0×10^{-3} mL; H_2O; 0.27 mmol, HCl; 0.01 mmol, 1 M = 1 mol dm^{-3}). First, $Ti[OCH(CH_3)_2]_4$ and Z-L-Ile-$NHC_{18}H_{37}$ were added to half of the prescribed amount of ethanol. The other half was mixed with a 2 M HCl aqueous solution as a catalyst; the mixture was added dropwise to the former solution and stirred under an ice-cooled condition. Then, the mixture was heated at 80 °C and the resultant homogeneous solution was slowly cooled to 25 °C to form a gel. The gel was dried at 25 °C for 10 d, followed by heating at 50 °C for 5 h in a vacuum to obtain a *dried gel*. The process for making a *calcined gel* involved heating at 200 °C for 2 h, following by calcination at 450 °C for 2 h to remove any organic components and to completely convert the gel into TiO_2.

Transmission Electron Microscopy and Scanning Electron Microscopy. The calcined gel was dispersed in water and a droplet of the solution was put on a carbon-coated grid (copper, 400-mesh). The solvent was evaporated in a vacuum for 3 h. Transmission electron microscopy (TEM) was performed with a JOEL JEM-2010 electron microscope.

Scanning electron microscopy (SEM) was performed with a Hitachi S-5000 field emission scanning electron microscope and a Hitachi S-2380N scanning electron microscope. The samples were dried overnight in a vacuum before the observation. The dried gels were sputtered using a gold target.

Powder X-Ray Diffraction. The crystal structures of the calcined gels were analyzed by powder X-ray diffraction (XRD) using a Rigaku Geigerflex and Cu $K\alpha$ radiation.

Results and Discussion

Gelation Ability and Minimum Gel Concentration. Table 1 summarizes the results of gelation tests for Z-L-Ile-$NHC_{18}H_{37}$. Z-L-Ile-$NHC_{18}H_{37}$ was capable of gelling alcohols and metal alkoxides at 25 °C. The amounts of Z-L-Ile-$NHC_{18}H_{37}$ necessary to solidify 1 mL of $Ti[OCH(CH_3)_2]_4$, $Ti(OCH_2CH_3)_4$, $Ti[O(CH_2)_3CH_3]_4$, $Ti[OCH(CH_2CH_3)(CH_2)_4CH_3]_4$, $Si(OCH_2CH_3)_4$, $Si[O(CH_2)_2CH_3]_4$, and $Si[O(CH_2)_3CH_3]_4$ were 6, 4, 3, 3, 7, 7, and 6 mg, respectively. We are convinced that Z-L-Ile-$NHC_{18}H_{37}$ is an excellent gelator for metal alkoxides. Furthermore, Z-L-Ile-$NHC_{18}H_{37}$ can gelate the solutions for the sol–gel polymerization of $Ti[OCH(CH_3)_2]_4$. All gels exhibited a thermally reversible sol-to-gel phase transition. Considering the thermoreversible gelation behavior of Z-L-Ile-$NHC_{18}H_{37}$ in solutions of the sol–gel polymerization, we believe that Z-L-Ile-$NHC_{18}H_{37}$ is likely to form a three-dimensional fibrous network, which is stabilized by the intermolecular hydrogen-bonding of the amide and urethane groups in the solutions.

Observation of TEM and SEM. Figure 1 shows an SEM image of dried gel prepared with Z-L-Ile-$NHC_{18}H_{37}$ ([Ti] : [gelator] = 1 : 1), where [Ti] and [gelator] are the concentrations of $Ti[OCH(CH_3)_2]_4$ and Z-L-Ile-$NHC_{18}H_{37}$ in the solution for the sol–gel polymerization. The well-grown fibrous aggregates, whose diameters are 300—1500 nm, form a three-dimensional network structure. The dried gel aggregates are formed by gelator-fibers surrounded by TiO_2 components.

FT-IR spectra confirmed that all organic components could be thoroughly removed from the calcined gels.

Figure 2 shows an SEM image of the calcined gel prepared without the gelator. The calcined gel of the ordinary sol–gel polymerization of a $Ti[OCH(CH_3)_2]_4$ solution without the gelator exhibits a smooth surface (Fig. 2). On the other hand, the calcined gel, prepared by sol–gel polymerization with the addition of Z-L-Ile-$NHC_{18}H_{37}$ ([Ti] : [gelator] = 1 : 0.1), possesses a surface with a pleated structure (Fig. 3). The diameters of the pleats are 300—1200 nm. Furthermore, the calcined gel prepared in the presence of a large amount of the gelator ([Ti] : [gelator] = 1 : 1) reveals a gathering of fibrous structures (Fig. 4), and the well-grown titania fibers form a

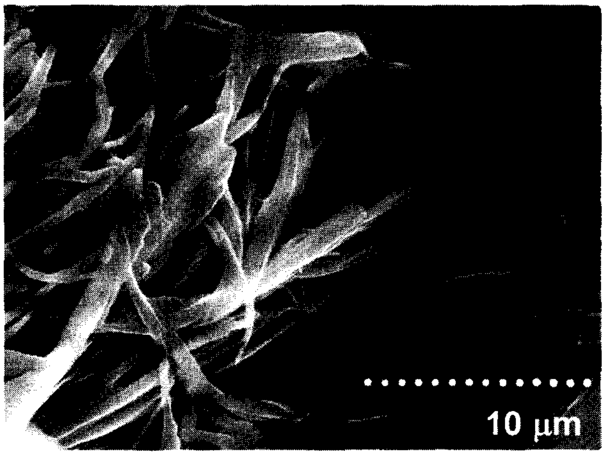


Fig. 1. SEM image of the dried gel prepared with the gelator ([Ti] : [gelator] = 1 : 1).

Table 1. Gelation Test of Z-L-Ile-$NHC_{18}H_{37}$ and Minimum Gel Concentration [in g dm^{-3} (gelator/organic fluid)] Necessary for Gelation at 25 °C[13]

Organic fluid	MGC	Organic fluid	MGC
Methanol	19	1-Decanol	22
Ethanol	20	Benzyl alcohol	20
1-Propanol	20	$Ti(OCH_2CH_3)_4$	4
2-Propanol	10	$Ti[O(CH_2)_3CH_3]_4$	3
1-Butanol	19	$Ti[OCH(CH_3)_2]_4$	6
2-Methyl-1-propanol	22	$Ti[OCH(CH_2CH_3)(CH_2)_4CH_3]_4$	3
1-Pentanol	17	$Si(OCH_2CH_3)_4$	7
1-Hexanol	20	$Si(OCH_2CH_2CH_3)_4$	7
1-Octanol	24	$Si(OCH_2CH_2CH_2CH_3)_4$	6

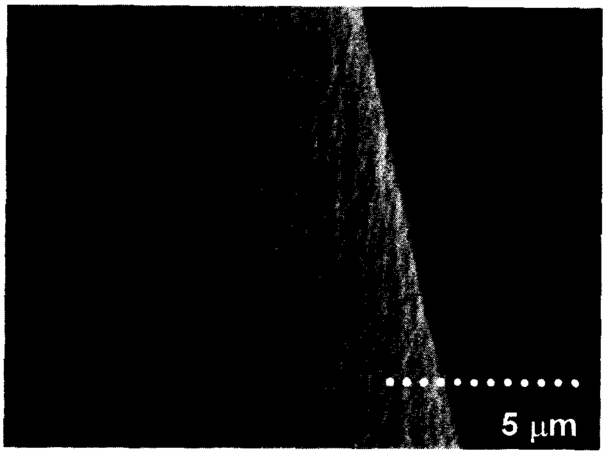


Fig. 2. SEM image of the calcined gel prepared without the gelator ([Ti] : [gelator] = 1 : 0).

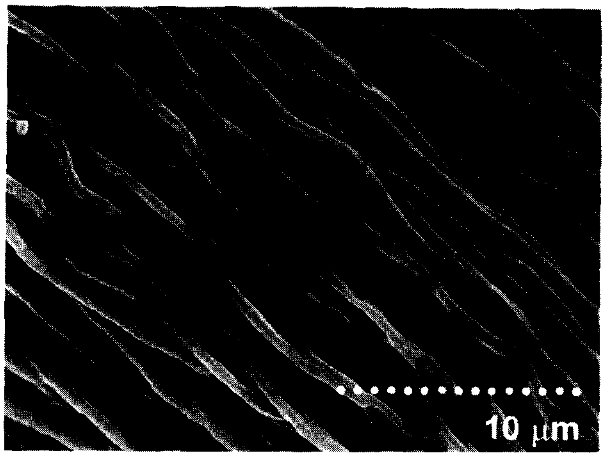


Fig. 3. SEM image of the calcined gel prepared with the gelator ([Ti] : [gelator] = 1 : 0.1).

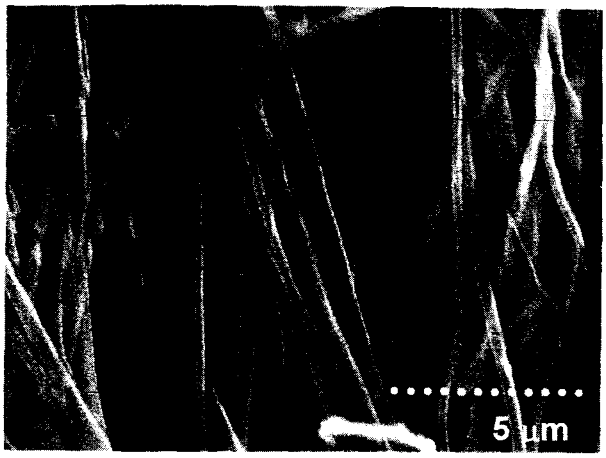


Fig. 4. SEM image of the calcined gel prepared with the gelator ([Ti] : [gelator] = 1 : 1).

steric and deep network structure. Since the diameter of the titania fiber of the calcined gel is 200—1200 nm, a slight shrinkage of fibrous aggregates seems to occur during the preparation of the calcined sample during the heat treatment.

The TEM photographs, which can reflect the small-scale structure of the TiO_2 fiber when compared with the SEM photographs, of the calcined gel show several filaments whose diameters are 15—400 nm (Fig. 5). These filaments consist of TiO_2 particles of 15—30 nm. We presume that the aggregates are formed by intermolecular hydrogen-bonds from numerous gelator molecules; Thus, they are juxtaposed and interlocked to form wide aggregates, and the oligomeric titania species are adsorbed onto these several wide aggregates through hydrogen-bonding interactions between the titanias and amide units of the gelator.

Figure 6 shows an SEM image of the silicate dried gel prepared by sol–gel polymerization using $Si(OCH_2CH_3)_4$ and Z-L-Ile-$NHC_{18}H_{37}$ ([Si] : [gelator] = 1 : 0.1). The silicate dried gel had a surface with a pleated structure similar to the pleated one of the titania sol–gel system (Fig. 3). The diameters of the pleats are 500—2000 nm. The unique morphology of the silicate sample was also created by using the gelator aggregates as a structure-forming agent. However, the structure possibly constructed by the gelator aggregates was not found inside a dried gel. The unique structure inside dried gels may be lost due to shrinkage caused by the polycondensation and the drying processes.

Powder X-Ray Diffraction (XRD). Figure 7 shows the

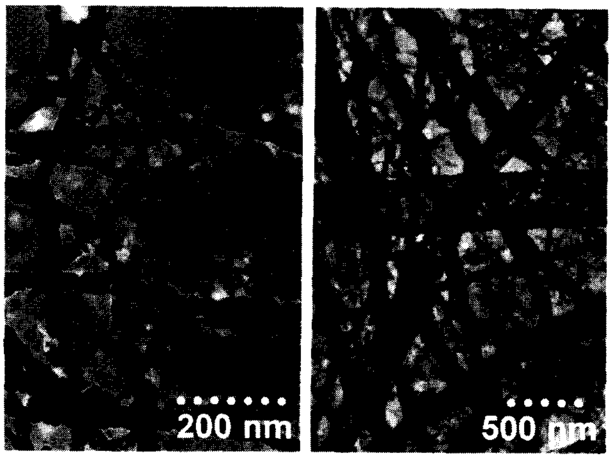


Fig. 5. TEM images of the calcined TiO_2 fiber prepared with the gelator ([Ti] : [gelator] = 1 : 1).

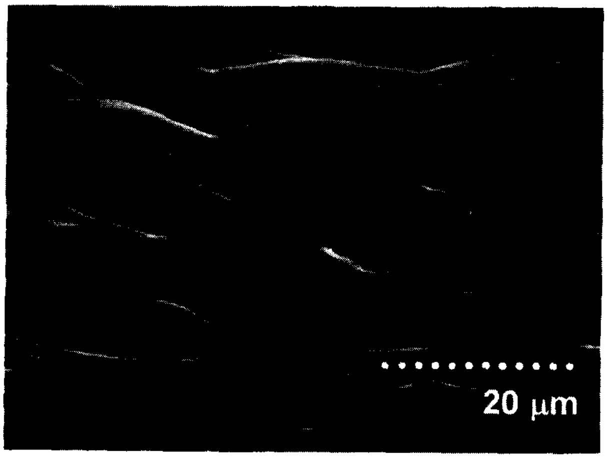


Fig. 6. SEM image of the silicate dried gel prepared with the gelator ([Si] : [gelator] = 1 : 0.1).

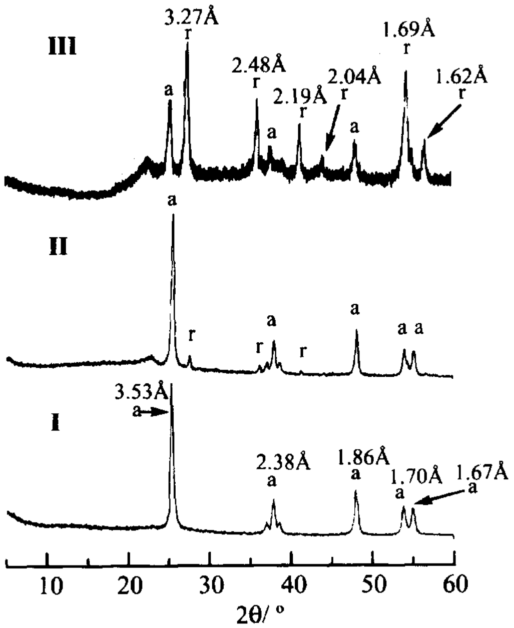


Fig. 7. Powder X-ray diffraction patterns of calcined gels at 450 °C for 2 h without Z-L-Ile-$NHC_{18}H_{37}$ (I) and with the gelator (II), (III) ([Ti] : [gelaror] = 1 : 0.1, 1 : 1, respectively). a: anatase type, r: rutile type.

XRD patterns for the crystal structures of the TiO_2 calcined gels. The calcined gel without the gelator has crystallized into an anatase crystal structure, while the calcined TiO_2 in the presence of the gelator consists of the anatase and rutile ones. It should be noted that the rulite component of the calcined gel increases with the concentration of the gelator. Obviously, the rutile TiO_2 was formed with the help of the Z-L-Ile-$NHC_{18}H_{37}$ molecules, suggesting that there are interactions between the titania molecules and the gelator molecules. The reason why the rutile structure was formed in the presence of Z-L-Ile-$NHC_{18}H_{37}$ is unclear at this time.

Since Z-L-Ile-$NHC_{18}H_{37}$ has no charge, it is unlikely that titania ion species are adsorbed onto the gelator fibers by electrostatic interactions during the sol–gel polymerization. However, the formation of the titania fiber and the presence of the rutile crystal structure indicate that there are interactions of gelator fibers and oligomeric titanias. It is thought that the oligomeric titanias were gathered around the frameworks of the gelator aggregates in a similar fashion to the hydrogen-bonding interaction between amino acid derivatives and titania.[15]

Conclusion

The organogelator Z-L-Ile-$NHC_{18}H_{37}$ gelled a variety of alcohols, titanium alkoxides, and silane alkoxides.

SEM and TEM observations of the calcined gel of $Ti[OCH(CH_3)_2]_4$ or $Si(OCH_2CH_3)_4$ with Z-L-Ile-$NHC_{18}H_{37}$ revealed that the sol–gel polymerization of the metal alkoxide using the gelator affords a well-grown fibrous structure of TiO_2 or a pleated structure of SiO_2. The calcined TiO_2 gels in the presence of the gelator consist of the anatase and rutile crystal structures. The rutile TiO_2 was formed with the help of Z-L-Ile-$NHC_{18}H_{37}$ molecules, suggesting that an interaction between the titania molecules and the gelator molecules occurs. The unique structure of the fibrous TiO_2 material may be created by the hydrogen-bonding interactions of the fibrous gelator aggregates and the oligomeric titanias.

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