Gelation of Ionic Liquids with a Low Molecular-Weight Gelator Showing T_{gel} above 100 °C

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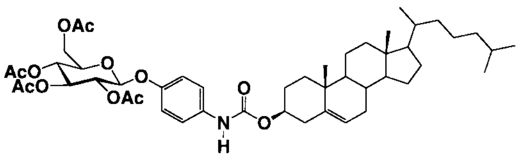
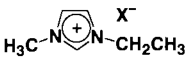
In an attempt to obtain solidified ionic liquids a cholesterol-based gelator has been applied to gelation of these liquids. By addition of a small amount of low molecular-weight gelator **1**, ionic liquids such as *N*,*N*'-dialkyl-substituted imidazolium ions and *N*-alkyl pyridinium ions are easily gelated to give the sufficiently thermostable physical gels.

Recently ionic liquids have attracted much attention through technological applications as electrolytes in batteries, photoelectrochemical cells, and other wet electrochemical devices.[1–3] In particular, ionic liquid systems based on *N*,*N*'-dialkyl-substituted imidazolium ions and *N*-alkyl pyridinium ions have realized unique properties such as high stability, high ionic conductivity, and negligible volatility.[4,5] There remains one important problem that is a control of the fluidity of ionic liquids for development of wet devices. One potential approach is to use a sol–gel system. To the best of our knowledge, however, there are only a few attempts to develop new gelators of ionic liquids.[5–7] Furthermore, most of the studies have been limited to chemical gels.[5] It thus occurred to us that low molecular-weight gelaters[8,9] would act as an alternative system to offer the physical gels of ionic liquids. It is known that compound **1** can form a gel in some organic solvents.[9] The primary driving force for aggregation of **1** is provided by one-dimensional stacking of the cholesterol moieties. This finding suggests that if **1** is dissolved in ionic liquids, **1** forms a network structure consisting of its one-dimensional aggregates and eventually can act as a gelator of ionic liquids.

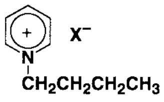
The preparation of gels is as follows. Since compound **1** with 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl group was insoluble in all ionic liquids **2**–**4** below 100 °C,[10] acetone solution of **1** was added to ionic liquids. Acetone was evaporated under reduced pressure (ca. 10^{-4} torr) for 12 h and the ionic liquids gelled after evaporating acetone from the sols. The acetone content of the gels was experimentally determinable to be < 0.5 mol% by the peak intensities in the NMR spectra of **1**/**2**–**4** systems in $CDCl_3$. Ionic liquid **2** formed a turbid gel, and **3** and **4** formed transparent gels at galator concentrations above [**1**] = 0.4, 0.2, and 0.1 wt%, respectively.



1



2: X⁻ = OTf⁻



3: X⁻ = OTf⁻
4: X⁻ = BF₄⁻

We thus examined the influence of the gelator concentration on the sol–gel phase transition temperature (T_{gel}). The results are shown in Figure 1 as plots of T_{gel} vs **1** concentration. The phase above each curve is the sol whereas the phase below each curve is the gel. In general, the T_{gel} values rose with increasing **1** concentration and reached almost the same level at high **1** concentration. It is clearly shown that at [**1**] > 0.4 wt%, the gels have high thermostability showing T_{gel} > 100 °C, which is sufficiently applicable as "ionic solid" to the field of material chemistry. On the other hand, at [**1**] < 0.4 wt%, T_{gel} is correlated with **1** concentration, i.e., the phase transition could be reversibly controlled by temperature.[9]

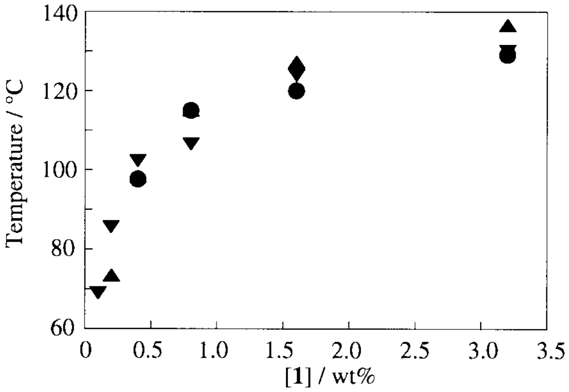


Figure 1. Plots of T_{gel} vs [**1**]: **2** (●), **3** (▲), and **4** (▼).

To obtain visual insights into the gel structures, we carried out observations with transmission electron microscopy (TEM). The sample was obtained by washing with water to remove ionic liquids and then by staining with phosphotungstic acid (5%). The typical pictures are shown in Figure 2. It is clearly seen from Figure 2a that in **1**/**2** system, the gelator forms warped fibers with 40–80 nm diameters. On the other hands, Figures 2b and 2c show that both **1**/**3** and **1**/**4** systems give twisted fibers of ca. 30 nm diameter: the fibers of **1**/**3** system consist of bundles whereas those of **1**/**4** system consist of helical tapes. The fibers in **1**/**2** system are somewhat bigger than those in **1**/**3** system or **1**/**4** system. These results are consistent with the findings that **1**/**2** system formed a turbid gel, whereas **1**/**3** and **1**/**4** systems formed transparent gels.

To obtain more direct visual insights into the aggregation mode in gels, we prepared wet samples for dark-field micrograph

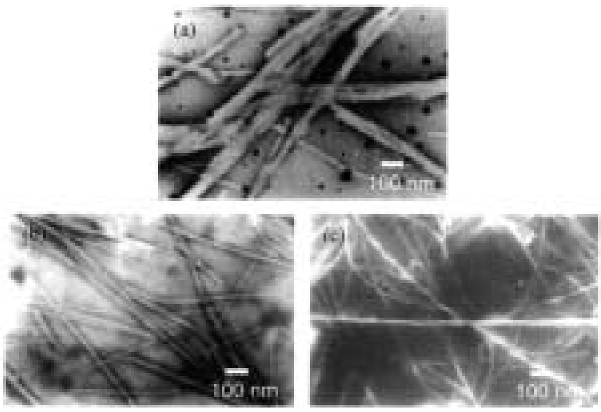


Figure 2. TEM images of (a) **1/2** system, (b) **1/3** system, and (c) **1/4** system: [**1**] = 0.4 wt%.

observation. Following a standard treatment procedure, we spread one drop of a **1** (0.8 wt%) and ionic liquid mixture on a cover glass. The drop was sandwiched with another cover glass. In the sample thus obtained (Figure 3a), the well-grown fibrous structures were abundantly observed for **1**/**2** system. On the other hand, the fibrous structures were scarcely observed for **1**/**3** system (Figure 3b). One can regard that the fiber size of **1** in **1**/**3** system is too small to detect with the dark-field micrograph method. These results are also consistent with those of TEM pictures.

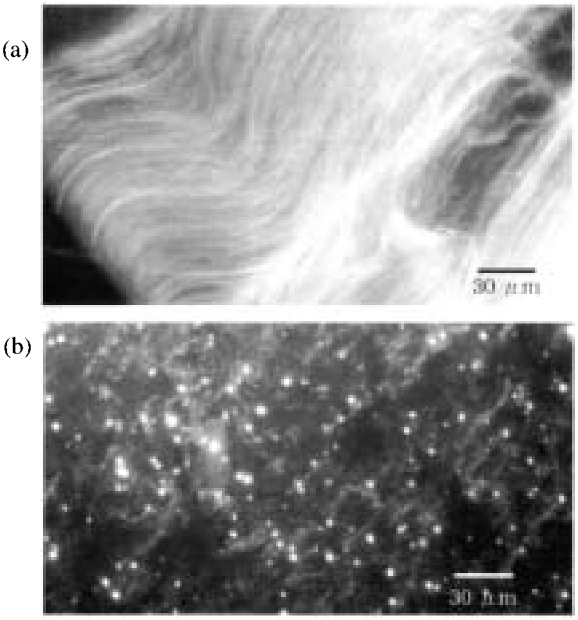


Figure 3. Dark-field micrographs of (a) **1/2** system and (b) **1/3** system : [**1**] = 0.8 wt%.

In conclusion, the present study demonstrated that the ionic liquid gels are easily prepared by addition of **1**. At [**1**] > 0.4 wt%, the gels have sufficient thermostability, whereas at [**1**] < 0.4 wt% the sol–gel phase transition can be reversibly controlled by temperature. Since the sol–gel phase transition phenomena in the low molecular-weight gelators are easily contlloed by temperature and concentration, further applications of these systems as electrolytes in photocurrent generators and photochemical reactions, etc. can become feasible targets.

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10 Over 100 °C, the ionic liquids slowly changed from colorless to brown color because of Hofmann degradation.