

Self-assembled *N*-Alkylimidazolium Perfluorooctanesulfonates

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(Received November 17, 2004; CL-041386)

Thermostability of a smectic A phase composed of *N*-alkylimidazolium heptadecafluorooctanesulfonate was improved by the formation of nonpolar layer composed of mixed perfluoroalkyl and aliphatic chains.

N,N'-Dialkylimidazolium salts composed of charge-delocalized anions are well known as room temperature ionic liquids.¹ They have been investigated in various research fields^{2,3} because of their attractive properties such as high ionic conductivity, non-volatility, and non-flammability. In order to obtain excellent ionic liquids showing low viscosity and low melting point, fluorinated anion such as TFSI⁻, PF₆⁻, CF₃SO₃⁻, and BF₄⁻ are often employed.² Generally, ionic liquids composed of trifluoromethanesulfonate anions shows lower melting point and viscosity than those composed of methanesulfonate anions.⁴ Such fluorinated anions show weaker Coulombic interaction with cations because of electron-withdrawing property to delocalize the anionic charge.

It is known that a number of amphiphilic imidazolium salts form thermotropic liquid-crystalline phase with nano-order phase separation of nonpolar aliphatic or perfluoroalkyl chain and polar ionic groups.⁵ In our previous study, we have investigated specific ion conductive behavior of monodomain orientated liquid-crystalline imidazolium salts.⁶ In order to attain both high ionic conductivity in these aggregated ionic domain and stabilized liquid-crystalline phases, it should be effective to introduce perfluoroalkyl chain toward anion. Furthermore, there has been no study on self-assembled structure of amphiphilic imidazolium salts having long perfluoroalkyl and aliphatic chain so far. Here we report the effect of aliphatic chain length of neutralized imidazolium salts prepared from heptadecafluorooctanesulfonic acid and *N*-alkylimidazole (Figure 1; **a-n**.) on the phase transition behavior, self-assembled structure, and ionic conductivity.

Salts **a-n** were prepared by neutralization of *N*-alkylimidazole⁷ with heptadecafluorooctanesulfonic acid in ethanol at room temperature. The mixture was stirred for 12 h, then the solvent was removed in vacuo. The obtained white powder was purified by recrystallization from chloroform or chloroform/diethyl ether depending alkyl chain length. The product was collected by filtration and dried in vacuo at 45 °C for 4 days. The structure of the samples was confirmed by ¹H NMR and elemental analysis. Phase transition behavior was characterized by DSC meas-

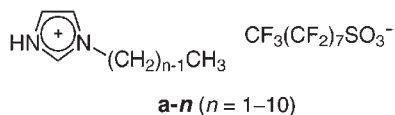


Figure 1. *N*-alkylimidazolium heptadecafluorooctanesulfonate.

urement and polarized optical microscopic observation. X-ray diffraction measurement was carried out at the temperature 10 °C lower than clearing point. Dynamic ionic conductivity in parallel direction of ionic layer was carried out by complex impedance method over frequency range from 10 to 5×10^6 Hz, using comb-shaped gold electrode cell system.⁶ Cell constants of these cells were calibrated by 0.01 M KCl solution before using.

All of **a-n** showed an enantiotropic smectic A (*S_A*) phase. The *S_A* phase for **a-1** was seen in wider temperature range than that for *N*-methyl-*N'*-alkylimidazolium trifluoromethanesulfonate.⁸ Figure 2 shows a phase diagram as a function of aliphatic chain length of **a-n** on heating.⁹ When carbon number was fewer than 3, melting points and clearing points fell with increasing the aliphatic chain length. Short aliphatic chains on imidazolium cation decreased molecular symmetry and disturbed the molecular packing. On the other hand, when $n \geq 3$, clearing points was raised with increasing the aliphatic chain length. Because perfluoroalkane is immiscible with hydrocarbons, the increase of thermostability of the *S_A* phase composed of **a-n** is attributed to enhancement of molecular orientation which is based on the formation of aliphatic chain layer phase-separated each from ionic and perfluoroalkyl chain layer.

The smectic layer spacing of **a-2** was determined from diffraction peak in the smallest-angle. Layer spacing of **a-2** was 23.2 Å. This spacing is approximately twice the length of the fully extended anion (12 Å). In the case of **a-n** having short aliphatic chain, their layer spacing suggested that perfluoroalkyl chains form bilayer structure.

Effect of aliphatic chain length on smectic layer spacing was

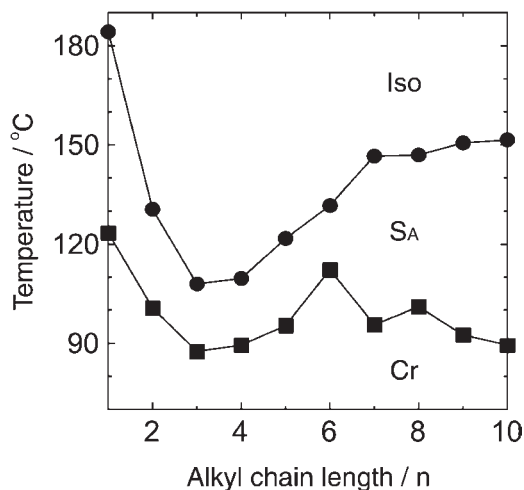


Figure 2. Phase diagram of **a-n** as a function of alkyl chain length of imidazolium cation. Iso = Isotropic liquid, *S_A* = smectic A phase, Cr = crystal.

investigated. It is expected that smectic layer spacing would increase with increasing chain length, when phase-separated structure is composed of three components of ionic groups, perfluoroalkyl, and aliphatic chains (**a-n** ($n \geq 4$)). X-ray diffraction peaks of **a-2**, **a-4**, **a-6**, and **a-8** were observed at almost the same angle. Layer spacing of **a-4**, **a-6**, and **a-8** were 23.0, 23.0, and 24.5 Å respectively. It was thus clarified that aliphatic chain length did not largely affect the layer spacing of **a-n** when $n \leq 8$. From this result and Figure 2, it is considered that enhancement of thermostability with increasing aliphatic chain length of **a-n** ($n \geq 3$) is attributable to the formation of nonpolar layer structure composed of perfluoroalkyl and aliphatic chains in the same plane. It has already been reported that steric effect also allows formation of mixed layer composed of fluoroalkyl and aliphatic chains.¹⁰ In the present study, strong electrostatic interaction should be the major force to form the mixed layer in the case of **a-n** ($n \geq 4$).

In the ¹H NMR spectra, peak due to long aliphatic chain was observed around $\delta = 1.3$ as multiplet. Intensity of this multiplet peak increased with increasing the chain length. In the case of **a-n**, this multiplet was observed when $n \geq 4$. This result indicates that aliphatic chain on imidazolium ring longer than *n*-butyl acts to prepare nonpolar moiety. These aliphatic chains would be phase-separated from ionic layer and prefer nonpolar layer.

Temperature dependence of ionic conductivity for **a-2** is shown in Figure 3 (○). Activation energy in crystalline phase was high, while low activation energy was observed in the S_A phase. In particular, ionic conductivity decreased after phase transition from a S_A phase to an isotropic phase. The decrease of ionic conductivity might be due to lower ionic density in an isotropic phase than is in aggregated ionic layer formed in the S_A phase. This suggests that successive ionic layers act as ion conductive pathway. Ionic conductivity of **a-4**, **a-6**, **a-8**, and **a-10** is also shown in Figure 3. Ionic conductivity decreased with

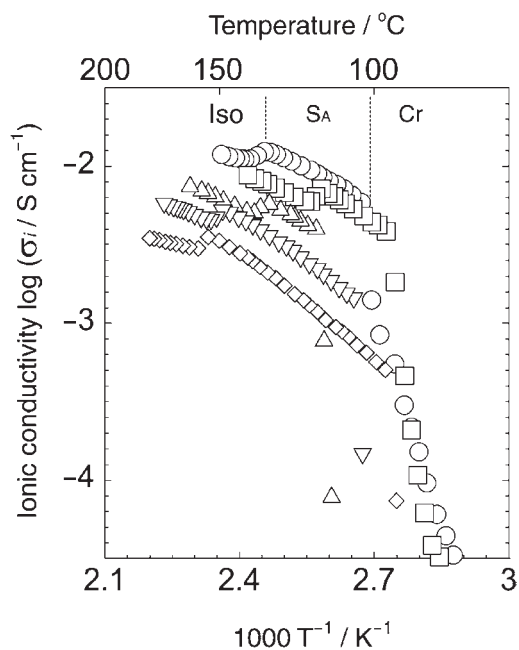


Figure 3. Temperature dependence of ionic conductivity of a series of **a-n** at heating process. ○: **a-2**, □: **a-4**, △: **a-6**, ▽: **a-8**, ◇: **a-10**.

increasing aliphatic chain length. Similar to **a-2**, discontinuous points of ionic conductivity for **a-4**, **a-6**, **a-8**, and **a-10** agreed with their melting point and clearing point.

N-Alkylimidazolium heptadecafluorooctanesulfonate shows the enantiotropic smectic A phase. Ionic conduction in ionic layer is faster than was observed in an isotropic phase. From thermodynamic and X-ray diffraction study, it was clarified that high thermostability of the smectic A phase was attained by the formation of nonpolar layer composed of perfluoroalkyl and aliphatic chains.

One of authors (T. M.) acknowledges the financial support from the Japan Society for the Promotion of Science (Research Fellowships for Young Scientists). This study was carried out under the 21st Century COE program for "Future Nanomaterials" at Tokyo University of Agriculture and Technology. The present study was also supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 14205136).

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