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Tailoring Liquid-crystalline Supramolecular Structures by Ionic Interactions

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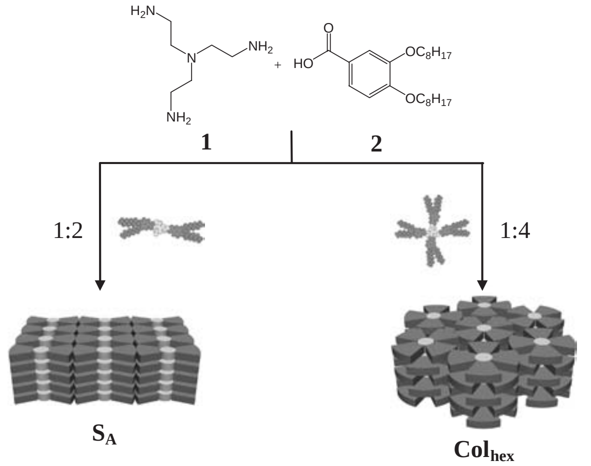
The binary ionic liquid crystal composed of tris(2-aminoethyl)amine (**1**) and 3,4-dioctyloxybenzoic acid (**2**) was investigated. The type of the mesophases with the highest thermal stability was found to be specific to the **1**–**2** molar ratios; 1:2 for the smectic A phase and 1:4 for the hexagonal columnar phase.

The ionic liquid crystals[1] are a class of liquid-crystalline materials constituting of cation and anion species via ionic interaction. This kind of liquid crystal has been of interest for their application to dimension-restricted ion conductive materials.[2,3] Although a wide variety of ionic liquid-crystalline molecules have been achieved by an elaborate molecular design and synthesis, a limited number of reports have described the creation of extended supramolecular assemblies by ionic interaction between oppositely charged molecular building blocks.[4–6] Such a binary supramolecular system enables us to modify the liquid-crystalline properties by simply varying one of the components. This simplicity also provides us a clue to apprehend the essential requirement necessary for the generation of the liquid crystal phases.

Here, we present a simple binary ionic liquid crystal composed of tris(2-aminoethyl)amine (**1**) and 3,4-dioctyloxybenzoic acid (**2**) (Scheme 1). The molar ratio of the two components could be a parameter to manipulate the mesomorphic behavior. The shape or interfacial curvature of the ionic complex can be adjusted by changing the molar ratio of **2** to **1**, which alters the mesophase morphologies. We assumed that the stoichiometric 1:3 complex as we previously reported[4] could not be always suitable for the mesomorphic structure of the ionic complex **1**•**2**. In tihis study, the highest clearing temperature was observed at a particular ratio specific to mesophase morphologies, not necessarily to be stoichiometric. These results suggest that an appropriate volume balance is required for the efficiently microsegregated structures in the mesophases.[7]



Scheme 1. Schematic representation of the ratio-dependent organization for the ionic liquid crystals.

The ionic supramolecular complexes **1**•**2** were prepared by mixing **1** and **2** in chloroform at appropriate molar ratios followed by evaporation of the solvent. The formation of the ion-pair was confirmed by FT-IR measurement.[8] It showed the carboxylate (COO^-) absorption bands at $1543\,cm^{-1}$ (ν_{as}) and $1379\,cm^{-1}$ (ν_s), suggesting that proton transfer from the acid to amine occurred. The mesomorphic properties were investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD).

The type of mesophase, smectic or columnar, and its clearing temperature were strongly dependent on the **1**–**2** molar ratios. The highest clearing temperatures were obtained at the molar ratios of 1:2 for the smectic A (S_A) phase, and 1:4 for the hexagonal columnar (Col_{hex}) phase.[8] These complexes showed enantiotropic mesomorphic behavior (Table 1). At the clearing point a single transition peak was observed on their DSC thermograms.[8] This indicates that the ratios, 1:2 for the S_A phase and 1:4 for the Col_{hex} phase, are significant. The stoichiometric 1:3 complex did not afford a stable mesophase even though its discotic shape seemed to be favorable for the formation of a columnar phase. It is important to note that the amine–acid stoichiometric ratio is not the most suitable for the generation of thermally stable mesophases.

On POM investigation, the 1:2 complex exhibited a *pseudo*-isotropic texture. Shearing gave an oily streaks texture indicative of a S_A phase (Figure 1a). In contrast, a spherulitic texture typical to a Col_{hex} phase was observed for the 1:4 complex (Figure 1b).

To elucidate the packing structure of the complexes in the mesophases, XRD measurements were carried out. The XRD pattern of the 1:2 complex in the S_A phase (Figure 2A) showed three reflections in the small-angle region with *d*-spacings of 27.9 (100), 14.0 (200), and 9.4 Å (300), indicating a well-defined periodic layer structure. In addition, a broad halo was observed

Table 1. The most suitable composite ratio (**1**:**2**) for the selective generation of mesophases

1–**2** ratio	Phase-transition behavior[a]
1:2	Cr 111 (41.8) S_A 152 (2.4) Iso
1:4	Cr 94 (1.3) Col_{hex} 153 (2.5) Iso

[a]The transition temperatures (°C) and corresponding enthalpies (in parentheses, $kJ\,mol^{-1}$) were determined by DSC on second heating scan (scan rate: $5\,°C\,min^{-1}$). Cr, S_A, Col_{hex}, and Iso indicate crystal, smectic A, hexagonal columnar, and isotropic liquid phases, respectively.

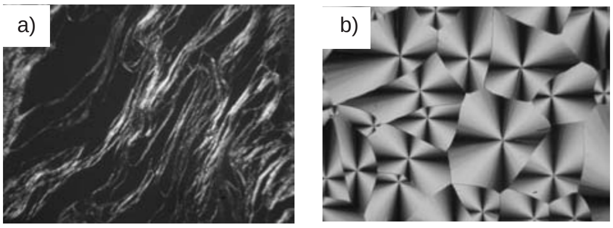


Figure 1. a) Oily streaks texture of the 1:2 complex at 130 °C. b) Spherulitic texture of the 1:4 complex at 140 °C (magnification: ×300).

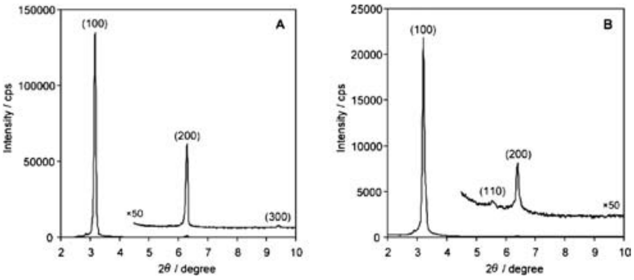


Figure 2. XRD patterns of the 1:2 complex at 120 °C (A) and the 1:4 complex at 125 °C (B).

in the wide-angle region around 4.5 Å corresponding to the conformational disorder of the alkyl chains. The cross section of the 1:2 complex can be deduced to be 57.4 Å^2 based on its volume ($V_{1:2} \approx 1600$ Å^3) and the layer spacing of the S_A phase ($d = 28.0$ Å) with the assumption that the two octyl chains are on opposite sides of **1** in the 1:2 supramolecular structure (i.e. rod-like shape). The cross-sectional area per one chain was calculated to be 28.7 Å^2. This value is in agreement with the cross-sectional area of a molten alkyl chain in a smectic liquid crystal.[9] The model for the S_A phase is illustrated in Scheme 1. The rod-shaped 1:2 complexes are estimated to form the layer structure, in which the polar ionic cores segregate from the alkyl chains to form the alternating microsegregated sublayers.

On the other hand, the XRD pattern of the 1:4 complex measured at 125 °C (Figure 2B) was characteristic of a Col$_{hex}$ phase. It showed three reflections in the small-angle region with d-spacings of 27.4, 15.9, and 13.8 Å. The three d-spacings were in the reciprocal ratio of $1{:}\sqrt{3}{:}\sqrt{4}$, which were respectively indexed as (100), (110), and (200) reflections of a 2D hexagonal lattice with the lattice constant $a = 31.8$ Å. A broad halo was also observed in the wide-angle region around 4.5 Å corresponding to the liquid-like order of the alkyl chains. The number of the 1:4 complex in a unit cell with a height of 4.0 Å[4] was calculated to be ≈1. This ratio suggests that one 1:4 complex is packed as one disk unit to form the columns, in which the polar ionic cores are surrounded by the alkyl chains (Scheme 1).

It is notable that the 1:4 complex was, in fact, a mixture of the 1:3 ionic complex and the non-ionized acid **2** at room temperature.[8] Its FT-IR spectrum showed the carbonyl absorption band of the non-ionized COOH group at 1672 cm^{-1} together with the carboxylate (COO$^-$) absorption band. This observation is in agreement with the previous report that the protonation of **1** preferentially occurs at the three primary amino groups and subsequent protonation of the tertiary amino group hardly proceeds.[10] The wavenumber of the non-ionized carbonyl absorption band is consistent with that of the pure acid **2**, which indicates that the non-ionized acid **2** in the 1:4 mixture exists as a hydrogen-bonded dimer at room temperature. To understand the role of the non-ionized acid **2** for the Col$_{hex}$ phase formation, temperature-variable FT-IR measurements were performed (Figure 3). A higher wavenumber shift of the carbonyl absorption band (ca. 20 cm^{-1}) was observed at 75 °C before its own melting point. This temperature corresponded to the initial endothermic transition (Cr$_1$–Cr$_2$) observed by DSC on first heating. These results suggest that the preorganized dimeric acid rearranged at this temperature into the mesomorphic columnar supramolecular structures. Ionic hydrogen bonds[11] between the non-ionized COOH and charged NH$_3$$^+$ (donor) or COO$^-$ (acceptor) could furnish the formation of the disk-shaped 1:4 complexes in the columnar structures.

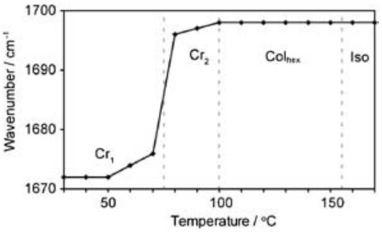


Figure 3. Temperature-dependent carbonyl stretching vibration of a non-ionized COOH group in the 1:4 complex.

In this study, we demonstrated the tailoring of ionic liquid-crystalline structures by varying the molar ratio of **2** to **1**. The types of mesophase structures to be generated were defined by the specific **1**–**2** molar ratio; 1:2 for the S_A phase and 1:4 for the Col$_{hex}$ phase. A particular emphasis should be placed on the importance of the suitable volume balance between polar and apolar microsegregated regions.

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