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Volume Effect of Alkyl Chains on Organization of Ionic Self-Assemblies toward Hexagonal Columnar Mesophases

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Upon ionic complexation of tris(2-aminoethyl)amine and di- or trialkoxybenzoic acids with normal and branched chains, hexagonal columnar mesophases were generated. The two parameters, the length and the cross-sectional area of the alkyl chains, were investigated to unveil the volume effect of the alkyl chains on the formation and stabilization of the columnar mesophases. The thermal stabilities of the columnar phases were strongly depended on the molar ratio of the acids to the amine. The highest clearing temperature (the most stable mesophase) was obtained at a ratio specific to the alkyl chain volume, not necessarily stoichiometric. We estimated the packing fraction (V_{comp}/V_{cell}) on the basis of the volume of the ionic complexes at these particular ratios (V_{comp}) and that of the unit cell of the Col_{hex} phases (V_{cell}). The most suitable packing fractions for the Col_{hex} phases of the present ammonium carboxylates were estimated to be in a range of 0.63–0.66.

Columnar aggregates are one of the fundamental structural motifs in nature as well as in artificial systems.[1] In the field of materials science they are expected to act as channels capable of mass-transportation because of their one-dimensional architecture. Functional columnar aggregates can be obtained by self-organization of molecules into columnar mesophases.[2] Disc-shaped molecules or supramolecular entities composed of molecular components that have flexible alkyl chains attached to a rigid core have a propensity to form one-dimensional columns via π–π stacking of cores and van der Waals interaction between alkyl chains. Typical discotic mesogens are benzene,[3] triazine,[4] triphenylene,[5] perylene,[6] hexabenzocoronene,[7] and phthalocyanine[8] derivatives. In addition, extended columns showing mesomorphisms have supramolecularly been obtained by noncovalent attractive forces such as hydrogen bonds,[9] donor–acceptor aromatic interactions,[10] metal complexations,[11,12] and ionic interactions.[13–15]

Ionic liquid crystals capable of forming columnar mesophases have been spotlighted because they are fascinating candidates for application to ion-transporting nanomaterials.[16] Recent reports have described one-dimensional ion-conductivity in a columnar mesophase[13c] and its polymerized thin film.[17] Since an ionic compound can be regarded as an amphiphile, a self-assembly process of amphiphiles into columnar mesophases is quite different from that of conventional anisometric disc-shaped molecules. In amphiphilic systems, the formation of columnar mesophases is mainly governed by the interfacial curvature of polymolecular aggregates, which can be controlled by the volume fractions of incompatible (hydrophilic/hydrophobic) subunits.[18]

We have been interested in liquid crystalline ionic self-assemblies comprised of different molecular building blocks via ionic interactions.[19] Based on the concept of supramolecular liquid crystals, the stoichiometric ratio of them is the key factor for mesomorphic properties. Indeed, most liquid crystalline ionic complexes consist of 1:1 stoichiometry per ionic interaction.[14] However, volumetric contributions of incompatible (ionic/nonionic) subparts are not negligible in the mesophase formation because of the amphiphilic nature of the resulting ionic complexes.[15]

In this study, we report on the best packing fractions required for the formation of stable hexagonal columnar mesophases. The columnar mesophases were generated by ionic complexes based on ammonium carboxylates composed of tris(2-aminoethyl)amine (**1**) and benzoic acids with various alkyl chain volume **2a**–**3k** (Figure 1). We previously reported hexagonal columnar mesophases based on **1**·**3a** with a stoichiometric amine–acid ratio of 1:3.[20] The discotic shapes of the 1:3 complexes seem to be favorable for the formation of columnar mesophases in view of the stoichiometry. However, if microsegregation is an important organizing force in the col-

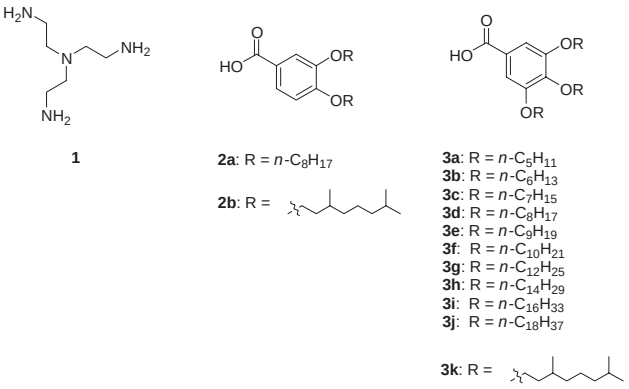

Figure 1. Chemical structures of amine **1** and acids **2a**–**3k**.

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Table 1. Phase-Transition Behavior of the Ionic Complexes at the Most Suitable Molar Ratios and Their Structural Parameters in Mesophase

Complex (ratio)	M_w[a)]	Transition behavior[b)]	Lattice constant a/Å (T/°C)[d)]	V_{cell}/Å^3 [e)]	V_{comp}/Å^3 [f)]	Packing fraction (V_{comp}/V_{cell})
1·2a (1:3.8)	1585	Cr 94 (0.3) Col_{hex} 153 (0.6) Iso	31.8 (120)	3941	2632	0.67
1·2b (1:3)	1450	G—[c)]Col_{hex} 153 (0.8) Iso	31.2 (115)	3794	2408	0.63
1·3a (1:3)[20]	1288	Cr 94 (0.2) Col_{hex} 119 (0.9) Iso	25.8 (100)	2594	2138	0.82
1·3b (1:2.6)	1245	Cr 90 (1.5) Col_{hex} 133 (1.1) Iso	26.9 (105)	2820	2067	0.73
1·3c (1:2.3)	1215	G 84 Col_{hex} 139 (1.1) Iso	27.8 (105)	3012	2018	0.67
1·3d (1:2.2)	1261	G 85 Col_{hex} 141 (1.0) Iso	28.9 (110)	3255	2094	0.64
1·3e (1:2.1)	1299	G 82 Col_{hex} 140 (1.2) Iso	30.2 (110)	3554	2157	0.61
1·3f (1:2)	1328	G—[c)]Col_{hex} 139 (1.1) Iso	31.1 (110)	3769	2205	0.59
1·3g (1:2)	1496	Cr 21 (10.8) Col_{hex} 134 (1.1) Iso	33.4 (110)	4347	2485	0.57
1·3h (1:2)	1665	Cr 42 (17.8) Col_{hex} 128 (0.9) Iso	35.6 (105)	4939	2764	0.56
1·3i (1:2)	1833	Cr 58 (31.7) Col_{hex} 122 (1.3) Iso	37.3 (100)	5422	3044	0.56
1·3j (1:2)	2001	Cr 67 (36.3) Col_{hex} 116 (1.1) Iso	39.1 (100)	5958	3323	0.56
1·3k (1:2)	1328	G—[c)] Col_{hex} 111 (1.0) Iso	28.8 (85)	3232	2205	0.68

a) M_w = molecular weight of the ionic complex at the ratio indicated. b) The transition temperatures (°C) and the corresponding enthalpies (in parentheses, kcal mol^{-1}) were determined by DSC on the second heating scan (rate: 5 °C min^{-1}). G, Cr, Col_{hex}, and Iso indicate glassy, crystal, hexagonal columnar, and isotropic liquid phases, respectively. c) Not detectable. d) a = lattice constant of the Col_{hex} phase. e) V_{cell} = volume of a unit cell for the Col_{hex} phase calculated by the following equation: $V_{cell} = \sqrt{3}a^2h/2$, where h is the height of the unit cell assumed to be 4.5 Å. f) V_{comp} = volume of the ionic complex at the ratio indicated: $V_{comp} = M_w/\rho N_A$, where ρ is density ($\approx$1 g cm^{-3}), and N_A is Avogadro's number.

umnar aggregates, the volume ratio, the volume of the ionic core vs. that of the peripheral alkyl chains, would strongly influence the stability of the columnar organization. We assume that the most suitable volume balance for the mesomorphic structures would provide an appropriate packing fraction of the ionic complex suitable for columnar organization.

In order to elucidate the importance of the packing fraction, we examined the effect of the molar ratio of the acids **2a**–**3k** to **1** on the thermal stability of the resulting columnar mesophases. The ratio affording the thermally most stable columnar mesophase could be an indicator of suitable volume balance appropriate to the columnar mesophase. From the volumetric viewpoint of the alkyl chains, we considered the following two parameters: (1) the alkyl chain length (**3a**–**3j**) and (2) the cross-sectional area of alkyl chains (**2a**, **2b**, **3d**, and **3k**). In addition, the ternary complex **1·2a·3d** was investigated to ensure the volume effect of the alkyl chains. The effects of alkyl chains have previously been studied for columnar ionic liquid crystals.[21] The highest clearing temperatures of the columnar mesophases (the most stable mesophases) were observed at a particular composite ratio specific to the alkyl chain volume. This result indicates that adjustment of the acid ratio to **1** can provide a suitable packing fraction of the ionic complexes for stable columnar mesophases.

Experimental

The commercially available amine **1** was of reagent grade and used without further purification. All acids employed, **2a**–**3k**, are known compounds and were synthesized according to previously reported procedures.[22] Ionic complexation of **1** and **2a**–**3k** was performed by mixing **1** and **2a**–**3k** in chloroform with appropriate molar ratios followed by evaporation of the solvent to afford the corresponding ionic complexes **1·2a**–**3k**, respectively. The formation of the ionic complexes was confirmed by FT-IR measurements using a JASCO FT/IR410 spectrometer, which showed the carboxylate (COO^-) absorption bands at 1543 (ν_{as}) and 1379 cm^{-1} (ν_s).

Thermal transitions of the ionic complexes were investigated by differential scanning calorimetry (DSC) using a MAC Science DSC3100S differential scanning calorimeter. The heating and cooling rates were 5 °C min^{-1}. A Nikon ECLIPSE E400POL optical polarized microscope equipped with an INSTEC HCS400 hot stage was used to verify thermal transitions and characterize anisotropic textures. X-ray diffraction (XRD) experiments were performed with Cu Kα radiation by using a Rigaku RINT 2200 diffractometer.

Results and Discussion

Mesomorphic Properties. The ionic complexes exhibited hexagonal columnar mesophases (Col_{hex}). Their thermal stabilities were strongly dependent on the molar ratio of the acid components. The highest clearing temperatures were observed at a molar ratio specific to the alkyl chains of the acid components. The phase-transition temperatures and the corresponding enthalpy values of the ionic complexes at the most suitable ratios, and the lattice parameters of the Col_{hex} phases are summarized in Table 1. The XRD results are collected in the Supporting Information.

Influence of the Alkyl Chain Length. The effect of the molar ratio of the acids **3a**–**3j** to **1** on the clearing temperature of the columnar mesophases was examined. Figure 2a shows the phase diagram of **1·3d** as an example. The highest clearing temperature was observed at the amine–acid molar ratio of 1:2.2 for **1·3d**. Such molar ratio-dependent stability of mesophase was previously examined for supramolecular liquid-crystalline systems incorporating pyridine/benzoic acid.[23] On POM investigation, the ionic complex at this ratio showed a spherulitic texture typical of a Col_{hex} phase (Figure 2b). On its DSC thermogram, a single phase-transition peak was observed at its clearing temperature. This specific ratio affording the highest clearing temperature can be defined as the most suitable ratio for the formation of the Col_{hex} phase. It is re-

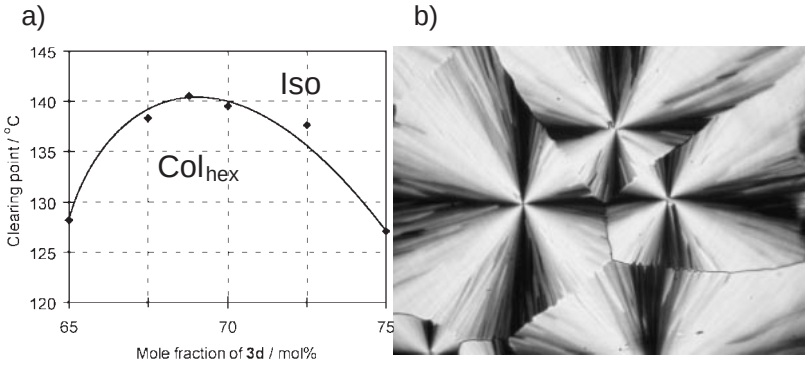

Figure 2. a) Phase diagram of **1·3d**. b) Polarized optical microphotograph of **1·3d** at a molar ratio of 1:2.2 (135 °C, ×600).

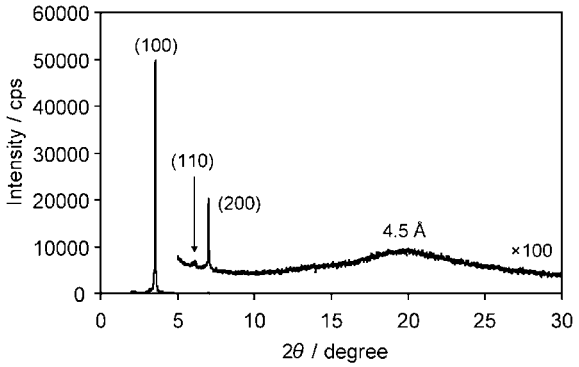

Figure 3. XRD pattern of **1·3d** (1:2.2) at 110 °C.

markable that the most suitable molar ratio for the Col$_{hex}$ phase decreased with increasing alkyl chain length; 1:3 for **1·3a**, 1:2.6 for **1·3b**, 1:2.3 for **1·3c**, 1:2.2 for **1·3d**, 1:2.1 for **1·3e**, and 1:2 for **1·3f**. For complexes with alkyl chain length longer than dodecyl, the molar ratio remained at 1:2 (**1·3g**–**1·3j**).

XRD measurements in mesophases were performed to investigate the packing structures of the ionic complexes at the most suitable ratios. Figure 3 shows the XRD profile of the **1·3d** complex (1:2.2). It shows three reflections in the small-angle region with *d*-spacings of 25.0, 14.4, and 12.6 Å. The three *d*-spacings were in a reciprocal ratio of $1:\sqrt{3}:\sqrt{4}$, which were respectively indexed as (100), (110), and (200) reflections of a 2D hexagonal lattice with a lattice constant $a = 28.9$ Å. The observed lattice constant (a) is approximately 74% of the calculated column diameter (D) with the assumption of fully extended alkyl chains ($D = 39.0$ Å, $a/D = 0.74$). This is often observed for columnar mesophases owning to the disordered conformation of the alkyl chains and some degree of their interdigitation between the columnar aggregates. In the Col$_{hex}$ phase, a column is comprised of polymolecular cylindrical aggregates where the ionized **1** and acid **3d** form a column surrounded by alkyl chains. For non-stoichiometric complexes of amine and acids in Col$_{hex}$ phases, non-ionized free amino groups could participate in ionic hydrogen bonds[24] with charged species such as NH_3^+ and COO^-. In this study, however, these types of interactions were hardly detected in the FT-IR measurements.

We estimated the packing fraction of the ionic complex in a unit cell of the Col$_{hex}$ phase. Commonly, the number of complexes per unit cell (z-value, $z = V_{cell}/V_{complex}$) is calculated to estimate their packing structures. In fact, the reciprocal z-value ($V_{complex}/V_{cell}$) is the packing fraction. A complex at the most suitable ratio is assumed as an averaged constitutional unit packed in a unit cell with a height of 4.5 Å. The density of substances is deduced to be equal to 1.0 g cm^{-3}.[25,26] It was found that the volumetric amount of the ionic complex for the most stable mesophase was constant regardless of the chain length of the acid substituents with decreasing molar ratio of the acid components (Figure 4a, $n = 5$–10, solid line). The unit cell volumes have a linear correlation with increasing chain length (Figure 4b, solid line). This causes a decrease in the packing fraction. In contrast, further increase in the chain length keeps the packing fraction constant (Figure 5, solid line). This constant value implies the limit of the packing fraction at which the columnar aggregates retain stability. These results suggest that the specific amine–acid ratios of the ionic complexes are essential to their packing fractions suitable for the Col$_{hex}$ phases. The plots of clearing temperature allow us to optimize the packing requirement of the ionic complexes for the Col$_{hex}$ phase (Figure 5, dashed line). Since the **1·3d** complex (1:2.2) affords the highest clearing temperature of all the complexes investigated, it is suggested that octyl chain and the corresponding packing fraction (0.64) are the most suitable packing requirement for the Col$_{hex}$ phase generated by the amine **1** and alkoxy-substituted benzoic acid system. There is no correlation between the packing fraction and the clearing temperature.

Influence of the Cross-Sectional Area of Alkyl Chains. In order to confirm the existence of a suitable packing fraction for stable Col$_{hex}$ phases, we examined the effect of the chain volume of the acid. This was carried out by varying the cross-sectional area of the alkyl chains of the acid derivatives. For this purpose, we investigated the acids with normal (**2a** and **3d**) and branched (**2b** and **3k**) octyl groups. Figure 6a shows the phase diagram of **1·2a** as an example. The highest clearing temperature was observed at an amine–acid molar ratio of 1:3.8 for **1**–**2a**. On POM investigation, the ionic complexes at this specific ratio showed a spherulitic texture (Figure 6b). On their DSC thermograms, a single phase-transition peak was observed at their clearing temperature. The results indicate that this specific ratio is the most suitable ratio for the formation of the Col$_{hex}$ phase. It is remarkable that the most suitable ratio for the highest clearing temperature decreased with increasing cross-sectional area of the alkyl chains; 1:3.8 for **1·2a**, 1:3 for **1·2b**, 1:2.2 for **1·3d**, and 1:2 for **1·3k**.

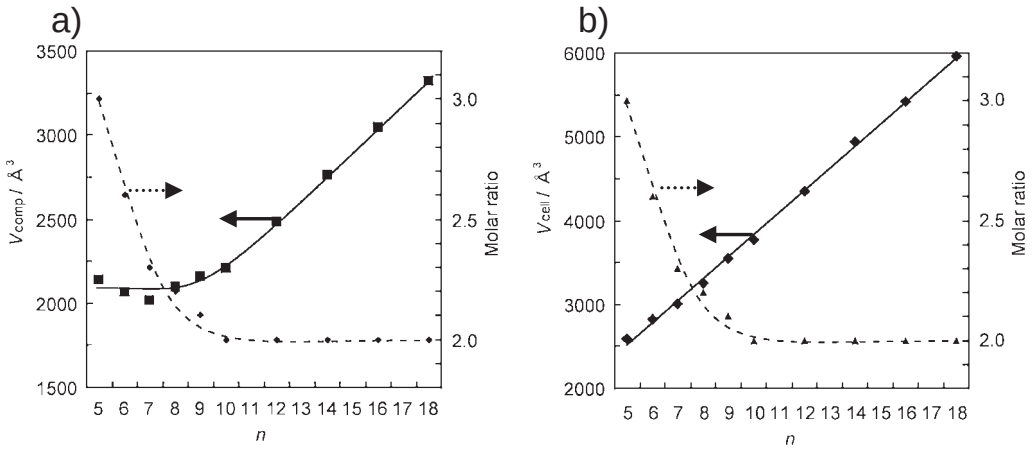

Figure 4. a) Plots of the volume of the ionic complexes at the most suitable molar ratio (solid line, left axis) against the chain length of the acid (*n*: the number of carbon atoms in a chain). b) Plots of the unit cell volume of the Col_{hex} phase (solid line, left axis) against the chain length (*n*). Dashed lines indicate the relation between chain length (*n*) and the most suitable molar ratio of the acid for the corresponding Col_{hex} phase (right axis).

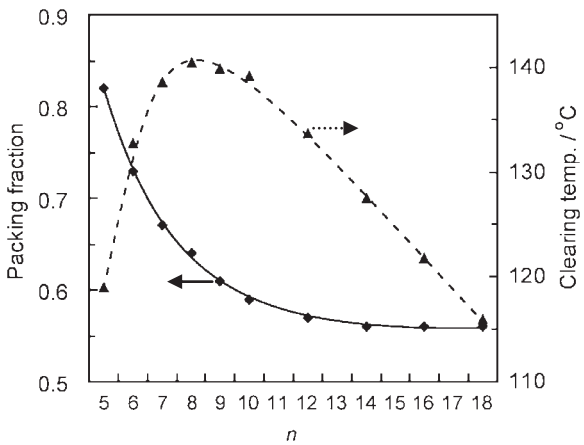

Figure 5. Plots of the packing fraction of the ionic complex at the most suitable ratio in the unit cell of the Col_{hex} phase (solid line) and the corresponding clearing temperature (dashed line) against the alkyl chain length of the acid (*n*).

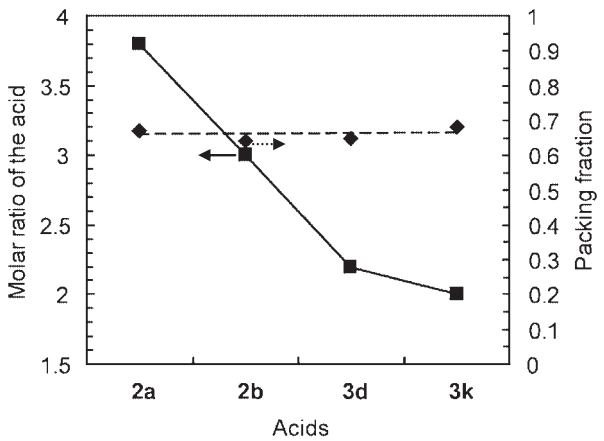

Figure 7. Relationship between the most suitable packing fraction (dashed line) and the molar ratio of the acids to **1** (solid line).

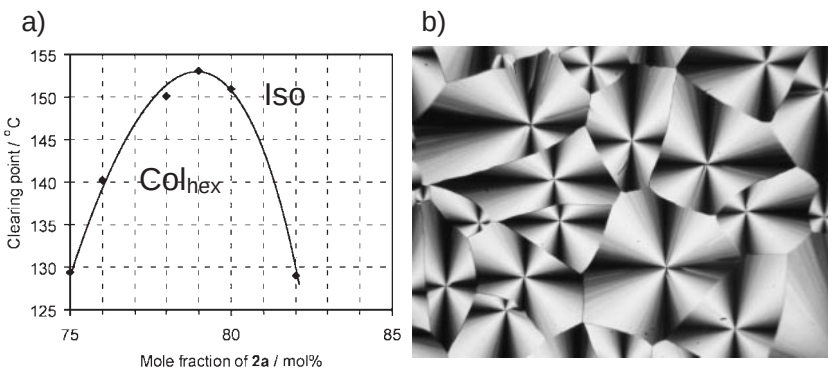

Figure 6. a) Phase diagram of **1**·**2a**. b) Polarized optical microphotograph of **1**·**2a** at the molar ratio of 1:3.8 (140 °C, ×300).

To understand the occurrence of the most suitable ratio of the acids for the Col_{hex} phases, we estimated the packing fraction of the ionic complexes in the unit cell. It was found that the packing fraction of the ionic complex in a unit cell kept a fixed value ca. 0.66 (Figure 7, dashed line). This indicates that the most suitable packing fraction for the formation of the Col_{hex} phase is embodied in specific amine–acid molar ratios.

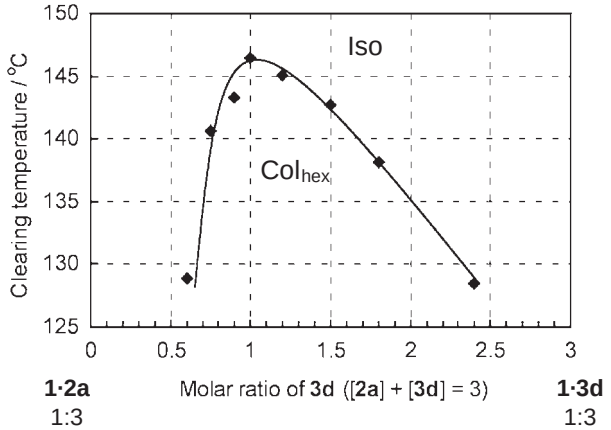

Figure 8. Phase diagram of the ternary complex **1·2a·3d**.

Volume Effect of the Alkyl Chains. A ternary complex **1·2a·3d** was investigated to ensure that the composite ratio of the acids could govern the volume of the alkyl chains accommodated into a unit cell of the Col_{hex} phases. The ternary ionic complex was prepared in such a way that the sum of the molar ratio of **2a** and **3d** to **1** was kept at three so that the three primary amino groups involved could function in the corresponding protonation.[27] The ternary complex exhibited a Col_{hex} phase. Figure 8 shows the dependence of the molar fraction of the acids on the clearing temperature of the Col_{hex} phase. A decrease in the alkyl chain volume by introducing **2a** into the ternary ionic complexes caused an incremental increase in the clearing temperature. The highest clearing temperature was obtained at a molar ratio 1:2:1 (**1·2a·3d**). At this ratio, a spherulitic texture was observed on POM (Figure 9a). The XRD profile showed a characteristic pattern of the Col_{hex} phase with the lattice constant $a = 30.8$ Å (Figure 9b). On the basis of the volumetric amount of the ternary complex (1:2:1) and the volume of a unit cell of the Col_{hex} phase, the packing fraction of the ternary complex **1·2a·3d** (1:2:1) in the unit cell of the Col_{hex} phase is estimated to be 0.63. The value is almost the same as the most suitable packing fraction of the binary complexes. This is caused by the volumetric adjustment with the alkyl chain volume leading to the stable Col_{hex} phase.

Conclusion

We have demonstrated that the volume of peripheral alkyl chains tunable by the molar ratio of an acid component is a decisive factor for the creation and stabilization of hexagonal columnar mesophase. Stable columnar mesophase was formed with a particular amine–acid composite ratio, not necessarily stoichiometric. The occurrence of a specific ratio, ionic/nonionic unit, results in the most suitable packing fraction which is a constant value (0.63–0.66) for the hexagonal columnar mesophase. This study emphasizes that the ratio-controlling approach in an ionic supramolecular system is a powerful method to unveil a principle underlying the formation of columnar mesophases.

Supporting Information

Phase diagrams and XRD results. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

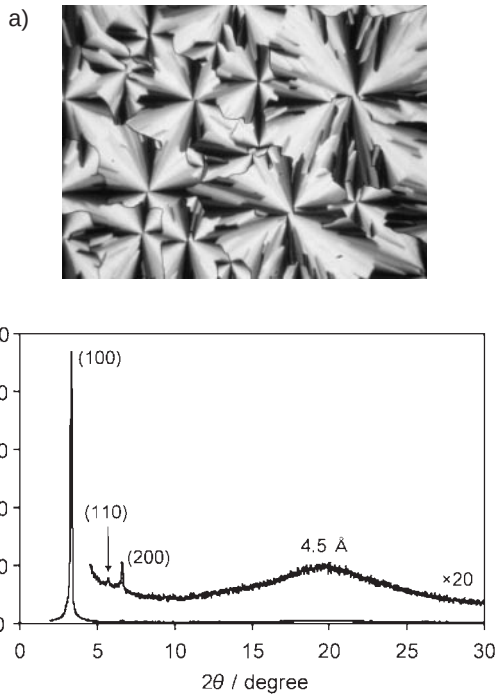

Figure 9. a) Polarized optical microphotograph of the ternary complex **1·2a·3d** (1:2:1) (135 °C, ×600). b) XRD pattern of **1·2a·3d** (1:2:1) at 115 °C.

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