Formation of Supramolecular Assemblies by Complementary Association of Octadecyloxy Tartaric Acid and Bispyridyls

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Formation properties of molecular assemblies from chiral amphiphile, 2,3-dioctadecyloxy-L-tartaric acid (**1**) are studied. Organization of **1** was achieved by self-complementary association, as well as with the aid of 2,2′ and 4,4′ bispyridyl components (**2** and **3,** respectively). Thermally induced formation of molecular assemblies in the solid state is reported. The results show that by modifying the geometry and angle of headgroup interaction one can control the microscopic morphologies, adding thus another facet to the design and manipulation of supramolecular polymers and liquid crystals. Amphiphile **1** produced ordered birefringent smectic texture in the solid state when heated to 90 °C; mixtures of **1** with **2** produced helices and needles, and **1** with **3** produced birefringent fan-shaped crystalline textures. X-ray diffraction data showed two motifs in observed reflections: smectic layer ordering as well as long-range in-plane ordering. An order parameter of 1000 Å in in-plane reflection indicated the existence of helices. Optical microscopic results confirmed the X-ray findings. The results suggest that microscopic features of the molecular assemblies can be modulated by involving a bifunctional molecular director (**2** or **3**) capable of hydrogen bonding with amphiphiles.

Introduction

A major scientific challenge in the miniaturiaztion of technology is how to build molecular assemblies precisely and predictably. A promising approach resides in the implementation of the self-organization of suitably designed components.[1] Phospholipids and amphiphiles are excellent vehicles for making well-defined microscopic structures by self-assembly.[1,2] However, the utility of phospholipids is limited due to their cost, complexity in synthesis, and short shelf life. Moreover, in mixed lipid systems, the self-assembling process becomes complex and placement or ordering of individual molecules in bilayer membranes cannot be controlled. Nonconventional association of molecules using complementary functionalities provides an efficient route for generating supramolecular microstructures through recognition-directed association.[1−7] The overall goal is to control the microscopic morphologies by altering the nature and geometry of headgroup interaction. We present here results along these lines that involve noncovalent, hydrogen bond-mediated association of *O*-alkyl tartaric acid with bispyridines (bipys) (Figure 1). In this system, the function of bipys is to direct the packing order of amphiphiles. Tartaric acid-derived amphiphiles have been used in the formation of chiral molecular assemblies.[8,9] The goal of the present study is to understand the properties of molecular assemblies formed from chiral amphiphile 2,3-dioctadecyloxy-L-tartaric acid (**1**) alone and in mixtures with 4,4′ and 2,2′ bipy components (**2** and **3**, respectively) in the solid state. Related studies concerning hydrogen-bonded association between various carboxylic acids and pyridine or bispyridine derivatives have been reported.[10−14]

Experimental Section

Materials. All chemicals and reagents were procured from Aldrich Chemical Co. and were used as received. Both 2,2′ and

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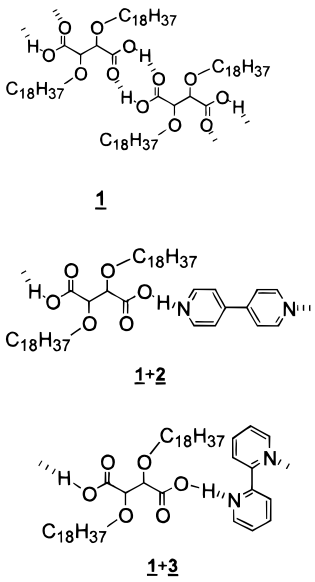

Figure 1. Hydrogen bond-mediated molecular association.

4.4′ bispyridyl were crystallized from toluene and vacuum-dried. 2,3-Dioctadecyloxy-L-tartaric acid was synthesized following a literature procedure.[9] **1** was recrystallized with hexane and thoroughly dried under vacuum. Purity of the materials was confirmed by their NMR spectra and melting points.

Sample Preparation. Only the anhydrous materials were used in the sample preparation. Complementary mixtures were prepared by mixing equimolar amounts of **1** and **2** or **3** in methylene chloride. The solvent was removed under a gentle stream of nitrogen and the resulting solid was heated to 170 °C for 30 s. The resulting solid samples were cooled and stored under nitrogen at room temperature.

Characterization of Association Materials. Thermal properties of pure **1** and its mixtures with **2** and **3** were studied using a Perkin-Elmer DSC-7 differential scanning calorimeter. DSC scans were used as guide to probe the textures at temperatures around phase changes under an optical microscope (Olympus BX50) fitted with a thermal stage (Linkam TP-92) and a camera. These samples were further examined by collecting X-ray diffraction data on polycrystalline materials using a Rigaku RU200B rotating anode Cu Kα X-ray generator. Samples were deposited on an aluminum plate by supplying a little heat to make the sample stick to surface. For temperature scans, the samples was heated with an accuracy of ±1 °C.

Results and Discussion

2,3-Bis(Octadecyloxy)-L-tartaric acid, **1**, by virtue of its two 18-carbon-long alkyl chains and polar headgroup, belongs to the class of natural surfactants. The presence of two carboxylic acids in the headgroup region renders this amphiphile versatile: (1) carboxylic acids through hydrogen bonding may self-complement to initiate the self-assembling process, and (2) self-assembling motif may be altered by adding molecules capable of interacting with carboxylic acids via hydrogen bonding or ionic interactions. Bispyridyls (2,2′ and 4,4′) form hydrogen-bonded complexes with **1** and influence its self-assembling properties. Differential scanning calorimetry, optical microscopy, and X-ray diffraction techniques were used in the investigation of the molecular assembling behavior of pure **1** and its equimolar mixture with **2** and **3**.

As a first step, infrared spectra were recorded to confirm hydrogen-bond association. Freshly crystallized **1** showed a carbonyl frequency at 1705 cm^{-1}, but in mixed systems, this band shifted to 1750 cm^{-1} and two additional O−H stretching frequencies emerged at 2410 and 1960 cm^{-1}, indicating the existence of hydrogen-bonding association.[10] A number of solvents have been used for mediating the molecular association including dioxane, THF, chloroform, and methylene chloride.[8−11] We have selected methylene chloride as mixing solvent due to its relatively nonhygroscopic nature, ability to dissolve molecular components, and ease of its complete removal from the mixture. The molecular components consisting of substituted benzoic acid and pyridyl functionality were mixed by heating, which induced and stabilized the formation of liquid crystalline phases.[13−15] Circular dichroism spectra of dodecyloxy tartaric acids containing uracil and diaminopyridine as complementary units revealed the existence of hydrogen bond-mediated association in ethanol.[8,9] Compound **1** and its mixture with **2** showed similar molar ellipticity in both, ethanol and methylene chloride. However, a solution of **1** + **2** in absolute ethanol (*c*, 40 mg/mL) produces needlelike structures upon slow cooling change of a clear, warm solution (A. Singh, unpublished results). In contrast to earlier report,[8] we did not observe helical structure in air-dried thin-layer films prepared from chloroform solution.

Differential scanning calorimetric (DSC) thermograms for **1** showed main transition at 91.4 °C and a pretransition at 67.1 °C. In the solid state, **1** underwent heat-induced self-complementary association to produce ordered birefringent smectic texture at 82 °C (Figure 2a). These textures appear at this temperature during the heating cycle. After the formation of heat-induced textures, the temperature was lowered to 25 °C, which caused the structures to distort and resulted in featureless textures. Reproducibility in the formation of these structures within the same temperature range indicates the formation of higher order assemblies mediated by intermolecular hydrogen bonding.

Equimolar mixture of **1** with **2** produced helices and needles at 145 °C, whereas mixtures with **3** produced birefringent fan shaped crystalline textures at 53 °C (Figure 2 b and c). The formation of birefringent, higher order structures is observed within a select range of temperatures, above which they melt and below which they distort. In previous studies, the formation of helical strands was observed in solid materials obtained after evaporating the polar solvents on a solid substrate.[8,9] Textures shown in Figure 2a−c clearly demonstrate the influence of molecular components on the resultant microscopic morphologies. For the mixture with **2**, DSC scans show multiple transitions, the main transition being at 157.4 °C. Other transitions of smaller but almost equal size occurred at 152, 102.3, 73.9, and 63.1 °C. In fact, a higher melting-transition temperature of the mixed system from **1** + **2** (157.4 °C) than that of **1** (91.4 °C) or **2** (111−114 °C) and the absence of transition due to individual components (due to phase separation) reveal that the mixed material is a new compound, probably an association polymer. Smaller multiple transitions may be attributed to short segments of associated monomers. Different batches of the mixed

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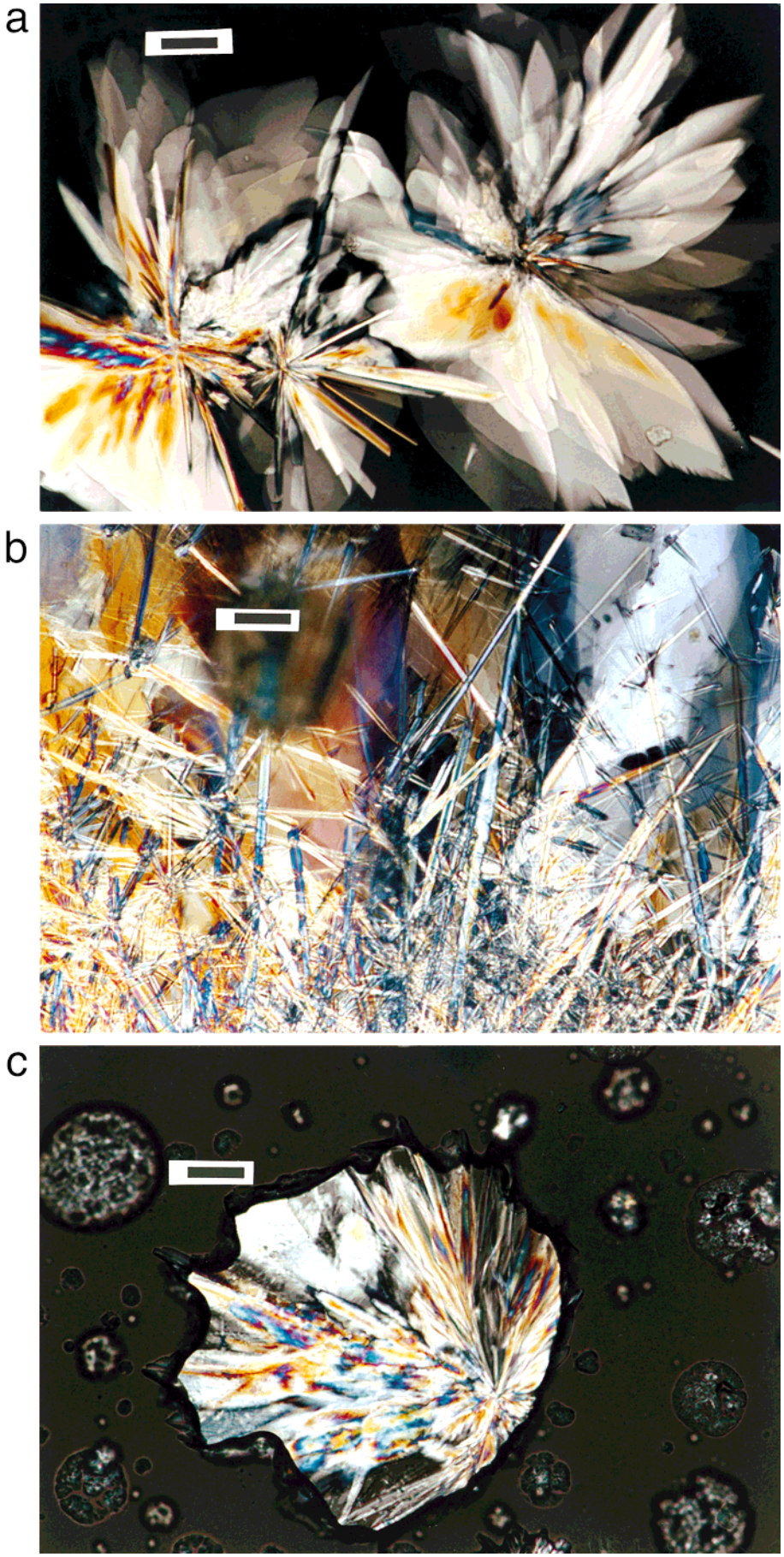

Figure 2. Microscopic textures formed from **1** (a) at 82 °C, **1** + **2** (b) at 145 °C, and **1** + **3** (c) at 53 °C (bar = 2 μm).

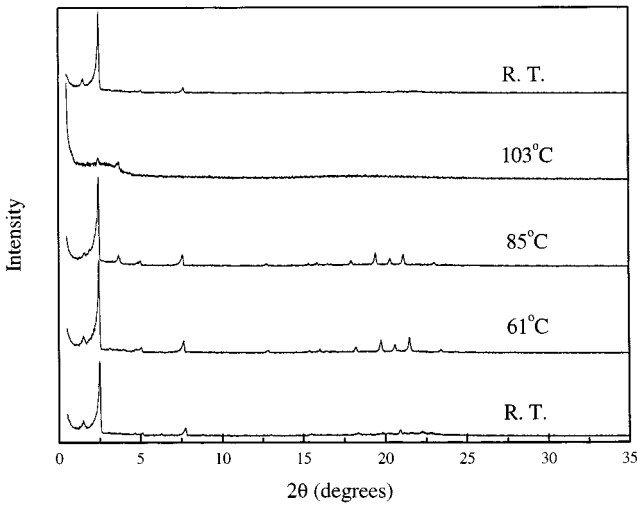

Figure 3. Temperature scans of X-ray diffraction patterns for **1**.

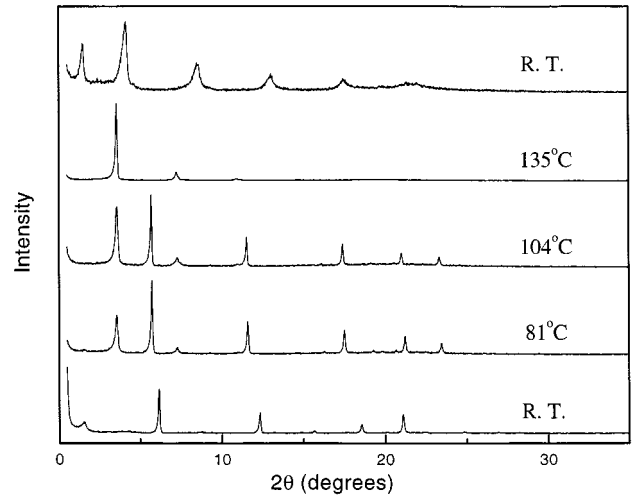

Figure 4. Temperature scans of X-ray diffraction patterns for 1:1 mixture of **1** and **2**.

materials show a range in the main transition temperature (155−157 °C), which may be due to the difference in the number of associated monomers present in the material. Similarly, all batches show cooling transitions in the range of 38−41 °C. A DSC scan for the mixture of **1** and **3** shows two transitions of comparable enthalpy at 63.0 and 75.6 °C. Again, none of these transitions is due to the precursor monomer. This sample shows a cooling transition at 54.7 °C. Therefore, the mixing of **1** with the bipys **2** and **3** results in the formation of new polydispersed association polymers.

Figures 3 and 4 show an overlay of 2θ X-ray scans of association polymer materials at selected temperatures, namely at room temperature, around phase-transition temperature, melting-transition temperature, and back to room temperature after cooling. From the positions of Bragg peaks, we calculated a spacing (d) corresponding to periodicity in our materials and from the peak's width, a radius of long-range ordering Rc, i.e., a correlation length in propagation of the periodicity.

From the room temperature scan in Figure 3, we identify one wide low-angle reflection with $d = 59$ Å and Rc = 290 Å. It is larger than the molecular dimension and may be attributed to a poor supramolecular periodicity, such as a bilayer (smectic 1). Three orders of sharper middle-angle reflections give $d = 35.5$ Å with better long-range ordering Rc = 660 Å (smectic 2). A reflection around 20°gives $d = 4.3$ Å. It is due to alkyl tail packing.

Upon heating the sample to 61 °C, we observed a low-angle reflection shift that indicates a decrease in smectic 1 periodicity. Middle-angle reflections indicate an increase in smectic 2 periodicity. Chain packing reflection splits to three values at 4.2, 4.3, and 4.5 Å that point to changes in hydrocarbon tail packing.

At 85 °C, the low-angle reflections disappeared and even better middle-angle (smectic 2 ordering) and tail packing reflections are obtained. The texture shown in Figure 2a appeared at this temperature. Upon heating to 103 °C, melting occurred and smectic 2 ordering (medium-angle reflections) as well as tail packing maxima disappeared. Quick cooling to room temperature brought the original ordering features minus the chain packing reflection, which usually requires more time for restoration.

Figure 4 shows the temperature X-ray scans for the mixed system derived from **1** and **2**. In general, ordering in **1** + **2** system is better than that in **1** alone and new ordering feature with $d = 14.2$ Å was observed. This spacing cannot be attributed to the system **1** alone and indicates supramolecular **1** + **2** organization. At room-temperature one wide, low-angle reflection with $d = 58.1$ Å (smectic 1) was observed. Three orders of sharp equidistant reflections with $d = 14.2$ Å are seen in the medium-angles, indicating good in-plane ordering. Reflection with spacing 4.1 Å is due to closely packed hydrocarbon tails. Thus, three levels of ordering motifs are observed, probably related to multilayer organization, in-plane ordering (possibly helical) and hydrocarbon chain packing.

After being heated to 81 °C, three sharp, medium-angle reflections were shifted to a lower angle, resulting in an increase of periodicity to $d = 15.5$ Å and Rc = 1000 Å. The low-angle reflection was replaced by two orders of reflection with $d = 25.2$ Å (probably resembling smectic **2** from **1**). It may be associated with conversion of smectic **1** structure to a smectic multilayer with tail interdigitation. Observation of better in-plane long-range ordering comparable with the multilayer ordering could indicate the presence of strong supramolecular periodicity in the system, such as helical structures. At 104 °C, the diffraction pattern remains the same, indicating no changes in the system.

At 135 °C, two orders of 25.2 Å spacing remains, indicating the presence of multilayer structure, but the chain packing maximum as well as the in-plane ordering (medium angle reflections) disappeared. Optical microscopy reveals the existing of needlelike structures (Figure 2b). When the sample is quenched to room temperature, all of the phases reappeared, except that due to hydrocarbon tail packing (similar to **1**).

The room temperature X-ray scan of the mixture of **1** and **3** was compared with room temperature scans of pure **1** and its mixture with **2** (Figure 5). The pattern of **1** + **3** appears more like that of system **1** than that of **1** + **2**. The low-angle reflection with $d = 74.8$ Å was rather smeared and with Rc = 300 Å and was similar to the smectic **1** ordering. Sharp reflections with 33.9 Å

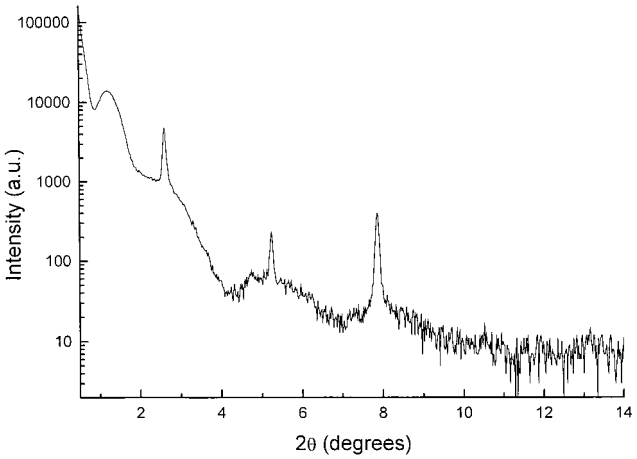

Figure 5. Room-temperature X-ray diffraction patterns for 1:1 mixture of **1** and **3**.

spacing correspond to medium-angle reflections of **1** itself. However, a large difference in the intensity distribution of reflections was observed indicating a difference in the in-plane organization. In particular, the intensity of the third reflection was larger than the intensity of the first and second reflections. This could be attributed to superhelical molecular organization, but X-ray data alone cannot confirm this. Optical microscopic observation of birefringent crystal confirms the discussed difference in the X-ray patterns.

Conclusions

The results reported here demonstrate the versatility of the approach for making molecular self-assemblies. They illustrate the ability to direct self-assembling process by altering the molecular packing with the aid of bipys. They show that by modifying the geometry and angle of headgroup interaction one can control the microscopic morphologies, adding thus another facet to the design and manipulation of supramolecular polymers and liquid crystals.[1,4] Combined data from microscopy, DSC, and X-ray diffraction on the systems show that textures, physical properties, and molecular packing of **1** are affected differently when 2,2′ or 4,4′ bipy interacted with carboxylic groups. One may also use carboxylic headgroup of an amphiphile for bipy-like compounds for building an ordered array. Efforts are underway to incorporate photochromic complementary molecules with the aid of **1**, including the stabilization of assemblies to render them technologically attractive.

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