Supramolecular Organization of ±Camphor-10-sulfonic Acid and *N*,*N*-Dimethyl Formamide into Giant Spherulites

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Received: March 16, 2004; In Final Form: April 23, 2004

Cast films of ±camphor-10- sulfonic acid (CSA) from *N*,*N*-dimethyl formamide (DMF) produced giant spherulites (diameter ≈ 1 cm) after isothermal crystallization at 50−62 °C. They did not exhibit any color under ordinary visible light, but when observed through a polarizing microscope, they showed different colors at different angles of the polarizer. The color also depends on thickness of the film from which giant spherulites are produced. IR study indicates supramolecular organization of CSA and DMF by H bonding, and elemental analysis suggests that the complex be produced in a 1:1 molar ratio of the components. The X-ray and differential scanning calorimetry study concludes that the supramolecular crystal is different from that of CSA. Similar results are obtained when cast films of CSA from *N*,*N*-dimethyl acetamide are crystallized but casting from methyl formamide/formamide produce only liquid crystalline texture.

Over the past quarter century, the supramolecular chemistry field has grown very fast, bridging the gap between the macro world and the atomic world.[1] Its aim is to gain progressive control over structural and dynamic features of matter through noncovalent interactions.[2] The formation of smart supramolecular materials by the self-assembly process is a new and important area of research in material science. Many supramolecular architectures with mesomorphic property,[3] functionizable nanoporous material,[4] sensors and nanoelectrodes,[5] etc. are produced. Here the noncovalent interactions such as hydrogen bonding, donor−acceptor interaction, etc., and molecular recognition processes are used to generate the above materials.[6] In this communication, we report a new system of self-assembly that can produce spherulites of centimeter size, showing different colors at different polarized lights and also at different film thicknesses.

±Camphor-10-sulfonic acid (Fluka) (CSA) dissolved in *N*,*N*-dimethyl formamide (DMF) (2% w/v) is dried on a hot plate at 60 °C and finally in a vacuum at 60 °C for 3 days. The sample taken on a microscopic glass slide is melted at 140 °C and is spread fully with a coverslip. The sample on isothermal crystallization at 50−62 °C in a Mettler hot stage (FP-82) produced giant spherulites (Figure 1), filling the entire coverslip. Crystallization at lower temperature, however, produces spherulites of a smaller size, and above 62 °C, no such spherulites are produced. For thin samples, the spherulites did not exhibit any color (Table 1), but thicker samples produced color that changes at different polarization angles (Figure 2). Also, the thicker samples produced smaller-sized spherulites probably because of higher nucleation density.

The formation of giant spherulites from small molecules is interesting, and it might be due to formation of supramolecular polymers from the CSA and DMF molecules. The proton of the sulfonic acid group of CSA makes hydrogen bonds with the carbonyl group of DMF as evidenced from the IR spectra of the samples (Supporting Information Figure 1). The −OH stretching frequency of the sulfonic acid group at 2966 cm^{-1} decreased by 8 cm^{-1}, and the carbonyl peak position of DMF decreased from 1666 to 1630 cm^{-1} in the DMF/CSA complex.

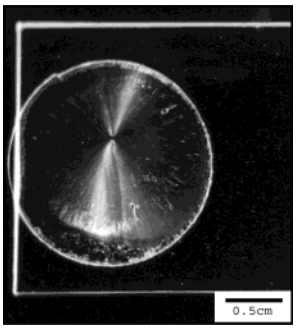

Figure 1. A normal picture of a giant spherulite produced by isothermal crystallization at 50 °C on a glass slide under a nitrogen atmosphere of CSA−DMF system. (Thickness = 0.024 mm.)

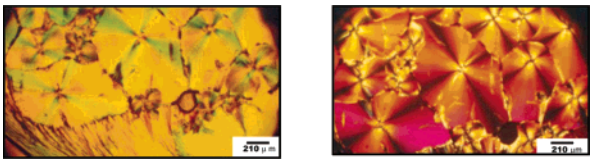

Figure 2. Optical micrograph of CSA−DMF giant spherulites (thickness = 0.110 mm) under (a) 45° crossed and (b) 90° crossed polarized light.

TABLE 1: Variation of Color of CSA−DMF Giant Spherulites with Polarization Angle and Thickness of the Film

thickness of film (mm)	90° crossed polarizer	45° crossed polarizer
0.04	colorless	colorless
0.06	yellow	colorless
0.092	orange	yellow
0.103	red	yellow
0.115	purple	greenish yellow
0.128	indigo	orange
0.134	bluish green	brick red
0.147	fluorescent green	red

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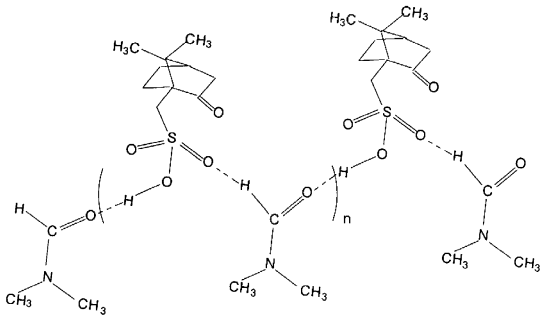
10.1021/jp048824g CCC: $27.50
Published on Web 05/08/2004

CHART 1: A Schematic Model of CSA−DMF Supramolecular Polymer



(the value of n is not known)

Also, the C−H deformation peak at 1389 cm^{-1} of DMF disappeared in the complex, indicating some interaction of this hydrogen with the S═O group of CSA.[7] The elemental analysis of the complex (Perkin-Elmer Series II, CHNS/O analyzer, 2400) indicates 4.78% nitrogen, 7.80% hydrogen, and 51.2% carbon. The results correspond to a 1:1 complex (molar ratio) of the components. A schematic model of the complex is shown in Chart 1.

The wide-angle X-ray scattering (WAXS) pattern of the supramolecular complex (Figure 3) is quite different from that of CSA used in this work. Thus, the giant spherulite has a different crystal structure than that of pure CSA. The melting behavior of the complex is quite different from the pure CSA (Figure 4). The complex (melted at 200 °C and quenched to −10 °C) exhibits both an exotherm and an endotherm upon heating from −10 °C at the heating rate of 10 °C. The exotherm appeared at 55 °C, whereas the endotherm appeared at 107 °C. The ΔH values in the exotherm and endotherm are almost equal to each other, indicating the supramolecular crystals are produced during heating (cold crystallization). Isothermal crystallization at 62 °C indicates a very high growth rate (0.563 mm/min) measured from polarized optical microscopy. Also the growth rates measured at different temperatures do not exhibit any negative temperature coefficient.[8] This indicates that the process is not nucleation controlled;[9] rather, it might occur during the supramolecular polymerization process, the supramolecular polymer being produced first followed by its rapid crystallization. As observed in the optical microscope, the giant spherulite is produced from the nucleation at a point as a small fibril followed by an evaluation of sheaflike and hedritic structures, and finally the growth and dendritic branching of radiating fibrils filled the whole space.

The optical property of the giant spherulites is very interesting (Table 1). The giant spherulites (thick or thin) do not exhibit any color under ordinary visible light. Also, the giant spherulites made from thin film have not exhibited any color by varying the polarization angle, but spherulites made from the thick films exhibit different colors at different polarization angles when viewed from the microscope (Leitz Biomed). For example, at a 90° angle of the polarizer (fully crossed), it is purple, and at a 45° angle (half crossed), it has a greenish-yellow color. This is probably due to the variation of the refractive index at different polarization angles. However, the reason for the difference in behavior of thick and thin film might be due to the different crystallite orientations of the polycrystals in the thick film, making the system optically anisotropic. This may cause the formation of orthogonal beams with their vibrations parallel to the extreme refractive index. When these are passed through an analyzer, interference colors are produced in the image and

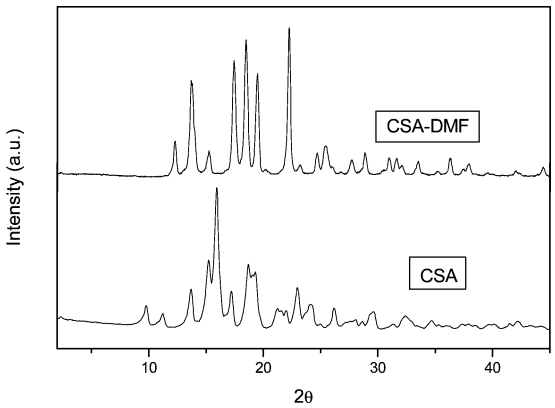


Figure 3. WAXS pattern of pure CSA and CSA−DMF giant spherulites produced at 50 °C.

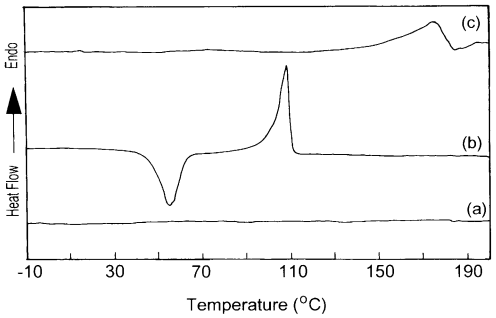


Figure 4. DSC thermograms of the CSA−DMF system: (a) cooled from the melt at 200 °C to −10 °C at the rate of 5 °C/min and (b) heated from −10 °C at the heating rate 10 °C/min to 200 °C. (c) DSC thermogram of CSA at the heating rate 10 °C/min.

it changes with thickness. Such a large spherulite may find its use in optical filters. The giant spherulites are somewhat hygroscopic, but adding some amount of poly(vinylidine fluoride) (PVF_2) sample (5% w/w) to it prohibits its hygroscopicity without losing the optical property and giant spherulitic structure.[10]

The formation of giant spherulites is interesting because such large-sized spherulites are not usually observed in conventional polymers. Apart from the CSA−DMF complex, the CSA−dimethyl acetamide complex produced a similar giant spherulite. But CSA−methyl formamide and CSA−formamide do not exhibit such giant spherulite structures under identical conditions; rather, a liquid crystalline texture appears. Probably in the former two systems molecular recognition and rigidity of the chain permit the formation of giant spherulites. A detailed study is in progress.

Acknowledgment. Swarup Manna acknowledges CSIR, New Delhi for providing the fellowship.

Supporting Information Available: FTIR spectra of the samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) In a previous publication,[11] we reported the formation of giant spherulites in the PVF_2−CSA system. The blends were made by casting from DMF and slowly cooled (5 °C/min) from the melt to 30 °C. The formation of giant spherulites in the PVF_2−CSA system probably may be due to either the PVF_2−CSA, PVF_2−DMF, or CSA−DMF systems. Here we observe no such structure if PVF_2 and CSA are mixed in the melt states. PVF_2 film cast from DMF does not exhibit a giant spherulite under isothermal crystallization. So it may be possible that CSA−DMF was the key part in forming the giant spherulites and PVF_2 being miscible there. A detailed mechanistic study of formation of such spherulites is under progress.

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