Novel Liquid-Crystal Phases Formed with Introduction of Chirality

Smectic liquid-crystalline systems are molecular structures whose constituent molecules are arranged in a series of layers with the molecules' axes perpendicular to the plane of the layers. The introduction of chiral, or "handed," compounds into such a system can lead to a wide variety of helical, polar, and frustrated macrostructures. I. Nishiyama of the Yokoyama Nano-structured Liquid-Crystal Project at JST in Japan, J.W. Goodby of the University of Hull, and their colleagues have recently demonstrated how the introduction of chirality into smectic liquid crystals can lead to novel liquid-crystal phases.

As reported in the August 24 issue of *Chemistry of Materials* (p. 3212), Nishiyama, Goodby, and JST colleagues J. Yamamoto and H. Yokoyama have investigated the molecular assembly of mixtures of the *R* and *S* chiral enantiomorphs (handedness) of bis{4′-(1-methylheptyloxycarbonyl)biphenyl-4-yl}alkanedioates. Five homologues of this chiral molecule can be distinguished: SS*n* (n = 2–5) and RR*n* (n = 4), each of which demonstrates a different phase-transition behavior.

All forms of this enantiomorphic compound are present as an isotropic liquid at temperatures above ~105°C and as a smectic liquid crystal at sufficiently low temperatures. Beyond that, interesting new phase transformations were observed, depending on the chiral composition of the materials. The even-membered chiral molecules (SS2, SS4, and RR4) were seen to transition into a mesophase, denoted as M_2, that exhibited a striped "parquet-like" texture. In addition, SS4 and RR4 formed another mesophase (M_1) between the isotropic liquid phase and M_2. This M_1 phase is characterized by its optical isotropy, regardless of orientation. Peaks observed during differential scanning calorimetry (DSC) experiments verify that M_1 and M_2 are thermodynamically real phases rather than simply transient or metastable molecular organizations. Furthermore, these phases represent "highly chiral" versions of the conventional antiferroelectric phase observed at intermediate temperatures. The SS4–RR4 phase diagram (Figure 1) summarizes the compositional and temperature features of this enantiomorphic liquid-crystal system.

X-ray diffraction (XRD) analysis of the M_1 and M_2 phases showed only broad scattering features, indicating a liquidlike short-range order in both. The pattern obtained from M_1, the optically isotropic phase, is a ring of scattered intensity, indicating the possible formation of a layered structure. In contrast, discrete diffraction spots are observed for the M_2 phase, indicating that the assembled molecules with "parquet-like" texture have some three-dimensional (3D) crystalline order as well. These results were further investigated by measuring the frequency dependence of Young's modulus for the two mesophases. M_2 clearly demonstrated elastic behavior, consistent with the previously assigned 3D structure. M_1, on the other hand, had no elasticity, ruling out the existence of a layered or 3D structure. Although the nature of the structure remains unclear, the researchers suggested a "sponge" phase of randomly interconnected layer planes as a possibility. The combined results of DSC, XRD, and mechanical testing confirm the existence of new liquid-crystalline phases produced by the introduction of chirality into a smectic system.

ANDY FRANCIS

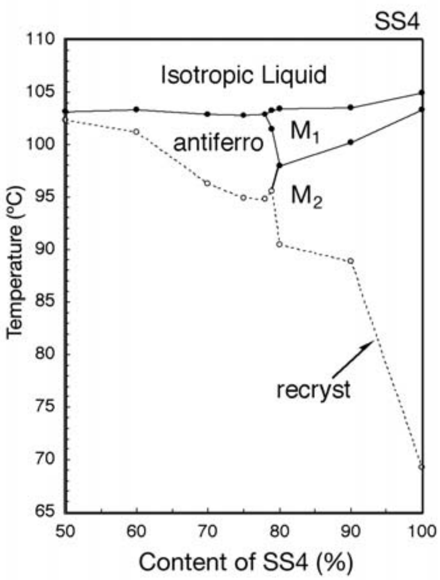

Figure 1. Phase diagram between chiral molecule SS4 and the racemic mixture (SS4:RR4 = 1:1). Reprinted in part with permission from Chem. Mater. ***16*** *(17) (August 24, 2004) p. 3213. ©2004 American Chemical Society.*

High-Strength Reticulated Porous Ceramics Fabricated by Two-Step Centrifuge Process

Reticulated porous ceramics (RPCs) are technologically important materials for a wide range of applications, including supports for space mirrors, molten metal fillers, catalyst supports, and heating elements. High-temperature stability and excellent thermal shock resistance are the properties responsible for their use in such diverse applications. RPCs are typically produced by the impregnation of a polyurethane sponge with a ceramic slurry. After slurry removal and drying, the sponge is burned out and the ceramic skeleton (struts surrounding pores) is sintered at high temperature followed by pressing. However, with traditional techniques such as the roll-press process, uniform, flaw-free structures are difficult to produce. X. Pu, X. Liu, F. Qiu, and L. Huang of the Chinese Academy of Sciences in Shanghai have developed a two-step process to increase the strength and further enhance the applications of RPCs.

The researchers used β-silicon nitride powder (mean particle diameter, d_{50} = 3 μm) as the matrix material, with 7 wt% alumina (d_{50} = 0.62 μm), 23 wt% silica sol, 1.5 wt% carboxymethylcellulose, and 0.2 wt% of Nopco 267-A, used as the sintering aid, binder, thickening agent, and antifoaming agent, respectively.

These results are reported in the July 2004 issue of the *Journal of the American Ceramic Society* (p. 1392). In the first coating stage, the polyurethane sponge was immersed in the ceramic slurry, compressed to ensure all pores were filled, and centrifuged to remove excess slurry. After drying the preform, the previous procedure was repeated. According to their results, the two-step process increases the structural integrity of the RPC due to enhanced adhesion between the body and slurry after the first coating. Pu and co-workers compared the weight of the sample between coating procedures and observed a twofold increase after the second coating procedure. To maintain structural integrity during centrifuging, the researchers suggested that the recoating step be done as quickly as possible.

According to Pu, the strut diameter and coating uniformity is strongly influenced by the viscosity of the slurry, especially after the second coating procedure. Optical photographs of the samples, taken after coating with slurries of various viscosities, show the increase in strut diameter and coating uniformity after the second coating. Furthermore, more viscous slurries produced thicker, more uniform struts with fewer flaws. The researchers said that in contrast to conventional processing techniques, this two-step process should also be successful in fabricating RPCs of irregular shape.

JEREMIAH T. ABIADE

Cracks in Rubber Propagate Faster than the Speed of Sound

Since the classical work by Griffith, Inglis, and Irwin on the physics of crack-