Macromolecules **2005,** *38,* 1525−1527

Communications to the Editor

Smectic Layered Polymer Networks Based on Side Chain Liquid Crystalline Polymers Having Thermally Reversible Urea Bonds

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Received November 15, 2004
Revised Manuscript Received January 18, 2005

Introduction. Layered solids having two-dimensional sheet arrangements, in which the constituents of the sheets are connected via strong bonds, e.g., covalent bonds, and the interactions between the sheets are relatively weak, are of great interest due to their having nanosized spaces between the layers.[1] Many layered inorganic or coordination compounds are known to exist, but layered structures are rarely found in synthetic organic materials.[2]

In this communication, we report the synthesis of a layered polymer network with a void space between the layers (Figure 1). We prepared a side chain liquid crystalline polymer showing a smectic phase. Mesogenic pendants were attached to the polymer backbone via thermally reversible urea bonds. Thermal annealing of the polymer in its smectic phase caused the urea bonds to be cleaved, generating isocyanato groups at the side chains. The subsequent reaction of the isocyanato groups in the same layer resulted in the creation of a polymer network sheet. The reaction between successive layers was not possible because of the wide layer spacing, except in the structural defects. The smectic layered structure was maintained even after the removal of the dissociated mesogenic side groups by solvent extraction. Various anisotropic materials have been prepared by liquid crystalline state polymerization,[3] but to our knowledge, this is the first example of a layered polymer network with a void space between successive layers.

Synthesis. Pendent mesogenic compounds (**3a**,**b**) were synthesized by the esterification reaction between biphenyl derivatives (**2a**,**b**) and 4-chlorocarbonylimidazole (**1**) (Scheme 1). The monomers (**4a**,**b**) were synthesized by the reaction between compound **3a** or **3b** and 2-isocyanatoethyl methacrylate (IEM). They were copolymerized with MMA by radical initiation to yield copolymers **5a** and **5b**. Copolymers **5a** and **5b** with 65% MMA units were readily dissolved in common organic solvents including THF and chloroform. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined by GPC in THF with polystyrene standards to be 11 000 and 33 300 for **5a** and 8310 and 20 800 for **5b**, respectively.

Mesomorphic Behaviors. The thermotropic properties of compounds **3a**,**b** and copolymers **5a** and **5b** were investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Compound **3a** showed enantiotropic mesophases at 222 ($\Delta H = 60$ J/g) ~ 231 °C ($\Delta H = 52$ J/g) on heating and 210 ($\Delta H = 63$ J/g) ~ 176 °C ($\Delta H = 11$ J/g) on cooling. Compound **3b** with a longer alkyloxy tail, also showed similar thermotropic mesophases, at 209 ($\Delta H = 52$ J/g) ~ 231 °C ($\Delta H = 51$ J/g) on heating and 198 ($\Delta H = 54$ J/g) ~ 173 °C ($\Delta H = 10$ J/g) on cooling.

The POM study showed that copolymers **5a** and **5b** had mesophases from 131 to 167 °C and from 125 to 168 °C, respectively, on heating. Phase transitions on cooling were not observed because the copolymers were partially cross-linked in the melt state. In the DSC thermograms, the strong endothermic peaks at 210 °C for **5a** and 200 °C for **5b** were attributed to the melting of the mesogenic pendent groups (**3a** or **3b**) dissociated from the polymer backbones. The dissociation of the urea bonds was also confirmed by IR spectroscopy. Above 130 °C, the characteristic peak for the isocyanato groups at 2274 cm^{-1} became stronger, showing that the urea bonds were cleaved to generate isocyanato groups.

Figures 2(a1) and 2(a2) show the small-angle X-ray diffractograms of copolymers **5a** and **5b**, respectively, which were measured at room temperature after quenching from their LC states (155 °C), respectively. Two reflection peaks appeared, with d spacings of 35.1 and 17.6 Å (for **5a**) and 38.9 and 19.4 Å (for **5b**), indicating that these copolymers had smectic layered structures.

Preparation of Polymer Networks. The copolymers were annealed for 5 h in their smectic phases (155 °C). Following this, they became insoluble in common organic solvents, including THF, chloroform, and DMSO, indicating the formation of a network structure. In the IR spectra of the copolymers, a strong band appeared at 3420 cm^{-1}, corresponding to the N−H stretching vibration of urea groups, confirming that the polymer chains in the same layer were cross-linked by the reaction of the regenerated isocyanato groups. No reaction between successive layers could occur because of the wide layer spacing, except in the structural defects. We presume that part of the dissociated isocyanato groups were converted to amino groups by their reaction with moisture during the annealing process. The amino groups would be expected to react with the isocyanato groups, resulting in cross-linking between the polymer chains.[4] The annealed polymers showed the same diffraction pattern as that of the polymers in the LC states [Figures 2(b1) and 2(b2)].

The annealed polymers were washed in THF to remove the released side groups. Interestingly, they still maintained their smectic layered structures. The X-ray analysis showed five reflection peaks corresponding to

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10.1021/ma047645u CCC: $30.25

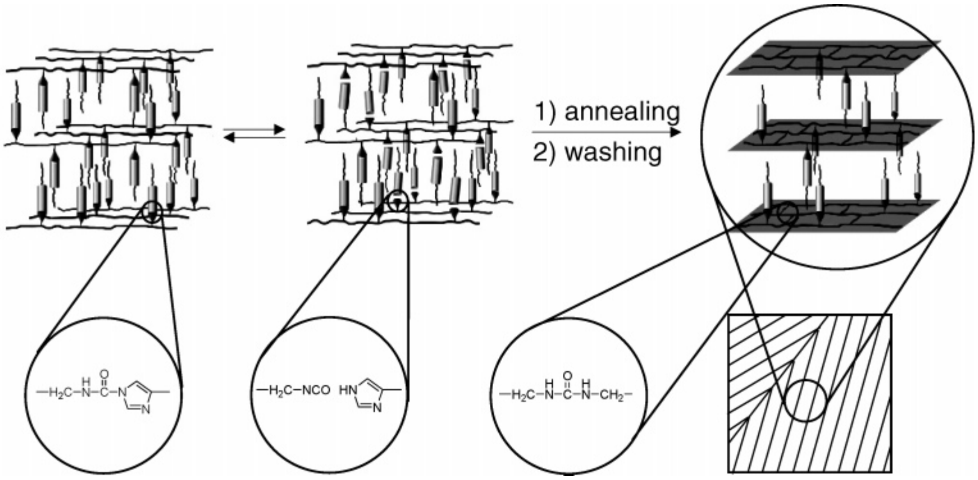
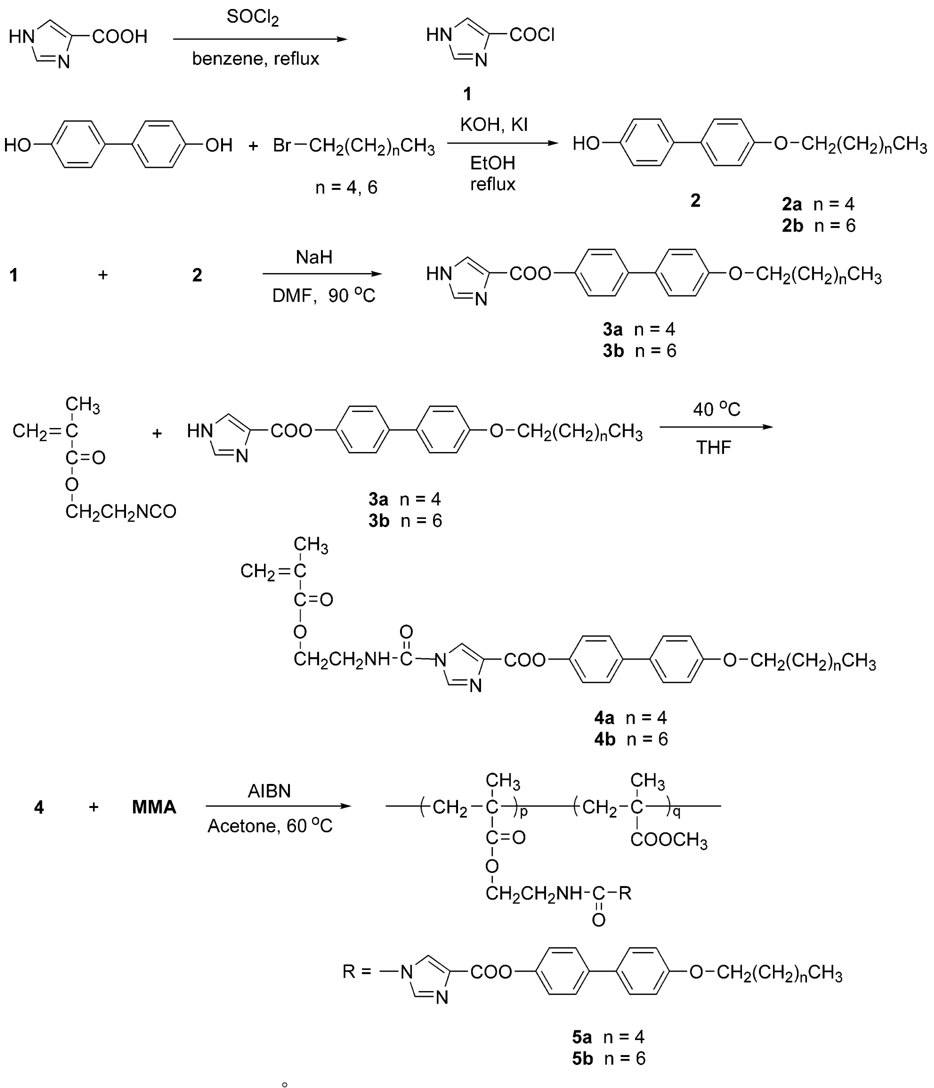


Figure 1. Schematic representation of the smectic layered network formed from **5a** or **5b**.

Scheme 1



d spacings of 38.6, 19.3, 12.9, 9.7, and 7.7 Å with a ratio of 1:2:3:4:5 for **5a** and two reflection peaks corresponding to *d* spacings of 40.1 and 20.5 Å with a ratio of 1:2 for **5b** [Figures 2(c1) and 2(c2)]. The slight increase in the layer spacing was attributed to the swelling of the polymer network during the process of washing in THF. Based on the weighing of the samples, 50% of the pendent mesogenic side groups (**3a** or **3b**) were found to have been removed from the polymer backbones. The removal of the mesogenic side groups by washing was also confirmed by solid-state ^{13}C NMR spectroscopy. The intensities of the peaks corresponding to the imidazole carbons at 141, 139, and 134 ppm and the phenyl carbons at 130, 129, and 126 ppm were reduced after washing.

The intriguing question was how the polymer network maintained its layered structure even after one-half of the mesogenic side groups were removed. The most

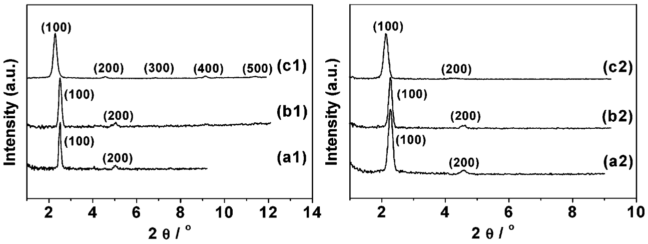


Figure 2. X-ray diffractograms of **5a** (left) and **5b** (right) measured at room temperature after quenching from LC states (155 °C) (a1, a2), annealing for 5 h at 155 °C (b1, b2), and washing in THF after annealing (c1, c2).

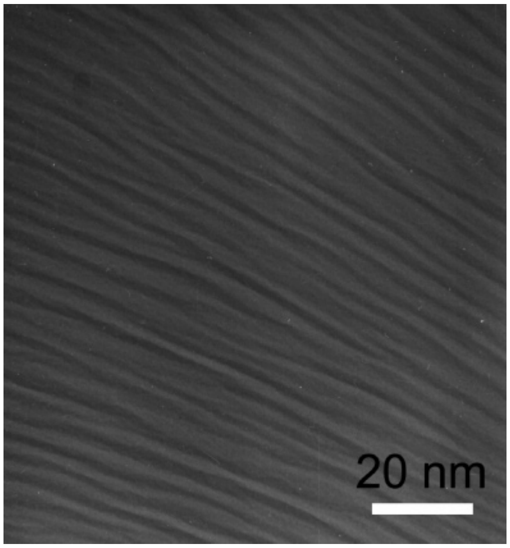


Figure 3. TEM image of the smectic layered polymer network obtained from polymer **5a**.

probable answer was provided by the TEM measurement. The bright-field TEM image of the smectic layered polymer network obtained from polymer **5a** is shown in Figure 3. Clear laminations with variations in the gaps are visible. The mean distance of the lamellar structure was about 4 nm, which corresponds to the distance shown in the XRD measurement. Variations in the lamination gaps suggested that a reaction between successive layers in areas of structural defects and/or the 3-dimensional warping of the lamellar structure likely occurred, thus preventing the collapse of the layered structure.

In summary, we prepared nanospaced polymer networks from side chain liquid crystalline polymers having thermally reversible urea bonds between the polymer backbones and the pendent mesogenic groups. The polymers had smectic layered structures in the LC state. The polymer networks formed through the reaction between the isocyanato groups dissociated from the urea bonds, when the polymer was annealed in the LC state. The polymer networks still showed smectic layered structures, even after the removal of the released side groups by solvent extraction. The approach described herein constitutes a new route to the synthesis of polymeric materials with voids.

Acknowledgment. This work was financially supported by the Hyperstructured Organic Materials Research Center at Seoul National University and National R&D Project for Nano Science and Technology.

Supporting Information Available: Experimental procedures of compounds **1**–**5**, DSC thermograms and POM images of compounds **3** and copolymers **5**, and solid-state ^{13}C NMR spectra of polymer **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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