

Preparation of Smectic Layered Polymer Networks Using Side Chain Liquid Crystalline Polymers Having Latent Reactive Monomeric Units

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Abstract: We prepared side-chain liquid crystalline polymers comprising two monomeric units, one having a mesogenic side group that could form a smectic mesophase and the other having a phenolic group attached to the polymer backbone via a thermally reversible urethane bond. The urethane linkage between the isocyanate and phenol groups was stable at room temperature, but it cleaved to generate an isocyanate group when the temperature was increased. When annealed, the copolymers in their smectic mesophases became insoluble in common organic solvents, suggesting the formation of network structures. XRD analysis showed that the annealed polymers maintained their smectic LC structures. The crosslinking process probably proceeded via the reaction of the dissociated isocyanate groups. Some of the isocyanate groups would have first reacted with moisture in the atmosphere to yield amino groups, which underwent further reaction with other isocyanate groups, resulting in the formation of urea bonds. We presume that only polymer chains in the same layer were crosslinked by the reaction of the isocyanate groups, resulting in the formation of a layered polymer network structure. Reactions between the layers did not occur because of the wide layer spacing.

Keywords: layered polymer network, side chain liquid crystalline polymer, thermally reversible bond, crosslinking reaction, pyrolysis.

Introduction

The synthesis of ordered polymeric networks is a challenging subject in materials chemistry. The most feasible way of synthesizing such materials is that molecules containing multi polymerizable groups are oriented before instigating polymerization. During the polymerization step, structural alterations need to be kept to a minimum. With this in mind, there has been intensive research focused on liquid crystalline (LC) state polymerization.¹ Liquid crystals have properties of both crystals and liquids. For instance, they have fluidity but simultaneously their molecules have orientational order like in crystals.² Small mass mesogenic compounds having vinyl groups attached to both of their ends through flexible spacers have been used for the polymerization. The polymerization of the compounds in a LC state was started by light activation of a photoinitiator to yield a network structure. In another approach, a side chain liquid crystalline polymer having functional groups was aligned in a LC state and then crosslinked by reaction with a bifunctional compound. Both methods offered satisfactory results in the sense that the rigid parts of mesogenic molecules

remained aligned in the network.

In our previous communication,³ we reported a novel way to synthesize layered polymer networks with nanospaces between the layers. Layered solid structures having two dimensional sheet arrangements, where the components of the sheet are connected via strong bonds (e.g. covalent bonds) and the interactions between the sheets are relatively weak, are frequently found in inorganic materials.⁴ However, these structures have been rarely achieved for synthetic organic compounds.⁵ For the layered polymer network synthesis, we used side chain liquid crystalline polymers having thermally reversible urea bonds between mesogenic imidazole pendants and vinyl polymers with isocyanate groups. The polymers showed smectic phases, and their thermal annealing in the LC state resulted in the formation of layered polymer networks.

In this work, we extended our approach to more general systems. We prepared side chain liquid crystalline polymers comprising two monomeric units, one having a mesogenic side group and the other having a phenolic group attached to the polymer backbone via a thermally reversible urethane bond. The urethane linkage between the isocyanate group and the phenol group was stable at room temperature, but when the temperature was increased, it cleaved to generate

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an isocyanate group. The mesogenic side groups were needed to induce smectic layered mesophases. We expected that the regenerated isocyanate groups in the LC phase would react with each other, leading to the formation of a layered network.

Experimental

Materials and Instrumentations. 1-Bromododecane (98%), hydroquinone (99%), 4,4'-biphenol (97%), methyl 4-hydroxybenzoate (99%), phenol (99%), dibutyltin dilaurate (95%), methacryloyl chloride (97%), 2-isocyanatoethyl methacrylate (98%), thionyl chloride (99%) were purchased from Aldrich Chem. Co. and used without further purification. Reagent-grade solvents were dried and purified as follows. Tetrahydrofuran (THF), acetone, and *N,N'*-dimethylformamide (DMF) were dried over sodium metal and distilled. Triethylamine (TEA), chloroform, and methylene chloride (MC) were distilled over calcium hydride. Methanol (MeOH) were dried over molecular sieves 4 Å and distilled. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were measured by using a Bruker Avance DPX-300 (300 MHz for ¹H NMR) spectrometer and Bruker Avance DPX-500 spectrometer (125 MHz for ¹³C NMR). IR spectra were obtained with the use of a PERKIN ELMER Spectrum 2000 Fourier transform infrared (FT-IR) spectrometer. Gel permeation chromatography (GPC) was carried out with a Viscotek Model 250 equipped with a RI750F refractive index detector from Younglin Instrument Co., Ltd. Styragel HR 4E and Styragel HR 5E columns from Waters were used as GPC columns with a flow rate of 1 mL/min at 35 °C by using THF as an eluent. Approximate calibration of the column was accomplished by means of narrow molecular weight polystyrene standards. X-ray diffraction (XRD) patterns were recorded by Bruker Xps GADDS (Cu K α radiation, $\lambda=1.54$ Å). Thermogravimetric analysis (TGA) was performed on a TA modulated TGA2050 with a heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) measurement was performed by a TA modulated DSC Q10 with a scanning rate of 10 °C/min under nitrogen. Elemental analyses were performed by an EA1110 analyzer (CE instrument). An optical microscopy study was performed by a Leica DM LP equipped with a Mettler Toledo FP 82HT heating stage and a Mettler Toledo FP 90 central process controller. Raman spectrum was obtained from a Jobin Yvon T64000 Raman system. The excitation was at 514 nm. The laser power was set to 35 mW.

Compound 1. To a solution of hydroquinone (20.0 g, 181.6 mmol) and triethylamine (30 mL, 215.2 mmol) in THF (200 mL) was added dropwise methacryloyl chloride (10.0 mL, 102.4 mmol) at 0 °C. The mixture was stirred for 2 h at room temperature. After filtration and evaporation, the product was isolated by column chromatography on silica gel (EA: *n*-hexane=1 : 2). Yield: 55%. ¹H NMR (CDCl₃): δ 6.94

(d, 2H, Ar), 6.75 (d, 2H, Ar), 6.34, 5.76 (s, 2H, vinyl protons), 5.53 (s, 1H, -OH), 2.05 (s, 3H, vinyl-CH₃). ¹³C NMR (CDCl₃): δ 167.21, 153.7, 144.26, 135.98, 127.85, 122.54, 116.35, 18.61. IR (KBr pellet, cm⁻¹): 3460, 1876, 1714, 1600, 1490, 1180. Anal. Calcd. for C₁₀H₁₀O₃: C; 67.41, H; 5.66. Found: C, 67.72, H, 5.67.

Compound 2. To a solution of methyl 4-hydroxybenzoate (5.0 g, 32.9 mmol) and potassium carbonate (5.9 g, 42.7 mmol) in acetone (120 mL) was added 1-bromododecane (8.1 mL, 33.7 mmol). The mixture was stirred for 24 h at 80 °C. After filtration and evaporation, the product was isolated by column chromatography on silica gel (EA : *n*-hexane = 1 : 9). Yield: 96%. ¹H NMR (CDCl₃): δ 7.97 (d, 2H, Ar), 6.89 (d, 2H, Ar), 4.02 (t, 2H, ArOCH₂-), 3.88 (s, 3H, COOCH₃), 1.77 (m, 2H, -OCH₂CH₂-), 1.26 (m, 18H, -CH₂-), 0.88 (t, 3H, -CH₃). ¹³C NMR (CDCl₃): δ 167.15, 163.19, 131.78, 122.53, 114.28, 68.43, 52.03, 32.14, 29.77, 26.20, 22.91, 14.33. IR (KBr pellet, cm⁻¹): 2920, 2850, 1726, 1600, 1260. Anal. Calcd. for C₂₀H₃₂O₃: C; 74.96, H; 10.06. Found: C; 74.64, H; 10.08.

Compound 3. To a solution of compound 2 (10.56 g, 33.0 mmol) in MeOH (100 mL) was added a solution of potassium hydroxide (5.4 g, 96.2 mmol) in water (100 mL). The mixture was refluxed for 2 h and then acidified by 1 N HCl. After filtration and evaporation, the product was isolated by column chromatography on silica gel (EA : *n*-hexane = 1 : 3). Yield: 97%. ¹H NMR (CDCl₃): δ 8.06 (d, 2H, Ar), 6.94 (d, 2H, Ar), 4.02 (t, 2H, ArOCH₂-), 1.77 (m, 2H, OCH₂CH₂), 1.26 (m, 18H, -CH₂-), 0.88 (t, 3H, -CH₃). ¹³C NMR (CDCl₃): δ 171.97, 163.92, 132.55, 121.59, 114.42, 68.52, 32.14, 29.77, 26.20, 22.91, 14.33. IR (KBr pellet, cm⁻¹): 2918, 2850, 2664, 2563, 1686, 1606, 1256. Anal. Calcd. for C₁₉H₃₀O₃: C; 74.47, H; 9.87. Found: C; 74.47, H; 9.99.

Compound 4. To a solution of compound 3 (6 g, 19.3 mmol) in chloroform (60 mL) was added a catalytic amount of DMF. The reaction flask was cooled in an ice bath and thionyl chloride (5.0 mL, 66.0 mmol) was added dropwise. Then, the ice bath was removed and the reaction mixture was stirred for 4 h at room temperature. After filtration and evaporation, the product was used for the next step without further purification.

Compound 5. To a solution of compound 1 (2.0 g, 11.2 mmol) in THF (80 mL) was added triethylamine (7.0 mL, 50.2 mmol). After stirring for 1 h at room temperature, compound 4 (3.2 g, 9.8 mmol) was added to the solution. The reaction mixture was stirred for 4 h at room temperature. After filtration and evaporation, the product was isolated by column chromatography on silica gel (EA : *n*-hexane = 1 : 2). Yield: 74%. ¹H NMR (CDCl₃): δ 8.14 (d, 2H, Ar), 7.18-7.21 (d, 4H, Ar), 6.95 (d, 2H, Ar), 6.38, 5.78 (s, 2H, vinyl protons), 4.04 (t, 2H, ArOCH₂-), 2.05 (s, 3H, vinyl-CH₃), 1.77 (m, 2H, -OCH₂CH₂-), 1.28 (m, 18H, -CH₂-), 0.89 (t, 3H, -CH₃). ¹³C NMR (CDCl₃): δ 165.97, 165.04, 163.82, 148.65, 136.01, 132.51, 127.58, 122.66, 114.54, 68.52, 32.14, 29.77, 26.20, 22.91, 18.61, 14.33. IR (KBr pellet, cm⁻¹): 2918, 2850, 1730,

1610, 1510, 1294, 1258, 1196. Anal. Calcd. for $C_{29}H_{38}O_5$: C, 74.65, H; 8.21. Found: C; 74.38, H; 7.79.

Compound 6. To a solution of 4,4'-biphenol (10.0 g, 53.7 mmol) and triethylamine (9.0 mL, 64.5 mmol) in THF (150 mL) was added dropwise methacryloyl chloride (3.7 mL, 37.9 mmol) at 0 °C. The mixture was stirred for 2 h at room temperature. After filtration and evaporation, the product was isolated by column chromatography on silica gel (EA : *n*-hexane = 1 : 2). Yield: 51%. 1H NMR ($CDCl_3$): δ 7.54 (d, 2H, Ar), 7.45 (d, 2H, Ar), 7.17 (d, 2H, Ar), 6.89 (d, 2H, Ar), 6.38, 5.77 (s, 2H, vinyl protons), 4.89 (s, 1H, -OH), 2.08 (s, 3H, vinyl- CH_3). ^{13}C NMR ($CDCl_3$): δ 166.35, 155.50, 150.1, 138.74, 136.10, 133.32, 128.57, 127.97, 127.91, 122.03, 115.92, 18.63. IR (KBr pellet, cm^{-1}): 3470, 1890, 1720, 1610, 1498, 1170. Anal. Calcd. for $C_{16}H_{14}O_3$: C; 75.57, H; 5.55. Found: C; 75.69, H; 5.64.

Compound 7. To a solution of compound **6** (1.5 g, 5.9 mmol) in THF (80 mL) was added triethylamine (5.6 mL, 40.2 mmol). After stirring for 1 h at room temperature, compound **4** (1.4 g, 4.3 mmol) was added to the solution. The reaction mixture was stirred for 4 h at room temperature. After filtration and evaporation, the product was isolated by column chromatography on silica gel (EA : *n*-hexane = 1 : 5). Yield: 71%. 1H NMR ($CDCl_3$): δ 8.18 (m, 2H, Ar), 7.63 (m, 4H, Ar), 7.18-7.29 (m, 4H, Ar), 7.00 (d, 2H, Ar), 6.38, 5.78 (s, 2H, vinyl protons), 4.05 (t, 2H, $ArOCH_2-$), 2.09 (s, 3H, vinyl- CH_3), 1.80 (m, 2H, $-OCH_2CH_2-$), 1.27 (m, 18H, $-CH_2-$), 0.90 (t, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ 166.13, 165.22, 163.83, 150.81, 138.38, 136.01, 132.53, 128.36, 127.57, 122.36, 121.69, 114.55, 68.57, 32.14, 29.88, 26.20, 22.91, 18.63, 14.34. IR (KBr pellet, cm^{-1}): 2918, 2850, 1732, 1610, 1500, 1292, 1218, 1170. Anal. Calcd. for $C_{35}H_{42}O_5$: C; 77.46, H; 7.80. Found: C; 77.65, H; 7.78.

Compound 8. To a solution of phenol (2.0 g, 21.3 mmol) and 2-isocyanatoethyl methacrylate (2.8 mL, 19.8 mmol) in THF (25 mL) was added dibutyltin dilaurate (2 mL) at room temperature. The reaction mixture was stirred for 5 h at 40 °C. After evaporation, the product was isolated by column chromatography on silica gel (EA : *n*-hexane = 1 : 3). Yield: 94%. 1H NMR ($CDCl_3$): δ 7.11-7.39 (m, 5H, Ar), 6.16, 5.63 (s, 2H, vinyl protons), 5.31 (t, 1H, -NH-), 4.33 (m, 2H, $-OCH_2-$), 3.61 (m, 2H, $-NHCH_2-$), 1.98 (s, 3H, vinyl- CH_3). ^{13}C NMR ($CDCl_3$): δ 167.55, 154.82, 151.13, 136.16, 129.54, 126.42, 125.64, 121.76, 63.77, 40.71, 18.55. IR (KBr pellet, cm^{-1}): 3336, 1740, 1700, 1542, 1494, 1306, 1256, 1210. Anal. Calcd. for $C_{13}H_{15}NO_4$: C; 62.64, H; 6.07, N; 5.62. Found: C; 62.51, H; 6.12, N; 5.55.

Polymerization. A typical procedure is as follows. Compound **5** (0.67 g, 1.44 mmol), compound **8** (0.04 g, 0.16 mmol), and AIBN (0.03 g, 0.18 mmol) were dissolved in THF (5 mL) in a 15 mL polymerization tube. After three freeze-thaw cycles, the tube was sealed under vacuum. The solution was stirred for 24 h at 60 °C. The polymer (**9**) was isolated by precipitation in methanol and purified by reprecipitation from the polymer solution in THF into methanol twice (yield: 75%). Polymer **10** was also prepared from compound **7** (0.70 g, 1.29 mmol), compound **8** (0.18 g, 0.72 mmol), and AIBN (0.03 g, 0.18 mmol) in a similar manner (yield: 72%). Polymer **9**: 1H NMR (CD_2Cl_2): δ 7.96(Ar, compound 5), 7.15(Ar, compound 5, 8), 6.85(Ar, compound 5), 4.22($-OCH_2-$, compound 8), 4.01($ArOCH_2-$, compound 5), 3.42($-NHCH_2-$, compound 8), 1.82($-OCH_2CH_2-$, compound 5), 1.56-1.31($-CH_2-$, compound 5, 8), 0.92($-CH_3$, compound 5, 8). Polymer **10**: 1H NMR (CD_2Cl_2): δ 8.03(Ar, compound 7), 7.49(Ar, compound 7), 7.19(Ar, compound 7, 8), 6.98(Ar, compound 7), 4.01($ArOCH_2-$, compound 7), 3.44($-NHCH_2-$, compound 8), 1.81($-OCH_2CH_2-$, compound 7, 8), 1.54-1.15 ($-CH_2-$, compound 7, 8), 0.90($-CH_3$, compound 7, 8).

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Results and Discussion

Synthesis. Figure 1 shows a schematic representation of a crosslinkable side chain liquid crystalline polymer. The polymer has two monomeric units, bearing a mesogenic pendent group and a latent reactive group. The former can induce the alignment of the polymer chains and the latter the crosslinking reaction between the polymer chains.

Synthetic routes for the mesogenic monomers (**5** and **7**) and the latent reactive urethane monomer (**8**) are outlined in Scheme I. Monomer **5** was prepared according the literature procedures.⁷ Hydroxyphenyl methacrylate **1** was synthesized by the reaction of methacryloyl chloride with hydroquinone. A long alkoxy tail was introduced onto the phenyl ring of methyl 4-hydroxybenzoate, by reaction with 1-bromodecane in acetone in the presence of potassium carbonate, to give compound **2**. The ester group of compound **2** was hydrolyzed and the resulting carboxyl group was converted to an acyl chloride using thionyl chloride to give compound **4**. Hydroxyphenyl methacrylate **1** was reacted with compound **4** to give mesogenic monomer **5**. Another mesogenic monomer **7** was prepared by the reaction of hydroxybiphenyl methacrylate **6**, which was prepared from methacryloyl chloride and 4,4'-biphenol, with compound **4**. The latent reactive urethane monomer **8** was prepared by the reaction of phenol with 2-isocyanatoethyl methacrylate, in THF, in the presence of a catalytic amount of dibutyltin dilaurate (DBTDL).

Monomers **5** and **7** were copolymerized with monomer **8** by free radical polymerization with AIBN as an initiator, in

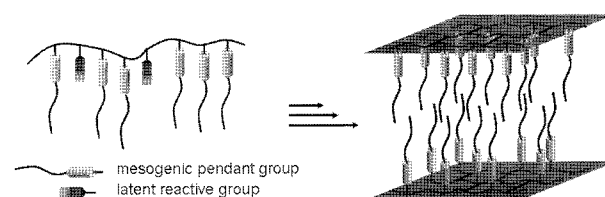
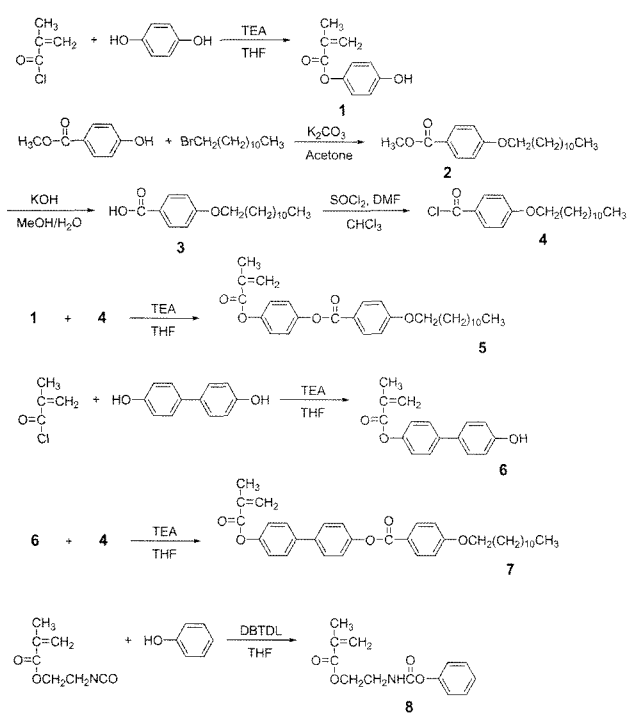
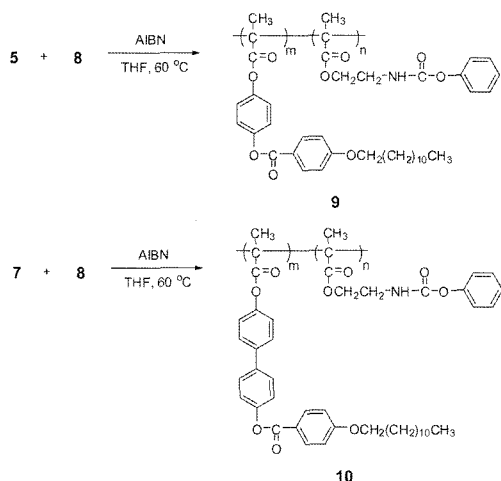


Figure 1. Schematic representation of the synthesis of a smectic layered polymer network from a crosslinkable side-chain liquid crystalline polymer.

Scheme I



Scheme II



THF and chloroform, respectively, at 60 °C. The number average molecular weight (M_n) and weight average molecular weight (M_w), measured by GPC in THF with polystyrene standards, were 19,000 and 70,000 for polymer **9** (obtained from monomers **5** and **8**) and 20,000 and 43,000 for polymer **10** (obtained from monomers **7** and **8**), respectively. The compositions of monomer **8** in the copolymers were determined by ¹H NMR spectroscopy to be 13% for polymer **9** and 25% for polymer **10**.

Thermal Reaction. The thermal dissociation of the urethane bond of monomer **8** into an isocyanate group and phenol was investigated by ¹H NMR spectroscopy in DMF-

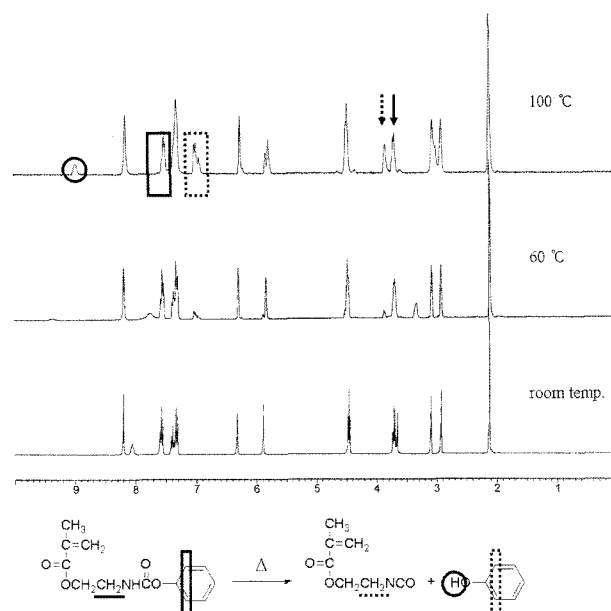


Figure 2. ¹H NMR spectra of compound **8** measured in DMF-*d*₇ at various temperatures.

*d*₇.⁶ The ¹H NMR spectra were measured at room temperature, 60 °C, and 100 °C (Figure 2). At room temperature, the peak associated with the methylene protons adjacent to the urethane bond showed up at 3.71 ppm. As the temperature was increased, a new peak corresponding to the same methylene protons appeared at 3.85 ppm. In addition, peaks for the OH and *ortho*-CH protons of phenol showed up at 7.0 and 8.9 ppm, respectively, indicating dissociation of the urethane bond.

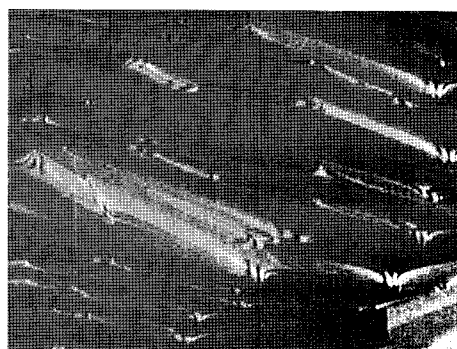
Mesomorphic Behaviors. The LC property of compound **5** has been previously reported.⁷ We reinvestigated the mesomorphic behavior of compound **5** in order to confirm its smectic layered LC structure. The compound showed a monotropic transition. In the differential scanning calorimetry (DSC) thermogram, two small peaks at 80 and 74 °C appeared on cooling. These correspond to an isotropic liquid to nematic phase transition and a nematic to smectic phase transition, respectively. Crystallization occurred at 67 °C. In the small-angle X-ray diffractogram of compound **5**, obtained after quenching from its LC state (70 °C), three reflection peaks corresponding to *d* spacings of 2.9, 1.5, and 1.0 nm appeared.

Compound **7** showed an enantiotropic transition. In the DSC thermogram, two sharp peaks at 111 and 118 °C and two small peaks at 152 and 203 °C appeared on heating, while two small peaks at 198 and 147 °C and two sharp peaks at 111 and 105 °C appeared on cooling. In the small-angle X-ray diffractogram of compound **7**, obtained after quenching from its LC state (130 °C), three reflection peaks corresponding to *d* spacings of 3.4, 1.7, and 1.1 nm, respectively. This suggests that the compound had a smectic layered

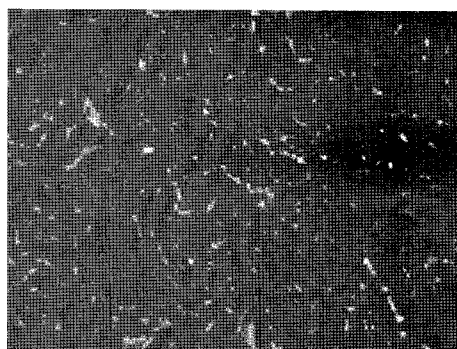
Table I. Phase Transition Temperatures and Enthalpies (in parentheses) for Compounds 5 and 7 as Determined by DSC (scan rate 10 °C min⁻¹)

Compound	Phase Transition Temperature (°C) and ΔH (kJ/mol)	
	2 nd Heating (°C)	2 nd Cooling (°C)
5	Cr 83 (56.7) I	I 80 (0.9) N 74 (0.7) Sm 67 (41.7) Cr
7	Cr 111 (6.8) Cr 118 (1.6) Sm 152 (0.2) N 203 (0.9) I	I 198 (0.8) N 147 (0.1) Sm 111 (2.3) Cr 105 (4.8) Cr

Cr: crystal; Sm: smectic phase; N: nematic phase; I: isotropic liquid.



(a)

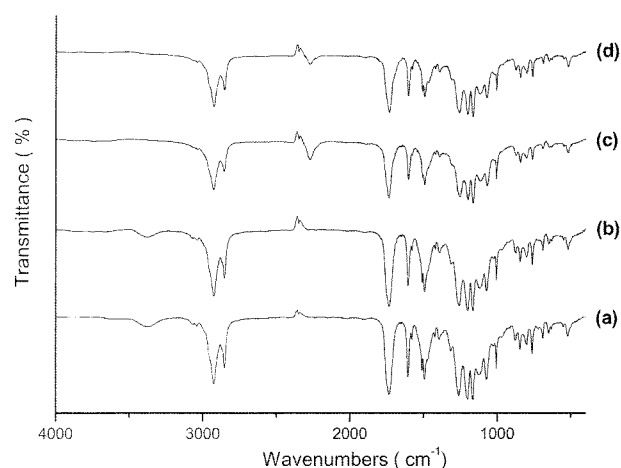


(b)

Figure 3. Polarized optical micrographs of (a) compound 5 obtained at 70 °C and (b) compound 7 obtained at 135 °C during the second cooling.

structure. Phase transition temperatures and corresponding enthalpy values for compounds 5 and 7 are given in Table I. Figure 3 shows the textures of the smectic phases of compound 5 and 7, as observed by polarized optical microscopy (POM) on cooling.

Copolymers 9 and 10 also showed liquid crystalline behaviors. The POM showed birefringent phases with non-specific textures in the range of about 100 to 180 °C for 9 and about 100 to 200 °C for 10. In the DSC thermogram of polymer 9, only one broad peak appeared at around 180 °C on heating and at around 175 °C on cooling. This corresponds to a LC phase to isotropic liquid transition and the reverse transition, respectively. Polymer 10 showed a broad

**Figure 4.** FT-IR spectra of polymer 10 obtained at (a) room temperature, (b) 100 °C, (c) 240 °C, and (d) 100 °C on cooling from 240 °C.

peak at around 220 °C on heating and a broad peak at around 200 °C on cooling. This again corresponds to a LC phase to isotropic liquid transition and the reverse transition, respectively. Since the transitions were observed over a wide range of temperatures, it was difficult to determine their enthalpy values. On the second cycle, the transition peaks became much broader than those observed in the first cycle. This is likely due to the copolymers being partially crosslinked in the melt state.

Figure 4 shows the IR spectra of polymer 10, obtained at various temperatures. For the IR measurement, a thin polymer film on a KBr pellet was prepared by the casting of a polymer solution in chloroform and subsequent drying. The spectra were recorded as the pellet temperature was increased at a rate of 10 °C/min. A characteristic peak for isocyanate groups, resulting from the dissociation of the urethane groups, began to show up at 2274 cm⁻¹ above 160 °C. However, the intensity of this peak was very low. This was attributed to the fact that the isocyanate groups were consumed rapidly by reacting with moisture, and thereby forming amino groups. The isocyanate groups could also react with the dissociated phenol, which would remain in the polymer film at temperatures below its boiling point (184 °C). A more distinct peak for the isocyanate group was observed when the sample was heated to 240 °C, in which case the dissociated phenol would have evaporated.

The small-angle X-ray diffractogram of polymer 9 showed that the polymer had a smectic layered structure in the LC state. In the small angle region, one reflection peak with a d spacing of 4.0 nm appeared, which corresponded to the layer thickness (Figure 5(a)). The polymer annealed at 155 °C for 5 h exhibited the same diffraction pattern to that of the polymer in the LC state (Figure 5(b)). The layered structure appeared to be disrupted after washing the annealed

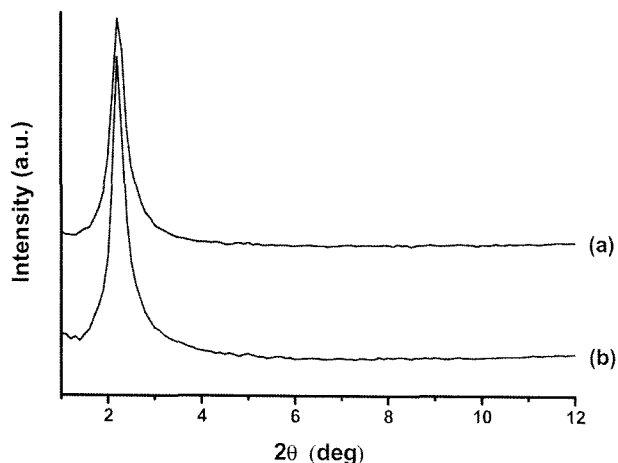


Figure 5. X-ray diffractograms of polymer **9** obtained at room temperature after (a) quenching from 155 °C and (b) annealing at 155 °C for 5 h.

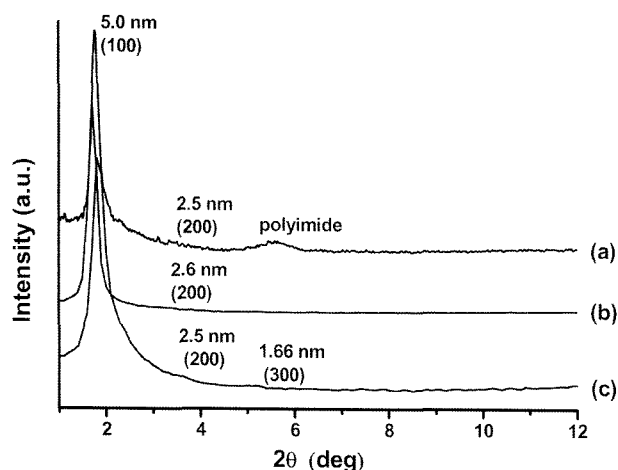
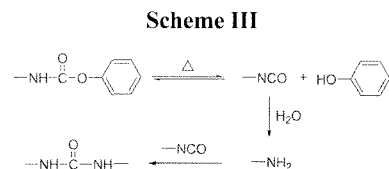


Figure 6. X-ray diffractograms of polymer **10** obtained at room temperature after (a) quenching from 155 °C, (b) annealing at 175 °C for 5 h, and (c) washing with methylene chloride after annealing.

sample in chloroform to remove the dissociated phenol molecules. This result was attributed to the low crosslinking density since only 13% of the repeating units had a thermally cleavable urethane bond. We attempted to increase the crosslinking density by incorporating more urethane monomer **8** into the polymer chain, but the resulting polymers didn't have layered structures.

Figure 6(a) shows the small-angle X-ray diffractogram of polymer **10**, which was measured at room temperature, after quenching from 155 °C. Two reflection peaks corresponding to d spacings of 5.0 and 2.5 nm appeared, indicating that the copolymer had a smectic layered structure. The copolymer was annealed at 175 °C, for 5 h. Following this, it became insoluble in THF, chloroform, and DMSO. This indicates the formation of a network structure. The annealed polymer showed a similar diffraction pattern to the polymer in the LC state, having two reflection peaks corresponding to d



spacings of 5.2 and 2.6 nm. The annealed polymer was washed with methylene chloride to remove the released phenol after which it still maintained its smectic layered structure, as shown in Figure 6(c).

The crosslinking process likely proceeded via the reaction of the dissociated isocyanate groups. Some of the isocyanate groups would have first reacted with moisture in the atmosphere to yield amino groups, which undergo further reaction with other isocyanate groups, resulting in the formation of urea bonds (Scheme III). Isocyanates are also known to undergo self-addition reactions to form dimers or trimers.⁸ We presume that only polymer chains in the same layer were crosslinked by the reaction of the dissociated isocyanate groups, resulting in the formation of a layered polymer network structure. Reactions between the layers would not occur because of the wide layer spacing.

The thermal degradation of polymer **10** was investigated by thermogravimetric analysis (TGA). Figure 7 shows TGA thermograms of polymer **10**. Before annealing, the polymer showed a weight loss at around 220 °C (corresponding to the evaporation of phenol) and had completely degraded above 420 °C. The annealed polymer showed greatly improved thermal stability. It was stable up to 300 °C and had a char yield of about 11% at 800 °C.

We explored the possibility of using the layered polymer network as a precursor of a carbon material. Annealed polymer **10** was pyrolyzed at 800 °C, for 5 min, under nitrogen.⁹ Preliminary experiments showed that the polymer was carbonized, having both ordered and disordered structures. A Raman scattering spectrum of carbonized polymer **10**

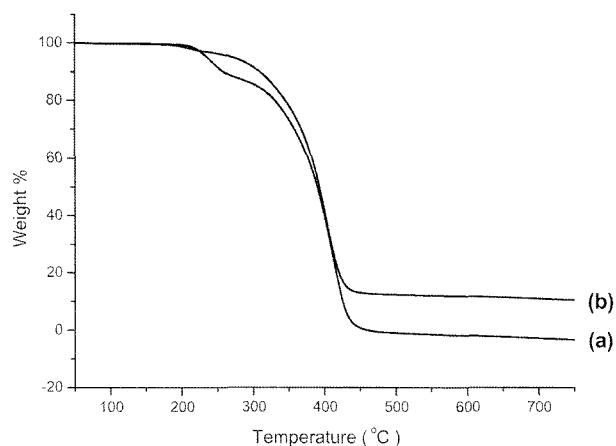


Figure 7. TGA thermograms of polymer **10**: (a) before annealing and (b) after annealing at 175 °C for 5 h.

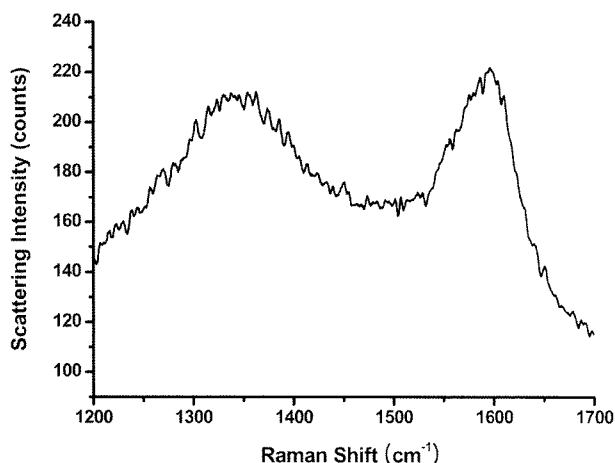


Figure 8. Raman scattering spectrum of polymer **10** after pyrolysis at 800 °C for 5 min under nitrogen.

exhibited partially graphitic carbon characteristics, with the D-band corresponding to disordered structures at 1362 cm^{-1} and graphitic G-band at 1595 cm^{-1} ,¹⁰ as shown in Figure 8.

Conclusions

We prepared polymer networks having nano-sized spacings between the layers using a side chain liquid crystalline polymer showing a smectic mesophase. We were able to control the spacing between the successive layers by changing the molecular length of the mesogenic unit. The pyrolysis of the layered polymer network yielded a partially graphitic carbon material. The approach described herein constitutes a new route to the synthesis of a layered organic material with a controlled spacing. This type of material has potential application as a catalyst support, a gas absorbent, or a precursor of a carbon nanomaterial.

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