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Macromolecules
NOTE

Preparation of Layered Polymer Networks by Cross-Linking Reaction of a Liquid Crystalline Polyphosphazene in a Smectic Phase

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Introduction

Liquid crystalline state polymerization of polymerizable mesogenic molecules is an attractive way to synthesize thermally and mechanically stable, anisotropic polymeric materials because of their unique phase properties showing both fluidity and molecular ordering.[1,2] They are macroscopically oriented by electric or magnetic fields, shearing, and on mechanically rubbed substrates.[3−8] In the synthesis of mesogenic monomers, polymerizable groups are attached to a mesogenic unit through a flexible spacer or introduced into a rigid part of a mesogene. The former will minimize the structural alterations during the polymerization.

For some time, we have studied the synthesis of nanomaterials using polymerizable mesogenic compounds.[9−16] For example, nanomaterials with columnar structures were obtained by polymerization of disklike mesogenic monomers in the columnar liquid crystalline state.[11,12] As part of this research, we became interested in the liquid crystalline state reaction of side-chain liquid crystalline polymers. In contrast to the polymerization of mesogenic monomers, the reaction of side-chain liquid crystalline polymers leads to cross-linking of the polymer chains, thereby resulting in the network structure. Given that the polymer has a layered liquid crystalline structure, the reaction produces layered polymer networks with a nanospace between the layers. Recently we synthesized the layered polymer network using side-chain liquid crystalline polymers in which mesogenic pendants were attached to the polymer backbone through thermally reversible urea bonds.[17] Upon thermal annealing in their smectic phases, isocyanate groups on the polymer backbone generated by dissociation of the urea bonds were reacted with each other to form layered polymer networks. Layered solid structures having two-dimensional sheet arrangements, where the components of the sheet are connected via strong bonds and the interactions between the sheets are relatively weak, are frequently found in inorganic materials.[18] However, these structures have rarely been achieved for synthetic organic compounds.[19]

In the present study, we report the synthesis of layered polymer networks from a liquid crystalline polyphosphazene. Polyphosphazenes are an interesting class of polymers with flexible backbones composed of alternating phosphorus and nitrogen. Various side groups can be attached onto the −P═N− polymer backbone by a substitution reaction of poly(dichlorophosphazene), which allows the polymers to exhibit a wide range of properties.[20,21] The most important advantage of using a polyphosphazene system for the layered polymer network synthesis is that mesogenic nucleophiles and thermal or photoreactive substituents can be attached simultaneously to the polyphosphazene backbone in one pot. Side-chain liquid crystalline polyphosphazenes bearing various mesogenic pendants were reported by Allcock and co-workers.[22−25] Several cross-linking routes are also available including chemical and photoirradiation methods and have been used to improve the physicochemical properties of functional polyphosphazenes.[26] Taking these synthetic advantages, we were able to synthesize a cross-linkable side-chain liquid crystalline polyphosphazene with ease. We report here the liquid crystalline state cross-linking reaction of the polyphosphazene and the structure of the resulting polymer network.

Experimental Section

Materials and Instruments. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (99%), 4,4′-biphenol (97%), 2-iodopropane (99%), 2-[2-(2-chloroethoxy)ethoxy]ethanol (99%), 2,2,2-trifluoroethanol (99+%), acetoxystyrene (99%), and sodium hydride (dry 95%) were purchased from Aldrich Chemical Co. Tetrahydrofuran (THF) was dried over sodium metal and distilled. ^{1}H and ^{31}P nuclear magnetic resonance (NMR) spectra were measured by a Bruker Avance DPX-300 (300 MHz for ^{1}H NMR) spectrometer and a Bruker Avance DPX-500 (200 MHz for ^{31}P NMR) spectrometer. All chemical shifts were listed in ppm downfield from tetramethylsilane (^{1}H NMR) and phosphoric acid (^{31}P NMR). Gel permeation chromatography (GPC) was carried out at 35 °C with a Viscotek Model 250 equipped with a RI750F refractive index detector from Younglin Instrument Co. Two 5 μm Waters columns (300 × 4.6 mm, MW 50−100 000 and 2000−4 × 10^6) were used with tetrahydrofuran (THF) as the elution solvent at a flow rate of 1 mL/min. Approximate calibration of the column was accomplished by means of narrow molecular weight polystyrene standards. X-ray diffraction (XRD) patterns were recorded by a Bruker Xps GADDS (Cu Kα radiation, 1.54 Å). The differential scanning calorimetry (DSC) measurements were performed by a TA modulated DSC Q10 with a scanning rate of 5 °C/min under nitrogen. Melting temperatures reported here correspond to the temperatures of the endothermic maxima. All the thermograms were baseline corrected and calibrated against indium metal. An empty aluminum pan was used as a reference. Elemental analyses were performed by an EA 1110 (CE Instrument) and a Flash 1112 (Thermo Electron Corp.). An optical microscopy (POM) 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.

Synthesis of Poly(dichlorophosphazene). Hexachlorocyclotriphosphazene was purified by recrystallization from *n*-hexane and sublimation at 55 °C under vacuum. Hexachlorocyclotriphosphazene (15 g, 43 mmol) and a magnetic stirrer were put into a 50 mL ampule which was dried under vacuum for 1 h and then sealed. The sealed ampule was placed in an oil bath at 250 °C with stirring. Polymerization was carried out for 3 h, and then

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the ampule was moved to the glovebox filled with dry argon gas. The ampule was broken, and the trimer was removed by sublimation at 55 °C under vacuum to give poly(dichlorophosphazene) (5.5 g).

Synthesis of 4-(4-Isopropyloxyphenyl)phenol (1). This compound was prepared according to the procedures in the literature[23] with minor modifications. 4,4′-Biphenol (4.7 g, 25 mmol) and potassium hydroxide (1.4 g, 25 mmol) were dissolved in ethanol (300 mL). 2-Iodopropane (5.3 g, 31 mmol) was added to the solution and stirred overnight at reflux temperature. After being neutralized with 35% hydrochloric acid, the solvent was evaporated. The residue was dissolved in chloroform (500 mL), and the solution was washed with water several times. The organic layer was dried with anhydrous magnesium sulfate. After filtration and evaporation, the product was isolated by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1/5 v/v) and further purified by recrystallization from ethyl acetate/*n*-hexane. Yield: 2.7 g (47%). ^{1}H NMR (DMSO-d_6): δ 7.46 (d, 2H, H^3 and H^5 of phenol), 7.40 (d, 2H, H^2 and H^6 of phenyl), 6.93 (d, 2H, H^3 and H^5 of phenyl), 6.81 (d, 2H, H^2 and H^6 of phenol), 4.61 (m, −OCHH, 1H), 1.27 (d, $-CH_3$, 6H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.83; H, 7.12.

Synthesis of 2-(2-{2-[(4′-Isopropyloxybiphenyl-4-yl)oxy]ethoxy}ethoxy)ethanol (2). This compound was prepared according to the procedures in the literature[23] with minor modifications. 4-(4-Isopropyloxyphenyl)phenol (1.9 g, 8.3 mmol) and potassium carbonate (1.4 g, 10 mmol) were dissolved in *N,N*-dimethylformamide (100 mL). 2-[2-(2-Chloroethoxy)ethoxy]ethanol (2.23 g, 13.2 mmol) was added to the solution and stirred for 12 h at 80 °C. After evaporation, the product was isolated by column chromatography on silica gel ($CHCl_3$/MeOH = 24/1 v/v) and further purified by recrystallization from ethyl acetate/*n*-hexane. Yield: 2.7 g (90%). ^{1}H NMR (DMSO-d_6): δ 7.52 (d, 2H, $H^{2'}$ and $H^{6'}$ of bphenyl), 7.51 (d, 2H, H^2 and H^6 of bphenyl), 6.99 (d, 2H, H^3 and H^5 of bphenyl), 6.95 (d, 2H, $H^{3'}$ and $H^{5'}$ of bphenyl), 4.62 (m, −OCHH, 1H), 4.57 (t, −OH, 1H), 4.10−3.45 (m, $-OCHH_2$, 12H), 1.27 (d, $-CH_3$, 6H). Anal. Calcd for $C_{21}H_{28}O_5$: C, 69.98; H, 7.83. Found: C, 70.04; H, 7.78.

Synthesis of 4-Vinylphenol (3). This compound was prepared according to the procedures in the literature[27] with minor modifications. Acetoxystyrene (10.0 g, 61.7 mmol) and sodium hydroxide (4.0 g, 100 mmol) were dissolved in ethanol (100 mL). The reaction mixture was stirred for 5 h at room temperature. After evaporation, the residue was dissolved in ethyl acetate (600 mL), and the solution was washed with water several times. The organic layer was dried with anhydrous magnesium sulfate. After filtration and evaporation, the product was isolated by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1/9 v/v). Yield: 6.1 g (82%). ^{1}H NMR (DMSO-d_6): δ 5.23 (d, $-C{=}CH_2$, 1H), 5.66 (d, $-C{=}CH_2$, 1H), 6.60−6.66 (q, −CH=C, 1H), 6.83 (d, 2H, H^2 of C_6H_4), 7.16 (d, 2H, H^3 of C_6H_4). Anal. Calcd for C_8H_8O: C, 79.97; H, 6.71. Found: C, 79.81; H, 6.80.

Preparation of Liquid Crystalline Polyphosphazene (LCPP). A solution of 4-vinylphenol (0.52 g, 0.43 mmol) in THF (20 mL) was added dropwise to a suspension of sodium hydride (0.011 g, 0.43 mmol) in THF at room temperature. This sodium salt solution was added to a solution of poly(dichlorophosphazene) (0.5 g, 8.6 mmol of Cl) in THF (100 mL) at room temperature, and the mixture was refluxed for 24 h. In a separate reaction, compound **2** (2.17 g, 6.02 mmol) was added to a suspension of sodium hydride (0.144 g, 6.02 mmol) in THF (100 mL). This second sodium salt solution was added to the polyphosphazene solution at room temperature, and the mixture was refluxed for 24 h. Finally a solution of sodium trifluoroethoxide prepared from 2,2,2-trifluoroethanol (0.43 g, 4.3 mmol) and sodium hydride (0.11 g, 4.3 mmol) in THF (100 mL) was added to the polyphosphazene solution at room temperature, and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature, and the polymer was precipitated into water.

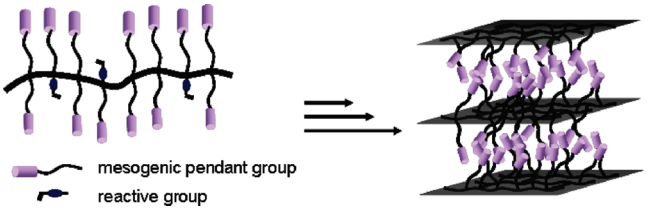


Figure 1. Preparation of the layered polymer networks from a cross-linkable, side-chain liquid crystalline polyphosphazene.

The polymer was purified further by precipitations from THF into water, methanol, and *n*-hexane and dried in vacuo to yield a rubbery solid. Yield: 82%. The number-average (M_n) and weight-average (M_w) molecular weight of the polymer measured by GPC in THF with polystyrene standards were 1.3×10^5 and 2.7×10^5, respectively. ^{1}H NMR (DMSO-d_6): δ 7.3, 6.8 (br, ArH), 5.2−5.7 (br, vinyl protons), (m, vinyl protons), 4.45 (br, $-CHMe_2$), 4.0 (br, CH_2CF_3), 3.6 (br, $-OCHH_2CH_2-$), 1.2 (br, $-C(CH_3)_2$). ^{31}P NMR (DMSO-d_6): δ −9.4, −7.5, −6.1.

Cross-Linking of LCPP. LCPP (0.1 g, $M_n = 1.3 \times 10^5$, $M_w = 2.7 \times 10^5$) and 2,2′-dimethoxy-2-phenylacetophenone (5 mg, 0.02 mmol) were dissolved in THF (20 mL). After evaporation of the solvent, the solid residue was dried at room temperature in vacuo. The mixture of the polymer and the photoinitiator was put on a quartz plate and heated up to 150 °C to become isotropic. The mixture was cooled to 115 °C to show the smectic phase and subjected to photoirradiation with a UV lamp (a high-pressure mercury arc lamp at 3 mW/cm^2) for 3 h. The cross-linked polymer film was peeled off from the quartz plate and washed with chloroform using a Soxhlet extractor for 12 h.

Results and Discussion

Figure 1 shows the preparation of the layered polymer networks from a cross-linkable, side-chain liquid crystalline polyphosphazene. The polymer has mesogenic pendants and cross-linkable side groups. The former induce the alignment of the polymer chains and the latter the cross-linking reaction between the polymer chains. We chose 2-(2-{2-[(4′-isopropyloxybiphenyl-4-yl)oxy]-ethoxy}ethoxy)ethanol (**2**) in Scheme 1 as a mesogenic substituent and 4-vinylphenol as a cross-linkable group. The liquid crystalline behaviors of the polyphosphazenes bearing biphenyl mesogenic compounds were studied in detail by Allcock and Kim.[23] The single substituent polyphosphazene bearing compound **2** was reported to show a smectic phase at relatively low temperatures probably due to the isopropyl tail. Although no X-ray analysis results have been presented in the literature,[23] we expected a wide layer distance based on the molecular length of compound **2**. On the contrary, a vinylphenoxy group could be attached directly to the polymer chain, which allowed a cross-linkable vinyl group to be close to the polyphosphazene backbone. Combined with the wide layer distance, this minimized the possibility of the cross-linking reaction between the polymer chains on the different layers in the smectic phase.

Biphenyl mesogenic compound **2** was prepared according to the literature procedure with minor modifications.[23] A reactive liquid crystalline polyphosphazene (LCPP) was prepared by sequential treatment of poly(dichlorophosphazene) with sodium salts of compound **2**, 4-vinylphenol (**3**), and trifluoroethanol in THF (Scheme 1). A sodium trifluoroethoxy group was used as a cosubstituent to impart flexibility as well as solubility to the polymer. In the ^{1}H NMR spectrum, the vinyl proton peaks appeared at 5.2−6.2 ppm. The peaks corresponding to methylene protons of 2,2,2-trifluoroethoxy and mesogenic groups appeared at 4.0 and 3.6 ppm, respectively. The substitution ratio of each side group was determined from the peak area ratio in the ^{1}H NMR spectrum.

The molar ratio of the cross-linkable group to the mesogenic group in the polymer was easily controlled through their sequential addition. We prepared a polymer having a ratio of 0.5/7.0/2.5 for the vinylphenoxy/mesogenic/trifluoroethoxy groups. ^{31}P NMR spectroscopy showed three resonances at around −6.1, −7.5, and −9.4 ppm. The biggest peak at −7.5 ppm was assigned to the mesogenic group substituted phosphorus nuclei. The other two peaks at −6.1 and −9.4 ppm were assigned to the trifluoroethoxy/mesogenic group and the vinylphenoxy/mesogenic group substituted phosphorus nuclei, respectively.

The single substituted polyphosphazene bearing mesogenic group **2** was reported to show a liquid crystalline phase between 106 and 125 °C on heating and between 121 and 101 °C on cooling.[23] The cosubstituted polymer (LCPP) also showed a similar enantiotropic transition. In the DSC thermogram, a sharp peak at 113 °C (ΔH = 12.39 J/g) and one broad peak at 136 °C (ΔH = 9.32 J/g) appeared on the heating scan, corresponding to a crystal to a liquid crystalline phase transition and a liquid crystalline to an isotropic phase transition, respectively. On cooling, two peaks also appeared at 130 °C (ΔH = −9.44 J/g) and 107 °C (ΔH = −12.36 J/g) (Figure 2). Uncharacteristic birefringent phases were observed on heating as well as cooling by POM.

In the small-angle X-ray scattering, obtained after quenching from its liquid crystalline state (115 °C), three reflection peaks corresponding to *d* spacings of 27.4, 13.7, and 9.12 Å were evident (Figure 3). The relative positions of these reflections were 1, 1/2, and 1/3, which were in good agreement with the (100), (200), and (300) reflections of a smectic phase. Since the fully extended length of the mesogenic unit was calculated to be about 23.7 Å using a simple molecular modeling (MM2 method), the X-ray analysis result suggests a well-ordered, partially interdigitated layer structure.

The polymer was cross-linked in the liquid crystalline phase by UV irradiation in the presence of a photoinitiator. The mixture of the polymer and the photoinitiator (2,2-dimethoxy-2-phenylacetophenone, 5 wt %) was put on a quartz plate and heated up to 150 °C to become isotropic. The mixture was cooled to 115 °C to show the smectic phase and subjected to photoirradiation with a UV lamp. For the X-ray analysis, the cross-linked polymer film was peeled off and washed with chloroform using a Soxhlet extractor. In the small-angle X-ray diffractogram, three peaks appeared broadened after cross-linking, but the layer distance

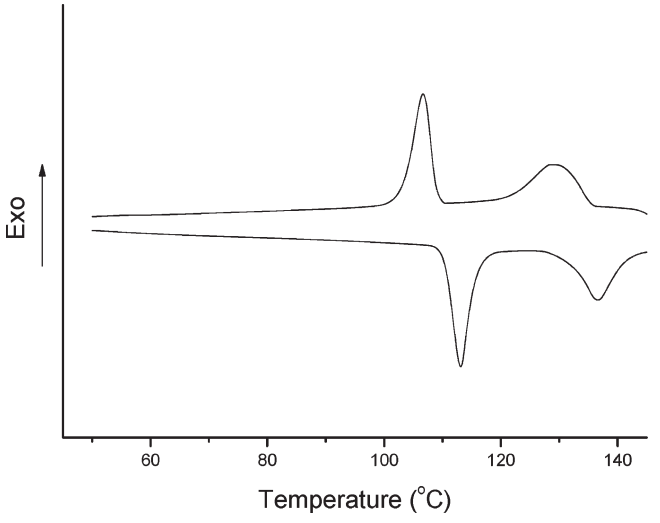


Figure 2. Differential scanning calorimetry thermograms of LCPP in Scheme 1 obtained on the second heating and on the second cooling.

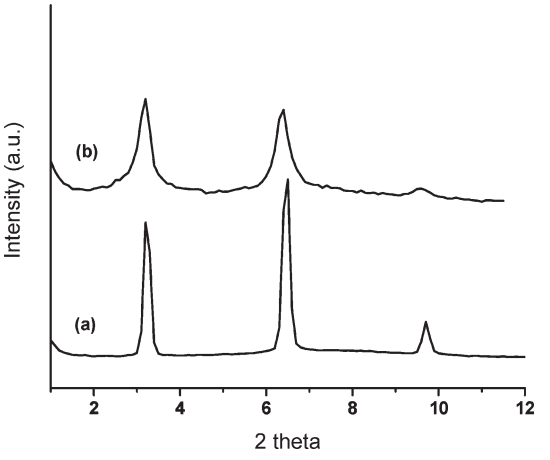
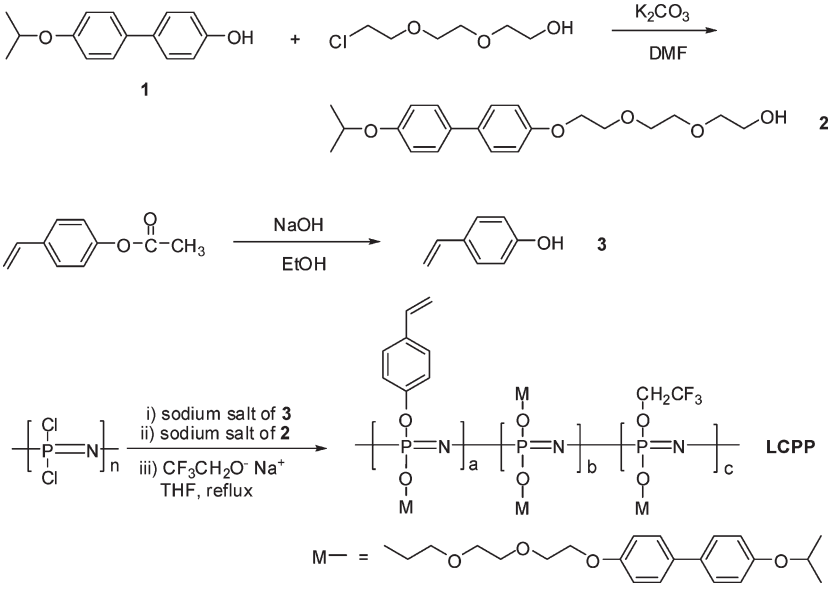


Figure 3. X-ray diffractograms of LCPP in Scheme 1 measured (a) after quenching from the liquid crystalline state (115 °C) and (b) after cross-linking reaction in the liquid crystalline state (115 °C) by UV irradiation for 3 h in the presence of 2,2′-dimethoxy-2-phenylacetophenone.

Scheme 1. Preparation of a Reactive Liquid Crystalline Polyphosphazene (DMF: *N*,*N*-Dimethylformamide; THF: Tetrahydrofuran)



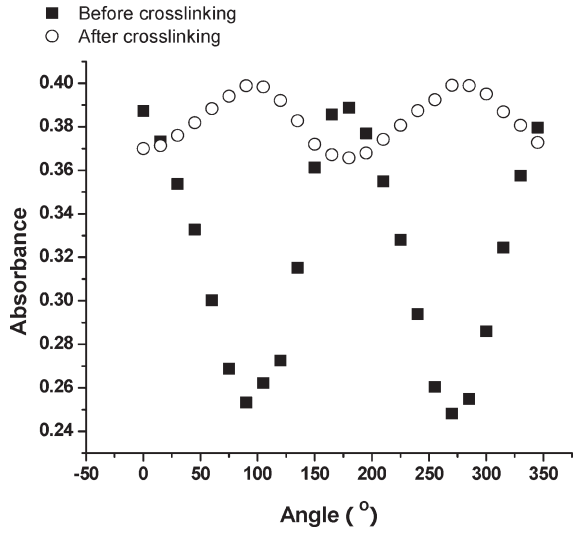


Figure 4. Polar plots of the absorbance of the IR peak of the biphenyl group of LCPP in Scheme 1 at 1607 cm^{-1} versus polarization angle.

was almost the same as that of the unreacted liquid crystalline phase of LCPP. We presumed that only the polymer chains in the same layer were cross-linked by the reaction between vinyl groups, resulting in the formation of layered polymer networks. Reactions between the layers did not occur because of the wide layer spacing.

We further investigated the structure of the cross-linked polymer film by IR spectroscopy. A mixture of LCCP and the photoinitiator (5 wt %) was placed between two KBr plates, heated to become isotropic, and cooled down to exhibit a smectic phase. The mesogenic groups of the polymer were aligned macroscopically by shearing. Figure 4 shows polar plots of the IR peak absorbance of the biphenyl groups at 1607 cm^{-1} versus the polarization angle,[28] measured before and after cross-linking. The angle $\theta = 0°$ corresponds to the polarization of the incident beam parallel to the shearing direction. This figure shows that the biphenyl mesogenic groups were mostly parallel to the shearing direction. After 3 h UV irradiation in the liquid crystalline state, however, this dichroism of the biphenyl band disappeared. Instead, very interestingly, weak dichroism was observed along the layer parallel direction. These results suggest that the aligned structure of the biphenyl mesogenic pendants was disrupted during cross-linking reaction between the vinyl groups on the polymer chains, but the layered structure was still maintained, as also observed in the X-ray analysis.

Conclusion

We prepared layered polymer networks from a side-chain liquid crystalline polyphosphazene having cross-linkable vinylphenoxy groups and mesogenic pendants. The polymer exhibited a smectic layered structure in the liquid crystalline state. The polymeric reaction was carried out by photoirradiation in the liquid crystalline state to produce layered polymer networks. The approach described herein constitutes a valuable route for the synthesis of nanospaced polymeric materials with potential applications in molecule storage.

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