Fixation of Multilayered Structures of Liquid-Crystalline 2:1 Complexes of Benzoic Acid Derivatives and Dipyridyl Compounds and the Effect of Nanopillars on Removal of the Dipyridyl Molecules from the Polymers

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A polymerizable benzoic acid derivative, 3,5-bis(propenoyloxymethyl)-4- hexadecyloxybenzoic acid (**1**), was synthesized and complexed in a molar ratio of 2:1 with each of the dipyridyl compounds 4,4′-bipyridyl (**2a**), 1,2-dipyridylethane (**2b**), 1,2-dipyridylethene (**2c**), and 1,3-dipyridylpropane (**2d**). All of these 2:1 complexes exhibited a monotropic smectic A liquid crystal phase. Complex compound $\mathbf{1}_2\cdot\mathbf{2b}$ (denoted **3b**) in the liquid crystal phase was photopolymerized by UV irradiation. As the polymerization proceeded, the multilayered structure of **3b** was maintained. In addition, the polymerizations of **3b** containing the polymerizable rodlike compound **PL** at concentrations of 5 and 10 mol % also proceeded in the smectic A phases while maintaining their multilayered structures. By treatment with dilute hydrochloric acid for 216 h, all of the **2b** molecules were removed from the polymer obtained from a mixture of **3b** and **PL** in a molar ratio of 90:10, though only 50% of **2b** could be removed from the polymer obtained from pure **3b**. This suggested that **PL** molecules cross-linked each pair of polymer sheets and functioned as nanopillars between the two sheets.

Introduction

Control of nanostructures has attracted much attention for preparation of functional materials,[1–7] and self-assembly in liquid-crystalline states is a very useful tool for constructing highly ordered nanostructures.[8–11] Polymerization of molecules that have been self-organized in liquid crystal phases is especially important for preparation of materials with excellent molecular alignment, thermal stability, and mechanical strength.[12–16] These polymers also exhibit specific features in their electronic[17–19] and optical[20–22] properties because of their well-organized nanostructures.

Polymerization in liquid crystal phases has also been applied in "molecular molding", in which polymerization of monomers doped with template molecules followed by removal of the template molecules forms "molecular molds" (empty nanospaces with the shape and size of the template molecules) in the polymer. Materials possessing molecular molds find application in molecular recognition, separation, and catalysis. Lyotropic liquid crystals are often used for preparation of these materials.[23–31] For example, in recent years, nanoporous polymers functioned as catalysts,[27–30] and

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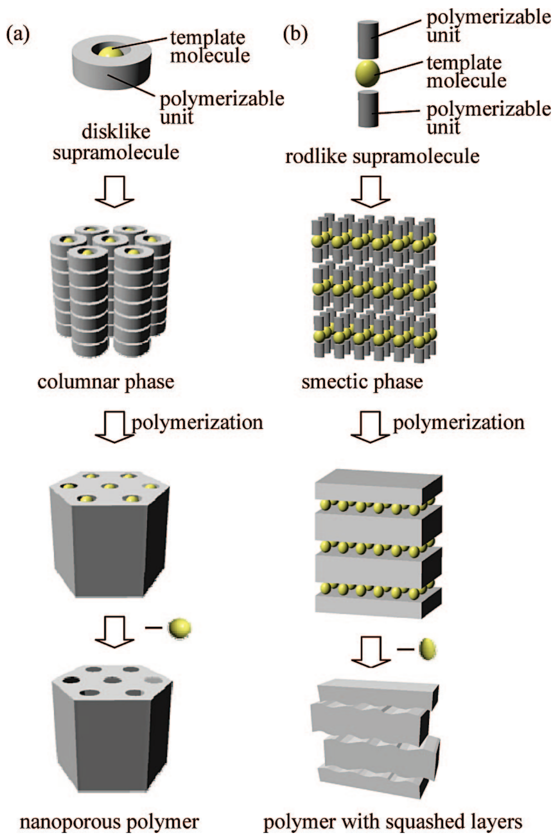

Figure 1. Schematic representation of the fabrication of molecular molds. (a) In a hexagonal columnar phase, polymerization followed by removal of the template molecules gives a nanoporous polymer. (b) In a smectic phase, a similar procedure gives a polymer with squashed layers.

nanoporous membranes[31] have been obtained by cross-linking of amphiphilic monomers in hexagonal columnar phases. Thermotropic supramolecular liquid-crystalline monomers in hexagonal columnar phases were also used for fabrication of nanoporous polymers.[32–34] It is assumed that these hexagonal columnar structures have the advantage that the pore size is maintained after removal of the template molecules because of the rigidity originating from their honeycomb structures (Figure 1a). Most of the template molecules can be removed from their inner spaces to give the nanoporous polymers without squashing the empty spaces. However, in the cases of lamellar (smectic) liquid crystal phases, the molecular molds in the polymer are squashed after removal of the template molecules (Figure 1b).

We have conceived a new methodology for preparing polymers with empty nanospaces using polymerization of smectic liquid-crystalline compounds. This approach involves introducing “nanopillars” between the layers in order to avoid squashing of the nanospaces after removal of template molecules. Figure 2 shows our concept in this study. We planned to synthesize a supramolecular compound exhibiting a smectic liquid crystal phase and having multiple polymerizable moieties in its constituent molecules from which a two- or three-dimensional polymer network could be obtained (**A1** in Figure 2). The supramolecular monomer would contain a rodlike template molecule between two polymerizable molecules. The template molecule would possess a hydrogen-bond acceptor at each end, and the polymerizable molecule would possess a hydrogen-bond donor, polymerizable units, and a flexible alkyl chain. A pillar molecule would also be designed as a rodlike molecule possessing a polymerizable unit at each end (**A2** in Figure 2). The **A1** supramolecules would be self-organized into a layered structure in the smectic liquid crystal phase (**B1** in Figure 2) and then photopolymerized to provide a sandwich structure having template molecules between the two polymer sheets (**B2** in Figure 2). The polymerization reaction would proceed only between polymerizable units within the layer because cross-linking between adjacent layers would be suppressed by the alkyl chain layers. In the past, most polymerizable

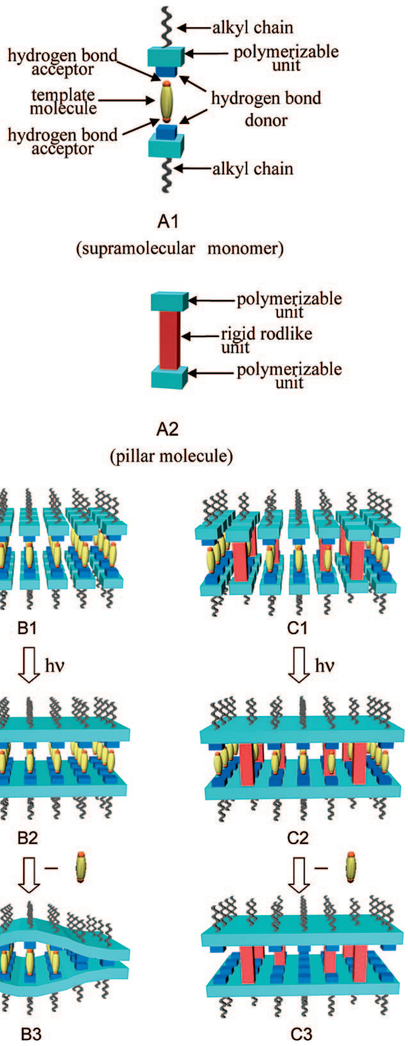

Figure 2. Schematic representation of the supramolecular monomer (**A1**), the pillar molecule (**A2**), and the processes (**B1** → **B2** → **B3** and **C1** → **C2** → **C3**) of constructing highly ordered polymers from **A1** and **A2**. **B1**: Smectic A phase of **A1** monomers. **B2**: Polymerized **A1** monomers with template molecules between the two polymer sheets. **B3**: Edge portions of the polymer sheets stick together after removal of some template molecules, preventing removal of the inner molecules from the polymer. **C1**: Smectic A phase of **A1** monomers doped with **A2** molecules. **C2**: Polymer obtained from the mixture of **A1** and **A2**. **C3**: Polymer sheets supported by nanopillars after removal of all of the template molecules.

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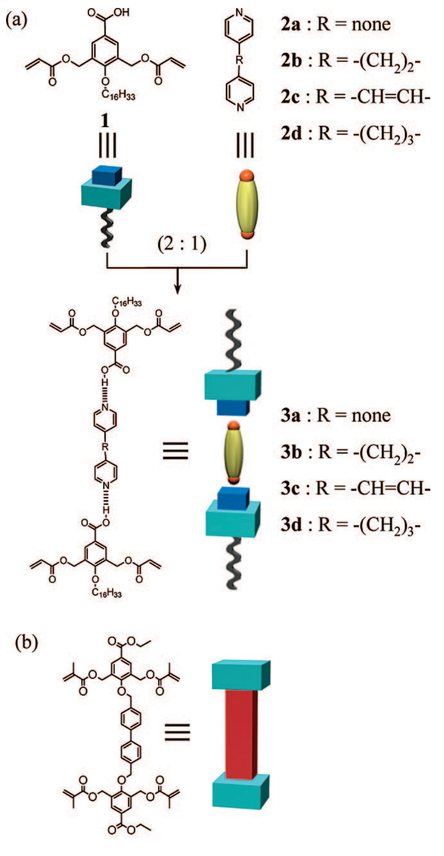

PL

Figure 3. Structures of (a) the supramolecular monomers **3a**−**d** and (b) the pillar molecule **PL**.

liquid-crystalline monomers possessed polymerizable moieties at the terminals of their alkyl chains,[18,24,26–34] and few of them possessed polymerizable units at the sides of the mesogenic cores.

We envisioned that removal of some of the template molecules from the sandwich structure **B2** would give a squashed layer structure (**B3** in Figure 2), preventing removal of the remaining template molecules from the inner spaces. In order to solve this problem, we planned to introduce nanopillars between the two polymer sheets by using photopolymerization of compound **A1** doped with **A2** in the smectic A phase (**C1** in Figure 2) to give pairs of polymer sheets cross-linked with nanopillars (**C2** in Figure 2). It was expected that smooth removal of the template molecules would be possible because the nanopillars would suppress the squashing of the empty space between the two polymer sheets (**C3** in Figure 2).

In order to implement our concept, we designed compounds **3a**−**d** as the rodlike supramolecular monomers (Figure 3a) and compound **PL** as the pillar molecule (Figure 3b). Compound **1** has two acrylate groups, a long alkyl chain, and a carboxyl group. Compounds **3a**−**d** are 2:1 complexes of **1** and the dipyridyl compounds **2a**−**d**, respectively. Compound **PL** has a rigid, rodlike core and four laterally introduced methacryloyloxy groups, and by design its two benzoate moieties point in the opposite direction from those of **3** in order to generate attractive intermolecular dipole–dipole interactions between the benzoate moieties of **PL** and **3**. In this paper, we describe the construction of unique multilayer structures reinforced by the nanopillars and successful removal of the template molecules.

Table 1. Phase Transition Behaviors of 3a−d[a]

compound	phase transition behavior
3a	$\mathrm{Cr\ 1} \xrightarrow{84.9\ (48.0)} \mathrm{Iso}$ $\mathrm{Cr\ 2} \xleftarrow[45.3\ (-2.3)]{} \mathrm{SmA} \xleftarrow[64.2\ (-2.0)]{} \mathrm{Iso}$
3b[b]	$\mathrm{Cr} \xrightarrow{71.6\ (14.1)} \mathrm{Iso}$ $\mathrm{SmA} \xleftarrow[66.1\ (-1.6)]{} \mathrm{Iso}$
3c[b]	$\mathrm{Cr} \xrightarrow{78.6\ (75.3)} \mathrm{Iso}$ $\mathrm{SmA} \xleftarrow[64.5\ (-1.0)]{} \mathrm{Iso}$
3d[b]	$\mathrm{Cr} \xrightarrow{67.7\ (54.3)} \mathrm{Iso}$ $\mathrm{SmA} \xleftarrow[65.8\ (-8.1)]{} \mathrm{Iso}$

[a] Transition temperatures (°C) and enthalpies of transition (in parentheses, kJ mol^{-1}) were determined by DSC (5 °C min^{-1}) and are given above or below the arrows. Cr1, Cr2, and Cr indicate various crystal phases. Iso and SmA indicate isotropic and smectic A phases, respectively. [b] The SmA−Cr transition was not observed.

Results and Discussion

Syntheses, Phase Behaviors, and Smectic-Layer Structures of 3a−d. Compound **1** was prepared from ethyl 4-hydroxybenzoate in four steps (see Scheme S1 in the Supporting Information) and mixed with each of the dipyridyl compounds **2a**−**d** in a 2:1 ratio to give the complexes **3a**−**d**, respectively, which had intermolecular hydrogen bonds between the pyridyl and carboxyl groups.[35]

The transition temperatures and enthalpies of **3a**−**d** were investigated using differential scanning calorimetry (DSC), and their phases were identified using polarized-light optical microscopy (POM). Whereas **1** itself did not exhibit any liquid crystal phase, complexes **3a**−**d** exhibited a smectic A liquid crystal phase only on cooling, and the supercooled mesophases of **3b**−**d** were maintained even at room temperature (Table 1). A microphotograph of **3b** in the smectic A phase is shown in Figure 4 and indicates the typical texture of the smectic A phases.

The superstructures of **3a**−**d** were investigated using X-ray diffraction (XRD) (Table 2). The XRD pattern of **3b** is shown in Figure 5. Most of the compounds showed a sharp *d*(100) peak with small *d*(200) and *d*(300) peaks in the small-angle region, indicative of a smectic layer structure (see Figure 5 and Figures S2−S4 in the Supporting Information). The *d*(100) spacings corresponded to the thicknesses of their layers. In all cases, each of the layer distances was much smaller than the molecular length of the corresponding supramolecule calculated by molecular modeling using Chem3D Ultra 7.0. This suggested that their alkoxy chains interdigitated between the adjacent layers (Figure 6).

Preparation of Mixtures of 3b and PL and Investigation of Their Layer Structures. Compound **3b** was selected as the monomer for the polymerization because its super-

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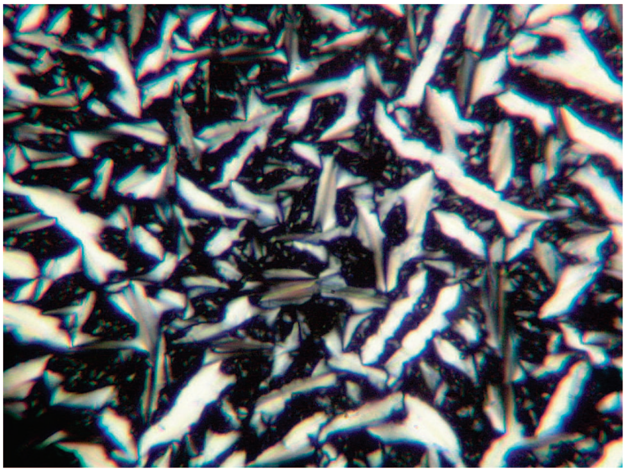

Figure 4. Microphotograph of **3b** (600×, 60 °C).

Table 2. Layer Distances [$d(100)_{obs}$] Observed Using XRD and Molecular Lengths Calculated by Molecular Modeling of 3a−d

compound	$d(100)_{obs}$ (Å)	molecular length (Å)[a]
3a	37.1	67.4
3b	37.4	69.6
3c	39.4	69.7
3d	36.4	62.1

[a] The molecular lengths of **3a**−**d** were calculated by molecular modeling using Chem3D Ultra 7.0.

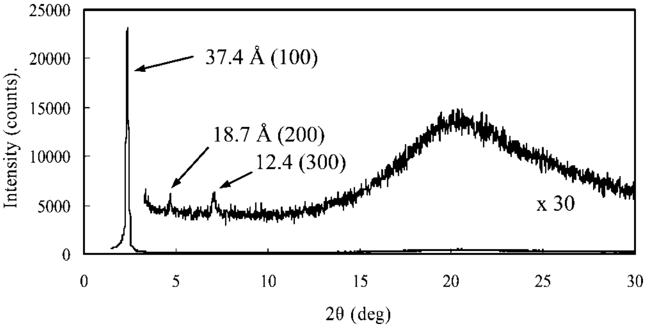

Figure 5. XRD pattern of **3b** at 40 °C. The numbers in parentheses are the Miller indices of the peaks.

cooled liquid crystal state was the most stable in the series **3a**−**d**. Compounds **3b** and **PL** were mixed in ratios of 95:5 and 90:10 to give mixtures **3b95**−**PL5** and **3b90**−**PL10**, respectively. In the POM of these mixtures, no segregation was observed, suggesting that the **PL** molecules were fully dispersed in these mixtures. Mixtures **3b95**−**PL5** and **3b90**−**PL10** also showed smectic A phases, and their thermodynamic behaviors and transition temperatures were similar to those of pure **3b** (see Table S1 in the Supporting Information). The XRD patterns of their smectic A phases (see Figure S5 in the Supporting Information and Figure 7, respectively) showed a single sharp *d*(100) peak corresponding to the layer distance, which was 0.7–0.8 Å longer than that of pure **3b**. These XRD data also suggested that the **PL** molecules were dispersed homogeneously in **3b95**−**PL5** and **3b90**−**PL10**, respectively, as shown in the molecular packing model (Figure 8).

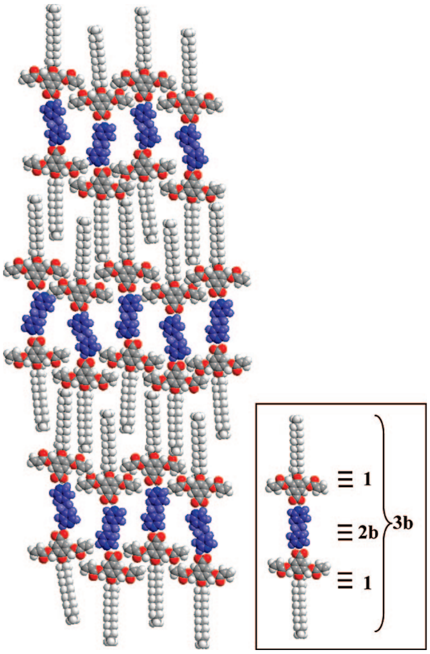

Figure 6. Molecular packing model of **3b** in the smectic A phase.

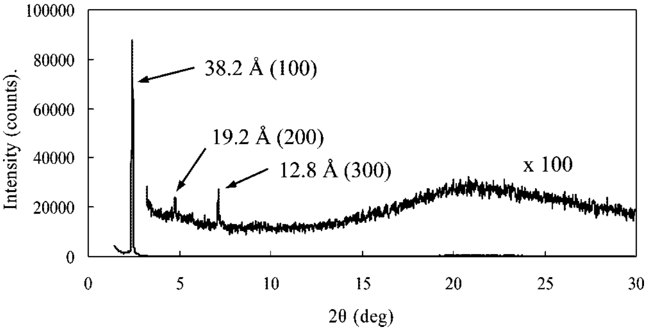

Figure 7. XRD pattern of **3b90**−**PL10** at 40 °C. The numbers in parentheses are the Miller indices of the peaks.

Photopolymerization of 3b, 3b95−**PL5, and 3b90**−**PL10 in Liquid Crystal States.** Samples of **3b**, **3b95**−**PL5**, and **3b90**−**PL10** in their smectic A liquid crystal phases were spread on glass plates, and polymerization was performed using a high-pressure mercury lamp at 40 °C for 8 h. The polymerization process was monitored using an IR spectrometer, and the acryloyl C═C stretch peak at 811 cm^{-1} disappeared after the irradiation. Polymerization of **3b**, **3b95**−**PL5**, and **3b90**−**PL10** proceeded to give the corresponding polymers, **P-3b**, **P-3b95**−**PL5**, and **P-3b90**−**PL10**, respectively. The polymers were pale-brown solids that were insoluble in common organic solvents. The XRD patterns of these polymers (see Figures S6−S8, respectively, in the Supporting Information) were similar to those of the respective monomer samples, although the layer distances of these polymers were 1.7, 1.0, and 0.8 Å longer than those of the corresponding monomers. Thus, it was confirmed that the layer structures of **3b**, **3b95**−**PL5**, and **3b90**−**PL10** were maintained upon polymerization.

Removal of the Template Molecules. To remove the template molecules (**2b**) from polymers **P-3b**, **P-3b95**−**PL5**, and **P-3b90**−**PL10**, samples of these polymers on glass plates were placed in 3 N hydrochloric acid, and the solutions were stirred at room temperature. The amount of **2b** extracted from each of the polymers into the solution was monitored using a UV–vis spectrometer. The intensity of the absorption band (λ_{max} = 255 nm) derived from the hydrochloride of **2b** increased

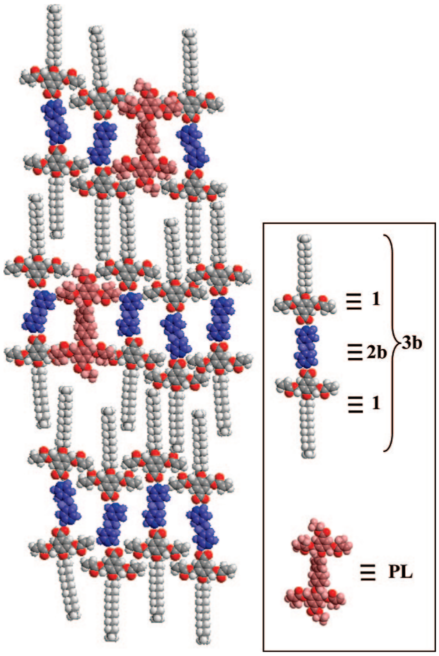

Figure 8. Molecular packing model of **3b**−**PL** in the smectic A phase.

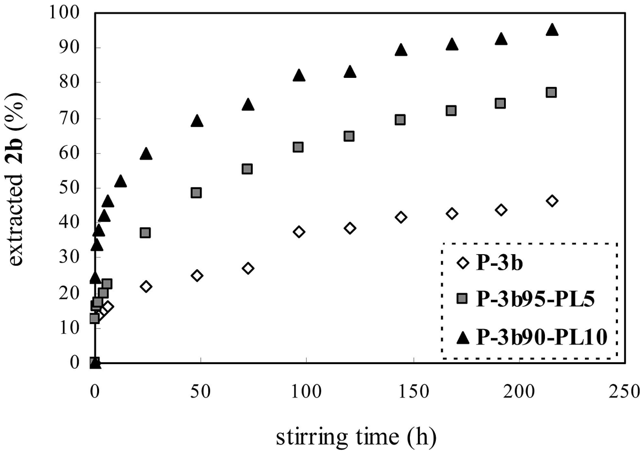

Figure 9. Plots of the percentage of **2b** extracted from polymers **P-3b**, **P-3b95**−**PL5**, and **P-3b90**−**PL10** into 3 N hydrochloric acid (as determined using UV–vis spectroscopy) as a function of stirring time. The thickness of the polymer films was 0.15 mm.

gradually. Figure 9 shows plots of the percentage of **2b** extracted from **P-3b**, **P-3b95**−**PL5**, and **P-3b90**−**PL10** as a function of stirring time. After the solutions were stirred for 216 h, 50% of the **2b** was removed from **P-3b**, whereas approximately 100% of the **2b** was removed from **P-3b90**−**PL10**. In the case of **P-3b95**−**PL5**, the extraction percentage at 216 h was 77%, which was almost halfway between those of the other two polymers. These results indicated that removal of the template molecules was improved by the addition of **PL** to **3b** because **PL** molecules played the role of nanopillars that kept intact the empty nanospaces between pairs of polymer sheets in the multilayered structure (see structure **C3** in Figure 2). After removal of the template, a portion of the polymer sample peeled off the glass plate, and the surface became rougher; nevertheless, two small peaks were obtained in the XRD pattern of **P-3b90**−**PL10** (Figure 10). Peak I (41.7 Å) was assigned to the layer distance, showing that the nanopillars supported the original layer distance even after removal of the template molecules.

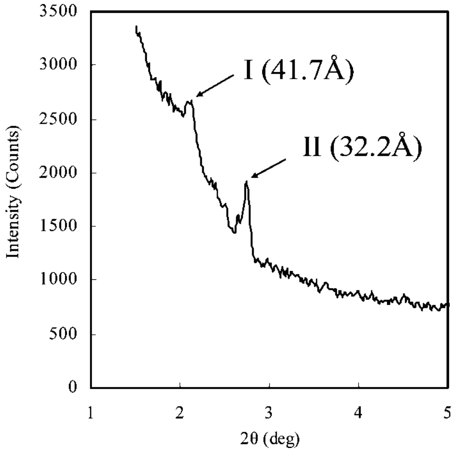

Figure 10. XRD profile of **P-3b90**−**PL10** after treatment with 3 N hydrochloric acid for 216 h.

This layer distance (41.7 Å) was slightly longer (2.7 Å) than that before removal of the template molecules (39.0 Å), and swelling of the polymers with water was thought to be the reason for this result. Water molecules from the hydrochloric acid solution could be included because the spaces possessed many hydrophilic carboxyl groups; the empty spaces should have been filled by water molecules. It was assumed that peak II (32.2 Å) was the layer distance for the pairs of the polymer sheets joined with hydrogen bonds between their carboxyl groups after removal of the template molecules. The difference between these two *d*(100) spacings was 9.5 Å, which was consistent with the molecular length of the template molecule **2b** (9.4 Å). These results suggested that the **PL** molecules functioned as nanopillars between pairs of polymer sheets and that there were empty nanospaces in the polymer after removal of **2b** molecules from **P-3b90**−**PL10**, although some of the empty spaces were squashed.

Conclusion

We have demonstrated that multilayer structures of polymerizable supramolecules in smectic A phases can be fixed by photopolymerization and that introduction of nanopillars improved the rates of removing template molecules. The layered polymers with empty spaces are assumed to be applicable for molecular recognition. Further work includes improvement of the strength of the nanostructures by introducing more-rigid pillar molecules and selective guest inclusion using the rigid nanostructures.

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Supporting Information Available: Procedures for the syntheses of **1** and **PL**, preparation of **3b**, **3b95**−**PL5**, and **3b90**−**PL10**, photopolymerization of **3b**, and removal of **2b**; phase transition behaviors of **3b**, **3b95**−**PL5**, and **3b90**−**PL10**; XRD patterns of **3a**, **3c**, **3d**, **3b95**−**PL5**, **P-3b**, **P-3b95**−**PL5**, and **P-3b90**−**PL10**; and microphotographs of **3c**, **3d**, **3b95**−**PL5**, **P-3b**, and **P-3b95**−**PL5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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