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Guest-Responsive Covalent Frameworks by the Cross-Linking of Liquid-Crystalline Salts: Tuning of Lattice Flexibility by the Design of Polymerizable Units

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Abstract: Cross-linked polymers prepared by the in-situ polymerization of liquid-crystalline salts were found to work as solid-state hosts with a flexible framework. As a component of such hosts, four kinds of polymerizable amphiphilic carboxylic acids bearing alkyl chains with acryloyloxy (A), dienyl (D), and/or nonreactive (N) chain ends (monomeric carboxylic acids; M_{AAA} , M_{ANA} , M_{DDD} , and M_{DND}) were used. The carboxylic acids were mixed with an equimolar amount of a template (1R,2S)-norephedrine unit, (guest amine; G_{RS}), to form the corresponding salts. Every salt exhibited a rectangular columnar LC phase at room tempera-

Introduction

Since the early stage of host–guest chemistry, solid-state hosts have attracted a lot of attention.^[1] Compared with homogeneous systems in dilute solutions, solid-state hosts find a wide range of practical applications, including catalysts, sensors, selectors, photonic/optoelectronic devices, ionic con-

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ture, which was successfully polymerized by ⁶⁰Co γ -ray-induced polymerization without serious structural disordering to afford the salt of cross-linked carboxylic acid (polymeric carboxylic acid; **P**_{AAA}, **P**_{ANA}, **P**_{DDD}, and **P**_{DND}) with **G**_{RS}. Owing to the noncovalency of the interactions between the polymer framework **P** and the template **G**_{RS}, the cross-linked polymers could reversibly release and capture a meaningful

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amount of G_{RS} . In response to the desorption and adsorption of G_{RS} , the cross-linked polymers dramatically switched their nanoscale structural order. A systematic comparison of the polymers revealed that the choice of polymerizable groups has a significant influence on the properties of the resultant polymer frameworks as solidstate hosts. Among these polymers, \mathbf{P}_{DDD} was found to be an excellent solid-state host, in terms of guest-releasing/capturing ability, guest-recognition ability, durability to repetitive usage, and unique structural switching mode.

ductors, an so forth.^[2] In addition, the dense integration of components in solid-state hosts often enables their synergetic motion in response to guest molecules, which would lead to sophisticated stimuli-responsive materials reminiscent of natural systems.^[3–5] These solid-state hosts are usually constructed through the spontaneous assembly of small building blocks by noncovalent interactions, such as hydrogen-bonding, coordination, electrostatic, π – π , and CH– π interactions. The reversibility of these noncovalent interactions plays an indispensible role to create frameworks with resilience and with few structural defects.^[6] At the same time, however, such reversibility inevitably limits the robustness, tunability, and processability of the resultant frameworks.

To overcome such limitation, a straightforward approach is to covalently connect the components of these architectures by in-situ polymerization. Unfortunately, this strategy is not applicable to traditional solid-state hosts with crystalline structures, as rigid frameworks rarely undergo in-situ reactions.^[7,8] On the other hand, liquid crystals (LCs) seem to be quite promising precursors of such polymeric solid-state hosts; molecules in LCs are aligned into an ordered structure with certain mobility, which often allows topologically controlled reactions to proceed in high probability.^[9] If a two-component LC composed of a polymerizable matrix unit and a template unit is available, a new type of porous material would be afforded by the in-situ polymerization of the LC and subsequent removal of the template unit. Indeed, pioneering works by Gin and co-workers have demonstrated the utility of this concept; several nano-channeled polymers with various applications, such as catalysts, nano-composites, separation membranes, and so forth, have been developed.^[9f,10]

Most of the materials developed by Gin et al. were formed by the cross-linking of lyotropic LCs.^[10] Considering the simplicity and ordering of supramolecular structures, thermotropic LCs might be more advantageous than lyotropic ones as the precursors of well-defined channels. At the present time, however, nanochanneled polymers from thermotropic LCs have been less systematically investigated.^[11] Recently, we have reported a cross-linked polymer by using a thermotropic LC salt, composed of an amphiphilic polymerizable carboxylic acid (monomeric carboxylic acid bearing three acryloyloxy groups; \mathbf{M}_{AAA}) with an enantiopure amino alcohol (Scheme 1).^[12] Owing to the noncovalency of the interactions between the polymer framework and the template, the resultant polymer was capable of releasing and re-capturing certain amounts of amino alcohols. Quite interestingly, the polymer showed unexpected dynamic properties, despite of its covalently cross-linked framework;^[13] in response to the adsorption/desorption of the template amino alcohol; the structure of the cross-linked polymer was reversibly transformed between rectangular columnar and amorphous states (Scheme 1c and d).

These encouraging results prompted us to expand the scope of our system. However, our previous system based on \mathbf{M}_{AAA} has the following problems and limitations, which



Scheme 1. Schematic representation for the structural switching of cross-linked polymers responsive to the desorption and adsorption of guest molecules. a) LC fomration: i) dichloromethane; ii) slow evaporation. b) Polymerization: 60 Co γ -ray (1.0 kGyh⁻¹) for 100 h in vacuo at RT. c) Desorption: HCOOH in EtOH (500 mm, 83 equiv) at 20 °C. d) Adsorption: **G** in MeOH (12 mm, 2 equiv) at 20 °C.

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would hamper further application as a solid-state host. 1) Through the in-situ polymerization of the LC salt, the original structure was disordered in a considerable level.^[12a] 2) A non-negligible amount of template molecule (about 30%) could not be removed from the cross-linked polymer by any means.^[12b] 3) The structural switching mode of the polymer was limited to only one type (rectangular columnar + amorphous), unlike the case of other supramolecular hosts, such as metal-organic frameworks.^[13] Therefore, we newly employed three kinds polymerizable carboxylic acids as the matrix unit and systematically varied the polymerizable (Scheme 1, M_{DDD} , M_{ANA} , and M_{DND}). Here we report a detailed study on the properties of the resultant polymers, which revealed that the modification of the polymerizable parts had an unexpectedly large effect on their performance as solid-state hosts.

Results and Discussion

Design of matrix and core units: In our previous work, a polymerizable amphiphilic carboxylic acid bearing three acryloyloxy groups (\mathbf{M}_{AAA}) was used as the matrix unit.^[13,14a] To clarify the effect of polymerizable functional groups on the properties of the resultant polymers, an analogue of \mathbf{M}_{AAA} , in which the acryloyloxy groups were replaced with conjugated dienyl groups (\mathbf{M}_{DDD}), was employed; polymerizable LCs bearing 1,3-dienyl groups have been recently reported by Gin and co-workers, in which the characteristic structure of 1,3-dienyl groups, similar to typical alkyl chains in polarity and size, has been shown to bring significant benefits, such as the stabilization of LCs.^[14b] In addition, the effect of the cross-linked density was also investigated by using analogous carboxylic acids with two polymerizable groups (\mathbf{M}_{ANA} and \mathbf{M}_{DND}).^[14c-e, 15]

As template units for the present template polymerization of two-component LCs, a number of amino alcohols are applicable. In fact, we have recently reported that the salts of tris(alkyloxy)benzoic acid derivatives with various amino alcohols have a general tendency to exhibit thermotropic LC phases.^[12,13,16] In this work, (1*R*,2*S*)-norephedrine (guest amine; **G**_{RS}) was selected, because an abundant amount of data have been accumulated by our group on the structure and properties of the LC salts of **G**_{RS} with amphiphilic carboxylic acids. In addition, easy access to its antipode ((1*S*,2*R*)-norephedrine, **G**_{SR}) and diastereoisomers ((1*R*,2*R*)and (1*S*,2*S*)-pseudonorephedrine, **G**_{RR} and **G**_{SS}) would allow us to investigate the chirality recognition ability of the resultant polymers.

Preparation and characterization of LC salts $\mathbf{M} \cdot \mathbf{G}_{RS}$: The carboxylic acids \mathbf{M}_{AAA} , \mathbf{M}_{DDD} , \mathbf{M}_{ANA} , and \mathbf{M}_{DND} were mixed with an equimolar amount of the amino alcohol \mathbf{G}_{RS} to give the corresponding salts (Scheme 1a). Every salt $\mathbf{M} \cdot \mathbf{G}_{RS}$ exhibited an LC phase at room temperature, which was confirmed by the combinational use of polarized optical microscopy, differential scanning calorimetry, and X-ray diffraction analysis (XRD). XRD studies revealed that the new salts ($\mathbf{M}_{DDD} \cdot \mathbf{G}_{RS}$, $\mathbf{M}_{ANA} \cdot \mathbf{G}_{RS}$, and $\mathbf{M}_{DND} \cdot \mathbf{G}_{RS}$) took an LC structure quite similar to that of $\mathbf{M}_{AAA} \cdot \mathbf{G}_{RS}$ (rectangular columnar; space group, *P2m*; lattice parameters, $43 \times 25-28$ Å), as unambiguously confirmed by nine or more refractions observed in a small-angle region (Figure 1).



Figure 1. XRD patterns of the salts of a) \mathbf{M}_{AAA} , b) \mathbf{M}_{ANA} , c) \mathbf{M}_{DDD} , and d) \mathbf{M}_{DND} with \mathbf{G}_{RS} : i) before and ii) after γ -ray irradiation.

The lattice size of these LC salts changed with a clear tendency, depending on the number of acryloyloxy groups in the carboxylic acid unit (Table 1). Among three types of the

Table 1. Structure and phase behavior of the LC salts $M \cdot G_{RS}$ before and after γ -ray irradiation.

Salt	Molecular structure of M			Clearing p	oint [°C] ^[a]	Lattice parameters, $a \times b$ [Å] ^[b]	
	А	D	$M_{ m r}$	monomer	polymer	monomer	polymer
$\mathbf{M}_{AAA} \cdot \mathbf{G}_{RS}$	3	0	843.1	73	>200 ^[c]	43.1×27.6	42.1×26.7
$M_{ANA} \cdot G_{RS}$	2	0	787.1	77	>200 ^[c]	43.0×26.4	41.7×26.3
$\mathbf{M}_{\text{DDD}} \cdot \mathbf{G}_{\text{RS}}$	0	3	663.0	99	$> 200^{[c]}$	42.9×24.8	41.9×24.2
$\mathbf{M}_{\text{DND}} \cdot \mathbf{G}_{\text{RS}}$	0	2	667.0	103	>200 ^[c]	43.0×24.9	42.2×24.6

[a] Determined by DSC on the first heating process. [b] Calculated from the *d*-spacings of the XRD reflections attributable to the (010) face and the overlapping of the (110) and (200) faces. [c] Transition into an isotropic melt was not observed up to 200 °C.

chain termini groups (acryloyloxy, dienly, and alkyl groups), acryloyloxy is bulkier than the others. As the number of acryloyloxy groups in the carboxylic acid decreases (\mathbf{M}_{AAA} , 3; \mathbf{M}_{ANA} , 2; \mathbf{M}_{DDD} , 0; \mathbf{M}_{DND} , 0), the *b* axis (=the shorter side) of the lattice became shorter (\mathbf{M}_{AAA} , 27.6; \mathbf{M}_{ANA} , 26.4; \mathbf{M}_{DDD} , 24.8; \mathbf{M}_{DND} , 24.9 Å). In contrast to this, the length of the *a* axis (=the longer side) was hardly influenced by the structure of the carboxylic acid units (\mathbf{M}_{AAA} , 43.1; \mathbf{M}_{ANA} , 43.0; \mathbf{M}_{DDD} , 42.9; \mathbf{M}_{DND} , 43.0 Å). Considering this tendency, the polymerizable end groups of the alkyl chains are likely to be mainly located on the *a*-side of the lattice, so that the bulkiness of the acryloyloxy group contributes only to the elongation of the length of the *b* axis (Figure 2).



Figure 2. Schematic representation for the possible arrangement of molecules in the LC salts $(\mathbf{M} \cdot \mathbf{G}_{RS})$ with a rectangular columnar structure (*P*2*m*).

In-situ polymerization of LC salts M·G_{RS}: The LC salts **M·G**_{RS} thus obtained were then subjected to radical polymerization (Scheme 1b). For the cross-linking of LC materials, photoinitiated polymerization has been widely used. However, we employed ⁶⁰Co γ -ray-induced polymerization due to the following advantages:^[12b,17,18] 1) γ -Ray-induced polymerization does not require any radical initiator, which sometimes induces undesired disordering of LC structures. 2) Unlike the case of UV light, γ -rays are highly penetrant and promote the polymerization in a homogeneous manner without depending on the depth from the surface.

Regardless of the structure of the carboxylic acid unit, the γ -ray irradiation converted the LC salts into hard solid masses that were insoluble in common organic solvents and nonmeltable up to 200 °C. Through the irradiation, the acryroyloxy and dienyl groups were consumed almost quantitatively, as confirmed by the disappearance of their characteristic IR absorptions (Figure 3, filled circles). The resultant cross-linked polymers were mechanically milled and washed with dichloromethane; the unreacted carboxylic acid and the template unit \mathbf{G}_{RS} were not detected in the washing.

For every salt, an XRD study showed that the original rectangular structure was disordered to some extent, as generally observed in the cross-linking of LC architectures.

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Figure 3. FT-IR spectra of the salts of a) M_{AAA} , b) M_{ANA} , c) M_{DDD} , and d) M_{DND} with G_{RS} : i) before and ii) after γ -ray irradiation.

However, it is worth noting that structural preservation in the cases of the carboxylic acids with dienyl groups was relatively better than those bearing acryloyloxy groups (Figure 1a vs. c and b vs. d). In general, the cross-linking of LC mesogens induced the congestion of polymerizable moieties, which are usually polar/rigid functionalities, to hinder dense molecular packing. However, the characteristic structure of the 1,3-dienyl group, less polar and less sterically demanding compared to usual polymerizable groups, would be favorable to retain the original molecular packing even after the polymerization

Desorption and adsorption of the guest G_{RS} on the crosslinked polymers P: With four kinds of cross-linked polymer frameworks (P_{AAA} , P_{ANA} , P_{DDD} , and P_{DND}) in hand, we next investigated their properties as solid-state hosts. To clarify the characteristics of these four polymers, we at first studied very simple consecutive processes, the desorption and adsorption of the template amino alcohol G_{RS} on the crosslinked polymers (Scheme 1c and d).

Owing to the noncovalency of the interactions between the template unit \mathbf{G}_{RS} and the polymer matrices \mathbf{P} , \mathbf{G}_{RS} could be easily extracted from the as-prepared holo-polymers (*holo*- $\mathbf{P}\cdot\mathbf{G}_{RS}$) to afford the corresponding apo-polymers (*apo*- \mathbf{P}) by treatment with a solution of formic acid (Table 2). The apo-polymers *apo*- \mathbf{P} thus obtained readily adsorbed the original guest \mathbf{G}_{RS} , when treated with a solution of \mathbf{G}_{RS} to afford the reconstituted polymers (*rec*- $\mathbf{P}\cdot\mathbf{G}_{RS}$). Through the desorption and adsorption, the mass transfer of

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Table 2. Capacity and structural change of P on the desorption and adsorption of $G_{\mbox{\tiny RS}}$

Salt	Amount of $\mathbf{G}_{RS} [\%]^{[a]}$					Lattice parameters, $a \times b \ [\text{Å}]^{[b]}$			
	holo		apo		rec	holo	apo	rec	
$\mathbf{P}_{AAA} \cdot \mathbf{G}_{RS}$	100	(-75)	25	(+70)	95	42.1×26.7	n.d.×n.d.	41.5×26.5	
$P_{ANA} \cdot G_{RS}$	100	(-96)	4	(+94)	98	41.7×26.3	$n.d. \times n.d.$	41.6×26.0	
$\mathbf{P}_{\text{DDD}} \cdot \mathbf{G}_{\text{RS}}$	100	(-95)	5	(+71)	76	41.9×24.2	n.d.×23.0	41.2×24.1	
$\mathbf{P}_{\mathrm{DND}}$ · \mathbf{G}_{RS}	100	(-97)	3	(+74)	77	42.2×24.6	n.d.×ca. $24^{[c]}$	n.d.×24.5	

[a] With respect to the carboxyl groups in the cross-linked polymer (mol%), which were calculated based on the change of the concentration of G_{RS} in the supernatant (determined by HPLC). Values in the parentheses represent the amounts of G_{RS} desorbed from (–) and adsorbed onto (+) the polymers. [b] Calculated from the *d*-spacings of the XRD reflections attributable to the (010) face and the overlapping of the (110) and (200) faces. [c] Calculated from a highly broadened XRD reflection.

 G_{RS} was monitored by the HPLC analysis of the supernatants. Hereafter, the amounts of G_{RS} are expressed with respect to the carboxyl groups in the cross-linked polymers (mol%). In all cases of these four polymers, the desorption and adsorption attained an equilibrium within 100 h, in spite of quite mild conditions (Figure S2 in the Supporting Information).^[19]

Efficiency of desorption/adsorption of the guest G_{RS} : In the desorption process, *holo*- P_{ANA} · G_{RS} , *holo*- P_{DDD} · G_{RS} , and *holo*- P_{DND} · G_{RS} released G_{RS} almost quantitatively [P_{ANA} , 100 \rightarrow 4% (-96%); P_{DDD} , 100 \rightarrow 5% (-95%); P_{DND} , 100 \rightarrow 3% (-97%)], while the desorption from *holo*- P_{AAA} · G_{RS} realized satisfactory but a little less conversion [P_{AAA} , 100 \rightarrow 25% (-75%)]. FT-IR studies clearly showed that the desorption process involved only a simple ion-exchange reaction (ammonium carboxylate \rightarrow carboxylic acid); at the equilibrium stage, the IR absorptions attributable to ammonium carboxylate disappeared, whereas those of free carboxylic acid newly emerged (Figure 4, a–d; i vs. ii).

In the following adsorption process, the apo-polymers composed of acryloyloxy groups (*apo*- \mathbf{P}_{AAA} and *apo*- \mathbf{P}_{ANA}) incorporated almost quantitative amounts of \mathbf{G}_{RS} , respectively [\mathbf{P}_{AAA} , 25 \rightarrow 95% (+70%); \mathbf{P}_{ANA} , 4 \rightarrow 98% (+94%)]. Meanwhile, the apo-polymers of dienyl groups (*apo*- \mathbf{P}_{DDD} and *apo*- \mathbf{P}_{DND}) showed saturation at a moderate level [\mathbf{P}_{DDD} , 5 \rightarrow 76% (+71%); \mathbf{P}_{ANA} , 3 \rightarrow 77% (+74%)]. FT-IR studies again showed that the adsorption progressed by a simple ion-exchange reaction (carboxylic acid \rightarrow ammonium carboxylate), accompanied with no detectable side reactions, such as the condensation of the carboxylic acid with the amine and the aminolysis of the poly(acrylate) moieties (Figure 4, a–d; ii vs. iii).

Overall, meaningful amounts of \mathbf{G}_{RS} could be cleanly desorbed (-75 to -97%) from and adsorbed (+70 to +94%) to all of the four polymers by simple treatment with an acidic solution and a \mathbf{G}_{RS} solution, respectively (Table 2). As described in the introductory part, our polymer \mathbf{P}_{AAA} could not release the original template quantitatively (up to about 70% with respect to the carboxyl groups in the polymer), which would be a fatal drawback as a solid-state host;^[12,13] the present study revealed that a small modification of the carboxylic acid unit, that is reducing cross-link density (\mathbf{P}_{ANA} and \mathbf{P}_{DND}) or changing polymerizable groups (\mathbf{P}_{DDD}), could solve this problem.



Figure 4. FT-IR spectra of a) \mathbf{P}_{AAA} , b) \mathbf{P}_{ANA} , c) \mathbf{P}_{DDD} , and d) \mathbf{P}_{DND} : i) the original state (holo-polymer), ii) after the desorption of \mathbf{G}_{RS} (apo-polymer), and iii) after the adsorption of \mathbf{G}_{RS} (reconstituted polymer). For each spectrum, the amount of \mathbf{G}_{RS} incorporated is shown with respect to the carboxyl groups in the polymer (mol%).

Structural switching mode through the desorption/adsorption of the guest G_{RS} : As we have reported, the desorption and adsorption of the guest G_{RS} induced the "melting" and "crystallization" of P_{AAA} (Scheme 1c and d).^[13] If the structural switching mode can be controlled by the cross-linking manner, it should further expand the scope of the present system. Therefore, the nanoscaled structures of the three new polymers (P_{DDD} , P_{ANA} , and P_{DND}) at the equilibrium stages of desorption and re-adsorption were investigated by XRD (Figures 5 and 6).

During the desorption, the polymer frameworks of acryloyloxy groups (\mathbf{P}_{AAA} and \mathbf{P}_{ANA}) were transformed into an amorphous-like structure. After the completion of the desorption, reflections originally observed at a small-angle region, characteristic of a rectangular columnar structure, became undetectable (Figure 5a and b; ii). The only detecta-

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Figure 5. 2D XRD images of a) \mathbf{P}_{AAA} , b) \mathbf{P}_{ANA} , c) \mathbf{P}_{DDD} , and d) \mathbf{P}_{DND} : i) the original state (holo-polymer), ii) after the desorption of \mathbf{G}_{RS} (apo-polymer), and iii) after the adsorption of \mathbf{G}_{RS} (reconstituted polymer). For each image, the amount of \mathbf{G}_{RS} incorporated is shown with respect to the carboxyl groups in the polymer (mol%).

ble reflection was a wide-angle halo peak due to the loose packing of the paraffin chains (the *d*-spacing = about 3.5 Å), which was inert toward the removal of \mathbf{G}_{RS} (Figure S1, a and b, ii). Unlike the polymer frameworks of the acryloyloxy groups, those of the dienyl groups (\mathbf{P}_{DDD} and \mathbf{P}_{DND}) exhibited a structural periodicity with a *d*-spacing of about 20 Å, even after the removal of \mathbf{G}_{RS} . Upon completion of the desorption, *apo*- \mathbf{P}_{DDD} showed a small but sharp reflection at a small-angle region, besides a wide-angle halo scattering due to the alkyl-chain packing (Figure 6c; ii). The corresponding reflection was also observed in the case of \mathbf{P}_{DND} , although its peak width highly broadened, compared with that of \mathbf{P}_{DDD} (Figure 6d; ii).

In the adsorption process, all of the polymers recovered their structural order. However, the efficiency of their structural reconstruction was highly influenced by the crosslinked density. In the cases of the highly cross-linked polymers \mathbf{P}_{AAA} and \mathbf{P}_{DDD} , an ordered rectangular columnar structure with lattice parameters essentially same as those of the original polymer was recovered (Table 2); a set of reflections characteristic of a rectangular columnar structure appeared again, of which the intensities were slightly lower but comparable to those of the pristine polymers (Figure 6a and c; iii). In contrast, the polymers with lower cross-linked density (\mathbf{P}_{ANA} and \mathbf{P}_{DND}) were not capable of recovering the original structure to such a high level. In the case of \mathbf{P}_{ANA} , most of the reflections owing to a rectangular columnar structure were recovered. At the same time, however, a broad peak newly emerged at the 2θ region of 3–4°, indicating a certain structural disordering during the desorption–adsorption cycle (Figure 6b; iii). Further considerable disordering was observed in the reconstitution of \mathbf{P}_{DND} . After the adsorption, the two reflections attributable to the (010) and (110)/(200) faces were significantly broadened, and other high-order reflections were barely detectable (Figure 6d; iii).

Thus, all of the four polymers generally changed the shape of their framework through the desorption and adsorption processes. However, the dynamic behavior of the polymers was highly influenced by the cross-linked density and the polymerizable functional group. In other words, we might be able to tune the flexibility of polymers derived from LC salts by the proper control of the following two factors. 1) Polymerizable functionality; the polymers of dienyl groups kept a certain structural order even after the desorption of the template (\mathbf{P}_{DDD} and \mathbf{P}_{DND}), whereas those of acryloyloxy groups turned into an amorphous-like state (\mathbf{P}_{AAA} and \mathbf{P}_{ANA}). 2) Cross-linked density; to construct frameworks with a satisfactory reconstitution ability, it was

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Figure 6. XRD patterns of a) \mathbf{P}_{AAA} , b) \mathbf{P}_{ANA} , c) \mathbf{P}_{DDD} , and d) \mathbf{P}_{DND} : i) the original state (holo-polymer), ii) after the desorption of \mathbf{G}_{RS} (apo-polymer), and iii) after the adsorption of \mathbf{G}_{RS} (reconstituted polymer). For each pattern, the amount of \mathbf{G}_{RS} incorporated is shown with respect to the carboxyl groups in the polymer (mol%).

essential to introduce three polymerizable groups per one carboxylic acid unit (\mathbf{P}_{AAA} and \mathbf{P}_{DDD}). Among these polymer frameworks, the highly cross-linked ones (\mathbf{P}_{AAA} and \mathbf{P}_{DDD}) showed a superior structural reconstitution ability, which seem more attractive than the less cross-linked types (\mathbf{P}_{ANA} and \mathbf{P}_{DDD}).

Intermediate states of the structural switching: To gain further insights into the dynamics of P_{AAA} and P_{DDD} , the intermediate structures of these polymers between the holo- and apo-states were thoroughly studied. For the estimation of structural order during the desorption and adsorption processes, we monitored the intensity of two strong reflections, attributable to the (010) face ($2\theta = 3.3 - 3.7^\circ$, *d*-spacing = 24-27 Å) and the overlapping of the (110) and (200) faces ($2\theta =$ $3.8-4.2^\circ$, *d*-spacing = 21-23 Å). Considering their Miller indices, these reflections should correspond to the structural order along the *a* and *b* axes of the rectangular lattice, respectively. Depending on the ordering/disordering along the two directions, the structural switching of the rectangular lattice can be classified into four extreme cases, as depicted in Figure 7.

In the case of \mathbf{P}_{AAA} , the two reflections changed their intensity synchronously with each other, in response to the amount of \mathbf{G}_{RS} incorporated in the polymer (Figure 8a). At the equilibrium stage of the desorption, no structural order remained in either of the directions, suggestive of the transformation into an amorphous-like structure (Figure 8a; v).



Figure 7. Schematic representation for the possible structural-switching patterns of a rectangular columnar lattice.

From these observations, we can deduce that the framework has similar "rigidity" in the directions of the *a* and *b* axes, so that the structural disordering/re-ordering proceeds in a directionally independent manner (Figure 7d and Scheme 2, left).

Quite interestingly and unexpectedly, the transformation of \mathbf{P}_{DDD} was more directionally dependent than that of \mathbf{P}_{AAA} . At the initial stage of the desorption, the reflection owing to the (110)/(200) faces showed a more drastic change than did the (010) face; the reflection of the (110)/(200) faces became almost undetectable even when the conversion was not sufficient (ca. 70% desorption, Figure 8b; iv). In contrast to this, the reflection of the (010) face was still visible at the equilibrium of the desorption process, at which an almost quantitative amount of \mathbf{G}_{RS} was removed (95% desorption, Figure 8b; v). Through the adsorption process, the reflection of the (010) face changed in proportion to the adsorption, whereas that of the (110)/(020) faces gained its intensity only at the final stage. Thus, \mathbf{P}_{DDD} had a tendency to



Figure 8. XRD patterns of a) P_{AAA} and b) P_{DDD} on the desorption (i–iv) and adsorption (v–xi) of G_{RS} . For each pattern, the amount of G_{RS} incorporated is shown with respect to the carboxyl groups in the polymer (mol%).

retain the structural order along the *b* axis more persistently than that along the *a* axis throughout the desorption and adsorption of \mathbf{G}_{RS} ; \mathbf{P}_{DDD} is considered to reversibly change its shape between a rectangular columnar structure and a lamellar structure (Figure 7b and Scheme 2, right).

Tolerance to repetitive desorption/adsorption of the guest G_{RS} : As described in the introductory part, traditional solid-



Figure 9. XRD patterns of a) $P_{\rm AAA}$ and b) $P_{\rm DDD}$ on the repetitive desorption/adsorption of $G_{\rm RS}$

state hosts attain reversible switchings of their ordered structures by an "error-correction" process, characteristic of supramolecular architectures based on noncovalent interactions between components.^[6]In contrast, covalently cross-linked frameworks, such as the present polymers, lack such an error-correction ability, in principle. Therefore, it might be intriguing to check the durability of the present polymers to the repetitive desorption and adsorption of the guest G_{RS} .

The two polymers (\mathbf{P}_{AAA} and \mathbf{P}_{DDD}) were subjected to two cycles of desorption and adsorption under conditions similar to those described above [Figure 9i ($holo-\mathbf{P}\cdot\mathbf{G}_{RS}$)—desorption—ii (apo_{1st} - \mathbf{P})—adsorption—iii (rec_{1st} - $\mathbf{P}\cdot\mathbf{G}_{RS}$)—desorption—iv (apo_{2nd} - \mathbf{P})—adsorption—v (rec_{2nd} - $\mathbf{P}\cdot\mathbf{G}_{RS}$)].^[20] Through the cycles, the nanoscaled structures of the polymers were monitored by XRD analyses. To our delight, the polymers showed an excellent durability to the repetitive usage, in which the frameworks switched their shape reversibly between two states; the polymers in the second cycle showed XRD patterns almost identical to those of the corre-



Scheme 2. Schematic representation for the structural switching of P_{AAA} and P_{DDD}

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sponding polymers in the first cycle (Figure 9a and b; ii vs. iv and iii vs. v).

These observations clearly proved that \mathbf{P}_{AAA} and \mathbf{P}_{DDD} have satisfactory tolerance to repetitive desorption and adsorption; the history of the polymers gives essentially no influence on the capability of switching their structures. Most likely, the cross-linked density of the present system, three polymerizable groups per one carboxylic acid unit, was suitable to cope with both flexibility and durability. Such knowledge provides us a clue to design next-generation covalent frameworks based on the present concept.

Ability to distinguish the shape of stereoisomeric guest molecules: As reported in our previous papers, $apo-P_{AAA}$ could incorporate not only the original template G_{RS} , but also other various amines.^[12] In addition, $apo-P_{AAA}$ was capable of recognizing subtle structural difference between the original template G_{RS} and its stereoisomers (G_{SR} , G_{RR} , and G_{SS}), so that the structural order of the reconstituted P_{AAA} was influenced by the shape of guests.^[13] These observations indicate the potential utility of our system as guest-responsive materials with a chirality recognition ability. In order to prove the generality and expansivity of this phenomenon, the new polymer P_{DDD} , exhibiting similar but different structural switching property from that of P_{AAA} , was also employed for the same experiment.

Thus, *apo*-**P**_{AAA} and *apo*-**P**_{DDD} were treated with the solutions of **G**_{RS}, **G**_{SR}, **G**_{RR}, and **G**_{SS}. To fairly evaluate the structural reconstitution efficiency, the adsorption was stopped before equilibrium, when the uptake reached a specific value (**P**_{AAA} (58±2)%; **P**_{DDD} (49±2)%).^[21] The nanoscaled structure of the resultant polymers was analyzed by XRD. Here, we again focused on the intensities of the two characteristic reflections in XRD patterns owing to the (010) and (110)/(200) faces, which represent the degree of the structural order along the *b* and *a* axes, respectively.

As we had expected, \mathbf{P}_{DDD} as well as \mathbf{P}_{AAA} showed an ability to recognize the difference between the guest molecules (Scheme 3); structural reconstitution by the matched guest (\mathbf{G}_{RS}) proceeded more efficiently than by the mismatched guests (\mathbf{G}_{SR} , \mathbf{G}_{RR} , and \mathbf{G}_{SS}). Quite interestingly, \mathbf{P}_{DDD} showed a different structural switching mode from that of \mathbf{P}_{AAA} , regarding directional dependence. In the case of \mathbf{P}_{DDD} , it always recovered the reflection of the (010) face independent of the guests, while the recovery of the reflection of the (110)/(200) faces was highly sensitive to the matching/ mismatching of the guests (Figure 10b; i vs. ii–iv). Thus, the



Figure 10. XRD patterns of a) P_{AAA} and b) P_{DDD} reconstituted with i) G_{RS} , ii) G_{SR} , iii) G_{RR} , and iv) G_{SS} . For each pattern, the amount of G captured by the polymer through the adsorption process is shown with respect to the carboxyl groups in the polymer (mol%).

guest specificity of \mathbf{P}_{DDD} was found to be expressed in the order along the *a* axis rather than in the order along the *b* axis. In contrast to this, the guest specificity of \mathbf{P}_{AAA} was reflected in the orders along both the *a* and *b* axes, since the two reflections synchronously varied their intensity depending on the matching of guests (Figure 10a; i vs. ii–iv).

Although such a difference in the structural switching mode was observed between \mathbf{P}_{AAA} and \mathbf{P}_{DDD} , both of these polymers showed an ability to distinguish the original template \mathbf{G}_{RS} from its stereoisomers (\mathbf{G}_{SR} , \mathbf{G}_{RR} , and \mathbf{G}_{SS}). Most likely, "best fitting" was achieved only when \mathbf{G}_{RS} was incorporated to the apo-polymers, because the cavities of the apo-polymers were tailored to accommodate the original



Scheme 3. Reconstitution of $apo-P_{AAA}$ and $apo-P_{DDD}$ by the adsorption of G_{RS} , G_{SR} , G_{RR} , and G_{SS} .

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template (G_{RS}). We should specifically mention here that the present polymers were capable of recognizing a quite subtle structural deviation of guests, reminiscent of enzymes; among the mismatched guest molecules, G_{RR} has the most similar shape to that of the original template G_{RS} , in which the only difference is the configuration of the C(2) methyl group.

Taking into account of the accurate template-memory effect, together with the tunability of lattice flexibility depending on the polymerizable units, the present system could lead to sophisticated sensors, actuators, and gate devices.

Origin of difference between P_{AAA} and P_{DDD} as solid-state hosts: As described above, the cross-linked polymers \mathbf{P}_{AAA} and \mathbf{P}_{DDD} were found to have favorable properties as solidstate hosts, regarding structural reconstitution ability, durability to repetitive usage, and guest-recognition ability. It is worth noting that the choice of the polymerizable functionalities (acryloyloxy or dienly groups) brought an unexpectedly large effect on the properties of the resultant polymer, particularly in the structural switching mode on the desorption and adsorption of the guest molecules (Scheme 2). Although analytical methods to study the structure of crosslinked polymers are generally limited, it might be important to examine the difference between P_{AAA} and P_{DDD} as solidstate hosts. Particularly, the molecular arrangement in the precursors of these polymers $(\mathbf{M}_{AAA} \cdot \mathbf{G}_{RS} \text{ and } \mathbf{M}_{DDD} \cdot \mathbf{G}_{RS})$ would give us some insights.

Supposing the molecular packing in these LC salts as shown in Figure 2, the polymerizable functionalities are prone to crowd along with the *a* axis of the rectangular lattice. Taking account of this localization and bulkiness/polarity of the polymerizable functionalities, the properties of \mathbf{P}_{AAA} and \mathbf{P}_{DDD} might be elucidated as follows. In the case of \mathbf{M}_{DDD} bearing dienly groups with less polar and less sterically demanding structure, the interdigitation of chain termini would easily take place, which allows the polymer network to grow along the *a* axis. Therefore, the resultant polymer \mathbf{P}_{DDD} is expected to retain the ordered structure along the b aixs more persistently than along the a axis. In contrast to this, the acryloyloxy groups in \mathbf{M}_{AAA} are bulkier and more polar, which would cause the steric/electrostatic repulsion with each other. As a result, the polymer network is anticipated to develop in a nondirectional manner.

Conclusion

In conclusion, solid-state hosts with a flexible framework (\mathbf{P}_{AAA} , \mathbf{P}_{ANA} , \mathbf{P}_{DDD} , and \mathbf{P}_{DND}) were prepared by the in-situ polymerization of the LC salts of polymerizable carboxylic acids (\mathbf{M}_{AAA} , \mathbf{M}_{ANA} , \mathbf{M}_{DDD} , and \mathbf{M}_{DND}) with a template amino alcohol (\mathbf{G}_{RS}). A systematic comparison of these polymers revealed that manner of the cross-linking has a significant effect on the properties as solid-state hosts. The following knowledge obtained in this work could lead to the

rational design of covalent frameworks with desired properties.

- 1) To reduce the structural disordering during the in-situ polymerization of the LC architecture, dienyl groups $(\mathbf{P}_{\text{DDD}} \text{ and } \mathbf{P}_{\text{DND}})$ were advantageous than the acryloyl-oxy groups $(\mathbf{P}_{\text{AAA}} \text{ and } \mathbf{P}_{\text{ANA}})$.
- 2) For the quantitative removal of the template, the reduction of cross-linked density (\mathbf{P}_{ANA} , and \mathbf{P}_{DND}) or the employment of dienyl groups as polymerizable functionalities (\mathbf{P}_{DDD}) was effective.
- 3) For the creation of frameworks with a sufficient structural reconstitution ability, it was essential to introduce three polymerizable groups per one carboxylic acid unit (\mathbf{P}_{AAA} , and \mathbf{P}_{DDD}).
- 4) The polymers of dienyl groups (\mathbf{P}_{DDD} and \mathbf{P}_{DND}) kept certain structural order even after the desorption of the template, whereas those of acryloyloxy groups (\mathbf{P}_{AAA} and \mathbf{P}_{ANA}) turned into an amorphous-like state.

Among these polymers, \mathbf{P}_{DDD} was found to be an excellent solid-state host, in terms of structural order, guest-releasing ability, guest-recognition ability, durability to repetitive usage, and a unique structural switching mode. Considering the beneficial features characteristic of covalently cross-linked systems, such as processability, physical/chemical robustness, kinetic stability, and size/shape tunability,^[22] the present system could lead us to further facile manipulation and more profound understanding of host–guest systems in the solid state.

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- [19] The rates of the desorption and adsorption were highly influenced by the concentrations of formic acid and G_{RS} in solutions, respectively. For all experiments except for the repetitive desorption and adsorption (see reference [20]), we intentionally used the relatively diluted solutions to retard the rates, which was suitable to monitor the time course by HPLC. Additionally, in the case of the adsorption process, the employment of excess G_{RS} prevented the accurate quantification of G_{RS} , since the change in the concentration became too small.
- [20] In the repetitive desorption and adsorption, the concentrated solutions of formic acid and G_{RS} (15 and 20 times more concentrated than those for the standard conditions) were used, respectively, in order to accelerate the reaction rates. For experimental details, see Supporting Information.
- [21] Our preliminary study showed that $apo-\mathbf{P}_{AAA}$ and $apo-\mathbf{P}_{DDD}$ have higher affinity to the original \mathbf{G}_{RS} than its stereoisomers ($\mathbf{G}_{SR}, \mathbf{G}_{RR}, \mathbf{G}_{SS}$). Although the selective binding implies the potential of these polymers as chiral selectors, such applications will be reported elsewhere, since the scope of the present work is specific transformation of these polymer frameworks.
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