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Switching of Structural Order in a Cross-Linked Polymer Triggered by the Desorption/Adsorption of Guest Molecules

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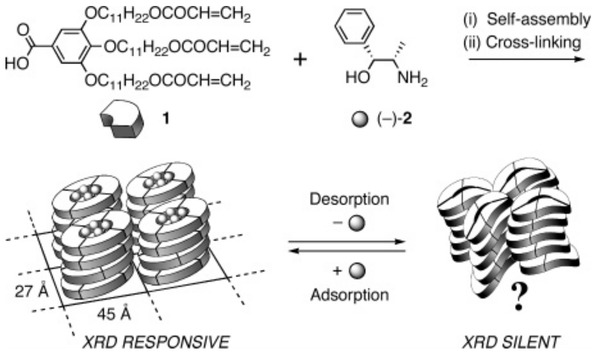
Host−guest chemistry in the solid state is one of the most classical areas in supramolecular chemistry but still attracts increasing attention as a key subject for the expansion of the scope of supramolecular chemistry to the next stage.[1] Contrary to the cases of homogeneous systems in dilute solutions, complexation/dissociation events in solid-state architectures sometimes trigger dramatic changes in the structure/property of whole systems, which might be directly related to the development of more sophisticated materials, such as sensors, logical gates, and stimuli−responsive actuators. In fact, solid-state hosts with dynamically variable frameworks, including graphites,[2a] clays,[2b] coordination polymers,[2c−e] and inclusion crystals,[2f,g] have been extensively studied for the last two decades. In these traditional intercalation hosts, components are usually connected with each other via noncovalent interactions, which are regarded as the origin of the resilience of the resultant architectures.[3] At the same time, however, the characteristics of noncovalent interactions inevitably limit the physical robustness and kinetic stability of the resultant architectures. Recently, we and other groups have devoted efforts to develop novel solid-state hosts based on the in situ polymerization of multicomponent liquid crystals.[4] Here we report an unexpected behavior of a cross-linked polymer, which was closely related to the behavior of conventional intercalation hosts; the columnar structural order in the cross-linked polymer was reversibly switched by desorption/adsorption of a guest (Scheme 1).

Scheme 1. Schematic Representation for the Guest-Responsive Transformation of a Cross-Linked Polymer



The cross-linked polymer with a columnar ordered structure was prepared by the in situ polymerization of a liquid crystalline material, the salt of a polymerizable carboxylic acid (**1**)[4a] with an enantiopure 1,2-amino alcohol ((−)-**2**).[4e,5,6] The powder XRD analysis of the resultant cross-linked polymer revealed that it still retained a rectangular columnar structure, of which the lattice parameters (a = 45.2 Å, b = 26.8 Å) were quite similar to those of the original liquid crystalline material (Figure 1b, i). From the cross-linked polymer, the amino alcohol (−)-**2** was desorbed by treatment with an acidic aqueous solution.[5,7] For example, upon soaking the finely milled cross-linked polymer (45.0 mg, calculated to contain 45 μmol of the carboxylic acid−amine pair) in a methanolic HCl solution at room temperature, the amino alcohol (−)-**2** in the cross-linked polymer was leached out to the supernatant, and an equilibrium was attained after 340 h, where 31 μmol of (−)-**2** (69% with respect to the original (−)-**2** in the cross-linked polymer) was desorbed from the cross-linked polymer (Figure 1a). Changes in the FT-IR spectra of the cross-linked polymer revealed that the desorption process involved only a quite simple ion-exchange reaction; as the desorption proceeded, the IR absorptions attributable to the ammonium−carboxylate salt decreased in intensity, whereas those of the free carboxylic acid newly emerged.[5] As might be expected for a porous composite with a flexible framework, a dramatic structural alteration was induced by the removal of the template (−)-**2** to diminish the intensities of the X-ray diffractions attributable to the (010), (110)/(200), and (300) faces of the rectangular columnar structure (Figure 1b, i−iii).[8] At the final equilibrium stage, the three diffractions became undetectable (Figure 1b, iv). Contrary to the behavior of the three diffractions at the small-angle region, a halo at the wide-angle region, attributed to the loosely packed aliphatic chains, was inert toward the removal of (−)-**2**.[5]

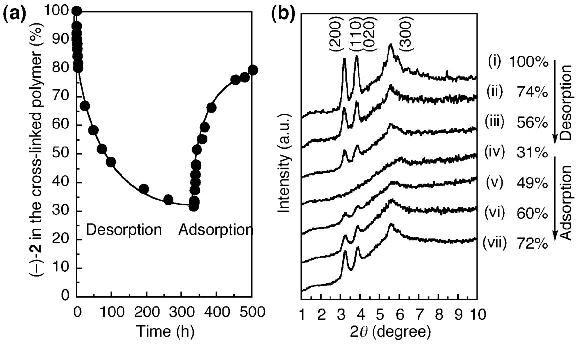


Figure 1. Desorption/adsorption of (−)-**2** from/to the cross-linked polymer: (a) time course of the desorption/adsorption monitored by HPLC and (b) XRD profiles of the cross-linked polymer.

In the next stage, we attempted the readsorption of the amino alcohol (−)-**2** to the apo-polymer, a polymer partially lacking the amine unit, obtained by the above procedure.[5,7] When the apo-polymer (35.5 mg, calculated to contain 40 and 12 μmol of the carboxylic acid unit and (−)-**2**, respectively) was soaked in a methanol solution of (−)-**2** at room temperature, the adsorption readily took place. At an equilibrium state, 20 μmol of (−)-**2** was adsorbed to the cross-linked polymer, indicating that the total amount of (−)-**2** in the cross-linked polymer was 79% with respect to the carboxylic acid units in the cross-linked polymer (Figure 1a). The IR spectroscopy of the resultant cross-linked polymer revealed that the adsorption progressed by the formation of the ammonium−carboxylate salt, without accompanying undesired side

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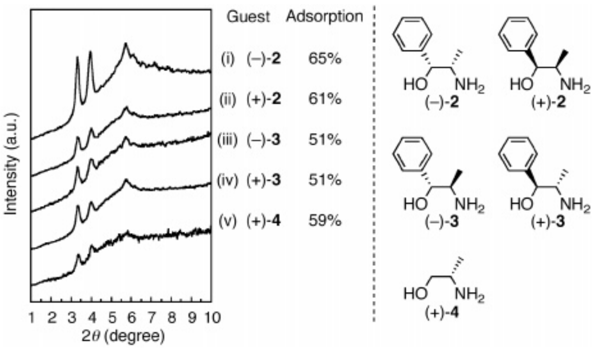

Figure 2. XRD profiles of the cross-linked polymers obtained by the reconstitution of the amine-deficient polymer with (i) (−)-**2**, (ii) (+)-**2**, (iii) (−)-**3**, (iv) (+)-**3**, and (v) (+)-**4**.

reactions such as the condensation of the two components to form an amide and the aminolysis/hydrolysis of the polyacrylate moiety.[5] To our surprise, the readsorption of (−)-**2** to the cross-linked polymer undoubtedly triggered the reconstitution of the ordered rectangular columnar structure ($a = 45$ Å, $b = 27$ Å), of which the lattice parameters were essentially identical to those of the original polymer before the desorption of (−)-**2**; three characteristic diffractions emerged even when only 49% of the carboxylic acid units in the cross-linked polymer participated in the salt-pair formation with (−)-**2**, and their intensities became stronger as the readsorption proceeded (Figure 1b, iv−vii). On the other hand, any other diffraction was not observed through the readsorption process; the phenomenon strongly suggests that there is little possibility of the transformation of the cross-linked polymer into another ordered structure. Thus, the cross-linked polymer prepared here was found to be highly resilient, although each unit in the polymer was connected with covalent bonds. As far as we know, this is an uncommon example of a cross-linked polymer with a dynamic nature, of which the structural order was reversibly changed by the adsorption/desorption of a guest.[8,9]

As reported in our previous work, 1,2-amino alcohols other than the original guest (−)-**2** could be incorporated in the cross-linked polymer,[4e] which prompted us to employ several 1,2-amino alcohols ((+)-**2**, (−)-**3**, (+)-**3**, and (+)-**4**) as triggers to induce the structural change of the apo-polymer obtained by the acidic desorption of (−)-**2** from the cross-linked polymer.[7] Quite interestingly, the resultant polymers exhibited three characteristic diffractions with *d*-spacings of 27, 22, and 15 Å, strongly suggesting the reconstruction of the rectangular lattice ($a = 45$ Å, $b = 27$ Å) (Figure 2, ii−v). Worth noting is that the adsorption of (+)-**4** triggered the reconstruction of the *rectangular* columnar structure, although our previous study revealed that the salt of monomeric **1** with (+)-**4** existed as a liquid crystal with a *hexagonal* one ($a = 42.2$ Å).[4e] Moreover, there was a significant difference in reconstitution ability between the original guest (−)-**2** and its enantio/diastereoisomers ((+)-**2**, (−)-**3**, and (+)-**3**); although the amounts of the re-adsorbed guests at an equilibrium state were almost identical in all of the four cases (51−65%), the intensities of the diffractions of the polymers, reconstituted with these three new guests, were about a half compared with the corresponding diffractions observed in the reconstitution with (−)-**2** (Figure 2, i vs ii−iv).[7] From these observations, we could deduce that the three-dimensional cross-linking might bring considerable structural constraint on the resultant polymer, which remained even after the removal of the original template. As a result, the apo-polymer had a strong tendency to take the rectangular columnar structure regardless of the structure of a guest to be incorporated, and yet the polymer host possessed an ability to sense the subtle structural difference between the diastereo/enantio isomers so that the "best fitting" was achieved only when (−)-**2** was used as the guest.

In conclusion, a cross-linked polymer, prepared by the in situ polymerization of the liquid crystalline salt **1**·(−)-**2** was found to work as a host with a flexible framework, of which the structural order was reversibly switched by changing the amount or shape of a guest incorporated in the polymer. The unique properties of the cross-linked polymers based on this concept, compared with conventional intercalation hosts, such as physical robustness, the kinetic stability, and size/shape tunability,[10] would lead us to the further facile manipulation and more profound understanding of host−guest systems in the solid state.

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Supporting Information Available: Experimental details for the preparation of the cross-linked polymer and the desorption/adsorption of guests from/to the cross-linked polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Different batches of the cross-linked polymer were found to vary their XRD profiles and the amounts of guest capable of releasing/capturing. The polymer samples for the experiments shown in Figure 2 were from the same batch, and the sample for the experiment shown in Figure 1 was from another batch.

(8) The packing mode of the ordered structure seems to be one of the crucial factors to determine the rigidity of the host framework. For examples of hexagonal columnar and lamellar structure systems, see refs 4b and 4d, respectively.

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