Host–Guest Systems

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Radical Polymerization of Vinyl Monomers in Porous Organic Cages

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Abstract: *The radical polymerization of vinyl monomers was performed in a tetrahedral imine-linked organic cage with extrinsic porosity (CC3). Because of its dynamic and responsive packing structure, CC3 endowed the polymerization with specific behaviors. The adsorption of styrene triggered a change in the CC3 assembly, resulting in a monomer arrangement that was suitable for polymerization within the host matrix. The polymerization reaction was strongly dependent on the crystallinity of CC3 and was promoted by amorphization of the host in a cooperative manner, which is not possible with conventional rigid porous materials. Furthermore, CC3 can recognize the polarity of substrates, and thus polar monomers, such as methyl methacrylate and acrylonitrile, could not induce the structural changes in CC3 that are required for polymerization. This monomer specificity governed by the flexibility of CC3 is useful to the prevent incorporation of unfavorable monomers into the polymeric products.*

There has been tremendous interest in nanoporous materials with molecular-sized pores because of their wide range of applications in storage, separation, and catalysis.[1] In particular, the preparation of nanoporous networks based on molecular precursors, such as metal–organic frameworks (MOFs),[2] covalent organic frameworks (COFs),[3] and polymers of intrinsic microporosity (PIMs),[4] has attracted much attention because their porous structures are stabilized by extended networks of covalent or coordination bonds. By contrast, nanoporous materials comprising discrete organic molecules have emerged as a new class of porous materials in recent years.[5] Different from organic clathrates, which are usually unstable against maintaining permanent pores upon guest removal, several porous organic molecules have shown permanent porosity, and their porous structures can be dynamically controlled depending on the packing of the component molecules.[5,6] For example, the molecular assembly of a cycloimine cage with a prefabricated cavity and pore window (CC3) is ambiguous, and thus the porous structure of CC3 changes greatly from amorphous to highly crystalline states upon guest inclusion or exposure to external stimuli (Figure 1).[6d–h] Interestingly, insufficient molecular packing of CC3 in the amorphous form results in an increase in the

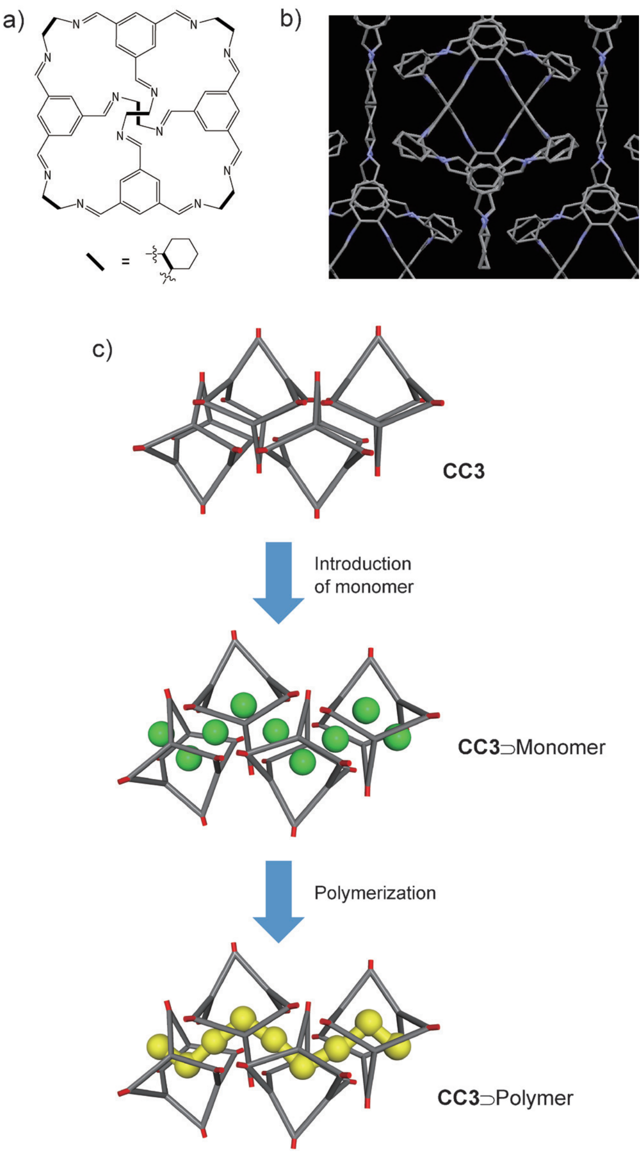

Figure 1. a) Molecular structure of CC3. b) The porous crystalline structure of CC3 shown as a stick model. Carbon gray, nitrogen blue. Hydrogen atoms are omitted for clarity. c) Polymerization of monomers in CC3.

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microporosity of CC3.[6e,f,i] Taking advantage of the properties of organic cages compared to conventional porous materials in terms of solubility and structural flexibility, CC3 and its derivatives have shown highly advanced adsorption/separation behavior with responsivity and selectivity.[6d–h,k]

In nature, all chemical reactions occurring in a living organism are governed by the catalytic action of enzymes.[7] Internal protein dynamics and flexibility are highly relevant to the enzymatic reactions, where subtle structural changes induced at the reactive site enhance the reactivity and selectivity of chemical reactions.[8] It is thus important to create reaction fields that can promote chemical reactions in a cooperative and responsive manner.[9] In this regard, porous organic cages have several excellent characteristics, such as designable porous structures and dynamic flexibility. Despite their useful advantages, there has been no report on regulating chemical reactions utilizing the flexibility of porous organic cages. Herein, we examined the radical polymerization of vinyl monomers in the porous structure of CC3 (Figure 1). Interestingly, the polymerization behavior was strongly dependent on the dynamic structural changes of CC3, which cannot be attained in conventional rigid porous materials, including zeolites and MOFs. Polymerization according to an induced-fit mechanism as well as specific selectivity was observed, highlighting the advantages of flexible porous organic cages.

Herein, we demonstrate the radical polymerization of styrene (St) using CC3. After dispersion of CC3 in St for the introduction of St into the pores, the excess monomers outside the host compound were removed by evacuation to give an adduct (CC3⊃St). X-ray powder diffraction (XRPD) was used to evaluate the crystallinity of CC3 upon inclusion of St in the pores (Figure 2; see also the Supporting Information, Figures S1 and S2). The crystallinity of CC3 could be finely tuned from 44 % to 87 % by changing the immersion time or by using a volatile cosolvent. Treatment of CC3 with neat St for a long period of time decreased the crystallinity of the host. The use of dichloromethane as a cosolvent maintained the crystallinity of CC3 during the introduction of St, and the volatile dichloromethane was thoroughly removed in the evacuation process. Note that CC3 could adsorb a larger amount of St with decreasing crystallinity, as revealed by ^{1}H NMR measurements after dissolving CC3⊃St in CDCl$_3$ (Figure S3). The loading amount of St was found to increase almost linearly with an increase in the amorphous ratio of CC3 (100–crystallinity [%]; Figure 3). This specific adsorption behavior promoted by amorphization of CC3 was strikingly different from that observed in conventional rigid porous materials.[6e,f,i]

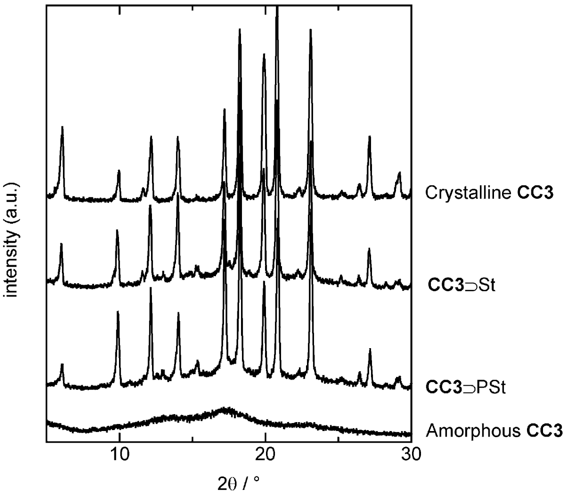

Figure 2. XRPD patterns of recrystallized CC3, CC3⊃St, CC3⊃PSt, and amorphous CC3 with crystallinities of 100, 54, 54, and 0 %, respectively.

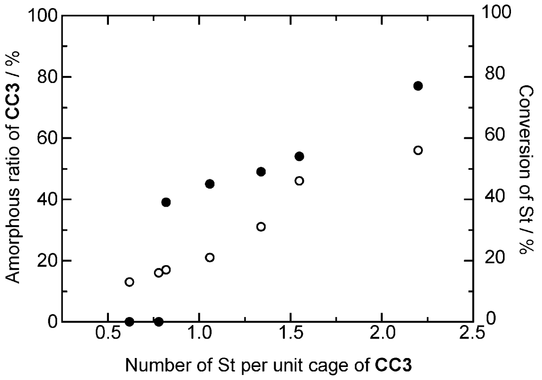

Figure 3. Plots of the amorphous ratio of CC3 (○) and the conversion of St (●) against the amount of St in CC3.

The obtained CC3⊃St was heated with azobisisobutyronitrile (AIBN) at 70 °C for 48 h to induce polymerization, forming polystyrene (PSt). The ^{1}H NMR spectrum of the product (CC3⊃PSt) in CD$_2$Cl$_2$ showed that the structure of CC3 was intact after the polymerization (Figure S4). Furthermore, the crystallinity of CC3 was retained during the polymerization, as confirmed by the XRPD measurement (Figure 2). CC3⊃PSt was then treated with 1 M HCl to decompose the CC3 framework, which provided PSt as a white powder. In Figure 3, the conversion of St is plotted against the amount of St accommodated in CC3. The significant effect of the crystallinity of CC3 on the polymerization of St is clearly revealed. In contrast to the linear relationship between the amorphous ratio of CC3 and the amount of St, a discontinuous change in the yield of PSt was observed as the amount of St increased. When the loading of St within CC3⊃St was small, the encapsulated St did not react until the loading of St reached approximately 0.8 styrene molecules per cage unit. After this threshold, the conversion of St gradually increased, and PSt could be efficiently obtained in highly amorphous CC3. Gel permeation chromatography showed that the molecular weight of the resulting PSt also became larger with decreasing crystallinity of CC3 (Figure S5). Although the number-averaged molecular weight (M_n) of the isolated PSt was not very high (several thousand Daltons), the molecular weight distribution (M_w/M_n) was relatively narrow (ca. 1.4–1.6) compared to that of PSt synthesized under usual solution conditions, probably because of the stabilization of the reactive propagation radicals in the CC3 host, as is often observed in confined polymerization systems.[10] In the case of conventional hard porous materials with network topologies, polymerization reactions cannot proceed efficiently in the amorphous forms because of the segregation of the nanochannel structures.[11] By contrast, CC3 favorably induced the polymerization in its amorphous form, and the polymerization of St in CC3 was triggered once the concentration of St exceeded the threshold.

CC3 forms a diamondoid pore network with intra- and inter-cage cavities.[6d,g,k] If monomer molecules could be trapped only in either of the cavities, polymeric products could not be produced in such a discontinuous channel structure of CC3. Considering the size, shape, and nature of styrene, this molecule can easily diffuse through the CC3 structure to be accommodated in intra- and inter-cage cavities.[6g,k] In fact, the presence of styrene in both cavities was supported by the reasonably high loading of styrene in low-crystalline CC3. To determine the polymerization mechanism, the molecular motion of the St monomers within CC3 was probed by solid-state ^{2}H NMR spectroscopy. The ^{2}H NMR spectra of St-d_5 (selectively deuterated at the phenyl ring) adsorbed in CC3 with different crystallinities (80 and 54%) were measured from 123 to 323 K (Figures 4 and S6). Interestingly, the sharp peaks observed above 243 K for both samples revealed the high mobility of the St guests with isotropic rotation in CC3, which suggests that the mobility of the monomer was high enough for polymerization at the polymerization temperature (70 °C). Whereas the ^{2}H NMR spectrum of the high-crystalline (80%) CC3⊃St-d_5 sample showed a single narrow Lorentzian line, the spectrum for a low-crystalline sample (crystallinity: 54%) was composed of narrow and broad Lorentzian components (Figures 4 a, b). For the latter sample, these two components were found to be substantially equivalent (Figure S7). The line width for the narrow component was almost the same as that of the corresponding component in high-crystalline CC3⊃St-d_5 (Figure 4 c). These results clearly suggest that St-d_5 adsorbed on crystalline and amorphous CC3 gives NMR resonances with narrow and broad Lorentzian shapes, respectively. As the line broadening of the ^{2}H NMR spectrum is caused by residual anisotropic interactions arising from the restriction of molecular motion,[12] the isotropic rotation of St-d_5 was relatively suppressed in amorphous CC3. Therefore, in our system, the accommodation of St monomers in crystalline CC3 increases the mobility of St. This result suggests the isolation of the St molecules in the compartmented cages, leading to the inhibition of polymerization. By contrast, St molecules in amorphous CC3 assemble closely enough to be polymerized in the extended diamondoid channels, despite the lower mobility that is due to the molecular packing of St. From the ^{2}H NMR measurements, we understood that the mobility of St in CC3 was affected by the crystallinity of CC3, which is the key to the polymerizability of St in CC3.

Aside from St, we attempted the polymerization of methyl methacrylate (MMA) and acrylonitrile (AN) in CC3 because these monomers have smaller molecular dimensions than St and should thus show high reactivity even in the narrow nanopores.[13] We introduced MMA and AN into CC3 in the same manner as St to give the composites CC3⊃MMA and CC3⊃AN, which were analyzed by XRPD and ^{1}H NMR spectroscopy (Figures 5, S8, and S9). The crystallinity of CC3 after the introduction of the monomers was almost 100% (Figure 5), and the amount of monomer adsorbed in the host was relatively low (Figure S9; 1.0 MMA and 1.4 AN monomers per cage unit). In contrast to St, the use of polar vinyl monomers, such as MMA and AN, could direct the CC3 cages to crystallize effectively, and the loading amounts of these monomers were independent of the immersion time in the monomers. CC3⊃MMA and CC3⊃AN were heated at 70 °C for 48 h in the presence of AIBN to induce polymerization. However, these substrates did not produce polymeric products in the CC3 host because of the unsuitable arrangement of the monomers in crystalline CC3, similarly to the case of St. Note that the polymerization of MMA proceeded smoothly (55% conversion, $M_n = 24200$, $M_w/M_n = 1.7$) when we employed low-crystalline CC3 (Figure 5; crystallinity: 44%) that was obtained by thorough grinding. These results strongly support our proposed mechanism, namely that the

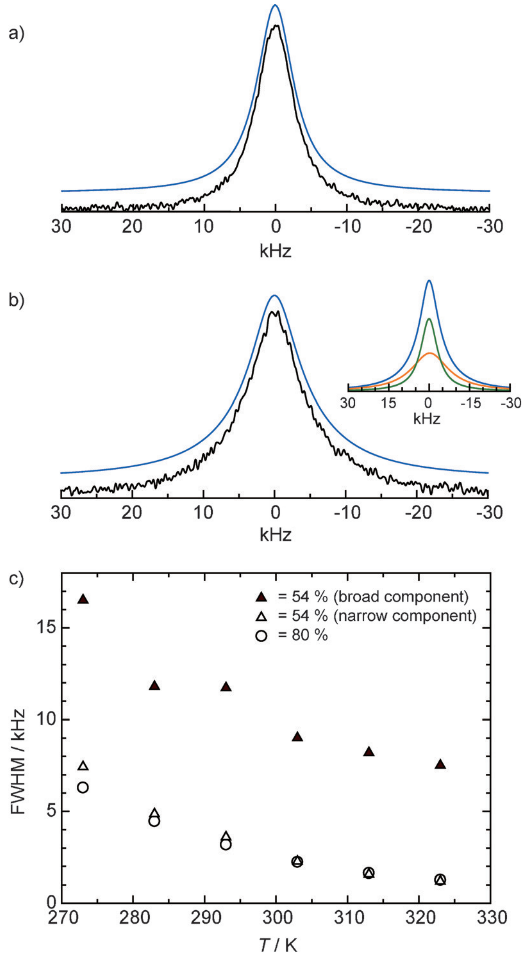

Figure 4. a, b) ^{2}H NMR spectra of St-d_5 adsorbed in CC3 with crystallinities of 80 (a) and 54% (b) at 273 K (black: observed, blue: simulated). The inset in (b) shows the simulated spectrum (blue) as a combination of narrow (green) and broad (orange) Lorentzian lines. c) Plots of the full widths at half maximum of the ^{2}H NMR spectra for CC3⊃St-d_5 with different crystallinities.

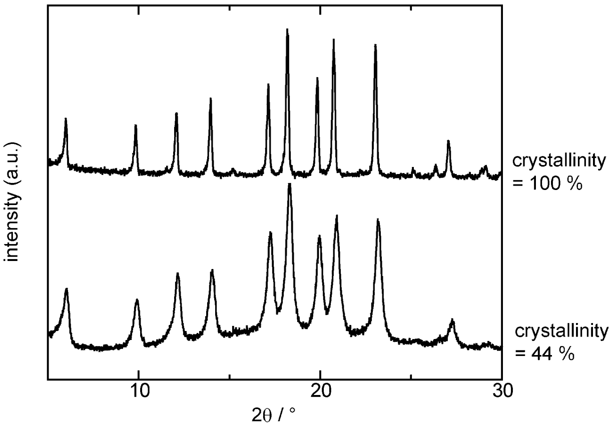

Figure 5. XRPD patterns of CC3⊃MMA with different crystallinities.

polymerizability of monomers strongly depends on the crystallinity of CC3.

As St can be easily copolymerized with MMA in the bulk and under solution conditions, the copolymerization of these two monomers adsorbed in CC3 was examined by changing the monomer ratio. The incorporation of MMA increased the crystallinity of CC3, which prevented the production of both the copolymer and the PSt homopolymer. Despite the high polymerizability of MMA, this monomer was regarded as an "inhibitor" in this copolymerization system, because polymerization was not observed even in the presence of only 20 mol% of MMA owing to the crystallinity of CC3 (Figure S8; crystallinity: 86%). Although the total number of monomer units in CC3 seemed high enough (Figure S9; 2.1 monomers per cage unit), the inability of CC3 to transform itself into the amorphous form prevented the polymerization. This substrate-specific polymerization process is governed by the structural flexibility of CC3, where only certain monomers can be involved in the polymerization by appropriate structural transformations of the host matrix. Therefore, CC3 has the potential to discriminate between monomers, enabling the highly selective production of requisite polymers.

In conclusion, we have described the first polymerization reaction in an organic cage with extrinsic porosity. In contrast to conventional rigid porous hosts, such as zeolites and MOFs, the use of discrete CC3 molecules leads to a packing structure that can be flexibly altered and is responsive to the quantity and type of accommodated vinyl monomers, which renders polymerization reactions in the pores dynamic and highly specific. We believe that these findings will contribute to significant progress in the utilization of porous organic cages for mediating strictly controlled reactions because of the high designability, versatility, and solubility of the organic cages.

Experimental Section

Polymerization of St in CC3: After drying the host compound CC3 (*S* configuration, 100 mg) in vacuo (< 0.1 kPa) at 110 °C for 5 h in a Pyrex reaction tube, a mixture of St (250 μL) and AIBN (2.5 mg) was added to the flask at room temperature. The mixture was left to stand to allow for the diffusion of the monomer and initiator into CC3, then excess St was removed in vacuo (0.35 kPa) for 1 h at room temperature. The reaction tube was filled with nitrogen and heated to 70 °C for 48 h for polymerization. The obtained composite was washed with MeOH to remove unreacted St inside the pores, and then stirred in a 1 M aqueous HCl solution (50 mL) for decomposition of the CC3. The resultant solid was dissolved in $CHCl_3$; then the solution was poured into a large amount of MeOH. The collected PSt product was dried under reduced pressure at room temperature.

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