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Controlled Cyclopolymerization of Difunctional Vinyl Monomers in Coordination Nanochannels

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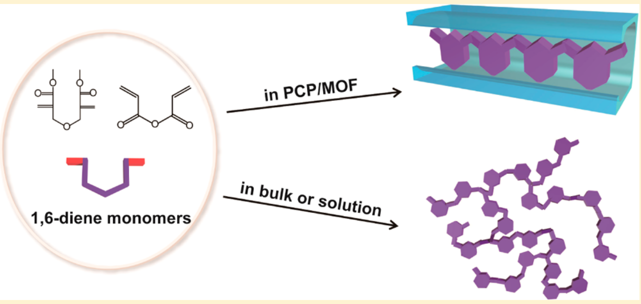
S *Supporting Information*

ABSTRACT: Radical cyclopolymerization of difunctional monomers based on 1,6-diene components was performed in one-dimensional channels of porous coordination polymers (PCPs). Although bulk or solution polymerization of the monomers usually gives cross-linked insoluble polymers, the unfavorable interpolymer reactions were effectively suppressed in the narrow nanochannels of PCPs to provide soluble linear polymers. The pore matrices and functionality of PCPs can be readily designed by changing the organic ligands, so that polymerization of the diene monomers in different sized pores was examined. The primary structures of the resulting polymers, such as branching, cyclic structure, and stereoregularity, were changed, depending on the pore characteristics of the PCPs.



INTRODUCTION

Radical polymerization of difunctional vinyl monomers often leads to insoluble polymers with uncontrollable mixtures of linear and cross-linked structures. Thus, it is important to develop polymerization methods for obtaining soluble linear polymers in controlled manners. Cyclopolymerization of divinyl monomers can provide linearly extended polymers containing cyclic structures in the polymer backbone.[1] As a result, it offers rigidity, solubility, and thermal stability of the resulting polymers, and enables the fine-tuning of the polymer properties depending on the degree of cyclization. The strategies for preparation of highly cyclized polymers have been developed so far based on monomer design.[2] Cyclopolymerization of 1,6-dienes with fewer cross-linking reactions is likely to proceed if their monofunctional counterparts do not polymerize.[3] However, the general drawback to these monomers is their low polymerizability because of the unconjugated structure. Polymerizations of designed monomers with two vinyl moieties in close proximity give a variety of linear polymers. In particular, the possibility of introducing cleavable units in the monomers allows chiral induction[4] and sequence regulation[5] after the removal of the template moieties. However, many polymerization systems suffer difficulties in inhibiting cross-linking reactions to give polymers with dominant cyclic structures.

Recently, the design and preparation of porous coordination polymers (PCPs) or metal organic frameworks (MOFs) that contain open-channel structures of controllable pore size, shape, and chemical environments have attracted much attention because of their wide applications in adsorption, separation, guest alignment, and sensors.[6] In particular, utilization of the regular micropores of PCPs for heterogeneous catalysis and ship-in-bottle reactions has shown many advantages to induce highly selective reactions in the pores, imposing specific size and shape effects of the pores on the reaction kinetics and selectivity.[7] Our recent research has revealed that radical polymerization of vinyl monomers in PCP channels can provide opportunities for controlling the primary structures of resulting polymers, such as molecular weight distribution, stereoregularity, reaction position, and copolymer composition.[8] The propagating radicals of vinyl polymers were remarkably stabilized in the narrow nanochannels, resulting in effective suppression of unfavorable side reactions, such as chain transfer and termination reactions.[8c,d] In addition, the rational design of nanochannels by functionalization of organic ligands enabled the production of well-regulated polymers that are unavailable in conventional polymerization systems in solution.[8e,f] Here, we performed controlled radical cyclopolymerization of 1,6-diene-type monomers, dimethyl 2,2′-[oxybis(methylene)]diacrylate (DO) and acrylic anhydride (AA), in one-dimensional nanochannels of $[Cu_2(L)_2(dabco)]_n$ (**1**: L = dicarboxylates, dabco = 1,4-diazabicyclo[2.2.2]octane) to give soluble linear polymers without cross-linked structures. Change of the dicarboxy ligands enabled controls of the pore

Received: June 14, 2014
Revised: October 7, 2014

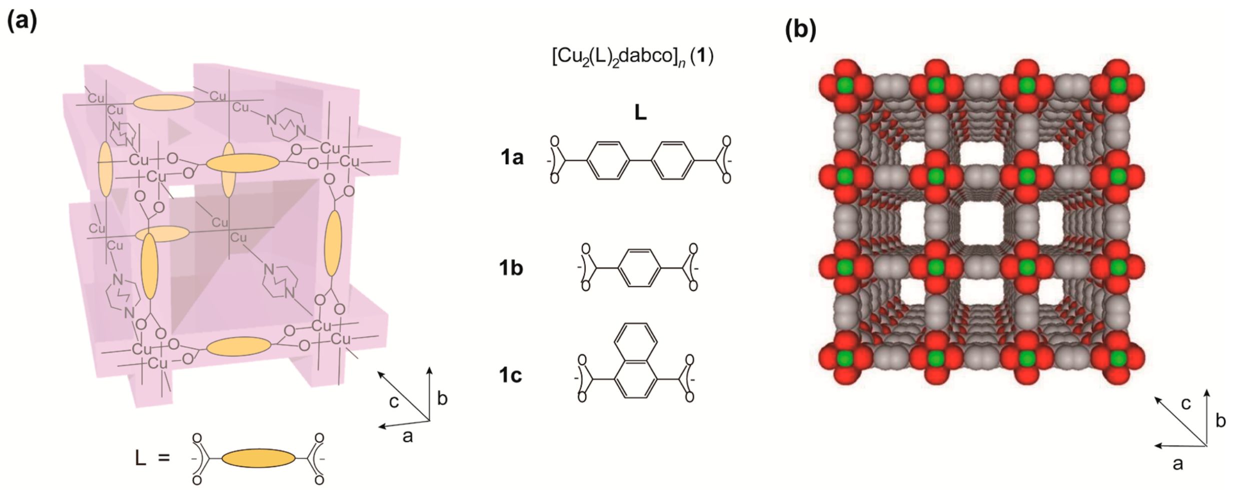


Figure 1. (a) Schematic illustration of $[Cu_2(L)_2(dabco)]_n$ (**1**). (b) One-dimensional nanochannel structure of **1b**. Copper, oxygen, nitrogen, and carbon atoms are denoted with green, red, blue, and gray, respectively. Hydrogen atoms were omitted for clarity.

size and shape of **1** (Figure 1: **1a**, L = biphenyl-4,4′-dicarboxylate; **1b**, *L* = 1,4-benzenedicarboxylate; **1c**, *L* = 1,4-naphthalenedicarboxylate), which allowed the tuning of solubility and cyclic structures of the obtained polymers.

EXPERIMENTAL SECTION

Materials. All of the reagents and chemicals used were obtained from commercial sources, unless otherwise noted. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from MeOH solution. The monomer AA was kindly donated by Kyoeisha Chemical Co., Ltd.

Preparation of 1. The hosts $[Cu_2(L)_2(dabco)]_n$ (**1**) were prepared using a previously described method.[8d] The PCPs with one-dimensional nanochannel structures were synthesized by mixing the component chemicals, such as Cu^{2+}, dabco, and various dicarboxylates in sealed vessels at elevated temperature. Formation of the regular porous structures of **1** was confirmed by X-ray powder diffraction (XRPD) measurement.

Synthesis of DO. DO was synthesized according to the literature.[9] *tert*-Butyl acrylate (22.9 g), paraformaldehyde (5.38 g), dabco (2.38 g), and *tert*-butyl alcohol (10.7 g) were added to a 200 mL round-bottomed flask. The mixture was stirred at 85 °C for 40 h. After adding CH_2Cl_2 (40 mL), the mixture was washed three times with 3% HCl (20 mL) and with water (20 mL). The resulting organic layer was separated and evaporated to give crude di-*tert*-butyl 2,2′-[oxybis(methylene)]diacrylate (17.3 g). Under a nitrogen atmosphere, this product was reacted with thionyl chloride (80 mL) and one drop of *N,N*-dimethylformamide at 45 °C for 24 h. After the removal of thionyl chloride under reduced pressure, anhydrous MeOH (70 mL) was added, and was stirred at 45 °C for 12 h. The mixture was evaporated, and then dissolved in CH_2Cl_2 (30 mL). After twice washing the mixture with saturated aqueous solution (20 mL) of sodium hydrogen carbonate and with water (20 mL), the organic layer was evaporated. The resulting product was purified by recrystallization from *n*-hexane to give pure DO (4.93 g, 26% yield).

Bulk Polymerization of DO. Under the nitrogen atmosphere, mixture of DO (33 mg), and AIBN (2 mg) was heated above the melting point of DO (47–48 °C)[9] to conduct the polymerization for 48 h at 70 °C. An insoluble polymeric product was quantitatively obtained after washing with MeOH.

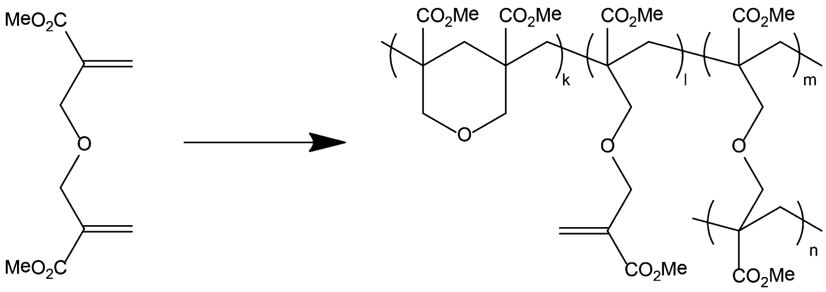
Polymerization of DO in 1. A typical procedure for polymerization of DO in **1** is as follows. After drying the host compound **1b** (200 mg) by evacuation (<0.1 kPa) at 135 °C for 5 h in a Pyrex reaction tube, **1b** was immersed in a MeOH solution (1 mL) of DO (103 mg) and AIBN (4 mg) at room temperature for 0.5 h. Then, MeOH was removed completely by evacuation (0.35 kPa) at room temperature for 1 h to introduce the monomer and initiator into the nanochannels. The reaction tube was filled with nitrogen and heated to 70 °C to perform the polymerization for 48 h. The obtained composite was vigorously stirred for 1 day in a 0.05 M aqueous solution (20 mL) of sodium ethylenediaminetetraacetate (Na−EDTA) for the complete dissolution of the frameworks of **1b**. White polymer product was released and was collected by centrifugation. Repeated washing with water and subsequent drying under reduced pressure at room temperature gave poly(dimethyl 2,2′-[oxybis(methylene)]-diacrylate) (PDO).

Solubility Test of PDO. We examined the solubility of PDO to determine if cross-linked polymer was contained in the product. Polymeric product (10 mg) was stirred in $CHCl_3$ (10 mL) for 10 min. After filtering the insoluble product, the filtrate was evaporated to give PDO that was weighed to determine the solubility.

Polymerization of AA in 1. Host **1** (200 mg) was dried by evacuation (<0.1 kPa) at 135 °C for 5 h in a Pyrex reaction tube. Subsequently, **1** was immersed in AA (1 mL) with AIBN (4 mg) at room temperature for 0.5 h to incorporate the monomer and initiator into the nanochannels. After excess monomer external to the host crystals was removed by evacuation (0.1 kPa) at room temperature for 0.5 h, the reaction tube was filled with nitrogen, and heated to 70 °C to perform the polymerization of AA for 24 h. The obtained product was then evacuated at 70 °C for 48 h to remove unreacted monomer, giving a polymer composite ($1 \supset$PAA).

Usually, polymeric product can be recovered from the composite by dissolution of the host matrix in Na−EDTA, acidic, or basic solutions. However, in this system, the resultant poly(acrylic anhydride) (PAA) is easily hydrolyzed to poly(acrylic acid) (PAAc) during the isolation process. Thus, conversion of AA was estimated using thermogravimetric analysis (TGA). The amount of AA monomer adsorbed in **1** without AIBN was calculated from the weight loss up to 200 °C by TGA. We compared the values of the weight loss corresponding to the adsorbed AA in **1** before and just after the polymerization to determine the conversion rate of AA.

Isolation of PAAc. **1b**-PAA composite (**1b**$\supset$PAA, 200 mg) was stirred in 1 M aqueous NaOH solution (50 mL) for 24 h to decompose the PCP framework. In this process, PAA was hydrolyzed to PAAc in the solution. After filtration, concentrated HCl was carefully added to neutralize the solution. Then, the precipitated terephthalic acid was removed by filtration, and the filtrate was evaporated to give a mixture of PAAc, dabco, and NaCl. For further purification, the mixture was dissolved in DMF (50 mL), and filtered to remove NaCl. After evaporation of the DMF, the obtained solid was washed with $CHCl_3$. Although the isolated PAAc was still contaminated with residual components of **1b** (terephthalic acid and dabco), the polymer could be characterized by ^1H and ^{13}C NMR in D_2O.



DO

Figure 2. Formation of six-membered cyclic, pendant double bond, and cross-linked structures in polymerization of DO.

Measurements. The XRPD data were collected using a Rigaku RINT 2000 Ultima diffractometer employing CuK*α* radiation. The IR spectra were measured using a Thermo Scientific Nicolet iS5. The ^1H and ^{13}C NMR spectra were obtained using a JEOL A-500 spectrometer operating at 500 MHz. The TGA was carried out from room temperature to 500 °C at a heating rate of 10 $°C\ min^{-1}$ using a Rigaku Instrument Thermo Plus TG 8120 in a nitrogen atmosphere. Gel permeation chromatography (GPC) measurements on the resulting polymers were performed in $CHCl_3$ at 40 °C on three linear-type polystyrene gel columns (Shodex K-805L) that were connected to a JASCO PU-980 precision pump, a JASCO RI-930 refractive index detector, and a JASCO UV-970 UV/vis detector set at 256 nm. The columns were calibrated against standard poly(methyl methacrylate) samples. Solid-state NMR measurements were carried out on 9.4T Bruker solid-state NMR instrument with an ADVANCE III 400 MHz spectrometer. ^{13}C cross-polarization magic angle spinning (CP MAS) spectra were obtained using a double resonance 7 mm magic angle spinning probe. A recycle delay and spinning rate are 2 and 7 kHz, respectively.

■ RESULTS AND DISCUSSION

Polymerization of DO. In the case of polymerization of dialkyl 2,2′-[oxybis(methylene)]diacrylate monomers, cyclization efficiency clearly depends on the bulkiness of their ester substituents, where the efficiency decreases with decreasing substituent size.[9,10] In fact, polymerization of DO with a dimethyl substituent by conventional methods gives polymers with mixtures of six-membered cyclic, cross-linked, and pendant double-bond structures in an uncontrolled manner (Figure 2).[9] Accordingly, solid-state bulk polymerization of DO at 70 °C provided a polymeric product that was completely insoluble in $CHCl_3$ because of the highly cross-linked structure. The free-radical polymerization of DO was attempted in benzene solution under a variety of monomer concentrations, giving insoluble cross-linked polymers as the predominant product. The solubility of the product was dependent on the initial monomer concentration, where the polymer product obtained from diluted monomer solution showed higher solubility in $CHCl_3$. However, the soluble part of the product showed a large polydispersity of the molecular weight ($M_w/M_n > 3$), which should be caused by the hyperbranched structure derived from intermolecular reactions.[2f,11]

Radical polymerization of DO was performed in **1** to inhibit the unfavorable cross-linking reaction. After introduction of the monomer into the channels of **1**, we measured the XRPD of the adduct (**1**⊃DO) to confirm the incorporation of the monomer into the nanochannels (Figure 3). The absence of diffractions characteristic of crystalline DO demonstrated that there was no leakage of the monomer from the nanochannels. We then carried out polymerization of DO by heating **1**⊃DO at 70 °C for 48 h to give polymer composites (**1**⊃PDO). XRPD measurements of **1**, **1**⊃DO, and **1**⊃PDO showed no change in the diffraction peak positions based on the host **1**, indicating that the crystalline porous structures of **1** was maintained without severe amorphization during the polymerization reaction (Figure 3). The resulting PDO was quantitatively released from the pores of **1** by dissolution of the host matrices of **1**⊃PDO in Na–EDTA solution.

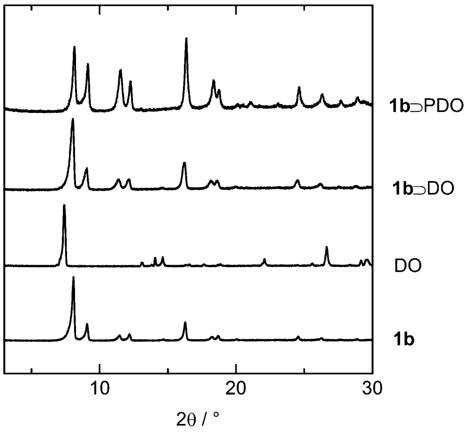


Figure 3. XRPD patterns of **1b**, neat DO, **1b**⊃DO, and **1b**⊃DO.

Table 1 summarizes the polymerization results of DO in **1** with different pore sizes. These experimental results clearly exhibit the significant pore size effects of PCPs on the polymerization of DO. Regarding the reactivity of DO in **1**, the yield of PDO decreases as the size of the pore narrows. The same tendency was also observed in the polymerization of other monomers in PCPs or nanopores because of the restricted mobility of monomers confined in narrower nanospaces.[8c,d,12] We also examined the solubility of PDO prepared in **1**. The product obtained from **1a** was partially soluble in $CHCl_3$, which

Table 1. Polymerization of DO in Bulk, Solution, and Nanochannels of 1 at 70 °C for 48 h

host (pore size [$Å^2$])	yield (%)	solubility[a]	M_n (M_w/M_n)[b]
bulk polymerization	100	0	–
0.6 M benzene solution[c]	79	5	–
0.1 M benzene solution	96	61	21 800 (3.4)[d]
1a (10.8 × 10.8)	65	36	8 300 (2.4)[d]
1b (7.5 × 7.5)	55	100	19 900 (1.5)
1c (5.7 × 5.7)	34	100	11 800 (1.4)

[a] Examined by dissolving the product (10 mg) in $CHCl_3$ (1 mL). [b] Obtained by GPC calibrated by poly(methyl methacrylate) standards. [c] Polymerization time was 1 h. [d] Analyzed on the soluble part.

is similar to the bulk and solution polymerization systems. In contrast, PDO isolated from **1b** and **1c** was completely soluble in $CHCl_3$. Thus, GPC analysis of the soluble part of PDO obtained from **1** was performed. Despite the polymerizations in narrow nanospaces, a polymeric product of PDO was obtained from every PCP. In addition, the polydispersity index (M_w/M_n) of PDO strongly depended on the pore size of **1**, where M_w/M_n of PDO obtained from **1b** and **1c** was relatively small. Because cross-linked or branched polymers usually show large polydispersity, this result is also suggestive of nonbranching structures in the PDO backbone.[2f,11]

We measured the IR spectra of the PDO from **1b** and **1c** to determine the microstructures (Figure 4), where the peak assignable to C═C double bonds of DO monomer at 1639 cm^{-1} was absent, probably because all of the double bonds in DO participated in the cyclopolymerization. A peak corresponding to C═O vibration for the PDO was clearly shifted to higher wavenumber compared with that of DO because of the formation of the cyclic structures. In the ^1H NMR spectra of the PDO isolated from **1b** and **1c**, no signals assignable to C═C double bonds were detectable, which is consistent with the IR result. In addition, conventional proton decoupled as well as distortionless enhancement by polarization transfer (DEPT)-135 ^{13}C NMR experiments revealed that the PDO prepared in these pores was contained only six-membered tetrahydropyran units (Figure 5).[13] Thus, the narrow one-dimensional channels of PCPs could suppress the unfavorable cross-linking and effectively direct the linearly extended cyclopolymerization of DO.

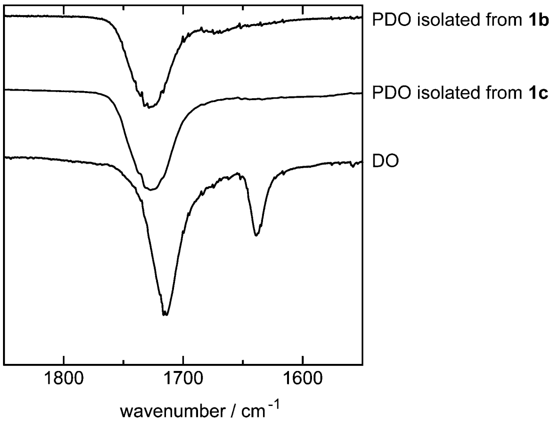


Figure 4. IR spectra of DO and PDO isolated from **1b** and **1c**.

Polymerization of AA.

Radical polymerization of AA in bulk produces cross-linked insoluble polymer. Solution polymerization of AA can provide a linear polymer (PAA) with less cross-linked or a branched structure; however, mixtures of five- and six-membered anhydride ring structures are formed in the main chain, via head-to-head and head-to-tail additions, respectively, during the intramolecular cyclization (Figure 6).[14] Detailed studies on the polymerization of AA showed that formation of six-membered rings is favored with increasing the monomer concentration, decreasing solvent polarity, and decreasing the polymerization temperature.[14b,c] The properties of PAA are significantly dependent on the ratio of five- and six-membered ring structures; thus, we performed polymerization of AA in the nanochannels of **1** to control the ring structures of PAA. In our system, increase in the proportion of six-membered rings in PAA is highly likely because of the condensed adsorption of AA in the hydrophobic channels of **1**. In addition, narrow nanochannels of **1** can lower the mobility of the embedded AA compared with that in solutions, which is presumably equivalent to the effect of decreasing the reaction temperature.

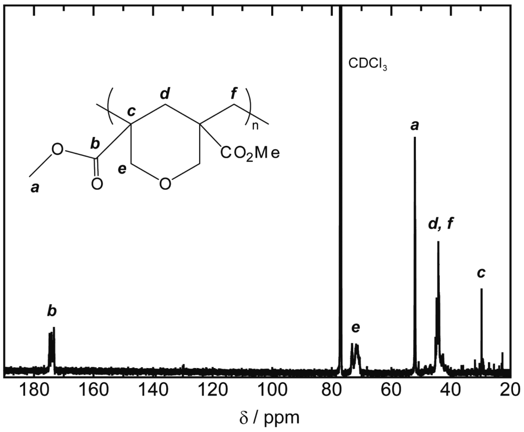


Figure 5. ^{13}C NMR spectrum of PDO obtained from **1b** in $CDCl_3$.

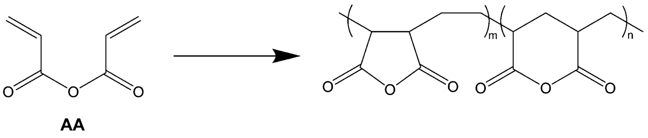


Figure 6. Formation of five- and six-membered cyclic structures in solution polymerization of AA.

Similar to the case of the polymerization of DO in **1**, polymerization of AA was carried out in **1** at 70 °C for 24 h to give the PAA composite (**1**⊃PAA) after the incorporation of AA into the channels. The maintenance of the PCP framework before and after the polymerization was confirmed by XRPD measurement of PAA (Figure 7). As was observed in the polymerization of DO, conversion of AA in **1** depended on the pore size of the PCPs. Although **1a** and **1b** gave PAA in relatively good yields (**1a**; 47%, **1b**; 43%), no polymeric product could be obtained in **1c**, which has the smallest pore size. Despite the relatively small monomer size, the conversions of AA in the PCP channels were found to be lower than those of DO in the corresponding channels (Table 1), which is presumably because of the effectively conjugated nature and the conformational rigidity of AA. Formation of PAA was confirmed by the IR measurement of **1**⊃PAA, in which structural assignment of cyclic structures in the polymer

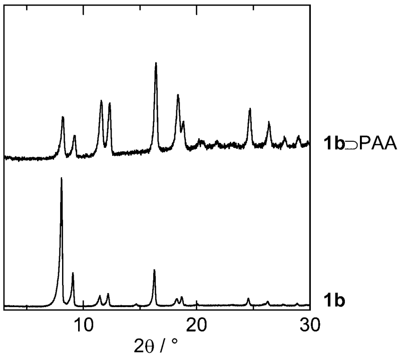


Figure 7. XRPD patterns of **1b** and **1b**⊃PAA.

backbone was also possible.[14a,c] Figure 8 shows the IR spectra of **1a**⊃PAA, **1b**⊃PAA, and the PAA prepared in benzene solution at 70 °C for 24 h. The previous paper has reported that the carbonyl absorption bands for five-membered anhydride in PAA appear at 1860 and 1780 cm^{-1}.[14a] These peaks were clearly found in the spectrum of the PAA synthesized in benzene; in contrast, neither **1a**⊃PAA nor **1b**⊃PAA had the bands corresponding to the formation of five-membered rings. The solution-polymerized PAA gave additional carbonyl peaks at 1810 and 1740 cm^{-1}, showing the existence of six-membered racemic anhydride in the polymer backbone.[14a,c] However, in the spectra of the **1**⊃PAA composites, absorption bands were only observed around 1805 and 1760 cm^{-1} in the carbonyl region, suggesting the predominant formation of six-membered meso anhydride in the PAA structure.[14a] Because polymerization in narrow nanochannels of PCPs has a propensity to give polymers with less sterically bulky meso moieties rather than racemic polymers,[8d,e] considerable difference in the stereoregularity of the resulting PAA was caused by effective through-space interaction by **1**. In the case of **1a**⊃PAA, an additional shoulder peak appeared at 1731 cm^{-1} in the region of the carbonyl absorption. Although the IR spectrum of propionic anhydride shows only two peaks corresponding to the carbonyl moiety, another carbonyl peak is observable at 1733 cm^{-1} in the spectrum of acrylic propionic anhydride, implying the existence of pendant double bonds in the structure of PAA in **1a**. These IR results show that cyclic structures of PAA can be finely regulated in the nanochannels of **1**, particularly in **1b**, which strongly supports our hypothesis. In addition to the IR measurement, we performed CP MAS solid-state ^{13}C NMR spectroscopy of **1b**⊃PAA. To avoid the paramagnetic effect of **1b** containing Cu^{2+}, we prepared PAA in channels of isostructural diamagnetic Zn^{2+} analogue of **1b** (**Zn1b**) as well,[8c,d] and characterized the structure of this composite. These solid-state NMR measurements also supported the formation of PAA with six-membered rings in the nanochannels of PCPs.[14c]

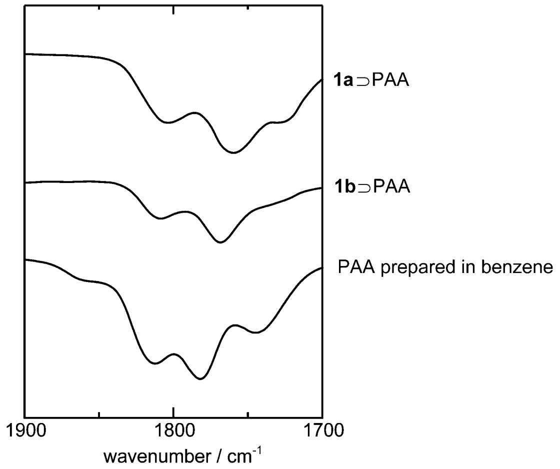


Figure 8. IR spectra of **1a**⊃PAA, **1b**⊃PAA, and PAA prepared in benzene at 70 °C.

To provide further confirmation of the microstructure of PAA, we attempted to recover the PAA included in **1** by treating the framework with aqueous Na−EDTA, acidic, or basic solution. However, this anhydride polymer was readily hydrolyzed to form PAAc during the isolation process. Despite the transformation of the polymer structure by hydrolysis, structural information on PAA can be transcribed into the daughter PAAc. In fact, hydrolysis of five- and six-membered anhydrides in PAA results in head-to-head and head-to-tail configurations of PAAc, respectively (Figure 9).[14c] It is thus evident that structural analysis on PAAc gives important fingerprints about the microstructure of PAA. A previous paper reported that, in the ^{1}H NMR spectrum of PAAc in D_2O, peaks corresponding to head-to-tail- and head-to-head-type methylene protons in the PAAc main chain appear at 1.8 and 1.6 ppm, respectively.[14c] After the isolation of PAAc from **1b**, we measured the ^{1}H NMR and could scarcely see the peak for methylene protons around 1.6 ppm (Figure 10). In addition, ^{13}C NMR spectrum of the product in D_2O gave weak signals corresponding to the syndiotactic triad (*rr*) of CH in the main chain of PAAc at 47 ppm, which is fairly consistent with the IR results.[15] Thus, these results showed that PAA was comprised of dominantly six-membered anhydride rings with high meso content.

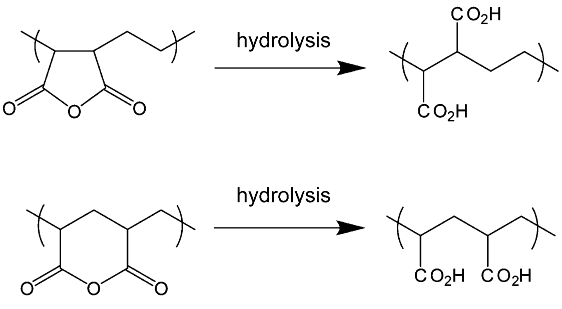


Figure 9. Hydrolysis of PAA with 5- and 6-membered rings gives head-to-head and head-to-tail type PAAc, respectively.

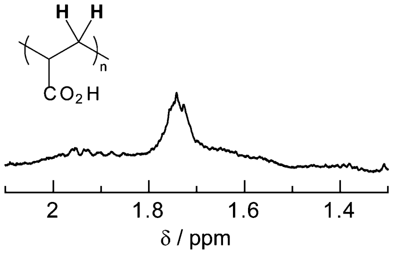


Figure 10. ^{1}H NMR spectrum of PAAc obtained from **1b** in D_2O. A peak corresponding to methylene protons of head-to-tail PAAc evidently appeared at 1.75 ppm.

■ CONCLUSION

This study has demonstrated that use of the nanochannels of PCPs for the polymerization of 1,6-diene monomers is a viable strategy for promoting cyclopolymerization without unfavorable cross-linking and branching reactions. The success of this strategy depended significantly on the pore size of the nanochannels in PCPs, where narrower nanochannels could effectively direct the linearly extended cyclopolymerization. Compared with conventional linear vinyl polymers, polymers with cyclic structures in the main chains usually show higher rigidity and thermal stability. We believe that the methodology presented here will be applicable to other cyclopolymerizations and/or multipolymerizable monomer systems for producing polymers with well-defined structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

XRPD patterns, GPC profiles, and IR, ^{1}H NMR, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by CREST-JST and Grant-in-Aids for Young Chemists (A) and for Scientific Research on Innovative Area "New Polymeric Materials Based on Element-Blocks (No. 2401)" from the Ministry of Education, Culture, Sports, Science and Technology, Government of Japan. The authors also acknowledge the financial supports from Sumitomo Chemical Co., Ltd. and Kuraray Co., Ltd., and insightful discussions with Mizuki Ito, Katsuhiko Iwasaki, and Hiroyuki Konishi.

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