Radical Polymerization of Vinyl Monomers in Porous Coordination Polymers: Nanochannel Size Effects on Reactivity, Molecular Weight, and Stereostructure

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ABSTRACT: Radical polymerization of vinyl monomers (styrene, methyl methacrylate, and vinyl acetate) was performed in various nanochannels of porous coordination polymers (PCPs), where relationships between the channel size and polymerization behaviors, such as monomer reactivity, molecular weight, and stereostructure, were studied. The capability for precise size tuning of nanospaces has afforded the first systematic study of radical polymerization in microporous channels based on PCPs. In this polymerization system, the polymer-growing radicals were remarkably stabilized by efficient suppression of termination reactions in the nanochannels, resulting in living radical polymerizations with relatively narrow molecular weight distributions. A significant nanochannel effect on the polymer stereoregularity was also seen, leading to a clear increase of isotacticity in the resulting polymers.

Introduction

Radical polymerization is the most widely employed process for obtaining organic polymeric materials, not only in industry but also in the laboratory because of its versatility in polymerizing a variety of monomers.[1,2] The industrial significance of radical polymerization is evident in the fact that it accounts for about 50% of all commercial polymers. To enhance and improve the properties of the polymeric materials, precision radical polymerization of vinyl monomers to control tacticity, sequence, molecular weight, etc. is currently an important topic;[3−6] however, control of the polymer primary structures to fabricate the desired regularities and topologies is very difficult, which is ascribed to the fact that the high reactivity of growing radical species usually causes unfavorable termination and chain transfer reactions. Recently, living radical polymerization of vinyl monomers in solution systems has emerged as an effective method for precision vinyl polymer synthesis because this polymerization is free from the side reactions resulting from the introduction of dormant species and can thus control the molecular weights, block copolymer sequences, and starburst structures of the resulting polymers.[7−12] It has also been demonstrated that the presence of fluoroalcohols or Lewis acids in reaction mixtures offers certain advantages for changing the tacticity in polymerization of a few specific vinyl monomers.[13−18]

All naturally occurring polymers are produced by enzymatic catalysis, where stereoselective, regioselective, and chemoselective polymerizations proceed effectively within regulated and well-organized molecular-scale spaces. Inspired by the elegant operations in these biological events, many synthetic chemists have focused their research interests on polymer synthesis in confined and designed nanospaces to attain precise structural controls of artificial polymers.[19−28] In particular, microporous materials (pore size <2 nm) with regular channel structures, such as porous organic crystals and zeolites, have imposed specific size and shape effects of the nanochannels on the reaction kinetics and selectivity in the solid-state inclusion polymerization processes because their pore dimensions are quite similar to the monomer sizes.[29−32] For example, much work has been devoted to polymerizations of diene monomers in channels of organic host compounds such as ureas, cyclotriphosphazenes, perhydrotriphenylene, and steroidal compounds, which have successfully accomplished regiocontrolled and stereocontrolled polymerizations by efficient through-space inductions.[33−42] However, inclusion polymerization of vinyl monomers in those microporous crystals seems difficult because the organic hosts exploit only hydrogen-bond or weak van der Waals interactions and generally produce narrow channels that often prevent the polymerization of bulky vinyl monomers or collapse during the vinyl polymerizations.[29,30] In the case of inorganic zeolites, most of them have discontinuous bottleneck channel structures that do not allow the vinyl monomers to be packed continuously. Thus, only a few microporous materials could have afforded polymerization of bulky vinyl monomers, such as styrene, acrylates, methacrylates, and vinyl esters, within the nanochannels.[32,36] From the viewpoint of industrial significance and versatility for organic polymer materials, development of new microporous materials with designable nanospace information, such as channel size, shape, and surface functionality, is highly desirable, as this can be applied to a tailor-made polymerization system to obtain preferred polymer structures; such a system is nanoinformation transcription polymerization (NITP).

The design and construction of metal−organic crystal architectures have been widely studied, and a variety of frameworks have emerged via self-assembly processes.[43,44] In particular, polymeric coordination frameworks with microporous regular channel structures, which are regarded as porous coordination polymers (PCPs), are currently receiving considerable attention in view of their possible functions in sorption, separation, and guest alignment.[45−50] Control of molecular reaction and transformation within the confined environments utilizing the regular

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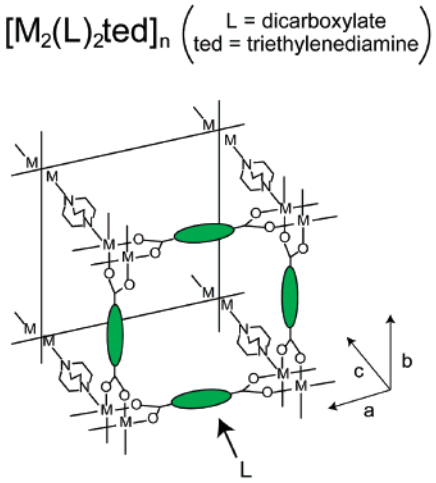
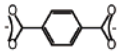
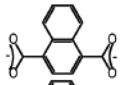
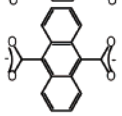
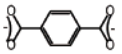
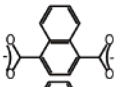
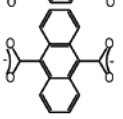
Scheme 1. Combination of Metal Ion (M) and Bridging Ligand (L)



	M	L
1a	Cu^{2+}	
1b	Cu^{2+}	
1c	Cu^{2+}	
1d	Cu^{2+}	
2b	Zn^{2+}	
2c	Zn^{2+}	
2d	Zn^{2+}	

nanochannels of PCPs is also an important topic in this area, prompting vigorous efforts in the development of PCPs for applications in heterogeneous catalysis, asymmetric reaction, and ship-in-bottle synthesis.[51−60] Although there are increasing demands for PCP materials with such catalytic and molecular conversion functions, systematic studies demonstrating how the PCP porous frameworks affect substrate reactivity and selectivity have been very limited so far. One of the most advantageous features of PCPs is their designable channel structures; the channel size, shape, and surface functionality can be systematically tuned by changing the organic ligands and metal ions, approximating molecular dimensions from 4 to 20 Å. This significance should be of key importance for the creation of unique nanospaces that can achieve NITP.[61] Recently, our initial researches revealed that application of a few PCPs to fields of radical vinyl polymerizations results in the achievement of living radicals and topotactic chain growth of multivinyl monomers.[62,63] To establish an NITP system based on PCPs, it is crucial to study detailed nanospace effects of the PCP nanochannels on the vinyl polymerization kinetics and the resulting polymer structures. In this paper, we demonstrate radical polymerization of common vinyl monomers, such as styrene (St), methyl methacrylate (MMA), and vinyl acetate (VAc), in nanochannels of host PCP compounds $[M_2(L)_2ted]_n$ (ted = triethylenediamine; **1**, M = Cu^{2+}; **2**, M = Zn^{2+}) whose channel size can be systematically controlled from 4.3 to 10.8 Å by changing the bridging dicarboxylate ligands L (Scheme 1). The main purpose of our approach here is to understand general relationships between the space size and space effects on the polymerization, such as monomer reactivity, molecular weight, and stereostructure.

Experimental Section

Materials. All reagents and chemicals were obtained from commercial sources. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from a methanol (MeOH) solution, and vinyl monomers were purified by vacuum distillation prior to use. The host PCP compounds $[Cu_2(L)_2ted]_n$ (**1a**, L = biphenyl-4,4′-dicarboxylate; **1b**, L = terephthalate),[64] $[Zn_2(L)_2ted]_n$ (**2b**, L = terephtalate; **2c**, L = 1,4-naphthalenedicarboxylate; **2d**, L = 9,10-anthracenedicarboxylate),[65,66] and a discrete copper(II) complex $[Cu_2(benzoate)_4(3\text{-picoline})_2]$ (**3**)[67] were prepared by previously described methods.

Preparation of $[Cu_2(1,4\text{-naphthalenedicarboxylate})_2ted]_n$ (1c) and $[Cu_2(9,10\text{-anthracenedicarboxylate})_2ted]_n$ (1d). These porous compounds were newly synthesized according to a reported preparation method for **1a** and **1b**.[64] The X-ray powder diffraction (XRPD) patterns of the obtained **1c** and **1d** are almost identical to those of the corresponding zinc analogues **2c** and **2d**,[65,66] showing that the framework structures of **1c** and **1d** are quite similar to those of **2c** and **2d**, respectively.

Polymerization in Nanochannels of PCPs. In a Pyrex reaction tube, a dried host compound (200 mg) was prepared by evacuation (0.08 kPa) at 130 °C for 5 h. Subsequently, this was immersed in a vinyl monomer liquid (0.5 mL) with AIBN (3 mg) at room temperature for 0.5 h to incorporate the monomer and the radical initiator into the nanochannels. After excess monomer external to the host crystals was completely removed by controlled evacuation (0.1−2.0 kPa) at room temperature for 1 h, the reaction tube was filled with nitrogen and was then heated to perform the polymerization. After the polymerization, the composite was stirred in a 0.05 M aqueous solution (15 mL) of ethylenediaminetetraacetic acid for 0.5 h for complete decomposition of the host porous framework. The resultant solid was dissolved in $CHCl_3$, then the solution was poured into a large amount of MeOH or *n*-hexane. The collected polymer product was dried under reduced pressure at room temperature.

Saponification of Poly(vinyl acetate) (PVAc). Saponification of PVAc to convert poly(vinyl alcohol) (PVA) was performed according to a reported method.[13] The saponification rate was 100%, determined by ^{13}C NMR measurement.

Measurements. XRPD data were collected on a Rigaku RINT 2000 Ultima diffractometer with Cu Kα radiation. Thermogravimetric analysis (TGA) was carried out from room temperature to 500 °C at 10 °C min^{-1} with a Rigaku Instrument Thermo plus TG 8120 in a nitrogen atmosphere. The amounts of monomers adsorbed in the hosts **1** and **2** without AIBN were calculated from the weight loss up to 200 °C. We compared the values of weight loss corresponding to adsorbed monomers in PCPs before and after the polymerization to determine the monomer conversion. Electron spin resonance (ESR) spectra were recorded on a JEOL JES-RE spectrometer in quartz capillaries of 4 mm internal diameter. ^1H and ^{13}C NMR spectra were obtained with a JEOL A-500 spectrometer operated at 500 MHz, and solid-state ^2H NMR spectra were measured by a Varian Chemagnetics CMX-300 spectrometer at 45.8 MHz. For the determination of molecular weights of polystyrene (PSt) samples, gel permeation chromatography (GPC) was carried out at 50 °C on a TOSOH 8020 (TSK-gel α-4000

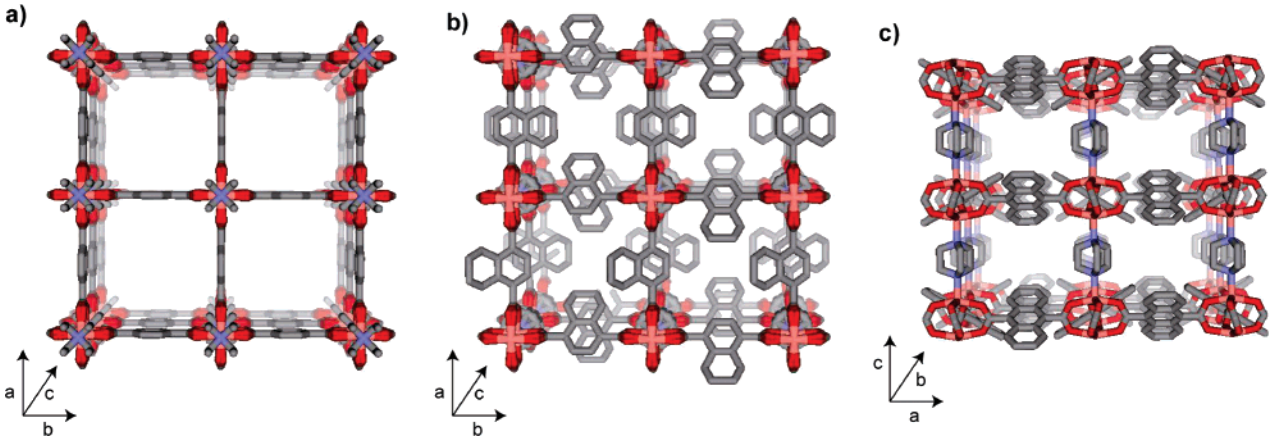


Figure 1. Nanochannel structures of (a) **2b**, (b) **2c**, and (c) **2d** displayed by stick models (Zn, pink; O, red; N, blue; C, gray). Hydrogen atoms and disordering atoms in the phenylene planes are omitted for clarity.

Table 1. Polymerization of Styrene (St) in Nanochannels of 1 and 2 at 70 °C for 48 h

host (pore size [Å^2])	adsorbed monomer amount (number/unit cell)[a]	conversion (%)[a]	M_n (M_w/M_n)[b]	tacticity[c] mm:mr:rr (m)
1a (10.8 × 10.8)	3.1	81	14 000 (3.3)	19:40:41 (39)
1b (7.5 × 7.5)	2.5	71	54 600 (1.6)	19:42:39 (40)
1c (5.7 × 5.7)	2.2	58	10 100 (1.6)	19:40:41 (39)
1d (4.8 × 4.3)	1.6	0		
2b (7.5 × 7.5)	2.5	71	56 200 (1.7)	16:43:41 (38)
2c (5.7 × 5.7)	2.1	56	11 100 (1.5)	17:42:41 (38)
2d (4.8 × 4.3)	1.6	0		
bulk polymerization[d]			37 600 (4.7)	16:42:42 (37)

[a] Determined by TGA. [b] Obtained by GPC calibrated by PSt standards. [c] Determined by ^{13}C NMR measurement in 1,1,2,2,-tetrachloroethane-d_2 at 100 °C. [d] Bulk polymerization was carried out under a comparable condition to those employed in PCPs.

column; exclusion limit = 1 × 10^6; particle size = 10 μm; 0.8 cm i.d. × 30 cm) with DMF as an eluent after calibration with PSt standards. The GPC measurements of poly(methyl methacrylate) (PMMA) and PVAc were performed in $CHCl_3$ at 40 °C on three linear-type polystyrene gel columns (Shodex K-805L; exclusion limit = 5 × 10^6; particle size = 10 μm; 0.8 cm i.d. × 30 cm) 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 PMMA samples. The absolute weight-average molecular weight (M_w) of PVAc prepared in **1b** was determined by multiangle laser light scattering (MALLS) coupled with GPC in DMF containing 10 mM LiBr at 40 °C on a Dawn E instrument (Wyatt Technology; Ga−As laser, λ = 690 nm). The refractive index increment (dn/dc) was measured in DMF at 40 °C on an Optilab DSP refractometer (Wyatt Technology; λ = 690 nm, c < 8.0 mg/mL). To investigate the branching structure of PVAc, a conventional GPC measurement of PVAc prepared in **1b** was performed under the same conditions, where the columns used were calibrated against standard PSt samples.

Results and Discussion

Preparation of Host PCPs. We have prepared host PCP compounds **1** and **2** by the solvothermal reaction of metal ions, ted, and dicarboxylate ligands, where two-dimensional layered structures based on paddle-wheel units are linked with ted as a pillar ligand (Scheme 1).[64−66] The crystal structures of **1** and corresponding **2** are almost the same,[64−66] as shown by XRPD analysis, and revealed three channels along the *a*-, *b*-, and *c*-axes. In all the crystals, one-dimensional aromatic nanochannels are formed along the *c*-axes and small apertures (approximately 4 Å) that are too narrow to polymerize vinyl monomers are also found along the *a*- and *b*-axes (Scheme 1 and Figure 1). The use of biphenyl-4,4′-dicarboxylate gave a host **1a** with larger nanochannels along the *c*-axis (pore size = 10.8 × 10.8 Å^2) compared with those of **1b** and **2b** (pore size = 7.5 × 7.5 Å^2).[64,65] The nanochannels of **1c** and **2c** with 1,4-naphthalenedicarboxylate ligand became narrower (pore size = 5.7 × 5.7 Å^2) because of steric hindrance of the inclined naphthalene moiety (Figure 1).[65] This inclination is associated with repulsion between the naphthalene ring and O atoms in the carboxylate group.[65] In the cases of **1d** and **2d**, the large anthracene unit filled the channels, resulting in nonporous structures along the *c*-axes; however, narrow two-dimensional channels with cross-sections of 4.8 × 4.3 Å^2 were still observed along the *a*- and *b*-axes.[66] Thus, in this experiment, we could prepare PCPs with precisely size-controlled nanochannels by changing the dicarboxylate ligands in **1** and **2**, approximately the dimensions of vinyl monomers. The pore dimensions of **1** and **2** are consistent with those evaluated by gas adsorption studies.[64−66]

Polymerization of Conjugated Monomers. Radical polymerizations of conjugated vinyl monomers such as St (molecular size = 6.8 × 4.4 Å) and MMA (molecular size = 5.9 × 4.1 Å) were performed in the nanochannels of **1** and **2** at 70 °C. From TGA, the adsorption amount of monomers was found to decrease as the size of the nanochannels narrowed, and the similar values of the monomer adsorption in **1** and corresponding **2** were also observed (Tables 1 and 2). XRPD measurements of the host compounds during the polymerizations indicated that the channel structures of PCPs were maintained upon the monomers' inclusion and their reaction (Figure 2). In the XRPD profiles, changes in the relative peak intensities and slight shifts of peak positions were detected after the introduction of monomers or their polymerizations in the host nanochannels, which clearly represented the effective encapsulations of the monomers or polymers in the nanochannels of PCPs.[32,62,63,66] We examined solid-state ^{2}H NMR measurements to study detailed motional behaviors of monomers adsorbed in the

Table 2. Polymerization of Methyl Methacrylate (MMA) in Nanochannels of 1 and 2 at 70 °C for 7 h

host (pore size [Å^2])	adsorbed monomer amount (number/unit cell)[a]	conversion (%)[a]	M_n (M_w/M_n)[b]	tacticity[c] mm:mr:rr (m)
1a (10.8 × 10.8)	3.2	76	93 000 (4.8)	6:38:56 (25)
1b (7.5 × 7.5)	2.6	74	73 100 (2.0)	8:40:52 (28)
1c (5.7 × 5.7)	2.3	58	30 600 (2.4)	10:43:47 (31)
1d (4.8 × 4.3)	1.8	0		
2b (7.5 × 7.5)	2.7	76	69 100 (2.4)	8:40:52 (28)
2c (5.7 × 5.7)	2.3	60	29 500 (2.4)	9:41:50 (30)
2d (4.8 × 4.3)	1.8	0		
bulk polymerization[d]			56 100 (6.4)	5:35:60 (22)

[a] Determined by TGA. [b] Obtained by GPC calibrated by PMMA standards. [c] Determined by ^{1}H NMR measurement in nitrobenzene-d_5 at 110 °C. [d] Bulk polymerization was carried out under a comparable condition to those employed in PCPs.

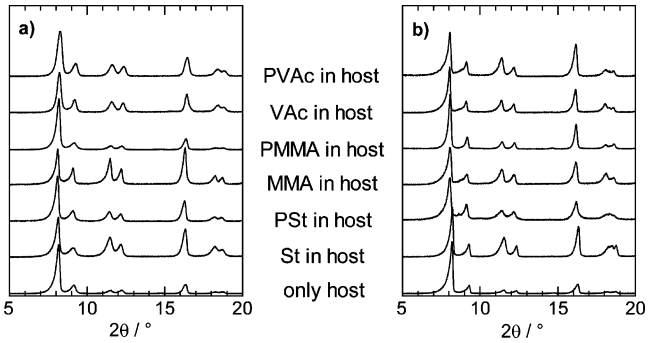


Figure 2. XRPD patterns of (a) **1b** and (b) **2b** during the polymerization of vinyl monomers.

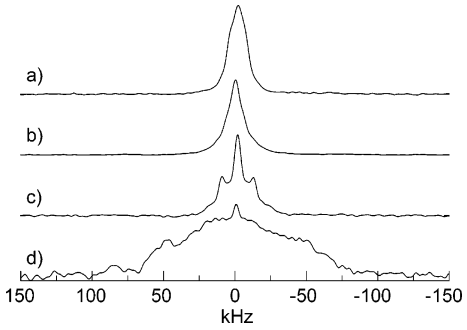


Figure 3. Solid-state ^{2}H NMR spectra of St-d_8 adsorbed in the nanochhanels of (a) **1a**, (b) **1b**, (c) **1c**, and (d) **1d** at 70 °C.

nanochannels. The solid-state NMR technique has been widely used for direct observation of mobility of guest molecules in various adsorbents[68−71] and is applicable to PCPs as well, even though the host frameworks contain paramagnetic species.[62,72] Molecular dynamics studies on the molecules bearing a benzene moiety by ^{2}H NMR measurements are also well established.[73−75] Figure 3 shows ^{2}H NMR spectra of St-d_8 adsorbed in the nanochannels of **1** at 70 °C. From the peak patterns of St-d_8 in **1a** and **1b**, the St molecules had near isotropic motions in the relatively large channels. On the other hand, the spectrum of St-d_8 in **1c** showed a broader line shape with shoulder peaks, indicating that the mobility of St in the slow motion regime becomes dominant. The extremely broad signal obtained from St-d_8 in **1d** is explained by the highly restricted mobility St experienced in **1d** compared with those in **1a**−**c**. From these experiments, we could understand that the mobility of the encapsulated St monomer strongly depended on the pore size of the PCPs.

Tables 1 and 2 summarize the polymerization results (conversion, molecular weight, and tacticity) of St and MMA in the nanochannels of the PCP hosts, respectively. In general, copper(II) compounds act as inhibitors for radical polymerizations,[1,2] and thus polymerizations of St and MMA never produce polymeric materials in the presence of [Cu_2(benzoate)$_4$(3-picoline)$_2$] (**3**) as a discrete copper(II) complex. In contrast, our radical polymerization system within the frameworks of polymeric copper(II) complexes **1a**−**c** has yielded PSt and PMMA in high conversions, which is probably because the copper(II) ions are embedded in highly crystalline three-dimensional solid frameworks of **1** without exposure on the pore surfaces. In addition, the polymerizations of St in the channels of zinc hosts **2** provide similar results to those from the systems using the corresponding copper hosts **1** with the same pore sizes (Table 1). Polymerization results of MMA obtained using **1** and corresponding **2** are also quite similar, as shown in Table 2. These experimental facts explain that the inclusion polymerizations of St and MMA are independent of the constituent metal ions in the PCP frameworks.

A strong correlation between the pore size of the PCPs and polymer yield is clearly seen, where the conversions for polymerizations of St and MMA decrease as the size of the nanochannels narrows (Tables 1 and 2). A detailed study on the pore size dependence of the polymerizations in PCPs by changing the reaction time shows that the yields of polymerizations saturate earlier in the larger pores of PCPs (Figure 4). On the other hand, molecular weights of the resulting polymers are independent of the reaction time in these systems, and high molecular weight polymers are obtained even in the early stage of the polymerizations (Figure 5). These experimental results strongly suggest that the pore size effect of PCPs on the polymer yield is predominantly dependent on the initiation step of the polymerizations rather than their propagation step. The lower conversions observed in the systems using narrower pores would be ascribed to low initiation efficiency in such narrow, restricted nanochannels. No polymeric product was obtained during the polymerizations in the nanochannels of **1d** and **2d**, which can also be explained by the frozen mobility of the monomers tightly encapsulated in the narrowest channels.[29,30,62]

Since thermal spontaneous polymerization of St in the bulk state commonly occurs at 70 °C,[76] we carried out the polymerization of St without AIBN in the channel of **1b** as a control experiment. However, this experiment showed a decreased conversion of St (approximately 10%), indicating the importance of the radical initiator residing inside the nanochannel to proceed the polymerization in our system.

From the viewpoint of molecular weight control, the small polydispersities (M_w/M_n) of the polymers prepared in PCPs compared with those of corresponding bulk-synthesized polymers is of great significance. The molecular weight distributions of PSt and PMMA were found to become narrower with a decrease in the host channel size, and eventually a value for M_w/M_n of 1.5 was attained in the polymerization of St using **2c**. To understand this unique phenomenon, we examined ESR measurements of propagating radicals in nonmagnetic hosts **2b**

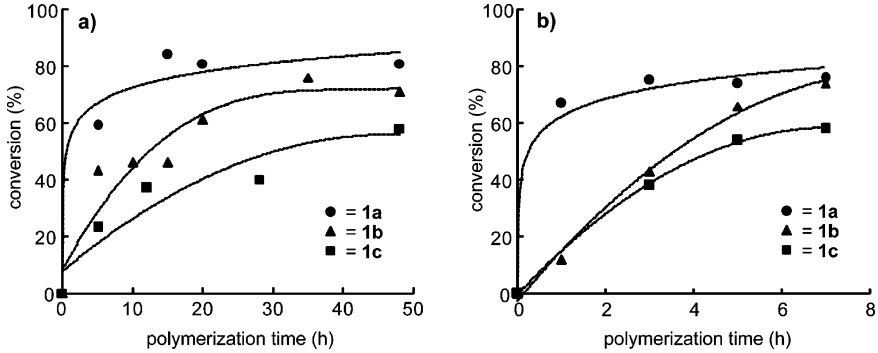


Figure 4. Dependence of monomer conversion on the polymerization time: (a) polymerization of St in **1** and (b) polymerization of MMA in **1**.

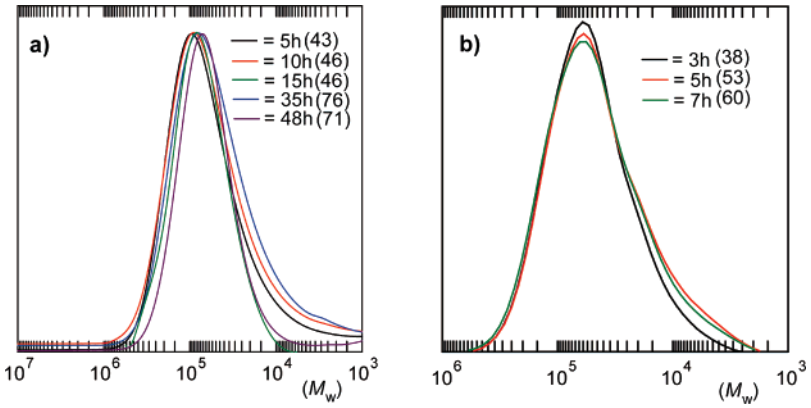


Figure 5. GPC profiles of (a) PSt prepared in **1b** and (b) PMMA prepared in **2c** for different reaction times. The values in parentheses show conversion (%) of the polymerization.

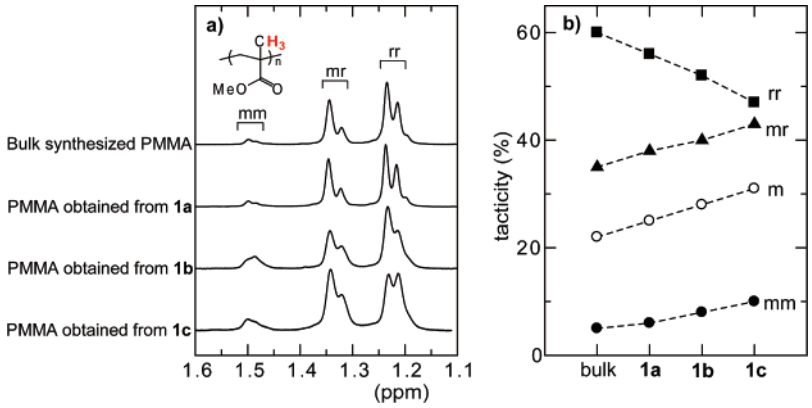


Figure 6. (a) ^{1}H NMR spectra of PMMA obtained from the nanochannels of **1** and the bulk condition in nitrobenzene-d_5 at 110 °C. (b) Plot of nanochannel effect on tacticity of PMMA.

during the polymerizations. In the ESR spectra, intense signals assigned to the propagating radical of both PSt and PMMA were observed and the maximum radical concentrations of PSt and PMMA in **2b** reached 2.6 and 0.48 mmol kg^{-1}, respectively, which are much higher than those detected in conventional solution radical polymerizations (10^{-4}−10^{-5} mmol kg^{-1}). It should also be noted that, after the polymerization of St in **2b**, the ESR signal for the propagating radical still appears for 3 weeks, even at 70 °C. In our polymerization system, PCPs with small pore sizes can significantly stabilize the propagating radicals by efficient suppression of termination reactions in the nanochannels,[29,62,77] realizing living radical polymerizations with small M_w/M_n values.

An important nanochannel effect on the polymer stereoregularity (tacticity) is also observed in our polymerization system, leading to an increase in isotacticity in the resulting polymers. In particular, the tacticity of PMMA strongly depends on the pore size of the PCPs; eventually an increase of 9% in meso dyads was achieved by using **1c** compared with that obtained from the bulk polymerization system (Figure 6). From the structural modeling study, it was seen that an isotactic polymer requires narrower conformational diameter (thickness) than the corresponding syndiotactic polymer.[78] Because there is no specific interaction between the adsorbed monomers and the pore walls, effective through-space interactions by the nanochannels of the PCPs successfully induced the polymerizations with less stereo-bulky isotactic units in our polymerization systems. Stereocontrolled radical polymerization of vinyl monomers is still very difficult; therefore, several research groups have intensively studied how to control the tacticities of vinyl polymers during solution radical polymerization by the addition of fluoroalcohols or Lewis acids to the reaction media.[13−18] In these systems, hydrogen bonding or coordinative interaction of the solvents or the additives with the polar groups in the monomers and/or the growing species would cause stereospecific chain growth; however, this method can only be applied

Table 3. Polymerization of Vinyl Acetate (VAc) in Nanochannels of 1 and 2 at 60 °C for 48 h

host (pore size [Å^2])	adsorbed monomer amount (number/unit cell)[a]	conversion (%)[a]	M_n (M_w/M_n)[b]	tacticity[c] mm:mr:rr (m)
1a (10.8 × 10.8)	5.3	49	48 000 (2.4)	22:49:29 (47)
1b (7.5 × 7.5)	3.3	47	41 500 (1.7)	29:50:21 (54)
1c (5.7 × 5.7)	2.7	0		
1d (4.8 × 4.3)	1.9	0		
2b (7.5 × 7.5)	3.4	66	36 000 (2.0)	30:49:21 (55)
2c (5.7 × 5.7)	2.6	0		
2d (4.8 × 4.3)	1.8	0		
bulk polymerization[d]			nd[e]	22:50:28 (47)

[a] Determined by TGA. [b] Obtained by GPC calibrated by PMMA standards. [c] Determined by ^{13}C NMR measurement in DMSO-d_6 at 100 °C after conversion to poly(vinyl alcohol) by saponification. [d] Bulk polymerization was carried out under a comparable condition to those employed in PCPs. [e] The obtained polymer had high-molecular weight portions over the exclusion limit (M_w > 5 000 000) of the GPC column with extremely wide polydispersity (M_w/M_n > 20).

to monomers with the carbonyl group, and it is still uncertain whether steric or electronic interaction works on the stereostructures. Although an organic host compound (cyclophosphazene) could affect the polymer stereoregularlity during the inclusion polymerization of vinyl monomers, no relationship between the channel size and the polymer stereostructures was observed because of the lack of capability for tuning the pore sizes.[36] In our polymerization system we could systematically study the nanochannel size effect on the tacticity of the vinyl polymers, showing that controlled increase of isotacticity became possible in the polymerizations utilizing the size-tunable pores of PCPs.

Polymerization of Nonconjugated Monomer. In spite of the useful practical application of poly(vinyl acetate) (PVAc) as a precursor of poly(vinyl alcohol) (PVA), VAc (molecular size = 5.5 × 4.0 Å^2) is known to be polymerized only via a radical mechanism. Unlike St and MMA, the propagating radical of PVAc shows intractably high reactivity and less stability because of the lack of a conjugated substituent in the VAc monomer. Thus, unfavorable chain transfer and termination reactions are particularly observed in the polymerization process of VAc, and the controlled radical polymerization of VAc has been considerably difficult to achieve.

Radical polymerization of VAc was carried out in the nanochannels of **1** and **2** at 60 °C for 48 h. From XRPD measurements, no framework transformation of the PCPs was observed during the polymerizations of VAc in these nanochannels (Figure 2). The results for the VAc polymerization are summarized in Table 3. Compared with the polymerizations of St and MMA, the polymer yields in this VAc system were relatively low; in particular, no trace of polymeric product was observed in the polymerizations utilizing even the nanochannels of **1c** and **2c**, although the monomer size of VAc is smaller than those of St and MMA. Addition of 10 times the amount of AIBN to the reaction system was also ineffective in producing PVAc. This inhibited conversion of VAc in the nanochannels can be ascribed to its low reactivity toward carbon radicals, where the reactivity of VAc with cyanopropyl radical generated from AIBN is 40 and 22 times as low as those of St and MMA, respectively, at 60 °C.[79] These facts thus suggest that the AIBN radical scarcely attacks VAc to initiate polymerization in such narrow channels as those of **1c** and **2c**.

The GPC measurements of PVAc obtained from the nanochannels (Figure 7) showed small M_w/M_n values (e.g., M_w/M_n of PVAc prepared in **1b** was 1.7), while PVAc prepared under the bulk conditions showed an extremely large polydispersity (M_w/M_n > 20) of the molecular weight caused by its hyperbranched structure derived from various side reactions (chain transfer and termination reactions). Because of the nonconjugated nature of the propagating radical, achievement of such a narrow molecular weight distribution of PVAc has still been limited, except for a few controlled living radical polymerization systems.[10,80−86] We also performed a GPC/MALLS measurement of PVAc isolated from **1b** to determine the absolute value of the molecular weight, obtaining an M_w of 95 500. This value is fairly consistent with that obtained from a conventional GPC measurement using the same column calibrated against standard PSt (M_w = 88 100), which clearly supports the less-branching linear structure of PVAc due to the constrained chain growth in the narrow one-dimensional nanochannel.[87]

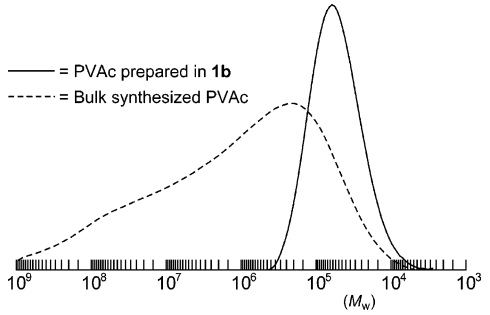


Figure 7. GPC profiles of PVAc prepared in **1b** and in the bulk condition. The profile of the bulk synthesized PVAc is extremely broad (M_w/M_n > 10) containing high molecular weight portions over the exclusion limit (M_w > 5 000 000) of the GPC column.

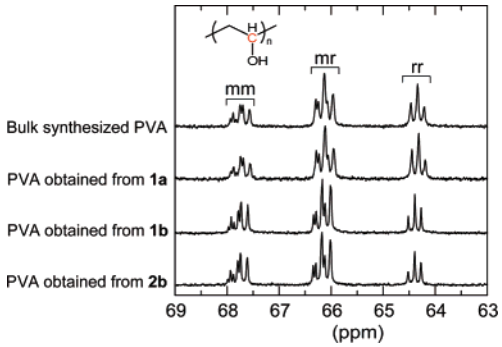


Figure 8. ^{13}C NMR spectra of PVA converted from PVAc by saponification in DMSO-d_6 at 100 °C.

After conversion of the obtained PVAc to PVA by saponification, ^{13}C NMR measurements were conducted to determine the polymer stereoregularlity (Figure 8), where the stereoregularlity of PVAc does not change by this treatment.[13] Similar to the cases of PSt and PMMA, the ratio of isotactic units in the polymer structure clearly increases when the VAc monomer is polymerized in the nanochannels of **1b** and **2b**. In the previous reports, the only possible way to change the tacticity of PVAc was addition of fluoroalcohols to the reaction media, which leads

to an increment of the syndiotactic units induced by the hydrogen-bonding interaction between the alcohols and VAc.[13,83] No method for increasing the isotactic units of PVAc has been reported so far. Therefore, the development of polymerizations in PCP nanochannels to produce a linearly extended PVAc not only with a narrow distribution of molecular weights but also with an increase of the isotactic unit is of considerable interest.

Conclusions

In this work, we performed radical polymerizations of vinyl monomers in size-tunable nanochannels of PCPs and demonstrated the significant effects of the channel size on the yield, molecular weight, and stereoregularity of the resulting polymers. The capability for precise size tuning of nanospaces is one of the most powerful advantages of PCPs, leading to the first systematic study of radical polymerization in microporous channels based on PCPs. From the viewpoint of polymerization, the narrow polydispersities of the obtained polymers as well as controlled increments of isotactic units in this polymerization system are noteworthy; these controls in polymer primary structures are very difficult in conventional bulk and solution polymerizations. We believe that our polymerization system can provide a new aspect of controlled radical polymerizations and is fundamentally important for the understanding of the role of pore size and geometry in attaining NITP.

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Supporting Information Available: XRPD, GPC, and ESR profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

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