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Effects of Unsaturated Metal Sites on Radical Vinyl Polymerization in Coordination Nanochannels

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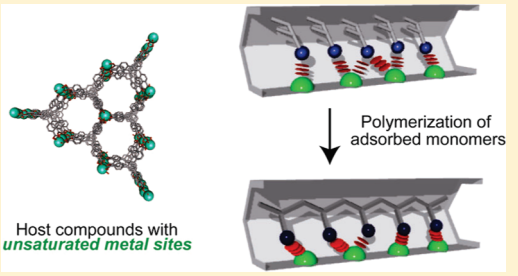
Supporting Information

ABSTRACT: Radical polymerization of vinyl monomers was performed in nanochannels of porous coordination polymers with unsaturated metal sites, [M(1,3,5-benzenetrisbenzoate)] (**1Al**, M = Al^{3+}; **1Eu**, M = Eu^{3+}; **1Nd**, M = Nd^{3+}; **1Y**, M = Y^{3+}; **1La**, M = La^{3+}; and **1Tb**, M = Tb^{3+}). In this system, the polymerization behaviors are strongly dependent on the Lewis acidity of the metal sites. For example, polymerizability of monomers was influenced by the metal sites because of the interaction with the monomers. From the viewpoint of streteoregularity, composition of isotactic unit in the resulting poly(methyl methacrylate) (PMMA) increased as the Lewis acidity of the hosts becomes higher. Although discrete Tb^{3+} ions are not effective for changing the stereoregularity of PMMA in solution polymerization system, nanochannels of **1Tb** gave PMMA with the increase in the isotactic unit, showing that the metal ions embedded in the pore walls of PCPs are useful for controlling stereoregularity of polymers.



INTRODUCTION

Porous coordination polymers (PCPs), comprised of metal ions and bridging organic ligands, have recently emerged as an important family of porous materials because of their unique structural and functional properties.[1−4] In many PCP structures, the coordination sphere around the metal ions is completely blocked by organic ligands; however, new synthetic strategies have been developed to overcome this problem by using volatile coordinative solvents that can be removed during the activation stage. The resulting unsaturated metal sites (UMS) or Lewis acidic sites can be successfully utilized for catalytic reactions and chemisorptions, where impregnation of the UMS in PCPs often enhances these properties because of their restricted and anisotropic nanoporous geometries.[5−9] In fact, catalytic reactions in PCP nanochannels with UMS showed high stereo-, regio-, and/or substrate-selectivities.[10−15]

Stereochemical control in radical polymerization is known to be very difficult because the highly reactive and neutral natures of free radical species induce uncontrolled chain growth.[16−18] However, several research groups have shown that addition of Lewis acids in reaction mixtures can effectively control the stereoregularity of the resulting polymer.[19−24] On the basis of the reported results, the Lewis acids would interact with the vinyl monomers and/or propagating radicals to induce stereospecific chain growth via coordination. However, Lewis acids are not always effective for controlling the stereoregularity despite their strong Lewis acidity, thus quantitative studies of the effects of Lewis acids on polymerizations are still necessary to understand the roll of Lewis acids in this controlled polymerization system.

Inclusion polymerizations in crystalline nanosized matrices has allowed spatial controls of primary structures of polymers and even two- or three-dimensional multilevel structuring.[25−31] In particular, polymerization in microporous channels based on organic host matrices has been extensively studied for controlling stereostructures of resulting polymers.[25−28] For example, radical polymerizations in cyclophosphazene channels have shown certain stereoregularity changes of vinyl polymers in several cases compared to the corresponding bulk or solution polymerization systems.[32] Highly stereoregular poly(acrylonitrile) could be also produced in urea channels at the low temperature reaction.[33] However, their narrow and fragile cavities often hamper the polymerization of large vinyl monomers. In addition, incorporation of Lewis acidic sites into the pore walls is fundamentally impossible.

We have developed controlled radical polymerizations in PCP nanochannels, showing that pore size and shape of PCPs have significant influences on the structures of the resulting polymers.[34−39] If PCPs with UMS can be utilized for the fields of radical polymerization, the UMS embedded in the pore walls would strongly interact with vinyl monomers, leading to restricted monomer arrangements with low mobility (Scheme 1). Hence, the polymerization behavior will be quite different from that observed in solution polymerization systems, and also in PCP nanochannels without UMS. Here, we report the radical

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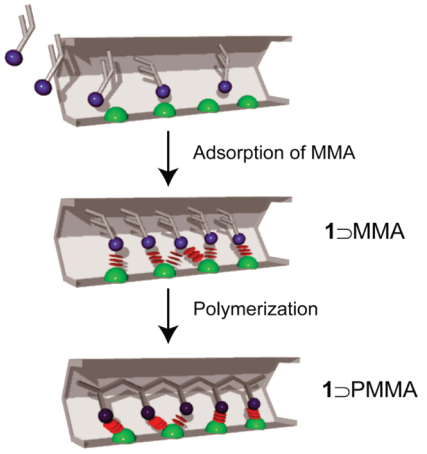
Scheme 1. Schematic Illustration for Polymerization of MMA in 1 with Unsaturated Metal Sites (UMS)



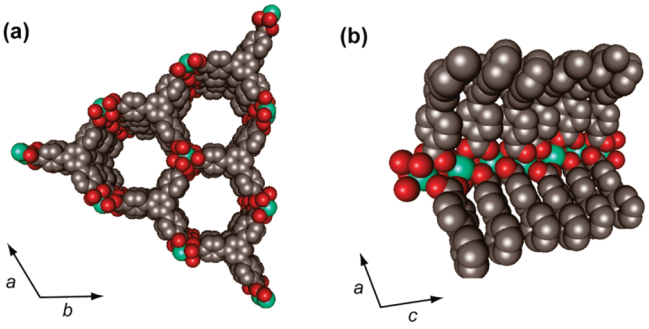


Figure 1. Views of (a) nanochannel structure and (b) pore wall structure of **1Tb** without guest and coordinative solvent molecules. Hydrogen atoms are omitted for clarity. Terbium, carbon, and oxygen atoms are denoted with green, gray, and red, respectively.

polymerization of vinyl monomers in one-dimensional nanochannels of a series of MIL-103, $[M(1,3,5\text{-benzenetrisbenzoate})]_n$ (**1Al**, M = Al^{3+}; **1Eu**, M = Eu^{3+}; **1Nd**, M = Nd^{3+}; **1Y**, M = Y^{3+}; **1La**, M = La^{3+}; and **1Tb**, M = Tb^{3+}). In these frameworks, UMS are located at the corners of the hexagonal-shaped channels (Figure 1).[40] It is noteworthy that such UMS effectively contributed to changing the polymer stereoregularity. We also demonstrate that the Lewis acidity of the UMS in **1** is highly relevant to the polymerization behavior, such as polymerizability and stereoregularity.

EXPERIMENTAL SECTION

Materials. All the reagents and chemicals used were obtained from commercial sources, unless otherwise noted. 2,2′-azobis(isobutyronitrile) (AIBN) was recrystallized from MeOH solution, and vinyl monomers were purified by vacuum distillation prior to use. The host PCPs, **1Eu**, **1Nd**, **1Y**, **1La**, and **1Tb**, were prepared using methods reported previously.[40]

Synthesis of 1Al. A mixture of $Al(NO_3)_3 \cdot 9H_2O$ (0.86 g, 2.3 × 10^{-3} mol), 1,3,5-tris(4-carboxyphenyl)benzene (H_3BTB; 1.0 g, 2.3 × 10^{-3} mol), and *N*,*N*-diethylformamide (DEF; 50 mL) was transferred into a 100 mL Teflon-lined autoclave and was stirring at 150 °C for 48 h. The resultant white precipitate was filtered, washed by DEF, and dried at reduced pressure to give **1Al** including solvent DEF in the pores (1.25 g). This host compound was activated by evacuation at 150 °C prior to use.

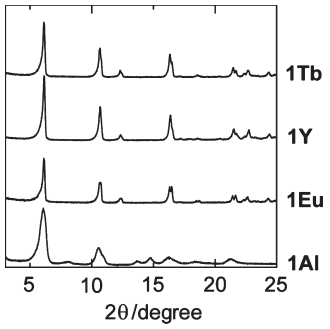


Figure 2. XRPD patterns of **1**.

Polymerization of Methyl Methacrylate (MMA) in 1. The dried host compound **1** (200 mg) was prepared by evacuation (<0.1 kPa) at 150 °C for 5 h in a Pyrex reaction tube. Subsequently, **1** was immersed in MMA (1 mL) with AIBN (10 mg) at room temperature for 0.5 h to incorporate MMA and the radical initiator into the nanochannels. After excess monomer external to the host crystals was removed completely by evacuation (2.0 kPa) at room temperature for 0.5 h, the reaction tube was filled with nitrogen, and heated to 70 °C to perform the polymerization for 24 h. To isolate the PMMA inside the channels, the composite was stirred overnight in a 0.05 M aqueous solution (40 mL) of sodium ethylenediaminetetraacetate (Na-EDTA) for the complete dissolution of the frameworks of **1**. The collected PMMA was washed with water (2 mL × 3) and dried under a reduced pressure at room temperature.

Measurements. The X-ray powder diffraction (XRPD) data were collected using a Rigaku RINT 2000 Ultima diffractometer employing CuKα radiation. The infrared spectra were measured using KBr disks employing a PerkinElemer Spectrum BX FT-IR system. The ^1H and ^{13}C NMR spectra were obtained using a JEOL A-500 spectrometer operating at 500 MHz. The 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-805 L) 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 or polystyrene samples.

RESULTS AND DISCUSSION

The porous compounds **1** with light rare-earth elements (**1Eu**, **1Nd**, **1Y**, **1La**, and **1Tb**) could be prepared under hydrothermal conditions according to the literature (Figure 2).[40] We tried to prepare the frameworks of **1** using other trivalent metal ions, such as Al^{3+}, Sc^{3+}, Ga^{3+}, and In^{3+}. In these experiments, the framework of **1** can be formed only when Al^{3+} was employed, and resulting **1Al** was characterized by XRPD (Figure 2). The pores of the as-synthesized **1** are lined with solvent molecules that complete the coordination sphere of M^{3+} ions.[40] These coordinative solvents can be removed by evacuation at 150 °C, leading to one-dimensional alignment of UMS in the hexagonal channels with a pore size of ca. 10 Å.

Introduction of MMA into the nanochannels of **1** was performed by immersion of **1** in MMA at room temperature followed by evacuation of excess MMA under reduced pressure. The XRPD patterns of the obtained host−guest composites (**1**⊃MMA) were almost the same as those of the corresponding **1** (Figure 3a). To evaluate the interaction between MMA and UMS in **1**, we carried out IR measurements of **1**⊃MMA in a region corresponding to the C═O stretching of MMA. Compared with neat MMA ($\nu_{C=O}$ = 1723 cm^{-1}), MMA incorporated in the channels of **1** showed clear peak shifts toward lower wavenumbers, except for the case of **1Al**

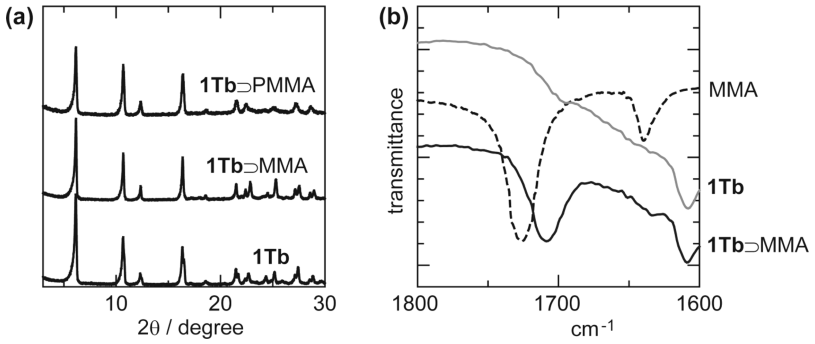


Figure 3. (a) XRPD patterns of **1Tb**, **1Tb**⊃MMA, and **1Tb**⊃PMMA. (b) IR spectra of neat MMA, **1Tb**, and **1Tb**⊃MMA.

Table 1. Polymerization of MMA in 1, 2, and Bulk at 70 °C for 24 h

host	C═O stretching of MMA (cm^{-1})	yield (%)	M_n (M_w/M_n)[a]	tacticity (%)[b] *mm*:*mr*:*rr* (m)	ΣP[c]	ρ[d]
1Al	1719	78	33 200 (3.1)	7:43:50 (29)	1.055	0.958
1Eu	1716	45	19 400 (6.5)	8:44:48 (30)	1.047	0.956
1Nd	1716	35	26 600 (9.4)	9:41:50 (30)	0.986	1.015
1Y	1715	27	29 500 (2.6)	10:42:48 (31)	0.981	1.019
1La	1715	10	7300 (3.2)	11:40:49 (31)	0.935	1.070
1Tb	1708	22	9600 (3.9)	10:44:46 (32)	1.012	0.989
2[e]	1719	76	93 000 (4.8)	6:38:56 (25)	1.013	0.987
bulk[f]	1723	-	56 100 (6.4)	5:35:60 (22)	1.004	0.996

[a] Obtained by GPC calibrated by PMMA standards. [b] Determined by ^{1}H NMR measurement in nitrobenzene-d_5 at 110 °C. [c] $\Sigma P = P_{m/r} + P_{r/m}$, where $P_{m/r} = [mr]/(2[mm] + [mr])$ and $P_{r/m} = [mr]/(2[rr] + [mr])$. [d] $\rho = 2[m][r]/[mr]$. [e] Polymerization for 7 h. [f] Bulk polymerization was carried out under a comparable condition.

(Figure 3b, Table 1). Note that MMA loaded in $[Cu_2(\text{biphenyl-4,4}'\text{-dicarboxylate})_2(\text{triethylenediamine})]_n$ (**2**) with a similar channel size (10.8 × 10.8 Å^2) did not show such a large peak shift because of lack of UMS in the channel (Table 1). Based on the IR peak positions, it is possible to list **1** in order of increasing interaction with MMA as follows: **1Al** < **1Eu**, **1Nd** < **1Y**, **1La** < **1Tb**. The weak interaction between **1Al** and MMA was probably because of the small ionic radius of Al^{3+} with low coordination numbers.

Polymerization of MMA accommodated in **1** was performed by heating **1**⊃MMA with AIBN at 70 °C for 24 h to provide polymer composites (**1**⊃PMMA) (Scheme 1). XRPD measurements of **1**⊃PMMA clearly showed that the original framework structures of **1** were retained during the polymerizations (Figure 3a). The resulting PMMA was quantitatively isolated from **1**⊃PMMA by dissolution of the frameworks of **1** in an aqueous Na-EDTA solution. In regard to the polymerizability of MMA in **1**, the conversion rates of MMA to PMMA in the channels of **1Y**, **1La**, and **1Tb** were found to be relatively low, although **1Al** produced PMMA with a satisfactory yield (Table 1). GPC measurement was carried out to determine the molecular weight of the recovered PMMA, showing a tendency that the molecular weight of the polymer seems to decrease with increase in the Lewis acidity of UMS in **1**.

Several control experiments were performed to understand the detailed polymerization behavior in **1**. For example, we examined polymerization of vinyl acetate (VAc) in the nanochannels of **1Al** and **1Tb**. Although the corresponding polymeric product was obtained (51% yield, M_n = 29,100) in the nanochannels of **1Al**, no polymer was produced from **1Tb**. We measured IR spectrum of **1Al**⊃VAc, and found that a peak corresponding to C═O of VAc was observed at the similar

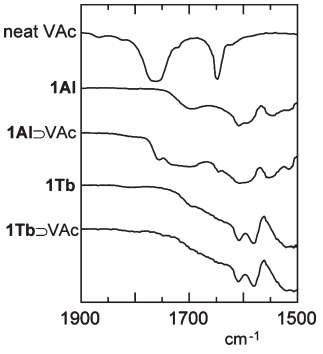


Figure 4. IR spectra of neat VAc, **1Al**, **1Al**⊃VAc, **1Tb**, and **1Tb**⊃VAc.

position of neat VAc, suggesting no significant interaction between **1Al** and VAc (Figure 4). In contrast, this peak was shifted to lower wavelength and might be overlapped with the host band in the spectrum of **1Tb**⊃VAc, probably because of strong interaction of **1Tb** with VAc (Figure 4). In addition, polymerization of styrene monomer without a carbonyl moiety in the channels of **1Tb** efficiently provided polystyrene (53% yield, M_n = 21,700), where styrene does not have an interactive site with UMS. We have also examined the polymerization of MMA in the channels of **2** without UMS, which gave a high molecular weight PMMA in high yield.[37] In a previous report, interaction of MMA with a Lewis acid reduced the electron density in the double bond of MMA, resulting in an increase of the monomer reactivity in the solution polymerization system.[19] In contrast, our results obtained here suggest that the interaction between UMS in **1** and the carbonyl group of

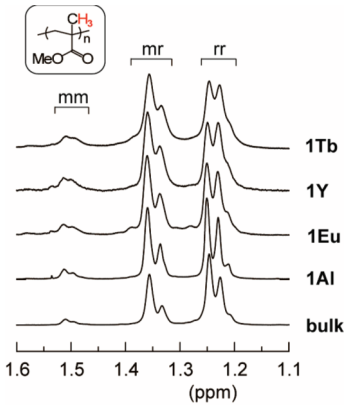


Figure 5. ^{1}H NMR spectra of PMMA prepared in nanochannels of **1** and in bulk condition (nitrobenzene-d_5, 110 °C).

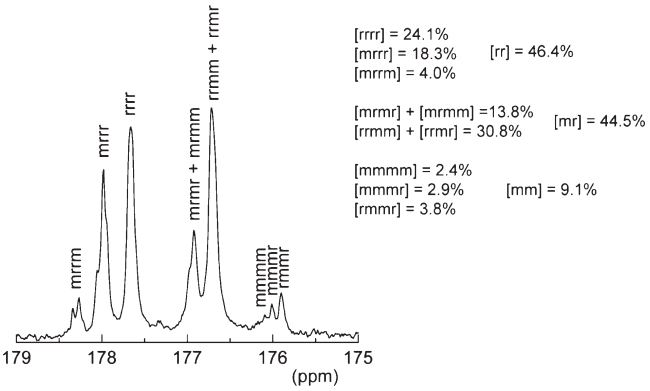


Figure 6. Carbonyl region of ^{13}C NMR spectrum of PMMA prepared in **1Tb** at 70 °C (toluene-d_8, 25 °C) and probabilities for the pentad sequence distributions.

the monomers causes a decrease in the polymerization rate, probably because the interaction between monomers and UMS leads to restricted monomer arrangements with low mobility in the channels. In solution polymerization system, monomer−Lewis acid complexes can freely diffuse to be polymerized; however, in case of polymerizations in nanoconfined geometries, mobility of monomers critically affects the conversion and molecular weight.[25,36,37]

Although the polymerizability of MMA was relatively low in the channels of **1**, interaction between MMA and UMS could enable significant change in the stereoregularity of PMMA. We checked the ^{1}H NMR spectra to determine the triad fractions corresponding to the methyl groups on the main chain of PMMA obtained from the channels of **1** (Table 1, Figure 5).[41] Interestingly, the tacticity of PMMA was found to be clearly changed; that is, the ratios of the isotactic (*mm*) and heterotactic (*mr*) triad fractions increased in comparison with those of bulk synthesized PMMA. Moreover, the changes of PMMA tacticity were larger than that occurred in the similar sized channels of **2** without UMS (Table 1).[37] Because the addition of Lewis acids to the reaction medium often leads to an increase in isotactic fractions of PMMA,[17−19,23] the relatively large change of tacticity observed here would be induced by the effective interaction between MMA and UMS in **1**. In addition, our system showed the order of tacticity change in PMMA corresponding to the Lewis acidity of UMS in **1**. The more strongly MMA interacts with UMS in **1**, the greater the PMMA tacticity changes, whereas stereoregularity change of the polymers seems irrelevant to Lewis acidity of additives in previous solution polymerizations. It should also be noted that discrete Tb complexes, such as $Tb(OTf)_3$ and $TbCl_3$, did not change the stereostructure of PMMA in solution polymerization.[19] In contrast, the Tb ion embedded in the framework of **1Tb** effectively induced the stereospecific chain growth of PMMA, showing the powerful effect of PCP nanochannel in changing the polymer stereostructure.

To understand the mechanism of stereocontrol during the polymerization of MMA in **1Tb**, we performed ^{13}C NMR measurement and determined the fractions of pentad sequences for the resulting PMMA (Figure 6).[42,43] Although we could obtain the values for the higher order tacticity, peaks corresponding to *rrrm*, *rrmr*, *mrmr*, and *mrmm* were found to be inseparable. However, the observed pentad values could provide more accurate triad distributions, thus we estimated the following parameters using the calculated triad fractions:

$$P_{m/r} = 1 - P_{m/m} = [mr]/(2[mm] + [mr])$$

$$P_{r/m} = 1 - P_{r/r} = [mr]/(2[rr] + [mr])$$

where $P_{m/r}$ is the probability that a racemo addition follows a meso addition, $P_{r/m}$ is the probability that a *meso* addition follows a *racemo* addition. In case of our polymerization in **1Tb**, the sum of $P_{m/r}$ and $P_{r/m}$ (ΣP) gave 1.034, showing a slight deviation from Bernoullian sequence distribution.[44,45] We also determined ΣP using ^{1}H NMR spectra of PMMA prepared in the other **1**, where the values of ΣP were not close to unity (Table 1). Therefore, in our polymerization system, it is unlikely that chain-end control is responsible for the resulting stereostructure of PMMA. To study the details of the polymerization mechanism, the Coleman−Fox parameter was calculated from the tacticity values of the PMMA.[46]

$$\rho = 2[m][r]/[mr]$$

The values of ρ for PMMA obtained in our experiments were found to be almost equal to $(\Sigma P)^{-1}$ (Table 1), suggesting that the polymerization of MMA in **1** can be applied to first-order Markov statistics.[44,45] Thus, a penultimate effect might be dominant in the stereoregulation of the polymerization in the nanochannels of **1**.

CONCLUSION

We have demonstrated the effects of UMS in PCPs on the polymerization of MMA, where UMS in **1** had influences on yield, molecular weight, and stereoregularity of resulting polymers. In particular, effect of UMS on the stereoregularity of PMMA is evident by comparison with a system using PCP without UMS. Although discrete Tb complexes are not effective for the stereocontrolled polymerization of MMA in solution system, Tb ions fixed on the pore wall of **1** could contributed to the change in the tacticity of resulting PMMA. Currently, PCPs with UMS are attracting much attention because of their useful applications as nanocatalysts or nanoreactors. Our results obtained here suggest that further control of polymerization will be possible by rational design of the arrangement of UMS in PCPs.

■ ASSOCIATED CONTENT

Supporting Information. XRPD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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