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Radical Copolymerization Mediated by Unsaturated Metal Sites in Coordination Nanochannels

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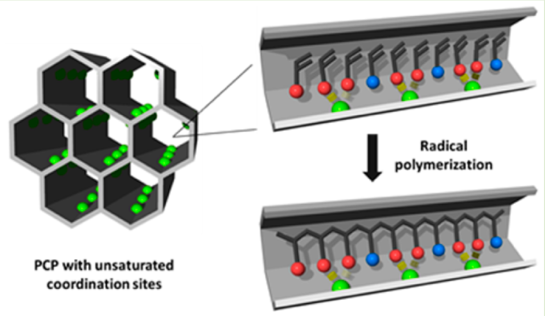
Supporting Information

ABSTRACT: Radical copolymerization of methyl methacrylate (MMA) and styrene was performed in [Tb(1,3,5-benzenetrisbenzoate)]$_n$ with coordinatively unsaturated metal sites (UMS) immobilized along the one-dimensional nanochannels. A drastic increase in the proportion of MMA units in the resulting copolymers was obtained compared with that obtained from the corresponding solution polymerization systems. Simultaneous coordination of MMA to the UMS is the key to increasing the MMA proportion during the copolymerization in the nanochannels, which was demonstrated by variable temperature IR measurements and several controlled experiments.



Controlled copolymerization for regulating monomer composition and sequence is very important in both fundamental polymer science and industrial applications because copolymerization can provide a powerful synthetic route for producing polymer materials with finely tunable properties.[1,2] Considerable experimental effort has been devoted toward controlled radical copolymerizations for inducing large changes of reactivity ratios and sequences of monomers.[3−6] For example, addition of Lewis acids in radical copolymerization of acrylates with other monomers allows control of the copolymer composition.[7−9] In this reaction system, complexation of Lewis acid to the ester functionality increases the reactivity and electron-accepting ability of acrylates, enhancing the tendency toward alternating copolymerization. One other promising strategy is template-assisted copolymerizations, where particular monomers are effectively recognized at preprogrammed sites in the templates.[10,11] This biomimetic approach has enabled drastic compositional changes and even sequence control of the resulting polymers.

The design and synthesis of porous coordination polymers (PCPs) with unique structures and functions using a self-assembly approach of metal ions and organic ligands have been the subjects of tremendous research efforts in recent decades because of their many potential applications in gas storage, separation, catalysis, and sensors.[12−16] In particular, utilization of PCPs for radical polymerization of monomers accommodated in the nanochannels has provided regulated polymers with controlled primary structures.[17−21] Copolymerization of commonly used monomers, such as methyl methacrylate (MMA), styrene (St), and vinyl acetate, has already been achieved in the nanochannels of a PCP, $[Cu_2(bdc)_2(ted)]_n$ (**1**; bdc = 1,4-benzenedicarboxylate, ted = triethylenediamine), showing a change of the monomer compositions in resulting copolymers compared with those obtained from free radical copolymerizations in solution and bulk.[18] This result was explained by the spatial confinement effect, where limited diffusivity of monomers affected their reactivity in the narrow nanochannels. However, the reported monomer reactivity ratios were not very different from those obtained in conventional free radical systems.

PCPs with coordinatively unsaturated metal sites (UMS) have often been utilized for high-performance catalysis and adsorbents because these Lewis acidic sites can bind to the target molecules selectively and strongly.[22−28] It is thus likely that UMS can significantly affect the monomer arrangement and reactivity during the copolymerization process. In this work, we performed radical copolymerization of MMA and St using [Tb(btb)]$_n$ (**2**; btb = 1,3,5-benzenetrisbenzoate) with UMS located at the corners of the hexagonal one-dimensional channels (Figure 1).[29] In the pores of **2**, MMA with a carbonyl group can interact with the metal sites, whereas St cannot. We aimed to achieve a large compositional change in the copolymer using not only the spatial effect of PCP, but also the anchoring effect of MMA at UMS.

For the copolymerization of MMA and St, the dried host **2** was prepared by evacuation at 120 °C for 8 h and was then immersed in MMA and St with different ratios to incorporate the monomers into the channels of **2**. Excess monomers

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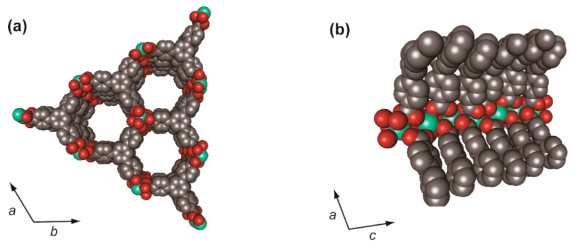

Figure 1. Views of (a) one-dimensional nanochannels and (b) pore wall structure of **2** without guest and coordinative solvent molecules. Hydrogen atoms are omitted for clarity. Terbium, carbon, and oxygen atoms are denoted with green, gray, and red, respectively.

outside the host particles were completely removed by evacuation (0.2 kPa), ensuring that the polymerization proceeds only inside the channels of **2**. However, in this process, the ratio of monomers accommodated in the channels is changed in comparison with the initial feed ratio because of the different vapor pressures between MMA and St. MMA with higher vapor pressure was predominantly removed by evacuation. Thus, the actual ratio of monomers encapsulated in **2** should be determined prior to the copolymerization. A part of the monomer composite was stirred in MeOH-d_4, followed by filtration, resulting in the extraction of all the monomers from **2**, which was confirmed by IR and thermogravimetric (TG) analyses (Figures S1 and S2). Then, the filtrate was analyzed using ^{1}H NMR to determine the monomer ratio accommodated in the pores of **2**. We performed copolymerization of the monomers initiated by azobis(isobutyronitrile) in the composite under a nitrogen atmosphere. X-ray powder diffraction (XRPD) measurements showed that the crystalline nanochannel structure of **2** was maintained during the copolymerization (Figure 2). MeOH was added to quench the polymerization, followed by the treatment with 0.05 M aqueous sodium ethylenediaminetetraacetate to digest the framework of **2**, resulting in the release of poly(MMA-*co*-St) from the nanochannels. Gel permeation chromatography (GPC) analysis for the copolymers revealed the production of polymeric materials with the molecular weight of several tens of thousands (Figure S3).

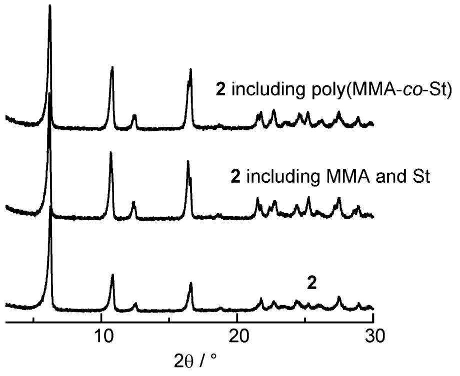

Figure 2. XRPD patterns of **2** before and after the copolymerization of MMA and St in the nanochannels (MMA/St = 15:85).

We performed ^{1}H NMR measurements on poly(MMA-*co*-St) in CD_2Cl_2 to determine the monomer ratio in the copolymer. In Figure 3, the proportions of MMA in the copolymer are plotted against those in the monomer feed. In the case of copolymerization at 70 °C, the monomer composition plots almost traced those obtained from free radical copolymerization. Only a slight increase in the MMA composition in the copolymer was found in the range of low feed ratios of MMA. In contrast, the composition of MMA in the copolymer remained high for a wide range of feed ratios when we carried out the copolymerization at room temperature initiated by light irradiation.

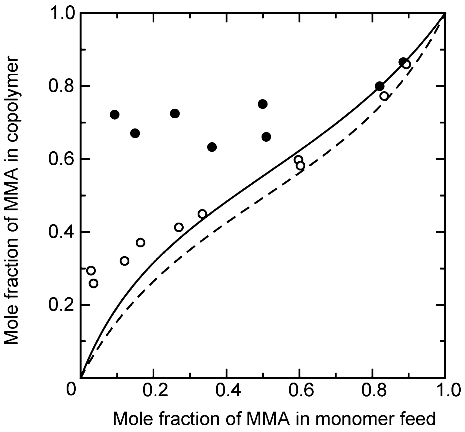

Figure 3. Copolymer composition plots obtained from copolymerizations of MMA and St in free radical condition (dot line), in **1** (solid line), in **2** at 70 °C (open circle), and in **2** at room temperature (filled circle). Conversion of monomers was controlled below 10%.

An initial study aiming to explore this interesting phenomenon was facilitated using variable temperature IR spectroscopy, where interaction between MMA and UMS in the nanochannels of **2** was investigated (Figure 4). In the measurement at 40 °C, a strong peak corresponding to C═O stretching of MMA was observed at 1713 cm^{-1} because of the effective coordination of MMA to UMS. The intensity of this peak gradually decreased, together with an increase in a peak for free MMA at 1723 cm^{-1}, with increasing analysis temperature. These IR results suggest that copolymerization of MMA and St in **2** should be strongly influenced by UMS at lower temperature (room temperature). In contrast, the effect of UMS on the copolymerization can be ignored at higher temperature (70 °C).

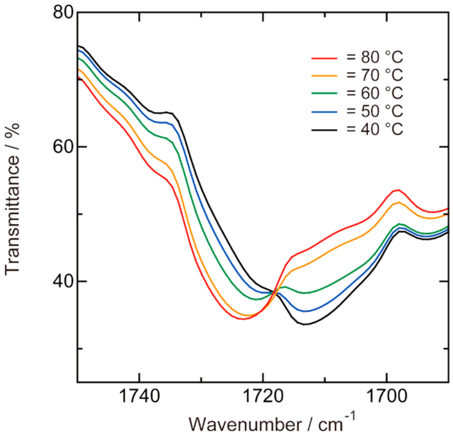

Figure 4. Variable temperature IR spectra for C═O stretching band of MMA in nanochannels of **2**.

As controlled experiments, copolymerizations of MMA and St in solvents, such as CH_2Cl_2 and toluene, with $Tb(OTf)_3$ as a discrete Lewis acid were carried out at room temperature.

Almost no effect of the metal ions on the composition of poly(MMA-*co*-St) was observed in any reaction conditions (Table 1). In the IR measurement of MMA with $Tb(OTf)_3$, the C═O stretching peak of MMA appeared at 1724 cm^{-1}, showing that MMA did not effectively interact with this Lewis acid (Figure S4). In addition, copolymerization of MMA and St using **1** without UMS in the pores did not give large changes of the monomer composition either at 70 °C and room temperature.[18] These results clearly showed the significant effect of **2** with UMS on radical copolymerization.

Table 1. Copolymerization of MMA and St in the Presence of $Tb(OTf)_3$[a]

solvent	Tb^{3+}/total monomer	MMA in monomer feed (mole fraction)	MMA in copolymer (mole fraction)
CH_2Cl_2	0.48	0.20	0.29
CH_2Cl_2	0.96	0.20	0.28
toluene	0.96	0.20	0.34
bulk		0.20	0.26

[a] Copolymerization was carried out at room temperature.

Many previous papers have reported that addition of Lewis acids to the radical homopolymerization of MMA led to an increase in the reactivity of the monomer as well as the isotacticity of the resulting PMMA because simultaneous complexation of several MMAs to the Lewis acid gives cyclic intermediates, resulting in the formation of meso diads upon polymerization.[30−33] In fact, the lanthanoid Tb ions in the UMS of **2** have a large coordination number, so that the isotacticity of PMMA prepared in the channels of **2** was indeed high.[19] In conventional radical copolymerizations of MMA and St in solutions, Lewis acids are generally effective in forming alternating copolymers.[7] However, it is unlikely that reaction of St with the large phenyl substituent can proceed smoothly at sterically hindered UMS in the corners of the hexagonal pores. Therefore, dimerization of MMA would be dominant at the UMS in **2**, rather than the heteroreaction between MMA and St. Because the UMS are periodically located with an interval of 12 Å along the one-dimensional channels, St monomers could be involved in the polymerization only at areas remote from UMS, resulting in the formation of an MMA-rich copolymer.

In conclusion, we have successfully demonstrated that radical copolymerization of MMA and St in the nanochannels of a PCP with UMS could provide poly(MMA-*co*-St) with a remarkably high fraction of MMA. Coordination of MMA monomers to the UMS during the copolymerization changed the reactivity of the monomers, promoting the incorporation of MMA units in the copolymer. We believe that the present work will open a new route to the design and control of microstructure and monomer composition in copolymer chains.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

IR, TG, and GPC data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00370.

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Notes

The authors declare no competing financial interest.

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