Radical Copolymerizations of Vinyl Monomers in a Porous Coordination Polymer

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Radical copolymerizations of vinyl monomers, such as styrene, methyl methacrylate, and vinyl acetate, in the nanochannels of a porous coordination polymer have been studied. The results are compared with those obtained for the corresponding free radical copolymerizations, which shows a spatial confinement effect on the monomer reactivity ratios in this system.

Inclusion polymerization has been successfully carried out with a variety of monomers and matrix compounds, and has proven to be a valuable tool to synthesize stereoregular and even optically active polymers.[1–3] However, the monomer diffusion mechanism as well as the subsequent polymerization process is not yet fully understood, because they depend on the constitutional and steric factors of the specific host–guest system. These factors become more critical if we carry out copolymerizations instead of homopolymerizations. However, relatively few studies have been reported so far on such inclusion copolymerizations.[4–7]

Porous coordination polymers (PCPs), built up by self-assembly of discrete metal centers with functional organic ligands, have developed rapidly in recent years because of their diverse topologies and unique properties, such as storage, separation, and heterogeneous catalysis.[8–11] Recently, our group adopted the functional nanochannels of PCPs to carry out homopolymerizations, in which stereoregularity, reaction site, and molecular weight of the product were successfully controlled.[12–14] Thus, attention has also been paid to the copolymerizations using the nanochannels of PCPs. Since the channel sizes of PCPs are quite similar to the monomer dimensions, the copolymerizations in PCPs would be strongly affected by competitive diffusion of monomers and the difference in their bulkiness. Therefore, such PCP-based copolymerization is expected to afford unique copolymers with compositions different from those obtained by the conventional copolymerizations.

In this communication, we report on the radical copolymerizations of commonly used vinyl monomers, such as styrene (St), methyl methacrylate (MMA), and vinyl acetate (VAc), using the nanochannels of $[Cu_2(bdc)_2(ted)]_n$ (**1**; bdc = 1,4-benzenedicarboxylate, ted = triethylenediamine), where the host **1** has regular and continuous one-dimensional (1-D) nanochannels with pore size of $7.5 \times 7.5\,\text{Å}^2$ along the *c* axis (Figure 1a).[15] An obvious nanochannel effect on the monomer reactivity is found for this unique copolymerization system.

The copolymerizations of vinyl monomers in the channels of **1** were carried out as follows.[16] The monomers were incorporated in the nanochannels by immersion of **1** in a mixture of monomers followed by removal of the excess monomers external to the host crystals under reduced pressure. The monomer incorporation ratio in the channel could be controlled by the initial feed ratio of the monomers. To induce copolymerization of the monomers accommodated, the adducts were heated with 2,2′-azobis(isobutyronitrile) (AIBN) as a radical polymerization initiator at elevated temperatures. The final polymer composites were obtained after a thorough washing with methanol and drying. The X-ray powder diffraction (XRPD) measurements of the monomer adducts and the polymer-composites showed that the channel structure of **1** is maintained during the copolymerization process (Figure 1b). The copolymer accommodated was then quantitatively released from the framework of **1** by the host decomposition in an ethylenediaminetetraacetic acid (EDTA) solution. The gel permeation chromatography (GPC) analysis of the resultant products showed that they are polymeric compounds with high molecular weights ($M_w > 30000$).

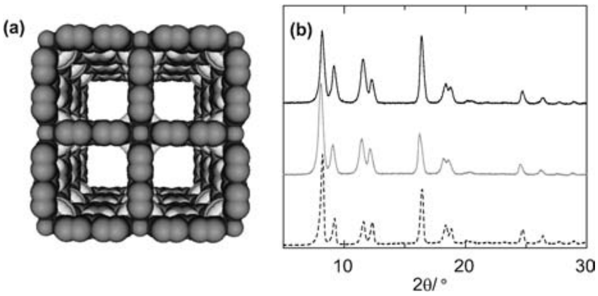

Figure 1. (a) Nanochannel structure of **1** displayed by CPK model. (b) XRPD patterns of only host **1** (dot line) and inclusion compound of **1** with St and MMA before (glay) and after polymerization (black). The molar ratio of St to MMA incorporated in the nanochannel was 1.0:1.2.

In order to obtain a copolymer composition curve, the copolymer compositions were determined from the initial polymerization ratios of monomers.[16] From these curves, the monomer reactivity ratios for the copolymerizations in the nanochannel of **1** were obtained using the Fineman–Ross method.[17] In case of the copolymerization of St and MMA at 70 °C (Figure 2a), the reactivities of St (r_{St}) and MMA (r_{MMA}) were calculated to be 0.39 and 0.72, respectively (Figure 2c). These r_{St} and r_{MMA} values are different from those obtained for the conventional bulk and solution radical polymerization systems: $r_{St} = 0.53$, $r_{MMA} = 0.49$.[18] Thus, the monomer reactivity ratio is dramatically affected by conducting the copolymerization in the nanochannels of **1**. Compared to free radical copolymerization, MMA-rich composition in the resultant copolymer was obtained in the corresponding monomer feed ratio.

Because of the lack of a conjugated substituent in the VAc monomer, free radical copolymerization of St and VAc produces a copolymer with much smaller amount of the VAc unit. Thus,

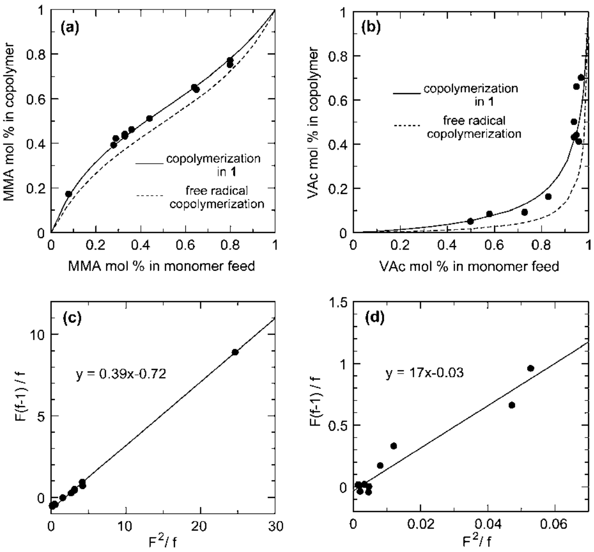

Figure 2. Copolymer composition curves obtained from copolymerizations of (a) St and MMA and (b) St and VAc in the nanochannels of **1**. Fineman–Ross plots for the copolymerizatios of (c) St and MMA and (d) St and VAc in the nanochannels of **1**, where F = monomer feed ratio ([St]/[MMA] or [St]/[VAc]) and f = monomer unit ratio in copolymer (d[St]/d[MMA] or d[St]/d[VAc]).

the monomer reactivity ratio of St ($r_{\mathrm{St}} = 55$) is much higher than that of VAc ($r_{\mathrm{VAc}} = 0.01$) in the copolymerization system.[19] In contrast, the copolymerization of St and VAc in the nanochannels of **1** at 60 °C provided copolymers with different monomer compositions, where the content of VAc certainly increased in comparison with that of a copolymer obtained from the corresponding bulk condition (Figure 2b). The monomer reactivity ratios r_{St} and r_{VAc} could be estimated to be 17 and 0.03, respectively (Figure 2d).

From these results, it is generally seen that the composition of St in a copolymer prepared in the host **1** becomes lower than that obtained from the corresponding free radical system. It seems very likely that the monomer reactivity in the nanochannels is controlled by the molecular size and the electronic property of each monomer. The interaction of the nanochannel of **1** with the St molecule is expected to be much stronger than those with other monomers, since the molecular size of St (6.8 × 4.4 Å) is clearly larger than of those of MMA (5.9 × 4.1 Å) and VAc (5.5 × 4.0 Å). An effective π–π interaction possibly formed between the phenyl ring of St and the pore may also be considered as another reason for the above observations. Thus, it is reasonable to consider that the diffusion of St in the channel is slower than those of MMA and VAc. In addition, the reactivity of St toward polymer chain terminals may be more restricted in the nanochannels because of its larger molecular size. Thus, our results suggest that the interactions between the PCP nanochannels and the vinyl monomers significantly affect the composition and the sequence of monomers in the resultant copolymerization products, possibly by efficient through-space inductions.

In conclusion, we have demonstrated that a spatial confinement effect can be achieved for the radical copolymerizations of vinyl monomers in 1-D nanochannels of a PCP. The detailed analysis of copolymer compositions showed obvious changes of the monomer reactivity ratios, compared to the corresponding free radical copolymerization system. We believe that the capability of precise channel design (channel size, shape, and surface functionality) is one of the most powerful advantages of using the PCPs in copolymerizations. We are currently targeting the tailor-made synthesis of copolymers with designable compositions and sequences using such microporous channels of PCPs.

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