

# Radical polymerisation of styrene in porous coordination polymers†

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The first radical polymerisation of styrene in porous coordination polymers has been carried out, providing stable propagating radicals (living radicals), and a specific space effect of the host frameworks on the monomer reactivity is demonstrated.

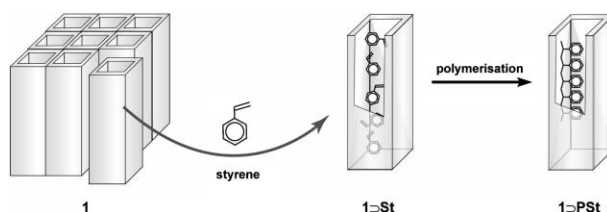
Since the early 1990s, the quest for porous coordination polymers (PCPs) composed of transition metal ions and bridging organic ligands has been the subject of intense research because of their potential applications in many areas, including molecular storage, separation, and exchange.<sup>1</sup> Recently, much effort has been devoted to developing characteristic features of PCPs that differ from those of conventional microporous materials, such as zeolites and activated carbons: 1) highly regular channel structures, 2) controllable channel size approximating molecular dimensions, and 3) designable surface potentials and functionality.<sup>1,2</sup> These features must be of key importance for the creation of unique nanosize reaction fields based on the PCP materials.<sup>3</sup> For example, PCPs with designed chiral porous channels are of practical use for heterogeneous asymmetric catalysis and have tremendous impact on chirotechnology.<sup>3a,b</sup> Our strategy for a successful application of PCPs is to utilize their regulated and tunable nanochannels in the field of polymerisation, which would not only allow multi-level control of polymerisation (control of stereoregularity, molecular weight, helicity, *etc.*), but also provide well-defined nanostructures permitting fabrication of next-generation materials. However, in spite of the potential advantages, successful attempts at polymerisation in the nanochannels of PCPs have not been reported to date.

Molecules in confined nanospace have properties clearly different from those of the corresponding bulk fluids, which is called a space effect. Recently, our interest has also been focused on specific behaviours of guest molecules accommodated in the nanochannels of PCPs.<sup>2b,4</sup> Such studies are essential for evaluation and understanding of the guest molecular properties (adsorption, reaction, conversion, alignment, *etc.*), and design of new functions based on PCPs. Nevertheless, little attention has been paid to guest behaviour in the nanochannels of PCPs,<sup>5</sup> and the relationship between the guest behaviour and its reactivity in the nanochannels has not been explored yet.

[M<sub>2</sub>(1,4-benzenedicarboxylate)<sub>2</sub>(triethylenediamine)]<sub>n</sub> (**1a**; M = Zn<sup>2+</sup>, **1b**; M = Cu<sup>2+</sup>)<sup>6</sup> and [Cu(pyrazine-2,3-dicarboxylate)<sub>2</sub>(4,4'-bipyridine)]<sub>n</sub> (**2**)<sup>7</sup> have regular and continuous one-dimensional nanochannels with cross-sections of 7.5 × 7.5 Å<sup>2</sup> and 8.2 × 6.0 Å<sup>2</sup>, respectively, which have been utilized for gas storage and guest molecular alignment. In this work, as the first stage of our strategy, we examine radical polymerisation of styrene (St; molecular size = 7.2 × 4.4 Å) in the nanochannels and study the link between reactivity and local dynamic behaviour of St in the nanochannels by a <sup>2</sup>H NMR technique.

The polymerisation of St in the channel of **1a** is carried out as follows.‡ The monomer St was fully adsorbed in the nanochannel by immersion of **1a** in liquid St followed by removal of excess St external to the host crystals under reduced pressure. The loading level of St in the nanochannel of **1a** (number of St/void volume of **1a**) is 2.8/nm<sup>3</sup>, determined by thermogravimetric analysis (TGA). To induce polymerisation of the accommodated St, the adduct (**1a**⊃PSt) was heated with 2,2'-azobis(isobutyronitrile) (AIBN) as a radical polymerisation initiator at 70 °C for 48 h (Scheme 1). The final polystyrene (PSt) composite (**1a**⊃PSt) was obtained after a thorough washing with MeOH and drying. We compare the X-ray powder diffraction (XRPD) pattern of **1a**⊃PSt with that of **1a** alone (Fig. 1). Although the peak positions of **1a**⊃PSt were in good agreement with those of **1a**, the relative peak intensities have obviously changed. Such a change in peak intensities is commonly observed for porous compounds when the pores are occupied by guest molecules, which is ascribed to the change of electron density in the pores.<sup>2b,8</sup> This result indicates that the channel structure of **1a** was maintained during the polymerisation and the resultant PSt chain is encapsulated in the nanochannel. The TGA data of **1a**⊃PSt show that conversion of the adsorbed St to PSt in the nanochannel of **1a** is 71%.

Quantitative recovery of the accommodated PSt from the host **1a** was performed by decomposition of the **1a** framework in 0.1 N NaOH.§ Characterisation of the resultant product by solution <sup>1</sup>H and <sup>13</sup>C NMR measurements showed the typical characteristics of pure PSt.† From the GPC measurement, the



**Scheme 1** Schematic illustration for polymerisation of St in the nanochannels of **1**.

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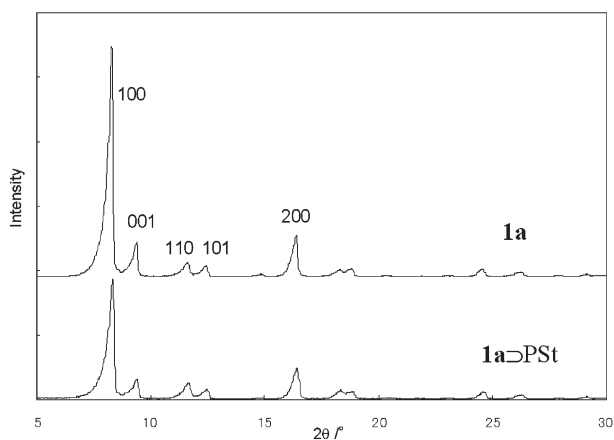


Fig. 1 XRPD profiles of **1a** and **1a**→PSt.

number-average molecular weight ( $M_n$ ) and the polydispersity ( $M_w/M_n$ ) of the recovered PSt were found to be 56,200 and 1.66, respectively (Fig. 2). In contrast, the GPC profile of bulk PSt synthesized under comparable conditions showed a broad fraction with a high polydispersity ( $M_w/M_n = 4.68$ ) (Fig. 2). This difference suggests a possibility of molecular weight control in the nanochannel of **1a**. The same experiment with use of copper complex **1b** also resulted in encapsulation of PSt in the nanochannel (**1b**→PSt; conversion = 71%). Extracted PSt from **1b**→PSt showed that  $M_n$  and  $M_w/M_n$  were 54,600 and 1.60, respectively. Interestingly, no difference in conversion, molecular weight, and polydispersity detected between the polymerisation in **1a** and **1b** indicates the polymerisation of St is not affected by metal ions in the frameworks. This polymerisation system can provide new opportunities for inclusion polymerisations, because polymerisation in the previous microporous zeolites and organic crystalline hosts, which has been extensively developed over the past few decades, still suffers from intrinsic issues of their narrow, discontinuous, and/or fragile cavities for allowing the polymerisation of large vinyl monomers ( $> 6 \text{ \AA}$ ).<sup>9</sup> In fact, polymerisation of St in their cavities has been very limited due to the bulkiness of St.<sup>10</sup>

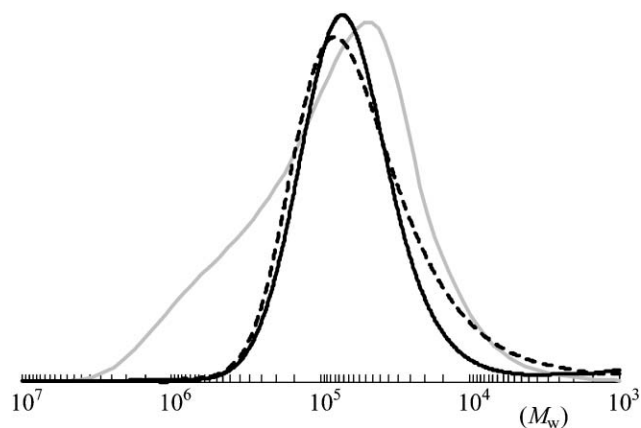


Fig. 2 GPC profiles of (dashed line) recovered PSt from **1a**, (black) recovered PSt from **1b** and (gray) bulk PSt synthesized under comparable conditions. Molecular weights are based on the calibration of standard PSt.

ESR measurement for the propagating radical was conducted by use of non-magnetic **1a**. It is of great interest that the ESR spectrum during the polymerisation showed an intense signal assigned to the propagating radical of PSt and the signal did not disappear over 3 weeks even at 70 °C.<sup>†</sup> In contrast to the case of bulk and solution polymerisations of St, the propagating radical in this system was remarkably stabilized due to suppressions of termination reaction and radical transfer in the nanochannel.<sup>9c,11</sup> Such a “living” radical nature is very important for controlling the molecular weight, which is consistent with the narrow polydispersities of the recovered PSt from **1**→PSt.

Next, we carried out the polymerisation of St under the same conditions in the nanochannel of **2** whose pore size is comparable to that of **1**. However, in this experiment, a trace amount ( $< 3\%$ ) of PSt was obtained (*ca.* 4% when the reaction was carried out at 100 °C), even though the channel was filled with the monomer St (number of St/void volume of **2** = 2.7/nm<sup>3</sup>). During the polymerisation, no evidence of framework change and radical transfer to the framework was observed. Since the reactivity of guest molecules in confined nanospaces is strongly dependent on the molecular behaviours,<sup>12</sup> comparison between <sup>2</sup>H NMR spectra of St-*d*<sub>8</sub> in the nanochannels of **1** and **2** was made. The solid-state <sup>2</sup>H NMR technique is a powerful tool for monitoring specific dynamics of guest molecules in nanospace.<sup>4,5,13</sup> Fig. 3a displays the selected <sup>2</sup>H NMR spectra for St-*d*<sub>8</sub> adsorbed in **1a** from -60 to 70 °C.<sup>14</sup> The characteristic spectra of an aromatic ring with quadrupole splitting of 13.4 kHz at 20 and 70 °C reveal that the guest St in the nanochannel has high mobility with mainly fast rotation around the C<sub>3</sub>-C<sub>6</sub> axis. With a decrease in the temperature to -60 °C, the spectrum shows a broader line shape, indicating that the mobility of St in the slow motion regime becomes dominant.<sup>13d</sup> It is also observed that the spectra of St-*d*<sub>8</sub> in **1a** and **1b** show similar line shapes,<sup>†</sup> supporting the same results in the polymerisation of St in those nanochannels. However, the spectra of St-*d*<sub>8</sub> in **2** whose dipolar interaction with the paramagnetic Cu(II) is negligibly weak, exhibit obvious broad

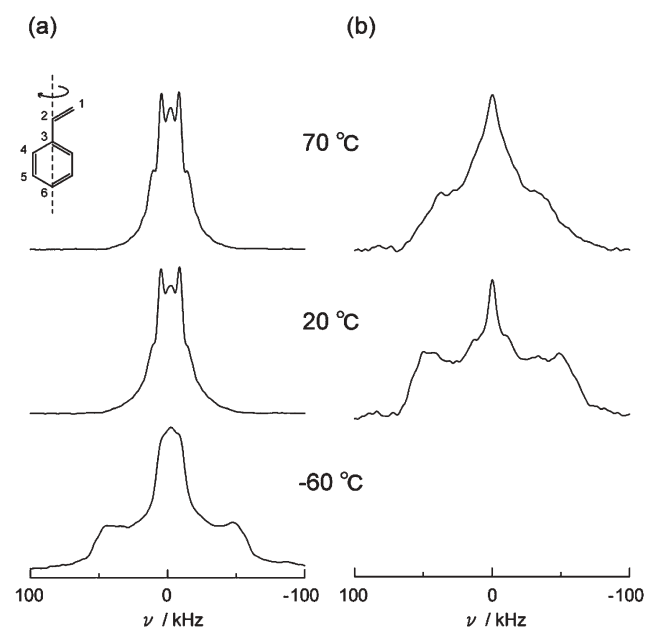


Fig. 3 Solid-state <sup>2</sup>H NMR spectra of St-*d*<sub>8</sub> adsorbed in **1a** (a) and **2** (b).

signals, indicating that the mobility of St in **2** is highly restricted compared with that in **1** (Fig. 3b). Note that the line shape of **2** at 70 °C is comparable to that of **1a** at -60 °C, showing the almost frozen motion of St in the nanochannel of **2** even at the polymerisation temperature. This strong space (confinement) effect in **2** can be explained by the unique periodical channel potential of **2** which is different from the smooth and uniform potential of **1**.<sup>4,7b</sup> The values for the monomer loading level (degree of monomer packing) in both of the hosts are almost the same, so that the restricted arrangement of the St in the nanochannel of **2** should result in the poor reactivity of St, although thermal spontaneous polymerisation of St in the bulk state commonly occurs at 70 °C.<sup>15</sup>

In conclusion, we have established a novel approach to polymerisation in the nanochannels of PCPs, and demonstrated that 1) the propagating radicals of PSt showed living radical nature and 2) reactivity of St can be determined by the confinement effect in the nanochannels. The results obtained here provide valuable information for understanding the detailed reaction mechanism of guest molecules in PCPs and designing new PCPs for molecular confinement, alignment and conversion. The advantageous porous features of PCPs encourage us to apply this system to various polymerisations, which will lead to not only new controlled polymerisation systems but also significant model systems for a single polymer chain isolated from its surroundings.

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## Notes and references

‡ Synthesis of **1a**→PSt: In a Pyrex reaction tube, dried complex **1a** (200 mg) was prepared by evacuation (80 Pa) at 130 °C for 3 h; subsequently, it was immersed in styrene (0.5 ml) with 2,2'-azobis(isobutyronitrile) (AIBN; 3 mg) at room temperature. After excess styrene was completely removed by evacuation (80 Pa) at room temperature for 2 h, the reaction tube was filled with nitrogen and was then heated at 70 °C for 48 h. The resultant powder was washed repeatedly with MeOH to remove unreacted St and dried at room temperature.

§ Recovery of PSt from **1a**→PSt: The composite **1a**→PSt (1.05 g) was stirred in 0.1 N NaOH for 10 h to decompose completely the porous framework of **1a**, then the resultant solid was dissolved in CHCl<sub>3</sub>. After filtration of the mixture, the filtrate was evaporated and poured into a large amount of MeOH. The collected precipitate was washed several times with MeOH and subsequent drying under reduced pressure at room temperature gave pure PSt (197 mg).

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- 14 We have also measured <sup>2</sup>H NMR spectra of St-*d*<sub>5</sub> (C<sub>6</sub>D<sub>5</sub>CH=CH<sub>2</sub>) adsorbed in **1a** and **2**. These results tell us that in the case of **1a**, peaks around 0 kHz at 20 and 70 °C of Fig. 3a are identified with the deuterons of the vinyl group of St-*d*<sub>5</sub>, and the mobility of the vinyl moiety is in a slow motion regime at -60 °C. On the other hand, we observed that most of the aromatic deuterons of St-*d*<sub>5</sub> in **2** are already quiescent at 20 and 70 °C; hence, we concluded that St adsorbed in **2** is strongly confined compared with that in **1a**.
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