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Topotactic Polymerization

Topotactic Linear Radical Polymerization of Divinylbenzenes in Porous Coordination Polymers**

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In memory of Yoshihiko Ito

Porous coordination polymers (PCPs) built by the self-assembly of discrete metal centers with functional organic ligands have received increasing attention in recent years because of their diverse topologies and unique properties.[1] One of the most advantageous features of PCPs is their designable frameworks: their pore size, shape, and surface properties are readily tunable by changing the bridging ligands.[1] Another intriguing feature of PCPs is that their flexible dynamic frameworks are responsive to guest molecules, something which does not occur with conventional microporous materials, such as zeolites and activated carbons.[2] For example, drastic structural transformations of PCPs with gated channels are triggered by various guest gas molecules at specific pressures,[2c] and in a few cases the guest molecules induce highly selective shrinking/breathing processes of the functional PCP frameworks that involve simultaneous changes of their electronic properties.[2a,d,e] The unique porous properties of such PCP frameworks, along with their designable structures and flexibility, could be key factors that make them useful for the highly selective recognition, accommodation, and reaction of target molecules.

Radical polymerization is the most widely employed process for obtaining polymeric organic materials in industry and the laboratory, therefore radical polymerization of vinyl monomers that allows control of properties which include tacticity, sequence, and molecular weight, is currently an important topic. Control of the polymer primary structures, which is essential for the fabrication of desired regularities and topologies, is, however, incredibly difficult owing to the high reactivity of the growing radical species.[3] In particular, controlled radical polymerization of divinylbenzenes (DVBs) to attain a regulated low-dimensional chain growth is still undeveloped because both vinyl moieties in these DVBs are equally reactive and therefore radical polymerization results in the formation of a hyperbranched network polymer.[4] In contrast to the conventional use of DVBs as cross-linkers, further progress in this field depends crucially on the development of an efficient method for directing low-dimensional regulated radical polymerization. Such a technique would not only contribute significantly to the field of synthetic polymer chemistry but would also provide novel materials with properties that are very different from those of other network polymers.[5]

Recently, polymerization in confined nanocavities, such as inclusion crystals, mesoporous silica, and porous organic nanostructures, has emerged as an attractive technique for the control of polymer structures and the design of well-defined nanostructures.[6] We have been studying controlled polymerization within functional nanospaces based on PCP materials[7]as a strategy to overcome the difficulties in conventional polymerization reactions (Scheme 1). Herein we demonstrate a selective linear radical polymerization of DVBs in the channels of $[M_2(1,4\text{-bdc})_2(\text{ted})]_n$ (bdc = benzenedicarboxylate; ted = triethylenediamine; M = Zn^{2+} (**1a**), Cu^{2+} (**1b**)), which have regular and continuous one-dimensional nanochannels with a pore size of 7.8×7.8 Å^2 along their *c* axes.[2f,8] Note that the key to this selective polymerization is an appropriate channel size for monomer inclusion and/or specific framework flexibility.

Polymerization of *p*-DVB (molecular dimensions: 8.5×4.4 Å) in the nanochannels of **1a** was performed as follows. After the adsorption of *p*-DVB into the nanochannels, the hybrid (**1a**⊃*p*-DVB) was heated at 100 °C for five days in a closed system in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) as the radical initiator. Compared to the reported polymerization of styrene in the channels of **1**,[7b] polymerization of *p*-DVB requires a higher temperature and longer

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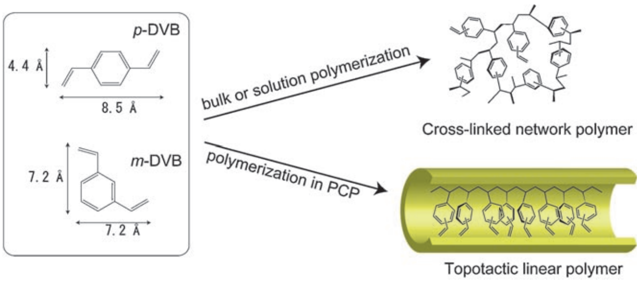

Scheme 1. The usual cross-linked network polymerization of DVBs and our topotactic linear polymerization in the one-dimensional channels of PCPs.

reaction time, probably because the large DVB monomers are tightly encapsulated in the channel. The poly(*p*-DVB) thus formed was then quantitatively released from the framework of **1a** by decomposing the host in ethylenediaminetetraacetic acid (EDTA) solution. It is noteworthy that the recovered poly(*p*-DVB) is soluble in various organic solvents (e.g. THF, $CHCl_3$, DMF, DMSO), which contrasts with the insoluble product usually obtained from the radical polymerization of DVBs in solution and bulk.[4]

Gel-permeation chromatography (GPC) measurement of the resultant poly(*p*-DVB) showed a weight-average molecular weight (M_w) and number-average molecular weight (M_n) of 20300 and 2000, respectively, with respect to a polystyrene standard.[9] Spectroscopic characterization of the resultant poly(*p*-DVB) (see the Supporting Information) indicated a unique polymer structure that suggests a selective linear polymerization of *p*-DVB in the nanochannel .[5a] For example, the IR spectrum of poly(*p*-DVB) contains absorption bands similar to those of *p*-DVB and polystyrene, and an absorption at 1629 cm^{-1} suggests the existence of residual vinyl moieties in poly(*p*-DVB). The UV absorption spectrum of poly(*p*-DVB) in THF is similar to that of the monomeric model compound 4-methylstyrene, as result which also indicates that the polymer contains vinylphenyl groups in its repeating units. In the ^{1}H NMR spectrum of poly(*p*-DVB), signals can be assigned to protons at the β-carbon of vinyl groups ($\delta = 5.1$ and 5.7 ppm; Figure 1). Comparison of the integrated peak intensities of the aromatic and the vinyl regions clearly shows that only one vinyl group of *p*-DVB is selectively polymerized to form the linear polymer and that hardly any undesired kink structures (branching and/or bonding through both vinyl groups) are formed during the reaction.[10] Thus, the porous compound **1a** successfully directs the linearly extended polymerization of a divinyl monomer through an effective entrapment of the reactive propagating radical mediator in the one-dimensional nanochannel of this complex.

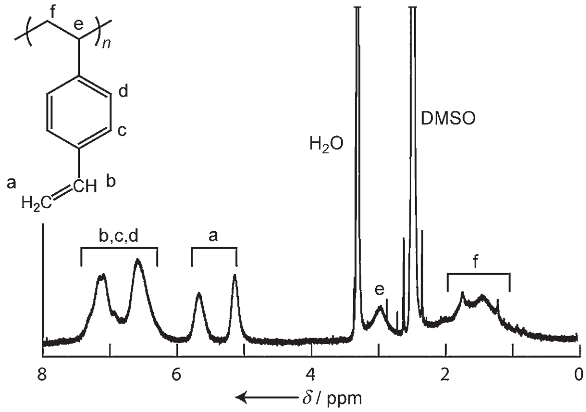

Figure 1. ^{1}H NMR spectrum (in [D$_6$]DMSO) of poly(*p*-DVB) obtained from the nanochannels of **1a**. The ratio of the intensities of signal a to those of signals b, c, and d is 2:5.

Next, we carried out the polymerization of *p*-DVB in an isostructural copper complex (**1b**) under the same conditions. However, no trace of polymeric product was observed in this experiment even though the porous structure of **1b** is almost the same as that of **1a**. To understand the different reactivities of *p*-DVB in **1** we performed thermogravimetric analysis (TGA) and X-ray powder diffraction (XRPD) measurements during the course of the polymerization. In the TGA profile of **1a**⊃*p*-DVB (Figure 2a), the observed weight loss of around 30% up to 250°C corresponds to removal of *p*-DVB from the host framework, which shows that the loading level of *p*-DVB in the nanochannel of **1a** is 2.0 (i.e. the number of *p*-DVB molecules per unit cell of **1a**).[11] A marked difference in weight loss is seen after the polymerization compared with the initial **1a**⊃*p*-DVB sample, thus indicating the transformation into thermally stable poly(*p*-DVB) in the nanochannel (68% conversion).[11] The TGA data for **1b**⊃*p*-DVB, however, indicate a lower amount of adsorbed *p*-DVB in **1b** (the number of *p*-DVB molecules per unit cell of **1b** is 0.9) than for **1a**. Moreover, that no change takes place in the profiles of **1b**⊃*p*-DVB before and after the polymerization is indicative of unpolymerized *p*-DVB remaining in the nanochannel (Figure 2b), a finding which is consistent with the experimental results obtained with **1b**. The XRPD measure-

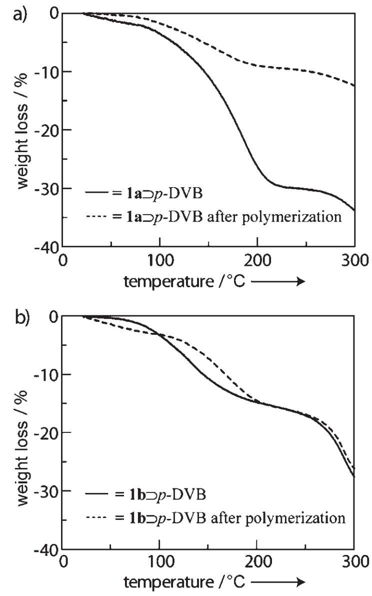

Figure 2. TGA profiles of a) **1a**⊃*p*-DVB and b) **1b**⊃*p*-DVB before and after polymerization. The heating rate of this measurement was 10 K min^{-1}.

ments gave an important clue to the different adsorption/polymerization properties of **1** as small changes of peak positions were observed after the introduction of *p*-DVB into the nanochannel of **1a** (Figure 3a), whereas the framework of **1b** did not show such structural changes (Figure 3b).

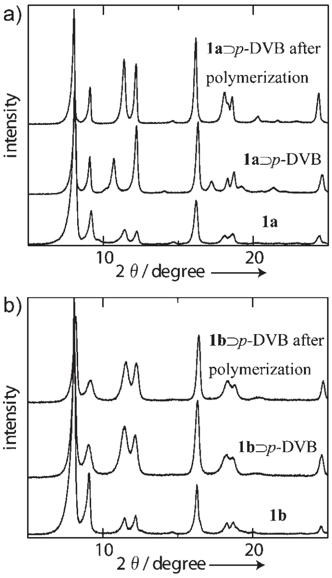

Figure 3. XRPD patterns of a) **1a** and b) **1b** during the polymerization of *p*-DVB in their nanochannels.

The detailed framework change of **1a** was examined by using synchrotron XRPD. A Le Bail fitting analysis of the diffraction data gave the unit-cell parameters of **1a**⊃*p*-DVB, which show that introduction of *p*-DVB into the channel does not affect the porous nature of the framework but induces a small amount of lattice expansion compared with the original host **1a** (see the Supporting Information).[12,13] PCPs containing Zn often show similar flexible and dynamic properties upon guest inclusion.[2f,g] The amount of *p*-DVB adsorbed and the cell parameters allowed us to calculate the average distance between *p*-DVB molecules in the channels (along the *c* axes) of **1a** and **1b** as being 4.5 and 10.6 Å, respectively, which suggests a polymerizable close-packed distribution of *p*-DVB in the channel of **1a** (Figure 4). The reactivity of monomers encapsulated in host matrices depends strongly on the distance between the monomers—the shorter the distance, the easier the reaction.[6a,b] The flexibility of **1a** allows adsorption of the relatively large *p*-DVB molecules by expansion of the host structure such that the monomer molecules are arranged adjacent to each other, which is essential for the polymerization. Even though much attention has been paid to flexible frameworks of PCPs, a relationship between host flexibility and guest reactivity has not yet been reported.

To determine the feasibility of this polymerization method we examined the radical polymerization of *m*-DVB (molecular dimensions: 7.2 × 7.2 Å) that is slightly smaller than the channel size, in the nanochannels of **1**. Introduction of the monomer into the channels does not trigger a framework change in **1**, as confirmed by the XRPD measurements (see the Supporting Information). In addition, TGA studies of the monomer adducts showed that the amount of *m*-DVB adsorbed in **1a** and **1b** is similar—the number of *m*-DVB molecules per unit cell in **1a** and **1b** is 1.7 and 1.8, respectively—and suggests an adjacent arrangement of the monomer (Figure 4; the average distance between *m*-DVB molecules in the channels of **1** is about 5.4 Å). Hence, in contrast to the case of *p*-DVB polymerization, *m*-DVB is polymerized in the channels of both **1a** and **1b** to give soluble polymeric products (polymerization in **1a**: 47 % conversion, $M_w = 48300$, $M_n = 9500$; polymerization in **1b**: 48 % conversion, $M_w = 10900$, $M_n = 5800$). Full spectroscopic characterization of the resultant poly(*m*-DVB) clearly indicated that only one vinyl moiety of *m*-DVB participates in the polymerization, analogous to the polymerization of *p*-DVB in **1a**.[5a]

To elucidate the importance of the channel size for this topotactic polymerization we prepared $[Cu_2(4,4'\text{-bpdc})_2(ted)]_n$ (**2**; bpdc = biphenyldicarboxylate), which has a large open channel (10.8 × 10.8 Å^2),[8] and attempted to polymerize DVBs in this framework. Conventional TGA confirmed the polymerization of *p*-DVB with high conversion (63 %), although the polymeric product obtained from **2** proved to be insoluble in all solvents tested, thereby showing that semi-branching cross-linked structures are probably formed in this large channel. This result suggests that a channel size suitable for the side-by-side accommodation of single molecules of DVBs should also be a key factor for obtaining selective linear polymerization (Figure 4).

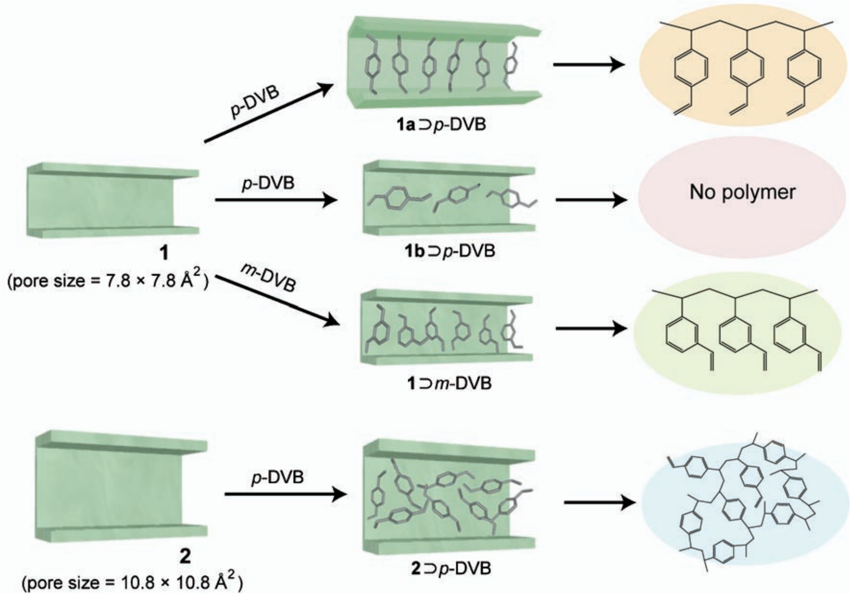

Figure 4. Encapsulation and polymerization of DVBs in the nanochannels of **1** and **2**.

In conclusion, we have successfully achieved the topotactic selective radical polymerization of DVBs inside the one-dimensional nanochannels of PCPs. The prerequisites for this polymerization are an appropriate channel size for the adsorbed monomer and/or framework flexibility to allow monomer adsorption and arrangement. Linear polymers bearing pendant vinyl groups in their backbone are attractive in light of the potential reactivity of the olefinic double bonds and for application as polymer precursors of functional materials.[14]

Experimental Section

Polymerization: Compound **1** (500 mg) was dried in a Pyrex reaction tube by heating to 130 °C under vacuum (80 Pa) for 4 h. A CH_2Cl_2 solution (2.0 mL) of *p*-DVB (250 mg) and 2,2′-azobis(isobutyronitrile) (AIBN; 8 mg) was then added at room temperature. The CH_2Cl_2 was evaporated at 30 kPa and the monomer was adsorbed into the nanochannel of **1** at 35 °C for 20 min at ambient pressure. Excess *p*-DVB was then removed under reduced pressure (80 Pa) at 35 °C for 30 min. The reaction tube was subsequently filled with nitrogen and heated at 100 °C for five days.

Recovery of poly(DVB)s: After the polymerization the powder composite (200 mg) was washed repeatedly with MeOH and then stirred in an aqueous solution (30 mL) of EDTA (0.05 M) for 30 min to decompose the porous framework of **1**. The solid obtained was dissolved in DMF (2 mL) and this solution was poured into a large amount of MeOH. The precipitate was collected and washed several times with MeOH and subsequently dried under reduced pressure at room temperature to give the poly(DVB). The structures of the poly(DVB)s obtained are similar to those produced by controlled anionic polymerization.[5a]

Poly(*p*-DVB): IR (KBr): $\tilde{\nu} = 2919, 1629, 1606, 1510, 1447, 1408, 1016, 988, 904, 838\ \mathrm{cm^{-1}}$; ^{1}H NMR ([D$_6$]DMSO): $\delta = 7.1$ (2H), 6.6 (3H), 5.7 (1H), 5.1 (1H), 3.0 (1H), 1.0–2.0 ppm (2H). Elemental analysis (%) calcd for $C_{10}H_{10}$: C 92.26, H 7.74; found: C 91.02, H 7.81.

Poly(*m*-DVB): IR (KBr): $\tilde{\nu} = 2925, 1630, 1600, 1579, 1484, 1441, 1391, 989, 903, 798, 711\ \mathrm{cm^{-1}}$. ^{1}H NMR ([D$_6$]DMSO): $\delta = 7.1$ (2H), 6.5 (3H), 5.6 (1H), 5.1 (1H), 3.0 (1H), 1.0–2.0 ppm (2H).

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[10] It seems unlikely that polymerization would occur through both vinyl groups of DVBs to form ladder-type polymers in the nanochannels of **1** owing to the lower reactivity of the pendant vinyl groups in poly(DVB)s than those of DVB monomers as well as the large steric hindrance between adjacent benzene rings in the polymer backbones, see: a) J. K. Fink, *J. Polym. Sci. Polym. Chem. Ed.* **1981**, *19*, 195; b) V. A. Harmandaris, N. P. Adhikara, N. F. A. van der Vegt, K. Kremer, *Macromolecules* **2006**, *39*, 6708.

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