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Polymer Synthesis in Coordination Nanospaces

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In nature, biopolymers are efficiently synthesized by multilevel arrangements of monomers within constrained molecular-level spaces. These biological systems produce regio- and stereoregular polymers with uniform molecular weights, and can also arrange the higher order structures of the resulting polymers. Inspired by the elegant operations of polymerization in biological systems, polymer synthesis in artificial confined geometries is a promising strategy for the control of polymer primary structures and the design of well-defined nanostructures. Recently, we have established a new methodology for controlling polymer synthesis using microporous coordination compounds. In this account, recent progress and future perspectives of polymerizations in these coordination nanospaces are reviewed.

1. Introduction

The synthesis of well-defined polymers with accurately controlled primary and three-dimensional structures is an increasingly important aspect of polymer science due to the continuing desire to prepare materials with new and/or improved physical properties.[1] In general, polymer synthesis is conducted in bulk or solution systems, and a variety of artificial catalysts has been employed to control the resulting polymer structures. In contrast, all naturally occurring polymers are produced by enzymatic catalysis, where stereo-, regio-, and chemoselective polymerizations proceed effectively within regulated and well-organized molecular-scale spaces. Inspired by the elegant operations in biological events, many chemists have focused their research interests on polymer synthesis in confined and designed nanospaces in an attempt at controlled polymerization.[2] Such template polymerizations in nanosized geometries can often allow spatial controls of primary structures of polymers and even two- and three-dimensional multilevel structuring. Several nanoporous matrices, such as organic hosts, zeolites, clays, and mesoporous materials, have played important roles so far to regulate the polymer structures by through-space interactions between the pore walls and the monomers.[3] However, there are still many issues that need to be improved in regard to the pore size, stability, surface functionality, and so on. For example, large strains or topological changes during inclusion polymerization in organic hosts often result in decomposition of the host channel structures because these organic hosts exploit only hydrogen bonding or weak van der Waals interactions. Mesopores are much larger than the size of conventional monomers, so that primary structures of polymers cannot be efficiently controlled in mesopores. Thus, development of new microporous materials with designable nanospace is highly desirable for attaining a precisely controlled polymerization that is applicable to a variety of monomers.

Recently, porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) composed of transition-metal ions and bridging organic ligands have been extensively studied.[4] The characteristic features of PCPs are highly regular channel structures, controllable channel sizes approximating molecular dimensions, and designable surface potentials and functionality (Figure 1). These features differ from those of conventional porous materials, such as zeolites, activated carbons, and organic supramolecular hosts. Because of these advantages, PCP materials have been studied for applications in storage, separation, delivery, and heterogeneous catalysts.[4] Our strategy for a successful application of PCPs is to utilize their regulated and tunable nanochannels for a field of polymerization (Figure 2).[5] Since 2004, we have been exploring polymerization reactions utilizing PCP channels, which can allow control of molecular weight, stereoregularity, reaction position, copolymer sequence, and chain arrangement of resulting polymers. In this account, I will show the essence of what particular properties can be achieved in the various types of polymerizations performed in PCPs, by reviewing key results from the literatures of recent years, as well as proposing some promising applications.

2. Controlled Radical Polymerization

Free radical polymerization has been a very important industrial process because of low requirements on monomer and reactant purity, facile copolymerization, and the fact that polymerizations can be conducted in either emulsion or

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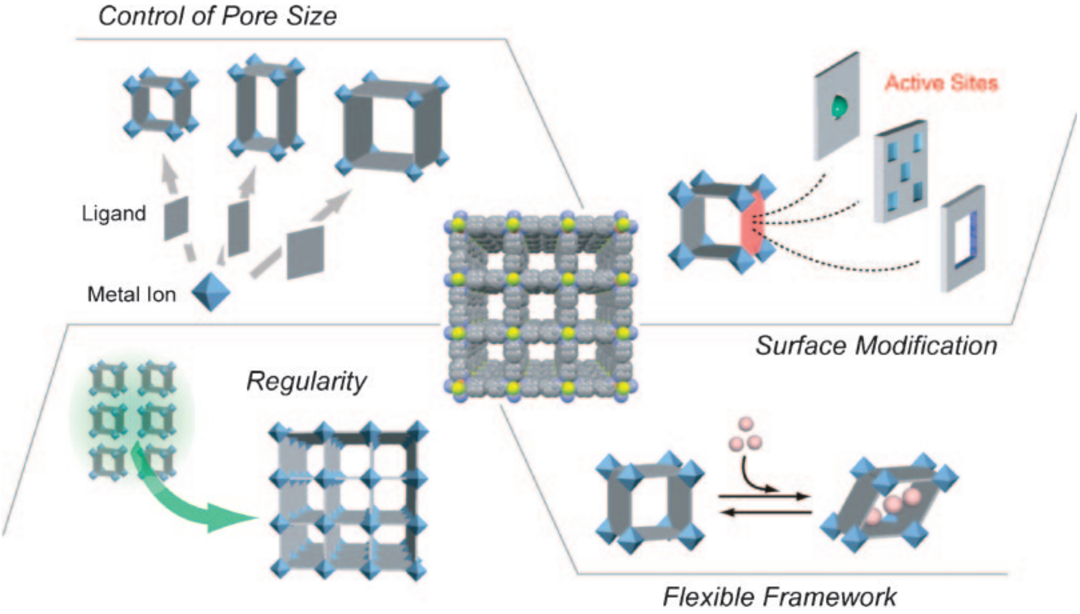

Figure 1. Characteristic features of PCPs.

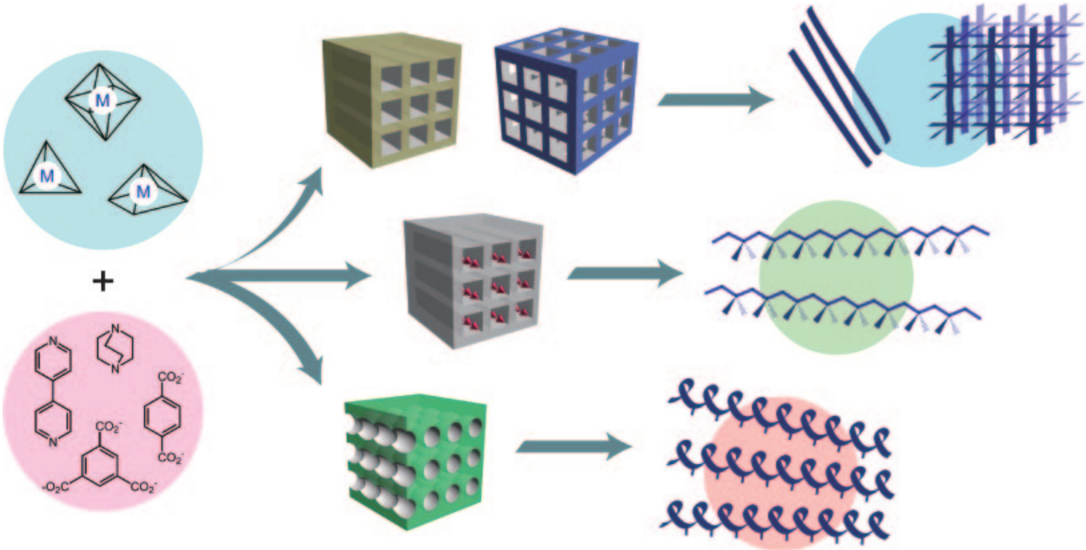

Figure 2. Schematic image for controlled polymerization in PCP nanochannels.

suspension using water as the medium. The significant drawback to these free radical polymerization processes is that polymers with uncontrolled stereoregularity and molecular weights are usually obtained. Thus, much attention has been paid to development of efficient methods for taming radical polymerizations.[6]

As a first work, we have performed polymerization of styrene (St) in nanochannels of $[M_2(bdc)_2(ted)]_n$ (**1a**, M = Cu^{2+}; **1b**, M = Zn^{2+}; bdc: 1,4-benzenedicarboxylate; ted: triethylenediamine (=1,4-diazabicyclo[2.2.2]octane); pore size = 7.5×7.5 Å^2) (Figure 3).[7] After St (molecular dimensions = 6.8×4.4 Å) was included in the PCP pores, the host-monomer adduct was heated with a radical initiator at 70 °C for 48 h to conduct the polymerization (conversion = 71%). Quantitative recovery of the accommodated polystyrene (PSt) with molecular weight (M_n) of ca. 55000 could be attained by decomposition of the host framework in NaOH or Na–EDTA solution. During this polymerization, the propagating radical was found to be remarkably stabilized because of effective entrapment in the nanochannels. This was shown by electron spin resonance (ESR) measurements for propagating radicals of PSt in the nanochannels of **1b**. In the ESR spectrum, intense signal corresponding to the propagating radical of PSt was detected, and the maximum radical concentration of PSt in **1b** reached 2.6 mmol kg^{-1}, which is much higher than that found in conventional solution polymerization (10^{-4}–10^{-5} mmol kg^{-1}). It should also be noted that the ESR signal did not disappear over three weeks, even at 70 °C. Because of this living nature, molecular weight distributions (M_w/M_n) of PSt obtained using **1a** and **1b** were 1.60 and 1.66, respectively, which are much smaller than those of PSt synthesized in bulk or solution.

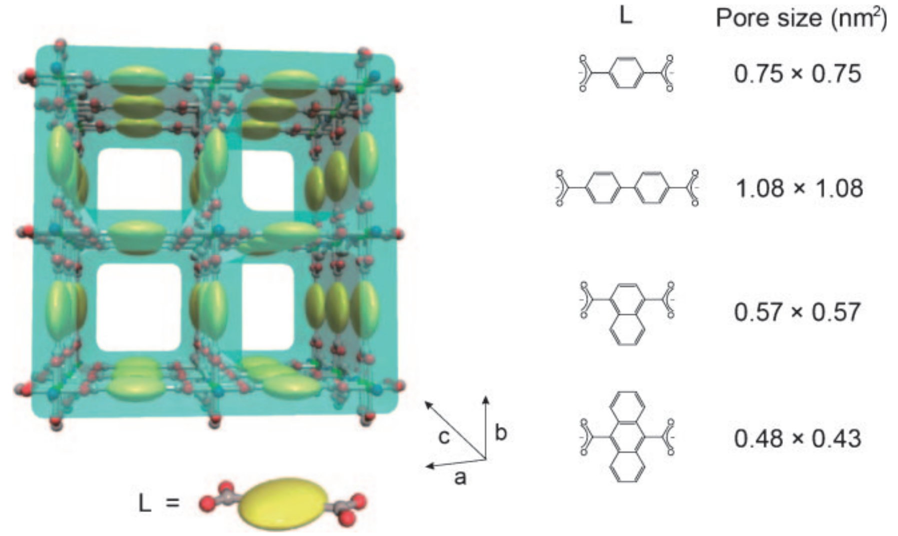

Figure 3. Nanochannel structures of $[M_2(L)_2(ted)]_n$ ($M = Cu^{2+}$ or Zn^{2+}, L = dicarboxylate, ted: triethylenediamine).

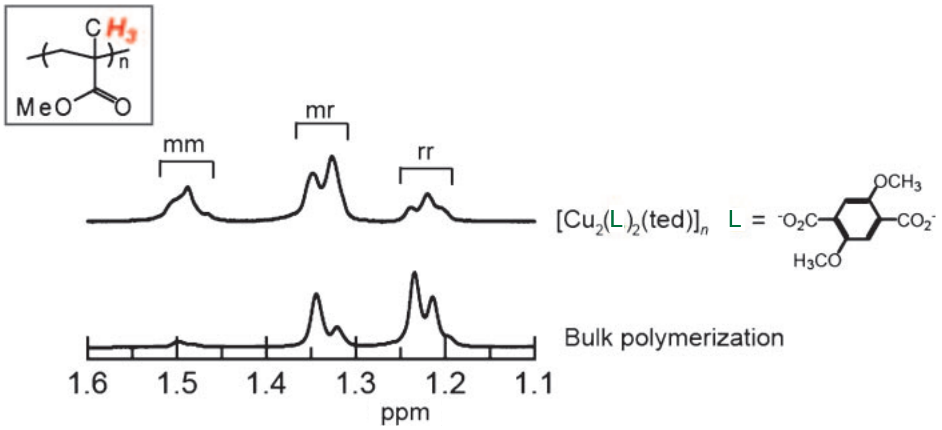

Figure 4. ^{1}H NMR spectra of α-methyl protons of PMMA in nitrobenzene-d_5 at 110 °C prepared in the bulk condition and in the nanochannels of $[Cu_2(1,4\text{-}\{2,5\text{-}(CH_3O)_2C_6H_2\}(CO_2)_2)_2(ted)]_n$. The polymerizations were carried out at 70 °C.

The nanochannel structure can be systematically controlled by changing the bridging dicarboxylate ligands of **1**.[8] In fact, the channel size of $[M_2(L)_2(ted)]_n$ can be tuned from 0.4 to 1.1 nm using various dicarboxylates (L = biphenyl-4,4′-dicarboxylate, pore size = 10.8×10.8 Å^2; L = 1,4-naphthalenedicarboxylate, pore size = 5.7×5.7 Å^2; L = 9,10-anthracenedicarboxylate, pore size = 4.8×4.3 Å^2) (Figure 3). A strong correlation between the pore size of $[M_2(L)_2(ted)]_n$ and polymer yield was observed, where conversions for polymerizations of St, methyl methacrylate (MMA, molecular dimension = 5.9×4.1 Å), and vinyl acetate (VAc, molecular dimension = 5.5×4.0 Å) decreased as the size of the pore narrowed.[9] No polymeric products were obtained during polymerizations in the narrowest pores of $[M_2\{9,10\text{-}C_{14}H_8(CO_2)_2\}_2(ted)]_n$. This is because of the reduced mobility of monomers in the narrow pores, as shown by solid-state NMR measurements. Interestingly, $[M_2(L)_2(ted)]_n$ was useful enough to control the stereoregularity (tacticity) of the vinyl polymers, such as PSt, poly(methyl methacrylate) (PMMA), and poly(vinyl acetate) (PVAc).[9,10] For example, the tacticity of PMMA strongly depends on the pore size of the PCPs, eventually an increase of 9% in isotacticity was achieved in $[Cu_2\{1,4\text{-}C_{10}H_6(CO_2)_2\}_2(ted)]_n$ compared with that obtained in the bulk polymerization.[9] In the case of the polymerization of VAc, the ratio of isotactic units of the resultant PVAc structure certainly increased, where this is the first example of an increase in the isotactic units in the radical polymerization of VAc.[9] These stereospecific polymerizations in $[M_2(L)_2(ted)]_n$ can be explained by through-space interaction between the pore walls and the monomers. Because an isotactic unit requires a narrower conformational diameter (thickness) than the corresponding syndiotactic unit, the polymerizations in nanochannels of $[M_2(L)_2(ted)]_n$ would result in increase in the less stereobulky isotactic moiety. A remarkable effect of substituted ligands in $[Cu_2(L)_2(ted)]_n$ on stereoregularity of the resulting PMMA was observed, in which the tacticity of the PMMA was strongly dependent on the number and position of the substituent.[10] In particular, polymerization of MMA in $[Cu_2(1,4\text{-}\{2,5\text{-}(CH_3O)_2C_6H_2\}(CO_2)_2)_2(ted)]_n$ yielded PMMA with isotacticity of 0.54 that is 32% higher than that obtained in the bulk polymerization (Figure 4). Note that this change of PMMA tacticity was much larger than those previously reported in controlled radical polymerization systems, thus, the utilization of PCPs is one of the most effective methods for

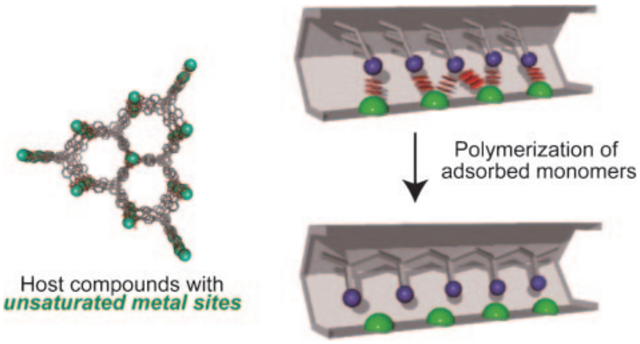

Figure 5. Schematic image for polymerization in PCPs with unsaturated metal sites.

controlling tacticity in radical polymerization. On the basis of IR, N_2 adsorption, a statics study, and MD calculations, the drastic increase of the isotacticity of PMMA obtained in $[Cu_2(1,4\text{-}\{2,5\text{-}(CH_3O)_2C_6H_2\}(CO_2)_2)_2(ted)]_n$ can be explained by the regular, narrow, and helical nature of the pores.[10]

There have been many attempts at controlling the tacticity by addition of polar molecules or Lewis acids to the reaction medium.[11] In these systems, the additives are supposed to interact with vinyl monomers and/or around the propagating radical species to induce a stereospecific chain growth via coordination. This fact inspired us to perform a stereocontrolled polymerization in nanochannels of PCPs with unsaturated metal sites, $[M\{1,3,5\text{-}(4\text{-}PhCO_2)_3C_6H_3\}]$ ($M = Al^{3+}$, Eu^{3+}, Nd^{3+}, Y^{3+}, La^{3+}, and Tb^{3+}) (Figure 5).[12] In these frameworks, the unsaturated sites are located at the corners of the hexagonal-shaped channels.[13] We found that the polymerization behaviors are strongly dependent on the Lewis acidity of the metal sites. For example, yield and molecular weight of resulting PMMA tended to decrease with the increase in the Lewis acidity of the component metal sites because of the restricted mobility of monomer. However, from the viewpoint of stereoregularity, composition of isotactic units in PMMA increased when we used hosts with higher Lewis acidity. It is interesting that a PCP composed of Tb^{3+} gave PMMA with significant increase in the isotactic unit, although discrete Tb^{3+} complexes are not effective for changing the stereoregularity of PMMA in solution polymerization.[14] Thus, our results showed that the metal ions embedded in the pore walls of PCPs are useful for controlling stereoregularity of polymers.

Control of composition and sequence in artificial copolymerization systems is a great challenge. In this regard, radical copolymerizations of vinyl monomers, such as St, MMA, and VAc, were examined in the nanochannels of **1a**.[15] In this system, it is likely that compositions of St in the copolymers prepared in the host are lower than those obtained from the corresponding free radical systems. This change of monomer reactivity in the nanochannels can be explained by the molecular size and electronic properties of the monomer. The interaction potential between the St molecule and the nanochannel of **1a** seems large because the molecular size of St is similar to that of the pore, and an effective π–π interaction between the monomer and the pore is also expected. This would result in a decrease in the diffusion speed of St in the channel, compared with those of MMA and VAc. In addition, the reactivity of the large St toward polymer chain terminals may be more restricted in the nanochannels. Thus, these results suggest a possibility that copolymerization utilizing PCP nanochannels could have a significant influence on the composition and sequence in the copolymer structures.

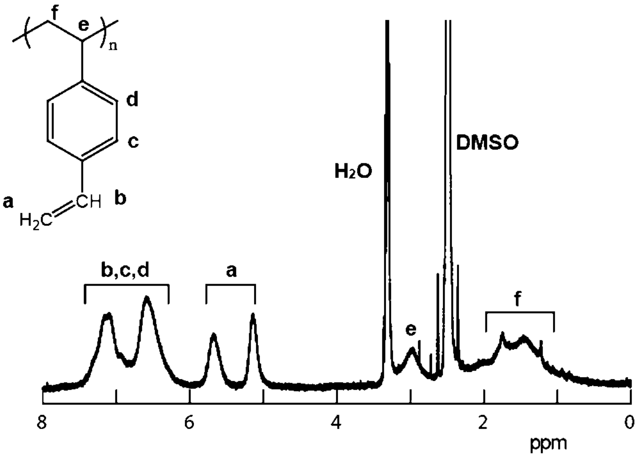

Figure 6. ^1H NMR spectrum of poly(p-DVB) obtained from the nanochannel of **1b** in DMSO-d_6.

The advent of efficient methods for controlling or suppressing crosslinking structures in polymerization is required for the further development of functional polymer materials. Usually, radical polymerization of divinylbenzenes (DVBs) in bulk or solutions leads to the unavoidable formation of hyperbranched network polymers, because the reactivity of the two vinyl moieties in DVBs is equivalent.[16] In contrast, radical polymerization of DVBs in one-dimensional channels of **1** has produced linear polymers leaving one pendant vinyl groups in each benzene ring (Figure 6).[17] Because of the linearly extended formations, the obtained polymers were highly soluble in various organic solvents, such as THF, $CHCl_3$, DMF, and DMSO, which greatly contrasts with insoluble crosslinked polymers obtained from the usual radical polymerization of DVBs in solution and bulk. Thus, it is of considerable interest that the one-dimensional nanochannels of **1** could successfully direct the linear polymerization of multivinyl monomers because of effective entrapment of the reactive propagating radical mediators in the narrow nanochannels. In this polymerization system, unique effects of pore size and flexibility were observed (Figure 7). Although polymerization of 1,3-disubstituted DVB (m-DVB; molecular dimension $= 7.2 \times 7.2$ Å) could produce linear polymer in **1a** (pore sizes $= 7.5 \times 7.5$ Å^2), polymerization of 1,4-disubstituted DVB (p-DVB; molecular dimension $= 8.5 \times 4.4$ Å) did not give any polymeric materials in **1a**. Unfortunately, polymerization of p-DVB in larger open channels (pore size $= 10.8 \times 10.8$ Å^2) of $[Cu_2\{4,4'\text{-}C_{12}H_8(CO_2)_2\}_2(ted)]_n$ gave insoluble polymeric product because of the formation of semibranching crosslinked structures in this large channel. To overcome this problem, **1b**, a zinc analog of **1a**, with flexible framework upon inclusion of specific guest molecules was employed. Introduction of p-DVB in the channels of **1b** induces a lattice expansion compared with the original host, however, the corresponding copper compound **1a** did not show such structural changes.[18] In addition, the adsorbed amount of

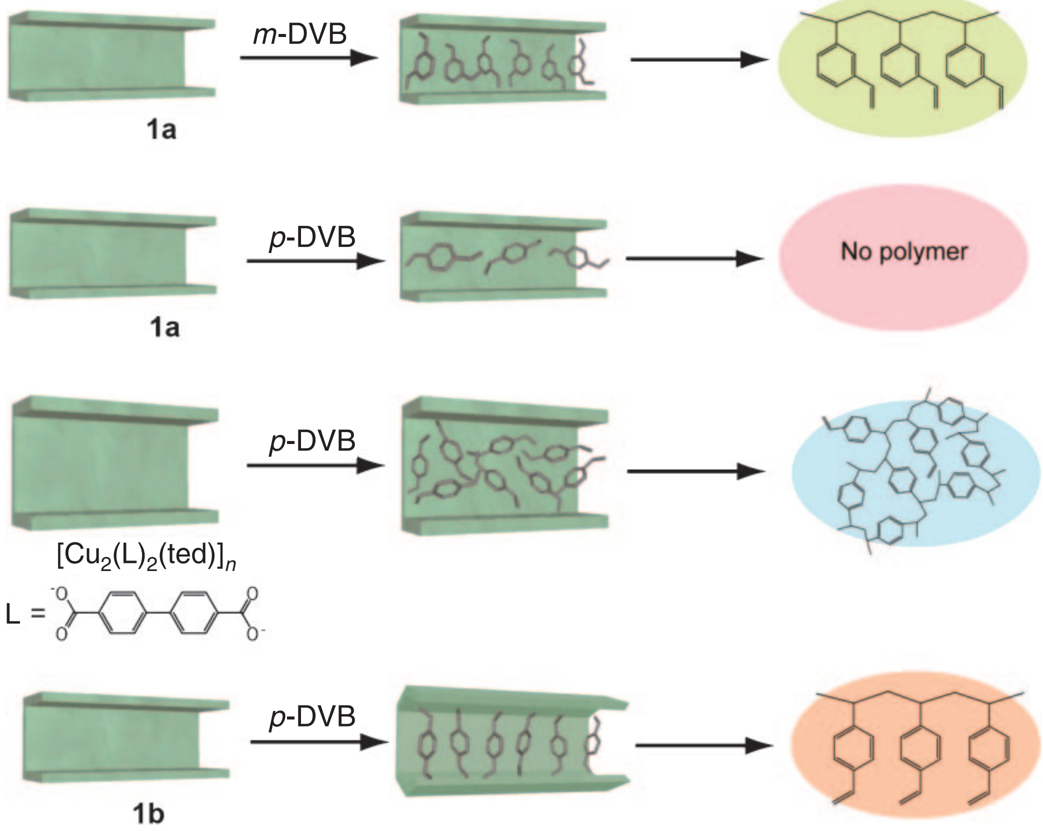

Figure 7. Effects of pore size and flexibility on polymerization of DVBs.

p-DVB in **1b** was much larger than that in **1a**. Average distance between *p*-DVB in the channel (along the *c* axis) of **1b** could be estimated to be 4.5 Å. Such a closed packing structure of *p*-DVB could allow the linear polymerization in the channels of **1b**. The host flexibility of **1b** is strongly associated with adsorption of the monomer by expanding the pore structure suited for adjacent arrangement of the monomer, resulting in the successful polymerization of *p*-DVB in the channels of **1b**.

3. Channel-Promoted Polymerization and Reaction

There is a growing interest in the study of PCPs with functionalized pore surfaces. The versatile pore features of PCPs, such as redox activity, Lewis acidity, basicity, and chirality, can be tailored by regularly arranged functional organic ligands and metal ions. Thus, PCPs bearing active sites in nanochannels have been envisioned for useful catalytic applications in organic synthesis.[19] Utilization of catalytic PCPs for preparation of functional polymeric materials is of current interest.

Much attention has been directed to poly(substituted acetylenes) for a wide range of applications, such as conducting materials, nonlinear optics, and polymer sensors.[20] The controlled polymerization of substituted acetylenes using several types of catalysts has been investigated with the aim of controlling the stereostructure (the *cis* and *trans* chain sequence) and decreasing the formation of cyclic trimer by-products (substituted benzenes) because the characteristic properties of poly(substituted acetylenes), such as conjugation length, suprastructures, and processability, can be precisely controlled by changing the substituents and stereoregularity.[21] Recently we have performed a spontaneous and stereoselective polymerization of substituted acetylenes in $[Cu_2(pzdc)_2(L)]_n$ (pzdc: pyrazine-2,3-dicarboxylate, L = bipyridine-type ligand; **2a**, L = 4,4′-bipyridine, pore size = 8.2×6.0 Å^2; **2b**, L = 1,2-di(4-pyridyl)ethylene, pore size = 10.3×6.0 Å^2) (Figure 8).[22] In this polymerization, the basic oxygen atoms of carboxylate ligands located at the pore wall strongly interact with substituted acetylenes to produce reactive acetylide species that subsequently initiates anionic polymerization in the nanochannels.[23] Compared with a controlled experiment, this polymerization system exhibited drastic acceleration of the polymerization. For example, the reaction of methyl propiolate with a model catalyst (sodium benzoate) at room temperature gave only a trace amount of product even after one month reaction. We have attempted the reaction at 70 °C, however, could not obtain polymeric product, where only unfavorable trisubstituted benzenes and a *cis*-geometric polymer were produced in very low yields. In contrast, **2** with narrow nanochannel structure could successfully direct the polymerization with *trans*-geometric addition. The experiments with various combinations of acetylene monomers and host PCPs showed that appropriate channel size, as well as the basic carboxylate moiety, is important for this spontaneous polymerization.

The utility of basic sites of PCPs has been also demonstrated for controlled polymer reaction. Densely arranged carboxylate moieties on pore walls of **1b** and its derivatives acted as basic sites and allow the efficient elimination reaction of the terminal group of oligo(vinylidene fluoride) (OVDF) (Figure 9).[24] The

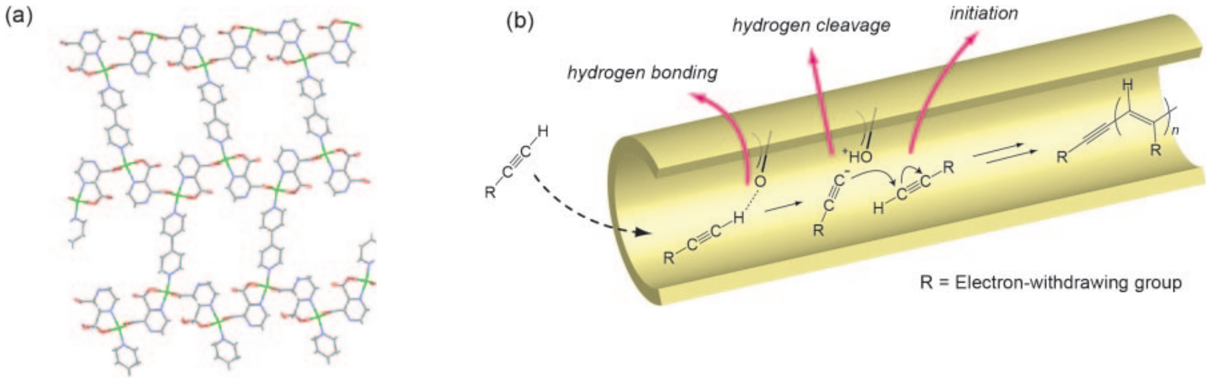

Figure 8. (a) Nanochannel structure of **2a**. (b) Spontaneous anionic polymerization of substituted acetylenes in **2**.

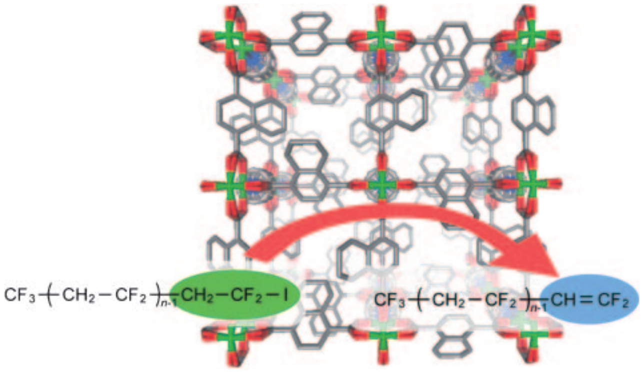

Figure 9. Elimination reaction at terminal group of oligo(vinylidene fluoride).

reaction of an OVDF in the PCP nanochannels was evidenced using solid-state ^{19}F NMR spectroscopy. From ^{19}F and ^{1}H NMR and IR measurements of the product isolated from the composite, the terminal –CH_2CF_2I moiety of OVDF was shown to be successfully converted to a –$CH{=}CF_2$ group. Because of the large surface area of the PCP materials, the OVDF precursor easily accessed the basic sites, resulting in a large increase in the rate of the elimination reaction. In addition, a notable effect of the porous structure of PCPs upon the elimination reaction was observed. In this system, the reaction conversion increased with increasing pore size, however, the selectivity became lower if a larger pore was employed.

The component metal ions in PCPs can work as effective activation sites for promoting polymerizations. $[Ni(dmen)_2]_2[Fe^{III}(CN)_6](PhBSO_3)$ (**3**; dmen: 1,1-dimethylethylenediamine; $PhBSO_3{}^-$: *p*-phenylbenzenesulfonate) has redox-active $[Fe^{III}(CN)_6]$ units within the two-dimensional layered framework.[25] In this framework, pyrrole monomers can be intercalated into the nanoslits and are oxidized by the Fe^{III} ions.[26] As a consequence of the host–guest redox reaction, the Fe^{III} ions are reduced to the Fe^{II} ions, accompanied by polymerization of the monomers to polypyrrole (PPy) and the release of the pillar counter anions for charge compensation (Figure 10). Although PCPs with redox-active metal ions might be capable of providing controlled reactions for oxidized/reduced products in the resulting composites, only a few reports on the use of PCPs for redox reactions have been reported because of the low framework stability of PCPs during the redox reaction.[27]

An interesting template effect of **3** on morphology and assembly of polymer objects was observed in this work.[26] Removal of the host framework of **3** in EDTA solution allowed

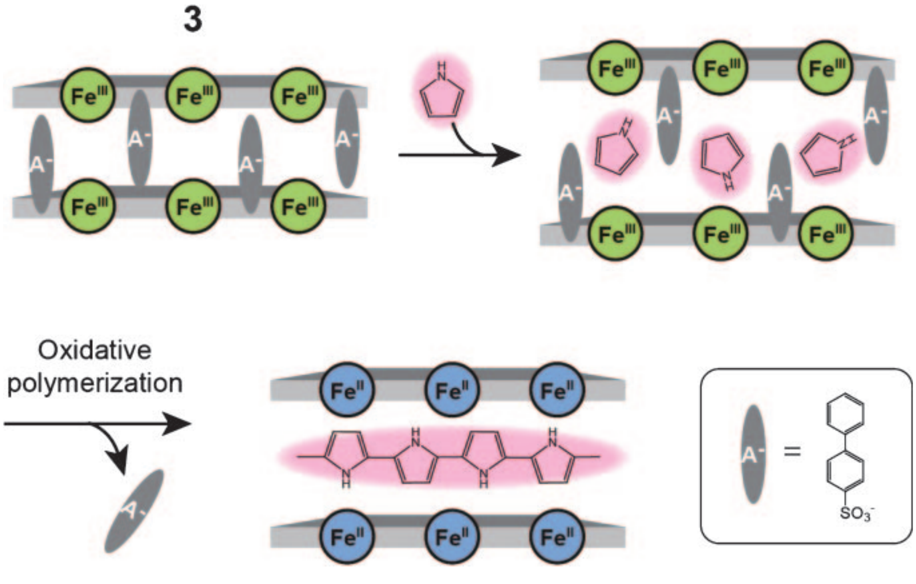

Figure 10. Oxidative polymerization of pyrrole in **3**.

isolation of the intercalated PPy as an insoluble black precipitate. When we conducted SEM measurements, the morphology of the isolated PPy was found to be platy in contrast to the granular morphology of the bulk PPy prepared by oxidation of Py with $K_3[Fe^{III}(CN)_6]$ in water (Figure 11). Although this bulk PPy was completely amorphous, the XRPD profile of the isolated PPy showed a peak corresponding to the accumulation of aromatic planes of PPy. In addition, the obtained PPy microsheet object showed anisotropic conductivity; the conductivity parallel to the sheet was 20 times higher than that along the direction perpendicular to the sheet. Therefore, in this system, the crystalline PCP template successfully directed 2-D oriented organization of PPy assembly at the molecular level.

Templating techniques for generating porous solids have been extensively studied in materials science. In particular, template synthesis of porous organic polymers has emerged as a promising subject because of the great potential of porous polymers in chromatography, sensing, and membranes.[28] Very recently, a feasible method for providing a porous structure of PPy has been reported by using three-dimensional channels of $[Cu_3(btc)_2]_n$ (**4**; btc: benzene-1,3,5-tricarboxylate) as a template (Figure 12).[29] In this work, the accessible Cu(II) sites on the pore surface catalyzed the oxidative polymerization of pyrrole in the framework of **4**, and finally provided a black powder composite. Isolation of the accommodated polymer from the composite was performed by complete dissolution of the host framework in various basic solutions. Porosity of the resulting polymer materials was examined by nitrogen adsorption measurements at 77 K. Although PPy prepared in the bulk condition did not adsorb the gas, PPy materials prepared in the PCP clearly showed adsorption, and the amount of adsorption gradually increased as weaker bases were employed for the isolation of PPy. Interestingly, the pore-size distribution for the PPy isolated by ammonia showed a peak at 1.3 nm, where this pore size might reflect the thickness of pore walls of **4** (ca. 1.2 nm). The porous structure of PPy was found to be very stable, and not affected by treatments with heating at 120 °C or common solvents.

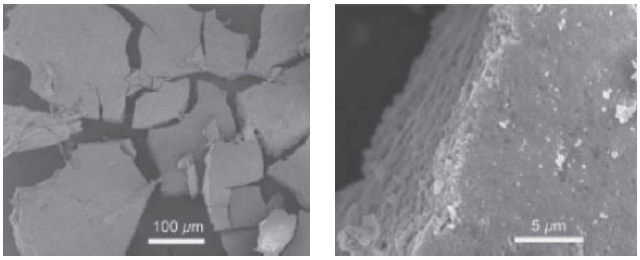

Figure 11. SEM images of PPy isolated from **3**.

4. Inorganic Polymers

Metals and metal oxides, which can be regarded as inorganic polymers, display many interesting optical, electronic, chemical, and catalytic properties in the nanometer-size regime. The synthesis and study of such inorganic particles with diameters in the nanometer region has become a major interdisciplinary area of research over the past 20 years.[30] Semiconductor nanoparticles promise to play a major role in several new technologies. The intense interest in this area derives from their unique chemical and electronic properties, which gives rise to their potential use in nonlinear optics, luminescence, electronics, catalysis, solar energy conversion, and optoelectronics, as well as other areas. The small dimensions of these particles result in different physical properties from those observed in the corresponding bulk material. It is widely recognized that surface of the nanoparticles plays an important role in the properties of the material, because the ratio of surface atoms to those in the interior increases. Recently, much research activity has been seen in the area of host–guest nanocomposites based on nanosized inorganic polymers and various host matrices because of specific size-dependent properties and host–guest synergistic functions. One promising idea is the preparation of inorganic polymers in the pores of PCPs, which would lead to potential applications ranging from fundamental physical studies to trace molecular detection and high-surface-area catalysis.[31]

We performed sol–gel polycondensation of tetramethoxysilane in nanochannels of PCPs, such as **2b** and **4**, resulting in the formation of nanosized silica dispersed homogeneously inside the channels.[31] In this system, the sol–gel condensation successfully proceeded only inside the channels, without destruction of the host framework or deposition of silica particles outside the pores, as demonstrated by XRD, N_2 adsorption, laser light diffraction, and electron microscope measurements. Moreover, study of the crystal phase transformation of silica in **2b** revealed a drastic decrease of its crystallization temperature as a result of its miniaturized size.[31a] ^{29}Si magic angle spinning NMR measurements clearly show

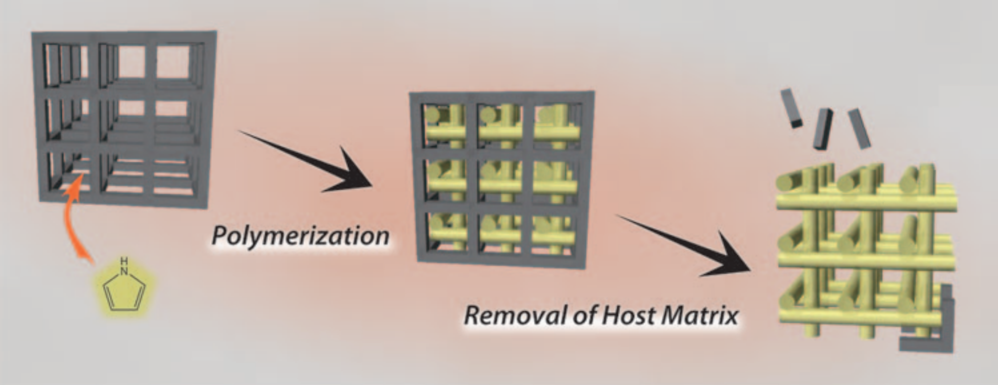

Figure 12. Schematic image for template synthesis of porous PPy.

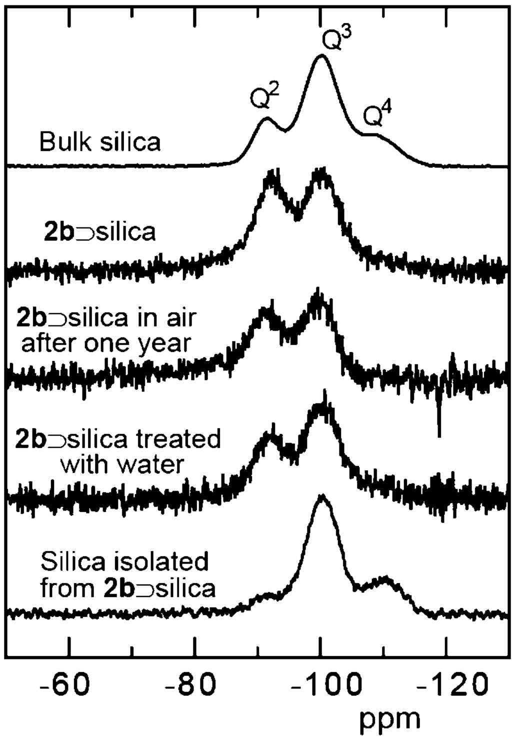

Figure 13. ^{29}Si MAS NMR spectra of silica in bulk and in **2b**. Chemical shifts are relative to external tetramethylsilane (TMS).

that the growth of silica was effectively constrained, and thus the hydrophilic silanol moieties on the surface of silica particles remarkably increased (Figure 13). Interestingly, the low-dimensional silica structure in a PCP has been stable over one year in air, and was not seriously changed upon treatment with water. However, removal of the host matrix in EDTA solution immediately led to further condensation of the active silanol moiety (Figure 13). Deposition of silica particles into the nanochannels of PCPs could allow the interesting alternations of the properties of the PCPs. For example, the obtained composite based on **2b** was found to be stable up to 238 °C, which is higher than the onset temperature (214 °C) of decomposition for the host alone.[31a] Compared to the original PCP systems, adsorption of water was greatly enhanced because of the strong interaction between silica and water (Figure 14).[31b] The PCP–silica nanocomposites preferred to adsorb 1,4-dioxane rather than cyclohexane, showing the remarkable affinity of PCP–silica hybrids to hydrophilic molecules. It is noteworthy that pore dimensionality of PCPs have large effects on the adsorption properties of PCP–silica hybrids. Compared to **4** with three-dimensional interconnecting nanochannels, **2b** with one-dimensional porous system showed more significant gate effects on selectivity for the adsorbates.[31b]

5. Conclusion and Perspectives

This review account described recent progress of controlled polymerizations using PCP nanochannels, which has been developed by our research group. Utilization of the regular crystalline nanochannels of PCPs has proven that not only primary structures of the resulting polymers but also polymer arrangement and alignment can be controlled. We believe that this methodology will contribute to the development of polymerization systems that can provide new features for controlled polymerizations. Multiple controls of polymer structures, such as molecular weight, stereostructure, reaction position, and monomer sequence, will be possible using our methodology. Highly designed PCP nanopores would produce regio- and stereoregular polymers with unique monomer sequences, as is seen in biological systems (peptides and DNA). It is also interesting to develop efficient synthetic methods for topological polymers, such as cyclic and ladder polymers, using the PCP pores. Repeating the use of PCPs for polymerizations should be of key importance, and will be very useful for future applications in industry.

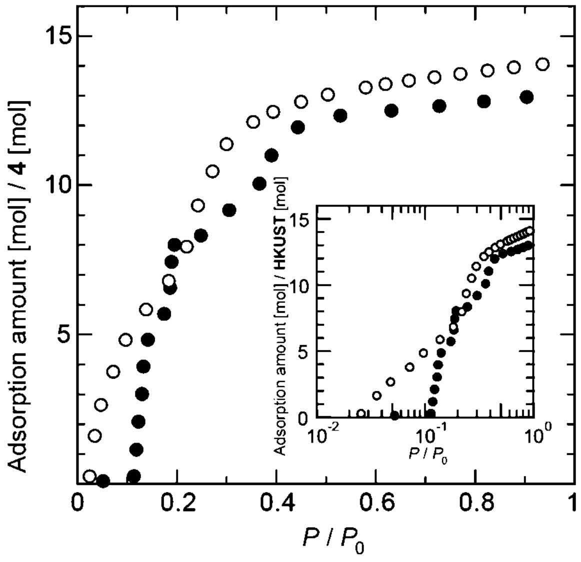

Figure 14. H_2O adsorption isotherms of **4** (●) and **4**⊃silica composite (○) at 77 K. The inset shows the adsorption isotherms plotted against a logarithmic relative pressure.

In addition to these polymerization systems, our research interest is focusing on the quest for specific properties of the polymer assemblies accommodated in these nanochannels and construction of host–guest nanocomposites.[32] Understanding and controlling the polymer properties in PCPs will enhance knowledge regarding their application to advanced functional materials and nanosized molecular-based devices.[32]

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