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Polymerization in Coordination Nanospaces

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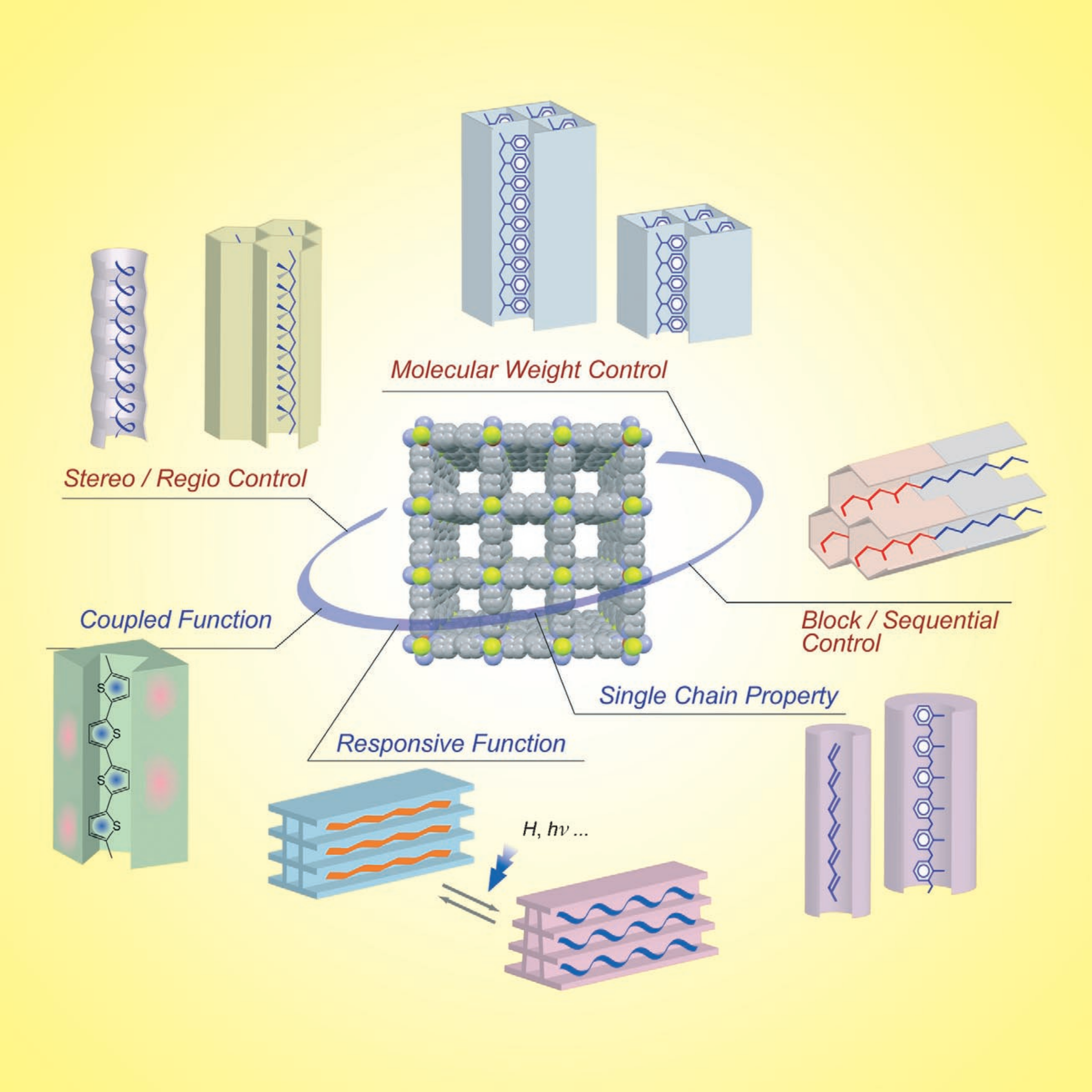

Abstract: Inspired by elegant polymerizations in biological systems, polymer synthesis in confined artificial nanospaces is a key challenge in the control of polymer structures and the design of well-defined nanostructures. In this regard, porous coordination polymers (PCPs) have a wide range of advantages, such as regular channel structures, controllable pore size, dynamic and flexible pores, and unique surface potentials and functionality, which can be utilized for precisely controlled polymerization and polymer arrangement. This Focus Review describes recent progress in polymerization in the nanochannels of PCPs and demonstrates why this polymerization system is so attractive and promising, from the viewpoints of three essential polymerization processes in PCPs, that is, monomer arrangement, polymerization methods, and control of polymer structure.

Keywords: coordination polymers • inclusion compounds • microporous materials • nanostructures • polymerization

1. Introduction

When one-dimensional nanochannels of crystalline porous compounds are filled with guest molecules with polymerizable groups, these monomers can be polymerized in the confined nanospaces. The host components provide a specific molecular-level flask for the reaction of the monomeric guest molecules. This reaction allows low-dimensional restrained polymerization, which is different from bulk and solution polymerization in conventional flasks but similar to polymer synthesis in natural biological systems. Typical examples are polymerizations in the microporous channels of organic hosts and zeolites.[1] Extensive studies on polymerization in organic hosts were carried out from the 1960s to the 1980s and focused on radical polymerization of conjugated diene and triene monomers irradiated with γ-rays.[1a–c] In the case of zeolites, impregnation of transition-metal ions, such as Cu^{II}, Fe^{III}, Ni^{II}, and Co^{II}, into the nanochannels is effective for oxidative polymerizations to produce many conjugated (semi)conducting polymers.[1c–e] In these systems, the inclusion polymerizations in the microporous hosts have shown specific size and shape effects of the nanochannels on the kinetics and selectivity of the polymerization.

Since the early 1990s, porous coordination polymers (PCPs) composed of transition-metal ions and organic ligands have been developed extensively owing to the scientific interest in the creation of nanometer-sized spaces for investigating novel phenomena, as well as for the commercial interest in their applications for molecular storage, separation, and heterogeneous catalysis.[2] The remarkable progress in the field of PCPs has paved the way for functional chemistry in the area of porous materials because their porous frameworks can essentially be designed at will on the basis of the variety of coordination geometries at the metal centers and the multifunctionality of the organic bridging ligands. Therefore, PCPs exhibit significant characteristic features, such as 1) highly regular channel structures, 2) controllable pore size approximating molecular dimensions, 3) flexible pores that respond to guest molecules, and 4) unique surface potentials and functionality, which are beyond the scope of conventional microporous materials (Figure 1).

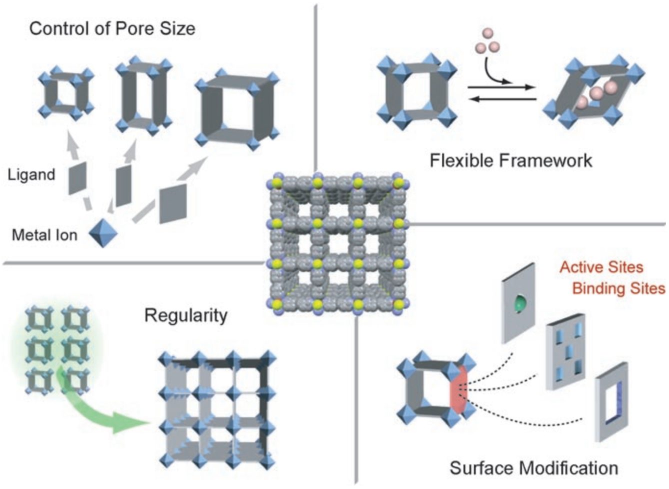

Figure 1. Characteristic functions of porous coordination polymers (PCPs).

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Considering the attractive features of the channels of PCPs, the utilization of PCPs should be of key importance for the creation of unique nanosized reaction cavities.[3] In particular, the use of PCP nanochannels as a cavity for polymerization is an attractive idea for many reasons, and would not only allow multilevel control of polymerization (control of stereochemistry, regiochemistry, molecular weight, helicity, etc.), but would also provide well-defined nanostructures and nanohybrids to enable the fabrication of new-generation materials. Such polymerization in the functional nanospaces of PCPs consists of three stages. The first stage is encapsulation of the monomers in the host PCPs. The second is polymerization by one of several mechanisms. The last stage is characterization of the resulting polymers in or out of the host frameworks. In this short account, we describe the essence of what particular properties can be achieved at all the stages of polymerization in PCPs; we review key results from the literature of recent years and propose some promising applications.

2. Encapsulation of Monomers

2.1. Confinement Effect

The reactivity of guest molecules in confined nanospaces is strongly dependent on the molecular states and behavior. Generally, the pore sizes of PCPs range from 4 to 20 Å.[4] Such nanosize pores are suitable for the confinement of guest molecules, even when the intermolecular interaction between guest and host molecules is governed only by dispersion forces, the so-called van der Waals forces.[5] By tuning the pore size and the shape of PCPs, we can create a nanospace with a strong confinement capability for a wide variety of monomers, ranging from gas molecules (acetylene, ethylene) to larger molecules (methyl methacrylate, styrene) even at room temperature. With the aid of this confinement, the density of adsorbed molecules in the pore is often larger than in the bulk solid. Therefore, the design and synthesis of a pore architecture that is well-suited to target monomers is a kind of "polymerization-cavity engineering".

On the other hand, PCPs with functional groups such as open metal sites or metal-free organic groups in the pores allow stronger guest trapping as well as control of the orientation of guest molecules.[6] There is no doubt that an adsorption system specific for a target molecule can be realized when multiple specific interaction sites are located at suitable positions on the regular micropore. The attractive sites of pores can initiate polymerization of the trapped monomers as well as ensure their anisotropic binding to the attractive sites of the pores. For instance, acetylene derivatives adsorbed in a PCP whose pore surface bears basic

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"My vision for Chemistry—An Asian Journal *is that it should become a leading journal with high impact and influence not only in chemistry but in science in general."*

Abstract in Japanese:

近年、有機配位子と金属イオンから分子サイズ程度の細孔をもつ多孔性結晶（多孔性配位高分子）が合成できるようになっている。これらは従来の多孔性物質（ゼオライト、活性炭）では実現しにくい「細孔サイズ、形状、表面構造の設計」、「完璧に近い規則性」、「動的で柔軟な骨格」が達成できることが大きな特徴である。このような機能性ナノ空間は有機高分子鎖がちょうど一本で包接される程度の大きさであり、重合反応場として利用することで、得られる高分子の立体規則性、定序性、分子量が制御可能になるだけではなく、多数の高分子鎖の配列や高次構造が精密に制御された新たな有機無機ナノ複合体になることが期待される。この総説ではモノマーの配列、重合、高分子構造の制御といった観点から、本重合法の新規性、有用性、および将来の展開について述べる。

oxygen atoms undergo spontaneous polymerization through RC≡C-H···O hydrogen bonding with the pore walls (see Section 3.1).[7] This reaction is caused by the combination of confinement effect in the restricted space and electron transfer through the hydrogen bond.

2.2. Regularity

In most cases, self-assembly processes of building blocks made up of metal ions and organic ligands afford PCP microcrystals with particle dimensions of at least 1 μm^3. Given a cross-section of even 1 nm for channels, a particle with a size of 1 μm^3 automatically contains millions of regular channels. Such regular channels, with a sharp distribution of PCP pore size and diameter owing to the high crystallinity, provide advantages for controlled polymerization.[8] Densely adsorbed monomers inside the channels are favorably amenable to highly reactive and regulated polymerization because all the channels can be used as a reaction cavity. If an assembled guest structure can be prepared with one-directional orientation or heteroguest accommodation (e.g., AAABBB, ABABAB…) by employing specific regular micropores, block or alternating copolymerization and sequence-controlled polymerization is achieved.

Recently, a series of pillared-layer-type PCPs $[\{Cu_2(pzdc)_2(L)\}_n]$ (pzdc = 2,3-pyrazinedicarboxylate; **1a**: L = pyrazine, channel size = 4.0 × 6.0 $Å^2$; **1b**: L = 4,4′-bipyridine, channel size = 8.2 × 6.0 $Å^2$; **1c**: L = 1,2-di(4-pyridyl)ethylene, channel size = 10.3 × 6.0 $Å^2$) with highly regular 1D micropores was prepared in which characteristic guest inclusions are realized. In the case of **1a**, which has the narrowest channel, small gas molecules (O_2, N_2, Ar, CH_4) are adsorbed in a 1D array fashion and show a crystalline phase at relatively high temperature (~100 K).[9] This phenomenon is due to the size matching between the shapes of the host surface potential and guest molecules. By tuning the regularity of the potential field of the channels, we can create well-ordered monomer assemblies inside the PCP channels toward the target polymerization.

2.3. Monomer Behavior

In the case of conventional adsorbents such as zeolites or activated carbon, many reports on the correlation between adsorbed guest dynamics and their reactivity inside the pore have been discussed. However, such studies in the area of PCPs are still rare. It is well known that the strong micropore field shifts the melting and freezing temperatures of the adsorbate in a confined nanospace. Benzene molecules in several zeolites show solidlike behavior at room temperature, whereas benzene in mesoporous silica (SBA-15) behaves as a liquid phase, even at 236 K.[10] To investigate the reactivity of polymerization, a detailed observation of monomer behavior inside the PCP is essential.

Standard methods for analyzing the guests inside the pores of adsorbents are thermodynamic or spectroscopic techniques such as differential scanning calorimetry and FTIR or NMR spectroscopy. In particular, ^2H NMR spectroscopy has been widely used for direct observation of the mobility of guests in various adsorbents and is also available for PCPs, even though the host frameworks contain paramagnetic species. Several observations about guest behavior in PCPs have been reported. The motions of adsorbed guests are sensitive to the pore walls, and the mobility of monomers adsorbed in several PCPs strongly depends on the size/shape of the porous frameworks, which determines the propensity of the incorporated monomers to undergo polymerization (see Section 3.1). Furthermore, computer simulation based on MO, MM, and MD methods is a powerful aid for the design of well-controlled and efficient reactions in nanospaces by showing how monomers are accommodated, orientated, and loosely trapped therein.[7,11]

3. Polymerization in PCPs

In general, polymerization methods are classified into three categories: addition polymerization, polycondensation, and polyaddition, all of which can potentially take place in the nanochannels of PCPs. In this Focus Review, we concentrate on radical polymerization and spontaneous catalytic polymerization (anionic polymerization) in PCPs, because the advantages of PCP nanochannels can be fully utilized in those systems.

3.1. Radical Polymerization

Polymerization of vinyl monomers in conventional microporous crystals (zeolites and organic hosts) still seems difficult, because 1) their channel sizes are often smaller than the monomer and/or resulting polymers, 2) most zeolites have discontinuous bottleneck channel structures that do not allow the monomers to be packed continuously, and 3) the channel structures of the organic hosts are held together by weak supramolecular interactions (hydrogen bonding and van der Waals interactions) and are typically fragile.[1a–c] Recently, the advantages of PCPs were exploited for a polymerization reaction: the radical polymerization of styrene was performed in regular, continuous, robust, and relatively wide one-dimensional channels of $[\{M_2(1,4\text{-benzenedicarboxylate})_2\text{triethylenediamine}\}_n]$ (**2a**: M = Cu^{2+}; **2b**: M = Zn^{2+}; channel sizes = 7.5 × 7.5 $Å^2$) (Figure 2).[12] In this system, polymerization proceeds in high conversion (71 %) without collapse of the channel structures, and the resultant polystyrene is completely encapsulated in the nanochannels. Interestingly, the polymerization of styrene does not proceed efficiently in complex **1b**, whose pore size is, however, comparable to that of **2**. To understand the difference between **1b** and **2**, solid-state NMR spectroscopy measurements were conducted (Figure 3). The line shape of the ^2H NMR spectra for $[D_8]$styrene adsorbed in **2** reveals that the guest styrene molecules have high mobility and fast rotation in the nanochannels. However, the spectra of $[D_8]$styrene in **1b** show completely solidlike behavior, even at the polymerization

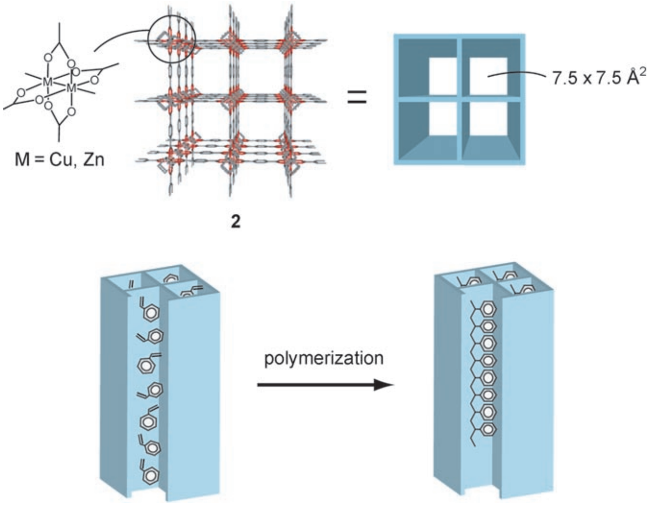

Figure 2. Radical polymerization of styrene in the nanochannels of **2**.

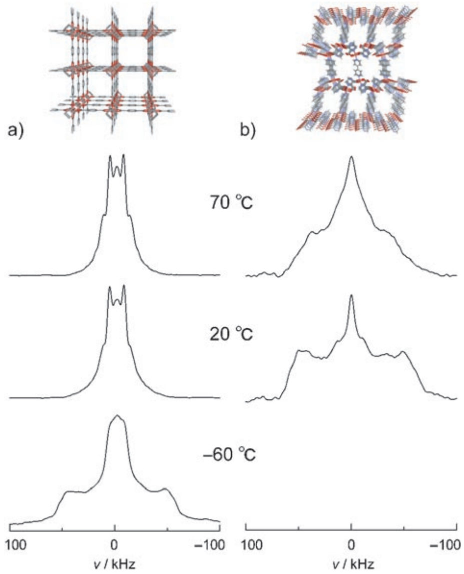

Figure 3. ^{2}H NMR spectra of [D$_8$]styrene in the nanochannels of a) **2b** and b) **1b**.

temperature, indicating that the mobility of styrene is much more restricted in **1b** than in **2**. This restricted arrangement of the styrene in the nanochannel of **1b** resulted in the poor reactivity of the former. The pore size and shape strongly affect the dynamics of the monomer, and the behavior of the monomer is a key factor in promoting polymerization in the porous framework.

3.2. Catalytic Spontaneous Polymerization

In contrast to conventional porous materials, an intriguing feature of PCPs is that their pore surfaces can be rationally designed and functionalized on the basis of its constituents (Figure 4).[6,13] The versatile pore features (redox activity, Lewis acidity, basicity, hydrophobicity, chirality, etc.) of PCPs are of key importance for the creation of unique nanosized reaction cavities based on the PCP materials. This is realized by the appropriate choice and the precise and regular arrangement of the metal ions and the organic functional groups. Thus, functionalized PCPs that bear specific interactive sites in/on the nanochannels have been envisioned for useful catalytic applications in organic and polymer syntheses.[3a–c] Recently, it was demonstrated that the pillared-layer complex **1b** catalyzed the spontaneous polymerization of substituted acetylenes in the nanochannels.[7] In the case of acidic monosubstituted acetylenes, the basic oxygen atoms from the carboxylate ligands in **1b** produce reactive acetylide species that subsequently initiate anionic polymerization in the nanochannel (Figure 5). In contrast to a control experiment with a discrete model catalyst (sodium benzoate), system **1b** leads to drastic acceleration of the polymerization. For example, the reaction of methyl propiolate with the model catalyst at room temperature for 1 month gave only a trace amount of product. An increase in the reaction temperature to 70 °C was also ineffective for polymerization. However, the reaction of the acetylene monomer with **1b** for 12 h at room temperature successfully provided the polymeric product. This unique catalytic poly-

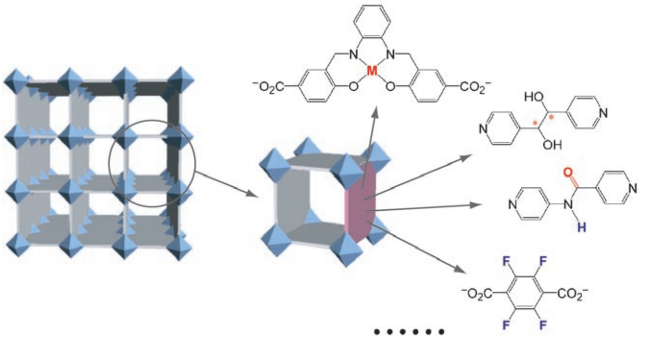

Figure 4. Functionalization of the surfaces of PCP pores.

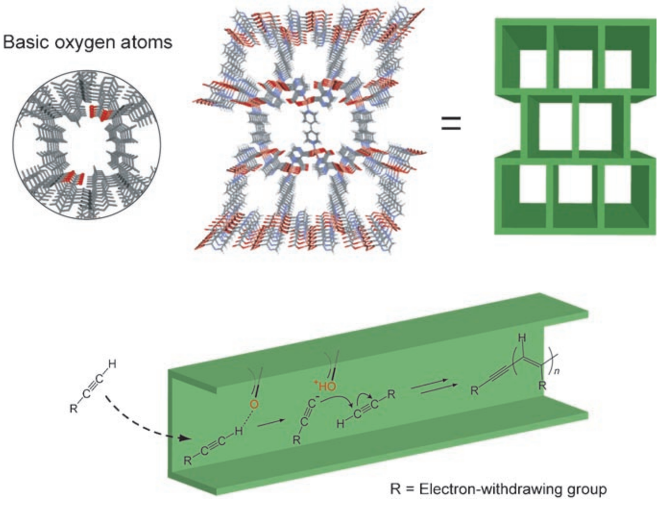

Figure 5. Catalytic spontaneous polymerization of substituted acetylenes in **1b**.

merization mechanism in **1b** is supported by IR spectroscopy measurements and computer simulation with a universal force field. Experiments with various combinations of acetylene monomers (methyl propiolate, cyanoacetylene, and 2-ethynylpyridine) and host PCPs (**1a–c** and **2a**) showed that appropriate channel size as well as the basic carboxylate moiety are important for this spontaneous polymerization.

4. Control of Polymer Structures and Organization

Needless to say, understanding the effects of the nanochannel on the structures of the polymers prepared in PCPs is of significant importance in this subject. However, to determine the structure of the polymers synthesized in PCPs, the polymers must be separated from the host frameworks without structural change. In this regard, the polymers accommodated in PCPs can be easily recovered by decomposition of the host frameworks in appropriate media, such as acid, base, water, or organic solvents.[3e,12] A simple extraction method is also available for the isolation of the encapsulated polymers.[7]

4.1. Primary Structures of Polymers

In the processes of polymerization in PCPs, the arrangement and orientation of the monomer molecules along the direction of the nanochannels could determine the regio- and stereospecificity of the obtained polymers (Figure 6). When polymerization of vinyl monomers is carried out in the nanochannels of PCPs, one can realize that the tacticity of the resulting polymers is controlled by effective through-space induction. The rational design of PCPs by judicious choice of connecting ligands leads not only to the tuning of the channel size and shape but also introduces interactive sites on the pore walls, which should be a promising approach to demonstrate the stereocontrolled polymerization of vinyl monomers.[14] Furthermore, functional PCPs with homochiral porous channels can be prepared by introduction of chiral ligands and/or asymmetric coordination geometry into the frameworks for application to enantioselective separation and catalysis.[2b,3a,c,15] Polymerizations in such chiral channels yield optically active polymers. Of considerable interest is the use of chiral PCPs to effect asymmetric polymerization such as asymmetric selective polymerization of racemic monomers as well as asymmetric polymerization of prochiral monomers, which may give helical polymer conformations.[16]

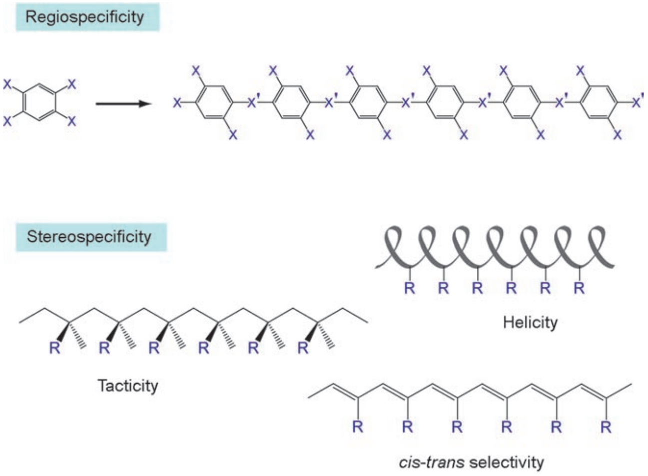

Figure 6. Examples of regio- and stereoselective polymerization.

Much effort has also been devoted to the stereocontrolled polymerization of substituted acetylene monomers in the past few decades, because stereoregularity (*cis* and *trans* chain sequence) of resulting polyacetylenes affects their characteristic properties, such as conjugation length, conductivity, suprastructures, and processibility.[17] The polymerization of substituted acetylenes in the nanochannels of **1b** proceeded with remarkably high stereoselectivity. The narrow nanochannel structure could successfully direct the polymerization with *trans* addition, which strikingly contrasts with the result obtained when using a model catalyst (sodium benzoate), for which only unfavorable cyclic byproducts (trisubstituted benzenes) and *cis* polyMP were obtained in very low yields.[7]

4.2. Molecular Weight

One of the most effective methods for precise molecular-weight control in polymer synthesis is living polymerization that is free from side reactions such as termination and chain transfer.[18] Unlike ionic polymerization, in which the growing species inherently repel each other, free-radical polymerization usually suffers from the recombination and disproportionation of the growing radical species.[18] Therefore, generation of long-lived stable radicals is very important to allow a precise molecular weight. In this regard, the radical polymerization of styrene in **2** showed an intense signal for a propagating radical in the ESR spectrum, and the signal did not disappear over three weeks, even at 70 °C.[12] In contrast to the case of bulk and solution polymerization, the propagating radical in this system was "living" owing to effective protection in the nanochannel. In fact, the number-average molecular weight (M_n) and the polydispersity (M_w/M_n) of the recovered polystyrene from **2** were determined to be $\approx 55\,000$ and 1.6, respectively, by gel-permeation chromatography (GPC) measurements. However, the GPC profile of bulk polystyrene synthesized under comparable conditions showed a broad fraction of polymer with a high polydispersity ($M_w/M_n = 4.7$). This difference suggests the possibility of molecular-weight control in the nanochannel of **2** (Figure 7).

On the other hand, construction of PCPs with the desired crystal sizes promises precise guest inclusion, which would enable the control of the number of incorporated guest molecules in the nanochannels. When organic monomers are employed as the guest molecules, this size change should be particularly useful, because the channel length would affect the molecular weight of the resultant polymers. Recently,

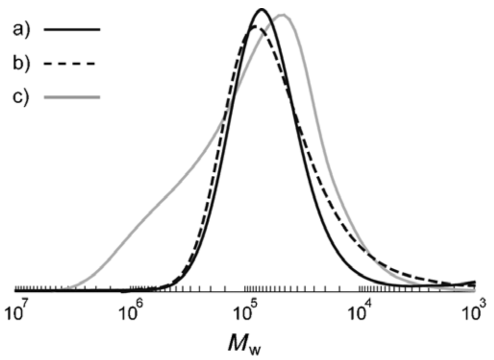

Figure 7. Gel-permeation chromatography profiles of a) recovered polystyrene from **2a**, b) recovered polystyrene from **2b**, and c) bulk polystyrene synthesized under the comparable condition.

our group demonstrated the successful tuning of the crystal growth of a PCP and, consequently, controlled its crystal size to between 2 and 70 µm.[19] The material employed in this study was **1a** with 4.0×6.0-Å^2 microporous one-dimensional channels in the framework, so that polymerization in those crystals would give some clues to precise molecular-weight control.

4.3. Isolation of a Single Polymer Chain

Increased attention is being focused on the fundamental properties of single polymer chains for their future applications in nanosized molecular-based devices.[20] Because the characteristic properties of amorphous bulk polymers are derived from entangled chain aggregates with distinct interchain interactions, encapsulation of a polymer in a one-dimensional crystalline microporous channel can provide a model system for a single polymer chain isolated from its surroundings, which would allow fundamental studies on inherent polymer properties, such as stability, mobility, conductivity, and fluorescence, for the isolated single chains.

In particular, encapsulation of functional conjugated polymers in PCP nanochannels offers several significant advantages. Studies on the fundamental properties of the incorporated polymers in host matrices are of current interest.[1d,e] Clearly, the simplest reason for this study is to understand the mechanism of conduction. It has been said that studies of the conduction mechanism would benefit substantially if the low-dimensional polymer structures were available as decoupled, structurally well-defined entities. The design of molecularly isolated conducting structures can potentially decrease the size of electronic circuitry to molecular dimensions. Thus, if encapsulation of conducting polymers in PCPs enables the separation of individual polymer chains, various contributions to conductivity can be disentangled. In particular, incorporation of conducting polymers in PCP channels is a fascinating one, not only because it would yield a true molecular nanowire, but also because it would allow us to study selectively the charge-transport mechanisms along the polymer chains. The easy alignment of the single chain assembly in PCPs, owing to their highly regular channel structures, could also result in the measurement of the anisotropic conduction in a single crystal. Furthermore, another purpose of the encapsulation is to protect the polymers from atmospheric attack. It is well known that polyacetylene is attacked by oxygen, and even more-stable polymers, such as polythiophene or polypyrrole, show spectroscopic changes upon exposure to air. This encapsulation can also offer protection from other types of chemical attack and greatly enhance thermal and mechanical properties.

5. Conclusions and Perspectives

This Focus Review has summarized an early but evolving stage of polymerization in PCPs and has shown why this subject is so attractive. Currently, most research in this area is focused on polymer synthesis and on control of the structure of the polymer in the nanochannels of PCPs. Another significant goal is to prepare encapsulated polymers in the nanochannels with unique targeted physical properties, which has yet to be fully realized. To exploit fully all the potential applications offered by polymer chains embedded in the regular micropores of PCPs, future research efforts will also be directed at the discovery of unprecedented properties of the confined polymers as well as at the construction of polymer–PCP nanohybrids. On the basis of these important points, polymerizations in PCPs can be classified into the following three categories (Figure 8):

Class I—Structure-controlled polymerization: Rational design and preparation of PCP hosts would permit precision syntheses of various polymers with controlled architectures in a predictable and reliable manner, which can lead to multiple structure controls (primary structure and molecular

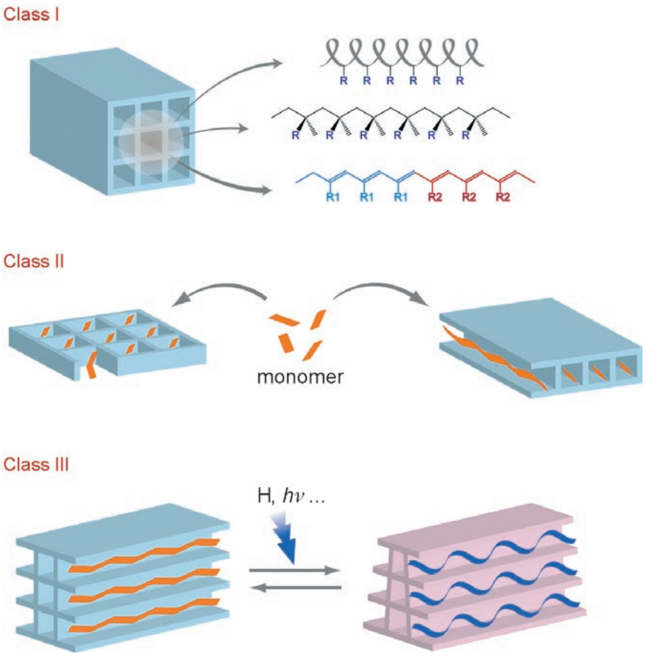

Figure 8. Classification of polymerization in PCPs.

weight) of the resulting polymers, size- and shape-selective polymerization, effective activation of encapsulated monomers, and so on. Furthermore, higher dimensional polymerization (2D- and 3D-polymerization) can also be effected in layered or 3D intersecting channel structures composed of PCPs. This is quite fascinating because conventional polymers do not have regular three-dimensional structures. In contrast, PCPs could yield regular 3D channel structures for controlled polymerization, providing regular 3D nets.

Class II—Orientation-controlled polymerization: PCP materials are among the most plausible candidates for the formation of polymer arrays because of their highly crystalline regular channel structures. This class of polymerization is aimed at polymer suprastructures (isolation of polymer chains and well-ordered alignment in the nanochannels) that will provide useful information for the application of the polymers in modules, circuitries, and devices. Therefore, preparation of PCPs with desired crystal sizes and geometries is of significant importance as they can act as intelligent building blocks to control the alignment of the encapsulated polymers in the programmed nanochannel networks. The crystal size and morphology changes would also be important to control the molecular weight of the prepared polymers in the nanochannels (see Section 4.2).

Class III—Structural and electronic hybrid polymerization: In contrast to conventional zeolites and activated carbon, several studies of the framework properties of PCPs have been reported (magnetism, spin crossover, fluorescence, chromism, etc.).[21] From this point of view, class III polymerization is aimed at combining advanced porous frameworks with functional guest polymers to produce new types of nanohybrid materials with unprecedented cooperative properties. For example, encapsulation of π-conjugated conducting polymers in the magnetic frameworks of PCPs could enable enhanced magnetic interactions of localized d electrons in the framework owing to exchange interactions with organic π-electron systems. Of considerable interest is the interplay of two motifs: interactions between porous frameworks and guest polymers through magnetic, electrostatic, or other relevant properties result in the bi- or multistability of the phases, which respond to external stimuli. In other words, this is a type of third-generation compound.[22]

The concept of polymerization in PCPs is rather simple. This simplicity should strongly encourage researchers in the areas of organic, inorganic, materials, supramolecular, and polymer chemistry, as designable nanochannels of PCPs will offer unique and attractive cavities for a variety of polymerizations.

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