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Thermal ring-opening polymerization of an unsymmetrical silicon-bridged [1]ferrocenophane in coordination nanochannels †

Yuichiro Kobayashi,[a] Kayako Honjo,[a] Susumu Kitagawa,[b] Jessica Gwyther,[c] Ian Manners,*[c] and Takashi Uemura*[ad]

Thermal ring-opening polymerization of the unsymmetrically substituted [1]ferrocenophane was performed in one-dimensional nanochannels of porous coordination polymers (PCPs). In contrast to conventional thermal polymerization in bulk, formation of cyclic polymer was inhibited in the channels. In addition, the tacticity of the resulting polymer was dependent on the pore size of PCPs.

Metal-containing polymers have been employed in a wide range of fields in sensory materials, information storage materials, synthetic metalloenzymes, electrocatalysts and stimuli-responsive materials because of their unique electrochemical, magnetic and catalytic properties.[1] Polyferrocenylsilanes (PFSs) containing ferrocene units in the polymer main chain together with organosilicon spacers can be prepared by ring-opening polymerization of sila[1]ferrocenopane monomers for their widespread applications such as high refractive index materials, electroactuated redox-active gels, precursors to nanostructured ceramics, and etch resists.[2] In order to address various demands for PFSs, efficient synthetic methodologies to produce a variety of PFSs has been developed. For example, thermal ring-opening polymerization (ROP) is a versatile approach to many functional PFSs and can also be performed in mesoporous silica with large (ca. 30 - 40 Å) channels.[3] Transition metal-catalysed ROP can also allow the use of many monomers that would otherwise decompose under harsh reaction conditions and living anionic ROP has been employed to obtain PFSs with controlled molecular weight.[4] However, control of the primary structure of PFSs is generally difficult, and often a mixture of linear and cyclic polymer is formed.[5] In addition, stereoregular PFSs are not available except for the case of solid-state topotactic ROP using the rather inconvenient technique of γ-ray irradiation.[6]

To overcome these problems, we have focused on ROP in nanoconfined spaces because the effective spatial regulation of the primary structures in resulting polymers.[7] For example, polymerization of multifunctional diene, phenol, and ethylene monomers has been conducted in one-dimensional channels of organic crystals and mesoporous silica, providing the corresponding linear polymers.[8] It has also been demonstrated that stereoregularity of polymers is controlled during the polymerization of acrylic monomers within the channels of cyclotriphosphazenes, urea, and montmorillonite.[9] The crucial point in the nanoconfined polymerization system is the design of the nanochannel structures with the size approximating monomer sizes. Porous coordination polymers (PCPs), prepared by the self-assembly of organic ligands and metal ions, have emerged as a new class of porous materials with variety of potential applications.[10] The advantages of PCPs are controllable channel size, shape, and surface functionality through the precise choice of organic ligands and metal ions. Because of the highly designable nanochannels structure, PCPs can also be utilized in the field of polymerization to regulate the primary and secondary structures of the resulting polymers.[11] In this work, we performed thermal ROP of the unsymmetrically substituted [1]ferrocenophane monomer $Fe(\eta\text{-}C_5H_4)_2SiMePh$ (**FM**), in one-dimensional nanochannels of PCPs (Figure 1) and investigated the structure of the obtained PFS using GPC, MALDI-TOF MS, and NMR spectroscopy. Interestingly, the thermal ROP of **FM** in the PCPs effectively inhibited the cyclization of the polymeric product. In addition, the tacticity of the resulting PFS could be successfully varied depending on the pore structure of the selected PCP.

a. Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: uemura@sbchem.kyoto-u.ac.jp
b. Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan.
c. School of chemistry, University of Bristol, Bristol, BS8 1TS, UK. E-mail: Ian.Manners@bristol.ac.uk
d. CREST, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
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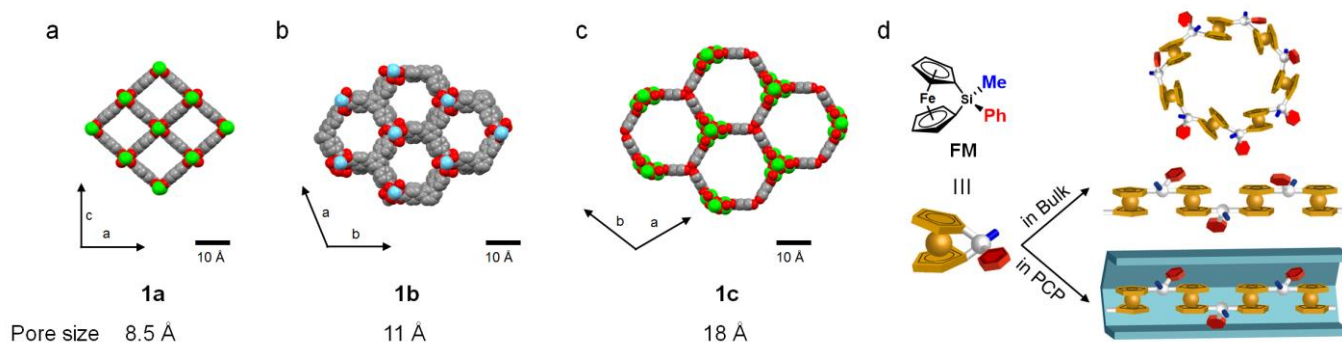
Fig. 1. View of one-dimensional nanochannel structures of **1** (a, **1a**[12]; b, **1b**[13a]; c, **1c**[14]) displayed by a space filing model based on published structure (Al, green; O, red; C, gray; La, blue). Hydrogen atoms are omitted for clarity. (d) Schematic image for polymerization of **FM** in bulk and one-dimensional nanochannels of PCP.
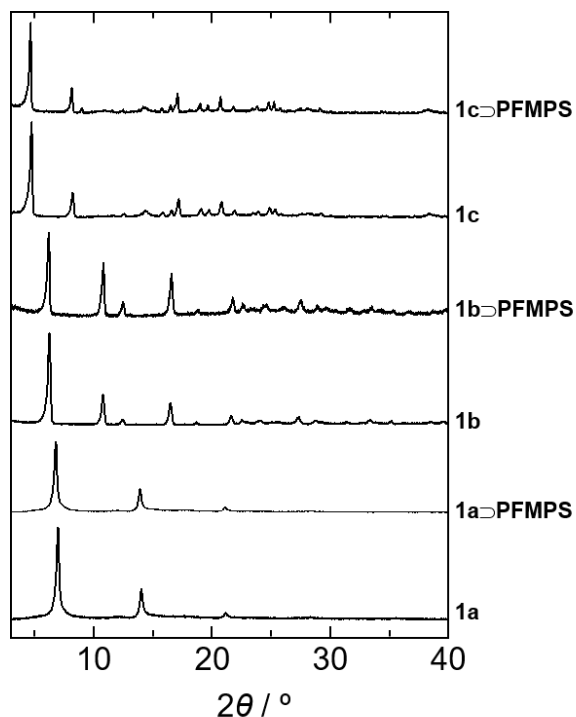

Fig. 2 XRPD patterns of **1** and **1⊃PFMPS**.

Thermal ROP of **FM** to poly(ferrocenylmethylphenylsilane) (**PFMPS**) was performed in one-dimensional nanochannels of three types of PCPs, [Al(OH)(2,6-naphthalenedicarboxylate)]$_n$ (**1a** ; pore size = 8.5 Å, Figure 1a),[12] [La(1,3,5-benzenetrisbenzoate)]$_n$ (**1b** ; pore size = 11 Å, Figure 1b),[13] and [Al$_8$(OH)$_{12}$(1,3,5-benzene tricarboxylate)$_3$]$_n$ (**1c** ; pore size = 18 Å, Figure 1c)[14]. **FM** monomer with the molecular dimension of *ca*. 8 Å, which is determined from the crystal structure[15], was introduced into the channels by immersion of **1** in dry benzene solution of **FM**, followed by complete removal of benzene by N$_2$ flow at room temperature (**1⊃FM**, Figure S1). The introduction of **FM** into the nanochannels was confirmed by the absence of diffraction peaks for **FM** in the X-ray powder diffraction (XRPD) measurement of **1⊃FM** (Figures S2). The inclusion compound was heated at 130 °C for 48 h in evacuated, sealed flask (**1⊃PFMPS**). During the ROP reaction, the colour of the sample changed from orange to brown, suggesting the conversion of **FM** to **PFMPS**. The XRPD
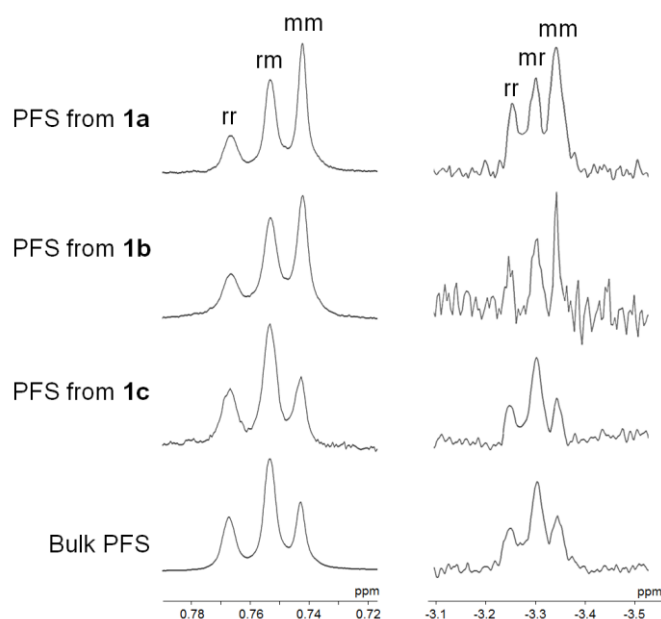
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Table 1. Polymerization of **FM** in the bulk and in nanochannels of **1** at 130 °C to yield **PFMPS**.[a]

Polymerization medium	Pore size (Å)	Yield (%)	M_n (×10^4)[b]	M_w/M_n[b]	Tacticity (%)[c] rr : rm : mm	$^2E_{1/2} - {}^1E_{1/2}$ (mV)[d]
1a	8.5	31	1.21	1.21	13:37:50	242
1b	11	48	2.38	1.30	16:38:46	242
1c	18	60	3.82	1.32	23:50:27	236
Bulk	-	91	12.0	1.87	26:49:25	235

[a] For 1 h in the bulk and 48 h in PCP. [b] Obtained by GPC calibrated by polystyrene standards. [c] Calculated from the integral ratio of ^{1}H NMR spectra (benzene-d$_6$) for methyl moiety in **PFMPS** corresponding to mm, mr, and rr triads. Curve fitting was applied using nonlinear least-squares method (See Fig. S7). [d] $^1E_{1/2}$ and $^2E_{1/2}$ refer to the half-wave potentials for the first and second oxidation waves, respectively.
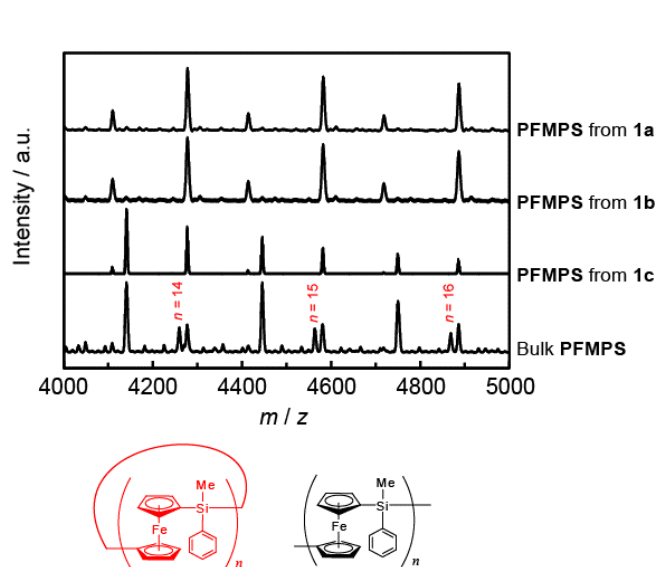
Fig. 3 MALDI-TOF MS spectra of **PFMPS** obtained from **1a**, **1b**, **1c**, and bulk. Cyclic polymer assigned in red.

Fig. 4 (Left) ^{1}H and (right) ^{13}C NMR spectra focusing on the methyl moiety of **PFMPS** obtained from **1a**, **1b**, **1c**, and bulk in C$_6$D$_6$.

measurement of **1⊃PFMPS** clearly showed that the original framework structure of **1** was retained during ROP (Figures 2 and S2). The changes in the relative intensities in the XRPD pattern were detected after the monomer introduction and ROP, which was ascribed to the accommodation of **PFMPS** in **1** due to the change of electron density in the pores.[16] SEM-EDX and N$_2$ adsorption measurements of the **1⊃PFMPS** assured that the ROP of **FM** proceeded only inside the channels of **1** (Figures S3 and S4).[17] The accommodated polymer could be released from the frameworks of **1** by the treatment with a tetrasodium ethylenediaminetetraacetate aqueous solution, followed by purification of the polymeric product by reprecipitation. Observed IR spectra of the product obtained from **1** was similar to that of bulk-synthesized **PFMPS** (Figure S5).[18] ^{1}H and ^{13}C NMR measurements of the product in C$_6$D$_6$ also ensured the formation of **PFMPS** in **1** (Figure S6).[19] Table 1 summarizes the ROP results (yield, molecular weight, molecular weight distribution, and tacticity) of **PFMPS** obtained in the nanochannels of **1**. An interesting relationship between polymer yield and pore size of **1** was observed, where the yield decreased with decreasing the pore size of **1**. In addition, GPC measurements were carried out to determine the molar mass of the isolated **PFMPS** from **1**, and showed the trend that **PFMPS** chain length decreased with decreasing the

pore size. This is probably because the mobility (and hence reactivity) of **FM** decreases as the size of the nanochannels is reduced.[20] The molar mass distributions (M_w/M_n) were also substantially narrower as reflected in the M_w/M_n values which suggests that random termination reactions are suppressed.

Although the actual mechanism of thermal ROP of sila[1]ferrocenophanes has yet not been fully understood, previous experimental data suggested that a nucleophilically-assisted process could be the most plausible.[2a] In this system, cyclopentadienyl (Cp) anions are generated by nucleophilic attack at a silicon atom to promote the ROP reaction, which is often accompanied by back-biting reactions, resulting in the formation of cyclic polymers (Scheme S1).[2a,5a,21] Therefore, PFS materials prepared in bulk condition in the melt consist of a mixture of linear polymers with different end groups and cyclic polymers, as is observed in the MALDI-TOF MS measurement (Figure 3).[2a,5b] In contrast, **PFMPS** isolated from **1** showed peaks for only linear polymers with the repeating unit of **FM** (m/z 304) without the formation of cyclic structures. This effective inhibition of cyclic PFS formation is presumably suppressed due to the inaccesibility of the α and ω end groups of polymer chains accommodated in the PCP channels.

Polymerization in nanoconfined geometries often gives polymers with the stereoregularity different from those obtained in bulk/solution polymerization.[7a, 9, 20a, b] We carried out ^{1}H and ^{13}C NMR spectroscopic analysis to determine the triad fractions corresponding to the methyl groups on the main chain of **PFMPS** (Table1, Figures 4, S6, and S7). Since the pore size of **1c** is very large for the monomer, tacticity of **PFMPS** obtained from **1c** was comparable to that of the bulk-synthesized polymer. However, the tacticity of **PFMPS** obtained from **1a** and **1b** with smaller pores was found to be clearly modified and, moreover, based on the NMR data (Figure 4) the enriched tacticity is the opposite to that formed exclusively via the ROP of **FM** induced by γ-ray irradiation.[6] Although the assignment of specific PFMPS tacticity has not yet been fully elucidated,[6] ROP of **FM** in PCPs with narrow nanopores would be expected to lead **PFMPS** with higher isotactic (meso) fractions based on steric considerations associated with the configuration of the Ph groups, allowing the induction of isotactic **PFMPS** in narrower channels of **1**.[20a,b] As only a syndiotactic **PFMPS** was obtained from the ROP of **FM** induced by γ-ray irradiation,[6] utilization of PCPs is significantly important to tune the tacticity of **PFMPS**, increasing the fraction of isotactic units.

The redox properties of PFS might be expected to be affected by conformational changes.[2a,22] We performed cyclic voltammetry of **PFMPS** obtained from **1** and found two reversible peaks because of stepwise oxidation process at alternating iron centres.[2a] The difference between the two oxidation potentials ($^2E_{1/2} - {}^1E_{1/2}$) was slightly increased in comparison with that of bulk synthesized **PFMPS** (Figure S8, Table 1). The difference in redox potential is indicative of the extent of the interaction between the ferrocene units and this might be interpreted as being a consequence of a decreasing distance between two adjacent ferrocenyl moieties in the isotactic environments.

In summary, we have demonstrated that ROP of **FM** in the one-dimensional nanochannels of PCP is a useful synthetic strategy to control of the resulting PFS primary structure. Thus **PFMPS** obtained from PCP did not contain a cyclic component, unlike the material synthesized by thermal ROP in the melt, and the resulting linear polymer was of lower polydispersity. In addition, the stereoregularity of the resulting **PFMPS** was significantly affected by the pore size of PCP and this led to a slight change in the redox coupling. Moreover, the preferred tacticity (isotactic) was opposite to that arising from γ-radiation experiments.[6]

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