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Mechanistic Studies on Template Polymerization in Porous Isotactic Poly(methyl methacrylate) Thin Films by Radical Polymerization and Postpolymerization of Methacrylate Derivatives

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ABSTRACT: The postpolymerization of various vinyl monomers was applied for mechanistic studies of the template polymerization of methacrylic acid (MAA) in porous isotactic (it-) poly(methyl methacrylate) (PMMA) thin films on quartz crystal microbalance (QCM) substrates and on silica gels, which were prepared by the alternative layer-by-layer (LbL) assembly of it-PMMA/syndiotactic- (st-) poly(methacrylic acid) (PMAA). In this study, QCM analyses, FT-IR/ATR spectra, ^{1}H NMR spectra, and SEC were employed to investigate the polymerization mechanism, and they highlighted the following points: (1) the livingness of polymer radicals by postpolymerization on a QCM, (2) substituent effects on the polymerizability in porous it-PMMA thin films, and (3) partial stereocomplex formations of polymerized MMA with host it-PMMAs. Stabilities of porous it-PMMA thin films on QCM substrates and on silica gels are also discussed herein.

Introduction

The development of controlled polymerization methods is an important research area because physical and chemical characters of polymers are influenced by their structures, such as molecular weight and stereoregularity. Challa et al. investigated the stereospecific polymerization of methyl methacrylate (MMA)[1,2] and methacrylic acid (MAA)[3] in the presence of stereoregular poly(methyl methacrylate) (PMMA) because isotactic- (it-) PMMA and syndiotactic- (st-) PMMA form stereocomplexes whose structures were reported as double-stranded helices by X-ray[4] and triple-stranded helices by AFM measurements.[5] In 2004, almost perfectly controlled radical polymerizations of methacrylates were reported in porous thin films.[6,7] Surprisingly, free radical polymerization principally controlled both molecular weights and stereoregularities, although little stereoregularity control was achieved in solution. Therefore, the elucidation of template polymerization mechanisms in thin films would provide significant finds. These aforementioned complexes were prepared by layer-by-layer (LbL) assembly as a critical approach.

LbL assembly, which is achieved by simple alternative immersions, was first reported by Decher et al.[8,9] as a convenient technique for fabricating thin films using polycation−polyanion interactions. Because of its simplicity and high applicability, the LbL assembly method is applied to a wide research area such as multilayer preparations,[10] metal particles,[11] virus,[12] proteins,[13] silica colloids,[14] and so on. However, weak polymer−polymer interactions, such as van der Waals interactions of it-PMMA and st-PMMA in stereocomplex formation,[15] were applied to LbL assembly by our group.[16] Then, thin films were successfully fabricated on quartz crystal microbalance (QCM) substrates by it-PMMA/st-poly(alkyl methacrylate) stereocomplexes[17] as well as it-PMMA/st-PMMA stereocomplexes. Among the successive research, it-PMMA/st-poly(methacrylic acid) (PMAA) stereocomplex formation[18] was the most important because the polymer possesses quite different solubilities in organic/alkali water solvents, which enabled us to extract only one component from stereocomplex thin films. Therefore, porous it-PMMA thin films were prepared, bearing st-PMAA-shaped nanospaces inside,[19−21] to lead the isospecific polymerization of MMA with porous st-PMAA thin films[6] and the syndiospecific polymerization of MAA.[7]

To investigate the mechanism of template polymerization, molecular weight growth during polymerization was monitored,[6] and oligomeric adsorption behaviors in porous it-PMMA thin films were analyzed.[22] These studies showed that the system proceeds in a living radical polymerization manner; however, the stereospecific mechanism has attracted attention for the possibility of stereocontrol of other polymers bearing similar structures.

Usually, molecular designs of monomers, catalysts, and additives are important to achieve stereospecific polymerization, which is why the molecular design of substituents[23−26] and the structural design of catalyst ligands[27−30] has been intensively researched for controlled polymerization. The use of porous reaction fields is another important approach for the controlled polymerization.[31−33] Basically, the aforementioned strategies are based on constructing and curving nanospaces at the molecular level along polymer main chains. In previous work, it was reported that porous it-PMMA thin films could partially associate with st-PMAA derivatives, such as st-PMMA, st-poly(ethyl methacrylate), and st-poly(propyl methacrylate).[19] Therefore, the application of other vinyl monomer polymerization to the template polymerization system would provide useful information on the mechanism.

In this article, we first confirmed the living manner in porous it-PMMA thin films by postpolymerizing of MAA on QCM substrates. Then, radical polymerizations were performed on MAA, MMA, acrylic acid (AA), and methacrylamide (MAm) with it-PMMA thin films on QCM substrates (Scheme 1). The polymerizability was compared on QCM, and ^{1}H NMR spectra were measured for the obtained PMMA to discuss the template polymerization mechanism.

Experimental Section

Materials. MMA (Tokyo Chemical Industry), MAA (Tokyo Chemical Industry), AA (Tokyo Chemical Industry), trimethylsi-

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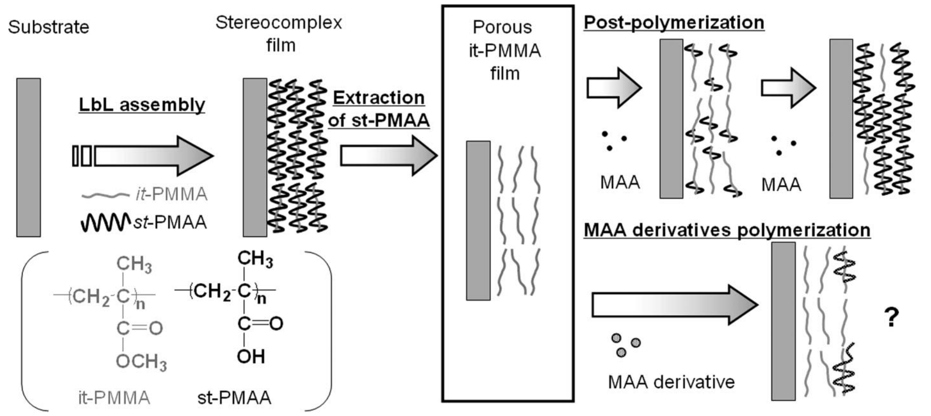
Scheme 1. Preparation of Porous it-PMMA Thin Film and Post-Polymerization of Methacrylic Acid and Its Derivatives



lylmethacrylate (Aldrich), and toluene (Tokyo Chemical Industry) were distilled just before use. MAm (Tokyo Chemical Industry), anhydrous acetonitrile (Wako Pure Chemical Industries, Japan), and anhydrous methanol (Wako Pure Chemical Industries, Japan) were used without further purification. Ultrapure distilled water was provided by the MILLI-Q laboratory (MILLIPORE). it-PMMA in this study was synthesized by anionic polymerization of MMA in toluene at −78 °C for 5 days with t-BuMgBr[34] ($mm/mr/rr = 96{:}3{:}1$, $M_n = 36\,000$, $M_w/M_n = 1.20$ was used for QCM substrate, $mm/mr/rr = 96{:}2{:}2$, $M_n = 22\,900$, $M_w/M_n = 1.21$ was used for silica gels substrate). st-PMAA was synthesized by anionic polymerization of trimethylsilylmethacrylate with t-BuLi/Bis(2,6-di-*tert*-butylphenoxy)methyl aluminum,[35] and the obtained polymer was methylated by diazomethane to be characterized ($mm/mr/rr = 1{:}6{:}93$, $M_n = 32\,400$, $M_w/M_n = 1.59$ was used for QCM substrate, $mm/mr/rr = 1{:}5{:}94$, $M_n = 33\,700$, $M_w/M_n = 1.45$ was used for silica gels substrate). Tacticities of polymers were determined by ^{1}H NMR spectra of alpha methyl protons in nitrobenzene-d_5 at 110 °C.

Polymerization on a Quartz Crystal Microbalance Substrate. The preparation of porous it-PMMA thin films on a QCM by LbL assembly and the subsequent template polymerization on a QCM were conducted as reported in the literature.[6,7] A typical experimental procedure of postpolymerization is described for the polymerization in MAA. A QCM substrate was immersed in an it-PMMA solution in acetonitrile (0.017 unitM) for 5 min at 25 °C, washed gently with acetonitrile, and dried with nitrogen gas to measure the frequency. The substrate was immersed in a st-PMAA solution in acetonitrile/water (4:6 v/v; 0.017 unitM) for 5 min at 25 °C. Alternate immersions were repeated for 16 steps (8 cycles); the selective extraction of st-PMAA in a 10 mM NaOH aqueous solution for 5 min was performed to obtain the porous it-PMMA film as a template polymerization field. This film was immersed in 6.8 mL of degassed ultrapure water with 85 mg MAA (1 mmol) in a glass vial capped by a septum rubber for 30 min at room temperature; then, 3.2 mL of radical initiator VA-044 (16.5 mg, 0.05 mmol) solution in the degassed ultrapure water was combined to heat up to 70 °C for polymerization reactions. The additional 2.5 mL of MAA solution in ultrapure water (8.5 mg/mL) was introduced to the reaction glass vial after 30 min and kept at 70 °C for more than 2.5 h. The QCM substrate was gently washed by ultrapure water to measure frequency.

Polymerization on Macroporous Silica Gels. The preparation of porous it-PMMA thin films on silica gels, and subsequent template polymerizations on silica gels were conducted as reported in the literature.[6,36] LbL-assembled it-PMMA/st-PMAA stereocomplex on macroporous silica gels (2.0 g) was introduced to 300 mL of ampule, and 250 mL of aqueous 10 mM NaOH solution was introduced to purge nitrogen for 2 h. After removed of NaOH solution by syringe, the silica gels were washed by ultrapure water twice to obtain porous it-PMMA film on silica gels. MeOH (50 mL) and ultra pure water (50 mL) were then combined with silica gels in ampule, and MMA (0.3 mL, 2.8 mmol) was introduced and nitrogen was purged for 1.5 h. VA-044 (37.9 mg, 0.14 mmol) was added to the mixture, and an additional 10 min of nitrogen purge was performed. The polymerization was initiated by heating up to 40 °C. After 3 h of reaction and removal of the supernatant solution, the ampule was cooled to room temperature, and silica gels were washed by 40 mL of acetonitrile three times. After centrifugation, the separated silica gels were then washed by 40 mL of chloroform three times again. The recovered solutions by each step were condensed to obtain polymers: the extracted NaOH(aq) soluble part, 318 mg (100 mg NaCl was included); supernatant solution part, 35 mg; acetonitrile soluble part, 71.3 mg; chloroform soluble part, 95.4 mg.

Quartz Crystal Microbalance. An AT-cut quartz crystal with a parent frequency of 9 MHz was obtained from USI (Japan). A crystal (9 mm in diameter) was coated on both sides with gold electrodes 4.5 mm in diameter, which was of mirrorlike polished grade. The frequency was monitored by an Iwatsu frequency counter (model SC7201) and was recorded manually. The amount of polymers adsorbed, Δm, could be calculated by measuring frequency decreases in the QCM, ΔF, using Sauerbrey's equation[37] as follows

$$\Delta F = 2F_0^2/(A\rho_q\mu_q)^{1/2})\Delta m$$

where F_0 is the parent frequency of the QCM (9 MHz), A is the electrode area (0.159 cm^2), ρ_q is the density of the quartz (2.5 g cm^{-3}), and μ_q is the shear modulus (2.95×10^{11} dyn cm^{-2}). This equation was reliable when measurements were made in air as described in this study because the mass of solvent is never detected as frequency shifts, and the effect of the viscosity of the absorbent on the frequency can be ignored.

Measurements. Attenuated total reflection (ATR) IR spectra of the thin films were obtained with a Spectrum 100 FT-IR spectrometer (Perkin-Elmer). The interferograms were coadded 64 times and were Fourier transformed. ^{1}H NMR spectra were measured by JNM-GSX400 system (JEOL, Japan). Static contact angles were measured using an automatic contact angle meter apparatus (Drop Master 100, Kyowa Interface Science, Japan) at room temperature. A drop of ultrapure water was introduced to the film using a microsyringe.

Results and Discussion

The stereospecific template polymerization of methacrylates using the complementary interaction of stereocomplex formation is significant because of the simple free-radical polymerization without any harmful organometal reagents under strict polymerization conditions.[6] However, the stereocomplex film formation prior to the polymerization by LbL assemblies was affected by subtle condition changes such as molecular weights of template polymers, the combination of polymers, concentrations, solvents, temperatures, and so on. On the research series of

Table 1. Radical Polymerization with Porous it-PMMA Film on QCM[a]

run	monomer	concn	temp	polymerization	time	C.E.[b]
		(mol/L)	(°C)	t_1 (h)	t_2 (h)	(%)
1[c]	MAA	0.1	70	3	0	–3
2[d]			70	3	0	–4
3	MAA	0.02	40	2	0	2
4	MAA	0.02	70	2	0	2
5	MAA	0.1	70	3	0	27
6	MAA	0.1	70	3	3	50
7	MAA	0.1	70	4	2	65
8	MAA	0.1	70	0.5	2.5	59
9	MAm	0.1	70	2	0	8
10	MAm	0.1	70	0.5	2.5	12
11	AA	0.1	70	2	0	66
12	AA	0.1	70	0.5	2.5	71
13[e]	MMA	0.1	70	0.5	2.5	90

[a] Solvent: water. After the reaction for t_1 (h) was initiated, monomer solution (1.0 M, 2.5 mL) was added for postpolymerization for t_2 (h). [b] Yields were determined as complex efficiency (C.E.). [c] Blank polymerization without VA-044. [d] Blank polymerization without monomer. [e] MeOH/water (1:1 v/v) was used as solvent.

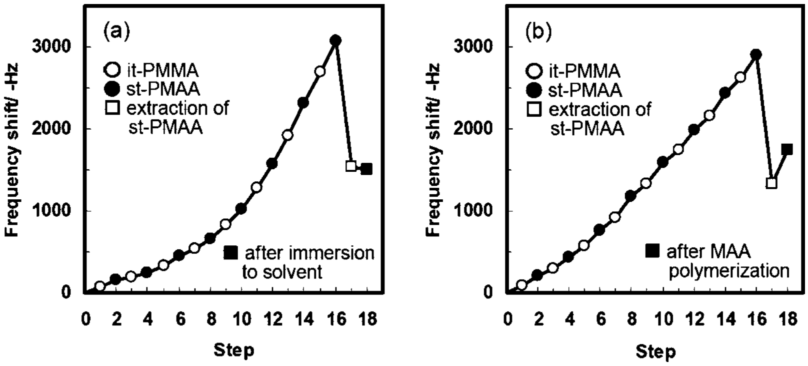


Figure 1. QCM analyses of LbL assembly, selective extraction, and template polymerization with (a) blank (Table 1, entry 2) and (b) 27% yield (Table 1, entry 5).

polymerization mechanistic studies, we initially had difficulties in controlling and estimating polymerizations. Besides, it-PMMA and st-PMAA did not form clear 2:1 stereocomplexes on the QCM in all cases, but 1.22 ± 0.34:1 ($n = 29$), implying a mixture of 2:1 and 1:1 stereocomplexes.[15,18,38] Therefore, the complex efficiency (C.E.) was determined to evaluate the polymerization value in this study as the following

$$\text{C.E.} = (\text{increased weight after polymerization})/(\text{extracted st-PMAA weight}) \times 100 \quad (1)$$

The results of template polymerization of methacrylate derivatives are listed in Table 1.

Because every LbL assembly step and extraction step differed for each substrate, it would be difficult to compare polymerizabilities with frequency changes when only small amounts of monomer polymerized. For this reason, blank polymerizations were run to check if the defined C.E. formula (1) was appropriate for evaluations. Following the reported polymerization conditions,[7] MAA in ultrapure water (0.1 mol/L) was heated to 70 °C for 3 h on QCM substrates with porous it-PMMA films without an azo-initiator (VA-044) (Table 1, entry 1). The resulting QCM analysis showed a −3% C.E. value, suggesting that there was no polymerized PMAA incorporated into the porous it-PMMA film and that very slight it-PMMA peeled on the substrate. The aforementioned tendency was also confirmed under conditions with an azo-initiator but without an MAA monomer to obtain −4% C.E., as depicted in Figure 1a (Table 1, entry 2). These data show that porous it-PMMA thin films are relatively stable, and most host template polymers remained on QCM substrates.

First, MAA polymerizations were performed under diluted conditions (0.02 M) for the purpose of polymerization analyses with low conversions. At both 40 and 70 °C, 2% C.E. values were observed (Table 1, entries 3 and 4). Considering the slight it-PMMA peeling (Table 1, entries 1 and 2) and oligomer adsorptions,[22] the C.E. values were appropriate to the explanation that the initially generated oligomers immediately adsorbed into porous it-PMMA thin films, and there were no further polymerizations that proceeded in the film, whereas the MAA monomer was consumed in solution. Under five times concentrated conditions (0.1 M), the increased value was apparently confirmed with 27% C.E., which demonstrated that actual polymerizations in films had taken place. (Table 1, entry 5). In Figure 2, the speculation of FT-IR/ATR spectra of the films with 27% C.E. are shown and compared with those of porous it-PMMA films and st-PMAA cast films.

Because of the fact that the amount of polymerized MAA was smaller than that of originally attached it-PMMA films, it was difficult to find changes in spectral patterns. Then, the differential spectrum (Figure 2d) was compared with that of it-PMMA/st-PMAA stereocomplex films (Figure 2b), which were obtained by subtracting the IR spectrum of porous it-PMMA films (Figure 2a) from those of originally measured IR spectra. Whereas the spectrum of st-PMAA cast film, which should possess a random conformation, showed a peak at 1695 cm^{-1}, differential spectra of both template polymerized films (27% C.E., Figure 2d) and stereocomplexes (Figure 2b) exhibited peaks at around 1720 cm^{-1}. This result shows that the circumstances of carbonyl groups of the obtained PMAA are similar to those of stereocomplexes, suggesting that stereocomplex formation is achieved during MAA polymerization.

However, the C.E. value in this study remained lower than that in a previously reported case,[7] probably because different stereoregular polymers were employed for stereocomplex formation and because the structure of the resulting porous it-PMMA film had variant balances of the oligomer adsorption,

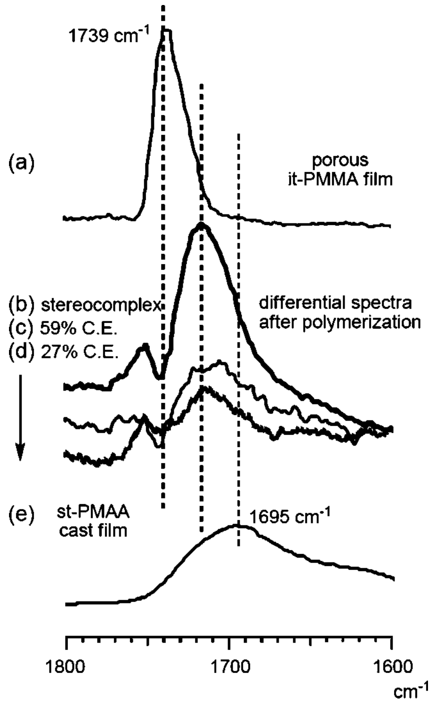


Figure 2. (a) FT-IR/ATR spectrum of the porous it-PMMA. The differential FT-IR/ATR spectra of (b) it-PMMA/st-PMAA, (c) MAA polymerized on it-PMMA film with 59% C.E. (Table 1, entry 8), and (d) MAA polymerized on it-PMMA film with 27% C.E. (Table 1, entry 5), which were obtained by the subtraction of the porous it-PMMA (a). (e) FT-IR/ATR spectrum of the st-PMAA cast film.

the mobility of it-PMMA chains, and the porosity that allowed monomer supply. In the solid polymer matrix, it is known that radicals are entrapped and gradually react.[39] To investigate the possibility of further polymerization, postpolymerization was applied because the polymerization system was reported in a living radical polymerization manner.

Additional MAA solution (2.5 mL, 8.5 mg/mL) was added 3 h, 4 h, and 0.5 h after initiation, respectively (Table 1, entries 6−8). In all cases, increased weights compared with that without added monomer were observed. Because no increasing weights were observed without radical initiators (Table 1, entry 1), 50% C.E. (Table 1, entry 6), 65% C.E. (Table 1, entry 7), and 59% C.E. (Table 1, entry 8) increasing weights should be attributed to the postpolymerization in porous it-PMMA thin films, implying that polymer radicals inside it-PMMA films still possessed reactivity and were ready to react if monomers were supplied (Figure 3a). To add to this, the intensity of differential IR spectra increased from that with 27% C.E. (Figure 2c,d). Furthermore, the contact angle on the surface changed from 49.2 ± 1.9 to 36.7 ± 2.8° compared with porous it-PMMA thin films, which hint that the surface hydrophilicity change came from stereocomplex formation. Therefore, postpolymerization would be a good approach to improving C.E. in this template polymerization system.

Another approach to investigating polymerization mechanisms is to change monomer structures and evaluate the effects of substituent bulkiness and polarities. Especially in this template polymerization system, van der Waals interactions were considered to be strong driving forces in stereocomplex formation, in which the molecular shape is very important. Porous it-PMMA thin films have incorporated st-PMAA derivatives to some extent,[19] and MAm and MMA were absorbed and acrylic acid (AA) was not absorbed into it-PMMA thin films when vinyl monomer concentrations were condensed (2 M).[22] Therefore, those MAA derivatives were applied to template polymerization of it-PMMA/st-PMAA systems (Table 1, entries 9−13).

MAm is a monomer with similar adsorption into porous it-PMMA thin films as MAA[22] because of its structural similarity with α-methyl groups, which should be associated with it-PMMA polymer chains.[40] However, the result of radical polymerization resulted in 8% C.E. (Table 1, entry 9), and it was slightly improved to 12% C.E., even when a postpolymerization was applied (Table 1, entry 10). It would be difficult for nonstereocomplex formation polymer combinations, such as it-PMMA/poly(MAm), to polymerize, although the monomer and limited oligomers were able to be incorporated. Reversely, polymerization using a smaller vinyl monomer, AA, made the weight increase to 71% C.E. (Table 1, entry 12), although AA itself did not incorporate into porous it-PMMA thin films.[22] Therefore, the size of porosity might strictly affect the polymerizability of MAA derivatives. However, a slightly bigger structure, MMA is expected to completely polymerize because of it-PMMA/st-PMMA stereocomplex formation as a driving force. After polymerization of MMA on QCM substrates, C.E. was 192% C.E. at first because of the adsorption of atactic-(at-) PMMA synthesized in MeOH/water (1:1 v/v). When the QCM substrate was rinsed with acetonitrile, which dissolved not only at-PMMA but also it-PMMA on the QCM, polymer still remained with 90% C.E., and it was stable in acetonitrile at 25 °C overnight (Figure 3b; Table 1, entry 13). Because it-PMMA/st-PMMA stereocomplexes do not dissolve in acetonitrile, the template polymerization of MMA in porous it-PMMA thin films was suggested.

To study the stereoregularity of obtained polymers, we chose the MMA polymerization on macroporous silica gels because the tacticity study of poly(AA) was difficult. Prior to the polymerization, we investigated the effect of steps in stereocomplex formation on silica gels by FT-IR/ATR spectra (Figure 4).

On the basis of the absorption intensity of silica gels at 1057 cm^{-1} (Supporting Information, Figure S1), the relative IR intensity of carbonyl groups at 1720 cm^{-1} proportionally grows, depending on the number of the alternative LbL assembly steps (Figure 4a,c,e,g), whereas each cast film of it-PMMA and st-PMAA has a peak at 1726 and 1695 cm^{-1}, respectively. The peak at each LbL step shifted to 1721 cm^{-1} with the same spectral patterns (Figure 4b,d,f,h), showing that the complete extraction of st-PMAA at each step and that the porous it-PMMA thin film do not depend on the thickness of the film. The stepwise weight increase to 80 steps was also confirmed by QCM analysis (Supporting Information, Figure S2).

MMA was then polymerized with porous it-PMMA thin films on 2 g of macroporous silica gels, prepared by an 80 step LbL assembly. The polymerization was conducted in MeOH/water (1:1 v/v) at 40 °C for 3 h. After polymerization, the supernatant was removed, and the polymer films on silica gels were washed with acetonitrile because at-PMMA and it-PMMA are soluble in acetonitrile, but the stereocomplex is insoluble. After it was separated from acetonitrile solution, the silica gel was then washed with chloroform to recover the rest of the polymers as an acetonitrile insoluble part. In this way, the reaction mixture was fractionated and separately analyzed as (1) the supernatant solution part, (2) the acetonitrile-soluble part, and (3) the chloroform-soluble part. Prior to the polymer analyses, the reaction was monitored by FT-IR/ATR spectra, as shown in Figure 5. The IR intensity of the polymer film on silica gels after MMA polymerization apparently increased compared with that of initial porous it-PMMA thin films on silica gels (Figure 5b). Silica gels with polymers were washed by 40 mL of acetonitrile three times, and IR spectra were measured again for carbonyl peaks in PMMA to see if they remained (Figure 5d), whereas initial porous it-PMMA films on macroporous silica gels totally washed away. This result indicates the

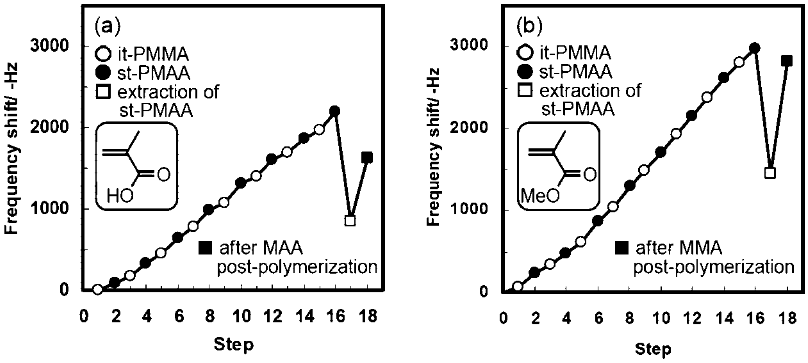


Figure 3. (a) QCM analyses of LbL assembly, selective extraction, and template polymerization of methacrylic acid with C.E. = 59% (Table 1, entry 8) and (b) template polymerization of methyl methacrylate with C.E. = 90% (Table 1, entry 13).

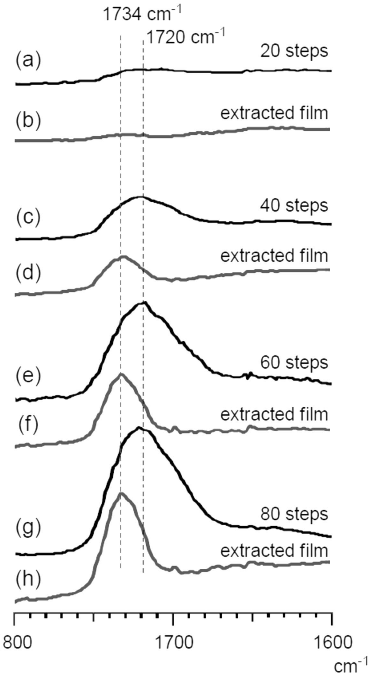


Figure 4. FT-IR/ATR spectra of it-PMMA/st-PMAA stereocomplex film on silica gels and the porous it-PMMA films on silica gels with (a,b) 20 steps, (c,d) 40 steps, (e,f) 60 steps, and (g,h) 80 steps.

synthesized PMMA formed stereocomplex with the initial porous it-PMMA. Finally, 40 mL of chloroform was used to recover PMMAs from silica gels (95 mg).

^{1}H NMR spectra of fractionated PMMAs are depicted in Figure 6. Together with a slight amount of it-PMMA, PMMAs recovered from supernatant solution showed typical at-PMMA (Figure 6a). However, the acetonitrile soluble part showed only it-PMMA, which was used to build the porous it-PMMA host film (Figure 6b). At last, ^{1}H NMR spectra of the rest of the film, collected as an acetonitrile-insoluble and chloroform-soluble part, showed that the equivalent amount of it-PMMA existed as slightly syndiotactic enriched PMMA (Figure 6c). The chloroform-soluble part (*mm*/*mr*/*rr* = 49:22:29) includes the synthesized PMMA with radical method and the original it-PMMA host as template film. The aforementioned experimental data suggest that enough MMA could be polymerized in it-PMMA film nanospaces and that the partially stereocomplex formed to change the total solubility in acetonitrile. However, taking the amount of it-PMMA host into account, the syndiotactic selectivity in Figure 6c was not so high, although almost perfect selectivities were achieved in the previous work.[6,7] The reason why selectivities varied between MMA and MAA polymerizations is that MMA possesses a bulky methyl group. Stereospecific template polymerization has been achieved only when the same polymer was synthesized as the polymer extracted from stereocomplex.[6,7] In this study, the porous nanostructure was created not by PMMA but by PMAA. In short, the porous nanostructure itself played an important role in stereoregulation in addition to stereocomplex formation. The substituent effect is supported by the fact that the porous it-PMMA film can incorporate st-PMAA with around 80% C.E., whereas st-PMMA and st-poly(ethyl methacrylate) are incorporated with only 43 and 8% C.E., respectively.[19,22] Therefore, the strict stereoregular control of PMMA during the polymerization was difficult under the present conditions. It is noteworthy that MMA was also polymerized in acetonitrile/water (4:6 v/v) and resulted in the same insoluble PMMA (13 mg), which was equivalent to the remaining it-PMMA (Supporting Information, Figure S3).

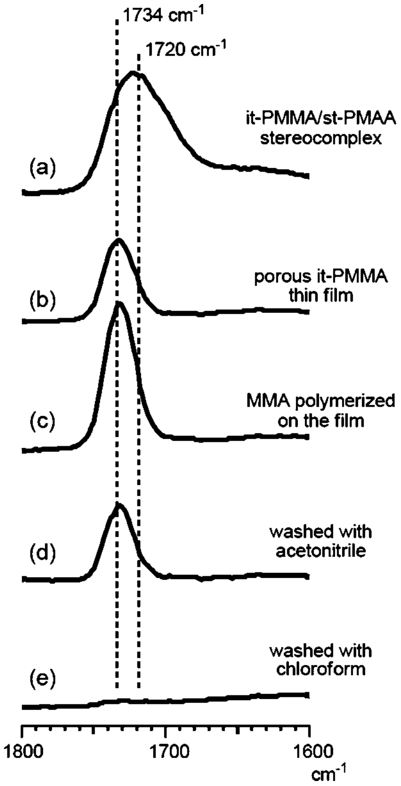


Figure 5. FT-IR/ATR spectra of the polymer film on silica gels, whose intensity corresponded at 1057 cm^{-1}: (a) it-PMMA/st-PMAA stereocomplex, (b) porous it-PMMA film, (c) MMA polymerized in the porous it-PMMA film, (d) acetonitrile insoluble part after the MMA polymerization in the porous it-PMMA film, and (e) after washing with chloroform on silica gels.

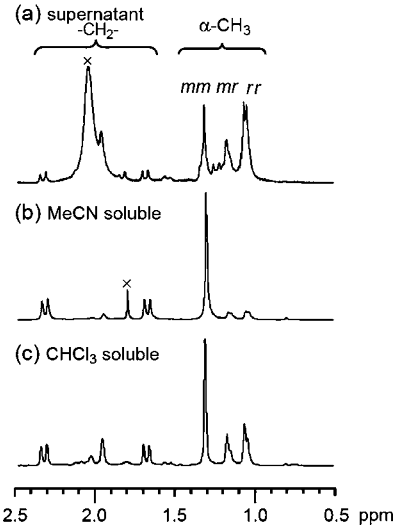


Figure 6. ^{1}H NMR spectra of PMMA obtained with it-PMMA thin film on macroporous silica gels in MeOH/water (1:1 v/v). (a) The supernatant solution part of the template polymerization, (b) the acetonitrile-soluble part of the host it-PMMA, and (c) the acetonitrile-insoluble and $CHCl_3$-soluble part of the obtained PMMA with the host it-PMMA (400 MHz, in nitrobenzene-*d* at room temperature).

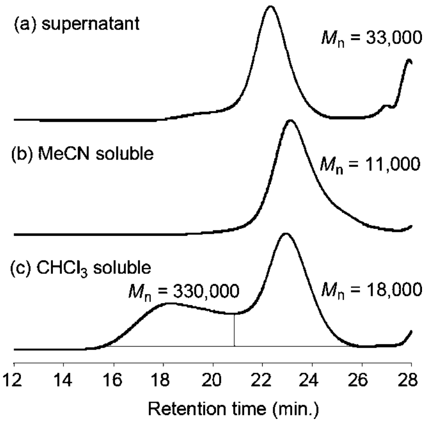


Figure 7. SEC traces of PMMA obtained with it-PMMA thin film on macroporous silica gels in MeOH/water (1:1 v/v): (a) The supernatant solution part of the template polymerization, (b) the acetonitrile-soluble part of the host it-PMMA, and (c) the acetonitrile-insoluble and $CHCl_3$-soluble part of the obtained PMMA with the host it-PMMA.

SEC charts of the resulting polymers are shown in Figure 7. The SEC analysis of the acetonitrile-soluble part depicted a unimodal pattern ($M_n = 11\,000$), indicating it-PMMA host in accord with ^{1}H NMR spectrum (Figure 7b). However, bimodal distribution was observed from the analysis of the chloroform-soluble part ($M_n = 330\,000$, $M_n = 18\,000$) (Figure 7c). The low-molecular-weight part ($M_n = 18\,000$), attributed to the rest amount of the it-PMMA host and associated with the synthesized PMMA, and the high-molecular-weight part ($M_n = 330\,000$) could be assigned to the synthesized PMMA. The value does not correspond to the expected molecular weight when the 1:2 stereocomplex formed with the it-PMMA host, suggesting that the methyl group of the MMA monomer also disturbed the molecular weight control in the template polymerization system as well as stereoregulation. Therefore, strict monomer structure is necessary for stereoregular control and molecular weight control at the same time, although the active living radicals cause postpolymerization.

Conclusions

LbL assemblies led to the successful formation of it-PMMA/st-PMAA stereocomplex films on QCM substrates and on silica gels to create the porous it-PMMA thin films as polymerization fields, although MAA polymerizability inside might depend on LbL assembly conditions. Without both azo-initiator and MAA monomer, blank polymerizations with the porous it-PMMA thin films showed that template polymerization fields, which created porous films, were stable in water at 70 °C for 3 h and that increased weights on substrates after polymerization were ascribed to the polymer associated with the host it-PMMA. The postpolymerization of MAA in porous it-PMMA thin films was successfully achieved, implying that the polymer radical in the film possessed an adequate activity in a living polymerization manner. When MAA derivatives were polymerized, the smaller-sized monomer (AA) was polymerized in good C.E. yield, whereas the bigger size monomer (MAm) remained a low C.E. value. Those substituent effects proposed that very slight size changes affected the polymerizabilities inside porous it-PMMA films during polymerization, although the adsorption at monomer structures resulted in differences. When MMA was polymerized, an almost equivalent amount of PMMA was obtained as an acetonitrile-insoluble part with the host it-PMMA, implying that the stereocomplex was partially formed. It was also revealed that the strict monomer structure was necessary for the stereocontrol and molecular weight control, whereas the active radical was entrapped in the porous it-PMMA host film. The mechanism investigation of template polymerization in this study should supply useful information on future template polymerization systems.

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Supporting Information Available: Experimental procedure of anionic polymerization, ^{1}H NMR spectra of it-PMMA and methylated st-PMAA for LbL assembly use, FT-IR/ATR spectra of it-PMMA/st-PMAA stereocomplex thin film on silica gels, QCM analysis of LbL assembly with 80 steps, ^{1}H NMR spectra of PMMA obtained with it-PMMA thin film on silica gels, QCM analyses of template polymerizations, and FT-IR/ATR spectra of thin films after template polymerizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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