

## ORIGINAL ARTICLE

# A study on template effects using irregular porous isotactic poly(methyl methacrylate) films constructed with syndiotactic rich poly(methacrylic acid) and isotactic poly(methyl methacrylate)

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To investigate the stereocomplex formation efficiency with various *syndiotactic*-poly(methacrylic acids) (*st*-PMAAs) after the extraction of the syndiotactic-rich PMAA from stereocomplex film, the low syndiotacticity of PMAA ( $rr=78\%$ ) was used to prepare irregular *isotactic* poly(methyl methacrylate) (*it*-PMMA)/*st*-PMAA ( $rr=78\%$ ) stereocomplex thin films on substrates. The resultant irregular porous *it*-PMMA thin films showed effective incorporation of *st*-PMAA ( $rr=78$  and  $96\%$ ), suggesting a structural rearrangement of the *it*-PMMA main chain. However, the template polymerization in porous *it*-PMMA thin films with a monomer of methacrylic acid resulted in a stereoregular replica of the *st*-PMAA, without any rearrangement of the *it*-PMMA. When irregular stereocomplex formation was employed, these results demonstrated a clear difference between polymer–polymer interactions and polymer–monomer interactions and indicated that a high stereoregularity was necessary to achieve strict control of the stereoregular template polymerization on the porous thin film.

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## INTRODUCTION

Template polymerization is a controlled polymerization method that uses a monomer in the presence of an interactive template polymer to control the rate of synthesis of the polymer structure.<sup>1,2</sup> This method has been studied for many decades, primarily to improve the reaction rate. For example, decades ago, Połowiński<sup>3,4</sup> and Takemoto<sup>5–8</sup> reported that the reaction rate had been improved by utilizing a hydrogen bond as the driving force. Sleiman and coworkers successfully polymerized bulky monomers, which had not been polymerized until then, by taking advantage of the hydrogen bonds of the base pairs.<sup>9</sup> Furthermore, Sawamoto and coworkers achieved monomer selective polymerization through electrostatic interactions by adding an initiator to the polymer template.<sup>10</sup> These studies utilized strong interactions between the template polymer and these monomers. Molecular design-based studies can be expected if the polymerization mechanism can be clarified. However, studies have also been performed that used weak interactions (Van der Waals). Recently, Kadokawa and colleagues<sup>11</sup> reported the polymerization of the helical complex of amylase and poly(glycolic acid-*co*- $\epsilon$ -caprolacton), such that the complex structure has a key conformation. This method of polymerization using complex formations has received much attention. However, the precise control of polymer structures using the template approach has been challenging.

We have focused on stereoregular poly(methyl methacrylate)s (PMMA)s, which form stereocomplexes by Van der Waals forces resulting in weak polymer–polymer interactions.<sup>12,13</sup> This complex is composed of a helical structure that is formed from an isotactic (*it*-) polymer and a syndiotactic (*st*-) polymer, which recognize one another's molecular structure.<sup>14–16</sup> The issue of how to achieve template polymerization with a stereocomplex conformation as the driving force has also been investigated. Challa and coworkers as well as other researchers have found a significant difference in reaction rate and stereoregularity,<sup>17–26</sup> but strict control of the polymer structure was not achieved in the solution state. However, we investigated porous thin films on a substrate, which were prepared by layer-by-layer (LbL) assembly using *it*-PMMA and *st*-poly(methacrylic acid) (*st*-PMAA),<sup>27–30</sup> and the subsequent extraction of one component through differential solubility. Surprisingly, we found that the porous film functions as an effective template for the polymerization system.<sup>31–34</sup> This technique gave strict control of the poly(methacrylate) structure, including a high stereoregularity and a low molecular weight distribution (polydispersity: PDI), measured by the radical method.

Recently, we focused on the template polymerization mechanism and a structural analysis of the porous film as a template field. As a comparison, we also investigated a suspension of crosslinked

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stereocomplexes without any substrate.<sup>35</sup> We reported that the molecular recognition capability of the porous thin film on a substrate was higher than the crosslinked polymer. Therefore, it is necessary to collect more detailed information on the template polymerization system, an LbL film on a substrate.

In this study, we used syndiotactic-rich PMAA (*rr* triad = 73 and 78%) and *it*-PMMA (*mm* triad = 95 and 99%) for the stereocomplex formation of porous *it*-PMMA thin films, and methacrylic acid (MAA) was polymerized with the template polymerization approach. We examined the effects of irregularity of the template and low stereoregularity, and the template polymerization mechanism is discussed.

## MATERIALS AND METHODS

### Materials

*it*-PMMA<sup>36</sup> and *st*-PMAA<sup>37</sup> were synthesized by conventional anionic polymerization (Table 1). The average molecular weights and distributions were measured by size exclusion chromatography using PMMA standards with a tetrahydrofuran eluant at 40 °C and a flow rate of 0.6 ml min<sup>-1</sup>. The tacticities were determined from the  $\alpha$ -methyl proton signal using 400 MHz NMR (nitrobenzene-*d*<sub>5</sub>, 110 °C). The characterization of *st*-PMAA was achieved after the carboxyl group was methylated. Acetonitrile, MAA, sodium hydroxide solution (NaOH *aq.*) and radical initiator VA-044 (2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride) were purchased from Wako Pure Chemical Industries (Kanagawa, Japan). Ultrapure distilled water was provided by the Milli-Q laboratory system (Darmstadt, Germany).

### Film preparation and incorporation of *st*-PMAA

An AT-cut quartz crystal microbalance (QCM) with a parent frequency of 9 MHz was obtained from USI (Fukuoka, Japan) and employed as the substrate. The frequency was monitored by an Universal Counter (Model 53131A, Hewlett-Packard Japan, Tokyo, Japan). The quartz crystal (9 mm diameter) was coated on both sides with mirror-like polished gold electrodes (4.5 mm in diameter). First, the QCM electrode was cleaned with a piranha solution, a mixed aqueous solution of 98% H<sub>2</sub>SO<sub>4</sub>/40% H<sub>2</sub>O<sub>2</sub> (3/1, v/v) for 3 min, followed by rinsing with ultrapure water and drying with N<sub>2</sub> gas.<sup>38</sup> The LbL films were prepared as follows: the substrate was alternatively immersed in an *it*-PMMA acetonitrile solution and an *st*-PMAA acetonitrile/water (4/6, v/v) solution at a concentration of 0.017 unitM for 5 min at 25 °C each. The substrate was rinsed with each solvent and dried with N<sub>2</sub> gas whenever taken out of each solution. This alternative deposition step was repeated 16 times to fabricate the stereocomplex of *it*-PMMA/*st*-PMAA on the substrate. Porous *it*-PMMA thin films were prepared by immersion into a 10 mM NaOH aqueous solution for 10 min and washed with ultrapure water.<sup>28,29,32</sup>

### Incorporation of *st*-PMAA into *it*-PMMA porous film

Porous *it*-PMMA thin films were immersed into an *st*-PMAA acetonitrile/water (4/6, v/v) solution at a concentration of 0.017 unitM at 25 °C. Total

immersion time was 2 h. The substrate was rinsed with each solvent, and dried with N<sub>2</sub> gas whenever it was removed from the solution.

### Template polymerization on QCM substrate

Distilled MAA was dissolved in ultrapure water to prepare a 35 mM monomer solution, and the porous *it*-PMMA thin films on the QCM substrate were added to the solution.<sup>32–34</sup> Dry nitrogen gas was handled at room temperature for more than 15 min before use. Then, VA-044 was added under nitrogen atmosphere and heated to 40 °C for 2 h ([I]/[M] = 1/20). After polymerization, the porous *it*-PMMA thin film was washed with ultrapure water, and the frequency shift and Fourier transform infrared spectroscopy (FT-IR) of the porous *it*-PMMA thin film were measured.

### Template polymerization on silica gel

To prepare porous *it*-PMMA thin films, silica gel (2 g, mean diameter 7  $\mu$ m) was alternatively immersed into an *it*-PMMA acetonitrile solution and an *st*-PMAA acetonitrile/water (4/6, v/v) solution at a concentration of 0.017 unitM for 5 min at 25 °C each.<sup>32–34</sup> The substrate was rinsed with each solvent, whenever it was taken out from each solution. This alternative deposition step was repeated 100 times (50 cycles) to fabricate the stereocomplex of *it*-PMMA/*st*-PMAA on the substrate. Porous *it*-PMMA thin films were prepared by immersing stereocomplex films into a 35 ml NaOH aqueous solution (10 mM) three times. Next, 0.3 ml of MAA was dissolved in 100 ml ultrapure water, and the porous *it*-PMMA thin films on silica gel were added to the solution. Dry nitrogen gas was handled for more than 15 min before use, and then VA-044 (57 mg) was added under nitrogen atmosphere and heated to 40 °C for 2 h. Afterwards, the mixture was vented and cooled down to 0 °C to stop the reaction. The silica gel was washed with water to recover recementitious PMAA, which was produced in solution. Then PMAA, which was synthesized in porous *it*-PMMA thin film, was extracted using 10 mM NaOH *aq.* The silica gel with the porous *it*-PMMA thin films was used three times as the template.

### Quartz crystal microbalance

The frequency was monitored by a frequency counter (Model 53131A) and was recorded manually. The QCM leads were sealed and protected with a rubber gel to prevent degradation from the solvent during immersion in the organic solutions and in the heated water. The amount of adsorbed polymers,  $\Delta m$ , could be calculated by measuring the frequency decreases in the QCM,  $\Delta F$  using Sauerbrey's<sup>39</sup> Equation (1)

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

where  $F_0$  is the parent frequency of the QCM (9 MHz),  $A$  is the electrode area (0.159 cm<sup>2</sup>),  $\rho_q$  is the density of the quartz (2.5 g cm<sup>-3</sup>), and  $\mu_q$  is the shear modulus (2.95  $\times 10^{11}$  dyn cm<sup>-2</sup>). This equation was reliable when measurements were taken in air, as described in this study, because the solvent mass is never detected as a frequency shift, and the effect of the viscosity of the absorbent on the frequency can be ignored.

### Infrared spectroscopy

The LbL assembled thin films of *it*-PMMA and *st*-PMAA were prepared on QCM substrates or silica gels. Attenuated total reflection IR spectra of the thin films were then obtained with a Spectrum 100 FT-IR spectrometer (Perkin-Elmer, Waltham, MA, USA). The interferograms were co-added eight times and Fourier transformed at a resolution of 4 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

We employed QCM analysis to calculate the amount of the stereocomplex film and the porous *it*-PMMA thin film assembled onto a gold substrate, and the amount of *st*-PMAA incorporated into porous *it*-PMMA thin films by Sauerbrey's equation.<sup>38,39</sup> A typical QCM analysis is shown in Figure 1. The stepwise stereocomplex assembly of *it*-PMMA/*st*-PMAA and the selective extraction of *st*-PMAA from the assembled films was confirmed in previous studies.<sup>28–35,40</sup> To confirm the preparation of porous films, another experiment

**Table 1** Material polymer in this study<sup>a</sup>

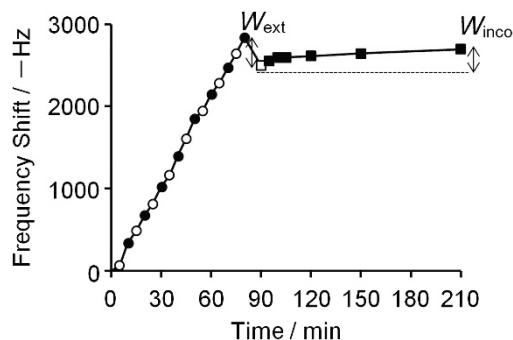
Polymer name	Tacticity <sup>b</sup> <i>mm:mr:rr</i>	$M_n^c$	PDI <sup>c</sup>
<i>it</i> -PMMA-1	95: 4: 1	14 700	1.50
<i>it</i> -PMMA-2	99: 1: 0	52 700	1.42
<i>st</i> -PMAA-1	3:24:73	18 200	2.20
<i>st</i> -PMAA-2	3:24:73	50 400	2.20
<i>st</i> -PMAA-3	1:21:78	60 800	1.41
<i>st</i> -PMAA-4	1: 3:96	15 200	1.71

Abbreviations: *it*-PMMA, isotactic-poly(methyl methacrylate); *st*-PMAA, syndiotactic-poly(methacrylic acid).

<sup>a</sup>*st*-PMAA were synthesized by anion polymerization and analyzed after methylation with diazomethane.

<sup>b</sup>Determined by <sup>1</sup>H NMR spectra in nitrobenzene-*d*<sub>5</sub> at 110 °C (400 MHz).

<sup>c</sup>Determined by size exclusion chromatography (SEC) with PMMA standard in tetrahydrofuran (THF) at 40 °C.



**Figure 1** Typical figure of quartz crystal microbalance (QCM) analysis of stepwise assembly from an *isotactic*-poly(methyl methacrylate) 2 (*it*-PMMA-2) ( $mm=99\%$ ) acetonitrile solution (white circle) and a *syndiotactic*-poly(methacrylic acid) 3 (*st*-PMAA-3) ( $rr=78\%$ ) solution of mixed acetonitrile/water (4/6, v/v) solvent (black circle), extraction of *st*-PMAA with 10 mM NaOH aq. (white square), and incorporation with porous *it*-PMMA film into *st*-PMAA-3 ( $rr=78\%$ ) solution of mixed acetonitrile/water (4/6, v/v) solvent (black square).

**Table 2** Results of complex efficiency (CE)

Run	Polymer	Tacticity <sup>a</sup> <i>mm:mr:rr</i>	$M_n^b$	CE (%)
1	<i>st</i> -PMAA-1	3:24:73	18200	66 ± 20
2	<i>st</i> -PMAA-3	1:21:78	60800	91 ± 39
3	<i>st</i> -PMAA-4	1:3:96	15200	> 100

Abbreviation: *st*-PMAA, *syndiotactic*-poly(methacrylic acid).

<sup>a</sup>Determined by <sup>1</sup>H NMR spectra in nitrobenzene-*d*<sub>5</sub> at 110 °C (400 MHz).

<sup>b</sup>Determined by SEC with PMMA standard in tetrahydrofuran (THF) at 40 °C.

was carried out and this result suggested that the extraction of *st*-PMAA from the assembled films was achieved within 10 min (see Supplementary Information; Supplementary Figure S1).

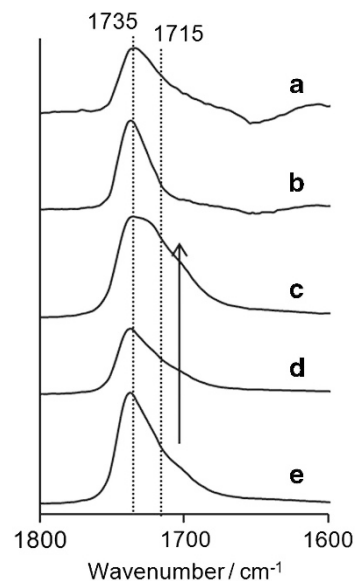
The incorporation capability was estimated using the complex efficiency (CE), which is defined as

$$CE(\%) = (W_{\text{inco}}/W_{\text{ext}}) \times 100 \quad (2)$$

where  $W_{\text{inco}}$  is the increased weight in the incorporation stages and  $W_{\text{ext}}$  is the decreased weight in the *st*-PMAA extraction stages.

Unlike previous reports, the amount of *st*-PMAA extracted at the NaOH aq. step was very low, most likely because it was difficult to form perfect stereocomplex pairs due to the low stereoregularity of the *st*-PMAA at the LbL assembly steps and because the *st*-PMAA-3 ( $rr=78\%$ ) might be rinsed away at each *it*-PMMA-2 assembly step. The small amount of extracted *st*-PMAA suggests that an excess amount of *it*-PMMA was present on the substrate. When the same stereoregularity, *st*-PMAA-3 ( $rr=78\%$ ), was incorporated after the extraction, the CE had reasonable values of 91 ± 39% ( $n=4$ ) (Table 2, Run 2). Thus, this film has nanoporous functionality within a large margin of error, fitting in with the syndiotactic-rich ( $rr=78\%$ ) stereoregularity. This result suggested that the molecules were not aligned in order and this porous *it*-PMMA thin film was unsound. This outcome most likely occurred because stereocomplex formation with the *it*-PMMA ( $mm>90\%$ ) and the *st*-PMAA ( $rr<90\%$ ) was only partially achieved.

Next, to investigate more functions of this porous film, other *st*-PMAAs with different tacticities and molecular weights were incorporated into ‘irregular’ porous *it*-PMMA films. Because a previous

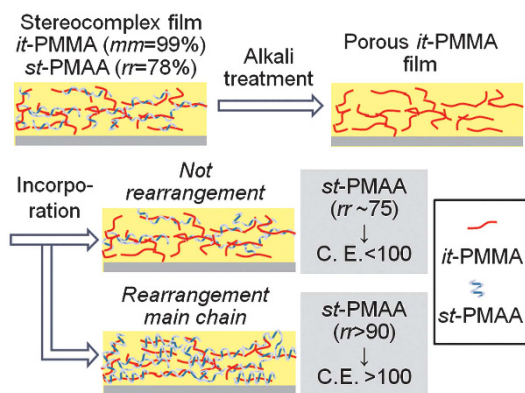


**Figure 2** FT-IR/attenuated total reflection (ATR) spectra of stereocomplex film (a), porous *isotactic*-poly(methyl methacrylate) (*it*-PMMA) film (b), incorporated with *syndiotactic*-poly(methacrylic acid) 4 (*st*-PMAA-4) ( $rr=96\%$ ) (c), incorporated with *st*-PMAA-3 ( $rr=78\%$ ) (d), and incorporated with *st*-PMAA-1 ( $rr=73\%$ ) (e).

report showed that low-*syndiotactic*-PMAA ( $rr \sim 60\%$ ) was hardly incorporated into ‘regular’ porous films,<sup>40</sup> we tried to compare with PMAA with an  $rr=73\%$  or greater, which is a similar  $rr$  value to *st*-PMAA in LbL preparation in current experiments. These results are shown in Table 2.

In the case of low stereoregularity *st*-PMAA, the polymer with a low molecular weight ( $rr=73\%$ ,  $M_n=18200$ ) has a lower CE; 66 ± 20% ( $n=4$ ) (Table 2, run 1) than that of *st*-PMAA-3 ( $rr=78$ ,  $M_n=60800$ ) (Table 2, run 2), most likely due to the low Van der Waals forces secondary to the low molecular weight. Surprisingly, highly stereoregular *st*-PMAA-4 ( $rr=96\%$ ,  $M_n=15200$ ) was incorporated into the porous *it*-PMMA thin film with a CE of >100%, estimated to be 680% from QCM frequency shift, against the extraction polymer (Table 2, run 3). This result indicates that the excess *it*-PMMA during the LbL process can be associated with the associating *st*-PMAA-3 ( $rr=78\%$ ), which was loosely constructed, suggesting that the stereocomplex formation was increased by a rearrangement of the *it*-PMMA. In other words, structural changes in the porous *it*-PMMA thin film toward the ideal stereocomplex were found, accompanied by a rearrangement of the polymer conformation on the substrate that was different from the solid and liquid phases.

To examine such a strange incorporation behavior, the FT-IR spectra were analyzed (Figure 2). Compared with the stereocomplex film (Figure 2a), the peak intensity under 1700  $\text{cm}^{-1}$  of porous *it*-PMMA film had decreased (Figure 2b). From this peak change, it is likely that the complete extraction of *st*-PMAA was achieved with NaOH solution. This result is consistent with the previous report.<sup>28</sup> Corresponding with an increase in *st*-PMAA incorporated into the porous thin films, the peak intensity near 1715  $\text{cm}^{-1}$  increased. This result was derived from the stereocomplexing *st*-PMAA (Figures 2c–e). In particular, Figure 2c indicates significant stereocomplex formation. If a large amount of *st*-PMAA physically adsorbed on the film surface, then the peak intensity at approximately 1650  $\text{cm}^{-1}$  would have been measured in the FT-IR spectra. How-



**Figure 3** Schematic illustrations of molecular structure in stereocomplex films and porous *isotactic*-poly(methyl methacrylate) (*it*-PMMA) film which were dependent on the tacticity of *syndiotactic*-poly(methacrylic acid) (*st*-PMAA). CE, complex efficiency.

ever, the increased peak intensity is barely visible in this area (Figure 2c). Therefore, the detected polymer weight increase in QCM could show incorporation and stereocomplexation.

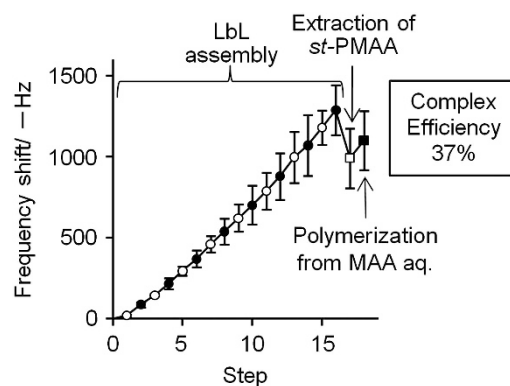
This result suggests that *st*-PMAA-4 ( $rr=96\%$ ) can form a stereocomplex with the *it*-PMMA in the porous film—which was prepared with *st*-PMAA-3 ( $rr=78\%$ )—more easily than normal physical absorption. A schematic illustration is shown in Figure 3 of the initial irregular stereocomplex due to the *st*-PMAA-3 ( $rr=78\%$ ) that leads to an excess incorporation of *st*-PMAA-4 ( $rr=96\%$ ).

Table 2 shows the possibility of synthesizing polymers with high tacticity. Therefore, we synthesized PMAA within porous *it*-PMMA thin film. At first, we employed a QCM substrate to confirm the template polymerization with the irregular film (Figure 4). The progress of polymerization was monitored by the frequency shift of the QCM measurements and the FT-IR spectra. The polymerization efficiency was estimated at 37%, which is lower than in the previous report, supporting the theory of random conformation of the polymer.<sup>28,31</sup>

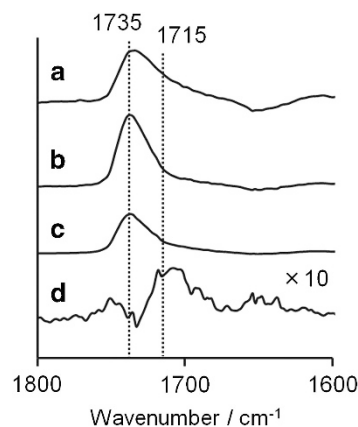
In addition, the FT-IR spectra showed the presence of polymerized PMAA in the porous films (Figure 5c). The spectrum of the thin film after polymerization showed a peak intensity increasing near  $1715\text{ cm}^{-1}$ . In this case, the peak intensity was so weak that the differential spectrum was investigated (shown in Figure 5d). The method of differential spectroscopy has been reported in a previous study.<sup>34</sup> This result implied that the polymerization of MAA occurred in porous *it*-PMMA thin films.

We were also interested in the stereoregularity of the synthesized PMAA, but the quantity of synthesized polymer in the porous *it*-PMMA thin film on the QCM substrate was too small to characterize. Therefore, to investigate the stereoregularity of the PMAA synthesized in the porous *it*-PMMA thin film, a larger amount of stereocomplex was prepared for NMR analysis on a silica gel as a substrate from 100 steps of LbL. The stereocomplex film on the silica gel was verified by FT-IR spectroscopy, including the intensities dependent on the LbL steps (Figure 6). In Figure 6, the gradual increase of the  $1735\text{ cm}^{-1}$  peak that suggests the formation of a stereocomplex and that the stereocomplex film was prepared on the silica gel surface sequentially.

Next, the *it*-PMMA porous thin film was prepared and examined. Template polymerization was achieved under the same polymerization conditions, temperature, and time as in the previous study.<sup>29,32,33</sup>



**Figure 4** Quartz crystal microbalance (QCM) analysis of stepwise assembly from an *isotactic*-poly(methyl methacrylate) (*it*-PMMA-2) ( $mm=99\%$ ) acetonitrile solution (white circle) and a *syndiotactic*-poly(methacrylic acid) 3 (*st*-PMAA-3) ( $rr=78\%$ ) solution of mixed acetonitrile/water (4/6, v/v) solvent (black circle), extraction of *st*-PMAA with 10 mM NaOH aq. (white square), and polymerization from MAA aq. in porous *it*-PMMA film (black square) ( $n=3$ ).



**Figure 5** FT-IR/attenuated total reflection (ATR) spectra of *isotactic*-poly(methyl methacrylate) 2 (*it*-PMMA-2) ( $mm=99\%$ )/*syndiotactic*-poly(methacrylic acid) 3 (*st*-PMAA-3) ( $rr=78\%$ ) stereocomplex film (a), porous *it*-PMMA film (b), after polymerized film (c), and differential spectrum from (c) to (b) shown in (d).

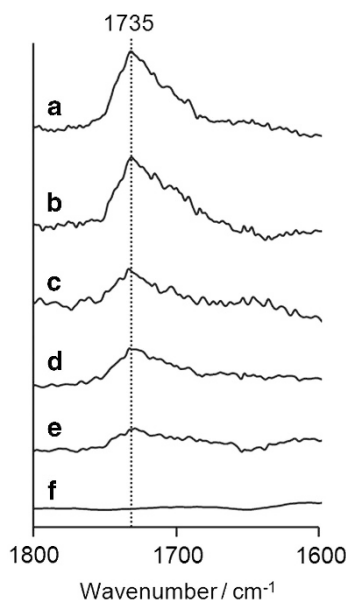
After polymerization, the synthesized polymer was extracted with an alkali solution and was purified by reprecipitation. This extraction method was established in previous studies as well.<sup>29,32,33</sup> The results of the template polymerization with  $^1\text{H}$  NMR and SEC are shown in Table 3, and the typical  $^1\text{H}$  NMR spectra are depicted in Figure 7.

The tacticity of the PMAA synthesized in porous *it*-PMMA thin films was close to that of the *st*-PMAA, which was employed for the initial LbL stereocomplex formation (Table 3, run 1). Interestingly, the tacticity of the synthesized PMAA showed a higher value than the PMAA, which was synthesized in solution (Table 3, run 1 and run 2). This result suggests that the tacticity of the synthesized PMAA is moderately controlled by the porous nano-space. Upon changing the solvent from water to a mixture of water and acetonitrile, the tacticity of the synthesized PMAA became closer to that of the extracted *st*-PMAA used with LbL assembly (Table 3, run 1 and run 3). However, the molecular weight changed dramatically and the molecular weight dispersion (PDI) increased, indicating that the solvent, which contributes to the solubility of the monomer, the



radical initiator, and the synthesized polymer, influenced the template efficiency. Next, we investigated the effect of surface area by changing the amount of the silica gel (Table 3, run 7 and run 8). These PMMA had tacticity and molecular weight values that were similar to the extracted *st*-PMAA. This similarity of tacticity and molecular weight value showed similar results to run 1 and run 2 in Table 3. In short, it was shown that the size of the porous *it*-PMMA thin film did not affect the product, and the irregular LbL film was mostly affected to synthesize PMAA.

Finally, we tried to reproduce the recycle reaction (Table 3, run 5 and run 6).<sup>33</sup> Notably, the tacticities ( $rr=77\%$  for run 5 and  $78\%$  for run 6 in Table 3) showed almost the same values, with slightly increased syndiotacticity. The details are still unclear, but this

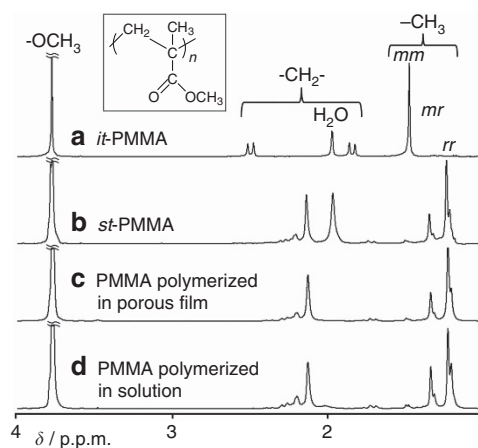


**Figure 6** FT-IR/attenuated total reflection (ATR) differential spectra of *isotactic*-poly(methyl methacrylate) 2 (*it*-PMMA-2) ( $mm=99\%$ )/*syndiotactic*-poly(methacrylic acid) 3 (*st*-PMAA-3) ( $rr=78\%$ ) stereocomplex film on silica particles with 50 cycles (a), 40 cycles (b), 30 cycles (c), 20 cycles (d), 10 cycles (e), and silica particles (f).

outcome could be due to a rearrangement of the *it*-PMMA in the irregular film, which approached a regular conformation through heating during the polymerization process.

## Conclusions

We investigated the behavior of *st*-PMAA incorporation into irregular porous *it*-PMMA thin films, which were constructed with *st*-PMAA-3 ( $rr=78\%$ ) and *it*-PMMA-2 ( $mm=99\%$ ). Interestingly, we observed reforming behavior of the *it*-PMMA conformation in the porous films upon stereocomplexation with the higher *st*-PMAA-4 ( $rr=96\%$ ). The presented results suggested that *it*-PMMA in porous films functions as an effective template for polymerization. However, this reforming ability was not observed for the polymerization reaction from monomer feeding. The stereocomplexation efficiency for polymerization might be different than that from polymer–polymer interactions. On the other hand, the irregular porous film, where the polymer structure was non-uniform,



**Figure 7**  $^1\text{H}$  NMR spectra of *isotactic*-poly(methyl methacrylate) 2 (*it*-PMMA-2) ( $mm=99\%$ ) (a), *syndiotactic*-PMMA (from *st*-PMAA-3) ( $rr=78\%$ ) (b), obtained poly(methacrylic acid) (PMAA) from radical polymerization in porous *it*-PMMA film (Table 3, run3) (c), and polymerized in acetonitrile/ $\text{H}_2\text{O}$  (4/6, v/v) solution (Table 3, run 4) (d). These samples were measured in nitrobenzene- $d_5$  at  $110^\circ\text{C}$  (400 MHz). PMMA of (b), (c), and (d) were synthesized from PMAA with methylation.

**Table 3** Results of polymerization<sup>a</sup>

Run	Polymer name	Polymerize solvent	Scale ml	Monomer mmol	Yield		Tacticity <sup>b</sup> mm:mr:rr	$M_n^c$	PDI <sup>c</sup>
					mg	%			
1	PMAA synthesized in porous film	$\text{H}_2\text{O}$	100	3.5	49	100 <sup>d</sup>	3:27:70	50800	1.44
2	PMAA synthesized in solution				53	75 <sup>e</sup>	4:31:65	65200	1.55
3	PMAA synthesized in porous film	$\text{MeCN}:\text{H}_2\text{O}$ (4:6)	100	3.5	53	88 <sup>d</sup>	2:22:76	19700	2.38
4	PMAA synthesized in solution				148	70 <sup>e</sup>	3:27:70	15700	3.30
5	Second recycle				52	87 <sup>d</sup>	2:21:77	27500	2.36
6	Third recycle				41	68 <sup>d</sup>	2:20:78	26000	2.84
7	PMAA synthesized in porous film	$\text{MeCN}:\text{H}_2\text{O}$ (4:6)	300	10.5	119	92 <sup>d</sup>	3:32:65	47500	1.80
8	PMAA synthesized in solution				736	80 <sup>e</sup>	5:33:62	34200	2.20

Abbreviations: *it*-PMMA, *isotactic*-poly(methyl methacrylate); PMAA, poly(methacrylic acid); *st*-PMAA-3, *syndiotactic*-poly(methacrylic acid) 3.

<sup>a</sup>Monomer concentration was 35 M ( $[M]/[I]=1/20$ ). Porous *it*-PMMA film were prepared from *it*-PMMA-2 ( $mm:mr:rr=99:1:0$ )/*st*-PMAA-3 ( $mm:mr:rr=1:21:78$ ) stereocomplex film (Run 1–6) and *it*-PMMA-1 ( $mm:mr:rr=95:4:1$ )/*st*-PMAA-2 ( $mm:mr:rr=3:24:73$ ) stereocomplex film (Run 7 and 8). PMAA were analyzed after methylation with diazomethane.

<sup>b</sup>Determined by  $^1\text{H}$  NMR spectra in nitrobenzene- $d_5$  at  $110^\circ\text{C}$  (400 MHz).

<sup>c</sup>Determined by SEC with PMMA standard in tetrahydrofuran (THF) at  $40^\circ\text{C}$ .

<sup>d</sup>Calculated by the equation: (synthesized PMAA)/(extracted *st*-PMAA from stereocomplex film)  $\times 100$ .

<sup>e</sup>These values mean conversion which were calculated by the equation: (synthesized PMAA)/(total reactant)  $\times 100$ .

can synthesize a low stereoregularity polymer with a value the same as the extracted polymer. In addition, strict control of the molecular weight and molecular weight distribution (PDI) was achieved using a low stereoregularity polymer. Furthermore, the present experiments revealed that polymerization in a porous film template can have narrow PDI values that are similar to the PDI values of free radical polymerization. Thus, it is important to use highly stereoregular polymers ( $mm > 90\%$  and  $rr > 90\%$ ) to form the initial stereocomplex film to transfer the stereoregularity of the polymer of the porous thin film. These results show the difference between polymer–polymer interactions and monomer–polymer interactions and give essential insights into template polymerization systems and nano-space synthesis chemistry.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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