

REVIEW ARTICLES

## Stereoregular Polymerization within Template Nanospaces

Takeshi SERIZAWA<sup>1</sup> and Mitsuru AKASHI<sup>2,†</sup>

<sup>1</sup>Research Center for Advanced Science and Technology (RCAST), The University of Tokyo,  
4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan

<sup>2</sup>Department of Molecular Chemistry, Graduate School of Engineering, Osaka University,  
2-1 Yamada-oka, Suita 565-0871, Japan

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**ABSTRACT:** Highly efficient stereoregular polymerizations within template nanospaces using free radical initiators, based on stereocomplexes formed between isotactic and syndiotactic methacrylate polymers are reviewed. Ultrathin films composed of double-stranded helical or van der Waals contacted stereocomplex nanostructures were successfully prepared by the layer-by-layer assembly method, and fundamental aspects of film preparation were summarized. Template nanospaces were prepared by the selective solvent extraction of a single component from stereocomplex films composed of it-poly(methyl methacrylate) and st-poly(methacrylic acid). The resulting porous films with designed nanospaces were used for template polymerizations. Methacrylate polymers with high iso- and syndiotacticities were synthesized within nanospaces. Structural information not only of template stereoregularity but also of template chain length was efficiently transferred to synthesized polymers. [DOI 10.1295/polymj.38.311]

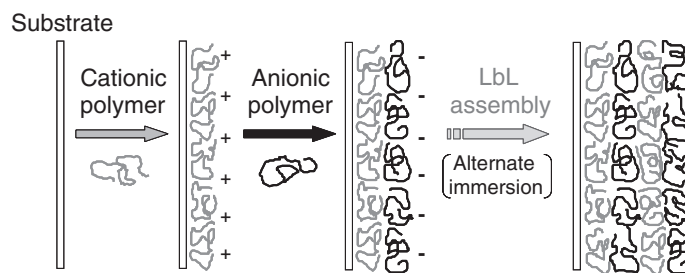
**KEY WORDS** Polymerization / Template / Stereocomplex / Film / Stereoregularity /

Template polymerization in regularly structured enzymatic nanospaces results in the efficient synthesis of biomacromolecules such as polynucleotides and proteins.<sup>1</sup> Multivalent and non-covalent interactions composed of hydrogen bonds and van der Waals interactions are frequently utilized for the coordination of monomer polymerization using biomacromolecule templates. This approach is attractive and challenging for the *in vitro* precision synthesis of synthetic and biorelated polymers.<sup>2–9</sup> Biomacromolecules have 3-dimensional and higher-order nanostructures which self-assemble in a given environment. Although molecularly regulated structures seem to be restricted to aqueous phase biomacromolecules, similarly regulated nanostructures, which self-assemble in certain organic solvents, are known to form combinations of synthetic polymers such as methacrylate polymers,<sup>10–19</sup> polyesters,<sup>20,21</sup> and poly(amino acid)s.<sup>22–24</sup> Stereocomplexes are formed between structurally well-defined synthetic polymers in certain solvents, or in films with structural fittings between polymer chains or between lateral functional groups with van der Waals contacts. For instance, isotactic (it) and syndiotactic (st) poly(methyl methacrylate)s (PMMA)s artificially form double stranded helical stereocomplexes in polar organic solvents on the basis of structural fitting with van der Waals interactions,<sup>10–14</sup> in which complex it-PMMA is surrounded by twice the length of st-PMMA.<sup>25–28</sup>

Researchers are highly interested in the double-stranded moiety of PMMA stereocomplexes as an adequate assembly system to perform *in situ* free radical template syntheses of stereoregular PMMA in the presence of a single PMMA.<sup>29–38</sup> Although the stoichiometry of the complex is different from that of nucleic acids, template polymerization is inspired by template syntheses of polynucleotides and proteins under mild physiological conditions.<sup>1</sup> However, the structural transcription of templates to polymers synthesized by this polymerization method has thus far been insufficient. Polymerization has been demonstrated under restrictive conditions such as low conversions, low temperatures, and high molecular weights of templates.<sup>29</sup> Since biological systems synchronously utilize sophisticated nanospaces produced by proper enzymes as well as template effects, solvated polymers with random and dynamic conformations are not suitable polymerization templates. In order to overcome this problem, we propose herein a free radical polymerization process within nanospaces fabricated by polymer templates as porous ultrathin films, based on double stranded or van der Waals contacted stereocomplexes formed between it-PMMA and st-poly(methacrylic acid) (st-PMAA).<sup>39,40</sup>

Our approach for precision template polymerization is comprised of the following three steps: step 1, which is the most important step, the fabrication of ultrathin films composed of stereocomplexes formed

<sup>†</sup>To whom correspondence should be addressed (Tel: +81-6-6879-7356, Fax: +81-6-6879-7359, E-mail: akashi@chem.eng.osaka-u.ac.jp).



**Figure 1.** Schematic representation of LbL assembly of polyelectrolyte multilayers.

between it-PMMA and st-PMAA; step 2, the selective extraction of a single component from films, to fabricate porous films with template nanopores; step 3, the free radical polymerization of monomers within nanopores and the characterization of selectively extracted resulting polymers. To fabricate ultrathin stereocomplex films on surfaces, we applied stereocomplex formation to layer-by-layer (LbL) assembly, which is normally used for the fabrication of polyelectrolyte multilayers through electrostatic polyion complex formation, as schematically shown in Figure 1.<sup>41–50</sup> LbL assembly can be demonstrated by the alternate immersion of substrates into interactive polymer solutions, which fabricates films with a controllable nanometer thickness. The concept of LbL assembly means that we can assemble certain polymers by stabilizing them on a substrate after adsorption due to polymeric interactions. Thus, this process should be potentially applicable to the formation of stereoregular PMMA stereocomplexes.

Although detailed studies of stereocomplex formation between structurally regular polymers have been performed,<sup>10–14</sup> no research has utilized stereocomplex characteristics for the stepwise fabrication of ultrathin polymer assemblies on a substrate. The stepwise stereocomplex assembly on a substrate would require the structural rearrangement of a pre-adsorbed polymer, possibly from a random conformation during the subsequent adsorption process of the second stereoregular PMMA, in order to form regular nanostructures. In this case, the polymers would have huge steric requirements during formation. The *in-situ* assembly of ultrathin stereocomplex films has more general implications regarding dynamic events involving polymeric interactions at ultrathin polymer film surfaces. In other words, the stereocomplex formation suggests that a dynamic conformational change in polymers adsorbed onto a film's surface is available for the ultrathin film assembly process. No one knows whether polymers at the interface can interact with other polymers exhibiting conformational changes. Resulting films, with regular structures, might have potential functions.

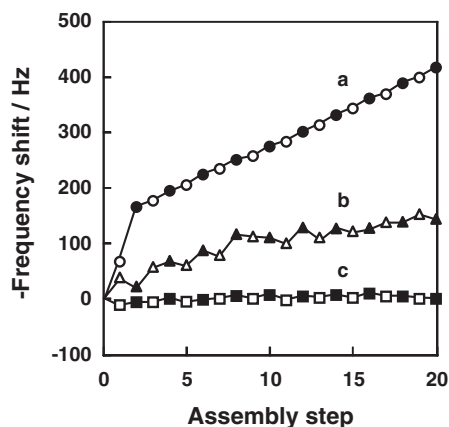
In this review, we will demonstrate a highly effi-

cient stereoregular polymerization process using free radical initiators within template nanopores, which can be prepared by the selective extraction of a single component from structurally regular ultrathin stereocomplex films composed of it-PMMA and st-PMAA. Before the preparation of nanopores, fundamental aspects of film fabrication based on the LbL assembly method are summarized. In order to quantify the amount of assembled polymers on surfaces to a nanogram level, we used a 9-MHz quartz-crystal microbalance (QCM) as a substrate. QCM frequency decreases ( $-\Delta F$ ) were converted to the mass of polymers assembled ( $\Delta m$ ) using Sauerbrey's equation,<sup>51</sup> in conjunction with the analysis of other measurements. The present system will not only lead to ultrathin polymer films with novel functions, but may also serve as a model for studying the novel concept of polymeric interactions at interfacial regions.

#### FUNDAMENTAL ASPECTS OF STEREOCOMPLEX ASSEMBLY ON SURFACES

##### *Quantitative Analysis of Assembly between It- and St-PMMA*

For the first fundamental combination, we selected the assembly of it- and st-PMMA.<sup>52</sup> Stereocomplex formation between it- and st-PMMA in organic solutions is known to be dependent on solvent species. Herein, we selected acetonitrile, acetone, and DMF, which are known to be strong complexing solvents.<sup>12</sup> Figure 2 shows the dependence of frequency shifts on assembly steps, when the QCM was alternately immersed in it-PMMA ( $M_n$  20750,  $M_w/M_n$  1.26,  $mm:mr:rr = 97:2:1$ ) and st-PMMA ( $M_n$  22700,  $M_w/M_n$  1.26,  $mm:mr:rr = 0:11:89$ ) solutions in three solvents at a PMMA concentration of  $1.7 \text{ mg mL}^{-1}$  for 15 min immersion times at ambient temperature. It is clear that acetonitrile was the best solvent for PMMA assembly in large amounts, as shown in Figure 2a. When the QCM was immersed in it- or st-solution alone for a much longer time, the frequency shift saturated to a level obtained during the first step of the assembly process. This observation suggests that the stereocomplex of stereoregular PMMA was produced



**Figure 2.** Frequency shift of QCM by the stepwise assembly from organic solutions of it- and st-PMMA at a concentration of  $1.7 \text{ mg mL}^{-1}$ : from (a) acetonitrile; (b) acetone; (c) DMF solutions. Open and closed symbols show it- and st-PMMA steps, respectively. Reprinted with permission from T. Serizawa *et al.*, *J. Am. Chem. Soc.*, **122**, 1891 (2000).<sup>52</sup> © 2000, American Chemical Society.

on the QCM. In the initial two steps, larger frequency shifts were observed, possibly due to the direct influence of the QCM gold substrate on the assembly amount. The frequency shift after a 20-step assembly was  $-416 \text{ Hz}$  with an experimental error of  $\pm 5\%$ . The shift corresponded to an adsorption of  $362 \text{ ng}$ , and the film thickness was estimated to be  $9.7 \text{ nm}$ , assuming a density for solid PMMA ( $1.188 \text{ g cm}^{-3}$ ). The estimated thickness was consistent with the thickness that was obtained by scratching the assembly on a QCM substrate using an AFM tip ( $9.7 \pm 0.3 \text{ nm}$ ). When the assembly was demonstrated without drying, the total frequency shift was not affected, indicating that the drying process is not essential for the stepwise assembly.

All of the solvents used in these experiments are known to promote complex formation in solutions.<sup>12</sup> Significantly, the amount of complex formed in DMF solution is almost the same as that formed in acetonitrile; although the formation in acetone was not studied under the same conditions. Accordingly, assembly on a QCM substrate is not related directly to the complex formation behavior in solutions. It is difficult to explain why we observed different behaviors between substrate surfaces and within solutions. A possible reason is derived from the solubility of PMMA in the above solvents, because the present assembly is based on physical adsorption of PMMAs onto a substrate. In general, both the solubility and the nature of the substrate affect polymer adsorption on surfaces. Studies have indicated that poor solubility and strong interaction with substrate surfaces promote polymer adsorption.<sup>53</sup> Herein, the substrate remained the same, and the solvent was changed. Acetonitrile was the

poorest solvent for PMMA,<sup>54</sup> when compared to other solvents. The poor solubility of PMMA in acetonitrile promoted assembly on the substrate, followed by the stepwise formation of stereocomplexes on substrate surfaces. The present data suggest that solvent selection is a key factor in the stepwise assembly of stereoregular PMMAs. A system using acetonitrile solutions was used in the following characterization of stereocomplex films.

The amount of PMMA adsorbed by each assembly step was analyzed using the QCM method. Researchers have experimentally and theoretically studied the length ratio between assembled it- and st-PMMA in mixed solutions, and have estimated it to be 1:2,<sup>25–28</sup> indicating that the amount of the stereocomplex formed between it- and st-PMMAs should be 1:2, due to the same chemical structure. In the case of the acetonitrile solvent, the mean ratio was obtained from it-PMMA to st-PMMA because stereocomplex formation seemed to occur during this step (see below). The mean ratio was determined as  $2.0 \pm 0.4$  from QCM measurements. The previous value is significantly consistent with values obtained in solution.<sup>25–28</sup> This observation strongly suggests that it- and st-PMMAs assembled on substrates by stereocomplex formation similar to what was observed in solution. In addition, frequency shifts of physically adsorbed it- and st-PMMAs on a QCM were  $-71$  and  $-23 \text{ Hz}$ , respectively, and the ratio did not approach 2. It is noted that we ignored the initial two steps in the estimation of the st/it ratio because of the relatively larger assembling amount.

Further details of the stepwise frequency shift shown in Figure 2a were evaluated by performing assembly in a system that started with st-PMMA. In aforementioned assemblies, we started from it-PMMA. For a detailed analysis, the st/it ratio was calculated both from the it-PMMA to st-PMMA step and from the st-PMMA to it-PMMA step. Mass ratios in Figure 2a were  $2.0 \pm 0.4$  and  $1.8 \pm 0.8$ , respectively. The former ratio was around 2 with a small experimental error as mentioned above, while the latter was close to 2, but had a larger experimental error. The aforementioned difference suggests that the stereocomplex formed during the step from it-PMMA to st-PMMA. When assembly was started with st-PMMA, ratios were  $2.0 \pm 0.3$  and  $2.3 \pm 1.0$ , respectively, which were similar to values obtained when starting with it-PMMA, suggesting that the stereocomplex was formed at the st-PMMA immersion step.

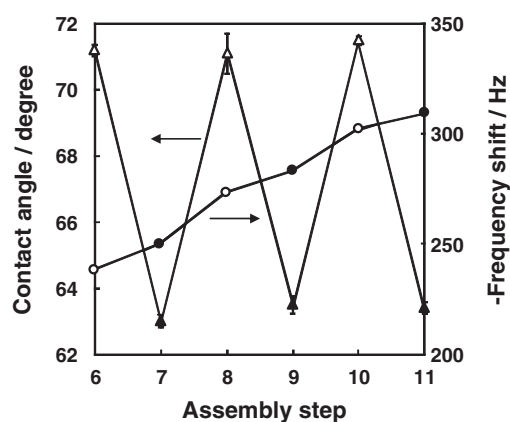
The frequency shift at each assembly step was analyzed in acetonitrile solutions at  $4^\circ\text{C}$ . A stepwise frequency shift was also observed. However, the amount of it- and st-PMMAs assembled at each step was three and two times greater than that assembled at ambient

temperature, respectively. The assembly mass ratio was  $1.4 \pm 0.6$ , which is smaller than that observed at ambient temperature. It is well known that it- and st-PMMA self-associate depending on solvent species.<sup>12</sup> In fact, when the PMMA solution was kept at 4 °C for a few weeks, a precipitate was observed. The larger assembly amount might be caused by precipitation on the surface. In addition, it- or st-PMMA may have difficulty rearranging into the complex, possibly due to a lower molecular mobility at the lower temperature. The stereocomplex might be formed in an interfacial region between it- and st-PMMA films, and may result in a structurally sandwiched assembly as the temperature changes. In fact, static contact angles of it- and st-steps were  $63.4 \pm 0.4$  and  $73.3 \pm 0.3$  degrees, respectively, which were consistent with values for each homogeneous film (see below). Temperatures as well as solvents affect the stepwise stereocomplex assembly of stereoregular PMMAs on a substrate. As a consequence, PMMAs were assembled at ambient temperature.

#### Structural Analysis of Assembled Films

Static contact angles on the air side of film surfaces of it- and st-PMMA are significantly different from each other due to the selective accumulation of functional groups at surfaces.<sup>55</sup> This characteristic is useful for monitoring the stepwise stereocomplex assembly of stereoregular PMMAs on substrates. In this section, static contact angles from ultrathin film surfaces that were prepared by the stepwise assembly of it- and st-PMMA from acetonitrile solutions were analyzed.

Figure 3 shows the dependence of the static contact angle, together with the frequency shift, on assembly



**Figure 3.** Static contact angle of the film assembled from acetonitrile solutions of it- and st-PMMA at a concentration of  $1.7 \text{ mg mL}^{-1}$ . Open and closed symbols show it- and st-PMMA steps, respectively. Reprinted with permission from T. Serizawa *et al.*, *J. Am. Chem. Soc.*, **122**, 1891 (2000).<sup>52</sup> © 2000, American Chemical Society.

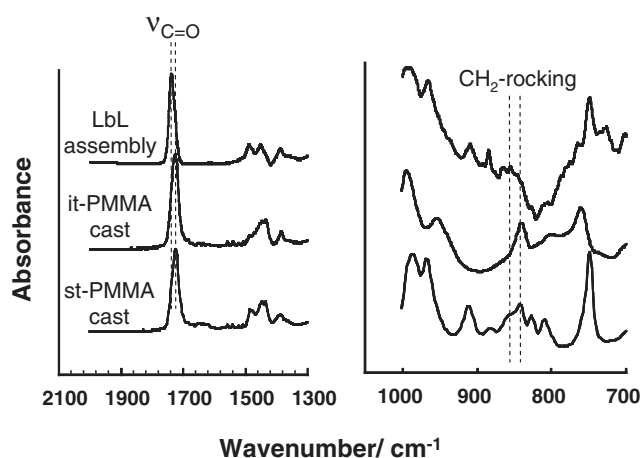
steps when the QCM was alternately immersed into acetonitrile solutions of it- and st-PMMA. The contact angle changed with the step number, thereby suggesting the stepwise assembly of stereoregular PMMAs on the substrate. Furthermore, the contact angle at an odd or even step, which corresponds to it- or st-PMMA assembly, was almost the same value within experimental error, indicating the same molecular composition or conformation at the film surface. The mean contact angle at odd it-PMMA assembly steps was  $63.3 \pm 0.3$  degrees. This value was comparable to  $63.0 \pm 0.3$  degrees, the angle of the adsorbed bulk it-PMMA film on the bare QCM substrate (in this case,  $\Delta F = -71 \text{ Hz}$ ). These are reasonable contact angle values compared to values for bulk films previously reported by Tretinnkov,<sup>55</sup> although the it-PMMA used in the present study had a higher isotacticity than reported polymers. The contact angle of the adsorbed it-PMMA was consistent with that of its cast film. Note that the contact angle of a bare gold surface of a QCM is  $44 \pm 1$  degrees in air. Accordingly, it may be considered that the surface of the it-PMMA step was completely covered by it-PMMA molecules alone. If the hypothesized structure of the stereocomplex<sup>25–28</sup> was assumed, it-PMMA will be buried in the helical structure of st-PMMA and the contact angle should change accordingly. Therefore, it-PMMA must be physically adsorbed onto the surface of the previously formed PMMA complex. It is significant that the it-PMMA layer was not replaced by st-PMMA in the complex film even after 1 h, although replacement may preferably have occurred in order to minimize the interfacial free energy (the static contact angle of the st-PMMA film is greater than that of the it-PMMA,<sup>55</sup> as also described below). These observations possibly indicate that the inner st-PMMA has a stable structure and is fixed by stereocomplex formation with inner it-PMMA, and never replaced the film surface.

On the other hand, the mean value at even st-PMMA assembly steps was  $71.2 \pm 0.4$  degrees, which was slightly smaller than a previously reported value of the st-PMMA film surface,<sup>55</sup> and smaller than that ( $73.2 \pm 0.8$  degrees) of a physically adsorbed st-PMMA film on a QCM ( $-\Delta F = 23 \text{ Hz}$ ) within experimental error. This observation is quite meaningful, because the contact angle of the st-PMMA step is possibly the real contact angle of the PMMA stereocomplex surface. Although the contact angle of the completed stereocomplex formed on the PMMA film surface has not been previously reported, the contact angle may be slightly smaller than that for the st-PMMA layer because the more hydrophilic ester group in st-PMMA than other groups in PMMA should point outwards in the molecular structure of



the stereocomplex.<sup>27</sup> Note that st-PMMA on film surfaces usually tends to direct alkyl main chains in air, in order to minimize the interfacial free energy.<sup>55</sup> Therefore, it is concluded that the surface composition of the ultrathin PMMA film was altered by the stepwise assembly of stereoregular PMMAs, possibly by the physical adsorption of it-PMMA without stereocomplex formation at it-PMMA steps and by the stereocomplex formation at st-PMMA steps on surfaces. The assembly mechanism was also supported by the aforementioned QCM quantitative results of ratios between assembled PMMAs.

Infrared spectroscopy is a powerful tool for analyzing stereocomplex formation of stereoregular PMMAs, as previously reported by other researchers.<sup>12,56–60</sup> When a film of a nm-order thickness is analyzed, the reflection absorption spectrum (RAS) is a powerful tool because it can detect the weaker absorption by ultrathin films. The absorption band of main-chain CH<sub>2</sub>-rocking vibrations at around 840–860 cm<sup>-1</sup> in addition to C=O-stretching vibrations at around 1700–1800 cm<sup>-1</sup> is available for evaluating stereocomplex formation.<sup>12</sup> Herein, we measured the RAS of assembled PMMA films in order to analyze the formation, as shown in Figure 4. PMMAs were 20-step assembled from acetonitrile-water mixed solutions (10/1.5, v/v), resulting in greater assembled amounts.<sup>52</sup> The main peak in CH<sub>2</sub>-rocking absorption for the assembly was at approximately 860 cm<sup>-1</sup>, together with a shoulder peak at approximately 840 cm<sup>-1</sup>. Peak positions were significantly different from those of cast films of it- and st-PMMAs, thereby suggesting stereocomplex formation between it- and st-PMMAs on the substrate. It was previously reported



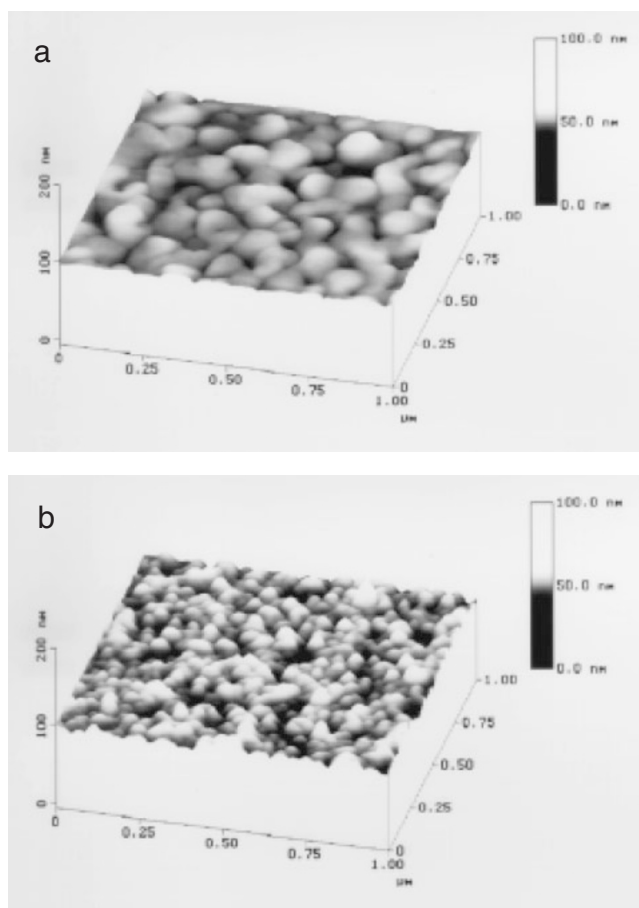
**Figure 4.** RAS of assembled films of it- and st-PMMAs at a concentration of 1.7 mg mL<sup>-1</sup> from acetonitrile/water, 10/1.5 (v/v) solutions, and attenuated total reflection (ATR) spectra of the cast films of it- and st-PMMA. Reprinted with permission from T. Serizawa *et al.*, *J. Am. Chem. Soc.*, **122**, 1891 (2000).<sup>52</sup> © 2000, American Chemical Society.

that the absorption band at 860 cm<sup>-1</sup> is observed when st-PMMA associates. However, acetonitrile is not a good solvent for self-association.<sup>12</sup> The absorption band at 860 cm<sup>-1</sup> for the self-association was also a shoulder peak appearing together with a main peak at 840 cm<sup>-1</sup>. On the other hand, CH<sub>2</sub>-rocking absorption bands for the present assembled films were different from those of the cast film obtained from the mixed solution. In the cast film, the main peak was at 840 cm<sup>-1</sup> and complex formation was not sufficiently promoted. Furthermore, C=O-stretching vibration bands for assembled films were shifted and the absorption peak was observed at a higher wavenumber compared to those of cast films. The band representing skeletal stretching vibrations observed at 758 cm<sup>-1</sup> might also be assigned to that of the stereocomplex. The previous observations strongly suggest that the stepwise assembly of stereoregular PMMAs is based on stereocomplex formation on surfaces.

Atomic force microscopy (AFM) is useful for the analysis of the surface topology of films. Herein, we analyzed PMMA assembled film surfaces that were prepared on the QCM from acetonitrile. Prior to the AFM analysis, the surface of a bare QCM gold surface was analyzed to investigate the roughness of the substrate. Figure 5a shows the AFM image of a bare QCM surface. The surface domain-like structure of the sputtered gold film on an electrode was observed. The mean diameter and height of the domain was analyzed to be 150 ± 60 and 5 ± 2 nm, respectively, and the mean roughness (*R<sub>a</sub>*) was 1.8 nm. On the other hand, Figures 5b shows the AFM image of a 20-step assembled PMMA film that was prepared from acetonitrile solutions on the QCM. It is significant that the image showed a domain-like structure that was different from those on a bare QCM electrode. The mean diameter and height of the domain was 60 ± 10 and 11 ± 2 nm, respectively, and the *R<sub>a</sub>* was 4.3 nm, which was more than three times greater than that of the bare QCM, but was nonetheless relatively smooth. The heights were smaller than the mean film thickness. It was therefore found that the PMMA assembled film showed a domain-like and smooth surface structure on the gold QCM substrate.

#### Assembly Mechanism of Stereocomplex Films

We have to discuss how the stereocomplex of stereoregular PMMAs forms on surfaces. On the basis of quantitative QCM and contact angle results, the stereocomplex appears to form during the assembly step from it-PMMA to st-PMMA, thereby resulting in an st-/it-PMMA mass ratio of 2. In this case, the physical adsorption of it-PMMA onto the assembly is reasonable if we consider that it adsorbs onto surfaces of stably formed stereocomplex assemblies as a result of



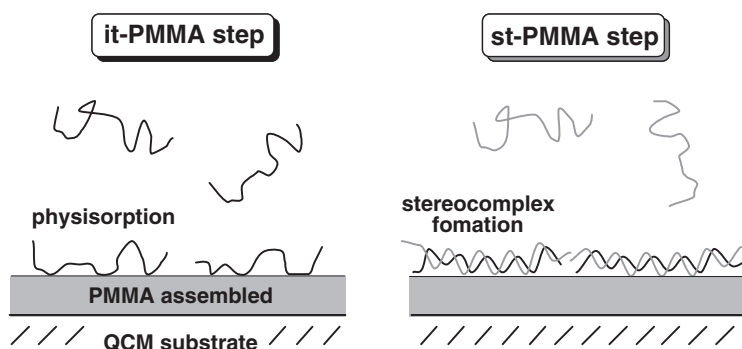
**Figure 5.** AFM images of (a) a bare QCM electrode and (b) the 20-step assembled film of it- and st-PMMA at a concentration of  $1.7 \text{ mg mL}^{-1}$  from acetonitrile. Reprinted with permission from T. Serizawa *et al.*, *J. Am. Chem. Soc.*, **122**, 1891 (2000).<sup>52</sup> © 2000, American Chemical Society.

poor-solvent driven physisorption.<sup>53</sup> In fact, the amount of it-PMMA adsorbed increased upon the addition of water as a poor solvent, so that the assembled amount of it- and st-PMMA increased.<sup>52</sup> However, this does not explain why excess or lower amounts of st-PMMA do not adsorb onto the it-PMMA layer. In other words, why does the amount of st-PMMA result in the observed complex stoichiometry? A possi-

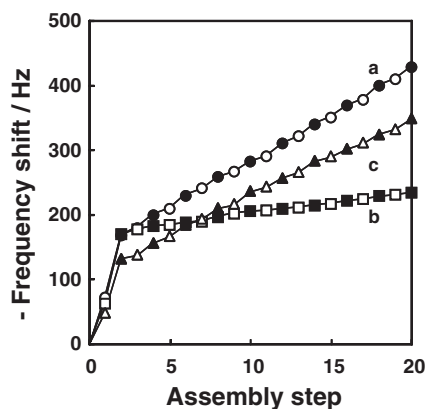
ble explanation is as follows. Less than one-third of the st-PMMA physically adsorbed onto a bare QCM surface than that observed with it-PMMA. Moreover, when the physical adsorption of each PMMA onto spin-coated atactic PMMA was analyzed, the amount of st-PMMA adsorbed was similarly smaller than that adsorbed by it-PMMA. These observations suggest that st-PMMA has a lower property for physical adsorption. Accordingly, st-PMMA can assemble onto it-PMMA on the film surface specifically by forming a strongly interactive stereocomplex. This must be the reason why excess or lower amounts of st-PMMA do not adsorb onto it-PMMA surfaces. It is significant that the stereocomplex assembly occurs during the step from it-PMMA to st-PMMA. If we recall the double stranded helical structure, in which it-PMMA is surrounded by twice the length or mass of st-PMMA, it-PMMA may have difficulty penetrating into physically adsorbed st-PMMA to form the complex. Both the physical adsorptive nature of the stereoregular PMMA and the double stranded structure seem to strongly affect the stepwise stereocomplex assembly onto surfaces. As a consequence, we concluded that assembly occurred during the step from physically adsorbed it-PMMA to st-PMMA with a molecular rearrangement that was initialized by the penetration of st-PMMA into the it-PMMA layer. The assembly mechanism of stereocomplex films is schematically shown in Figure 6.

#### Application to Other Stereocomplexes

Syndiotactic methacrylate polymers in double stranded helical stereocomplex do not necessarily need to be made with PMMA, because methyl ester groups of st-PMMA are oriented toward the outside of stereocomplexes. Therefore, combinations of it-PMMA and other st-poly(alkyl methacrylate)s also form similar stereocomplexes.<sup>15,16</sup> It is necessary to analyze the fabrication of stereocomplex films with st-polymers that have bulky side chains, to confirm the stepwise stereocomplex assembly on surfaces. In



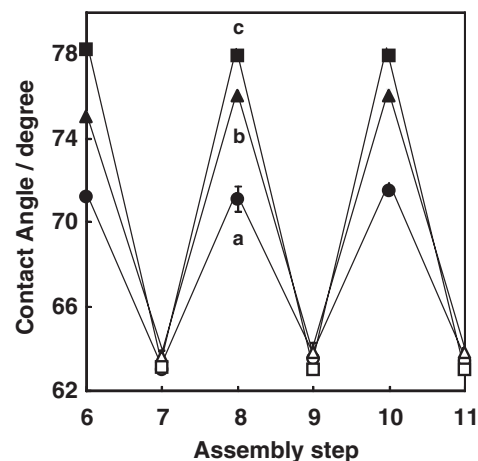
**Figure 6.** Schematic representation of the PMMA stereocomplex assembly on surfaces. Reprinted with permission from T. Serizawa *et al.*, *J. Am. Chem. Soc.*, **122**, 1891 (2000).<sup>52</sup> © 2000, American Chemical Society.



**Figure 7.** Frequency shift of QCM with a stepwise assembly from acetonitrile solutions at a concentration of  $1.7 \times 10^{-2}$  unitM composed of (a) it-PMMA and st-PMMA, (b) it-PMMA and st-PHEMA, (c) it-PMMA and st-PPMA ( $M_n$  23800). Open and closed symbols show it-PMMA and st-polymer steps, respectively. Reprinted with permission from K.-I. Hamada *et al.*, *Langmuir*, **17**, 5513 (2001).<sup>61</sup> © 2001, American Chemical Society.

this section, we analyzed the stepwise assembly of it-PMMA with st-poly(ethyl methacrylate) (PEMA) and st-poly(propyl methacrylate) (PPMA) on surfaces from acetonitrile solutions.<sup>61</sup> The QCM substrate was also used to quantify the amount of assembled polymers to a the nano-gram level, and to facilitate the analysis of static contact angles.

Figure 7 shows the dependence of frequency shifts on assembly steps when the QCM was alternately immersed in combinations between it-PMMA ( $M_n$  20750,  $M_w/M_n$  1.26,  $mm:mr:rr = 97:2:1$ ) and st-PMMA ( $M_n$  22700,  $M_w/M_n$  1.26,  $mm:mr:rr = 0:11:89$ ), st-PHEMA ( $M_n$  21340,  $M_w/M_n$  1.11,  $mm:mr:rr = 1:8:91$ ), or st-PPMA ( $M_n$  23800,  $M_w/M_n$  1.09,  $mm:mr:rr = 2:7:91$ ) solutions for 15 min at ambient temperature at a concentration of  $1.7 \times 10^{-2}$  unitM. Frequencies decreased with increasing assembly steps in all cases, thus indicating a stepwise polymer deposition possibly based on stereocomplex formation. In the initial two steps, larger frequency shifts were observed, due to the direct influence of the gold QCM substrate on the assembly process. When we immersed the QCM in an it- or st-polymer solution alone for a much longer time, the frequency shift saturated at a level obtained in a single step of the assembly process. The previous observations also suggest stereocomplex formation between stereoregular polymers on surfaces. Frequency shifts after a 20-step assembly between it-PMMA and st-PMMA, st-PHEMA, or st-PPMA were  $-416$ ,  $-239$ , and  $-402$  Hz, respectively. Film thickness was estimated from frequency decreases to be 9.7, 5.5, and 9.3 nm, respectively, assuming a density for solid PMMA ( $1.188 \text{ g cm}^{-3}$ ). These values were consistent with those obtained by scratching as-



**Figure 8.** The static contact angle of the film assembled from acetonitrile solutions at a concentration of  $1.7 \times 10^{-2}$  unitM of (a) it-PMMA and st-PMMA, (b) it-PMMA and st-PHEMA, (c) it-PMMA and st-PPMA. Open and closed symbols show it-PMMA and st-polymer steps, respectively. Reprinted with permission from K.-I. Hamada *et al.*, *Langmuir*, **17**, 5513 (2001).<sup>61</sup> © 2001, American Chemical Society.

semblies with an AFM tip ( $9.7 \pm 0.3$ ,  $5.4 \pm 0.5$ , and  $9.4 \pm 0.6$  nm, respectively). It is difficult to reasonably explain why the assembled amount was lowest with the combination of it-PMMA and st-PHEMA. Herein, the same it-PMMA was utilized for all assemblies. The stepwise assembly was generated by complex formation of the st-polymers with the physically adsorbed it-PMMA (see below). From these observations, the physical adsorptive property of it-PMMA on the complex surface prepared from it-PMMA and st-PHEMA seems to be the smallest.

In the quantitative QCM analysis, the possibility of stereocomplex formation on QCM surfaces was demonstrated. In each stereocomplex, the stoichiometry (length ratio) between it-PMMA and st-polymers of methacrylates is significant, because other research groups have experimentally and theoretically studied the ratio between stereoregular PMMAs in mixed solutions, and have estimated it to be 1:2 (it-PMMA:st-PMMA, length:length).<sup>25–28</sup> It is possible to discuss similar stereocomplex formations between it-PMMA and st-poly(alkyl methacrylate)s. In the case of the present assemblies, mean length ratios (st-/it-polymers) determined from QCM analyses were  $2.0 \pm 0.4$ ,  $1.8 \pm 0.5$ , and  $2.5 \pm 0.5$ , respectively, which were estimated from the it-PMMA to st-poly(alkyl methacrylate) step, except for the initial two steps, and which suggested stereocomplex formation.

We also analyzed static contact angles for monitoring the stepwise assembly of the stereoregular polymers on the substrate. Figure 8 shows the dependence of angles on each assembly step. The angle alternately changed with each step, indicating a stepwise assem-

bly on surfaces. Mean angles at odd it-PMMA steps using water droplets were  $63.3 \pm 0.3$ ,  $63.7 \pm 0.5$ , and  $63.0 \pm 0.3$  degrees for the it-PMMA assembly with st-PMMA, st-PEMA, and st-PPMA, respectively. These values were essentially the same within experimental error, and were consistent with  $63.0 \pm 0.3$  degrees, which is the angle of a bulk it-PMMA film. Therefore, we concluded the surface following immersion in it-PMMA to be completely covered by homogeneous it-PMMA.

On the other hand, mean angles at even st-poly(alkyl methacrylate) steps were  $71.2 \pm 0.4$ ,  $75.7 \pm 0.5$ , and  $78.0 \pm 0.6$  degrees, respectively, which differed from one another. These values were slightly smaller than  $73.2 \pm 0.8$ ,  $78.7 \pm 0.7$ , and  $80.3 \pm 0.6$  degrees, which represent angles for bulk st-PMMA, st-PEMA, and st-PPMA films, respectively. The aforementioned observations suggest that stereocomplex formation occurs at each even step, although the ideal contact angle of the stereocomplex surface has not been reported. It is significant that the angle for the present assemblies increased with increasing st-polymer alkyl chain lengths. It is noted that alkyl ester groups of st-poly(alkyl methacrylate)s point outward in assembled structures of double-stranded stereocomplexes, as Challa *et al.* reported.<sup>27</sup> Our observations support stereocomplex formation between it-PMMA and st-poly(alkyl methacrylate)s on surfaces. It was concluded that the surface composition of each ultrathin film was altered by the stepwise assembly, possibly due to the physical adsorption of it-PMMA and by stereocomplex formation between it-PMMA and st-poly(alkyl methacrylate)s on surfaces. Infrared spectra and AFM analyses also supported the stepwise stereocomplex assembly (data not shown).

As a consequence, we found that it-PMMA and st-poly(alkyl methacrylate)s also assembled on surfaces from acetonitrile solutions by the same assembly mechanism as that of stereoregular PMMAs. Furthermore, stereocomplexes formed between racemic crystals formed between D- and L-poly(lactide)s (the details are not described here) were also applicable to film formation.<sup>62,63</sup> It is therefore conceivable that there are generalizations in the stepwise preparation of ultrathin polymer films that use stereocomplex formations on surfaces.

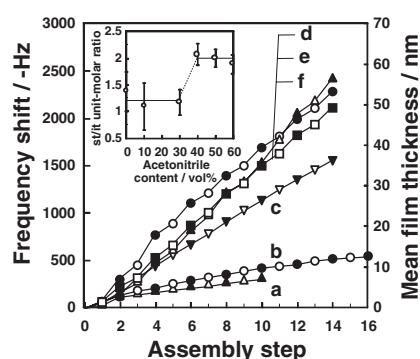
## STEREOREGULAR POLYMERIZATION IN POROUS TEMPLATE NANOSPACES

### *Stereocomplex Assembly of It-PMMA and St-poly(methacrylic acid)*

A stereocomplex is formed not only between it- and st-poly(alkyl methacrylate)s.<sup>10–16</sup> but also between it-PMMA and st-poly(methacrylic acid) (PMAA).<sup>17,18</sup>

Solvent selection for the latter polymer is a significant factor in stepwise assembly, because it-PMMA can dissolve in organic solvents, and st-PMAA in aqueous phases. If solvation of polymers at film surfaces affects stepwise stereocomplex formations, the complex assembly of polymers solubilized in different solvents can be used to manipulate stereocomplex film formation. In addition, the stepwise assembly of polymers includes various applications such as additional surface modification of the assembly through a carboxyl group of st-PMAA, and solvent extraction of one component based on differential solubility. The extracted film will thus have a porous structure, which can be utilized as a host film against stereoregular polymers of methacrylates<sup>64</sup> and as nanospaces for stereoregular template polymerization.<sup>39,40</sup> In this section, the stepwise assembly of it-PMMA and st-PMAA based on stereocomplex formation on surfaces was analyzed by the QCM technique on the basis of static contact angle analyses, RAS, and AFM observations.<sup>65</sup>

In previous studies of stereocomplex formation between it-PMMA and st-PMAA,<sup>17,18</sup> 1:2-stereocomplex formation using an 83 vol % ethanol/water mixed solvent was reported. However, the mixed solvent was unable to dissolve it-PMMA ( $M_n$  20750,  $M_w/M_n$  1.26, *mm:mr:rr* = 97:1:2) under the same conditions, possibly due to differences in molecular weights or tacticities. Furthermore, we have successfully assembled it- and st-polymers of methacrylates using acetonitrile or acetonitrile/water solvents.<sup>52,61</sup> Therefore, acetonitrile and acetonitrile/water mixtures were utilized as it-PMMA and st-PMAA ( $M_n$  37940,  $M_w/M_n$  1.77, *mm:mr:rr* = 1:2:97) solvents, respectively. Figure 9 shows frequency shifts corresponding to assembled amounts against each assembly step from



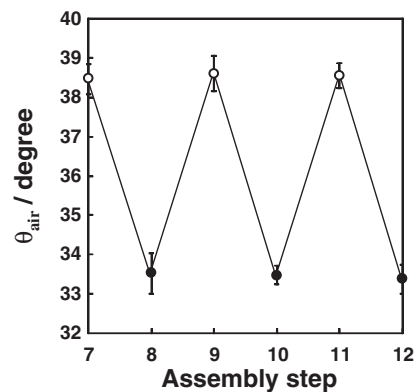
**Figure 9.** QCM analyses of a stepwise assembly from an it-PMMA acetonitrile solution and a st-PMAA solution of mixed acetonitrile/water (v/v) solvents: (a) water, (b) 10/90, (c) 30/70, (d) 40/60, (e) 50/50, (f) 60/40. Open and closed symbols show it-PMMA and st-PMAA steps, respectively. Reprinted with permission from T. Serizawa *et al.*, *Langmuir*, **16**, 7112 (2000).<sup>65</sup> © 2000, American Chemical Society.



both an it-PMMA acetonitrile solution ( $0.17 \text{ mg mL}^{-1}$ ,  $1.7 \times 10^{-2} \text{ unitM}$ ) and an st-PMAA acetonitrile/water mixed solution ( $0.15 \text{ mg mL}^{-1}$ ,  $1.7 \times 10^{-2} \text{ unitM}$ ) for each 15 min immersion at  $25^\circ\text{C}$ . An st-PMAA solution with an acetonitrile content of more than 60 vol % was not prepared due to the poor solubility of st-PMAA. The frequency decreased with each step due to the stepwise assembly of polymers, and the assembled amount increased with increasing contents of acetonitrile. The thickness of the assembly was controllable at each step within the order of a nanometer scale. The thickness in Figure 9d after the 14-step assembly was estimated to be 48 nm. A stepwise deposition was not observed by the repetitive immersion in each polymer solution. The inset of Figure 9 shows the length ratio of st-PMAA and it-PMMA assembled against the acetonitrile content. The length ratio was obtained from a mean value of mass ratios at the step from it-PMMA to st-PMAA. The ratio dramatically changed between 30 and 40 vol % of acetonitrile in the st-PMAA solution. Ratios ranged from 1 to 1.5 with less than 30 vol % acetonitrile, while they were approximately 2 above 40 vol %. Note the former ratio contains a larger experimental error.

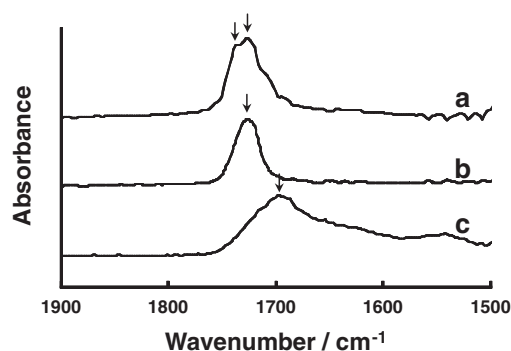
Challa *et al.*<sup>18</sup> analyzed stereocomplex formation between the present polymers with 1/1 or 2/1 length stoichiometry (st-PMAA/it-PMMA) depending on the solvent species, on the basis of solution viscosity measurements. The 2/1 stoichiometry was observed using the 83 vol % ethanol/water mixed solvent. Based on this knowledge, it is reasonable to suggest that the double-stranded stereocomplex formed above a 40 vol % acetonitrile content during the stepwise assembly. To form double-strands on film surfaces, drastic conformational changes in the pre-adsorbed it-PMMA are necessary, and/or penetration of st-PMAA into the it-PMMA layer is necessary. These observations are reasonable if we consider that it-PMMA on the film surface is slightly swollen by the acetonitrile contained in the mixed st-PMAA solvent. The solvation might facilitate the necessary change, even though it-PMMA does not dissolve in mixed acetonitrile/water (4/6–6/4, v/v) solvents. It is difficult to explain the increase in the amount of assembled polymers observed above 30 vol %, as shown in Figure 9. Although this observation can be explained by the difference in the amount of it-PMMA physically adsorbed onto the complex assembly, a further study of this topic is necessary.

Assemblies prepared from it-PMMA acetonitrile and st-PMAA acetonitrile/water (4/6, v/v) solutions were characterized in detail. Figure 10 shows the static contact angle with pure water droplets measured in atmospheric air at ambient temperature at each assembly step. The angle was alternately changed, therefore



**Figure 10.** Static contact angle analysis of stepwise assembly. Open and closed symbols show it-PMMA and st-PMAA steps, respectively. Reprinted with permission from T. Serizawa *et al.*, *Langmuir*, **16**, 7112 (2000).<sup>65</sup> © 2000, American Chemical Society.

confirming the stepwise polymer assembly. The angles were  $38.5 \pm 0.4$  and  $33.5 \pm 0.4$  degrees at the it-PMMA and st-PMAA steps, respectively. Polymer cast film contact angles were  $63.0 \pm 0.3$  and  $21.5 \pm 0.4$  degrees, respectively. The difference in measured angles between the stepwise assembly and the cast film may be due to the following reasons. At the it-PMMA step, the hydrophilic stereocomplex layer might be partially exposed on the surface, resulting in a smaller angle than measured on the it-PMMA cast film. On the other hand, swelling of the st-PMAA cast film by water molecules may render its angle smaller than that at the complex surface. In other words, st-PMAA in the assembly could be less swollen than in the cast film, possibly due to complex formation. Figure 11 shows RAS results from the assembled film and from each cast film. Two carbonyl vibration bands assigned to it-PMMA ( $1736 \text{ cm}^{-1}$ ) and st-PMAA ( $1726 \text{ cm}^{-1}$ ) were observed for the assembled film. The larger peak for st-PMAA was reliable based on



**Figure 11.** (a) RAS of a 14-step assembly in Figure 1d, (b) and (c) ATR spectra of it-PMMA and st-PMAA cast films, respectively. Arrows show each peak top. Reprinted with permission from T. Serizawa *et al.*, *Langmuir*, **16**, 7112 (2000).<sup>65</sup> © 2000, American Chemical Society.

quantitative QCM results. Each band in the assembled film shifted to a higher wavenumber compared to bands for cast films of it-PMMA ( $1726\text{ cm}^{-1}$ ) and st-PMAA ( $1695\text{ cm}^{-1}$ ). The aforementioned observation demonstrates stereocomplex formation according to previous papers.<sup>52,59,61</sup> AFM images of the QCM substrate and the resulting assembled film were clearly different from that of the QCM surface, indicating assembly of the polymers (data not shown).

Assembly of it-PMMA and st-PMAA from acetonitrile and acetonitrile/water mixed solutions with a suitable acetonitrile content, respectively, by alternate immersion of substrates was demonstrated based on stereocomplex formation. A 2/1 length stoichiometry (st-PMAA/it-PMMA) in the complex assembly was observed above a certain acetonitrile content in the mixed solvent of st-PMAA, suggesting that a double-stranded helical complex was prepared; other characteristics also support complex formation.

#### Fabrication of Template Nanospaces in Films

The creation of molecular recognition systems with a suitable chemical design formolecular assemblies is of great interest.<sup>66–70</sup> Most recognition systems target small molecules. The recognition of synthetic linear polymers using certain assemblies seems to be relatively difficult due to the lack of a regular conformation with spatially oriented functional groups. In this section, we demonstrate a macromolecular recognition system resulting from the incorporation of st-polymers of methacrylic acid or methacrylates into the ultrathin it-PMMA film designed by LbL assembly on the basis of stereocomplex formation (Figure 12).<sup>64</sup> The resulting molecular recognition concept can be

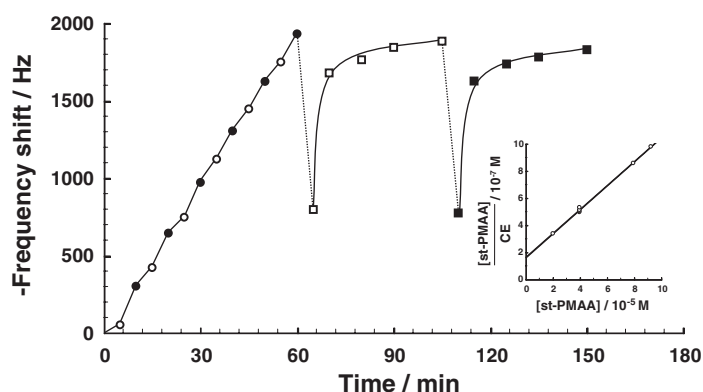


**Figure 12.** Schematic representation of the selective extraction of st-PMAA from the LbL assembly of it-PMMA and st-PMAA on the basis of stereocomplex formation, and the subsequent incorporation of st-polymers of methacrylic acid or methacrylates. Reprinted with permission from T. Serizawa *et al.*, *Angew. Chem., Int. Ed.*, **42**, 1118 (2003).<sup>64</sup> © 2003, Wiley-VCH.

applied to template polymerization in the following section.

After the stereocomplex assembly of it-PMMA ( $M_n$  20750,  $M_w/M_n$  1.26,  $mm:mr:rr = 97:1:2$ ) and st-PMAA ( $M_n$  37940,  $M_w/M_n$  1.26,  $mm:mr:rr = 1:2:97$ ) on the QCM surface, the immersion of the assembly in a 10 mM sodium hydroxide aqueous solution for 5 min resulted in a drastic frequency increase, thus indicating desorption of some of the polymers from the assembly (Figure 13). There was no additional frequency change with a longer term immersion, in which several hours had elapsed, thereby suggesting the selective extraction of st-PMAA, which can be readily dissolved in an aqueous alkaline solution (see following IR data). The extracted amount was consistent with that of st-PMAA assembled on the substrate, possibly indicating a 100% extraction of st-PMAA. St-PMAA was successfully extracted from the stereocomplex film assembled with it-PMMA and st-PMAA.

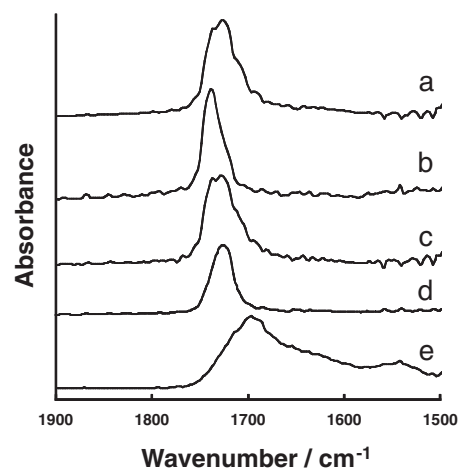
Subsequently, st-PMAA was incorporated into the



**Figure 13.** QCM analysis of the LbL assembly, the selective extraction, and the subsequent st-PMAA incorporation. The it-PMMA (○) in acetonitrile and st-PMAA (●) in an acetonitrile/water (4/6, v/v) were alternately assembled on a QCM substrate for a 12-step assembly at the concentration of 0.017 unitM at 25 °C, following to our previous study.<sup>65</sup> A dotted line shows the selective extraction process of st-PMAA in a 10 mM NaOH aqueous solution for 5 min, in order to obtain the designed host it-PMMA film. St-PMAA was subsequently incorporated in the it-PMMA film from the acetonitrile/water (4/6, v/v) solution at the concentration of 0.017 unitM at 25 °C (□). The extraction and incorporation was repeated again (■). The inset shows the apparent Langmuir plot, in order to obtain and the maximum complexing efficiency and the apparent incorporation constant. Reprinted with permission from T. Serizawa *et al.*, *Angew. Chem., Int. Ed.*, **42**, 1118 (2003).<sup>64</sup> © 2003, Wiley-VCH.

resulting it-PMMA film from the solution (0.017 unitM) with a complexing efficiency of approximately 80% (Figure 13). The efficiency was calculated as the percent incorporation of st-PMAA against the film it-PMMA, assuming that the complex was formed with an ideal stoichiometry (2/1 length ratio of st-PMAA/it-PMMA). The incorporation saturated over time. The extraction from the stereocomplex assembly was significantly repeated at least three times, and the subsequent incorporation of st-PMAA was also observed with the same complexing efficiency at the same concentration. This extraction-incorporation process could be repeated several times. Incorporation with the same efficiency suggests that the process was governed by a certain incorporation constant. The Langmuirian plot of the complexing efficiency showed a linear relationship (coefficient of variation;  $R^2 = 0.998$ ), as shown in the inset of Figure 13. The apparent incorporation constant was analyzed to be  $5.4 \times 10^4 \text{ M}^{-1}$ . This is the first time an affinity constant for the stereocomplex was estimated by structural fitting with van der Waals interactions. The maximum complexing efficiency was estimated to be 113%. The maximum efficiency was more than 100%. St-PMAA, which is partially incorporated into the host film, might be present on the film surface. In fact, the efficiency persisted even after a  $110^\circ\text{C}$  thermal treatment of the film, although the glass transition temperature of the it-PMMA film was approximately  $90^\circ\text{C}$ .<sup>71</sup> The aforementioned observation suggests that a structurally stable film was prepared using the present method. Furthermore, constants for st-PMAA with a smaller  $M_n$  of 14400 and 4650 were  $1.5 \times 10^4 \text{ M}^{-1}$  and  $7.0 \times 10^3 \text{ M}^{-1}$ , suggesting that the constant increased with increasing molecular weight. Atactic PMAA was not incorporated into the porous it-PMMA film, indicating that the above incorporation occurred by complementary stereocomplex formation.

RAS in carbonyl vibration band regions were utilized for the detection of complex formation and to obtain conformational information (Figure 14). There were two peaks for the assembled film at  $1737$  and  $1725 \text{ cm}^{-1}$ , which were assigned to it-PMMA and st-PMAA, respectively (Figure 14a). Only a single peak was observed at  $1739 \text{ cm}^{-1}$  after extraction using an alkaline solution (Figure 14b), meaning that a single polymer component was completely extracted from the assembled film. The peak position was almost the same at the higher wavenumber for the film, suggesting that st-PMAA was successfully extracted from the assembled film; the conformation (or micro environment) of it-PMMA remained after the extraction. The two peaks were also observed after immersion into an st-PMAA solution (Figure 14c), thereby resulting in a recovery of the complex assembly. It

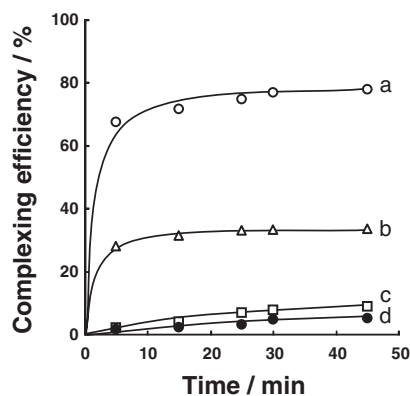


**Figure 14.** RAS of the LbL assembly of it-PMMA and st-PMAA for a 12-step assembly (a), the extracted film (b), the st-PMAA incorporated film (c), a cast film of it-PMMA (d), and a cast film of st-PMAA (e). Films were similarly prepared on a gold-sputtered poly(ethylene terephthalate) film, as shown above. Reprinted with permission from T. Serizawa *et al.*, *Angew. Chem., Int. Ed.*, **42**, 1118 (2003).<sup>64</sup> © 2003, Wiley-VCH.

is significant that the peak intensity corresponding to st-PMAA was smaller than that for the assembled film, which is reasonable because the complexing efficiency was smaller and around 80% at the incorporating st-PMAA concentration as shown in the QCM analysis.

Film surface topologies and thickness on QCM substrates were directly analyzed by AFM (original images not shown). The  $R_a$  of the surface of assembled films was 2.6 nm (1.8 nm for QCM). The thickness estimated by scratching with the AFM cantilever was  $43.6 \pm 4.3$  nm. The roughness after the extraction of st-PMAA was 3.2 nm, which was slightly rougher than before, indicating a molecular-level extraction at the surface. However, it is surprising that the thickness was  $44.1 \pm 3.8$  nm, which was not changed by the extraction. The previous observation strongly suggests that an it-PMMA film with a macromolecularly porous structure was obtained. It is however difficult to reasonably explain why the porous it-PMMA film is not compressed. The terminals of it-PMMA, which do not correlate with the stereocomplex, might support the 3-dimensional film structure even after the extraction of a single st-PMAA component. The roughness recurred with the incorporation of st-PMAA (2.6 nm), and the thickness was the same ( $42.9 \pm 4.6$  nm), thus suggesting a reversible change in only the surface topography.

The structurally regular porous it-PMMA film, which was prepared by the selective extraction of st-PMAA from the LbL assembled film composed of it-PMMA and st-PMAA, was utilized as a host for the incorporation of other st-poly(alkyl methacrylate)s



**Figure 15.** The time dependence of the complexing efficiency for the incorporation of st-PMAA (a), st-PMMA (b), st-PEMA (c), and st-PPMA (d) in the designed it-PMMA film at a concentration of 0.017 unitM at 25 °C. The LbL assembly and the selective extraction were similarly demonstrated in Figure 13. Reprinted with permission from T. Serizawa *et al.*, *Angew. Chem., Int. Ed.*, **42**, 1118 (2003).<sup>64</sup> © 2003, Wiley-VCH.

(Figure 15). St-poly(alkyl methacrylate)s similarly form a stereocomplex with it-PMMA.<sup>15,16</sup> If the stereocomplex is rapidly formed in the film, the host it-PMMA film will not dissolve in an acetonitrile phase. When a conventionally spin-coated it-PMMA film on the QCM substrate was immersed in polymer solutions of acetonitrile, only desorption of it-PMMA was observed. Since it-PMMA can dissolve in acetonitrile, the stereocomplex did not form on/in the film. On the other hand, incorporation into the designed porous it-PMMA film was observed depending on the lateral chain length of the st-polymers. Complex efficiencies for st-PMMA ( $M_n$  22700,  $M_w/M_n$  1.26,  $mm:mr:rr = 0:11:89$ ), st-poly(ethyl methacrylate) (PEMA) ( $M_n$  21340,  $M_w/M_n$  1.11,  $mm:mr:rr = 1:8:91$ ), and st-poly(propyl methacrylate) (PPMA) ( $M_n$  23800,  $M_w/M_n$  1.09,  $mm:mr:rr = 2:7:91$ ) at the same concentration that used in st-PMAA incorporation were 43, 8, and 6%, respectively. These values significantly decreased with increasing alkyl chain lengths. Since the it-PMMA film was designed using a template st-PMAA, a pore structure fitting to st-PMAA should be conserved in the film. Therefore, there must be steric hindrance associated with the incorporation of st-polymers of other alkyl methacrylates. St-PMMA was incorporated into the host with moderate efficiency, indicating that there may be a small difference between the proton and methyl groups as side chains for st-PMAA and st-PMMA, respectively. Note that the it-PMMA film did not dissolve even when the complexing efficiency was small for st-PEMA and st-PPMA, suggesting that the slight incorporation of the st-polymers possibly onto the film surface suppressed dissolution in an acetonitrile solvent.

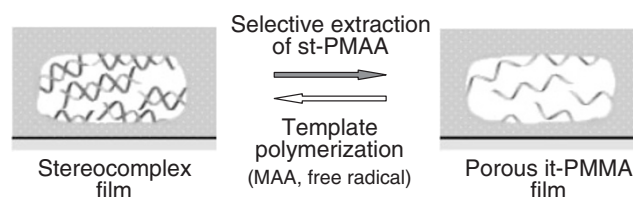
As a consequence, it has been demonstrated that the

selective extraction of st-PMAA in an aqueous alkaline solution from an LbL assembled stereocomplex film composed of it-PMMA and st-PMAA provides ultrathin it-PMMA films with macromolecularly porous and regulated conformations. The extraction and the subsequent incorporation of st-PMAA using suitable solvents were reversible. The porous it-PMMA film incorporated st-poly(alkyl methacrylate)s with a shorter alkyl side chain. This is the first report of the selective extraction of a single component in LbL assembled films in order to realize molecular recognition, and porous films can be utilized as polymerization templates.

#### *Polymerization within Template Nanospaces Using a Double Stranded Assembly*

Designed porous films fabricated by the selective solvent extraction of a single polymer component from ultrathin stereocomplex films composed of it-PMMA and st-PMAA were used as template nanospaces for polymerization.<sup>39</sup> LbL assembly of these polymers successfully led to the fabrication of ultrathin double stranded stereocomplex films with expected stoichiometries, as described above. St-PMAA was selectively extracted from assembled films in aqueous solutions of sodium hydroxide, followed by the fabrication of porous it-PMMA films. We applied the porous it-PMMA films for template syntheses of st-PMAAs, as schematically shown in Figure 16.

Polymerizations from MAAs ( $1.7 \text{ mg mL}^{-1}$ ) in porous it-PMMA ( $M_n$  20750,  $M_w/M_n$  1.2,  $mm:mr:rr = 97:2:1$ ) films (mean thickness, 44 nm) at 40 °C in the presence of the free radical initiator, 2,2'-azobis(*N,N*-dimethyleneisobutyramidine)dihydrochloride (VA-044) ( $5.0 \text{ mg mL}^{-1}$ ) ([monomer]/[initiator] = 20/1, mol/mol) in 10 mL acetonitrile/water (4/6, v/v) were preliminarily analyzed by immersing the QCM substrate coated with porous films. After 2 h polymerization periods in both solution and film, PMAAs synthesized were incorporated into porous films at an 80% fill rate (where, 100% indicates that st-PMAA extracted is equal to incorporated PMAAs).



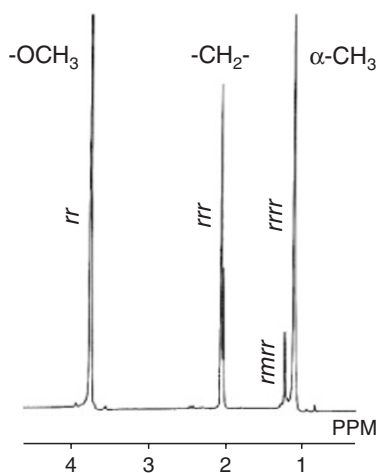
**Figure 16.** Schematic representation of template polymerization of st-PMAA using ultrathin porous it-PMMA films based on double stranded stereocomplexes. Reprinted with permission from T. Serizawa *et al.*, *Macromolecules*, **38**, 6759 (2005).<sup>39</sup> © 2005, American Chemical Society.



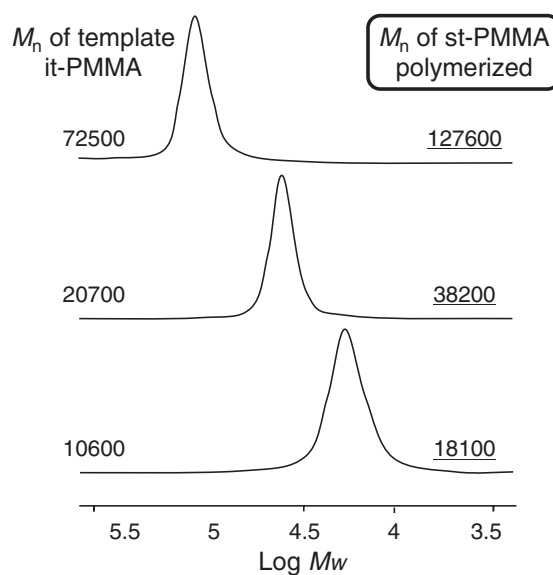
Attenuated total reflection (ATR) spectra in carbonyl vibration bands demonstrated the emergence of a newly observed peak at  $1725\text{ cm}^{-1}$  corresponding to PMAA in addition to the original peak of template it-PMMA at  $1737\text{ cm}^{-1}$ . Peak positions are significantly consistent with those for the stereocomplex film,<sup>64</sup> thus indicating st-specific polymerization of PMAA along template it-PMMA in the porous film.

In order to characterize the PMAA synthesized, porous it-PMMA films were prepared on silica colloids with greater surface areas (10 g, mean diameter: 1.6  $\mu\text{m}$ ). 1.5 g MAA was similarly polymerized in 500 mL solvent in the presence of coated silica. Polymerized PMAAs were extracted in an aqueous 10 mM sodium hydroxide solution. Approximately 0.2 g of PMAA was recovered, and yields were analyzed to be 13%. PMAAs were methylated using diazomethane to obtain PMMAs, and characterized by  $^1\text{H NMR}$ . Figure 17 shows an NMR trace for the PMMA prepared using template it-PMMA ( $M_n$  20750,  $M_w/M_n$  1.2,  $mm:mr:rr = 97:2:1$ ). Chemical shifts for  $\alpha$ -methyl groups at 1–1.5 ppm, which can be used as signals for analyzing tacticity, were almost single peaks at 1.2 ppm, thereby indicating that >96% syndiotactic PMAA had been prepared. Since PMAAs simultaneously prepared in bulk solution did not show a high syndiotacticity ( $mm:mr:rr = 8:69:23$ ), and since st-specific polymerization did not proceed using conventional non-porous it-PMMA films, structural information from template it-PMMA were successfully transferred to st-PMAA on the basis of a pre-memorized double stranded assembly.

Molecular weights of synthesized st-PMMA were analyzed by size exclusion chromatography (SEC) us-



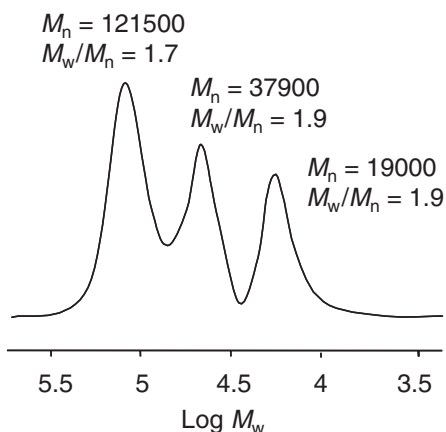
**Figure 17.** Typical  $^1\text{H NMR}$  spectrum of st-PMMA ( $mm:mr:rr = 0:2:98$ ) methylated from st-PMAAs polymerized in porous it-PMMA template films. Reprinted with permission from T. Serizawa *et al.*, *Macromolecules*, **38**, 6759 (2005).<sup>39</sup> © 2005, American Chemical Society.



**Figure 18.** SEC charts of st-PMMA polymerized in porous template films from it-PMMA with various molecular weights. Reprinted with permission from T. Serizawa *et al.*, *Macromolecules*, **38**, 6759 (2005).<sup>39</sup> © 2005, American Chemical Society.

ing a THF solvent. SEC charts are shown in Figure 18.  $M_n$  of st-PMMA were approximately twice those of template it-PMMA in all cases. It is surprising that the mass ratio was potentially consistent with the stoichiometry of double stranded 1:2 (it:st) stereocomplexes.<sup>19–22</sup> Molecular weights of PMMA simultaneously prepared in solution ( $M_n$  2300,  $M_w/M_n$  4.0) were obviously independent of template it-PMMA. The aforementioned observations strongly suggest that structural information from polymer chain length templates, which were derived from the double stranded stereocomplex, were successfully transferred to synthesized polymers. Although st-PMAAs with  $M_n$  of approximately 40000 ( $rr > 95\%$ ,  $M_w/M_n < 2.0$ ) were commonly utilized for nanospace creation,  $M_n$  of st-PMMA polymerized were clearly dependent on  $M_n$  of template it-PMMA. Furthermore, changes in MAA/initiator molar ratios did not affect the molecular weight of st-PMMA, supporting template synthesis in porous films. Template it-PMMA regulated molecular weights as well as tacticities. Molecular weight distributions of polymerized st-PMMA were narrow, and reached 1.5 in some case. The molecular weight distribution is characteristic of this system, and is better than following st-specific polymerizations with PMAAs using 1:1 stereocomplex assemblies<sup>40</sup> (see below).

Porous template films were reusable for further polymerizations with reproducibility lasting at least three times after the selective extraction of polymerized st-PMAAs. A pot polymerization in the presence of mixed silica coated with template it-PMMA with



**Figure 19.** SEC chart of a pot polymerized st-PMMA in porous template films from it-PMMA with  $M_n$  of 11000, 22800, and 68900. Reprinted with permission from T. Serizawa *et al.*, *Macromolecules*, **38**, 6759 (2005).<sup>39</sup> © 2005, American Chemical Society.

different  $M_n$  ( $M_w/M_n$ ) (11000 (1.5), 22800 (1.2), and 68900 (1.5)) resulted in the synthesis of st-PMMA mixtures with respective  $M_n$  of 19000, 37900, and 121500, as shown in Figure 19. The observations indicate that pot polymerizations prepare mixtures of stereoregular methacrylate polymers with various molecular weights, which can be readily separated by chromatographic methods. This type of stereoregular polymerization has never been realized with conventional polymerizations, and is characteristic to the present system.

The detailed polymerization mechanism is unknown. Since SEC curves with single and narrow peak widths shifted to higher molecular weights (original data not shown), a living radical (rather than free radical) polymerization might proceed within porous it-PMMA films. In other words, radical terminals of growing st-PMAA chains might stably exist in films during polymerization. On the other hand, affinity constants for double stranded stereocomplexes analyzed by using st-PMMA with various molecular weights against porous it-PMMA films following methods described in a previous paper<sup>64</sup> were maximal, when molecular weights of st-PMAAs were twice those of it-PMMA (data not shown). These observations suggest that zippers-likely formed one-to-one stereocomplex double strands are thermodynamically stable in the films. During polymerization, growing st-PMAAs might shuttle on template it-PMMA until the formation of stable double strands is completed, which might be the reason for the efficient transferring of molecular weights. Termination in films is an important factor that needs to be discussed. Since molecular weights of st-PMAAs polymerized were controlled by those of it-PMMA templates after

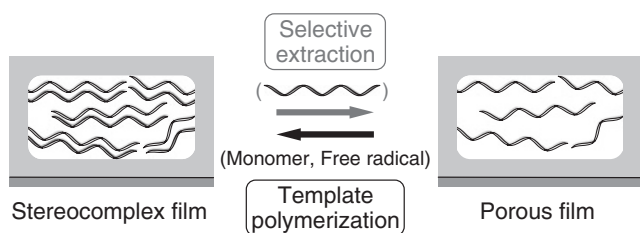
suitable polymerization times (2 h), radical terminals should “live” until polymerization ends. An influx of oxygen by opening the reaction media seemed to stop the polymerization. The interpretation is reasonable, because a SEC curve following polymerization for longer times (3 h) became bimodal, thereby suggesting that radicals were still “alive” after 2 h of polymerization.

Unfortunately, assembled it-PMMA could not be extracted using conventional organic solvents such as chloroform and toluene, possibly reflecting a difference in both polymers during the double stranded stereocomplex. Since it-PMMA are surrounded by st-PMAAs using van der Waals contacts between respective esters and  $\alpha$ -methyl groups,<sup>27</sup> dissociation seems to be difficult. Furthermore, since carboxyl groups of st-PMAAs point out of double strands, carboxyl anions in alkaline solutions might cause electrostatic repulsions between strands, thus resulting in the easy extraction of st-PMAAs. The present double stranded stereocomplex system was suitable for st-specific polymerization.

In conclusion, a highly st-specific template polymerization of PMAA along with template it-PMMA chains in porous films was demonstrated on the basis of double stranded stereocomplexes. Molecular weights of st-PMAAs were controlled by template it-PMMA following the stereocomplex stoichiometry, and molecular weight distributions were narrow. We confirmed that structural transcription of template polymers to polymers synthesized could be realized using structurally regular ultrathin porous films composed of template polymers. The solid-phase polymerization in ultrathin template films with regular nanospaces using interactive polymers potentiates novel methodologies for precision polymerization.

#### *Polymerization within Template Nanospaces Using van der Waals Contact Assembly*

In the case of the double-stranded 1:2 stereocomplex film composed of respective it-PMMA and st-PMAA, st-PMAA was selectively extracted from the film in an aqueous alkaline solution, resulting in a macromolecularly porous it-PMMA film.<sup>64</sup> Then, this porous film was used for st-specific polymerization of PMAA.<sup>39</sup> However, it-PMMA was not extracted from the film, indicating that a versatile host composed of it- or st-polymers for template polymerization cannot be fabricated by using the assembled film. In this section, we focused on the formation of a stereocomplex between it-PMMA and st-PMAA with a 1:1 length stoichiometry.<sup>17,18</sup> LbL assembly of polymers under suitable conditions produced a stereocomplex film with a 1:1 stoichiometry, and the subsequent selective extraction of a single polymer component successfully



**Figure 20.** Schematic representation of template polymerization using ultrathin porous films. LbL assembly prepares the ultrathin film of a stereocomplex comprised of it-PMMA and st-PMAA. Two polymer chains are drawn by rigid helical rods, and should be partially distorted and entangled in the film. There must be a disordered region of the stereocomplex. A single component is selectively extracted from the film, resulting in the preparation of the porous film with regular nanospaces. Then, the porous film is used as a reaction mold for free radical template polymerization of MMA or MAA, followed by the regeneration of the stereocomplex film. Reprinted with permission from T. Serizawa *et al.*, *Nature*, **429**, 52 (2004).<sup>40</sup> © 2004, Nature Publishing Group.

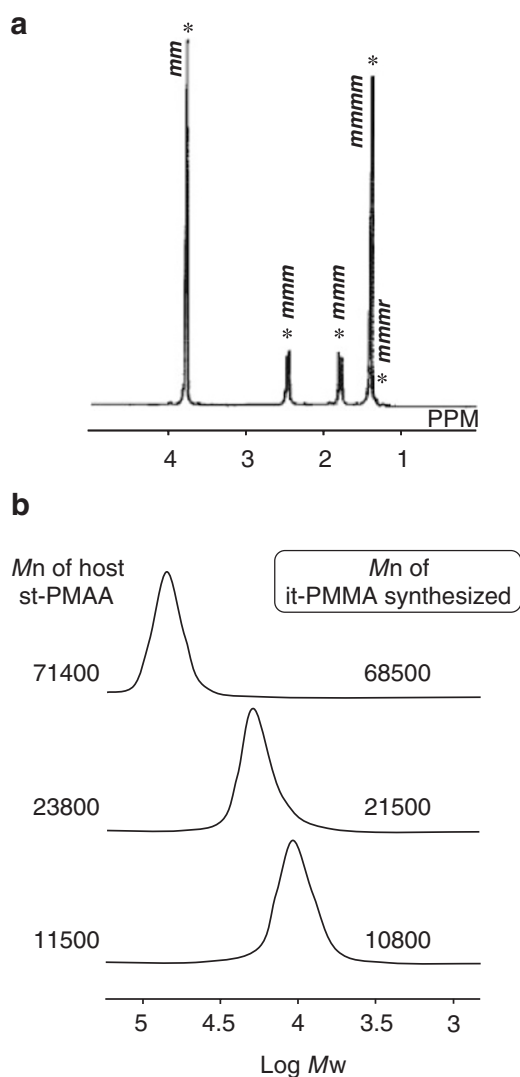
produced porous st-PMAA or it-PMMA films, of which nanospaces could be utilized in stereoregular template polymerization of it-PMMA and st-PMAA, respectively.<sup>40</sup> The present template polymerization method is schematically represented in Figure 20.

To obtain an assembly with a 1:1 stoichiometry, DMF and DMF/water (2/3, v/v) were selected as solvents for it-PMMA and st-PMAA, respectively. Solvents were determined by a detailed assembly analysis, following methods in a previous study.<sup>18</sup> LbL assembly in both solutions produced a film with the objective stoichiometry of  $1.0 \pm 0.2$  (st/it-length ratio). The thickness and the  $R_a$  for 6 cycles [(it-PMMA/st-PMAA)<sub>6</sub>] were analyzed to be  $20.1 \pm 0.3$  and  $3.2$  nm on the QCM substrate, respectively. Considering the assembly amount analyzed ( $4.1 \pm 0.1 \mu\text{g cm}^{-2}$ ), the mean density of the film was estimated to be  $1.0 \text{ g cm}^{-3}$ . The immersion of the assembled film in both chloroform and a 10 mM sodium hydroxide aqueous solution resulted in the desorption of approximately half of the polymers. The amount desorbed was consistent with the amount of each polymer totally assembled, thereby suggesting that it-PMMA and st-PMAA were selectively extracted from the film. ATR spectra in the carbonyl vibration region supported the selective disappearance of peaks at  $1731$  and  $1717 \text{ cm}^{-1}$ , corresponding to it-PMMA and st-PMAA, respectively. The thickness after the extraction of it-PMMA and st-PMAA was  $18.3 \pm 2.8$  and  $19.4 \pm 2.8$  nm, respectively. Values were consistent with the initial thickness of the film within experimental error. In addition, the  $R_a$  was  $2.1$  and  $2.8$  nm, respectively, and was slightly smoother than before. These observations indicate that a porous film com-

posed of st-PMAA or it-PMMA suitable for template polymerization was successfully prepared by the selective solvent extraction. It is also difficult to explain why films were not compressed by the extraction. Polymer terminals as well as some segments that did not join the complex might support the film structure, as described in the double-stranded system.<sup>64</sup>

For template polymerization, the QCM substrate coated with the porous st-PMAA film was immersed in a 10 mL DMF solution of MMA ( $1.7 \text{ mg mL}^{-1}$ ) for 3 h at  $70^\circ\text{C}$  in the presence of a free radical initiator, 2,2'-azobisisobutyronitrile ( $5 \text{ mg mL}^{-1}$ ). After rinsing with DMF, approximately 90% of the it-PMMA previously extracted was recovered. ATR spectrum of the obtained film showed the same band peaks as those observed for the stereocomplex film, possibly suggesting that it-PMMA was prepared, and that it formed a stereocomplex with st-PMAA in the film. In order to analyze the stereoregularity and the molecular weight of the PMMA, the porous film was prepared on silica particles (10 g, mean diameter:  $1.6 \mu\text{m}$ ). Then, MMA was polymerized in DMF, and the PMMA was characterized by extraction using chloroform. Approximately 0.4 g PMMA was obtained from feeding 1.5 g MMA/500 mL DMF, which yielded approximately 25% under these polymerization conditions. A  $^1\text{H NMR}$  chart of the PMMA clearly demonstrated the it-specific polymerization of MMA in the porous st-PMAA film (Figure 21a), indicating that an it-specific template polymerization was achieved on the basis of stereocomplex formation with the st-PMAA. SEC curves potentially demonstrate the control of molecular weights within a narrow distribution (Figure 21b). Isotacticities were greater than 92% in all cases. The  $M_n$  of the host st-PMAA controlled the  $M_n$  of the it-PMMA, and was almost the same. These observations are surprising because polymerization conditions, such as concentrations of monomers and initiators, were the same in all polymerizations except for the molecular weight of the template st-PMAA. Properties of template polymers corresponding to a 1:1 complex assembly were clearly transferred to synthesized PMMAs. The molecular weight distribution was also small, compared to conventional free radical polymerization systems. PMMA recovered from supernatants showed no stereoregularity ( $mm:mr:rr = 21:68:11$ ) and a different molecular weight with a larger distribution ( $M_n$  4670,  $M_w/M_n$  4.9). As a consequence, the control of the stereoregularity and of the molecular weight of it-PMMA was realized by the template polymerization method using porous template films.

The porous film of it-PMMA was similarly prepared from the 1:1 complex film to polymerize st-PMAA. Silica particles coated with the porous it-



**Figure 21.** Characterization of it-PMMA polymerized in porous st-PMAA films for 3 h at 70 °C. a, A typical <sup>1</sup>H NMR chart of it-PMMA polymerized in a porous st-PMAA ( $M_n$  23800) film. b, SEC curves of it-PMMA polymerized in porous films of st-PMAAs with various molecular weights. Reprinted with permission from T. Serizawa *et al.*, *Nature*, **429**, 52 (2004).<sup>40</sup> © 2004, Nature Publishing Group.

PMMA film were used for free radical polymerization of MAA in DMF/water (2/3, v/v) in the presence of a water-soluble free radical initiator, VA-044 for 2 h at 40 °C. St-PMAA was successfully prepared by using the template it-PMMA film, and the molecular weight of the host it-PMMA similarly regulated that of the st-PMAA. These observations indicate an alternative utilization of porous films for template polymerization. Note that conventionally prepared films did not realize the above template polymerization. Template polymerization of the combination between it-PMMA and st-PMAA in the solution only demonstrated the acceleration of polymerization rates, since the association is relatively weaker than that of stereoregular PMMA.<sup>37</sup> Accordingly, the potential of the present

porous films was confirmed.

If we speculate about the mechanism for template polymerization, two contradictory polymerization processes may be anticipated: (i) polymerization occurring after the sufficient coordination of monomers with templates<sup>38</sup> and (ii) a stepwise polymerization with incorporation (or slow diffusion) of monomers into porous films. The QCM measurement did not show the sorption of monomers into films, and did not support the former mechanism. Time-dependent SEC curves of it-PMMA prepared by st-PMAA hosts were obtained. Curves with single, narrow peak widths shifted to higher molecular weights, supporting the latter mechanism which is similar to living radical polymerization rather than conventional free radical polymerization. Curves were bimodal after 4 h, followed by the binding of terminal radicals in the film. Since the polymerization of MMA after 3 h was stopped by exposing the reaction media in air, radical terminals, which had been present in films, seemed to react with oxygen. A similar mechanism for st-PMAA polymerization was also supported.

In conclusion, porous template polymer films provided a reaction mold for the stereoregular polymerization of methacrylates. It- and st-polymers of methacrylates with high stereoregularity and with a narrow molecular weight distribution were successfully prepared by using a 1:1 stereocomplex assembly. Since particles coated with ultrathin template films are readily handled and reusable, large-scale syntheses of stereoregular polymers may be anticipated in the near future. Easier syntheses for stereoregular polymers potentiate novel applications in technological and biomedical fields.

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Takeshi Serizawa was born in 1969 (Yamanashi Prefecture, Japan), Serizawa received his B.Edu. and M.Edu. degrees in chemistry from Chiba University in 1991 and 1993, for his research on the synthesis of amino acid-containing amphiphiles and their assembly properties on the supervision of Prof. N. Yamada, and his Ph.D. from Tokyo Institute of Technology in 1996 on the supervision of Prof. Y. Okahata and Associate Professor T. Sato, who is now a professor in Keio University, for his research on the analysis of the recognition of biomolecules to ganglioside lipids. From 1996 to 2003, he worked as an assistant professor and an associate professor for Akashi laboratory in Kagoshima University. He moved to the University of Tokyo in 2004 as an associate professor, and manages his research group. His current research interests focus on the control of specific or non-specific interactions between synthetic polymers and biopolymers. He is the author and coauthor of *ca.* 100 original papers, *ca.* 20 reviews and books, and *ca.* 10 patents.



Mitsuru Akashi was born in Tokushima Prefecture, Japan in 1949. He received his B.S. degree in 1972 and Ph. D. degree in 1978 from Osaka University under the supervision of Professor Kiichi Takemoto. After working as a Postdoctoral Researcher at the National Institute of Health (United States) and Waterloo University (Canada), he engaged in assistant professor of Faculty of Engineering, Kagoshima University in 1981, where he started his career as a polymer chemist and devoted his energies to the education. He was promoted to associate professor in 1984 and full professor in 1989 at the same institution. In 2003, he moved to Graduate School of Engineering, Osaka University. So far, he has received the Award of the Society of Polymer Science, Japan concerning “*Design and Preparation of Novel Multiphase Polymeric Mterials Based on Polymer Assembling Techniques*” (1999) and then the Award of Japanese Society for Biomaterials on “*Design and Preparation of Novel Biomaterials by the Nanostructure Control of Polymeric Material Surfaces*” (2004). He is the author and coauthor of *ca.* 300 original papers, *ca.* 90 reviews and books, and *ca.* 100 patents.