

Stepwise Stereocomplex Assembly of Stereoregular Polymers of Methacrylates on a Substrate

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Isotactic (it-) and syndiotactic (st-) poly(methyl methacrylate)s (PMMA) were alternately assembled by the stepwise immersion of a 9-MHz quartz-crystal microbalance (QCM) into organic solutions at ambient temperature. Quantitative QCM analysis revealed that acetonitrile was the best solvent for assembly on the substrate and that growth of the assembly was linear. The ratio of st-/it-PMMA assembled, the static contact angle of the assembly at each step, and its reflection absorption spectrum (RAS) strongly implied stepwise assembly of stereocomplex. In addition, the combinations of it-PMMA and st-poly(methacrylic acid) (PMAA) were similarly assembled during their stereocomplex formation. In the PMAA assembly system, the st-PMAA was selectively extracted from the assembly, resulting in an it-PMMA host ultrathin film. Atomic force microbalance (AFM) observation showed the assembly was obtained by selective re-adsorption of st-polymer, because the it-PMMA host ultrathin film maintained suitable spaces between polymer chains.

Key words: Ultrathin film / stereocomplex / stereoregular / quartz-crystal microbalance / poly(methyl methacrylate) / stereo-memory

INTRODUCTION

Systematic design by self-organization of individual macromolecules with a highly ordered nano-structure in solutions or solids has been of great interest. Especially, fabrication of ultrathin polymeric films on surfaces of various materials is of current interest because of their potential for modification and functionalization and the scientific significance of the fabrication process. Langmuir-Blodgett (LB) technique is a promising method for obtaining molecularly layered structures. This method requires amphiphilic polymers and suitable apparatus. Therefore, regulated polymer assembly on certain substrates using other simple methodologies is of great interest not only because of potential applications in the synthesis of polymeric materials, but also because of scientific significance in the field of polymer surface chemistry. Recently, Decher et al. developed a simple technique for fabricating layer-by-layer ultrathin polymer films by alternate immersion of a substrate into an aqueous solution of anionic and cationic polyelectrolytes [1]. This method resulted in a layered film structure with a molecularly smooth surface, and film thickness was controllable to a polymer monolayer level.

Stereocomplexes are formed between sterically well-defined synthetic polymers in certain solvents, or in films with structural fittings between the polymer chains or between lateral functional groups with van der Waals contact. There have been previous studies of complex formation in isotactic (it-) / syndiotactic (st-) poly(methyl methacrylate)s (PMMA) [2], it-PMMA / st- poly(alkyl methacrylate) [3], it-PMMA / st-poly (methacrylic acid) (PMAA) [4] in the form of mixed solutions or solid films. The PMMA system has been particularly well studied by many researchers, revealing a double stranded helical structure, in which it-PMMA is surrounded by twice the

molar amount of st-PMMA. This structure was proposed by both Challa et al. based on theoretical and X-ray diffraction data [2], and by Spevacek et al. based on ¹³C-NMR measurements [5]. Stereocomplex formation between PMMA may be applied to studies of polymeric assembly from solutions on the basis of this molecularly characterized structure.

In this study, we analyzed the stepwise assembly of stereoregular PMMA and a combination of it-PMMA and st-PMAA onto a substrate. We used a quartz-crystal microbalance (QCM) as a substrate, and analyzed the static contact angle, reflection absorption spectra (RAS), and atomic force microscopic (AFM) measurements. We believe that the present system will not only lead to novel ultrathin polymer films, but may also serve as a model for studying the novel concept of polymeric interaction at the interfacial region.

EXPERIMENTAL

It-PMMA (M_n 20750; M_w/M_n 1.26), st-PMMA (M_n 22700; M_w/M_n 1.26) were synthesized by anionic polymerization in toluene at -78°C with $t\text{-C}_4\text{H}_9\text{MgBr}$ and $t\text{-C}_4\text{H}_9\text{Li}/(\text{C}_2\text{H}_5)_3\text{Al}$, respectively, as initiators. St-PMAA (M_n 37940; M_w/M_n 1.77) were synthesized by hydrolyzing poly(trimethylsilyl methacrylate) synthesized by anionic polymerization. Their tacticities (mm:mr:rr), which were analyzed from α -methyl proton signals using NMR measurements, were 97:2:1, 0:11:89, and 1:2:97, respectively. An AT-cut quartz crystal (9 mm in diameter) coated on both sides with gold electrodes, 4.5 mm in diameter and with a parent frequency of 9 MHz, was utilized (USI, Japan). The amount of polymer assembled, Δm , was calculated from the decrease in frequency of QCM, ΔF , using Sauerbrey's equation as follows,

$$-\Delta F = \frac{2F_0^2}{A\sqrt{\rho_q\mu_q}} \times \Delta m$$

where F_0 is the parent frequency of the QCM (9×10^6 Hz), A is the electrode area (0.159 cm^2), ρ_q is the density of the quartz (2.65 g cm^{-3}), and μ_q is the shear modulus ($2.95 \times 10^{11} \text{ dyn cm}^{-2}$). Film thickness was estimated by assuming the density to be that of PMMA solids 1.188 g mL^{-3} . A QCM substrate was immersed in each solution for 15 min at 25°C , washed with the same solvent, and dried with nitrogen gas. The frequency was then measured. In the present study, a 15 min immersion of the QCM achieved equilibrium adsorption of the polymers at each step. The polymer films were deposited by stepwise immersion of the substrate into each solution.

A reflection absorption spectrum (RAS) was obtained with a Herschel FT/IR-610, Jasco (Japan), at ambient temperature. Attenuated total reflection (ATR) spectra were obtained using the same apparatus by attachment of a ZnGe internal element ($60 \times 10 \times 3.75 \text{ mm}$) with an incidence angle of 45° . The polymer solutions were cast on the element. The interferograms were co-added 50 times and Fourier transformed at a resolution of 4 cm^{-1} . The static contact angle of the assembly at each step in stepwise deposition was measured by dropping water onto the films at ambient temperature. The AFM images were obtained using a Digital Instruments NanoScope III that was operated with a tapping mode in the air at ambient temperature. Image processing other than flat leveling was not performed. The mean roughness (R_a) in given observed areas was estimated from the following equation:

$$R_a = \frac{1}{L_x L_y} \int_0^{L_x} \int_0^{L_y} |F(x, y)| dx dy$$

RESULTS AND DISCUSSION

Stepwise stereoregular PMMAs assembly

Stereocomplex formation between it- and st-PMMA in solutions is well known to be dependent on solvent species. In general, stereocomplex formation is not determined by the polarity of the solvents, which can solubilize PMMA homogeneously. We selected acetonitrile, acetone, and *N,N*-dimethylformamide (DMF), which have already been shown to be strongly complexing solvents. In all cases, an immediate precipitation or turbidity with mixing of it- and st-PMMA solutions was not observed at ambient temperature.

Figure 1 shows the dependence of the frequency shift on the assembly steps when the QCM was alternately immersed in it-PMMA and st-PMMA solutions in the three solvents for 15 min at a PMMA concentration of 1.7×10^{-2} unitM. Acetonitrile was the best solvent for PMMA assembly in large amounts, as shown in Figure 1a. When we immersed the QCM in it- and st- solution alone for a much longer time, the frequency shift saturated at a level obtained at one step of the assembly process. In the initial two steps, we observed larger frequency shifts, possibly due to the direct influence of the gold substrate of the QCM on the assembly process. The frequency shift after 20-step assembly was 416 Hz. This shift corresponded to an adsorption amount of 362 ng. The film thickness was estimated to be 9.7 nm. This value was also consistent with the value that was obtained by scratching of PMMA assembly on a QCM substrate using contact-mode AFM

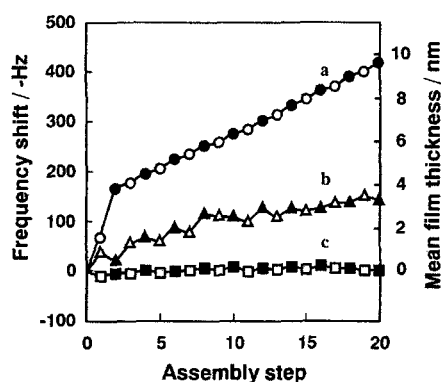


Figure 1. Frequency shift of QCM by the stepwise assembly from various organic solutions of it- and st-PMMA: (a) acetonitrile, (b) acetone, (c) DMF solutions. T. Serizawa et al. *J. Am. Chem. Soc.* **122**, 1891 (2000)

($9.7 \pm 0.3 \text{ nm}$). On the other hand, acetone and DMF gave less adsorption as shown in Figure 1b, 1c. All of the solvents used in these experiments are known to promote complex formation in mixed solutions of it- and st-PMMA. Accordingly, stepwise assembly on a QCM substrate is not related to complex formation behavior in solutions. A possible reason may be that acetonitrile was the poorest solvent of PMMA of the three solvents used. These data imply that suitable solvent selection is a significant factor in the stepwise assembly of stereoregular PMMA. The ratio between it- and st-PMMA in the stereocomplex assemblies of PMMA has been estimated to be 1:2, as reported by Challa, et al. [1]. With acetonitrile as a solvent, the mean ratio that was determined from the QCM measurements was 2.0 ± 0.4 , which is consistent with the value obtained by Challa, et al. This strongly implies that it- and st-PMMA were assembled on a QCM substrate by stereocomplex formation. Furthermore, the amount of PMMA assembly on the substrate was affected by concentration and molecular weight (shown in our previous paper [6]).

It is known that the static contact angles on the air-side of the film surface of it- and st-PMMA are significantly different from each other because of the selective accumulation of functional groups at the surfaces. Figure 2a shows the dependence of the static angle on the assembly step when the QCM was alternately immersed into acetonitrile solutions of it- and st-PMMA. The contact angle changed with the step number, indicating stepwise assembly of each polymer on the substrate. Furthermore, the contact angle with each alternate step (odd or even steps) was essentially the same, similarly indicating the same molecular composition or conformation at the film surface. The mean contact angle at the odd steps (it-PMMA assembly) was $63.3 \pm 0.3^\circ$. This value was comparable to $63.0 \pm 0.3^\circ$, the angle of the adsorbed bulk it-PMMA film on a bare QCM substrate. Therefore, it-PMMA must be physically adsorbed onto the surface of the preformed PMMA complex. This observation suggests that the inner st-PMMA has a stable structure and is fixed by the stereocomplex formation with inner it-PMMA, and never replaced to the film surface. On the other hand, the mean contact angle at the even steps (st-PMMA assembly) was $72.4 \pm 0.4^\circ$, which was slightly smaller than the reported value of the st-PMMA film surface and also smaller than that ($73.2 \pm 0.8^\circ$) of a physically adsorbed

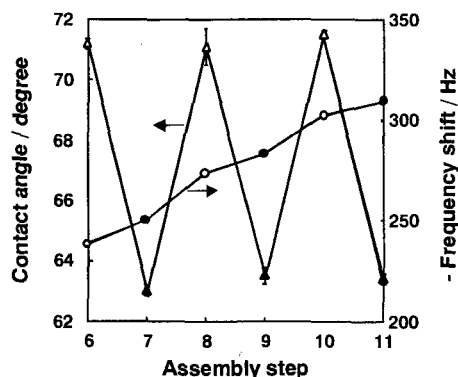


Figure 2. Static contact angle of the stepwise assembly from acetonitrile solutions of it- and st-PMMA. T. Serizawa et al. *J. Am. Chem. Soc.* **122**, 1891 (2000)

bulk st-PMMA film on a QCM. It may be slightly smaller than that for the st-PMMA layer because the ester group in st-PMMA should point outward in the molecular structure of the stereocomplex. Note that st-PMMA on film surfaces usually tends to direct alkyl main chains toward the air, to minimize the interfacial free energy. We surmised that the surface composition of the ultrathin PMMA film was altered by stepwise assembly of each polymer, possibly by physisorption of it-PMMA and by stereocomplex formation between it- and st-PMMA on a substrate. These observations were consistent with the QCM results.

Infrared spectroscopy is one of the most useful tools for evaluating stereocomplex formation of stereoregular PMMAs on a certain substrate, as previously reported by other researchers [7]. Analysis of the absorption band of main chain CH_2 -rocking vibrations at around 840-860 cm^{-1} in addition to the absorption band of $\text{C}=\text{O}$ -stretching vibrations at around 1700-1800 cm^{-1} , allowed evaluation of the stereocomplex formation (data was shown in our previous paper [6]). The main peak in CH_2 -rocking absorption for the PMMA assemblies was apparently at approximately 860 cm^{-1} , together with a shoulder peak at around 840 cm^{-1} . These peak positions were significantly different from those of cast films of it- and st-PMMA, indicating stereocomplex formation. Furthermore, the $\text{C}=\text{O}$ -stretching vibration bands for the stepwise assemblies were shifted and the absorption peak was observed at a higher wavenumber compared to those of the cast films. These observations strongly suggest that the stepwise assembly of stereoregular PMMA was based on stereocomplex formation on substrate surfaces.

Atomic force microscopy (AFM) imaging is a useful tool for analysis of the surface topology of polymer films. In the present study, we directly analyzed the surfaces of the PMMA assembly (data was shown in our previous paper [6]). The image of the PMMA assembly was obviously different from that of the QCM surface, indicating assembly of stereoregular PMMAs. The mean roughness of the PMMA assembly and the QCM substrate was 4.3 and 1.8 nm, respectively. The roughness of the assembly was relatively smooth considering its film thickness.

On the other hand, st-polymers in the stereocomplex are not necessary to be the PMMA, because the methyl ester group of st-PMMA is oriented toward the outside of the stereocomplex. We also analyzed the stepwise assembly between it-PMMA and st-poly(alkyl methacrylate) on a QCM substrate by alternate immersion in acetonitrile solutions. The st-/it-polymer ratio calculated from the

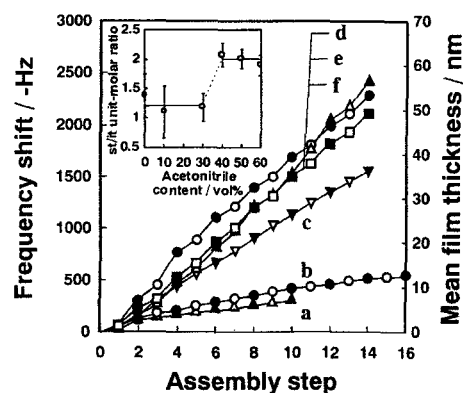


Figure 3. Frequency shift of QCM by the stepwise assembly from an it-PMMA acetonitrile solution and a st-PMAA solution of mixed acetonitrile/water (v/v) solvents: (a) water, (b) 10/90, (c) 30/70, (d) 40/60, (e) 50/50, and (f) 60/40. T. Serizawa et al. *Langmuir* **16**, 7112 (2000)

amount adsorbed at each step, the static contact angle and spectroscopic studies confirmed stepwise stereocomplex assembly (K. Hamada et al. to be submitted).

Stepwise assembly between it-PMMA and st-PMAA

A stereocomplex is also formed between it-PMMA and st-PMAA [3]. Figure 3 shows frequency shifts corresponding to assembled amounts with each assembly step from both an it-PMMA acetonitrile solution and a st-PMAA acetonitrile/water mixed solution (1.7×10^{-2} unitM). An st-PMAA solution with an acetonitrile content of more than 60 vol% was not prepared because of the poor solubility of st-PMAA. The mean thickness of the assembly was controllable at each step to a nanometer order. The thickness in Figure 3d after a 14-step assembly was estimated to be 48 nm. These polymers are not assembled by simply immersion only into each solution. The Figure 3 inset shows the unit-molar ratio of st-PMAA and it-PMMA assembled against the acetonitrile content. The ratio was obtained as a mean value of the ratios at the step from it-PMMA to st-PMAA. The ratios were around 2 above 40 vol%. Challa et al. [3] demonstrated stereocomplex formation between the present polymers with 1/1 or 2/1 unit-molar stoichiometry (st-PMAA/it-PMMA) depending on the solvent species. Based on this knowledge, it is reasonable to suggest that the double-stranded stereocomplex was formed above 40 vol% of acetonitrile content, while a mixture of the complexes was formed below 30 vol%. In order to form double-strands on the film surface, drastic conformational changes in the pre-adsorbed it-PMMA are necessary because the it-PMMA should have a random conformation on the film surface, and/or penetration of st-PMAA into the it-PMMA layer is needed. The present observations are reasonable if we consider that it-PMMA on the film surface is slightly swollen by the acetonitrile in the solvent mixture containing st-PMAA. The slight solvation might facilitate the necessary conformational change, even though it-PMMA is not dissolved in mixed acetonitrile/water (4/6-6/4, v/v) solvents. It is more difficult however to explain the increase in the amount of assembled polymer observed above 30 vol%, as shown in Figure 3. Although this observation can be partially explained by differences in the amount of it-PMMA physically adsorbed onto the assembly, further study of

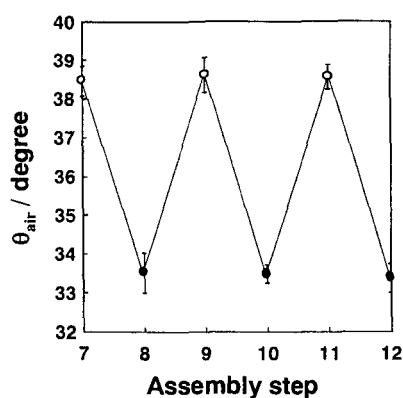


Figure 4. Static contact angle of the stepwise assembly from acetonitrile solutions of it-PMMA and st-PMAA. T. Serizawa et al. *Langmuir* **16**, 7112 (2000)

this topic is necessary.

Figure 4 shows the static contact angles on the air-side of the film surface at each assembly step. The angle was alternately changed, also confirming stepwise polymer assembly. At the it-PMMA and st-PMAA steps, the angles were 38.5 ± 0.4 and 33.5 ± 0.4 degrees, respectively. The angles of cast films of the polymers were 63.0 ± 0.3 and 21.5 ± 0.4 degrees. The difference in measured angles between the assembly and the cast film may be attributed to the following. At the it-PMMA step, the polymer might partially intercalate in the complex assembly resulting in a smaller angle than measured on the it-PMMA cast film. Even if intercalation did not occur, water might still swell the inner assembly. On the other hand, swelling of the st-PMAA cast film by water (st-PMAA was dissolved in water after water-swelling) may render its angle smaller than that at the complex surface. In other words, st-PMAA in the assembly step could be less swollen than in the cast film.

Figure 5 shows the results of infrared spectra analyses of the assembly and of each cast film. Two carbonyl vibration peaks assigned to those for it-PMMA (1736 cm^{-1}) and for st-PMAA (1726 cm^{-1}) were observed for the assembly using RAS. The larger peak for st-PMAA was reliable based on the QCM results. Each band in the assembly shifted to a higher wavenumber compared to those for cast films of it-PMMA (1726 cm^{-1}) and st-PMAA (1695 cm^{-1}) analyzed using ATR spectra. This observation also suggested stereocomplex formation in the assembly. AFM images of the assembly were obviously different from those of the QCM surface, indicating assembly of the polymers. The mean roughness of the assembly was 2.6 nm, and was relatively smooth considering its film thickness (48 nm).

Stereocomplex formation between it-PMMA and st-PMAA with different solubilities was also evaluated. The it-PMMA is a hydrophobic polymer, whereas st-PMAA is water soluble. When the assembly is immersed in 10 mM NaOH solution, hydrophilic st-PMMA is selectively extracted from the assembly, resulting in an it-PMMA host ultrathin film. The extraction process was affected by the pH of the extract solutions. Furthermore, st-PMAA was incorporated into the resulting ultrathin it-PMMA film with an efficiency of 80 %, because the it-PMMA host ultrathin film maintains suitable spaces between polymer chains (measured using AFM scratching). The complex efficiency after

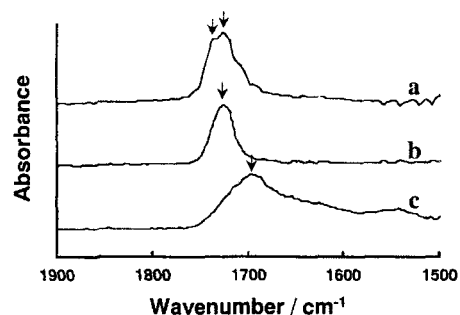


Figure 5. (a) RAS of a 14-step assembly in Figure 1d and (b) and (c) ATR spectra of it-PMMA and st-PMAA cast film, respectively. Arrows show each peak top. T. Serizawa et al. *Langmuir* **18**, 7112 (2000).

re-adsorption was dependent on the concentration of re-adsorbed st-PMAA. The st-poly(alkyl methacrylate) was also re-adsorbed, and the complex efficiency depended on the alkyl chain length of the side group.

CONCLUSION

We showed the stepwise assembly of stereoregular PMMA on a QCM substrate from various organic solvents. Furthermore, we also showed the stepwise assembly of it-PMMA and st-PMAA from acetonitrile and acetonitrile solutions. We found that stepwise assembly involving stereocomplex formation was dependent on the solvent used. In both systems, the st-/it-polymer ratio calculated from the amount adsorbed in each step, the static contact angle and FT-IR confirmed stepwise stereocomplex assembly. PMMA assembly was achieved by altering conditions such as the polymer concentration, the molecular weight of the st-PMMA, and the solvents. The surface topography of these assemblies which was analyzed by AFM, showed a domain-like structure, but was molecularly smooth. Moreover, in the combination of it-PMMA and st-PMAA, the st-PMAA was selectively extracted from the assembly, resulting in an it-PMMA host ultrathin film. The designed host it-PMMA film therefore, selectively incorporated st-polymer. The present system may be applied in the design of various molecular assembly.

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