Stepwise Stereocomplex Assembly of Stereoregular Poly(methyl methacrylate)s on a Substrate

**Takeshi Serizawa, Ken-ichi Hamada, Tatsuki Kitayama,[†] Nobutaka Fujimoto,[†]
Koichi Hatada,[†] and Mitsuru Akashi***

*Contribution from the Department of Applied Chemistry and Chemical Engineering,
Faculty of Engineering, Kagoshima University, Korimoto 1-21-40, Kagoshima 890-0065, Japan*

Received April 26, 1999

Abstract: Isotactic (it-) and syndiotactic (st-) poly(methyl methacrylate)s (PMMAs) were synthesized by anionic polymerization in toluene at −78 °C with t-C_4H_9MgBr and t-$C_4H_9Li/(C_2H_5)_3Al$, respectively, as initiators. Polymers were assembled by the stepwise immersion of a 9-MHz quartz-crystal microbalance (QCM) as a substrate into organic solutions at ambient temperature. Quantitative QCM analysis revealed that acetonitrile was the best solvent for assembly on the substrate compared to acetone and *N,N*-dimethylformamide (DMF). The analysis also showed linear growth of the assembly except during the initial two steps (possibly due to direct influence of the gold QCM substrate), indicating that the amount of assembly can be easily regulated at each step. A 5 min immersion of the QCM into each PMMA solution was enough to obtain stepwise assembly. The ratios of st-/it-PMMA assembled, the static contact angle of the assembly at each step, and its reflection absorption spectrum (RAS) strongly implied the stepwise formation of a stereocomplex between it- and st-PMMAs in the assembly. The amount of stereocomplex assembled was significantly affected by the addition of water to the organic solutions, the PMMA concentration, and its molecular weight, as well as the solvent species. Atomic force microscopic (AFM) examination of the assembly revealed a smooth surface. The assembly was formed at the step from the physically adsorbed it-PMMA to st-PMMA. A possible assembling mechanism was also proposed.

Introduction

Biopolymers such as DNA and proteins, which function in biological systems, have 3-dimensional and higher-order structures which self-assemble in a given environment. Although molecularly regulated structures seem to be restricted to biopolymers in an aqueous phase, similarly regulated nanostructures, which self-assemble in certain solvents, are known in the field of synthetic polymers. Stereocomplexes are formed between sterically well-defined synthetic polymers in certain solvents, or in a film 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/syndiotactic poly(methyl methacrylate)s (PMMAs),[1] isotactic PMMA/syndiotactic polymers of alkyl methacrylates,[2] isotactic PMMA/syndiotactic poly(methacrylic acid),[3] isotactic polymers of *R*-(+)-/*S*-(−)-α-methylbenzyl methacrylates,[4] enantiomeric poly(lactide)s,[5] isotactic polymers of *R*-(+)-/*S*-(−)-α-methyl-α-ethyl-*β*-propiolactones,[6] and poly(*γ*-benzyl L-/D-glutamate)s[7] 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 isotactic-PMMA (it-PMMA) is surrounded by twice the molar amount of syndiotactic-PMMA (st-PMMA). This structure was proposed by both Challa et al. based on theoretical and X-ray diffraction data[8] and Spevacek et al. based on ^{13}C NMR measurements.[9] Stereocomplex formation between PMMAs may be applied to studies of polymeric assembly from solutions on the basis of this molecularly characterized structure.

Regulated assembly of ultrathin polymer films on certain substrates is of great interest not only because of its potential applications in the synthesis of polymeric materials, but also because of its scientific significance in the field of polymer surface chemistry. Studies of polymer films of homogeneous

---

* To whom correspondence should be addressed. Tel: +81-99-285-8320. Fax: +81-99-255-1229. E-mail: akashi@apc.kagoshima-u.ac.jp.

[†] Present address: Graduate School of Engineering Science, Osaka University, Machikaneyama-cho 1-16, Toyonaka 560-0043, Japan

(1) (a) Watanabe, W. H.; Ryan, C. F.; Fleischer, P. C., Jr.; Garrett, B. S. *J. Phys. Chem.* **1961**, *65*, 896. (b) Liquori, A. M.; Anzuino, G.; Coiro, V. M.; D'Alagni, M.; Santis, P. D.; Savino, M. *Nature* **1965**, *206*, 358. (c) Spevacek, J.; Schneider, R. *Adv. Colloid Interface Sci.* **1987**, *27*, 81. (d) Feitsma, E. L.; De Boer, A.; Challa, G. *Polymer* **1975**, *16*, 515. (e) De Boer, A.; Challa, G. *Polymer* **1976**, *17*, 633.

(2) (a) Bosscher, F.; Keekstra, D.; Challa, D. *Polymer* **1981**, *22*, 124. (b) Kitayama, T.; Fujimoto, N.; Terawaki, Y.; Hatada, K. *Polym. Bull.* **1990**, *23*, 279.

(3) (a) Lohmeyer, J. H. G. M.; Kransen, G.; Tan, Y. Y. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 725. (b) Lohmeyer, J. H. G. M.; Tan, Y. Y.; Lako, P.; Challa, G. *Polymer* **1978**, *19*, 1171.

(4) Hatada, K.; Shimizu, S.; Terawaki, Y.; Ohta, K.; Yuki, H. *Polym. J.* **1981**, *13*, 811.

(5) Ikada, Y.; Jamshidi, K.; Tsuji, H.; Hyon, S.-H. *Macromolecules* **1987**, *20*, 904.

(6) Grenier, D.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 577.

(7) (a) Fukuzawa, T.; Uematsu, I. *Polym. J.* **1974**, *6*, 537. (b) Takahashi, T.; Tsutsumi, A.; Hikichi, K.; Kaneko, M. *Macromolecules* **1974**, *7*, 806. (c) Nomori, H.; Tsuchihashi, N.; Takagi, S.; Hatano, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2522. (d) Lotz, B.; Colonna-Cesari, F.; Heits, F.; Spach, G. *J. Mol. Biol.* **1976**, *106*, 915. (e) Baba, Y.; Kagemoto, A. *Macromolecules* **1977**, *10*, 458. (f) Heitz, F.; Cary, P. D.; Crane-Robinson, C. *Macromolecules* **1977**, *10*, 526.

(8) (a) Bosscher, F.; Brinke, G. T.; Challa, G. *Macromolecules* **1982**, *15*, 1442. (b) Brinke, G. T.; Schomaker, E.; Challa, G. *Macromolecules* **1985**, *18*, 1925. (c) Schomaker, E.; Challa, G. *Macromolecules* **1989**, *22*, 3337.

(9) Spevacek, J.; Schneider, B.; Straka, J. *Macromolecules* **1990**, *23*, 3042.

10.1021/ja9913535 CCC: $19.00 © 2000 American Chemical Society
Published on Web 02/18/2000

nanoscale thickness and/or molecularly regulated assembling structures have been especially attractive to many researchers.[10] Detailed studies of the molecular assembly of certain polymers should lead to new scientific insights regarding the molecular events involved in assembly. Recently, Decher et al. found that the stepwise immersion of substrates such as mica and glass into aqueous solutions of positively and negatively charged polymers produced layered ultrathin polymer films with a thickness of less than several tenths of a nanometer.[11] In each step, the adsorbed polymer is insolubilized and stabilized by electrostatic complex formation on the substrate, and is not washed out by rinsing with water, resulting in a stable ultrathin film. Because this technique involves the simple immersion of a substrate into an oppositely charged polymer solution, researchers extended this process to include deposition not only of water-soluble linear charged polymers,[12] but also of viruses,[13] proteins,[14] silica colloids,[15] metal nanoparticles,[16] dyes,[17] metal oxides,[18] amphiphiles,[19] and clays.[20] We also studied the electrostatic adsorption of polystyrene nanospheres onto the surface of alternately deposited polymer films, and analyzed their regulated monolayer structures.[21] Furthermore, other research groups have utilized charge transfer[22] and hydrogen-bonding[23] interactions between certain polymers to facilitate ultrathin film deposition. The concept of stepwise deposition 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 formation of stereocomplexes of stereoregular PMMAs, as well as to other interaction systems.

Although detailed studies of stereocomplex formation between stereoregular PMMAs have been performed, no research has utilized the characteristics of the stereocomplex for stepwise fabrication of ultrathin polymer assemblies on a substrate. The resulting ultrathin films would have a molecularly regulated, novel structure, because the charged polymers in the electrostatically prepared ultrathin films formed by stepwise fabrication are believed to have random conformation structures. Furthermore, the stepwise stereocomplex assembly of PMMAs on a substrate would require structural rearrangement of a preadsorbed stereoregular PMMA, possibly from random conformation during the subsequent adsorption process of the second stereoregular PMMA, to form the double stranded nano-structure described above. In this case, the polymers would have huge steric requirements during formation. In situ assembly of ultrathin PMMA films with stereocomplex formations has more general implications regarding the dynamic events involving polymeric interaction at the surface of ultrathin polymer films. In other words, stereocomplex formation suggests that a dynamic conformational change in polymers adsorbed onto a film's surface is available for the ultrathin film deposition process. We do not know, however, whether polymers at the interface can interact with other polymers exhibiting conformational changes.

In this study, we analyzed the stepwise assembly of isotactic (it-) and syndiotactic (st-) PMMAs onto a substrate from their organic solutions. We used a quartz-crystal microbalance (QCM) as a substrate to quantify the amount of PMMA adsorbed to a nano-gram level using Sauerbrey's equation,[24] in conjunction with the analysis of 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 Section

Materials. Isotatic and syndiotactic PMMAs were synthesized by anionic polymerization in toluene at −78 °C with t-C_4H_9MgBr[25a] and t-$C_4H_9Li/(C_2H_5)_3Al$,[25b] respectively, as initiators. Characteristics such as the number-average molecular weights (and their distribution), which were measured by size exclusion chromatography with polystyrene standard in THF, are listed in Table 1. The tacticities (mm:mr:rr), which were measured by ^{1}H NMR signals of the α-methyl protons, are also

---

(10) (a) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932. (b) Andrade, J. D., Ed. *Polymer Surface Dynamics*; Plenum Press: New York, 1988. (c) Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir−Blodgett to Self-Assembly*; Harcourt Brace Jovanovich: Boston, 1991. (d) Tsukruk, V. V. *Prog. Polym. Sci.* **1997**, *22*, 247. (e) Grainger, D. W. *Prog. Colloid Polym. Sci.* **1997**, *103*, 2243.

(11) (a) Decher, G.; Hong, J.-D. *Makromol. Chem., Macromol. Symp.* **1991**, *46*, 321. (b) Decher, G.; Hong, J.-D. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1430. (c) Decher, G. *Compr. Supramol. Chem.* **1996**, *9*, 507. (d) Decher, G. *Science* **1997**, *277*, 1232.

(12) (a) Kaschak, D. M.; Mallouk, T. E. *J. Am. Chem. Soc.* **1996**, *118*, 4222. (b) Advincula, R.; Aust, E.; Meyer, W.; Knoll, W. *Langmuir* **1996**, *12*, 3536. (c) Hoogeveen, N. G.; Stuart, M. A. C.; Fleer, G. J. *Langmuir* **1996**, *12*, 3675. (d) Caruso, F.; Niikura, K.; Furlong, D. N.; Okahata, Y. *Langmuir* **1997**, *13*, 3422. (e) Delcorte, A.; Bertrand, P. *Langmuir* **1997**, *13*, 5125. (f) Chen, W.; McCarthy, T. J. *Macromolecules* **1997**, *30*, 78. (g) Cheung, J. H.; Stockton, W. B.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2712. (h) Lvov, Y.; Onda, M.; Ariga, K.; Kunitake, T. *J. Biomater. Sci. Polym. Ed.* **1998**, *9*, 345.

(13) Lvov, Y.; Haas, H.; Decher, G.; Möhwald, H.; Mikhailov, A.; Mtchedlishvily, B.; Morgunova, E.; Vainshtein, B. *Langmuir* **1994**, *10*, 4232.

(14) (a) Lvov, Y.; Ariga, K.; Kunitake, T. *Chem. Lett.* **1994**, 2323. (b) Lvov, Y.; Ichinose, I.; Ariga, K.; Kunitake, T. *J. Am. Chem. Soc.* **1995**, *117*, 6117. (c) Onda, M.; Lvov, Y.; Ariga, K.; Kunitake, T. *Biotech. Bioeng.* **1996**, *51*, 163. (d) Sano, M.; Lvov, Y.; Kunitake, T. *Annu. Rev. Mater. Sci.* **1996**, *26*, 153. (e) Hodak, J.; Etchenique, R.; Calvo, E. J. *Langmuir* **1997**, *13*, 2708. (f) Caruso, F.; Niikura, K.; Furlong, D. N.; Okahata, Y. *Langmuir* **1997**, *13*, 3427. (g) He, J.-A.; Samuelson, L.; Li, L.; Kumar, J.; Tripathy, S. K. *Langmuir* **1998**, *14*, 1674.

(15) (a) Ariga, K.; Lvov, Y.; Onda, M.; Ichinose, I.; Kunitake, T. *Chem. Lett.* **1997**, 125. (b) Lvov, Y.; Ariga, K.; Onda, M.; Ichinose, I.; Kunitake, T. *Langmuir* **1997**, *13*, 6195.

(16) (a) Yang, H. C.; Aoki, K.; Hong, H.-G.; Sackett, D. D.; Arendt, M. F.; Yau, S.-L.; Bell, C. M.; Mallouk, T. E. *J. Am. Chem. Soc.* **1993**, *115*, 11855. (b) Kotov, N. A.; Dékány, I.; Fendler, J. H. *J. Phys. Chem.* **1995**, *99*, 13065. (c) Feldheim, D. L.; Grabar, K. C.; Natan, M. J.; Mallouk, T. E. *J. Am. Chem. Soc.* **1996**, *118*, 7640. (d) Sun, Y.; Hao, E.; Zhang, X.; Yang, B.; Gao, M.; Shen, J. *J. Chem. Soc., Chem. Commun.* **1996**, 2381. (e) Sun, Y.; Hao, E.; Zhang, X.; Yang, B.; Gao, M.; Shen, J.; Chi, L.; Fuchs, H. *Langmuir* **1997**, *13*, 5168. (f) Yonezawa, T.; Onoue, S.; Kunitake, T. *Adv. Mater.* **1998**, *10*, 414.

(17) (a) Sun, Y.; Zhang, X.; Sun, C.; Wang, Z.; Shen, J.; Wang, D.; Li, T. *J. Chem. Soc., Chem. Commun.* **1996**, 2379. (b) Ariga, K.; Onda, M.; Lvov, Y.; Kunitake, T. *Chem. Lett.* **1997**, 25. (c) Ariga, K.; Lvov, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1997**, *119*, 2224. (d) Linford, M. R.; Auch, M.; Möhwald, H. *J. Am. Chem. Soc.* **1998**, *120*, 178.

(18) (a) Ichinose, I.; Senzu, H.; Kunitake, T. *Chem. Lett.* **1996**, 831. (b) Ichinose, I.; Tagawa, H.; Mizuki, S.; Lvov, Y.; Kunitake, T. *Langmuir* **1998**, *14*, 187.

(19) (a) Ichinose, I.; Fujiyoshi, K.; Mizuki, S.; Lvov, Y.; Kunitake, T. *Chem. Lett.* **1996**, 257. (b) Sohling, U.; Schouten, A. J. *Langmuir* **1996**, *12*, 3912.

(20) (a) Keller, S. W.; Kim, H.-N.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 8817. (b) Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *Langmuir* **1996**, *12*, 3038. (c) Kotov, N. A.; Haraszti, T.; Turi, L.; Zavala, G.; Geer, R. E.; Dékány, I.; Fendler, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 6821. (d) Fang, M.; Kaschak, D. M.; Sutorik, A. C.; Mallouk, T. E. *J. Am. Chem. Soc.* **1997**, *119*, 12184.

(21) (a) Serizawa, T.; Akashi, M. *Chem. Lett.* **1997**, 809. (b) Serizawa, T.; Takeshita, H.; Akashi, M. *Chem. Lett.* **1998**, 487. (c) Serizawa, T.; Takeshita, H.; Akashi, M. *Langmuir* **1998**, *14*, 4088. (d) Serizawa, T.; Kamimura, S.; Akashi, M. *Colloids Surf.* In press.

(22) (a) Shimazaki, Y.; Mitsuishi, M.; Ito, S.; Yamamoto, M. *Langmuir* **1997**, *13*, 1385. (b) Shimazaki, Y.; Mitsuishi, M.; Ito, S.; Yamamoto, M. *Langmuir* **1998**, *14*, 2768.

(23) Stockton, W. B.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2717.

(24) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.

(25) (a) Hatada, K.; Ute, K.; Okamoto, Y.; Kitayama, T. *Polym. J.* **1986**, *18*, 1037. (b) Kitayama, T.; Shinozaki, T.; Sakamoto, T.; Yamamoto, M.; Hatada, K. *Makromol. Chem* **1989**, *15*, 167.

Table 1. Stereoregular Poly(methyl methacrylate)s Synthesized in This Study

			tacticity/%		
	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	mm	mr	rr
it-PMMA	20750	1.26	97	2	1
st-PMMA	5540	1.14	1	12	87
	7230	1.12	1	11	88
	10600	1.24	1	11	88
	22700	1.26	0	11	89
	34100	1.22	1	12	87
	72430	1.40	1	13	86

included in Table 1. Acetonitrile, acetone, and *N*,*N*-dimethylformamide (DMF) of spectral grade were purchased from Nacalai Tesque (Japan) and used for measurements without further purification. Ultrapure distilled water was provided by the MILLI-Q labo.

Quartz Crystal Microbalance. An AT-cut quartz crystal with a parent frequency of 9 MHz was obtained from USI (Japan). A crystal (9 mm in diameter) was coated on both sides with gold electrodes 4.5 mm in diameter, which was of a mirrorlike polished grade. The mean roughness of the electrode surface was estimated to be 1.938 nm from contact-mode AFM analysis. The frequency was monitored by an Iwatsu frequency counter (Model SC7201), and was recorded by a personal computer (NEC PC-9801 DX). The leads of the QCM were sealed and protected with a rubber gel to prevent degradation as a result of the solvent contact during immersion in organic solutions. The amount of PMMAs adsorbed, Δm, could be calculated by measuring the frequency decrease in the QCM, ΔF, using Sauerbrey's equation[24] 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 (2.95×10^{11} dyn cm^{-2}). This equation was reliable when measurements were made in air as described in this study, because the mass of the solvents is never detected as the frequency shift, and the effect of the viscosity of the absorbent on the frequency can be ignored.

Stepwise Adsorption. Before assembly measurements, QCM electrodes were treated 3 times with a piranha solution (H_2SO_4:H_2O_2 = 3:1) for 1 min each time, followed by rinsing with pure water and drying with N_2 gas, to clean its surface. The QCM obtained following cleaning was then immersed in an it-PMMA solution of adequate concentration (0.17−2.6 mg mL^{-1}) for an adequate time (15 min in almost every case) at ambient temperature, taken out, thoroughly rinsed with the same solvent, and dried with N_2 gas. The frequency decrease was then measured. The QCM was then immersed again into an st-PMMA solution and the same procedure was repeated. This stepwise cycle was repeated for film deposition. The assembling temperature was lower than the dissociation temperatures of PMMA stereocomplexes in various organic solutions, which were higher than 60 °C in almost every case.[26] The film thickness of the resulting PMMA assemblies was estimated from the frequency shifts, assuming the film density[27] to be 1.188 g cm^{-3} and the film surface to be flat. The assembling ratio between it-PMMA and st-PMMA was basically obtained as a mean value of the ratios at the step from it-PMMA to st-PMMA, because stereocomplex formation seemed to occur during this step (see Results and Discussion).

Others. Reflection Absorption Spectrum (RAS) spectra were obtained with a Herschel FT/IR-610, Jasco (Japan) at ambient temperature. First, one side of a glass slide (13 × 26 mm), which was used as a substrate for RAS measurement, was coated with gold to obtain a reflective surface. The PMMA films were deposited by stepwise immersion of the substrate into acetonitrile solutions of it- and st-PMMA in the absence or presence of water; the formation procedure was the same as that on QCM. Attenuated total reflection (ATR) spectra were obtained by the same apparatus attached with a ZnGe internal reflection element (60 × 10 × 3.75 mm) with an incidence angle of 45°. PMMA solutions were cast on the element. In both measurements, the interferograms were co-added 128 times and Fourier transformed at a resolution of 8 cm^{-1}. The static contact angle of PMMA ultrathin films at each step in stepwise deposition was measured by dropping water onto the films. The AFM images were obtained in a Digital Instruments NanoScope III that was operated with a tapping or a contact mode in the air at ambient temperature. We have not performed any image processing other than flat leveling. The mean square roughness (*Ra*) in given observed areas was estimated from the following equation:

$$Ra = \frac{1}{LxLy}\int_0^{Ly}\int_{Lx}^{0} |F(x,y)|\,\mathrm{d}x\,\mathrm{d}y$$

where *F(x,y)* is the surface relative to the center plane that is a flat plane parallel to the mean plane, and *Lx* and *Ly* are the dimensions of the surface.

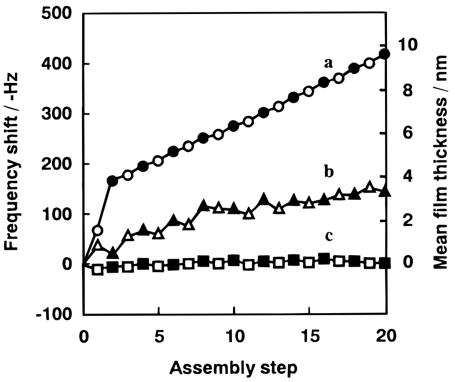

Figure 1. Frequency shift of QCM by the stepwise assembly from various organic solutions of it- ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700) at the concentration of 1.7 mg mL^{-1} from (a) acetonitrile, (b) acetone, and (c) DMF solutions.

Results and Discussion

Assembly from Organic Solvents. 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 DMF, which have already been shown to be strongly complexing solvents.[1c] In all cases, an immediate precipitation or turbidity by mixing of it- and st-PMMA solutions was not observed at ambient temperature. Before the stepwise assembly, we analyzed the stability of the resonance frequency of the QCM in organic solvents, because the QCM might not work when immersed for a long time in these solvents. We immersed the QCM in pure solvents for 15 min and then dried the surface with N_2 gas before measuring the resonance frequency shift. We observed a shift of only a few hertz after repeated immersion (more than 10 times) in solvent alone. As a consequence, we were able to determine the amount of assembled PMMA from the QCM shift.

Figure 1 shows the dependence of the frequency shift on the assembly steps when the QCM was alternately immersed in it-PMMA ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700) solutions in the three solvents for 15 min at a PMMA concentration of 1.7 mg mL^{-1} (in this case, we used a combination of stereoregular PMMAs that had similar molecular weights). Acetonitrile was the best solvent for PMMA assembly in large amounts, as shown

---

[26] Spevacek, J.; Schneider, B. *Makromol. Chem.* **1974**, *175*, 2939.

[27] Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook,* 3rd ed.; John Wiley & Sons: New York, Chichester, Brisbane, Toronto, Singapore, 1989.

in Figure 1a. When we immersed the QCM in it- or st- solution alone for a much longer time, the frequency shift saturated at a level obtained at one step of the assembly process. This observation implies that the stereocomplex of stereoregular PMMAs was formed on the QCM. 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 a 20-step assembly ($-\Delta F_{20\mathrm{steps}}$) was 416 Hz with an experimental error of ±5%. The error was also the case in subsequent experiments using acetonitrile solvent. This shift corresponded to an adsorption amount of 362 ng. The film thickness that was estimated by assuming the films' molecular smoothness was 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 (9.7 ± 0.3 nm). When the assembly was performed without the drying process, the total frequency shift was not affected, indicating the drying process is not essential for the stepwise assembly. The thickness at each it- and st-PMMA step, which was estimated at all steps except for the initial two, was 0.23 ± 0.04 and 0.44 ± 0.05 nm, respectively.

On the other hand, acetone gave less adsorption ($-\Delta F_{20\mathrm{steps}} = 143$ Hz, of which an experimental error was 15%), and we could not observe any assembly from the DMF solution ($-\Delta F_{20\mathrm{steps}} = 0$ Hz), as shown in Figure 1, parts b and c, respectively. All of the solvents used in these experiments are known to promote complex formation in mixed solutions of it- and st-PMMA.[1c] Notably, the amount of complex formed in DMF solution is almost the same as that formed in acetonitrile, although formation in acetone was not studied under the same conditions. Accordingly, stepwise assembly on a QCM substrate is not related to complex formation behavior in solutions. It is difficult to explain why we observe different behavior on the QCM and in solutions. A possible reason may be solubility of PMMA in the above solvents, because the present assembly is based on physisorption of PMMAs onto a substrate. In general, both solubility and the nature of the substrate affect polymer adsorption. Studies have indicated that poor solubility and strong interaction with the substrate promote polymer adsorption.[28] In the present study, the substrate remained the same, and the solvent was varied. Acetonitrile was the poorest solvent of PMMA,[27] compared to acetone and DMF. The poor solubility of PMMA in acetonitrile may promote stepwise assembly on the substrate. The data imply that suitable solvent selection is a significant factor in the stepwise assembly of stereoregular PMMA. We selected a system using acetonitrile solutions for use in the following experiment.

The amount of PMMA adsorbing in each assembly step was analyzed by using the QCM technique. Other research groups have experimentally and theoretically studied the ratio between assembled it- and st-PMMA in mixed solutions, and have estimated it to be 1:2.[1] In the case of acetonitrile solvent, the mean ratio that was determined from the QCM measurements was 2.0 ± 0.4 (for the estimation procedure, see the Experimental Section), which is consistent with the value obtained previously in this solution.[1] This strongly implies that it- and st-PMMAs were assembled on a QCM substrate by stereocomplex formation similar to that observed in solution. In addition, the frequency shifts of physically adsorbed it- and st-PMMAs on a QCM, as estimated by simple immersion of QCM into each acetonitrile solution, were −71 and −23 Hz, respectively, and the molar ratio did not become 2. Although we ignored the initial two steps in the estimation of the st/it ratio because of the relatively larger assembling amount (in the following sections as well), the ratio was still 1.6. The ratio observed in acetone was not used because of fairly large fluctuations in the data. When we assembled the PMMAs from acetonitrile solutions with 5 min immersing time, we observed constant frequency shifts, indicating that 5 min of immersion was sufficient for stepwise assembly of the PMMAs (data not shown). PMMAs were assembled using 15 min of immersing time in the present study.

On the other hand, when we repeated immersion (15 min) of QCM with drying processes into a mixed solution of it- and st-PMMAs (of which concentration was 0.85 and 1.7 mg mL^{-1}, respectively), we observed stepwise deposition. The frequency shift after a 10-step assembly was approximately 420 Hz, and the mean shift at each step was 29 ± 10 Hz. However, the mixed solution became turbid at the time of step 9. The mechanism of this deposition might be different from that of the stepwise assembly described in the present study. Further research of deposition from a mixed solution of stereoregular PMMAs is necessary.

Further details of the stepwise frequency shift shown in Figure 1a were evaluated by performing assembly in a system that started with st-PMMA (in all other assemblies, we started from it-PMMA). For a detailed analysis, we calculated the st/it ratio both from the it-PMMA to st-PMMA step (discussed above) and from the st-PMMA to it-PMMA step. Assembly ratios in Figure 1a were 2.0 ± 0.4 and 1.8 ± 0.8, respectively. Significantly, 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. This difference may indicate that stereocomplex formation preferentially occurred during the step from it-PMMA to st-PMMA. When we started with st-PMMA (QCM data not shown), the ratios were 2.0 ± 0.3 and 2.3 ± 1.0, respectively, which were similar to values obtained when starting with it-PMMA. In the following experiments, the ratio was estimated from the it-PMMA to st-PMMA step.

The frequency shift at each assembly step was also measured at 4 °C in acetonitrile solutions. A stepwise frequency shift was also observed in this analysis. However, the amount of it- and st-PMMA assembled at each step was three and two times larger than that assembled at ambient temperature, respectively. The molar assembly ratio was 1.4 ± 0.6, which is smaller than that observed at ambient temperature. It is known that it- and st-PMMAs undergo self-association in their solutions, depending on the solvent species.[1c] In fact, when we kept the PMMA solutions at 4 °C for a few weeks, precipitation was observed. The larger assembling amount might be caused by such precipitation on the film surface. In addition, it- or st-PMMA may have difficulty rearranging into a complex formation possibly due to lower molecular motion at the lower temperature. The stereocomplex might be formed in an interfacial region between each it- and st-PMMA assembly. This might lead to a structurally sandwiched assembly as temperature is changed. In fact, the static contact angles of the it- and st-steps were 63.4 ± 0.4° and 73.3 ± 0.3°, respectively. These values were consistent with the values for each bulk film (see below). Temperatures as well as solvents affect the stepwise assembly of stereoregular PMMA on a substrate. Further research regarding the temperature effect will be performed soon. As a consequence, we assembled PMMAs at ambient temperature in the present study.

---

(28) Fleer, G. D.; Stuart, M. A. C.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, Glasgow, New York, Tokyo, Melbourne, Madras, 1993.

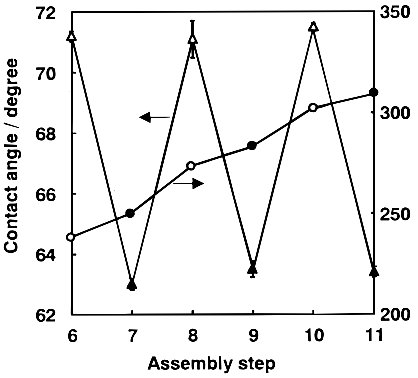

Figure 2. Static contact angle of the stepwise assembly from acetonitrile solutions of it- ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700) at the concentration of 1.7 mg mL^{-1}.

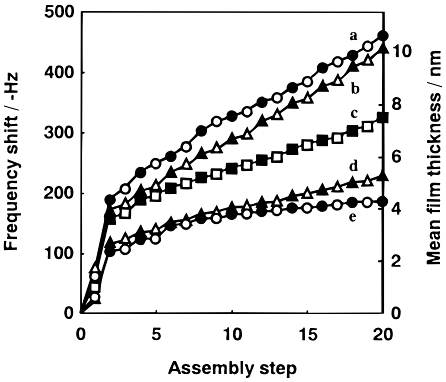

Figure 3. Frequency shift of QCM by the stepwise assembly from acetonitrile solutions of it- ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700) at various concentrations: (a) 2.6, (b) 1.7, (c) 0.85, (d) 0.34, and (e) 0.17 mg mL^{-1}.

Static Contact Angle Measurement. 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 surface.[29] We think this characteristic is useful for monitoring the stepwise assembly of stereoregular PMMAs on a substrate. Here, we analyzed the static contact angle of the ultrathin film surface that was prepared by the stepwise assembly of it- and st-PMMAs from acetonitrile solutions.

Figure 2 shows the dependence of the static contact angle, together with the frequency shift, on assembling steps when the QCM was alternately immersed into acetonitrile solutions of it-PMMA ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700). The contact angle changed with the step number, indicating stepwise assembly of stereoregular PMMA on the substrate. Furthermore, the contact angle of each stereoregular PMMA step (an odd or even step) was almost the same value, also indicating the same molecular composition or conformation at the film surface. The mean contact angle at odd steps (it-PMMA assembly) was 63.3 ± 0.3°. This value was comparable to 63.0 ± 0.3°, the angle of the adsorbed bulk it-PMMA film on a bare QCM substrate ($-\Delta F = 71$ Hz). This was a reasonable value compared to values for bulk films reported by Tretinnkov,[29] although the it-PMMA described in the present study had higher stereoregularity than the 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 ± 1° in the air. Accordingly, we may consider the surface upon the it-PMMA adsorption step to be completely covered by it-PMMA molecules alone. If we assume the hypothesized structure of the stereocomplex,[8,9] it-PMMA will be buried in the helical structure of st-PMMA and the contact angle should be altered accordingly. Therefore, it-PMMA must be adsorbed onto the surface of the preformed PMMA complex. Significantly, the it-PMMA layer was not replaced by st-PMMA in the complex film even after 1 h, although replacement may preferably have occurred to minimize the interfacial free energy (the static contact angle of the st-PMMA film is larger than that of the it-PMMA one, as described below). That might mean 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 value at even steps (st-PMMA assembly) was 71.2 ± 0.4°, which was slightly smaller than the reported value of the st-PMMA film surface[29] and also smaller than that (73.2 ± 0.8°) of a physically adsorbed bulk st-PMMA film on a QCM ($-\Delta F = 23$ Hz) within the range of experimental error. The contact angle of the adsorbed st-PMMA was also consistent with that of its cast film. We think this observation is quite meaningful, because the contact angle of the st-PMMA step is possibly the true contact angle of the stereocomplex-formed PMMA film surface. Although the contact angle of the completed stereocomplex formed on the PMMA film surface has not been previously reported, it may be slightly smaller than that for the st-PMMA layer because the ester group in st-PMMA should be pointed out in the molecular structure of the stereocomplex.[8,9] Note that st-PMMA on film surfaces usually tends to direct alkyl main chains in the air, to minimize the interfacial free energy.[29] We concluded that the surface composition of the ultrathin PMMA film was altered by the stepwise assembly of stereoregular PMMAs, possibly by physisorption of it-PMMA without stereocomplex formation and by stereocomplex formation between it- and st-PMMA on a substrate. These observations were consistent with the QCM results.

Effect of PMMA Concentration. The PMMA assembly in this study is based on stepwise adsorption of each stereoregular PMMA. Accordingly, PMMA concentrations of each solution may affect assembling behavior. Even in the solution system, we obtain clear solutions, precipitation, or gels depending on the concentrations.[1c] Here, we analyzed the effect of PMMA concentration on stepwise assembly from acetonitrile solutions at ambient temperature, in which the assembly was successively performed as described in the previous section.

Figure 3 shows the dependence of the frequency shift on assembling steps when the QCM was alternately immersed into acetonitrile solutions of it- ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700) at various PMMA concentrations. The frequency shifted in proportion to assembling steps at all concentrations, indicating the stepwise assembly of stereoregular PMMAs on the QCM with clear dependence on the PMMA concentration. The shift in the initial two steps at all concentrations was greater than that in the latter steps, as was described above. Figure 4 shows the dependence of $-\Delta F_{20\mathrm{steps}}$ and the ratio of st-/it-PMMA assembled on PMMA concentration. The $-\Delta F_{20\mathrm{steps}}$ clearly increased and was gradually saturated with increased concentration, indicating that the assembly was based on concentration-dependent adsorption. On the other hand, the ratios were constant at around 2 within experimental error at all concentrations studied. The observations are reasonable if we consider the stereocomplex formation between it- and st-PMMAs. At the concentration of 0.17 mg mL^{-1}, the experimental error was fairly large due to a small frequency shift, as is shown in Figure

---

(29) Tretinnikov, O. N. *Langmuir* **1997**, *13*, 2988.

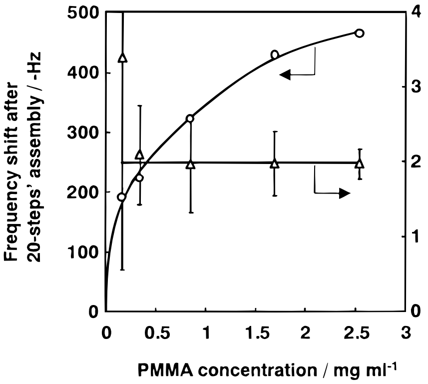

Figure 4. Dependence of the frequency shift after a 20-step assembly and the ratio of st-/it-PMMA on the concentration.

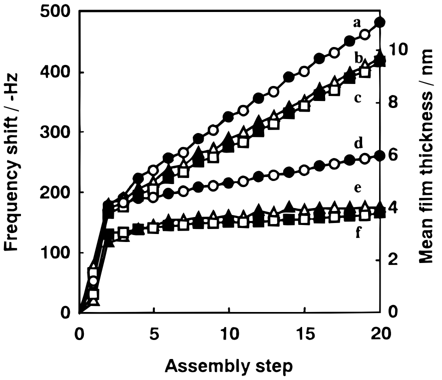

Figure 5. Frequency shift of QCM by the stepwise assembly from acetonitrile solutions of it- ($\bar{M}_n$ 20750) and st-PMMA with various molecular weights: (a) $\bar{M}_n$ 72430; (b) 34100; (c) 22700; (d) 10600; (e) 7230; and (f) 5540.

3e. We found the stepwise assembly of stereoregular PMMAs could be performed at the various PMMA concentrations studied, although the amount of adsorption increased with an increase in concentration.

When we assembled it- and st-PMMAs at concentrations of 0.85 and 2.55 mg mL^{-1}, respectively, the st/it-PMMA ratio became 2.1 ± 0.4, also indicating stereocomplex (QCM data not shown). This indicates that twice the amount of st-PMMA as it-PMMA assembles on the substrate, even when the st-PMMA concentration is greater than that of it-PMMA. On the other hand, when we assembled it- and st-PMMAs at the reversed concentrations of 2.55 and 0.85 mg mL^{-1}, the ratio became 1.1 ± 0.4 (QCM data also not shown). This indicates that at least the same concentration of st-PMMA as that of it-PMMA is necessary for stepwise stereocomplex formation.

Effect of Molecular Weight of st-PMMA. Researchers have previously studied the effect of molecular weight on the stereocomplex formation of highly isotactic and syndiotactic PMMAs in solutions, where it did not significantly affect stereocomplex formation if the PMMAs had sufficient stereoregularity and high enough molecular weights.[1c]

Figure 5 shows the dependence of the frequency shift on the assembly steps when the QCM was alternately immersed in acetonitrile solutions of it- ($\bar{M}_n$ 20750) and st-PMMAs with various molecular weights. The frequency shifted more as the number of assembly steps increased regardless of molecular weight, indicating stepwise assembly of stereoregular PMMAs on the QCM. Moreover, adsorption was clearly dependent on molecular weight. The shift in the initial two steps was greater with all molecular weights, compared to the shifts in the latter steps, as described previously. Figure 6 shows the dependence of $-\Delta F_{20\text{steps}}$ and the ratio of st-/it-PMMA on the molecular weight. The $-\Delta F_{20\text{steps}}$ clearly increased with the molecular weight until reaching a molecular weight of around 20000 and tended to saturate at around 500 Hz at higher molecular weights. On the other hand, the st-/it-PMMA ratios were constant around 2 within experimental error for all the molecular weights studied. Below a molecular weight of 7230, the experimental error was fairly large due to the small shift in frequency, as shown in Figures 5e and 6f. It is clear that st-PMMAs of various molecular weights can be alternately assembled with it-PMMA on a substrate, possibly due to stereocomplex formation. However, it is significant that it-PMMA utilized in the present study was the same in all experiments. This suggests that it-PMMA adsorption is strongly affected by the molecular weight of st-PMMA assembled on a substrate. It is difficult to reasonably explain this observation. The terminal residue of PMMA during assembly on a substrate might be affected by polymer adsorption. Further research will be needed.

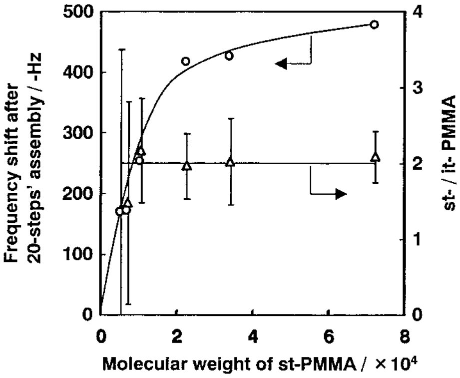

Figure 6. Dependence of the frequency shift after a 20-step assembly and the ratio of st-/it-PMMA on the molecular weight of st-PMMA.

In the stereocomplex formation between it- and st-PMMAs, one molecule of st-PMMA, which is twice the length of it-PMMA, can assemble with one molecule of it-PMMA in acetonitrile.[1c] On the basis of this estimation, the it-PMMA ($\bar{M}_n$ 20750) used here might assemble with st-PMMA with a molecular weight of around 40000 by way of 1-to-1 assembly. This means that it- and st-PMMAs might cross-link each other in assembly on a QCM substrate.

Assembly from Water-Mixed Organic Solvents. There have been sufficient advances in regulation of the amount of assembled PMMAs that form stereocomplex structures on a substrate. If a greater amount of PMMA can be assembled in the same number of steps, formation processes can be shortened. We have already studied the electrostatic alternate-assembly of water-soluble naturally occurring polymers such as chitosan (as a cationic polymer) and poly(γ-glutamic acid) (as an anionic polymer) onto QCM.[30] In these cases, the addition of water-soluble organic solvents to aqueous solutions, in which the polymers are less soluble, caused assembly of a greater amount of the polymers. The concept should be primarily applied to PMMA assemblies. The observation of greater assemblies from less soluble solvents suggests that the physisorption process is a significant process in assembly. Accordingly, we added water, as a less soluble solvent of PMMA, to acetonitrile solutions. Water was added until limitations in PMMA solubility had been reached, as judged with the naked eye. When we mixed the solutions of it- ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700) at

---

(30) Serizawa, T.; Goto, H.; Kishida, A.; Endo, T.; Akashi, M. *J. Polym. Sci. Polym. Chem. Ed.* **1999**, *36*, 801.

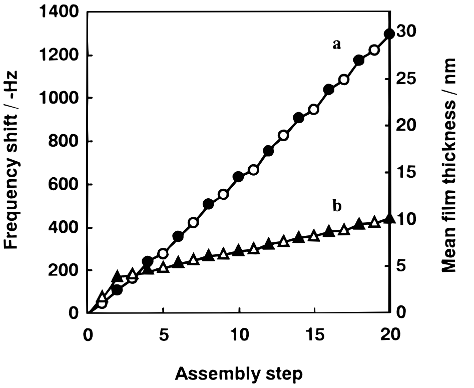

Figure 7. Frequency shift of QCM by the stepwise assembly from water-mixed organic solutions of it- ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700) at the concentration of 1.7 mg mL^{-1}: (a) acetonitrile/water, 10/1.5 (v/v) and (b) acetonitrile (the same as Figure 1a).

concentrations of 1.7 mg mL^{-1} at ambient temperature, the polymers immediately precipitated. As the polymers were not precipitated immediately in the absence of water (pure organic solutions), assembly seemed to be enhanced by the addition of water.

Figure 7 shows the dependence of the frequency shift on assembling steps when the QCM was alternately immersed in it-PMMA ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700) solutions with an acetonitrile/water (10/1.5, v/v) solvent system at a PMMA concentration of 1.7 mg mL^{-1} at ambient temperature, together with the shift observed in pure acetonitrile solutions. The amount of assembled PMMA after 20 steps was approximately three times greater in the water-mixed solutions than in the pure acetonitrile solutions. The st/it-PMMA ratio from water-mixed acetonitrile solutions was 1.8 ± 0.4, which is the same as that from pure acetonitrile solutions, within experimental error. This implies stepwise stereocomplex formation between it- and st-PMMA even from water-mixed acetonitrile solutions on a substrate. Although detailed discussion of this enhanced assembling is difficult, the physisorption of it-PMMA seemed to be facilitated by the addition of water. Further research on the effect of mixed solvents or other solvents on the stepwise assembly is in progress.

Absorption Spectra Measurement. 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.[1c,31] When we analyze a film of nanometer-order thickness, reflection absorption IR spectroscopy (RAS) is a powerful tool because it can detect the weaker absorption by thinner PMMA films. The absorption band of main-chain CH$_2$-rocking vibrations at around 840−860 cm^{-1} in addition to C=O-stretching vibrations at around 1700−1800 cm^{-1} is available for evaluating the formation of the stereocomplex. Here, we measured the RAS of ultrathin films of assembled PMMAs to analyze the formation.

Figure 8 show the RAS data for the PMMA assemblies that were prepared from the acetonitrile and water−acetonitrile mixed solutions, together with the ATR spectra of cast films obtained from it-PMMA, st-PMMA, and their mixed acetonitrile solutions (the mixture ratio was 1/2, w/w). In each assembly, the assembling step was controlled to obtain films with a similar thickness (around 15 nm). The main peak in CH$_2$-rocking absorption for both 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-PMMAs, indicating stereocomplex formation between it- and st-PMMAs on the substrate. It is known that the band at 860 cm^{-1} is observed when st-PMMA associates with itself. However, acetonitrile is not a good solvent for self-association at ambient temperature, as previously reported.[1c] The band at 860 cm^{-1} for the self-association was a shoulder peak appearing together with a main peak at 840 cm^{-1}. On the other hand, the CH$_2$-rocking absorption peaks for both assemblies were different from those of the cast film obtained from the mixed solution. In the latter case, the main peak was at 840 cm^{-1} and complex formation was not promoted sufficiently. Furthermore, the C=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. The band representing the skeletal stretching vibration observed at 758 cm^{-1} might also be assigned to that of the stereocomplex. These observations strongly suggest that the stepwise assembly of stereoregular PMMA in this study was based on stereocomplex formation on substrate surfaces.

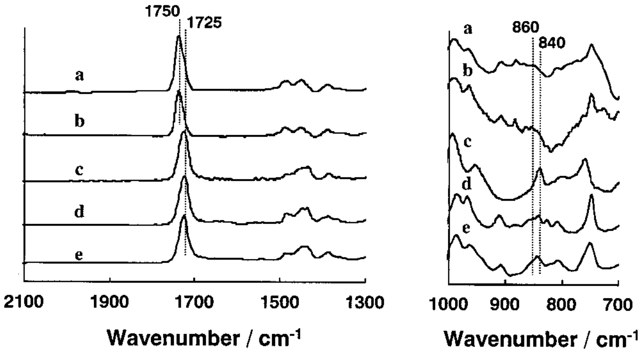

Figure 8. RAS spectra of the stepwise assemblies of it- ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700) at the concentration of 1.7 mg mL^{-1} from (a) acetonitrile and (b) acetonitrile/water, 10/1.5 (v/v) solutions, and ATR spectra of the cast films of (c) it-PMMA, (d) st-PMMA, and (e) their mixed (1/2, w/w) acetonitrile solutions.

AFM of PMMA Assembly. Atomic force microscopy (AFM) is a useful tool for analysis of the surface topology of polymer films. In the present study, we directly analyzed the surface of the PMMA assemblies that were prepared on the QCM from the acetonitrile and its water-mixed solutions. To study the surface topology of certain ultrathin polymer films by AFM, researchers usually deposit polymers onto a molecularly smooth substrate such as mica or HOPG. However, as we do not know how substrate species affect PMMA assembly, we analyzed the assemblies that were deposited on the QCM. Consequently, prior to AFM analysis of the PMMA assemblies, we analyzed the surface of a bare QCM gold surface to study the roughness of the substrate. Figure 9a shows the AFM image of a bare QCM surface. We observed the domain-like surface structure of the sputtered gold film on an electrode. The mean diameter and height of the domain were revealed to be 150 ± 60 and 5 ± 2 nm, respectively. The mean square roughness (*Ra*) was 1.8 nm. These values show that the surface of a QCM electrode is relatively smooth.

Figures 9b and 9c show the AFM images of the PMMA assemblies that were prepared from the acetonitrile and acetonitrile/water (10/1.5, v/v) solutions on the QCM, respectively. Significantly, both of the images also showed domain-like structures that were apparently different from those on a bare

---

[31] (a) Dybal, J.; Štokr, J.; Schneider, B. *Polymer* **1983**, *24*, 971. (b) Spevacek, J.; Schneider, B.; Dybal, J.; Štokr, J. *Croat. Chem. Acta* **1987**, *60*, 11. (c) Schneider, B.; Spevacek, J.; Straka, J.; Štokr, J. *Makromol. Chem., Macromol. Symp.* **1990**, *34*, 213. (d) Spevacek, J. *Makromol. Chem., Macromol. Symp.* **1990**, *39*, 71. (e) Tretinnikov, O. N.; Nakao, K.; Ohta, K.; Iwamoto, R. *Macromol. Chem. Phys.* **1996**, *197*, 753.

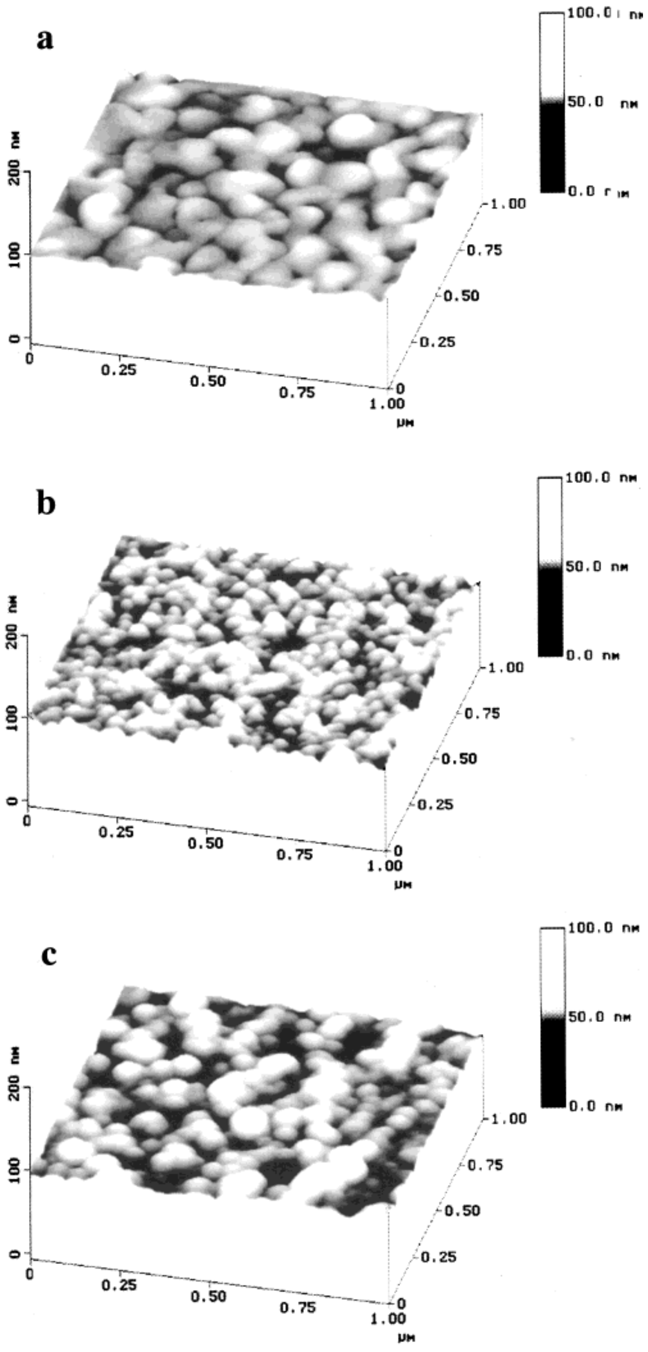

Figure 9. AFM images of the 20-step assembly of it- ($\bar{M}_n$ 20750) and st-PMMA ($\bar{M}_n$ 22700) at a concentration of 1.7 mg mL^{-1}: (a) a bore QCM electrode and (b) from acetonitrile and (c) acetonitrile/water, 10/1.5 (v/v), solutions.

QCM electrode, as shown in Figure 9a. The diameter of the domains seemed to differ depending on the solvent species. The mean diameter and height of the domain that was prepared from acetonitrile solutions was 60 ± 10 and 11 ± 2 nm, respectively. In addition, the *Ra* was 4.3 nm which was more than three times larger than that of the bare QCM but was nonetheless relatively smooth. On the other hand, those films formed from water−acetonitrile solutions had domains of 98 ± 11 and 12 ± 3 nm, respectively. The *Ra* was 4.8 nm, which was slightly larger than that of the assembly prepared from acetonitrile solutions. In both cases, the heights were smaller than the mean film thickness and were estimated by the surface flat. We found that the PMMA assemblies showed a domain-like and smooth surface structure on the gold QCM substrate. As the topology of the QCM substrate may potentially affect PMMA assembly, further analysis using other smoother substrates, such as mica and HOPG, is required.

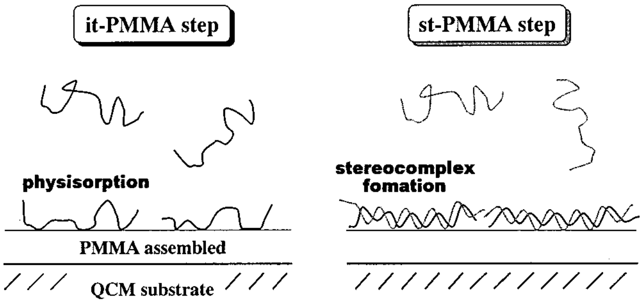

Figure 10. Schematic representation of a PMMA assembly at each step.

Assembling Mechanism. Why the stepwise stereocomplex of stereoregular PMMAs forms on the substrate surface remains the subject of discussion. On the basis of the quantitative QCM and contact angle results, the stereocomplex appears to form during the assembly step from it-PMMA to st-PMMA, resulting in an st-/it-PMMA ratio of 2. In this case, it-PMMA physisorption onto the assembly is reasonable if we consider that it adsorbs onto the surface of the stably formed assembly as a result of poor solvent-driven physisorption.[28] In fact, the amount of it-PMMA adsorbed increased with the addition of water as a less soluble solvent, so that the amount of stepwise assembly increased. However, this does not explain why excess or lower amounts of st-PMMA do not adsorb onto the it-PMMA layers. In other words, why does st-PMMA adsorption result in such complex stoichiometry? One possible explanation is as follows. As described above, less than one-third the amount of st-PMMA was physically adsorbed onto a bare QCM surface than it-PMMA. Moreover, when we analyzed physisorption of each PMMA onto spin-coated atactic PMMA, the amount of st-PMMA adsorbed was similarly smaller than it-PMMA. These observations suggest that st-PMMA has less ability to physically adsorb and perhaps has higher solubility in acetonitrile solutions. Accordingly, st-PMMA can adsorb (or assemble) onto it-PMMA on the film surface only by the formation of a strongly interactive stereocomplex. This must be the reason excess or lower amounts of st-PMMA do not adsorb onto the it-PMMA surface. In fact, the stereocomplex assembly was observed from a higher concentration of st-PMMA than it-PMMA as described above. It is also significant that the 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 st-PMMA, it-PMMA may have difficulty penetrating into the physically adsorbed st-PMMA to form the complex. Both the physisorption nature of the stereoregular PMMAs and the double stranded nano-structure seem to strongly affect stepwise assembly onto substrates.

Conclusions

The stepwise assembly of stereoregular PMMA on a QCM substrate from various organic solvents was studied. A quantitative analysis by using the QCM technique showed stepwise stereocomplex assembly of it- and st-PMMAs on the substrate. The static contact angle and spectroscopic studies also confirmed assembly. We found that the assembly occurred during the step from physically adsorbed it-PMMA to st-PMMA, and included a molecular rearrangement that was initialized by the penetration of st-PMMA into the it-PMMA layer, as schematically shown in Figure 10. Assembly was affected by conditions such as solvent species, PMMA concentrations, and PMMA molecular weight. The surface topography of these assemblies that were analyzed by AFM showed a domain-like structure, but were relatively smooth. We proposed a possible mechanism for stepwise stereocomplex formation on a substrate. Moreover, we remain interested in the mechanical properties or thermal stability of assembled PMMAs with a nanoscale thickness, because such polymers should be stronger as a result of stereocomplex formation. The present study showed that the QCM technique can be used for polymer assembly from the organic phase and for systems that require molecular rearrangement. Further study of other stereocomplex systems including combinations between it-PMMA and st-poly(alkyl methacrylate)s, and on the novel applications of molecularly regulated stereocomplex assemblies, such as biomedical or technological uses, are now in progress.

Acknowledgment. We would like to acknowledge Dr. A. Kishida (Kagoshima University, Japan) for grateful discussions. This work was financially supported in part by Grant-in-Aid for Scientific Researches in the Priority Areas of “New Polymers and Their Nano-Organized Systems” (No. 277/101266248) and “Molecular Synchronization for Design of New Materials System” (No. 404/11167270) from the Ministry of Education, Science, Sports and Culture, Japan.

JA9913535