Porous Ultrathin Polymer Films

Recognition of Stereoregular Polymers by Using Structurally Regulated Ultrathin Polymer Films**

*Takeshi Serizawa, Ken-ichi Hamada, Tatsuki Kitayama, and Mitsuru Akashi**

The creation of molecular recognition systems with suitably designed molecular assemblies is of great interest.[1–6] Most of the recognition systems target small molecules except for those that use combinations of biomacromolecules. Recently, chain length recognition of synthetic polymers was reported on the basis of the electrostatic interaction between oppositely charged polymers in polyion complex micelles.[7] The recognition of synthetic linear polymers using certain assemblies is relatively difficult because of their lack of regulated conformations with spatially oriented functional groups.

The layer-by-layer (LbL) assembly of interactive polymers on surfaces results in constructions of multilayered ultrathin polymer films and is performed by simple alternate immersion of substrates into various solutions.[8] Electrostatic interactions between water-soluble polyelectrolytes are normally used for LbL assembly. Most of the assembled polymers seem to have random-coiled conformations in the films, although biomacromolecules, such as proteins and DNA, have also been applied in LbL assemblies. Recently, we studied LbL assembly by using stereocomplexes between isotactic (it) and syndiotactic (st) poly(methyl methacrylate)s (PMMAs).[9] The PMMAs in the assembly showed a double-stranded helical structure, in which it-PMMA was surrounded by twice the molar amount of st-PMMA, and these polymers had a molecularly regulated conformation. Stereocomplex formation was also applied in LbL assembly between it-PMMA and st-poly(methacrylic acid) (PMAA) with different solvent solubilities,[10] and between it-PMMA and st-poly(alkyl methacrylate)s[11]. Herein, we report a macromolecular recognition system resulting from the incorporation of st-polymers of methacrylic acid or methacrylates into an ultrathin it-PMMA film designed by LbL assembly on the basis of stereocomplex formation (Figure 1).

Figure 1. A 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.

The first step in the preparation of the designed ultrathin it-PMMA film is the LbL assembly between it-PMMA and st-PMAA by stereocomplex formation. The alternate immersion of a quartz crystal microbalance (QCM) substrate into both solutions resulted in a stepwise decrease of the frequency (Figure 2). The molar ratio of the unit assembled from st-PMAA and it-PMMA calculated from the QCM analysis was 2.1($\pm$0.2):1 (st-PMAA/it-PMMA), which is consistent with that of an ideal complex stoichiometry with a double-stranded helical structure.[12] The mean thickness of the LbL assembly after 12-steps was calculated to be 48 nm, after the density was assumed to be the same as that of the glass state solid PMMA (1.118 g cm^{-3}). The subsequent immersion of the assembly in an aqueous solution of sodium hydroxide (10 mM) for 5 min resulted in a drastic increase in frequency, which indicates a desorption of some of the polymers from the assembly (Figure 2). There was no frequency change with long-term immersion even after several hours had elapsed. This observation indicates selective extraction of st-PMAA, which can be readily dissolved in

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[*] Prof. M. Akashi, Prof. T. Serizawa, K.-i. Hamada
Department of Nanostructured and Advanced Materials
Graduate School of Science and Engineering
Kagoshima University
1-21-40 Korimoto, Kagoshima 890-0065 (Japan)
Fax: (+81) 99-255-1229
E-mail: akashi@apc.kagoshima-u.ac.jp

Prof. T. Kitayama
Graduate School of Engineering Science
Osaka University
1-16 Machikaneyama-cho, Toyonaka 560-0043 (Japan)

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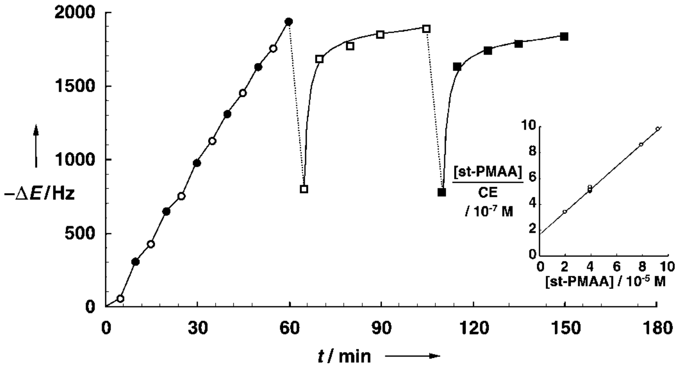

Figure 2. QCM analysis of the LbL assembly, selective extraction, and subsequent st-PMAA incorporation. The it-PMMA (○) in acetonitrile and st-PMAA (●) in an acetonitrile/water (4/6, v/v) were alternately assembled on a QCM substrate for a 12-step assembly at the concentration of 0.017 unitM at 25 °C, in accordance with our previous study.[10] •••••: The selective extraction process of st-PMAA in a 10 mM NaOH aqueous solution for 5 min, to obtain the designed host, the it-PMMA film. □: The subsequent incorporation of st-PMAA 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, which is explained in reference [13], to obtain the maximum CE and the apparent incorporation constant. −Δ*F* = frequency shift.

an aqueous alkaline solution (see reflection absorption spectra (RAS)). The amount extracted was also consistent with the amount of st-PMAA assembled on the QCM substrate, thus indicating a 100 % extraction of st-PMAA. Since an aqueous alkaline solution was used for extracting st-PMAA, the remaining it-PMMA should not swell with water molecules. However, st-PMMA was successfully extracted from the assembly to give an ultrathin it-PMMA film.

The polymer st-PMAA was incorporated into the ultrathin it-PMMA film by immersing the film in a solution of st-PMAA (0.017 unitM), with a complexing efficiency of around 80 % (Figure 2). The efficiency was calculated as the percentage of the incorporated st-PMAA against the host it-PMMA under the assumption that the complex was formed with ideal stoichiometry (2:1 unit ratio st-PMAA/it-PMMA), and incorporation became saturated over time. The extraction was repeated again, and subsequent incorporation of st-PMAA was also observed with the same complexing efficiency (CE). This extraction–incorporation cycle could be repeated several times. Incorporation with the same efficiency indicated that the process was governed by the apparent incorporation constant. The Langmuir plot showed a linear relationship (coefficient of variation; $R^2 = 0.998$; inset in Figure 2).[13] The apparent incorporation constant was estimated to be $5.4 \times 10^4\,\text{M}^{-1}$. This is the first case of an estimation of an affinity constant for the present stereocomplex, which was obtained by a structural fitting with van der Waals interactions. The maximum value of the complexing efficiency was estimated to be 113 %, assuming 2:1 st-PMAA/it-PMAA stoichiometry. Although the maximum efficiency was more than 100 %, the st-PMAA partially incorporated into the host might also be present on the film surface. In fact, the complexing efficiency was maintained even after thermal treatment of the it-PMMA film until a temperature of 110 °C was reached, although the glass transition temperature of it-PMMA films on surfaces was approximately 90 °C.[14] This result suggests that a structurally stable film was prepared by using the present process. Furthermore, the incorporation constants for the st-PMAA with smaller $\bar{M}_n$ values of 14400, and 4650 were $1.5 \times 10^4\,\text{M}^{-1}$ and $7.0 \times 10^3\,\text{M}^{-1}$, respectively, which indicates that the incorporation constant increases with increased molecular weight. On the other hand, the fact that atactic PMAA was not incorporated into the it-PMMA film suggests that the above incorporation occurred by stereocomplex formation.

The RAS in the carbonyl vibration region were used to detect complex formation, and obtain conformational information, as described in our previous studies (Figure 3).[9–11] There are two peaks in this region of the spectrum arising from the LbL assembly at 1737 and 1725 cm⁻¹, which are assigned to it-PMMA and st-PMAA, respectively (Figure 3 a). The peak intensity at the lower wavenumber was larger than that at the higher wavenumber. This suggests that the designation of these peaks is reasonable because the larger molar amount of st-PMAA was assembled for stereocomplex formation as shown in the QCM analysis. The RAS peaks shifted to a higher wavenumber compared to those for their individual cast films, which also indicates stereocomplex formation (Figure 3 d and e). After the film was immersed in an alkaline solution, only one peak was observed at 1739 cm⁻¹ in the reflection absorption spectrum (Figure 3 b), thus, one component was completely extracted from the LbL assembly. The position of the peak in the spectrum in Figure 3 b was almost the same as that at the higher wavenumber in the spectrum of the LbL assembly (Figure 3 a). These observations suggest that st-PMAA was extracted from the LbL assembly with an alkaline solution, and that the conformation (or microenvironment) of it-PMMA was maintained after the extraction.

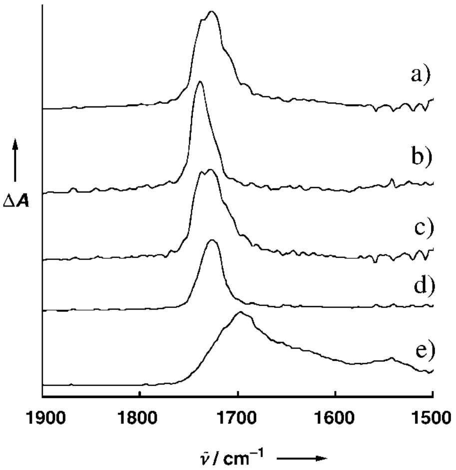

Figure 3. RAS of a) the LbL assembly of it-PMMA and st-PMAA for a 12-step assembly, b) the extracted film, c) the st-PMAA incorporated film, d) a cast film of it-PMMA, e) a cast film of st-PMAA. The films were similarly prepared on a gold-sputtered poly(ethylene terephthalate) film.

The two peaks were observed again after the film was immersed in a solution of st-PMAA (Figure 3c), thus indicating the reformation of the two-component complex. However, the peak intensity corresponding to st-PMAA was smaller than that for the LbL assembly, which is reasonable because the complexing efficiency was smaller and around 80% at the st-PMAA concentration as shown in the QCM analysis.

The surface topology and the thickness of the above assemblies on the QCM were directly analyzed by atomic force microscopy (AFM). The mean roughness (Ra) of the surface of the LbL assembly was 2.6 nm (1.8 nm for QCM). The thickness estimated by scratching the film with a cantilever was 43.6 ± 4.3 nm, which is consistent with that calculated from the QCM analysis (48 nm). This result means that the LbL assembly in the present study has a similar density to that of solid PMMA. The roughness of the surface of the film after the extraction of st-PMAA was 3.2 nm, rougher than before the extraction, which indicates that a molecular-level extraction occurred even at the surface. However, the thickness (44.1 ± 3.8 nm) was not significantly altered by the extraction. This finding strongly suggests that an ultrathin it-PMMA film with a macromolecular porous structure was obtained. It is difficult to explain why the porous it-PMMA film was not squashed. The terminals of it-PMMA, which do not form the stereocomplex, might support the film structure even after the extraction of st-PMAA. The roughness reoccurred with the incorporation of st-PMAA (2.6 nm), and the thickness was the same (42.9 ± 4.6 nm), thus indicating a reversible change in only the surface topography.

The structurally regulated ultrathin it-PMMA film, prepared by the selective extraction of st-PMAA from the LbL assembly between it-PMMA and st-PMAA, was used as a host for the incorporation of other st-poly(alkyl methacrylate)s (Figure 4). St-poly(alkyl methacrylate)s also form stereocomplexes with it-PMMA. If the complex is rapidly formed in the film, the host it-PMMA film should not dissolve in an acetonitrile phase. When a normally spin-coated it-PMMA film on QCM was immersed in solutions of polymer in acetonitrile, which is a polar solvent that accelerates complex formation, rapid desorption of it-PMMA was observed. Since it-PMMA can readily dissolve in acetonitrile, the stereocomplex was not formed on/in the film. On the other hand, incorporation of st-poly(alkyl methacrylate)s into the designed it-PMMA film was dependent on the chain length of the lateral group. The complexing efficiencies for st-PMMA, st-poly(ethyl methacrylate) (PEMA), and st-poly(propyl methacrylate) (PPMA) at the same concentration as used in the st-PMAA incorporation system were 43, 8, and 6%, respectively. These values were significantly decreased with increased alkyl chain length. Since the it-PMMA film was designed using st-PMAA as a template, a porous structure fitting to st-PMAA should be conserved in the film. There must be steric hindrance associated with the incorporation of st-poly(alkyl methacrylate)s. Although st-PMMA was incorporated into the host with moderate efficiency, there may be a small difference between the proton and methyl groups as side chains for st-PMAA and st-PMMA, respectively. The apparent incorporation constant and the maximum complexing efficiency of st-PMMA similarly estimated by the Langmuir plot were $4.0\times10^{3}\,\text{M}^{-1}$ and 47%, respectively, which indicates weaker and smaller incorporation of st-PMMA compared to st-PMAA. Notably, the it-PMMA film did not dissolve, even though the complexing efficiency was small for st-PEMA and st-PPMA. This observation suggests that the slight incorporation of the st-polymers onto the film surface suppressed dissolution in the acetonitrile phase.

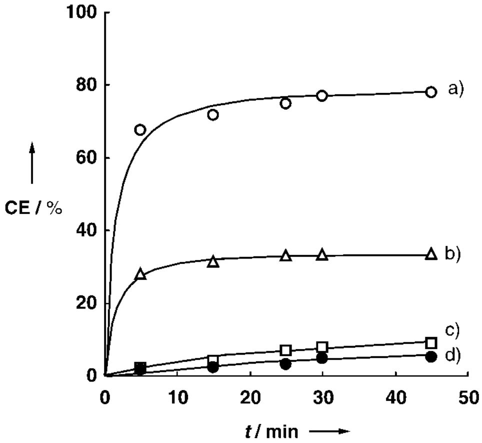

Figure 4. The time dependence of CE for the incorporation of a) st-PMAA, b) st-PMMA, c) st-PEMA, d) st-PPMA in the designed it-PMMA film at the concentration of 0.017 unitM at 25 °C. The LbL assembly and the selective extraction were similarly demonstrated in Figure 2.

Preliminary experiments revealed reversible incorporation and extraction of st-PMAA using spin-coated it-PMMA. However, an it-PMMA film prepared by a similar st-PMAA extraction did not show any alkyl-chain recognition, and in the corresponding reflection absorption spectrum, the peak representing the carbonyl vibration band was also reversibly shifted after the incorporation and extraction processes, thus indicating a reversible conformational change (i.e. no conservation of conformation). The present system is based on the characteristic property of LbL assemblies, which permits tight deposition of interactive polymers at the molecular level.

In summary, we have demonstrated that st-PMAA is selectively extracted in an aqueous alkaline solution from an LbL assembly of it-PMMA and st-PMAA with stereocomplex formation. The resulting ultrathin it-PMMA film is molecularly porous and has a regulated conformation. The extraction and the subsequent incorporation of st-PMAA were reversible. The designed host it-PMMA film incorporated st-poly(alkyl methacrylate)s with shorter alkyl side chains. This is the first report of selective extraction of one component in an LbL assembly giving rise to macromolecular recognition. The present concept may be applied to various systems of interactive polymers, not only synthetic polymers but also biomacromolecules, with differential solubility, or different properties of degradation. Detailed parameters for demonstrating the present macromolecular recognition such as pH for extraction film thickness, stability of porous films, solvent incorporation, incorporation of other polymers will appear in the near future. The present host film might be applied to template polymerization for the preparation of stereoregular polymers. This method also facilitates easy preparation of a molecularly porous ultrathin film by using selective extraction of one component from LbL assemblies.

Experimental Section

Materials: it-PMMA, st-PMAA, and other st-poly(alkyl methacrylate)s were synthesized by conventional anionic polymerization using suitable monomers and initiators. The $\bar{M}_n$ values, molecular weight distributions ($\bar{M}_w/\bar{M}_n$), tacticities (*mm:mr:rr*) were as follows: it-PMMA 20750, 1.26, 97:2:1; st-PMAA 37940, 1.26, 1:2:97 (mainly used); 14400, 1.25, 1:3:96; 4650, 1.21, 0:4:96; st-PMMA 22700, ,1.26, 0:11:89; st-PEMA 21340, 1.11, 1:8:91; st-PPMA 23800, 1.09, 2:7:91.

LbL assembly: The assembly was carried out in accordance with our previous studies.[9–11] For details, see Experimental Section of the preceding communication.[15] The it-PMMA film was prepared by the selective extraction of st-PMAA in an aqueous alkaline solution from the LbL assembly between it-PMMA and st-PMAA. Frequency shifts were measured after drying a QCM substrate by using nitrogen gas in all experiments.

Characterization: RAS were measured with a Herschel FT/IR-610, Jasco (Japan) in nitrogen atmosphere at ambient temperature. The interferograms were superimposed 50 times and Fourier transformed at a resolution of 4 cm^{-1}. AFM images were obtained by 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 Ra in given observed areas was estimated from the following Equation (1)

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

in which *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.

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$$\frac{[\text{st}-\text{PMAA}]}{\text{CE}} = \frac{1}{\text{CE}_{\max}}\,[\text{st}-\text{PMAA}] + \frac{1}{\text{CE}_{\max} K_{\text{app}}} \qquad (2)$$

efficiency, $\text{CE}_{\max}$ is the maximum complexing efficiency, and K_{app} is the apparent affinity constant.
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