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Template Polymerization Using Artificial Double Strands

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Template syntheses of synthetic polymers are interesting targets for precision polymerization. Isotactic (it) and syndiotactic (st) poly(methyl methacrylate)s (PMMAs) artificially form double-stranded helical stereocomplexes in polar organic solvents on the basis of structural fitting with van der Waals interactions,[1] in which complex it-PMMAs are surrounded by twice length of st-PMMAs.[2] Polymer chemists are strongly interested in this double-stranded moiety as an adequate assembly system to perform in situ free radical template syntheses of stereoregular PMMAs in the presence of a single PMMA.[3,4] Although the stoichiometry of this complex is different from that of nucleic acids, template polymerization is inspired by template syntheses of nucleic acids and proteins under mild physiological conditions.[5] However, the structural transcription of templates to polymers synthesized by this method has thus far been insufficient. Polymerization has been demonstrated under restrictive conditions (low conversions, low temperatures, and high molecular weights of templates).[3]

Since biological systems synchronously utilize sophisticated nanospaces formed by proper enzymes as well as template effects, solvated polymers with random and dynamic conformations are not suitable polymerization templates. To overcome this problem, we proposed polymerization within nanospaces formed by polymer templates as porous ultrathin films and realized highly efficient template synthesis of stereoregular methacrylate polymers.[6] Polymerization proceeded along with stereocomplexes formed with van der Waals contacts between it-PMMA and st-poly(methacrylic acid) (PMAA) with 1:1 (length/length) stoichiometry. The molecular weights of methacrylate polymers synthesized were almost the same as those of template polymers, suggesting that length information was transferred to synthesized polymers. However, since we have insufficient information for the assembly structure of 1:1 stereocomplexes,[7] the absolute transfer of structural information was not convincing. It is therefore desirable to aim for applications with other significant assemblies for template polymerization. Herein, we report the stereoregular template polymerization in template nanospaces using free radical initiators, based on double-stranded helical stereocomplexes formed between it-PMMA and st-PMMA (1:2, length/length). By using double strands, structural transfer can be clearly discussed.

Ultrathin porous films fabricated by the selective solvent extraction of single polymer components from ultrathin stereocomplex films were designed as template nanospaces. it-PMMA and st-PMAA were selected as adequate stereocomplex combinations because of their different solubilities. The alternate layer-by-layer assembly[8] of these polymers successfully fabricated ultrathin double-stranded stereocomplex films with expected stoichiometries.[9−11] We previously demonstrated that st-PMAAs were selectively extracted from double strands in aqueous solutions of sodium hydroxide, fabricating porous it-PMMA films. Then, st-PMAA could be reincorporated into films until nanospaces were filled with st-PMAAs.[12] This incorporation was specific for st-PMAA, and other st-polymers of methacrylates were not incorporated. Accordingly, nanospaces were potentially fitted into st-PMAAs for the formation of pores. Herein, we apply porous it-PMMA films for template syntheses of st-PMAAs, as schematically shown in Figure 1.

it-PMMA and st-PMAA for assembly were synthesized by conventional anionic polymerization using suitable monomers and initiators. Substrates were alternately immersed into it-PMMAs (1.7 mg $\mathrm{mL^{-1}}$) and st-PMAAs (1.5 mg $\mathrm{mL^{-1}}$) solutions of acetonitrile and acetonitrile/water (4/6, v/v), respectively, at 25 °C for 5 min. After each immersion, substrates were rinsed with the same solvent and dried under nitrogen gas. The assembly was initiated from it-PMMA steps in all cases. Here, polymers were assembled for 12 steps, and the mean thickness was estimated to be 43.6 ± 4.3 nm from a scratching mode of the atomic force microscope. The porous it-PMMA film was prepared by immersion of the assembly into aqueous solution of 10 mM sodium hydroxide.

Polymerizations from MAAs (1.7 mg $\mathrm{mL^{-1}}$) in porous it-PMMA films (mean thickness, 44 nm) at 40 °C in the presence of the free radical initiator, 2,2′-azobis(*N*,*N*-dimethyleneisobutyramidine) dihydrochloride (5.0 mg $\mathrm{mL^{-1}}$) ([monomer]/[initiator] = 20/1, mol/mol), in 10 mL of acetonitrile/water (4/6, v/v) were preliminarily analyzed by immersing a quartz crystal microbalance (QCM) substrate coated with porous films. The QCM detected amounts of assembled polymers on its surface from decreases in frequency.[6,9−13] After 2 h polymerization periods in both solution and film, synthesized PMAAs were incorporated into porous it-PMMA films at an 80% fill rate (where 100% indicates st-PMAA extracted = incorporated PMAAs). Attenuated total reflection (ATR) spectra in carbonyl vibration regions demonstrated the emergence of a new peak at around 1725 $\mathrm{cm^{-1}}$, corresponding to PMAA in addition to the original peak of template it-PMMA at around 1737 $\mathrm{cm^{-1}}$. These peak positions were significantly consistent with those for the stereocomplex film,[12] strongly suggesting st-specific polymerization of PMAA along template it-PMMAs in the porous film (see Supporting Information, Figures S1 and S2).

To characterize the synthesized PMAA in detail, porous it-PMMA films were prepared on silica colloids (10 g, mean diameter 1.6 μm), following methods outlined in previous report.[6] 1.5 g of MAA was similarly

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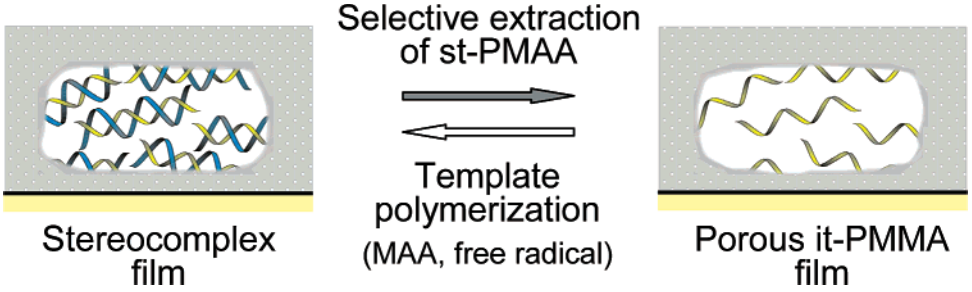

Figure 1. Schematic representation of template polymerization of st-PMAA using ultrathin porous it-PMMA films based on double-stranded stereocomplexes.

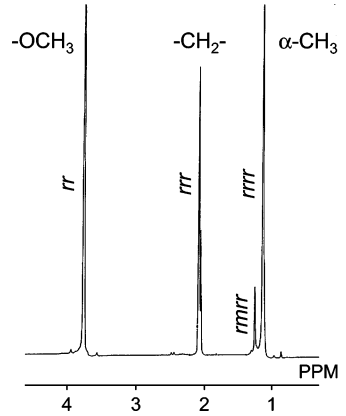

Figure 2. Typical ^{1}H NMR spectrum of st-PMMA (*mm*:*mr*:*rr* = 0:2:98) methylated from st-PMAAs polymerized in porous it-PMMA template films.

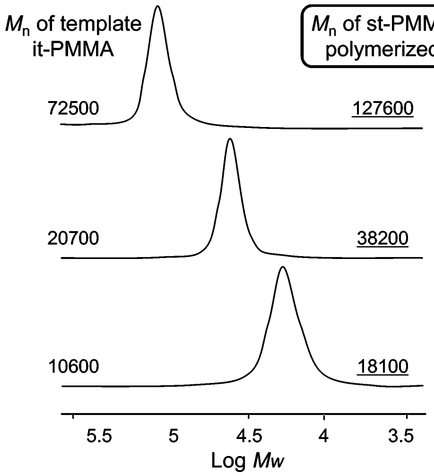

Figure 3. SEC charts of st-PMMAs polymerized in porous template films from it-PMMAs with various molecular weights.

Table 1. Analytical Data of St-PMAA Prepared by Template Polymerization

template it-PMMA		[M]$_0$/[I]$_0$[a]	st-PMMA polymerized	
M_n, M_w/M_n	*mm*:*mr*:*rr*	(mol/mol)	M_n, M_w/M_n	*mm*:*mr*:*rr*
10 600, 1.4	96:3:1	20	18 300, 2.7	0:4:96
20 700, 1.3	96:3:1	20	38 200, 1.5	0:2:98
21 500, 1.3	97:2:1	10[b]	36 000, 1.9	1:2:97
20 900, 1.3	96:3:1	5[b]	39 100, 2.0	0:3:97
72 500, 1.3	95:4:1	20	125 800, 1.9	0:3:97

[a] [M]$_0$ and [I]$_0$ indicate initial amounts of monomer MAA and an initiator, respectively. [b] For changing the ratio, [I]$_0$ was decreased.

polymerized in 500 mL of solvent in the presence of coated silica. After rinsing the silica with solvent, polymerized PMAAs were extracted in an aqueous 10 mM sodium hydroxide solution. Approximately 0.2 g of PMAA was recovered, and yields were estimated to be 13%. Subsequently, PMAAs were methylated using diazomethane to obtain PMMAs and then characterized by ^{1}H NMR. Figure 2 shows a typical NMR chart for the PMMA prepared using template it-PMMAs (M_n 20 750, M_w/M_n 1.2, *mm*:*mr*:*rr* = 97:2:1) (M_n: average number molecular weight; M_w: average weight molecular weight; *mm*:*mr*:*rr*: tacticity referring triads). Chemical shifts for α-methyl groups at 1−1.5 ppm, which can be used as signals for tacticity, were almost single peaks at 1.2 ppm, indicating that >96% syndiotactic PMAA had been prepared. Since PMAAs simultaneously prepared in solution did not show high syndiotacticity (*mm*:*mr*:*rr* = 8:69:23) and since st-specific polymerization did not proceed using conventionally spin-coated it-PMMA films, structural information from template it-PMMAs was successfully transferred to st-PMAA on the basis of prememorized double strands. Syndiotacticity as well as yields was significantly superior to previous reports.[3,4]

Synthesized st-PMMAs molecular weights were analyzed by size exclusion chromatography (SEC) using a THF solvent. Typical SEC charts are shown in Figure 3, and resulting molecular weights as well as tacticities are summarized in Table 1. M_n of st-PMMAs were approximately twice those of template it-PMMAs in all cases. Surprisingly, this mass ratio was potentially consistent with the stoichiometry of double-stranded 1:2 (it:st) stereocomplexes.[2] In fact, molecular weights of PMMAs simultaneously prepared in solution (M_n 2300, M_w/M_n 4.0) were independent of template it-PMMAs. These observations strongly indicate that information from polymer chain length templates, which were derived from stereocomplex structures, were successfully transferred to synthesized polymers. Although st-PMAAs with M_n of ~40000 (rr > 95%, M_w/M_n < 2.0) were commonly utilized for the creation of nanospaces, M_n of st-PMMAs polymerized were clearly dependent on M_n of template it-PMMAs. Furthermore, changes in MAA/initiator molar ratios did not affect the molecular weight of st-PMMAs, also supporting template synthesis in porous films, as shown in Table 1. Accordingly, molecular weights as well as tacticities were regulated by template it-PMMAs. Molecular weight distributions from polymerized st-PMMAs were narrow and reached 1.5 in some case. The narrow molecular weight distribution is characteristic of the present system and is better than previous st-specific polymerizations with PMAAs using 1:1 stereocomplex assemblies.[6] These observations suggest that 1:2 stereocomplexes have more suitable assembly structures for template polymerization compared to 1:1 stereocomplexes.

Porous films were reusable for further template polymerizations with reproducibility lasting at least

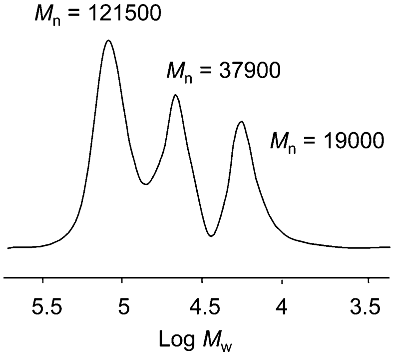

Figure 4. SEC chart of a pot polymerized st-PMMAs in porous template films from it-PMMAs with M_n of 11 000, 22 800, and 68 900.

three times, based on the selective extraction of polymerized st-PMAAs. A pot polymerization in the presence of mixed silica coated with template it-PMMAs with different M_n (M_w/M_n) (11 000 (1.5), 22 800 (1.2), and 68 900 1.5)) significantly resulted in the synthesis of st-PMMA mixtures with respective M_n of 19 000, 37 900, and 121 500, as shown in Figure 4. This observation indicates that a pot polymerization prepares mixtures of stereoregular methacrylate polymers with various molecular weights, which can be readily separated by conventional chromatographic methods. This type of stereoregular polymerization has never been realized with conventional polymerization systems and is characteristic of the present system.

The detailed polymerization mechanism is unknown. However, since SEC curves with single and narrow peak widths shifted to higher molecular weights (see Supporting Information, Figure S3), a living radical (rather than free radical) polymerization might proceed within the porous films. In other words, radical terminals of growing st-PMAA might stably exist in the porous films during polymerization. On the other hand, affinity constants for double-stranded stereocomplexes, which were analyzed by using st-PMMAs with various molecular weights against porous it-PMMA films following methods described in a previous paper,[12] were maximal when molecular weights of st-PMAAs were approximately twice those of it-PMMAs.[14] These observations suggest that zippers likely formed one-to-one double strands that are thermodynamically stable in films. During polymerization, growing st-PMAAs should shuttle on template it-PMMAs until the formation of stable double strands is completed. This might be the reason for the efficient transfer of molecular weight information. Polymerization termination is also an important factor that needs to be discussed. Since molecular weights of st-PMAAs polymerized were regulated by those of it-PMMA templates after constant polymerization times (2 h), radical terminals should be "live" until polymerization ends. An influx of oxygen by opening reaction media seemed to stop the polymerization. This interpretation is reasonable because a SEC curve following polymerization for longer times (3 h) became bimodal (presence of polymers with higher molecular weights), suggesting that radicals were still "alive" after polymerization for 2 h (see Supporting Information, Figure S3).

Unfortunately, it-PMMAs could not be extracted using conventional organic solvents such as chloroform and toluene, possibly reflecting an difference in both polymers during the double-stranded stereocomplex assembly. Since it-PMMAs are surrounded by st-PMAAs using van der Waals contacts between respective esters and α-methyl groups,[2] complex dissociation of (solvation of it-PMMAs) seems to be difficult. Furthermore, since carboxyl groups of st-PMAAs point out toward double strands,[2] the formation of carboxyl anions in alkaline solution might cause electrostatic repulsions between strands, resulting in the easy extraction of st-PMAAs. It was found that the present double-stranded stereocomplex system was suitable for st-specific polymerization.

In conclusion, a highly st-specific template polymerization of PMAA along with complementary it-PMMA chains in ultrathin porous films was demonstrated on the basis of double-stranded stereocomplexes. Molecular weights of st-PMAAs were regulated by template it-PMAAs following the stereocomplex stoichiometry, and molecular weight distributions were narrow. It was confirmed that structural transcription of template polymers to polymers synthesized can be realized using structurally regular ultrathin porous films composed of template polymers. Although we had insufficient information for the assembly structure of 1:1 stereocomplexes used for template polymerization,[6] the present study convinced that the structural information on templates could be absolutely transferred to polymers synthesized. The present solid-phase polymerization in ultrathin polymer films with regular nanospaces using interactive polymers potentiates novel methodologies for precision polymerization.

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Supporting Information Available: ATR spectral analyses and SCE chart. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Spěváček, J.; Schneider, R. *Adv. Colloid Interface Sci.* **1987**, *27*, 81.
(2) Schomaker, E.; Challa, G. *Macromolecules* **1989**, *22*, 3337.
(3) Buter, R.; Tan, Y. Y.; Challa, *J. Polym. Sci., Part A1* **1972**, *10*, 1031.
(4) Buter, R.; Tan, Y. Y.; Challa, G. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1003.
(5) Alberts, B.; Bray, D.; Hopkin, K.; Johnson, A.; Lewis, J.; Raff, M.; Roberts, K.; Walter, P. *Essential Cell* Biology, 2nd ed.; Garland Publishing: New York, 2003.
(6) Serizawa, T.; Hamada, K.-I.; Akashi, M. *Nature (London)* **2004**, *429*, 52.
(7) Lohmeyer, J. H. G. M.; Tan, Y. Y.; Lako, P.; Challa, G. *Polymer* **1978**, *19*, 1171.
(8) *Multilayer Thin Films*; Decher, G., Schlenoff, J. B., Eds.; Wiley-VCH: Weinheim, 2003.
(9) Serizawa, T.; Hamada, K.-I.; Kitayama, T.; Fujimoto, N.; Hatada, K.; Akashi, M. *J. Am. Chem. Soc.* **2000**, *122*, 1891.
(10) Serizawa, T.; Hamada, K.-I.; Kitayama, T.; Katsukawa, K.-I.; Hatada, K.; Akashi, M. *Langmuir* **2000**, *16*, 7112.
(11) Hamada, K.-I.; Serizawa, T.; Kitayama, T.; Fujimoto, N.; Hatada, K.; Akashi, M. *Langmuir* **2001**, *17*, 5513.
(12) Serizawa, T.; Hamada, K.-I.; Kitayama, T.; Akashi, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1118.
(13) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.
(14) Serizawa, T.; Hamada, K.-I.; Noguchi, K.; Akashi, M., unpublished data.

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