

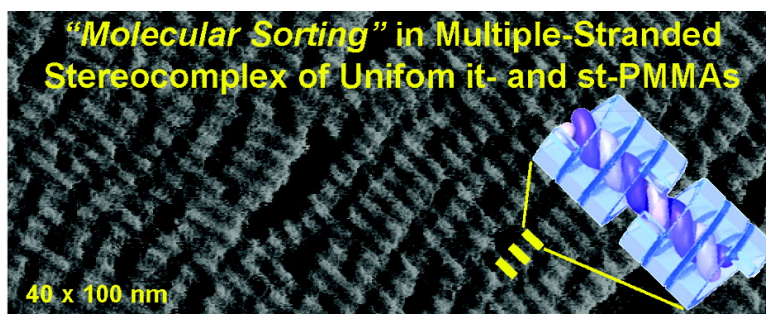
Article

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Molecular Weight Recognition in the Multiple-Stranded Helix of a Synthetic Polymer without Specific Monomer–Monomer Interaction

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Abstract: Stereoregular isotactic and syndiotactic poly(methyl methacrylate)s (it- and st-PMMA) are known to form a multiple-stranded complementary helix, so-called stereocomplex (SC) through van der Waals interactions, which is a rare example of helical supramolecular structures formed by a commodity polymer. In this study, we prepared SCs by using uniform it- and st-PMMA and those with a narrow molecular weight distribution having different molecular weights and investigated their structures in detail using high-resolution atomic force microscopy as a function of the molecular weight and molecular weight distribution of the component PMMAs. We found that complementary it- and st-PMMA with the longer molecular length determine the total length of the SC, and molecules of the shorter component associate until they fill up or cover the longer component. These observations support a supramolecular triple-stranded helical structure of the SCs composed of a double-stranded helix of two intertwined it-PMMA chains included in a single helix of st-PMMA, and this triple-stranded helix model of the SCs appears to be applicable to the it- and st-PMMA having a wide range of molecular weights we employed in this study. In homogeneous double-stranded helices of it-PMMA, it has been found that, in mixtures of two it-PMMA with different molecular weights, chains of the same molecular weight selectively form a double-stranded it-PMMA helix, or recognize the molecular weights of each other (“molecular sorting”). We thus demonstrate that molecular weight recognition is possible, without any specific interaction between monomer units, through the formation of a topological multiple-stranded helical structure based upon van der Waals interaction.

Introduction

In molecular recognition or intermolecular information transfer between polymer chains, multiple-stranded helices of polymers may provide a very important specific role. Typical examples are double-stranded helices of DNA, which recognize precisely the monomer sequence and the molecular weight of pairing chains via complementary base-pair formation through hydrogen bonds, and which perform important functions in biological systems such as replication and information transfer.¹ Synthetic artificial double-stranded helices formed via strong interactions of metal coordinate bonds between pairing oligomer chains, called helicates, are also known to form the double-stranded helices by selective

association,² recognizing the structure and molecular weight (molecular length) of the pairing molecules; such behavior is referred to as “molecular sorting”.³ However, studies on molecular sorting have so far been limited to metal-coordinate-bonded helicates of oligomers consisting of a few monomer units^{4,5} or peptide nucleic acids (PNAs) driven by hydrogen bond formation.⁶ Polymers that do not have such strong interactions between monomers as metal-coordinate or hydrogen bonds might also recognize molecular weight through topological interaction, if they can form a multiple-stranded helix structure.

More than half a century ago, it was shown that stereoregular isotactic and syndiotactic poly(methyl methacrylate)s (it-PMMA

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(1) Watson, J. D.; Crick, F. H. C. *Nature* **1953**, *171*, 737–738.

(2) Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565–2569.

(3) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995.

(4) Krämer, R.; Lehn, J.-M.; Marquis-Rigault, A. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 5394–5398.

(5) Caulder, D. L.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1997**, *36*, 1440–1442.

(6) Wittung, P.; Nielsen, P. E.; Buchardt, O.; Egholm, M.; Nordén, B. *Nature* **1994**, *368*, 561–563.

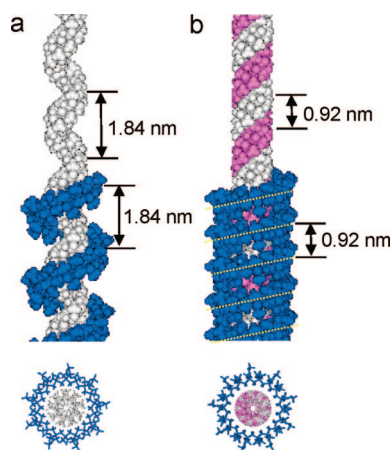


Figure 1. Space-filling models (top, side view) and stick models (bottom, cross-section) of an it-PMMA and st-PMMA SC ($it/st = 1/2$). (a) Double-stranded helix; (b) triple-stranded helix. White and pink, it-PMMA helix; blue, st-PMMA helix. The upper part of the st-PMMA helix has been omitted for clarity.

and st-PMMA, respectively) can form a stereocomplex (SC) with a definite melting point at a stoichiometric composition of $it/st = 1/2$ through van der Waals interactions in specific solvents or in solids.⁷ After the initial proposal of a nonhelical structure model,⁸ in 1989 Shomaker and Challa⁹ proposed a double-stranded helix structure (Figure 1a), in which a 9/1 helix (nine monomer units per turn) of it-PMMA is wound by an 18/1 helix of st-PMMA with a monomer ratio of 1/2. This model has long been accepted, because it can explain rationally (1) the stoichiometry,¹⁰ (2) the template-polymerization phenomena,¹¹ and (3) the stereocomplexation between it-PMMA and st-PMMA derivatives.¹² However, we recently proposed a triple-stranded helix model from the observation by high-resolution atomic force microscopy (AFM) of SCs prepared by the Langmuir–Blodgett (LB) technique, which shows that a double-stranded helix of it-PMMA is included in a single helix of st-PMMA, forming an inclusion complex with a triple-stranded helix structure (Figure 1b).¹³ The SC of PMMA is a rare example of helical supramolecular structures formed by a commodity polymer. In this study, we prepared SCs using uniform it- and st-PMMA fractionated by chromatography¹⁴ and those with a narrow molecular weight distribution (narrow-dispersity it-

and st-PMMA) synthesized by anionic living polymerization (see Experimental Section) and investigated their supramolecular structures in detail by AFM^{17,18} as a function of the molecular weight and molecular weight distribution of the component PMMA. We first show that the size of the SC precisely depends on the molecular weights of the component PMMA to form a triple-stranded helical SC. In addition, we demonstrate that an it-PMMA chain can recognize the molecular weight of the paring it-PMMA chain through topological interaction in their double-stranded helix structure in the SC. Interactions between the it- and st-PMMA chains are also discussed based on the detailed AFM observations of the SCs as a function of the molecular weight of the component PMMA.

Experimental Section

Preparation of Uniform PMMA (it22, it28, it43, st44, and st72). The uniform it-PMMA and st-PMMA were prepared according to a previously reported method.¹⁵ Highly stereoregular it- and st-PMMA with a narrow molecular weight distribution were

- (7) For reviews: (a) Spěváček, J.; Schneider, B. *Adv. Colloid Interface Sci.* **1987**, *27*, 81–150. (b) te Nijenhuis, K. *Adv. Polym. Sci.* **1997**, *130*, 67–81. (c) Hatada, K.; Kitayama, T. *Polym. Int.* **2000**, *49*, 11–47.
- (8) Liquori, A. M.; Anzuino, G.; Coiro, V. M.; D’Alagni, M.; de Santis, P.; Savino, M. *Nature* **1965**, *206*, 358–362.
- (9) Schomaker, E.; Challa, G. *Macromolecules* **1989**, *22*, 3337–3341.
- (10) Vorenkamp, E. J.; Bosscher, F.; Challa, G. *Polymer* **1979**, *20*, 59–64.
- (11) (a) Buter, R.; Tan, Y. Y.; Challa, G. *J. Polym. Sci., Part A1* **1972**, *10*, 1031–1049. (b) Buter, R.; Tan, Y. Y.; Challa, G. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1003–1011. (c) Serizawa, T.; Hamada, K.; Akashi, M. *Nature* **2004**, *429*, 52–55. (d) Hamada, K.; Serizawa, T.; Akashi, M. *Macromolecules* **2005**, *38*, 6759–6761.
- (12) (a) Lohmeyer, J. H. G. M.; Tan, Y. Y.; Lako, P.; Challa, G. *Polymer* **1978**, *19*, 1171–1175. (b) Bosscher, F.; Keekstra, D.; Challa, G. *Polymer* **1981**, *22*, 124–126.
- (13) Kumaki, J.; Kawachi, T.; Okoshi, K.; Kusanagi, H.; Yashima, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 5348–5351.
- (14) Hatada, K.; Kitayama, T.; Ute, K.; Nishiura, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 416–431.
- (15) Ute, K.; Miyatake, N.; Osugi, Y.; Hatada, K. *Polym. J.* **1993**, *25*, 1153–1160.
- (16) Ute, K.; Niimi, R.; Matsunaga, M.; Hatada, K.; Kitayama, T. *Macromol. Chem. Phys.* **2001**, *202*, 3081–3086.

- (17) Because of the difficulty in the synthesis of high molecular weight uniform PMMA by fractionation, high molecular weight it- and st-PMMA with a narrow molecular weight distribution were also prepared and used for SC formation (see Experimental Section).
- (18) AFM is a powerful tool to study polymer chains on substrate, and various isolated and self-assembled synthetic polymers deposited on substrates have been observed from linear polymers to specially structured polymers, such as polymer brushes, monodendron-jacketed polymers, polyelectrolytes, heteroarm star copolymers, helical polymers, fullerene end-capped polymers, and block copolymers composed of architecturally different components, etc. For examples, see: (a) Kumaki, J.; Nishikawa, Y.; Hashimoto, T. *J. Am. Chem. Soc.* **1996**, *118*, 3321–3322. (b) Sheiko, S. S.; Gerle, M.; Fischer, K.; Schmidt, M.; Möller, M. *Langmuir* **1997**, *13*, 5368–5372. (c) Percec, V.; Ahn, C.-H.; Ungar, G.; Yearley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161–164. (d) Gerle, M.; Fischer, K.; Roos, S.; Müller, A. H. E.; Schmidt, M.; Sheiko, S. S.; Prokhorova, S.; Möller, M. *Macromolecules* **1999**, *32*, 2629–2637. (e) Prokhorova, S. A.; Sheiko, S. S.; Ahn, C.-H.; Percec, V.; Möller, M. *Macromolecules* **1999**, *32*, 2653–2660. (f) Prokhorova, S. A.; Sheiko, S. S.; Mourran, A.; Azumi, R.; Beginn, U.; Zipp, G.; Ahn, C.-H.; Holerca, M. N.; Percec, V.; Möller, M. *Langmuir* **2000**, *16*, 6862–6867. (g) Sheiko, S. S.; Prokhorova, S. A.; Beers, K. L.; Matyjaszewski, K.; Potemkin, I. I.; Khokholov, A.; Möller, M. *Macromolecules* **2001**, *34*, 8354–8360. (h) Minko, S.; Kiriy, A.; Gorodyska, G.; Stamm, M. *J. Am. Chem. Soc.* **2002**, *124*, 3218–3219. (i) Kiriy, A.; Gorodyska, G.; Minko, S.; Jaeger, W.; Štěpánek, P.; Stamm, M. *J. Am. Chem. Soc.* **2002**, *124*, 13454–13462. (j) Samorí, P.; Ecker, C.; Gössl, I.; de Witte, P. A. J.; Cornelissen, J. J. L. M.; Metselaar, G. A.; Otten, M. B. J.; Rowan, A. E.; Nolte, R. J. M.; Rabe, J. P. *Macromolecules* **2002**, *35*, 5290–5294. (k) Kumaki, J.; Hashimoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 4907–4917. (l) Sheiko, S. S.; da Silva, M.; Shirvanians, D.; LaRue, I.; Prokhorova, S.; Möller, M.; Beers, K.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2003**, *125*, 6725–6728. (m) Kiriy, A.; Gorodyska, G.; Minko, S.; Stamm, M.; Tsitsilianis, C. *Macromolecules* **2003**, *36*, 8704–8711. (n) Sakurai, S.; Ohira, A.; Suzuki, Y.; Fujito, R.; Nishimura, T.; Kunitake, M.; Yashima, E. *J. Polym. Sci. A: Polym. Chem.* **2004**, *42*, 4621–4640. (o) Zhuang, W.; Ecker, C.; Metwelaar, G. A.; Rowan, A. E.; Nolte, R. J. M.; Samorí, P.; Rabe, J. P. *Macromolecules* **2005**, *38*, 473–480. (p) Kawachi, T.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2005**, *127*, 9950–9951. (q) Pyun, J.; Tang, C.; Kowalewski, T.; Fréchet, J. M. J.; Hawker, C. J. *Macromolecules* **2005**, *38*, 2674–2685. (r) Roiter, Y.; Minko, S. *J. Am. Chem. Soc.* **2005**, *127*, 15688–15689. (s) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1245–1248. (t) Kajitani, T.; Okoshi, K.; Sakurai, S.-i.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 708–709. (u) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 5650–5651. (v) Sakurai, S.-i.; Ohsawa, S.; Nagai, K.; Okoshi, K.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 7605–7608. For reviews of single chain observations, see: (w) Schlüter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864–883. (x) Sheiko, S. S.; Möller, M. *Chem. Rev.* **2001**, *101*, 4099–4123. (y) Samorí, P.; Surin, M.; Palermo, V.; Lazzaroni, R.; Leclère, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3927–3938.

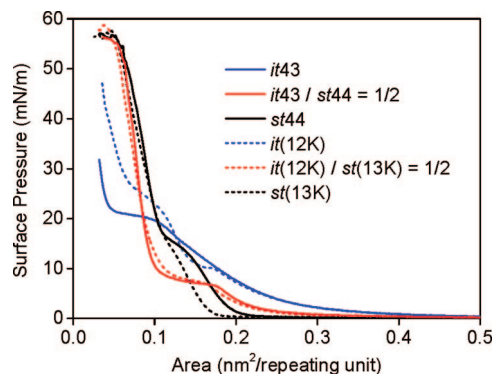


Figure 2. π -A isotherms of it-PMMA, st-PMMA, and it-PMMA and st-PMMA mixtures (it/st = 1/2 in unit-molar base) on water. The π -A isotherms were measured at a compression rate of 0.5 mm/s (45 cm²/min) using filter paper as the Wilhelmy plate. Solid lines indicate a uniform polymer pair, it43 and st44. Broken lines indicate a narrow-dispersity polymer pair, it(12K) and st(13K).

first synthesized by stereospecific anionic living polymerization and were then subjected to fractionation to collect the oligomers with specific degrees of polymerizations by supercritical fluid chromatography using carbon dioxide/ethanol as the eluent. The abbreviation it22 corresponds to an it-PMMA 22-mer, for example. The tacticities (*mm/mr/rr*) of the it- and st-PMMA uniform polymers were 95.9/3.5/0.6 and 0/1.9/98.1, respectively.

Preparation of Narrow-Dispersity it- and st-PMMA (it(6.7K), it(12K), st(13K), and st(24K)). The narrow-dispersity it-PMMA, it(6.7K) and it(12K), were prepared by the isotactic-specific anionic living polymerization of MMA in toluene at -78 °C with *tert*-butylmagnesium bromide as an initiator.¹⁹ The narrow-dispersity st-PMMA, st(13K) and st(24K), were synthesized by the syndiotactic-specific anionic living polymerization of trimethylsilyl methacrylate in toluene at -78 °C with *tert*-butyllithium in the presence of bis(2,6-di*tert*-butylphenoxy)methylaluminum, followed by hydrolysis of the pendant esters, and methylation with diazomethane.²⁰ The number-average molecular weights (M_n), molecular weight distributions (M_w/M_n), and tacticities (*mm/mr/rr*) were as follows: it(6.7K), $M_n = 6700$, $M_w/M_n = 1.19$, and *mm/mr/rr* = 97/3/0; it(12K), $M_n = 12\,000$, $M_w/M_n = 1.11$, and *mm/mr/rr* = 97/3/0; st(13K), $M_n = 13\,000$, $M_w/M_n = 1.13$, and *mm/mr/rr* = 0/4/96; st(24K), $M_n = 23\,800$, $M_w/M_n = 1.10$, and *mm/mr/rr* = 0/4/96. The M_n and M_w/M_n values were measured by size exclusion chromatography (SEC) in chloroform using PMMA standards (Shodex, Tokyo, Japan) for the calibration. The tacticities were determined from the ¹H NMR signals of the α -methyl protons.

Surface Pressure-Area (π -A) Isotherm Measurements and LB Film Preparations for AFM. The π -A isotherms of it-PMMA, st-PMMA, and it- and st-PMMA mixtures (it/st = 1/2) in Figure 2 were measured in a way similar to that previously reported.^{13,21} LB film preparations for AFM measurements of SCs are described below. About 250–900 μ L of an it- and st-PMMA mixed solution (it/st = 1/2 in unit-molar ratio) in chloroform having a total polymer concentration of 3×10^{-5} to 1×10^{-4} g/mL was spread on a water surface at 25 °C in a commercial LB trough with an area of 60×15 cm², and an effective moving barrier length of 15 cm (FSD-300AS, USI, Japan). The film was compressed to a surface pressure of 10 mN/m at a moving barrier rate of 0.5 mm/s, corresponding to a compression rate of 45 cm²/min, and deposited onto a freshly cleaved mica by pulling it out of the water at a rate

of 4.2 mm/min, while compressing the monolayer at the same pressure (the vertical dipping method) (Figure 3a, left). To obtain well-organized SC monolayers, extremely slow compression conditions were also used. To save time, the monolayer was first compressed at the normal compression rate of 0.5 mm/s (45 cm²/min) to a surface pressure of 1 mN/m, where no stereocomplexation started. Next, the compression rate was reduced to 0.001 mm/s (0.09 cm²/min), and the film was compressed to 10 mN/m and deposited in the same way (Figures 3a, center and right columns, 3c,d, 4, and 5a,c; Figure S1, the same conditions except deposition at 5 mN/m). Note that the compression rate was 1/500 of the normal conditions, and it took about 45 h for compression to 10 mN/m under the two-step compression conditions (cf. about 18 min for the normal compression rate of 0.5 mm/s).

AFM Observations. AFM observations were done using a commercial AFM (NanoScope IIIa or IV/multimode AFM unit, Veeco Instruments, Santa Barbara, CA) with standard silicon cantilevers (PointProbe, NCH, NanoWorld, Neuchâtel, Switzerland) in air in the tapping mode. The typical settings of the AFM observations were as follows: a drive amplitude of 1.0 V, a set point of 0.85 V, and a scan rate of 2–2.5 Hz. The AFM images obtained are presented without any image processing except flattening. The resolutions of the images strongly depended on the quality of the tips. Only tips that clearly resolved the spacing of the SC axis (ca. 2.4 nm) were selectively used. The blind tip estimation of the resultant images using DECONVO 1.1, a public domain software by A. Efimov (NT-MDT Co., Moscow, Russia) based on published algorithms,²² showed that effective tip radii typically ranged from 0.4 to 1.2 nm; this small tip size rationalizes the high-resolution images obtained in our conditions. The lengths of the SCs were measured manually using the NIH ImageJ program, developed at the National Institutes of Health (available on the Internet at <http://rsb.info.nih.gov/nih-image/>). Typically, the lengths of the 300–700 SCs in the AFM images were measured, and the number- and weight-average lengths (L_n , L_w) and the length distribution (L_w/L_n) were estimated. These values were measured without compensation for the tip radius, and the measured values might be overestimated by around 1 nm because of the broadening effect of the tip. Repeated evaluations for different AFM images of the same SCs showed that the error in evaluating L_n of the SCs was less than 1 nm.

Results and Discussion

π -A Isotherms of Uniform and Narrow-Dispersity it-PMMA, st-PMMA, and Their Mixtures. A mixed monolayer of it-PMMA and st-PMMA spread on a water surface is known to form an SC upon compression.^{13,23,24} Figure 2 shows typical π -A isotherms of uniform and narrow-dispersity it-PMMA, st-PMMA, and their mixtures (it/st = 1/2 in unit-molar base) on water. A high molecular weight it-PMMA with a narrow molecular weight distribution, it(12K), showed a typical expanded π -A isotherm with a transition at around 10 mN/m, corresponding to its crystallization,^{13,21} whereas low molecular weight uniform it-PMMA 43-mer (it43), did not show such a transition because it43 is too small to crystallize. A narrow-dispersity st-PMMA, st(13K), and a uniform st-PMMA, st44, showed condensed π -A isotherms, and formed amorphous films on compression;^{13,21} st44 had an unassigned shoulder at around 15 mN/m. The it(12K)/st(13K) and it43/st44 mixtures (it/st = 1/2) showed almost the same π -A isotherms, with a clear transition at around 7

(19) Hatada, K.; Ute, K.; Tanaka, K.; Okamoto, Y.; Kitayama, T. *Polym. J.* **1986**, *18*, 1037–1047.
 (20) Kitayama, T.; He, S.; Hironaka, Y.; Iijima, T.; Hatada, K. *Polym. J.* **1995**, *27*, 314–318.
 (21) Kumaki, J.; Kawauchi, T.; Yashima, E. *J. Am. Chem. Soc.* **2005**, *127*, 5788–5789.

(22) Villarubia, J. S. *J. Res. Natl. Inst. Stand. Technol.* **1997**, *102*, 425–454.
 (23) Brinkhuis, R. H. G.; Shouten, A. *J. Macromolecules* **1992**, *25*, 2725–2731.
 (24) Liu, J.; Zhang, Y.; Zhang, J.; Shen, D.; Guo, Q.; Takahashi, I.; Yan, S. *J. Phys. Chem. C* **2007**, *111*, 6488–6494.

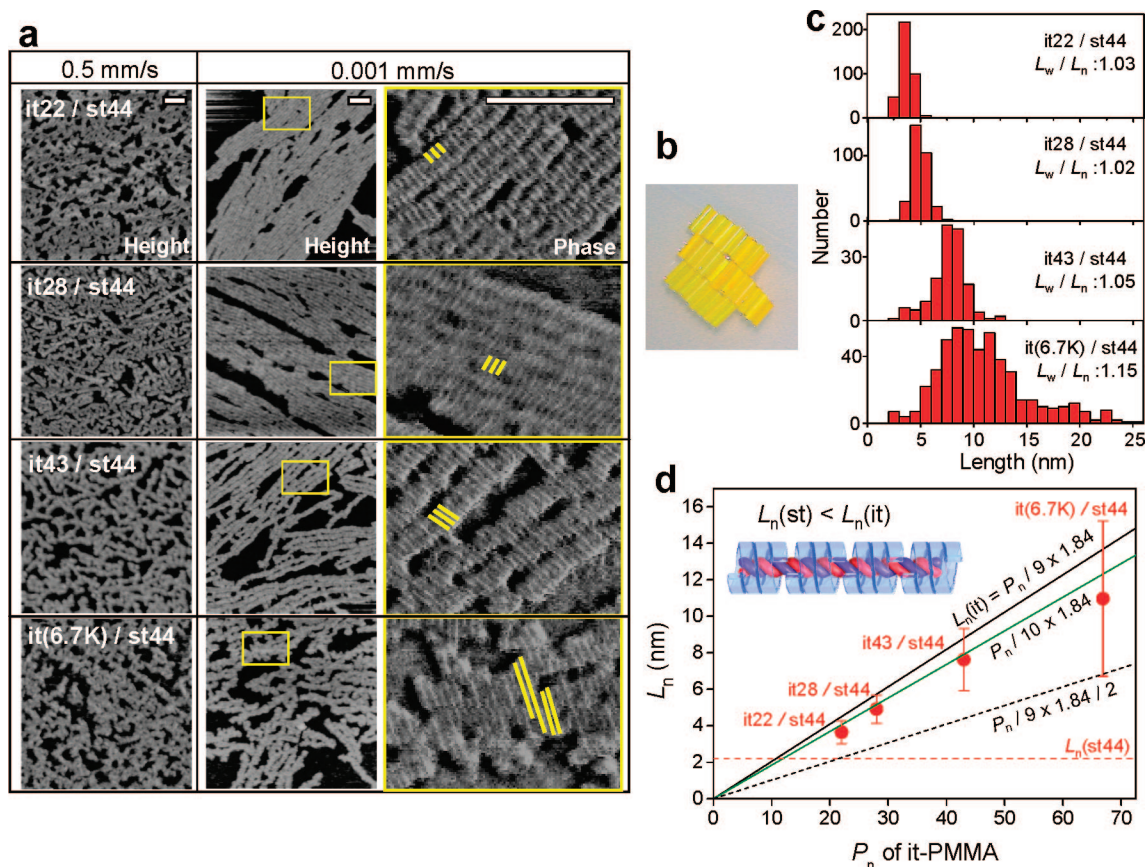


Figure 3. SCs composed of a uniform st-PMMA (st44) and an it-PMMA selected from uniform (it22, it28, and it43) and narrow-dispersity (it(6.7K)) it-PMMA. (a) AFM height and phase images of monolayers of an it-PMMA and st-PMMA mixture (it/st = 1/2 in unit-molar base) compressed at a rate of 0.5 mm/s (left column) or 0.001 mm/s (centre and right columns), and deposited on mica at 10 mN/m. Right column: magnified phase images of the areas indicated by the yellow squares in the centre columns; yellow lines indicate single SC molecules. Scale bar: 40 nm. Height range for the height images: 4 nm. (b) Photograph of 30 macroscopic PMMA rods (diameter, 3 mm; length, 10 mm), self-assembled on a water surface, the structures of which are similar to the nanometer-scale assemblies of the SCs formed from uniform PMMA compressed at a rate of 0.001 mm/s (a) (centre and right columns, upper three rows). (c) Molecular length distributions of the SCs directly determined by AFM. (d) Number-average lengths (L_n) of the SCs plotted against the number-average degrees of polymerization (P_n) of it-PMMA (red circles; error bars indicate the standard deviation). Lines indicate the lengths of a 9/1 it-PMMA double helix composed of one and two it-PMMA chains (black dotted and solid lines, respectively), and an 18/1 st44 single helix (red dotted line) calculated on the basis of the triple-stranded helix model in Figure 1b. The length of an it-PMMA double helix composed of two 10/1 it-PMMA chains is also shown (green line).

mN/m, corresponding to stereocomplexation. Note that the low molecular weight it43 did not crystallize by itself, but the low molecular weight pair it43/st44 formed a stereocomplex, indicating that the stereocomplex is thermodynamically more stable than the it-PMMA crystal. None of the isotactic uniform polymers used in the present study also crystallized by themselves at the water surface, but instead, they formed SCs with the st-PMMA used here.

AFM Study of Stereocomplex Formation: Molecular Weight Effect of it-PMMA Components on Molecular Length of the Stereocomplex. We used a uniform st-PMMA (st44) as an st-PMMA component and a series of uniform it-PMMA (it22, it28, and it43), or a narrow-dispersity it-PMMA, it(6.7K), as an it-PMMA component to investigate the effect of the molecular weights of it-PMMA component on the molecular lengths of the resulting SCs. Mixtures of it- and st-PMMA with the mole ratio (it/st = 1/2) in chloroform solutions were spread on a water surface and compressed to 10 mN/m to form SCs. The LB films deposited on mica were then examined by AFM (Figure 3).

All of the AFM images in Figure 3a show SCs with a thickness of about 1.4 nm. SCs formed from uniform polymer pairs adopt irregular structures at a normal monolayer compression

rate (0.5 mm/s; Figure 3a, left column, rows 1–3). At a slow compression rate of 0.001 mm/s (Figure 3a, center and right columns, rows 1–3), in contrast, lamellae with a uniform width are formed from SCs aligned in parallel (yellow lines in the magnified images of the right column) and show a regular aggregation structure by stacking of lamellae. The compression at the rate of 0.001 mm/s required about 136 h (cf. 18 min for the normal compression rate of 0.5 mm/s; for details, see Experimental Section). Figure 3b shows a photograph of macroscopic PMMA rods (3-mm diameter, 10-mm length), self-assembled on a water surface by gently rocking the water surface. The PMMA rods were regularly self-assembled due to interfacial tension. Interestingly, the macroscopic aggregation of the rods resembles the nanometer-scale structure of SCs formed by the slow compression. The lamella structure of an SC composed of a PMMA with a molecular weight distribution, it(6.7K), is very irregular even at the slow compression rate (Figure 3a, bottom row).

The length distributions of SCs are shown in Figure 3c. For the uniform it-PMMA, the ratios of the weight-average length (L_w) and the number-average length (L_n) are 1.02–1.05, showing a narrow distribution, and the SCs lengthen as the molecular weight of it-PMMA increases. Because uniform polymers have

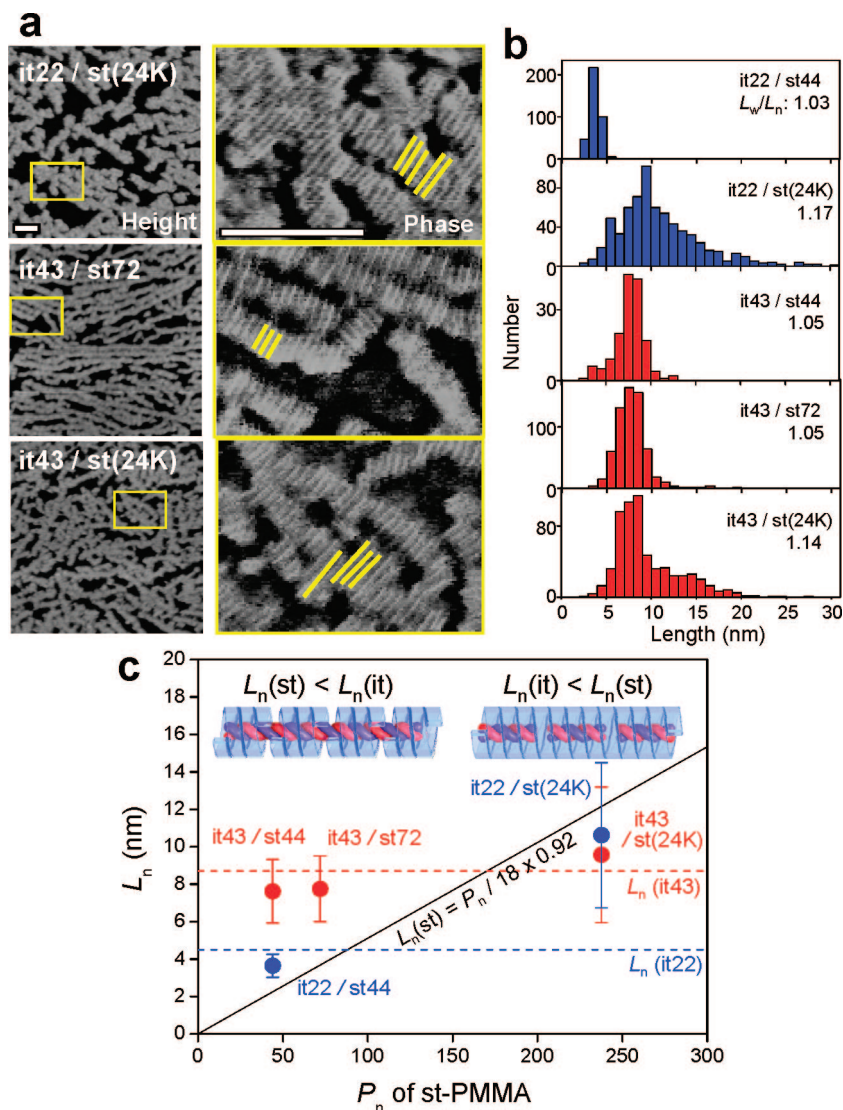


Figure 4. SCs composed of an it-PMMA selected from uniform it-PMMA (it22 and it43) and an st-PMMA selected from uniform (st44 and st72) and narrow-dispersity (st(24K)) st-PMMA. (a) AFM height and magnified phase images of monolayers of an it-PMMA and st-PMMA mixture (it/st = 1/2) compressed at a rate of 0.001 mm/s and deposited on mica at 10 mN/m. The magnified images correspond to the areas indicated by the yellow squares in the height images. Scale bar: 40 nm. Height range for the height images: 4 nm. (b) Molecular length distributions of the SCs directly determined by AFM corresponding to Figures 3a (it22/st44 and it43/st44) and 4a (it22/st(24K), it43/st72, and it43/st(24K)). (c) Number-average lengths (L_n) of the SCs plotted against the number-average degrees of polymerization (P_n) of st-PMMA (red circles; error bars indicate the standard deviation). Lines indicate the lengths of 9/1 it-PMMA double helices composed of two it22 chains (blue dotted line, $L_n(\text{it22})$) and two it43 chains (red dotted line, $L_n(\text{it43})$), and an 18/1 st-PMMA single helix (black line, $L_n(\text{st})$) calculated on the basis of the triple-stranded helix model in Figure 1b. Representations of SCs for it-PMMA and st-PMMA dominant regions are also shown in the graph. it-PMMA, inner red and blue helices; st-PMMA, outer transparent blue helices.

no molecular weight distribution, the SCs obtained should have no length distribution in the ideal case. In reality, however, the SCs do have a distribution, which together with the fact that the SCs obtained from uniform PMMA by the slow compression had a regular structure and showed almost no irregular multiple aggregates through intermolecular connections (close association, not open association) indicates that the SCs certainly have a thermodynamically stable and regular structure, although the perfect thermodynamically stable structure has not yet been attained in spite of the slow compression. For it(6.7K), in contrast, the distribution is considerably broad with $L_w/L_n = 1.15$, which corresponds to the molecular weight distribution $M_w/M_n = 1.19$ of it(6.7K).

Figure 3d shows the relation between L_n and the degree of polymerization (P_n) of it-PMMA. Here we compare the lengths of the double-stranded helix of it-PMMA and the single helix

of st-PMMA, calculated on the basis of the triple-stranded helix model (Figure 1b), with the experimental results. In the triple-stranded helix model, the it-PMMA helix is a 9/1 helix with a helical pitch of 1.84 nm, and the st-PMMA helix is an 18/1 helix with a helical pitch of 0.92 nm.¹³ The length of the outer helix of st-PMMA, $L_n(\text{st44})$, is estimated to be 2.2 nm (dotted red line), which is considerably shorter than the experimental values. For the inner it-PMMA helix, the observed lengths of

(25) The solid green line in Figure 3d shows the calculated length for a 10/1 double helix of two it-PMMA chains. The experimental values fit well with the calculated ones, suggesting that the it-PMMA helix seems to be wound more loosely than 9/1.

(26) If one assumes that a single it-PMMA chain folds back on itself to form a double-stranded helix, followed by inclusion by an st-PMMA helix to produce an SC, the length of the resulting SC will be reduced by half (dotted black line in Figure 3d), and therefore, this possibility can be excluded.

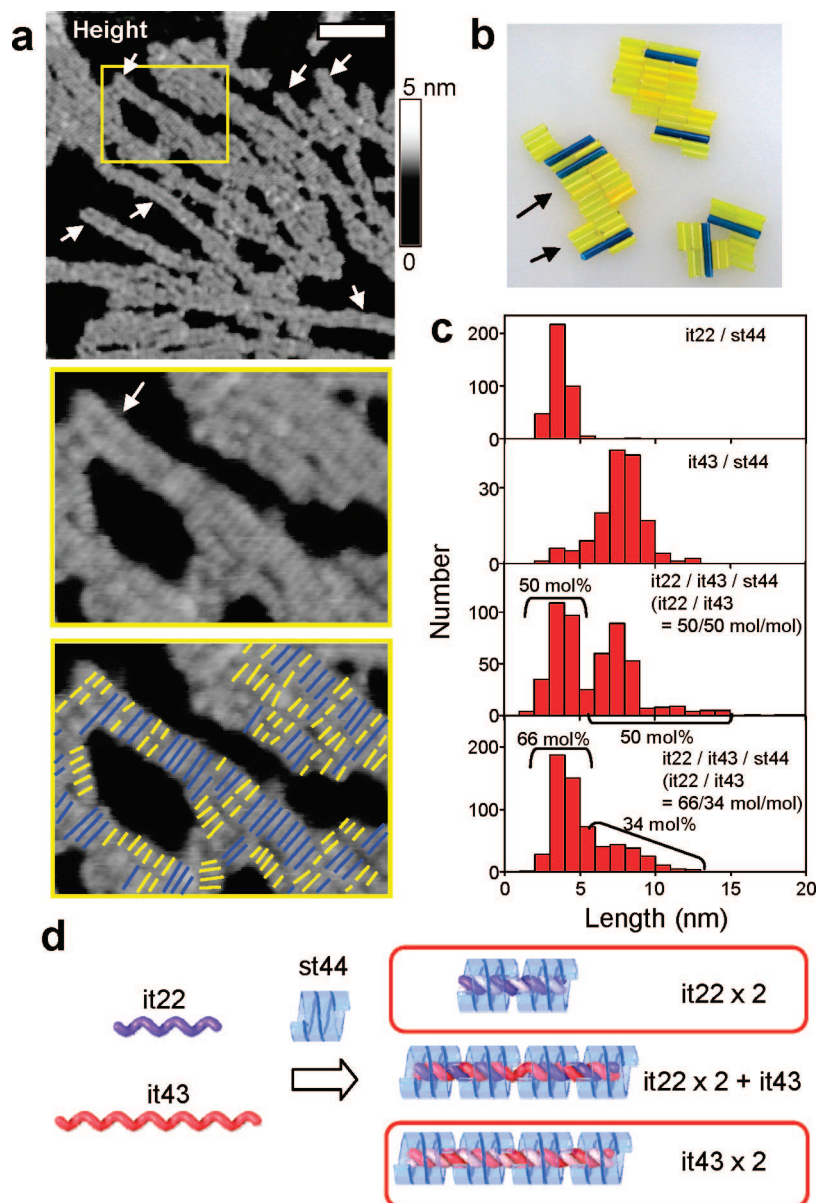


Figure 5. SCs composed of it22/it43/st44 mixtures. (a) AFM height images of a monolayer of an it22/it43/st44 mixture compressed on a water surface at a rate of 0.001 mm/s and deposited on mica at 10 mN/m. The composition was it22/it43/st44 = 0.34/0.66/2 in weight; this composition corresponds to it/st = 1/2 on a unit molar basis and it22/it43 = 50/50 on a polymer-molar basis. Magnified height images of the area indicated by a yellow square in the upper image are shown (middle and bottom) with short (yellow) and long (blue) SC packing (bottom). Scale bar: 40 nm. (b) Photograph of PMMA macroscopic rods (diameter, 3 mm) with two different lengths (10 mm, yellow; 20 mm, blue) self-assembled on a water surface. Characteristic structures of paired lamellae indicated by arrows are seen in panels a and b, for details, see the text. (c) Molecular length distributions of the SCs directly determined by AFM. The compositions of the SCs were it22/st44 (1/2 in weight), it43/st44 (1/2 in weight), it22/it43/st44 (0.34/0.66/2 in weight, corresponding to it/st = 1/2 in weight and it22/it43 = 50/50 on a polymer-molar basis) and it22/it43/st44 (0.5/0.5/2 in weight, corresponding to it/st = 1/2 in weight and it22/it43 = 66/34 on a polymer-molar basis) from top to bottom, respectively. (d) Representation of possible chain arrangements in an SC made of an it22/it43/st44 mixture.

the SCs (red circles) are in agreement with the values calculated under the assumption that two it-PMMA molecules with a 9/1 helix form a double-stranded helix (solid black line), although the values are slightly smaller than the calculated ones.²⁵ These observations indicate that two it-PMMA chains form a double-stranded helix (red and blue helix in the center), which determines the total length of an SC. Subsequently, several shorter helices of st44 (transparent blue helices) wind around the double-helix of the it-PMMA to complete the triple-stranded SC as shown by the schematic representation of a triple-stranded helical SC in Figure 3d.²⁶

AFM Study of Stereocomplex Formation: Molecular Weight Effect of st-PMMA Components on Molecular Length of the Stereocomplex. Next, we investigated the effect of molecular weights of st-PMMA component on the molecular lengths of the resulting SCs using a uniform it22 or it43 as an it-PMMA component and a uniform st44 or st72, or a narrow-dispersity st(24K) as an st-PMMA component. Figure 4a shows the AFM images of the SCs compressed at the rate of 0.001 mm/s. The molecular length distributions of the SCs determined by AFM corresponding to Figure 4a (it22/st(24K), it43/st72, and it43/st(24K)) together with those of Figure 3a (it22/st44 and it43/

st44) are summarized in Figure 4b. Figure 4c shows the relation between L_n of the SCs and P_n of the st-PMMA. In the region where the length of it-PMMA ($L_n(\text{it}22)$, $L_n(\text{it}43)$) is longer than that of st-PMMA ($L_n(\text{st})$) (Figure 4c, left side of graph), the length of SCs is determined by the length of it-PMMA. In a comparison of the results for it22/st44 and it43/st44, the length of SCs is determined by the dominant it-PMMA. A comparison of the results for it43/st44 and it43/st72 shows that the length of SCs is also determined by it43 and not affected by the shorter component of st44 or st72. The length distributions of SCs obtained from the uniform polymers are narrow; L_w/L_n varied from 1.03 to 1.05 (Figure 4b, first, third, and fourth from top).

From Figure 4c, the P_n of an st-PMMA whose length becomes dominant to that of it-PMMA, is 90 for it22 and 170 for it43, respectively. Because such a high molecular weight uniform polymer is difficult to obtain by fractionation, we used an st-PMMA with a narrow molecular weight distribution, st(24K), for investigation in the st-PMMA dominant region. The length of the SC of it22/st(24K) is longer than that of it22 (it22/st44) across almost all of the distribution range, and has a single broad distribution (Figure 4b, first and second graphs from the top). The distribution of the length of SCs is estimated as $L_w/L_n = 1.17$, which is comparable to that of the molecular weight of st(24K), $M_w/M_n = 1.10$. The number-average length of SCs, $L_n = 10.9 \pm 4.6$ nm, is in fair agreement with the length of 12.1 nm for an st-PMMA 18/1 helix, estimated on the basis of the triple-stranded helix model. In contrast, the length distribution of the SC from it43/st(24K) is unusual, a broad distribution with a sharp peak at around 8 nm (the bottom of Figure 4b). This is probably because the length distribution of st(24K) is so broad that, in the lower molecular weight region, the length of st(24K) is shorter than that of it43; therefore, the length of the SC at this regime should be determined by it43. In fact, the peak of the length distribution around 8 nm for it43/st(24K) is similar to the distributions for it43/st44 and it43/st72 (Figure 4b, third and fourth from the top).

Consequently, the length of an SC is determined by that of the st-PMMA in the region where a helix of st-PMMA is longer than that of it-PMMA (see the schematic representation of the triple-stranded helix model of an SC in Figure 4c (right)), and the length of the SC is in fairly good agreement with the value estimated from the triple-stranded helix model (Figure 1b). These observations also support the supramolecular triple-stranded helical structure of the SCs composed of a double-stranded helix of two intertwined it-PMMA chains included in a single helix of st-PMMA.²⁷ The structure and the interaction between the helices of SCs are very different from those of the intertwined triple-stranded helices observed in biopolymers such as schizophyllan.²⁸ The observed behavior of SC formation, such that the longer component determines the length of the SC and the shorter component supplements the longer one to complete the SC, seems reasonable, taking into account the inclusion complex structure of the SC. For instance, a poly(ethylene glycol) chain is known to penetrate numbers of α -cyclodextrin molecules to form a rotaxane (a so-called 'molecular necklace'), the length of which is determined by the poly(ethylene glycol);²⁹ this behavior is similar to the formation process of inclusion-type SCs from it-PMMA and st-PMMA.

Molecular Sorting of it-PMMA with Different Molecular Weights to Form Double-Stranded Helices Included in the st-PMMA Helices. Next, we consider how the double-stranded helix of it-PMMA included in the st-PMMA helix is formed.

To investigate this, we examined the formation of SCs from a mixture of uniform it- and st-PMMA, it22 and it43, and st44. In this system, st44 (2.2 nm) is shorter than it22 (4.5 nm) and it43 (8.8 nm) (Figures 3d and 4d). The molecular length of an SC is expected to reflect the length of a double-stranded helix formed from a mixture of it-PMMA with different molecular lengths. Here, it43 is nearly twice as long as it22. Molecular sorting experiments were performed as described below. A chloroform solution of a mixture of it22, it43, and st44 in a weight ratio of 0.34/0.66/2 or 0.5/0.5/2 was spread on a water surface and then compressed to 10 mN/m at the slow compression rate of 0.001 mm/s to form an SC. This composition corresponds to the it/st = 1/2 stoichiometry and it22/st43 = 50/50 or 66/34 on a polymer-molar basis, respectively. AFM images of the LB film (it22/it43/st44 = 0.34/0.66/2) deposited on mica are shown in Figure 5a. A characteristic structure of paired thin lamellae composed of parallel array of short SCs was observed (Figure 5a, top and middle, arrows). The packing of SCs determined from the AFM image is shown schematically in the bottom image of Figure 5a. The short SCs (yellow lines) and the twice-as-long SCs (blue lines) are observed as a mixture, resulting in the lamella structure.

Figure 5b shows a self-assembled macroscopic structure on a water surface, composed of PMMA rods (3-mm diameter) of two different lengths: 10 mm (yellow) and 20 mm (blue). Long blue PMMA rods stabilize the structure of paired lamellae of yellow short rods (arrows). This macro-

(27) In addition to the triple-stranded helix model, we compared the observed lengths of the SCs with those calculated on the basis of the double-stranded (Figure 1a) and quadruple-stranded (Figure S2 in Supporting Information) helix models. As shown in Figure 3d, the molecular lengths of the it-PMMA double-stranded helix in the triple-stranded helix can be expressed as $L_n^{\text{triple,two-it}}(\text{it}) = P_n/9$ (monomer units/turn) $\times 1.84$ (nm/pitch) = $0.204P_n$ and $L_n^{\text{triple,one-it}}(\text{it}) = P_n/9$ (monomer units/turn) $\times 1.84$ (nm/pitch)/2 = $0.102P_n$ for an it-PMMA double-stranded helix composed of two it-PMMA chains and a folded single it-PMMA chain, respectively. The experimental results support the former structure, the it-PMMA double-stranded helix composed of two it-PMMA chains (Figure 3d). In the same way, the molecular lengths of the st-PMMA in the triple-stranded helix can be expressed as $L_n^{\text{triple}}(\text{st}) = P_n/18 \times 0.92 = 0.051P_n$, which is in fairly good agreement with the observations (Figure 4c). On the basis of the double-stranded helix model in Figure 1a, the lengths of the it-PMMA and st-PMMA chains are estimated to be $L_n^{\text{double}}(\text{it}) = P_n/9 \times 1.84 = 0.204P_n$ and $L_n^{\text{double}}(\text{st}) = P_n/18 \times 1.84 = 0.102P_n$, respectively. The calculated chain lengths of the it-PMMA agree well with the experimental values, but those of the st-PMMA disagree with the observed ones; therefore, the double-stranded helix model can be ruled out. As mentioned in our previous report,¹³ another model for the PMMA SC, a quadruple-stranded helix (Figure S2 in Supporting Information) can be possibly constructed. In this model, the same double-stranded helix of it-PMMA is surrounded by a double-stranded st-PMMA helix composed of two intertwined 18/1 st-PMMA helices with the helical pitch of 0.92 nm, which also satisfies the AFM results (0.92 nm) and the stoichiometry of it/st = 1/2. Therefore, the chain lengths of the st-PMMA chains can be calculated as $L_n^{\text{quadruple,two-st}}(\text{st}) = P_n/18 \times 1.84 = 0.102P_n$ and $L_n^{\text{quadruple,one-st}}(\text{st}) = P_n/18 \times 1.84/2 = 0.051P_n$ for the st-PMMA double helix composed of two st-PMMA chains and a folded single st-PMMA chain, respectively. Thus, if we assume that an st-PMMA double-helix is composed of a folded single st-PMMA chain, the experimental results ($\sim 0.051P_n$) also agree, in principle, with those based on the quadruple-stranded helix model. Although we could not completely rule out this possibility, the formation of such a complicated double-stranded helix with a single st-PMMA chain by folding, followed by inclusion of a double-stranded it-PMMA helix to produce an SC seems highly unlikely. A major difference between the triple- and quadruple-stranded helix models is the difference in the tilt angle of the outer st-PMMA helix with respect to the axis of the SC main chain. The observed tilt angle by AFM was in fair agreement with the tilt angle of the triple-stranded-helix model,¹³ which also supports the triple-stranded-helix as a plausible model for the SC.

(28) Deslandes, Y.; Marchessault, R. H.; Sarko, A. *Macromolecules* **1980**, *13*, 1466–1471.

(29) Harada, A.; Li, J.; Kamachi, M. *Nature* **1992**, *356*, 325–327.

scopic structure is similar to the nanostructure of the SCs (Figure 5a, arrows). Figure 5c shows the length distributions of SCs composed of mixtures of a single it-PMMA (it22 or it43) and st44 (top and upper-middle) and it22/it43/st44 mixtures with different mixing ratios (lower-middle and bottom). In every case, the molar ratio of it-PMMA to st-PMMA was kept at a stoichiometric composition of 1/2. SCs obtained from a mixing ratio of it22/it43 = 50/50 on a polymer molar basis show a bimodal length distribution: the respective peaks are in good agreement with the distribution obtained for a mixture of it22 and st44, and a mixture of it43 and st44. The numbers of SCs contained in the respective peaks are 1 to 1, and correspond exactly to the mixing ratio of it-PMMA. A similar tendency has been found for a different mixing ratio, it22/it43 = 66/33 on a polymer molar basis (bottom), and the numbers of SCs contained in the respective peaks also correspond exactly to the mixing ratio of it-PMMA.

A representation of the possible SC formed from a mixture of it22, it43, and st44 is shown in Figure 5d. If the homogeneous double-stranded helices of it22 and it43 were predominantly formed from mixtures of it22 and it43, SCs with a bimodal length distribution reflecting the mixing ratio of it22 and it43 would be produced as supported by the experimental results (Figure 5c). Therefore, the formation of heterogeneous double-stranded helices comprising two it22 chains and a single it43 chain (Figure 5d, right-middle) can be ruled out. These results clearly show that it-PMMA

molecules recognize the molecular weight of each other exactly and form double-stranded helices only with molecules of the same molecular weight.³⁰

Conclusions

In summary, we investigated the PMMA SC, the molecular basis of the structure, and the mechanism of complex formation using uniform it- and st-PMMA and those with a narrow molecular weight distribution having different molecular weights by high-resolution AFM, and found that (1) uniform it- and st-PMMA form SCs with a discrete supramolecular structure, (2) the size of the SC precisely depends on the molecular weights of the component PMMA, (3) the it- or st-PMMA with the longer molecular length determines the total length of the SC and molecules of the shorter component associate until they fill up or cover the longer component, and (4) the it-PMMA chain recognizes the molecular weight of the paring it-PMMA chain through topological interaction in their double-stranded helix structure in the SC ("molecular sorting"). These observations support the supramolecular triple-stranded helical structure of SCs that we have recently proposed,¹³ which is composed of a double-stranded helix of two intertwined it-PMMA chains included in a single helix of st-PMMA. This triple-stranded helix model of SCs appears to be applicable to it- and st-PMMA having the wide range of molecular weights we employed in this study. The present system is, to the best of our knowledge, the first example of a multiple-stranded helical structure showing molecular weight recognition based on the complementary complex formation of polymers without specific monomer–monomer interaction. This finding suggests that the multiple-stranded helical structure itself may play an essential role in realization of functions such as replication and information transfer, although the mechanism differs from that of the complementary double-stranded helix formation in DNA.³¹ We are currently investigating the helix-sense-selective synthesis of the PMMA SC.

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Supporting Information Available: High-resolution AFM images of an SC formed from it43 and st44 and a quadruple-stranded helix model for an SC. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(30) One may suspect that, if the it-PMMA in SCs are not the double-stranded helices shown in Figure 1b but are the single helices shown in Figure 1a, then the same mixtures of short and long SCs corresponding to the mixing ratio of it-PMMA shown in Figure 5c,d should be obtained without specific molecular weight recognition between it-PMMA because, in this case, formation of double-stranded helices between it-PMMA is not necessary. Here, we therefore reconsider the experimental results without any hypothesis to make clear which model, the single- or double-stranded helix, is reasonable for it-PMMA chains. Let us consider the degree of polymerizations of an it-PMMA and st-PMMA that form an SC with the same length on the basis of the experimental results of the length of SCs given as a function of the molecular weights of it-PMMA and st-PMMA (Figures 3d and 4c). For instance, an SC of 10 nm corresponds to a 58-mer of it-PMMA and a 224-mer of st-PMMA, respectively. Note that only the experimental data are used. Assuming that an SC is composed of a single it-PMMA and a single st-PMMA chain, the ratio becomes it/st = 58/224 = 1/3.9, which does not agree with the experimentally determined stoichiometry of 1/2. To agree with 1/2, it is reasonable to assume that an SC is composed of two it-PMMA chains and one st-PMMA chain, i.e., the SC is composed of a double-stranded helix of it-PMMA and a single helix of st-PMMA.

(31) Orgel, L. E. *Nature* **1992**, *358*, 203–207.