Stereocomplexes

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Stereospecific Cyclic Poly(methyl methacrylate) and Its Topology-Guided Hierarchically Controlled Supramolecular Assemblies**

Jing Ming Ren, Kotaro Satoh, Tor Kit Goh, Anton Blencowe, Kanji Nagai, Kenji Ishitake, Andrew Joseph Christofferson, George Yiapanis, Irene Yarovsky, Masami Kamigaito, and Greg Guanghua Qiao**

Abstract: *In this study, the stereocomplexation between a novel stereospecific cyclic vinyl polymer, that is, cyclic syndiotactic poly(methyl methacrylate) (st-PMMA), with the complementary linear isotactic (it-) PMMA was investigated. Surprising new insight into the effects of the topology (i.e., end groups), size, and tacticity of the assembling components on stereocomplex formation was obtained. Characterization of the stereocomplexes revealed that the self-assembly of cyclic st-PMMAs and linear it-PMMAs resulted in the formation of an unprecedented "polypseudorotaxane-type" supramolecular assembly. This stereocomplex exhibited remarkably different physical properties as compared to the conventional PMMA triple-helix stereocomplex as a result of the restricted topology imposed by the cyclic st-PMMA assembling component.*

Naturally occurring macromolecules possess a precisely regulated molecular weight, composition, monomer sequence, and stereostructure (i.e. tacticity). The meticulous structural controls grant them a unique structure, distinct properties, and the ability to form intricate and exquisite supramolecular assemblies (e.g., DNA[1] and proteins[2]), which regulate important bioprocesses within living organisms. The ultimate goal in polymer chemistry is to match and emulate nature by synthesizing macromolecules with a precisely controlled primary structure that may serve as basic building blocks for the assembly of advanced nanostructured materials with novel properties and functions.[3] So far, success towards this end has been limited, and the synthesis of polymers with a highly controlled primary structure still remains challenging.

Cyclic polymers present in both natural[4] and synthetic forms[5] are among the most fascinating classes of macromolecules. They possess simple molecular structures but exhibit intriguing chemical and physical properties[6] as a consequence of the topology control imposed by the tethering of chain ends. Remarkable progress has been made in the development of synthetic techniques that offer efficient routes to well-defined cyclic polymers with high purity.[7] Cyclic polymers with well-defined molecular weights (MWs) and compositions (i.e., homopolymers, copolymers, and gradient polymers) have been extensively investigated.[8] However, with the exception of cyclic poly(oligo)peptides,[9] cyclic polymers that consist of monomeric units with a controlled stereochemical arrangement have been less explored.[10] Herein, we report the synthesis of a novel cyclic syndiotactic poly(methyl methacrylate) (*c*-*st*-PMMA) with simultaneous control over MW, tacticity, and topology through polymerization of the vinyl monomer methyl methacrylate (MMA). The synthesis of well-defined stereospecific cyclic polymers from vinyl monomer building blocks has not previously been demonstrated. Furthermore, the controlled tacticity endows the cyclic *st*-PMMA with the ability to stereocomplex with complementary linear isotactic (*it*-) PMMA to form an unprecedented "polypseudorotaxane-type"[11] supramolecular assembly with a controlled crystallization mode dictated by the topology of the *st*-PMMA component.

The novel cyclic *st*-PMMA was synthesized by the use of a combination of stereospecific living radical polymerization (SLRP)[12] and "click" end-to-end cyclization.[7a] The cyclic *st*-PMMA polymers were obtained in high purity (cyclic purity > 93 %) through cyclization of the heterotelechelic *st*-PMMA precursors containing alkyne and azide end groups (Scheme 1). In this study, a copper-catalyzed (Cu-)SLRP was devised (see Figure S1 in the Supporting Information) and exploited for the preparation of heterotelechelic polymer precursors. The implemented Cu-SLRP system provided living *st*-PMMAs with triad syndiotacticity (*rr*) values of up

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[*] J. M. Ren, Dr. T. K. Goh, Dr. A. Blencowe, Prof. G. G. Qiao
Polymer Science Group, Department of Chemical and Biomolecular Engineering, University of Melbourne
Melbourne, VIC 3010 (Australia)
E-mail: gregghq@unimelb.edu.au
Homepage: http://www.chemeng.unimelb.edu.au/polymer-science

Prof. K. Satoh, Dr. K. Nagai, Dr. K. Ishitake, Prof. M. Kamigaito
Department of Applied Chemistry
Graduate School of Engineering, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603 (Japan)
E-mail: kamigait@apchem.nagoya-u.ac.jp

Dr. A. J. Christofferson, Dr. G. Yiapanis, Prof. I. Yarovsky
School of Aerospace, Mechanical and Manufacturing Engineering
RMIT University
GPO Box 2476, Victoria 3001 (Australia)

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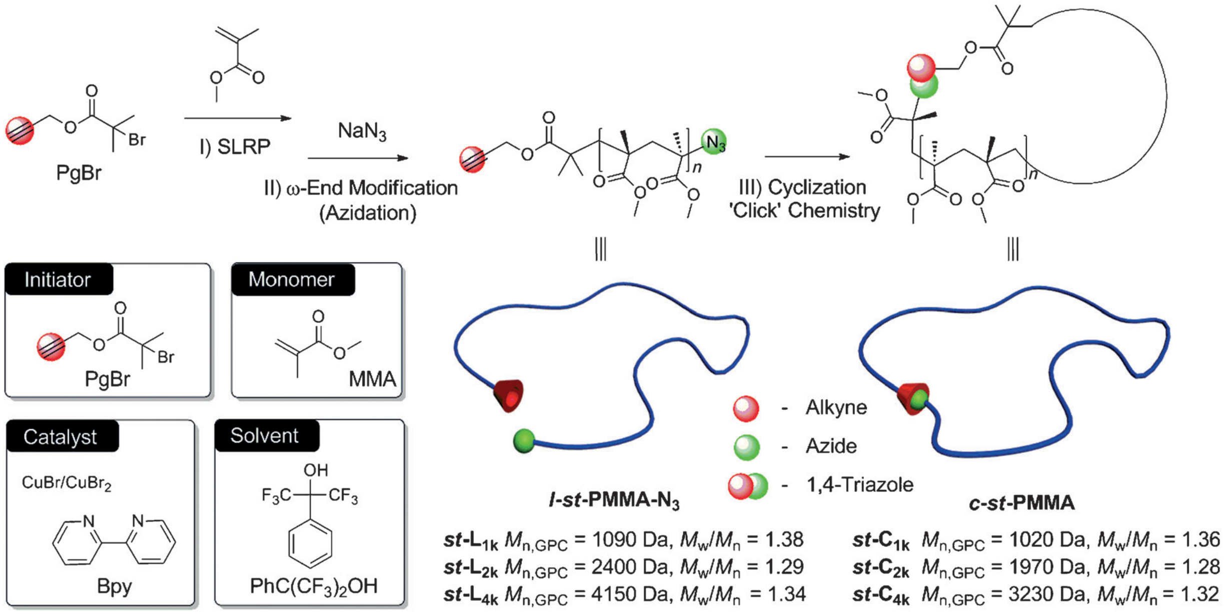

Scheme 1. Preparation of cyclic syndiotactic poly(methyl methacrylate) (*c*-*st*-PMMA) by I) stereospecific living radical polymerization (SLRP), II) azidation, and III) "click" cyclization.

to 72 %. Although living anionic polymerization[13] is able to provide *st*-PMMAs with higher levels of syndiotacticity (*rr* up to 96 %) than those observed for Cu-SLRP, the heterotelechelic functional groups at the polymer chain ends could be introduced conveniently in the Cu-SLRP approach by the use of a functional initiator and end-group substitution (Scheme 1).[14] For the Cu-SLRP, the bulky fluorinated cumyl alcohol $PhC(CF_3)_2OH$ was used as the solvent, which coordinates to the carbonyl groups of MMA and the growing polymer side chain to generate a syndiospecific environment for living polymerization to proceed (see Scheme S1 in the Supporting Information).[15] The dual control of MW and tacticity is therefore achieved simultaneously. The cyclization of heterotelechelic *st*-PMMA was performed after quantitatively transforming the "living" ω-bromo chain end into an azide through azidation (see Figure S2 in the Supporting Information). The ring closure of the "clickable" heterotelechelic *st*-PMMA was verified by gel permeation chromatography (GPC), matrix-assisted laser desorption ionization time-of-flight (MALDI ToF) mass spectrometry, ^{1}H NMR spectroscopy (Figure 1), FT-IR spectroscopy, and differential scanning calorimetry (DSC; see Figure S3 in the Supporting Information).

It is well-known that linear PMMAs are able to form a triple-stranded helical supramolecule[16] consisting of an intertwined double-stranded helix of *it*-PMMA polymers wrapped by a single strand of *st*-PMMA in an *it*-/*st*- 1:2 stoichiometry.[17] In the present study, we initially anticipated that the *c*-*st*-PMMA would not be able to form a conventional stereocomplex[18] with the complementary linear *it*-PMMA, since the absence of chain ends on the *c*-*st*-PMMA component would hinder molecular wrapping. To test this hypothesis, we synthesized two linear (*l*-) *it*-PMMA polymers (*it*-L_{10k}: $M_n = 10.3$ kDa, $M_w/M_n = 1.12$, *mm*/*mr*/*rr* 93:3:4; *it*-L_{44k}: $M_n = 44.3$ kDa, $M_w/M_n = 1.30$, *mm*/*mr*/*rr* 97:2:1; see Figure S4

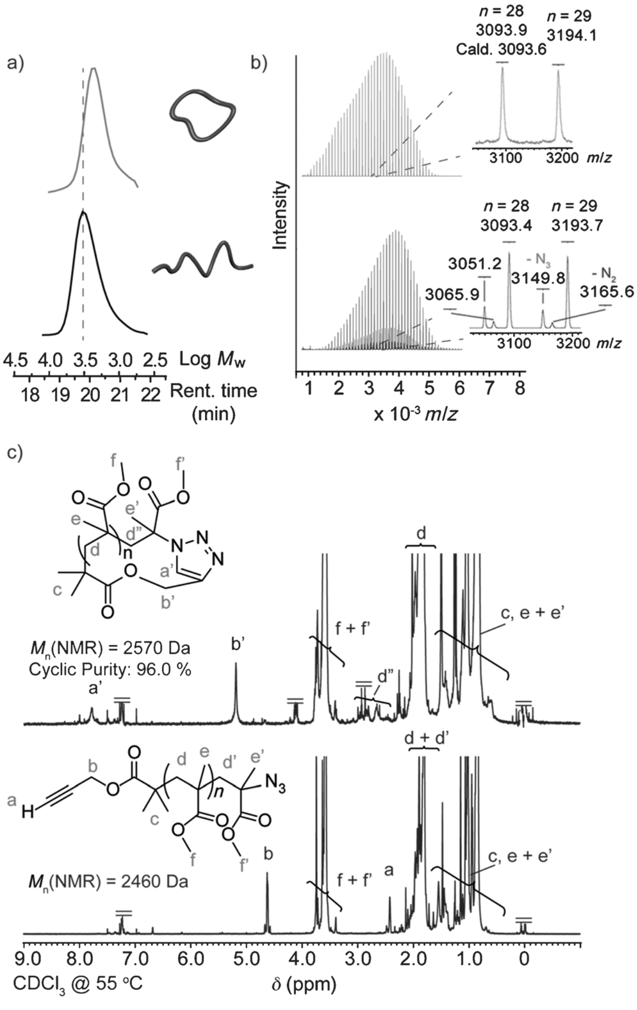

Figure 1. a) GPC differential refractive index (DRI) response and molecular-weight distribution, b) MALDI ToF mass spectra, and c) ^{1}H NMR spectra of the cyclic syndiotactic poly(methyl methacrylate) *st*-C_{2k} and its linear polymer precursor *st*-L_{2k}.

and Table S1 in the Supporting Information) through living anionic polymerization for stereocomplexation with the *c-st*-PMMA polymers. Previously, it has been demonstrated that *st*-PMMAs with low syndiotacticity ($rr < 80\,\%$) are capable of forming stereocomplexes, whereas the complementary *it*-PMMAs with high degrees of isotacticity are essential for stereocomplex formation to occur.[18a,c] The *l-it*-PMMAs were prepared by anionic rather than living radical polymerization, as a synthetic route to highly isotactic ($mm > 90\,\%$) polymers by the latter method has not been established. The PMMA stereocomplexes were prepared by the simple mixing of the separately dissolved *it*- and *st*-PMMA components in 1:2 *it*/*st* stoichiometry; acetonitrile/water (9:1) was used as the complexation solvent.[19] Unexpectedly, the DSC and X-ray diffraction (XRD) profiles (Figure 2a) of the stereocomplex sample prepared from *c-st*-PMMA (*st*-C$_{4k}$: $M_n = 3.2$ kDa, $M_w/M_n = 1.32$, *mm*/*mr*/*rr* 2:26:72, cyclic purity: 93% by ^{1}H NMR spectroscopic analysis) and *l-it*-PMMA (*it*-L$_{10k}$) revealed a crystalline structure that is essentially different from the structures of the individual PMMA precursors (Figure 2c,d). Furthermore, large nanoscale objects (100×100 nm^2) were observed in the 1:2 stoichiometric mixture of *it*-L$_{10k}$ and *st*-C$_{4k}$ by atomic force microscopy (AFM) as a direct result of the aggregation of complexed supramolecules through strong van der Waals interactions.[18a] Such phenomena were entirely absent in the samples of individual stereoregular PMMAs (see Figure S5 in the Supporting Information). This set of important results indicates that *c-st*-PMMA is able to stereocomplex with complementary *l-it*-PMMA in spite of its cyclic topology.

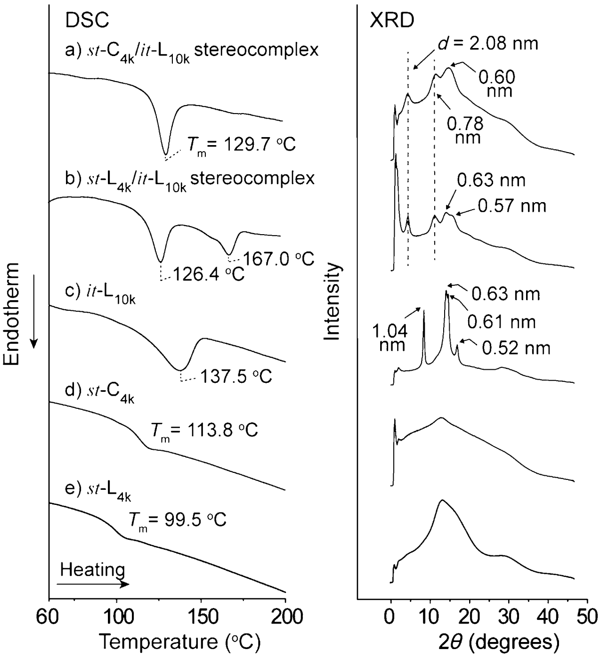

Figure 2. DSC thermograms and X-ray powder diffraction (XRD) patterns of a) the *st*-C$_{4k}$/*it*-L$_{10k}$ stereocomplex, b) the linear *st*-L$_{4k}$/*it*-L$_{10k}$ stereocomplex, c) the linear *it*-PMMA *it*-L$_{10k}$, d) the cyclic *st*-PMMA *st*-C$_{4k}$, and e) the linear *st*-PMMA *st*-L$_{4k}$.

More interestingly, the *st*-C$_{4k}$/*it*-L$_{10k}$ stereocomplex and the *st*-L$_{4k}$/*it*-L$_{10k}$ stereocomplex (i.e., the stereocomplex that is constructed from *it*-L$_{10k}$ and *st*-L$_{4k}$ ($M_n = 4.0$ kDa, $M_w/M_n = 1.32$, *mm*/*mr*/*rr* 2:26:72)—the corresponding linear polymer precursor of *st*-C$_{4k}$) share similar XRD profiles (Figure 2a,b) with a characteristic PMMA-stereocomplex *d*-spacing value at 2.08 nm. The *d*-spacing value correlates well with the chain–chain lateral spacing (2.4 ± 0.1 nm) of the linear PMMA triple-helix stereocomplexes observed by AFM.[16] Furthermore, the unit quantity of the complexed sequence in the *st*-C$_{4k}$/*it*-L$_{10k}$ stereocomplex is less than that in the *st*-L$_{4k}$/*it*-L$_{10k}$ stereocomplex, as supported by the DSC thermograms (the total endothermic heat released (ΔH_{tot}) through melting of the stereocomplex upon heating; see Table S2, entries 1 and 5 in the Supporting Information).[20] On the basis of these results, we hypothesized that the *c-st*-/*l-it*-PMMA stereocomplex possesses a distinct "polypseudorotaxane-type" or "molecular-necklace" structure that is comprised of a double-stranded helix of *it*-PMMA[21] onto which discrete *st*-PMMA rings are threaded (Figure 3a, I).

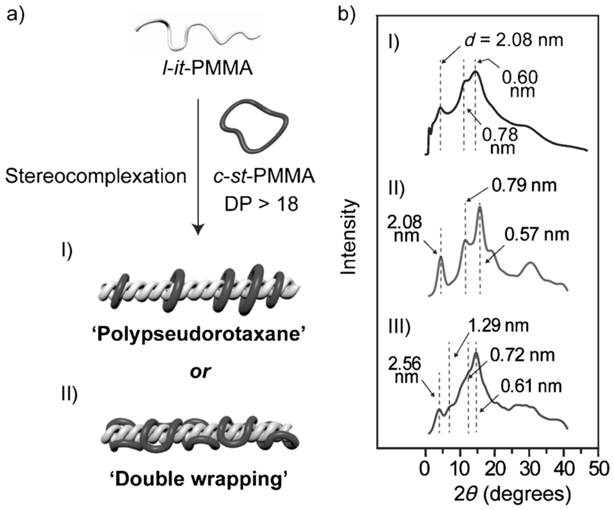

Figure 3. a) Schematic illustration of two possible stereocomplexes prepared from *l-it*-PMMA and *c-st*-PMMA, with a I) "polypseudorotaxane-type" and II) "double-wrapping" arrangement; b) XRD profiles of I) the *st*-C$_{2k}$/*it*-L$_{10k}$ stereocomplex, II) the simulated *c-st*-/*l-it*-PMMA stereocomplex with a "polypseudorotaxane-type" arrangement, and III) the simulated *c-st*-/*l-it*-PMMA stereocomplex with a "double-wrapping" arrangement (degree of polymerization (DP) of *c-st*-PMMA in II and III: 18).

We obtained further evidence for the proposed "polypseudorotaxane-type" stereocomplex structure by carefully examining the effect of the *c-st*-PMMA ring size on stereocomplex formation. In the conventional linear PMMA triple-helix stereocomplex, each helical turn of the wrapping *st*-PMMA consists of approximately 18 MMA repeat units (MW: 1.8 kDa).[16] Hence, it was expected that as the MW of *c-st*-PMMA approached this limiting value, reduced complex formation would arise from ineffective threading of the *c-st*-PMMA as a result of steric restrictions. In fact, a decrease in MW below the limiting value may result in no stereocomplex formation, since the threading of *c-st*-PMMA would be impossible. To verify this prediction, the *c-st*-PMMA polymers *st*-C$_{2\mathrm{k}}$ ($M_\mathrm{n} = 1.9$ kDa, $M_\mathrm{w}/M_\mathrm{n} = 1.28$, *mm*/*mr*/*rr* 2:26:72, cyclic purity: 96%) and *st*-C$_{1\mathrm{k}}$ ($M_\mathrm{n} = 1.0$ kDa, $M_\mathrm{w}/M_\mathrm{n} = 1.36$, *mm*/*mr*/*rr* 2:27:71, cyclic purity: 97%) were synthesized and stereocomplexed with *it*-L$_{10\mathrm{k}}$. The DSC and XRD results obtained for the resulting stereocomplexes matched our prediction rather well. The *st*-C$_{2\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$ stereocomplex had a lower ΔH_tot value than that of *st*-C$_{4\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$ (Figure 4a,b). This lower ΔH_tot value is indicative of a lower degree of (crystalline) complex formation, which was confirmed by the observation that the XRD profile of *st*-C$_{2\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$ showed weakened peak intensity as compared to that of *st*-C$_{4\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$ (Figure 4a,b). No stereocomplex was formed when *st*-C$_{1\mathrm{k}}$ and *it*-L$_{10\mathrm{k}}$ were used as precursors, as supported by both the DSC and XRD profiles (Figure 4d).

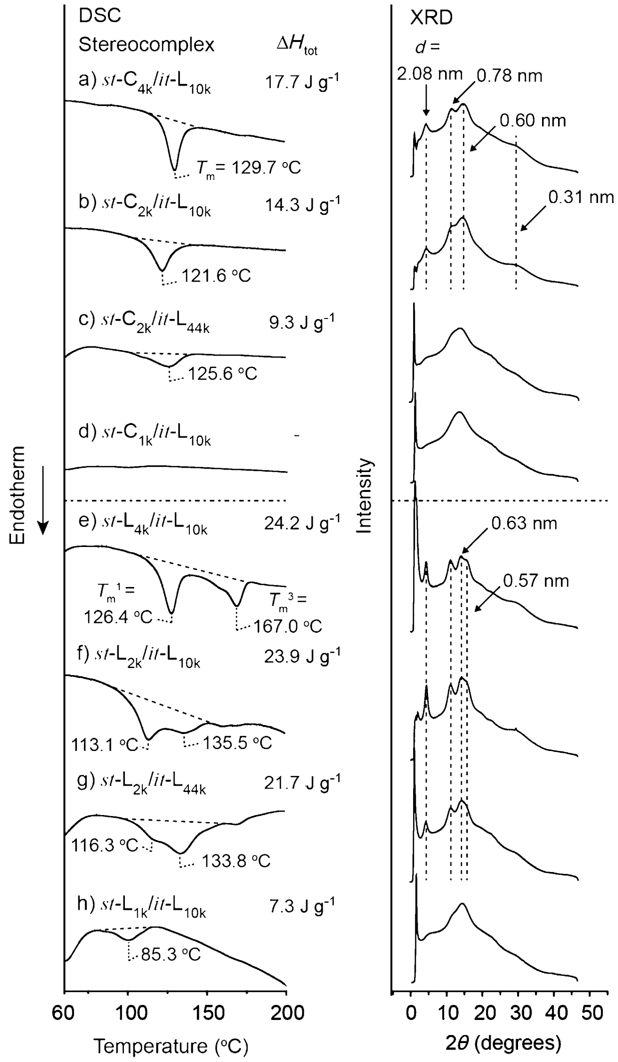

Figure 4. DSC and X-ray powder diffraction profiles of the *c-st-/l-it*-PMMA stereocomplexes a) *st*-C$_{4\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$, b) *st*-C$_{2\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$, c) *st*-C$_{2\mathrm{k}}$/*it*-L$_{44\mathrm{k}}$, and d) *st*-C$_{1\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$, and the *l-st-/l-it*-PMMA-stereocomplex counterparts e) *st*-L$_{4\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$, f) *st*-L$_{2\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$, g) *st*-L$_{2\mathrm{k}}$/*it*-L$_{44\mathrm{k}}$, and h) *st*-L$_{1\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$.

In contrast, variation in the chain length of *l-st*-PMMA had negligible impact on the amount of stereocomplexes formed with the same *it*-PMMA (Figure 4e,f). The only exception is when the average chain length of the *l-st*-PMMA component is shorter than 18 MMA units, in which case only the partially stabilized PMMA stereocomplex can be prepared (see Scheme S2b in the Supporting Information). One typical example of the partially stabilized stereocomplex is *st*-L$_{1\mathrm{k}}$/*it*-L$_{10\mathrm{k}}$, which has lower thermal stability and crystallinity than the other PMMA stereocomplexes, as indicated by its DSC and XRD profiles (Figure 4h). Although these results cannot rule out the possibility that *c-st*-PMMA forms a partially stabilized stereocomplex with the *l-it*-PMMA (i.e., a "double-wrapping" stereocomplex; Figure 3a, II), they suggest the stereocomplexation of *c-st*-PMMA and *l-it*-PMMA predominantly affords the "polypseudorotaxane-type" complex in support of the proposed model.

The degree of complexation of the *c-st-/l-it*-PMMA stereocomplex varies with the chain length of *l-it*-PMMA (Figure 4b,c), whereas that of the linear stereocomplex remains almost constant (Figure 4f,g). The increased chain length of the molecular axle would lead to a reduced number of threaded cyclic components owing to steric effects.[22] These results provide additional evidence that *c-st-/l-it*-PMMA stereocomplexes adopt the proposed "polypseudorotaxane-type" supramolecular structure. The present system indicates one possible formation mechanism for the conventional PMMA triple-helix stereocomplex: a double-stranded helix of *it*-PMMA molecules is included in a preformed single-stranded helix of *st*-PMMA, and the termini of the *st*-PMMA are not essential in facilitating stereocomplexation.

Previous studies have demonstrated that the conventional linear stereocomplex can also be prepared by solvent-free thermal annealing at reaction temperatures above the glass transition temperatures (ΔT_gs) of the PMMA components.[20b] In this study, the amount of stereocomplexes formed by thermal annealing, as determined by means of DSC (ΔH_m), was less than the amount prepared in solvent (see Figure S6 and Table S2 in Supporting Information) as a direct consequence of reduced system mobility, in good agreement with previous studies.[20] Notably, no *c-st-/l-it*-PMMA stereocomplex could be obtained by thermal annealing under the same conditions. We propose two possible explanations for this observation. First, the stereocomplexation system involving the cyclic polymer has a higher system immobility than the linear counterpart as a result of the imposed topology constraint. Second, in the absence of a solvent, the *c-st*-PMMA component is not able to form the "opened ring" (solvated) structure, hence it cannot thread the complementary *it*-PMMA polymers to afford the "polypseudorotaxane-type" stereocomplex.

Two-dimensional rotating frame nuclear Overhauser effect spectroscopy (2D ROESY)—a common characterization technique for inclusion complexes[23]—was utilized to characterize the resultant *c-st-/l-it*-PMMA stereocomplexes. However, no cross-peak interactions were detected between nuclei on the complementary *st*- and *it*-PMMA components owing to their low mobility and solubility upon stereocomplexation.

There is a subtle difference between the DSC profiles of the *c-st-*/*l-it-*PMMA stereocomplex and the linear stereocomplex. Except for *st-*L_{1k}/*it-*L_{10k}, all of the linear stereocomplexes had two melting temperatures (T_m^1 and T_m^3). The high-temperature melting point T_m^3 was not observed for the corresponding *c-st-*/*l-it-*PMMA stereocomplexes (T_m^1 only; Figure 4). Such difference is ascribed to the different crystallization modes of the two stereocomplexation systems. Schomaker and Challa investigated the origin of the multiple endothermic peaks of the PMMA stereocomplex in detail and proposed that T_m^1 and T_m^3 could be assigned to the formation of fringed-micellar structures (clusters of stereocomplexes) and lamellar crystallites, respectively.[20,24] In the linear system, the *st-*PMMA component has free chain ends that might bridge[25] adjacent stereocomplexes to aid the formation of lamellar superstructures (see Scheme S3 in the Supporting Information). In contrast, the bridging is suppressed by the cyclic topology of *c-st-*PMMA in the *c-st-*/*l-it-*PMMA stereocomplexes, so its crystallization mechanism follows that of fringed-micellar growth only (see Figure S7a,b in the Supporting Information). This difference accounts for the observation that the stereocomplexation solution became turbid immediately after the mixing of two complementary linear PMMA components, whereas that of the *c-st-*/*l-it-*PMMA stereocomplex remained clear even after prolonged periods (170 h; see Figures S8.1 and S8.2 in the Supporting Information). The clarity of the mixture in the latter case is attributed to the suppression of intercomplex interactions. The average hydrodynamic radius (R_h) of dispersed particles in a dilute solution of the *st-*L_{4k}/*it-*L_{10k} stereocomplex was significantly (approximately 15 times) larger than that in a dilute solution of the *st-*C_{4k}/*it-*L_{10k} stereocomplex (see Figure S7c,d in the Supporting Information). The difference in the crystallization mode is also reflected in the XRD profiles of the *c-st-*/*l-it-*PMMA stereocomplexes (Figure 4). The XRD profiles showed relative weak intensity of the diffraction peaks with *d*-spacing values at 2.08 and 0.57 nm, thus suggesting low ordering perpendicular to the helix axis in the absence of lamellar crystallite growth, in agreement with the DSC analysis.[20a]

It is difficult to design experiments to enable observation of the exact structure of the *c-st-*/*l-it-*PMMA stereocomplex. Therefore, we constructed molecular models of the two proposed structures of the *c-st-*/*l-it-*PMMA stereocomplex (Figure 3a, I and II; see also Figures S9.1 and S9.2 in the Supporting Information). The XRD profiles (Figure 3b) of the corresponding crystal structures of those proposed stereocomplexes were simulated and compared with the experimental result. The simulations demonstrated that the "polypseudorotaxane-type" arrangement reproduces the experimental XRD pattern of the *st-*C_{2k}/*it-*L_{10k} stereocomplex (Figure 3b, II and I, respectively). The "double-wrapping" model failed to reproduce the experimental *d* spacings, particularly the peak at 2.08 nm (Figure 3b, III). The "double-wrapping" model has a unique diffraction peak at 1.29 nm, which is associated with the spacing of the *st-*C_{2k} rings in the *xy* plane (see Figure S9.2 in the Supporting Information). Additionally, the "double-wrapping" configuration has a lower calculated density (1.20 $g\,cm^{-3}$) and solubility parameter (19.1 $J^{1/2}\,cm^{-3/2}$) than the "polypseudorotaxane-type" configuration (1.22 $g\,cm^{-3}$ and 20.7 $J^{1/2}\,cm^{-3/2}$, respectively; see Table S3 in the Supporting Information). On the basis of an examination of both structural and thermodynamic characteristics, the simulation results indicate that the "polypseudorotaxane-type" configuration is the most plausible arrangement of the stereocomplex of *c-st-*PMMA and the complementary *it-*PMMA double helix and support the experimental evidence.

Finally, it is anticipated that stereocomplexation between *l-it-*PMMA and *c-st-*PMMA with a significantly higher degree of polymerization (DP; e.g., DP > 200) may afford the "cross-linked" triple-stranded and/or the quadruple-stranded helix[16] stereocomplex (see Scheme S4 in the Supporting Information) as a direct effect of the diminished rigidity of *c-st-*PMMA with a large ring size. The resultant *c-st-*/*l-it-*PMMA stereocomplexes are expected to crystallize in both the fringed-micellar and lamellar modes in a similar way to the corresponding linear stereocomplex counterparts, since the suppression of intercomplex cross-linking by topological constraint of the *c-st-*PMMA will be compensated by its chain length and mobility.

In summary, we have described a synthetic route for the preparation of a syndiospecific cyclic vinyl polymer (up to 40 repeat units) with high cyclic purity (> 93 %). The highly regulated microstructure enables the cyclic polymer to form an unprecedented supramolecular assembly with linear isospecific counterparts through stereocomplexation. We propose that the resulting stereocomplex has a "polypseudorotaxane-type" structure. The presented self-assembly system demonstrates hierarchical control over the microstructure of the polymers, their supramolecular assembly, and the morphology of the resulting crystalline structure. The hierarchical control imposed by topological restriction of the macromolecular building blocks is anticipated to provide new directions of research in supramolecular chemistry. Practically, we emphasize that the reported synthetic strategy may pave the way for the development of a novel class of cyclic inclusion materials for molecular-separation, catalytic, and electronic and optoelectronic applications. Further investigations, including AFM imaging of the present individual stereocomplex, are currently under way.

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