DNA-Inspired Strand-Exchange for Switchable PMMA-Based Supramolecular Morphologies

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MATERIALS

L-ascorbic acid (reagent grade, Sigma Aldrich), copper(I) bromide (CuBr, Sigma Aldrich, 99.999%), copper(II) bromide (CuBr₂, Sigma Aldrich, 99.999%), magnesium turnings (Aldrich, > 99.5%), polyethylene glycol monomethyl ether (Sigma-Aldrich, average MW ~ 5,000), sodium azide (NaN₃, Sigma Aldrich, ≥ 99.5%), t-butyldimethylsilane (Alfa Aesar, > 98%), n-butyllithium solution (1.6 M in hexanes, Aldrich), ethyl α-bromoisobutyrate (Ebib, Sigma Aldrich, 98%), chloro(indenyl)bis(triphenylphosphine)ruthenium(II), dichloromethane adduct (Strem Chemicals, 98%), and aluminium oxide (neutral, Fisher Scientific) were used as received. Methyl methacrylate (MMA, TCI, > 99.8%) and 1,1-diphenylethylene (DPE, Alfa Aesar, 98%) were distilled under reduced pressure over calcium hydride (CaH₂, Sigma-Aldrich, ≥ 97%) before use. Tributylamine (Sigma Aldrich, ≥ 98.5%) was distilled and stored in sealed ampoules as 0.4 M solutions in dry toluene before use. Toluene and tetrahydrofuran (THF) were collected under Ar atmosphere from solvent purification system (PureSolv, Innovative Technology Inc.) for polymerization use. Other solvents including acetonitrile (MeCN, Fisher Scientific, 99.5%), diethyl ether (Et₂O, anhydrous, Sigma-Aldrich, ≥ 99%), dichloromethane (DCM, Fisher Scientific, ≥ 99.5%), toluene (Sigma-Aldrich, 99.5%), ethyl acetate (EtOAc, Sigma-Aldrich, 99.5%), n-hexane (Fisher Scientific, 55% as hexane), methanol (Fisher Scientific, ≥ 99.8%) and anhydrous methanol (Alfa Aesar, 99.9%) were used as received.

CHARACTERIZATION METHODS

¹H and ¹³C NMR spectroscopy measurements were conducted in CDCl₃ at 25 °C or 55 °C on a Varian spectrometer operating at 600 (or 500) and 125 MHz for ¹H and ¹³C, respectively. For PMMA, the triad tacticity was estimated by the integration of area under the C=O carbon resonance at 175–180 ppm in the ¹³C NMR spectra of the polymers. Small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) measurements were conducted using a custom constructed SAXS instrument in the X-ray diffraction facility in the Materials Research Laboratory (MRL) at University of California, Santa Barbara (UCSB). The instrument used a 50 micron microfocus, Cu target X-ray source with a parallel beam multilayer optics and monochromator (Genix from XENOCS SA, France), high efficiency scatterless hybrid slits collimator developed in house,¹ and Pilatus100k and Eiger 1M solid state detectors (Dectris, Switzerland). SAXS and WAXS data were collected at sample-to-detector distances of 1.7 m and 150 mm, respectively, and calibrated with a silver behenate standard. SAXS data were also acquired at beamline 1–5 at the Stanford Synchrotron Radiation Lightsource (SSRL). The beamline was configured with an X-ray wavelength of λ = 0.974 Å and focused to a spot size of 300 μm × 300 μm. 2D-scattering patterns were collected on a Rayonix 165 CCD detector. Sample-to-detector distances were 2.7 m and calibrated with a silver behenate standard. The 2D data were reduced by azimuthal averaging to give \( I(q) \), where \( I \) is intensity and \( q \) is the momentum transfer vector \( q = (4π/λ) \sin \theta \). For SAXS measurements, data reduction and model fitting were carried using the NIKA and IRENA software.
packages developed at Argonne National Laboratory. The number-average molecular weight ($M_\text{n}$) and weight-average molecular weight ($M_\text{w}$) of the product polymers were determined by GPC in 0.25 wt% triethylamine/chloroform using a Waters 2695 separation module with a Waters 2414 differential refractive index detector. The columns were calibrated against PMMA standards (Agilent Technologies; $M_p = 875–1677000$ Da; $M_w/M_n = 1.02–1.09$). TEM micrographs were acquired on an FEI Tecnai G2 Sphera Microscope with an accelerating voltage of 200 kV. Dynamic light scattering (DLS) measurements were performed using a BI-200SM multi-angle detector system (Brookhaven Instruments) equipped with a Cobolt Samba 500 mW continuous-wave diode pumped laser ($\lambda = 532$ nm). The applied laser intensity could be modulated by passing the laser through an optical filter (1, 10, 20, 50 or 100% transparency). The type of filter and detector pinhole size were chosen such that the average count rate during a measurement was 150 – 500 kcps. Measurements were performed at a fixed detector angle of 90°. Temperature control was provided by an externally connected circulating water bath ($\pm 0.5$ °C precision) set at 25 °C. Dilute polymer solutions (2 – 5 mg/mL, MeCN/H$_2$O 9 : 1 v/v) were filtered through a 0.45 μm Teflon syringe filter into the glass sample tube immediately before the measurement. Autocorrelation functions were collected and if required fitted to a cumulant model to obtain Z-average diameters and corresponding polydispersity indices (PDIs).

**GENERAL EXPERIMENTAL SECTION**

**POLYMER SYNTHESIS**

**Bromine end-functionalized syndiotactic poly(methyl methacrylate) (st-PMMA-Br) synthesis**

*st*-PMMA-Br was synthesized by anionic polymerization according to the previously published procedure with modifications: the initiator 1,1-diphenyl-n-hexyllithium (n-Hex(Ph)$_2$Li) was prepared in-situ by adding DPE (500 mM in THF, 2.6 mL), and n-butyllithium (1.6 M in hexane, 0.9 mL) to anhydrous THF (50 mL) in a Schlenk tube at room temperature under Ar. The initiator solution was stirred for 2 h before cooling down to -78 °C in a MeOH/dry ice bath. MMA was then added dropwise (5.3 mL in 5 min) to start polymerization. The reaction solution was kept at -78 °C for 2 h, and BrCCl$_3$ (2.7 M in THF, 18.4 mL) was added. The reaction was then allowed to warm up to room temperature overnight (~ 15 h) and then quenched with degassed anhydrous methanol (5 mL). The crude solution was diluted with toluene (50 mL), passed through a silica gel plug, and precipitated twice in cold MeOH (200 mL) to obtain *st*-OMMA-Br as a white powder, 4.8 g (91 %), *st*-PMMA5k-Br; GPC: $M_n = 5.2$ kDa, $D = 1.10$; $^1$H NMR (600 MHz, CDCl$_3$): $M_n = 5.3$ kDa, $\delta_{1H} 0.59–0.67$ (s, 3H, CH$_3$ n-hexyl chain end), 0.70–1.45 (m, CH$_3$- backbone, and CH$_3$ of n-hexyl di(phenyl) chain end), 1.70–2.40 (m, -CH$_2$- backbone, and d, 1H, -(Ph)$_2$CCH$_2$-), 2.64–2.80 (m, 1H, -(Ph)$_2$CCH$_2$- and 2H -CH$_2$-MMA-Br chain end), 3.30–3.80 (m, -COOC$_3$), 7.06–7.25 (m, 10H, n-hexyl di(phenyl) chain end); $^{13}$C NMR: $mm/rr$ (%) = 2/21/77. GPC data, $^1$H and $^{13}$C NMR, and FT-IR spectra are provided in Figures S1 – 4. *st*-20k was prepared via the same experimental procedure by changing monomer-to-initiator ratio [M/I ~ 200] without chain end modification; GPC: $M_n = 21.2$ kDa, $D = 1.10$; $^{13}$C NMR: $mm/rr$ (%) = 2/21/77.
Synthesis of st-PMMA-N$_3$ via azidation of st-PMMA-Br

st-PMMA-Br (2.0 g, $M_n = 5.2$ kDa, 0.38 mmol), NaN$_3$ (0.25 g, 3.8 mmol) and L-ascorbic acid (0.011 g, 0.060 mmol) were dissolved in 34 mL of CH$_3$CN/H$_2$O (9 : 1) in a round bottom flask, and the mixture was degassed by bubbling N$_2$ for 10 min. A standard catalyst solution of CuBr/CuBr$_2$/Bpy (0.1/0.067/0.33 M in CH$_3$CN/H$_2$O (9 : 1), 2.3 mL) was then added and the reaction solution was stirred at 40 °C for 24 h. The crude product solution was extracted with EtOAc (50 mL × 3), and the organic layers were collected, combined and then washed with HCl (1 M, 50 mL × 3) and H$_2$O (50 mL × 3). The solution was then concentrated (to ~50 mL), and passed through a short neutral alumina column before being dried in vacuo to afford st-PMMA-N$_3$ as a white powder (1.8 g, 90%). GPC: $M_n = 5.3$ kDa, $D = 1.10$. $^1$H NMR (600 MHz, CDCl$_3$): $M_n = 5.2$ kDa, $\delta_H$ 0.59–0.65 (s, 3H, CH$_3$ n-hexyl chain end), 0.70–1.45 (m, CH$_3$ - backbone, and CH$_3$ of n-hexyl di(phenyl) chain end), 1.70–2.40 (m, -CH$_2$- backbone, and d, 1H, -(Ph)$_2$CCH$_2$-), 2.64–2.80 (m, 1H, -(Ph)$_2$CCH$_2$-), 3.30–3.80 (m, -OCH$_3$), 7.06–7.25 (m, 10H, n-hexyl di(phenyl) chain end). GPC data, $^1$H NMR, and FT-IR spectra are provided in Figures S1–4.

Figure S1. GPC trace overlay of st-PMMA5k-Br and st-PMMA5k-N$_3$. 

\[ \text{st-PMMA5k-Br} \]
\[ M_n = 5200 \]
\[ D = 1.10 \]

\[ \text{st-PMMA5k-N$_3$} \]
\[ M_n = 5300 \]
\[ D = 1.10 \]
Figure S2. $^1$H NMR traces of st-PMMA5k-Br and st-PMMA5k-N$_3$, respectively.
**Figure S3.** Partial $^{13}$C NMR spectra of $i$-PMMA-5k and $s$-PMMA-5k illustrating the tacticity determination.

**Figure S4.** FT-IR traces of $s$-PMMA5k before and after azidation.

Alkyne end-functionalized poly(ethylene glycol) monomethyl ether (PEG-Alkyne) synthesis

PEG-Alkyne was synthesized according to previously published procedure:5 To a solution of PEG monomethyl ether ($M_n \sim 5000$ Da) (5.0 g, 1.0 mmol) in toluene (38 mL) was added crushed KOH (0.40 g, 7.1 mmol), and the reaction mixture was allowed to stir at 50 °C for 30 min under an Ar atmosphere. Propargyl bromide (4.5 g, 38 mmol) was added to the reaction mixture, and heating continued for 16 h. The hot reaction mixture was then passed through Celite. The Celite was washed with acetone, the combined organic layer was concentrated under reduced pressure, and the crude product was precipitated in Et$_2$O. The solid polymer was filtered, dried, and transferred to a Soxhlet thimble, where it was extracted with Et$_2$O to ensure removal of excess propargyl bromide. PEG-Alkyne was obtained as a white solid: yield 5 g (> 99%); GPC: $M_n = 10.7$ kDa, $D$ = 1.04 (relative to PMMA standards); $^1$H NMR (600 MHz, CDCl$_3$): $M_n = 5.9$ kDa, $\delta_{H} 4.20$ ($d$, O-CH$_2$-Alkyne), 3.80–3.45 ($m$, PEG CH$_2$), 3.37 ($s$, CH$_3$-O-PEG), 2.43 ($t$, acetylene proton). GPC data, $^1$H NMR, and FT-IR spectra are provided in Figures S5 – 7.
**Figure S5.** GPC trace overlay of PEG5k-OH before and PEG5k-Alkyne after the chain end modification.

**Figure S6.** $^1$H NMR spectra of PEG5k-OH and PEG5k-Alkyne before and after the chain end modification.
Synthesis of st-PMMA5k-b-PEG5k (1) via click chemistry

st-PMMA5k-N₃ (0.66 g, $M_{n \text{,NMR}} = 5200$, 0.13 mmol), PEG5k-Alkyne (0.50 g, $M_{n \text{,NMR}} = 5900$, 0.085 mmol), and CuBr (18 mg, 0.13 mmol) were added into a round bottom flask equipped with a 3-way stopcock in a glovebox. Degassed DMF (7.5 mL) and PMDETA (27 µL, 0.13 mmol) were subsequently added. The reaction mixture was stirred at rt. for 10 min and then at 65 °C for 24 h. The crude product was poured into H₂O (100 mL), and extracted with EtOAc (20 mL × 3). The organic extracts were combined, washed with HCl (1M, 50 mL × 3) and H₂O (50 mL × 3), and dried under reduced pressure to yield a yellowish powder as the crude product.

Automatic flash chromatography isolation of st-PMMA5k-b-PEG5k (1) was performed on a Biotage Isolera One unit coupled with a Biotage ESLD-A120 detector using Biotage KP-SIL SNAP/SNAP Ultra cartridge series (10 g), eluting with MeOH/DCM using the gradient profile in Table S1:

| % MeOH (Start) | % MeOH (End) | Column Volume (CV) |
|----------------|--------------|--------------------|
| 0              | 0            | 2                  |
| 0              | 10           | 12                 |
| 10             | 10           | 20                 |

The separated fractions (CV 12 – 30) containing the product polymer were combined and concentrated to give 1 as a white powder (0.57 g, 60 %). GPC: $M_n = 14.8$ kDa, $D = 1.05$ (relative to PMMA standard). $^1$H NMR (600 MHz, CDCl₃): 11.2 kDa. FT-IR, GPC and $^1$H NMR traces for PEG5k-b-st-PMMA5k (1) are provided in Figures S7–9.
Figure S7. FT-IR spectra of PEG5k-Alkyne, st-PMMA-5k-N₃, and st-PMMA-5k-b-PEG-5k (1), respectively.
Figure S8. Schematic of synthesis of \textit{st-}PMMA5k-b-PEG5k (1) via click chemistry and GPC traces of PEG5k-Alkyne, \textit{st-}PMMA-5k-N\textsubscript{3}, and \textit{st-}PMMA-5k-b-PEG-5k (1), respectively.

Figure S9. \textsuperscript{1}H NMR spectrum of \textit{st-}PMMA-5k-b-PEG-5k (1) showing integration of all key characteristic resonance peaks.
Isotactic poly(methyl methacrylate) (\textit{it}-PMMA) synthesis

\textit{it}-PMMA was synthesized by anionic polymerization according to our previous publications.\textsuperscript{6-7} The Grignard reagent, \textit{t}-C\textsubscript{4}H\textsubscript{9}MgBr, was prepared as follows: anhydrous Et\textsubscript{2}O (28 mL) and \textit{t}-butylbromide (14 g, 0.10 mol) were added consecutively into a dry addition funnel under N\textsubscript{2}. Separately, Mg turnings (3.7 g, 0.15 mol) were added to a dry round bottom flask under N\textsubscript{2} via a funnel with a flushing adapter, followed by the addition of anhydrous Et\textsubscript{2}O (60 mL). The \textit{t}-butylbromide solution was then added slowly at 25 °C over 1 h. The solution was stirred for an additional hour and then left to stand for 12 h. The Grignard reagent ([\textit{t}-C\textsubscript{4}H\textsubscript{9}MgBr]_{eff} = 210 mM determined via polymerization) was stored in a dry round-bottom flask equipped with a 3-way stopcock under Ar atmosphere at 0 °C before use.

The general procedure employed for the synthesis of \textit{it}-PMMA was as follows: the initiator solution (2.7 mL) was added to anhydrous toluene (8.5 mL) in a Schlenk tube at -78 °C under Ar. MMA was then added slowly (1.2 mL in 5 min) causing the mixture to turn orange. The polymerization solution was kept at -78 °C for 24 h, and then degassed methanol (1 mL) was added to the Schlenk flask to quench the reaction. The reaction solution was diluted with toluene (20 mL), washed with 1 M HCl (20 mL × 3) and distilled water (20 mL × 3), dried over MgSO\textsubscript{4}, filtered, and precipitated into hexane to afford \textit{it}-PMMA (\textit{it}-2.5k) as a white powder, 1.0 g (94 %); GPC: \(M_n = 2.7 \text{ kDa}, D = 1.16\); \textit{\textsuperscript{1}H} NMR (500 MHz, CDCl\textsubscript{3}): \(M_n = 2.2 \text{ kDa}, \delta_1\) 0.97–0.93 (s, 9H, (CH\textsubscript{3})\textsubscript{3} chain end), 0.95–1.40 (m, CH\textsubscript{3}- backbone), 1.40–2.25 (m, -CH\textsubscript{2}- backbone), 2.40–2.50 (br, 1H, chain end), 3.40–3.80 (m, -OCH\textsubscript{3}). \textit{\textsuperscript{13}C} NMR (125 MHz, CDCl\textsubscript{3}): \textit{mm}/\textit{mr}/\textit{rr} (\%) = 86/12/2.

The same reaction was repeated to afford PMMA with different \(M_n\) ranging from 2.2 – 44 kDa by varying the initiator to monomer ratio. Please refer to Table S2 for an overview of the polymerization results. A representative partial \textit{\textsuperscript{13}C} NMR spectrum of the \textit{it}-PMMA is provided in Figure S3 to show the tacticity determination (using \textit{it}-5k as an example).

| Sample | \(M_{n,NMR}\) | \(M_{n,GPC}\) | \(D_{GPC}\) | Tacticity |
|--------|--------------|--------------|-------------|-----------|
| \textit{isotactic (\textit{i})} | \(M_{n,NMR}\) | \(M_{n,GPC}\) | \(D_{GPC}\) | \textit{mm} | \textit{mr} | \textit{rr} |
| \textit{it}-2.5k | 2700 | 2200 | 1.16 | 86 | 12 | 2 |
| \textit{it}-5k | 5000 | 4600 | 1.21 | 92 | 5 | 3 |
| \textit{it}-20k | \footnotesize{\textit{a}} | 20700 | 1.13 | 93 | 4 | 3 |
| \textit{it}-40k | \footnotesize{\textit{a}} | 44000 | 1.30 | 97 | 2 | 1 |

* \(M_{n,NMR}\) cannot be accurately determined due to high molecular weight

Preparation of PMMA stereocomplex micelles via crystallization driven self-assembly
The general procedure employed for the preparation of PMMA stereocomplex micelles was adopted from a literature procedure with modification as follows: I (20 mg based on the st-PMMA segment) and it-PMMA (20 mg) precursors were separately dissolved in MeCN:H₂O (9:1) at concentrations of 10 mg/mL and combined to an it:st molar ratio of 1:2. The mixture was heated to reflux, cooled back to rt., and left to stand overnight. For WAXS analysis, the samples were dried under reduced pressure (0.05 mmHg) for 24 h before measurement. For SAXS analysis, the sample solutions were used as prepared. For DLS analysis, the sample solutions were diluted to 2 – 5 mg/mL. For TEM imaging, the sample solution were diluted to 0.5 – 2 mg/mL, before negative staining using a procedure adapted from literature: TEM grids were glow discharged (15 mA, 20 sec) and exposed to 3 µL of sample followed by two water droplets and two droplets of uranyl formate before drying overnight.

TEM images of stereocomplexed micelles, WAXS analysis, and SAXS profiles provided in Figures S10 – 14, 19 and 20. DLS autocorrelation functions and intensity-average hydrodynamic diameter distributions of stereocomplex micelles along with the controlled experiments are provided in Figures S15 – 18.

Figure S10. TEM images (a – d) for the stereocomplex micelles prepared from diblock copolymer I with it-PMMA with MWs of ~2.5, 5, 20 and 40 kDa, respectively (scale bar 200 nm) and e) the intensity average hydrodynamic diameter distribution of these micelles.
Figure S11. Additional TEM images (a – c, at various magnification) for the sphere stereocomplex micelles (prepared from 1 and it-2.5k), and d) dried state size distribution for the sphere micelle (particle count = 100). Scale bar = 200 nm.
Figure S12. Additional TEM images (a – c, at various magnification) for the sphere stereocomplex micelles (prepared from 1 and it-5k), and d) dried state diameter distribution for the sphere micelle (particle count = 100). Note: the worm length distribution is not determined due to a small amount of worm-like micelles present. Scale bar = 200 nm.
Figure S13. Additional TEM images (a – c, at different magnification) for the worm-like stereocomplex micelles (prepared from 1 and it-20k), and d) dried state length and diameter distributions for the worm-like micelle (particle count = 100). Scale bar = 200 nm.
Figure S14. Additional TEM images (a – c) for the worm-like stereocomplex micelles (prepared from I and it-40k), and d) dried state diameter distribution for the worm-like micelle (particle count = 100). Note: The length distribution of the worm-like micelles cannot be determined due to aggregation.
Figure S15. Dynamic light scattering (DLS) autocorrelation plots of the stereocomplex micelles from three separate acquisitions (using the worm-like micelle prepared form 1 and it-20k as example) to determine the average micelle size (see Figure S10c).

Figure S16. Dynamic light scattering (DLS) autocorrelation plot of the solution mixture of 1 and st-20k, showing no stereocomplex micelle formation.
Figure S17. Dynamic light scattering (DLS) autocorrelation plot of the solution mixture of 1 and α-PMMA (DP 200), showing no stereocomplex micelle formation.

Figure S18. Additional dynamic light scattering (DLS) autocorrelation plots of various it- and st-PMMA alone, indicating these polymers are all soluble in the stereocomplexation solvent (i.e., MeCN/H₂O 9:1) without their assembling counterparts.
Figure S19. WAXS and solution SAXS diffraction traces for sphere- and worm-like stereocomplex micelles prepared from 1 and it-2.5k, and 1 and it-20k, respectively. The experimental data was fitted with models for objects with spheroid and cylindrical geometry (solid lines).

Figure S20. Solution SAXS diffraction traces for sphere- and worm-like stereocomplex micelles prepared from 1 & it-5k, and 1 & it-40k, respectively. The experimental data was fitted with models for objects with spherical and cylindrical geometry (solid lines).
**Figure S21.** a) Proposed cylindrical model for the worm-like micelle prepared from 1 and it-20k (diameter and length determined by TEM), and b) the cross-sectional view of the micelle. c) The schematic showing the average length of the it-20k double helix calculated based on the Yashima’s model.  

**PMMA triple-helix strand displacement experiment**

To a solution of st-5k (2 mg/ml), it-20k (2 mg/ml) was added via syringe to reach an it:st molar ratio of 1:2. The solution was heated to reflux in a sealed vial, then allowed to cool down to r.t. slowly and left stand overnight. The precipitate was collected via centrifugation, dried under reduced pressure (0.05 mmHg) for 24 h to give a white powder as the initial stereocomplex (yield: 8 mg, 62%). A small fraction of the initial stereocomplex (1 mg) was taken for WAXS analysis before being redissolved in chloroform for GPC analysis. The initial stereocomplex sample was charged into a 4 ml vial, to which a solution of st-20k (2 mg/ml, ~2.3 ml) was added to adjust the it:st stoichiometry ratio to 1:1 (Note: the stereocomplex is insoluble in the stereocomplexing solvent at r.t.). The solution vial was carefully sealed and heated to reflux (until all polymers dissolved and the reaction solution became clear), slowly cooled down to r.t., and left to stand overnight. The precipitate i.e., the new stereocomplex was collected via centrifugation and dried under reduced pressure (0.05 mmHg) overnight (yield: 9 mg, 70%), before being characterized via WAXS and GPC analysis. Please refer to Figure S22 for schematic illustration of the strand displacement and the GPC results. WAXS diffraction traces of the stereocomplexes are provided in Figures S23 and S24.
**Figure S22.** Schematic illustration of PMMA strand displacement and GPC traces of the input stereocomplex (it-20k/st-5k), input long st-PMMA strand (st-20k), output short st-PMMA strand (st-5k), and output stereocomplex (it-20k/st-5k).
**Figure S23.** (a) Wide angle X-ray scattering (WAXS) $2\theta$ plot of the input stereocomplex ($itr-20k/st-5k$) showing characteristic PMMA stereocomplex diffraction peaks with d-spacing values of 2.1, 0.80, 0.63 and 0.56 nm. (b) The raw WAXS diffraction pattern.

**Figure S24.** (a) Wide angle X-ray scattering (WAXS) $2\theta$ plot of the input stereocomplex ($itr-20k/st-20k$) showing characteristic PMMA stereocomplex diffraction peaks with d-spacing values of 2.1, 0.79, 0.62 and 0.56 nm. (b) The raw WAXS diffraction pattern.
Switching PMMA stereocomplex micelle morphology via PMMA triple-helix strand displacement

For the first transition from micellar spheres to worms, to a solution of sphere PMMA stereocomplex micelle (10 mg/mL), *it*-PMMA solution (10 mg/ml) was added via syringe to reach an *it*:st molar ratio of 1:1. The solution was heated to reflux in a sealed vial, slowly cooled back to r.t., and left to stand overnight. For the reverse switching, st-PMMA (10 mg/mL) solution was added via syringe to re-balance the overall *it*:st molar ratio to 1:2. The solutions were heated to reflux in a vial, slowly cooled back to rt. and left to stand overnight. The precipitate – the ‘waste’ PMMA triple-helix was collected via centrifugation and dried under reduced pressure (0.05 mmHg) for 24 h to give a white powder. SAXS diffraction profiles and DLS autocorrelation plots of the PMMA stereocomplex micelle before and after morphology switching are provided in Figures S25 and S27, respectively. WAXS diffraction profile of the ‘waste’ PMMA triple-helix can be found in Figure S28.

Figure S25. Solution SAXS diffraction traces for spherical micelle prepared from 1 and *it*-2.5k, the sample after the first switch (sphere to worm-like morphology) through strand exchange with *it*-20k, and after the second switch (worm-like to sphere) through strand extraction using st-20k.
Figure S26. Schematic illustration of stereocomplex micelle morphology switching mechanisms: a) from sphere to worm-like morphology, and b) from worm-like structure back to spherical micelles through PMMA triple-helix strand exchange. For the sphere to worm-like micelle transition, 3 replaces 2, while for the reverse switching, 6 extracts 3 yielding a PMMA triple-helices that precipitate as ‘waste’.
Figure S27. Dynamic light scattering (DLS) autocorrelation plots of the stereocomplex micelles switching between sphere and worm-like morphologies through three forward and two reverse switching cycles.

Figure S28. WAXS traces of the precipitates collected after each reverse switching (i.e., 2 → 3, and 4 → 5, see Figure 6 main text) showing characteristic peaks of crystallized PMMA triple-helices at 2θ = 4, 11, 14 and 16°.
ADDITIONAL SYNTHESIS AND CHARACTERIZATION

Preparation of *atactic* PMMA (DP 200) via atom transfer radical polymerization. Ebib (18 µL, 0.13 mmol), MMA (5.3 mL, 50 mmol), and tributylamine (0.4 M in toluene) (0.31 mL, 0.13 mmol) were dissolved in toluene (20 mL). The mixture was degassed with Ar for 40 min. The catalyst, chloro(indenyl)bis(triphenylphosphine)ruthenium(II), dichloromethane adduct (9.7 mg, 0.012 mmol) was added and the reaction mixture was degassed for an additional 5–10 minutes, then left stirring at 80 °C for 16 h. The reaction vessel was cooled to room temperature, the solution diluted with toluene, filtered over a column of neutral alumina, and concentrated under reduced pressure. The crude polymer was dissolved in DCM and purified by precipitation in cold MeOH (3 times) to afford the desired pure polymer (monomer conversion = 58\% by \textsuperscript{1}H NMR, 3.0 g, 60 \%). GPC: $M_n = 23.9$ kDa, $D = 1.12$. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): $\delta$\textsuperscript{H} 0.70–1.45 (m, -CH\textsubscript{3} backbone and CH\textsubscript{3} polymer chain end), 1.70–2.20 (m, -CH\textsubscript{2} backbone), 3.30–3.80 (m, -COOC\textsubscript{H}\textsubscript{3}); 3.95–4.15 (b, -CH\textsubscript{2} chain end). \textsuperscript{13}C NMR: \textit{mm/mr/rr} (%) = 7/36/57. FT-IR, GPC and \textsuperscript{1}H NMR traces for the a-PMMA (DP 200) are provided in Figure S29 – 31.

![FT-IR spectra of a-PMMA (DP 200)](image)

**Figure S29.** FT-IR spectra of *a*-PMMA (DP 200).
Figure S30. Reaction scheme and GPC trace of $\alpha$-PMMA (DP 200).

Figure S31. $^1$H and partial $^{13}$C NMR (C=O group) spectra of $\alpha$-PMMA (DP 200).
FURTHER DISCUSSION

A general upward trend can be observed in the DLS plot across the switching cycles (Figure 6a, main text), which we attribute to the accumulation of PMMA homopolymer triple-helix stereocomplexes (waste products) that do not precipitate well from the solution.7,11 To test our hypothesis, small aliquots of the solution were taken, and analyzed via SAXS for the first forward and reverse switching cycle. The SAXS profile of the initial solution and the solution after the first forward switching closely resemble the scattering profiles of the previously established sphere and worm-like micelle solutions (Figure S25). However, the profile of the ‘reverse switched’ sample solution shows a non-zero slope at low \( q \) range (0.007-0.03 Å\(^{-1}\)), suggesting the presence of large objects attributable to the unremoved PMMA stereocomplex aggregates. Small aliquots of the reaction solution were collected and diluted (~0.2 mg/mL) for TEM for each switching step. A closer examination on the TEM images revealed the resolution of the stereocomplex micelles decreases across the switching cycles, and this is more apparent in the worm-like micelle samples. The resolution loss of the micelle structures is likely due to the ‘fouling’ of the unremoved PMMA triple-helix aggregates during TEM sample preparation.

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