Supporting Information

Facile Synthesis and Visualization of Janus Double-Brush Copolymers

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Experimental Section

Measurements. $^1$H NMR (500 MHz) spectra were acquired in CDCl$_3$ using a Varian INOVA-500 spectrometer at 25 °C. Tetramethylsilane (TMS) was used as an internal reference for $^1$H NMR spectroscopy. FT-IR spectra were obtained on a Bruker Tensor 27 system using attenuated total reflectance (ATR) sampling accessories. High resolution mass spectrum was obtained on a ThermoFinnigan MAT XL spectrometer.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) was measured on a Bruker Biflex IV (Billerica, MA) MALDI mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). Mass spectrum was acquired in the reflection mode with a mass range of 2000–12000 m/z, and the mass scale was calibrated externally using the peaks of peptide calibration standard II purchased from Bruker. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich; ≥99%) served as matrix and was dissolved in CHCl$_3$ at a concentration of 20 mg/mL. Sodium trifluoroacetate (NaTFA, Aldrich; ~98%) served as cationizing agent and was dissolved in MeOH/CHCl$_3$ (1/3, v/v) at a concentration of 10 mg/mL. The polymer was dissolved in CHCl$_3$ at a concentration of 10 mg/mL. The matrix solution, polymer solution, and NaTFA solution were mixed in the ratio of 10/1/1 (v/v/v). The sample preparation involved depositing 1 μL of the mixture on the steel plate, and allowing the spot to dry.

Gel permeation chromatography (GPC) was conducted using Viscotek GPC system equipped with a VE-3580 refractive index (RI) detector, a 270 dual detector system having a viscometer detector and a dual-angle (7 ° and 90 °) laser light scattering (LS) detector, a VE 1122 pump, and two mixed-bed organic columns (PAS-103M with exclusion limit of 70 kDa and PAS-105M with exclusion limit of 4 MDa). N,N’-dimethylformamide (HPLC grade) with 0.1 M
LiBr was used as solvent for polymers and eluent for GPC with a flow rate of 0.50 mL/min at 55 °C. Polymer solutions were prepared at a known concentration (ca. 3 mg/mL) and an injection volume of 100 μL was used. The instrument was calibrated with linear polystyrene standards. The refractive index increment (dn/dc) was measured for polymers and used to determine the molecular weights and polydispersities.

Atomic force micrography (AFM) were performed on an Asylum Research MFP-3D AFM instrument operating in tapping mode. The measurements were conducted in air at ambient conditions by using Si cantilevers with a spring constant of ca. 20-95 N/m and a resonance frequency of about 145-230 kHz. The tip purchased from Nanoscience Instruments with a radius of smaller than 10 nm was used. The AFM samples were prepared from dilute sample solutions (0.02-0.1 mg/mL in CH₂Cl₂) by either spin-coating or solvent casting on fresh cleaved mica.

Transmission electron microscopy (TEM) images were obtained by using a JEOL 2010 microscope. TEM samples were prepared by solvent casting on 300 mesh carbon-coated copper grids from dilute sample solutions (0.02 mg/mL in CH₂Cl₂). Some of the TEM samples were stained without thermal annealing. The other TEM samples were annealed under vacuum at 150 or 180 °C for 12 h before staining. Fresh 0.2 % solution of ruthenium tetroxide prepared by reaction between sodium periodate and hydrated ruthenium dioxide in water was used as the staining agent for TEM samples. The dried samples were treated with the volatile vapors of ruthenium tetroxide overnight prior to TEM measurements.

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q200 system with a RCS-90 cooling device in the temperature range of 25-200 °C with a heating rate of 10 °C/min under nitrogen. Thermogravimetric analysis (TGA) was
conducted on a TG209F1 instrument (NETZSCH, Inc.), and the total mass losses samples (~6 mg) were measured from 25 to 550 °C at a heating rate of 10 °C/min in a nitrogen flow of 50 mL/min.

Dynamic light scattering (DLS) measurements were performed using a Nano ZS90 Zetasizer (Malvern Instruments). A 4 mW 633 nm HeNe laser was used as the light source and all experiments were performed at a temperature of 25.0 °C at a measuring angle of 90° to the incident laser beam. The correlation decay functions were analyzed by cumulants method to obtain size distribution. All determinations were repeated five times.

**Materials.** 4-Dimethylaminopyridine (DMAP; 99+%), $N,N'$-dicyclohexyl-carbodiimide (DCC, 99%), and ethyl vinyl ether (99%) were purchased from Acros. L-Lactide (LA, 98%), 2,2'-azobisisobutyronitrile (AIBN, 98%), styrene (99+%), 1,2-dichloroethane (99.8%) and the 2\textsuperscript{nd} generation Grubbs’ catalyst were purchased from Aldrich. Diethyl ether (HPLC), dichloromethane (DCM; HPLC), and ethyl acetate (EtOAc, HPLC) were purchased from Fisher Chemical. LA was recrystallized in dry ethyl acetate four times prior to use. Styrene was purified by passing through a column packed with neutral alumina gel prior to use. Dry ethyl acetate, dichloromethane and 1,2-dichloroethane were distilled from CaH\textsubscript{2} (s)-1-Dodecyl-(s')-(α, α'\textsuperscript{-}dimethyl-α’’-acetic acid) trithiocarbonate (DDMAT), an exo-NB-based diol and 3\textsuperscript{rd} generation Grubbs catalyst were synthesized following literature methods.$^{2-4}$
Synthesis of NB-functionalized RAFT-ROP Dual Agent/Initiator (1). The synthesis was conducted following Scheme S1. The exo-NB-based diol (1.84g, 4.28 mmol), DDMAT (0.549 g, 1.43 mmol), and DMAP (0.017 g, 0.143 mmol) were mixed in 30 mL of dichloromethane under nitrogen atmosphere. N,N'-Dicyclohexylcarbodiimide (0.324 g, 1.57 mmol) was added. The reaction was allowed to react at room temperature for 24 h. The filtrate was evaporated, and the product (0.90 g) was obtained as yellow oil in 79% yield, after column separation by eluting with 50:50 (v/v) ethyl acetate/hexane over silica gel. \(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, δ): 6.10-6.14 (m, 2H, CH=CH of NB), 4.18-4.31 (m, 6H, 3 × CH\(_2\)OCO), 3.64-3.71 (m, 14H, all OCH\(_2\)CH\(_2\) and CH\(_2\)OH except CH\(_2\)OCO), 3.26 (t, 2H, CH\(_2\)S from DDMAT), 3.04 (m, 1H, CH from NB), 2.92 (s, 1H, CH from NB), 2.72 (s, 1H, OH and from NB-based diol), 2.24 (m, 1H, CH from NB), 1.94 (m, 1H, 0.5 × CH\(_2\) from NB), 1.52-1.69 (m, 8H, 2 × CH\(_3\), and SCH\(_2\)CH\(_2\) from DDMAT), 1.50-1.52 (d, 1H, 0.5 × CH\(_2\) from NB), 1.20-1.38 (m, 23H, 9 × CH\(_2\) from DDMAT; CH\(_3\) and 2 × 0.5 × CH\(_2\) from NB), 0.86-0.89 (m, 3H, CH\(_3\) from DDMAT). FT-IR (cm\(^{-1}\)): ν = 3700-3200 (strong), 3050-2800 (strong), 1730 (strong), 1463 (medium-strong),
1258 (medium-strong), 1125 (strong), 1058 (medium-strong), 945 (medium-strong), 867 (medium), 820 (medium), 720 (medium). HRMS (ESI, m/z): [M + Na]$^{+}$ calcd for $C_{38}H_{64}O_{10}S_{3}Na$, 799.3554; found, 799.35571.

**Synthesis of Diblock Macromonomer PSt$_{23}$-b-PLA$_{21}$ (2).** NB-functionalized RAFT-ROP dual agent/initiator 1 (0.500 g, 0.640 mmol), LA (3.23 g, 22.4 mmol), DMAP (0.313 g, 2.56 mmol), and AIBN (0.011 g, 0.064 mmol) were added into a 25 mL Schlenk flask, evacuated and refilled with nitrogen three times. Styrene (4.66 g, 44.8 mmol) and dry 1,2-dichloroethane were then added under nitrogen. The reaction mixture was degassed by at least six cycles of freeze-pump-thaw and then heated with an oil bath at 59 °C. At time intervals, liquots of reaction mixtures were withdrawn by using a dry syringe for $^1$H NMR determination. After 24 h of reaction, the polymerization mixture was cooled to room temperature. The conversion of St of 34% was determined based on the resonance intensities of a vinyl proton of the remaining monomer at 5.73 ppm. The conversion of LA of 71% was determined based on the comparison of the resonance intensities of protons from PLA at 5.12 to 5.40 ppm (the resonance intensities of styrenyl protons at 5.24 ppm was substracted) with the resonance intensities of LA monomer at 5.06- 5.12 ppm. The reaction mixture was precipitated in methanol to give 2.89 g of 2 as a slightly yellow solid in 66% isolated yield. $^1$H NMR (500 MHz, CDCl$_3$, 25 °C, δ): 6.34-7.40 (m, all aromatic protons), 6.10-6.20 (m, 2H, $\text{CH}=\text{CH}$ of NB), 5.18-5.32 (m, 46H, all CH of LA except the one at ω-terminal of PLA), 3.95-4.45 (m, 9H, 4 × $\text{CH}_2$OCO and $\text{CHOH}$ of ω-terminal of PLA), 3.41-3.83 (m, 12H, all $\text{OCH}_2\text{CH}_2$, except $\text{CH}_2$OCO), 3.20-3.33 (2H, $\text{CH}_2$S from DDMAT), 3.05 (m, 1H, $\text{CH}$ from NB), 2.94 (s, 1H, $\text{CH}$ from NB), 0.81-2.40 (br m, 10 × $\text{CH}_2$ and 3 × $\text{CH}_3$ from DDMAT, $\text{CH}$ and 2× $\text{CH}_2$ from NB, all $\text{CH}_3$ from PLA and aliphatic alkyl protons from PSt). FT-IR (cm$^{-1}$): ν = 3700-3685 (strong), 3050-2760 (strong), 1757 (strong),
1605 (strong), 1494 (medium-weak), 1459 (medium-strong), 1383 (medium-strong), 1250 (medium-strong), 1214 (medium-strong), 1178 (strong), 1094 (strong), 1049 (medium-strong), 996 (medium), 887 (weak), 813 (weak), 760 (medium), 711 (strong). DP_{n,NMR} (PSi) = 23, DP_{n,NMR} (PLA) = 21, M_{n,NMR} = 6.2 kDa, M_p^{Maldi-TOF} = 6319.83 Da, M_{n,GPC} = 8.6 kDa, PDI^{GPC} = 1.14.

**General Procedure for the Synthesis of Janus Double-Brush Copolymers (3).**

Macromonomer PSt_{23}-NB-PLA_{21} 2 (150 mg, 0.024 mmol) was added into a flame-dried Schlenk flask, and dissolved in fresh dry CH$_2$Cl$_2$ (1.3 mL) under nitrogen. Grubbs’ 3$^{rd}$ generation catalyst (0.121 mg, 0.136 µmol) was added as a solution in fresh dry CH$_2$Cl$_2$ (0.2 mL). The polymerization mixture was stirred at room temperature for 1 h, and then quenched by the addition of 0.3 mL of ethyl vinyl ether. As measured by GPC analysis of the reaction mixture, the conversion of 86% was determined for 2. The reaction mixture was precipitated in diethyl ether, redissolved in dichloromethane, and passed through a column packed with silica gel (~4.5 g; pore size ≈ 60 Å) using CH$_2$Cl$_2$ as eluent. The first portion of eluted solution (~18 mL, R$_f$ ~ 1.0) was concentrated under reduced pressure to yield 121 mg of DBC (3c; isolation yield: 94%, based on 86% conversion of 2). $^1$H NMR (500 MHz, CDCl$_3$, 25 °C, δ): 7.50-6.32 (aromatic protons), 5.00-5.38 (m, 48H, all CH of LA except the one at ω-terminal of PLA), 3.98-4.45 (m, 9H, 4 × CH$_2$OCO and CHOH of ω-terminal of PLA), 3.40-3.87 (m, 12H, all OCH$_2$CH$_2$, except CH$_2$OCO), 3.20-3.33 (2H, CH$_2$-S from DDMAT of 1), 2.94 (m, 1H, CH from PNB), 2.87 (s, 1H, CH from PNB), 0.78-2.42 (br m, 10 × CH$_2$ and 3 × CH$_3$ from DDMAT, CH and 2× CH$_2$ from PNB, all CH$_3$ from PLA and aliphatic alkyl protons from PSt). FT-IR (cm$^{-1}$): ν = 3700-3400 (strong), 3110-2760 (strong), 1948 (weak), 1868 (weak), 1752 (strong), 1601 (medium-weak), 1494 (medium), 1454 (medium-strong), 1383 (medium), 1360 (medium), 1267 (medium-strong),
1183 (strong), 1125 (medium-strong), 1089 (strong), 1054 (medium-strong), 911 (medium-weak), 871 (medium), 818 (weak), 756 (medium), 698 (strong).

References:


Figure S1. $^1$H NMR (500 MHz) spectra of: a) 1, b) 2, and c) 3c.
Figure S2. GPC curves of 3c before and after purification by passing through a short silica gel column.

Figure S3. DLS number-average a) and intensity-average b) size distribution profiles of 3a-c.
Figure S4. DSC curves of 2 and 3c.
Figure S5. Thermolytic profiles of 2 and 3c.
Figure S6. GPC curves of 3c before and after heating in DMSO at 180 ºC for 12 h.

Note: The essentially identical GPC curves suggested that 3c were chemically stable at annealing condition.
Figure S7. AFM images of 3c samples prepared by spin-coating a) and by solvent casting b) on mica.
Figure S8. TEM images of 3c samples annealed at 150 °C (a and b) and 180 °C (c and d).