Synthesis of Bipyridine-Centered Diblock Copolymers

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ABSTRACT: A series of bipyridine-centered diblock copolymers, bpy(A)(B), containing PMMA, PS, PCL, PLA, and PEG chains were synthesized via sequential, orthogonal strategies from unsymmetrical, difunctional bipyridine ligands. Specifically, the combination of atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP) generally produced bpy(PCL)(PMMA) (**16**) and bpy(PS)-(PCL) (**14**) samples with anticipated molecular weights and low polydispersities (PDIs = 1.1−1.2). ROP or ATRP was also used in conjunction with a polymer coupling strategy to synthesize bpy(PEG)(R) diblocks with a bipyridine binding site at the block junction where R = PCL (**12**), PLA (**13**), or PMMA (**21**). Polymers with low PDIs were again generated in all cases (PDI ∼ 1.2−1.3). The particular design explored in this study could ultimately lead to block copolymeric metal complexes that form ordered assemblies with metal ions at microdomain interfaces.

Introduction

Presently, there is great interest in block copolymers for their ability to self-assemble into nanoscale morphologies.[1−4] Significant advances have been made in recent years in generating new macromolecular compositions and architectures[5−9] and correlating these with aggregate microstructures;[10−12] inorganic−organic composites are also known.[13−18] Yet even the simplest of synthetic systems—those made from just a few different kinds of monomers that lead to copolymers with as many compositional domains (i.e., blocks)—still often pose significant challenges for synthesis and structural characterization.

Recently, we described a modular metal template approach to block copolymer synthesis.[19,20] An almost unprecedented diversity[21] of block copolymer architectures may be easily accessed by coupling different polymeric ligands with metal ions. In addition to serving as a template for synthesis, the resulting metal centers also introduce functionality into macromolecular materials.[22−24] Site-isolated chromophores and reactive centers may be inert[25−27] or labile,[20,28,29] leading to macromolecular assemblies that can function as nanoscale templates for mineralization[30] or can change their structure in response to environmental stimuli (e.g., temperature).[31] One approach to block copolymer synthesis involves chelation of two different kinds of homopolymeric macroligands to a metal center,[19,20] whereas another entails coordination of polymeric ligands that themselves are block copolymers.[32,33] Previously, we described the synthesis of triblock copolymer macroligands generated by sequential monomer addition to ligand initiators that were protected by metal chelation for cationic polymerization of 2-oxazolines.[28,29] Other triblock macroligands, BA-bpy-AB, have been prepared using alternative ring-opening polymerization (ROP)[34] and atom transfer radical polymerization (ATRP) mechanisms that do not require protection of the bipyridine donor.[35] Ligand-centered triblocks lead to metal-centered star-shaped polymers that, upon self-assembly, are predicted to position metals in the compositional domain to which the metal is directly attached, whereas diblock copolymers, A-bpy-B, with donors at the block junction may lead to assemblies with metals at the domain interfaces. First examples of the latter include ligand-centered diblocks, polystyrene-*b*-poly(ϵ-caprolactone)[32] and polystyrene-*b*-poly(methyl methacrylate).[33] Here, we demonstrate modularity in the synthesis of block copolymer macroligands by showing that diverse diblock subunits may be generated from a small set of unsymmetrical, difunctional bipyridine reagents with hydroxyl and halide functionalities. Combination of these macroligands with metal ions and exploration of metal position in functional nanoscale assemblies will serve as the subjects of future accounts.

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Experimental Section

Materials. All chemicals were obtained from Aldrich Chemical Co., Inc., and used as received unless otherwise indicated. Silica gel used for flash chromatography (particle size 0.040−0.063 mm) was obtained from Merck. Silica chromatography columns were deactivated with 10% Et_3N in hexanes and then were washed with hexanes prior to use where noted. THF was dried and purified by distillation over sodium/benzophenone ketyl. Dry *N*,*N*-dimethylformamide (DMF) and anisole were obtained from Aldrich in Sureseal bottles. Chloroform-*d* ($CDCl_3$) was passed through a plug of activated basic alumina (Brockmann I; flame-dried in vacuo) prior to use. Styrene and methyl methacrylate were dried over CaH_2 and purified by distillation and then stored in a refrigerator inside a drybox prior to use. 3,6-Dimethyl-1,4-dioxane-2,5-dione (DL-lactide) was recrystallized twice from ethyl acetate. ϵ-Caprolactone was dried over CaH_2 and distilled prior to use. CuBr was purified as described by Keller.[36] Poly(ethylene glycol) 2000 monomethyl ether was obtained from Fluka. The ligands 4,4′-bis-(chloromethyl)-2,2′-bipyridine,[37] 4,4′-bis(hydroxymethyl)-2,2′-bipyridine (**1**),[38] and 4-chloromethyl-4′-hydroxymethyl-2,2′-bipyridine (**2**)[32] and the macroligands[32] bpy(CH_2OH)(PS) (**10**), bpy(PS)(PCL) (**14**), bpy(CH_2Cl)(PCL) (**17**), and bpy(PCL)(PS) (**18**) were prepared as previously reported. For an explanation of macroligand nomenclature[39] and its relationship to synthetic sequence, see ref 39.

Methods. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a General Electric QE-300 spectrometer in $CDCl_3$. ^1H NMR and ^{13}C NMR spectra were referenced to the signal for residual protiochloroform at 7.260 and 77.0 ppm, respectively, and ^1H NMR coupling constants are re-

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ported in hertz. Elemental analyses were performed with a Perkin-Elmer series II 2400 CHN analyzer. Polymer molecular weights were determined by GPC in $CHCl_3$ (25 °C; flow rate 1.0 mL/min) using a Hewlett-Packard 1100 system equipped with a vacuum degasser, a diode array detector with a Polymer Labs 5μ "mixed C" guard column and two "mixed C" GPC columns, Wyatt Technology Corp. DAWN multiangle laser light scattering (MALLS) (5 mW polarized He−Ne laser, λ = 633 nm), and an Optilab refractive index detector and diode-array UV/vis detection along with accompanying Wyatt Technology Corp. Astra software. The d*n*/d*c* values for PMMA (0.059 mL/g, λ = 633 nm)[40] and PS (0.145 mL/g, 35 °C, λ = 633 nm)[41] in $CHCl_3$ were used to calculate MALLS molecular weights. The d*n*/d*c* value for bpy(PCL)(PMMA) (0.057 mL/g, λ = 633 nm in $CHCl_3$) was determined by a single injection method that assumed 100% mass recovery from the columns. Indicated reaction temperatures refer to oil bath settings.

Initiators. 4-Hydroxymethyl-4′-[(*tert*-butyldimethylsiloxy)methyl]-2,2′-bipyridine, bpy(CH_2OH)(CH_2OTBS) (3). The monoprotected diol was prepared according to a modified literature procedure.[42] A DMF solution (10 mL) of 4,4′-bis(hydroxymethyl)-2,2′-bipyridine, **1** (0.414 g, 1.92 mmol), was combined with NaH (41.8 mg, 1.74 mmol) and stirred for 1 h at 25 °C. After adding TBSCl (0.262 g, 1.74 mmol), the resulting solution was stirred at 25 °C for 18 h and then transferred to a separatory funnel containing EtOAc (200 mL) and a 10% aqueous K_2CO_3 solution (100 mL). The aqueous layer was extracted with additonal EtOAc (2 × 100 mL), and then the combined organic fractions were dried over Na_2SO_4. Filtration and purification on deactivated silica gel (EtOAc) provided the monoprotected diol **3** as a white crystalline solid: 0.270 g (48%). ^{1}H NMR δ: 0.13 (s, 6 H, Si(CH_3)$_2$), 0.97 (s, 9 H, SiC(CH_3)$_3$), 4.83 (m, 4 H, CH_2), 7.35 (d, J = 5.0, 1 H, bpy*H*), 7.39 (d, J = 5.0, 1 H, bpy*H*), 8.28 (s, 1 H, bpy*H*), 8.35 (s, 1 H, bpy*H*), 8.64 (d, J = 5.0, 2 H, bpy*H*). ^{13}C NMR δ: −5.4, 18.3, 25.8, 63.1, 63.6, 118.3, 118.6, 120.9, 121.1, 149.0, 149.1, 151.6, 152.0, 155.6, 155.8. Anal. Calcd for $C_{18}H_{26}N_2O_2Si$: C, 65.42; H, 7.93; N, 8.48. Found: C, 65.30; H, 8.05; N, 8.68.

4-[(*tert*-Butyldimethylsiloxy)methyl]-4′-(2-bromo-2-methylpropionoxymethyl)-2,2′-bipyridine, bpy(CH_2OTBS)($CH_2OCOC(CH_3)_2Br$) (4). A THF (10 mL) solution of the initiator, **3** (0.109 g, 0.33 mmol), was combined with Et_3N (0.14 mL, 0.99 mmol). After stirring at 25 °C for 15 min, the solution was cooled to 0 °C and 2-bromo-2-methylpropionyl bromide (80 μL, 0.66 mmol) was added. The resulting solution was stirred for 18 h as it slowly warmed to room temperature. The reaction mixture was diluted with CH_2Cl_2 (∼100 mL) and washed with 1% $NaHCO_3$ (3 × 20 mL) before drying over Na_2SO_4. Filtration and purification on deactivated silica gel (EtOAc) afforded **4** as a clear colorless oil: 0.129 g (79%). ^{1}H NMR δ: 0.14 (s, 6 H, Si(CH_3)$_2$), 0.97 (s, 9 H, SiC(CH_3)$_3$), 2.00 (s, 6 H, CH_3), 4.87 (s, 2 H, CH_2), 5.33 (s, 2 H, CH_2), 7.40 (t, J = 5.4, 1 H, bpy*H*), 7.49 (d, J = 4.2, 1 H, bpy*H*), 8.35 (s, 1 H, bpy*H*), 8.48 (s, 1 H, bpy*H*), 8.71 (t, J = 5.0, 2 H, bpy*H*). ^{13}C NMR δ: −5.4, 18.3, 25.8, 30.8, 55.2, 63.1, 65.8, 155.6, 156.3, 120.8, 121.7, 151.6, 151.3, 118.3, 119.5, 149.1, 149.5, 171.2. Anal. Calcd for $C_{22}H_{31}N_2BrO_3Si$: C, 55.11; H, 6.52; N, 5.84. Found: C, 55.32; H, 6.39; N, 6.07.

4-Hydroxymethyl-4′-(2-bromo-2-methylpropionoxymethyl)-2,2′-bipyridine, bpy(CH_2OH)($CH_2OCOC(CH_3)_2Br$) (5). A DMF (60 mL) solution of 4,4′-bis(hydroxymethyl)-2,2′-bipyridine, **1** (0.424 g, 1.96 mmol), was combined with Et_3N (0.596 g, 5.89 mmol). After stirring at room temperature for 30 min, 2-bromo-2-methylpropionyl bromide (0.451 g, 1.96 mmol) was added, and the resulting yellow solution was stirred for 12 h. The reaction mixture was diluted with CH_2Cl_2 (∼100 mL), and the resulting solution was washed with 1% $NaHCO_3$ (3 × 100 mL) before drying over Na_2SO_4. Filtration and purification on deactivated silica gel (EtOAc) afforded **5** as a pale yellow oil: 0.250 g (35%). ^{1}H NMR δ: 1.99 (s, 6 H, CH_3), 4.82 (d, J = 3.1, 2 H, CH_2OH), 5.30 (s, 2 H, CH_2OCO), 7.36 (t, J = 6.0, 2 H, bpy*H*), 8.36 (s, 1 H, bpy*H*), 8.38 (s, 1 H, bpy*H*), 8.64 (d, J = 5.0, 1 H, bpy*H*), 8.67 (d, J = 5.0, 1 H, bpy*H*). ^{13}C NMR δ: 30.8, 55.2, 63.6, 65.7, 118.6, 119.4, 121.4, 121.7, 145.6, 149.3, 149.5, 151.2, 155.6, 156.3, 171.3.

4-[(*tert*-Butyldimethylsiloxy)methyl]-4′-chloromethyl-2,2′-bipyridine, bpy(CH_2OTBS)(CH_2Cl) (6). Chlorination of **3** was effected by the method of Cram et al.[43] as follows. Triphenylphosphine (0.257 g, 0.98 mmol), *N*-chlorosuccinimide (0.153 g, 1.14 mmol), and THF (50 mL) were combined and stirred at 25 °C for 30 min before adding the monoprotected diol, **3** (0.270 g, 0.82 mmol). After stirring for 20 h, the reaction mixture was transferred to a separatory funnel containing EtOAc (200 mL) and H_2O (100 mL). The aqueous layer was extracted with additonal EtOAc (100 mL), and the combined organic layers were dried over Na_2SO_4. Concentration and purification on silica gel (EtOAc) afforded **6** as a white powder: 0.256 g (90%). ^{1}H NMR δ: 0.14 (s, 6 H, Si(CH_3)$_2$), 0.97 (s, 9 H, SiC(CH_3)$_3$), 4.63 (s, 2 H, CH_2Cl), 4.84 (s, 2 H, CH_2OTBS), 7.36 (d, J = 5.0, 1 H, bpy*H*), 7.40 (d, J = 4.6, 1 H, bpy*H*), 8.30 (s, 1 H, bpy*H*), 8.42 (s, 1 H, bpy*H*), 8.65 (d, J = 5.0, 1 H, bpy*H*), 8.68 (d, J = 5.0, 1 H, bpy*H*). ^{13}C NMR δ: −5.4, 18.4, 25.9, 44.0, 63.7, 118.7, 120.8, 121.4, 123.3, 147.3, 148.3, 149.7, 153.3, 154.3, 155.3. Anal. Calcd for $C_{18}H_{25}N_2ClOSi$: C, 61.96; H, 7.22; N, 8.03. Found: C, 61.61; H, 7.40; N, 8.35.

Macroligands. Bpy(PMMA)(CH_2OH) (8). *Method A*. An anisole solution (10 mL) of CuBr (38.5 mg, 0.268 mmol), HMTETA (65.3 mg, 0.283 mmol), and MMA (2.758 g, 27.55 mmol) was stirred until the copper salt had dissolved (∼2 h). After adding the initiator **4** (0.105 g, 0.174 mmol) and stirring for 5 min, the reaction mixture was delivered to a Kontes tube, sealed under nitrogen, and stirred at 70 °C for 40 min. The reaction was quenched by cooling and removing residual monomer under vacuum. The resulting crude polymer was dissolved in THF, run through a plug of neutral alumina, and precipitated by dropwise addition of a concentrated CH_2Cl_2 solution to stirring hexanes. Reaction of bpy(CH_2OTBS)(PMMA), **7**, thus produced, with TBAF in THF (an excess of a 1.0 M solution) for 30 min, followed by aqueous workup and precipitation (THF/MeOH) afforded bpy(PMMA)(CH_2OH), **8A**, as a white powder: 0.860 g (30%).[44] M_n = 15 160, M_w = 16 760, PDI = 1.11. ^{1}H NMR δ: 0.76−2.23 (complex m, CH_3, CH_2), 3.60 (s, PMMA OCH_3), 5.07 (s, bpyCH_2, 2 H), 5.32 (s, bpyCH_2, 2 H). *Method B*. An anisole solution (10 mL) of CuBr (25.2 mg, 0.18 mmol), HMTETA (44.0 mg, 0.18 mmol), and MMA (1.899 g, 19.0 mmol) was stirred for 1 h. The resulting solution was transferred to a reaction vessel containing **5** (69.0 mg, 0.19 mmol). The reaction vessel was sealed under nitrogen with a Teflon cap and stirred at 80 °C for 11 min until the reaction was quenched by diluting with cold (0 °C) THF and stirring over neutral alumina. Removal of the alumina via filtration, followed by concentration and precipitation (THF/MeOH; THF/1:3 saturated aqueous NH_4Cl:MeOH; THF/MeOH), afforded bpy(CH_2OH)(PMMA), **8B**, as a white powder: 0.570 g (29%).[45] GPC: M_n = 10 440, M_w = 12 570, PDI = 1.20. ^{1}H NMR δ: 0.73−2.17 (complex m, CH_3, CH_2), 3.60 (s, PMMA OCH_3), 4.87 (s, bpyCH_2), 5.18 (s, bpyCH_2), 7.36−8.76 (complex m, bpy*H*).

Bpy(PS)(CH_2OH) (10). *Method A*. The ATRP of styrene from bpy(CH_2Cl)(CH_2OH), **2**, to produce bpy(CH_2OH)(PS), **10A**, was previously reported.[32] *Method B*. Bipyridine-centered polystyrene samples bpy(PS)(CH_2OH), **10B**, were prepared from bpy(CH_2OTBS)(CH_2Cl), **6**, by a similar procedure with the following exceptions. After polymerization, the purified intermediate, bpy(CH_2OTBS)(PS), **9**, was reacted with TBAF in THF for 30 min as above for **8** (prepared by method A) to provide **10** as a white solid: 0.427 g (79%). GPC: M_n = 25 360, M_w = 28 100, PDI = 1.11. ^{1}H NMR was consistent with that reported for **10**.[32]

Bpy(PEG)(CH_2OH) (11). A THF solution (15 mL) of poly(ethylene glycol) 2000 monomethyl ether (0.572 g, 0.32 mmol) was combined with NaH (10.9 mg, 0.45 mmol). A THF solution (10 mL) of **6** (0.125 g, 0.35 mmol) was added, and the mixture was refluxed for 19 h. After allowing the solution to cool to room temperature, TBAF in THF (0.8 mL of a 1.0 M solution) was added, and the resulting solution was stirred at 25 °C for 18 h. The reaction mixture was adjusted to pH ∼8 with saturated $NaHCO_3$ and then concentrated to dryness. The crude product was dissolved in CH_2Cl_2 and filtered to remove salts. Purification by precipitation (CH_2Cl_2/hexanes) and flash chromatography on silica gel (acetone) afforded **11** as a white

solid: 0.427 g (67%). M_n(NMR) = 1740, PDI = 1.15.[45] ^{1}H NMR δ: 3.38 (s, PEG OCH_3), 3.64 (br s, PEG OCH_2), 4.68 (s, bpyCH_2), 4.82 (d, J = 4.2, bpyCH_2), 7.38 (d, J = 4.2, bpy$H$), 8.39 (s, bpy$H$), 8.44 (s, bpy$H$), 8.68 (m, bpy$H$).

Bpy(PEG)(PCL) (12). The macroinitiator, **11** (0.100 g, 51 μmol), was dissolved in THF (10 mL) and then cooled to −78 °C. Triethylaluminum (32 μL, 61 μmol, 1.9 M solution in toluene) was added, and the resulting solution was allowed to stir for 2 h as it slowly warmed to 25 °C. After adding ϵ-caprolactone (1.13 mL, 10.2 mmol), the solution was stirred at room temperature for 48 h until the polymerization was quenched with the addition of a 0.02 M HCl solution (3.0 mL). Purification by precipitation (THF/MeOH) provided **12** as a white powder: 1.22 g (97%). GPC (MALLS):[46] M_n = 24 350, M_w = 31 510, PDI = 1.29; M_n(NMR) = 26 140. ^{1}H NMR δ: 1.25−1.72 (complex m, PCL CH_2), 2.31 (t, J = 7.3, PCL COCH_2,), 3.38 (s, PEG OCH_3), 3.64 (s, PEG OCH_2), 4.06 (t, J = 6.6, PCL OCH_2).

Bpy(PEG)(PLA) (13). The bpy(PEG)(CH_2OH) macroligand **11** (50.0 mg, 0.025 mmol) was dried with three toluene azeotropic distillations and then dissolved in THF (5 mL). After cooling the solution to −78 °C, triethylaluminum (15 μL, 0.028 mmol, 1.9 M solution in toluene) was added, and the solution was allowed to stir for 13 h as it slowly warmed to 25 °C. Lactide monomer (0.733 g, 5.09 mmol) was added, and the solution was stirred at 70 °C for 4 days until the polymerization was quenched with 0.02 M aqueous HCl (1.5 mL). Purification by precipitation (THF/hexanes) provided **13** as a white solid: 0.657 g (83%). GPC (MALLS):[47] M_n = 29 340, M_w = 34 490, PDI = 1.18; M_n(NMR) = 28 150. ^{1}H NMR δ: 1.48−1.81 (m, PLA CH_2), 3.38 (s, PEG OCH_3), 3.65 (s, PEG OCH_2), 4.99−5.30 (m, bpyCH_2, PLA CH).

Bpy(CH_2OCOC(CH_3)$_2$Br)(PCL) (19). The bromoester end-functionalized poly(ϵ-caprolactone) was synthesized according to the procedure for bpy(CH_2Cl)(PCL), **17**.[32] Reagent loadings: **5**, 27.0 mg (74 μmol); ϵ-caprolactone, 1.69 g (14.8 mmol); triethylaluminum, 47 μL (88 μmol, 1.9 M solution in toluene); THF, 10 mL. The product **19** was purified via precipitation (THF/MeOH) and was obtained as a white solid: 1.52 g (89%). GPC (MALLS): M_n = 37 510, M_w = 42 680, PDI = 1.14. ^{1}H NMR δ: 1.25−1.48 (m, PCL COCH_2CH_2CH_2CH_2CH$_2$O), 1.55−1.75 (m, PCL COCH_2CH_2CH$_2$CH_2CH$_2$O), 2.00 (s, CH_3), 2.30 (t, J = 7.3, PCL COCH_2), 4.06 (t, J = 6.5, PCL OCH_2), 5.20−5.33 (m, bpyCH_2), 7.96−8.73 (m, bpy$H$).

Bpy(PCL)(PMMA) (16). An anisole (5 mL) solution of CuBr (1.4 mg, 9.9 μmol), HMTETA (2.3 mg, 9.9 μmol), and MMA (1.025 g, 10.2 mmol) was stirred in a drybox for 1 h. After adding the bromoester end-functionalized PCL **19** (0.370 g, 9.9 μmol) and stirring for 5 min, the reaction mixture was transferred to a Teflon-sealed reaction vessel and stirred at 80 °C for 7 h. The viscous solution was diluted with THF and stirred over alumina. Filtration and purification via precipitation (THF/MeOH) provided **16** as a white solid: 0.570 g (41%).[44] GPC (MALLS): M_n = 75 620, M_w = 86 530, PDI = 1.14; M_n(NMR) = 71 600. ^{1}H NMR δ: 0.78−2.01 (complex m, PMMA CH_3, CH_2; PCL CH_2), 2.30 (t, J = 6.9, PCL COCH_2), 3.60 (s, PMMA OCH_3), 4.06 (t, J = 6.2, PCL OCH_2), 5.30 (s, bpyCH_2).

Bpy(PEG)(CH_2OCOC(CH_3)$_2$Br) (20). A CH_2Cl_2 (15 mL) solution of bpy(PEG)(CH_2OH) (0.427 g, 0.22 mmol), **11**, was combined with Et_3N (0.176 g, 1.74 mmol). After stirring at room temperature for 30 min and then cooling to 0 °C, 2-bromo-2-methylpropionyl bromide (0.200 g, 0.87 mmol) was added, and the resulting solution was stirred for 18 h as it slowly warmed to 25 °C. Purification on deactivated silica gel (acetone) afforded the bromoester functionalized PEG **20** as a white solid: 0.405 g (88%). ^{1}H NMR δ: 1.94 (s, CH_3), 3.38 (s, PEG OCH_3), 3.64 (br s, PEG OCH_2).

Bpy(PEG)(PMMA) (21). An anisole (8 mL) solution of CuBr (14.1 mg, 0.098 mmol), HMTETA (23.0 mg, 0.100 mmol), and MMA (2.357 g, 23.5 mmol) was stirred in a drybox for 30 min. The poly(ethylene glycol) macroinitiator **20** (0.200 g, 0.095 mmol) was added, and then the reaction mixture was sealed in a Kontes tube under nitrogen and stirred at 80 °C for 1 h. The reaction was quenched by diluting with THF and stirring over neutral alumina. Filtration and concentration in vacuo, followed by precipitation (THF/MeOH), afforded the PEG−PMMA diblock, **21**, as a white solid: 0.792 g (38%).[44] GPC:[48] M_n = 35 630, M_w = 42 520, PDI = 1.19; M_n(NMR) = 32 280. ^{1}H NMR δ: 0.56−2.15 (complex m, PMMA CH_3, CH_2), 3.60 (s, PMMA OCH_3), 3.64 (s, PEG OCH_2).

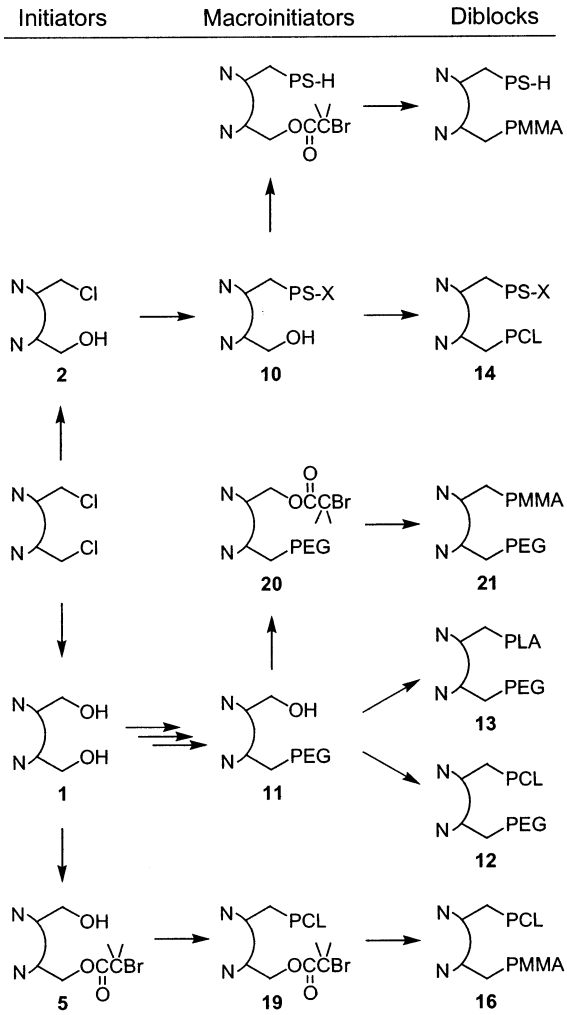
Results and Discussion

We previously described the synthesis of a bipyridine-centered polystyrene-*b*-poly(ϵ-caprolactone) diblock copolymer via atom transfer radical polymerization of styrene, followed by sequential aluminum-mediated polymerization of ϵ-caprolactone from the unsymmetrical, difunctional ligand, 4-chloromethyl-4′-hydroxymethyl-2,2′-bipyridine, **2**.[32] Because the two polymerization mechanisms were compatible with both initiating sites (i.e., CH_2OH and CH_2Cl) and catalyst systems (i.e., CuBr/HMTETA and Et_3Al), no chain modifications were necessary between growth of the first and second polymer blocks. In this study, the concept of sequential polymerization from orthogonal initiator sites[49−52] is extended to the synthesis of other bpy-centered diblocks. First, unsymmetrical difunctional bipyridine initiators were prepared using monofunctionalization strategies, similar to those employed in the synthesis of **2**. Next, one site (i.e., an initiator substituted at the 4-position) was utilized for the synthesis of block A, before growing block B from the other initiating site (i.e., at the 4′-position of the bipyridine). Thus, diblock copolymers with combinations of PMMA, PS, PCL, PEG, and PLA chains have been prepared, all with a bipyridine functional group at the block junction. A flowchart illustrating how bpy initiators, macroinitiators, and diblock products are interconnected appears in Scheme 1. Representative molecular weight data for macroinitiators and bpy-centered diblock copolymers prepared in this study are collected in Table 1.

PMMA samples with narrow molecular weight distributions have been prepared using α-bromoester initiators in controlled ATRP reactions.[5,6,19,27,53] The synthesis of an unsymmetrical initiator with this α-bromoester group is illustrated in Scheme 2. First, 4,4′-bis(hydroxymethyl)-2,2′-bipyridine (**1**) was protected at one site to provide 4-hydroxymethyl-4′-[(*tert*-butyldimethylsiloxy)methyl]-2,2′-bipyridine, **3**, by reaction with just less than 1 equiv of sodium hydride (NaH) followed by trapping of the anion with chloro-*tert*-butyldimethylsilane (TBSCl) (or chloro-*tert*-butyldiphenylsilane, DPSCl).[54] Although a near statistical distribution of unreacted, half-protected, and fully protected diol was obtained when equal equivalents of base and **1** were used, the use of an excess of **1** decreased the amount of the fully protected ligand. The desired product, **3**, was isolated by flash chromatography on silica gel, and any unreacted diol and difunctional byproduct were recovered for use in future studies. The free hydroxymethyl functionality of **3** was then converted to the α-bromoester moiety with 2-bromo-2-methylpropionyl bromide and triethylamine in THF to provide the initiator **4**.

Subsequent polymerization of MMA via copper-catalyzed ATRP from ligand **4** produced bpy-functionalized PMMA macroligands, **7**, with a protected hydroxyl group at one end of the polymer chain (Scheme 3). To remove the silyl group from this PMMA polymer intermediate, samples were reacted with tetrabutylammonium fluoride (TBAF) in THF. Reaction times greater than 1 h promoted undesired reaction between TBAF and the PMMA backbone, as indicated by the

Scheme 1. Schematic Representation of the Relationship between Initiators, Macroinitiators, and Bpy-Centered Diblocks



appearance of a high molecular weight shoulder in the GPC trace (MALLS) and an increase in polymer PDI. However, when a shorter reaction time of 30−60 min was employed, deprotection was evident by ^{1}H NMR, and there was little change in the molecular weight data for the product, bpy(PMMA)(CH_2OH), **8A** (Table 1).

Because initiators with primary alcohols are compatible with copper-catalyzed ATRP reaction conditions,[32,55,56] we tested whether methyl methacrylate might also be polymerized directly from the bromoester ligand, **5**. This ligand was conveniently prepared in one step from **1** by reaction with 1 equiv of 2-bromo-2-methylpropionyl bromide (Scheme 2). While this transformation provides a mixture of **1**, **5**, and the bis(α-bromoester) ligand, careful selection of solvent biased the reaction toward the synthesis of **5**. When run in THF, even with less than 1 equiv of the butyryl bromide, virtually all product was a mixture of the symmetric bis(α-bromoester) and unreacted diol. Increased solubility of the 4-bromoester-4′-hydroxymethyl-bpy in THF relative to **1** (and thus, greater likelihood toward reaction) may explain this result. When DMF was employed as the solvent, the solubility of diol increased, and a mixture of **1**, **5**, and bis(α-bromoester) was generated. The targeted ligand **5** was separated from the two byproducts by flash chromatography on deactivated silica gel. The resulting unsymmetrical, difunctional ligand was subsequently utilized as an ATRP initiator

Table 1. Molecular Weight Data[a] for Representative Bpy-Functionalized Macroligands

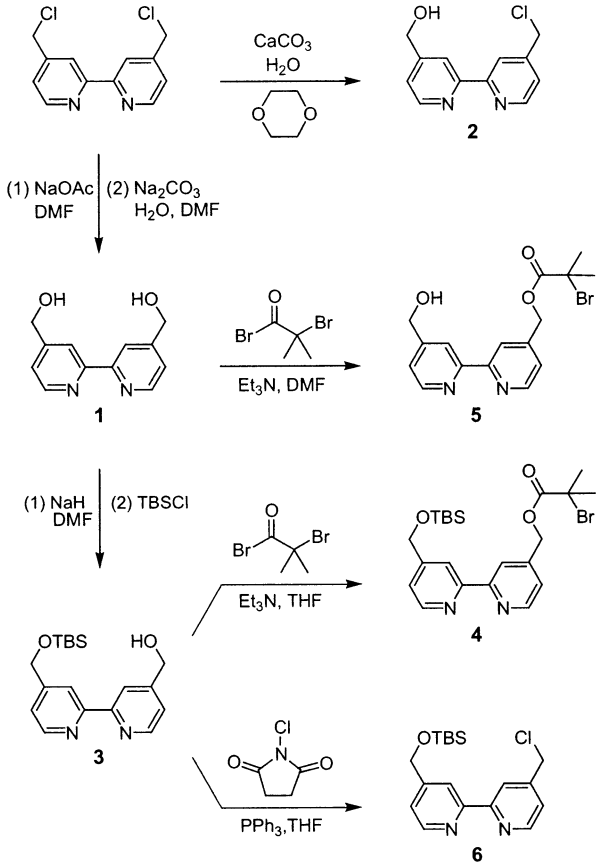
compd	polymer	calcd M_n (kDa)	M_n (kDa)[a]	M_w/M_n
7[b−d]	bpy(PMMA)(CH_2OTBS)	16.3	16.6	1.08
8A	bpy(PMMA)(CH_2OH)	16.2	15.2	1.11
8B[e,c]	bpy(CH_2OH)(PMMA)	10.4	10.4	1.20
15[f,c]	bpy(PMMA)(PCL)	72.3	30.2	1.38
9[g]	bpy(PS)(CH_2OTBS)	16.0	25.4	1.11
10A	bpy(PS)(CH_2OH)	25.3	26.8	1.07
10B[h,c]	bpy(CH_2OH)(PS)	5.3[i]	6.0	1.23
14[j]	bpy(PS)(PCL)	63.0	57.3	1.13
11	bpy(PEG)(CH_2OH)		1.7	1.15[k]
12[l]	bpy(PEG)(PCL)	24.6	24.4[m]	1.29
13[n]	bpy(PEG)(PLA)	30.7	29.3[o]	1.18
21[p]	bpy(PEG)(PMMA)	26.8	35.6	1.19
17[q]	bpy(CH_2Cl)(PCL)	44.8	5.5	1.19
18[r]	bpy(PCL)(PS)	20.8	161.4	1.39
19[s]	bpy($CH_2OCOC(CH_3)_2Br$)(PCL)	23.2	37.5	1.14
16[t,c]	bpy(PCL)(PMMA)	140.7	75.6	1.14

[a] Molecular weights were determined by GPC with MALLS/RI detection unless otherwise indicated. [b] Kinetics data for bpyPMMA$_2$[22] used to estimate reaction time; calcd MW based on ∼50% conversion at ∼50% initiator efficiency. [c] Reaction stopped prior to completion. [d] Method A. MMA/**4** = 160; 70 °C, 40 min. [e] Method B. MMA/**5** = 100; 80 °C, 11 min. [f] CL/**8A**= 500; 25 °C, 3 days. [g] Method B. styrene/**6** =150; 110 °C, 18 h. [h] Method A. styrene/**2** = 200; 110 °C, 4.5 h. [i] Kinetics data for bpyPS$_2$ used to estimate reaction time; calcd based on ∼30% conversion. [j] CL/**10A** = 500; 25 °C, 10 days.[32] [k] Molecular weight data (M_n) obtained by ^{1}H NMR. Molecular weight data for the commercially available MeO−PEG−OH starting material (vs PEG standards): M_n = 1770, M_w = 2030, PDI = 1.15. [l] CL/**11** = 200; 25 °C, 2 days. [m] Molecular weight data estimated using the d*n*/d*c* value for PCL; M_n(NMR) = 26 144. [n] DL-Lactide/**11** = 200; 70 °C, 4 days. [o] Molecular weight data estimated using the d*n*/d*c* value for PLA. [p] MMA/**20** = 250; 80 °C, 1 h. [q] CL/**2** = 200; 25 °C, 2 days.[32] [r] Styrene/**17** = 200; 25 °C, 18 h.[32] [s] CL/**5** = 200; 25 °C, 2 days. [t] MMA/**19** = 1000; 80 °C, 7 h.

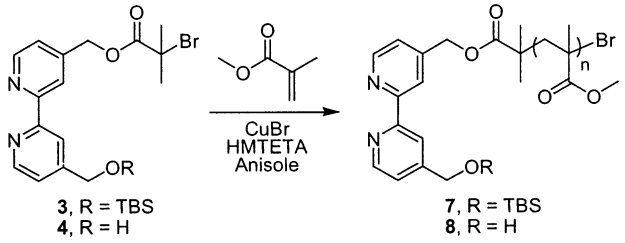
for the polymerization of MMA (Scheme 3) and directly produced hydroxymethyl-bpy end-functionalized polymers, bpy(CH_2OH)(PMMA), **8B**, likewise with narrow polydispersities (Table 1) and anticipated weights,[57] based on previous findings for bpyPMMA$_n$ reactions.[22] This preferred method not only takes advantage of a more effective synthesis of the initiator **5** relative to **4**, it eliminates the final deprotection step with TBAF.

As for the preparation of functionalized PMMA homopolymers, two methods were screened for the synthesis of bpy end-functionalized polystyrene macroinitiators (Scheme 4). One involved a protected alcohol initiator **6** and the other employed a bpy ligand with a free alcohol substituent, **2**. Both unsymmetrical bipyridine ligand initiators, **2** and **6**, have chloromethyl substituents, which are functional groups that have previously been utilized in the construction of PS chains with narrow polydispersities by ATRP.[5,6,25] The initiator **6** was synthesized through transformation of the monoprotected ligand, **3** (Scheme 2). Specifically, the free hydroxymethyl group was converted to a picolyl chloride functionality with *N*-chlorosuccinimide and triphenylphosphine in THF. This chloride ligand effectively initiated the polymerization of styrene to produce bpy(CH_2OTBS)(PS) intermediates, **9** (Scheme 4). The resulting PS chains exhibited low PDIs. Unlike with PMMA, removal of the silyl protecting group from PS products with TBAF to generate the desired PS macroinitiators, bpy(PS)(CH_2OH) (**10A**), did not significantly alter the molecular weight, even with long (>12 h) reaction times (Table 1). Deprotection was again moni-

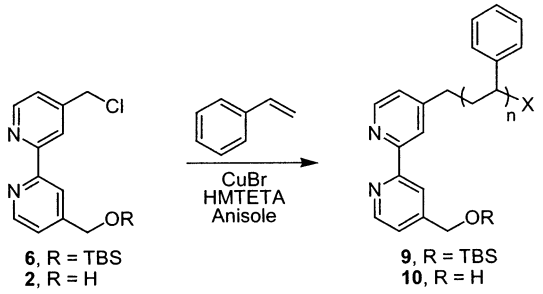
Scheme 2. Synthesis of Unsymmetrical, Difunctional Bipyridine Initiators, 1−6



Scheme 3. Synthesis of Hydroxymethyl-Bpy End-Functionalized Poly(methyl methacrylate), 8



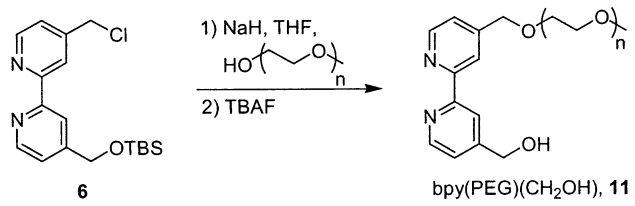
Scheme 4. Synthesis of Hydroxymethyl-Bpy End-Functionalized Polystyrene, 10



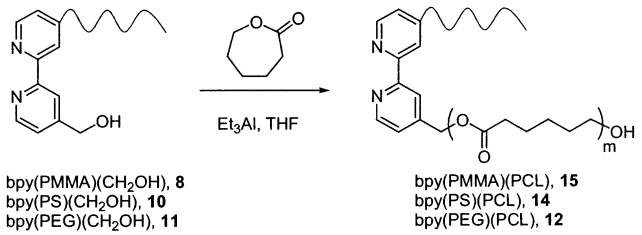
tored with ^{1}H NMR and typically proceeded to completion in less than 5 h.

The second route to hydroxymethyl bpy end-functionalized polystyrenes employed the chloromethyl-substituted initiator, **2**. Because the hydroxyl group is compatible with the ATRP reaction conditions (CuBr/HMTETA in anisole), it proved more efficient to prepare hydroxyl-end functionalized polystyrenes, **10**, in this manner (Scheme 4; Table 1, **10B**).[32] Again, reactions

Scheme 5. Synthesis of a Hydroxymethyl-Bpy End-Functionalized PEG Macroligand, Bpy(PEG)(CH$_2$OH), 11



Scheme 6. Synthesis of Poly(ϵ-caprolactone)-Containing Diblocks from Alcohol Macroinitiators, Bpy(CH$_2$OH)(PMMA) (8), Bpy(CH$_2$OH)(PS) (10), and Bpy(PEG)(CH$_2$OH) (11)



showed good control and molecular weights close to anticipated values,[57] based on reaction stoichiometry and previous findings with related bpy chloride initiators.[25,26] Even though the preparation of PS samples from **6** was less resourceful, nonetheless, bpy(OTBS)(Cl) was valuable for the synthesis of PEG macroligands.

Poly(ethylene glycol) was introduced by reaction of MeO−PEG−OH with NaH, followed by addition to **6** to produce bpy(CH$_2$OTBS)(PEG). (If the hydroxyl group of **2** were not protected, it too would be deprotonated by NaH and could react with chloride sites to generate ether linkages.) After coupling, bpy(CH$_2$OTBS)(PEG) was deprotected with either TBAF or dilute HCl to give the hydroxyl end-functionalized polymer, bpy(PEG)(CH$_2$OH), **11** (Scheme 5).[58] As expected, molecular weight data for the bpy-tagged product were comparable to the linear MeO−PEG−OH starting material (Table 1).

Because biocompatible polymers are of interest to us, block copolymers with poly(ϵ-caprolactone) (PCL) and poly(lactic acid) (PLA) were also targeted. Bipyridine binding sites have previously been incorporated into these biodegradable polyesters via the controlled ring-opening polymerization of ϵ-caprolactone and DL-lactide cyclic esters from primary alcohols with either tin[34] or aluminum[32] catalysts.[59] To explore the scope of this methodology, the available alcohol functionalities in bpy(PEG)(CH$_2$OH), **11**, bpy(CH$_2$OH)(PS), **10**, and bpy(CH$_2$OH)(PMMA), **8**, were utilized as initiating sites for Al-mediated ring-opening polymerization. Specifically, poly(ϵ-caprolactone) was grown from bpy(PEG)(CH$_2$OH) in the presence of triethylaluminum in THF at room temperature to provide bpy(PEG)(PCL), **12** (Scheme 6). Comparison of the GPC traces indicated both consumption of the macroinitiator and the anticipated increase in molecular weight for the diblock product (Figure 1). Resonances corresponding to both the PCL and PEG chains of bpy(PEG)(PCL) are evident in the ^{1}H NMR spectrum (Figure 2), and integration of specific peaks (PCL: $-COCH_2(CH_2)_4O-$; PEG: $-OCH_2CH_2-$) reveals good agreement between GPC and NMR molecular weight data: M_n(MALLS) = 24 350; M_n(NMR) = 26 140. The bpy(PEG)(CH$_2$OH) macro-

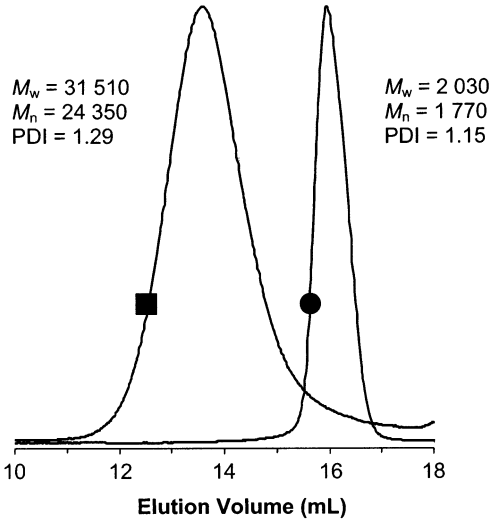


Figure 1. Overlay of the GPC traces for a bpy(PEG)(CH_2OH) macroinitiator, **11** (●), and the corresponding bpy(PEG)(PCL) diblock, **12** (■).

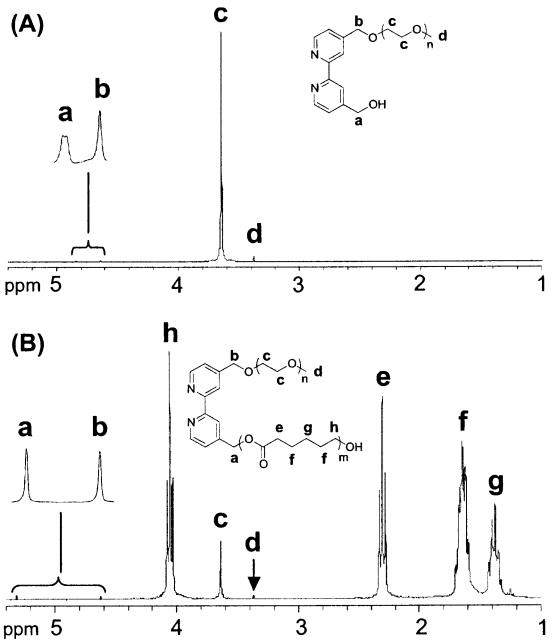


Figure 2. ^{1}H NMR spectrum of (A) a bpy(PEG)(CH_2OH) macroinitiator, **11**, and (B) the corresponding diblock, bpy(PEG)(PCL), **12**.

initiator also effectively polymerized DL-lactide in the presence of Et_3Al catalyst in THF at 70 °C[60] to provide bpy(PEG)(PLA), **13**. Again, both polymer blocks were evident in the ^{1}H NMR spectrum and integration of selected peaks (PLA: $-OCOCH(CH_3)O-$; PEG: $-OCH_2CH_2-$) indicated a molecular weight that was consistent with that reported by GPC: M_n(MALLS) = 29 340; M_n(NMR) = 28 150 (Table 1).

Polymerization of ϵ-caprolactone from the hydroxyl-functionalized polystyrene macroinitiator, **10**, was also controlled and generated bpy(PS)(PCL) samples, **14**, with low PDIs (Scheme 6) and comparable molecular weights by ^{1}H NMR integration and GPC methods: M_n(MALLS) = 57 250; M_n(NMR) = 59 500 (Table 1).[32]

While bpy(CH_2OH)(PMMA), **8**, also initiated the growth of PCL samples via aluminum-mediated ring-opening polymerization of ϵ-caprolactone to produce bpy(PMMA)(PCL), **15**, the rate of monomer consumption was much slower than for bpy(CH_2OH)(PS) and bpy(CH_2OH)(PEG) initiators. In addition, PDIs of the resulting samples were typically greater than 1.30. However, when PCL was polymerized from the unsymmetrical alcohol, **5**, before polymerizing MMA, the resulting diblock product, bpy(PCL)(PMMA), **16**, exhibited a higher level of molecular weight control and lower PDIs (<1.3). This is in contrast to the bpy(PS)(PCL) bpy-centered diblock, where polymerizing styrene via ATRP prior to conducting ROP generated products with lower PDIs. It was previously reported that the pyridyl chloride functionality of bpy(CH_2Cl)(CH_2OH), **2**, was relatively sensitive to ROP and subsequent workup, providing product with only a small fraction of active initiator chain ends. This, in turn, made it difficult to efficiently prepare bpy(CH_2Cl)(PCL), **17**, and thus bpy(PCL)(PS), **18** (Table 1).[32] Conversely, the α-bromoester functionality of bpy($CH_2OCOC(CH_3)_2Br$)(PCL), **19**, obtained from compound **5** remains a viable initiator following polyester synthesis, and subsequent polymerization of MMA gave diblock samples, **16**, with lower PDIs (∼1.14) relative to bpy(PMMA)(PCL) (∼1.38). In addition, molecular weight data for bpy(PCL)(PMMA) (M_n(MALLS) = 74 290; M_w = 85 010; PDI = 1.14) were consistent with that targeted based on monomer loading[57] and in agreement with data calculated from ^{1}H NMR: M_n(NMR) = 71 600 (Table 1).

Methyl methacrylate was also polymerized as a second step from a bromoester-functionalized PEG chain, bpy(PEG)($CH_2OCOC(CH_3)_2Br$), **20**. This PEG macroinitiator was synthesized by reacting bpy(PEG)(CH_2OH), **11**, with 2-bromo-2-methylpropionyl bromide in Et_3N/CH_2Cl_2. GPC molecular weight data for the resulting bpy-centered diblock, bpy(PEG)(PMMA), **21**, were again consistent with ^{1}H NMR spectral analysis (Table 1) and MMA loading, given initiator efficiencies anticipated based on previous findings with related α-bromoester systems.[33]

Conclusions

Various bipyridine-centered diblock copolymers were synthesized via sequential polymerization of two monomers from orthogonal initiator sites. Homopolymers with active end groups were synthesized from functional bipyridine initiators. These macroinitiators were then utilized to generate low-polydispersity diblock copolymers with a bipyridine binding site at the block junction. Use of these block copolymer subunits in combination with each other or other known macroligands in modular metal template synthesis could lead to functional block copolymer materials and thus film morphologies of unprecedented complexity. The coordination chemistry of the reported diblock macroligands and self-assembly properties of the block copolymeric metal complex products that result will serve as subjects of future reports.

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(46) MALLS molecular weight data were estimated using the d*n*/d*c* value for PCL (0.056 mL/g, λ = 633 nm in $CHCl_3$).
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