Well-Defined Acetylene-Functionalized Oxanorbornene Polymers and Block Copolymers

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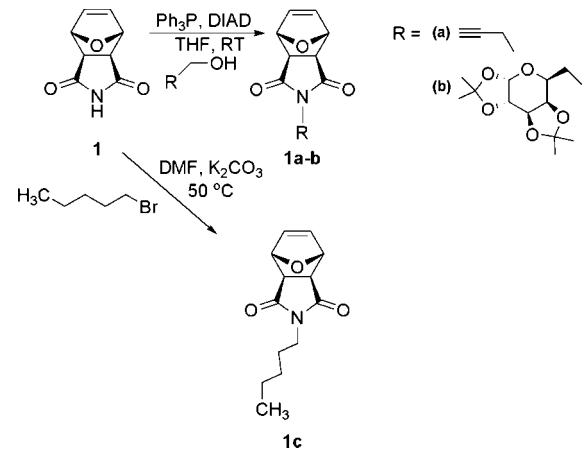
ABSTRACT: Well-defined and high molecular weight acetylene-functionalized poly(oxanorbornenes) were synthesized using ring-opening metathesis polymerization (ROMP) of cobalt-functionalized *exo*-oxanorbornene monomer **2a**. Dicobalt hexacarbonyl, $Co_2(CO)_6$, was used as a protecting group for the acetylene moiety. This protecting group was found to be compatible with third-generation Grubbs' catalyst, offering well-defined homopolymers and block copolymers in high yields (up to 97%). Equally important, it was removed (>99%) by treating the polymers with ceric(IV) ammonium nitrate (CAN), under mild conditions, with no observable unwanted side reactions. This approach yields high fidelity polymers containing the acetylene functionality which is incompatible with Ru-based catalysis. The explosion of click chemistry makes these polymers attractive starting macromolecules for postpolymerization chemistry.

Introduction

Ring-opening metathesis polymerization (ROMP) of strained bicyclic norbornene monomers, assisted by various Grubbs' catalysts, has attracted great attention.[1] This is mainly due to the efficiency, control, and tolerability of the ruthenium catalysts to a variety of pendant functional groups.[2] However, the controlled ring-opening metathesis polymerization of acetylene-functionalized monomers has not yet been reported in the literature due to the incompatibility of the acetylene moiety with the Ru catalyst. With the rediscovery of Sharpless "click" chemistry which has proven to be a versatile postmodification method in polymer chemistry,[3] the synthesis of well-defined acetylene-functionalized polymers and block copolymers will find significant use in the generation of highly functional materials.[4] Previously, Binder and co-workers[5] attempted to polymerize acetylene-functionalized oxanorbornene **1a** by ROMP. However, their efforts were hampered by the lack of controlled polymerization of the acetylene-functionalized oxanorbornene monomer, leading to polymers with broad PDI. Alternatively, acetylene-functionalized poly(oxanorbornene)s were prepared by polymerizing **1** followed by treatment with propargyl bromide, but due to insolubility of the polymer precursor, molecular weights (MW) were limited.

To circumvent the incompatibility of the ruthenium catalyst with the acetylene moiety, an easy to install and removed protecting group for the acetylene functionality is needed. Dicobalt octacarbonyl forms a stable complex with acetylene functionality, yielding the dicobalt hexacarbonyl−acetylene complex. This chemistry has been used to synthesize cobalt-containing polymers and block copolymers by postpolymerization methods.[6] Although dicobalt hexacarbonyl has also been used as a protecting group for the acetylene moiety in small molecules,[7] its applicability in polymers remains unknown. In this paper, we report for the first time the ring-opening metathesis polymerization of an acetylene-protected oxanorbornene. The protecting group, dicobalt hexacarbonyl, was found to be compatible with the third generation Grubbs' catalyst used for the polymerization which proceeded in a controlled manner offering well-defined polymers and block copolymers with narrow polydispersity indices (PDI) and excellent control over molecular weight (MW). Removal of the protecting group was carefully characterized by NMR, IR, and UV−vis spectroscopy and was found to be quantitative with no adverse influence on the polymer's PDI.

Scheme 1. Synthesis of Monomers 1a−c



Results and Discussion

Monomers Synthesis. Monomers **1a** and **1b** were prepared via Mitsunobu coupling.[8] Treatment of the corresponding alcohol derivatives with *exo*-10-oxa-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (**1**) in the presence of triphenylphosphine and diisopropylazodicarboxylate (DIAD) afforded the corresponding functionalized monomers **1a** and **1b** in 90% and 65% yield, respectively. Monomer **1c** was prepared in 80% yield by nucleophilic substitution of **1** with 1-bromopentane using DMF/K_2CO_3 (Scheme 1).

Monomer **1a** was treated with dicobalt octacarbonyl to afford **2a** in 75% yield (Scheme 2) which was confirmed by NMR. The ^{1}H NMR spectrum, in $CDCl_3$, showed a significant downfield shift for the acetylenic resonance from δ 2.17 to δ 6.00 ppm upon complexation, which is consistent with previously reported values (Figure 1).[9] The methylene proton resonances also shifted downfield from δ 4.19 to 4.80 ppm along with a slight downfield shift of the proton signals corresponding to the bicyclic oxanorbornene structure. The ^{13}C NMR spectrum of complex **2a** (Figure 2) gave rise to a new peak at δ 198.93

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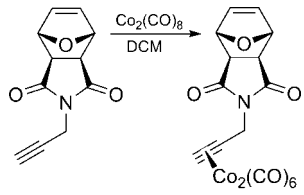
Scheme 2. Protection of the Acetylene with Dicobalt Hexacarbonyl



1a 2a

ppm due to the carbonyls of the cobalt complex. At the same time, the signals for the acetylenic and the methylene carbons also shifted downfield to δ 88.20, 72.23, and 41.16 ppm. Monomer **2a** is readily soluble in common organic solvents such as THF, $CHCl_3$, and CH_2Cl_2 due to the neutral metal complex.

Polymerization Studies. Third generation Grubbs' catalyst was used to polymerize monomer **2a** (Scheme 3), and the polymerization was initially monitored by NMR. After 8 min, the polymerization was complete as indicated by the disappearance of the vinyl proton signal at δ 6.50 ppm (H_1) as shown in Figure 3 and the emergence of the trans and cis vinyl proton resonances at δ 6.01 and 5.71 ppm, respectively. In agreement, the ^{13}C NMR analysis (Figure 4) showed the loss of the vinyl carbon signals at δ 136.62 ppm and the appearance of a new broad peak at δ 131.32 ppm that was attributed to the carbon double bonds of the polymer backbone. As expected, the allylic

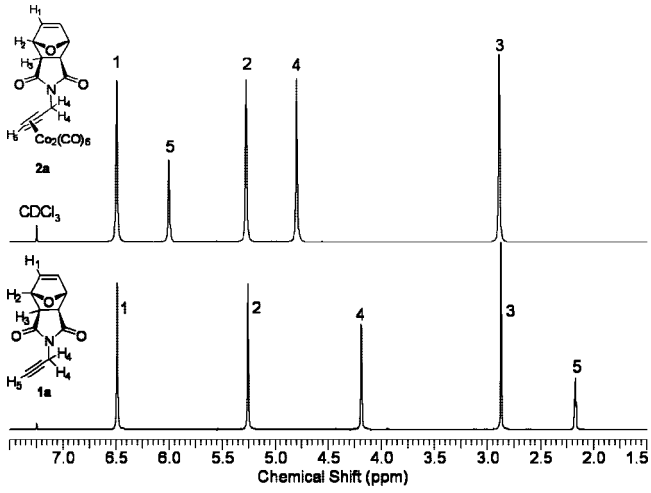


Figure 1. ^1H NMR spectra in $CDCl_3$ of **1a** and **2a** showing the downfield shift of the acetylenic (H_5) and the methylene protons (H_4) of **1a** from 2.17 and 4.19 to 6.00 and 4.80 ppm, respectively.

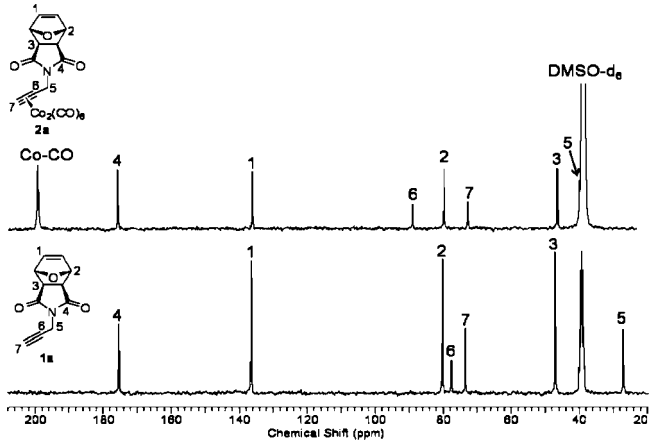
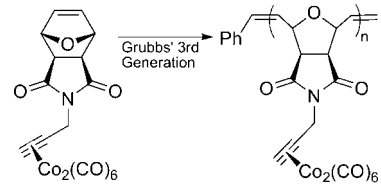


Figure 2. ^{13}C NMR spectra of **1a** and **2a** taken in DMSO-d_6.

Scheme 3. Ring-Opening Metathesis Polymerization of 2a



2a 3

carbon, labeled C_2, gave rise to two signals at δ 80.89 and 77.60 ppm which were ascribed to C_{trans} and C_{cis}, respectively. The C_3 signal (see Figure 4) also shifted downfield from δ 47.56 to 52.44 ppm. There was no change in the carbon signals of the acetylene moiety after polymerization. Beyond NMR, the GPC analysis of the heavily metalized polymer **3** showed a monomodal distribution of MWs with a narrow PDI of 1.09 (Figure 5). To our knowledge, this is the first example that demonstrates the compatibility of the third generation Grubbs' catalyst with the novel dicobalt hexacarbonyl complex.

A series of homopolymers with different [M]/[I] ratios, and thus MW, were synthesized to evaluate the "livingness" of the polymerization. The results shown in Table 1 and plotted in Figure 6 indicate that the polymerizations were well-controlled, resulting in narrow polydispersities for all samples, good isolated yields (85−90%), and MW's spanning 20−100 kDa. In all cases, the targeted number-average molecular weight (M_n) were close to the theoretical values, and the plot of M_n vs [M]:[I] ratio was linear, suggesting that the polymerizations were living (Figure 6).

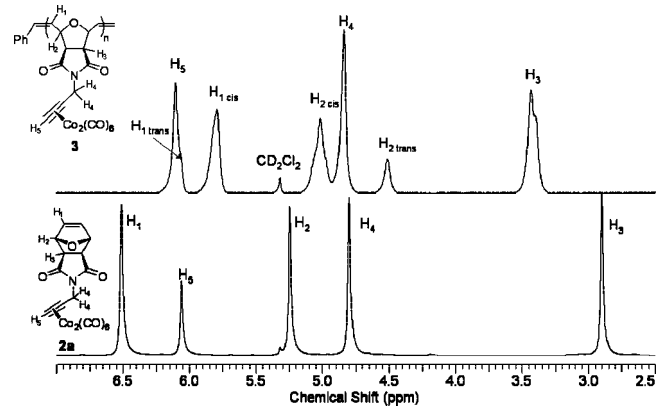


Figure 3. ^1H NMR analysis of monomer **2a** and polymer **3** taken in CD_2Cl_2.

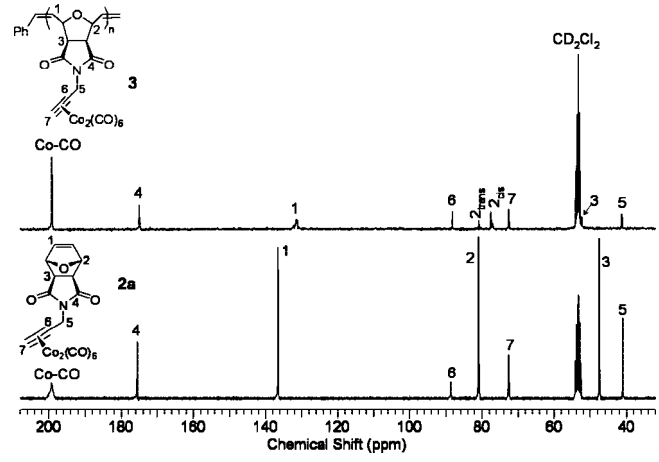


Figure 4. ^{13}C NMR analysis of monomer **2a** and polymer **3**. The spectrum was taken in CD_2Cl_2.

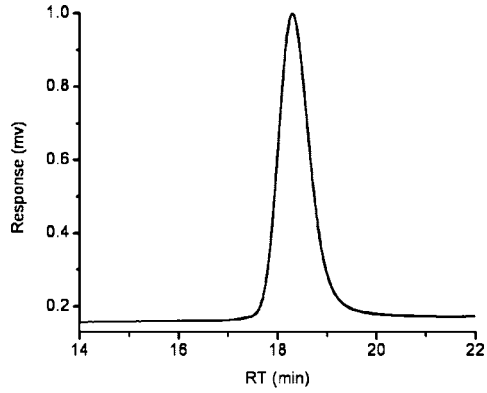


Figure 5. GPC chromatogram of homopolymer **3**. [M]:[I] ratio = 208; M_n = 100 kDa; PDI = 1.09.

Table 1. M_n, DP, M_w, $M_{n,th}$, and PDI of 3

entry	M_n (kDa)	M_w (kDa)	[M]:[I]	DP	$M_{n,th}$ (kDa)	PDI
1	20	21	40:1	41	20	1.07
2	41	42	81:1	82	40	1.06
3	59	64	117:1	120	60	1.08
4	80	87	159:1	163	80	1.09
5	102	113	202:1	208	100	1.09

To gain further evidence that the polymerization of **2a** was living, a block copolymer was synthesized via a two-step polymerization sequence according to Scheme 4. A 10:1 [M]:[I] ratio of monomer **2a** was allowed to polymerize to completion after which 50 equiv of monomer **1b** was added to the reaction. After complete consumption of monomer **1b**, the AB block copolymer **4** was isolated by precipitation from pentane. Figure 7 shows the GPC analysis of block copolymer **4**. Using similar reaction conditions, another block copolymer, **5**, was prepared (Scheme 5). A 10:1 [M]:[I] ratio of monomer **2a** was polymerized to completion followed by the addition of 20 equiv of monomer **1c** to afford a block copolymer with 1:2 molar ratio.

Deprotection. Deprotection of the acetylene−cobalt complex of polymer **3** (M_n = 100 kDa) was accomplished via oxidative removal of the cobalt carbonyl by treating the polymer with ceric(IV) ammonium nitrate (CAN).[7] 5 equiv per monomer of CAN was dissolved in acetone and added to a solution of **3**, which effervesced mildly for 10 min before the polymer precipitated as white solid (Scheme 6). This white precipitate was collected and redissolved in DMSO, upon which an additional 1 equiv of CAN per monomer was added. The solution was stirred at room temperature for 1 h, and the resulting ^{1}H NMR (DMSO-d_6) of **6** showed the reemergence of the methylene (H_4) and acetylenic protons (H_5) with signals at δ 4.13 and 3.17 ppm, respectively (Figure 8). The assignment of the acetylenic proton signal at δ 3.17 ppm was confirmed by collecting NMR spectrum for **1a** in $CDCl_3$ and DMSO-d_6. The chemical shift of the acetylenic proton signal in **1a** was solvent dependent, shifting downfield from δ 2.17 ppm (in $CDCl_3$) to δ 3.17 ppm (in DMSO-d_6), which validates the assignment of the acetylenic proton for **6**. In addition, the integration shown in Figure 8 is consistent with the structure of **6**, and careful inspection shows no residual signal for the proton of the acetylene−$Co_2(CO)_6$ complex. ^{13}C NMR analysis of **6** shows complete removal of the cobalt carbonyl peak at δ 198.93 ppm and the upfield shift of the methylene and the acetylenic carbon signals to δ 29.30, 78.40, and 72.30 ppm, respectively (Figure 9).

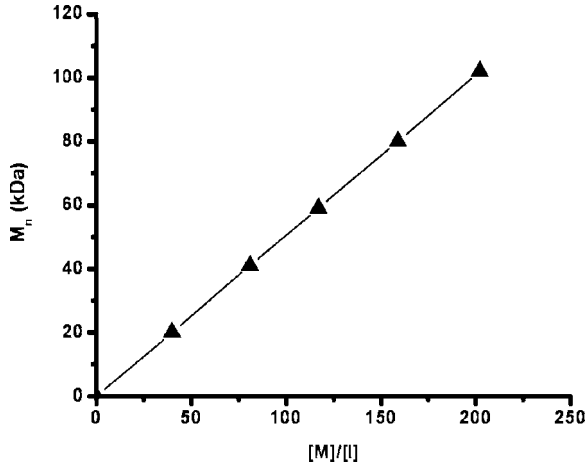


Figure 6. Plot of M_n vs [M]:[I].

The deprotection of **3** was also confirmed by IR and UV−vis spectroscopy. The IR spectra of **3** and **6** (Figure 10) show the disappearance of the strong metal−carbonyl stretches at 2097, 2056, and 2020 cm^{-1} and the appearance of the acetylene stretch at 2126 cm^{-1}. The UV−vis spectrum of **6** also shows the disappearance of the absorptions at 292, 350, and 417 nm (Figure 11) from the cobalt complex following deprotection. Unfortunately, the GPC analysis of **6** was hindered due to the insolubility of the deprotected polymer in common organic solvents like THF, which is the mobile phase for the GPC. To circumvent this problem, a statistical copolymer containing a 1:2 molar ratio of **2a**:**1c** was synthesized (Scheme 7). The GPC analysis of this deprotected copolymer, **8**, shows a reduction in the M_n due to removal of the $Co_2(CO)_6$ protecting group, but no change in the PDI (Figure 12). The block copolymer, **4**, was also treated with CAN to afford acetylene deprotected copolymer **9** (Scheme 8), which remained soluble due to the short acetylenic block following analysis before and after the deprotection (Figure 13). There is only a small change in the retention time for **9** due to the small acetyelinic block. The deprotection of block copolymer **5** also proceeded cleanly (see Supporting Information).

Conclusion

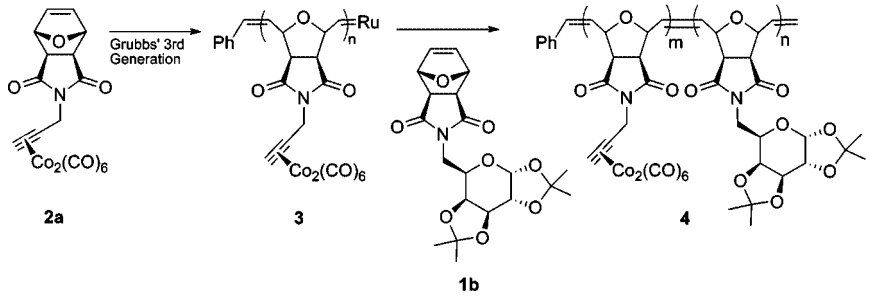
Using third generation Grubbs' catalyst for ROMP of monomer **2a**, a novel and indirect approach to the synthesis of well-defined acetylene-functionalized oxanorbornene polymers and block copolymers has been developed. The polymerization of the acetylene-functionalized oxanorbornene monomer was made possible by protecting the acetylene moiety of **1a** with dicobalt hexacarbonyl. The ROMP of **2a** proceeded cleanly with no side reaction and excellent control over molecular weights and polydispersities. The dicobalt hexacarbonyl complex was oxidatively removed by treating the protected polymers with CAN to obtain acetylene-functionalized oxanorbornene polymers. NMR, IR, and UV−vis spectroscopy indicated quantitative removal of the protecting group and GPC analysis after deprotection showed no change in the PDIs.

Experimental Section

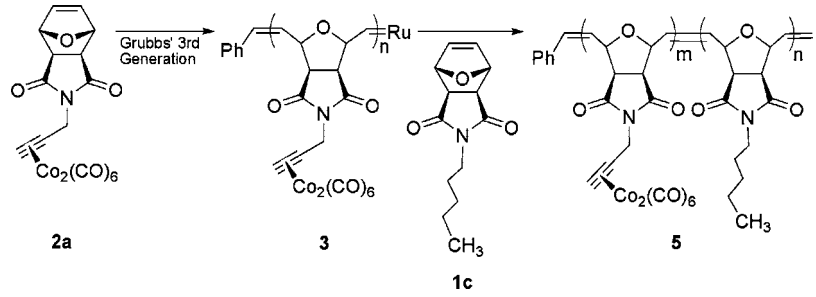
Instrumentation. NMR spectra were recorded on a Bruker DPX-300 MHz (^{1}H NMR; ^{13}C NMR, 75 MHz) spectrometer. Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (of residual protons) and ^{13}C signals of deuterated solvents. Molecular weights and PDIs were measured by GPC in THF relative to polystyrene standards on systems equipped with two-column sets (Polymer Laboratories) and refractive-index detectors (HP1047A) at 40 °C with a flow rate of 1 mL/min. UV−vis spectra were obtained using a Perkin-Elmer Lambda 2 series spectrophotometer with PECSS software. IR spectra were obtained using a Bio-Rad FTS 3000 Excalibur Series.

Materials. All reagents were purchased either from Acros Organics, Aldrich, or Strem and used without further purification.

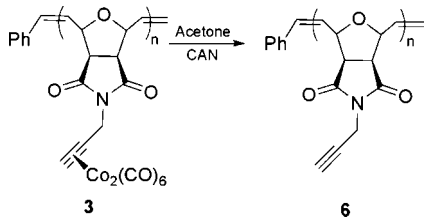
Scheme 4. Synthesis of Block Copolymer 4 with Total M_n by GPC = 17.9 kDa, PDI = 1.04, and m = 10, n = 50



Scheme 5. Synthesis of Block Copolymer 5



Scheme 6. Deprotection Reaction of 3 with CAN



Dichloromethane and THF were dried over CaH_2 and sodium benzophenone ketyl, respectively. Third generation Grubbs' catalyst[10] and *exo*-oxanorbornene **1**[11] were synthesized according to the literature.

General Synthesis Procedure for Monomers 1a and 1b. To a round-bottom flask charged with compound **1**, alcohol derivatives, and 1.5 equiv of triphenylphosphine, THF was added. The solution mixture was then immersed in an ice bath, and 1.5 equiv of diisopropyl azodicarboxylate (DIAD) was added dropwise. After the addition of DIAD, the ice bath was removed and the reaction was allowed to stir at room temperature for 24 h. The solvent was removed under reduced pressure, and the product was crystallized from diethyl ether. The mother liquor was concentrated, and the remaining product was isolated by column chromatography.

Synthesis of Compound 1a. Compound **1** (6.51 g, 39.4 mmol), propargyl alcohol (2.1 mL, 35.8 mmol), triphenylphosphine (15.5 g, 59.1 mmol), diisopropylazodicarboxylate (DIAD) (11.5 mL, 59.1 mmol). The product was isolated by repeated crystallization from diethyl ether. The mother liquor was chromatographed (SiO_2 ethyl acetate/hexane = 2/3). The pure product is white solid. Yield: 6.5 g (32.2 mmol, 90%). ^{1}H NMR ($CDCl_3$): δ 6.50 (s, 2H), 5.25 (s, 2H), 4.20 (s, 2H), 2.91 (s, 2H), 2.17 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 176.0, 136.6, 81.5, 78.0, 74.0, 47.0, 28.0.

Synthesis of Compound 1b. Compound **1** (6.34 g, 38.4 mmol), 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (9.84 g, 34.9 mmol), triphenylphosphine (15.1 g, 57.6 mmol), diisopropyl azodicarboxylate (DIAD) (11.2 mL, 57.6 mmol). The product was isolated by repeated crystallization from diethyl ether. The mother liquor was chromatographed (SiO_2 ethyl acetate/hexane = 2/3). The pure product is white solid. Yield: 9.24 g (22.7 mmol, 65%). ^{1}H NMR ($CDCl_3$): δ 6.44 (s, 1H), 5.39 (d, 1H), 5.19 (d, 1H), 4.53 (s, 1H), 4.12 (dd, 2H), 3.95−3.88 (m, 1H), 3.36 (d, 1H), 2.80 (s, 2H), 1.42 (s, 3H), 1.38 (s, 3H), 1.27 (s, 3H), 1.21 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 176.2, 175.8, 136.4, 109.5, 108.5, 96.1, 80.7, 71.2, 70.7, 70.3, 64.1, 47.3, 47.1, 39.3, 25.8, 25.6, 24.9, 24.3.

Synthesis of Compound 1c. A mixture of 1-bromopentane (6.00 g, 39.7 mmol), potassium carbonate (5.48 g, 39.7 mmol), and compound **1** (4.41 g, 26.5 mmol) was stirred in anhydrous DMF

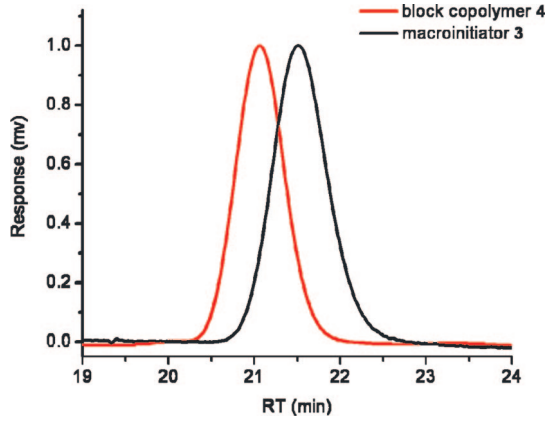


Figure 7. GPC analysis of block copolymer **4** (M_n = 17.9 kDa; PDI = 1.04) and macroinitiator **3** (M_n = 5.32 kDa; PDI = 1.07).

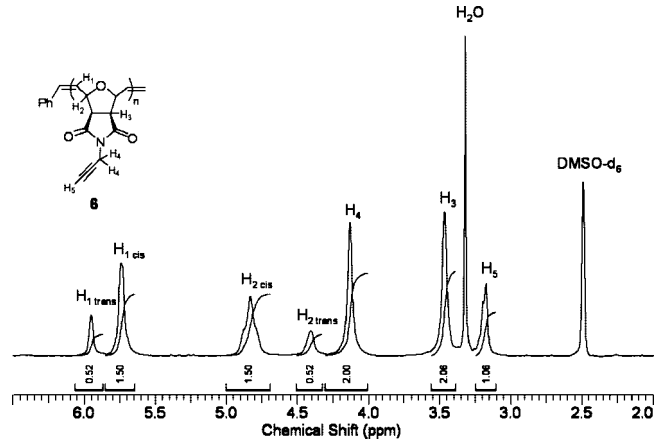


Figure 8. ^{1}H NMR spectra of **6**.

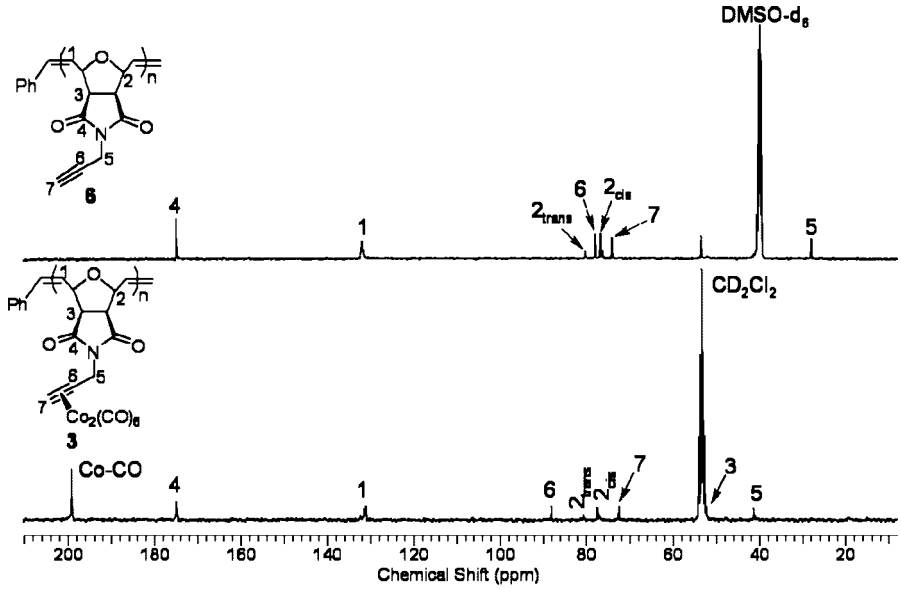


Figure 9. ^{13}C NMR spectra of **3** before deprotection and **6** after deprotection.

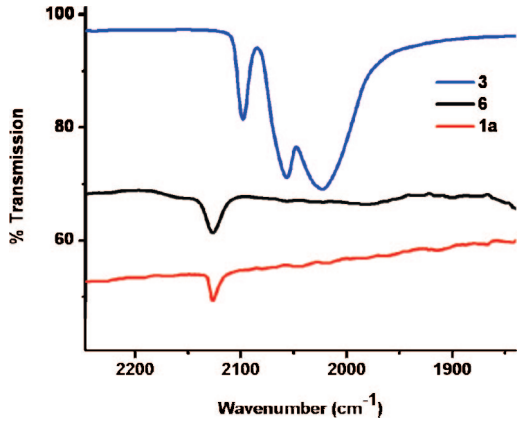


Figure 10. IR analyses of monomer **1a**, protected polymer **3**, and the deprotected polymer **6**.

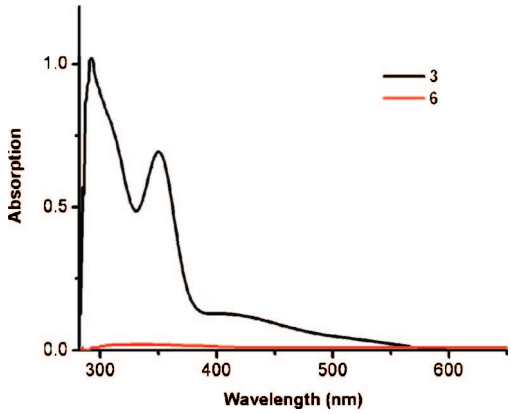


Figure 11. UV−vis analysis of **3** before and **6** after treatment with CAN.

(300 mL) at 50 °C for 4 h. The reaction mixture was evaporated to dryness, and the crude product was purified by chromatography (SiO_2, hexane/ethyl acetate) 1/1). Pure **1c** was obtained as a white solid. Yield: 4.99 g (21.2 mmol, 80%). ^1H NMR ($CDCl_3$): δ 6.45 (s, 2H), 5.19 (s, 2H), 3.38 (t, 2H), 2.77 (s,2H), 1.53−1.38 (m, 2H), 1.28−1.10 (m, 4H), 0.80 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 176.1, 136.4, 80.7, 47.2, 38.8, 31.1, 27.4, 26.1, 22.3, 13.8.

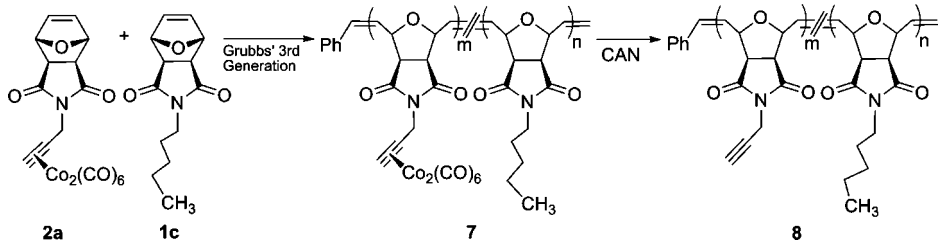
Synthesis of Compound 2a. To a round-bottom flask charged with compound **1a** (3.62 g, 17.8 mmol), CH_2Cl_2 (100 mL) was added. The flask was immersed in an ice bath, and $Co_2(CO)_8$ (12.2 g, 35.6 mmol) was added and the reaction mixture was allowed to stir in an ice bath for 2 h and at room temperature for another 2 h. The solvent was removed under nitrogen flow; pentane (200 mL) was then added to remove the excess of $Co_2(CO)_8$ and to precipitate the product. The pure product was isolated by chromatography (SiO_2, CH_2Cl_2/acetone) 9/1). Pure **2a** was obtained as a red solid. Yield: 6.53 g (13.4 mmol, 75%). ^1H NMR ($CDCl_3$): δ 6.50 (s, 2H), 6.00 (s, 1H), 5.27 (s, 2H), 4.80 (s, 2H), 3.89 (s, 2H). ^{13}C NMR (DMSO-d_6): δ 199.3, 175.9, 136.6, 89.6, 80.4, 73.4, 47.1, 40.7.

General Polymerization Procedure. A known amount of monomer was weighed into a Schlenk flask, placed under an atmosphere of nitrogen, and dissolved in anhydrous CH_2Cl_2 (1 mL per 100 mg of monomer). Into a separate Schlenk flask, a desired amount of third generation Grubbs' catalyst was added, flushed with nitrogen, and dissolved in a minimum amount of anhydrous CH_2Cl_2. Both flasks were degassed three times by freeze−pump−thaw cycles. The monomer was transferred to the flask containing the catalyst via a cannula. The reaction was allowed to stir at room temperature until the polymerization is complete (~8 min), after which ethyl vinyl ether (0.2 mL) was added to quench the polymerization. An aliquot was taken for GPC analysis, and the remaining product was precipitated from pentane.

General Procedure for Block Copolymer Synthesis. Known amounts of monomers A and B were weighed into two separate Schlenk flasks, placed under an atmosphere of nitrogen, and dissolved in anhydrous CH_2Cl_2 (1 mL per 100 mg of monomer). Into another Schlenk flask, a desired amount of third generation Grubbs' catalyst was added, flushed with nitrogen, and dissolved in minimum amount of anhydrous CH_2Cl_2. All three flasks were degassed three times by freeze−pump−thaw cycles. Monomer A was transferred to the flask containing the catalyst via a cannula. The reaction was allowed to stir at room temperature until the polymerization is complete (~8 min), after which the second monomer B was added to the flask via a cannula. The polymerization was allowed to continue for another 8 min before it was quenched with ethyl vinyl ether (0.2 mL). An aliquot was taken for GPC analysis, and the remaining product was precipitated from pentane or evaporated to dryness.

General Deprotection Procedure. To a round-bottom flask charged with a known molar amount of polymer or block copolymer in acetone, a 5 mol equiv of ceric(IV) ammonium nitrate (CAN) solution in acetone was added. The reaction mixture was allowed to stir at room temperature for 15 min. The product, white

Scheme 7. Synthesis of Statistical Copolymer 8 with *m*:*n* = 1:2 and Total MW of 12.4 kDa



precipitate, was isolated by filtration, and redissolved in minimum amount of DMSO. 1 mol equiv of CAN solution in DMSO was added. The solution was allowed to stir at room temperature for 1 h. The deprotected product was isolated by dropwise addition into methanol. The product was dried under vacuum to the deprotected polymer as white solid.

UV−vis analyses were conducted on solutions of **3** (1×10^{-6} g/mL) and **6** (3×10^{-6} g/mL) which were prepared in $CHCl_3$ and DMSO, respectively.

Polymer 3. ^{1}H NMR (CD_2Cl_2): δ 6.26−6.01 (br, 1.5 H), 5.53−5.72 (br, 1.52 H), 5.16−4.93 (br, 1.58 H), 4.84 (s, 2H), 4.51(br s, 0.46 H), 3.55−3.31 (br, 2 H). ^{13}C NMR (CD_2Cl_2): δ 199.2, 175.1, 131.6, 88.3, 80.9, 77.6, 72.6, 52.4, 41.4. IR: 2097, 2056, and 2020 cm^{-1}. UV−vis: 292, 350, and 417 nm. M_n = 100 kDa, PDI = 1.09.

Block Copolymer 4. ^{1}H NMR (CD_2Cl_2): δ 6.08−5.93 (br m, 1.07 H), 5.70 (br s, 1.30 H), 5.42−5.28 (br m, 1H), 5.08−4.67 (br m, 1.69 H), 4.60−4.47(br m, 1H), 4.37 (br s, 1 H), 4.28−3.98 (br m, 4H), 3.98−3.75 (br m, 1H), 1.39 (s, 3H), 1.26 (s, 3H), 1.21)s, 3H), 1.19 (s, 3H). ^{13}C NMR (CD_2Cl_2): δ 199.3, 175.5, 131.0, 109.7, 108.8, 96.3, 87.7, 80.8, 77.2, 72.7, 71.4, 71.0, 70.6, 64.0, 52.4, 39.2, 25.8, 25.7, 24.8, 24.2. M_n = 17.9 kDa, PDI = 1.04.

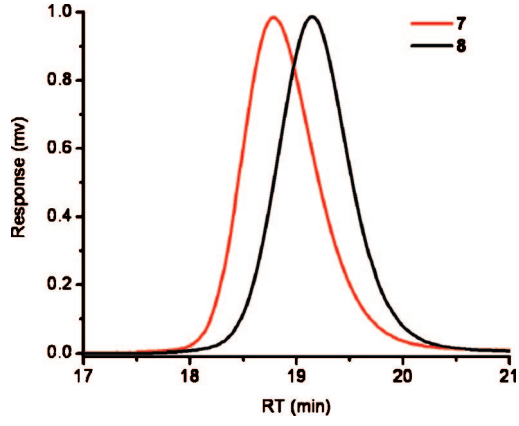
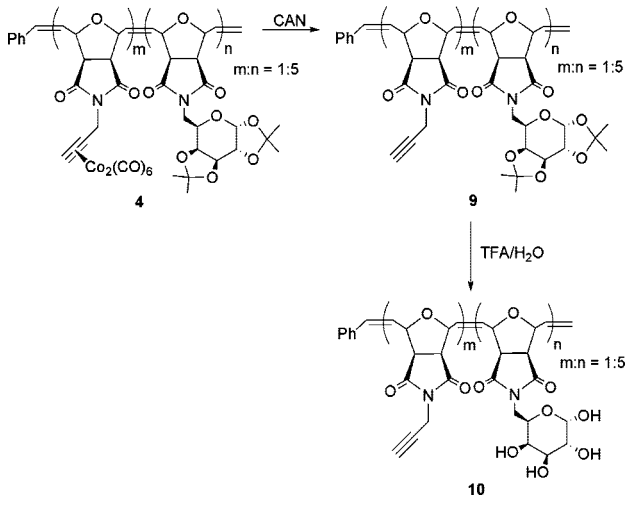


Figure 12. GPC analysis of **7** (M_n = 12.4 kDa; PDI = 1.08) and **8** (M_n = 9.63 kDa; PDI = 1.09).

Scheme 8. Deprotection of the Acetylene and Isopropylidene Moieties of Block Copolymer 4



Block Copolymer 5. ^{1}H NMR ($CDCl_3$): δ 6.03 (s, 1.55H), 5.75 (s, 1.82H), 4.99 (br s, 1.67H), 4.79 (s, 1H), 4.43(br m, 1H), 4.37 (s, 1H), 3.60−3.11 (br m, 5H), 1.52 (s, 2H), 1.25 (s, 4H), 0.85 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 198.8, 175.6, 174.9, 131.7, 130.9, 87.8, 72.2, 53.3, 52.2, 41.2, 38.9, 28.8, 27.2, 22.1, 13.9. IR: 2097, 2056, and 2020 cm^{-1}. UV−vis: 292, 350, and 417 nm. M_n = 15.7 kDa, PDI = 1.05.

Polymer 6. ^{1}H NMR (DMSO-d_6): δ 5.95 (s, 0.52H), 5.74 (s, 1.5H), 4.83 (br s, 1.50H), 4.41 (br s, 0.52H), 4.13(s, 2H), 3.47 (s, 2H), 3.17 (br s, 1H). ^{13}C NMR (DMSO-d_6): δ 174.6, 131.6, 79.9, 77.6, 76.4, 73.8, 53.1, 27.6. IR: acetylene stretch at 2126 cm^{-1}. UV−vis: no peaks were observed between 280 and 700 nm.

Polymer 7. ^{1}H NMR ($CDCl_3$): δ 6.05 (s, 1.57H), 5.76 (s, 1.85H), 4.99 (br s, 1.69H), 4.79 (s, 1H), 4.45 (br m, 1H), 4.37 (s, 1H), 3.59−3.9 (br m, 5H), 1.54 (s, 2H), 1.26 (s, 4H), 0.86 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 198.6, 175.5, 174.7, 131.6, 130.7, 87.9, 72.1, 53.5, 52.3, 41.5, 38.6, 28.7, 27.4, 22.3, 13.6. M_n = 12.4 kDa, PDI = 1.08.

Copolymer 8. ^{1}H NMR ($CDCl_3$): δ 6.04 (s, 0.47H), 5.75(s, 0.93H), 4.94 (br s, 1H), 4.43 (br s, 0.41H), 4.23 (s, 0.98H), 3.70−3.10 (br m, 5H), 2.21 (br s, 0.5H), 1.53 (br s, 2H), 1.27 (br s, 4H), 0.88 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 176.4, 132.2, 80.6, 78.1, 76.7, 74.2, 53.6, 52.7, 49.3, 38.8, 28.8, 27.2, 14.3. IR: acetylene stretch at 2126 cm^{-1}. UV−vis: no peaks were observed between 280 and 700 nm.

Block Copolymers 9 and 10. ^{1}H NMR ($CDCl_3$): δ 6.06 (s, 0.93H), 5.75(s, 1.26H), 5.42 (s, 1H), 5.20−4.75 (br m, 1.40H), 4.58 (s, 0.94H), 4.45 (s, 1H), 4.35−3.85 (br m, 4.38H), 3.58−3.05 (br m, 3.17H), 2.26 (br s, 0.21H), 1.60−1.10 (m, 12H). ^{13}C NMR (DMSO-d_6): δ 175.6, 131.2, 108.7, 108.1, 95.7, 80.4, 77.5, 76.5, 73.8, 70.2, 63.5, 53.1, 51.9, 25.9, 25.6, 24.8, 24.3.

The deprotection of the isopropylidene moiety was removed by treating copolymer **9** with an aqueous solution of TFA (TFA/H_2O,

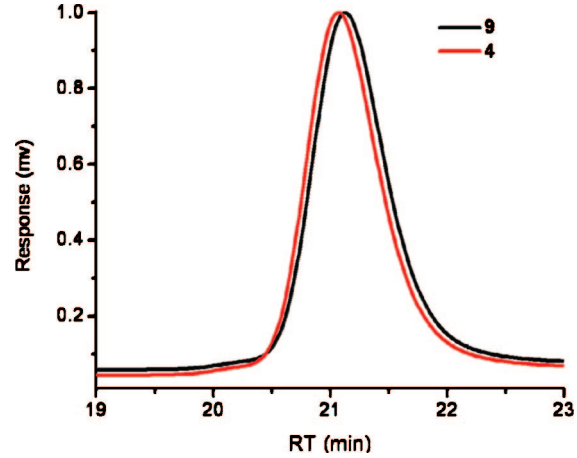


Figure 13. GPC analysis of **4** (M_n = 17.9 kDa; PDI = 1.04) and **9** (M_n = 17.3 kDa; PDI = 1.05).

5:1 v/v). The solution was allowed to stir at room temperature for 1 h. The deprotected polymer, **10**, was isolated by dropwise addition into anhydrous diethyl ether. ^{1}H NMR (DMSO-d_6): δ 5.95 (s, 0.81H), 5.73 (s, 1.11H), 5.36−4.55 (br d, 6.52H), 4.39 (s, 1H), 4.23−3.97 (br, 1H), 3.96−3.0 (br m, 6.59H).

Block Copolymer 11. ^{1}H NMR ($CDCl_3$): δ 6.05 (s, 0.47H), 5.76(s, 0.93H), 4.96 (br s, 1H), 4.44 (br s, 0.41H), 4.21 (s, 0.98H), 3.70−3.10 (br m, 5H), 2.25 (br s, 0.5H), 1.53 (br s, 2H), 1.27 (br s, 4H), 0.87 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 176.4, 132.3, 80.8, 78.1, 76.9, 74.2, 53.6, 52.6, 49.1, 38.6, 28.8, 27.2, 14.3.

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Supporting Information Available: NMR and GPC characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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