Synthesis and Self-Assembly of Conjugated Polymer Precursors Containing Dichlorocarbonate Groups by Living Ring-Opening Metathesis Polymerization

Hassan S. Bazzi and Hanadi F. Sleiman*

Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, H3A 2K6 Canada

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ABSTRACT: We have used the living ring-opening metathesis polymerization reaction with $Cl_2(PCy_3)_2$-Ru=CHPh to generate a new class of conjugated polymer precursors containing the reactive group 1,2-dichlorocarbonate in their backbone. These polymers possess narrow molecular weight distributions and are easily processable. We have incorporated the 1,2-dichlorocarbonate monomers into block copolymers and have shown that these systems can self-assemble in selective solvents to generate spherical micellar aggregates (TEM). Mild hydrolytic treatment of these precursor polymers converts them into novel low-band-gap conjugated polymers and block copolymers containing 1,2-diol groups in their backbone.

1. Introduction

Block copolymers containing dissimilar blocks have recently been the subject of intense research interest. In this unique class of compounds, two or more polymer properties are intimately blended into one covalent assembly, while at the same time being physically segregated into different domains.[1] The propensity of the copolymer blocks to phase-separate can result in self-assembly of these molecules into a variety of nanoscale micellar structures, such as spheres, cylinders, vesicles, lamellae, etc.[1] A particularly interesting class of materials for incorporation into block copolymers are conjugated polymers.[2] The self-assembly of conjugated polymers is especially desirable, because it allows the rational design and use of these polymers in electronic and electrooptical devices.[3] However, most conjugated polymers to date have been synthesized via polycondensation or polyaddition reactions, and thus obtaining homopolymers and block copolymers with narrow molecular weight distributions has been difficult.[2] The ring-opening metathesis polymerization reaction[4] (ROMP) has been successfully used as a living method to generate conjugated polymer precursors.[5−8] In most cases, however, these studies have been complicated by difficult monomer synthesis or vigorous conditions for the conversion of precursors to the conjugated materials.

One promising class of monomers for the facile generation of conjugated polymers via ROMP are norbornenes **1**[9] and **2**[10] (Chart 1). These monomers can be readily prepared via Diels−Alder reaction of cyclopentadiene or furan with dichlorovinylene carbonate. The ROMP of **1** or **2** is expected to yield polymers containing dichlorocarbonate units. Mild hydrolytic treatment converts this dichlorocarbonate unit to 1,2-diketone. The latter species can undergo a favorable keto−enol tautomerism to produce a conjugated polymer containing diol units in its backbone[11] (Scheme 1). Importantly, this 1,2-diol group allows for the potential incorporation of new functionalities, such as chromophores, metal centers, or luminescent units into the resulting conjugated polymers.[9,12] The ROMP of **1** has been previously reported using $WCl_6/Sn(CH_3)_4$[11] and Mo alkylidene[13] catalysts to only yield polydisperse mixtures or short oligomers, and the ROMP of **2** is unreported.

Here, we report the living ring-opening metathesis polymerization of dichlorocarbonate-substituted norbornene and oxanorbornene **1** and **2** as a method to construct conjugated polymer precursors with narrow molecular weight distributions. (Scheme 1). We also report the synthesis of block copolymers of **1** and the self-assembly of one of these copolymers into spherical micelles. The precursor polymers can undergo mild hydrolysis to generate a novel class of low-band-gap conjugated polymers and block copolymers.

2. Experimental Section

General Considerations. All reactions were carried out either under a dry nitrogen atmosphere, using standard Schlenk techniques, or in an inert-atmosphere glovebox unless otherwise noted. ^1H NMR spectra were recorded on a Varian M400 spectrometer operated at 400.140 MHz and ^{13}C NMR spectra on a Varian M300 spectrometer operated at 75.459 MHz. Chemical shifts are reported in ppm relative to the deuterated solvent resonances. IR spectra were recorded on a Perkin-Elmer 16PC series FT-IR spectrometer in the range between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1}. UV/vis spectra were recorded on a Varian Cary 300 spectrophotometer, and UV/vis/NIR spectra were recorded on a Varian Cary 5E spectrophotometer. MALDI-TOF spectra were recorded on a Kratos Kompact MALDI 3 V4.0.0 spectrometer. GPC spectra were recorded using a Waters 510 pump equipped with two polystyrene-packed Styragel columns (HR4 and HR1, 7.8 × 300 mm) in series and in-line with a Varian RI-4 detector. THF was used as the eluent at a flow rate of 0.6 mL/min, and the instrument was calibrated with polystyrene standards from Aldrich.

Transmission Electron Microscopy. The diblock copolymer **11** was first dissolved in THF (1% w/v of copolymer **11** in THF), then hexanes or water was added dropwise until the turbidity of the solution indicated the onset of aggregation (THF:hexanes = 1:2, THF:H_2O = 1:0.2). Samples were prepared by placing a drop of this solution (final concentration of copolymer **11** after addition of hexanes or water is 0.33% and 0.83% w/v, respectively) onto transmission electron microscopy (TEM) copper grids (400 mesh, carbon-coated, purchased from Electron Microscopy Sciences). The grids were air-dried for 12 h. The aggregates were then examined using a JEOL 2000FX electron microscope operated at 80 kV. Computerized image analysis was carried out using Jandel Sigma ScanPro 4.0. The average size and distribution of a sample of 340 micellar aggregates from two TEM grids were determined.

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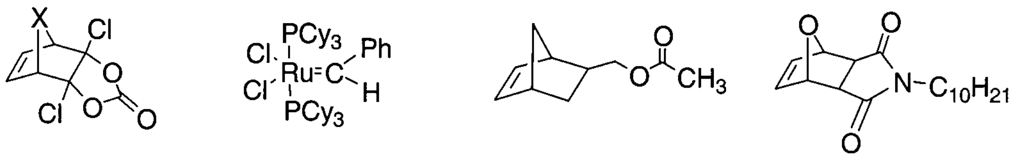
Chart 1



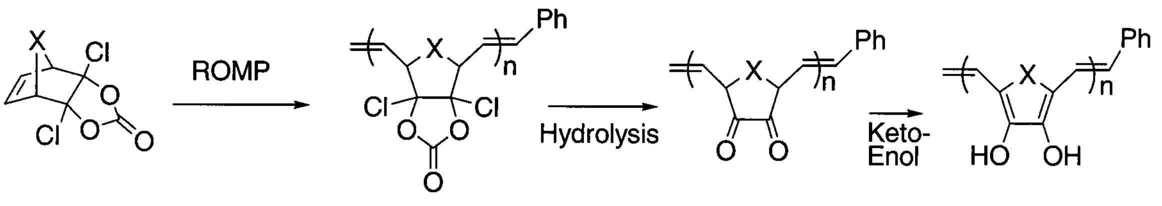
1: $X=CH_2$
2: $X=O$

3

4

5

Scheme 1



1: $X=CH_2$
2: $X=O$

6: $X=CH_2$
7: $X=O$

8: $X=CH_2$
9: $X=O$

Table 1. GPC[a] Traces of Polymer 6 (See Figure 1)

[M]/[I]	calcd M_n	obsd $M_n \times 10^{-4}$	PDI
200	44 304	5.2	1.07
150	33 254	3.7	1.10
125	27 729	3.1	1.10
120	26 624	2.9	1.06
100	22 204	2.4	1.08
50	11 154	1.2	1.09

[a] THF, polystyrene standards.

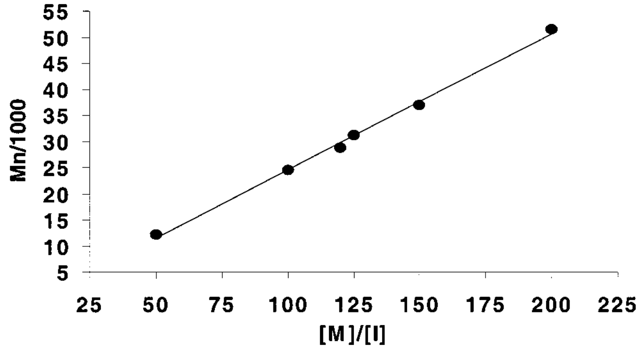


Figure 1. Number-average molecular weight vs monomer/initiator ratio.

Materials. All reagents were purchased from Aldrich and used as received. The Grubbs' catalyst **3**[15] was purchased from Strem Chemicals. Monomers **1**,[9] **2**,[11] and **4**[14] were synthesized according to literature procedures. Tetrahydrofuran (THF) was distilled from sodium/benzophenone, and dichloromethane (CH_2Cl_2) was distilled from CaH_2. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification.

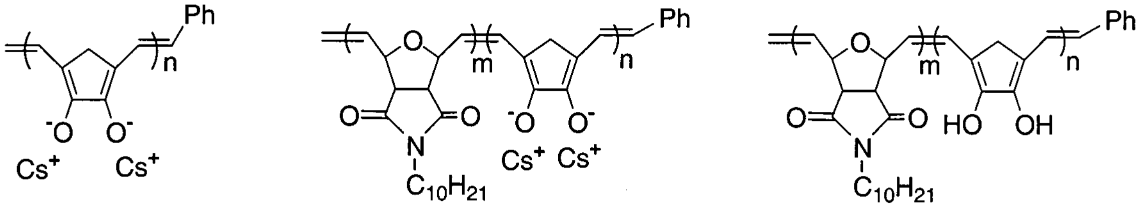
Synthesis of Polymer 6. Catalyst **3** (15 mg, 0.018 mmol) was dissolved in 5 mL of dry THF and stirred for 15 min. It was then added dropwise to monomer **1** (different ratios ranging from 50 to 200 equiv for each equivalent of initiator) with vigorous stirring. The solution was placed in an oil bath at 65 °C. The color of the solution turned from purple to brown in a few minutes, indicating initiation. The reaction was carried out at 65 °C for 12 h. The solution was then cooled to room temperature, and ethyl vinyl ether (600 equiv) was added dropwise. The resulting mixture was stirred for 1 h and precipitated by dropwise addition into heptane. The precipitated polymer was purified by reprecipitation from THF/heptane and dried in vacuo (85% yield). ^1H NMR: δ (CD_2Cl_2) 5.88 (br, 2H), 3.42 (br, 2H), 2.46 (br, 1H) and 1.55 (br, 1H). ^{13}C NMR: δ (CD_2Cl_2) 148.37, 128.80, 128.67, 108.29, 55.28, 55.16 and 32.92. IR (neat): 2936, 1843 (C=O), 1456, 1280, 1236, 1194, 1174, 1105, 1079, 1009, 977, 928, 890, 750, 608 cm^{-1}. MALDI-TOF: repeat unit 221.2 g/mol. GPC data: see Table 1 and Figure 1.

Synthesis of Polymer 7. Catalyst **3** (12 mg, 0.015 mmol) was dissolved in 5 mL of dry CH_2Cl_2 and stirred for 15 min, then added dropwise to monomer **2** (135 mg, 0.605 mmol, 40.3 equiv), and allowed to stir for 12 h at room temperature. Ethyl vinyl ether (600 equiv) was added and the solution stirred for 1 h, followed by precipitation in heptane. The polymer was purified by reprecipitation from CH_2Cl_2/heptane and dried in vacuo (90% yield). ^1H NMR: δ (CD_2Cl_2) 6.12 (br, 2H), 4.62 (br, 2H). ^{13}C NMR: δ (CD_2Cl_2) 147.11, 127.25, 104.60, and 86.55. IR (neat): 1843, 1699, 1652, 1558, 1539, 1506, 1197, 1116, 1065, 1010, 985, 969, 908, 745 cm^{-1}. MALDI-TOF: repeat unit 222.98 g/mol. GPC (THF, polystyrene standards): one peak at $M_n = 6.7 \times 10^3$ (calculated $M_n = 9351$) and PDI = 1.16.

Hydrolysis of Polymers 6 or 7. 10 mg of the polymer was dissolved in 2 mL of dry THF, and then 2 mL of degassed H_2O was added. The solution was refluxed for 6 h in a nitrogen atmosphere, during which a dark solid precipitated. The solvent was removed under reduced pressure and the product dried. Polymer **8**: IR (KBr pellet): 3500 and 1650 (broad peaks), 2923, 2852, 1457, 1395, 1261, 1098, 1023, 802 cm^{-1}. Polymer **9**: IR (KBr pellet): 3500 (broad peak), 2961, 2921, 2849, 1709, 1604, 1510, 1433, 1261, 1096, 1021, 805 cm^{-1}. Microanalysis: calculated for $3(C_6H_4O_3)\cdot(THF)\cdot2(H_2O)$: C, 55.00%; H, 5.04%. Found: C, 55.38%; H, 5.25%. MALDI-TOF spectrometry of a LiOH solution of **9**: $[PhCH{=}(C_6H_4O_3)_5{=}CH_2 + 4Li^+]$ 752.9; $[PhCH{=}(C_6H_4O_3)_6{=}CH_2{-}2H^+ + 6Li^+]$: 887.0.

Synthesis of Copolymer 10. Catalyst **3** (15 mg, 0.018 mmol) was dissolved in 5 mL of dry THF and stirred for 15 min and then added dropwise to monomer **1** (161 mg, 0.729 mmol) while stirring vigorously. The solution was placed in an oil bath at 65 °C. After 3 h, an aliquot was taken out of the solution and quenched with ethyl vinyl ether. The remaining solution was cooled to room temperature, and the solvent was evaporated under reduced pressure; then monomer **4** (394 mg, 2.37 mmol) in 5 mL of dry CH_2Cl_2 was added dropwise via a syringe. The solution was stirred at room temperature and monitored by ^1H NMR, which showed the disappearance of **4** after 30 min. Ethyl vinyl ether (600 equiv) was added, along with a small volume of CH_2Cl_2 to prevent precipitation, and the solution was stirred for 1 h. Copolymer **10** was precipitated in methanol, purified by reprecipitation from CH_2Cl_2/heptane, and dried in vacuo (435 mg, 78%). ^1H NMR: δ ($CDCl_3$) 5.84

Chart 2



12 13 14

(br), 5.32 (br), 4.02 (br), 3.87 (br), 3.18 (br), 2.98 (br), 2.80 (br), 2.67 (br), 2.45 (br), 2.30 (br), 2.03 (br), 1.92 (br), 1.58 (br), 1.20 (br). ^{13}C NMR: δ ($CDCl_3$) 171.28, 148.15, 134.77, 134.18, 132.87, 131.76, 128.40, 107.98, 67.30, 54.98, 46.57, 44.06, 43.52, 42.20, 41.33, 36.67, 35.80, 21.05. IR (neat): 2944, 1841 and 1740 (C=O), 1456, 1385, 1365, 1238, 1104, 1077, 1032, 1010, 971, 890, 751, 605 cm^{-1}. GPC (THF, polystyrene standards): the homopolymer (isolated from the quenched aliquot) gave a peak of $M_n = 8.6 \times 10^3$ (calculated $M_n = 8944$) and PDI = 1.09; the copolymer trace shifted to $M_n = 4.4 \times 10^4$ (calculated M_n = 30 535) and PDI = 1.38.

Synthesis of Copolymer 11. Catalyst **3** (15 mg, 0.018 mmol) was dissolved in 5 mL of dry THF, stirred for 15 min, and then added dropwise to monomer **1** (201.6 mg, 0.912 mmol) while stirring vigorously. The solution was placed in an oil bath at 65 °C. After 3 h, half of the solution (2.5 mL) was removed and quenched with ethyl vinyl ether. The remaining solution was cooled to room temperature, and then monomer **5**[16] (exo isomer, 140 mg, 0.456 mmol) in 2.5 mL of dry THF was added dropwise via a syringe. The solution was stirred at room temperature and monitored by ^{1}H NMR (aliquots in CD_2Cl_2), which showed the disappearance of **5** after 1 h. Ethyl vinyl ether (600 equiv) was added, and the solution was stirred for 0.5 h. Copolymer **11** was precipitated in methanol, purified by reprecipitation from THF/hexanes, and dried in vacuo (250 mg, 75%). ^{1}H NMR: δ (CD_2Cl_2) 6.09 (br), 5.88 (br), 5.82 (br), 4.95 (br), 4.42 (br), 3.46 (br), 3.31 (br), 3.23 (br), 2.25 (br), 1.81 (br), 1.55 (br), 1.25 (br), 0.87 (br). ^{13}C NMR: δ (CD_2Cl_2), 175.77, 148.20, 131.21, 108.05, 81.18, 52.58, 44.62, 39.08, 32.11, 30.27, 29.71, 29.52, 29.36, 27.83, 27.02, 22.91, 14.13. GPC (THF, polystyrene standards): homopolymer (isolated from the quenched aliquot) $M_n = 9.1 \times 10^3$ (calculated M_n = 8944) and PDI = 1.10; the copolymer $M_n = 4.8 \times 10^4$ (calculated M_n = 24 194) and PDI = 1.20.

Preparation of 12, 13, and 14 for UV/vis/NIR Characterization (Chart 2). Polymer **12**: Polymer **6** (6 mg) was dissolved in CH_2Cl_2 (1 mL) and was spin-coated on quartz slides to give transparent films. Aqueous CsOH solution (0.1 N) was added dropwise to cover the whole surface of the slide (slide in 45° position). The color of the polymer film changed to pale gray immediately. The slide was then washed with deionized water and dried. Copolymer **13**: In a screw-capped vial equipped with a stirring bar, copolymer **11** (1 mg) was dissolved in THF (1 mL) and stirred for 5 min. Aqueous CsOH solution (0.005 N, one drop) was added while stirring to the colorless solution. The color of the solution became dark purple immediately. An aliquot was taken out of the solution, diluted with THF, and transferred to a quartz cell. Copolymer **14**: 1 mg of copolymer **11** was dissolved in 1 mL of dry THF, and then 1 mL of degassed and deionized H_2O was added. The solution was stirred at room temperature under a nitrogen atmosphere for 4 days and turned dark red-purple.

3. Results and Discussion

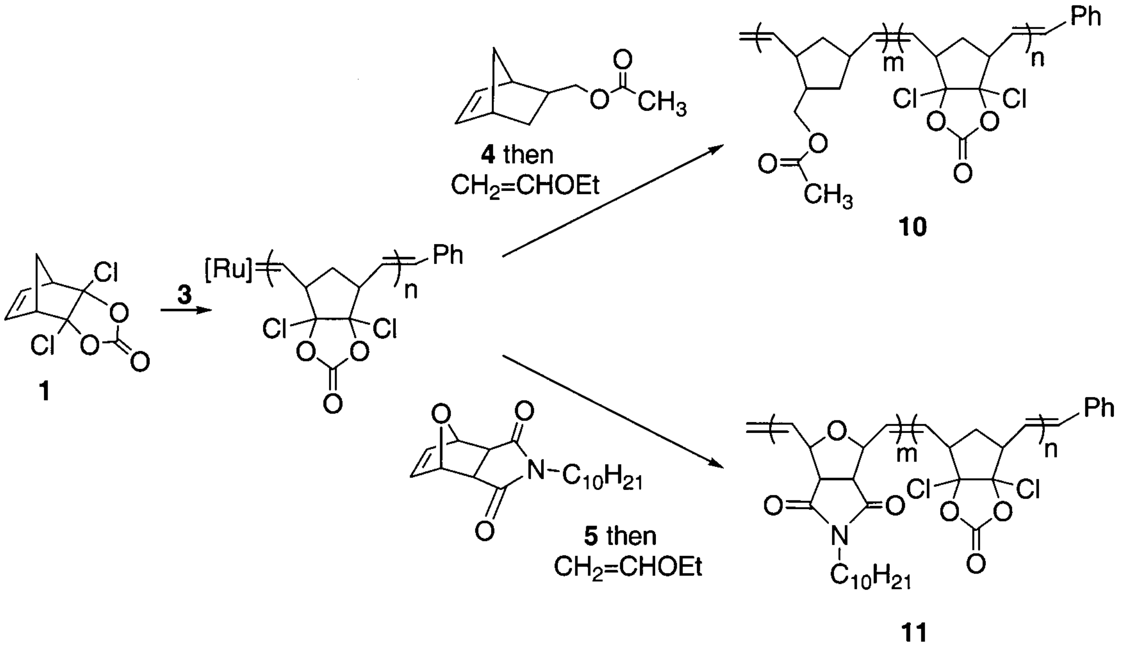
Homopolymer Synthesis. The ring-opening metathesis polymerization of monomer **1** (carbonate group endo) with the Grubbs ruthenium alkylidene initiator **3**[15] (50:1 ratio) was examined in THF at 65 °C for 12 h (Scheme 1). This results in the formation of polymer **6**, with conversions ranging from 90 to 95% (by ^{1}H NMR). The reaction can be quenched with the addition of ethyl vinyl ether, and polymer **6** can be isolated by precipitation with heptane (85% yield). Polymer **6** is soluble in a range of organic solvents (e.g., CH_2Cl_2, THF, DMSO) and has been characterized by ^{1}H and ^{13}C NMR (75% trans), FTIR, and MALDI-TOF mass spectrometry.

Monitoring the polymerization of **1** by ^{1}H NMR (d_8-THF) reveals the rapid disappearance of the alkylidene peak (20.2 ppm)[15] of the initiator and the appearance of a broad signal at 19.6 ppm which is due to the α-alkylidene proton of the propagating polymer chain. The latter resonance persists throughout the entire polymerization process at 65 °C and does not diminish even upon allowing the resulting solution to stand at room temperature for 24 h.[17] This is an indication that the growing polymer chain remains living throughout the polymerization and that chain termination/transfer is slow. The polydispersities of **6** have been determined by GPC to be quite narrow (1.06−1.10, Table 1),[18] and a plot of the average molecular weight of the polymer against the monomer:initiator ratio shows a linear relationship (Figure 1). All these findings provide strong evidence for the living nature of this polymerization.

It is of note that ROMP reactions using ruthenium alkylidene catalysts have almost exclusively been carried out in CH_2Cl_2, CH_3OH, or H_2O as solvents/dispersants.[4] In the case of monomer **1**, however, the ROMP reaction in CH_2Cl_2 at room temperature gave polymers in low yields and with significantly higher polydispersities (e.g., PDI = 1.8). Using THF as solvent allowed for the attainment of higher temperatures, which proved necessary for **1**, likely because of the endo arrangement of the carbonate moiety in this monomer. In addition, a number of studies have shown that THF may enhance the living character of ROMP reactions. This coordinating solvent has been shown to accelerate initiation in the case of the Ru catalyst **3**[19] and to slow propagation in studies with the Mo catalyst (Mo(NAr)($CHCMe_2Ph$)-[$OCMe(CF_3)_2$]$_2$).[20] Indeed, the ROMP of **1** with catalyst **3** in THF (65 °C, 12 h) yields polymers with narrow molecular weight distributions and in high yields (vide supra).[21] These studies demonstrate that THF can be used as a solvent for living ROMP reactions, allowing for an even larger spectrum of functionality in ROMP monomers.

To test the generality of this method for the preparation of a variety of dichlorocarbonate containing polymers, the ROMP of oxanorbornene monomer **2**[10] (carbonate group exo) was examined (Scheme 1). The reaction of **2** (40.3 equiv) with initiator **3** in CH_2Cl_2 at room temperature for 12 h results in nearly complete conversion to polymer **7** (^{1}H NMR). This previously unreported polymer can be obtained in 90% isolated yield and was characterized by ^{1}H and ^{13}C NMR (70% trans), FTIR, and MALDI-TOF spectrometry. Polymer **7** is soluble in CH_2Cl_2 and THF, and its GPC trace shows a narrow molecular weight distribution (M_n =

Scheme 2



6.7×10^3, PDI = 1.16), consistent with the generation of **7** via a living ROMP process.

Synthesis of Block Copolymers. The living nature of the ROMP of **1** suggested this system may allow for the novel controlled incorporation of dichlorocarbonate units into block copolymers (Scheme 2). We thus examined the generation of block copolymers containing poly(**1**). Monomer **1** (40 equiv) was reacted with initiator **3** in THF at 65 °C for 3 h. A ^{1}H NMR spectrum of the product in CD_2Cl_2 reveals the presence of the α-alkylidene signal of the propagating chain (19.3 ppm). An aliquot of this solution was quenched and precipitated, and its GPC trace shows an average molecular weight $M_n = 8600$ g/mol and PDI = 1.09. To the remaining solution of poly(**1**) in CD_2Cl_2 was added monomer **4**[14] (130 equiv). ^{1}H NMR reveals the complete reaction of monomer **4** after 30 min at room temperature and the continued presence of the α-alkylidene proton signal of the growing polymer. After quenching and precipitation, GPC analysis of copolymer **10** shows the disappearance of the homopolymer peak at $M_n = 8.6 \times 10^3$ g/mol and the presence of a single peak at $M_n = 4.4 \times 10^4$ g/mol and PDI = 1.38.[22] The ^{1}H NMR of the copolymer ($CDCl_3$) contains two olefinic peaks with very similar chemical shifts to those of the individual homopolymers (5.32 and 5.84 ppm, 5:1 ratio). In addition, the IR spectrum of **15** shows two peaks in the carbonyl region at 1841 cm^{-1} (C=O in **6** is 1843 cm^{-1}) and 1740 cm^{-1} (C=O in poly(**4**) is 1737 cm^{-1}), confirming the identity of **10** as poly[**1**-*block*-**4**]. This prompted us to generate another block copolymer **11** using monomer **5** (exo isomer)[16] in a similar fashion to give poly-[**1**-*block*-**5**]. The presence of the long alkyl chains (monomer **5**) along the backbone of the second block provides the copolymer with amphiphilic character, hence allowing for the possibility of self-assembly in solution. Thus, the ROMP of **1** gives efficient access to diblock copolymers containing a precursor block to a conjugated polymer and greatly simplifies typical procedures employed to generate these materials.[3]

Hydrolysis of the Precursor Polymers. Feast and Harper[11] have previously reported the ROMP of monomer **1** using the catalyst $WCl_6/Sn(CH_3)_4$, and the acid- or base-promoted hydrolysis of the obtained polydisperse poly(**1**), to lead to the insoluble conjugated diol form. The conductivity of the hydrolyzed form was found to increase significantly, consistent with conversion of poly(**1**) to its conjugated diol form.[11] We have conducted studies on the conversion of precursors **6** and **7** to their conjugated form. The hydrolysis of these polymers in a boiling THF/water mixture (1:1) gives polymers **8** and **9** as dark insoluble solids (Scheme 1). The IR spectra of these polymers show disappearance of the carbonyl band of the dichlorocarbonate group at 1843 cm^{-1} and the appearance of broad peaks around 1650 and 3500 cm^{-1} (OH bending and stretching) for all polymers obtained. No new carbonyl band is apparent, suggesting the complete conversion to the conjugated enol forms **8** and **9**. The insolubility of polymer **8** prevented any further spectral characterization. However, polymer **9** was found to be sparingly soluble in aqueous LiOH and showed the correct repeat unit by MALDI-TOF mass spectrometry of the resulting solution.[23]

Interestingly, hydrolytic conversion of the precursor polymers can be carried out at room temperature using aqueous base and allows for the development of a new mild route to the conjugated polymers. Colorless thin films of **6** were spin-cast from dichloromethane on quartz substrate. Addition of 0.1 N aqueous CsOH causes immediate darkening to a pale gray color, indicating the onset of hydrolysis. Under these conditions, polymer **6** is likely to be obtained in its deprotonated anionic form **12**, due to the acidity of its hydroxyl protons.[11] UV/vis/NIR spectra of the resulting film show a low-energy absorption band centered at $\lambda_{max} = 1242$ nm (Figure 3). This is consistent with the generation of a low-band-gap conjugated polymer (0.85 eV band gap derived from the energy absorption edge of the band).

In addition, hydrolysis of the precursor block copolymer **11** was carried out by dissolving the copolymer in THF and adding a dilute aqueous CsOH solution (0.005 N). Interestingly, the solution immediately darkens to a deep purple color, but the resulting conjugated copolymer **13** remains soluble in the medium. This

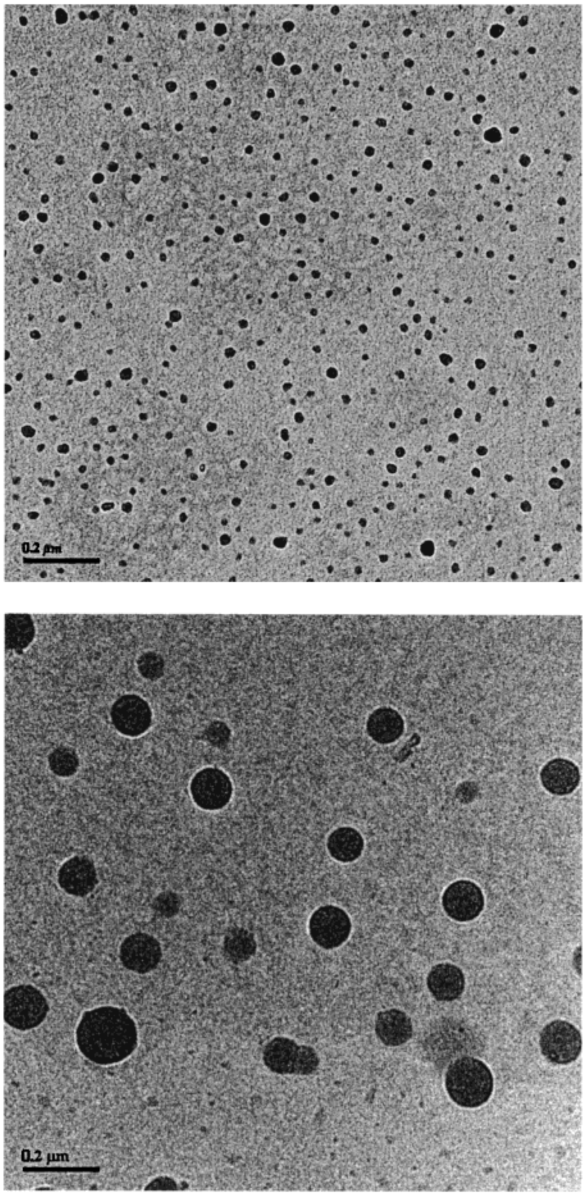


Figure 2. Transmission electron micrographs (TEM) of copolymer **15**: (a, top) in THF:hexanes, 1:2 and (b, bottom) in THF:water, 1:0.2.

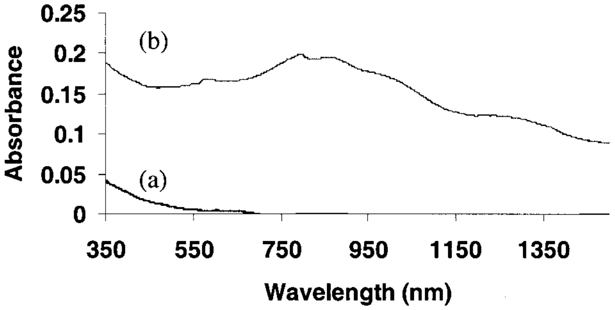


Figure 3. UV/vis/NIR of homopolymer **6**: (a) spin-coated film on quartz and (b) after treatment with 0.1 N CsOH.

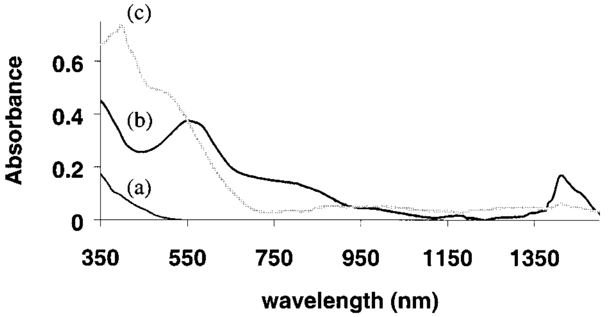


Figure 4. UV/vis/NIR of copolymer **11**: (a) in THF, (b) after addition of aqueous 0.005 N CsOH to **11**, and (c) after addition of deionized water to **11**.

indicates that the poly(**5**) block in this conjugated diblock copolymer acts as a solubilizing moiety. UV/vis/NIR spectra of the solution show a low-energy band at $\lambda_{max} = 1409$ nm and a corresponding band gap of 0.82 eV (Figure 4). Similar spectral features can also be observed for the neutral conjugated diblock **14**, which was generated by stirring a solution of copolymer **11** in THF/H_2O (3% H_2O in THF v/v, room temperature, 4 days) (Figure 4).

The above studies demonstrate that precursors **6** and **11** give ready access to a new class of low-band-gap conjugated polymers and block copolymers. To our knowledge, **13** is the first example of a diblock copolymer containing a low-band-gap conjugated block.[24] These features, in addition to their ease of generation, provide the basis for a range of novel applications of these polymers as high-performance components for electronic and optoelectronic devices.[3]

Preliminary Studies on Micelle Formation. With block copolymers containing the dichlorocarbonate units in hand, studies were performed on their self-organization into micellar aggregates.[1] In copolymer **11**, the two blocks possess different solubility behaviors. While both are soluble in THF, the homopolymer of **1** (polymer **6**) is soluble in polar solvents such as methanol, while the hydrophobic homopolymer of **5** is soluble in hexanes. Micelle solutions of **11** were prepared by adding hexanes slowly to a solution of copolymer **11** in THF, until the observed turbidity indicated the onset of aggregation (0.3% w/w in 1:2 THF/hexanes). Transmission electron micrographs of the resulting solution of copolymer **11** are shown in Figure 2a. The TEM studies show that micellar aggregates of spherical shape are formed. The sphere diameters show a monomodal distribution, ranging from 16 to 27 nm, with an average of 21.9 nm and a standard deviation of 5.4 nm (computerized image analysis). In the 1:2 THF/hexane mixture, it is expected that copolymer **11** self-assembles in a way to expose the hydrophobic poly(**5**) block to the solvent and to minimize the interaction between poly(**1**) and the hexane-rich medium. Thus, the core is expected to be the dichlorocarbonate-containing polymer and the corona the hydrophobic block. The self-assembly of copolymer **11** was also studied in THF/H_2O (1:0.2). Spherical particles of larger diameter (average of 85.2 nm, standard deviation 19.0 nm) are obtained (TEM, Figure 2b), indicating possible aggregation into large compound micelles (LCM). With micellar formation both possible in more hydrophobic (THF/hexane) and more hydrophilic media (THF/H_2O), precursor copolymer **11** is expected to generate a range of aggregates containing nanodomains of conjugated polymers. These are anticipated to be useful both as fundamental probes for the behavior of conjugated polymers confined in micellar structures and as a facile method to pattern conjugated polymers on the nanoscale for applications in novel optical and electronic devices.[3]

4. Conclusion

We have shown that the living ring-opening metathesis polymerization of **1** and **2** provides an efficient method to generate conjugated polymer precursors with low polydispersities. We have also demonstrated the suitability of this method for the synthesis of block copolymers and have shown that poly-[**1**-*block*-**5**] can self-assemble to form spherical micelles. Hydrolysis studies of the precursor polymers have resulted in the generation of a new class of low-band-gap conjugated homopolymers and block copolymers. We are currently studying the properties and functionalization of these conjugated materials as well as their self-assembly into micellar aggregates containing conjugated domains.

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Supporting Information Available: MALDI-TOF MS spectra of polymers **6** and **7**; kinetic data and NMR spectra of the polymerization of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(16) Monomer **5** can be polymerized using **3** to give homopolymers with low polydispersities. Dalphond, J.; Bazzi, H. S.; Kahrim, K.; Sleiman, H. F., manuscript in preparation.

(17) See Supporting Information.

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(21) Preliminary kinetic studies (^{1}H NMR) were performed on the reaction of **1** with catalyst **3** (50:1 ratio) in d_8-THF at 65 °C. Under these conditions, monomer consumption did not follow a first-order rate law.[17] However, all our data are consistent with the living ROMP of **1** (monomodal molecular weight distributions, low PDI's, linear dependence of M_n on monomer/initiator ratio, propagating alkylidene detected by NMR throughout polymerization). The kinetics obtained may be the result of using a relatively low monomer/initiator ratio[18] and are under further investigation.

(22) The increase in PDI for copolymer is most likely due to the polymerization step of norbornene ester **4**; indeed, the PDI for the ROMP homopolymer of **4** was found to be 1.67.

(23) Polymer **9** also gave a correct elemental analysis (See Experimental Section).

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