Norbornenyl-Substituted Thiophenes and Terthiophenes: Novel Doubly Polymerizable Monomers

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ABSTRACT: The synthesis and polymerization of norbornenyl-substituted thiophenes (**2** and **4**) and terthiophenes (**3** and **5**) are reported. All monomers readily undergo ring-opening metathesis polymerization (ROMP) using the ruthenium catalyst, $Cl_2(PPCy_3)_2$ Ru=CHPh (**1**). The terthienyl monomers **3** and **5** were directly polymerized onto the surface of a gold electrode via electrochemical oxidation of the capping terthienyl units, while the direct electrochemical homopolymerization of **2** was not achievable, which is consistent with previous literature reports for similarly substituted thiophenes. Chemical polymerization of the terthienyl segments of **3** and **5** using $FeCl_3$ yielded insoluble materials. Finally, polymers obtained from the ROMP procedure were further cross-linked using the oxidative techniques described above, yielding highly networked materials which displayed an increase in thermal stability and electrical conductivity relative to their single-chain polymeric precursors.

Introduction

Conducting organic polymers have received a great deal of attention due to their potential in a number of technological applications.[1] Processability, corrosion resistance, and availability of inexpensive starting materials make these polymeric materials important synthetic targets.[1] In particular, polymers obtained from the oxidative polymerization of thiophenes,[2] bithiophenes,[3] and terthiophenes[4] have been intensely studied because of the highly conjugated nature of the resulting materials. Poly(thiophenes) are readily synthesized either by simple chemical oxidation[5] or via electrochemical methods[6] and have been used in the development of electronic devices,[7] energy storage batteries,[8] photochromic devices,[9] sensors,[10] and nonlinear optical devices[11] and in the modification of electrodes.[12] Numerous substituted thiophenes have been reported, ranging from those which make the resulting polymers water-soluble and self-doped[13] to those containing transition metals which interact with either the substituents on the polymer backbone or the propagating thienyl units.[14]

Recently, we reported on the synthesis of a novel class of nanoparticle−polymer hybrid materials.[15] In this approach, we used ring-opening metathesis polymerization (ROMP),[16] and specifically the ruthenium catalyst **2**,[17] to functionalize 2−3 nm gold nanoparticles[18] with redox-active norbornenyl-modified ferrocenes. We envision that other generations of these hybrid materials will be useful in the fabrication of nanoscale structures that are the basis for electronic and diagnostic devices. These polymer-coated nanoparticles are dispersible in a variety of solvents and, hence, are quite easy to manipulate and process. Many oligo- and poly(thiophene) materials are highly insoluble and, therefore, difficult to process. We rationalized that, by forming conducting polymers on the surface of gold nanoparticles, we could isolate a new form of poly(thiophene) with highly desirable properties and processability. Toward this goal, it is desirable to be able to fabricate nanoparticles with conducting polymer shells within the context of our nanoparticle−polymer hybrids. The first step in achieving this objective is to construct doubly polymerizable monomers that can undergo ROMP chemistry followed by a second cross-linking reaction to give a conducting polymer composite. Herein, we report the synthesis of new ROMP monomers that, when ring-opened, serve as precursor polymers to graft copolymers of norbornene and terthiophene. Specifically, the syntheses of norbornenyl-substituted thiophenes (**2** and **4**) and norbornenyl-substituted terthiophenes (**3** and **5**) as well as our subsequent investigations into the reactivity of these novel compounds toward ROMP and thienyl coupling are described. The controlled cross-linking of the ROMP polymers gives materials with conductivities that are within the range of conductivities associated with other poly(thiophenes).[1]

Experimental Section

General Considerations. All reactions were carried out under a dry nitrogen atmosphere using either standard Schlenk techniques or in an inert-atmosphere glovebox unless otherwise noted. Acetonitrile and CH_2Cl_2 were distilled over calcium hydride. Tetrahydrofuran (THF), toluene, and diethyl ether were distilled over sodium/benzophenone. All solvents were distilled under nitrogen and saturated with nitrogen prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification, except for $CDCl_3$, which was distilled over calcium hydride and vacuum transferred into an airtight solvent bulb prior to transfer into the inert-atmosphere glovebox. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 FT-NMR spectrometer (300 MHz for ^1H NMR, 75 MHz for ^{13}C NMR). ^1H NMR data are reported as follows: chemical shift (multiplicity: b = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet, integration, and peak assignments). ^1H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the residual solvent resonances as internal standards, while peak assignments were made using ACD Laboratories software. GC-MS experiments were recorded on a Hewlett-Packard HP 6980 series instrument equipped with an HP-5 column (initial temperature was set at 50 °C for 2 min with a ramp of 20 °C per min and a final temperature of 280 °C). High-resolution electron impact mass spectrometry (HREIMS) data were obtained on a VG 70-SE instrument. Gel permeation chroma-

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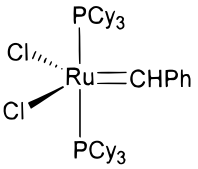
tography (GPC) was performed on a Hewlett-Packard HP1090 liquid chromatograph equipped with two Supelco Progel-TSK columns in series and an in-line UV detector. (Column dimensions were 30 cm × 7.5 mm × $^3/_8$ in. (length × i.d. × o.d.); THF was used as the eluent at a flow rate of 1.0 mL/min, and the instrument was calibrated with polystyrene standards from Aldrich.) Thermal gravimetric analysis was carried out on a TA Instruments DSC 2920 calorimeter. Cyclic voltammetry was performed on either a Pine AFRDE4 or Pine AFRDE5 bipotentiostat with either a Kipp en Zonen BD90 X−Y or a Linseis LY 1400 recorder. A conventional three-electrode cell was used for all electrochemical experiments (Au/Si working electrode, Ag wire reference electrode, and Pt gauze counter electrode). Elemental analysis was done by Atlantic Microlab Inc., Norcross, GA. All flash column chromatography was carried out using a 56 mm inner-diameter column containing 200 mm of silica gel under a positive pressure of nitrogen, unless otherwise noted. Conductivity measurements were performed on a standard four-point probe apparatus by pressing ~20 mg of polymer into a rectangular pellet (measurements were corrected for pellet size/shape).

Materials. The ruthenium catalyst **1**,[17] 3′-(2-hydroxyethyl)-2,2′:5′,2″-terthiophene,[19] *exo*-5-norbornene-2-carboxylic acid,[20] 2,5-dibromo-3-bromomethyl-thiophene,[21] (2-thienyl)magnesium bromide,[22] and *exo*-5-norbornene-2-ol[23] were synthesized from published procedures. All other reagents were purchased from either the Aldrich Chemical Co. or Lancaster and used without further purification.



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Preparation of *exo*-5-Norbornene-2-yl-2-(3-thiophenyl)acetate (2). In a 100 mL Schlenk flask was added 5-*exo*-norbornene-2-ol (1.10 g, 10 mmol), 3-thiopheneacetic acid (1.42 g, 10 mmol), and *p*-toluenesulfonic acid monohydrate (80 mg, 0.42 mmol). The three solids were dissolved in toluene (60 mL), and a Dean−Stark trap was fitted to the top of the flask. A cold water condenser was placed on top of the Dean−Stark trap, and the mixture was heated to reflux. Over a period of 6 h, the reaction volume was reduced to 20 mL by occasionally collecting solvent from the bottom of the Dean−Stark trap. The mixture was cooled to room temperature, poured into water (50 mL), and extracted with ether (3 × 50 mL). The organic portions were combined, washed with brine (50 mL), dried over sodium sulfate, and filtered into a 500 mL round-bottom flask. The solvent was removed under vacuum using a rotary evaporator. The pale yellow oil was chromatographed on silica using a 1:1 solution of CH_2Cl_2 and hexanes as an eluent to yield the desired product (1.68 g, 7.2 mmol, 72%) as a clear oil. ^1H NMR ($CDCl_3$): 1.40−1.71 (m, 4H, 3- and 7-norbornenyl-H_2), 2.83 (b, 1H, 1-norbornenyl-*H*), 2.91 (b, 1H, 4-norbornenyl-*H*), 3.65 (b, 2H, methylenyl-H_2), 4.70 (d, 1H, 2-norbornenyl-*H*), 5.97 (m, 1H, 6-norbornenyl-*H*), 6.24 (m, 1H, 5-norbornenyl-*H*), 7.05 (d, 1H, 4-thienyl-*H*), 7.15 (b, 1H, 5-thienyl-*H*), 7.30 (m, 1H, 2-thienyl-*H*). ^{13}C NMR ($CDCl_3$): 34.7 (3-norbornenyl-*C*), 36.3 (methylenyl-*C*), 40.7 (4-norbornenyl-*C*), 46.3 (1-norbornenyl-*C*), 47.3 (7-norbornenyl-*C*), 75.8 (2-thienyl-*C*), 122.7 (2-thienyl-*C*), 125.7 (5-thienyl-*C*), 128.5 (4-thienyl-*C*), 132.6 (6-norbornenyl-*C*), 133.9 (3-thienyl-*C*), 141.2 (5-norbornenyl-*C*), 171.3 (carbornyl-*C*). Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02; S, 13.68. Found: C, 66.91; H, 6.15; S, 13.86.

Preparation of 2-(3′-(2,2′:5′,2″-Terthienyl))ethyl *exo*-5-Norbornene-2-carboxylate (3). In a 100 mL Schlenk flask was added 5-*exo*-norbornene-2-acetic acid (450 mg, 3.0 mmol). The flask was placed under nitrogen, and dry CH_2Cl_2 (20 mL) was added via cannula, followed by oxalyl chloride (5 mL of a 2 M solution in CH_2Cl_2, 10 mmol). The mixture was allowed to stir for 2 h at room temperature. The solvent and excess oxalyl chloride were removed under vacuum, and the resulting acid chloride was redissolved in dry diethyl ether (20 mL). In a separate 100 mL Schlenk flask was added 3′-(2-hydroxyethyl)-2,2′:5′,2″-terthiophene (850 mg, 2.91 mmol). The flask was placed under nitrogen, and diethyl ether (20 mL) was added, followed by triethylamine (0.84 mL, 6 mmol). The flask was fitted with a pressure-equalizing dropping funnel. The norbornenyl−acid chloride solution was transferred to the dropping funnel via cannula and subsequently added to the stirring solution of the terthienyl solution dropwise over a period of 10 min. The mixture was stirred for an additional 10 min at room temperature, poured into water (50 mL), and extracted with ether (3 × 50 mL). The organic portions were collected, washed with brine (50 mL), dried over sodium sulfate, and filtered into a 500 mL round-bottom flask. The solvent was removed under vacuum using a rotary evaporator. The resulting oil was chromatographed on silica using 1:1 CH_2Cl_2:pentane as an eluent to yield the desired product (1.15 g, 2.79 mmol, 96%) as a light green oil. ^1H NMR (CD_2Cl_2): 1.32−1.86 (m, 4H, 3- and 7-norbornenyl-H_2), 2.87 (b, 1H, 4-norbornenyl-*H*), 2.98 (b, 1H, 1-norbornenyl-*H*), 3.10 (t, 2H, O−CH_2−CH_2), 4.32 (t, 2H, O−CH_2−CH_2), 6.11 (m, 2H, 5- and 6-norbornenyl-*H*), 7.05 (m, 1H, 4′-thienyl-*H*), 7.10 (m, 2H, 3- and 4-thienyl-*H*), 7.19 (m, 2H, 2- and 4″-thienyl-*H*), 7.26 (d, 1H, 3″-thienyl-*H*), 7.37 (d, 1H, 5″-thienyl-*H*). HREIMS: Calcd for $C_{22}H_{20}O_2S_3$: 412.06. Found: 412.06. Anal. Calcd for $C_{22}H_{20}O_2S_3$: C, 64.04; H, 4.89; S, 23.32. Found: C, 63.41; H, 4.89; S, 23.31.

Preparation of 2,5-Dibromo-3-(*exo*-5-norbornene-2-oxy)methylthiophene (4). In an inert atmosphere glovebox, *exo*-5-norbornene-2-ol (710 mg, 6.45 mmol) was weighed into a 50 mL Schlenk flask. THF (15 mL) was added, and the solution was stirred vigorously while oil-free sodium metal (160 mg, 6.96 mmol) was added to it. The mixture was then taken out of the glovebox, refluxed for 12 h under a nitrogen bubbler, and allowed to cool to room temperature. In a separate 100 mL Schlenk flask, 2,5-dibromo-3-bromomethylthiophene (2.01 g, 6.00 mmol) was dissolved in THF (15 mL), and the flask was capped with a pressure-equalizing dropping funnel. The cooled solution of deprotonated *exo*-5-norbornen-2-ol was then transferred to the pressure-equalizing dropping funnel via cannula filtration and slowly added to the thienyl solution with vigorous stirring over a period of 10 min. The dropping funnel was then replaced with a cold water condenser, and the mixture was refluxed for an additional 12 h under a nitrogen bubbler. Upon cooling to room temperature, the reaction mixture was poured into ether (50 mL) and washed successively with water (50 mL), 0.1 M NaOH (50 mL), 1.0 M HCl (50 mL), and brine (50 mL). The organic layer was collected, dried over sodium sulfate, and filtered through a Buchner funnel. The solvent was removed on a rotary evaporator. Column chromatography of the slightly yellow oil on silica gel with 20% CH_2Cl_2 in hexanes as the eluent gave the desired product (1.88 g, 5.16 mmol, 86%) as a clear oil. ^1H NMR ($CDCl_3$): 1.41−1.71 (m, 4H, 3- and 7-norbornenyl-H_2), 2.82 (b, 1H, 4-norbornenyl-*H*), 2.93 (b, 1H, 1-norbornenyl-*H*), 3.56 (m, 1H, 2-norbornenyl-*H*), 4.40 (m, 2H, O−CH_2), 5.93 (m, 1H, 6-norbornenyl-*H*), 6.20 (m, 1H, 5-norbornenyl-*H*), 6.99 (m, 1H, 3-thienyl-*H*). ^{13}C NMR ($CDCl_3$): 34.53 (3-norbornenyl-*C*), 40.47 (4-norbornenyl-*C*), 46.06 (7-norbornenyl-*C*), 46.50 (1-norbornenyl-*C*), 65.12 (O-CH_2), 80.31 (2-norbornenyl-*C*), 109.59 (2-thienyl-*C*), 111.21 (5-thienyl-*C*), 131.03 (6-norbornenyl-*C*), 133.10 (4-thienyl-*C*), 139.80 (3-thienyl-*C*), 140.87 (5-norbornenyl-*C*). HREIMS: Calcd for $C_{12}H_{12}Br_2OS$: 361.94. Found: 361.92.

Preparation of 3′-(*exo*-5-Norbornene-2-oxy)methyl-2,2′:5′,2″-terthiophene (5). (1,1′-Bis(diphenylphosphino)ferrocene)-$PdCl_2$ (39 mg, 0.05 mmol) was weighed into a 100 mL Schlenk flask containing a magnetic stir bar and fitted with a cold water reflux condenser and an addition funnel. The flask was placed under nitrogen, and a solution of **4** (1.00 g, 2.75 mmol) in dry diethyl ether (20 mL) was added via cannula. The flask was cooled to −20 °C in an acetone/ice bath, and a solution of (2-thienyl)magnesium bromide[25] (1.54 g, 8.22 mmol) in dry diethyl ether (20 mL) was added by addition funnel over a 30 min period. The reaction was allowed to warm to room temperature and then refluxed overnight under a nitrogen bubbler. The excess Grignard reagent was quenched by the slow addition of a saturated solution of aqueous ammonium chloride (40 mL) to the organic layer, followed by washes with water (3 × 50 mL). The organic layer was collected, dried over sodium sulfate, and filtered into a 500 mL round-bottom flask. The solvent was removed under vacuum using a rotary evaporator. The resulting dark brown oil was chromatographed on silica using 1:1 CH_2Cl_2 and hexanes as an eluent to yield the desired product (870 mg, 2.35 mmol, 86%) as a green oil. ^{1}H NMR ($CDCl_3$): 1.47−1.78 (m, 4H, 3- and 7-norbornenyl-*H*$_2$), 2.84 (b, 1H, 1-norbornenyl-*H*), 2.98 (b, 1H, 4-norbornenyl-*H*), 3.65 (m, 1H, 2-norbornenyl-*H*), 4.56 (m, 2H, O−C*H*$_2$), 5.94 (m, 1H, 6-norbornenyl-*H*), 6.20 (m, 1H, 5-norbornenyl-*H*), 7.03 (m, 1H, 4′-thienyl-*H*), 7.09 (m, 1H, 4″-thienyl-*H*), 7.18 (m, 1H, 3-thienyl-*H*), 7.21 (m, 1H, 5″-thienyl-*H*), 7.22 (m, 1H, 4-thienyl-*H*), 7.24 (m, 1H, 2-thienyl-*H*), 7.35 (m, 1H, 3″-thienyl-*H*). ^{13}C NMR ($CDCl_3$): 34.47 (3-norbornenyl-*C*), 40.51 (4-norbornenyl-*C*), 46.19 (7-norbornenyl-*C*), 46.47(1-norbornenyl-*C*), 65.21 (O-*C*H$_2$), 80.42 (2-norbornenyl-*C*), 123.87 (2-thienyl-*C*), 124.65 (5″-thienyl-*C*), 126.15 (3″-thienyl-*C*), 126.61 (4-thienyl-*C*), 126.64 (4′-thienyl-*C*), 127.76 (3 -thienyl-*C*), 127.91 (4″-thienyl-*C*), 132.63 (2′-thienyl-*C*), 133.20 (6-norbornenyl-*C*), 135.07 (5′-thienyl-*C*), 135.67 (3′-thienyl-*C*), 136.28 (5′-thienyl-*C*), 137.02 (2″-thienyl-*C*), 140.80 (5-norbornenyl-*C*). Anal. Calcd for $C_{20}H_{18}OS_3$: C, 64.83; H, 4.90; S, 25.96; Found: C, 64.78; H, 4.99; S, 26.00. GC-MS: retention time 18.73 min, *m*/*z* 370.

ROMP of 2. A solution of **2** (400 mg, 1.7 mmol) in CH_2Cl_2 (2 mL) was injected into a stirring solution of **1** (19 mg, 0.023 mmol) in CH_2Cl_2 (3 mL). The mixture was allowed to stir for 30 min. The polymerization was irreversibly terminated by the addition of ethyl vinyl ether (1 mL), and the volatiles were removed under vacuum using a rotary evaporator. The polymer was precipitated twice from CH_2Cl_2 (2 mL) with pentane (100 mL) and dried under vacuum to yield a clear sticky polymer (**ROMP-poly2**, 352 mg, 88%). ^{1}H NMR ($CDCl_3$): 1.15 (b, 1H), 1.75 (b, 2H), 1.99 (b, 1H), 2.55 (b, 2/3H), 2.65 (b, 2/3H), 2.95 (b, 2/3H), 3.65 (b, 2H), 4.86 (b, 1H), 5.30 (m, 2H), 7.03 (m, 1H), 7.12 (b, 1H), 7.27 (b, 1H). Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02; S, 13.68. Found: C, 66.10; H, 6.00; S, 13.57. GPC analysis: $M_n = 14\,400$; PDI = 1.4.

ROMP of 3. A solution of **3** (400 mg, 0.96 mmol) in CH_2Cl_2 (2 mL) was injected into a stirring solution of **1** (21 mg, 0.026 mmol) in CH_2Cl_2 (3 mL). The mixture was allowed to stir for 30 min. The polymerization was irreversibly terminated by the addition of ethyl vinyl ether (1 mL), and the volatiles were removed under vacuum using a rotary evaporator. The polymer was precipitated twice from pentane (100 mL) and dried under vacuum to yield a light green powder (**ROMP-poly3**, 328 mg, 82%). ^{1}H NMR ($CDCl_3$): 1.10 (b, 1H), 1.57 (b, 1H), 1.85 (b, 1H), 2.00 (b, 1H), 2.50 (b, 2H), 2.65 (b, 1H), 3.05 (b, 2H), 4.28 (b, 2H), 5.26 (b, 2H), 6.95 (b, 1H), 7.01 (b, 2H), 7.12 (b, 2H), 7.18 (b, 1H), 7.29 (b, 1H). Anal. Calcd for $C_{22}H_{20}O_2S_3$: C, 64.04; H, 4.89; S, 23.32. Found: C, 63.92; H, 4.92; S, 23.19. GPC analysis: $M_n = 10\,500$; PDI = 1.6.

ROMP of 4. A solution of **4** (300 mg, 0.82 mmol) in CH_2Cl_2 (2 mL) was injected into a stirring solution of **1** (23 mg, 0.027 mmol) in CH_2Cl_2 (3 mL). The mixture was allowed to stir for 30 min. The polymerization was irreversibly terminated by the addition of ethyl vinyl ether (1 mL), and the volatiles were removed under vacuum using a rotary evaporator. The polymer was precipitated twice from methanol (100 mL) and dried under vacuum to yield a white powder (**ROMP-poly4**, 273 mg, 91%). ^{1}H NMR ($CDCl_3$): 1.15 (b, 1H), 1.60 (b, 1H), 1.94 (b, 2H), 2.53 (b, 2/3H), 2.69 (b, 2/3H), 3.00 (b, 2/3H), 3.65 (b, 1H), 4.35 (b, 2H), 5.35 (m, 2H), 6.94 (b, 1H). Anal. Calcd for $C_{12}H_{12}Br_2OS$: C, 39.59; H, 3.32; S, 8.81. Found: C, 39.67; H, 3.34; S, 8.54. GPC analysis: $M_n = 11\,800$; PDI = 1.4.

ROMP of 5. A solution of **5** (300 mg, 0.81 mmol) in CH_2Cl_2 (2 mL) was injected into a stirring solution of **1** (19 mg, 0.023 mmol) in CH_2Cl_2 (3 mL). The mixture was allowed to stir for 30 min. The polymerization was irreversibly terminated by the addition of ethyl vinyl ether (1 mL), and the volatiles were removed under vacuum using a rotary evaporator. The polymer was precipitated twice from pentane (100 mL) and dried under vacuum to yield a light green powder (**ROMP-poly5**, 270 mg, 90%). ^{1}H NMR ($CDCl_3$): 1.10 (b, 1H), 1.60 (b, 1H), 1.95 (b, 2H), 2.59 (b, 2/3H), 2.71 (b, 2/3H), 3.71 (b, 1H), 4.45 (m, 2H), 5.33 (m, 2H), 6.95 (b, 1H), 7.01 (b, 1H), 7.12 (m, 4H), 7.25 (b, 1H). Anal. Calcd for $C_{20}H_{18}OS_3$: C, 64.83; H, 4.90; S, 25.96. Found: C, 64.33; H, 5.15; S, 26.45. GPC analysis: $M_n = 12\,000$; PDI = 1.3.

Oxidative Polymerization of 3 Using $FeCl_3$. $FeCl_3$ (350 mg, 2.18 mmol) was placed in a 50 mL Schlenk flask containing a magnetic stirring bar, and CH_2Cl_2 (10 mL) was added. A solution of **3** (150 mg, 0.36 mmol) in CH_2Cl_2 (5 mL) was injected into the flask, and the mixture was stirred under nitrogen for 24 h. The reaction solution was poured into MeOH (100 mL) and filtered to give a black powder. The crude polymer was further purified via a Soxhlet extraction (MeOH, 24 h) to yield a dark brown powder (107 mg, 71%).

Oxidative Cross-Linking of ROMP-poly3 Using $FeCl_3$. $FeCl_3$ (234 mg, 1.45 mmol) was placed in a 50 mL Schlenk flask containing a magnetic stirring bar, and CH_2Cl_2 (10 mL) was added. A solution of **ROMP-poly3** (100 mg, 0.24 mmol of terthienyl units) in CH_2Cl_2 (5 mL) was injected into the flask, and the mixture was stirred under nitrogen for 24 h. The reaction solution was poured into MeOH (100 mL) and filtered to give a bright red-orange powder. The crude polymer was further purified via a Soxhlet extraction (MeOH, 24 h) to yield a dark powder (97 mg, 97%).

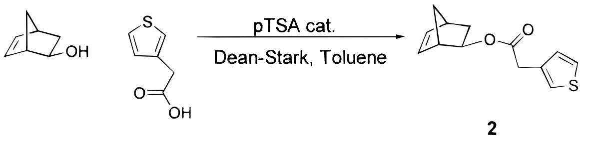
Oxidative Polymerization of 5 Using $FeCl_3$. $FeCl_3$ (263 mg, 1.62 mmol) was placed in a 50 mL Schlenk flask containing a magnetic stirring bar, and CH_2Cl_2 (10 mL) was added. A solution of **5** (100 mg, 0.27 mmol) in CH_2Cl_2 (5 mL) was injected into the flask, and the mixture was stirred under nitrogen for 24 h. The reaction solution was poured into MeOH (100 mL) and filtered to give a black powder. The crude polymer was further purified via a Soxhlet extraction (MeOH, 24 h) to yield a dark brown powder (87 mg, 87%).

Oxidative Cross-Linking of ROMP-poly5 Using $FeCl_3$. $FeCl_3$ (263 mg, 1.62 mmol) was placed in a 50 mL Schlenk flask containing a magnetic stirring bar, and CH_2Cl_2 (10 mL) was added. A solution of **ROMP-poly5** (100 mg, 0.27 mmol of terthienyl units) in CH_2Cl_2 (5 mL) was injected into the flask, and the mixture was stirred under nitrogen for 24 h. The reaction solution was poured into MeOH (100 mL) and filtered to give a bright red-orange powder. The crude polymer was further purified via a Soxhlet extraction (MeOH, 24 h) to yield a dark powder (98 mg, 98%).

Electrochemical Polymerizations/Cross-Linking Experiments. The electrochemical polymerization of **3** (12 mg, 0.029 mmol) was carried out in 0.1 M $TBAPF_6/CH_3CN$ (8 mL) by repeated scanning between −0.3 and 1.8 V at a scan rate of 100 mV/s. The electrochemical polymerization of **5**, the cross-linking of **ROMP-poly3**, and the cross-linking of **ROMP-poly5** were carried out under similar conditions.

Results and Discussion

Monomer Preparation. The ester-linked norbornenyl-substituted thiophene monomer **2** was prepared in one step by an acid-catalyzed esterification of the commercially available 3-thiopheneacetic acid and *exo*-5-norbornene-2-ol (eq 1). The thienyl starting material was modified in the 3-position to allow for oxidative polymerization, which primarily occurs in the 2,5-



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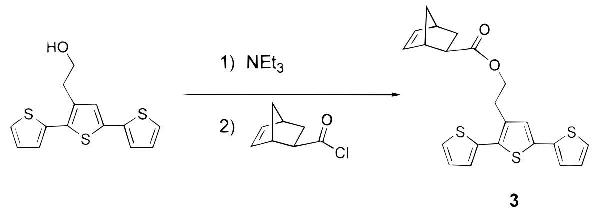
(1)

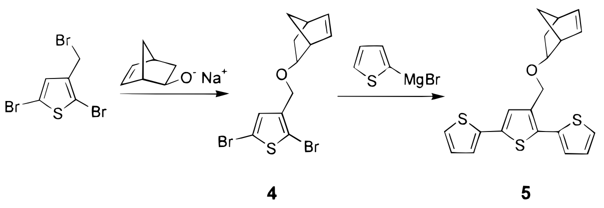
positions.[1] The exo-isomer of the norbornenyl alcohol was chosen in order to maximize ROMP activity.[24] The coupling was carried out under Dean−Stark conditions in refluxing toluene and required less than 6 h to complete, allowing for isolation of the desired product in moderate to high yield after column chromatography on silica gel. This reaction also can be performed by refluxing the reagents in benzene over molecular sieves; however, the yield of the desired product is only about half that found for the Dean−Stark conditions. In both cases, the monomer was purified (as confirmed by ^{1}H NMR spectroscopy and elemental analysis) prior to polymerization.

The ester-linked norbornenyl-substituted terthiophene **3** was prepared via a condensation reaction (eq 2). *exo*-5-Norbornene-2-acetic acid was converted to an acid chloride using oxalyl chloride. The acid chloride route to **3** was chosen over the Dean−Stark method used for the synthesis of **2** in order to prevent the epimerization of the exo-isomer of the norborneneacetic acid. Immediate reaction of this acid chloride with 3′-(2-hydroxyethyl)-2,2′:5′,2″-terthiophene in the presence of triethylamine afforded, in essentially quantitative yield, the desired product in under 20 min.



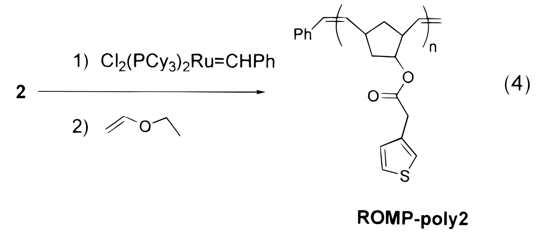
(2)

To form a more robust link between the norbornenyl and thienyl/terthienyl segments, ether-linked compounds were targeted. The syntheses of the ether-linked norbornenyl-substituted thiophene **4** and terthiophene **5** were accomplished using well-established synthetic techniques (eq 3). Displacement of bromine from 2,5-dibromo-3-bromomethylthiophene with the sodium salt of *exo*-5-norbornen-2-ol yielded **4** in high yield. This compound is polymerizable via ROMP of the norbornenyl group and potentially through a dehalogenation polycondensation through the brominated thienyl group.[3] A simple Grignard displacement of the 2,5-dibromide groups of **4** using (2-thiophenyl)magnesium bromide gave **5** in nearly quantitative yield. Both compounds **4** and **5** were isolated via column chromatography in sufficient purity for polymerization purposes.



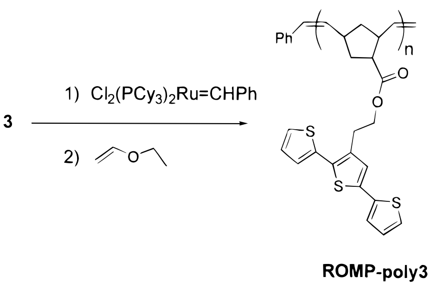
(3)

Ring-Opening Metathesis Polymerizations. Considering the well-documented coordination chemistry of the thienyl moiety for transition metals,[25] and in particular for Ru(II),[26] there was some uncertainty as to whether **2**−**5** would be ROMP-active with the ruthenium catalyst **1**. However, the polymerization of **2** was found to occur readily under conditions used for the polymerization of other nonthienyl-containing norbornenyl derivatives (eq 4).[17] The monomer was dissolved in dry CH_2Cl_2 under an inert atmosphere of nitrogen and injected into a stirring solution of **1** (1.4 mol %). The complete polymerization of the monomer occurred in less than 30 min, as indicated by ^{1}H NMR spectroscopy. After this time, the polymerization was irreversibly terminated with ethyl vinyl ether, a known ROMP terminating agent for catalysts such as **1**.[27] Purification of the polymer was afforded by two precipitations from CH_2Cl_2 with pentane, yielding a polymer (**ROMP-poly2**) with a PDI of 1.4 and an average molecular weight of approximately 14 400 (versus polystyrene standards) as determined by GPC.

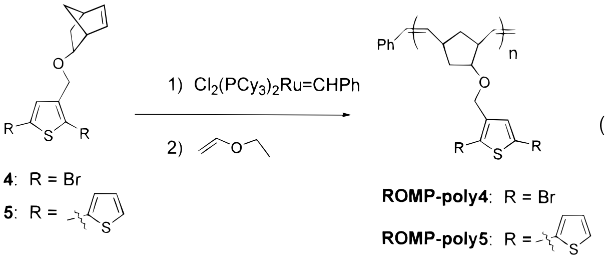


(4)

Monomers **3**−**5** displayed similar ROMP activity to that of **2** (eqs 5 and 6). In each case, the polymers were obtained in quantitative yields after 30 min of reaction time. Their structures and purities were verified by ^{1}H NMR spectroscopy and elemental analyses, respectively. The ether-linked monomers gave polymers that were most easily isolated via precipitation from CH_2Cl_2 with methanol (**ROMP-poly4** and **ROMP-poly5**, respectively), while **ROMP-poly3** was isolated from CH_2Cl_2 after pentane precipitation. The terthienyl-substituted ROMP polymers were light green solids, while the thienyl-substituted ROMP polymers were white. GPC analyses revealed PDIs ranging from 1.3 to 1.6 and M_n's between 10 000 and 12 000 (versus polystyrene standards).

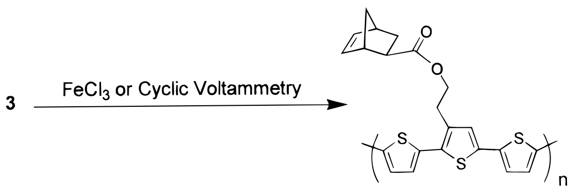


(5)

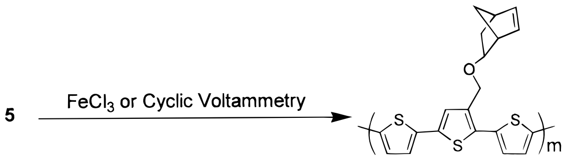


(6)

Oxidative Polymerizations Using $FeCl_3$. A common chemical reagent used to polymerize thienyl compounds is $FeCl_3$.[1] Treatment of either **3** or **5** with 6 equiv of $FeCl_3$ in CH_2Cl_2 for 24 h at room temperature yielded dark brown solids, consistent with the oxidative polymerization of their terthienyl segments (eqs 7 and 8). In a typical preparative procedure, the mixture was poured into MeOH and filtered to give the desired crude product. Purification of the respective polymers was



(7)



(8)

accomplished using a Soxhlet extraction apparatus with MeOH as the solvent. This apparatus allowed for the removal of soluble impurities, as evidenced by the change in color of the MeOH solution from green to clear as it was passed through the Soxhlett thimble over a period of 24 h. The resulting insoluble polymers were obtained in high yield (71−87%). The insolubility of these materials prohibited further spectroscopic characterization.

Electrochemical Polymerizations. Another common route to poly(thiophenes) is to electrochemically oxidize (and hence deposit onto an electrode) monomer starting units.[1] Of the monomers reported in this study, **4** is not a candidate for such a procedure because it is substituted in the 2- and 5-positions with Br. The direct electrochemical homopolymerization of **2** was not achievable under our conditions, a result which is consistent with previous reports of thiophenes substituted with esters in the 3-position.[28] However, the terthienyl monomers **3** and **5** were readily polymerized using similar techniques. This stems from the extended π-structure of the terthienyl moiety, which lowers the oxidation potentials of **3** and **5**, as compared with **2**. The terthienyl unit also is less sterically challenged with respect to coupling in the 2- and 5″-positions, relative to the 2- and 5-positions of a single thienyl unit. Repeated cycling of a small Au electrode between −0.3 and 1.8 V, while immersed in a dilute solution of **3**, resulted in the deposition of a polymer film and a concomitant growth of a redox wave in the cyclic voltammogram (Figure 1). With each scan, more material deposits onto the electrode, resulting in an increase in the anodic and cathodic peak currents associated with the polymer. Similar polymerization results were obtained for **5**.

Polymer Cross-Linking. Unlike the polymers obtained from **3** and **5** using oxidative techniques, **ROMP-poly3** and **ROMP-poly5** were soluble in a number of organic solvents, allowing for the controlled cross-linking of these materials (eq 9). When an Au electrode was immersed in a solution of **ROMP-poly3** while the potential of the electrode was cycled between −0.3 and 1.8 V, an insoluble film with a voltammetric response consistent with cross-linked polymers was deposited onto the electrode (Figure 2). Rapid growth of this film continued with each scan, and similar results were obtained using **ROMP-poly5** as the starting polymer.

$$\left.\begin{array}{l}\textbf{ROMP-poly3}\\ \\ \textbf{ROMP-poly5}\end{array}\right\}\xrightarrow{\text{FeCl}_3\text{ or Cyclic Voltammetry}}\begin{array}{c}\textbf{Cross-Linked}\\ \textbf{Polymers}\end{array}\qquad(9)$$

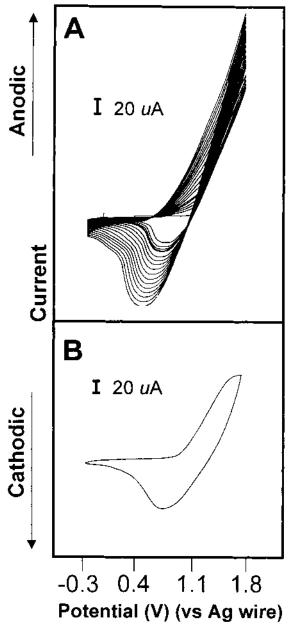


Figure 1. (A) Electrochemical polymerization of **3** and (B) the CV of the resulting polymer (0.1 M TBAPF$_6$ in CH$_3$CN, internal Fc standard).

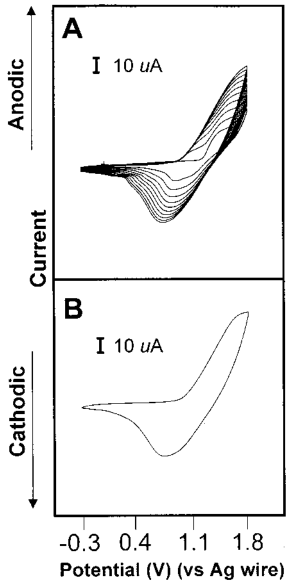


Figure 2. (A) Electrochemical cross-linking of **ROMP-poly3** and (B) the CV of the resulting material (0.1 M TABPF$_6$ in CH$_3$CN, internal Fc standard).

Cross-linking also was achieved by treating **ROMP-poly3** and **ROMP-poly5** with FeCl$_3$. When the polymers were cross-linked in this fashion, their color changed from green to black. The solids were purified and isolated in quantitative yield via a Soxhlet extraction. These materials displayed a general increase in thermal stability, especially at high temperatures, as compared to their ROMP polymer precursors, as demonstrated by a comparison of the thermal gravimetric analysis (TGA) plots of **ROMP-poly5** and its corresponding cross-linked product (Figure 3). The TGA plot of oxidatively polymerized **poly5** over the same temperature range (Figure 3) is essentially the same as that of the cross-linked product of **ROMP-poly5**, suggesting that the two materials are of the same nature. The conductivity of the cross-linked product of **ROMP-poly5**, as measured using a standard four-point probe

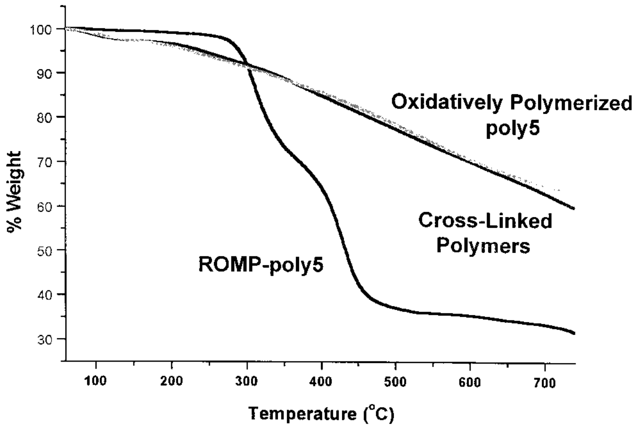


Figure 3. TGA plot of **ROMP-poly5**, its cross-linked product, and the oxidatively polymerized **poly5**.

apparatus on a pressed pellet of the material, also showed an increase as compared to the single-chain polymeric starting material. **ROMP-poly5** showed a conductivity of less than 10^{-9} S cm^{-1}, while the cross-linked material displayed a conductivity on the order of 10^{-4} S cm^{-1}.

Conclusions

The novel doubly polymerizable monomers presented herein constitute a bridge between ROMP and poly(thiophene) chemistries. They provide both a demonstration of the functional group tolerance of **1** and a new route to polymers substituted with terthienyl units. The recent developments in the field of surface initiated ROMP,[15,29] both from flat and nanoparticle gold substrates, could benefit greatly from this development. We envision grafting ROMP polymers from such surfaces using **3**−**5** as monomer feedstocks and then cross-linking the propagating materials to form conducting polymer wires (on flat substrates)[30] and shells (around nanoparticle templates). These studies, as well as a more exhaustive evaluation of the electronic properties of these novel materials, will be discussed in future reports.

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