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Communications

Oxidative Cross-Linking and Grafting of Polymethacrylates with Pendent Thiophene Groups

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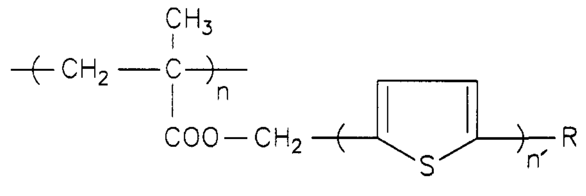
Introduction

In recent years polythiophene and polypyrrole derivatives have received considerable attention owing to their nonlinear optical properties in the neutral state and their high electronic conductivities in the partially oxidized (doped) state,[1–4] but very little has been done to produce polymers with pendent thiophene and pyrrole residues.[5] We are attempting to synthesize a variety of polymethacrylates with pendent thiophene groups (1; n' = 1–6) with the intention of using these polymers to produce new electroactive and nonlinear optical materials. It is anticipated that due to the high reactivity of the α-H of the thiophene, these polymers can be grafted with other thiophene and pyrrole monomers to give interesting composites. Furthermore, since thiophene residues are known to photo-cross-link (rendering the light exposed areas insoluble without loss of electrical conductivity),[6] side-chain polymers with thiophene groups may also be useful in the fabrication of electronically conducting polymeric "wires" or "channels" of defined resistivity for microchips and printed circuitry.



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In this communication we describe the optical properties of doped and undoped poly(2-thienylmethyl methacrylate) (1; n' = 1) and oxidative cross-linking/grafting reactions of this polymer.

Experimental Section

General Considerations. All UV–vis spectra were recorded on a Perkin-Elmer Lambda 6 Model 80524P spectrophotometer. Infrared spectra were recorded on a Mattson Polaris FT-IR Model NU-1000 spectrophotometer using NaCl cells for liquid samples and KBr pellets for polymer (solid) samples at ambient conditions. ^{1}H NMR and ^{13}C NMR spectra were obtained on a 200-MHz Bruker AC-200 spectrometer using deuterated chloroform solvent with TMS internal standard. ^{13}C solid-state NMR (cross-polarization, magic angle spinning) spectra were obtained on a 200-MHz Bruker MSL-200 NMR spectrometer. Molecular weights were estimated by gel permeation chromatography (polystyrene standard) with a Waters Model 410 GPC, eluting THF through a ultrastyrogel column. Thin films of the polymer were spin cast from THF on quartz plates using a Headway Research Inc. Model EC101D spin-coater. Films were spun at 2000 rpm to give a peak optical density of ca. 0.8.

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Materials. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride under Argon atmosphere. Benzene (thiophene free) and all other reagents were obtained from Aldrich Chemical Co. All the solvents were stored over fresh molecular sieves. Freshly distilled methacryloyl chloride (Aldrich) was used.

Monomer. To a solution of 2-thienylmethanol (6.853 g, 0.06 mol) and Et_3N (10 mL) in dry THF (50 mL) cooled to 0 °C, was added methacryloyl chloride (7.952 g, 0.066 mol) over 1 h with stirring. After the solution was stirred for an additional 1 h at 0 °C, H_2O (about 50 mL) was added to dissolve the amine salt. The product was extracted with ether. The combined extracts were washed with aqueous HCl, $NaHCO_3$, H_2O, and saturated NaCl and dried over Na_2SO_4. After removal of the solvent, the product was chromatographed on silica gel with benzene: chloroform (9:1) as eluant. The product (pale yellow oil, 8.958 g, 82%) was the first band off the column and was stored at 0 °C. IR (NaCl) 1719 cm^{-1} (ester CO); ^1H NMR ($CDCl_3$) δ 1.9 (s, 3 H, CH_3), 5.3 (s, 2 H, $-CH_2-$), 5.5 and 6.1 (2 H, $=CH_2$, geminal coupling), 6.95–7.3 (m, 3 H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 166.94 (*C*O), 138.07 ($-C=CH_2$), 135.99 (substituted thiophene C), 128.27 ($CH_2=C$), 126.69, 126.63, 125.95 (3 remaining thiophene C's), 60.72 ($-CH_2-O-$), 18.20 (CH_3); UV–vis (cyclohexane): two bands at λ_{max} 213 nm and λ_{max} 232 nm, MS m/z (rel intensity) 184 (2.5), 183 (5.9), 182 (M^+, 48.1), 164 (8.2), 137 (34.5), 113 (6.0), 97 (100), 69 (27.2).

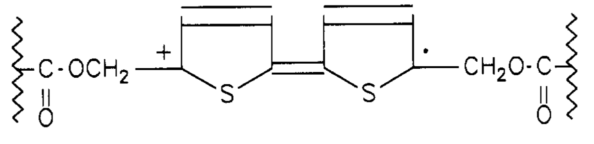
Polymer. The monomer (2.105 g, 11.6 mmol) was combined with azobisisobutyronitrile, AIBN (0.0898 g, 0.55 mmol) in dry benzene (25 mL) and the mixture was stirred at 60 °C for several hours (until most of the monomer disappeared). The polymer was then recovered by addition of the reaction mixture to excess methanol. The polymer was filtered, washed with methanol, and dried in vacuo. The yield of the polymer (2.011 g) was essentially quantitative neglecting mechanical losses. The molecular weight of the polymer was low (M_w = 5000; M_w/M_n = 1.32). A second polymerization with 1.087 g (6 mmol) of monomer in 5 mL benzene with 1.5 mol % AIBN (0.0148 g) yielded a very high molecular weight material ($M_w = 3 \times 10^5$). IR (KBr) 1727 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.0 (m, 3 H, CH_3), 1.77–2.03 (broad, 2 H, $-CH_2-$), 5.1 (s, 2 H, $-CH_2-OCO-$), 7.3–6.95 (m, 3 H, aromatic protons); ^{13}C NMR (CP/MAS) δ 15.91 (CH_3), 45.25 (CH_2), 55.33 ($-CH_2-O-$), 127.85 (unsubstituted thiophene C's), 137.69 (substituted thiophene C), 177.48 (*C*O); UV–vis: one band at λ_{max} 233 nm. Anal. Calcd for $C_9H_{10}O_2S$ (repeat unit): C, 59.32; H, 5.53; S, 17.59. Found: C, 59.22, H, 5.51, S, 17.25.

Results and Discussion

The reaction of 2-thienylmethanol with methacryloyl chloride in the presence of triethylamine base proceeded readily at 0 °C giving high yields of 2-thienylmethyl methacrylate. Free radical polymerization of the monomer gave high yields of colorless poly(2-thienylmethyl methacrylate). The molecular weight of the polymer could be controlled by varying the amount of AIBN initiator and the amount of the solvent used for the reaction. The spectral and elemental analysis of the polymer are consistent with the structure of poly(2-thienylmethyl methacrylate).

Poly(2-thienylmethyl methacrylate), spin-cast from tetrahydrofuran (THF) on quartz plates, gave uniform, colorless films. The UV–vis spectrum of the polymer films shows a band at λ_{max} 237 nm at 25 °C, which is red-shifted by ca. 5 nm as compared to the dilute solutions of the same polymer in organic solvents.[7] The colorless thin films of the polymer, upon doping with $SbCl_5$, turned bright pink-violet. The UV–vis spectrum of the doped polymer films displays a new band at 469 nm and a broad band from ca. 750 nm which grows beyond the range of our monitoring system. The doped films were stable up to 30 min under ambient conditions but turned yellow upon longer exposure to the atmosphere. The doped films, upon treatment with triethylamine, turned yellow and became insoluble in common organic solvents.

We have observed that the absorption spectrum of the radical cation of 2,5′-dimethylbithiophene, generated in CH_2Cl_2 by oxidation of the oligomer with $SbCl_5$, shows a strong band at λ_{max} 446 nm and a broad weak band from 580 to 750 nm.[8] The similarity of these transitions to those observed in the doped films of poly(2-thienylmethyl methacrylate) suggests that the thiophene radical cations, initially generated upon doping of the polymer films, rapidly couple[9] with the neutral species on neighboring chains to yield the radical cations of 2,5′-disubstituted bithiophene, **2**. Thus, the doped films upon neutralization with triethylamine yield the highly cross-linked, insoluble polymer. As expected, the solid-state ^{13}C NMR spectrum of the cross-linked material (^{13}C NMR (CP/MAS) δ 177.6, 137.9, 128.1, 55.6, 45.3, 16.1) is similar to that of poly(2-thienylmethyl methacrylate).



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The doping of a dilute solution (0.1 g/5 mL) of the low molecular weight poly(2-thienylmethyl methacrylate) (M_n ~ 3800) in dry and deaerated thiophene[10] with $SbCl_5$ yielded a soluble polymer (0.14 g after purification) with higher molecular weight (M_w ~ 14300; M_n ~ 8400; M_w/M_n = 1.7). The ^1H NMR spectrum of this polymer is essentially the same as the starting material except it shows an increase in the ratio of aromatic protons: aliphatic protons (6.8:7) as compared to poly(2-thienylmethyl methacrylate) (3:7). This indicates successful grafting of ca. 2 additional thiophene moieties per repeat unit of the polymer. Apparently, oxidative cross-linking does not occur under the conditions of the grafting reaction, because of the higher concentration of the thiophene solvent molecules as compared to the thiophene side chains.

The UV–vis spectrum of $SbCl_5$-doped thin films of the grafted polymer shows two bands at λ_{max} 350 and 528 nm. These are in good agreement with the values reported for neutral α-terthiophene (350 nm) and α-terthiophene radical cation generated in pentasil zeolites (522 nm).[11] Apparently, cross-linking does not occur very efficiently in this case, possibly due to the higher stability of the polymer-bound terthiophene radical cation.

The chemically initiated grafting/cross-linking reactions as well as photochemical and photophysical properties of

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(7) This bathochromic shift could be due to aggregation of thiophene chromophores: Kasha, M. *Radiat. Res.* **1963**, *20*, 55.

(8) These transitions are in accord with those observed in photochemically generated radical cation of bithiophene: Evans, C. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2694.

(9) Radical cations of short-chain oligothiophenes are known to undergo facile dimerization/polymerization with neutral species to yield radical cations of higher oligomers.[3]

(10) The solution was stirred at 35 °C for 30 min, neutralized with triethylamine, and the polymer recovered by addition to methanol. The polymer was purified by size exclusion chromatography (Sephadex G-15) to remove the low molecular weight oligothiophenes.

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several other carbon–carbon chain polymers with pendent thiophene groups are under current investigation.

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Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra of 2-thienylmethyl methacrylate and poly(2-thienylmethyl methacrylate), absorption spectra of doped and undoped THF cast poly(2-thienylmethyl methacrylate) films, absorption spectrum of the radical cation of 2,5′-dimethylbithiophene in CH_2Cl_2, and absorption spectrum of doped thin film of the grafted polymer (8 pages). Ordering information is given on any current masthead page.