

## Synthesis of New Polymers with Polymethacrylate Backbone and Polythiophene Side Chains

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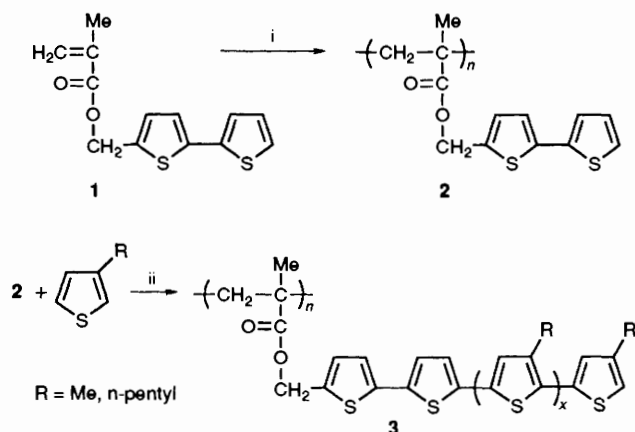
Poly(2,2'-bithienylmethyl methacrylate) has been prepared and used as an initiator in electrochemical and chemical oxidative polymerization of 3-alkylthiophenes.

Polythiophenes are among the most important conductive polymers. Both their syntheses and properties have been investigated extensively.<sup>1,2</sup> Recently, we have discovered that a small amount of 2,2'-bithiophene greatly facilitates the rate of polymerization of thiophene monomers<sup>3,4</sup> and proposed an electrophilic aromatic substitution mechanism for the polymerization.<sup>3</sup> According to this mechanism, the added bithiophene is oxidized first to form a radical cation, because it has a lower oxidation potential than the thiophene monomers. The polymer growth is accomplished by the electrophilic attack of the radical cation on the incoming neutral monomers. The bithiophene essentially functions as an initiator in the polymerization. Therefore, we decided to explore the possibility of using a conventional polymer bearing the bithienyl pendant groups as a polymeric initiator in the polymerization of thiophene monomers to afford new comb-like polymers. In this communication, we report the first synthesis of poly(2,2'-bithienylmethyl methacrylate) and its application as an initiator in both electrochemical and chemical polymerization

of 3-alkylthiophenes to afford new electroactive polymers as illustrated Scheme 1.

2,2'-Bithienylmethyl methacrylate **1** was prepared by reacting methacryloyl chloride with 2,2'-bithienyl methanol<sup>5</sup> in pyridine-methylene chloride at 0 °C. After purification by column chromatography on silica gel with hexane-ethyl acetate (95:5 by volume) as eluant, the product was obtained in 76% yield and was thoroughly characterized.† Poly(2,2'-bithienylmethyl methacrylate) **2** was synthesized by anionic polymerization of **1** using Bu<sup>n</sup>Li as initiator in tetrahydrofuran (THF) at -78 °C.<sup>6,7</sup> As a typical procedure, to a solution of

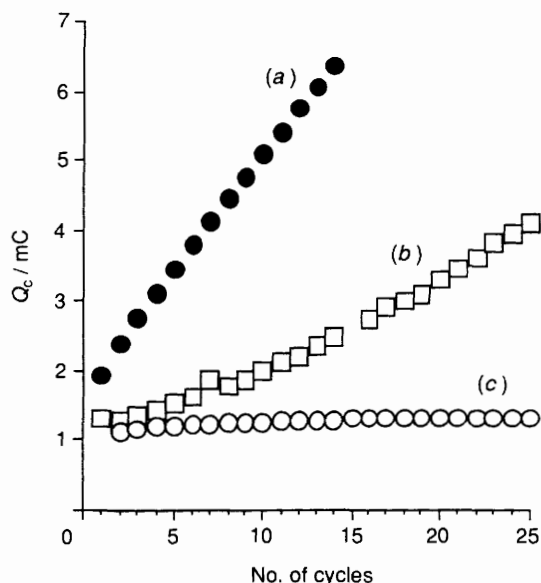
† Selected data for **1**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.2–6.8 (m, 5H, thienyl), 6.2 (s, 1H, vinyl), 5.5 (s, 1H, vinyl), 5.1 (s, 2H, -O-CH<sub>2</sub>-), 1.9 (s, 3H, -CH<sub>3</sub>). IR (thin film ν/cm<sup>-1</sup>): 1730 (C=O stretching), ca. 3100 (thienyl ring C-H stretching), 1640 (vinyl C=C stretching), 1162 (ester C-O stretching). MS: *m/z* 264 (M<sup>+</sup>). Satisfactory elemental analysis was obtained.



**Scheme 1** Reagents and conditions: i,  $\text{Bu}^n\text{Li}$ , THF,  $-78^\circ\text{C}$ ; ii, [O]

2.8 g (10.6 mmol) of **1** in 15 ml of dry THF, precooled to  $-78^\circ\text{C}$  under argon was added  $\text{Bu}^n\text{Li}$  (0.20 ml, 0.50 mmol) solution in hexane. After stirring at  $-78^\circ\text{C}$  for 6 h, the reaction was quenched with methanol. The polymer was isolated as a white solid upon precipitation in methanol and was purified by repeated process of redissolving in THF and precipitating in methanol twice. After drying *in vacuo* at room temp. overnight, 1.8 g of the polymer **2** was obtained in 64% yield. The polymer is soluble in common organic solvents such as methylene chloride, chloroform and benzene. The  $\bar{M}_n$  of the polymer was 6900 with a polydispersity of 1.7 as determined from gel-permeation chromatography in THF using monodispersed polystyrene calibration. The IR spectrum of the polymer shows all the characteristic absorption bands of the corresponding monomer **1** except the disappearance of the C=C stretching band at  $1640\text{ cm}^{-1}$ .  $^1\text{H NMR}$  spectrum of the polymer also shows the disappearance of the vinyl proton signals of the monomer. ‡ Based on the integration of the  $\alpha$ -methyl signals, the polymer consists of 65 syndio-, 8 iso- and 27% hetero-tactic triads, which are close to the literature values for poly(methyl methacrylate) prepared under the similar conditions.<sup>7</sup> In the UV-VIS spectra of both the monomer **1** and the polymer **2**, an absorption band was observed at a  $\lambda_{\text{max}}$  of 310 nm, which is assigned to the  $\pi$ - $\pi^*$  transition of the bithiophene units. All the results are consistent with the proposed structure of the polymer.

The polymer **2** was introduced to both electrochemical and chemical polymerization of 3-methylthiophene and 3-n-pentylthiophene. The electrochemical polymerization was carried out in a single compartment cell with a saturated calomel electrode (SCE) as reference and platinum plates as both working and counter electrodes.<sup>3,4</sup> The electrolyte consisted of  $0.20\text{ mol dm}^{-3}$  3-alkylthiophenes,  $0.10\text{ mol dm}^{-3}$  tetrabutyl ammonium hexafluorophosphate and a small amount ( $0.2$ – $2.0\text{ mmol dm}^{-3}$ , based on the repeating unit) of **2** in methylene chloride. The potential was cycled continuously between  $-0.2$  and  $1.6\text{ V vs. SCE}$  at a sweeping rate of  $100\text{ mV s}^{-1}$ . The cathodic charge ( $Q_c$ ), which is indicative of the amount of electroactive polymer formed on the electrode,<sup>3</sup> was recorded for each potential cycle. Fig. 1 shows some typical plots of  $Q_c$  against number of cycles (*i.e.* reaction time  $t$ ) for the electrochemical polymerization of 3-methylthiophene in the absence and in the presence of the polymer **2**. The plot for the electrochemical oxidation of **2** alone [Fig. 1(c)] is also shown for comparison. The rate of polymer formation (*i.e.*  $dQ_c/dt$ ) in the presence of **2** [Fig. 1(a)] is significantly increased from that in the absence of **2** (b). The



**Fig. 1** Plots of the cathodic charge ( $Q_c$ ) in mC against the cycle number for the electrochemical polymerization of  $0.2\text{ mol dm}^{-3}$  3-methylthiophene (a) in the presence of  $0.2\text{ mmol dm}^{-3}$  poly(2,2'-bithienylmethyl methacrylate) (**2**) and (b) in the absence of **2** and (c) for the polymerization of  $0.2\text{ mmol dm}^{-3}$  of **2** alone. The potential cycling range:  $-0.2$  to  $1.6\text{ V vs. SCE}$  at a sweeping rate of  $100\text{ mV s}^{-1}$ .

increase in the amount of **2** leads to higher rate of polymerization. Furthermore, in the absence of **2**, no appreciable cathodic charge could be measured from the polymerization of 3-methylthiophene at an up-switch potential of  $1.4\text{ V}$  even after cycling for a long time. However, in the presence of a small amount of **2**, the polymerization proceeded at  $1.4\text{ V}$ . The presence of **2** also increases the rate of chemical polymerization of 3-methylthiophene in acetonitrile-methylene chloride solvent with iron(III) perchlorate as oxidant. Similar results were obtained for the polymerization of 3-n-pentylthiophene.

All the observations are in excellent agreement with the predictions based on the polymerization mechanism we have proposed.<sup>3</sup> Thus, the bithiophene pendant group in the polymeric initiator **2** is oxidized first to form a radical cationic species in the system because it has a lower oxidation potential ( $1.3\text{ V vs. SCE}$ ) than that of 3-methylthiophene ( $1.8\text{ V}$ ). The radical cation would then react with neutral monomers leading to the polymer chain growth. Since the slow step of oxidizing the monomers with high oxidation potentials is avoided in the presence of **2**, the overall rate of polymerization is increased as observed. The function of **2** as the initiator is also consistent with the scanning electronic microscopy results. During the electrochemical polymerization, the electroactive poly(3-alkylthiophene) films grew smoothly and uniformly over the electrode surface in the presence of **2** because the bithiophene groups in **2** provided the nucleation sites. In contrast, in the absence of **2** the polymers appeared as discontinuous and irregular coatings.<sup>8</sup> It is interesting to note that both electrochemical and chemical oxidation of **2** alone afforded an insoluble green product, owing probably to the crosslinking reactions between the bithiophene pendant groups.

In summary, we have successfully prepared a new family of polymers with polymethacrylate backbone and electroactive polythiophene side chains. The results also support the mechanism proposed for the oxidative polymerization of thiophene monomers. Because of their unique structural combination, the new polymers could have many interesting electronic, optical and mechanical properties. For example, these polymers are electrically conductive ( $\sigma \sim 0.3$  to  $40\text{ S cm}^{-1}$ ). We are currently investigating the physical and chemical properties of these polymers and exploring their

‡ Selected data for **2**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.2–6.8 (5H, thienyl), 5.0 (2H,  $-\text{O}-\text{CH}_2-$ ), 2.3–1.3 (2H,  $-\text{CH}_2-$ ), 1.1, 0.9 and 0.7 (3H, respectively for iso-, hetero- and syndio-tactic  $-\text{CH}_3$ ). Satisfactory elemental analysis was obtained.

potential applications in the fabrication of non-linear optical and electronic devices.

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