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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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To cite this Article Martinez, F. and Neculqueo, G.(1999) 'Synthesis and Polymerization of 3-Octylsubstituted Thiophene, Bithiophene and Terthiophene', *International Journal of Polymeric Materials*, 44: 3, 265 – 274

To link to this Article: DOI: 10.1080/00914039908009698

URL: <http://dx.doi.org/10.1080/00914039908009698>

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Synthesis and Polymerization of 3-Octylsubstituted Thiophene, Bithiophene and Terthiophene

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(Received 15 April 1998)

The synthesis of 3-octyl-thiophene, 3,3'-dioctyl-bithiophene and 3,4',3''-tri(3-octyl)-terthiophene has been carried out by using the cross coupling reaction, catalyzed by nickel. These oligomers were polymerized by chemical oxidative method with FeCl₃ and electrochemically. The products were characterized by UV, ¹H-NMR, ¹³C-NMR and GPC. The behavior and optical properties of the polymers obtained by different polymerization methodologies is discussed.

Keywords: Thiophene oligomers; alkylthiophene; polyalkylthiophene; spectroscopic characterization

INTRODUCTION

The synthesis of alkylthiophene oligomers is receiving considerable attention due to the application on electronic devices such as transistors, light emitting diode or photovoltaic cells [1–5]. The introduction of the hydrocarbon side chain improves solubility and builds up regio and regular structures for the modulation of the electrical and optical properties of these materials [6–10]. On the other hand, the polythiophene derived from well defined oligomers, where a regio and stereochemical control is desirable, result in polymer with a significantly higher

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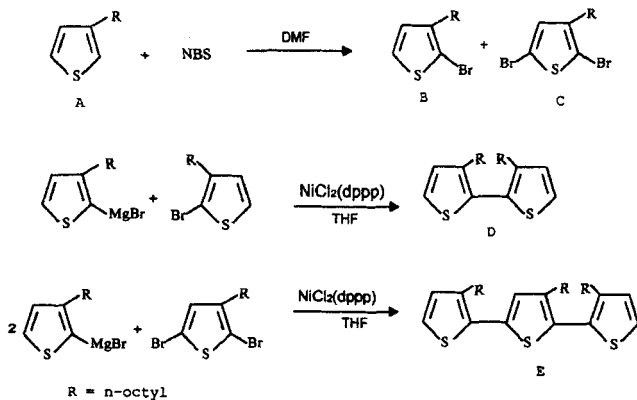
conductivity, due to regiospecific synthesis of $\sim 100\%$ head-to-tail polyalkylthiophene [11–15]. The processability of these polyalkylthiophene is also highly improved due to the flexible side chains which reduces both the chain intractability and the β -coupling during polymerization.

The nickel-catalyzed cross-coupling reaction of thienyl bromides with thienyl magnesium bromides reagents has been employed.

In this paper the spectroscopic data of 3-octylthiophene, 2-bromo-3-octylthiophene, 2,5-dibromo-3-octylthiophene, 3,3'-di(3-octyl)-2,2'-bithiophene and 3,4',3''-tri(3-octyl)-2,2':5',2''-terthiophene is given including UV, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ analysis. The UV-visible absorption spectra and GPC chromatograms of the polymers are discussed in terms of the oligomer size and chemical or electrochemical methodology used for the polymerization.

RESULTS AND DISCUSSIONS

The alkyl substituted thiophene oligomers were synthesized as shown in Scheme 1. In all these couplings reactions the mono or dihalogenated alkylthiophene are required as starting materials, so the monobromo or dibromo oligothiophenes were obtained with *N*-bromosuccinimide (NBS). A high selectivity of bromination can be achieved when the reactions are carried out in dipolar-aprotic solvents



Scheme 1 Synthesis of 3-octyl-thiophene oligomers.

such as dimethylformamide (DMF) and an adequate temperature control reaction.

The cross-coupling reactions afforded some small amount of byproducts and the separation and purification of the reaction mixture was possible by column chromatography. The UV absorption maxima, λ_{\max} of these oligomers have a smaller λ_{\max} than the unsubstituted equivalent thiophene oligomers [16], probably due to the steric hindrance of the alkyl chain which results in a more or less pronounced twisting between the adjacent rings and do not allow a complete coplanarity of the rings. An hypsochromic shift of the longest wave length absorption has been observed for the alkylthiophene [17] and some theoretical calculation have shown that the oligomer conformation change upon introduction of alkyl substituents in different positions [18]. The polymers of the three alkyl substituted thiophenes were all soluble in common organic solvents such as THF; chloroform, dichloromethane, dioxane, *etc.*, giving yellow to orange solutions. The UV-visible spectra of the polymers, in chloroform solution, electrochemically polymerized are presented in Figure 1. Under the polymerization conditions, the polymers showed absorption maxima between 400–430 nm, however, when the chemically and electrochemically polymers are compared, Figure 2, a slightly higher λ_{\max} , is observed for the poly-di(3-octyl)bithiophene chemically obtained, about 20–30 nm, above the electrochemical one. The conjugation length of this polymer would be higher compared with the same polymer obtained *via* electrochemically where the possibility of α , β coupling has been previously demonstrated [19], and by this way the interruption of the conjugation length proceeds. On the other hand, by comparison of the poly(3-octyl)bithiophene with the poly-di(3-octyl)bithiophene, both chemically polymerized, Figure 3, we observe a red shift of about 20 nm for the bithiophene based polymer. This phenomenon confirms the greater conjugation length that is obtained when the starting material is richer in α , α' coupling and can be extended to the trimer of tetramer based polymers.

Table I summarizes the molecular weight (M_n , M_w) of the poly(3-octyl)thiophene and poly-di(3-octyl)bithiophene under different polymerization methods. The GPC chromatograms of electropolymerized polymers (poly-di(3-octyl)bithiophene) showed a fraction of high molecular weight which was not observed in those polymers obtained

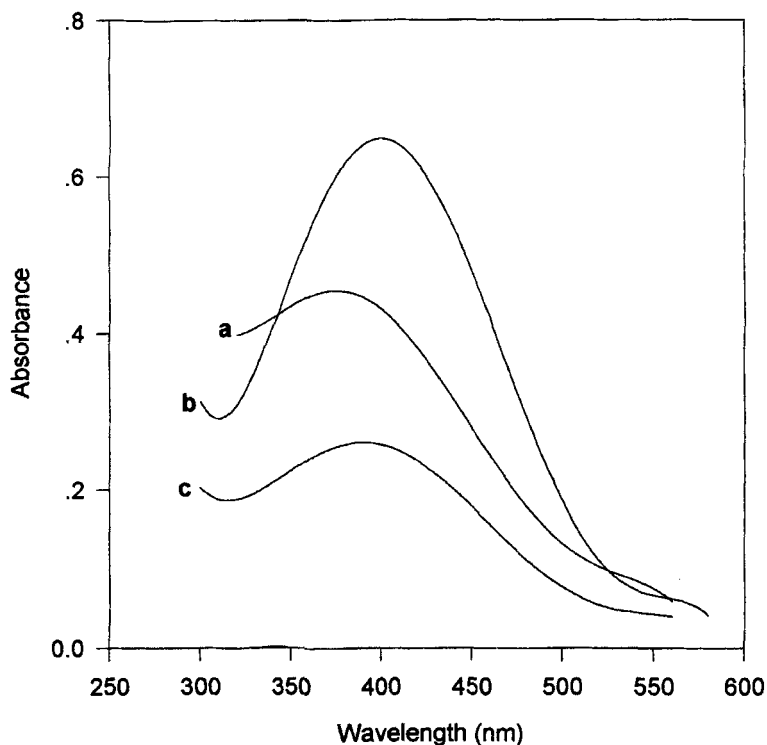


FIGURE 1 Absorption spectra of (a) poly(3-octyl)thiophene (b) poly-di(3-octyl)bithiophene (c) poly-tri(3-octyl)terthiophene, electrochemically polymerized.

via chemical oxidation, Figure 4. This behavior can be associated to the crosslinking process of the electropolymerization which has been observed in other electroobtained alkylthiophene polymers, the one finally produce insoluble materials, when the polymerization time exceeds 30 or more hours [19].

CHARACTERIZATION

The ^1H and ^{13}C -NMR spectral data were obtained from Bruker WP-270 NMR spectrometer. The ultraviolet-visible spectra were recorded using a Perkin Elmer Lambda 11 UV spectrophotometer. The molecular weights were determined using a gel permeation chromatograph

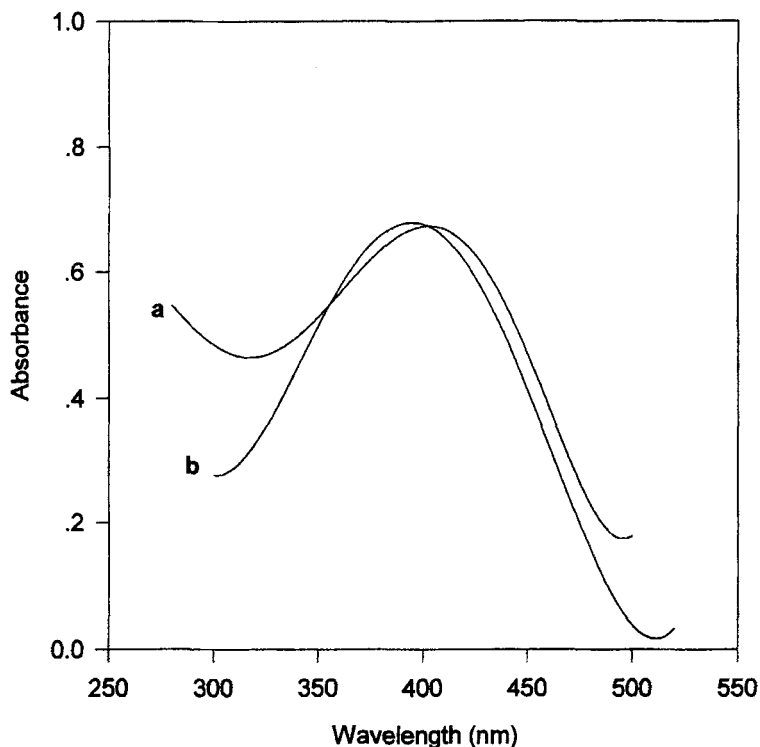


FIGURE 2 Absorption spectra of poly-di(3-octyl)bithiophene (a) chemically polymerized (b) electrochemically polymerized.

(GPC Bruker LC-2B, refractive index detector and $10^3 - 10^5$ Å Bruker columns relative to polystyrene standards). The polymers samples were dissolved and eluted with tetrahydrofuran.

EXPERIMENTAL

3-octylthiophene (a)

Into a dry flask was placed 5.6 g (0.23 mmol) of magnesium turnings and iodine in diethyl ether (60 ml) which was purged with argon. Then 40 ml, (0.23 mol) of 1-bromooctane was slowly added maintaining reflux for 2 h. Then the octylmagnesium bromide obtained was added

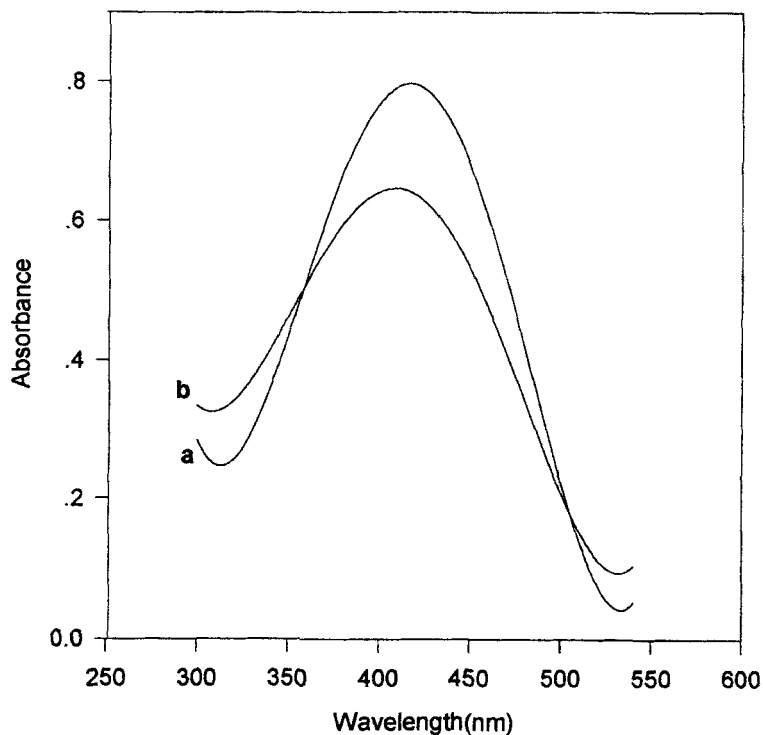


FIGURE 3 Absorption spectra of (a) poly-di(3-octyl)bithiophene (b) poly(3-octyl)thiophene, both chemically polymerized.

TABLE I Gel permeation chromatographic results of chemically and electrochemically thiophene polymers

	<i>Poly(3-octyl)thiophene</i>		<i>Poly-di(3-octyl)bithiophene</i>	
	<i>chemical</i>	<i>electrochem.</i>	<i>chemical</i>	<i>electrochem.</i>
Mw (g/mol)	37.000	59.000	52.000	90.100 *
Mn (g/mol)	23.300	44.000	24.400	93.000 *

*high molecular weight fraction.

slowly to an ice-cooled solution of (18 ml, 0.19 mol) 3-bromothiophene and 100 mg, 0.019 mol) of Ni (dppp) Cl₂ in 80 ml of diethyl ether. The mixture was refluxed for 18 h, cooled to room temperature, and hydrolyzed with 1M HCl. The organic phase was separated, washed

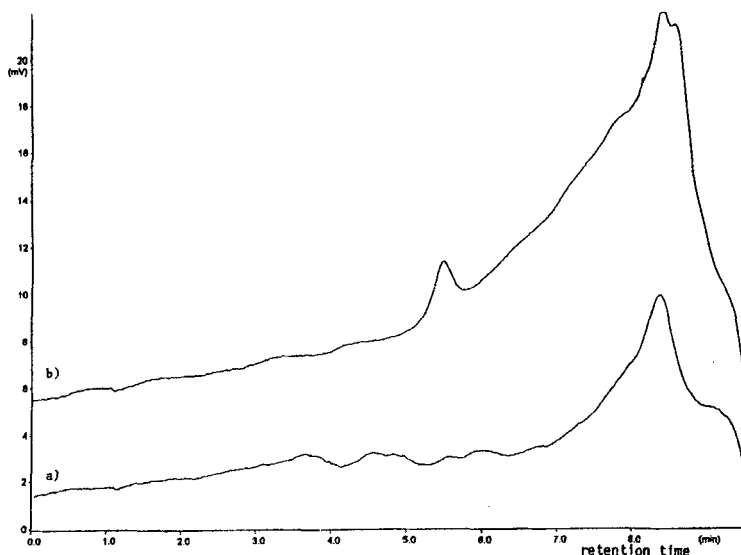


FIGURE 4 GPC chromatograms of poly-di(3-octyl)bithiophene (a) chemically polymerized (b) electrochemically polymerized.

with distilled water until pH neutral, dried over MgSO_4 for 3 h and then the solvent was removed by rotary evaporation. The product was purified by distillation under reduced pressure yielded 23.17 g, 62% of 3-octylthiophene obtained as a liquid colorless. $\lambda_{\text{max}} \text{CHCl}_3$, 236.8 nm. $^1\text{H-NMR}$ (270 MHz, CDCl_3 , ppm) 0.96 (t, 3H); 1.34–1.63 (m, 10H); 2.68 (t, 2H); 6.96 (d, 1H, thiophene ring, H-4); 6.97 (d, 1H, thiophene ring, H-5), 6.98 (s, 1H, thiophene ring, H-2). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , ppm): Aromatics: 143.2 C(3); 128.3 C(4); 125.0 C(5); 119.5 C(2). Aliphatics: 31.89; 30.56; 30.27; 29.71; 29.44; 29.36; 22.68; 14.10.

2-bromo-3-octylthiophene (b)

In the absence of light, to a solution of 16.81 g. (0.085 mol) 3-octylthiophene in 35 ml of dimethylformamide (DMF) were slowly added 15.24 g. (0.085 mol) of *N*-bromosuccinimide in 50 ml of DMF. The mixture was stirred for 40 h, and poured onto ice, and extracted several times with diethyl ether. The organic phase was washed with

distilled water and dried over sodium sulfate, the solvent was extracted and the product was purified by vacuum fractional distillation. The product, 19 g of yellow liquid was obtained in 79% yield. λ_{\max} CHCl_3 , 240.4 nm. $^1\text{H-NMR}$ (270 MHz, CDCl_3 , ppm) 0.9 (t, 3H); 1.25–1.39 (m, 10H); 2.59 (t, 2H); 6.80 (d, 1H, thiophene ring, H-4); 7.19 (d, 1H, thiophene ring, H-5). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , ppm) Aromatics: 141.86 C(3); 128.13 C(4); 125.03 C(5); 108.79 C(2). Aliphatics: 31.96; 31.90; 29.75; 29.39; 29.26; 29.25; 22.69; 14.11.

2,5-dibromo-3-octylthiophene (c)

In the absence of light, to a solution 15.14 g (0.077 mol) of 3-octylthiophene in 30 ml of DMF was slowly added 27.79 g (0.15 mol) of NBS in 130 ml of DMF. The mixture was stirred for 3 h at 40°C, and poured onto ice, and extracted several times with dichloromethane. The organic phase was washed with distilled water and dried over sodium sulfate, the solvent was extracted and the product was purified by vacuum fractional distillation. λ_{\max} CHCl_3 , 245.2 nm. $^1\text{H-NMR}$ (270 MHz, CDCl_3 , ppm) 0.91 (t, 3H), 1.30 (m, 10H), 1.53 (m, 2H), 2.52 (t, 2H), 6.78 (s, 1H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , ppm) Aromatics: 142.90 C(3); 130.87 C(4); 110.28 C(2); 107.90 C(5). Aliphatics: 31.86; 29.56; 29.45; 29.33; 29.21; 29.11; 22.26; 14.13.

3,3'-di(3-octyl)-2,2'-bithiophene (d)

3.9 g, (0.014 mol) of 3-octylthiophene magnesium bromide was added slowly to an ice-cooled solution 3.1 g (0.011 mol) of 2-bromo-3-octylthiophene and 100 mg. of $\text{NiCl}_2(\text{dppp})$ in 60 ml THF. The mixture was refluxed for about 40 h, hydrolyzed with 1 M HCl, washed with distilled water, dried with MgSO_4 and extracted the solvent. The product an brown oil was purified by silica gel chromatography using hexane-chloroform mixture yielded 3,3'-dioctyl bithiophene as a slightly yellow liquid (oil). λ_{\max} CHCl_3 , 247.6 nm. $^1\text{H-NMR}$ (270 MHz, CDCl_3 , ppm) 0.9 (m, 6H), 1.2 (m, 20H), 1.5 (m, 4H), 2.5 (m, 4H), 6.93 (d, 2H), 7.24 (d, 2H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , ppm): Aromatics: 142.32 C(3); 128.76 C(4); 128.52 C(2); 125.87 C(5). Aliphatics: 31.91; 30.76; 29.47; 29.44; 29.26; 28.33; 22.70; 14.13.

3,4',3''-tri(3-octyl)-2,2':5',2''-terthiophene (e)

3.9 g (0.014 mol) 3-octylthiophene magnesium bromide was added slowly to an ice-cooled solution of g. of 2,5-dibromo-3-octylthiophene and 120 mg. of NiCl₂(dppp) in ml THF. The mixture was observed by chromatography. The mixture was then hydrolyzed with 1M HCl, washed with distilled water and dried over MgSO₄. λ_{\max} CHCl₃, 314.5 nm. ¹H-NMR (270 MHz, CDCl₃, ppm) 0.9 (t, 9H), 1.3 (m, 30H), 1.6 (m, 6H), 2.5 (m, 4H), 2.7 (m, 2H), 6.93 (d, 1H), 6.95 (d, 1H), 6.97 (s, 1H), 7.14 (d, 1H), 7.3 (d, 1H). ¹³C-NMR (75 MHz, CDCl₃, ppm). Aromatics: 142.9 C(4', 3''); 140.0 C(3); 130.5 C(2); 129.1 C(4, 4''); 128.6 C(5', 2''); 127.6 C(3'); 125.8 C(5''); 124.2 C(2'); 123.9 C(5). Aliphatics: 32.7; 31.3; 31.2; 30.2; 29.9; 29.8; 29.4; 23.4; 23.2; 14.6.

POLYMERIZATION

The 3-octylthiophene, 3,3'-dioctylbithiophene and 3,4',3''-tri(3-octyl)-terthiophene were polymerized, using 0,2 M solution of FeCl₃ in acetonitrile/chloroform mixture (5:1) at room temperature under argon atmosphere. After being stirred for 48 h., the polymer were precipitated in methanol, filtered, washed thoroughly with methanol-acetone mixture and then dried under vacuum at 60°C during 12 h. The electrochemical polymerization was carried out using 0.1 M of oligomers, acetonitrile or acetonitrile/dichloromethane mixture and 0.05 M of tetrabutylammonium perchlorate (TBAClO₄) as electrolyte. A two compartment cell was used with platinum working electrodes. Current densities of 3 mA/cm² were used and the polymerizations were performed at room temperature and purged with argon or nitrogen for about 10 minutes before applying the current. The polymer films were carefully separated from electrodes, washed with methanol and then dried under vacuum at 60°C during 12 h.

Acknowledgments

The authors wish to thank the Commission of the European Communities, Project N° C11-CT94-0070 for financial support.

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