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Synthesis and characterization of side chain liquid crystalline polymer with a polythiophene backbone

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Abstract

Poly{3-(4-methoxy-4′-hexyloxybiphenyl)oxymethylthiophene} (PolyMHOT) has been prepared to examined the effect of liquid crystalline properties on the conducting polymer structure. This monomer exhibited enantiotropic smectic liquid crystalline mesophase. Polymerization was carried out by chemical and electrochemical methods. In chemical method, polymer yield were quite high and the polymerization required 3 eq. of oxidant to monomer. In the electrochemical procedure, the monomer exhibits an anodic peak due to the formation of radical cation with onset potential about 1.10 V and form electroactive polymer film. However, poly(MHOT) was insoluble organic solvents and not observed liquid crystalline properties due to small portion of crosslinked polymer structure and inherently rigid polythiophene backbone. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Recently, π-conjugated polymers have received considerable attention mainly due to their interesting electrical and optical properties which makes them good candidates for applications in microelectronic devices. Discovery of fusibility [1, 2], solubility [3–5] and unique properties in poly(thiophene)s by the attachment of pendant substituents have stimulated synthesis of new types of conducting polymers. Since poly(3-alkylthiophenes) were introduced as an unique electroactive polymer, they have attractive interest in material science for practical as well as potential applications. For example, poly(3-alkylthiophenes) have been utilized in prototype devices such as Schottky diodes, metal–insulator–semiconductor field effect transistors, light emitting diodes [6], rechargeable battery electrodes [7], electrochromic devices, chemical and optical sensors [8]. Furthermore, the introduction of functional groups into the 3-position of the thiophene units in polythiophene not only influence solubility and meltability but also control and modify other physical, electronic, and electro-optical properties of polythiophene. A variety of polymers with functionalized substituent on the 3-position of the thiophene units have been synthesized. For example, the crown ether side chain resulted in ionochromic activity in the polythiophene [9], the chiral side chain yielded an optically active polythiophenes [10], and an alkanesulfonic acid side chain produced a water soluble polymer which was a self-doping conducting polymer [11].

In our previous works, we reported the synthesis and electro-optical properties of a side chain liquid crystal polymers, based on a poly(1,6-heptadiyne) backbone by transition metal catalyst systems [12–15]. In an attempt to investigate the effect of the more ordered liquid crystalline phase on the electrooptical

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properties of polymers, we are now expanding considerable effort toward the synthesis of side chain liquid crystalline polymers with mesogenic polythiophene.

In this article, we described the synthesis of conducting polymeric side chain liquid crystal polythiophenes by chemical and electrochemical procedure, and the results of optical, physical and spectroscopic data are reported.

2. Experimental

2.1. Materials and instruments

Solvents were purified by normal procedures and handled under moisture free atmosphere. The polymerization solvents, chloroform or nitrobenzene were distilled from calcium hydride. Ferric chloride (Junsei Co) was dried with vacuum pump immediately prior to use. The other materials were commercial products and used without further purification. The polymerization glassware and syringes were dried at 150°C for at least 24 h before use. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AM-300 spectrometer. Infrared (IR) spectra were taken on a Bomen Michelson MB-100 spectrometer in KBr pellet or neat. Thermogravimetric analysis (TGA) was performed with a DuPont 951 TGA in nitrogen atmosphere at a rate of 10°C/min up to 800°C. Thermal transition was measured with a DuPont 910 differential scanning calorimeter (DSC) under nitrogen atmosphere as a heating rate of 20°C/min. Electrical conductivity was calculated by 4-point probe method.

2.2. Preparation of 3-(4-methoxy-4′-hexyloxybiphenyl)oxy methylthiophene (MHOT)

Thiophene derivative with mesogenic and spacer group were synthesized by modified Williamson ether synthesis (Scheme 1).

2.2.1. 3-(6-bromohexyloxy)methylthiophene

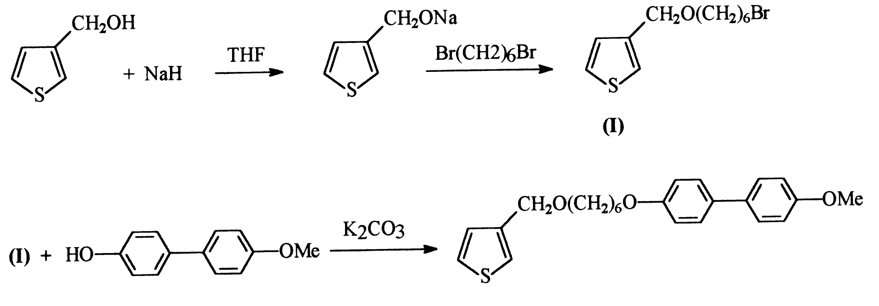
3-thiophene methanol (22.80 g, 0.2 mol) was converted into its sodium salt by reaction with sodium hydride in tetrahydrofuran (THF) (200 ml). This solution stirred at 40°C for 6 h, then added catalytic amount potassium hydride. The reaction mixture was added dropwise 1,6-dibromohexane (97.6 g, 0.4 mol) in THF (100 ml) during 10 min and further reacted for 12 h at room temperature with stirring. After solvent was removed with evaporator, water (50 ml) was carefully added, and the organic layer was extracted three times with methylene chloride (50 ml, each). Product was isolated by evaporating the solvent after drying the solvent with magnesium sulfate. The crude product was purified by vacuum distillation. b.p. 104°C/0.2 mmHg, yield, 65%., ^{1}H-NMR ($CDCl_3$, 60 MHz, ppm); 1.5 (m, 8H), 3.3 (m, 4H), 4.4 (s, 2H), 7.1 (m, 3H).

2.2.2. 3-(4-Methoxy-4′-hexyloxybiphenyl)oxymethylthiophene (MHOT)

To the mixture of 4-methoxy-4′-hydroxybiphenyl (10 g, 0.05 mol) as previously synthesized [16] and K_2CO_3 (21 g) in DMF (200 ml) was added dropwise 3-(6-bromohexyloxy)methylthiophene (13.85 g, 0.05 mol) followed by heating to 80°C for 24 h. After cooling, the reaction mixture was poured into water (300 ml) and formed solid was filtered, then recrystallization with methanol (200 ml). m.p. 95 ~ 97°C, yield 84.3%, ^{1}H-NMR ($CDCl_3$,300 MHz, ppm), δ 1.49 (m, 4H), 1.65 (m, 2H), 1.76 (m, 2H), 3.48 (t, 2H), 3.81 (s, 3H), 3.97 (t, 3H), 4.51 (s, 2H), 6.96 (d, 4H), 7.09 (d, 1H), 7.18 (s, 1H), 7,25 (d, 1H), 7.48 (d, 4H), IR (KBr pellet, cm^{-1}); 3100: C–H thiophene stretching band, 1603, 1466: C=C aromatic stretching, 1252: C–O stretching, 821: C–H *para* substituted benzene out of plane, 782: C–H thiophene out of plane.

2.3. Chemical polymerization of MHOT

The general procedure was as follows; A two-neck round bottom flask was equipped with a syringe. A



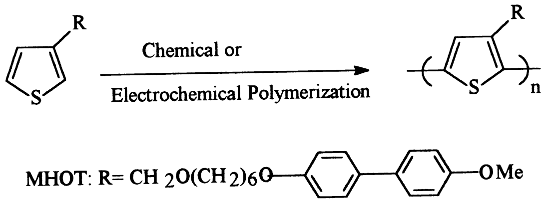
Scheme 1.

synthetic grade anhydrous metal halogenide was pulverized and put into the flask under a dry nitrogen atmosphere. The reaction vessel was then connected to a vacuum line and evacuated at about 100°C under vigorous mechanical agitation of the metal halogenide in the flask prior to the reaction (dry metal halogenide). Dry nitrogen was then reintroduced into the reaction vessel and a dry distilled solvent (0.4 M), such as nitrobenzene or chloroform, was added into the flask under the dry nitrogen flow. 0.1 M of the monomer was added dropwise into the metal halogenide solution (or suspension) through the syringe under vigorous agitation with a magnetic stirrer. After all the monomer was added, the metal halogenide solution (or suspension) was further stirred for about 24 h at room temperature to ensure the complete of the reaction. After completing the reaction, the reaction mixture was precipitated into methanol. The resulting black precipitate (an as-grown material) was collected by filtration and dried to a constant under vacuum at 40°C for 12 h. The polymer yield was calculated by gravimetric. Typical example of the polymerization procedure is described below.

Dry $FeCl_3$ (1.458 g, 9 mmol) was suspended in 20 ml of dry, distilled $CHCl_3$ and stirred for 15 min. To the partially dissolved solid, was added dropwise MHOT (1.18 g, 3 mmol) dissolved in 10 ml of dry, distilled $CHCl_3$. The reaction mixture was warmed in an oil bath to 30°C and was stirred for 48 h. Methanol (200 ml) was then added with stirring. Stirring was stopped and after the black solid had settled, and the solid filtered. Poly(MHOT) was obtained in 76.3% yield.

2.4. Electrochemical polymerization of MHOT

Electrochemical polymerization was carried out by using an EG&G Princeton Research Model 273 poteniostat galvanostate. A constant current density of 2.0 mA/cm^2 was employed to conduct electopolymerization on a platinum working electrode with a platinum strip counter electrode and Ag/AgCl reference electrode. Acetonitrile, distilled over P_2O_5, and tetrabutylammonium perchlorate, recrystallized from methanol, were used as the supporting electrolyte. The monomer concentration was 0.1 M in each case, and the electrolyte was 0.1 M $TBAClO_4$ in CH_3CN. Polymerization was carried out at 40°C for 3 days. More precise electrochemical polymerization analysis was discussed at result part.



Scheme 2.

3. Results and discussion

3.1. Polymerization

Scheme 2 outlines the polymerization of MHOT by using both chemical and electrochemical methods.

3.1.1. Chemical polymerization

Polythiophene derivatives were prepared organo synthetically via dehydrogenation condensation, i.e. chemical oxidation, of monomers in the presence of metal halogenide ($FeCl_3$, $AlCl_3$, etc) in an appropriate medium such as nitrobenzene and chloroform solution (or suspension) [4]. These methods are advantageous because unstable intermediates or multistep reaction processes are not required. Furthermore, the yield of polymers is quite high. The high reactivity of the available α-positions on the thiophene rings affords a significant amount of synthetic flexibility for the various oxidative polymerization methods.

In Table 1, the results for the chemical polymerization are listed. For the MHOT, $FeCl_3$ is more effective oxidant than $AlCl_3$ at the thiophene derivatives polymerization. Also, the results of polymerization by variation of the oxidant to monomer mole ratio are recorded. Low oxidant ratio give poor yield. Therefore, oxidant was required a minimum of three times equivalent than monomer. Same result were known in the polymerization of 3-alkylthiophene [17], di-2-thienylphenylene. Since it is easier to oxidize the conjugated polymer than the monomer, at least 3 eq. of $FeCl_3$ was used for polymerization to allot enough reagent for the oxidation coupling and to oxidize the polymeric backbone.

The solvents and initial monomer concentrations may affect on the polymer yield. The polymerization temperature was independent on the polymer yield. The use of $FeCl_3$ as the oxidizing agent in the polymerization of 3-alkylthiophene has been shown to give exceptionally high molecular weight polymers [18]. However, sparingly soluble in common organic solvents, the resulting polymers were not determined of the molecular weight.

3.1.2. Electrochemical analysis and polymerization

Anodic electropolymerization is useful for the preparation of both electrode-supported and free-standing conducting polyheterocycle films and has been applied here. The monomer was studied electropolymerization

Table 1
Polymerization of MHOT by chemical method

Exp. No.	Monomers (mmol)	Oxidants (mmol)	Solvent (ml)	Temperature (°C)	Polymer yield[a] (%)
1	MHOT (2)	$FeCl_3$ (8)	$CHCl_3$ (40)	60	95
2	MHOT (3)	$FeCl_3$ (9)	$CHCl_3$ (30)	25	76
3	MHOT (1.3)	$FeCl_3$ (3.9)	NB[b]	60	82
4	MHOT (1.3)	$FeCl_3$ (1.3)	$CHCl_3$ (39)	25	–
5	MHOT (1.3)	$FeCl_3$ (3.9)	$CHCl_3$ (33)	25	10

[a] Methanol insoluble polymer.
[b] Nitrobenzene.

to form electroactive polymer films. The behavior of the monomer was examined systematically by cyclic voltammetry (CV) under standard conditions. For MHOT, a series of scans was made, observing the initial scan only and varying the scan-rate from 20 to 90 mV/S. In a first series of experiments, consecutive scans were observed at a fixed scan rate of 50 mV/S (when a platinum working electrode is used). The monomer exhibits an anodic peak due to the formation of radical cations with onset potentials of 1.12 V, and (various Ag/AgCl) for MHOT.

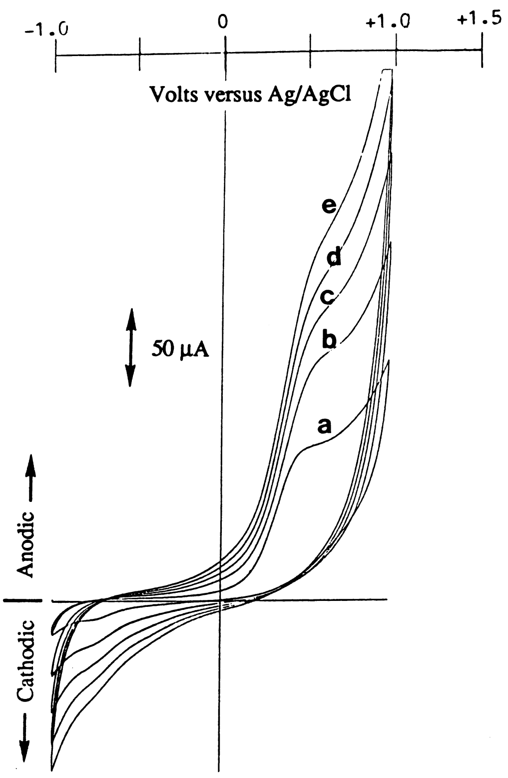


Fig. 1. Cyclic voltammogram of poly(MHOT) thin film in 0.1 M $TBAClO_4$. Scan rate; (a) 20, (b) 30, (c) 50, (d) 70, (e) 90 mV/s.

Two cathodic peaks are observed about –0.4 and 0.95 V on the return scans due to reduction of oxidized polymer on the electrode surface. Switching potentials were maintained < 1.5 V in all cases to avoid overoxidation and deactivation of the polymers electroactivity [19]. The consecutive scans show anodic current much lower potentials as the reduced polymer on the electrode surface are oxidized, followed by a higher current during monomer oxidation. This overall increase in current with repeating scanning is due to the fact that the depositing conducting polymer is increasing the effective surface area of the electrode.

The electrochemically prepared poly(MHOT) film was subsequently thoroughly washed with CH_3CN to remove excess monomer and its electroactivity examined in monomer free electrolyte. This is shown in Fig. 1 as a function of scan rate and is again representation of all polymers studied.

In most of the systems studied, a simple CV trace was observed where the anodic current associated with monomer oxidation exhibited a clear $V^{1/2}$ dependence consistent with control by reactant diffusion to the electrode.

3.1.3. Polymer structure

Polymer structure was identified by FT-IR, ^1H-NMR spectroscopy. In MHOT, IR spectrum gives the C–H out-of-plane band on the 3-substituted thiophene at 782 cm^{-1} and also shown an absorption band 824 cm^{-1} owing to the phenylene C–H out-of-plane band [20]. In poly(MHOT), 782 cm^{-1} peak shifts to 2,3,5-trisubstituted thiophene out-of-plane band at 814 cm^{-1} and phenylene C–H out-of-plane band (824 cm^{-1}) is unchanged. An absorption at about 3100 cm^{-1}, due to the α-hydrogen of the thiophene rings, is observed in the monomer. The intensity of this absorbance is significantly reduced in the polymer. This indicates that the oxidative coupling polymerization is occurring extensively at the α-sites on the thiophene yielding the fully conjugated polymer as desired. In ^1H-NMR spectrum, poly(MHOT) shows a dominant signal at 7.15 ppm and,in addition, weaker signals at around. The other peaks are unchanged by polymerization. One major peak (at 7.15 ppm) assigned

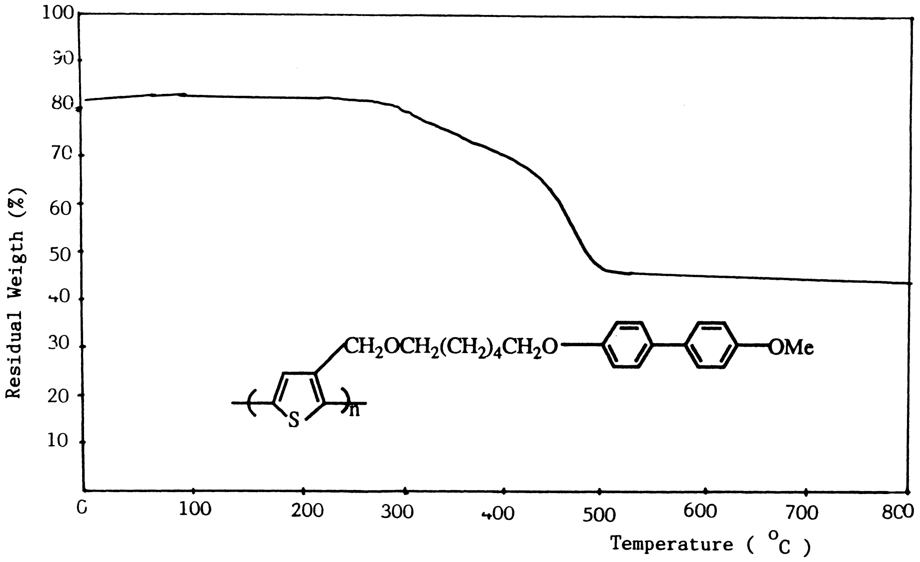


Fig. 2. TGA thermogram of poly(MHOT), under nitrogen.

head-to-tail linkage structure. Defects can occur in these chains during polymerization, such as the formation of β-linkage or crosslinking, which disrupt conjugation and structure order in the materials.

3.1.4. Thermal and liquid crystalline properties

The thermal stabilities of polymer was analyzed using thermogravimetry. A thermograms is shown in Fig. 2 for poly(MHOT). Poly(MHOT) exhibits an onset of degradation of at least 280°C in the reduced form, which is comparable to substituted polythiophene. The most striking difference is the char residue, with the MHOT polymers leaving about 45% residue after heating up to 1000°C. The MHOT observed an enantiotropic smectic mesophase. A typical DSC curve and optical polarization micrographs of MHOT are shown in Figs. 3 and 4. In the second heating, apart from the T_g at about 9.9°C only one broad endotherm is seen at $T_m = 102°C$ (ΔH = 31.57 cal/g). This is probably due to the high viscosity and rigid backbone of the polymeric product [21]. Although some organized phase was observed in the optical polarization micrograph below the transition temperature (T_m). During the observation of the texture of MHOT at about 100°C, the morphology was a viscous fluid and easily assembled. Thus, the texture is a probably smectic phase but not the crystallinity. In DSC studies, the poly(MHOT) is not observed phase transition peak. The lack of liquid crystalline behavior for this polymer is attributed to the inability of the spacer linkage to decouple the chain motions from those of the side groups. In such polymer, the main chain polythiophene is considerably rigid compared with poly(meth)acrylate, which seems to make it difficult to organize mesogenic groups. Further study is needed to find a suitable condition for obtaining the liquid crystalline state.

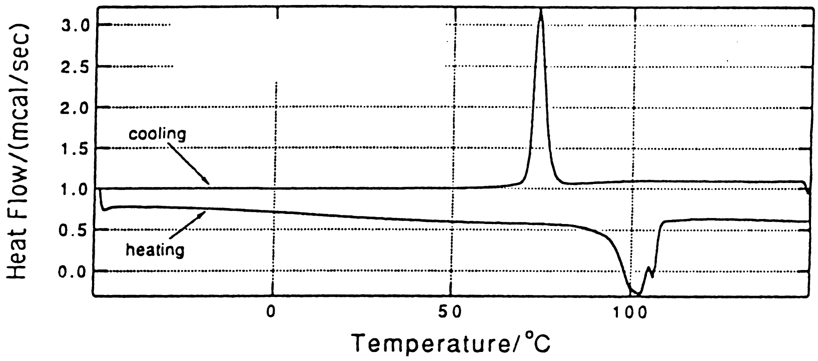
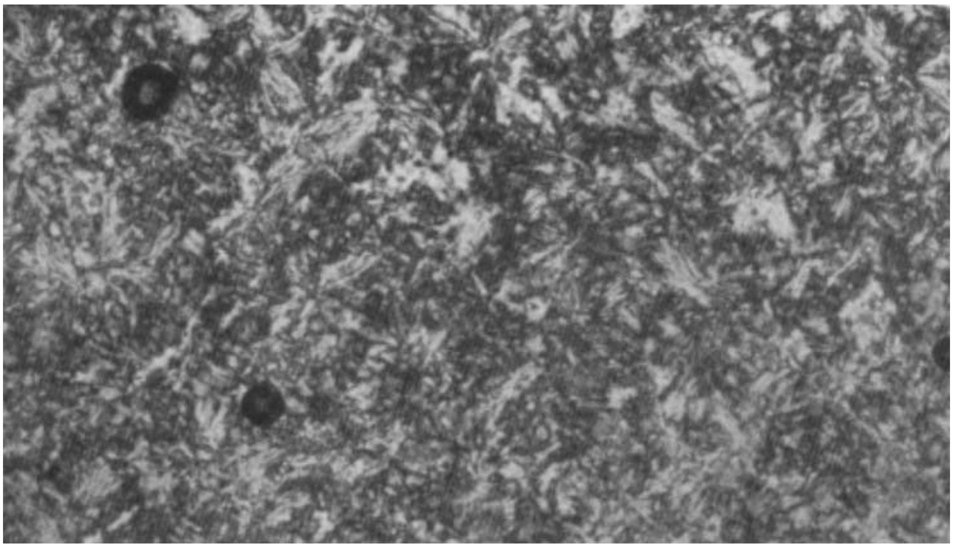


Fig. 3. DSC thermogram of MHOT (scanning rate = 10°C).



3.1.5. Electrical properties

The polymer was isolated in their insulating form by treatment of the $FeCl_3$-polymerized product with NH_4OH. As such, pressed pellets of the polymer powders exhibit electric conductivities $< 10^{-9}$ S/cm. Though insoluble, the powders could be oxidatively doped, with a concurrent elevation in conductivity, by dispersing the polymer in an oxidizing solution. A conductivity of 10^{-3} S/cm is observed for the polymers when oxidized with $FeCl_3$. Significantly lower conductivity (10^{-6} S/cm) is observed when I_2 is used as the dopant, which is most likely due to the lower oxidation power of I_2 when compared to $FeCl_3$ in solution.

Acknowledgements

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