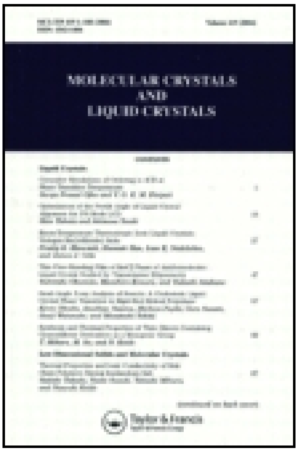

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Synthesis and Properties of Polythiophene Containing Mesogenic Group at 3-Position of Thiophene Ring

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SYNTHESIS AND PROPERTIES OF POLYTHIOPHENE CONTAINING MESOGENIC GROUP AT 3-POSITION OF THIOPHENE RING

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Abstract Various kinds of polythiophene derivatives were synthesized and thermal properties were examined by DSC, polarized microscopic and X-ray diffraction observations. Fusibility and solubility of these polymers deeply depends upon the polymerization methods and polarity of the mesogenic group. Polymerization was carried out by oxidation and polycondensation methods.The polarity at the end of mesogenic group plays an important role for solubility and fusibility of the polymer in the case of oxidative polymerization. 3-Substituted polythiophene having polar group such as cyano or nitro at the end of mesogenic group was soluble in polar solvent and fusibility at higher temperature. The polymer having polar group at the end of mesogenic group prepared by mild polymerization condition such as polycondensation exhibited a clear smectic texture and also showed electrochemically active by cyclic voltammograms.

1. Introduction

A number of papers have been published on the side-chain type liquid crystalline polymers (sLCP) with a flexible polymer backbone such as acrylate, methacrylate, styrene siloxane, and so on.[1] However, the synthesis and characterization of sLCP with a rigid polymer backbone have been studied on a few polymers. Among them, the conjugated polymers with a mesogenic group in the side chain would be considered a new functional polymer owing to an improvement of the orientation of the polymers.

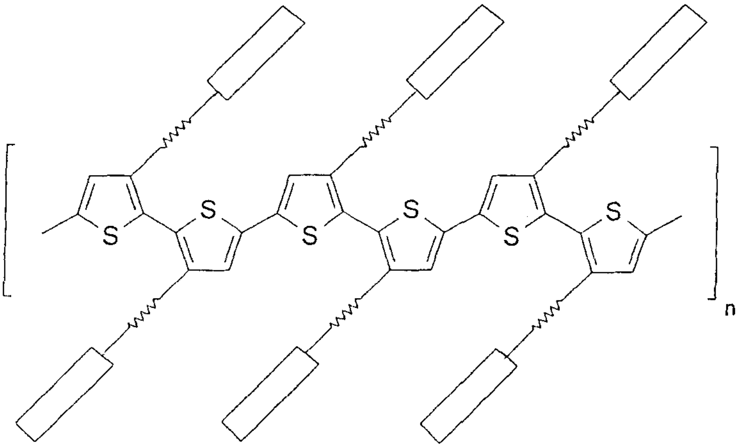
One example for functional materials is a conducting polymer. A conducting polymer have attracted much attention from both industrial and academic viewpoints. However, most conducting polymers are non-soluble in any solvents and no fusible. Recently polythiophenes substituted at the 3-position for alkyl,[2,3] alkoxy,[4,5] butanesulfonic acid[6] or phenyl[7] groups make it possible to add functionality such as solubility and thermochromism. Many poly(3-substituted thiophene)s have been studied for their various properties in this advantages.

It is well-known that the conductivity of conductive polymers would be improved by controlling the orientation of the polymer backbone.[8] The methods to control the orientation of conducting polymer are known for stretching[9] and polymerization under a magnetic field or liquid crystalline phase.[10]

Examples that the liquid crystalline phase was applied for the control of orientation of electrically conducting polymer are almost application for oriented field, and there is only one report about electrically conducting polymer which shows liquid crystalline property for polyacetylene with a phenylcyclohexyl mesogenic moiety in the side chain.[11]

From these experimental results, the solubility of polythiophene and conductivity of *oriented polyacetylene*, it can be expected that the conductive liquid crystalline polymers would be improved their conductivity and one candidate for functional film. Conductive liquid crystalline polymers would be obtained by the combination of conjugated material with mesogenic group.[12]

In this paper, polythiophene was selected as a conjugated main chain. The side-chain type polythiophene containing mesogenic group which shows liquid crystalline property by itself at the 3-position of the thiophene ring were prepared and investigated their thermal and electrochemical properties, as shown in the following.



Side-Chain Type Polythiophene

2. Experimental

Thiophene derivatives which were substituted by mesogenic group through ester bond (ester type) or ether bond (ether type) were synthesized, as shown in Figure 1. Cyanobiphenyl- or butoxybiphenyl moiety were used as a mesogenic group. 3-Thiophene methanol(aldrich) used as a starting material of thiophene derivatives without purification. A typical reaction scheme for the synthesis of polythiophene derivatives were shown in Figure 2.

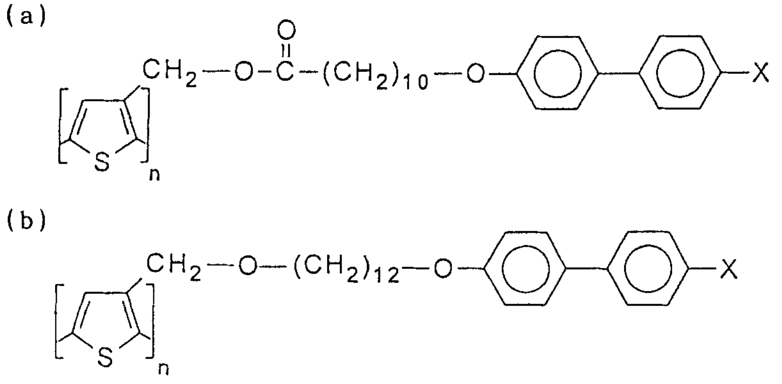


Figure 1. Structures of poly(3-substituted thiophene)s (a)ester type, (b)ether type, $X=OC_4H_9$, CN

Separation and purification were carried out by both elution column chromatography (silica gel, methylene chloride or mixed solvent,ethylacetic acid:hexane as eluent) and recrystallization. Their products in each reaction steps were detected by thin layer chromatography.

Polymerization were conducted by three methods, such as oxidative polymerization, electrochemical polymerization and dehalogenation polymerization with Ni(0)-complex.[10]

Relative molecular weights of chloroform soluble parts of these polymers were measured by GPC(Toso HLC-8020) with an instrument equipped with a Toso 254nm lump and a refractive index detector at 40°C. Polystyrene standards were used for the calibration plots for molecular weights and elusion time..

Optical textures and phase transition temperatures were observed with Nikon polarizing microscope equipped with a mettler FP-52 hot stage and Mettler FP-80 temperature controller. Phase transition temperature of these polymers was also studied utilizing a differential scanning

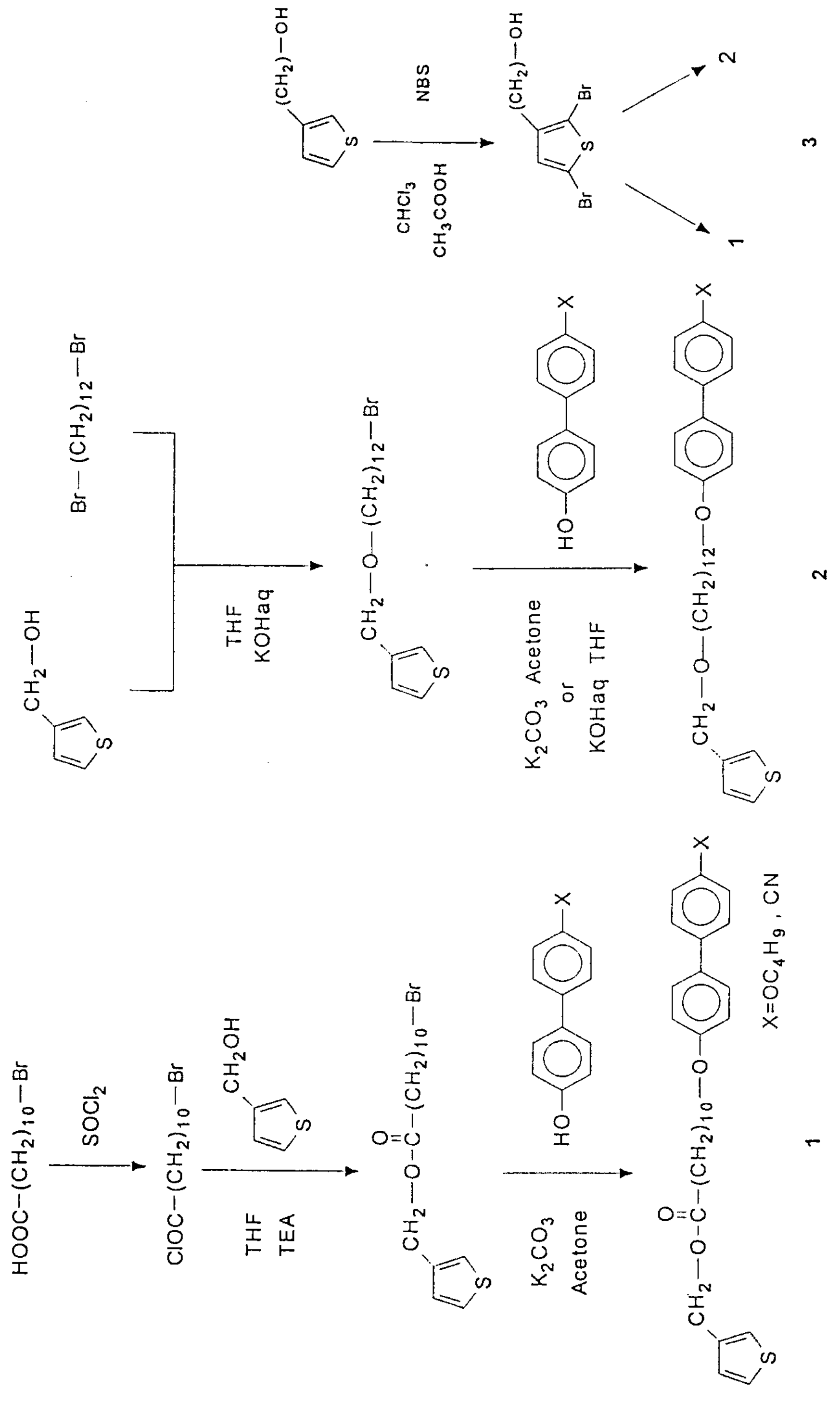


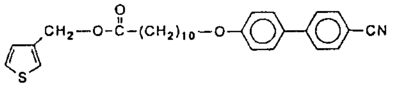
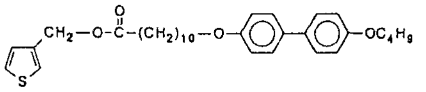
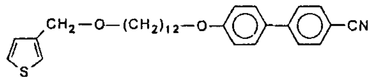
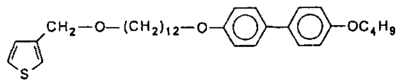
Figure 2. Synthetic routes of typical polythiophene derivatives

calorimetric method with a Mettler TA-3000 systems with a scanning rate of 10°C/min.

3. Results and Discussion

The phase transition temperature of monomers and polymers were shown in Tables 1 and 2, respectively. Polymerization was carried out by oxidative polymerization. All monomers did not show any mesomorphic phase. However, polymers exhibited different solubilities and fusibilities depending upon the polarity at the end of mesogenic group, as shown in Table 2. Polymers having butoxy group at the end of mesogenic group were insoluble and infusible, while polythiophene derivatives having cyano group at the end of mesogenic group were partially soluble in polar solvent such as chloroform or tetrahydrofuran and melted partially at 110 °C-140°C. However, polythiophene derivatives did not show any mesophase at the molten state. These results would occurred by the side reaction such as the reactive for 4-position of thiophene ring or crosslinking reaction in the oxidation or electrochemically polymerization methods.

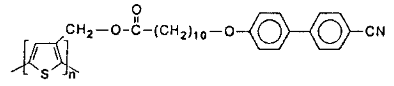
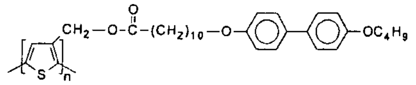
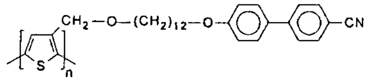
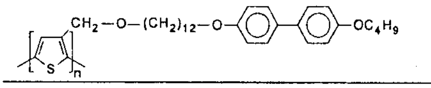
Table 1. Phase transition temperature of monomers

Monomer	Transition Temperature (°C)
	$K \underset{53.6}{\overset{77.6}{\rightleftharpoons}} K' \underset{55.2}{\overset{79.8}{\rightleftharpoons}} I$
	$K \underset{92.2}{\overset{101.3}{\rightleftharpoons}} I$
	$K \underset{52.8}{\overset{64.6}{\rightleftharpoons}} I$
	$K \underset{87.9}{\overset{102.7}{\rightleftharpoons}} I$

K: Crystal, I: Isotropic

From these results, solvable and fusible polythiophene derivatives would be created if polymerization will carry out by mild condition such as dehalogenation polycondensa-

Table 2. Phase transition temperature of polymers

Polymer	Yield (%)	Solubility in $CHCl_3$ (wt%)	Tm(℃)
	30.8	47.7 Mn=34,800	110-140
	54.5	—	—
	45.7	22.8 Mn= 8,200	110-140
	30.7	—	—

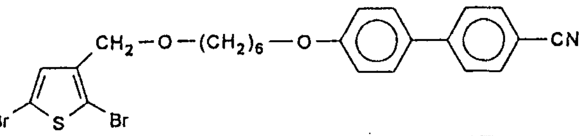
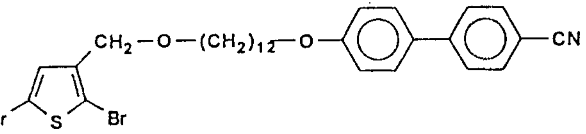
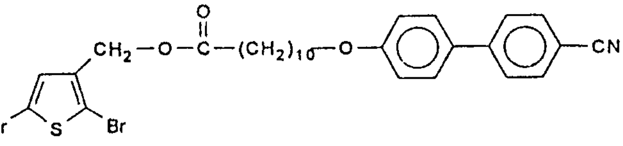
tion for the thiophene derivative monomer having a polar group at the end of mesogenic group. The dehalogenation polycondensation of 3-substituted thiophene was carried out by using Ni(0)-complex as the dehalogenating reagent under an atmosphere of nitrogen. The synthesis of dehalogenating reagent and polycondensation were carried out as follows.[13,14] Dried two-necked flask was charged with Nickel chloride, triphenylphosphine, and zinc dust. The flask was evacuated and filled with nitrogen several times carried out in the vacuum line. Dry DMF was added via syringe. The reaction flask as then placed in an oil bath at 50°C and stirred magnetically. After the red-brown catalyst had formed, a nitrogen-purged solution of thiophene derivative in DMF was added via syringe to the reaction mixture. The reaction was conducted at 60°C for 20 hours. After the reaction, the mixture was concentrated and poured into methanol in order to obtain the polymer.

The phase transition temperature of 2,5-dibromothiophene derivative monomers was shown in Table 3.

Monomers for 2,5-dibromothiophene substituted mesogenic group at the 3-position of thiophene ring showed lower melting point than the monomers which were not brominated. Especially ether type monomer showed a monotropic smectic phase. Brominated polymers were soluble in polar solvent such as chloroform, THF and the color of polymers were bright orange at the room temperature.

DSC thermogram of both ether and ester type polymers showed two peaks , as shown in Figure 3. The one peak of the low temperature side was assigned as the glass

Table 3. Phase transition temperature of 2,5-dibromothiophene derivatives and their polymers

Structure	DP	Transition Temperature (℃)	
		monomer	polymer
	5	$K \underset{64}{\overset{84}{\rightleftharpoons}} I$	$g \underset{?}{\overset{110}{\rightleftharpoons}} I$
	9	$K \underset{?}{\overset{55}{\rightleftharpoons}} K' \underset{?}{\overset{59}{\rightleftharpoons}} I$	$g \underset{20}{\overset{21}{\rightleftharpoons}} S$
	11	$$\begin{tikzcd} K \arrow[rr, "56"] & & I \arrow[dl, "38"] \\ & S \arrow[ul, "?"] & \end{tikzcd}$$	$g \underset{22}{\overset{25}{\rightleftharpoons}} S$

transition temperature based on the baseline shift, and the other one of the higher temperature side originated from the transition from mesophase to isotropic phase. Mesophase of these polymers would be assigned smectic phase owing to the large transition enthalpy change from mesophase to isotropic fluid.

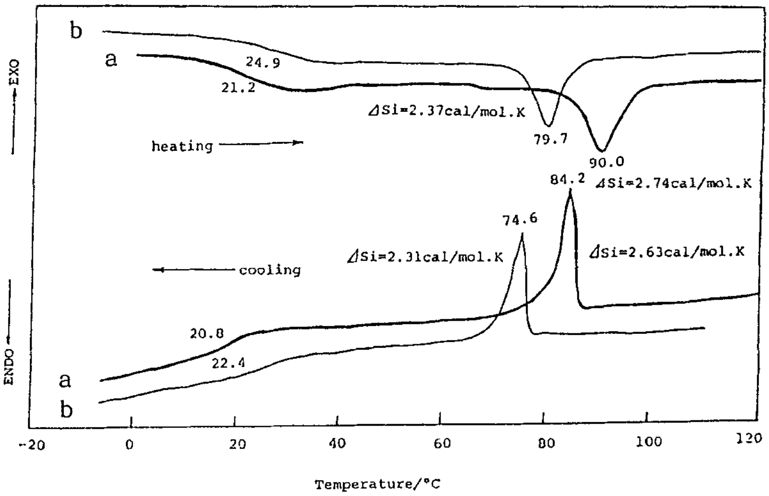
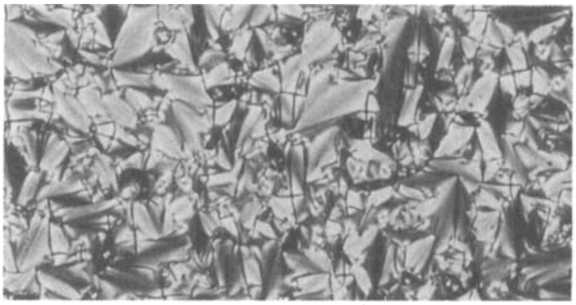


Figure 3. DSC thermogram of polymers: (a) ether type; (b) ester type.

Ether type polymer exhibited a clear fan texture characteristic of smectic phase, as shown in Figure 4.



Cooling 80.6°C

Figure 4. Polarized photomicrograph of polymer. See Color Plate IX.

The phase transition temperature of these polymers was shown in Table 3 based on the DSC and polarized microscopic observations. In spite of low degree of polymerization, liquid crystalline temperature range for ether type polymer showed a wider temperature range than that for ester type polymer.

A cast film of ether type polymer showed absorption peaks in the UV-visible range at 400nm which is due to π-π^* electric transition and 293nm which is due to cyanobiphenyl moiety. The maximum position of π-π^* transition shifted to longer wavelength (410nm) for the film cooled slowly from isotropic melt. This implies an effective conjugate length became longer by improvement of orientation of polymer backbone.

In order to obtain the electrochemical properties of ether type polymer, cyclic voltammetric measurements were performed as shown in Figure 5. Here (a) was prepared by solvent casted film, and (b) was prepared from the isotropic melt. Both cyclic voltammograms had anodic and cathodic wave. The color of the polymer changed into orange. Compared between (a) and (b), it is found that (a) can reach doping state more smoothly than (b). This seems to be due to that liquid crystalline phase is smectic phase which form layer structure, but details about this phenomena have not been found yet. This polymer was found to be active in electrochemically.

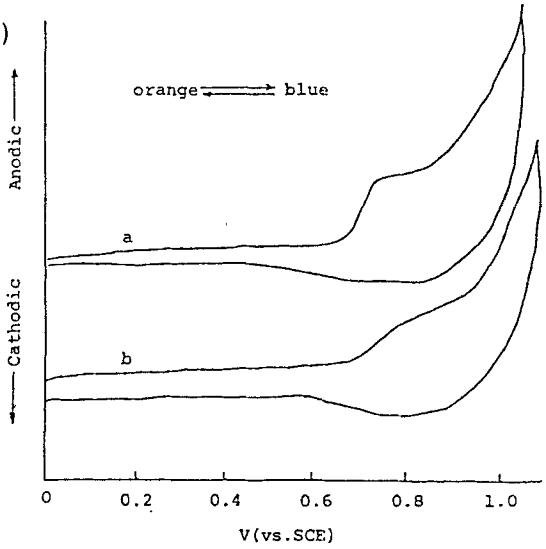


Figure 5. Cyclic voltammograms
a; without heat treatment;
b:after heat treatment

This is the first example of liquid crystalline 3-substituted polythiophenes.

Acknowledgment

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