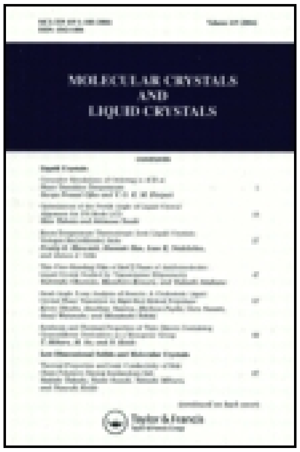

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Syntheses and Properties of Polythiophene Derivatives with Phenylalkyl and Liquid Crystalline Groups

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Syntheses and Properties of Polythiophene Derivatives with Phenylalkyl and Liquid Crystalline Groups

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We have synthesized a series of mono-substituted thiophene derivatives with phenylalkyl and liquid crystalline groups and polymerized them through a chemical oxidative polymerization and a dehalogenative polycondensation, respectively. Poly(phenylalkyl-substituted thiophene)s were found to have highly stereoregular configurations composed of head to tail linkages. The dehalogenative polycondensation of the 2,5-dibrominated thiophene monomer with the liquid crystalline group at the 3-position of thiophene ring showed a monotropic nematic phase with a schlieren and droplet texture in polarizing optical micrograph. All polymers were characterized in terms of chemical and spectroscopic properties as well as electrical conductivities before and after iodine doping.

Keywords: mono-substituted polythiophenes; solubility; liquid crystallinity; spectroscopic properties; stereoregularity; electrical conductivity

INTRODUCTION

The significant progress in the control and modification of properties of conjugated polymers has been accomplished recently towards advanced molecular devices and molecular electronics. Polythiophene with functional group at the 3-position of thiophene ring has been of current interest because of solubility in organic solvent, molecular rectifying effect, ionic or molecular recognition, and inherent electrical conductivity of the polymer [1-4].

Meanwhile, as has been extensively studied in polyacetylene, the alignment of conjugated chains is one of the key factors to enhance the electrical conductivity [5]. Introduction of liquid crystalline groups into the side chain of the conjugated polymer is expected to afford a higher electrical conductivity and a notable electrical anisotropy [6-9]. This is because the polymer main chain can be aligned by the virtue of spontaneous orientation of liquid crystalline side chains and further by macroscopic orientation of liquid crystalline domains under external force, such as shear stress and electric or magnetic field [9].

Previously, we reported syntheses of soluble conducting poly(2,5-thienylene) derivatives through electrochemical and chemical polymerizations of 3-(2-phenylethyl) and 3-(3-phenylpropyl)thiophene monomers [10].

In the present study, to develop novel liquid crystalline poly(2,5-thienylene) derivatives, we have synthesized two kinds of thiophene monomers substituted with (i) phenylalkyl group with methylene chain length of 2 ~ 5, and (ii) with liquid crystalline group consisting of phenoxycyclohexyl moiety as a mesogenic core. Chemical oxidative polymerizations or dehalogenative polycondensation for these monomers were carried out. Characterizations were carried out by means of IR, UV-Vis, ^{1}H- and ^{13}C-NMR, element analyses, as well as evaluations of molecular weights and electrical conductivities upon iodine doping. First, we report the syntheses and properties of polythiophene derivatives prepared with the chemical oxidative polymerizations. Second, we report the liquid crystalline polythiophene derivative prepared with the dehalogenative polycondensation of 2,5-dibrominated thiophene monomer with the liquid crystalline group.

EXPERIMENTAL

General Aspects

All reactions were carried out under an argon atmosphere. FT-IR spectra were recorded on a JASCO FT/IR 8000 spectrometer using KBr method. NMR spectra were recorded on a JEOL FT-NMR 100 MHz spectrometer using $CDCl_3$ as a solvent and TMS as an internal standard for both ^{1}H and ^{13}C measurements. Molecular weights were determined on gel permeation chromatography (GPC) with a Shodex A-80M column using THF as an eluent. Based on GPC curves, number- and weight-average molecular weights were calculated using a calibration curve for a standard polystyrene. Differential scanning calorimeter (DSC) thermograms were measured by a Perkin-Elmer DSC7. UV-visible absorption spectra were measured with a Hitachi U-3500 spectrometer in THF. The electrical conductivity of the cast film prepared from

$CHCl_3$ solution was measured through four-probe method at room temperature, where changes of conductivity were monitored as a function of doping time.

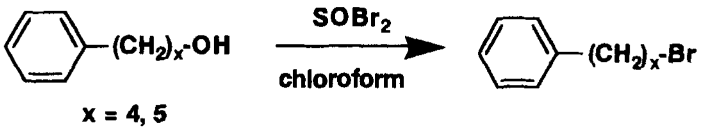
Reagents and Solvents

All reagents were used as received, except bis(1,5-cyclooctadiene)-nickel(0), $Ni(cod)_2$, which was prepared according to the literature [11]. All solvents used in reactions were distilled from appropriate drying agents under argon gas before use.

Section 1

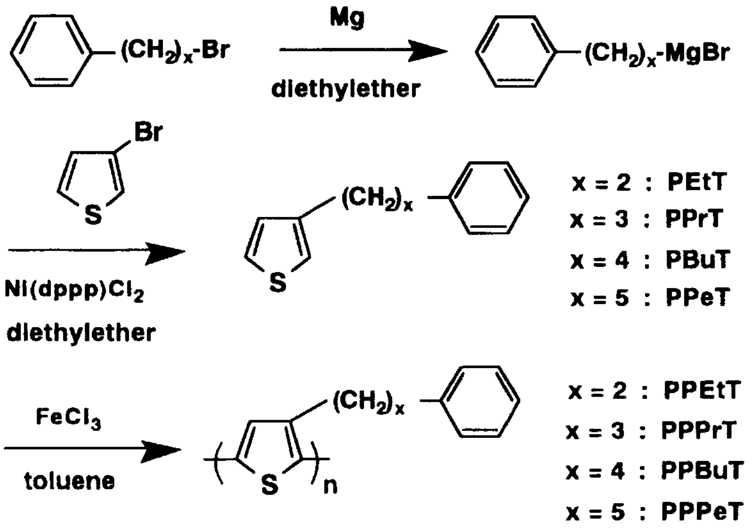
1. Synthesis of 3-(ω-phenylalkyl)thiophenes

ω-Phenylalkylbromides, C_6H_5-$(CH_2)_x$-Br, (x= 4, 5), were synthesized through bromination of the ω-phenylalkylalcohols with thionylbromide [$SOBr_2$] in chloroform, except ω-phenylethyl and ω-phenylpropylbromides that are commercially available (Scheme 1).



Scheme 1

3-(ω-Phenylalkyl)thiophenes (x = 2 ~ 5) [PEtT, PPrT, PBuT, PPeT] were synthesized by Grignard cross-coupling reactions between ω-phenylalkylbromides and 3-bromothiophene in the presence of dichloro[1,3-bis-(diphenylphosphino)propane]-nickel (II) [$Ni(dppp)Cl_2$]. Chemical oxidative polymerizations of the 3-(ω-phenylalkyl)thiophenes were carried out using an iron trichloride [$FeCl_3$] as a catalyst in toluene at room temperature (Scheme 2). The reaction mixture was added into an excess amount of methanol with stirring to precipitate the neutral undoped polymer. It should be noted that the previous electrochemical polymerizations of 3-(ω-phenylethyl)thiophene [PEtT] and 3-(ω-phenylpropyl)thiophene [PPrT] yielded insoluble polymers in doped and undoped states [10], implying that the electrochemical polymerization must accompany a cross-linking reaction. Therefore, we employed here the chemical polymerization. Actually, the polymers prepared by the chemical polymerization were soluble in organic solvent such as THF, chloroform, and benzene.



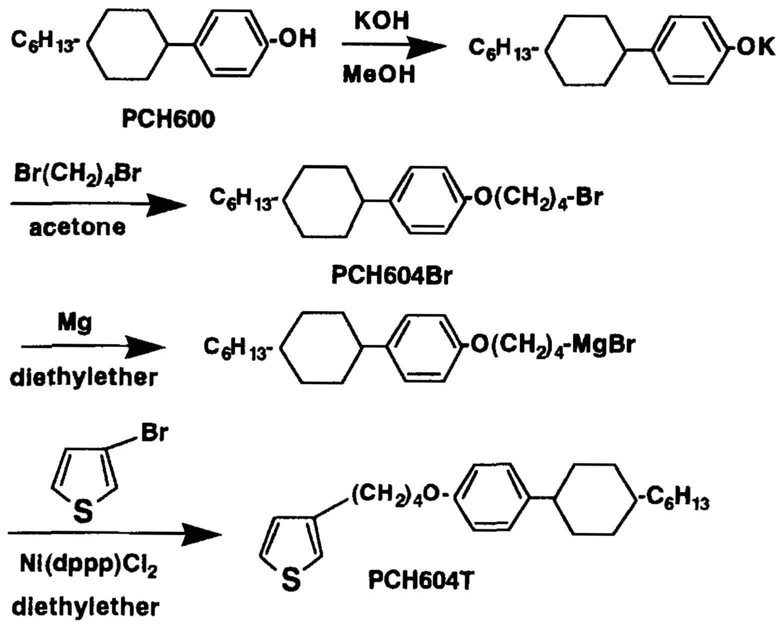
Scheme 2

2. Synthesis of 3-(4-phenoxybutyl)-thiophene

3-(4-Phenoxylbutyl)thiophene [POBuT] was synthesized through the same procedure as shown in Scheme 2, for which commercially available 4-phenoxybutylbromide was used in stead of 3-(ω-phenylalkyl)bromide. Chemical polymerization of POBuT was carried out using the same procedure mentioned above. However, the polymer produced was insoluble in organic solvent, making it impossible to evaluate molecular weight and spectroscopic properties in solution.

3. Synthesis of PCH604-thiophene

Subsequently, we tried to introduce the liquid crystalline substituent into the thiophene ring (Scheme 3). The substituent consists of the phenoxycyclohexyl mesogen, which is abbreviated PCH604. The precursor of PCH604-thiophene, abbreviated PCH604Br, was synthesized by reacting *para*-(*trans*-4-*n*-hexylcyclohexyl)phenol [PCH600] with dibromobutane [$Br(CH_2)_4Br$] in KOH. The Grignard reagent of PCH604Br was coupled with 3-bromothiophene to yield PCH604-thiophene. It is worthy noting that although the PCH604-thiophene showed no mesogenic phase, the precursor, PCH604Br, showed nematic liquid crystalline phase in range of 26 - 29 °C.



Scheme 3

The measurements of DSC and polarizing optical microscope confirmed that the nematic liquid crystal of PCH604Br was only observable in the cooling process but not in the heating process, indicating a monotropic liquid crystal. It may be rationalized that the difference in occurrence of mesogenic phase between PCH604Br and PCH604-thiophene is due to the difference in molecular shape, in which the former is very close to rod-like molecule.

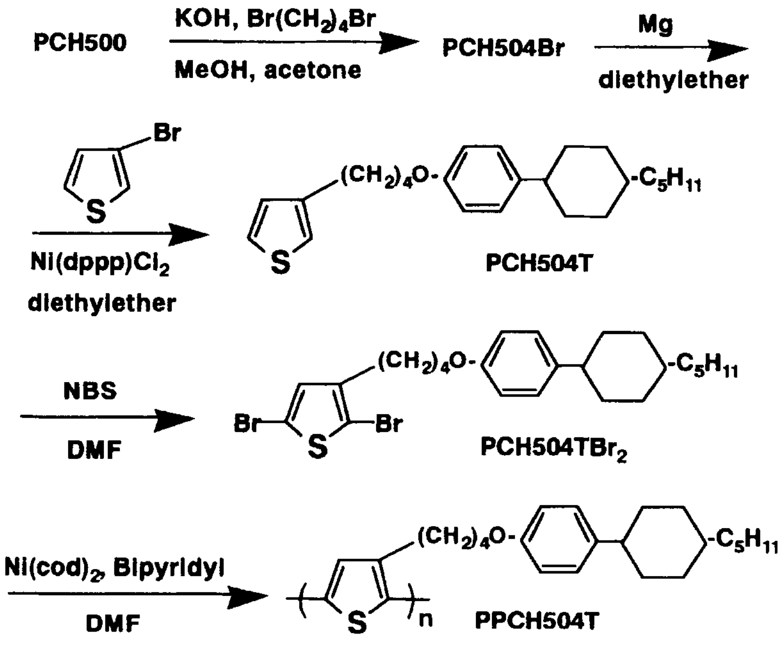
The chemical polymerization of PCH604-thiophene gave insoluble powder polymer. This result is similar to the case of POBuT. Infrared spectrum of the polymer dispersed in KBr was also similar to that of polymerization product of POBuT, suggesting an occurrence of cross-linking in both polymers.

In contrast, PBuT has the substituent that is free from ether-type oxygen atom neighboring the phenyl ring. The polymerization of PBuT yielded soluble polymer with stereoregularly linked 2,5-thienylene structure. Ether-type oxygen, especially linked with phenyl ring, may tend to behave as a Lewis base and to interact with $FeCl_3$ used as a catalyst that is a Lewis acid. This sort of charge transfer interaction should interfere the polymerization to cause cross-linkings between the side chains during the polymerization.

Section 2

In the previous section, the thiophene derivative (PCH604T) with the liquid crystalline group, consisting of cyclohexylphenoxy moiety as a mesogen, tetramethylene chain as a spacer, and *n*-hexyl group as a terminal group, was synthesized. The chemical oxidative polymerization of this monomer using $FeCl_3$ as a catalyst gave an insoluble and infusible polymer. Although the polymer became soluble by extensive washing in an alkaline solution, the insolubility of the crude polymer was attributed to a formation of charge transfer complex between $FeCl_3$ and the phenoxy oxygen moiety of LC group, resulting in a $FeCl_3$-doped polymer.

Recently, Yamamoto et al. developed a dehalogenative polycondensation of 2,5-dihalothiophene using a Ni(0) catalyst. It is expected that this method enables us to synthesize a soluble polymer of PCH604T where there is no need to use a Lewis acid as a polymerization catalyst [12]. Here we have synthesized the thiophene derivative PCH504T (Scheme 4), which is similar to PCH604T, and polymerized it by the dehalogenative polycondensation.



Scheme 4

The polymer of PCH504T, abbreviated PPCH504T, was soluble in common organic solvents. In this study the chemical and electrical properties of this polymer are discussed.

1. Synthesis of 4-(*trans*-4-*n*-pentylcyclohexyl)-4-bromobutoxybenzene, PCH504Br

The brominated intermediate compound was prepared by the Williamson method for etherification [13]. A solution of *p*-(*trans*-4-*n*-pentylcyclohexyl)phenol, PCH500 (48.8 g, 0.2 mol) in acetone (100 ml) was mixed with potassium hydroxide (14.0 g, 0.25 mol) dissolved in methanol (100 ml). The mixture was added dropwise into a four-necked round bottom flask, containing a solution of 1,4-dibromobutane (172.8 g, 0.8 mol) in acetone (100 ml), over 3 hrs under moderate stirring. After refluxing the reaction mixture for 2.5 hrs on a hot water bath, water was poured in and the organic products were extracted with diethylether. After drying the extraction with anhydrous calcium chloride, diethylether was removed and the residue was distilled under reduced pressure to remove surplus dibromobutane. The solid residue was recrystallized from ethanol, and dried under vacuum to give PCH504Br in ca. 60% yield.

Anal. Calcd for $C_{21}H_{33}OBr$: C, 66.14; H, 8.66. Found: C, 65.96; H, 8.80.

2. Synthesis of 4-(*trans*-4-*n*-pentylcyclohexyl)-4-(β-thienyl)-butoxybenzene, PCH504T

The thiophene derivative was synthesized via Grignard coupling. Bis(1,3-diphenylphosphinopropane)nickel(II)-dichloride, Ni(dppp)Cl_2 (1.6 g, 3 mmol) was added to a solution of 3-bromothiophene (9.8 g, 60 mmol) in diethylether (50 ml) in a four-necked round bottom flask. The flask was cooled on an ice bath with stirring the mixture. To this mixture, a Grignard reagent prepared from magnesium (1.5 g, 60 mmol) and PCH504Br (22.9 g, 60 mmol) in diethylether (130 ml) and THF (10 ml) was added dropwise over 2.5 hrs followed by refluxing for 3.5 hrs on a hot water bath. 2N-hydrochloric acid (40 ml) was added to the reaction mixture, and the organic products were extracted with diethylether. After drying the extraction with anhydrous calcium chloride, diethylether was removed, and the residue was recrystallized from ethanol. The product was dried under vacuum to give PCH504T in ca. 73% yield. Anal. Calcd for $C_{25}H_{36}OS$: C, 78.13; H, 9.37. Found: C, 78.52; H, 9.70.

3. Dibromination of PCH504T

The 2,5-dibrominated thiophene derivative, PCH504TBr$_2$, was prepared by dibromination of PCH504T with *N*-bromosuccinimide (NBS) in DMF at 40°C according to the literature [14]. The organic products were extracted with ether, dried over anhydrous calcium chloride, evaporated, and the residue was recrystallized from ethanol. The product was dried under vacuum to give PCH504TBr$_2$ in ca. 13% yield. Anal. Calcd for $C_{25}H_{34}OSBr_2$: C, 55.39; H, 6.27. Found: C, 54.64; H, 6.15.

4. Synthesis of Poly(PCH504T), PPCH504T

The polymer was obtained by a dehalogenative polycondensation of the monomer according to the literature[12c,d]. The catalyst Ni(cod)$_2$ and the ligand 2,2'-bipyridyl were added 1.2 times that of the monomer. The reaction took place for 24 hrs at 120°C under moderate stirring in a hot oil bath. The reaction mixture was poured into a 2N HCl / MeOH solution, and the resulting dark precipitate was filtered and washed with 2N HCl / MeOH solution for several times until the solution became colorless. The polymer was reprecipitated from a chloroform solution poured into an excess of acetone and was dried under vacuum to give PPCH504T in ca. 43% yield. Anal. Calcd for $(C_{25}H_{34}OS)_n$: C, 78.49; H, 8.96. Found: C, 71.63; H, 8.05.

RESULTS AND DISCUSSION

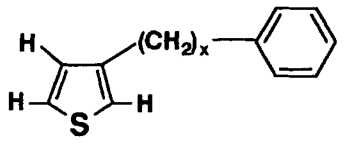
Polythiophenes with phenylalkyl groups

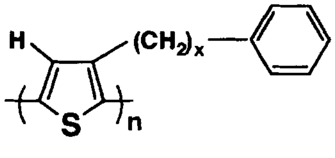
IR spectra of the monomers and the corresponding polymers are measured. The results are shown in Table I. The monomer, PBuT, showed the absorption peaks at 770, 835, and 857 cm^{-1} which are assigned to C-H out-of-plane vibrations of the thiophene ring substituted at the 3-position. In the polymer, PPBuT, the three peaks disappeared and the new peak appeared at 831 cm^{-1} which is assigned to the C-H out-of-plane vibration of the thiophene ring with substitutions at the 2-, 3-, and 5-positions. No other remarkable difference was observed compared with the spectrum of the monomer. These results indicate the formation of polythiophene derivatives with linkages at the 2- and 5-positions of thiophene ring. Similar results were also obtained in PPEtT, PPPrT, and PPPeT.

TABLE I Infrared absorption bands of monomers and polymers of 3-(ω-phenylalkyl)-thiophenes. (units of cm^{-1})

	Monomer[a]			Polymer[b]
PEtT	858	839	777	822
PPrT	862	835	774	829
PBuT	857	835	770	831
PPeT	858	833	772	833

a : C-H out of plane vibrations in mono-substituted thiophene ring.
b : C-H out of plane vibration in tri-substituted thiophene ring.





In poly(2,5-thienylene), there are three different linkages such as head-to-tail (HT), head-to-head (HH), and tail-to-tail (TT), which are attributed to 2-5', 2-2', and 5-5' couplings of adjacent thiophene rings, respectively. Wegner et al.[15] pointed our that chemical shifts of protons attached at α-carbon of alkyl group in poly(alkylthiophene) are split into two signals, and the signal with larger intensity that is located at lower magnetic field is attributed to HT linkage. Wudl et al.[16] also pointed out that in addition to the dominant signal of proton chemical shift at 6.98 ppm owing to stereoregularly linked HT-HT sequence, there are three smaller signals due to HT-HH, TT-HT, and TT-HH sequences.

Figure 1 shows ^{1}H-NMR spectrum of PPPrT, by focusing on the lower magnetic field. According to assignments of poly(3-alkylthiophene) reported by Wudl et al, the present chemical shifts at 6.92. 6.97 7.01, and 7.05 ppm are attributed to protons of the thiophene rings with HT-HT, HT-HH, TT-HT, and TT-HH sequences, respectively, as illustrated in Fig. 2. Integrated intensities of the chemical shifts gave values of 85, 5, 5, and 5 % for HT-HT, HT-HH, TT-HT, and TT-HH sequences, respectively. It is clear that PPPrT is a highly stereoregular polymer consisting of HT-HT sequence. Similar degrees of the stereoregularity were obtained in PPBuT and PPPeT polymers.

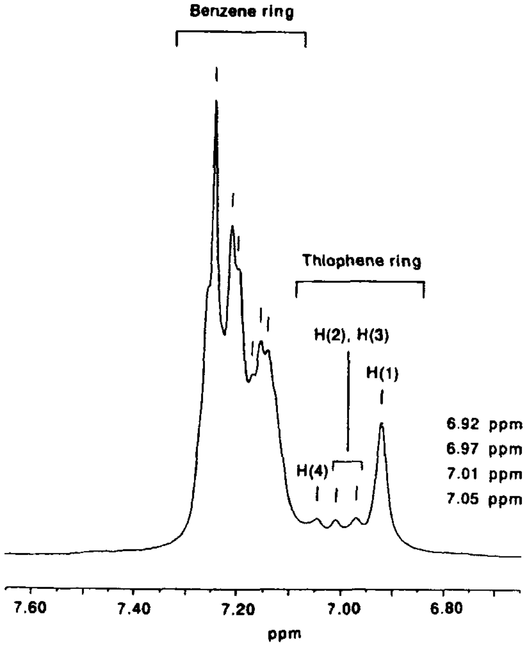


FIGURE 1 ^{1}H-NMR spectrum of PPPrT in the region of lower magnetic field.

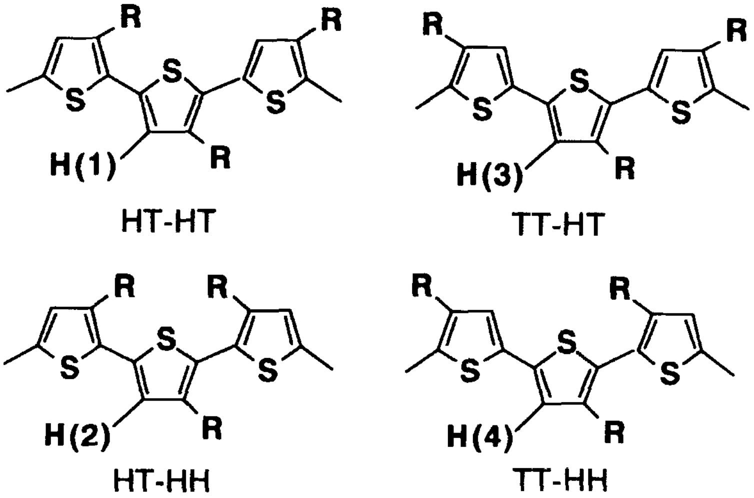


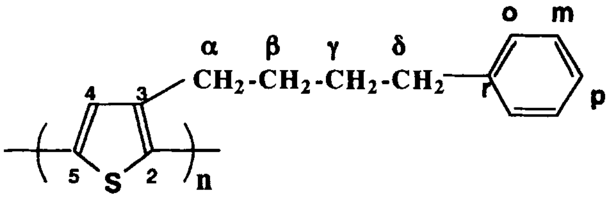
FIGURE 2 Four kinds of stereospecific sequences of the thiophene rings in poly(3-substituted thiophene).

The overall ^{13}C-NMR signals and their assignments for the representative monomer, PBuT, and the polymer, PPBuT, are summarized in Table II. In the polymer, the signals at 130.7 and 133.8 ppm are due to the carbons at 2- and 5-positions of the thiophene ring, and are notably shifted by 9 - 11 ppm towards the lower magnetic field, compared with the monomer. On the other hand, the signal at 128.7 ppm due to the carbon at 4-position of the thiophene ring showed no notable shift. This result indicates that the polymer is composed of fundamental structure of 2,5-thienylene monomer units.

TABLE II ^{13}C-NMR chemical shifts (ppm) of 3-(4-phenylbutyl)thiophene monomer, PBuT, and corresponding polymer, PPBuT

Monomer (PBuT)	Polymer (PPBuT)	Difference in chemical shift[a]	Assignment
30.1	29.3	-0.8	α
30.1	30.1	0.0	β
31.0	31.2	+0.2	γ
35.8	35.7	-0.1	δ
119.9	130.7	+10.8	2
125.1	133.8	+8.7	5
125.7	125.8	+0.1	p
128.2	128.7	+0.5	4
128.3	128.3	0.0	o
128.4	128.4	0.0	m
142.5	142.4	-0.1	r
142.9	139.6	-3.3	3

a : The positive and negative signs stand for the down-field and up-field shifts, respectively, after the polymerization.



The formation of poly(2,5-thienylene) derivatives was also confirmed in the polymers of PPrT and PPeT, except PEtT that includes a little amount of branched structure due to the linkage of adjacent units in the 2,4-positions of the thiophene ring. The ^{1}H-NMR measurements also supported the above ^{13}C-NMR results.

The molecular weights of the polymers were evaluated through GPC using THF as a developing solvent. The values of molecular weights were calibrated by polystyrene standards. In Table III are shown these results, as well as absorption bands and electrical conductivities upon iodine doping. The molecular weight of PPEtT is smaller than those of other polymers, although its molecular weight distribution is relatively narrow.

TABLE III Number-average and weight-average molecular weights, absorption bands, and electrical conductivity upon iodine doping of poly[3-(ω-phenylalkyl)-2,5-thienylenes)]

Polymer	Mn	Mw	Mw/Mn	λ_{max} (nm)	log ε	σ (S/cm)
PPEtT	3900	20000	5.1	423	3.89	0.03
PPPrT	6700	69000	10.3	432	3.89	0.37
PPBuT	5500	63000	11.5	427	3.75	0.12
PPPeT	6000	77000	12.8	430	3.53	0.34

The absorption band due to the lowest π-π* transition in the thiophene main chain was observed at 420 - 430 nm. The conjugation of the polythiophene derivatives was also confirmed by an appearance of doping effect in electrical conductivity. The cast films of PPPrT, PPBuT, and PPPeT showed electrical conductivities with orders of 10^{-7} S/cm and 10^{-1} S/cm before and after iodine doping, respectively. The relatively lower conductivity with an order of 10^{-2} S/cm in the doped film of PPEtT may be due to its lower molecular weight and/or partly irregularly linked 2,4-thienylene branched structure.

Polythiophene with liquid crystalline group

The dehalogenative polycondensation of PCH504T gave a soluble and fusible polymer. The polymer obtained by reprecipitation from a chloroform solution was a red-brown powder, and was soluble in common organic solvents such as chloroform, THF, toluene, etc. at room temperature. In Table IV are summarized results of the polymerization of PCH504TBr$_2$. The degree of polymerization, evaluated from number average molecular weight, was ca. 100, assuming that there are no bromine atoms in the terminal of polymer chains. Meanwhile, the polymer synthesized by the chemical oxidative polymerization using FeCl$_3$ gave some insoluble fractions even after repeated washing in a concentrated alkaline solution. The soluble fraction had a less degree of polymerization (ca. 90) and a lower solubility, than the dehalogenatively polycondensed polymer.

TABLE IV Polymerization results of PPCH504T

M_n	M_w	M_w/M_n	DP[a]	yield (%)	color
39000	82000	2.1	102	25	dark red brown

[a] Degree of polymerization calculated from M_n, assuming that all bromines have been condensed.

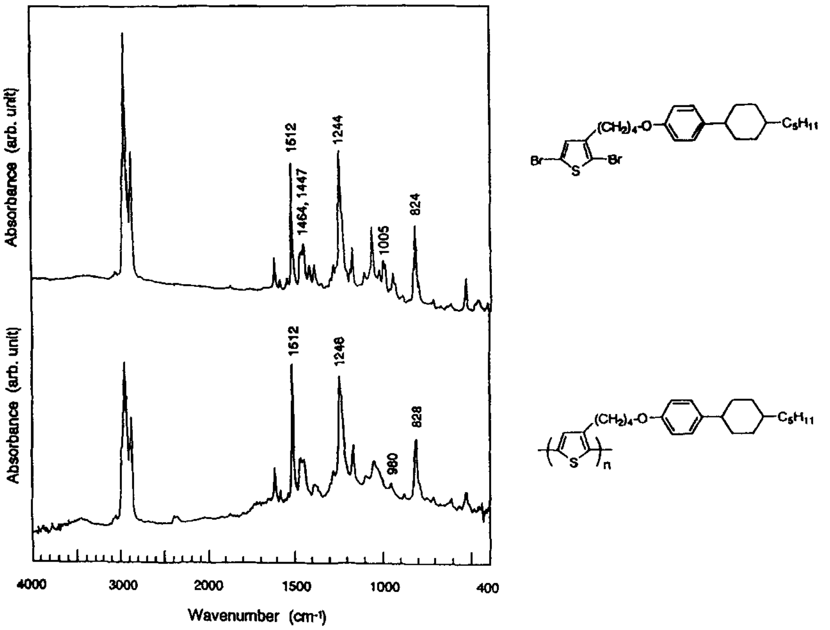


FIGURE 3 IR spectra of PCH504TBr$_2$ (upper) and PPCH504T (below).

IR absorption spectra of the dibrominated monomer (PCH504TBr$_2$) and the polymer (PPCH504T) are shown in Fig. 3. Absorption band due to C-H out-of-plain vibrations of the 2,5-disubstituted thiophene ring was observed at 824 and 828 cm^{-1} for the monomer and the polymer, respectively [17]. Bands around 3054 cm^{-1} are due to C-H stretching vibrations of the thiophene ring. The ring stretching vibrations of the substituted thiophene of the polymer can be seen at 1449 and 1468 cm^{-1}. Small intensity band at 951 cm^{-1} is due to C-Br stretching vibration, and its intensity became weaker in the polymer, which indicates that the dehalogenation has occurred in most of the thiophene rings [18]. Absorption band at 1244 cm^{-1} is well assigned to C-O-C stretching vibration.

^{1}H-NMR spectrum of PPCH504T solution is shown in Fig. 4. ^{1}H- and ^{13}C-NMR spectroscopy are essential on discussing the regioregularity of poly(3-mono-substituted thiophene)s, because they provide information on the substitution patterns in the polymer backbone. There are four different chemical environments for the proton in the 4-position of the thiophene ring, which gives four signals in the vicinity of 7 ppm in the ^{1}H-NMR spectrum [19,20]. In the present polymer, however, the liquid crystalline substituent contains the phenyl

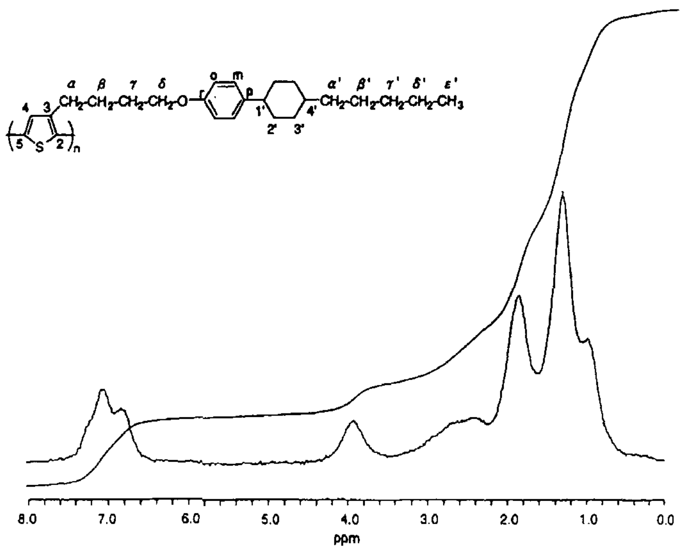


FIGURE 4 ^{1}H-NMR spectrum of PPCH504T.

moiety which has chemical shifts similar to those of the thiophene ring. This makes it difficult to identify the signals of the polymer backbone. For this reason, it was not possible to determine the exact regularity of the polymer. Nevertheless, the dehalogenative condensed polymer seems to be much more stereoregular than the chemically oxidative polymer. In fact, the spectrum of the latter polymer showed a very broad signals near 7 ppm, implying an existence of several kinds of protons due to the stereo-irregularity.

Figure 5 shows ^{13}C-NMR spectrum of the polymer. Similar to the ^{1}H-NMR, chemical shifts of the carbons of the phenyl group and those of the thiophene ring appeared to be very close. Considering the DEPT 135 spectrum, there was a small signal at 128 ppm due to the carbon in the 2-position of the thiophene ring. A large signal at 127 ppm is due to the carbon of the phenyl group. A small signal at 137 ppm is due to the carbon in the 5-position of the thiophene ring. Signals due to the carbons in 3- and 4-positions of the thiophene ring can be seen at 143 and 124 ppm, respectively [20,21].

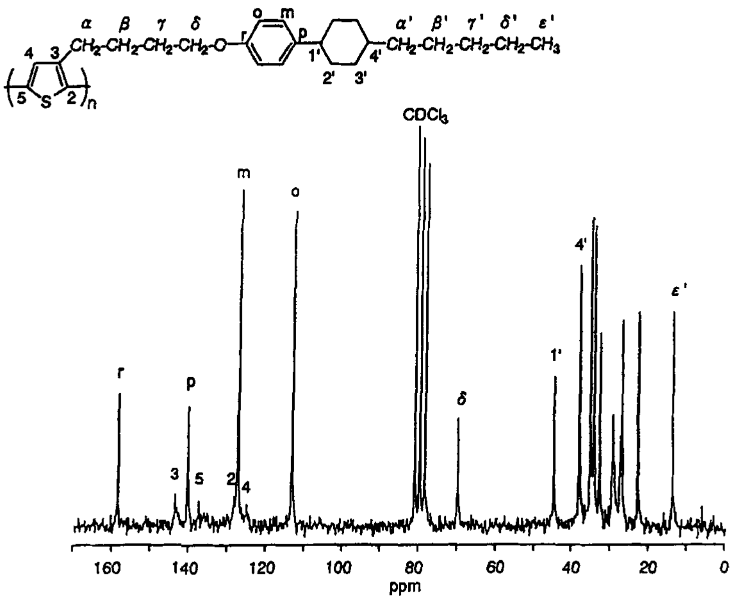


FIGURE 5 ^{13}C-NMR spectrum of PPCH504T.

Table V summarizes phase transition temperatures of the polymer (PPCH504T), determined from polarizing optical micrograph, as well as those of the precursor (PCH504Br) and the monomer (PCH504T) discussed in the previous section. PCH504Br exhibited a schlieren texture in the cooling process, indicating a monotropic nematic liquid crystal. PCH504T showed no mesophase. On the other hand, the PPCH504T showed a monotropic liquid crystal; In the heating process, the polymer changed directly to the isotropic phase from the solid state at 136°C. In the cooling process, the polymer exhibited schlieren and droplet textures at 110~130 °C, as shown in Fig. 6, demonstrating a formation of nematic liquid crystalline phase.

TABLE V Phase transition temperatures (°C) determined by polarizing optical micrography

	the second cooling process					the second heating process		
PCH504Br	K	31.1	N	31.3	I	K	46.0	I
PCH504T	K	35.2	I			K	37.6	I
PPCH504T	G	109.8	N	131.8	I	K	136.2	I

K: crystal, G: glassy, N: nematic, I: isotropic

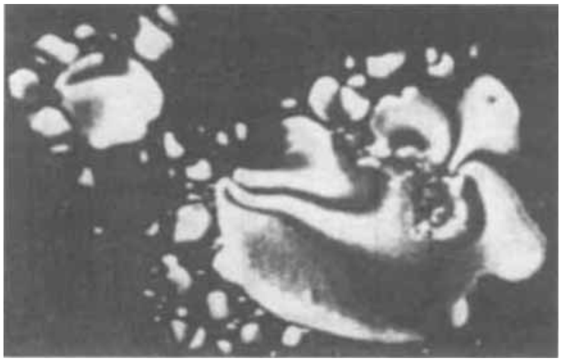


FIGURE 6 Polarizing optical micrograph of PPCH504T; Schlieren texture at 124 °C in the cooling process.

The existence of the mesophase for PPCH504T was also confirmed in the differential scanning calorimeter (DSC) thermograms (Fig. 7). The glass to isotropic phase transition in the heating process was observed as the broad endothermic peak ranging from 75 to 100 °C, which is substantially lower than that observed in the polarizing optical microscope (Table V). Nevertheless, the small exothermic peak can be seen in the cooling process around 113 °C, which corresponds to the phase transition from the isotropic to the nematic phase.

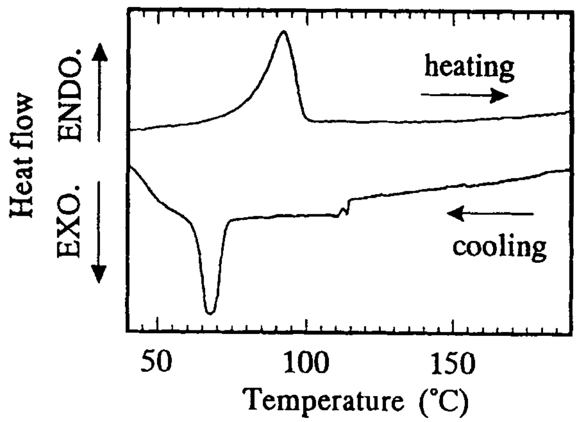


FIGURE 7 DSC thermograms of PPCH504T.

It should be noted here that the liquid crystalline phase of the present polymer was less reproducible. Another trial of synthesis under the same polymerization conditions gave a polymer with no liquid crystalline phase. One of the reasons for such a low reproducibility of the liquid crystalline phase is that the spacer length of the PCH504 substituent is not enough for allowing a flexible motion of the liquid crystalline group. In fact, the subsequent work, by treating longer methylene chains as spacers, gave well reproducible liquid crystalline polythiophene derivatives [22]. It has also been reported by Finkelmann et al. that in case of side chain liquid crystalline polymers, it becomes much easier to achieve an anisotropic orientation of mesogenic groups by linking them to the main chain via flexible spacer groups, compared with direct linkages [23]. Hence, it must be important for the mesogenic group to have a high flexibility so as to behave as if it were independent to the main chain.

UV-Vis absorption spectra of PPCH504T in solution and cast film are shown in Fig. 8. The THF solution of the polymer has a maximum at 410 nm due to π–π* transition of the conjugated backbone, by which band-edge bandgap was evaluated to be 2.6 eV [24]. In contrast, the cast film prepared from chloroform has a maximum at 417 nm, indicating a longer effective conjugation compared with the polymer solution. In other words, this may be due to an increase of coplanarity of the main chain in the cast film.

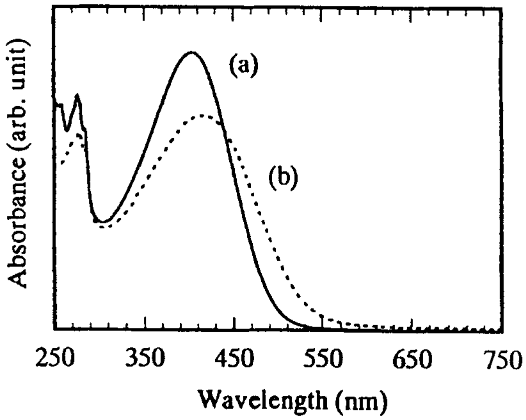


FIGURE 8 UV-Vis absorption spectra of PPCH504T;
(a) THF solution, (b) cast film.

The cast film of PPCH504T showed an electrical conductivity of 10^{-6} ~10^{-5} S/cm before doping. Iodine doping was carried out by exposing the film to a vapor of iodine. Maximum conductivity after doping was 10^{-3} S/cm. It took more than 30 hours to attain the maximum doping, probably because the bulky substituent such as PCH504 group might disturb the attack of the dopant to the polymer chains.

CONCLUSION

1. A series of 3-(ω-phenylalkyl)thiophenes with methylene chain lengths of 2 ~ 5 as a spacer were synthesized. The chemical oxidative polymerizations of these monomers gave soluble polymers with stereoregularly linked 2,5-thienylene structure. Especially, PPPrT, PPBuT, and PPPeT were found to have a high stereoregularity in which the HT-HT sequence is as high as 85 %.

The cast films of the polymers showed electrical conductivities of an order of 10^{-1} S/cm upon iodine doping. Among the polymers, PPEtT has a relatively smaller average molecular weight and a lower electrical conductivity in the doping. Therefore the length of more than 3 in the methylene spacer is recommended for synthesis of highly conjugated poly(substituted thiophene)s.

2. The thiophene monomer with the liquid crystalline group was synthesized by introducing the phenoxycyclohexyl mesogenic core into the 3-position of the thiophene ring. The chemical polymerization of the monomer yielded insoluble polymer. Similar result was found in the polymerization of 3-(4-phenoxybutyl)thiophene, POBuT. It may be argued that the existence of ether-type oxygen atom linked with phenyl ring interferes the polymerization through charge transfer interaction with $FeCl_3$ used as a catalyst. This might cause cross-linkages between the side chains of the polythiophene derivatives, giving insoluble polymers in organic solvents.

3. The liquid crystalline polythiophene derivative, PPCH504T, was synthesized through the dehalogenative polycondensation of 2,5-dibrominated thiophene monomer. The polymer was soluble in common organic solvents, and it exhibited schlieren and droplet textures in the cooling process at 110 ~ 130 °C, demonstrating a formation of monotropic nematic liquid crystalline phase. However, the reproducibility of the mesophase remained low, suggesting that it is required to adopt a longer methylene spacer in the liquid crystalline group.

The THF solution of PPCH504T showed an absorption maximum at 410 nm, and the energy gap was evaluated to be 2.6 eV. The neutral film of PPCH504T had an electrical conductivity of 10^{-6} ~ 10^{-5} S/cm, which increased to 10^{-3} S/cm after iodine doping.

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References

[1.] (a) K.-Y. Jen, G. G. Miller, and R. L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, 1346 (1986); (b) R. L. Elsenbaumer, K.-Y. Jen, and R. Oboodi, *Synth. Met.*, **15**, 169 (1986).

[2.] M. Feldhues, G. Kämpf, H. Litterer, T. Mecklenburg, and P. Wegener, *Synth. Met.*, **28**, C487 (1989).

[3.] J. Roncali, R. Garreau, D. Delabouglise, F. Garnier, M. Lemaire, *Synth. Met.*, **28**, C341 (1989).

[4.] B. Zinger, Y. Greenwald, and I. Rubinstein, *Synth. Met.*, **41-43**, 683 (1991).

[5.] T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 11 (1974).

[6.] K. Akagi, H. Tanaka, R. Toyoshima, and H. Shirakawa, *Trans. Mat. Res. Soc. Jpn.*, **15A**, 513 (1994).

[7.] R. Toyoshima, M. Narita, K. Akagi, and H. Shirakawa, *Synth. Met.*, **69**, 289 (1995).

[8.] N. Koide and H. Iida, *Mol. Cryst. Liq. Cryst.*, **261**, 427 (1995).

[9.] (a) S.-Y. Oh, K. Akagi, H. Shirakawa, and K. Araya, *Macromolecules*, **26**, 6203 (1993); (b) K. Akagi, S.-Y. Oh, H. Goto, Y. Kadokura, and H. Shirakawa, *Trans. Mat. Res. Soc. Jpn.*, **15A**, 259 (1994); (c) H. Shirakawa, Y. Kadokura, H. Goto, S.-Y. Oh, K. Akagi, and K. Araya, *Mol. Cryst. Liq. Cryst.*, **255**, 213 (1994); (d) K. Akagi, H. Goto, Y. Kadokura, H. Shirakawa, S.-Y. Oh, and K. Araya, *Synth. Met.*, **69**, 13 (1995); (e) K. Akagi, H. Goto, H. Shirakawa, T. Nishizawa, and K. Masuda, *Synth. Met.*, **69**, 33 (1995); (f) H. Goto, K. Akagi, H. Shirakawa, S.-Y. Oh, and K. Araya, *Synth. Met.*, **71**, 1899 (1995); (g) K. Akagi, H. Goto, K. Iino, H. Shirakawa, and J. Isoya, *Mol. Cryst. Liq. Cryst.*, **267**, 277 (1995); (h) K. Yoshino, K. Kobayashi, K. Myojin, M. Ozaki, K. Akagi, H. Goto, and H. Shirakawa, *Jpn. J. Appl. Phys.*, **35**, 3964 (1996); (i) K. Akagi and H. Shirakawa, *Macromolecular Symposia*, **104**, 137, (1996); (j) K. Akagi and H. Shirakawa, *The Polymeric Materials Encyclopedia. Synthesis, Properties and Applications* (CRC Press, 1996), Vol. 5, p. 3669; (k) K. Akagi and H. Shirakawa in *Current Trends in Polymer Science*, edited by J. C. Alexander (Research Trends, 1997), Chap. 2, p. 107.

[10.] H. Shirakawa, S. Fukumoto, H. Tanaka, Y. Ugawa, K. AKagi, K. Kaeriyama, and H. Masuda, *J. Macromol. Soc. -Chem.*, **A28**, 1245 (1991).

[11.] R. A. Schunn, *Inorg. Synth.*, **15**, 5 (1974).

[12.] (a) T. Yamamoto, K. Osakada, T. Wakabayashi, and A. Yamamoto, *Makromol. Chem., Rapid Commun.*, **6**, 671 (1985); (b) T. Yamamoto, Y. Miyazaki, T. Fukuda, Z.-H. Zhou, T. Maruyama, T. Kanbara, and K. Osakada, *Synth. Met.*, **55-57**, 1214 (1993); (c) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.-H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992); (d) Y. Miyazaki and T. Yamamoto, *Synth. Met.*, **64**, 69 (1994).

[13.] P. Bäuerle, F. Würthner, and S. Heid, *Angew. Chem. Int. Ed. Engl.*, **29**, 419 (1990).

[14.] P. Bäuerle, F. Pfau, H. Schlupp, F. Würthner, K.-U. Gaudl, M. B. Caro, and P. Fischer, *J. Chem. Soc., Perkin Trans.*, **2**, 489 (1993).

[15.] M. Leclerc, F. M. Diaz, and G. Wegner, *Macromol. Chem.*, **190**, 3105 (1989).

[16.] R. M. Souto Maior, K. Hinklemann, H. Eckert, and F. Wudl, *Macromolecules*, **23**, 1268 (1990).

[17.] K. E. Schulte, A. Kreutzberger, and G. Bohn, *Chem. Ber.*, **97**, 3263 (1964).

[18.] J. W.-P. Lin and L. P. Dudek, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2869 (1980).

[19.] (a) R. M. Souto Maior, K. Hinkelmann, H. Eckert, and F. Wudl, *Macromolecules*, **23**, 1268 (1990); (b) M. Sato and H. Morii, *Polym. Commun.*, **32**, 42 (1991).

[20.] T.-A. Chen, X. Wu, and R. D. Rieke, *J. Am. Chem. Soc.*, **117**, 233 (1995).

[21.] (a) S. Hotta, M. Soga, and N. Sonoda, *Synth. Met.*, **26**, 267 (1988); (b) M. Leclerc, F. M. Diaz, and G. Wegner, *Makromol. Chem.*, **190**, 3105 (1989).

[22.] R. Toyoshima, S. Shibata, I. Osaka, K. Akagi, and H. Shirakawa, to be submitted for publication.

[23.] H. Finkelmann, M. Happ, M. Portugal, and H. Ringsdorf, *Makromol. Chem.*, **179**, 2541 (1978).

[24.] T.-C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, *Phys. Rev. B*, **30**, 702 (1984).