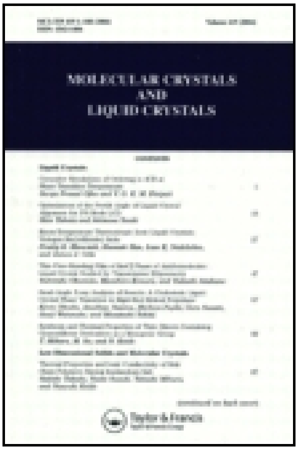

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Synthesis and Physical Properties of Side-Chain Type Liquid Crystalline Polythiophene Derivatives

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Synthesis and Physical Properties of Side-Chain Type Liquid Crystalline Polythiophene Derivatives

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Side-Chain type liquid crystalline polythiophenes containing a mesogenic group at 3-position of the thiophene ring were synthesized. Homopolymers were obtained by the dehalogenation polycondensation with zero valence nickel as a catalyst, and copolymers were synthesized by the Stille coupling reaction with zero valence palladium as a catalyst. Homopolymers and copolymers involved a cyano group at the end of the mesogenic group exhibited a nematic phase, while a smectic phase was shown for the homopolymer having the ester bond between the thiophene ring and an alkyl spacer. After annealing of the polymer, the oxidation-reduction potential peaks of the polymer were lower than that of the neat samples. The conductivity of I_2 doped thermal treated homopolymers and copolymers were 10^{-2}S/cm and 10^{-1}S/cm, respectively.

Keywords: polythiophene; nematic phase; smectic phase; conductivity; side-chain type liquid crystalline polymer

INTRODUCTION

Recently, π-conjugated polymers have attracted a considerable interest and have been the research subject of numerous investigations for their electrical conductivity and non-linear optical property[1-3]. In general, π-conjugated

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polymers, such as polyacetylene, polyphenylene, polythiophene and polypyrrole are insoluble and infusible for their rigid structures. As for polythiophene , the solubility and fusibility are improved remarkably by lateral substitution of the thiophene ring with alkyl or alkoxy group [4].

It is well-known that the conductivity of π-conjugated polymers is changed remarkably by the orientation of the polymer backbone. Two methods to control the orientation of a π-conjugated polymers are known, the stretching of the polymer film and the polymerization in a liquid crystalline medium under a magnetic field [5]. So, in those backgrounds it can be expected that the solubility and fusibility of the polythiophenes are improved by introducing the self-organizing group, that is mesogenic group, at the 3-position of the thiophene ring. Consequently, the polymer backbone of the polythiophene derivatives can be easily oriented to the direction of the external fields, and furthermore their conductivity was increased drastically [6-8].

As for polymerization methods of the thiophene, oxidative polymerization [9-11], electrolytic polymerization[12-15] and polycondensation[16-20] are well-known. Both oxidative polymerization and electrolytic polymerization of thiophene are undesirable in terms of that irregular coupling was caused

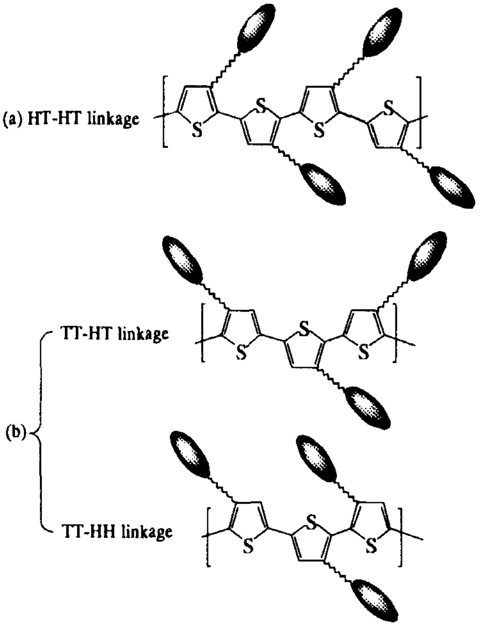
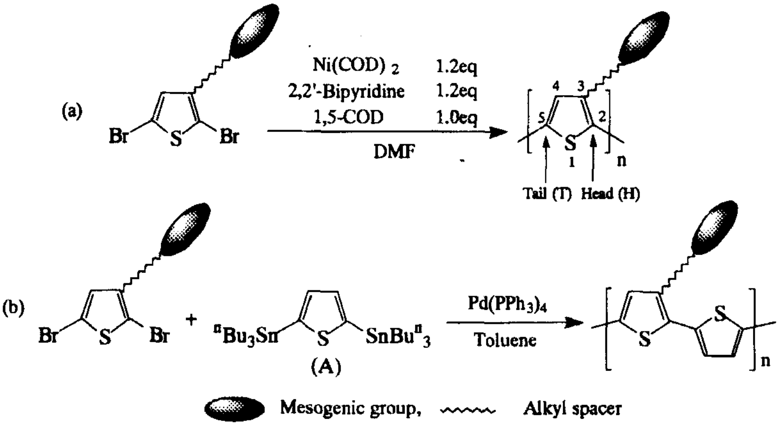


FIGURE 1 Possible regiochemical linkage in polythiophenes (regioregular-(a),and regiorandom polythiophenes(b))

during polymerizations, or having a difficulty to remove the catalyst in the polymers such as Lewis acid and electrolyte worked as a dopant [6-7]. So, thiophene homopolymers were synthesized by the dehalogenation polycondensation which progresses in the mild condition and didn't happen the irregular coupling except for 2,5 position, as shown in Scheme 1(a) [21]. However, the regiorandom polymer shown in Fig. 1(b) can be synthesized rather than the regioregular polymer shown in Fig. 1(a) by the polymerization method of Scheme 1(a) [21].



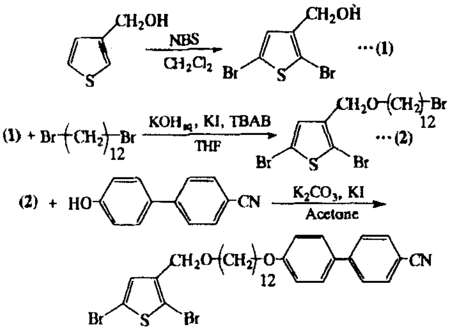
SCHEME 1 Synthesis of homopolymer and copolymer

The π-conjugated length are expanded for high planarity of the thiophene rings which adjoined each other in the head-to-tail {H-T(2,5)} linkage of the main chain. On the other hand, the existence of the head-to-head {H-H(2,2)} linkage in the polymer chain causes the shorter π-conjugated of the thiophene rings adjoined each other [22], and the π-conjugated length were shortened. These disorders of the regioregularity in the main chain of polythiophene derivatives can reduce the desired physical properties of the materials, for instance the electroconductivity [23a] and electroluminescence [23b].

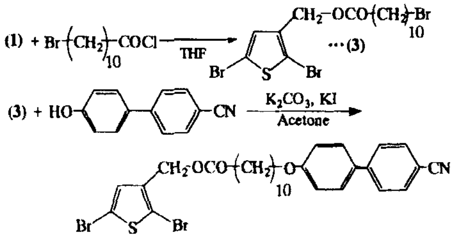
In this report, in order to get a higher planarity and longer conjugated length,, the copolymers having a mesogenic side chain arranged alternately were synthesized, as shown in Scheme 1(b), and the thermal and optical properties of the polymers were investigated.

Results and discussion

The path for synthesis is shown in Scheme 2(a) and 2(b) ,respectively. 3-Thiophenemethanol was the starting material for dibromothiophene monomers. Bromination of 3-thiophenemethanol was carried out using N-bromosuccineimide(NBS) at room temperature. The mesogenic group was introduced into 3-position of the thiophene ring through an alkyl spacer, and connected with ether or ester bond as shown in scheme 2(a) and 2(b) ,respectively. We used a cyano biphenyl group as a rigid core which was superior to alkoxy biphenyl group regarding solubility and fusibility [6]. Their products in each reaction step were confirmed by ^{1}H-NMR and IR measurements.



(a) Ether type monomer[Th12CB]



(b) Ester type monomer[Th11CB]

SCHEME 2 Synthesis of mesogenic dibromothiophene monomers

The transition temperatures of dibromothiophene monomers are shown in Table I . The monomer having the ether bond between the thiophene ring and an alkyl spacer (Th12CB) exhibited a homeotropic orientation on the cooling scan confirmed by the conoscopic measurement. On the other hand, liquid crystalline phase of the monomer(Th11CB) having the ester bond between the thiophene ring and an alkyl spacer was not observed.

TABLE I Phase transition temperatures of monomers

Monomers	Phase transition temperatures (℃)
Th12CB	$\mathrm{Cr} \xrightarrow{57} \mathrm{I} \xrightarrow{37} \mathrm{H} \xrightarrow{30} \mathrm{Cr}$
Th11CB	$\mathrm{Cr} \xrightleftharpoons[?]{62} \mathrm{I}$

Cr:crystal, H:homeotropic, I:isotropic

The colors of the homopolymers and the copolymers are reddish brown and red, respectively. These polymers are soluble in common organic solvents, such as chloroform, toluene, THF and DMF.

Table II shows the phase transition temperatures and number-average molecular weights of the polymers. Both of the ether bond type homopolymer(PTh12CB) and copolymer(CPTh12CB) had a higher molecular weight than that of the ester bond type homopolymer(PTh11CB) and copolymer(CPTh11CB).

TABLE II Phase transition temperatures of polymers

Polymers	Molecular weight ($\overline{Mn}$)	Phase transition temperatures (℃)
PTh12CB	71,100	$\mathrm{g} \xrightleftharpoons[?]{?} \mathrm{N} \xrightleftharpoons[101]{106} \mathrm{I}$
PTh11CB	5,400	$\mathrm{g} \xrightleftharpoons[?]{?} \mathrm{Sm} \xrightleftharpoons[74]{76} \mathrm{I}$
CPTh12CB	6,500	$\mathrm{g} \xrightleftharpoons[?]{92} \mathrm{N} \xrightleftharpoons[123]{123} \mathrm{I}$
CPTh11CB	2,200	$\mathrm{g} \xrightleftharpoons[97]{97} \mathrm{N} \xrightleftharpoons[124]{124} \mathrm{I}$

g:glassy, N:nematic, Sm:smectic, I:isotropic

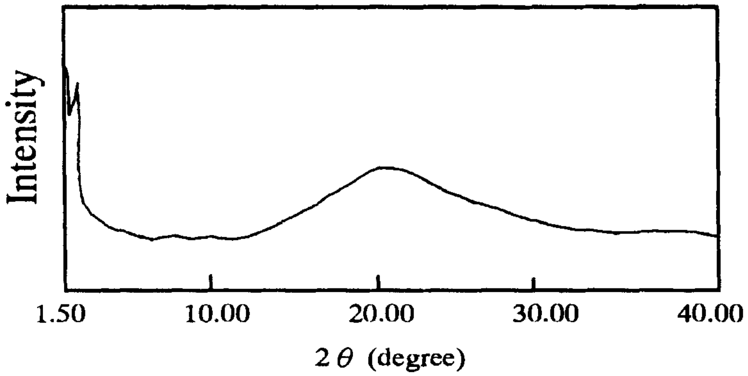


FIGURE 2 X-ray diffraction pattern of PTh11CB

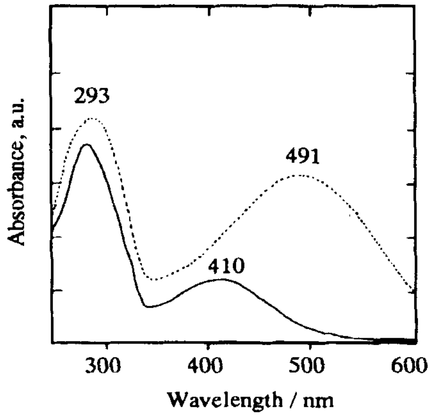


FIGURE 3 UV-vis absorption spectra of PTh11CB (solid line) and CPTh11CB(broken line)

A schlieren texture characteristic of nematic phase was observed for PTh12CB, CPTh12CB and CPTh11CB, while PTh11CB exhibited a focal conic fan type texture. From the X-ray diffractogram measurement of PTh11CB, as shown in Fig. 2, a broad peak was observed in the wide-angle range, furthermore a sharp peak was detected in the small-angle range. The layer spacing of PTh11CB was 51 Å corresponding to the double length of the side chain. Consequently, it would be identified that PTh11CB formed the bilayer structure at the mesophase.

The thermal stability of the mesophase for the ether bond type copolymer was superrior to that for the ester bond type copolymer.

Fig. 3 shows the UV-visible absorption spectra of PTh12CB and CPTh12CB. Two absorption peaks were observed at 293nm and 410nm for PTh11CB. The absorption peaks at 293nm and 410nm were attributed to a cyano group and the π-π* absorption peak, respectively. While, the π-π* absorption peak of CPTh11CB was 491nm. In spite of the lower molecular weight of CPTh11CB than that of PTh11CB, the π-π* absorption peak for CPTh11CB was shifted to the longer wavelength at 491nm compared with that of PTh11CB at 410nm. This demonstrates that the copolymer has a longer effective conjugated length than that of the homopolymer.

The fluorescence spectra of PTh11CB and CPTh11CB are shown in Fig. 4. The emission peak top of PTh11CB and CPTh11CB were 577nm and 630nm, respectively. The emission peak top for CPTh11CB was longer wavelength than that for PTh11CB.

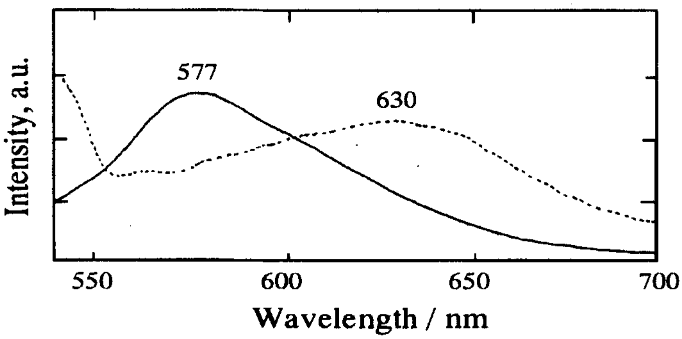


FIGURE 4 Fluorescence spectra of PTh11CB (solid line) and CPTh11CB (broken line). Excitation wavelength 525nm.

The electrochemical properties of the polymers were examined using a cyclic voltamogram measurements. The CV curves of CPTh12CB are shown in Fig. 5. The oxidation /reduction peaks of the neat CPTh12CB were detected at 0.64V and at 0.56V, respectively. However, the oxidation/reduction peaks of

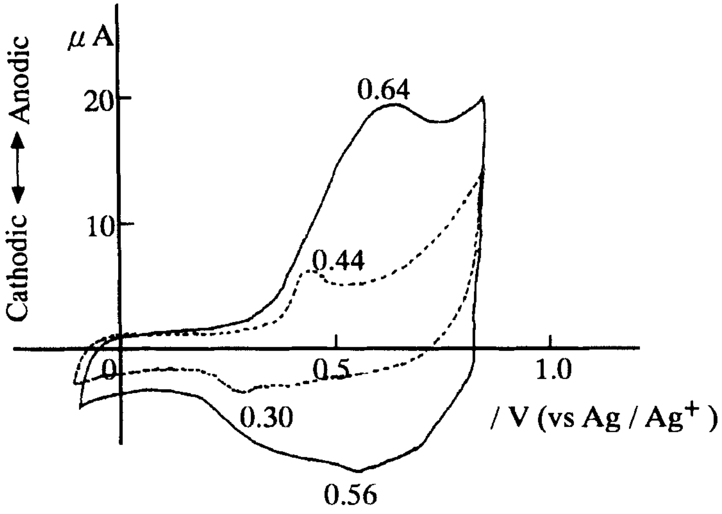


FIGURE 5 Cyclic voltamograms of etherbond type copolymer (CPTh12CB)

the thermal treated CPTh12CB were shifted to the lower potentials, 0.44V and 0.30V, respectively, than that of the neat sample. These shifts suggested that the planarity of the polymer backbone was enhanced via annealing. Consequently, doping and undoping of the electrolyte to the main chain of the thiophene derivatives were caused more smoothly after annealing. The oxida-

TABLE Ⅲ Oxidation-reduction peaks of polymers

Polymers	Oxidation peak (V versus Ag/Ag$^+$)	Reduction peak (V versus Ag/Ag$^+$)
PTh12CB	1.03 (0.85)*	0.68 (0.61)
CPTh12CB	0.64 (0.44)	0.56 (0.30)
PTh11CB	0.81 (0.81)	0.69 (0.69)
CPTh11CB	0.70 (0.41)	0.48 (0.36)

*( ):after annealing

tion /reduction peaks of the polymers are summarized in Table Ⅲ. The oxidation/reduction peaks of the copolymers were lower than that of the homopolymers. This demonstrates that doping/undoping of the electrolyte for the copolymers having a longer effective conjugated length is caused smoothly than that for homopolymers. The oxidation /reduction peaks of the polymers were observed reversibly, and the doping/undoping were accompanied by color changes. During the p-doping, the color of the polymer film was changed from red to blue, while the undoped polymer films the color was changed from blue to red. These color changes of the polymer film were observed by repeating the redox cycle with unchanged the potential value, so the polymers can be oxidized and reduced reversibly.

TABLE Ⅳ Conductivity of polymers

Polymers	Molecular weight	π - π * absorption (λ_{max}) (nm)	mesophase	Conductivity a)(S/cm)	
				neat	After annealing
PTh12CB	71,100	425	Nematic	10^{-6}	10^{-2}
PTh11CB	5,400	410	Smectic	10^{-6}	10^{-3}
CPTh12CB	6,500	501	Nematic	10^{-3}	10^{-1}
CPTh11CB	2,200	491	Nematic	10^{-4}	10^{-3}

a) Iodine doped

The electrical conductivity of the polymers was shown in Table Ⅳ. The polymer films were doped under I_2 atmosphere. The conductivity of the virgin homopolymers (PTh12CB and PTh11CB) were independent of the mesomorphic structures and their values were about 10^{-6} S/cm. However, the conductivity of the annealed homopolymers increased drastically to 10^{-2} S/cm for nematic phase (PTh12CB) and 10^{-3} S/cm for smectic phase (PTh11CB). As for molecular weight of PTh11CB, it was about 1/14 of PTh12CB's, and for maximum absorption wavelength of π-π* transition of the main chain was shorter about 15nm. In spite of these results, the conductivity of the annealed PTh11CB was only 1/10 than that of thermal treated PTh12CB. Therefore it was supposed that there was some possibility of showing the higher conductivity for the smectic phase which formed the layer structure than that of the nematic phase. In the case of copolymers,the conductivities of virgin CPTh12CB and CPTh11CB were 10^{-3} S/cm and 10^{-4} S/cm, respectively. Furthermore, after annealing the polymers , the conductivity of CPTh12CB increased to 10^{-1} S/cm, and of CPTh11CB to 10^{-3} S/cm. The molecular weight of CPTh12CB was smaller than that of PTh12CB as shown in Table Ⅳ ,it was about 1/10 of PTh12CB, and that of CPTh11CB was about 1/2 of PTh11CB, and also the maximum absorption wavelength of π–π^* transition of CPTh12CB was 76nm longer than that of PTh12CB, and of CPTh11CB was 81nm longer than that of PTh11CB. From the above results, it would be expected that the higher molecular weight copolymers have the possibility of higher conductivity.

Conclusion

A nematic phase was observed for homopolymer having the ether bond between an alkyl chain and the thiophene ring, while a smectic phase was shown for homopolymer connected with the ester bond between the thiophene ring and an alkyl spacer. As for copolymers, only a nematic phase was observed. The π–π^* absorption peak of the copolymers introduced the mesogenic group to the thiophene ring alternately was shifted to longer wavelengths than that of homopolymers having the same mesogenic group. The oxidation-reduction peaks of the annealed copolymers was shifted to lower potentials than the virgin samples. The conductivity of the annealed liquid crystalline polymers were about $10 \sim 10^4$ times larger than that of the neat samples.

Experimental

Measurements

^{1}H-NMR spectra were obtained from a JEOL JNM-PMX60 type spectrometer using $CDCl_3$ as a solvent. Infrared(IR) spectra were taken on a JEOL

JIR7000 type FT-IR spectrometer. DSC measurements were conducted with a Mettler 3000 series. Optical microscopy was performed on a Nikon polarizing optical microscopy equipped with a Mettler FP80 controller and a FP82 hot stage. Gel permeation chromatography(GPC) was carried out with a Tosoh HLC-8020 instrument using chloroform as the eluent. The instrument was calibrated with a polystyrene standard. X-ray diffraction patterns were recorded with a Rigaku X-ray diffractometer RAD-2B system with Ni-filtered Cu-K α radiation. UV-vis spectra were taken on a HITACHI U-3410 spectrophotometer and fluorescence spectra were obtained on a HITACHI F-4500 spectrophotofluorometer with polymer thin films cast from $CHCl_3$ solutions on a quarts plate. Cyclic voltamograms(CVs) were measured by using a Hokuto Denko HB-111 function generator and a HA-501 potentiostat/galvanostat. A polymer was cast from a $CHCl_3$ solution onto a ITO glass plate, and this working electrode was heated to 95% of the clearing temperature of a sample annealed for 1h, and subsequently cooled to room temperature. After that, the electrode which was thermal treated or not was set in an acetonitrile solution of 0.1M $LiClO_4$ as an electrolyte. A platinum electrode was used as a counter electrode and an Ag/Ag^+ electrode was used as a reference electrode. The electroconductivities were measured with a Mitsubishikagaku Loresta HP (MCP-T410) electrometer by using four-probe (Mitsubishikagaku MCP-TP06P) technique at room temperature under N_2 atmosphere.

Materials

The synthesis route for mesogenic dibromothiophene monomers and polymers are shown in Scheme 2 and Scheme 1, respectively.

Compounds(1)~(3) ,mesogenic thiophenemonomers,(a)and(b), and homopolymers,(PTh12CB) and (PTh11CB) were synthesized according to the literature[6]-[8],[24]. The procedure of compound(A), copolymers,(CPTh12CB) and (CPTh11CB) are described below.

Synthesis of copolymers

Copolymers were prepared according to Scheme 1(b)[25].

[2,5-bis(tri-n-butylstannyl)thiophene(A)][26]

In a three-necked flask was charged with 2,5-dibromothiophene (5.4g, 2.3×10^{-2} mol) and 50ml of dry THF under nitrogen. After cooling to -78℃, 29.8ml(5.0×10^{-2} mol) of 1.6M n-butyllithium in hexane was dropped to this solution and the mixture was stirred for 0.5h. 7.5ml(5.0×10^{-2} mol) of N,N,N',N'-tetramethylethylenediamine(TMEDA) was dropped to the mixture and stirred for 0.5h at the same temperature. 16.3g(5.0×10^{-2} mol) of tri-n-butyltinchloride in 10ml of dry THF. The mixture was allowed to warm to -50 ℃ and was stirred at this temperature for 4h. The reaction was quenched with 100ml of water at 0℃ with vigorous stirring. The organic layer was separated and then evaporated. 100ml of chloroform and 100ml of 10% HCl_{aq} were added to the residue, and washed with water until organic layer was neutral. The organic layer was dehydrated with $MgSO_4$ and solvent was removed under reduced pressure, and the excessive tri-n-butyltinchloride was removed from the residue by the fractional distillation. 12.0g(77.9% yield) of light yellow oil was obtained.

^{1}H-NMR ($CDCl_3$, δ ppm):0.7-2.0(m,54H), 7.7(s,2H)

Copolymerization

[CPTh12CB]: Dried shlenk flask was charged with compound Th12CB (0.70g, 1.0×10^{-3} mol), tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$,(24mg, 2.1×10^{-5} mol). 10ml of dry toluene and compound A (0.68g, 1.0×10^{-3} mol) were then added via syringe. The reaction mixture was stirred at 85℃ for 48h in a stream of nitrogen. After the reaction, the solution was poured into hexane to precipitate the polymer. The polymer was washed with methanol, 10% $EDTA_{aq}$, water and finally acetone. The polymer was further purified by dissolution in chloroform and reprecipitation with hexane. 0.44g(70.7% yield) of CPTh12CB was obtained as red powder.

IR(KBr,cm^{-1}):2921,2850(C-H),2223(CN),1602,1494(C-C, Ar),1249(C-

O,Ar),1097(C-O,Aliphatic),850(C-H, hetero- cyclic),821(C-H,Ar)

The copolymer **(CPTh11CB)** was prepared in a similar to above way. 0.71g(76.5% yield) of CPTh11CB was obtained as red powder. IR(KBr,cm^{-1}):2925,2852(C-H), 2223(CN), 1735(C=O), 1602,1494(C-C, Ar), 1249(C-O,Ar),1112(C-O,Aliphatic),850(C-H, heterocyclic),823(C-H,Ar)

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