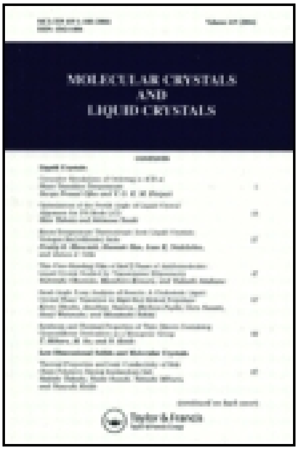

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Synthesis and Properties of Liquid Crystalline Polythiophene and Polythienylenevinylene Derivatives

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Synthesis and Properties of Liquid Crystalline Polythiophene and Polythienylenevinylene Derivatives

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Liquid crystalline polythiophene (LC-PTs) and polythienylenevinylene (LC-PTVs) derivatives with various length of methylene spacer in the LC substituents were synthesized. LC-PTs were prepared through dehalogenative polycondensation using Ni(0) complex, and LC-PTVs through Stille reaction followed by Heck reaction. The polymers showed enantiotropic smectic phase. Both LC-PTs and LC-PTVs were fluorescent with greenish yellow and/or green colors. The polymers were macroscopically aligned under magnetic field of 10 Tesla. Alignment of the polymers was confirmed by polarizing optical microscope, X-ray diffraction and polarized infrared spectra. The aligned polymers showed not only anisotropic electrical conductivity but also dichroic fluorescence. It is found that the LC conjugated polymers synthesized here are promising materials with linearly polarized luminescence.

Keywords: polythiophene; polythienylenevinylene; liquid crystallinity; anisotropic conductivity; dichroic fluorescence

INTRODUCTION

Polythiophene (PT) derivatives are representative five-membered conjugated polymers and regarded as promising materials for advanced electrical and optical devices. The alignment of conjugated polymer main chain is one of the key factors to enhance the electrical conductivity. Introduction of liquid crystals into π-conjugated polymer is expected to afford anisotropies in both electrical and optical properties. This is because the orientation of liquid crystalline (LC) side chain could lead the macroscopic alignment of the conjugated backbone.

LC polyacetylenes previously synthesized [1-3] exhibited an enhancement and an anisotropy in electrical conductivity after magnetically forced alignment. Meanwhile the LC-PTs [4,5] and poly-*p*-phenylene derivatives (PPPs) [6,7] are anticipated to exhibit dichroic luminescence as well as anisotropic conductivity. In this work, we report the synthesis and properties of LC-PT and LC-polythienylenevinylene (PTV) derivatives with LC substituents such as cyanobiphenyl (CB) and phenylcyclohexyl (PCH) mesogenic cores. The polymers synthesized were subjected for macroscopic alignment under magnetic field.

SYNTHESIS

Synthesis of 2,5-Dibrominated Thiophenes with CB Type LC Side Chain

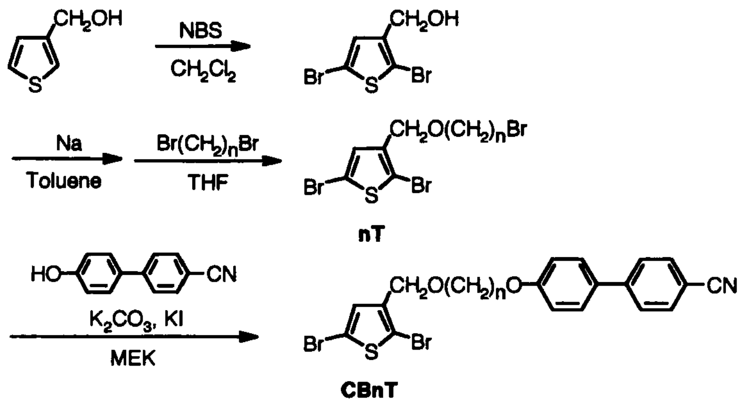
3-Thiophenemethanol was brominated at 2 and 5 positions of thiophene ring by using N-bromosuccineimide (NBS) and dichloromethane. The brominated thiophenemethanol was linked with 1,n-dibromoalkane (n = 6, 8, 10, 12) through etherification, to give nT. CBnT was synthesized by etherification of nT and 4-cyano-4'-hydroxybiphenyl using K_2CO_3 and KI (SCHEME 1).

Synthesis of 2,5-Dibrominated Thiophenes with PCH Type LC Side Chain

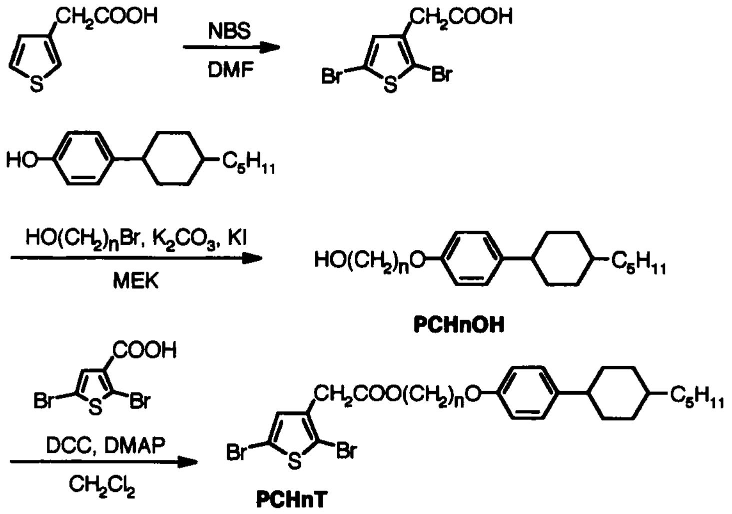
3-Thiopheneacetic acid was brominated at 2 and 5 positions of thiophene ring. PCHnOH was synthesized by etherification of n-bromo-1-alkanol (n = 6, 8, 10, 12) and 4-(*trans*-4'-*n*-pentylcyclohexyl)phenol using K_2CO_3 and KI, and then coupled with brominated thiopheneacetic acid using dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP), giving PCHnT (SCHEME 2).

Polymerization

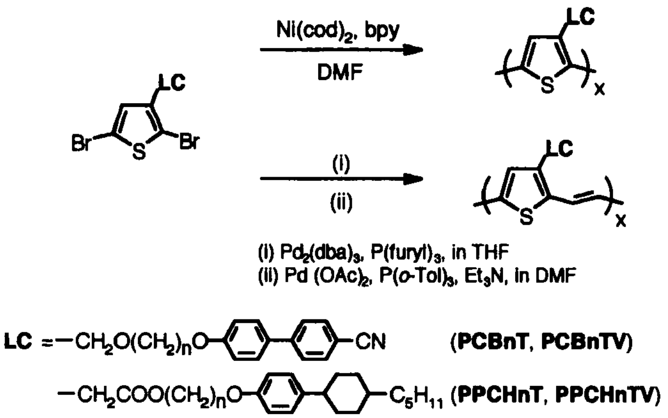
Polymerizations of CBnT and PCHnT were carried out through dehalogenative polycondensation using bis(1,5-cyclooctadiene)nickel



SCHEME 1 Synthetic route of CBnT (n = 6, 8, 10, 12)



SCHEME 2 Synthetic route of PCHnT (n = 6, 8, 10, 12)



SCHEME 3 Synthetic routes of LC-PTs (upper) and -PTVs (lower)

[Ni(cod)$_2$], and 2,2'-bipyridine [bpy], yielding PCBnT and PPCHnT, respectively (SCHEME 3, upper).

CBnT and PCHnT were coupled with tributyl(vinyl)tin, tris(dibenzylideneacetone)dipalladium(II) [Pd$_2$(dba)$_3$] and tri(furyl)phosphine [P(furyl)$_3$] as catalysts according to Stille reaction, and subsequently polymerized through Heck reaction using palladium acetate [Pd(OAc)$_2$] and tri(*o*-tolyl)phosphine [P(*o*-Tol)$_3$] as catalysts, yielding PCBnTV and PPCHnTV, respectively (SCHEME 3, lower).

RESULTS AND DISCUSSION

Chemical, optical, electrical and thermal properties of the polymers

All polymers synthesized were fusible and soluble in organic solvents. Their chemical, optical and electrical properties are summarized in Table I. The molecular weights of the polymers were evaluated through GPC calibrated by polystyrene standards. The degrees of polymerization of LC-PTs were larger than those of LC-PTVs. Thus the absorption bands due to π-π^* transition of main chain of LC-PTs were located at longer wavelength than those of LC-PTVs. Electrical conductivities of the iodine doped polymers were 10^{-8} - 10^{-5} S/cm.

The polymers exhibited greenish-yellow fluorescence at 490 - 530 nm in CHCl$_3$. Emission maxima of LC-PTs were observed at longer

TABLE I Properties of LC-PTs and LC-PTVs

polymers	$\overline{Mn}$	DP[a]	λ_{max} (nm)	log ε	PL_{max} (nm)	Φ (%)[c]	σ (S/cm)[d]	Phase transition temperatures (°C)[e,f]
PCB6T	5200	13	350 (sh)[b]	3.50	500	3.5	-	G 35 (30) S_A 70 (48) I
PCB8T	3700	9	372	3.61	517	5.3	-	G 36 (30) S_A 60 (45) I
PCB10T	11000	25	400	3.76	536	6.3	3.5×10^{-6}	G 60 (55) S_A 98 (94) I
PCB12T	6700	14	364	3.66	519	2.5	-	G 60 (55) S_A 75 (68) I
PPCH6T	36000	76	401	4.19	533	7.6	1.0×10^{-6}	G 70 (60) S_A 82 (72) I
PPCH8T	7800	16	373	3.71	518	4.0	-	G (-) - S_B 62 (58) S_A 75 (73)
PPCH10T	20000	38	395	3.78	527	7.6	2.0×10^{-6}	G (-) - S_B 56 (52) S_A 61 (59)
PPCH12T	6500	12	366	3.58	508	1.4	-	G (-) - S_B 73 (68) S_A 95 (91)
PCB6TV	3400	8	364	3.59	493	3.0	-	G 60 (55) I
PCB8TV	3000	7	355 (sh)	3.61	485	2.7	-	G 70 (65) I
PCB10TV	7200	15	360	3.60	494	3.6	2.7×10^{-5}	G 60 (55) S_A 75 (68) I
PCB12TV	4300	9	360 (sh)	3.39	477	5.0	-	G 45 (40) S_A 62 (60) I
PPCH6TV	4800	10	378	4.10	495	3.2	5.9×10^{-8}	G 65 (55) S_A 80 (70) I
PPCH8TV	5000	10	373	3.17	480	3.5	-	G (-) - S_B 84 (74) S_A 90 (82)
PPCH10TV	8200	15	353	3.57	485	2.5	1.5×10^{-5}	G (-) - S_B 56 (51) S_A 65 (63)
PPCH12TV	5500	10	366	3.41	470	2.4	-	G (-) - S_B 61 (52) S_A 73 (65)

[a] Degree of polymerization calculated from $\overline{Mn}$. [b] sh; shoulder. [c] Fluorescence quantum yield evaluated by using quinine sulfate standard sample. [d] Electrical conductivity after iodine doping. [e] G; glassy, S_A; smectic A, S_B; smectic B, I; isotropic. [f] Values without with parentheses correspond to heating and cooling process, respectively.

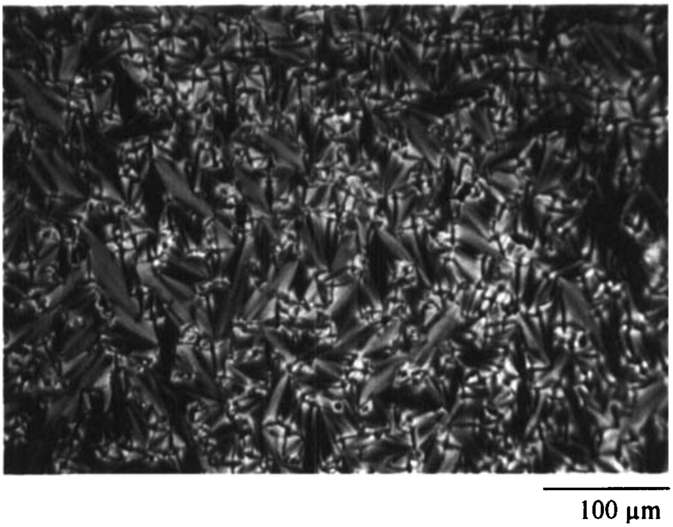


FIGURE 1 Polarizing optical micrograph of PCB10T at 88 °C in cooling process.
See Color Plate XX at the back of this issue.

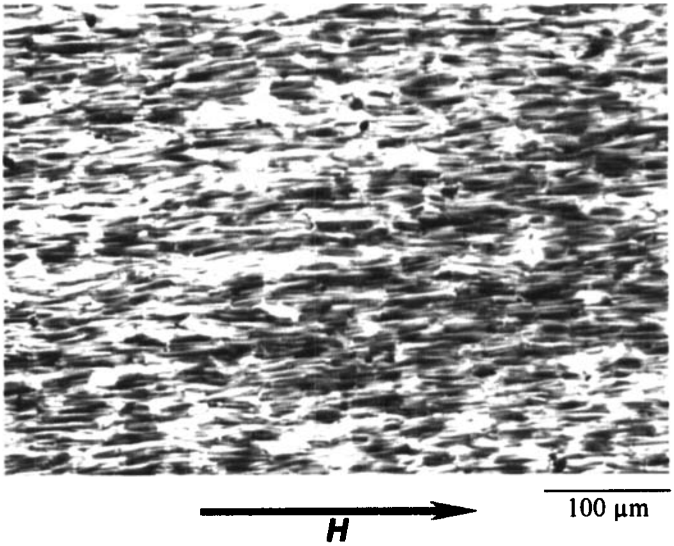


FIGURE 2 Polarizing optical micrograph of PCB10T at room temperature after magnetically forced alignment.
See Color Plate XXI at the back of this issue.

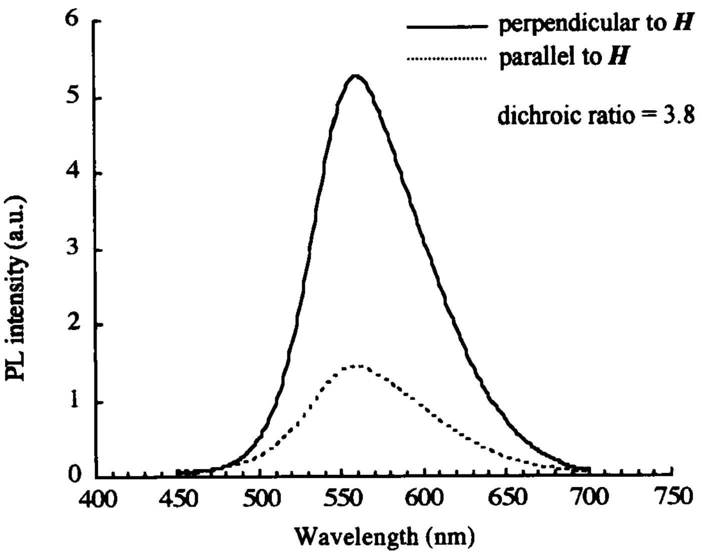


FIGURE 3 Polarized PL spectra of aligned PPCH10T

wavelength than those of LC-PTVs, as expected from the behavior in UV-Vis absorption spectra. The fluorescence intensity of LC-PTs was larger than that of LC-PTVs. Fluorescence quantum yields were evaluated by using quinine sulfate as a standard sample. Excitation wavelength used for both the polymers and quinine sulfate was 366 nm. The values of quantum yields were 1.4 - 7.6 %.

The phase transition temperatures are also listed in Table I. Measurements indicate that the polymers with CB type LC group have enantiotropic smectic A phase. Those with PCH type LC group have smectic A and B ones, although PCH6T with methylene spacer of 6 show only smectic A phase. Similar results were observed in LC-PTV, except PCB6TV and PCB8TV that exhibit no mesophase. Figure 1 shows a typical fan-shaped texture of PCB10T.

Magnetically forced alignment of the polymers

In order to realize polarized luminescence and anisotropic electrical conductivity, we carried out magnetically forced alignment of the polymers. Magnetic field (*H*) of 10 Tesla was applied to the polymers under LC temperature during both heating and cooling processes.

Figure 2 shows polarizing optical microscope (POM) of aligned polymer of PCB10T. It is clear that domains were aligned parallel to the direction of ***H***. Measurements of XRD, polarized IR and UV-Vis spectra indicated that LC side chains are aligned parallel to ***H*** and consequently the main chains are aligned perpendicular to ***H***. The aligned polymers showed an anisotropy in electrical conductivity, where the ratio of perpendicular to parallel conductivity ($\sigma_{\perp}/\ \sigma_{//}$) was 2.0 - 8.5. Note that $\sigma_{\perp}$ stands for conductivity perpendicular to the magnetic field, i.e., parallel to main chain, and hence $\sigma_{//}$ stands for perpendicular to main chain. Lastly, the aligned polymer films of LC-PTs and LC-PTVs showed dichroic fluorescence with dichroic ratios of 2.0 - 3.8 and 1.4 - 1.8, respectively, as shown in Figure 3.

CONCLUSION

A series of LC-PTs and LC-PTVs were synthesized. The polymers exhibited dichroic fluorescence with greenish-yellow color when they were macroscopically aligned by magnetic field. It is suggested that they are useful for novel optical advanced materials with polarized luminescence.

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