

## Synthesis of Liquid Crystalline Helical Polythienylene Derivatives with Circularly Polarized Fluorescence

I. Osaka, A. Nakamura<sup>†</sup>, Y. Inoue<sup>†</sup> and K. Akagi<sup>\*</sup>

Institute of Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

Fax: 81-298-55-7440, e-mail: akagi@ims.tsukuba.ac.jp

<sup>†</sup>Exploratory Research for Advanced Technology, Japan Science and Technology Corporation

Several kinds of polythienylene and its copolymers of both *R* and *S* configurations were synthesized by introducing chiral alkoxy substituent in their side chain. Some of the polymers showed enantiotropic liquid crystallinity. The polymers synthesized exhibited blue to orange fluorescent colors. White fluorescence was observed in the mixture of some of the polymers. In CD spectra of both polymer solution and film were shown Cotton effects due to the inherent helical structure in the region of  $\pi$ - $\pi^*$  transition of conjugated backbone. All of the polymers and the mixture of the polymers showed circularly polarized fluorescence in both solution and film state. From these results, the present polymers, when well mixed, are available for both linearly and circularly polarized white luminescent materials.

**Key words:** polythienylene, liquid crystal, white luminescence, circularly polarized fluorescence

### 1. INTRODUCTION

Polythiophenes and poly-*p*-phenylenes, are representative aromatic  $\pi$ -conjugated polymers and they are regarded as promising for advanced materials in electronics and optoelectronics due to their profound electrical and optical properties. The polarized optical properties or red, green, blue (RGB) colored luminescence of the conjugated polymers have been attracting current interest in both industrial and academic view point. Recently, we have reported the syntheses of a series of side chain type liquid crystalline (LC) conjugated polymers<sup>1</sup> and their linearly polarized fluorescence generated by macroscopic alignment of the polymers under magnetic field.<sup>2</sup>

Circularly polarized luminescence is one of the most fruitful properties of aromatic conjugated polymers, as well as the linearly polarized one. The circular polarization of the luminescence comes from the chirality or a helicity of the conjugated polymers and hence requires no macroscopic alignment of the polymers. The helical conjugated polymer can be prepared by using chiral nematic reaction field composed of nematic liquid crystals and chiral dopant.<sup>3</sup> Introduction of chiral moiety into the side chain of the polymer is another approach for the formation of helical structure on conjugated polymers.<sup>4</sup> Although LC conjugated polymers with chiral group linked to the mesogenic core via long alkyl spacer exhibited chiral smectic C phase,<sup>5</sup> they showed no circular polarization at the  $\pi$  -  $\pi^*$  transition band. This suggests that it might be essential for the formation of helical main chain to locate the chiral center of the side chain as close as possible to the conjugated backbone.

Here polythiophene derivatives and their copolymers of both *R* and *S* configurations, as shown in Fig. 1, were synthesized by introducing chiral nonyloxy carbonyl group in their side chains. It is expected that  $\pi$ -electrons of the carbonyl group locating between the chiral center and conjugated main chain would make an

indispensable contribution to bring chiral environment to the backbone by ways of "through space" and "through bond" interactions, giving an induced chirality and even helicity on the conjugated backbone. The variation of the backbone structure affords various conjugation lengths, enabling color tuning of the fluorescence. Addition and/or increase of thienylene ring in the phenylene repeating unit may give rise to the red shift of both absorption and fluorescence band. Besides, the generation of RGB colored luminescence in the conjugated polymers should allow us to have white colored one by mixing the corresponding polymers in appropriate ratio. On the other hand, the backbone of aromatic conjugated polymer plays a role of mesogenic core of liquid crystal. Thus the polymers shown in Fig. 1 exhibit main chain type liquid crystallinity. From these

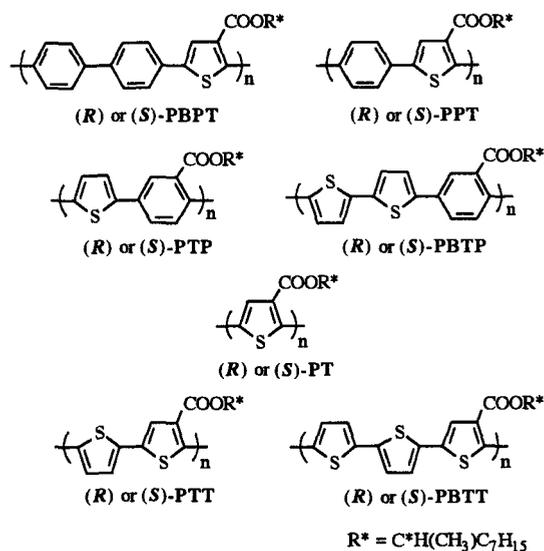
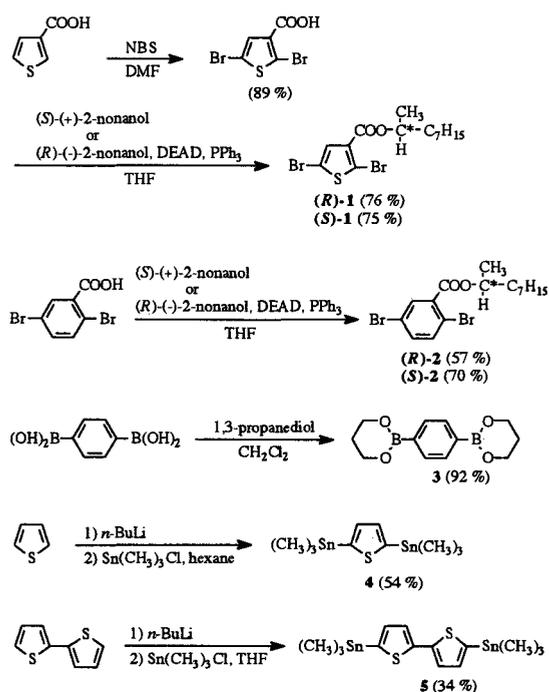


Fig.1 Chemical structure of the synthesized polymers



Scheme 1 Synthetic routes of the monomers

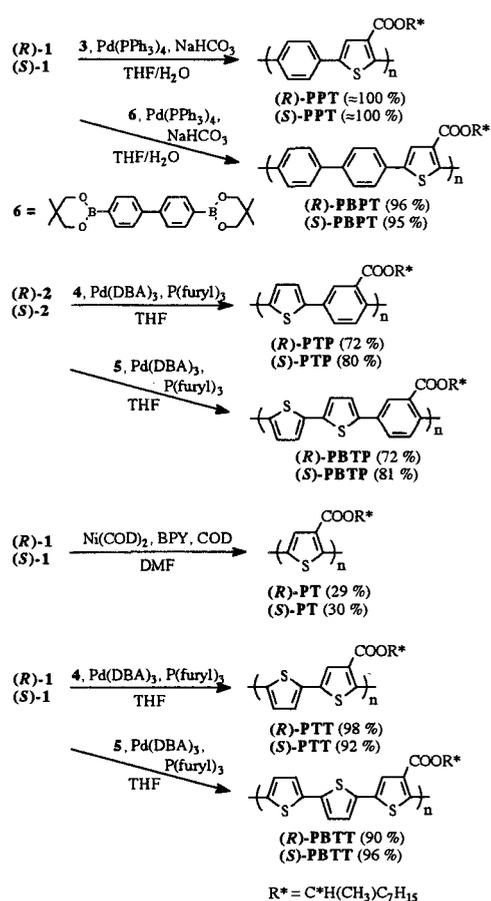
aspects, the polymers might exhibit both linearly and circularly polarized white luminescence when well mixed.

## 2. SYNTHESIS

The syntheses of the chiral monomers and the coupling monomers for copolymerization are shown in Scheme 1. All compounds were well characterized with IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  spectroscopies, and elemental analysis.

3-Thiopheneacetic acid was dibrominated at 2 and 5 positions by using *N*-bromosuccinimide (NBS) and DMF, and followed by esterification with (*S*)-(+)-2-nonanol and (*R*)-(-)-2-nonanol using azodicarboxylic acid diethyl ester (DEAD) and triphenylphosphine ( $\text{PPh}_3$ ) as catalysts according to Mitsunobu reaction, giving (*R*)-(-)- and (*S*)-(+)-2,5-dibromo-3-(2-methyloctyloxy)-carboxythiophene [(*R*)-1 and (*S*)-1], respectively. The esterifications of 2,5-dibromobenzoic acid with (*S*)-(+)- and (*R*)-(-)-2-nonanol were carried out in the same way to give (*R*)-(-)- and (*S*)-(+)-2,5-dibromo-3-(2-methyl-octyloxy)carboxybenzene [(*R*)-2 and (*S*)-2], respectively. 1,4-Benzenediboric acid bistrimethylene cyclic ester (**3**) was obtained by refluxing the mixture of 1,4-benzenediboric acid and 1,3-propanediol in dichloromethane. Thiophene was treated with *n*-BuLi, and followed by an addition of trimethyltin chloride to give 2,5-bis(trimethylstannyl)thiophene (**4**). The synthesis of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**5**) was carried out in the same way as mentioned above.

In Scheme 2 are shown the synthetic routes of the polymers. The polymers synthesized were characterized by using IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopies. (*R*)-1 and (*S*)-1 were coupled with **3** by using tetrakis(triphenylphosphine)palladium(II)



Scheme 2 Synthetic routes of the polymers

[ $\text{Pd}(\text{PPh}_3)_4$ ] and  $\text{NaHCO}_3$  as catalysts in mixture of THF and  $\text{H}_2\text{O}$ , according to Suzuki coupling reaction, to give (*R*)-PPT and (*S*)-PPT, respectively. (*R*)-PBPT and (*S*)-PBPT were prepared by coupling (*R*)-1 and (*S*)-1 with 4,4'-biphenyldiboric acid bis(neopentyl glycol) cyclic ester (**6**) in the same way, respectively. (*R*)-2 and (*S*)-2 were copolymerized with **4** through Stille coupling reaction, in which tris(dibenzylideneacetone)dipalladium(0) [ $\text{Pd}_2(\text{DBA})_3$ ] and tri(2-furyl)phosphine [ $\text{P}(\text{furyl})_3$ ] were used as catalysts to give (*R*)-PTP and (*S*)-PTP, respectively. The preparations of PBTPs, PTTs, and PBTTs of both *R* and *S* configurations were also carried out through Stille reaction. (*R*)-PT and (*S*)-PT were synthesized from (*R*)-1 and (*S*)-1, respectively, through dehalogenative polycondensation using bis(1,5-cyclooctadiene)nickel(0) [ $\text{Ni}(\text{COD})_2$ ], 2,2'-bipyridine (BPY), and cyclooctadiene (COD) as catalysts.

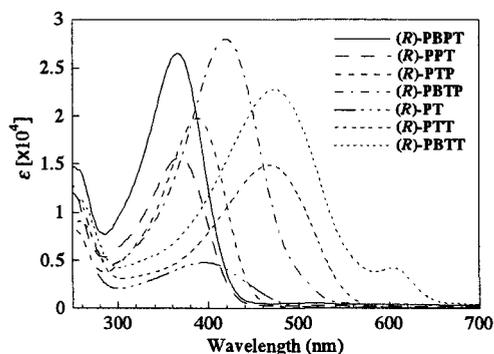
## 3. RESULTS AND DISCUSSION

All polymers synthesized were fusible and soluble in organic solvents such as THF and chloroform. In Table I are summarized chemical properties of the polymers of *R* configuration. Similar results (not cited here) for the *S* polymers were also obtained. The molecular weights of the polymers were evaluated through gel permeation chromatography (GPC) calibrated by polystyrene standard. The values of degree of polymerization (DP) stand for the quantity of the unit cell of the

Table I Chemical properties of the polymers

Polymer	$M_n$	$M_w/M_n$	DP <sup>a</sup>
(R)-PBPT	4700	1.6	15 (45)
(R)-PPT	11100	2.3	34 (68)
(R)-PTP	8500	2.8	25 (50)
(R)-PBTP	3500	1.4	8 (24)
(R)-PT	3200	1.4	13 (13)
(R)-PTT	8100	1.7	24 (48)
(R)-PBTT	2700	1.3	6 (19)

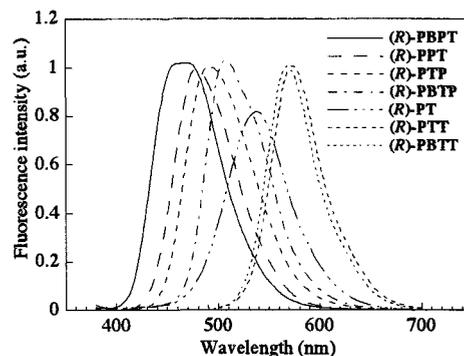
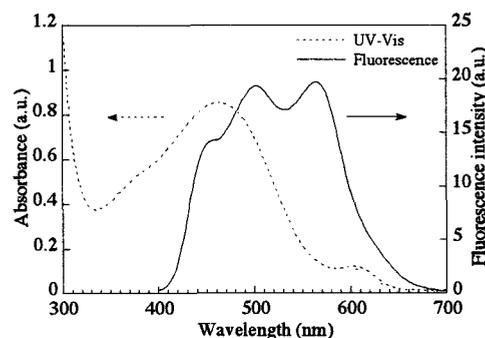
a) The values in the parentheses are numbers of aromatic rings in the main chain.

Fig. 2 UV-Vis absorption spectra of the polymers in CHCl<sub>3</sub>

corresponding polymers. The quantities of aromatic rings, which were evaluated by multiplying DP by the number of rings in the unit cell, are shown in the parentheses.

All polymers, except PTs and PTTs, showed enantiotropic LC phase through wide and high temperature region in polarizing optical microscopy. The LC phase was maintained even over 300 °C, indicating the thermal stability common to main-chain type LC polymer. Meanwhile, the glass-LC phase transition temperatures of the polymers were found to be around 100 °C. The explicit assignment of the LC phase remains unsolved and hence it is currently investigated.

Fig. 2 shows the UV-Vis absorption spectra of R polymers in chloroform. The absorption bands corresponding to the  $\pi - \pi^*$  transition were red shifted with an increase of the ratio of thienylene to phenylene ring in the unit cell. The absorption bands of the spin cast polymer films were located in longer wavelength by 10 ~ 50 nm than those of polymer solutions as shown in Table II. This probably comes from the situation that the conjugated polymer in film can form more ordered

Fig. 3 Fluorescence spectra of the polymers in CHCl<sub>3</sub>Fig. 4 UV-Vis absorption and fluorescence spectra of the mixture of (R)-PBPT, (R)-PBTP, and (R)-PBTT in CHCl<sub>3</sub>

conformation than in solution, resulting in enhanced interchain interactions. Fig. 3 is the fluorescence spectra of R polymers in chloroform. The red shift correlated with the ratio of thienylene to phenylene ring in the unit cell was also observed in fluorescence. The fluorescent colors of the polymers are listed in Table II. It should be noted here that the variety in absorption and/or fluorescence wavelengths cited in Table II is primary due to the difference of the repeating unit in each polymer, although these values are substantially shifted by additional macroscopic alignment through LC phase. In Table II are also summarized fluorescence quantum yields of the polymers evaluated by using quinine sulfate in 1.0 M sulfuric acid as standard sample, where the excitation light of 366 nm was commonly used. The polymers having at least one phenylene ring showed relatively higher quantum yield such as 0.2. PBPT, PBTP, and PBTT with the same R configuration were mixed in suitable ratio. The mixing ratio was determined from the comparison of their quantum yields.

Table II Optical properties of the polymers

Polymer	$\lambda_{max}$ (nm)		$\log \epsilon$	$E_{m_{max}}$ (nm)		$\Phi^a$	fluorescent color <sup>c</sup>
	in CHCl <sub>3</sub>	film		in CHCl <sub>3</sub>	film		
(R)-PBPT	365	376	4.33	469	479	0.26	blue
(R)-PPT	375	385	4.25	480	491	0.24	greenish-blue
(R)-PTP	389	411	4.29	492	532	0.26	green
(R)-PBTP	420	443	4.45	509	557	0.23	yellowish-green
(R)-PT	400	407	3.69	539	546	0.039	yellow
(R)-PTT	468	533	4.17	574	632	- <sup>b</sup>	orange
(R)-PBTT	474	526	4.34	570	643	- <sup>b</sup>	orange

a) fluorescence quantum yield b) could not measure c) fluorescent color observed in CHCl<sub>3</sub>

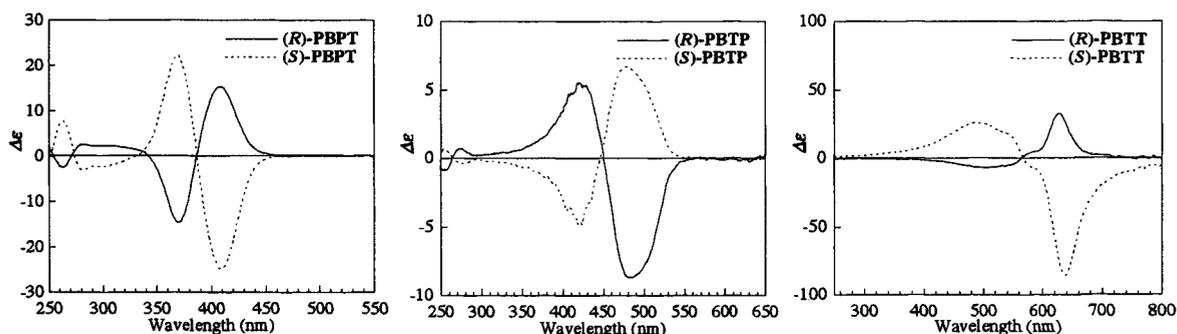


Fig. 5 CD spectra of PBPTs (left), PBTPs (center), and PBTTs (right) in  $\text{CHCl}_3$

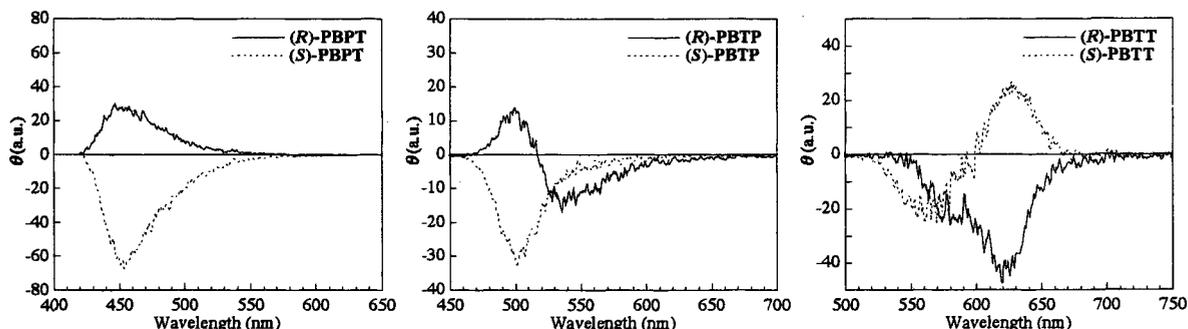


Fig. 6 CPF spectra of PBPTs (left), PBTPs (center), and PBTTs (right) in  $\text{CHCl}_3$

The chloroform solution of the mixture exhibited white fluorescence upon irradiation of UV light. The polymer mixture also showed white emission in film when the mixture was dispersed into polystyrene to avoid and depress the feasible interchain interactions between polymers. Fig. 4 shows the UV-Vis absorption and fluorescence spectra of the mixture of the *R* polymers in chloroform. The fluorescence spectrum covers the visible region of 400 ~ 700 nm, indicating that the mixture emits white colored fluorescence.

Circular dichroism (CD) spectra of PBPTs, PBTPs, and PBTTs of both *R* and *S* configurations are shown in Fig. 5. In (*R*)-PBTT, positive and negative Cotton effects were observed in longer and shorter wavelength, respectively. The completely reversed CD spectra were observed in (*S*)-PBTT. PBPTs and PBTPs also exhibited bisignate CD spectra in mirror image between *R* and *S* configurations. The rest of the polymers showed weak CD peaks. The dissymmetry factors,  $g_{\text{abs}} = 2(\epsilon_L - \epsilon_R)/(\epsilon_L + \epsilon_R) = 2\Delta\epsilon/\epsilon$ , the degree of circular polarization in absorption, were  $|2 \times 10^{-3}| \sim |0.1|$ . These results suggest that the polymers synthesized possess intrinsic helicity in their conjugated backbones. The films of the polymers also indicated Cotton effects in the region of  $\pi - \pi^*$  transition. In Fig. 6 are shown circularly polarized fluorescence (CPF) spectra of PBPTs, PBTPs, and PBTTs of both *R* and *S* configurations, where excitation light of 360 ~ 390 nm was used. They exhibited the circular polarization in their fluorescence bands, which originated from the inherent helical structure of the backbone. The dissymmetry factors of CPF,  $g_{\text{em}} = 2(I_L - I_R)/(I_L + I_R)$ , of the polymers in chloroform were  $|1 \times 10^{-3}| \sim |4 \times 10^{-3}|$ . The  $g_{\text{em}}$  factors in film were one order higher than those in solution. This may be due to the enhancement of inter chain interaction associated with aggregation in solid state. In addition, the mixture of the polymers

exhibited CD and CPF in both solution and film and generated circularly polarized white fluorescence.

#### 4. Conclusion

Various kinds of aromatic conjugated polymers with chiral nonyloxy carbonyl group in the side chain were synthesized. Some of the polymers showed enantiotropic liquid crystalline phase. The polymers exhibited RGB colored fluorescence with the quantum yields of 0.04 ~ 0.26. White fluorescence was observed when some of the polymers were mixed in suitable ratio. CD spectra of both film and solution of the polymers indicated Cotton effects, suggesting that they are inherently helical. The polymers exhibited circularly polarized fluorescence in both solution and film even in the mixture. From these results, the polymers synthesized here might be advanced materials with both linearly and circularly polarized white luminescence when well mixed.

#### 5. References

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