

## Segmented conjugated polymer based on poly( $\alpha$ -thiophenediyl)benzylidene

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### Summary

Segmented polymers with random sequences of conjugated and non-conjugated blocks are produced by partial dehydrogenation of poly( $\alpha$ -thiophenediyl)benzylidene. The fraction of conjugated block was controlled by the elimination time. The polymers gave photoluminescence. Absorption coefficients of the polymers increased with the rate of dehydrogenation, and the highest fluorescence intensity were achieved around 9 % conjugation conversion. The polymers were characterized by <sup>1</sup>H- and <sup>13</sup>C-n.m.r. and infrared spectra, and were soluble in common organic solvents, which suggests a good processability.

### Introduction

Among the many conjugated polymers, poly(*p*-phenylenevinylene) (PPV) and its derivatives exhibit relatively high photoluminescence (PL) efficiencies. Many investigators have previously reported the photoluminescence characteristics (1-3) and polymer laser dye (4) of PPV. Recently, Burroughes et al. developed a polymer electroluminescence (EL) device with PPV films as the emitting layer (5). Thereafter, many groups investigated polymer EL based on PPV (6-14). These PL and EL efficiencies were attributable to the delocalized electrons. The introduction of long alkyl chains to polymer skeleton was an effective way to achieve high efficiencies of PL. Another successful method for high efficiencies of PL utilized oligomers of the conjugated polymer. These oligomers, however, had problems including recrystallization and poor thermal stability.

Recently, Burn et. al. developed a successful method (9-10) for achieving high efficiency of EL by using a segmented conjugated polymer based on PPV derivatives. The efficiency was 0.3 % in an EL device, but the ratio of conjugated blocks and non-conjugated blocks was not clearly determined.

Jenekhe (15-19) reported in 1987 that fully conjugated derivatives of poly( $\alpha$ -thiophenediyl)-benzylidene (PTB) could be produced by the elimination of PTB with bromine gas. No luminescence was reported in these reports because the bromine ions acted as luminescence quencher. Herein, we described the first synthesis of the polymer based on PTB that has conjugated blocks and non-conjugated blocks, and the ratio of the conjugated blocks is controlled by the reaction time with acid catalyst. The relationship between the intensity of photoluminescence and the rate of conjugated segment is also discussed.

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## Experiment

Dichloromethane was purified by distillation after dried by calcium hydride for 24 hours and removal of methanol by silica column. Other chemicals and solvents were of reagent grade quality, purchased commercially and used without further purification. Chloroform was of spectral grade quality, purchased commercially and used without further purification.

The u.v.-vis.-n.i.r. absorption spectra were recorded on a Hitachi U-4000 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer System 2000 spectrometer. The fluorescence spectra were recorded on a Nihon Bunko FP-777 spectrofluorometer.

$^1\text{H}$  and  $^{13}\text{C}$ -n.m.r. spectra were recorded on a Varian VXR300 spectrometer.

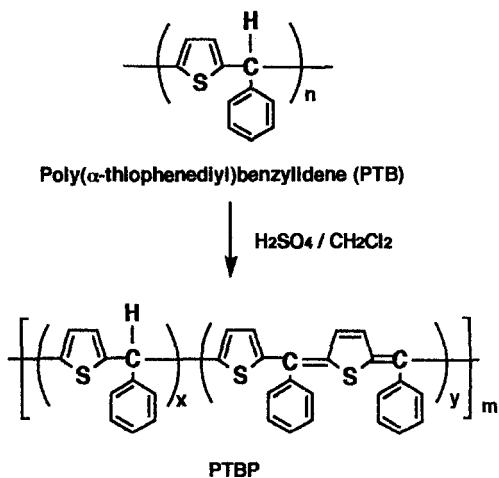
The precursor polymer, PTB was synthesized from thiophene and benzaldehyde by acid condensation. The details of this preparative method were previously described (20).

Elimination of PTB was carried out by chemical dehydrogenation. Sulfuric acid (0.46 % by weight) was added to a dichloromethane solution of PTB (0.75 % by weight) under an inert atmosphere. The mixture was stirred at room temperature for a definite time. After the reaction mixture was neutralized with pyridine, the solvent was removed by reduced pressure. The residue was resolved in dichloromethane and poured into methanol. The precipitates were filtered off, washed with methanol, and dried in vacuo.

The determination of absorption coefficient and the fluorescence intensity were carried out in the  $5.13 \times 10^{-3}$  mol/l toluene solutions at room temperature.

## Results and Discussion

The  $^1\text{H}$ -n.m.r. spectrum of PTB was shown in Figure 1. The peak of  $\delta$  7.20 ppm was assigned to five adjacent aromatic protons of benzene ring, the peak of  $\delta$  6.53 ppm was assigned to two adjacent protons of thiophene ring, and the peak of  $\delta$  5.59 ppm was assigned to the proton of methine. The  $^{13}\text{C}$ -n.m.r. spectrum was shown in Figure 2. The peaks of  $\delta$  146.3 and 143.3 ppm were assigned to the carbons of thiophene ring, the peaks from  $\delta$  128.6 to 125.3 ppm were assigned to the carbons of benzene ring, and the peak of  $\delta$  46.7 ppm was assigned to carbon of methine. The infrared spectrum was shown in Figure 3. The aliphatic C-H stretching vibration peaks in the  $2800 \sim 3000 \text{ cm}^{-1}$  region are significantly observed. The peaks of  $1491 \sim 1494 \text{ cm}^{-1}$  were assigned to C-H stretching of



**Scheme 1. Synthesis of copolymer (PTBP) with conjugated and unconjugated blocks by elimination from PTB**

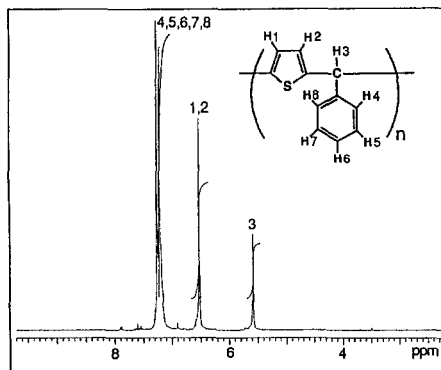


Figure 1 The  $^1\text{H}$ -n.m.r. spectrum of PTB benzene rings and the peak of  $698\text{ cm}^{-1}$  was assigned to C-H bending of five adjacent aromatic protons of benzene rings.

Figure 4 shows the infrared spectrum of the polymer obtained by the reaction in dichloromethane solution containing PTB with sulfuric acid for half an hour. The new broad peaks of  $1000 \sim 1600\text{ cm}^{-1}$  and the sharp peak of  $999\text{ cm}^{-1}$  were observed. The peaks were assigned to polyene. In its  $^1\text{H}$ -n.m.r. spectrum, the peak at  $\delta 5.59\text{ ppm}$  that was assigned to the proton of methine was weakened compared with the peak at  $\delta 6.53\text{ ppm}$  that was assigned to two adjacent protons of thiophene ring. The results suggest us that some protons of methine were eliminated and conjugation length of this polymer increased.

The proportions of conjugated blocks of these polymers could be controlled by the reaction time with sulfuric acid. The proportions were estimated by  $^1\text{H}$ -n.m.r. with the relative intensity between the peak at  $\delta 6.53\text{ ppm}$  and the peak at  $\delta 5.59\text{ ppm}$ .

Figure 5 shows the optical absorption spectrum and the fluorescence spectrum of PTBP with 8.7% conjugated segments. Two absorption spectrum peaks were observed at 464 and 494 nm. A fluorescence spectrum peak was observed at 570 nm by the pumping lights at 464 nm. The same fluorescence spectrum was observed by the pumping lights at 494 nm.

The relationships of absorption coefficient and fluorescence intensity with the proportions of conjugated blocks of PTBP were demonstrated in Figure 6. The relationship between the

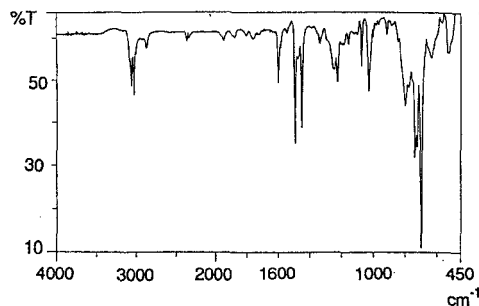


Figure 3 The infrared spectrum of PTB

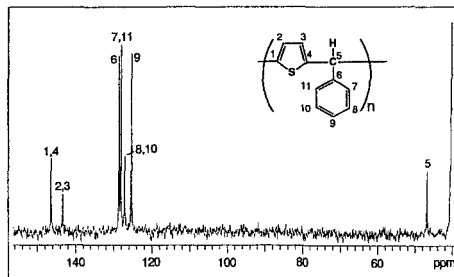


Figure 2 The  $^{13}\text{C}$ -n.m.r. spectrum of PTB

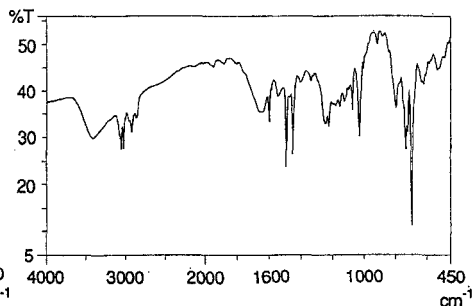


Figure 4 The infrared spectrum of PTBP

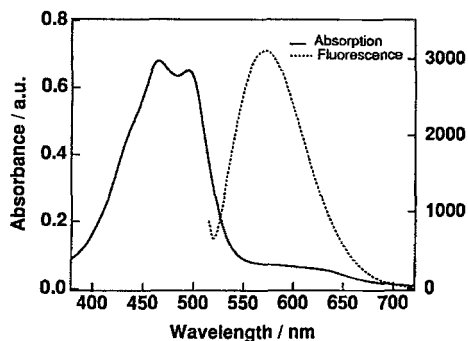


Figure 5 The absorption spectrum and fluorescence spectrum of PTB in toluene

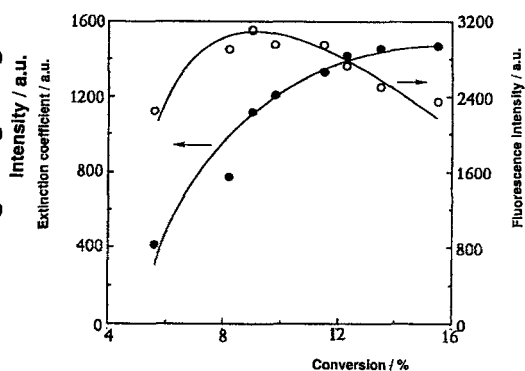


Figure 6 The change of extinction coefficient and fluorescence intensity with conversion rate to conjugation form

extinction coefficient, fluorescence intensity, and the wavelength of both peaks of PTBP with around 10 % conjugated blocks were summarized in Table 1. The absorption maxima was blue shifted and the fluorescence maxima was red shifted as the conversion. So, the conjugation length increased with greater reaction time in the presence of sulfuric acid. Consequently, the conjugation length was extended.

Table 1 The relationship between the fluorescence intensity and the conversion rate to conjugation.

conjugation conversion %	absorption maxima nm	extinction coefficient	fluorescence maxima nm	fluorescence intensity
5.6	497	413	570	250
8.2	494	773	571	2900
8.7	494	1120	572	3110
9.8	494	1210	572	2960
11.5	494	1330	572	2950
12.3	494	1420	572	2730
13.5	493	1460	572	2510
15.5	493	1470	573	2350

The absorption coefficient increased proportionally with greater number of conjugated blocks. On the contrary, the intensity of fluorescence did not simply increase but had an upper limit around 9 % conversion to conjugated structure. These results suggest that 9 % is the most suitable rate to introduce the delocalization in this polymer and the polymer with 9 % conjugated blocks have highest luminescence efficiency.

Table 2 shows the solvent effect to the absorption maximum and fluorescence maximum. Solvatochromism could be seen in these PTBP solutions. This result suggests us that the conformation of the polymer chain structure might be change as the solubility of PTBP in these solvents.

Table 2 The solvent effects of the absorption and fluorescence spectra.

Solvent	absorption	fluorescence	fluorescence intensity
	maxima nm	maxima nm	
Toluene	494, 464	571	3000
Tetrahydrofuran	490, 462	570	950
Dioxane	490, 462	568	2700
Chloroform	491, 464	571	1200

## Conclusion

Copolymers with conjugated and non-conjugated blocks were synthesized and characterized. The rate of conjugated blocks and non-conjugated blocks was controlled. The polymers are soluble in common organic solvents required for good film-forming properties.

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