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Synthesis of poly(α-thiophenediyl)benzylidene with high molecular weight and its thermal stability

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Summary

The synthesis of poly(α-thiophenediyl)benzylidene (PTB) with high molecular weight is described. Number-average degrees of polymerization reached about 74. The characterizations of the polymer was investigated by ^{1}H-NMR, ^{13}C-NMR, IR, and UV-VIS spectra. The polymer with well-defined structure and high molecular weight was obtained by polymerization at low temperature and in polar solvent. This polymer was thermally stable and a thermal decomposition took place at 391 °C under nitrogen and at 370 °C under air. The glass transformation temperature was 117 °C and this PTB was nonfusible.

Introduction

Recently special interest has been drawn to small bandgap polymers. Poor solubility of these polymers, however, in any solvent was limited for their application. In recent years, poly(p-phenylenevinylene) and poly(p-thienylenevinylene) have been prepared through soluble precursor polymer (1,2). So their uses were accepted for electroluminescence devices (3) and field effect transistors (4).

Among conducting polymers, poly(isothianaphthene) was known so far to have the smallest bandgap found experimentally and theoretically (5,6). Thereafter theoretical approach toward small bandgap polymers have been widely investigated (7-12). Kertesz et al. calculated by using the model of Longuet-Higgins and Salem (LHS) that the polymer modified the hetero-aromatic molecules by introducing the methine linkage, had a smaller bandgap than unmodified molecules (13-15). Polyarylmethines were predicted to show a small bandgap and they were synthesized via a precursor (16-21). Though a few syntheses have been reported for polyarylmethines and their precursors, no well-defined synthetic route has been developed.

Jenekhe has described a system of formula of the polyarylmethine precursors by condensation of thiophene, bithiophene and terthiophene with benzaldehyde (16-20), but the condensed materials from thiophene and bithiophene were followed only by UV- absorption spectroscopy. The reported properties were not of those of the polymer's because the resulting materials from terthiophene had a low molecular weight (about 4-mer).

In this paper, we report the synthesis and the thermal properties of high molecular weight poly(α-thiophenediyl)benzylidene (PTB) that was a precursor of a conductive polyarylmethine.

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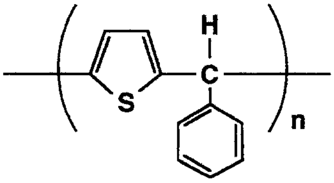


Scheme 1 Poly(α-thiophenediyl)benzylidene (PTB)

Experiment

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

The absorption spectra were recorded on a Hitachi U-4000 spectrophotometer. ^1H and ^{13}C-NMR spectra were recorded on a Varian VXR300 spectrometer. The infrared spectra were recorded on a Perkin-Elmer system 2000 spectrometer. The differential scanning calorimetry was recorded on a Perkin–Elmer DSC-7 and the thermogravimetric analysis was recorded on a Perkin–Elmer TGA7.

Molecular weights were measured at 40 °C by gel permeation chromatogram (GPC) analyses performed on a Waters liquid chromatograph equipped RI detector on Shodex KF802,3,4 by uses of tetrahydrofuran as solvent and polystyrene as the standard.

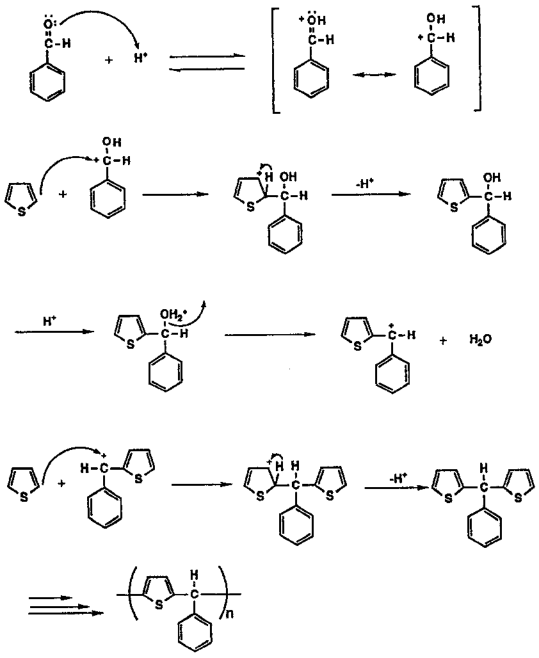
The general procedure is described for the preparation of PTB. A standard reaction was performed in a 100 ml, two-necked, round-bottomed flask with a three-way tube. After replacement with nitrogen gas, the flask was charged with freshly prepared dichloromethane (15 ml), thiophene (3.0 ml, 3.75×10^{-2} mol) and benzaldehyde (3.8 ml, 3.75×10^{-2} mol). The mixture was magnetically stirred and cooled in an ice bath, and boron trifluoride etherate (1.6 ml, 1.3×10^{-2} mol) was added dropwise to this solution. The resulting solution was instantly turned yellow and then red in 10 minutes. After stirring for 17 hours under an inert atmosphere at room temperature, the solvent was evaporated in vacuo. The residue was resolved in dioxane and poured into methanol. The precipitates were filtered off, washed with methanol, and dried in vacuo. A yellowish polymer was obtained. (4.98 g, yield 70 %) ^1H-NMR ($CDCl_3$) 7.20,6.53,5.59, ^{13}C-NMR ($CDCl_3$) 146.3, 143.3, 128.6, 128.0, 127.0, 125.3, 46.7, IR : 3059, 3024, 3923, 2865, 1947, 1875, 1805, 1757, 1700, 1598, 1583, 1545, 1492, 1472, 1450, 1387, 1335, 1245, 1224, 1201, 1155, 1074, 1029, 1002, 841, 798, 777, 738, 723, 696, 648, 629 cm^{-1}, elemental analysis : calcd. for ($C_{11}H_8S_1$):C,76.8; H,4.6; S,18.6 %, found : C,76.3; H,4.6; S,18.1 %

Results and Discussion

Polymer Synthesis

This polymerization is a typical Friedal–Crafts reaction. Scheme 2 shows a proposed polymerization mechanism by acid catalyst.

In the previous study (16-20), the characterizations of PTB were insufficient. Only the absorption maxima was reported.



Scheme 2 The proposed mechanism of PTB polymerization.

We tried to prepare PTB according to Jenekhe's method (18) using hydrogen sulfate as a catalyst and dioxane as a solvent. When the reaction was run in ice bath, no precipitate was obtained. When the reaction was carried out at about 80 °C for 8 hours, a black condensed material was obtained. The NMR peaks were broadened ones. This equivocal structure was resulted from the dehydrogenation of methine that was gone on simultaneously with condensation. To depress this dehydrogenation, the polymerization should be carried out at low temperature with a strong catalyst such as boron trifluoride etherate was considered. When the condensation polymerization was carried out according to this idea, a clear-defined structural polymer was obtained.

Polymer Structure

The ^{1}H-NMR spectrum of this polymer obtained by the polymerization conditions described in the experimental section is shown in Figure 1. The peak of δ 7.20 ppm was assigned to five adjacent aromatic protons of benzene ring, the peak of δ 6.53 ppm was assigned to two adjacent protons of thiophene ring, and the peak of δ 5.59 ppm was assigned to the proton of methine. Also, the ^{13}C-NMR spectrum is shown in Figure 2. The peaks of δ 146.3 and 143.3 ppm were assigned to the carbons of thiophene ring, the peaks from δ 128.6 to 125.3 ppm were assigned to the carbons of benzene ring, and the peak of δ 46.7 ppm was assigned to carbon of methine. The infrared spectrum is shown in Figure 3. The aliphatic C-H stretching vibration peaks in the 2800 ~ 3000 cm^{-1} region are significantly observed. The peaks of 1491 ~ 1494 cm^{-1} were assigned to C-H stretching of benzene rings and the peak of 698 cm^{-1} was assigned to C-H bending of five adjacent aromatic protons of benzene rings.

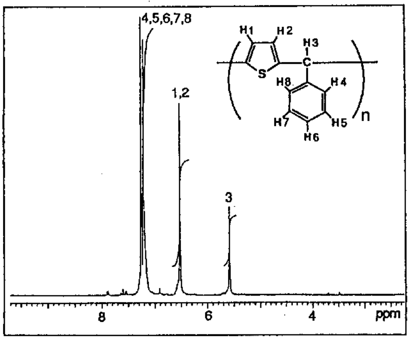


Figure 1. ^{1}H-NMR spectrum of PTB

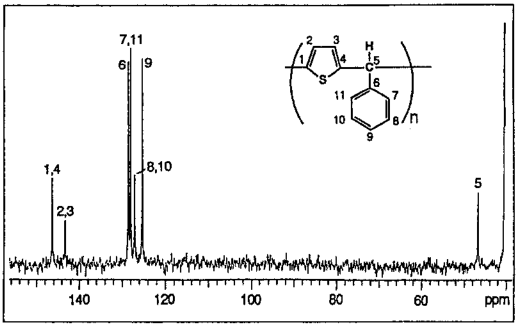


Figure 2. ^{13}C-NMR spectrum of PTB

From these results of ^{1}H-NMR, ^{13}C-NMR, infrared spectrum, and elemental analysis, the resulting polymer has a well-defined PTB structure that is shown in Scheme 1.

Molecular Weight

When dioxane and boron trifluoride etherate were used as a solvent and a catalyst, respectively, the resulting polymer was yellow and soluble in a polar solvent. Its molecular weight was measured by GPC. The molecular weight of this polymer was estimated to Mw 1100 and Mn 1900 (polystyrene as the standard). This molecular weight was relatively low.

When we used dichloromethane and boron trifluoride etherate as the solvent and the catalyst, respectively, the brownish polymer was obtained, and it is in a polar solvent. The molecular weight of this polymer was estimated to Mw 13000 and Mn 22000 (polystyrene as the standard) by GPC. This polymer had a relatively high molecular weight.

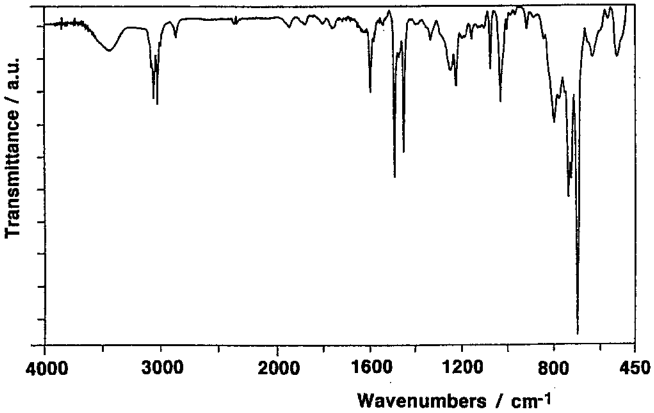


Figure 3. The infrared spectrum of PTB

These results are summarized in Table 1. They suggest that the polarity of the used solvent affects the molecular weight of the resulting polymers.

Table 1 Molecular weight and yield of the resulting PTB is obtained in dioxane and dichloromethane.

Solvents	Mw	Mn	Mw/Mn	DPn	Yield(%)
Dioxane	1900	1100	1.70	6.6	23.8
Dichloromethane	21600	12800	1.69	74.2	70.0

Solubility

Solubility and processability of conjugated polymer are of great importance for characterization of the materials as well as for fabrication of novel devices. PTB synthesized in dichloromethane is soluble in common organic solvents as summarized in Table 2.

Table 2 Solubilities of PTB in various organic solvents

Solvents	Dichloromethane	Dioxane
Chloroform	Soluble	Soluble
Dichloromethane	Soluble	Soluble
THF	Soluble	Soluble
Dioxane	Soluble	Soluble
Xylene	Soluble	Soluble
Metahnol	Insoluble	Insoluble

Absorption Spectrum

The absorption spectrum of the PTB in chloroform was shown in Figure 4. There was no absorption band in longer wavelength. From the optical absorption edge, the band-gap of PTB was estimated about 4.3 eV.

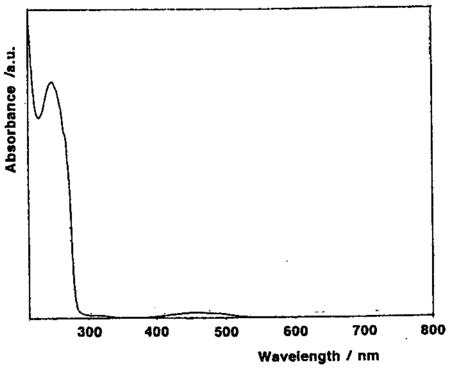


Figure 4. The optical absorption spectrum of PTB

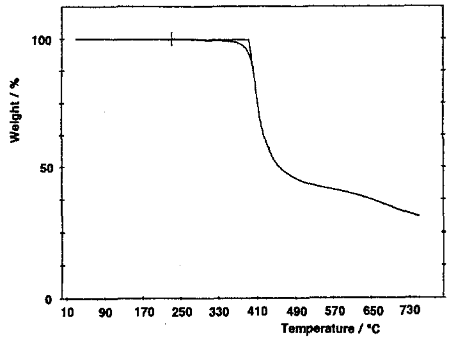


Figure 5. The thermal stability of PTB in nitrogen.

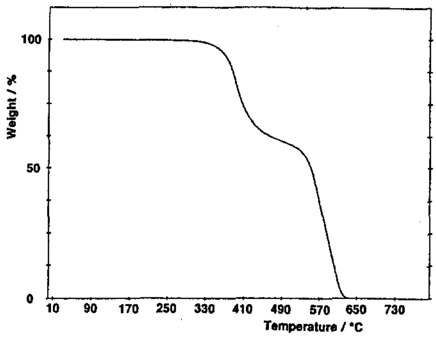


Figure 6. The thermal stability of PTB in air.

Thermal Properties

Figures 5 and 6 show the thermal stability of PTB that was recorded on the thermogravimetric analysis of PTB under nitrogen and air, respectively. Thermal decomposition took place at 391 °C under nitrogen and at 370 °C under air. These results show us that PTB is rather stable in air. Onset of weight loss in the temperature range of 150-250 °C (18) was not detected in the present experiment. This thermal stability is considered to be attributed to high molecular weight.

Figures 7 and 8 show the differential scanning calorimetries of PTB under nitrogen and air atmosphere, respectively. The glass transformation temperature of PTB was 117 °C and this polymer was nonfusible.

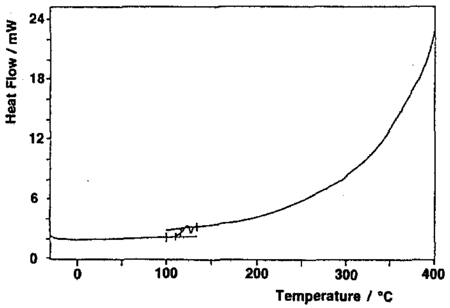


Figure 7. The differential scanning calorimety investigation of PTB in nitrogen.

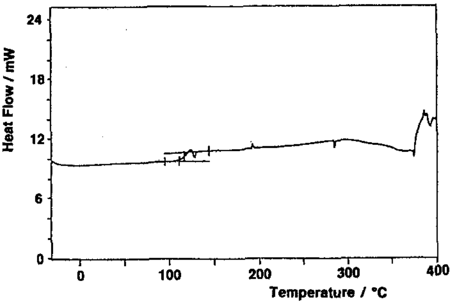


Figure 8. The differential scanning calorimety investigation of PTB in air.

Conclusion

Poly(α-thiophenediyl)benzylidene with high molecular weight and well-defined structure was synthesized. The important feature of the present polymerization condition is that the polymerization is carried out at low temperature and in a polar solvent. Both the well-defined structure and the high molecular weight (DPn about 74) were achieved in the above conditions. This polymer is thermally stable and is soluble in common organic solvents. This suggests that the present polymer has a big applicablity to fabrications of novel optical and electrical device.

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