

SYNTHESIS AND CHARACTERIZATION OF SOLUBLE POLYPHENYLENE COMPOSED OF *p*-PHENYLENE AND *m*-PHENYLENE UNITS

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Abstract NiCl₂(bpy) catalyzed polycondensation between *p*-dibromobenzene and *m*-dibromobenzene has been carried out under various conditions. The polycondensation endows the copolymer with an M_n of 2300 (by GPC, polystyrene standards) and good solubility in organic solvents. The fluorescence spectra of the copolymer measured with tetrahydrofuran solution shows an emission maximum ($\lambda_{\max}$) at 372.8 nm, whereas for the film the maximum shifts to 436.6 nm.

Keyword Polyphenylene, Copolycondensation, Conjugated polymer

INTRODUCTION

In the field of conjugated polymer, polyphenylene continues to receive considerable attention due to its outstanding physical and chemical properties^[1–3]. It is known for its exceptional thermal stability in the neutral state, good chemical stability and very wide conductive range and optical properties. But a major problem in the application of polyparaphenylene (PPP) is its insolubility in most organic solvents. The most important and attractive study goal is the synthesis of soluble polyphenylene.

In order to modify its solubility in organic solvents, a long-chain PPP derivative has been synthesized^[4, 5]. But the steric demand of the alkyl chain leads to a considerable torsion on the phenyl-phenyl bonds, which seriously inhibits the conjugated interaction along the polymer chain.

More recent approaches have been tried to overcome this problem^[6–8]. A novel and particularly promising approach toward the planarization of the PPP backbone is the incorporation of a ladder-type structure.

In this paper, the synthesis of a new soluble polyphenylene that is based on the copolymerization between *p*-dibromobenzene and *m*-dibromobenzene using the Yamamoto reaction is described^[9].

EXPERIMENT

Copolymerization

When 25 mg of NiCl₂(bpy) was added to a mixture of the products obtained by the reaction of 5.9 g (25 mmol) of a mixture of *p*-dibromobenzene and *m*-dibromobenzene with 0.61 g (25 mmol) magnesium in dry THF(30 mL), the copolymerization was started. Copolymerization was completed after refluxing for 4–48 h. The reaction mixture was poured into 200 mL methanol. The copolymer was precipitated and collected on a glass filter, washed with dilute hydrochloric acid, distilled water and methanol, and dried in vacuum at room temperature to yield light yellow or white copolymer. The yield is in the range of 40%–90% based on the amount of carbon taken into the copolymer.

Characterization of Copolymer

IR spectra were recorded on a Jasco IR-810 spectrometer. UV spectra were taken with a Shimadzu UV-3100pc

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scanning spectrophotometer. DSC and TGA were performed with a Shimadzu DSC-50 differential scanning calorimeter and a TG-50 thermo-gravimetric analyzer, respectively. X-ray diffraction patterns were obtained with a Philips PC-APD X-ray diffractometer. The anode material was Cu, α_1 wavelength was 0.154 nm and α_2 wavelength was 0.154439 nm. Molecular weight and molecular weight distribution were performed with Toson HLC-8020 GPC and the detector was Toson UV-8020. Solvent for determination was LiBr solution in *N,N*-dimethylformamide (0.5 g/L), flow rate of the solvent was 0.5 mL/min and pressure of pump was 7.0 MPa. Fluorescence spectra were obtained with Hitachi F-4010 fluorescence spectrophotometer. The solution of copolymer in THF for UV analysis was controlled in the range of 0.1%–0.3%.

RESULTS AND DISCUSSION

Polycondensation

Table 1 summarizes the influence of molar ratio of *m*-segment in copolymer on its solubility in organic solvents. It is presumed that we could get soluble polyphenylene using copolycondensation of two monomers. However, as shown in Fig. 1 when the reaction time was 4 h for all polycondensation, with an increase in molar ratio of *p*-dibromobenzene in monomers, the yield was increased. This fact suggests that *m*-dibromobenzene is more difficult to polymerize than *p*-dibromobenzene. It was known that polyparaphenylene is insoluble in any organic solvent. This means that during the synthesis of polyphenylene precipitation concurs with the polycondensation preventing the copolymer from attaining a high degree of polymerization. But when the molar ratio between *p*-dibromobenzene and *m*-dibromobenzene in the reaction mixtures was in the range of *p*:*m* = 3-1:7-9, the reaction became a solution polycondensation. This fact means that the increase of reflux time of the reaction favors this polycondensation and copolymer with higher molecular weight can be obtained. The influences of reaction time and the amount of catalyst on molecular weight and MWD are shown in Table 2 and 3, respectively.

Table 1. The solubility of copolymer in organic solvent

<i>p</i> / <i>m</i>	100/0	80/20	60/40	50/50	40/60	30/70	20/80	10/90	0/100
THF	○	○	○	○	●	●	◎	◎	○
DMF	○	○	○	○	●	●	◎	◎	○
DMSO	○	○	○	○	●	●	◎	◎	○
CHCl ₃	○	○	○	○	○	●	◎	◎	○
H ₂ SO ₄	◎	◎	◎	◎	◎	◎	◎	◎	◎

Note: ○ Insoluble; ● Poor solubility in organic solvent; ◎ Soluble in organic solvent

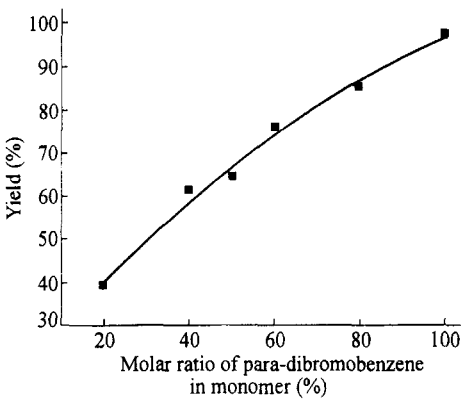


Fig. 1 The influence of molar ratio of *p*-dibromobenzene in monomers on the yield of copolymer

As shown in Table 2, with the increase of reflux time, the molecular weight and yield of copolymer both increase and the copolymer formed has narrower molecular weight distribution. But too long a reaction time does

not increase the yield and the molecular weight of copolymer again.

Table 2. Influence of reactive time on molecular weight and yield of copolymer

Run	Reactive time (h)	Yield (%)	M_n	M_w/M_n
1	4	39.31	1265	1.7
2	10	38.0	1313	1.52
3	24	67.1	2595	1.15
4	40	67.0	2301	1.21

Note: *p*-dibromobenzene:*m*-dibromobenzene = 2:8 (molar ratio)

The GPC analysis of soluble polyphenylene shows a narrow molecular weight distribution with a weight-average molecular weight of approximately 2800 and number-average molecular weight of 2300 ($M_w/M_n = 1.21$).

As shown in Table 3, with increasing amount of catalyst, the molecular weight of formed copolymer increased and molecular weight distribution becomes narrower.

Table 3. The influence of the amount of catalyst on molecular weight and MWD of soluble polyphenylene

Run	M_n	M_w	M_z	M_w/M_n	Amount of cat. (mg)
1	2594.75	2980.95	3442.00	1.15	12.5
2	2397.45	2920.43	3511.14	1.20	6.1
3	1823.39	2385.46	3063.98	1.31	3.1

Note: *p*-dibromobenzene: *m*-dibromobenzene = 2:8 (molar ratio)

IR and X-ray Diffraction Analysis

It was known^[10–12] that if PPP has a strictly linear structure, it should display an IR spectrum without absorption at 850–900 and 1590–1600 cm^{-1} , and should have a single weak band at 900 cm^{-1} . The band at 808 cm^{-1} is the out-of-plane vibration of *p*-phenylene units and that at 1475 cm^{-1} is the C=C stretching vibration absorption band of 1,4 substituted benzene ring. But there are two absorption bands at 1594 cm^{-1} ($\nu_{\text{C}=\text{C}}$) and 775 cm^{-1} ($\delta_{\text{C-H}}$) for polymetaphenylene (PMP). From the analysis of IR for PPP, PMP and polyphenylene copolymer, we can assign characteristic absorption bands for *p*-phenylene units (1471 cm^{-1} and 812 cm^{-1}) and characteristic bands for *m*-phenylene (1594 cm^{-1} and 775 cm^{-1}) in the copolymer. As shown in Fig. 2, when the ratio of *p*-phenylene and *m*-phenylene units in copolymer is changed, the $I_{1470\text{ cm}^{-1}} / I_{1597\text{ cm}^{-1}}$ will be changed too.

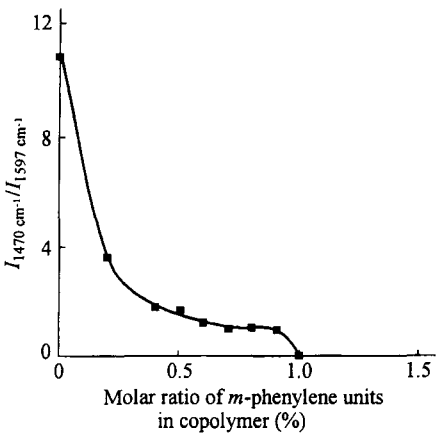


Fig. 2 The influence of molar ratio of *m*-phenylene units in copolymer on the $I_{1470\text{ cm}^{-1}} / I_{1597\text{ cm}^{-1}}$

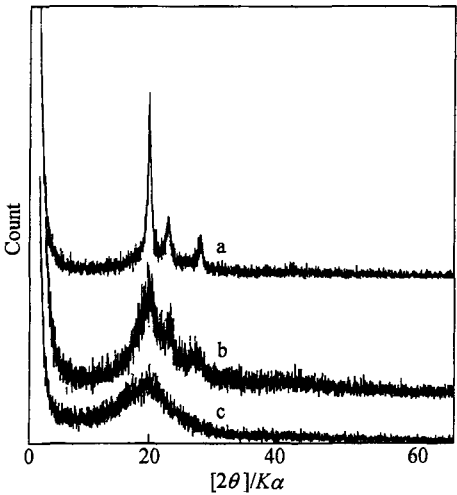


Fig. 3 X-ray diffraction analysis of copolymer a) Polyparaphenylene; b) Copolymer (*p*:*m* = 5:5); c) Polymetaphenylene

Figure 3 shows X-ray diffraction patterns of the powdery polymer. The data indicate that PPP has high crystallinity while PMP is an amorphous polymer. With the increase of *m*-phenylene units in the copolymer, the crystallinity of the copolymer will decrease while its solubility in organic solvents will increase.

UV Absorption and Fluorescence Spectra

UV-vis spectra of the copolymer depend highly on the molar ratio of *p*-phenylene units in the copolymer. As shown in Fig. 4, the absorption maximum appears at 257.6 nm in the copolymer composed of 30% *p*-phenylene

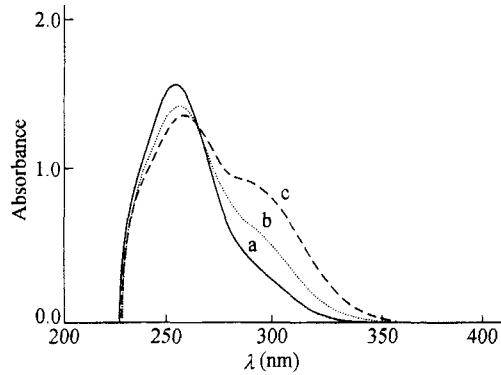


Fig. 4 The UV spectra of copolymers
a) *p*:*m* = 1:10; b) *p*:*m* = 2:8; c) *p*:*m* = 3:7

Table 4. The absorption maximum of *p*-phenylene group in copolymer

Run	Para/Meta (molar ratio)	λ_{max} (nm)	Average of repeatedly linked <i>p</i> -phenylene units
1	30/70	257.6	2.22
2	20/80	255.4	2.15
3	10/90	253.2	2.09

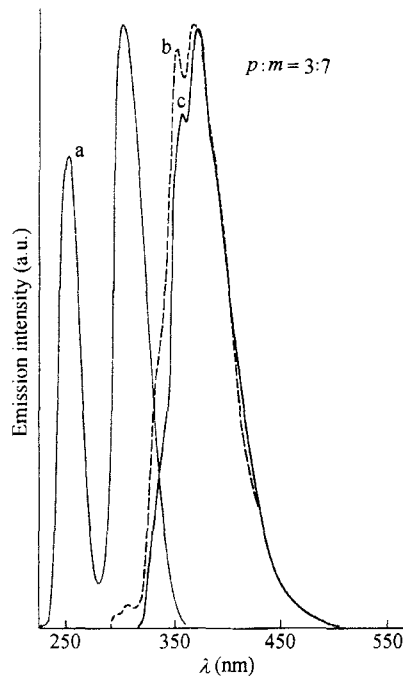


Fig. 5 Fluorescence spectra of copolymer in THF

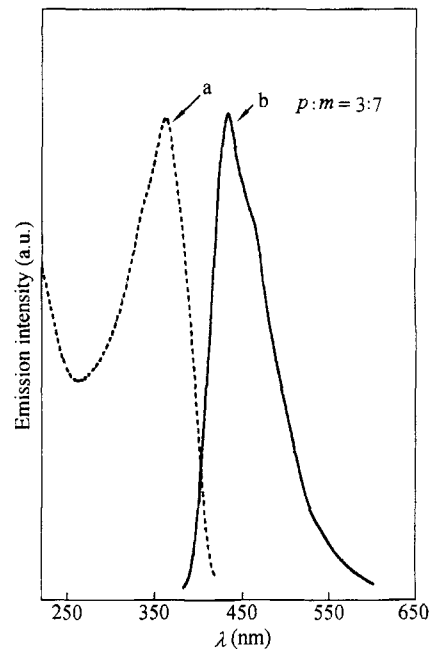


Fig. 6 Fluorescence spectra of polyphenylene copolymer film cast on a quartz plate

and 70% *m*-phenylene units. When *meta*-linked phenylene units are presented in the polymer chain, conjugation along the chain backbone is prohibited. With the increase of molar ratio of *m*-phenylene units in the polymer, the number of repeatedly linked *p*-phenylene units will decrease and the absorption maximum will be blue shifted (as shown in Fig. 4). According to the absorption maximum of *p*-phenylene units in the copolymer, the calculated average of repeatedly linked *p*-phenylene units in the copolymer is shown in Table 4^[13, 14].

Figure 5 shows the fluorescence spectra of copolymer in THF. As shown in Fig. 5 curve a, there are two peaks at 248.6 nm and 298.2 nm for excitation spectra of copolymer in THF. The peak at 248.6 nm belongs to *meta*-units in copolymer and the peak at 298.2 nm is for *para*-units in copolymer. Curve b ($\lambda_{\text{max}} = 371.2$ nm) is the fluorescence emission spectrum for excitation wavelength 248.6 nm and curve c ($\lambda_{\text{max}} = 372.8$ nm) is the fluorescence emission spectrum for excitation wavelength 298.2 nm. Because of the low quantum efficiency for polymetaphenylene, the emission intensity at 248.6 is lower than that at 298.2 nm although the content of *m*-units in the copolymer is higher than that of *p*-units.

Figure 6 shows the fluorescence spectrum (curve b, $\lambda_{\text{max}} = 436.6$ nm at excitation wavelength 369 nm) measured using a thin film cast on a quartz plate. Here a bathochromic shift of nearly 64 nm to 436.6 nm is observed

REFERENCES

- 1 Speight, J.G., Kovacic, P. and Coch, F.W., *J. Macromol. Sci., Rev. Macromol. Chem.*, 1971, C5: 295
- 2 Kovacic, P. and Jones, M.B., *Chem. Rev.*, 1987, 87: 357
- 3 Lacaze, P.C., Aeiya, S. and Lacroix, J.C., in "Handbook of Organic Conductive Molecules and Polymers: Conductive Polymer: Synthesis and Electrical Properties", ed. by Nalwa, H.S., John Wiley & Sons Ltd., Chichester, 1997, p.205
- 4 Ibuki, E., Ozasa, S. and Murai, K., *Bull. Chem. Soc., JPN*, 1975, 48: 1868
- 5 Berlin, A.A., *J. Polym. Sci.*, 1961, 55: 621
- 6 Scherf, U. and Mullen, K., *Synthesis*, 1992, 23
- 7 Tour, J.M. and Lamba, J.J.S., *J. Am. Chem. Soc.*, 1993, 115: 4935
- 8 Kreyenschmid, M.T., Frank Ucket and Klaus Mullen, *Macromolecules*, 1995, 28: 4577
- 9 Takakazu, Y., Yasuhiro, H. and Akio Y., *Bull. Chem. Soc. JPN*, 1978, 51: 2091
- 10 Aeiya, S., Laze, P. C., *J. Chem. Phy.* 1989, 86: 143; *J. Polym. Chem. Ed.* 1989, 27:, 515
- 11 Soubiran, P., Aeiya S., Aaron J.J., M. Delamar and P.C.Lacaze, *J. Electroanal. Chem.*, 1988, 251: 89
- 12 Socrates, G., "Infrared Characteristic Group Frequencies", John Wiley & Sons Ltd, Chichester, 1980, p.90
- 13 Suzuki, H., *Bull. Chem. Soc. JPN*, 1969, 33: 109
- 14 Tieke, B., Bubeck, C. and Lieser, G., *Makromol. Chem. Rapid Commun.*, 1982, 3: 261