

## A New Simple Synthesis of Soluble Poly(*p*-diethynylbenzene) Catalyzed by Cobalt-Phosphine

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**ABSTRACT:** *p*-Diethynylbenzene was polymerized in the presence of cobalt-phosphine in diethylamine at room temperature. The polymer had a molecular weight of ~13000 and the yield was 73.1—73.6% (M/Cat. = 100; for 10 h at 25°C). The polymers, highly soluble in polar organic solvents, possess the main chain containing  $\pi$ -conjugated linear polyene and the side chains consisting of the *p*-ethynylphenylene pendant groups. The effect of concentration and reaction time on the yield and product solubility were investigated.

**KEY WORDS** Polydiethynylbenzene / Cobalt Catalyst /  $\pi$ -Conjugated Polymers /

Preparation of  $\pi$ -conjugated polymers and clarifying their chemical and physical properties are the subjects of recent interest. Reports on the  $\pi$ -conjugated polymers having nonlinear optic and fluorescence properties have increased.<sup>1–5</sup>

Investigations in the field are mainly oriented to improve deficient properties and to find new possibilities for obtaining  $\pi$ -conjugated systems corresponding to the requirements for applications.<sup>6,7</sup>

Research devoted to methods of synthesizing the poly(*p*-diethynylbenzene) has been reported. However, the reported procedures including  $\gamma$ - and UV-radiation induced or electroinitiated polymerizations generally lead to insoluble and infusible products or result in partially soluble products with low yield. The electroinitiated procedure is complicated and platinum has to be used as electrodes.<sup>8–10</sup>

In the present paper, *p*-diethynylbenzene is polymerized in a simple catalytic procedure in mild conditions with the yield of 73.1—73.6%. The polymer is highly soluble in organic solvents such as toluene, tetrahydrofuran, chloroform and dimethylformamide, and possess outstanding thermal stability.

### EXPERIMENTAL

#### Materials

CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> were prepared according to the literature.<sup>11</sup> *p*-Diethynylbenzene (*p*-DEB) was synthesized by the reported procedure<sup>12</sup> and purified by sublimation immediately before use. Diethylamine was distilled over calcium hydride and stored under nitrogen. Tri-*n*-butylphosphine was purchased from Tokyo Chemical Industry Co., Ltd. All other reagents and solvent were purchased from commercial sources and used without further purification.

#### Instrumentation

UV-visible spectra were taken using a Beckman DU-50 spectrophotometer, Infrared spectra were obtained on a PE983 infrared spectrophotometer (film cast onto NaCl plates).

Molecular weight was determined at 25°C from gel-permeation chromatography in tetrahydrofuran (THF) using Waters 208 chromatograph vs. polystyrene standard. <sup>1</sup>H NMR and <sup>13</sup>C NMR measurement was carried out on a Varian Unity 200 MHz NMR spectrometer. Thermogravimetry analysis was recorded on a Perkin-Elmer 7 apparatus at a heating rate of 20°C min<sup>-1</sup>.

#### Preparation of Catalyst CoX<sub>2</sub>-2PBu<sub>3</sub>/EtOH

3 mmol CoX<sub>2</sub>·6H<sub>2</sub>O (X=Cl, Br) were dissolved in 5 mL hot absolute ethanol and 6 mmol tri-*n*-butylphosphine were added under nitrogen atmosphere. The mixture was stirred for 2—5 min at room temperature and stored under N<sub>2</sub> at 0°C.

#### General Polymerization Procedure

All polymerizations were conducted under N<sub>2</sub>. In a general procedure dry diethylamine (8 mL) was injected to *p*-DEB (10 mmol) in a presence of a solution of CoX<sub>2</sub>-2PBu<sub>3</sub>/EtOH (containing 0.12 mmol catalyst, X=Cl or Br) and reacted for 5—10 h at room temperature (17—28°C). The brown polymer was precipitated into petroleum ether (30—60°C fraction) and dried under vacuum at room temperature for 24 h.

### RESULTS AND DISCUSSION

#### Polymer Synthesis

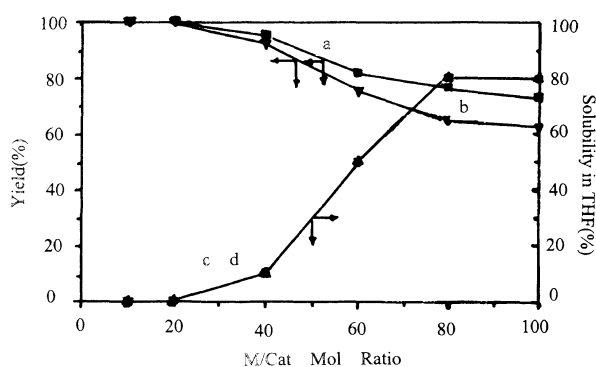
Based on the data in Table I, the yield and molecular weight distribution (MWD) of the polymer obtained by CoCl<sub>2</sub>-2PBu<sub>3</sub>/EtOH are different from those of the polymers obtained by directly adding CoCl<sub>2</sub> and PBu<sub>3</sub>. This suggests that CoCl<sub>2</sub>-PBu<sub>3</sub> complex may be the active species in this catalytic process. As seen from Table I, in the case of CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> or CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, the yield is much lower. This may be due to the fact that these complexes are almost insoluble in reaction solution diethylamine. From Table I, catalyst CoCl<sub>2</sub>-2PBu<sub>3</sub> possesses higher activity, but gave polymers with broader MWD compared to catalyst CoBr<sub>2</sub>-2PBu<sub>3</sub>.

Table II and Figure 1 show the results of polym-

**Table I.** Polymerization of *p*-DEB with different catalysts<sup>a</sup>

Catalyst	Yield/%	Solubility in THF/% <sup>b</sup>	$\bar{M}_w$ ( $\times 10^3$ )	$\bar{M}_n$ ( $\times 10^3$ )	MWD
CoBr <sub>2</sub> -2PBu <sub>3</sub> <sup>c</sup>	66.5	80	5.8	3.9	1.49
CoCl <sub>2</sub> -2PBu <sub>3</sub> <sup>c</sup>	73.1	80	5.1	2.2	2.32
CoBr <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> <sup>d</sup>	Trace	—	—	—	—
CoCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> <sup>d</sup>	Trace	—	—	—	—
CoCl <sub>2</sub> +PBu <sub>3</sub> <sup>c</sup>	59.6	80	5.0	2.9	1.72
CoCl <sub>2</sub> ·6H <sub>2</sub> O	No polym.	—	—	—	—

<sup>a</sup> Solvent, HNEt<sub>2</sub>; M/Cat. Mole ratio, 100; temperature, 25°C; reaction time, 10 h. <sup>b</sup> At room temperature. <sup>c</sup> Newly prepared catalyst. <sup>d</sup> Almost insoluble in HNEt<sub>2</sub>. <sup>e</sup> CoCl<sub>2</sub> and tri-*n*-butylphosphine were added directly at molar ratio of 1:2.



**Figure 1.** Effects of molar Ratio of M/Cat. on yield (a,b) and solubility (c,d) of PDEB by CoCl<sub>2</sub>-2PBu<sub>3</sub> (a,c) and CoBr<sub>2</sub>-2PBu<sub>3</sub> (b,d) ( $C = 1.2 \text{ mol L}^{-1}$ , 10 h at 25°C).

erization of *p*-DEB by Cobalt-phosphine catalyst with variation in reaction time (Table II) and monomer to catalyst (M/Cat.) molar ratio (Figure 1). The yield, solubility, molecular weight and MWD of the polymers by CoCl<sub>2</sub>-2PBu<sub>3</sub> are influenced by the reaction conditions. The yield increased but solubility decreased with decreasing monomer/catalyst ratio. Although longer reaction time leads to a higher yield, it has an unfavorable effect on the MWD. Using the reaction conditions listed in Table II, polymerizations could be carried out smoothly. The polymers were readily prepared by CoCl<sub>2</sub>-2PBu<sub>3</sub>/EtOH in diethylamine with 80–100 of M/Cat. at molar ratio and  $1.2 \text{ mol L}^{-1}$  of initial monomer concentration at 10 h at room temperature (17–28°C). The weight-average molecular weights and molecular weight distributions ranged from  $5.1 \times 10^3$  to  $1.3 \times 10^3$  and 2.32 to 3.20, respectively with the yield of 73.1–73.6%. The polymers, brown in color, are soluble in common organic solvents including toluene, chloroform, dimethylformamide, and tetrahydrofuran.

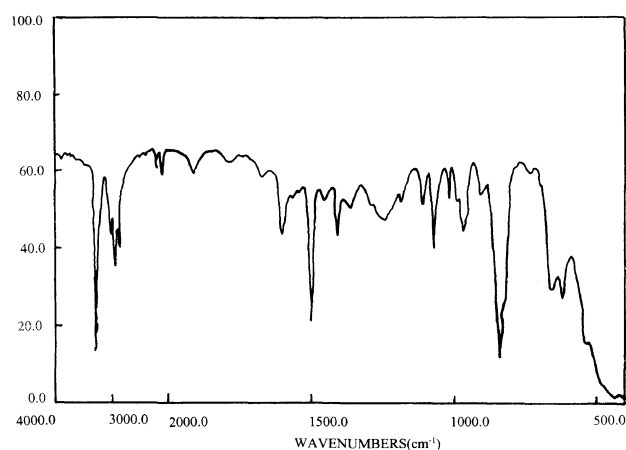
#### Polymer Characterization

The polymers were investigated by IR, UV, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. As shown in Figure 2, the IR spectrum of polymer PDEB-5 are different from that of *p*-DEB. By polymerization, the ethynyl  $\nu(\equiv\text{C-H})$  band of the monomer at  $3264 \text{ cm}^{-1}$  shifted to a higher frequency of  $3275 \text{ cm}^{-1}$ . The intense absorption bands of the polymers at about  $3275 \text{ cm}^{-1}$  prove the presence of a great number of unreacted triple bonds. This indicates that the polymers obtained by cobalt-phosphine catalyst system are different from those (which show disappearance of

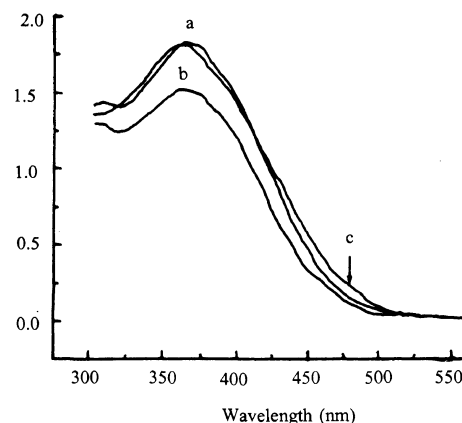
**Table II.** Effects of reaction time on product yield, solubility, molecular weight, and molecular weight distribution<sup>a</sup>

Polymer	M/Cat. Mol.ratio	Time/h	Yield/%	Solubility in THF/% <sup>b</sup>	$\bar{M}_w$ ( $\times 10^3$ )	MWD
PDEB-1	100	10	73.1	80	5.1	2.32
PDEB-2	100	20	73.9	80	6.8	2.67
PDEB-3	80	2	30.1	~100	10.2	2.67
PDEB-4	80	5	53.6	90	11.2	2.85
PDEB-5	80	10	73.6	80	13.3	3.20
PDEB-6	80	15	75.7	80	17.5	3.31
PDEB-7	80	20	77.1	~50	13.9	3.03

<sup>a</sup> Solvent, HNEt<sub>2</sub>; concentration,  $1.2 \text{ mol L}^{-1}$ ; temperature, 17–25°C; Cat., CoCl<sub>2</sub>-2PBu<sub>3</sub>/EtOH. <sup>b</sup> At room temperature.



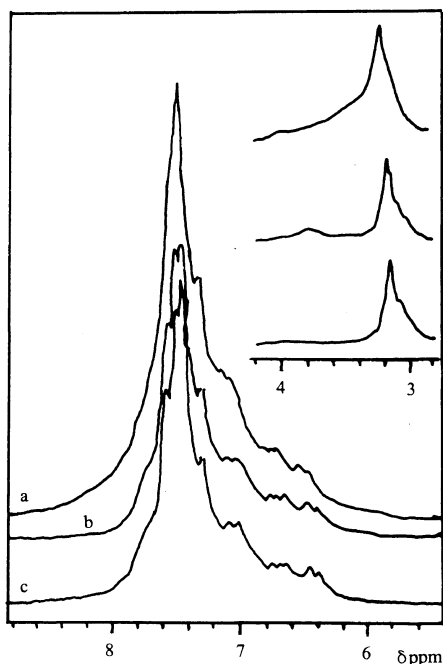
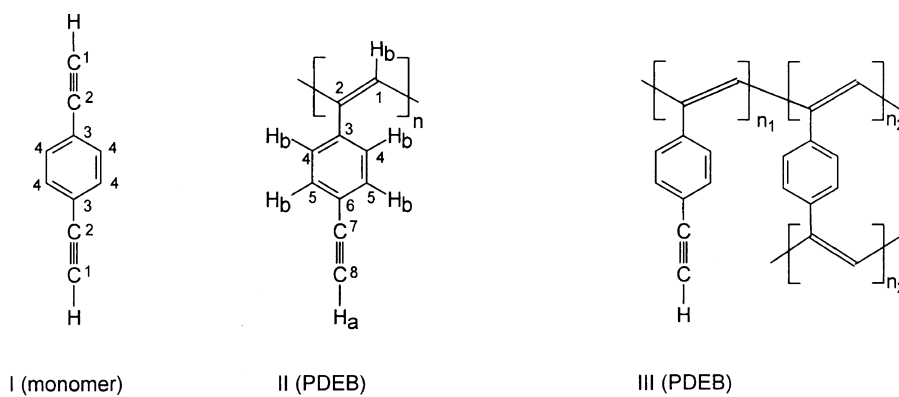
**Figure 2.** IR spectrum of PDEB (film cast onto NaCl plates).



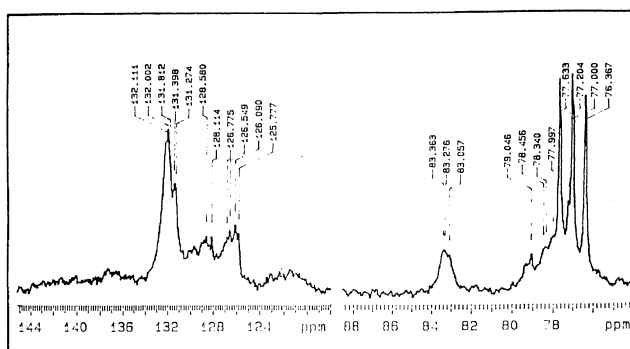
**Figure 3.** UV spectra of PDEB. a,  $\bar{M}_n = 3.8 \times 10^3$ ; b,  $\bar{M}_n = 4.2 \times 10^3$ ; c,  $\bar{M}_n = 5.3 \times 10^3$ .

bands due to  $\nu_{\equiv\text{C-H}}$ ) by other catalyst system.<sup>13</sup> The characteristic bands of  $\delta_{\text{C-H}}$  (*p*-disubstituted benzene ring) did not shift significantly. The new band at  $847 \text{ cm}^{-1}$  is ascribed to the  $\delta_{\text{C-H}}$  absorption of  $\text{C}=\text{C}-\text{H}$ . The appearance of bands at  $1600\text{--}1660 \text{ cm}^{-1}$  suggests the formation of extended  $\pi$ -conjugated linear polyene.<sup>14–16</sup> From infrared spectra, the polymers by cobalt-phosphine catalyst were found to contain both linear  $\pi$ -conjugated polyene main chain and *p*-ethynylphenylene pendant groups.

The appearance of  $\pi\text{-}\pi^*$  absorption band at  $\sim 370 \text{ nm}$  in THF in the UV-Vis absorption spectra (Figure 3) of these polymers confirmed that the extended  $\pi$ -conjugated



**Figure 4.**  $^1\text{H}$  NMR spectra (200 MHz,  $\text{CDCl}_3$ ) of PDEB, a,  $\bar{M}_w = 1.0 \times 10^4$ ; b,  $\bar{M}_w = 1.3 \times 10^4$ ; c,  $\bar{M}_w = 1.8 \times 10^4$ .



**Figure 5.**  $^{13}\text{C}$  NMR spectra (50 MHz,  $\text{CDCl}_3$ ) of PDEB ( $\bar{M}_w = 1.3 \times 10^4$ ).

systems were formed. The peak position showed no variation with change of the molecular weight of PDEB in a range of  $\bar{M}_w = 1.0 \times 10^4 - 1.8 \times 10^4$  or  $\bar{M}_n = 3.8 \times 10^3 - 5.3 \times 10^3$ .

$^1\text{H}$  NMR spectra of PDEB with  $\bar{M}_w = 1.0 \times 10^4$  and  $1.8 \times 10^4$  (by  $\text{CoCl}_2-2\text{PBu}_3$  for 2 h, 10 h, and 15 h, respectively) are shown in Figure 4a–4c. The  $^1\text{H}$  NMR spectrum of the monomer shows proton signals at  $\delta = 3.20$  ppm (s, 2H,  $\equiv\text{C}-\text{H}$ ) and  $\delta = 7.43$  ppm (s, 4H,

aromatic protons). By polymerization ethynyl  $\text{H}_a$  ( $\equiv\text{C}-\text{H}$ ) and conjugated double bond protons  $\text{H}_b$  (Ph-H and  $\text{C}=\text{C}-\text{H}$ ) have signals in the region of  $\delta = 2.93-3.46$  ppm and  $\delta = 6.42-7.41$  ppm respectively. Compared with those of the monomer, the proton signals of the polymers are all extended and multiple.

The proportion of integration high of signals at conjugated double bonds ( $\text{H}_b$ ) and at the ethynyl ( $\text{H}_a$ ) regions in the  $^1\text{H}$  NMR spectra of the polymers with  $\bar{M}_w = 1.0 \times 10^4$ ,  $1.3 \times 10^4$ , and  $1.8 \times 10^4$  are 5:1, 5.1:1, and 5.6:1 (calcd.  $\text{H}_b:\text{H}_a = 5:1$  for structure II) respectively.  $^1\text{H}$  NMR analysis indicated that the polymers by  $\text{CoCl}_2-2\text{PBu}_3$  for a relatively short polymerization period of  $\leq 10$  h possess the structure of II (in accordance with the IR and UV analysis), and those for a longer reaction time of  $> 10$  h have the structure of III with  $n_1:n_2 = 10:1$ . This is in accordance with IR and UV analysis.

The  $^{13}\text{C}$  NMR spectrum of the monomer shows carbon signals at  $\delta = 79.2$  ppm (structure, I,  $\text{C}_1$ ), 83.0 ppm ( $\text{C}_2$ ), 122.4 ppm ( $\text{C}_3$ ), and 131.9 ppm ( $\text{C}_4$ ). As shown in Figure 5, the  $^{13}\text{C}$  NMR spectrum of the polymer ( $\bar{M}_w = 1.3 \times 10^4$ ) shows carbon signals at  $\delta = 78.0-80.1$  ppm (structure II,  $\text{C}_8$ ), 82.6–84.2 ppm ( $\text{C}_7$ ), 119–123.6 ppm ( $\text{C}_1$ ), and 125.8–133.6 ppm ( $\text{C}_3-\text{C}_6$ ). This confirms the conclusions from  $^1\text{H}$  NMR analysis.

Thermogravimetric analysis curves under  $\text{N}_2$  for PEDB ( $\bar{M}_w = 1.3 \times 10^4$  and  $\bar{M}_n = 4.2 \times 10^3$ ) revealed weight loss in one stage in the temperature range of 398 to  $900^\circ\text{C}$ . The weight loss was approximately 90% at  $900^\circ\text{C}$ . TGA measurements indicate that PDEB by  $\text{CoCl}_2-2\text{PBu}_3$  exhibits a remarkable thermal stability.

## CONCLUSIONS

Soluble  $\pi$ -conjugated poly(*p*-diethynylbenzene) was readily synthesized by  $\text{CoCl}_2-2\text{PBu}_3$  catalysis in diethylamine at room temperature with high yield and high molecular weight. IR, UV,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR analysis as well as the fact that a large part of the product remains soluble in common organic solvents indicate that one ethynyl group of the *p*-DEB takes part in to the reaction, while the other one remains unreacted. The resulting polymers containing  $\pi$ -conjugated polyene main chain and free ethynyl substituted benzene side chains.

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