

# Cyclopolymerization of 2-Ethynyl-*N*-propargylpyridinium Tetraphenylborate by Transition Metal Catalysts

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Received January 18, 2005; Accepted March 22, 2005

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**Abstract:** A new conjugated ionic cyclopolymer having a bulky tetraphenylborate counter ion, poly (2-ethynyl-*N*-propargylpyridinium tetraphenylborate), was synthesized via ring-forming polymerization of the corresponding diacetylenic monomer. The polymerization of 2-ethynyl-*N*-propargylpyridinium tetraphenylborate was performed using various transition metal catalysts. In general, the polymerization of this diacetylenic monomer proceeded well to give a high yield of polymer. The catalytic activities of a W-based catalyst were similar with those of Mo-based catalysts. The resulting polymers were mostly brown or black powders. The polymer structure was characterized through elemental analysis and NMR, IR, and UV-visible spectroscopies to confirm the conjugated cyclopolymer structure and its tetraphenylborate counter ions. The inherent viscosities of the resulting polymers were in the range 0.09~0.16 dL/g, depending on the polymerization conditions. The thermal and morphological properties of the polymers were also studied and are discussed.

**Keywords:** cyclopolymerization, 2-ethynylpyridine, transition metal catalyst, morphology

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## Introduction

Conjugated polymer systems have been used as candidate materials for applications such as organic semiconductors, chemical sensors, light-emitting diodes, nonlinear optical materials, liquid crystalline materials, membranes for optical resolution of racemic mixtures, and membranes for the separation of gases and liquid mixtures [1-7]. Ionic conjugated polymers also have potential for use as materials for mixed ionic and electronic conductivity, and in energy storage devices such as batteries and permselective membranes [8,9].

Various polyacetylenes carrying different functionalities have been prepared and characterized [1,2,10,11].

Cyclopolymerization is a type of chain-growth addition polymerization that forms cyclic structures in the polymer main chain via an alternating intramolecular intermolecular chain propagation [12]. In 1949, Butler and Bunch found that diallyl ammonium salts were polymerized with free-radical initiators to give water-soluble, non-crosslinked polymers [13]. The cyclopolymer obtained from nonconjugated dienes having various functionalities have many potential applications, such as photoresponsive coatings, antistatic agents, positively charged electrophotographic toners, basic anion exchangers, demineralization agents, and interferon inducers [13]. The cyclopolymerization of nonconjugated diynes has also been investigated extensively in an attempt to prepare polymers that would contain alternating double and single bonds along the polymer main chain possessing a cyclic recurring unit [2,14,15].

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The cyclopolymerization of dipropargyl monomers containing an ionic moiety is a facile synthetic method for the preparation of self-doped conjugated ionic polymers [16,17]. In a previous study, we synthesized various conjugated ionic polymers via the cyclopolymerization of some quarternary dipropargyl ammonium salts [18]. We have also reported the synthesis of such ionic conjugated polymers as poly(propargyltriphenylphosphonium bromide) [19], poly(*N*-propargylpyridinium bromide) [20], and poly(propargyltrimethylammonium bromide) [21].

In recent years, we reported the synthesis of a novel conjugated ionic polymer via an interesting cyclopolymerization reaction of 2-ethynyl-*N*-propargylpyridinium bromide having two different acetylenic functional groups (acetylenic and propargyl) in the same monomer [22,23]. In this article, we report on the polymerization behavior for the cyclopolymerization of 2-ethynyl-*N*-propargylpyridinium tetraphenylborate (EPP-TPB), which has a bulky counter anion, and the properties of the resulting poly(EPP-TPB).

## Experimental

### Materials

2-Ethynylpyridine (Aldrich Chemicals, 98%) and NaBPh<sub>4</sub> (Aldrich Chemicals, 99.5+%) were used as received. Propargyl bromide (Aldrich Chemicals, 80 wt% solution in toluene) was dried with calcium hydride and fractionally distilled. WCl<sub>6</sub> (Aldrich Chemicals, 99.99+%), MoCl<sub>5</sub> (Aldrich Chemicals, 99.99+%), MoCl<sub>4</sub>, PdCl<sub>2</sub> (Aldrich Chemicals, 99.995%), PtCl<sub>2</sub> (Strem), RuCl<sub>3</sub> (Aldrich Chemicals), EtAlCl<sub>2</sub> (Aldrich Chemicals, 25 wt% solution in toluene) were used without further purification. (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> was prepared by a reported method [24]. The solvents were analytical grade materials; they were dried with an appropriate drying agent and fractionally distilled.

### Synthesis of 2-Ethynyl-*N*-propargylpyridinium Bromide

2-Ethynyl-*N*-propargylpyridinium bromide was prepared according to a reported method [22].

### Synthesis of EPP-TPB

EPP-TPB was prepared by the ion-exchange reaction of 2-ethynyl-*N*-propargylpyridinium bromide with sodium tetraphenylborate in methanol solvent as follows. To a stirred methanol solution (200 mL) containing 20 g (90.1 mmol) of 2-ethynyl-*N*-propargylpyridinium bromide, a methanol solution (150 mL) containing sodium tetraphenylborate (34.2 g, 100 mmol) was added slowly at room temperature. A light-brown EPP-TPB powder was immediately formed and precipitated. The product was filtered and dried under vacuum (38.3 g, 92%). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, δ, ppm): 3.75 (1H), 3.95 (1H), 5.38 (2H),

6.73~7.28 (20H), 7.55~9.27 (4H). IR (KBr pellet, cm<sup>-1</sup>): 3300, 3054, 2226 (acetylenic C-H stretching of -CH<sub>2</sub>-C≡C-H), 2131 (acetylenic C-H stretching of -C≡C-H), 1620 (aromatic =C-H stretching of pyridyl moiety), 1578, 1540, 1479, 1427, 1154, 1032, 846, 735, 707, 612.

### Polymerization of EPP-TPB by MoCl<sub>5</sub>

In a 20-mL reactor containing EPP-TPB 1.0 g, (2.17 mmol) and chlorobenzene (2.9 mL, [M]<sub>0</sub> = 0.5 M), 0.433 mL (0.0433 mmol, M/C = 50) of 0.1 M chlorobenzene solution was injected. The polymerization was carried out at 80°C for 24 h. After the polymerization time, the reaction solution was diluted by adding 10 mL of chloroform and precipitated into a large excess of methanol. The precipitated polymer was filtered and dried under vacuum at 40°C for 24 h. The polymer yield was 82%.

### Polymerization of EPP-TPB by WCl<sub>6</sub>-EtAlCl<sub>2</sub>

In a 20-mL flask containing EPP-TPB 1.0 g, (2.17 mmol) and chlorobenzene 2.47 mL, ([M]<sub>0</sub> = 0.5 M), a mixture of 0.433 mL of WCl<sub>6</sub> (0.1 M solution, 0.0433 mmol, M/C = 50) and 0.433 mL of EtAlCl<sub>2</sub> (0.2 M solution, 0.0866 mmol, the mole ratio of EtAlCl<sub>2</sub>/WCl<sub>6</sub> = 2) was injected. The reaction and work-up procedures were same with that used for the polymerization with MoCl<sub>5</sub>. The polymer yield was 85%.

### Polymerization of EPP-TPB by PdCl<sub>2</sub>

In a 20-mL reactor equipped with a rubber septum, EPP-TPB (1.0 g, 2.17 mmol), PdCl<sub>2</sub> (12.8 mg, 0.072 mmol, M/C:30), and DMF (3.84 mL, [M]<sub>0</sub> = 0.25 M) were added, in that order, and sealed with a rubber septum after flushing with purified argon. The polymerization was carried out at 80°C for 24 h. After a given polymerization time, 10 mL of DMF was added to the polymerization solution. The polymer solution was precipitated into a large excess of methanol, filtered, and then dried under vacuum at 40°C for 24 h. The polymer yield was 95%.

### Instruments and Measurement

<sup>1</sup>H-NMR spectra of the monomer and polymer were recorded on a Bruker AM-200 spectrometer in DMSO-*d*<sub>6</sub>; the chemical shifts are reported in ppm with tetramethylsilane as an internal standard. IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. Elemental analyses were performed using a Perkin-Elmer 240DS Elemental Analyzer. UV-visible spectra were recorded on a JASCO V-530 spectrophotometer in DMF solvent. The inherent viscosities of the polymers were determined at a concentration of 0.5 g/dL in DMF at 30°C. Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10°C/min up to 700°C with a DuPont 2200 thermogravimetric analyzer.

**Table 1.** Cyclopolymerization of EPP-TPB by Mo- and W-Based Transition Metal Catalysts<sup>a</sup>

Exp. No	Catalyst System (mole ratio) <sup>b</sup>	M/C <sup>c</sup>	Solvent	Polymer Yield <sup>d</sup> (%)
1	MoCl <sub>5</sub>	50	Chlorobenzene	82
2	MoCl <sub>5</sub>	30	Chlorobenzene	85
3	MoCl <sub>5</sub> -Ph <sub>4</sub> Sn (1:1)	50	Chlorobenzene	87
4	MoCl <sub>5</sub> -EtAlCl <sub>2</sub> (1:2)	50	Chlorobenzene	90
5	MoCl <sub>4</sub> -EtAlCl <sub>2</sub> (1:2)	50	Chlorobenzene	85
6	Cp <sub>2</sub> MoCl <sub>2</sub> -EtAlCl <sub>2</sub> (1:2)	50	Chlorobenzene	80
7	WCl <sub>6</sub>	50	Chlorobenzene	55
8	WCl <sub>6</sub> -Ph <sub>4</sub> Sn (1:1)	50	Chlorobenzene	67
9	WCl <sub>6</sub> -( <i>n</i> -Bu) <sub>4</sub> Sn (1:1)	50	Chlorobenzene	73
10	WCl <sub>6</sub> -EtAlCl <sub>2</sub> (1:2)	50	Chlorobenzene	85
11	MoCl <sub>5</sub>	50	Toluene	80
12	MoCl <sub>5</sub>	50	Benzene	75

<sup>a</sup>Polymerization was carried out at 80°C for 24 h. Initial monomer concentration ([M]<sub>0</sub>) was 0.5 M.

<sup>b</sup>The mixture of catalyst and cocatalyst was aged for 15 min at 30°C before use.

<sup>c</sup>Monomer-to-catalyst mole ratio.

<sup>d</sup>Methanol-insoluble polymer yield.

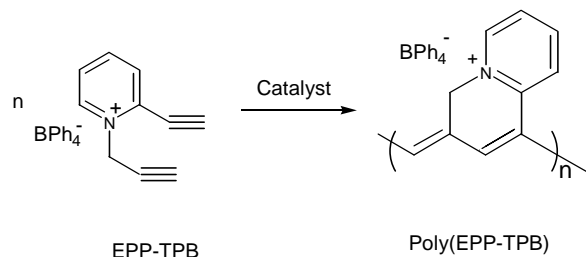
DSC thermograms were recorded on a DuPont 910 differential scanning calorimeter under a nitrogen atmosphere at a scanning rate of 10°C/min. The photoluminescence spectra of poly(EPP-TPB) were obtained using a 488-nm Ar laser for excitation and a Perkin-Elmer luminescence spectrometer LS50 (Xenon flash tube). The emission signal was collected by using the conventional photoluminescence arrangement of a laser, samples, a cryostat (Air Products 1R02-A dispex), a monochromator (Spex 750M), and a photomultiplier (Hamamatsu R943-02). The signal from the photomultiplier was amplified by an EG&G 5101 lock-in amplifier with the chopping frequency of 170 Hz, and converted to a digital signal in the autoscan system.

## Results and Discussion

The cyclopolymerization of EPP-TPB having two different acetylenic functional groups and a bulky counter anion (tetraphenylborate) was performed using various transition metal catalysts (Scheme 1).

In previous studies, we found that Mo-based catalysts are very effective for the cyclopolymerization of some dipropargyl monomers, such as 1,6-heptadiyne [15], dipropargyl ether [25], diethyl dipropargylmalonate [26], and dipropargylfluorene [27]. In addition, the catalytic activity of Mo-based catalysts was found to be greater than those of W-based catalysts for the cyclopolymerization of these dipropargyl monomers. From these viewpoints, systematic studies on the polymerization behavior of a diacetylenic monomer having a bulky tetraphenylborate counter anion are very interesting.

Initially, we used the Mo-based catalysts for the present cyclopolymerization of EPP-TPB. Table 1 shows the results for the polymerization of EPP-TPB by the Mo- and

**Scheme 1.** Cyclopolymerization of EPP-TPB.

W-based transition metal catalysts. In general, the polymerization of EPP-TPB by these Mo- and W-based catalysts proceeded well to give high yields of polymer. The catalytic activities of the Mo-based catalysts were similar to those of the W-based catalysts. Similar catalytic activities of Mo- and W-based catalysts have also been observed for the polymerization of some acetylene derivatives, such as propargyltriphenylphosphonium bromide [19], propargyltriphenylphosphonium tetraphenylborate [28], and 1-ethynylcyclohexene [29]. Of the molybdenum-based catalysts, MoCl<sub>5</sub> itself showed a high catalytic activity; the polymer yields were increased slightly when organotin and organoaluminum cocatalysts such as Ph<sub>4</sub>Sn and EtAlCl<sub>2</sub> were used. Other molybdenum catalysts, such as MoCl<sub>4</sub> and Cp<sub>2</sub>MoCl<sub>2</sub>-based catalysts showed similar catalytic activity when compared with that of MoCl<sub>5</sub>.

On the other hand, for the polymerization of EPP-TPB using tungsten-based catalysts, WCl<sub>6</sub> alone gave a moderate yield of polymer (55%). The organotin and organoaluminum cocatalysts (especially EtAlCl<sub>2</sub>) displayed good cocatalytic activities. EtAlCl<sub>2</sub> showed the best cocatalytic activity in the present polymerization. The enhanced cocatalytic activity of EtAlCl<sub>2</sub> has also been observed in the polymerization of similar ionic acetylenic monomers, such as propargyltriphenylphosphonium

**Table 2.** Cyclopolymerization of EPP-TPB by Palladium, Platinum, and Ruthenium Chlorides<sup>a</sup>

Exp.No	Catalyst	Solvent	M/C <sup>b</sup>	Temp.	P.Y. (%) <sup>c</sup>	$\eta_{inh}^d$
1	PdCl <sub>2</sub>	DMF	30	80	95	0.15
2	PdCl <sub>2</sub>	DMF	50	80	84	0.13
3	PdCl <sub>2</sub>	DMF	100	80	61	0.09
4	PdCl <sub>2</sub>	DMF	30	100	99	-
5	PdCl <sub>2</sub>	DMF	30	120	99	-
6	PdCl <sub>2</sub>	DMSO	30	80	99	0.15
7	PdCl <sub>2</sub>	Pyridine	30	80	87	0.14
8	PdCl <sub>2</sub>	NMP	30	80	93	0.15
9	PtCl <sub>2</sub>	DMF	30	80	91	0.14
10	RuCl <sub>3</sub>	DMF	30	80	96	0.16
11	(Ph <sub>3</sub> P) <sub>2</sub> PdCl <sub>2</sub>	DMF	30	80	78	0.10

<sup>a</sup>Polymerization was carried out for 24 h. Initial monomer concentration ( $[M]_0$ ) was 0.25 M.

<sup>b</sup>Monomer-to-catalyst mole ratio.

<sup>c</sup>Methanol-insoluble polymer yield.

<sup>d</sup>The inherent viscosities of polymers were measured at a concentration of 0.5 g/dL in DMF solvent at 30°C.

bromide [19], tripropargylammonium bromide [30], di-propargylammonium bromide [18], and dihexyldipropargylammonium bromide [16].

We also attempted the polymerization of EPP-TPB by using such classical transition metal catalysts as palladium, platinum, and ruthenium chlorides. Table 2 shows the results for the polymerization of EPP-TPB by these catalyst systems. In most cases, the polymer yields were relatively high. As the mole ratio of monomer-to-catalyst increased, the polymer yield and inherent viscosity decreased. The polymerization performed at elevated temperatures (100, 120°C) yielded mostly insoluble product, although the polymer yields were quantitative. We also tested the solvent effect for this polymerization. This polymerization proceeded well in organic solvents such as DMF, DMSO, and NMP, because they are good solvents for the monomer and the resulting polymer system.

We characterized the molecular structure of poly (EPP-TPB) by using various instrumental methods, such as NMR (<sup>1</sup>H and <sup>13</sup>C-), IR, and UV-visible spectroscopies and by elemental analysis. The elemental analysis data of the reprecipitated poly(EPP-TPB) agrees with the theoretical values; Calcd for (C<sub>34</sub>H<sub>28</sub>NB): C, 88.50%; H, 6.12%; N, 3.04%; B, 2.34%, Found: C, 87.80%; H, 6.10%; N, 3.05%.

In general, <sup>1</sup>H-NMR spectra of conjugated polymers possessing pyridyl substituents are of poor quality because of line-broadening effects caused by the ionic pyridyl moieties [31]. Figure 1 shows the <sup>1</sup>H-NMR spectrum of the reprecipitated poly(EPP-TPB) recorded in DMSO-d<sub>6</sub>. It shows characteristic aromatic proton peaks of tetraphenylborate counter anion at 6.65–7.35 ppm. It also shows broad peaks due to the aromatic pyridyl protons at 7.50–9.48 ppm; the methylene protons of the cyclic repeating units are observed at ca. 5.0 ppm.

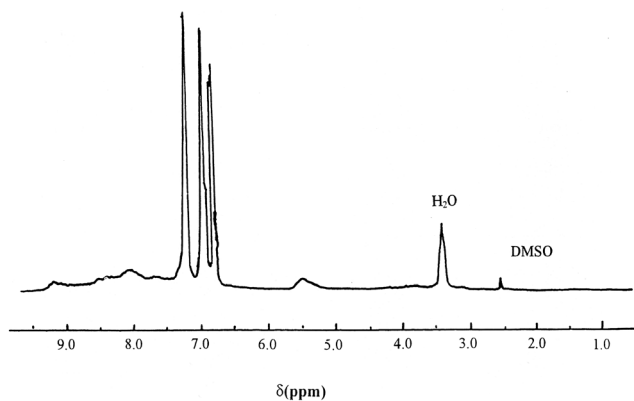
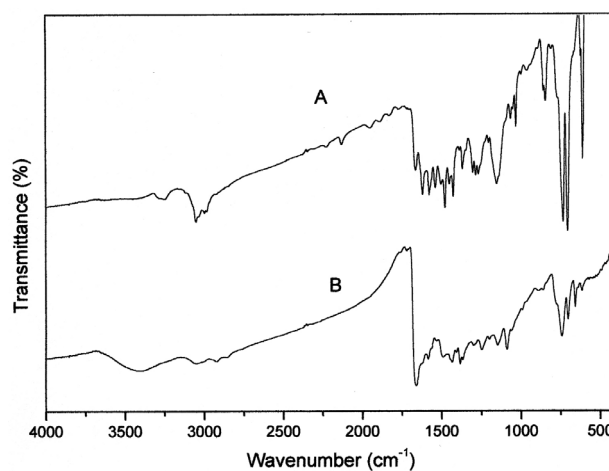
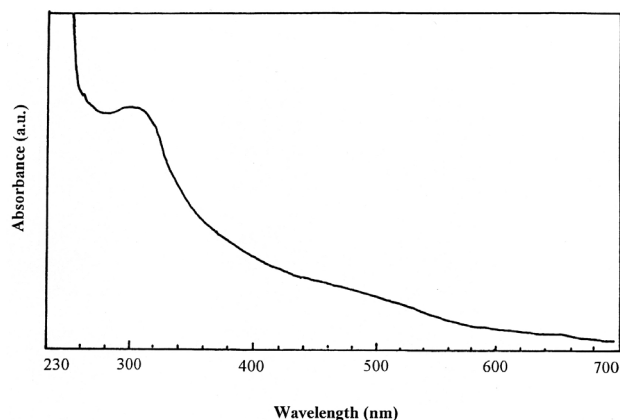
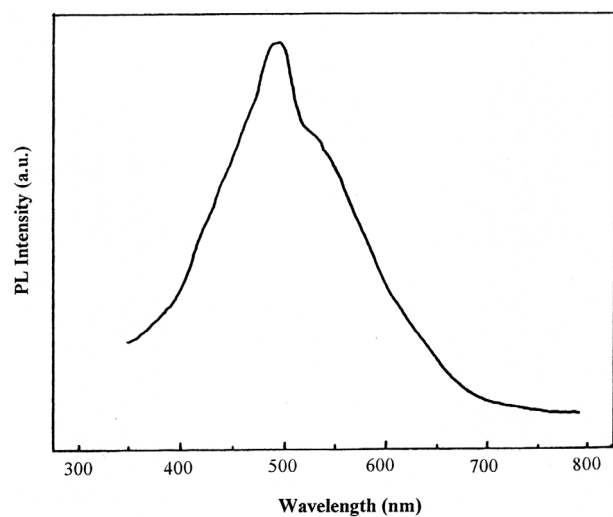
**Figure 1.** <sup>1</sup>H-NMR spectrum of poly(EPP-TPB) in DMSO-d<sub>6</sub>.**Figure 2.** FT-IR spectra of EPP-TPB (A) and poly(EPP-TPB) (B) in KBr pellets.

Figure 2 shows the IR spectra of EPP-TPB and poly (EPP-TPB) recorded in KBr pellets. The IR spectrum of poly (EPP-TPB) did not show the acetylenic C≡C bond stretching frequencies at 2226 and 2131 cm<sup>-1</sup> or the



**Figure 3.** UV-visible spectrum of poly(EPP-TPB) in DMF.



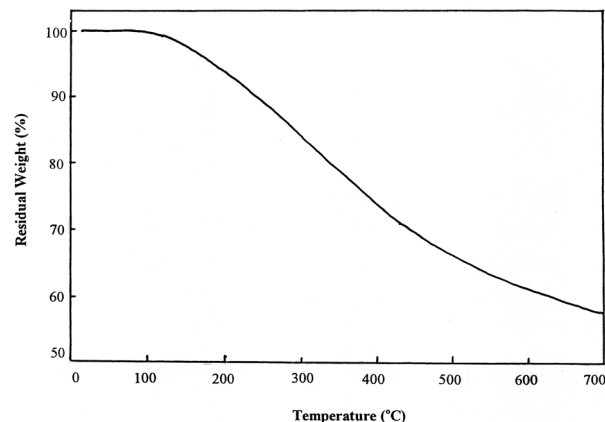
**Figure 4.** PL spectra of poly(EPP-TPB) in DMF solution using an excitation wavelength of 390 nm.

acetylenic  $\equiv\text{C-H}$  stretching frequencies at about  $3250\text{ cm}^{-1}$ . Instead, the  $\text{C}=\text{C}$  double bond stretching frequency peak of conjugated polymer backbone at  $1620\text{ cm}^{-1}$  became more intense than those ( $\text{C}=\text{C}$  and  $\text{C}=\text{N}$  stretching frequencies) of the pyridyl moiety.

The UV-visible spectrum of poly(EPP-TPB) is shown in Figure 3. It was measured using DMF as solvent. The UV-visible spectrum of poly(EPP-TPB) showed a characteristic broad absorption peak of  $400\sim 700\text{ nm}$ , which originates from the  $\pi\rightarrow\pi^*$  transition of the polyene main chain; such a signal was not observed in the UV-visible spectrum of the monomer, EPP-TPB.

From these analytical results, we conclude that the present poly(EPP-TPB)s have a conjugated polyene backbone structure with cyclic recurring units, which are bonded ionically with bulky tetraphenylborate anions.

The resulting poly(EPP-TPB)s were mostly brown or black powders, depending on the polymerization conditions and the catalysts used. The inherent viscosities of the resulting poly(EPP-TPB)s were in the range  $0.09\sim$



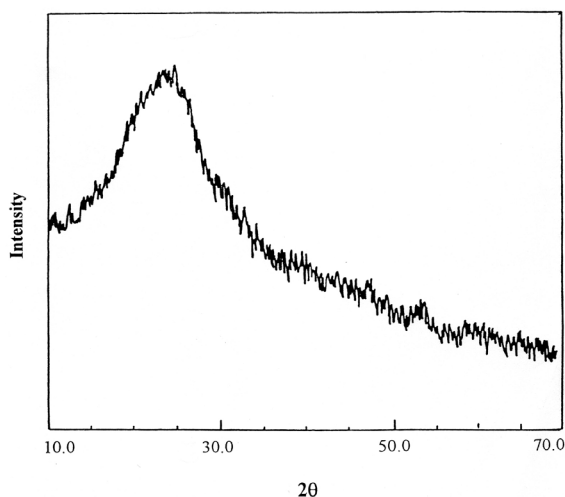
**Figure 5.** TGA thermogram of poly(EPP-TPB) recorded under a nitrogen atmosphere (heating rate:  $10^\circ\text{C}/\text{min}$ ).

$0.16\text{ dL/g}$ . The solubility test was performed for powdery samples in excess solvents. The resulting poly(EPP-TPB)s were mostly soluble in such solvents as DMF, DMSO, and NMP.

Figure 4 shows the typical photoluminescence (PL) spectra of poly(EPP-TPB) solution (solvent: DMF). Poly(EPP-TPB) showed a green PL spectrum at  $495\text{ nm}$  corresponding to a photon energy of  $2.51\text{ eV}$ . The shape and maximum value of the PL spectra did not change when using a different excitation wavelength. The temperature-dependent photoluminescence spectra of poly(EPP-TPB) film were also measured. The photoluminescence intensity increased as the temperature increased. This phenomenon arose because the non-radiative decay channels increased as the temperature increased. However, there were no changes in the location of the peak and the line shape of the spectrum as the temperature was varied. This observation means that the temperature does not affect the excitation states of the present ionic polymer. Similar results have also been observed for another pyridine-containing conjugated polymer, poly(2-ethynylpyridinium bromide), having a propargyl side chain [32].

The thermal properties of poly(EPP-TPB) were studied by using the TGA/DSC method. Figure 5 shows a typical TGA thermogram of poly(EPP-TPB) measured at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. The small weight loss at low temperature ( $\leq 120^\circ\text{C}$ ) may originate from the moisture absorbed during the process and/or the organic residues in the polymer. This polymer began to decompose at ca.  $120^\circ\text{C}$ . This result indicates that the polymer retains 95% of its original weight at  $191^\circ\text{C}$ , 90% at  $252^\circ\text{C}$ , 80% at  $351^\circ\text{C}$ , 70% at  $442^\circ\text{C}$ , and 58% at  $700^\circ\text{C}$ , respectively. The DSC thermogram of poly(EPP-TPB) exhibited that some exothermic decomposition began to occur at ca.  $120^\circ\text{C}$ , probably due to the thermal cross-linking reaction and decomposition.

We also studied the morphology of poly(EPP-TPB) powder by X-ray diffraction analysis. Figure 6 shows the



**Figure 6.** XRD spectrum of poly(EPP-TPB) powder.

typical X-ray diffractogram of poly(EPP-TPB) powder. Because the peak in the diffraction pattern is broad and the ratio of the half-height width to diffraction angle ( $\Delta 2\theta/2\theta$ ) is greater than 0.35 [10], the present poly(EPP-TPB)s are considered to be amorphous.

## Conclusions

The cyclopolymerization of EPP-TPB, an interesting diacetylenic monomer having bulky tetraphenylborate as its counter anion, was performed using various transition metal catalysts. The polymerization of EPP-TPB proceeded well to give mostly high yields of polymers. The molybdenum- and tungsten-based catalysts displayed high catalytic activities, regardless of the ionic nature of the monomer. These observations may be explained by the shielding effect brought about by the ionic nature of the bulky tetraphenylborate. Such classical transition metal catalysts as PdCl<sub>2</sub>, PtCl<sub>2</sub>, and RuCl<sub>3</sub>, were also very effective for the present cyclopolymerization. Various spectral data on the poly(EPP-TPB) revealed that the present polymers have a conjugated cyclic backbone structure and a bulky tetraphenylborate as counter ion. The poly(EPP-TPB)s were mostly brown or black powders and were soluble in organic solvents such as DMF, DMSO, and NMP. X-Ray diffraction analysis revealed that the present poly(EPP-TPB)s are mostly amorphous.

## Acknowledgment

This work was supported by the Regional R&D Cluster Project designed by the Ministry of Science and Technology and the Ministry of Commerce, Industry, and Energy.

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