Synthesis and Properties of Poly(2-ethynyl-*N*-propargylpyridinium bromide)

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Ionic conjugated polymer, poly(2-ethynyl-*N*-propargylpyridinium bromide), was prepared by the cyclopolymerization of 2-ethynyl-*N*-propargylpyridinium bromide on using various transition metal catalysts, or by thermal methods without adding catalyst. The polymerization of 2-ethynyl-*N*-propargylpyridinium bromide catalyzed by $PdCl_2$ gave the resulting polymers in relatively high yields. The polymer structure was characterized by various instrumental methods to confirm the conjugated polymer backbone structure carrying cumulated pyridine moiety. The polymers prepared by $PdCl_2$ in DMSO or *m*-cresol were completely soluble in DMF, DMSO, and formic acid. The inherent viscosities of the resulting polymers were in the range of 0.07-0.19 dL/g. Thermal properties of the polymers were also discussed.

Keywords : Conjugated polymer, 2-Ethynyl-*N*-propargylpyridinium bromide, Cyclopolymerization, Transition metal catalyst.

Introduction

Cyclopolymerization (ring-forming polymerization) is a type of chain-growth addition polymerization that leads to cyclic structure into the polymer main chain *via* an alternating intramolecularintermolecular chain propagation.[1,2] During the past four decades, studies on the cyclopolymerization of nonconjugated dienes have been extensively made.[3-7] In 1951, Butler and Ingley found that diallyl ammonium salts were polymerized with free-radical initiators to give water-soluble, noncrosslinked polymers.[8] The cyclopolymers obtained from nonconjugated dienes having various functionalities have many potential applications such as photoresponsive coating,[9,10] antistatic agent,[11] positively charged electrophotographic toners,[12] basic anion exchangers,[13] demineralization agent,[14] and interferon inducer[15] etc.

These concepts on the cyclopolymerization has been effectively applied to the nonconjugated diacetylene compound more than 35 years ago, which was before the current enthusiasm for investicating the electrical,[16-22] electro-optical,[23] and optical[24-33] properties of unsaturated polymers.[34-36] The cyclopolymerization of nonconjugated diynes were extensively investigated in an attempt to prepare polymers that would contain alternating double and single bonds along the polymer main chain with a cyclic recurring unit.[37-40]

The cyclopolymerization of dipropargyl monomers carrying ionic moiety is one of facile synthetic method for an self-doped conjugated ionic polymers.[41,42] In a series of our recent studies, various dipropargyl quarternary ammonium salts were polymerized to yield the unusual conjugated polymers. The various counterions are ionically bound to the polymer.[40,42-45] And also we reported the synthesis of water-soluble poly(2-ethynylpyridine) by the simple polymerization of 2-ethynylpyridine by W- and Mo-based catalysts[46] and the synthesis of poly(*N*-propargylpyridinium bromide) by palladium- and platinum chlorides.[47]

In recent years, we reported briefly the synthesis of a novel conjugated ionic polymer *via* an interesting cyclopolymerization reaction of 2-ethynyl-*N*-propargylpyridinium bromide (EPPB) having two different acetylenic functional groups (acetylenic and propargyl) in the same monomer.[48] The present article report the full accounts for the cyclopolymerization of EPPB by using various catalyst systems including thermal polymerization, the characterization and physical properties of the polymers.

Experimental Section

Materials. 2-Vinylpyridine (Aldrich Chemicals, 97%), bromine (Aldrich Chemical, A.C.S. reagent, 99.5 + %), and sodium amide ($NaNH_2$, Aldrich Chemicals, tech., 90%) were used as received. Propargyl bromide (Aldrich Chemicals, 80 wt% solution in toluene) was dried with calcium hydride and fractionally distilled. $PdCl_2$ (Aldrich Chemicals, 99.995%), $PtCl_2$ (Strem), and $RuCl_3$ (Aldrich Chemicals) were used without further purification. $(Ph_3P)_2PdCl_2$ was

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prepared by a reported method.[49] The solvents were analytical grade materials. They were dried with an appropriate drying agent and fractionally distilled.

Preparation of 2-Ethynylpyridine. 2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method.[46]

Preparation of EPPB. The monomer, EPPB, was prepared by the nucleophilic substitution reaction of 2-ethynylpyridine with propargyl bromide in ethyl ether solution. The brownish crude product was purified by the recrystallization from methanol/ether mixed solvent (3 : 1, V : V). Yield: 78%, ^{1}H-NMR (CF_3COOD): 1.10 (1H, $-CH_2-C\equiv C-\underline{H}$), 3.60 (1H, $\equiv C-\underline{H}$), 5.40 (2H, $-C\underline{H}_2-$), 7.4-9.2 (4H, pyridyl proton), IR (KBr, cm^{-1}): 2224 (acetylenic C-H stretching of $-CH_2-C\equiv C-H$), 2120 (acetylenic C-H stretching of $-C\equiv C-H$), 1620 (aromatic =C-H stretching of pyridyl moiety).

Polymerization of EPPB by $PdCl_2$. In a 50 mL flask equipped with reflux condenser, thermometer, and rubber septum, EPPB (1.0 g, 4.50 mmol), $PdCl_2$ (16.0 mg, 0.09 mmol, M/C mole ratio: 50), and DMF (8.0 mL, $[M]_0 = 0.5$) were added in that given order and sealed with a rubber septum. The polymerization was carried out at 90 °C for 24 hrs under nitrogen atmosphere. After a given time of polymerization, 10 mL of ethanol was added to the polymerization solution. The polymer solution was prepicipitated into an excess of ethyl ether, filtered, and then dried under vacuum at 40 °C for 24 hrs. The polymer yield was 90%. Calcd for ($C_{10}H_8NBr$): C, 54.08%; H, 3.64%; N, 6.31%; Br, 35.98%, Found: C, 53.21%; H, 3.55 %; N, 6.30%; Br, 35.51%.

Thermal Polymerization of EPPB. EPPB (1.0 g, 4.50 mmol) and DMF (3.50 mL, $[M]_0 = 1.00$) were added in the test tube and sealed with rubber septum after purging with purified nitrogen. The polymerization was carried out in 120 °C oven. The polymerization proceeded in a heterogeneous manner. The work-up procedure was identical with that of polymerization of EPPB by $PdCl_2$. The polymer yield was 56%.

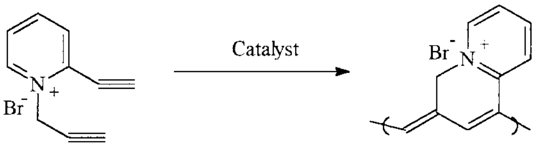
Instruments and Measurement. ^{1}H-NMR spectra of monomer and polymer were recorded on a Bruker AM-200 spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. Magic angle spinning, cross polarization ^{13}C-NMR spectra of insoluble polymer were also recorded on a Bruker AM-200 spectrometer (5-s repetition time, 3.5-ms cross polarization mixing time, 8-W decoupler power, and 3.8-KHz spinning). IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. Elemental analyses were performed with Perkin-Elmer 240DS Elemental Analyzer. UV-visible spectra were taken on a JASCO V-530 spectrophotometer in DMF solvent. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dl in DMSO solvent at 25 °C. Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min upto 800 °C with a DuPont 2200 thermogravimetric analyzer. DSC thermograms were taken on a DuPont 910 differential scanning calorimeter under nitrogen atmosphere at a scanning rate of 10 °C/min.

Results and Discussion

The polymerization of EPPB having two acetylenic functional groups was carried out by using various catalyst systems including transition metal catalysts (Scheme 1).

Table 1 shows the results for the polymerization of EPPB by various transition metal catalysts. The polymerization of EPPB catalyzed by $PdCl_2$ yield the resulting poly (EPPB) in a relatively high yield. The polymer yield generally decreased as the monomer to catalyst mole ratio (M/C) increased (exp. No; 1-3). The inherent viscosity of the resulting poly (EPPB)s were in the range of 0.07-0.19dL/g.

In general, the polymerization of EPPB by $PdCl_2$ in solvents such as DMF, HCO_2H, and pyridine proceeded heterogeneously. Some black products were precipitated into the bottom of reactor and/or adhered to the side wall of reactor during the polymerization. The soluble portion of these polymeric products were mostly below 40%. However, when DMSO or *m*-cresol was used as the polymerization solvent, the polymerization proceeded in a homogeneous manner.



EPPB Poly(EPPB)

Scheme 1

Table 1. Polymerization of EPPB by Transition Metal Catalysts[a]

exp. no	catalyst	M/C[b]	Solvent	$[M]_0$[c]	temp (°C)	yield[d]	η_{inh}[e]
1	$PdCl_2$	25	DMF	0.5	90	95	0.13
2	$PdCl_2$	50	DMF	0.5	90	90	0.14
3	$PdCl_2$	100	DMF	0.5	90	72	0.09
4	$PdCl_2$	25	DMF	0.5	90	53	0.07
5	$PdCl_2$	25	DMSO	0.5	90	100	0.19
6	$PdCl_2$	25	*m*-cresol	0.5	90	100	0.17
7	$PdCl_2$	25	HCO_2H	0.5	90	89	0.09
8	$(PPh_3)_2PdCl_2$	25	DMF	0.5	90	85	0.08
9	$PtCl_2$	25	DMF	0.5	90	87	0.08
10	$RuCl_3$	25	DMF	0.5	90	99	0.12
11	Thermal	–	DMF	1.0	120	56	–
12	WCl_6	50	chlorobenzene	2.0	90	–	–
13	WCl_6-$EtAlCl_2$[f]	50	chlorobenzene	1.0	90	–	–
14	WCl_6-Ph_4Sn[f]	50	chlorobenzene	1.0	90	–	–
15	$MoCl_5$	50	chlorobenzene	1.0	90	25	–
16	$MoCl_5$-$EtAlCl_2$[f]	50	chlorobenzene	1.0	90	35	–
17	$MoCl_5$-Et_2AlCl[f]	50	chlorobenzene	1.0	90	31	–

[a]Polymerization was carried out for 24 hours. [b]Monomer to catalyst mole ratio. [c]Initial monomer concentration (M). [d]Polymer yield (%). [e]Measured at a concentration of 0.5 g/dL in DMSO at 25 °C. [f]The mixture of WCl_6 and cocatalyst was aged for 15 min at room temperature before use.

The poly (EPPB)s prepared in DMSO or *m*-cresol were mostly soluble in such organic solvents as DMF, DMSO, and formic acid. Other catalysts such as $(Ph_3P)_2PdCl_2$, $PtCl_2$, and $RuCl_3$ were also effective to give a high yield of polymer.

We also tested the catalytic activity of W- and Mo-based transition metal catalysts for the polymerization of EPPB. In the case of a neutral tertiary amine, hexyldipropargylamine, it was reported that the polymeric products did not form with Lewis-acidic transition metal catalysts. This result may result from the deactivating effect of a basic nitrogen atom on catalysts. However, the $MoCl_5$-based catalyst showed some catalytic activity for this polymerization. Similar behaviors were also found for the polymerization of quarternary ammonium salt, dihexyldipropargylammonium bromide (or tosylate).[41,42] In general, the WCl_6-based catalysts did not show any catalytic activity in this polymerization. On the other hand, the $MoCl_5$-based catalyst system yield the resulting poly(EPPB) in some moderate yield of polymer. The $EtAlCl_2$ cocatalyst increased the polymer yield slightly. The enhanced cocatalytic activity of $EtAlCl_2$ were also observed in the polymerization of similar ionic acetylenic monomers such as propargyltriphenylphosphonium bromide,[51] tripropargylammonium bromide,[50] dipropargylammonium bromide,[44] and dihexyldipropargylammonium bromide.[41]

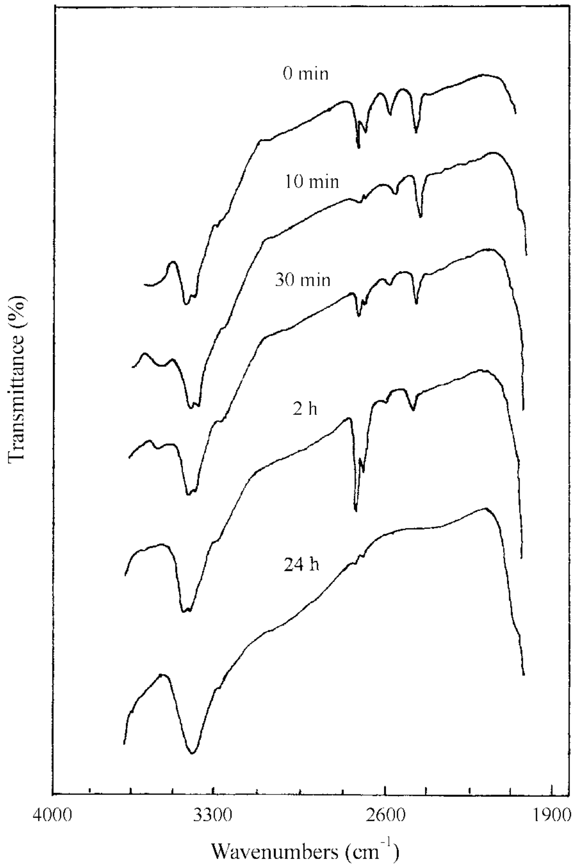


Figure 1. The consecutively measured IR spectra of EPPB monomer coated on KBr pellet as a function time at 120 °C.

The time dependence of polymer yield for the polymerization of EPPB by $PdCl_2$ in DMF was studied. The polymerization proceeded gradually upto 24 hrs, the polymer yield was 81% after 12 hrs of polymerization time and 90% after 24 hrs.

The EPPB monomer was also polymerized thermally without any initiator or catalyst at the elevated temperature (120 °C) to yield poly(EPPB) (polymer yield: 56%). Figure 1 shows the consecutively measured IR spectra of EPPB monomer coated on KBr pellet as a function of exposing time in 120 °C oven. In the IR spectrum of initial EPPB, the two types of acetylene moieties (ethynyl- and propargyl-) were observed. As the exposing time in 120 °C of oven increased, the intensity of acetylenic peaks gradually decreased because of thermal polymerization. The ethynyl group at 2224 cm^{-1} was found to be more reactive than that of the propargyl functional group at 2120 cm^{-1}. The peak of the ethynyl group of EPPB were mostly disappeared even after 2 hrs. Thus it was presumed that the first polymeric product of this reaction be the poly(2-ethynylpyridinium bromide) having propargyl side chain and then the cross-linked products was formed by the thermal cross-linking reaction of the acetylenic functional group of propargyl side chain. The poly(EPPB)s obtained by the thermal method were insoluble in most organic solvents.

The polymer structure of poly(EPPB) was characterized by various instrumental methods such as NMR (^1H and ^{13}C-), IR, UV-visible spectroscopies and elemental analysis.

Figure 2 shows the ^1H-NMR spectrum of poly(EPPB) prepared by $PdCl_2$ as the catalyst in DMSO. It showed braod peaks due to the conjugated double bonds and aromatic pyridyl protons at 6.0-9.2 ppm, and the methylene protons were observed at around 5.0 ppm.

Figure 3 shows the solid state ^{13}C-NMR spectrum of insoluble poly(EPPB). This exhibited the aromatic and vinyl carbon peaks of poly(EPPB) at around 125 ppm and the methylene carbon peaks at around 60 ppm.

The IR spectrum (Figure 4) of poly(EPPB) did not show the acetylenic C≡C bond stretching frequency at 2120 and

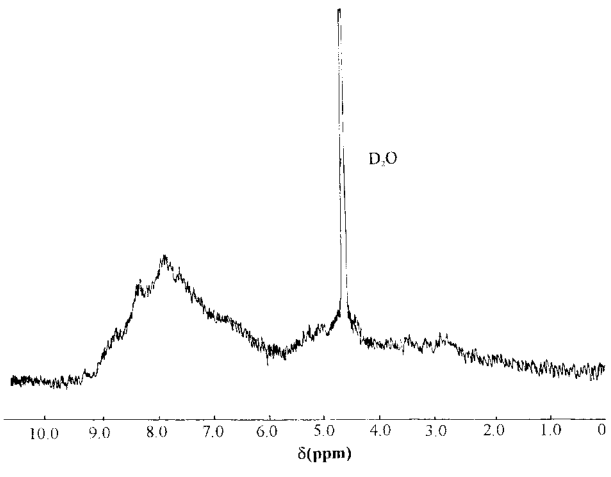


Figure 2. ^1H-NMR spectrum of poly(EPPB) prepared by $PdCl_2$ in DMSO (solvent: D_2O).

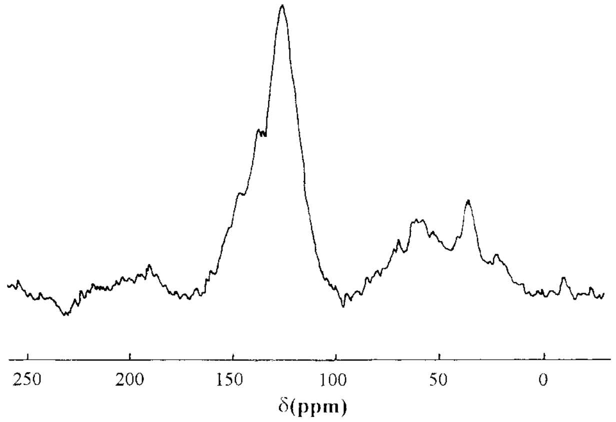


Figure 3. Solid-state ^{13}C-NMR spectrum of insoluble poly(EPPB).

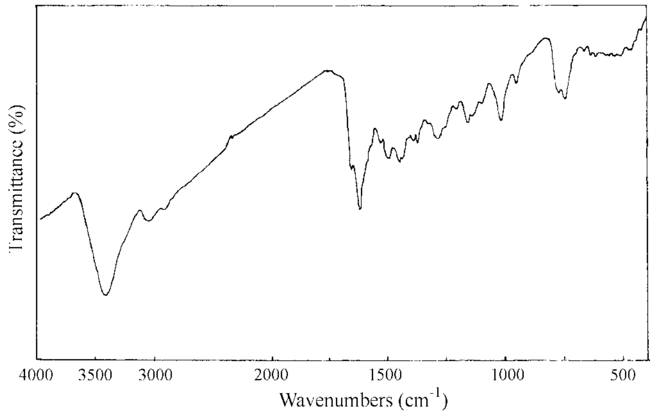


Figure 4. FT-IR spectrum of poly(EPPB) prepared by $PdCl_2$ in DMSO (KBr pellet).

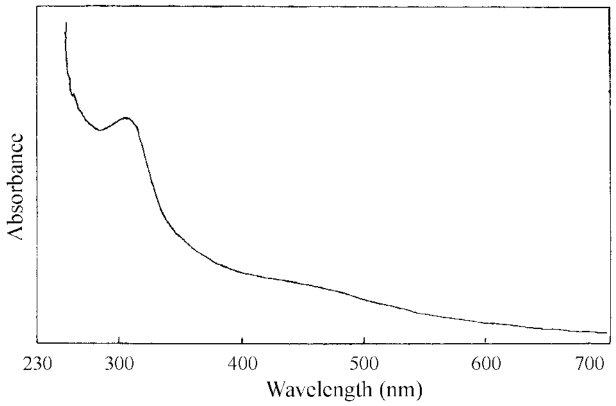


Figure 5. UV-visible spectrum of poly(EPPB) prepared by $PdCl_2$ in DMSO (solvent: DMF).

2224 cm^{-1} and the acetylenic ≡C-H stretching frequency at about 3300 cm^{-1}. Instead, the C=C double bond stretching frequency peak of conjugated polymer backbone at 1623 cm^{-1} became more intense than those (C=C and C=N stretching frequency) of pyridyl moiety.

Table 2. Solubility Behaviors of Poly(EPPB)s[a]

Sample Solvent	Poly(EPPB) prepared by $PdCl_2$ in DMSO	Poly(EPPB) prepared by $PdCl_2$ in DMF
H_2O	++	+–
DMSO	++	+–
DMF	++	+–
m-cresol	++	+–
methanol	+–	+–
acetone	+–	+–
chloroform	—	—
chlorobenzene	—	—
benzene	—	—
tetrahydrofuran	—	—

[a] ++: soluble, +–: partially soluble, —: insoluble

Figure 5 shows the UV-visible spectrum of poly(EPPB) in DMF. The UV-visible spectrum of poly(EPPB) showed the characteristic broad absorption peak of 400-700 nm which was originated from the $\pi \rightarrow \pi^*$ transition of the polyene main chain, which had not been observed at the UV-visible spectrum of monomer, EPPB. The elemental analysis data of reprecipitated poly(EPPB) agreed with the theoretical value.

These analytical results suggest that the poly(EPPB)s have a conjugated polyene backbone structure with cyclic recurring units fused with pyridyl substituent.

The resulting Poly(EPPB)s were generally dark-brown or black powders. The solubility test was performed for powdery samples in excess solvents. Table 2 shows the solubility behaviors of poly(EPPB)s prepared in DMSO or DMF by $PdCl_2$. As previously described, the polymerization at the solvent of DMSO or *m*-cresol proceeded in homogeneous manner. Thus the resulting polymers were completely soluble in the solvents of DMF, DMSO, *m*-cresol, and water. However the polymerization in DMF proceeded in heterogeneous manner regardless of catalysts. The resulting poly(EPPB)s were partially soluble in such solvents as DMF, DMSO, water, and methanol, but insoluble in chlorobenzene, toluene, benzene, carbon tetrachloride, chloroform, *n*-hexane, etc.

The inherent viscosities of the polymers were in the range of 0.07-0.19 dL/g depending on the catalyst and the polymerization conditions used. These values are superior to

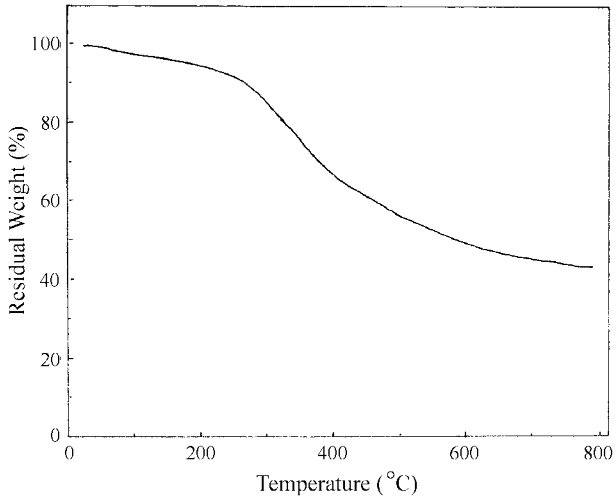


Figure 6. TG thermogram of poly(EPPB) prepared by $PdCl_2$ in DMSO under nitrogen atmosphere (heating rate: 10 °C/min).

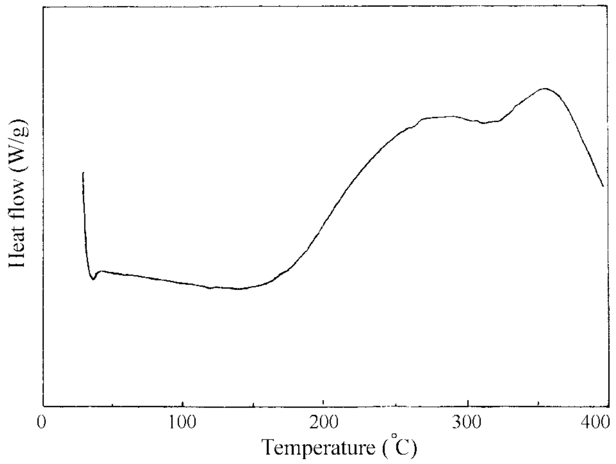


Figure 7. DSC theromgram of poly(EPPB) prepared by $PdCl_2$ in DMSO under nitrogen atmosphere (heating rate: 10 °C/min).

those of conjugated polymers from monopropargyl salt monomers such as propargyltriphenylphosphonium bromide[51] and propargylpyridinium bromide.[47] The polymer solutions could be cast into a thin homogeneous polymer film. However the resulting polymer films were too brittle to measure the mechanical properties.

Figure 6 shows the typical TG thermogram of poly(EPPB) under nitrogen atmosphere. It shows that the polymer retains 95% of its original weight at 191 °C, 90% at 271 °C, 80% at 326 °C, 60% at 457 °C, 41% at 800 °C, respectively. The small weight loss at low temperature ($\leq$ 200 °C) will be due to the absorbed moisture during the process and/or organic residues in the polymer.

Figure 7 shows the DSC thermogram of poly(EPPB) under nitrogen atmosphere. Some exothermic peak was observed from around 150 °C probably due to the thermal cross-linking reaction and thermal decomposition.

The morphology of poly(EPPB) was also investigated by X-ray diffraction analysis. 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,[52] the present poly(EPPB)s were considered to be amorphous

Conclusions

The polymerization of EPPB, an interesting cyclopolymerizable monomer having two acetylenic functionalities (acetylenic and propargyl) was carried out. We found that this ionic monomer could be easily polymerized by various transition metal catalysts and gave the poly(EPPB) in a relatively high yield. The solubility behaviors were dependent on the catalysts and polymerization conditions. The poly(EPPB)s prepared by $PdCl_2$ in DMSO or *m*-cresol were completely soluble in several organic solvents. The polymer structure was characterized by various instrumental methods to confirm the conjugated polymer backbone system carrying pyridyl moiety. The X-ray diffraction data indicated that the prepared poly(EPPB)s were mostly amorphous.

References

1. Stille, J. K.; Frey, D. A. *J. Am. Chem. Soc.* **1961**, *83*, 1697.
2. Hubert, A. J.; Dale, J. *J. Chem. Soc.* **1965**, 3160.
3. Butler, G. B.; Bunch, R. L. *J. Am. Chem. Soc.* **1949**, *71*, 3120.
4. Butler, G. B. *Acc. Chem. Res.* **1982**, *15*, 370.
5. Yokota, K.; Matsumura, M.; Yamaguchi, K.; Takada, Y. *Makromol. Chem. Rapid. Commun.* **1983**, *4*, 721.
6. Butler, G. B. *Cyclopolymerization and Cyclocopolymerization*; Marcel Dekker: New York, 1992.
7. Do, C. H.; Joo, Y. T.; Butler, G. B. *Korea Polym. J.* **1996**, *4*, 61.
8. Butler, G. B.; Ingley, F. L. *J. Am. Chem. Soc.* **1951**, *73*, 894.
9. Butler, G. B. *U.S. Patent* 3,288,770 (Nov. 29, 1966).
10. Hoover, M. F.; Carr, H. E. *Tappi* **1968**, *51*, 552.
11. Hoover, M. F. *Ger. Offen.* 1,814,597 (July 24, 1969).
12. Clingman, M. W.; Auclair, C. J. *U.S. Patent* 4,299,898 (1969).
13. Clingman, A. L.; Parrish, J. R.; Stevenson, R. J. *Appl. Chem.* **1963**, *13*, 1.
14. Weiss, D. E.; Bolto, B. A.; McNeill, R.; Macpherson, A. S.; Siudak, R.; Swinton, E. A.; Willis, D. *Aust. J. Chem.* **1966**, *19*, 561.
15. Breslow, D. S. *Pure and Appl. Chem.* **1976**, *45*, 103.
16. Cukor, P.; Krugler, J. I.; Rubner, M. F. *Makromol. Chem.* **1981**, *182*, 165.
17. Gal, Y. S.; Choi, S. K. *Bull. Korean Chem. Soc.* **1990**, *11*, 70.
18. Gal, Y. S.; Jung, B.; Choi, S. K. *J. Appl. Polym. Sci.* **1991**, *42*, 1793.
19. Gal, Y. S.; Choi, S. K. *J. Appl. Polym. Sci.* **1993**, *50*, 601.
20. Toshima, N.; Hara, S. *Prog. Polym. Sci.* **1995**, *20*, 155.
21. Roncali, J. *Chem. Rev.* **1997**, *97*, 173.
22. Chang, S. H.; Kang, S. K.; Jang, K. H.; Ryu, K. S. *Bull. Korean Chem. Soc.* **1998**, *19*, 261.
23. Koda, T.; Ishiguro, A.; Kaneta, N.; Kishida, H.; Tokura, Y.; Ishikawa, K. *Synth. Met.* **1995**, *71*, 1723.
24. Kaino, T.; Kubodera, K.; Kobayashi, H.; Kurihara. T.; Saito, S.; Tsutsuni, T.; Tokito, S.; Murata, H. *Appl. Phys. Lett.* **1988**, *53(21)*, 2002.
25. Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341.
26. Lee, H. J.; Oh, J. M.; Choi, S. J.; Kim, H. K.; Choi, S. K. *Polym. Bull.* **1994**, *32*, 433.
27. Samuel, D. W.; Ledoux, I.; Dhenaut, C.; Zyss, J.; Fox, H. H.; Schrock, R. R.; Silbey, R. J. *Science* **1994**, *265*, 1070.
28. Halvorson, C.; Hays, A.; Kraabel, B.; Wu, R.; Wudl, F.; Heeger, A. J. *Science* **1994**, *265*, 1215.
29. Lee, H. J.; Suh, M. C.; Shim, S. C. *Synth Met.* **1995**, *73*, 141.
30. Lee, H. J.; Kang, S. J.; Kim, H. K.; Cho, H. N.; Park, J. T.; Choi, S. K. *Macromolecules* **1995**, *28*, 4638.
31. Lee, H. J.; Won, Y. H.; Kang, S. J.; Choi, S. K.; Kim, H. K. *J. Polym. Sci., Polym. Chem. Ed.* **1996**, *34*, 2333.
32. Okawa, H.; Kurosawa, K.; Wada, T.; Sasabe, H. *Synth. Met.* **1995**, *71*, 1657.
33. Choi, S. K.; Lee, J. H.; Kim, H. K. *Macromol. Symp.* **1997**, *118*, 67.
34. Akagi, K.; Goto, H.; Kadokura, Y.; Shirakawa, H.; Oh, S. Y.; Araya, K. *Synth. Met.* **1995**, *69*, 13.
35. Pu, L. *Acta Polymer* **1997**, *48*, 116.

36. Joo, K. S.; Kim, S. Y.; Chin, C. S. *Bull. Korean Chem. Soc*. **1997**, *18*, 1296.
37. Jeon, S. J.; Shim, S. C.; Cho, C. S.; Kim, T. J.; Gal, Y. S. *J. Polym. Sci., Polym. Chem. Ed*. **2000**, *38*, 2663.
38. Jeon, S.J.; Shim, S. C.; Cho, C. S.; Kim, T. J.; Gal, Y. S. *Bull. Korean Chem. Soc*. **2000**, *21*, 980.
39. Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565,
40. Choi, S. K.; Gal, Y. S.; Jin, S. H.; Kim, H. K. *Chem. Rev.* **2000**, *100*, 1645.
41. Kim, B. S.; Chen, L.; Gong, J. P.; Osada, Y. *Korea Polym. J*. **2000**, *8*, 116.
42. Kang, K. L.; Kim, S. H.; Cho, H. N.; Choi, K. Y.; Choi, S. K. *Macromolecules* **1993**, *26*, 4539.
43. Gal, Y. S.; Jung, B.; Lee, W. C.; Choi, S. K. *Synth. Met*. **1995**, *69*, 549.
44. Gal, Y. S.; Choi, S. K. *Eur. Polymer J*. **1995**, *31*, 941.
45. Choi, D. C.; Kim, S. H.; Lee, J. H.; Cho, H. N.; Choi, S. K. *Macromolecules* **1997**, *30*, 176.
46. Gal, Y. S.; Cho, H. N.; Kwon, S. K.; Choi, S. K. *Polymer (Korea)* **1988**, *12*, 30.
47. Gal, Y. S.; Jung, B.; Lee, W. C.; Choi, S. K. *Bull. Korean Chem. Soc*. **1994**, *15*, 267.
48. Gal, Y. S.; Lee, W. C.; Lee, J. H.; Choi, S. K. *Bull. Korean Chem. Soc*. **1998**, *19*, 22.
49. Colguhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathway for Organic Synthesis*; Plenum Press: New York, 1984; p 384.
50. Gal, Y. S. *Macromol. Reports* **1994**, *A31*, 271.
51. Gal, Y. S. *J. Chem. Soc. Chem. Commun*. **1994**, 327.
52. Masuda, T.; Higashimura,T. *Acc. Chem. Res.* **1984**, *17*, 51.