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Polymerization of 4-Dimethylamino-N-propargylpyridinium Bromide by Transition Metal Catalysts

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ABSTRACT

The polymerization of an ionic propargyl derivative, 4-dimethylamino-N-propargylpyridinium bromide (DMAPPB), was carried out by palladium, platinum, and ruthenium chlorides. The polymerization of DMAPPB by these transition metal

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catalysts proceeded well to give a relatively high polymer yield. The chemical structure of the resulting polymer was characterized by such instrumental methods as elemental analysis, infrared, NMR, UV-visible spectroscopies to have conjugated polymer backbone system bearing 4-dimethylamino-N-methylenepyridinium bromide. The polymer was soluble in DMF, DMSO, and formic acid, and found to be less hygroscopic than those of similar homologues having more smaller substituents. The resulting polymers were mostly black powders and showed the amorphous morphology.

Key Words: Polymerization; Conjugated polymer; Ionic polymer; Transition metal catalyst.

INTRODUCTION

Conjugated polymer systems have been studied as organic semiconductors,^[1-3] as membranes for gas separation and for liquid-mixture separation,^[4-6] materials for enantioseparation for racemates by high performance liquid chromatography,^[7] side-chain liquid crystal,^[8-10] materials for chemical sensors,^[11] and as materials for nonlinear optical property and for photoluminescence and electroluminescence properties.^[12-19]

Various conjugated polymers from acetylene derivatives have been prepared and characterized.^[10,20,21] We have also reported on the synthesis and characterization of conjugated polymers from the monopropargyl monomers such as propargyl halides,^[22] propargyl ethers,^[23,24] and amines,^[25] and the dipropargyl monomers such as 1,6-heptadiyne,^[26] dipropargyl ethers,^[27,28] diethyl dipropargylmalonate,^[29,30] diphenyldipropargylmethane,^[31] 9,9-dipropargylfluorene,^[32] etc.

Conjugated ionic polymers have potential as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries and permselective membrane, and light-emitting devices, due to the their extensive conjugation and various functionalities.^[21]

The synthesis of simple mono- and di-substituted ionic polyethynylpyridines had been carried out with the activation of the acetylene bond in ethynylpyridines.^[33,34]

We have also studied the polyacetylene materials having pyridine moiety such as poly(2-ethynylpyridine),^[35] poly(N-propargylpyridinium bromide),^[36] poly(2-ethynyl-N-propargylpyridinium bromide),^[37,38] and poly(2-ethynylpyridinium bromide) having peculiar functional groups such as carbazolyl and glycidyl moieties.^[39,40]

In the polymerization of propargylamine derivatives such as propargylammonium bromide, dipropargylammonium bromide, and tripropargylamine by transition metal catalysts, the resulting polymers were mostly insoluble in organic solvents, although the polymer yields were very high.^[41-43] The ionic polymers from dipropargylammonium derivatives having two n-hexyl substituents at N-atom were found to be completely soluble in polar solvents such as methanol, DMSO, DMF, THF, chloroform, etc.^[44,45] This means that the solubility of polyacetylene derivatives depend on the substituents as well as the polymerization methods. The soluble ionic conjugated polymers will be very processible into thin homogeneous films, which may be an advantage for the applications as materials of organic semiconductors, chemical sensors, etc.



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The present article deals with the synthesis of soluble conjugated ionic polymer from a bulky ionic propargyl derivative, 4-dimethylamino-N-propargylpyridinium bromide (DMAPPB), and the characterization of the resulting poly(DMAPPB).

EXPERIMENTAL

Materials

4-Dimethylaminopyridine (Aldrich Chemicals, 99%) was used as received. Propargyl bromide (Aldrich Chemicals, 80 wt% solution of toluene) was dried with CaH_2 and distilled under reduced pressure. PdCl_2 (Aldrich Chemicals, 99%), PtCl_2 (Strem), RuCl_3 (Aldrich Chemicals) were used as received. MoCl_5 (Aldrich Chemicals, 99.9 + %), EtAlCl_2 (Aldrich Chemicals, 25 wt% (1.8M) solution in toluene), and Me_4Sn (Aldrich Chemicals, 95%) were used without further purification. The solvents were analytical grade materials. They were dried with an appropriate drying agent and fractionally distilled.

Synthesis of DMAPPB

The monomer, DMAPPB, was prepared by the reaction of 4-(dimethylamino)pyridine and propargyl bromide as follows. In a 500 mL flask, benzene (150 mL), 20 g (0.164 mol) of 4-(dimethylamino)pyridine, and 25.0 g (0.21 mol) of propargyl bromide were added with stirring. After a while, yellowish powder was precipitated to the bottom. The reaction was carried out for 6 hrs at 40°C. And then the reaction mixture was filtered with glass sintered filter, and washed twice by ethyl ether. The crude product was recrystallized twice using ethanol/ether cosolvent. 31 g (0.129 mol, yield: 78%) of pure DMAPPB was obtained. mp: 196.52°C.

$^1\text{H-NMR}$ (δ , ppm, DMSO-d_6): 3.20 (6H), 3.84 (1H), 5.24 (2H), 7.11 (2H), 8.36 (2H); $^{13}\text{C-NMR}$ (δ , ppm, DMSO-d_6): 40.07, 45.76, 77.28, 79.30, 108.12, 141.67, 156.19; FT-IR (wavenumber, cm^{-1}): 3220, 3063, 2934, 2118, 1652, 1572, 1179, 837, 665.

Polymerization of DMAPPB by PdCl_2

1 g ((4.15 mmol) of DMAPPB, 0.0292 g (0.1658 mmol) of PdCl_2 , and 10 mL DMF ($[\text{M}]_0 = 0.38 \text{ M}$) were added in the order given, and the polymerization was carried out at 90°C for 24 hrs under nitrogen atmosphere with magnetic stirring. The polymerization proceeded mostly in the homogeneous manner. After a given time of polymerization, additional 10 mL of DMF was added to the polymerization solution. The polymer solution was preprecipitated into a large excess of ether, filtered from the solution, then dried under vacuum at 40°C for 24 h. The polymer yield was 81%.

Instruments and Measurement

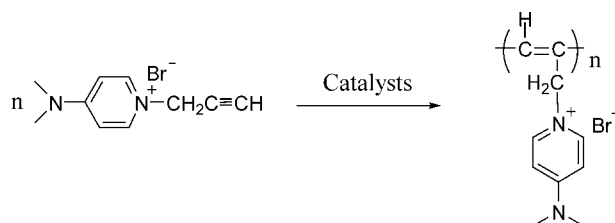
FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. NMR (^1H - and ^{13}C -) spectra of polymers were recorded on a Varian 500MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d_6 and the chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Elemental analyses were performed with a FISON S EA1110 Elemental Analyzer. UV-visible spectra of polymer solution were taken on a JASCO V-530 spectrophotometer. TGA/DSC thermograms were obtained under a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ up to 800°C with Rheometric Thermal Analyzer. X-ray diffractograms were measured with a PHILIPS X-ray diffractometer (Model: X'Pert-APD).

RESULTS AND DISCUSSION

Polymerization

The polymerization of DMAPPB, a typical ionic acetylenic monomer, was carried out by Pd, Pt, and Ru-chlorides (Sch. 1).

Table 1 shows a typical result for the polymerization of DMAPPB by Pd, Pt, and Ru-chlorides. PdCl_2 was found to be an effective catalyst for the polymerization of this ionic acetylenic monomer, DMAPPB, to give a relatively high yield of polymer (81%) although the reason is not clear in the present state. As the monomer to catalyst mol ratio (M/C) was increased, the polymer yield was gradually decreased. This trend is general for the transition metal-catalyzed polymerization of acetylenic monomers. A similar result was also observed in the polymerization of 4-hydroxy-N-propargylpiperidine by the same catalyst.^[46] However, the insoluble polymeric products were obtained at the reaction condition of relatively high initial monomer concentration ($[\text{M}]_0 = 1.0$, Exp. no : 4), although the highest polymer yield (92%) was obtained. We used other solvents such as DMSO, formic acid, and pyridine for the present polymerization. The polymerization behaviors were found to be similar, regardless of the solvents used. PtCl_2 , RuCl_3 , and $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ catalysts also polymerized DMAPPB to give a moderate yield of polymer. These polymerization behaviors were similar with those for the polymerization of similar homologue, propargylpyridinium bromide, which did not have 4-dimethylamine



Scheme 1. Polymerization of DMAPPB.

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Table 1. Polymerization of DMAPPB by transition metal catalysts.^a

Exp. no.	Catalyst	M/C ^b	[M] ₀ ^c (M)	Solvent	P.Y. ^d (%)
1	PdCl ₂	25	0.38	DMF	81
2	PdCl ₂	50	0.38	DMF	73
3	PdCl ₂	100	0.38	DMF	46
4	PdCl ₂	25	1.00	DMF	92 ^e
5	PdCl ₂	25	0.38	DMSO	85
6	PdCl ₂	25	0.38	Formic acid	74
7	PdCl ₂	25	0.38	Pyridine	62
8	PtCl ₂	25	0.38	DMF	65
9	RuCl ₃	25	0.38	DMF	77
10	(Ph ₃ P) ₂ PdCl ₂	25	0.38	DMF	57

^a Polymerization was carried out at 90°C for 24 hrs.^b Monomer to catalyst mol ratio.^c Initial monomer concentration (mol/L).^d Polymer yield (%).^e Mostly insoluble.

substituents.^[36] The poly(DMAPPB) was less hygroscopic, whereas the simple poly(propargylpyridinium bromide) was very hygroscopic.

We also attempted the polymerization of this ionic monomer by molybdenum and tungsten chlorides such as MoCl₅ and WCl₆, which had been used as very effective catalysts for the polymerization of some acetylene derivatives.^[20,21,32] However, Mo- and W-based catalyst systems did not give any polymeric products for the present polymerization of DMAPPB, even when the cocatalysts such as EtAlCl₂ and Me₄Sn were used. In our previous work,^[36] we also did not obtain any polymeric products for the polymerization of similar ionic acetylenic monomer by Mo- and W-based catalysts. The ionic nature of these acetylenic monomers were thought to poison the active site of Mo- and W-based catalyst system.

Polymer Structure

The chemical structure of a conjugated ionic polymer, poly(DMAPPB), was characterized by various instrumental methods such as NMR (¹H-, ¹³C-), IR, and UV-visible spectroscopies. The IR spectra of DMAPPB and poly(DMAPPB) are presented in Fig. 1. The IR spectrum of poly(DMAPPB) did not show the acetylenic C≡C bond stretching frequency at 2118 cm⁻¹ and the acetylenic ≡C-H stretching frequency at about 3220 cm⁻¹. Instead, the C=C double bond stretching frequency peak of conjugated polymer backbone at 1647 cm⁻¹ was more intensively observed, with the peaks of C=C double bond stretching frequency peak of pyridyl substituents. The peak at 808 cm⁻¹ is due to the C-H out-of-plane deformation of pyridyl substituents. The peaks at 1442 cm⁻¹ was originated from the CH₂ scissor vibration frequencies.

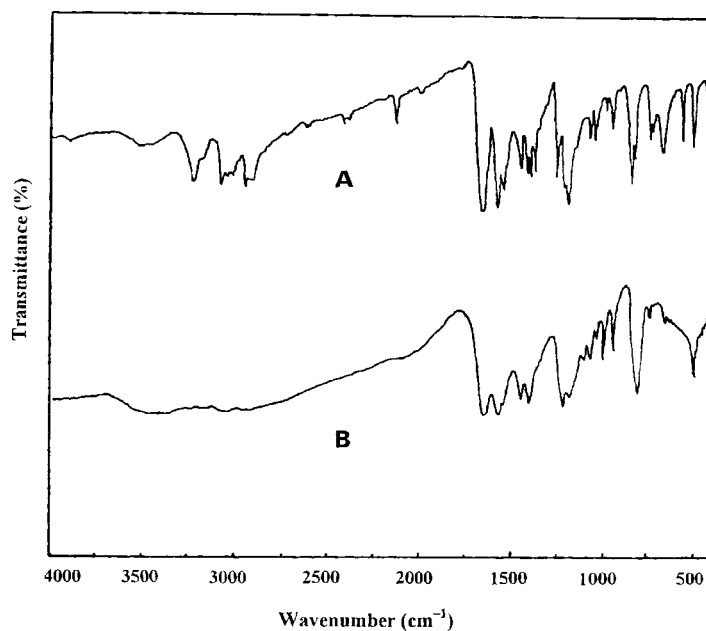


Figure 1. FT-IR spectra of DMAPPB (A) and poly(DMAPPB) in KBr pellet.

Figure 2 shows the $^1\text{H-NMR}$ spectrum of poly(DMAPPB) in DMSO-d_6 . In general, the NMR spectrum of conjugated polymers having pyridyl moieties showed poor quality due to the line-broadening effect of ionic pyridyl moieties.^[15] We obtained the NMR spectrum of reprecipitated poly(DMAPPB). The $^1\text{H-NMR}$ spectrum of poly(DMAPPB) showed the aromatic proton peaks of pyridyl moiety at 6.4–9.0 ppm. The vinyl proton of conjugated polymer backbone was also observed broadly at the aromatic region of pyridine moiety. The peaks of methylene protons adjacent to conjugated main chains was also observed at 4.4–6.0 ppm. The peaks at 2.5–3.8 ppm are originated from the methyl protons of 4-dimethylamine groups at the pyridyl substituents.

Figure 3 shows the $^{13}\text{C-NMR}$ spectrum of poly(DMAPPB) in DMSO-d_6 . The $^{13}\text{C-NMR}$ spectrum of poly(DMAPPB) showed the peaks of aromatic carbons of pyridyl substituents at 108, 142, and 156 ppm. This spectrum did not show any acetylenic carbon peaks that were seen at 77.3 and 79.3 ppm in the $^{13}\text{C-NMR}$ spectrum of DMAPPB monomer. Instead, the olefinic backbone carbon peaks of the conjugated polymer were observed broadly at 125–140 ppm. The peaks of the methylene carbons adjacent to the conjugated vinylic carbons was observed at 52.1–59.3 ppm.

Figure 4 shows the UV-visible spectra of DMAPPB and poly(DMAPPB) in DMF solvent. The UV-visible spectrum of poly(DMAPPB) showed the characteristic broad absorption peak at the visible region, which is originated from the $\pi \rightarrow \pi^*$ conjugation band transition of the polyene main chain, which had not been observed at the UV-visible spectrum of monomer, DMAPPB. The absorption peak of poly(DMAPPB) tailed upto 800 nm.

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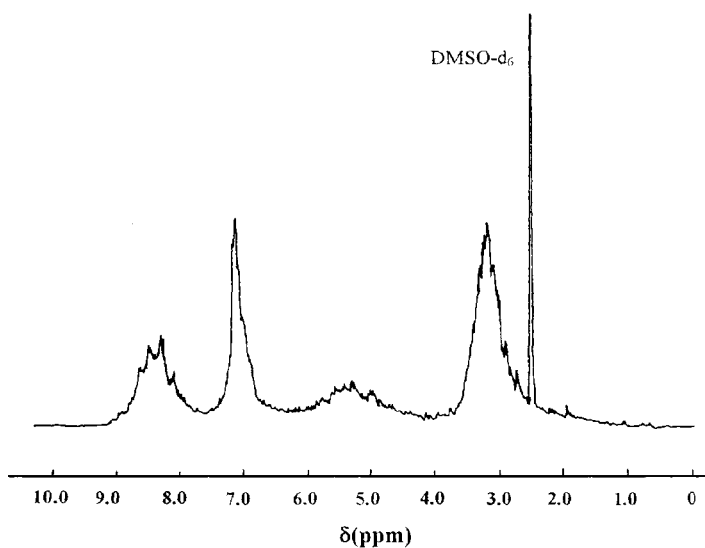


Figure 2. ^1H -NMR spectrum of poly(DMAPPB) in DMSO-d_6 .

The elemental analysis data of poly(DMAPPB) agreed well with the theoretical values: Calcd. for $(\text{C}_{10}\text{H}_{13}\text{N}_2\text{Br})_n$; C, 49.81%; H, 5.43%; N, 11.62%; Br, 33.14%, Found: C, 49.10%; H, 5.47%; N, 11.27%; Br, 33.16%.

These spectral data indicated that the present poly(DMAPPB) have a conjugated backbone system bearing the moiety of 4-dimethylaminopyridinium bromide.

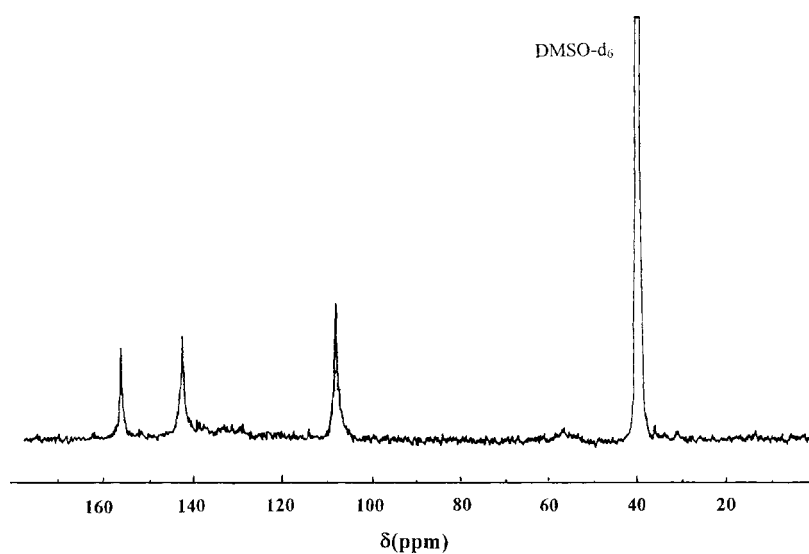


Figure 3. ^{13}C -NMR spectrum of poly(DMAPPB) in DMSO-d_6 .

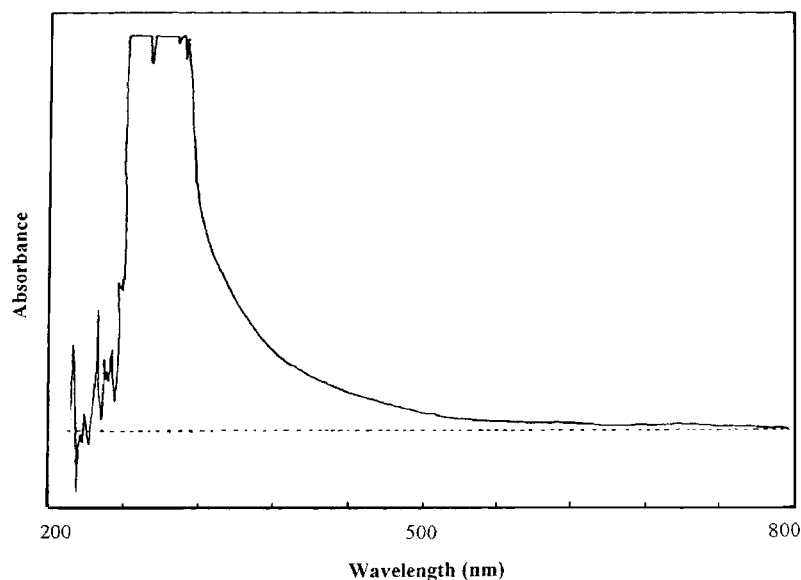


Figure 4. UV-visible spectra of poly(DMAPPB) in DMF solution.

Polymer Properties

The resulting poly(DMAPPB)s were generally black powders. This polymer was soluble in DMF, DMSO, formic acid, etc. In our another work,^[36] it was found that the similar poly(propargylpyridinium bromide)s are also completely soluble in polar solvents, whereas some conjugated polymers obtained from propargyl derivatives are insoluble in any organic solvents.^[25,27,42] These observations mean that the polymerization proceed in an ideal manner due to the bulky substituent under somewhat mild reaction conditions. However, the same polymers obtained at the reaction condition of high initial monomer concentration ($[M]_0 = 1.0\text{ M}$) was insoluble in organic solvents, which is originated from the cross-linking reaction of the labile allylic hydrogen atoms of polymers. The inherent viscosities were in the range of 0.06–0.15 dL/g, depending on the polymerization conditions. The poly(DMAPPB) was found to be less hygroscopic than that of similar homologue, poly(propargylpyridinium bromide), which did not have 4-dimethylamine substituent.^[36] The resulting poly(DMAPPB) were also found to be stable to air oxidation. Even after exposing for 3 months to air condition, the IR spectrum of poly(DMAPPB) did not show any carbonyl carbon absorption peak, which may be originated from the autooxidation of conjugated main chain.

Figure 5 shows the typical TGA/DSC thermogram of poly(DMAPPB) under nitrogen atmosphere. This ionic polymer shows some weight loss at initial low temperature (11% at 200°C). This weight loss at a relatively low temperature was assumed to be due to the absorbed moisture and/or organic residues, which is a characteristic phenomenon of the ionic conjugated polymer system.^[40] This polymer

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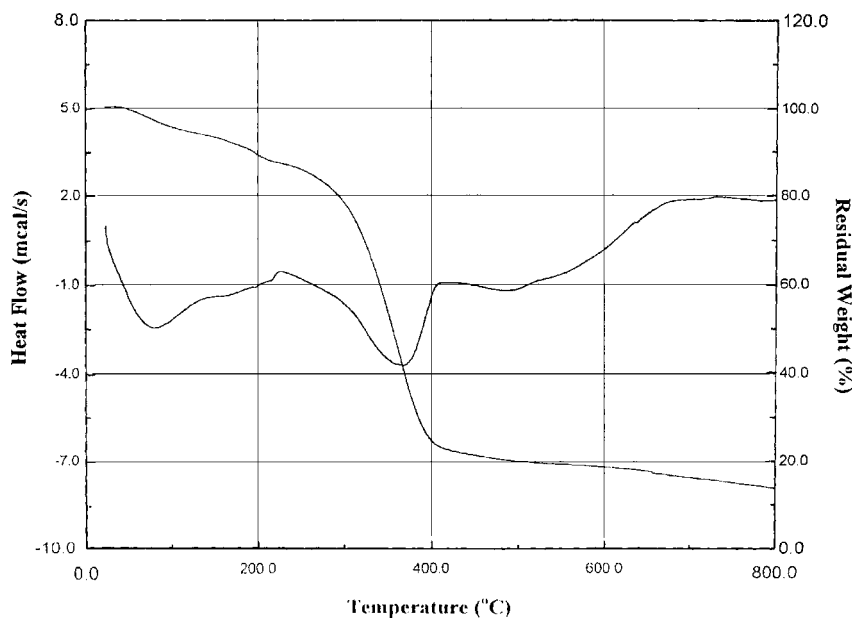


Figure 5. TGA/DSC thermogram of poly(DMAPPB).

showed an abrupt weight loss at the temperature range of 240–400°C. The char yield after heating up to 800°C was 13.5%.

The morphology of poly(DMAPPB) was also investigated by X-ray diffraction analysis (Fig. 6). 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,^[20] the present poly(DMAPPB)s are amorphous.

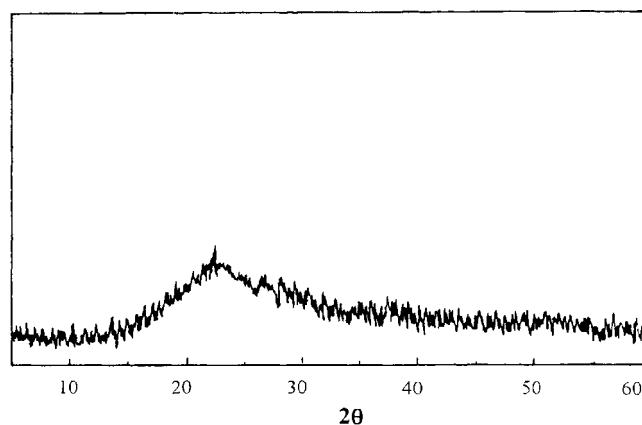


Figure 6. X-ray diffractogram of poly(DMAPPB).

CONCLUSION

The polymerization of an ionic acetylenic monomer, DMAPPB, was carried out by Pd, Pt, and Ru-chloride catalysts. These polymerizations proceeded well by the above catalysts to give a relatively high yield of polymer. On the other hand, the Mo- and W-based catalysts did not polymerized this ionic monomer, owing to the deactivation of MoCl₅ and WCl₆ catalyst by ionic pyridinium moieties. The resulting polymers were mostly black powder and soluble in such organic solvents as DMF, DMSO, and formic acid. The polymer structure was characterized by various instrumental methods to have the conjugated backbone system bearing the moiety of 4-(dimethylamino)pyridinium bromide. This polymer was found to be less hygroscopic than those of other similar simple homologues. X-ray diffraction analysis revealed that the present polymer is mostly amorphous.

ACKNOWLEDGMENT

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