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POLYMERIZATION OF 4-HYDROXY-N-PROPARGYLPIPERIDINE BY TRANSITION METAL CATALYSTS

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Key Words: 4-Hydroxy-N-propargylpiperidine, Transition Metal Catalysts, Con-jugated Polymer, Acetylene Derivative

ABSTRACT

The polymerization of 4-hydroxy-N-propargylpiperidine, having 4-hydroxypiperidine moiety, was carried out with various transition metal catalysts. The polymerizations proceeded well to give a relatively high yield of polymer (maximum polymer yield: 93%). Palladium, platinum, and ruthenium chlorides were found to be generally effective for this polymerization. On the other hand, the group 5 and 6 transition metal catalysts such as WCl_6 , $MoCl_5$, WCl_6 -organoaluminum compounds etc. fail to polymerize this monomer. The molecular structure of the resulting poly(4-hydroxy-N-propargylpiperidine) was characterized by the various instrumental analysis methods such as NMR (1H - and ^{13}C -), IR, and UV-visible spectroscopies. The IR spectrum of polymer shows neither the acetylenic hydrogen stretching (3197 cm^{-1}) nor the carbon-carbon triple bond stretching (2113 cm^{-1}) frequencies presented in the IR spectrum of monomer. Instead, the carbon-carbon double bond stretching frequency at 1611 cm^{-1} was newly observed. These polymers were mostly brown and black powders and were completely soluble in such polar solvents as formic acid, DMF, DMSO, and tetrahydrofuran. X-ray diffraction analysis of the resulting poly(4-hydroxy-N-propargylpiperidine) revealed that this polymer is mostly amorphous.

INTRODUCTION

The conjugated polymers from substituted acetylenes are expected to show unique properties such as electrical conductivity [1-3], gas and liquid mixture separation [4, 5], enantioseparation of racemates [6-8], metal ion-binding [9, 10], radiation degradation [11, 12], side-chain liquid crystalline [13-16], and nonlinear optical properties [17-21].

Various polyacetylenes have been prepared and characterized [22-24]. In our previous works, we have reported the polymerization of propargyl halides [25, 26], ethers [27-30], and amines [31], and the cyclopolymerization of dipropargyl derivatives such as dipropargyl ether [32], sulfide [33], silanes [34], diethyl malonate [35, 36], dihexylammonium salts [37, 38], etc.

The polymerization of acetylene derivatives having hydroxy functional group are of interest because of their unique structures and a facile modification



of hydroxy group with interesting multifunctional groups. The mostly simple hydroxy-containing polyacetylene, poly(propargyl alcohol) had been prepared by high pressure [39], PdCl₂ [40], Ni(CO)₂(PPh₃)₂ [41], NiI₂(PPh₃)₂ [42], Ni(NCS)(C≡C-R)(PPh₃)₂ [42], γ -ray [43], plasma [44], and MoCl₅ [45-47]. In most cases, the resulting poly(propargyl alcohol)s were insoluble in any organic solvents. A soluble poly(propargyl alcohol) was tentatively prepared by the homogeneous polymerization of propargyl alcohol with Pd(C≡CCH₂OH)₂(PPh₃)₂ [48, 49].

Various substituents at the symbol α -carbon of propargyl alcohol, have been introduced, in order to increase the solubility of polyacetylene derivatives having hydroxy functional group. Soluble poly(1-ethynyl-1-cyclohexanol) [50, 51], poly(ethynylfluorene) [52], poly(3-butyn-2-ol) [53], poly(1-octyn-3-ol) [53], and poly(2-phenyl-3-butyn-2-ol) [53] were prepared and characterized.

To our knowledge, there have been no reports on the polymerization of some acetylene derivatives having 4-hydroxypiperidine moiety. 4-Hydroxy-N-propargylpiperidine (HPP) is interesting acetylenic compound having tertiary amine and hydroxy functional group, which can react with functionalized compounds.

This article deals with the synthesis and its polymerization behaviors of HPP carrying 4-hydroxypiperidine moiety by transition metal catalysts and the characterization of the resulting poly(HPP).

EXPERIMENTAL

Materials

4-Hydroxypiperidine (Aldrich Chemicals, 98%) and K₂CO₃ (Aldrich Chemicals, 99.99%) were used as received. Propargyl bromide (Aldrich Chemicals, 80 wt% solution of toluene) was dried over calcium hydride and fractionally distilled. PdCl₂ (Aldrich Chemicals, 99.995%), PtCl₂ (Strem), RuCl₃ (Aldrich Chemicals,) were used without further purification. The polymerization solvents were analytical grade materials. They were dried with the appropriate drying agent and fractionally distilled.

Synthesis of HPP

To a flask charged with dried DMF solution (300 mL) of 4-hydroxypiperidine (20.23 g, 0.2 mol) containing K₂CO₃ (33.2 g, 0.24 mol) was slowly



added propargyl bromide (25 g, 0.21 mol) at room temperature. The reaction mixture was gently refluxed for additional 4 hours with vigorous stirring. After water was added, the solution was extracted three times with diethyl ether, then the extract was washed thoroughly with distilled water, dried over anhydrous MgSO_4 . The volatile materials were removed on a rotary evaporator and HPP was recrystallized from ether/hexane solution (yield: 80%).

$^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 1.44-1.70(2H), 1.78-1.93(2H), 2.20-2.39(3H), 2.49(1H), 2.68-2.80(2H), 3.24(2H), 3.57-3.72(1H).

$^{13}\text{C-NMR}$ (DMSO-d_6 , δ , ppm): 34.22, 46.28, 49.61, 66.07, 75.39, 79.80.

FT-IR (KBr pellet, wavenumbers, cm^{-1}): 3425, 3197, 2951, 2795, 2113, 1464, 1366, 1230, 1070, 784, 733.

Polymerization

A typical polymerization of HPP is as follows. Into a 20 mL ampule, HPP (0.5 g, 3.60 mmol), PdCl_2 (25.5 mg, 0.144 mmol, $\text{M/C} = 25$), and DMF (6.69 mL, $[\text{M}]_0 = 0.5\text{M}$) were added in that order given and sealed with a rubber septum after flushing with dry nitrogen. After standing at 90°C for 24 hours, 10 mL of ethanol was added to the ampule. This polymer solution was precipitated into an excess diethyl ether, filtered from the solution, and then dried under vacuum at 40°C for 24 hours. The polymer yield was calculated by gravimetry.

Instruments and Measurement

NMR (^1H - and ^{13}C -) spectra were recorded on Bruker AM-200 spectrometer in CDCl_3 . Infrared spectra were obtained with a Bruker EQUINOX 55 spectrometer using potassium bromide pellets. UV-visible spectra were obtained with a Shimadzu UV-3100S spectrophotometer in tetrahydrofuran. Inherent viscosities (η_{inh}) of the resulting poly(HPP)s were measured at a concentration of 0.5 g/dL in DMF at 30°C . Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ up to 800°C with a DuPont 2200 Analyzer. DSC thermograms were taken on a DuPont 910 differential scanning calorimeter under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. X-ray diffraction patterns of polymer samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Wahren flat-plate camera using Ni-filtered $\text{CuK}\alpha$ radiation at a scan speed of $4^\circ/\text{min}$.

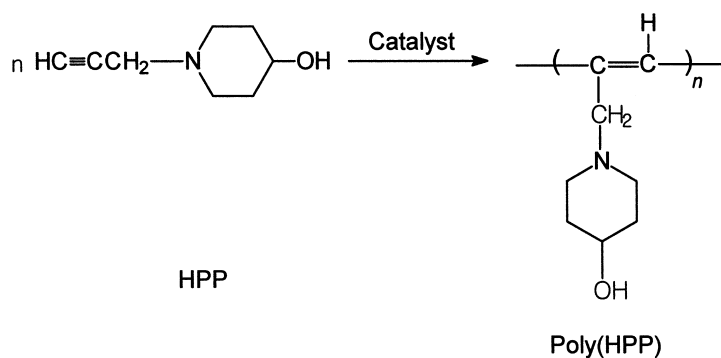


RESULTS AND DISCUSSION

The polymerization of HPP, an acetylene derivative having 4-hydroxy-piperidine moiety, was carried out by palladium, platinum, and ruthenium chlorides (Scheme 1).

Table 1 lists the results for the polymerization of HPP by palladium, platinum, and ruthenium chlorides. These catalysts were found to be effective for the present polymerization of HPP. The polymerization of HPP by these catalysts proceeded in homogeneous phase to give completely soluble poly(HPP)s. The effect (exp. no: 1-3) of initial monomer concentration ($[M]^0$) were tested. The polymer yield was slightly increased as the initial monomer concentration is increased from 0.5 to 2.0. However, the inherent viscosities were found to be similar, regardless of the initial monomer concentration. The effect of monomer to catalyst mole ratio (M/C) was also tested (exp. no: 1, 4, 5). As the M/C increased, the polymer yield and the inherent viscosities were decreased from 80% to 45% and from 0.19 to 0.14 dL/g, respectively. Other catalysts such as $(PPh_3)_2PdCl_2$, $PtCl_2$, and $RuCl_3$ also polymerized HPP effectively to give a moderate yield of polymer.

Figure 1 shows the time dependence curve for the polymerization of HPP by $PdCl_2$ and $PtCl_2$ catalyst systems. The polymerization of HPP by $PdCl_2$ catalyst proceeded gradually to reach 50% yield after the polymerization time of 5 hours. And then the polymerization rate decreased gradually reached a plateau after 12 hours. The polymerization behavior by $PtCl_2$ catalyst was similar with that by $PdCl_2$ catalyst although the polymer yield was somewhat lower. Similar polymerization behaviors were also observed in the polymerization of 5-phenyl-2-(2-propynylamino)-2-oxazolin-4-one by these catalyst systems [54].



Scheme 1



TABLE 1. Polymerization of HPP by Palladium, Platinum, and Ruthenium Chlorides^a

| Experiment No. | Catalyst | M/C ^b (mole ratio) | [M] ₀ ^c | Polymer Yield (%) | η_{inh} ^d |
|----------------|--|----------------------------------|-------------------------------|-------------------|---------------------------|
| 1 | PdCl ₂ | 25 | 0.5 | 80 | 0.19 |
| 2 | PdCl ₂ | 25 | 1.0 | 87 | 0.20 |
| 3 | PdCl ₂ | 25 | 2.0 | 93 | 0.17 |
| 4 | PdCl ₂ | 50 | 0.5 | 70 | 0.16 |
| 5 | PdCl ₂ | 100 | 0.5 | 45 | 0.14 |
| 6 | PdCl ₂ | 25 | 0.25 | 36 | 0.12 |
| 7 | (Ph ₃ P) ₂ PdCl ₂ | 25 | 0.5 | 47 | 0.13 |
| 8 | PtCl ₂ | 25 | 0.5 | 73 | 0.15 |
| 9 | RuCl ₃ | 25 | 0.5 | 63 | 0.17 |

^a Polymerization was carried out at 90°C for 24hrs in DMF.

^b Monomer to catalyst mole ratio.

^c Initial monomer concentration ([M]₀).

^d Inherent viscosities (η_{inh}) were measured at a concentration of 0.5g/dL in DMF at 30°C.

Table 2 shows the solvent effect for this polymerization of HPP by PdCl₂. The solvents such as DMF, DMSO, pyridine, m-cresol, and formic acid were tested and evaluated. In most cases, the polymerization proceeded homogeneously. DMF, DMSO, and m-cresol were found to be most effective for the present polymerization to give the polymer yield over 70%. Pyridine and formic acid also gave moderate yield of polymer (65%, 55%, respectively). The inherent viscosities of the poly(HPP)s according to the polymerization solvents were in the range of 0.12-0.20 dL/g.

We attempted the polymerization of HPP using Mo- and W-based catalysts. However, polymerization did not proceed in aromatic and halogenated hydrocarbon solvents. The reason was assumed to be the poor solubility of HPP



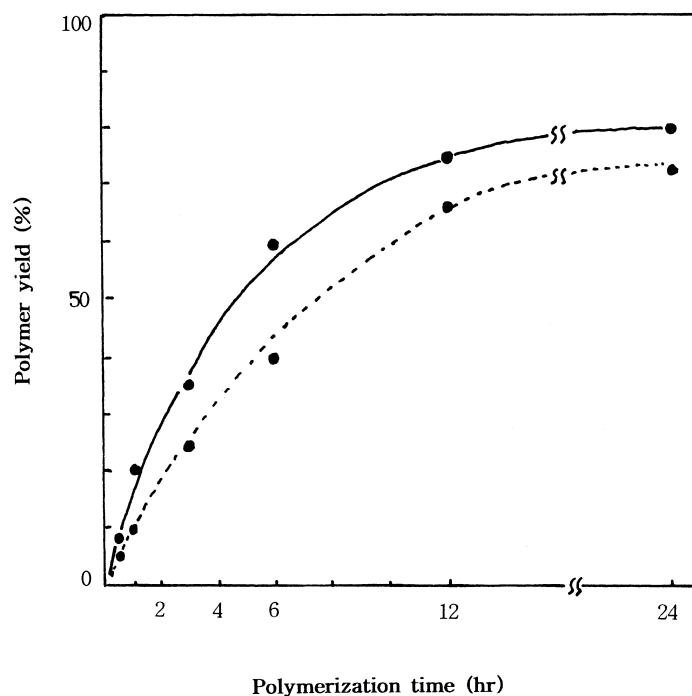


Figure 1. Time dependence curves of polymer yield for the polymerization of HPP by PdCl₂ (—) and PtCl₂ (-----) catalyst systems.

TABLE 2. Solvent Effect for the Polymerization of HPP by PdCl₂^a

| Experiment No. | Solvent | Polymer Yield (%) | η_{inh}^b |
|----------------|----------|-------------------|----------------|
| 1 | DMF | 80 | 0.19 |
| 2 | DMSO | 85 | 0.20 |
| 3 | Pyridine | 65 | 0.14 |
| 4 | HCOOH | 55 | 0.12 |
| 5 | m-Cresol | 75 | 0.16 |

^a Polymerization was carried out at 90°C for 24hrs. Monomer to catalyst mole ratio (M/C) and Initial monomer concentration ($[M]_0$) were 25 and 0.5 M, respectively.

^b Inherent viscosities (η_{inh}) were measured at a concentration of 0.5g/dL in DMF at 30°C.



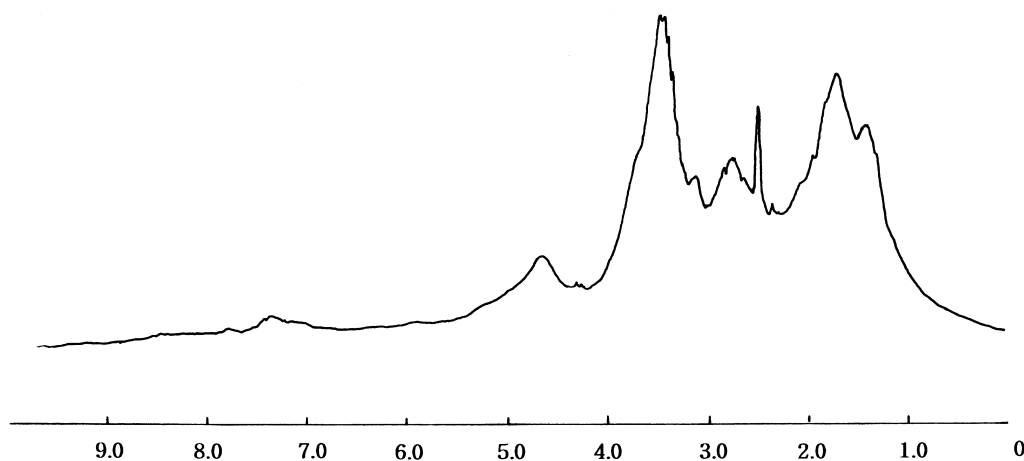


Figure 2. ^1H -NMR spectrum of poly(HPP) in DMSO-d_6 .

to the polymerization solvents (chlorobenzene, toluene, etc.) and/or the poisoning of the Mo- and W-catalysts by the heteroatom (N, O) of HPP.

The molecular structure of the resulting poly(HPP) was characterized by various instrumental methods such as NMR (^1H - and ^{13}C -), IR, and UV-visible spectroscopies.

Figure 2 shows the ^1H -NMR spectrum of poly(HPP) prepared by PdCl_2 . It shows the broad vinyl protons in the polymer backbone at about 7.4 ppm. The hydrogen peak of methylene carbon adjacent to the 4-hydroxy carbon was observed at 1.0–2.2 ppm. The methylene hydrogen of piperidine moiety adjacent to the nitrogen atom and the methylene hydrogen between nitrogen atom and vinyl carbon of polymer backbone were also observed at 2.3–2.9 ppm and 3.0–4.0 ppm, respectively. The broad peak at 4.4–5.4 ppm is due to the hydroxy proton peaks of piperidine moiety.

Figure 3 shows the ^{13}C -NMR spectrum of poly(HPP) prepared by PdCl_2 . The acetylenic carbon peaks of HPP at 75.39 and 79.80 ppm disappeared in the ^{13}C -NMR spectrum of poly(HPP). Instead, a new peak at region of 125–140 ppm, which is due to the carbon atom of conjugated polymer backbone, was observed in the ^{13}C -NMR spectrum of poly(HPP). The peak of 4-hydroxy carbon of piperidine moiety was observed at 66.2 ppm. The peaks of 2- and 3-methylene carbons of piperidine moiety were also observed at 51.1 and 34.4 ppm, respectively.

Figure 4 shows the FT-IR spectra of HPP and poly(HPP) in KBr pellet. The infrared spectrum of poly(HPP) shows neither the acetylenic hydrogen



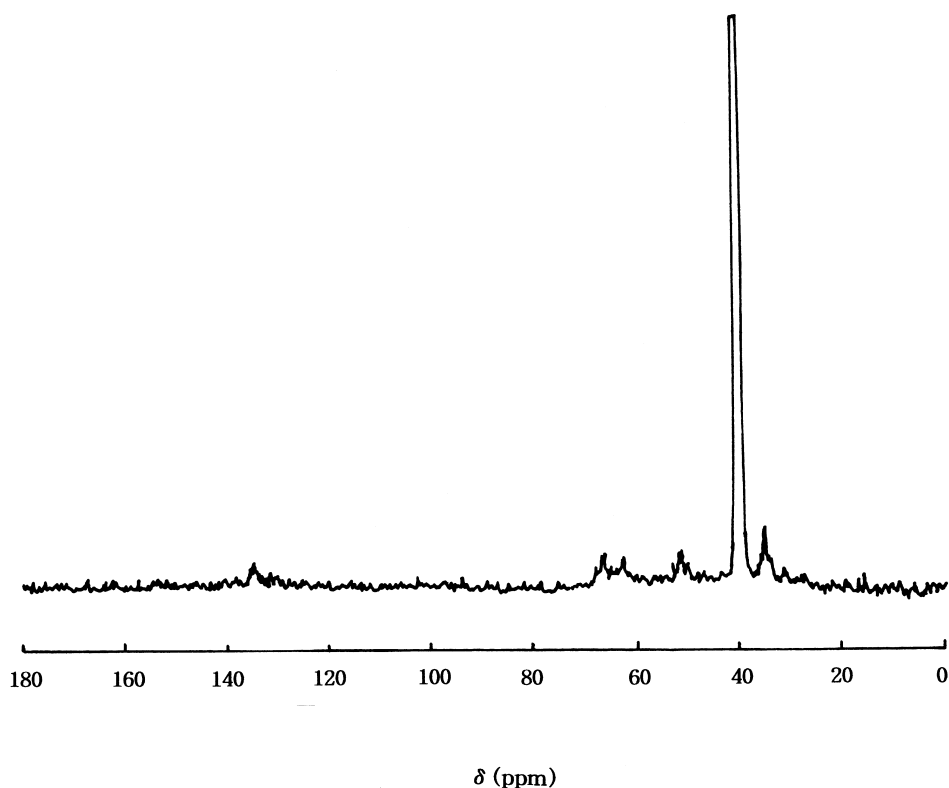


Figure 3. ¹³C-NMR spectrum of poly(PPO) in DMSO-d₆.

stretching (3197 cm⁻¹) nor the carbon-carbon triple bond stretching (2113 cm⁻¹) frequencies presented in the infrared spectrum of HPP. Instead, the carbon-carbon double bond stretching frequency at 1611 cm⁻¹ was newly observed. The strong broad peak observed at about 3367 cm⁻¹ is due to the O-H stretching of 4-hydroxypiperidine moiety and the moisture absorbed in the processes. And the peaks at 1449 cm⁻¹ and 1063 cm⁻¹ are due to the scissor vibration frequencies of -CH₂- and CH-O-H of cyclic alcohols, respectively.

The UV-visible spectrum (Figure 5) of poly(HPP) in tetrahydrofuran shows a characteristic absorption peak of conjugated polymer, $\pi \rightarrow \pi^*$ absorption at long wavelength (up to 700 nm).

From these analytical results, it was concluded that the present poly(HPP) have a conjugated backbone system carrying 4-hydroxypiperidine moiety.

Figures 6 and 7 show the TGA and DSC thermograms of poly(HPP), respectively. The TGA thermogram of poly(HPP) prepared by PdCl₂ showed



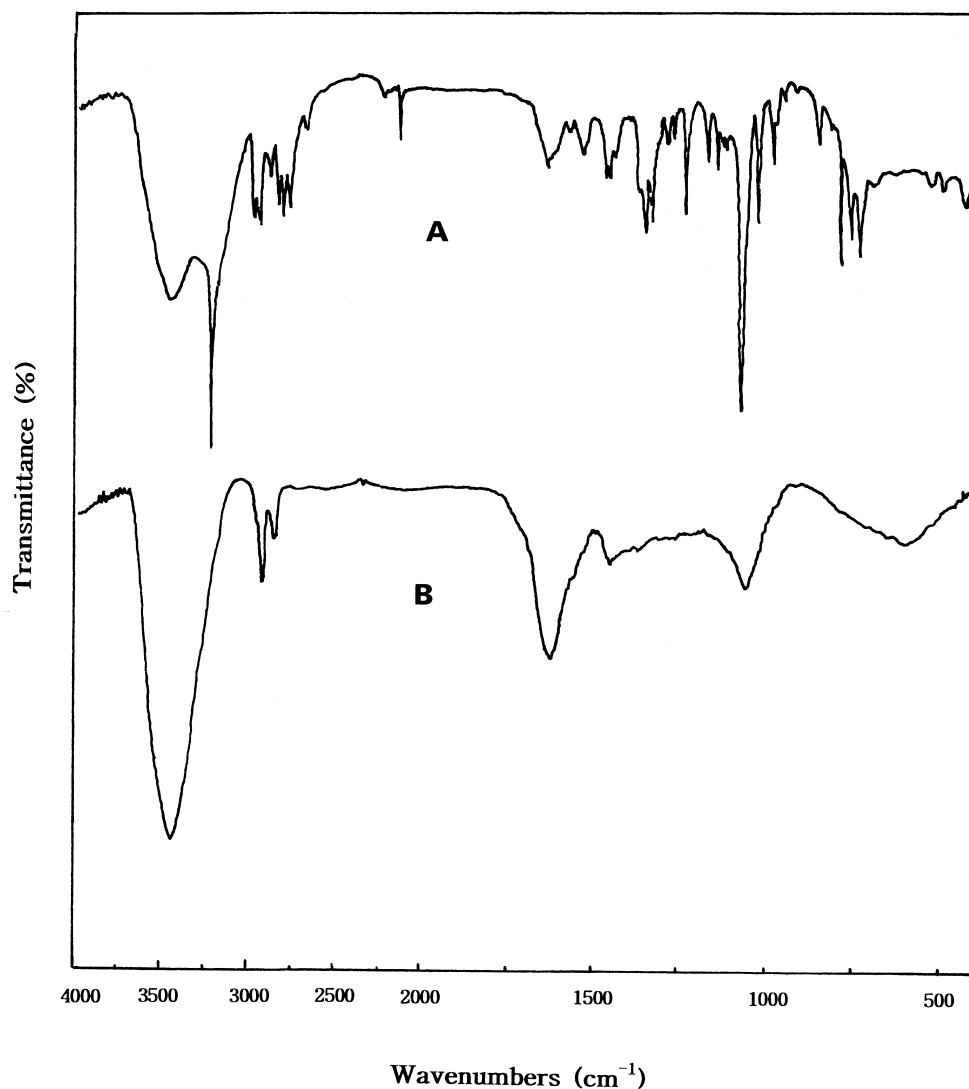


Figure 4. FT-IR spectra of HPP [A] and poly(HPP) [B] in KBr pellet.

that it retained 97.1% of its original weight at 150°C, 91.2% at 222°C, 62.7% at 300°C, 52.3% at 400°C, and 44.5% at 800°C.

The DSC thermogram (Figure 7) shows an exothermic peak at 193.7°C. This peak is originated from the thermal cross-linking and/or decomposition processes of conjugated polymer backbone with the 4-hydroxypiperidine moiety.

The solubility test was performed for the present polymer samples in excess solvent. The results are listed in Table 3. Poly(HPP) is soluble in formic acid, DMF, DMSO, and tetrahydrofuran, and partially soluble in water, but



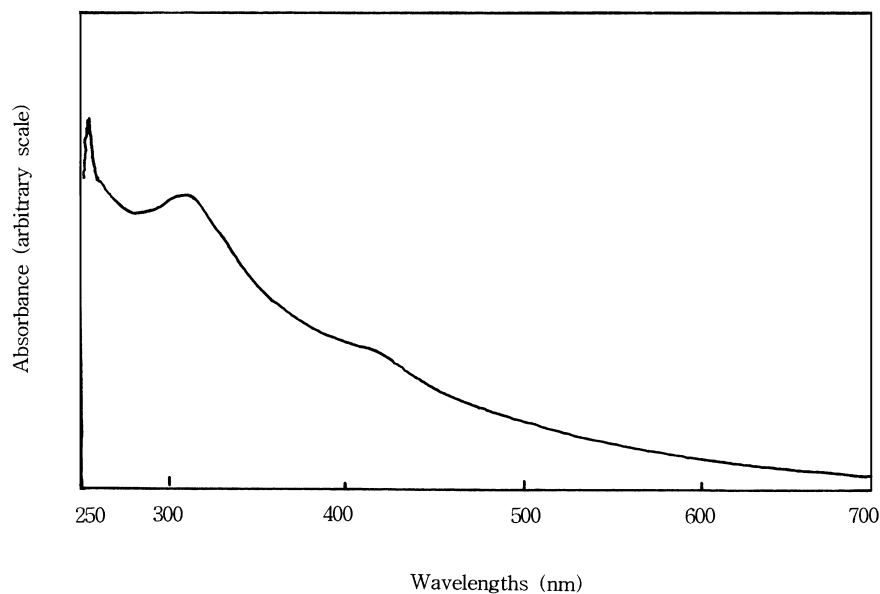


Figure 5. UV-visible spectra of poly(HPP) in tetrahydrofuran.

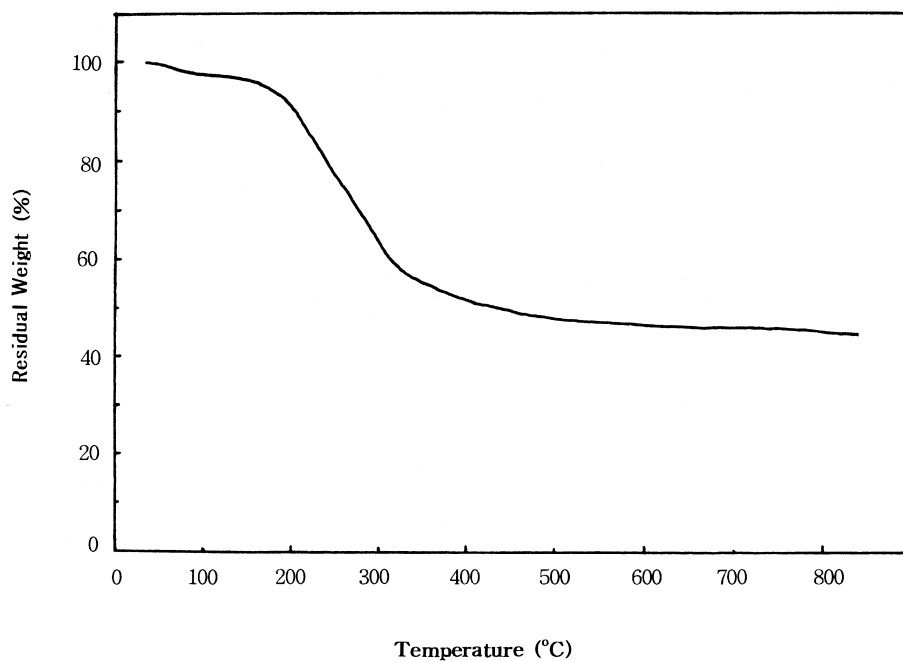


Figure 6. TGA thermogram of poly(HPP).

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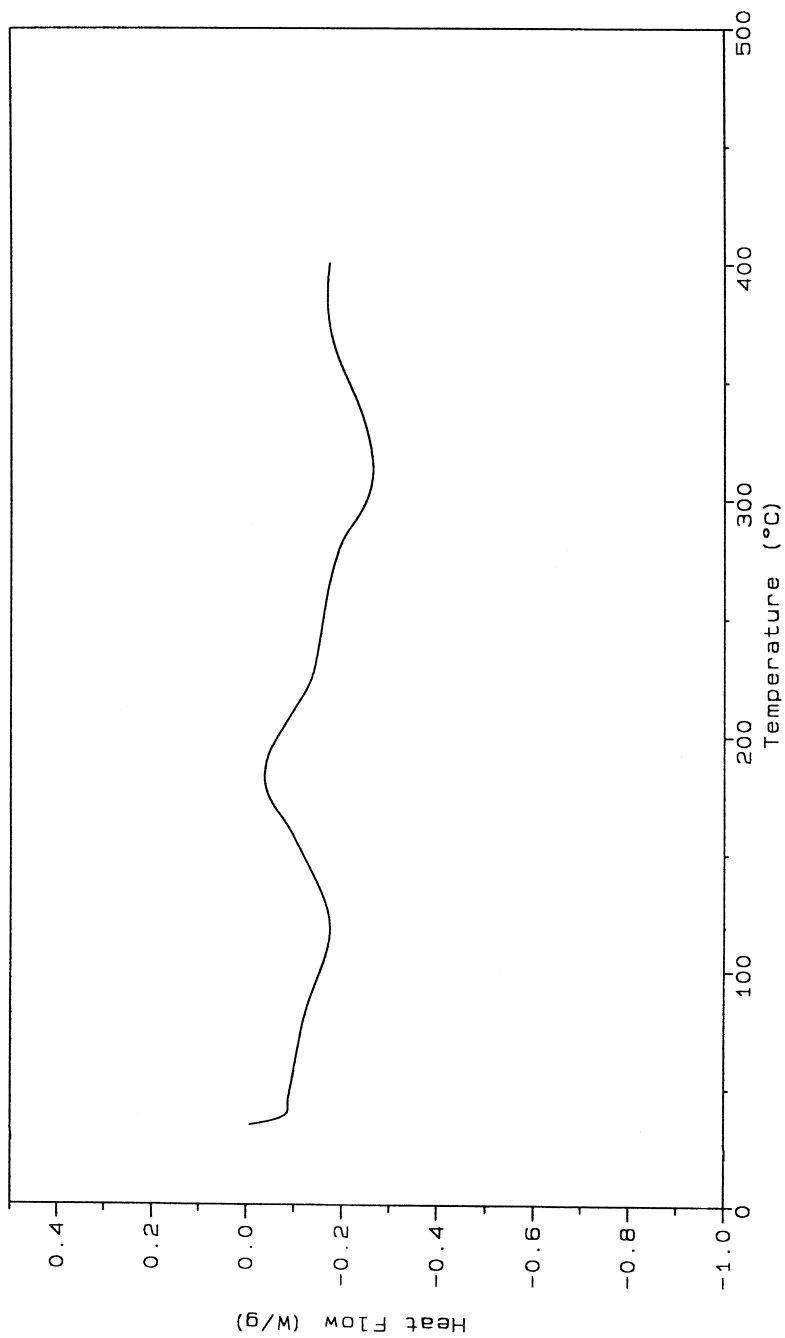


Figure 7. DSC thermogram of poly(HPP).

TABLE 3. Solubility Behaviors of Poly(HPP)^a

| Solvent | Solubility ^b |
|-------------------|-------------------------|
| DMSO | ++ |
| DMF | ++ |
| HCOOH | ++ |
| m-Cresol | ++ |
| H ₂ O | +- |
| CHCl ₃ | -- |
| Benzene | -- |
| Chlorobenzene | -- |
| Toluene | -- |
| Acetonitrile | -- |
| Formaldehyde | -- |

^a The solubility test was performed for the polymer samples in each excess solvent.

^b ++: soluble, +-: partially soluble, --: insoluble.

mostly insoluble in chlorobenzene, 1,1,1-trichloroethane, ethyl ether, n-hexane, and CCl₄.

The morphology of the resulting poly(HPP) was investigated by X-ray diffraction analysis. Figure 8 shows a typical X-ray diffractogram of poly(HPP). Because the peaks in diffraction patterns are all broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35 [55], the present polymers are amorphous.

CONCLUSION

HPP, an acetylene derivative having 4-hydroxypiperidine moiety was synthesized and polymerized. It was found that the PdCl₂, PtCl₂, and RuCl₃



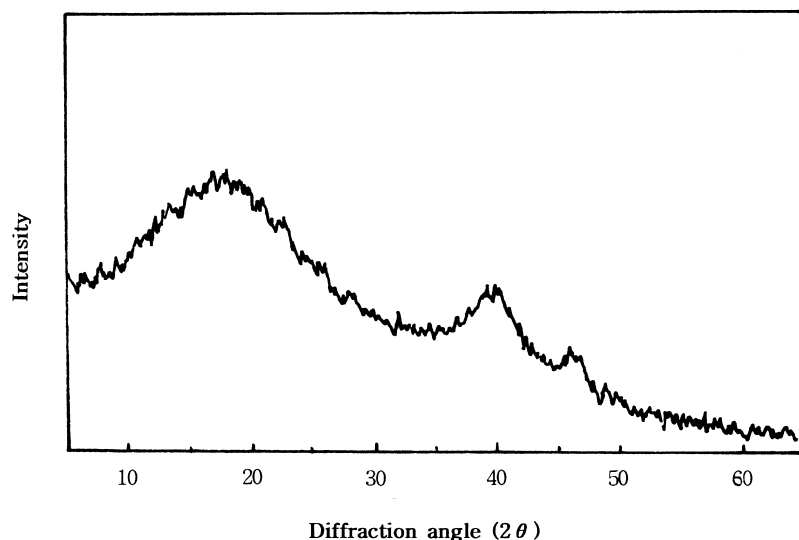


Figure 8. X-ray diffractogram of poly(HPP).

catalyst systems are effective for the polymerization of HPP, whereas the Mo- and W-based catalyst systems gave no polymer. DMF, DMSO, and m-cresol were found to be effective solvent for the present polymerization. The inherent viscosities of the resulting poly(HPP)s were in the range of 0.12-0.20 dL/g, depending on the catalyst system and the polymerization conditions used. From the spectroscopic data, it was concluded that the present polymer have a conjugated polymer backbone structure carrying a 4-hydroxypiperidine moiety. Poly(HPP)s were mostly soluble in formic acid, DMF, DMSO, and tetrahydrofuran and solution castable into thin film. It is anticipated that the applications of this polymer as semiconductors, polymeric electrolytes, and NLO materials.

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REFERENCES

- [1] P. Cukor, J. I. Krugler, and M. I. Rubner, *Makromol. Chem.*, **182**, 165 (1981).



- [2] Y. S. Gal, B. Jung, and S. K. Choi, *J. Appl. Polym. Sci.*, **42**, 1793 (1991).
- [3] A. Camus, V. Faruffini, A. Furlani, N. Marsich, G. Ortaggi, R. Paolesse, and M. V. Russo, *Appl. Organomet. Chem.*, **2**, 533 (1988).
- [4] T. Mizumoto, T. Masuda, and T. Higashimura, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 2555 (1993).
- [5] J. S. Yang and G. H. Hsiue, *J. Membrane Sci.*, **120**, 69 (1996).
- [6] E. Yashima, T. Matsushima, T. Nimura, and Y. Okamoto, *Korea Polymer J.*, **4**, 139 (1996).
- [7] L. Pu, *Acta Polymer*, **48**, 116 (1997).
- [8] T. Aoki, K. I. Shinohara, T. Kaneko, and E. Oikawa, *Macromolecules*, **29**, 4192 (1996).
- [9] T. Kakuchi, T. Watanabe, H. Kamimura, S. Matsunami, and K. Yokata, *Polymer*, **37**, 3767 (1996).
- [10] T. Kakuchi, S. Matsunami, H. Kamimura, F. Ishii, T. Uesaka, and K. Yokota, *J. Polym. Sci. Polym. Chem. Ed.*, **33**, 1431 (1995).
- [11] B. Z. Tang, T. Masuda, and T. Higashimura, *J. Polym. Sci. Polym. Chem. Ed.*, **27**, 1197 (1989).
- [12] Y. Mujie, Z. Jian, L. Aibing, S. Zhiquan, Z. Mingjian, and L. Senhao, *Ibid*, **27**, 3829 (1989).
- [13] S. H. Jin, S. H. Kim, H. N. Cho, and S. K. Choi, *Macromolecules*, **24**, 6040 (1991).
- [14] S. J. Choi, S. H. Jin, J. W. Park, H. N. Cho, and S. K. Choi, *Ibid*, **27**, 309 (1994).
- [15] S. H. Jin, S. W. Kang, J. G. Park, J. C. Lee, and K. S. Choi, *J. Macromol. Sci., Pure and Appl. Chem.*, **A32**, 455 (1995).
- [16] S. K. Choi, J. H. Lee, S. J. Kang, and S. H. Jin, *Prog. Polym. Sci.*, **22**, 693 (1997).
- [17] J. L. Moigne, A. Hilberer, and F. Kajzar, *Makromol. Chem.*, **192**, 515 (1991).
- [18] M. Jang and J. Liu, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 3155 (1993).
- [19] H. J. Lee, J. M. Oh, S. J. Choi, H. K. Kim, and S. K. Choi, *Polym. Bull.*, **32**, 433 (1994).
- [20] S. K. Choi, J. H. Lee, and H. K. Kim, *Macromol. Symp.*, **118**, 67 (1997).
- [21] H. J. Lee, Y. H. Won, S. J. Kang, S. K. Choi, and H. K. Kim, *J. Polym. Sci. Polym. Chem. Ed.*, **34**, 2333 (1996).
- [22] H. W. Gibson, F. C. Bailey, A. J. Epstein, H. Rommelmann, S. Kaplan, J.



- Harbour, X-Q. Yang, B. Tanner, and J. M. Pochan, *J. Am. Chem. Soc.*, *105*, 4147 (1983).
- [23] J. Kunzler and V. Percec, *J. Polym. Sci. Polym. Chem. Ed.*, *28*, 1043 (1990).
- [24] S. H. Jin, Y. S. Gal, and S. K. Choi, *Polymer Science and Technology (Korea)*, *3*, 455 (1992).
- [25] W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Bull. Korean Chem. Soc.*, *9*, 328 (1988).
- [26] W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Polymer (Korea)*, *12*, 720 (1988).
- [27] W. C. Lee, M. W. Huh, Y. S. Gal, and S. K. Choi, *Ibid*, *13*, 520 (1989).
- [28] W. C. Lee, Y. S. Gal, M. S. Ryoo, S. H. Han, and S. K. Choi, *Ibid*, *15*, 283 (1991).
- [29] W. C. Lee, J. H. Seo, Y. S. Gal, S. H. Jin, and S. K. Choi, *Bull. Korean Chem. Soc.*, *14*, 708 (1993)
- [30] W. C. Lee, Y. S. Gal, S. H. Jin, S. J. Choi, H. J. Lee, and S. K. Choi, *J. Macromol. Sci., Pure and Appl. Chem.*, *A31*, 737 (1994).
- [31] Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *J. Polym. Sci. Polym. Chem. Ed.*, *30*, 2657 (1992).
- [32] Y. S. Gal and S. K. Choi, *Polymer (Korea)*, *11*, 563 (1987).
- [33] Y. S. Gal and S. K. Choi, *J. Polym. Sci. Polym. Lett. Ed.*, *26*, 115 (1988)
- [34] Y. H. Kim, Y. S. Gal, and S. K. Choi, *Macromolecules*, *21*, 1991 (1988).
- [35] M. S. Ryoo, W. C. Lee, and S. K. Choi, *Ibid*, *23*, 4135 (1990).
- [36] Y. S. Gal, W. C. Lee, H. J. Lee, S. H. Jang, and S. K. Choi, *J. Mac. Sci.-Pure and Appl. Chem.*, *A34*, 2251 (1997).
- [37] K. L. Kang, S. H. Kim, H. N. Cho, K. Y. Choi, and S. K. Choi, *Macromolecules*, *26*, 4539 (1993).
- [38] S. H. Kim, S. J. Choi, J. W. Park, H. N. Cho, and S. K. Choi, *Macromolecules*, *27*, 2339 (1994).
- [39] R. K. Bartlett, G. O'Neill, H. S. Turner, and W. F. Wall, *Br. Polym. J.*, *4*, 503 (1972).
- [40] L. A. Akopyan, S. G. Grigoryan, G. A. Zhamkochyan, and S. G. Matsoyan, *Vysokomol. Soedin., Ser. A*, *17*, 2517 (1975).
- [41] L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, *27*, 3930 (1962).



- [42] A. Furlani, M. V. Russo, P. Carusi, S. Licoccia, E. Leoni, and G. Valenti, *Gazz. Chim. Ital.*, *113*, 671 (1983).
- [43] S. Okamura and K. Hayashi, Japan 7886 (1986); *Chem. Abst.*, *59*, 7671h.
- [44] K. Yoshimura, T. Kitade, K. Kitamura, and K. Hozumi, *J. Appl. Polym. Sci.*, *38*, 1011 (1989).
- [45] M. G. Voronkov, V. B. Pukhnarevich, S. P. Sushchinskaya, V. Z. Annenkova, V. M. Annenkova, and N. J. Andreeva, *J. Polym. Sci. Polym. Chem. Ed.*, *18*, 53 (1980).
- [46] Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *Polymer (Korea)*, *16*, 597 (1992).
- [47] Y. S. Gal, *J. Mac. Sci.-Pure and Appl. Chem.*, *A32*, 61 (1995).
- [48] M. Yang, M. Zheng, A. Furlani, and M. Russo, *J. Polym. Sci. Polym. Chem. Ed.*, *32*, 2709 (1994).
- [49] M. Yang, H. Sun, and W. Chen., *Polymer International*, *27*, 928 (1995).
- [50] A. Usanmaz and N. Kizilirmak, *J. Mac. Sci., Pure and Appl. Chem.*, *A29*, 1175 (1992).
- [51] Y. S. Gal, *Ibid*, *A31*, 703 (1994).
- [52] M. V. Russo, G. Iucci, G. Polzonetti, and A. Furlani, *Polymer*, *33*, 4401 (1992).
- [53] Y. S. Gal, B. Jung, J. H. Kim, W. C. Lee, and S. K. Choi, *J. Mac. Sci.-Pure and Appl. Chem.*, *A31*, 1177 (1994).
- [54] W. C. Lee, Y. S. Gal, and S. K. Choi, *Ibid*, *A34*, 99 (1997).
- [55] T. Masuda and T. Higashimura, *Acc. Chem. Res.*, *17*, 51 (1981).

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