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Polymerization of 5-Phenyl-2-(2-propynylamino)-2-oxazolin-4-one by Transition Metal Catalysts

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POLYMERIZATION OF 5-PHENYL-2-(2-PROPYNYLAMINO)-2-OXAZOLIN-4-ONE BY TRANSITION METAL CATALYSTS

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ABSTRACT

Polymerization of 5-phenyl-2-(2-propynylamino)-2-oxazolin-4-one, an acetylene derivative which can yield a conjugated polymer, was carried out with palladium and platinum chlorides. These catalyst systems gave a moderate yield of polymer (maximum polymer yield: 81%). In the polymerization of PdCl₂, as the monomer-to-catalyst mole ratio increased, the polymer yield and molecular weight decreased from 69 to 25% and from 2930 to 2010, respectively. The polymer structure was identified by various instrumental analyses (NMR, IR, UV-visible spectroscopies) to have a conjugated polymer backbone. The resulting poly-

mers were completely soluble in chloroform, formic acid, tetrahydrofuran, DMF, and DMSO, but insoluble in ethyl ether, *n*-hexane, and CCl_4 .

INTRODUCTION

Polymers having a conjugated backbone are expected to show unique properties such as electrical conductivity [1–3], gas and liquid mixture separation [4, 5], radiation degradation [6, 7], side-chain liquid crystallinity [8–10], and nonlinear optical properties [11–13].

A number of substituted polyacetylenes have been synthesized and characterized [14–16]. In recent years we have reported the polymerization of propargyl halides [17, 18], ethers [19–22], and amines [23], and the cyclopolymerization of dipropargyl derivatives such as dipropargyl ether [24], sulfide [25], silanes [26], diethyl malonate [27], dihexylammonium salts [28, 29], etc. To our knowledge, there have been no reports on the polymerization of 5-phenyl-2-(2-propynylamino)-2-oxazolin-4-one (PPO). PPO is an interesting propargyl compound having two nitrogen atoms which can react with alkyl bromides or methyl trifluoromethanesulfonate to give the corresponding salts.

In this paper, studies on the polymerization behaviors of PPO by transition metal catalysts and the physical and spectroscopic properties of the resulting poly(PPO) will be presented.

EXPERIMENTAL

Materials

PPO (Aldrich Chemicals, mp 166–170°C) was used after recrystallization with DMF/ethanol solvent. PdCl_2 (Aldrich Chemicals, 99.995%), PtCl_2 (Strem), and RuCl_3 (Aldrich Chemicals) were used without further purification. The polymerization solvents were analytical grade materials. They were dried with appropriate drying agent and fractionally distilled.

Polymerization

A typical polymerization of PPO is as follows. Into a 2-mL ampule, PPO (0.5 g, 2.33 mmol), PdCl_2 (13.8 mg, 0.078 mmol), and DMF (3.67 mL, $[\text{M}]_0 = 0.5 \text{ M}$) were added in the order given and sealed with a rubber septum after flushing with 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 of distilled water, filtered from the solution, and then dried under vacuum at 40°C for 6 hours. The polymer yield was calculated by gravimetry.

Instruments

NMR (^1H - and ^{13}C -) spectra were recorded on a Bruker AM-200 spectrometer in CDCl_3 . Infrared spectra were obtained with a Bio-Rad Digilab FTS spectrometer using potassium bromide pellets. UV-visible spectra were obtained with a Shimadzu

UV-3100S spectrophotometer in tetrahydrofuran. The average molecular weights of polymers were measured by means of a GPC-150C of Waters using a calibration curve for polystyrene. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min up to 700°C with a DuPont 1090 Analyzer. DSC thermograms were taken on a DuPont 910 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10°C/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 CuK α radiation at a scan speed of 4°/min.

RESULTS AND DISCUSSION

The polymerization of PPO, a propargyl derivative with an oxazoline moiety, was carried out by palladium and platinum chlorides.

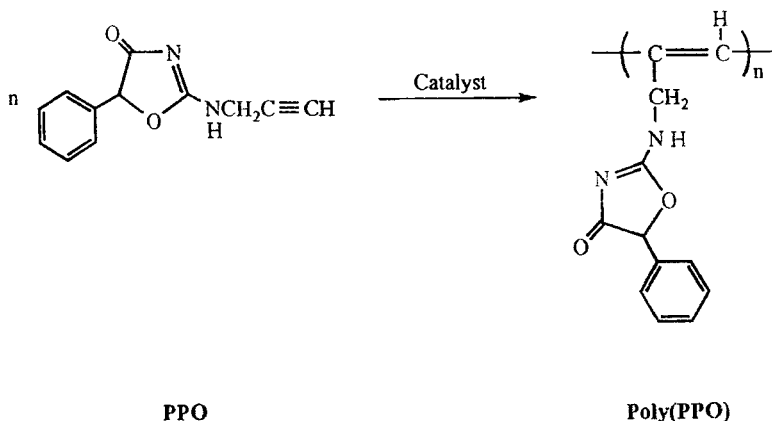


Table 1 lists the results for the polymerization of PPO by palladium, platinum, and ruthenium chlorides. These catalysts were found to be effective for the present polymerization of PPO. The initial monomer concentration ($[M]_0$) did not show a considerable effect on the polymer yield and average molecular weight (Exp. 1-4). The effect of monomer-to-catalyst mole ratio (M/C) was also tested (Exp. 4-6). As the M/C increased, the polymer yield and molecular weight decreased from 69 to 25% and from 2930 to 2010, respectively.

The solvent effect for the present polymerization was tested in such solvents as DMF, DMSO, pyridine, and HCO₂H (Exp. 2, 7-9). In the case of DMSO solvent, the resulting polymer was mostly insoluble although it shows the highest polymer yield (81%). Pyridine was also found to be a good solvent. On the other hand, formic acid gave only a low yield of polymer. (Ph₃P)₂PdCl₂, PtCl₂, and RuCl₃ were also found to be effective for the polymerization and gave a moderate yield of polymer. However, an insoluble polymer was mostly produced when RuCl₃ was used as catalyst.

We attempted the polymerization of PPO using Mo- and W-based catalysts. However, polymerization did not proceed in aromatic and halogenated hydrocar-

TABLE 1. Polymerization of PPO by PdCl₂, PtCl₂, and RuCl₃^a

Experiment	Catalyst	M/C ^b (mole ratio)	[M] ₀ ^c	Solvent	Polymer yield, %	\bar{M}_n ^d
1	PdCl ₂	30	0.25	DMF	57	3390
2	PdCl ₂	30	0.50	DMF	74	3360
3	PdCl ₂	30	0.75	DMF	75	2820
4	PdCl ₂	30	1.0	DMF	69	2930
5	PdCl ₂	50	0.50	DMF	54	2190
6	PdCl ₂	100	0.50	DMF	25	2010
7	PdCl ₂	30	0.50	DMSO	81	Insoluble
8	PdCl ₂	30	0.50	Pyridine	67	1950
9	PdCl ₂	30	0.50	HCO ₂ H	35	2080
10	(Ph ₃ P) ₂ PdCl ₂	30	0.50	DMF	51	1980
11	PtCl ₂	30	0.50	DMF	43	3060
12	RuCl ₃	30	0.50	DMF	65	Insoluble

^aPolymerization was carried out at 90°C for 24 hours in chlorobenzene.

^bMonomer-to-catalyst mole ratio.

^cInitial monomer concentration ([M]₀).

^dMeasured by means of a Waters GPC-150C using the calibration curves for polystyrene.

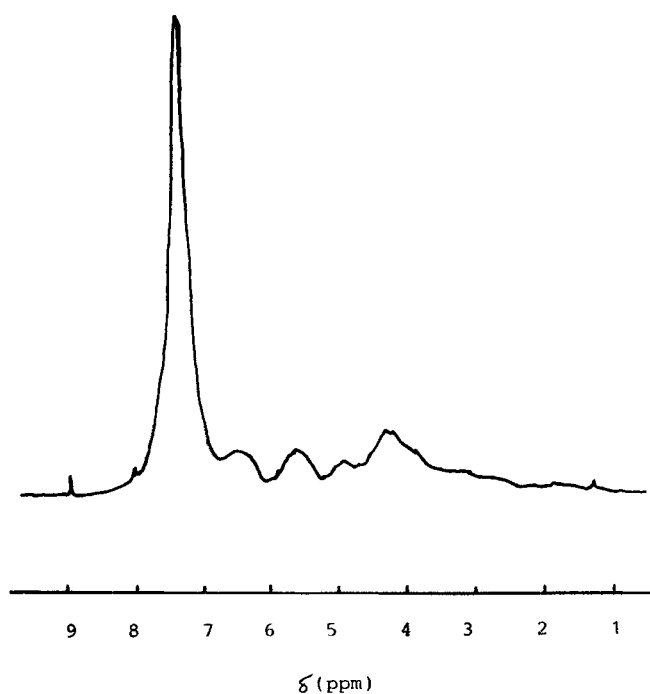


FIG. 1. ¹H-NMR spectrum of poly(PPO) in CDCl₃.

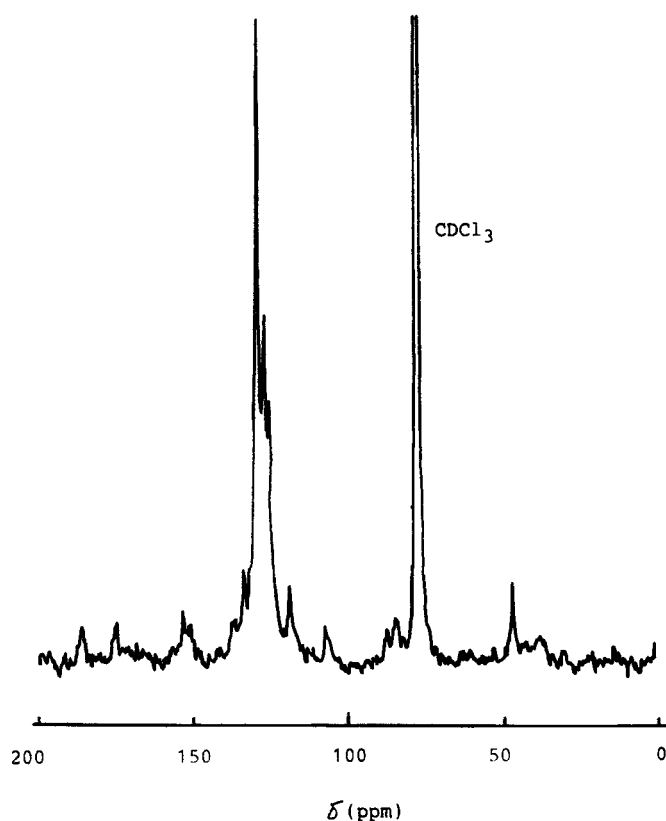


FIG. 2. ^{13}C -NMR spectrum of poly(PPO) in CDCl_3 .

bon solvents. The reason was assumed to be the poor solubility of PPO to the polymerization solvents (chlorobenzene, toluene, etc.) and/or the poisoning of the Mo- and W-catalysts by the heteroatom (N, O) of PPO.

Figure 1 shows the ^1H -NMR spectrum of poly(PPO) prepared by PdCl_2 . It shows phenyl protons and vinyl protons in the polymer backbone at 6-8 ppm. It also shows the protons adjacent to oxygen atom and methylene ($-\text{CH}_2-$) protons at 5.6 and 4.3 ppm, respectively.

Figure 2 shows the ^{13}C -NMR spectrum of poly(PPO) prepared by PdCl_2 . The carbon peak in the conjugated polymer backbone is observed at about 150 ppm. The carbonyl carbon peak and the carbon peaks adjacent to N-H and $-\text{O}-$ linkage were observed at 185 and 175 ppm, respectively. The peaks at 85 ppm originate from the carbon adjacent to the phenyl substituent.

Figure 3 shows the FT-IR spectra of PPO and poly(PPO). The infrared spectrum of poly(PPO) shows neither the acetylenic hydrogen stretching (3265 cm^{-1}) nor the carbon-carbon triple bond stretching (2128 cm^{-1}) frequencies present in the infrared spectrum of PPO. Instead, the carbon-carbon double bond stretching frequency at 1610 cm^{-1} was more intensively observed. The peak observed at about 3300 cm^{-1} is due to the N-H stretching of amines and the moisture absorbed in the process.

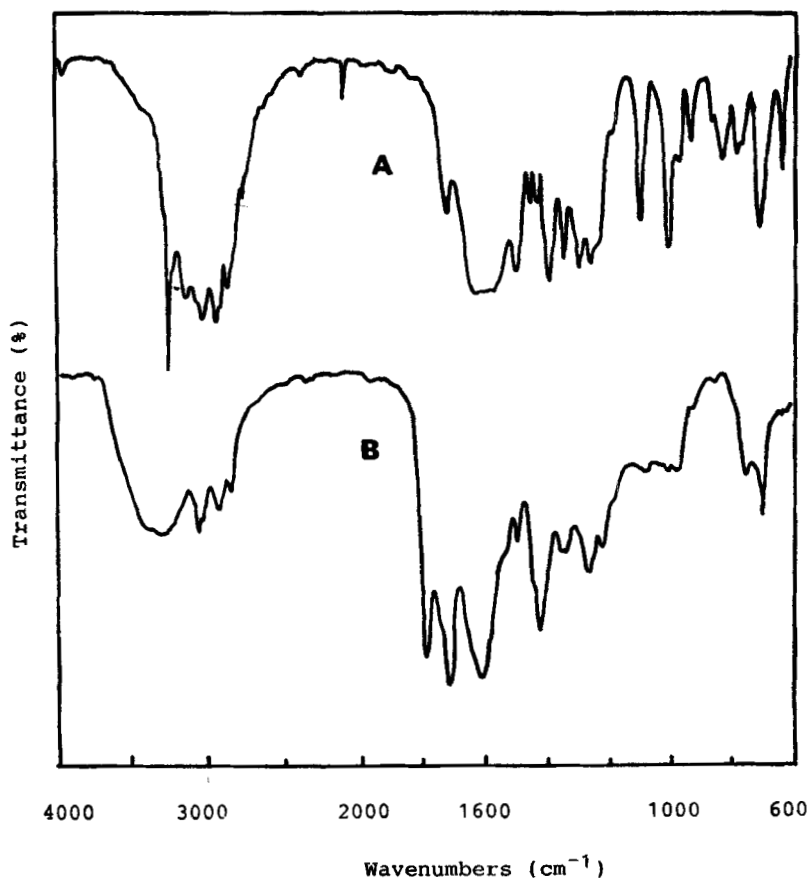


FIG. 3. FT-IR spectra of PPO (A) and poly(PPO) (B) in KBr pellets.

Figure 4 shows the UV-visible spectra of poly(PPO) in tetrahydrofuran. This spectrum shows a characteristic absorption peak of conjugated polymer: $\pi \rightarrow \pi^*$ absorption at a long wavelength (up to 650 nm).

TGA and DSC thermograms of poly(PPO) are shown in Figs. 5 and 6. The TGA thermogram of poly(PPO) prepared by PdCl_2 shows that it retains 95% of its original weight at 145°C, 90% at 222°C, 50% at 372°C, and 15% at 650°C. The DSC thermogram (Fig. 6) shows an exothermic peak at 240–300°C. This peak originates from the thermal decomposition process of the conjugated polymer backbone with the pendant oxazolin-4-one group.

The solubility test was performed for the present polymer samples in excess solvent. Poly(PPO) is soluble in chloroform, formic acid, DMF, DMSO, and tetrahydrofuran, and partially soluble in toluene, chlorobenzene, and 1,1,1-trichloroethane, but insoluble in ethyl ether, *n*-hexane, and CCl_4 .

The morphology of the resulting polymers was investigated by x-ray diffraction analysis. 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 [30], the present polymers are amorphous.

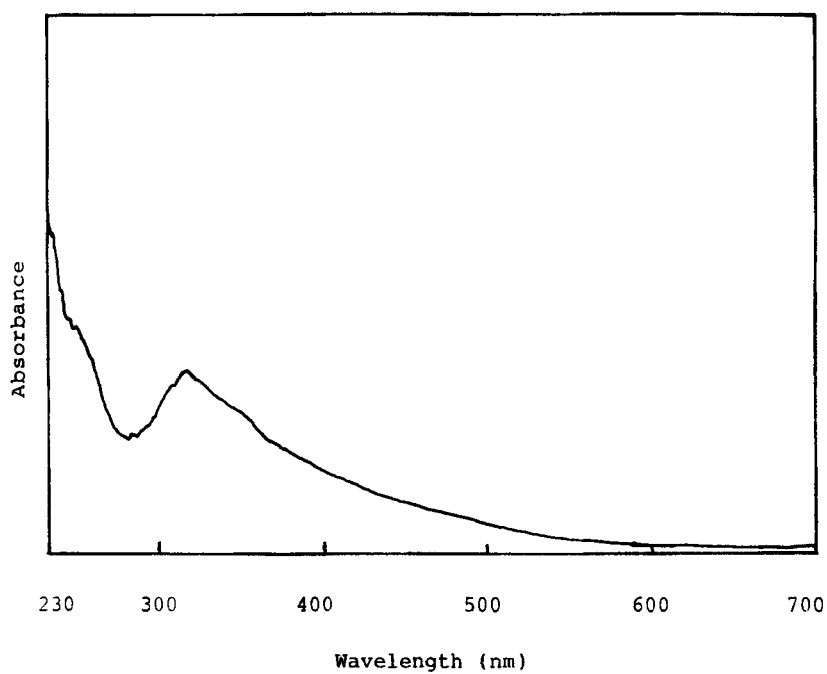


FIG. 4. UV-visible spectra of poly(PPO) in tetrahydrofuran.

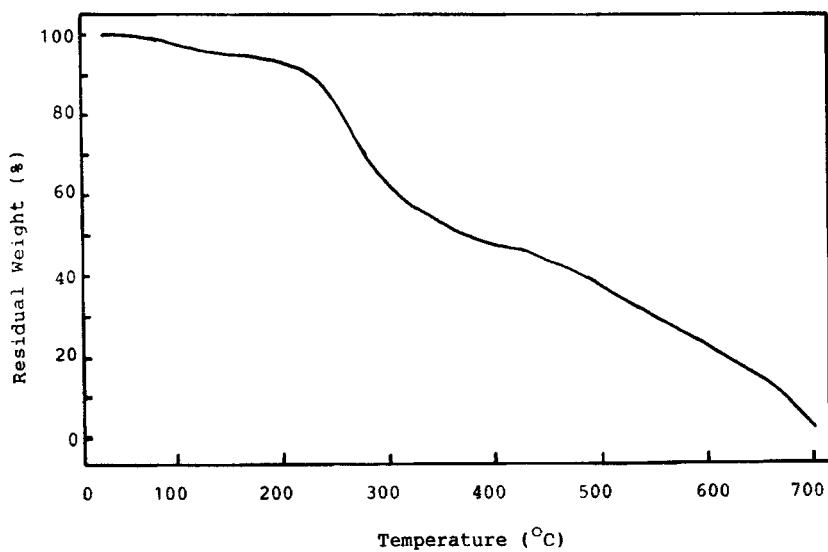


FIG. 5. TGA thermogram of poly(PPO).

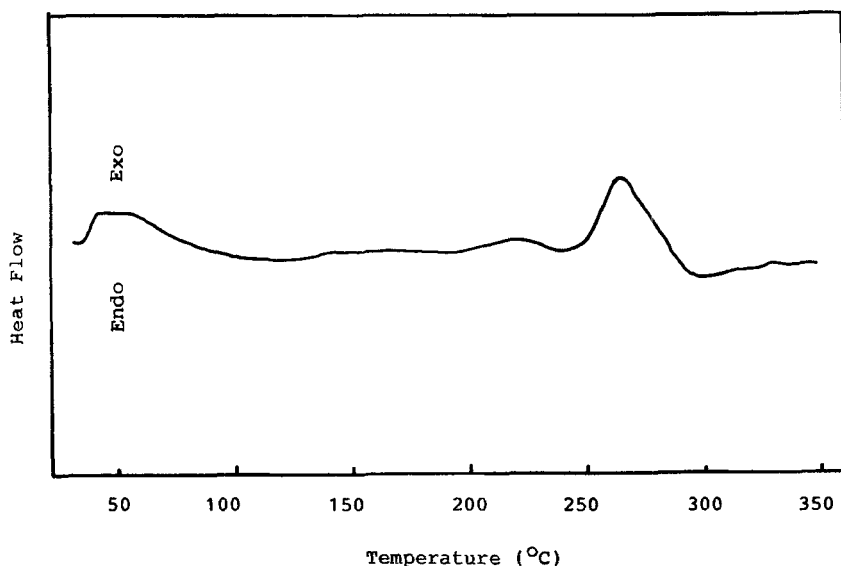


FIG. 6. DSC thermogram of poly(PPO).

Further works on the electrical and nonlinear optical properties of poly(PPO) are now in progress.

CONCLUSIONS

In this article we obtain a new conjugated polymer, poly(PPO), by the polymerization of a propynyl derivative having an oxazolin moiety by using transition metal catalysts. It was found that the PdCl_2 and PtCl_2 catalyst systems are effective for the polymerization of PPO, whereas the Mo- and W-based catalyst systems gave no polymer. From the spectroscopic data it is concluded that the present polymer has a conjugated polymer backbone structure carrying a pendant phenyl oxazoline moiety. It is anticipated that there will be applications of this polymer as polymer electrolytes, NLO materials, and semiconductors.

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