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SYNTHESIS AND PROPERTIES OF POLY(PHENYL PROPARGYL ETHER) AND ITS HOMOLOGUES

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ABSTRACT

Various para-substituted phenyl propargyl ethers (substitutent = H, OMe, and CN) were synthesized and polymerized by transition metal catalyst systems including $MoCl_5$, WCl_6, and $PdCl_2$. The catalytic activity of $MoCl_5$-based catalysts was greater than that of WCl_6-based catalysts for the present polymerization. The polymer yield increased in the following order: H $>$ OMe $>$ CN, according to substitutents. The poly(phenyl propargyl ether) [poly(PPE)] and poly(methoxy phenyl propargyl ether) [poly(OMe-PPE)] obtained are completely soluble in various organic solvents such as chloroform, methylene chloride, THF, and 1,4-dioxane. However, poly(cyanophenyl propargyl ether) [poly(CN-PPE)] is partially soluble in various organic solvents such as those mentioned above. The electrical conductivities of the undoped and iodine-doped polymers and found to be about 10^{-13} and 10^{-4}–10^{-5} S/cm, respectively. The solubilities, thermal properties, and morphologies of the resulting polymers were also studied.

INTRODUCTION

A large number of monosubstituted acetylenes has been polymerized using a wide range of catalysts and polymerization conditions [1, 2]. Polymerization systems include homogeneous and heterogeneous Ziegler–Natta catalysts, transition metal complexes (Pd, W, Mo, Ni, Co), free radical initiators, thermal initiators, and cationic and anionic initiators.

The conjugated olefinic polymers formed by homo- and copolymerization of acetylenes are interesting because they are generally organic semiconductors. The high conductivity of doped polyacetylenes was first observed by Shirakawa et al., about two decades ago [3], and now research on the applications of polyacetylene to such items as polymer batteries and solar cells are in progress in many laboratories. The polymerization of propargyl bromide, propargyl chloride, and propargyl ether derivatives containing methyl, ethyl, *n*-propyl, and *n*-butyl was attempted with $MoCl_5$- and WCl_6-based catalysts. However, these catalysts generally give only insoluble and intractable polymers [4–7]. In recent years we have also reported the polymerization of propargyl amines [8] and the cyclopolymerization of dipropargyl derivatives [9–14].

The present article deals with the polymerization of monosubstituted propargyl ethers containing various para-substituted phenyl derivatives and the physical properties of the resulting polymers.

EXPERIMENTAL

Materials

Propargyl bromide was dried and distilled by recommended procedures [15]. Phenol, 4-methoxy phenol, and 4-cyano phenol (Aldrich Chemical Co.) were used without further purification. Tungsten(IV) and molybdenum(V) chlorides (Aldrich Chemical Co., resublimed, 99%) and organoaluminum compounds (Aldrich Chemical Co., 25% solution in hexane) were used as received. Tetrabutyltin was distilled under reduced pressure. All solvents were purified in the usual manner.

Instruments for Characterization

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AM-300 spectrometer, and chemical shifts were reported in ppm units with tetramethylsilane as the internal standard. Infrared spectra were measured as neat oil or as KBr pellets on a Bomen MB-100 spectrometer, and frequencies are given in reciprocal centimeters. A Shimadzu UV-3100S spectrometer was used for UV spectral data. The number-average molecular weight (M_n) and polydispersity were determined by a Waters GPC-510 calibrated with polystyrene standards in THF solvent. Thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyzer in a nitrogen atmosphere at 10°C/min. Electrical conductivity was measured by the 4-point probe dc method. X-ray diffraction patterns of unoriented samples were obtained on a Rigaku Geigerflex x-ray diffractometer equipped with a Wahrus flat-plate camera using Ni-filtered CuK_α radiation at a scan speed of 4°C/min.

Preparation of Monomers

Scheme 1 outlines the synthesis of the monomers. In a three-neck flask equipped with an additional funnel for solid, a stirrer, and a thermometer, 47 g (0.5 mol) phenol, 77 g (0.65 mol) propargyl bromide, and 400 mL ethanol were added. Then mechanical powdered KOH (24 g, 0.6 mol) was added over 30 minutes to the vigorously stirred mixture. After this addition, the mixture was heated under reflux for 2 hours. The mixture was then cooled and 500 mL ice water added. The layers were separated, and the aqueous layer extracted one time with a small amount of ethyl ether. The extract and main portion were combined, washed with water, and dried over magnesium sulfate. PPE was obtained in 75% yield, bp 80°C/20 mmHg. ^1H NMR (δ, ppm): 2.7 (1H), 4.8 (2H), 7.0-7.7 (5H); IR (NaCl pellet, cm^{-1}): 3288 ($\equiv C-H$), 2122 ($C\equiv C$).

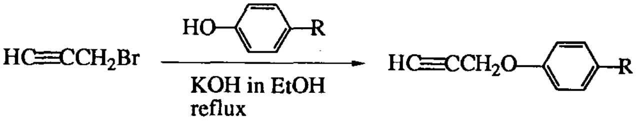
The procedures for OMe-PPE and CN-PPE were prepared by the same procedure used for the preparation of PPE.

OMe-PPE: ^1H NMR (δ, ppm): 2.5 (1H), 3.7 (3H), 4.6 (2H), 6.7-6.9 (4H); ^{13}C NMR (δ, ppm): 55 (OCH_3), 56 (CH_2O), 75 ($C\equiv$), 78 ($HC\equiv$), 114, 116, 149, 154 (phenyl carbons); IR (NaCl pellet, cm^{-1}): 3300 ($\equiv C-H$), 1000 (aromatic C—OMe).

CN-PPE: ^1H NMR (δ, ppm): 2.5 (1H), 4.9 (2H), 7.1-7.7 (4H); ^{13}C NMR (δ, ppm): 56 (CH_2O), 77 ($C\equiv$), 77 ($HC\equiv$), 105, 116, 119, 134 (phenyl carbons), 161 ($C\equiv N$); IR (NaCl pellet, cm^{-1}): 3200 ($\equiv C-H$), 2127 ($C\equiv C$), 1597 (C=C), mp 115°C.

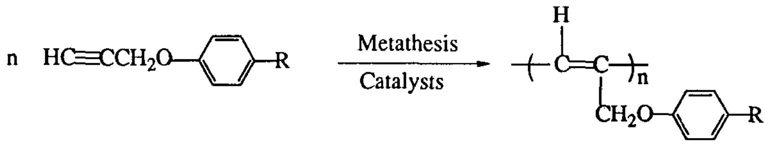
Polymerization

Polymerization was carried out in a dry nitrogen atmosphere because the active species of the catalysts are very sensitive to oxygen and moisture. The catalyst solution, which consisted of two components ($MoCl_5$ and $EtAlCl_2$), was aged at 30°C for 15 minutes before use. A typical polymerization procedure was as follows: In a 20-mL ampule equipped with a rubber septum, 3.04 mL of 0.05 M $MoCl_5$



R = H, PPE
R = OMe OMe-PPE
R = CN CN-PPE

SCHEME 1.



Catalyst: $MoCl_5$, WCl_6, $PdCl_2$

Cocatalyst: $(n\text{-}Bu)_4Sn$, $EtAlCl_2$

R = H, poly(PPE)
R = OMe poly(OMe-PPE)
R = CN poly(CN-PPE)

SCHEME 2.

solution, 0.76 mL of 0.2 M $(n\text{-}Bu)_4Sn$ solution, and 2.8 mL of 1,2-dichloroethane were injected. After aging at 30°C for 15 minutes, 1.0 g PPE was injected in this catalyst solution. After standing at 60°C for 24 hours, the polymerization was terminated with a small amount of methanol. Then 10 mL chlorobenzene was added, and the polymer was isolated by precipitation in a large excess of methanol. The precipitated polymer was filtered from the solution and dried under vacuum at 40°C for 24 hours. The polymer yield was calculated by gravimetry.

TABLE 1. Polymerization of PPE of Various Transition Metal Catalysts[a]

Experiment	Catalyst system[b] (mole ratio)	M/C[c]	$[M]_0$[d]	Polymer yield, %[e]
1	$MoCl_5$	50	1	52
2	$MoCl_5/EtAlCl_2$ (1/1)	50	1	10
3	$MoCl_5/EtAlCl_2$ (1/1)	50	2	18
4	$MoCl_5/(n\text{-}Bu)_4Sn$ (1/1)	50	1	72
5	$MoCl_5/(n\text{-}Bu)_4Sn$ (1/1)	50	2	86
6	WCl_6	50	1	5
7	$WCl_6/EtAlCl_2$ (1/1)	50	1	5
8	$WCl_6(n\text{-}Bu)_4Sn$ (1/1)	50	1	10
9	$PdCl_2$[f]	50	1	30

[a] Polymerization was carried out at 60°C for 24 hours in 1,2-dichloroethane.

[b] Mixture of catalyst and cocatalyst in 1,2-dichloroethane and chlorobenzene was aged for 15 minutes before use as catalyst.

[c] Monomer-to-catalyst mole ratio.

[d] Initial monomer concentration.

[e] Methanol-insoluble polymer.

[f] Polymerization was carried out at 90°C for 24 hours in DMF.

RESULTS AND DISCUSSION

Scheme 2 outlines the polymerization of various monomers with transition metal catalyst systems.

Table 1 shows the results for the polymerization of PPE by various transition metal catalysts. $MoCl_5$ alone gives some moderate yield of polymer. $EtAlCl_2$, which was an effective cocatalyst in the polymerization of 2-ethynylpyridine [16] and propargyl chloride [4] by $MoCl_5$, decreased the polymer yield. However, $(n\text{-Bu})_4Sn$ was found to be a very effective cocatalyst for this polymerization with $MoCl_5$. In general, WCl_6 alone and WCl_6-based catalysts were less effective than $MoCl_5$-based catalysts. $PdCl_2$ polymerized PPE to give poly(PPE) in a 30% yield.

The polymerization of OMe-PPE was carried out with $MoCl_5$- and WCl_6-based catalysts, and the results are summarized in Table 2.

$MoCl_5$-cocatalyst systems were found to be more effective for the polymerization of OMe-PPE than $MoCl_5$ alone. $(n\text{-Bu})_4Sn$ exhibited excellent cocatalyst activity compared to $EtAlCl_2$ for the polymerization of OMe-PPE. These results are similar to those reported for the polymerization of dipropargyl malonate [14, 17]. When WCl_6-based catalysts and $PdCl_2$ were used, the polymerization did not proceed.

TABLE 2. Polymerization of OMe-PPE by Various Transition Metal Catalysts[a]

Experiment	Catalyst system[b] (mole ratio)	M/C[c]	$[M]_0$[d]	Polymer yield, %[e]
1	$MoCl_5$	50	2	22.5
2	$MoCl_5$	100	2	10
3	$MoCl_5/(n\text{-Bu})_4Sn$ (1/1)	50	2	50
4	$MoCl_5/(n\text{-Bu})_4Sn$ (1/4)	50	2	50
5	$MoCl_5/EtAlCl_2$ (1/1)	50	2	15
6	$MoCl_5/EtAlCl_2$ (1/4)	50	2	20
7	WCl_6	50	2	–
8	$WCl_6/(n\text{-Bu})_4Sn$ (1/1)	50	2	Trace
9	$WCl_6/EtAlCl_2$ (1/1)	50	2	Trace
10	$PdCl_2$[f]	50	2	Trace

[a] Polymerization was carried out at 60°C for 24 hours in 1,2-dichloroethane.

[b] Mixture of catalyst and cocatalyst in 1,2-dichloroethane and chlorobenzene was aged for 15 minutes before use as catalyst.

[c] Monomer-to-catalyst mole ratio.

[d] Initial monomer concentration.

[e] Methanol-insoluble polymer.

[f] Polymerization was carried out at 90°C for 24 hours in DMF.

Table 3 shows the results for the polymerization of CN-PPE by transition metal catalysts. The polymer yields were low in comparison to those of PPE and OMe-PPE. The low catalytic activity may be due to the interaction of a heteroatom (CN unit of the phenyl group) with the catalyst, thus hindering triple bond coordination. In contrast to the above-mentioned monomers, $EtAlCl_2$ was found to be especially effective for the polymerization of CN-PPE by $MoCl_5$. In the polymerization of PPE and OME-PPE by $MoCl_5$, the high cocatalytic activity of n-Bu_4Sn was thought to be due to the activation of the $MoCl_5$-$(n\text{-}Bu)_4Sn$ catalyst system by monomer as the third component. On the other hand, in the polymerization of CN-PPE, it can be postulated that the cyano group preferably poisons the catalyst system composed of $MoCl_5$ and n-Bu_4Sn, and the $MoCl_5$-$EtAlCl_2$ catalyst system is not deactivated by the cyano group in the present polymerization. The influence of solvents was also examined by using $MoCl_5$-cocatalysts. It was found that 1,2-dichloroethane, toluene, and chlorobenzene are good solvents for these polymerizations. On the other hand, dioxane and monoglyme were found to be poor solvents.

Polymer Structure

Polymer structure was identified by NMR (^1H and ^{13}C), IR, and UV-visible spectroscopy. Figure 1 shows the ^1H-NMR spectra of poly(OMe-PPE) and poly(CN-PPE). As the polymerization proceeded, the acetylenic proton peak at about 2.5 ppm disappeared, and new vinylic proton peaks appeared at 6.4–7.7 ppm together with the aromatic phenyl ring. It also shows broad methylene protons at 3.5–5.2 ppm. Figure 2 shows the ^{13}C-NMR spectra of OMe-PPE and poly(OMe-PPE). While the acetylenic carbon peaks disappeared at 75 and 78 ppm, carbon peaks on

TABLE 3. Polymerization of CN-PPE by Various Transition Metal Catalysts[a]

Experiment	Catalyst system[b] (mole ratio)	M/C[c]	$[M]_0$[d]	Polymer yield, %[e]
1	$MoCl_5$	50	0.5	17
2	$MoCl_5$	50	1	30
3	$MoCl_5/EtAlCl_2$ (1/4)	25	0.5	20
4	$MoCl_5/EtAlCl_2$ (1/4)	50	0.5	50
5	$MoCl_5(n\text{-}Bu)_4Sn$ (1/4)	25	0.5	10
6	$WCl_6/EtAlCl_2$ (1/4)	25	0.5	15

[a] Polymerization was carried out at 60°C for 24 hours in 1,2-dichloroethane.

[b] Mixture of catalyst and cocatalyst in 1,2-dichloroethane and chlorobenzene was aged for 15 minutes before use as catalyst.

[c] Monomer-to-catalyst mole ratio.

[d] Initial monomer concentration.

[e] Methanol-insoluble polymer.

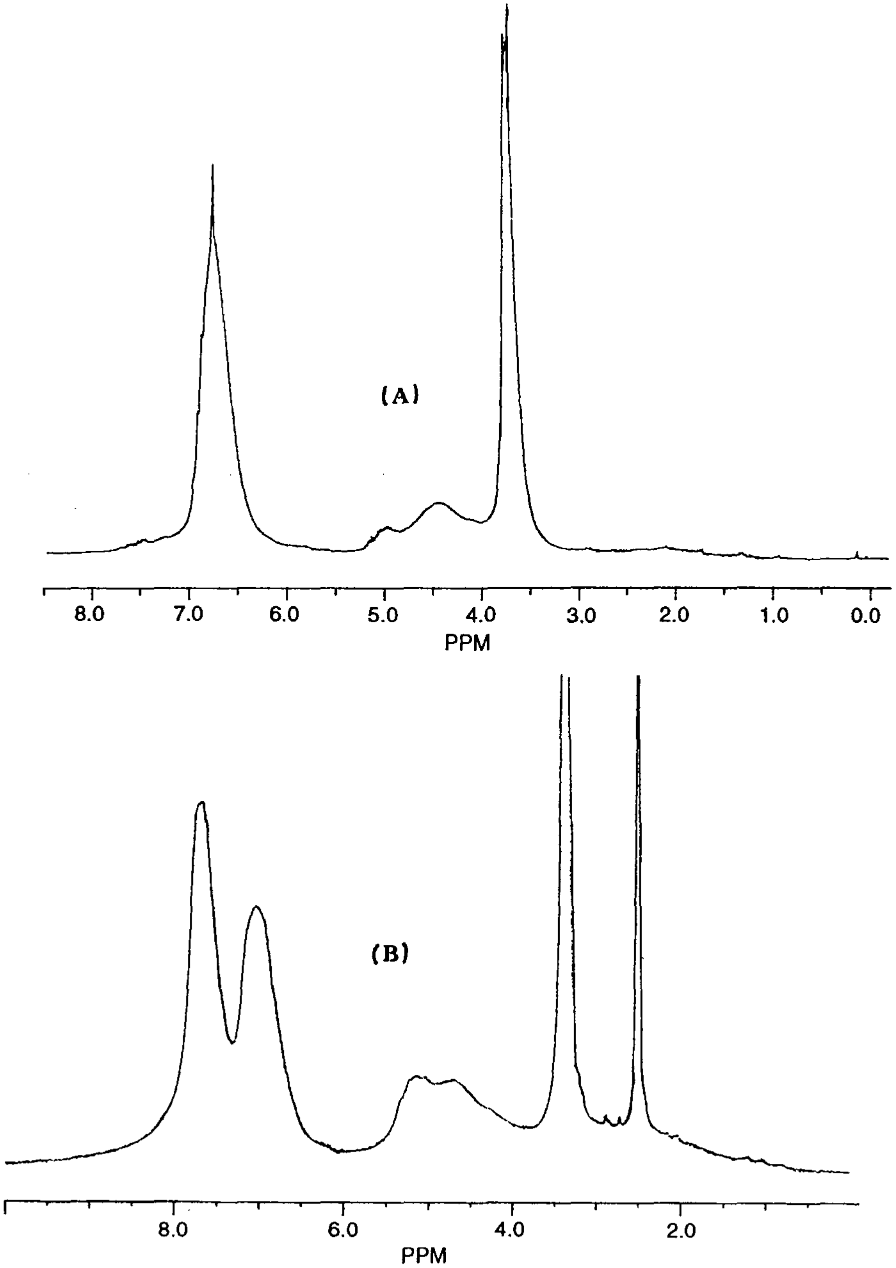


FIG. 1. ^{1}H-NMR spectra of poly(OMe-PPE) (A) and poly(CN-PPE) (B) in $CDCl_3$. (Sample: Experiment 3 in Table 2 and Experiment 5 in Table 3.)

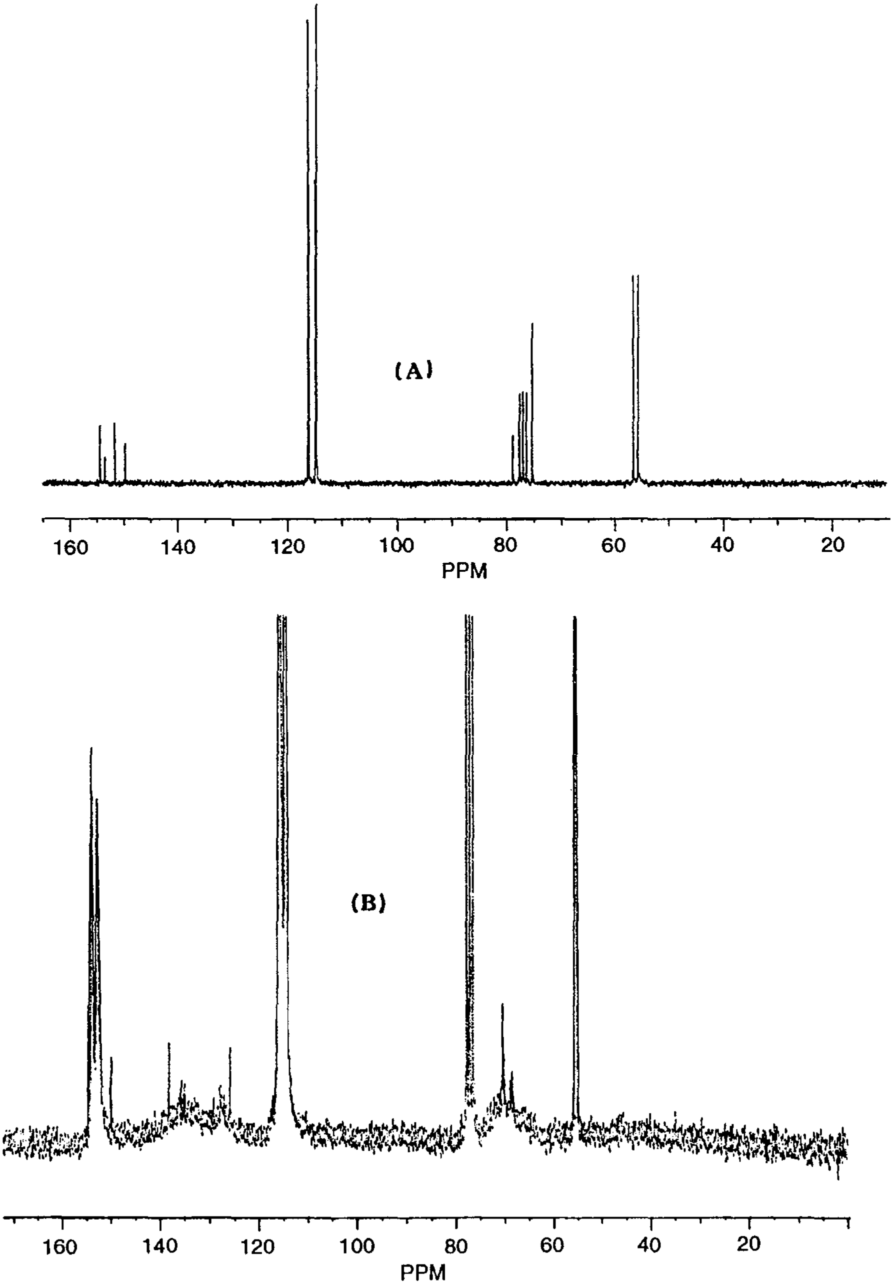


FIG. 2. ^{13}C-NMR spectra of OMe-PPE (A) and poly(OMe-PPE) (B) in $CDCl_3$. (Sample: Experiment 3 in Table 2.)

the conjugated double bond appeared at 128–138 ppm. The peak of the methylene carbon adjacent to the triple bond is shifted from 56 to 71 ppm by polymerization. Figure 3 shows the IR spectra of poly(OMe-PPE) and poly(CN-PPE). The IR spectrum of the polymers showed neither the acetylenic hydrogen stretching nor the carbon—carbon triple bond stretching presented in the IR spectrum of the monomer, respectively. The UV-visible spectra of the polymers were recorded in 1,2-dichloroethane (Fig. 4). A characteristic peak of conjugated polymers appeared in the visible region and is due to the $\pi \rightarrow \pi^*$ transition of conjugated polymers.

Physical Property

Poly(propargyl ethers) having such aliphatic substitutents as methyl, ethyl, *n*-propyl, *n*-butyl, and tetrahydrofuryl substituents were almost insoluble in any organic solvent except for the polymers prepared by $PdCl_2$ [5]. The insolubility of poly(propargyl ethers) prepared by Mo- and W-based catalysts is assumed to be due to the crosslinking of active allyl protons in polymers by catalysts or other factors. However, poly(PPE) and poly(OMe-PPE) were completely soluble in various organic solvents such as chloroform, methylene chloride, THF, and benzene, but insoluble in acetone, *n*-hexane, and ethyl ether. But poly(CN-PPE) was partially soluble in the above-mentioned solvents. The reason for the good solubility of poly(PPE) and poly(OMe-PPE) was deduced to be due to the introduction of a

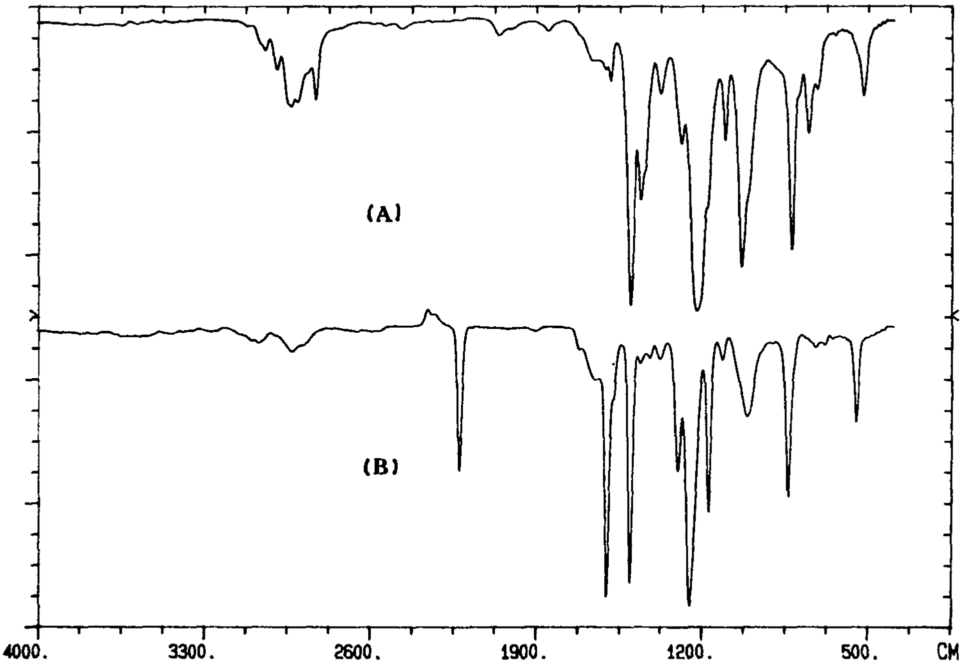


FIG. 3. IR spectra of poly(OMe-PPE) (A) and poly(CN-PPE) (B) in $CDCl_3$. (Sample: Experiment 3 in Table 2.)

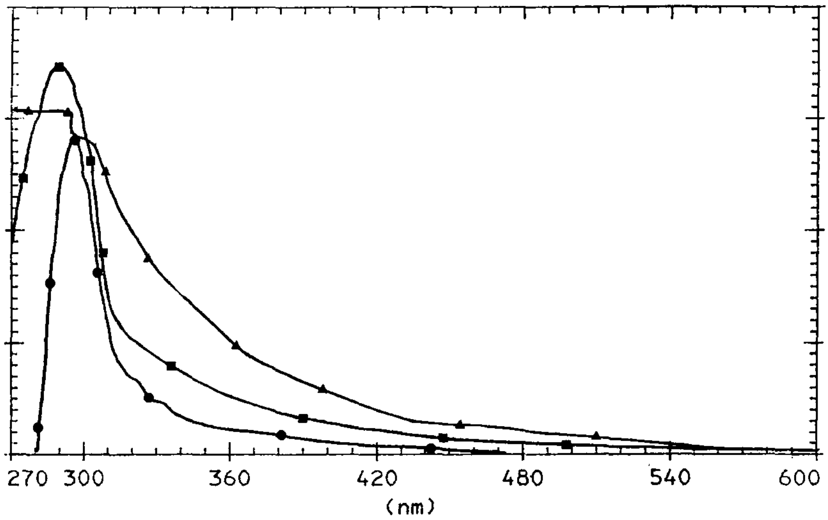


FIG. 4. UV-visible spectra of polymers in 1,2-dichloroethane. [Sample: Experiment 4 in Table 1 (▲), Experiment 3 in Table 2 (■), and Experiment 5 in Table 3 (●).]

substituent (phenyl and *p*-methoxyphenyl) which increased the solubility and/or the homogeneous polymerization by a transition metal and poly(OMe-PPE) to give an ideal conjugated polymer structure carrying each substituent. On the other hand, the poor solubility of poly(CN-PPE) was thought to originate from the crosslinking of the para-substituted cyano group in the polymer.

The molecular weights and colors of the resulting poly(PPE) and its homologues are listed in Table 4. The average molecular weights ($\overline{M}_n$) of poly(PPE) and poly(OMe-PPE) were in the 2,700–15,000 range with polystyrene standards. The polydispersities of these polymers were in the 1.9–3.5 range. Poly(PPE) and poly-

TABLE 4. The Average Molecular Weights and Color of PPE and Its Homologues

Sample	Sample no. (A-B)[a]	Molecular weight[b] (M_n)	M_w/M_n	Color
Poly(PPE)	1-1	2,700	3.5	Yellow
Poly(PPE)	1-4	3,200	3.3	Red
Poly(PPE)	1-5	5,700	2.6	Red
Poly(OMe-PPE)	2-1	12,500	1.9	Dark red
Poly(OMe-PPE)	2-4	15,000	2.5	Dark red
Poly(CN-PPE)	3-2	3,800	2.8	Black
Poly(CN-PPE)	3-4	5,300	3.0	Black

[a] A = Table number, B = sample number.

[b] Molecular weights were measured with a Waters GPC-510 calibrated with polystyrene standards in THF solvent.

(OMe-PPE) were yellow, red, and dark-red colored powders whereas poly(CN-PPE) was a black-colored powder.

Figure 5 shows the TGA thermogram of the resulting polymers. Poly(PPE) is thermally stable up to 200°C and decomposes above this temperature. Poly(PPE) retained 95% of its original weight at 225°C, 70% at 360°C, and 50% at 560°C. Pyrolysis of poly(OMe-PPE) and poly(CN-PPE) showed that 10% of the mass is lost at 208°C, 30% at 290°C, and 56% at 504°C.

Table 5 lists the electrical conductivities of the undoped and iodine-doped polymers. When pressed pellets of the polymers were doped with I_2 for 2 hours at room temperature, the electrical conductivity increased from 10^{-13} to 10^{-4}-10^{-5} S/cm.

We also investigated the morphologies of poly(OMe-PPE) and poly(CN-PPE) by x-ray diffraction analysis (Fig. 6). The data of x-ray diffraction analysis are as

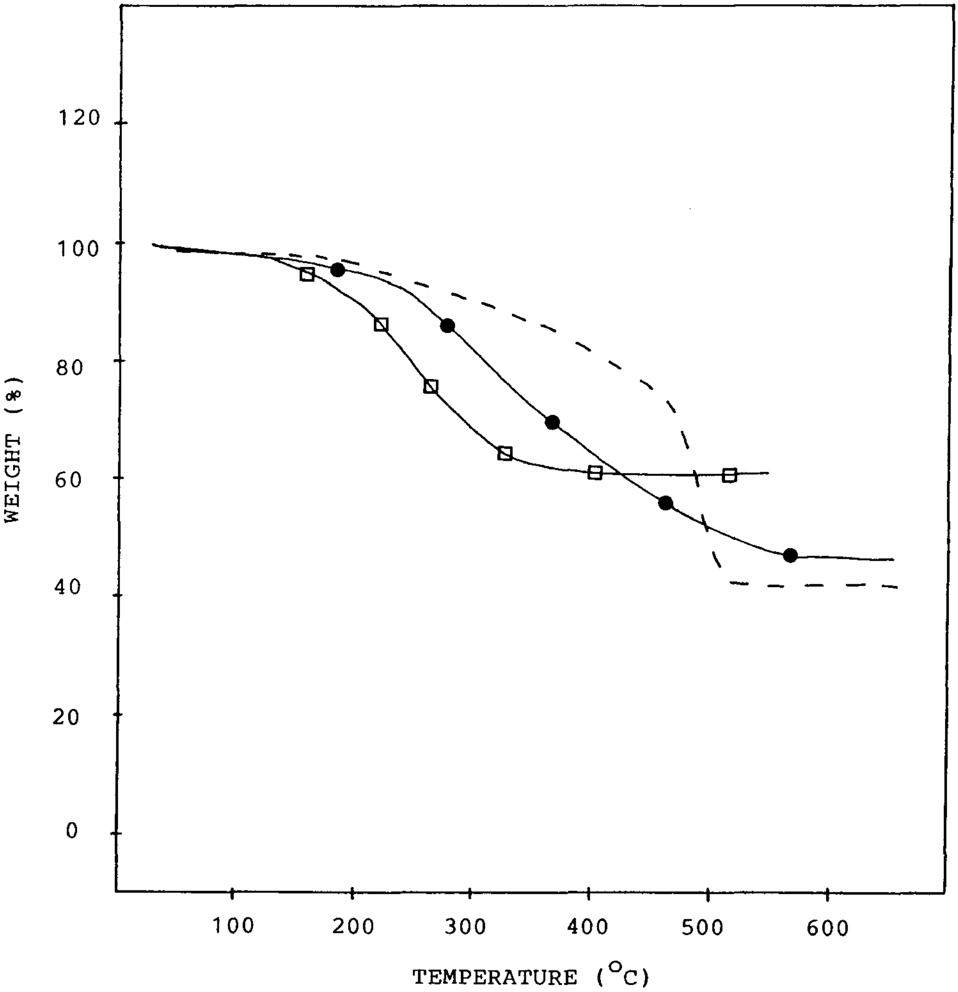


FIG. 5. TGA thermograms of poly(PPE) (●), poly(OMe-PPE) (□), and poly(CN-PPE) (- - -). (Sample: Experiment 4 in Table 1 and Experiment 3 in Table 2.)

TABLE 5. Electrical Conductivity of Poly(PPE) and Its Homologues[a]

Polymer	Composition of doped polymers[b]	Conductivity,[c] S/cm
Poly(PPE)	$(C_9H_8O)_1(I_2)_{0.43}$	6.1×10^{-4}
Poly(OMe-PPE)	$(C_{10}H_{10}O)_1(I_2)_{0.25}$	5.3×10^{-5}
Poly(CN-PPE)	$(C_{10}H_7N)_1(I_2)_{0.13}$	4.9×10^{-5}

[a] Pressed pellets of these polymer were doped by exposure to the vapor of iodine in a vacuum (10^{-1} mmHg).

[b] Extent of doping was obtained by the weight uptake method.

[c] Measured by the 4-point probe dc method.

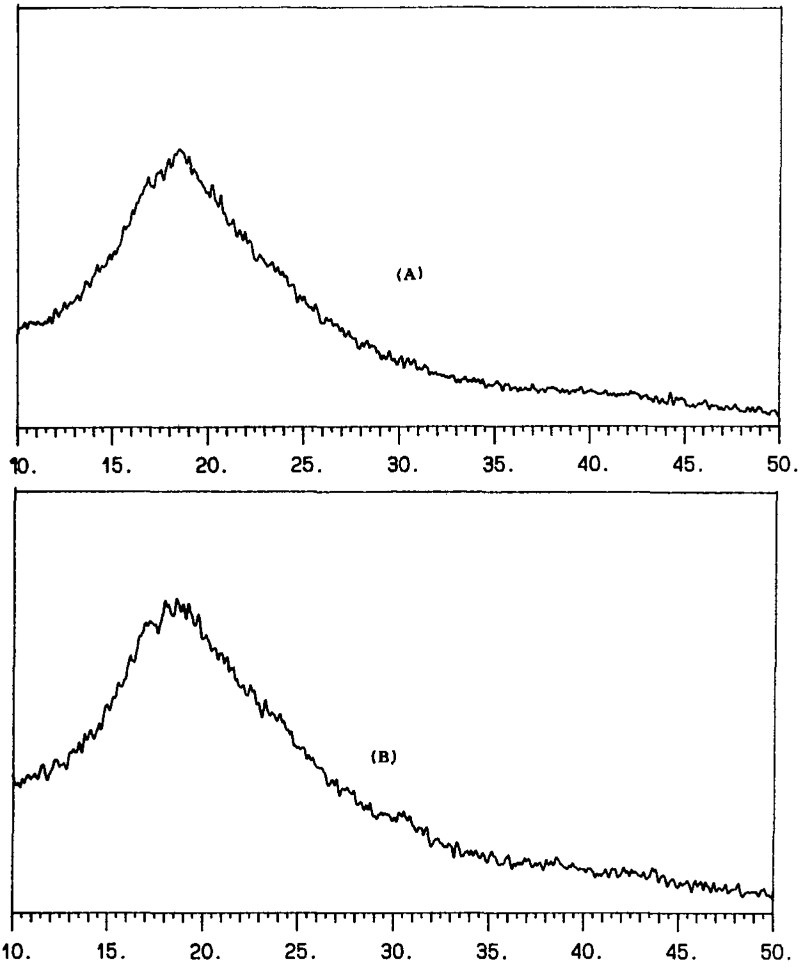


FIG. 6. X-ray diffractograms of poly(OMe-PPE) (A) and poly(CN-PPE) (B). [Sample: Experiment 3 in Table 2 and Experiment 5 in Table 3 (scanning rate = 4°C/min).]

follows: poly(OMe-PPE); 2θ, $(\Delta 2\theta/2\theta)$ = 18.5 (0.59); poly(CN-PPE); 2θ, $(\Delta 2\theta/2\theta)$ = 18.5 (0.68). Because the peaks in the diffraction patterns are all broad, the ratios of the half-height width-to-diffraction angle $(\Delta 2\theta/2\theta)$ are all greater than 0.35. In general, the crystalline diffraction peaks are sharp, hence their $\Delta 2\theta/2\theta$ values are usually smaller than 0.05 [18]. Consequently, it can be concluded that the present polymers are amorphous.

CONCLUSION

In this paper we described the synthesis and properties of monosubstituted polyacetylenes containing various para-substituted phenyl rings. The catalytic activities of Mo-based catalysts were greater than those of W-based catalysts. The polymer structure was identified by various instrumental methods to be a conjugated polyene structure in a polymer backbone. The polymerization yield increased in the following order of substituents: H > OMe > CN. The resulting polymers were colored powders, and the electrical conductivities of iodine-doped polymers increased from 10^{-13} to 10^{-4}-10^{-5} S/cm. X-ray diffraction analysis indicated that the resulting polymers have no crystallinity.

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