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POLYMERIZATION OF α-HYDROXYACETYLENES BY TRANSITION METAL CATALYSTS

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ABSTRACT

α-Hydroxyacetylenes (2-propyn-1-ol, DL-3-butyn-2-ol, 1-octyn-3-ol, 2-phenyl-3-butyn-2-ol) with a hydroxy functional group were polymerized by various Mo- and W-based catalysts. In general, the catalytic activities of Mo-based catalysts were greater than those of W-based catalysts for these polymerizations. In the polymerization of 2-propyn-1-ol, $MoCl_5$ alone and the $MoCl_5$–$EtAlCl_2$ catalyst system gave a quantitative yield of polymer. In the polymerization of 2-propyn-1-ol and its homologues by Mo-based catalysts, the polymer yield decreased as the bulkiness of the substituent increased. On the other hand, the polymer yield increased as the bulkiness of the substituent increased in WCl_6-$EtAlCl_2$-catalyzed polymerization. Polymers with a bulkier substituent showed better solubility in organic solvents than those without a substituent [e.g., poly(2-propyn-1-ol)]. The structures of the resulting polymers were characterized by various instrumental methods such as ^1H- and ^{13}C-NMR, IR, and UV-visible spectroscopies. Thermogravimetric analyses and thermal transitions of the resulting polymers were also studied.

INTRODUCTION

The polymerization of acetylene and its derivatives is a fundamental method for the synthesis of polymers with a conjugated system which can be used as organic semiconductors [1–5], membranes for gas separation [6, 7] and liquid mixture separation [8, 9], as sidechain liquid crystals [10, 11], and for radiation degradation (electron-beam resist) [12–14].

The polymerization of substituted acetylenes has been carried out with a number of catalysts: Mo-, W-, Ta-, Nb-based catalysts [15–19]; Rh^1 complexes [20], metal carbenes [21], metal carbyne [22], phosphine complexes [23, 24], etc.

The polymerization of propargyl derivatives, a monosubstituted acetylene, by other research groups has been restricted to propargyl halides [25], propargyl ethers [25], dipropargyl ether [26], and propiolic acid [27].

In recent years we have reported the polymerization of propargyl halides [28, 29], ethers [30], and amines [31], and the cyclopolymerization of such dipropargyl derivatives as dipropargyl ether [32], sulfide [33], silanes [34], germaniums [35], and diphenylmethane [36].

The polymerization of 2-propyn-1-ol (PO), which has a hydroxy functional group, has been carried out with $PdCl_2$ [25], $NiI_2(Ph_3P)_2$ [37], $Ni(NCS)(C\equiv CR)(Ph_3P)_2$ [37], γ-rays [38], plasma [39], etc. The polymerization of PO by $MoCl_5$ was briefly reported [40]. We also reported on the polymerization of PO by various Mo- and W-based catalysts [41]. The poly(2-propyn-1-ol) [poly(PO)] obtained was insoluble in any organic solvent. Thus, characterization of the polymer structure by various instrumental methods was not performed.

We now report results for the polymerization of PO and its homologues with such substituents as DL-3-butyn-2-ol (BO), 1-octyn-3-ol (OO), and 2-phenyl-3-butyn-2-ol (PBO), and the characterization of the resulting conjugated polymers which carry an α-hydroxy functional group.

EXPERIMENTAL

Materials

PO (Aldrich Chemicals, 99%), BO (Aldrich Chemicals, 99%), OO (Aldrich Chemicals, 96%), and PBO (Aldrich Chemicals, 98+ %) were dried and fractionally distilled by recommended procedures. $MoCl_5$ and WCl_6 (Aldrich Chemicals, resublimed, 99+ %), and organoaluminum compounds [Et_3Al, $(i\text{-}Bu)_3Al$, Et_2AlCl, and

$EtAlCl_2$, Aldrich Chemicals, 1.8 M solution in toluene] were used as received. Tetraphenyltin (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride, Tetra-*n*-butyltin (Aldrich Chemicals, tech., 93%) was used after simple distillation. Molybdenum alkoxide [$Mo(OEt)_5$, High Purity Chemicals] and $PdCl_2$ (Aldrich Chemicals, 99.995%) were used without further purification. All polymerization solvents were analytical-grade materials. They were dried with appropriate drying agents and fractionally distilled.

Preparation of Catalyst Systems

All procedures for catalyst system preparation were carried out under dry nitrogen atmosphere because the active species are sensitive to moisture or oxygen. Transition metal chlorides and ethoxides and organoaluminum compounds were dissolved in chlorobenzene as 0.2, 0.1, and 0.05 M solutions before use. $PdCl_2$ and Ph_4Sn were added as powders to the polymerization ampule.

Polymerization Procedures

A polymerization ampule equipped with a rubber septum was flushed with dry nitrogen. Injections of catalyst solution and monomer were by hypodermic syringes from which air and moisture were carefully excluded.

Polymerization of PO by $MoCl_5$

A solution of $MoCl_5$ (1.78 mL 0.05 M chlorobenzene solution, 0.0892 mmol) and chlorobenzene (2.18 mL, $[M]_0 = 2$) was prepared. To this solution was added PO (0.5 g, 9.33 mmol) at room temperature. The polymerization was carried out at 60°C for 24 hours. Then the polymer solution (inhomogeneous) was diluted with chloroform, and the polymer was purified by pouring it into a large excess of methanol. The polymer was filtered from the solution and dried to constant weight under vacuum at 40°C for 24 hours. The polymer yield was 87%.

Polymerization of BO by $MoCl_5$-$EtAlCl_2$ (1:2)

A catalyst solution was prepared by mixing $MoCl_5$ (0.715 mL 0.2 M chlorobenzene solution, 0.0143 mmol), $EtAlCl_2$ (1.43 mL 0.2 M chlorobenzene solution, 0.0286 mmol), and chlorobenzene (0.855 mL, $[M]_0 = 2.0$) and aged at 30°C for 15 minutes. To this solution was added BO (0.5 g, 7.13 mmol) at room temperature. The polymerization was carried out at 80°C for 24 hours. The polymerization was stopped by adding a small amount of methanol. The resulting polymer was dissolved in DMF/EtOH cosolvent (volume ratio = 1/1), followed by precipitation with excess water. The polymer was filtered from the solution and dried under vacuum at 40°C for 24 hours. The polymer yield was 50%.

Polymerization of OO by $Mo(OEt)_5$-$EtAlCl_2$ (1:2)

A catalyst solution was prepared by mixing $Mo(OEt)_5$ (0.792 mL 0.1 M chlorobenzene solution, 0.0792 mmol), $EtAlCl_2$ (0.792 mL 0.2 M chlorobenzene solution, 0.158 mmol), and chlorobenzene (2.38 mL, $[M]_0 = 2.0$) and aged at 30°C for 15 minutes. To this solution was added OO (0.5 g, 3.96 mmol) at room temperature. The polymerization was carried out at 80°C for 24 hours. The polymerization was stopped by adding a small amount of methanol. The solvent (mainly chlorobenzene) was removed under reduced pressure at 60°C. The resulting polymer was dissolved in DMF/EtOH cosolvent (volume ratio = 1/1), followed by precipitation with excess water. The polymer was filtered from the solution and dried under vacuum at 40°C for 24 hours. The polymer yield was 21%.

Polymerization of PBO by WCl_6-$EtAlCl_2$ (1:2)

A catalyst solution was prepared by mixing WCl_6 (0.684 mL 0.1 M chlorobenzene solution, 0.0684 mmol), $EtAlCl_2$ (0.684 mL 0.2 M chlorobenzene solution, 0.137 mmol), and chlorobenzene (1.55 mL, $[M]_0 = 1.0$) and aged at 30°C for 15 minutes. To this solution was added PBO (0.5 g, 3.42 mmol) at room temperature. The polymerization was carried out at 80°C for 24 hours. The polymerization was stopped by adding a small amount of methanol. The resulting polymer was dissolved in chloroform, followed by precipitation with excess ethyl ether. The precipitated polymer was filtered from the solution and dried under vacuum at 40°C for 24 hours. The polymer yield was 43%.

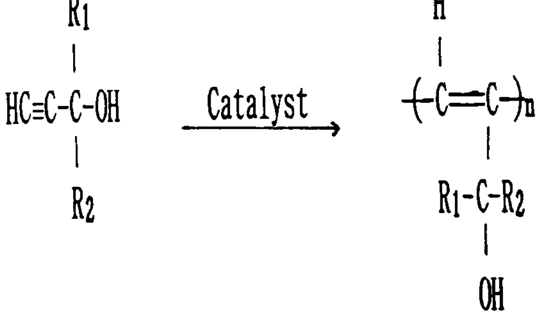
Instruments and Measurement

^1H- and ^{13}C-NMR spectra were recorded on Bruker AM-200 spectrometer in $CDCl_3$. Infrared spectra were obtained with a Bio-Rad Digilab FTS-60 spectrometer using potassium bromide pellets. Ultraviolet (UV) visible spectra were obtained using a Shimadzu UV-3100s spectrophotometer in THF. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min up to 800°C with a DuPont 1090 Analyzer. Inherent viscosities (η_{inh}) of polymers were measured at a concentration of 0.5 g/dL in $CHCl_3$ at 25°C.

RESULTS AND DISCUSSION

Polymerization

The polymerization of PO and its homologues was carried out by various transition metal catalysts.



$$HC{\equiv}C-\overset{R_1}{\underset{R_2}{C}}-OH \xrightarrow{\text{Catalyst}} \left(\overset{H}{C}=\underset{\underset{\underset{OH}{|}}{R_1-C-R_2}}{C} \right)_n$$

where R_1, R_2: H, H; CH_3, H; $(CH_2)_4CH_3$, H; CH_3, C_6H_5.

Table 1 shows the results for the polymerization of PO by Mo-based catalysts. Organotin and organoaluminum compounds, a typical cocatalyst for the polymerization of substituted acetylenes by WCl_6 and $MoCl_5$, were used. *n*-BuLi and ethanol were also used as a cocatalyst. $MoCl_5$ alone resulted in a high yield of polymer. Ph_4Sn showed enhanced cocatalytic activity. The polymer yields were somewhat increased when Et_2AlCl and $EtAlCl_2$ were used as a cocatalyst. The $MoCl_5$-$EtAlCl_2$ catalyst system showed a quantitative yield of polymer. When *n*-BuLi and ethanol were used as a cocatalyst, the polymer yields decreased. The high polymer yield in the polymerization of PO by $MoCl_5$ alone may be explained as the cocatalytic activity of PO reducing $MoCl_5$, although the mechanism is not now fully understood. Good polymerization results by Mo-based catalysts have also been observed in the polymerization of propiolic acid [27], dipropargyl ether [26], and dipropargylcarbinols [43]. Molybdenum ethoxides, such as $Mo(OEt)_5$ and $MoCl_5$-$EtAlCl_2$, polymerized PO to give a moderate yield of polymer.

Table 2 shows the results for the polymerization of PO by W- and Ti-based catalysts. These catalysts gave only a low yield of polymer. The $TiCl_4$-$EtAlCl_2$ catalyst system [29], which was found to be an effective catalyst system for the polymerization of propargyl bromide and propargyl chloride, gave no polymer for the present polymerization of PO.

Table 3 shows the results for the polymerization of PO and its homologues by $MoCl_5$. The polymerization was carried out for 24 hours in chlorobenzene at 80°C. The polymer yield decreased as a bulkier substituent was substituted at the hydroxy carbon. PBO was polymerized by $MoCl_5$ alone to give a 20% yield of polymer.

Tables 4 and 5 show the results for the polymerization of PO and its homologues by the $MoCl_5$-$EtAlCl_2$ and $Mo(OEt)_5$-$EtAlCl_2$ catalyst systems, respectively. The polymerization behaviors were similar to that by $MoCl_5$ alone. When the $Mo(OEt)_5$-$EtAlCl_2$ catalyst system was used, the polymer yield was generally lower compared to what was obtained when $MoCl_5$ and the $MoCl_5$-$EtAlCl_2$ catalyst system

TABLE 1. Polymerization of 2-Propyn-1-ol by Mo-Based Catalysts[a]

Experiment	Catalyst system[b] (mole ratio)	M/C[c]	$[M]_0$[d]	Polymer yield, %
1	$MoCl_5$	100	2	87
2	$MoCl_5$-Ph_4Sn (1:1)	100	2	90
3	$MoCl_5$-Et_2AlCl (1:2)	100	2	95
4	$MoCl_5$-$EtAlCl_2$ (1:2)	100	2	99
5	$MoCl_5$-*n*-BuLi (1:1)	100	2	73
6	$MoCl_5$-EtOH (1:2)	100	2	84
7	$Mo(OEt)_5$	50	1	42
8	$Mo(OEt)_5$-$EtAlCl_2$ (1:2)	50	1	64

[a] Polymerization was carried out for 24 hours in chlorobenzene at 60°C.
[b] Mixture of catalyst and cocatalyst was aged at 30°C for 15 minutes before use.
[c] Monomer-to-catalyst mole ratio.
[d] Initial monomer concentration (M).

TABLE 2. Polymerization of 2-Propyn-1-ol by W- and Ti-Based Catalysts[a]

Experiment	Catalyst system[b] (mole ratio)	M/C[c]	$[M]_0$[d]	Polymer yield, %
1	WCl_6	100	2	7
2	WCl_6-Ph_4Sn (1:1)	100	2	10
3	WCl_6-*n*-Bu_4Sn (1:2)	100	2	7
4	WCl_6-$EtAlCl_2$ (1:2)	100	2	5
5	$W(OEt)_6$	50	1	20
6	$W(OEt)_6$-$EtAlCl_2$ (1:2)	50	1	10
7[e]	$TiCl_4$	100	2	0
8[e]	$TiCl_4$-$EtAlCl_2$ (1:2)	100	2	0

[a] Polymerization was carried out for 24 hours in chlorobenzene at 60°C.
[b] Mixture of catalyst and cocatalyst was aged at 30°C for 15 minutes before use.
[c] Monomer-to-catalyst mole ratio.
[d] Initial monomer concentration (M).
[e] Polymerization solvent was benzene.

were used. The decreasing tendency of polymer yield with increasing bulkiness of the substituent in the polymerization of PO and its derivatives by Mo-based catalysts may be explained by the steric hindrance effect of monomer in the reaction. In addition, the good polymerization results for the polymerization by Mo-based catalysts originated from the activation of $MoCl_5$ by α-hydroxyacetylenes. In another work [43] it was found that PO activated by $MoCl_5$ in the polymerization of phenylacetylene gives an increased polymer yield. As previously described, the WCl_6-$EtAlCl_2$ catalyst system generally shows a relatively low polymer yield (Table 6). However, with a bulky monomer (PBO), the polymer yield was greater than with Mo-based catalyst systems. Similar polymerization behaviors were also observed in

TABLE 3. Polymerization of 2-Propyn-1-ol and Its Homologues by $MoCl_5$[a]

Experiment	Monomer	Polymer yield, %	η_{inh}[b]
1	PO	96	–
2	BO	35	0.10
3	OO	27	0.08
4	PBO	20	0.11

[a] Polymerization was carried out for 24 hours in chlorobenzene at 80°C. Initial monomer concentration ($[M]_0$) and monomer-to-catalyst mole ratio (M/C) were 2 M and 50, respectively.

[b] Measured at a concentration of 0.5 g/dL in chloroform at 25°C.

TABLE 4. Polymerization of 2-Propyn-1-ol and Its Homologues by $MoCl_5$-$EtAlCl_2$ (1:2)[a]

Experiment	Monomer	Polymer yield, %	η_{inh}[b]
1	PO	99	–
2	BO	50	0.13
3	OO	35	0.09
4	PBO	29	0.14

[a] Polymerization was carried out for 24 hours in chlorobenzene at 80°C. Initial monomer concentration ($[M]_0$) and monomer-to-catalyst mole ratio (M/C) were 2 M and 50, respectively. Mixture of catalyst and cocatalyst was aged at 30°C for 15 minutes before use.

[b] Measured at a concentration of 0.5 g/dL in chloroform at 25°C.

the cyclopolymerization of dipropargyl sulfide, sulfoxide, and sulfone which have or do not have an oxygen atom (due to the activation effect of oxygen and the steric effect) [44].

Polymer Structure

The molecular structure of polymers carrying an α-hydroxy functional group was characterized by IR, NMR, and UV-visible spectroscopies.

Figure 1 shows the infrared spectra of polymers from PO and its homologues obtained by $MoCl_5$-$EtAlCl_2$. The infrared spectra of these polymers show neither the acetylenic hydrogen stretching frequency nor the carbon—carbon triple bond

TABLE 5. Polymerization of 2-Propyn-1-ol and Its Homologues by $Mo(OEt)_5$-$EtAlCl_2$ (1:2)[a]

Experiment	Monomer	Polymer yield, %	η_{inh}[b]
1	PO	75	–
2	BO	40	0.07
3	OO	21	0.06
4	PBO	5	–

[a] Polymerization was carried out for 24 hours in chlorobenzene at 80°C. Initial monomer concentration ($[M]_0$) and monomer-to-catalyst mole ratio (M/C) were 2 M and 50, respectively. Mixture of catalyst and cocatalyst was aged at 30°C for 15 minutes before use.

[b] Measured at a concentration of 0.5 g/dL in chloroform at 25°C.

TABLE 6. Polymerization of 2-Propyn-1-ol and Its Homologues by WCl_6-$EtAlCl_2$ (1:2)[a]

Experiment	Monomer	Polymer yield, %	η_{inh}[b]
1	PO	9	–
2	BO	13	0.07
3	OO	15	0.05
4	PBO	43	0.15

[a] Polymerization was carried out for 24 hours in chlorobenzene at 80°C. Initial monomer concentration ($[M]_0$) and monomer-to-catalyst mole ratio (M/C) were 1 M and 50, respectively. Mixture of catalyst and cocatalyst was aged at 30°C for 30 minutes before use.

[b] Measured at a concentration of 0.5 g/dL in chloroform at 25°C.

stretching frequency appearing in the infrared spectra of monomers. Instead, the carbon—carbon double bond stretching frequencies at 1580–1700 cm^{-1} indicate the formation of a conjugated polymer.

The poly(PO) was insoluble in organic solvents regardless of the polymerization conditions and the catalysts used. Thus, the exact polymer structure was not characterized by NMR and UV-visible spectroscopies. Figure 2 shows the ^1H-NMR spectra of soluble poly(BO), poly(OO), and poly(PBO) in $CDCl_3$. The ^1H-NMR spectrum (A) of poly(BO) does not show the acetylenic proton peak at 2.6 ppm observed in the ^1H-NMR spectrum of BO. Instead, the broad vinyl proton peak in the conjugated polymer backbone is observed at about 6.5 ppm. The ^1H-NMR spectrum (B) of poly(OO) with its long alkyl (*n*-pentyl) chain shows alkyl proton peaks at 0.5–1.8 ppm and methine protons adjacent to the hydroxy carbon at 1.8–2.7 ppm. The two broad peaks at 5.9 and 6.9 ppm may be assignable to the vinyl protons in the conjugated polymer backbone. The ^1H-NMR spectrum (C) of poly(PBO) shows phenyl and vinyl protons at 6.5–8.3 ppm. It also shows methyl and hydroxy protons at 1.0–4.0 ppm with featureless broad peaks.

Figure 3 shows the ^{13}C-NMR spectra of soluble poly(BO), poly(OO), and poly(PBO) in $CDCl_3$. These spectra do not show the acetylenic C≡C peaks (81–87 and 71–74 ppm) observed in the ^{13}C-NMR spectra of monomers. Instead, in most cases the new characteristic C=C double bond peaks in the polymer backbone were observed between 120 and 147 ppm.

Figure 4 shows the UV-visible spectra of poly(BO), poly(OO), and poly(PBO) in THF. A $\pi \rightarrow \pi^*$ absorption peak of conjugated double bonds in the polymer main chain, which are absent in the monomers, appear in the visible region (400–600 nm).

Physical Properties

The solubility test was performed for the polymer samples in excess solvent. As previously described, poly(PO) is insoluble in any organic solvent regardless of

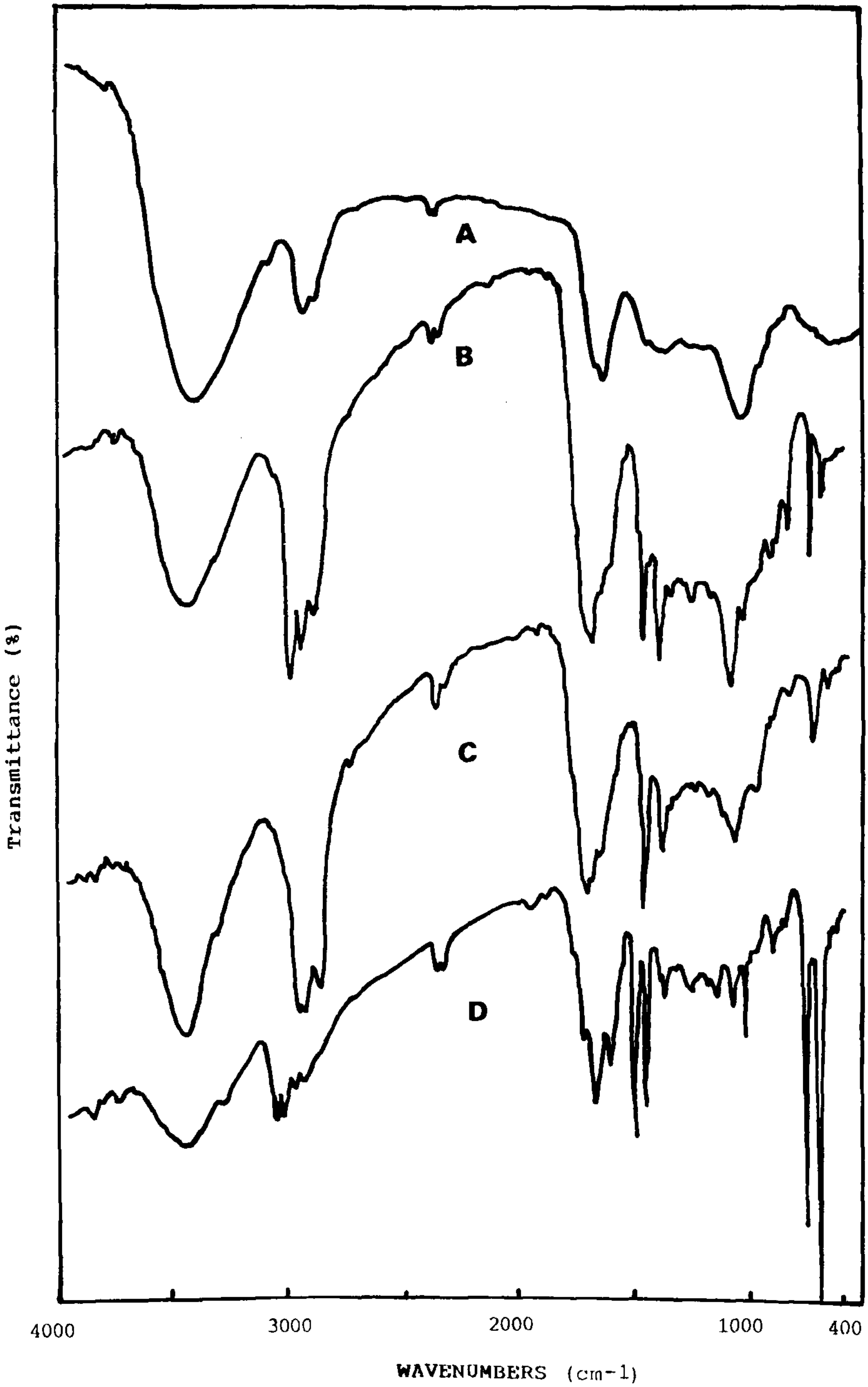


FIG. 1. Infrared spectra of poly(PO) [A], poly(BO) [B], poly(OO) [C], and poly(POB) [D] in KBr pellet.

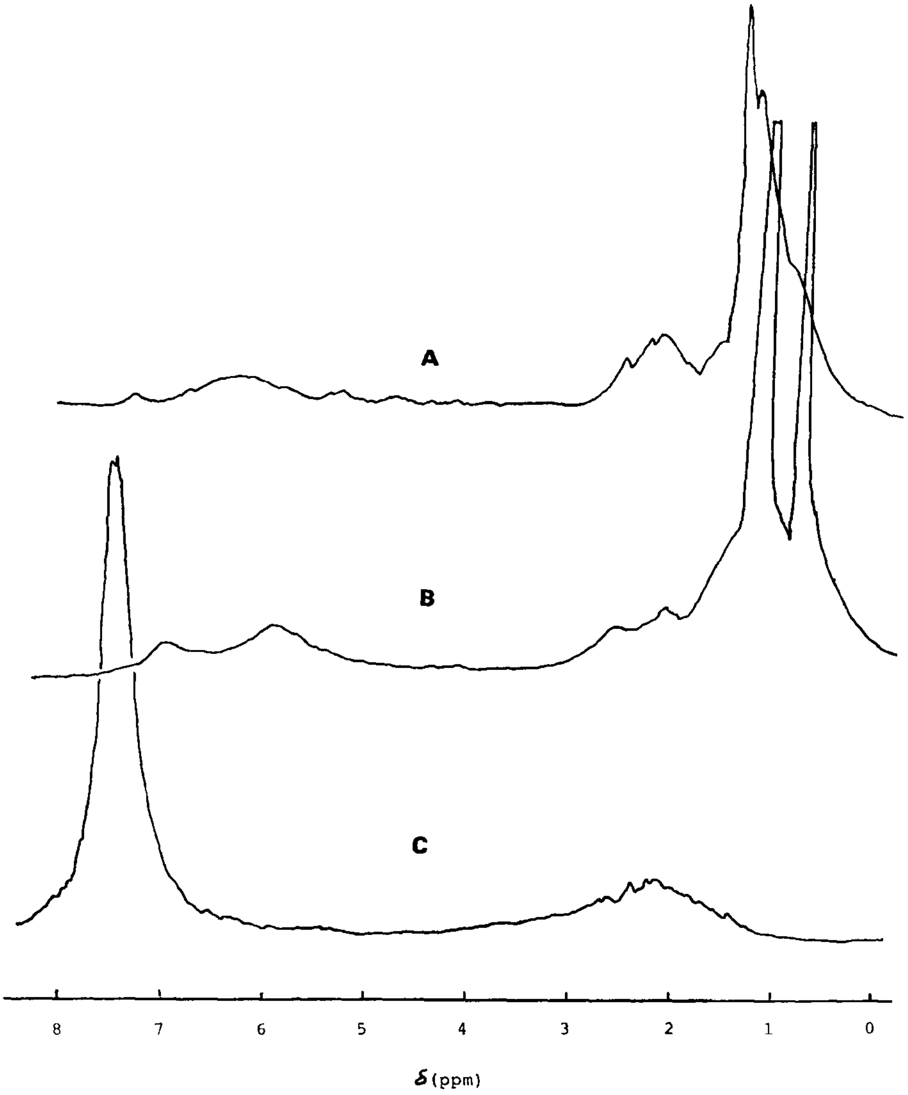


FIG. 2. ^{1}H-NMR spectra of poly(BO) [A], poly(OO) [B], and poly(PBO) [C] in $CDCl_3$.

the polymerization conditions and the catalysts used. This phenomenon was assumed to be caused by crosslinking of the resulting polymer by activated allyl protons. In general, poly(BO) was partially soluble (about 50% of the total polymer yield) in aromatic and halogenated hydrocarbon solvents such as chlorobenzene, benzene, chloroform, THF, etc. Poly(OO) and poly(PBO) were complete soluble in aromatic and halogenated hydrocarbon solvents. Poly(PO), poly(BO), and poly(PBO) were mostly brown or black powders. Poly(OO) was a black powder with a low melting temperature.

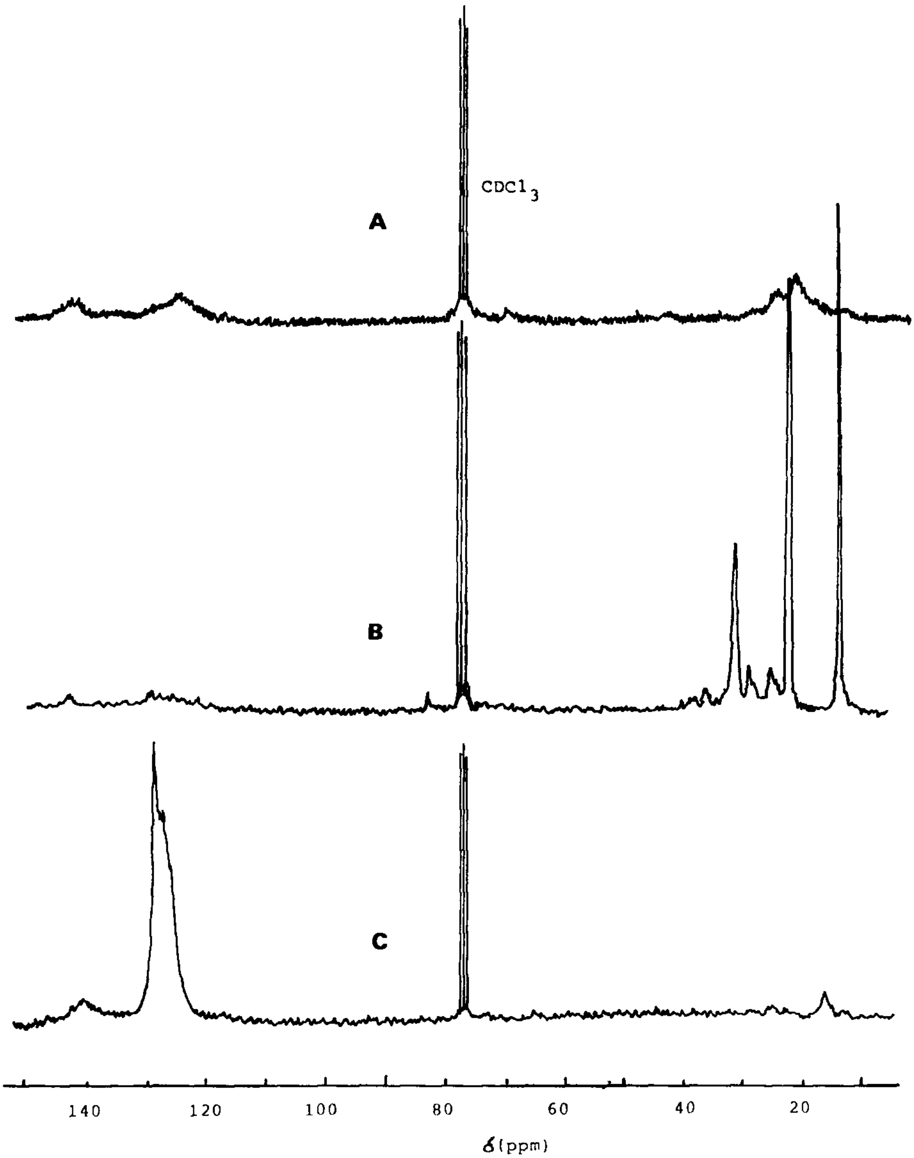


FIG. 3. ^{13}C-NMR spectra of poly(BO) [A], poly(OO) [B], and poly(PBO) [C] in $CDCl_3$.

Figure 5 shows the TGA thermograms of poly(PO), poly(BO), poly(OO), and poly(PBO). In the case of poly(PO), an enhanced weight loss below 200°C was observed. Poly(OO) also shows an enhanced weight loss at about 200°C, whereas poly(BO) and poly(PBO) exhibit a gradual weight loss up to 450°C. The weight loss at low temperature seems to be due to moisture, solvent, and catalyst residues although it has not been fully characterized.

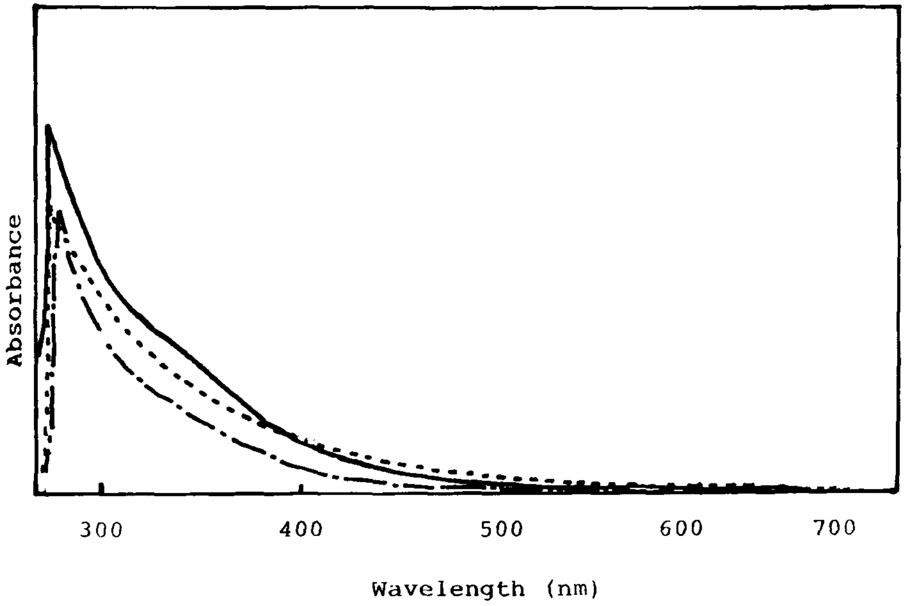


FIG. 4. UV-visible spectra of poly(BO) [——], poly(OO) [· –], and poly(PBO) [· · ·] in THF.

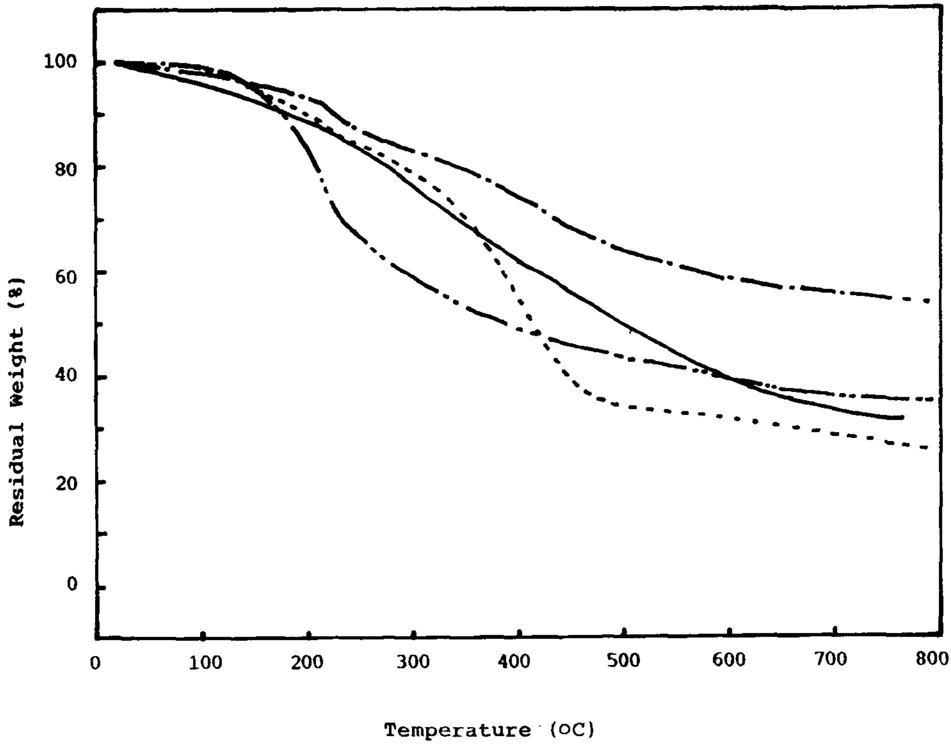


FIG. 5. TGA thermograms of poly(PO) [——], poly(BO) [– · –], poly(OO) [– · · –], and poly(PBO) [· · ·].

CONCLUSIONS

In this article we describe the polymerization behaviors of PO and its homologues by Mo- and W-based transition metal catalysts. PO was easily polymerized to give a quantitative yield of polymer with Mo-based catalyst systems, especially $MoCl_5$-$EtAlCl_2$. In most cases the catalytic activities of Mo-based catalysts were found to be more effective than those of W-based catalysts. The high polymer yield for the polymerization of Mo-based catalyst system originates from the activation of $MoCl_5$ by PO and its homologues with an α-hydroxy functional group. The decreasing phenomenon of polymer yield with increasing bulkiness of the substituent in the Mo-based catalyst systems was judged by the steric hindrance of α-hydroxyacetylene. However, in the case of W-based catalyst systems, a quite different polymerization behavior was observed. It originated through the poisoning effect of WCl_6 by the hydroxy group of monomer. It is believed that the extent of deactivation of WCl_6 by α-hydroxyacetylene increases with smaller substituents on the hydroxy carbon. The polymers, except poly(PO), were generally soluble in aromatic and halogenated hydrocarbon solvents when a substituent was introduced at the hydroxy carbon.

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