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POLYMERIZATION OF HYDROXYALKYLACETYLENES BY TRANSITION METAL CATALYSTS

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ABSTRACT

The polymerization of hydroxyalkylacetylenes [$HC{\equiv}C(CH_2)n$-OH, $n = 1$–4) was carried out with various transition metal catalysts. Mo-based catalysts and $PdCl_2$ were very effective for the polymerization of hydroxyalkylacetylenes. The polymer yields generally decreased as the number of methylene units between the hydroxy and acetylene functional groups increased from 1 to 4. Polymer solubility increased as the number of methylene units increased. The resulting polymers had a conjugated polyene structure with linear hydroxyalkyl substituents. The resulting polymers were black or light-brown powders. The thermal properties were studied by thermogravimetric analysis. X-ray diffraction analysis data indicated that the polymers are mostly amorphous.

INTRODUCTION

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

The polymerization of acetylene derivatives having a hydroxy functional group has been restricted to such cases as 2-propyn-1-ol [15–18], 3-butyn-2-ol [19], 1-ethynyl-1-cyclohexanol [20, 21], and 9-ethynyl-9-fluorenol [22]. Catalyst systems included $PdCl_2$ [16], $NiI_2(Ph_3P)_2$ [17], $Ni(NCS)(C{\equiv}CR)(Ph_3P)_2$ [17], $Ni(CO)_2$-

$(Ph_3P)_2$ [20], $Rh(COD)Cl_2/NaOH$ (COD: *cis,cis*-cyclooctadiene) [22], γ-rays [23], plasma [18], etc.

In recent years we have studied the polymerization behaviors of such α-hydroxyacetylenes as 2-propyn-1-ol [24, 25], 1-octyn-3-ol [26], 2-phenyl-3-butyn-2-ol [26], and 1-ethynyl-1-cyclohexanol [27] by molybdenum- and tungsten-based catalysts.

Now we report our results for the polymerization of acetylene derivatives having linear methylene between acetylene and hydroxy functional groups [$HC{\equiv}C\text{-}(CH_2)_nOH$, $n = 1\text{-}4$] and the characterization of the resulting polymers which carry the hydroxymethylene functional group.

EXPERIMENTAL

Materials

2-Propyn-1-ol (PO, Aldrich Chemicals, 99%), 3-butyn-1-ol (BO, Aldrich Chemicals, 99%), 4-pentyn-1-ol (PEO, Aldrich Chemicals, 98%), and 5-hexyn-1-ol (HO, Aldrich Chemicals, 96%) were dried and fractionally distilled by recommended procedures. $MoCl_5$ and WCl_6 (Aldrich Chemicals, resublimed, 99+%) and $EtAlCl_2$ (Aldrich Chemicals, 1.8 M solution in toluene) were used as received. $PdCl_2$ (Aldrich Chemicals, 99.995%) was used without further purification. The polymerization solvents were analytical grade materials. They were dried with appropriate drying agent and fractionally distilled.

Polymerization Procedures

All procedures for catalyst solution preparation and polymerization were carried out under a dry nitrogen atmosphere because the active species are sensitive to moisture and oxygen. $MoCl_5$, WCl_6, and $EtAlCl_2$ were dissolved in chlorobenzene as 0.1 and 0.2 M solutions before use. $PdCl_2$ was added as a powder to a polymerization ampule equipped with a rubber septum and which was flushed with nitrogen. Injections of catalyst solution and monomer were made by means of hypodermic syringes. The polymer yield was calculated by gravimetry.

Polymerization of PO by $MoCl_5$

A solution of $MoCl_5$ (1.78 mL of a 0.1 M solution, 0.178 mmol) and chlorobenzene (2.18 mL, $[M]_0 = 2$) was prepared. To this solution was added PO (0.5 g, 9.33 mmol). Polymerization proceeded at 60°C for 24 hours. After a given polymerization time, the polymer solution 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 under vacuum at 40°C for 24 hours. The polymer yield was quantitative.

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

A catalyst solution was prepared by mixing $MoCl_5$ (0.426 mL of a 0.1 M solution, 0.143 mmol), $EtAlCl_2$ (1.426 mL of a 0.2 M solution, 0.0286 mmol), and chlorobenzene (0.168 mL, $[M]_0 = 2$) and aged at 30°C for 15 minutes. To this solution was added BO (0.5 g, 7.134 mmol). The polymerization was carried out at 60°C for 24 hours. Then the polymerization solvent (chlorobenzene) was removed by vacuum pumping below 40°C. To this sample was added a cosolvent (DMF/ethanol, volume ratio of 3/1). The resulting polymer solution was precipitated into a large excess of distilled water. The polymer was filtered from the solution and dried under vacuum at 40°C for 24 hours. The polymer yield was 95%.

Polymerization of PEO by $PdCl_2$

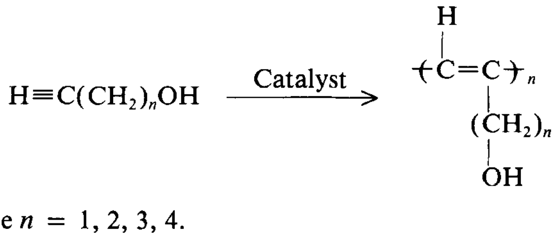
$PdCl_2$ (0.0211 g, 0.119 mmol) was dissolved in DMF (5.39 mL, $[M]_0 = 1.0$) at 90°C. To this catalyst solution was added PEO (0.5 g, 5.94 mmol). After 24 hours at 90°C, 10 mL cosolvent (DMF/ethanol, volume ratio of 1/1) was added. The polymer solution was precipitated into a large excess of distilled water. The polymer was filtered from the solution and dried under vacuum at 40°C for 24 hours. The polymer yield was 59%.

Instruments and Measurement

NMR (^1H and ^{13}C) spectra were recorded on a Bruker AM-200 spectrometer in $CDCl_3$, and chemical shifts were reported in ppm units with tetramethylsilane as the internal standard. Infrared spectra were obtained with a Bio-Rad Digilab FTS-60 spectrometer using potassium bromide pellets. Ultraviolet-visible spectra were obtained using chloroform in a Shimadzu UV-3100s spectrophotometer. The average molecular weights of polymers were measured by means of a Waters GPC-510 using calibration curves 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. X-ray diffraction patterns of the polymer 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°/min.

RESULTS AND DISCUSSION

The polymerization of acetylene derivatives carrying hydroxyalkyl functional groups was carried out with various transition metal catalysts.



$$\mathrm{H{\equiv}C(CH_2)_nOH} \xrightarrow{\text{Catalyst}} \left(\overset{\mathrm{H}}{\mathrm{C}}=\underset{\underset{\mathrm{OH}}{\mathrm{(CH_2)_n}}}{\mathrm{C}}\right)_n$$

where $n = 1, 2, 3, 4$.

Polymerization of Hydroxyalkylacetylenes

$MoCl_5$-based catalyst systems exhibited high catalytic activity in the polymerization of PO [25]. The polymerization of PO proceeded well in various aromatic and halogenated hydrocarbon solvents. However, the resulting poly(PO) was insol-

TABLE 1. Polymerization of $HC{\equiv}C(CH_2)_nOH$ by $MoCl_5$[a]

Experiment	n	Polymer yield, %	$\overline{M}_n$
1	1	100	–
2	2	91	–
3	3	45	2020
4	4	30	1650

[a] Polymerization was carried out at 60°C for 24 hours in chlorobenzene. Initial monomer concentration ($[M]_0$) and monomer-to-catalyst mole ratio (M/C) were 2 M and 50, respectively.

TABLE 2. Polymerization of $HC{\equiv}C(CH_2)_nOH$ by $MoCl_5$-$EtAlCl_2$ (1:2)[a]

Experiment	n	Polymer yield, %	$\overline{M}_n$
1	1	99	–
2	2	95	–
3	3	63	2600
4	4	35	1420

[a] Polymerization was carried out at 60°C for 24 hours in chlorobenzene. Initial monomer concentration ($[M]_0$) and monomer-to-catalyst mole ratio (M/C) were 2 M and 50, respectively. The mixture of $MoCl_5$ and $EtAlCl_2$ solution was aged at 30°C for 15 minutes before use.

TABLE 3. Polymerization of $HC{\equiv}C(CH_2)_nOH$ by $PdCl_2$[a]

Experiment	n	Polymer yield, %	$\overline{M}_n$
1	1	100	–
2	2	67	–
3	3	59	1710
4	4	55	1570

[a] Polymerization was carried out at 90°C in DMF for 24 hours. Initial monomer concentration ($[M]_0$) and monomer-to-catalyst mole ratio (M/C) were 1 M and 50, respectively.

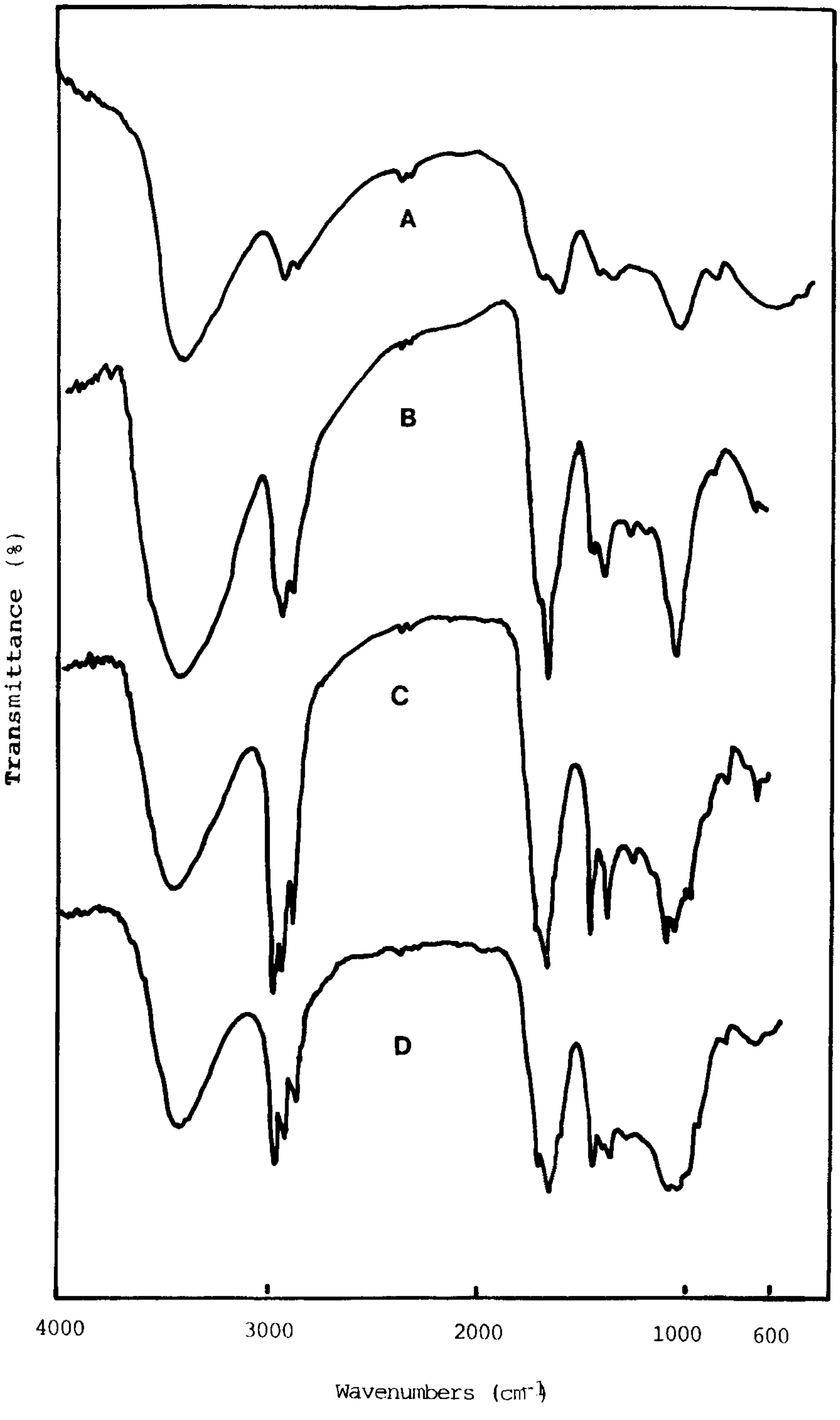


FIG. 1. FT-IR spectra of poly(PO) [A], poly(BO) [B], poly(PEO) [C], and poly(HO) [D] in KBr pellets.

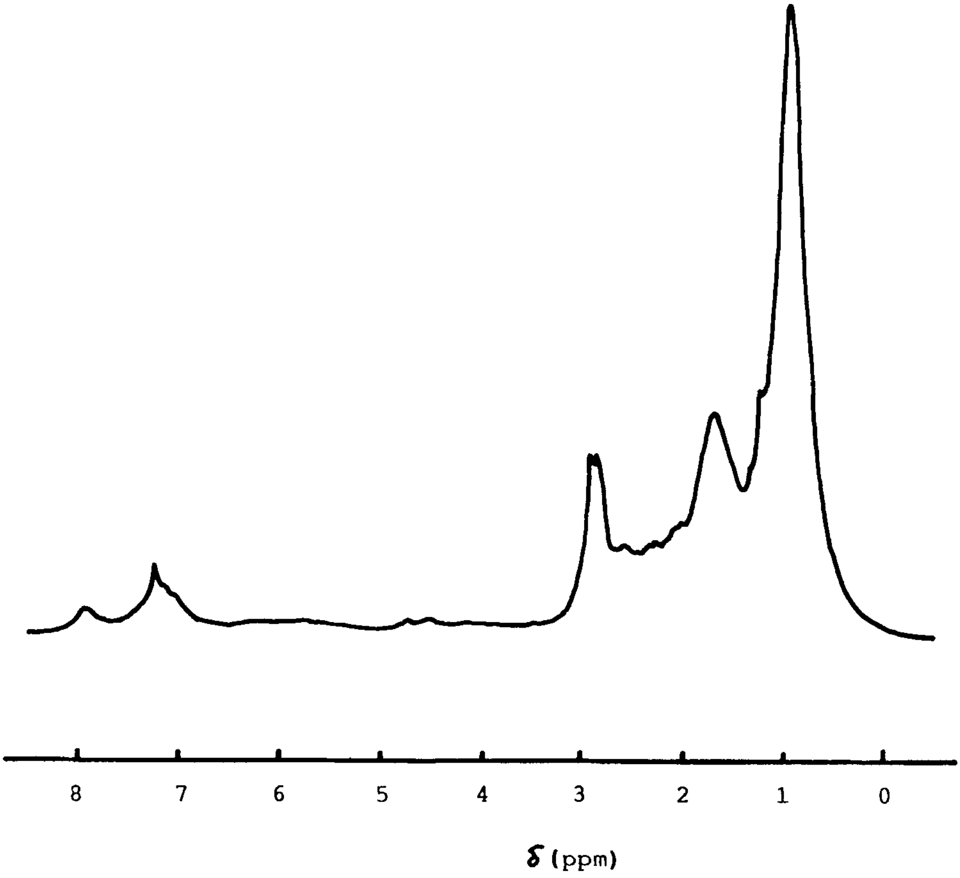


FIG. 2. ^{1}H-NMR spectrum of poly(PEO) in $CDCl_3$.

uble in such organic solvents as chloroform, THF, DMF, and DMSO, regardless of the polymerization conditions and the catalyst used.

Table 1 shows the results for the polymerization of hydroxylalkyl acetylenes by $MoCl_5$. It has been known that $MoCl_5$-based catalysts are very effective for the polymerization of some acetylene derivatives, especially those containing oxygen atoms, such as propiolic acid [28], dipropargyl ether [29], and dipropargylcarbinols [30]. When $n = 1$ or 2, the polymerizations gave a high polymer yield. However, the resulting polymers were mostly insoluble in organic solvents. As the alkyl chain length between the acetylene and hydroxy functional groups is increased, the polymerization reaction occurs more smoothly and the polymer yield is gradually decreased. However, when $n = 3$ or 4, the polymers were soluble in such organic solvents as chloroform, chlorobenzene, and THF.

Table 2 shows the results for the polymerization of hydroxyalkylacetylenes by the $MoCl_5$-$EtAlCl_2$ catalyst system. In previous work we found that organoaluminum compounds, especially $EtAlCl_2$, were very effective cocatalysts for the polymerization of such acetylene derivatives as 2-ethynylpyridine [31], propargyl halide

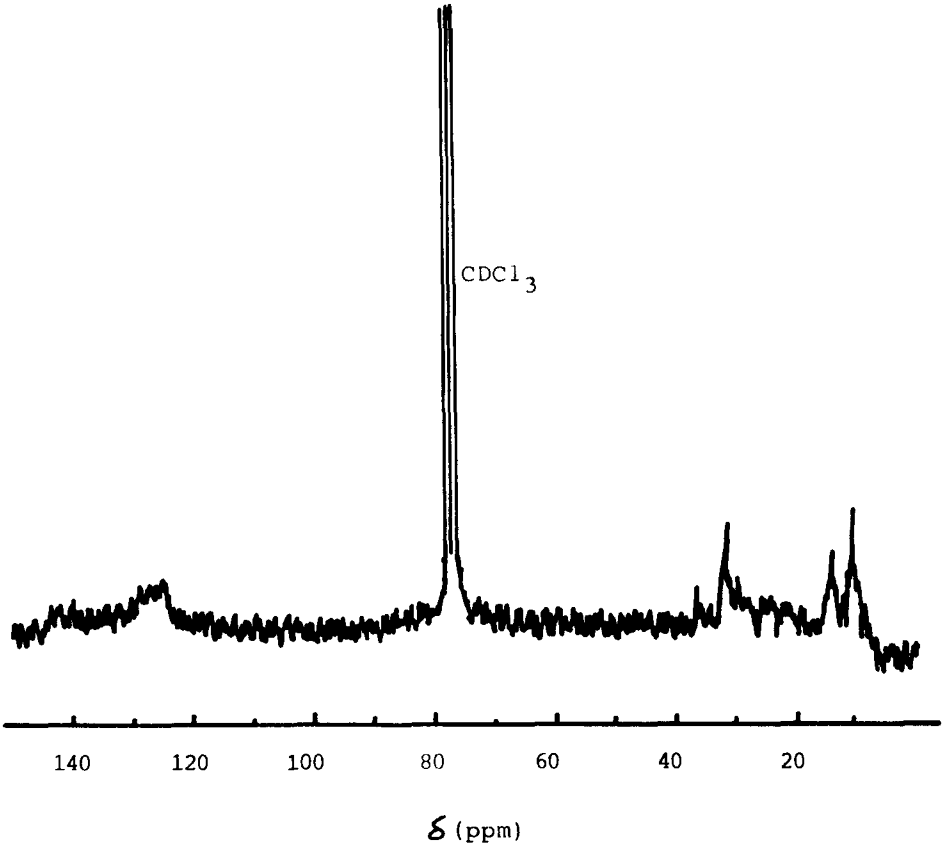


FIG. 3. ^{13}C-NMR spectrum of poly(PEO) in $CDCl_3$.

(halide = Br, Cl) [32], and dipropargylgermaniums [33] by $MoCl_5$ or WCl_6. In the present case the polymerization results obtained with $MoCl_5$-$EtAlCl_2$ were similar to those observed in the polymerization by $MoCl_5$.

The high catalytic activity of $MoCl_5$ and $MoCl_5$–$EtAlCl_2$ for the polymerization of hydroxyalkylacetylenes can be explained as being due to the activating role of an acetylene monomer with a hydroxy functional group, although the mechanism is not fully understood.

The polymerization of hydroxyalkylacetylenes by WCl_6–$EtAlCl_2$ was also carried out. The WCl_6–$EtAlCl_2$ catalyst system gave only a low yield (7%) of polymer for PO. On the other hand, polymerization did not proceed for other hydroxyalkylacetylenes. The low catalytic activity of WCl_6-based catalysts for the present polymerization of hydroxyalkylacetylenes is thought to be due to poisoning of WCl_6 by the hydroxy group. Similar results were observed for the polymerization of such hydroxy group-containing acetylenes as dipropargylcarbinol [30], 1-octyn-3-ol [26], and 1-ethynyl-1-cyclohexanol [27].

Table 3 shows the results for the polymerization of hydroxyalkylacetylenes by $PdCl_2$ in DMF. In most cases, polymerization proceeded well. When $n = 1$, the

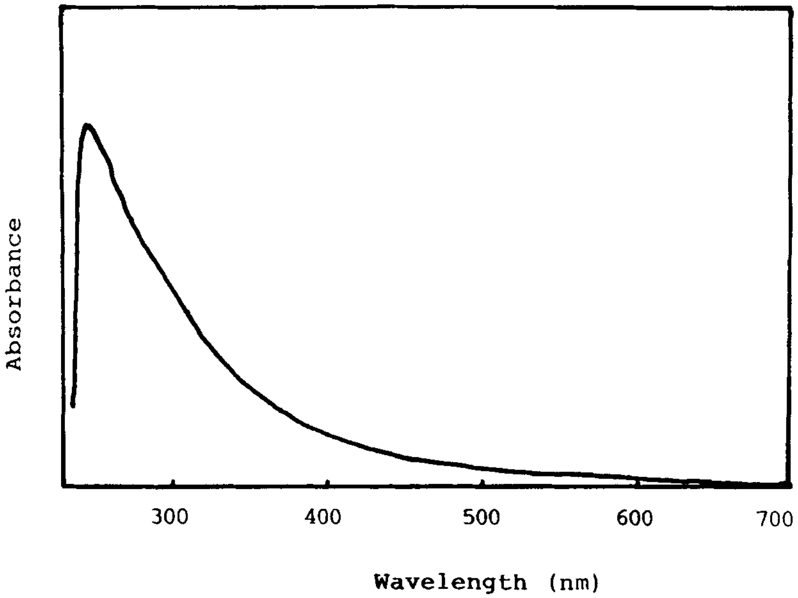


FIG. 4. UV-visible spectra of poly(PEO) in THF.

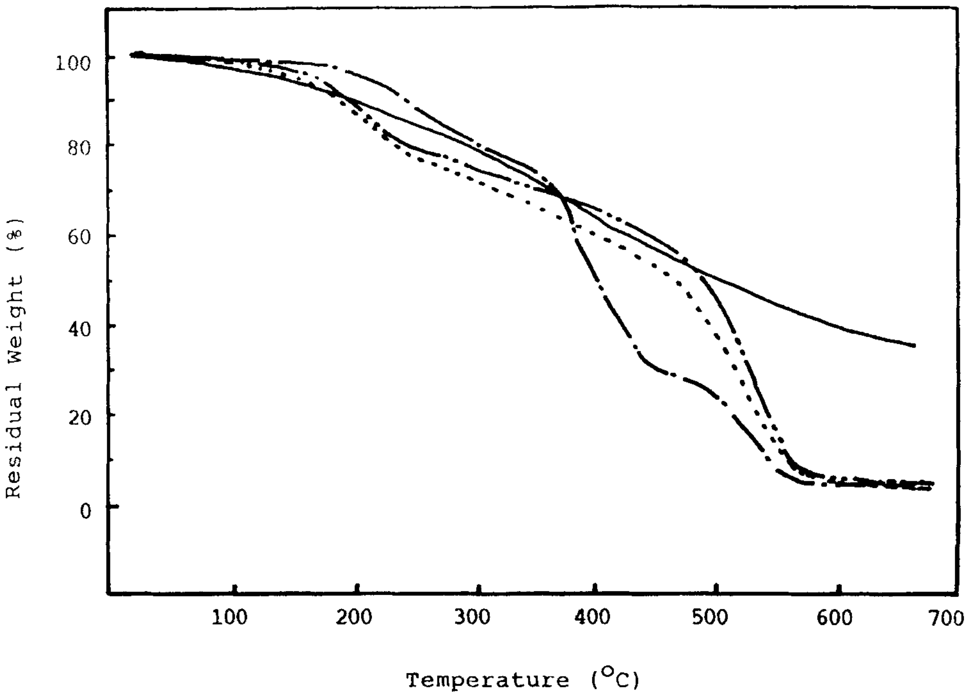


FIG. 5. TGA thermograms of poly(PO) [——], poly(BO) [– · –], poly(PEO) [– · · –], and poly(HO) [· · ·].

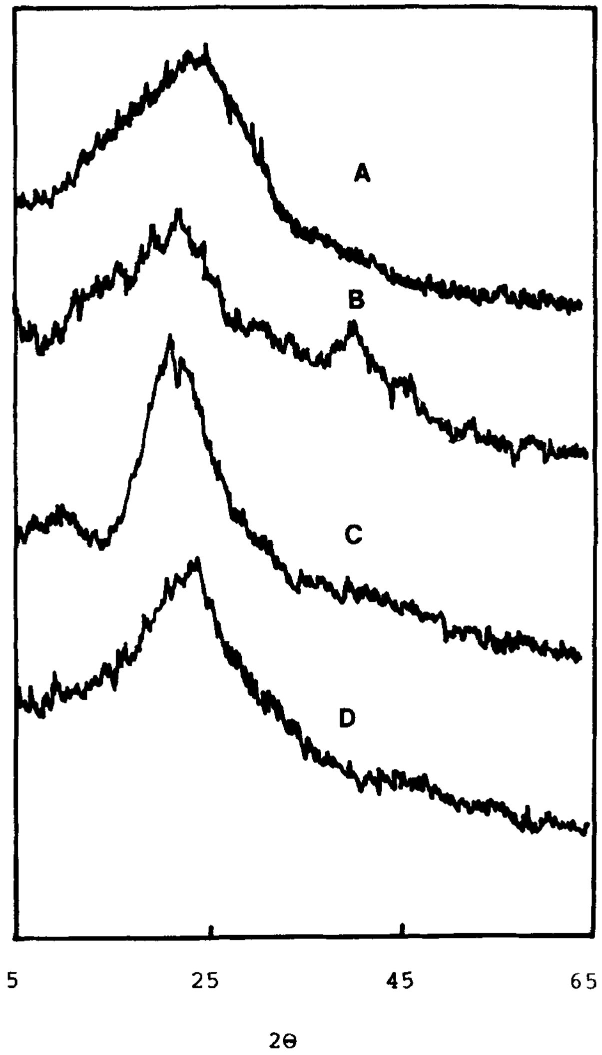


FIG. 6. X-ray diffractograms of poly(PO) [A], poly(BO) [B], poly(PEO) [C], and poly(HO) [D].

polymer yield was quantitative. The polymer yields gradually decreased as the length of the methylene chain between the hydroxy group and the acetylene group increased (from *n* = 1 to *n* = 4). The molecular weights of poly(PEO) and poly(HO) prepared by $PdCl_2$ were 1710 and 1570, respectively.

The structures of the resulting polymers with their hydroxyalkyl substituent were characterized by NMR (^1H and ^{13}C), IR, and UV-visible spectroscopies. In the case of *n* = 1 or 2, because of polymer insolubility, the identification of polymer structure by various instrumental methods (NMR, GPC, UV-visible) could not be carried out.

Figure 1 shows the FT-IR spectra of polymers prepared from hydroxyalkylacetylenes by $MoCl_5$. The infrared spectra of these polymers showed neither the acetylenic hydrogen stretching nor the carbon—carbon triple bond stretching frequencies in the infrared spectra of the monomers. Instead, new carbon—carbon double bond stretching frequencies appeared at about 1650 cm^{-1}, which indicates that a highly conjugated polymer was formed.

Figure 2 shows the ^1H-NMR spectrum of poly(PEO) prepared by $PdCl_2$. The peaks at 6.9-8.2 ppm are due to the vinyl protons on the polymer backbone. Methylene proton peaks were observed at 0.5-3.2 ppm.

Figure 3 shows the ^{13}C-NMR spectrum of poly(PEO) prepared by $MoCl_5$-$EtAlCl_2$. This shows the presence of vinyl carbons at the conjugated backbone at 125-145 ppm and also shows the methylene carbon peaks at 10-35 ppm.

Figure 4 shows the UV-visible spectra of poly(BO), poly(PEO), and poly(HO) in THF. These spectra show the characteristic absorption peak of a conjugated polymer, $\pi \rightarrow \pi^*$ absorption at long wavelength (up to 650 nm).

The solubility test for the present polymer samples was performed in excess solvent. As previously described, poly(PO) and poly(BO) were insoluble in any organic solvent regardless of the polymerization conditions and the catalysts used. However, poly(PEO) and poly(HO) were soluble in such solvents as chloroform, chlorobenzene, and THF, but insoluble in water, methanol, and *n*-hexane.

The color of polymers prepared by $PdCl_2$ was usually black. However, polymers prepared by Mo-based catalysts were light brown. The thermal stability of the resulting polymers, investigated by thermogravimetric analysis, showed a slight weight loss at the initial low temperatures. This may be due to the emission of absorbed moisture and/or residual organic solvents. In the TGA thermograms of poly(PEO) and poly(HO) (Fig. 5), the rapid weight loss at 150-200°C was judged to be due to dehydration.

The morphology of the resulting polymers was also investigated by x-ray diffraction analysis (Fig. 6). Because the peaks in the diffraction patterns are all broad and the ratio of the half-height width to the diffraction angle ($\Delta 2\theta / 2\theta$) is greater than 0.35 [34], the present polymers are amorphous.

CONCLUSIONS

The polymerization behaviors of four hydroxyalkylacetylenes and the properties of the resulting polymers have been described. In general, the catalytic activities of $MoCl_5$-based catalysts were greater than those of WCl_6-based catalysts. The high catalytic activity of Mo-based catalysts for the polymerization of hydroxyalkylacetylenes was thought to be due to the activating effect of $MoCl_5$ by the hydroxy functional group in the monomers. $PdCl_2$ was also found to be an effective catalyst. In general, the polymer yield gradually decreased as the number of methylene groups between the hydroxy and acetylene functional groups was increased from 1 to 4. The poly(PO) was insoluble in such organic solvents as chloroform, THF, DMF, and DMSO regardless of the polymerization conditions and the catalysts used. Poly(BO) was partially soluble, and poly(PEO) and poly(HO) were completely soluble in chloroform, THF, DMF, etc. Analytical data indicated that these polymers have a conjugated backbone structure with a hydroxyalkyl substituent.

X-ray analysis indicated that polymers from hydroxyalkylacetylenes are mostly amorphous.

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