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SYNTHESIS AND PROPERTIES OF POLY(1,6-HEPTADIYNE) DERIVATIVES CONTAINING HYDROXY FUNCTIONAL GROUP

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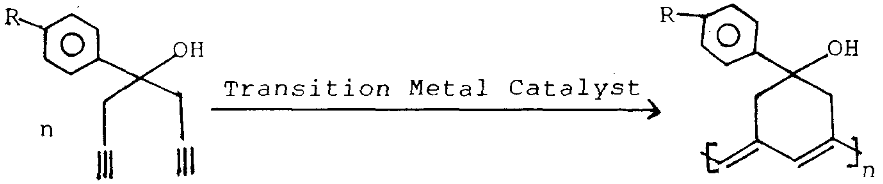
ABSTRACT

1,6-Heptadiyne derivatives containing hydroxy and aromatic substituents, 4-hydroxy-4-phenyl-1,6-heptadiyne (HPHD), 4-hydroxy-4-(4′-methylphenyl)-1,6-heptadiyne (HMHD), and 4-hydroxy-4-(4′-methoxyphenyl)-1,6-heptadiyne (HMOHD), were prepared and polymerized by various transition metal catalyst systems. A molybdenum complex was found to be the most effective catalyst for the cyclopolymerization of 4-hydroxy-1,6-heptadiyne derivatives. Polymerization of 4-hydroxy-1,6-heptadiyne derivatives by $MoCl_5$-based catalysts gave soluble and highly colored polymers. HMOHD containing the methoxy functional group showed the highest reactivity in cyclopolymerization. The structures of the resulting polymers were elucidated with IR, ^{1}H- and ^{13}C-NMR, and UV-visible spectroscopies. The present polymers were thermally and oxidatively more stable and had higher number-average molecular weights (M_n) of 2 × 10^4 to 3 × 10^4 than the corresponding 4-hydroxy-1,6-heptadiyne derivatives containing aliphatic substituents.

INTRODUCTION

Cyclopolymerization of nonconjugated diynes has been investigated in order to prepare polymers that contain conjugated double bonds along the backbone and a cyclic recurring unit [1, 2]. We found that $MoCl_5$- and WCl_6-based catalyst systems were very effective for the cyclopolymerization of 1,6-heptadiyne derivatives. In a previous paper we reported that 4-hydroxy-1,6-heptadiyne effectively cyclopolymerized by $MoCl_5$ alone [3]. It was interesting that the resulting cyclopolymer has a functional hydroxy group which has the capacity to show chemical reactivity, hydrophilicity, and complexing ability. However, the number-average molecular weight (M_n) of poly(4-hydroxy-1,6-heptadiyne) barely reached several thousand, and the polymer properties were relatively inferior [3]. In the present paper we deal with the cyclopolymerization of 4-hydroxy-1,6-heptadiyne derivatives containing aromatic substituents. The structure and properties of the product polymers are elucidated.



R: -H, $-CH_3$, $-OCH_3$

EXPERIMENTAL

Monomers were prepared as follows. Grignard reagent prepared from 1.22 mol magnesium turnings and 1.49 mol propargyl bromide was reacted with 0.5 mol methyl benzoate (methyl toluate and methyl anisiate) for 1 hour at 0°C. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with ethyl ether. The crude 4-hydroxy-4-phenyl-1,6-heptadiyne (HPHD) and 4-hydroxy-4-(4′-methylphenyl)-1,6-heptadiyne (HMHD) were purified by fractional distillation (HPHD: yield 63%, bp 84°C/10^{-2} mmHg; and HMHD: yield 60%, bp 93°C/10^{-2} mmHg) and 4-hydroxy-4-(4′-methoxyphenyl)-1,6-heptadiyne (HMOHD) was purified by distillation and recrystallization in ether (yield, 50%, white granular crystals, mp 40°C).

Tungsten(VI) and molybdenum(V) chloride (Aldrich Chemicals, resublimed, 99+%) were used without further purification. Tetra-*n*-butyltin (Aldrich Chemicals, 25% solution in hexane) was used as received. All solvents were purified in the usual manner.

Catalyst preparation and polymerization were carried out under a dry nitrogen atmosphere. Transition metal halides and organometallic compounds were dissolved to make a 0.2-M solution in each solvent before use. A typical polymerization procedure was as follows: solvent, catalyst solution, and cocatalyst solution (in case of need) were injected into a 20-mL ampule equipped with a rubber septum. When cocatalyst was used, these catalyst systems were aged at 30°C for 15 minutes. Finally, monomer was injected into the polymerization ampule. In the case of solid monomer, the catalyst solution was injected into the monomer and solvent mixture. After the mixture stood at 60°C for 24 hours, the polymerization was terminated by adding a small amount of methanol. The resulting polymer was dissolved in chloroform, followed by precipitation with a large excess of methanol. The polymer was filtered and dried under vacuum at 40°C for 24 hours. The polymer yield was calculated by gravimetry.

^{1}H- and ^{13}C-NMR spectra were recorded on a Varian FT-80A Spectrometer and a Bruker AM-200 Spectrometer, respectively. Infrared spectra were taken on a Perkin-Elmer model 267 grating spectrometer using an NaCl cell and potassium bromide pellets. UV-visible spectra were obtained with a Beckman DU-6 spectrometer. The number-average molecular weights (M_n) of the polymers were measured by means of a Waters GPC-150 C by use of polystyrene calibration. Thermogravimetric analysis (TGA) was done under a nitrogen atmosphere at a heating rate of 10°C/min up to 600°C with a Perkin-Elmer TGA. Elemental analysis (C, H) was made on a 240 C Elemental Analyzer. Molybdenum residues in the polymer were obtained on a Perkin-Elmer 5000.

RESULTS AND DISCUSSION

Table 1 shows the results of the polymerization of 4-hydroxy-1,6-heptadiyne derivatives by various catalysts. All $MoCl_5$-based catalysts have effective catalytic activity. However, polymers are hardly obtained by using WCl_6-based catalysts. It seems that the hydroxy functional group in 4-hydroxy-1,6-heptadiyne derivatives inhibits the catalytic activity of WCl_6, though the hydroxy group is considerably hindered by bulky aromatic substituents such as phenyl, 4-methylphenyl, and 4-methoxyphenyl. $(n\text{-Bu})_4Sn$ and $EtAlCl_2$ have been known to be excellent cocatalysts for the polymerization of mono- and disubstituted acetylenes [6, 7]. However, neither $(n\text{-Bu})_4Sn$ nor $EtAlCl_2$ has cocatalytic activity for the cyclopolymerization of 4-hydroxy-1,6-heptadiyne derivatives. 4-Hydroxy-1,6-heptadiyne derivatives are effectively polymerized by $MoCl_5$ alone. These results are similar to that reported for the cyclopolymerization of 4-hydroxy-1,6-heptadiyne [3]. In the polymerization of 4-hydroxy-1,6-heptadiyne derivatives by $MoCl_5$-based catalysts, it would seem that the reactivity of monomers does not depend on the steric hindrance but on the electronic nature of the substituents. The monomer containing the *p*-methoxyphenyl substituent is more reactive than those containing phenyl and *p*-methylphenyl substituents with similar steric hindrances. In the case where the polymerization temperature is 60°C and the initial monomer concentration, $[M_0]$, is 1.0 M, HMOHD was polymerized to an insoluble polymer in high yield within several minutes, and

TABLE 1. Substituent Effect in the Polymerization of 4-Hydroxy-1,6-heptadiyne Derivatives

Expt.	Catalyst system[a] (mole ratio)		Polymer yield, %		
			Poly(HPHD)	Poly(HMHD)	Poly(HMOHD)
1	$MoCl_5$		98	97	98[b]
2	$MoCl_5 \cdot (n\text{-Bu})_4Sn$	(1:2)	85	80	67[b]
3	$MoCl_5 \cdot EtAlCl_2$	(1:2)	76	72	65[b]
4	WCl_6		0	0	0
5	$WCl_6 \cdot (n\text{-Bu})_4$	(1:2)	0	0	0
6	$WCl_6 \cdot EtAlCl_2$	(1:2)	5	5	5

[a] Polymerization was carried out at 60°C for 24 hours. Initial monomer concentration was 1.0 M, and the monomer to catalyst mole ratio was 50.

[b] Crosslinked polymers, i.e., insoluble.

HPHD and HMHD were polymerized to soluble polymers after 6 hours. Thus, the polymerization of HMOHD was carried out under mild conditions; the polymerization temperature was 30°C and the initial monomer concentration $[M_0]$ was 0.125 M. Figure 1 shows the time dependence of polymer yield in the polymerization of HMOHD by $MoCl_5$. The mild polymerization conditions afforded soluble poly(HMOHD) in high yield after 6 hours. Similar results were obtained in the polymerization of 4,4-diphenoxy-1,6-heptadiyne [9]. 4,4-Diphenoxy-1,6-heptadiyne was more reactive for the polymerization than 4,4-diphenyl-1,6-heptadiyne [10]. Thus, we suppose that monomers containing the alkoxy or phenoxy group are more reactive than those containing the alkyl or phenyl substituent for the polymerization by $MoCl_5$-based catalysts.

The solvent effect on the polymerization of 4-hydroxy-1,6-heptadiyne derivatives was also investigated (Table 2). Oxygen-containing solvents such as tetrahydrofuran and dioxane are good solvents for the polymerization of 1,6-heptadiyne derivatives regardless of substituents, while they are not polymerized in pyridine and dimethylsulfoxide because they strongly coordinate to the active site of the catalyst through the lone pair electrons of nitrogen and oxygen, respectively.

The red-black colored poly(HPHD) and poly(HMHD) are completely soluble in common organic solvents except for polar protic and hydrocarbon solvents. On the other hand, the purple-black colored poly(HMOHD) is only completely soluble in dimethylsulfoxide and partially soluble in oxygen-containing solvents such as dioxane and tetrahydrofuran. These results explain why poly(HMOHD) was obtained in low yield in aromatic solvents which are generally known to be good solvents for polymerization by transition metal catalysts.

The structure of the resulting polymers was identified by NMR (^1H and ^{13}C), IR, UV-Vis spectroscopies, and elemental analysis. The ^1H-NMR spectra of poly(4-hydroxy-1,6-heptadiyne) derivatives are shown in Fig. 2 The broad peaks at 6.0–7.8 ppm are due to protons on the conjugated double bond and to phenyl protons. Figure 3 shows the IR spectra of poly(4-hydroxy-1,6-heptadiyne) derivatives. The infrared spectra of the polymers showed neither acetylenic carbon—hy-

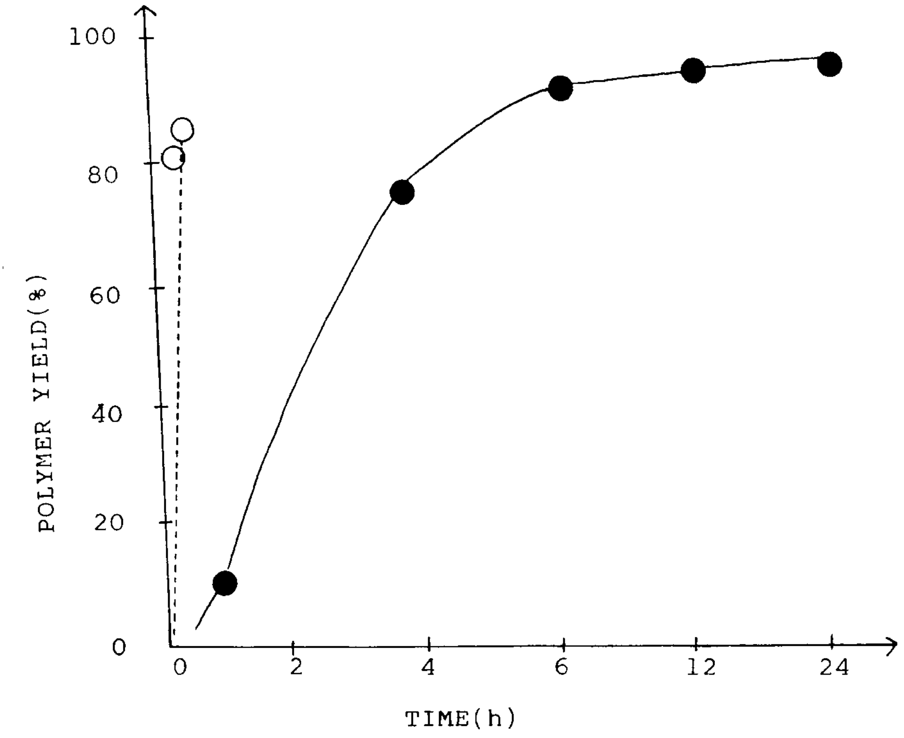


FIG. 1. The time dependence of polymer yield in the polymerization of 4-hydroxy-4-(4′-methoxyphenyl)-1,6-heptadiyne by $MoCl_5$. (○) Polymerization carried out at 60°C with an initial monomer concentration of 1.0 M: (●) Polymerization carried out at 30°C with an initial monomer concentration of 0.125 M.

TABLE 2. Solvent Effect in the Polymerization of 4-Hydroxy-1,6-heptadiyne Derivatives by $MoCl_5$

		Polymer yield, %		
Expt.	Solvent	Poly(HPHD)[a]	Poly(HMHD)[a]	Poly(HMOHD)[b]
1	Chlorobenzene	83	48	28
2	Toluene	62	63	18
3	Benzene	78	25	20
4	Carbon tetrachloride	36	48	5
5	Chloroform	53	65	24
6	Ethyl acetate	90	87	62
7	Tetrahydrofuran	95	92	80
8	Dioxane	98	98	83
10	Dimethylsulfoxide	0	0	0
11	Pyridine	0	0	0

[a] Polymerization was carried out by $MoCl_5$ at 60°C for 24 hours. Initial monomer concentration $[M_0]$ was 1.0 M.

[b] Polymerization was carried out by $MoCl_5$ at 30°C for 24 hours. Initial monomer concentration $[M_0]$ was 0.125 M.

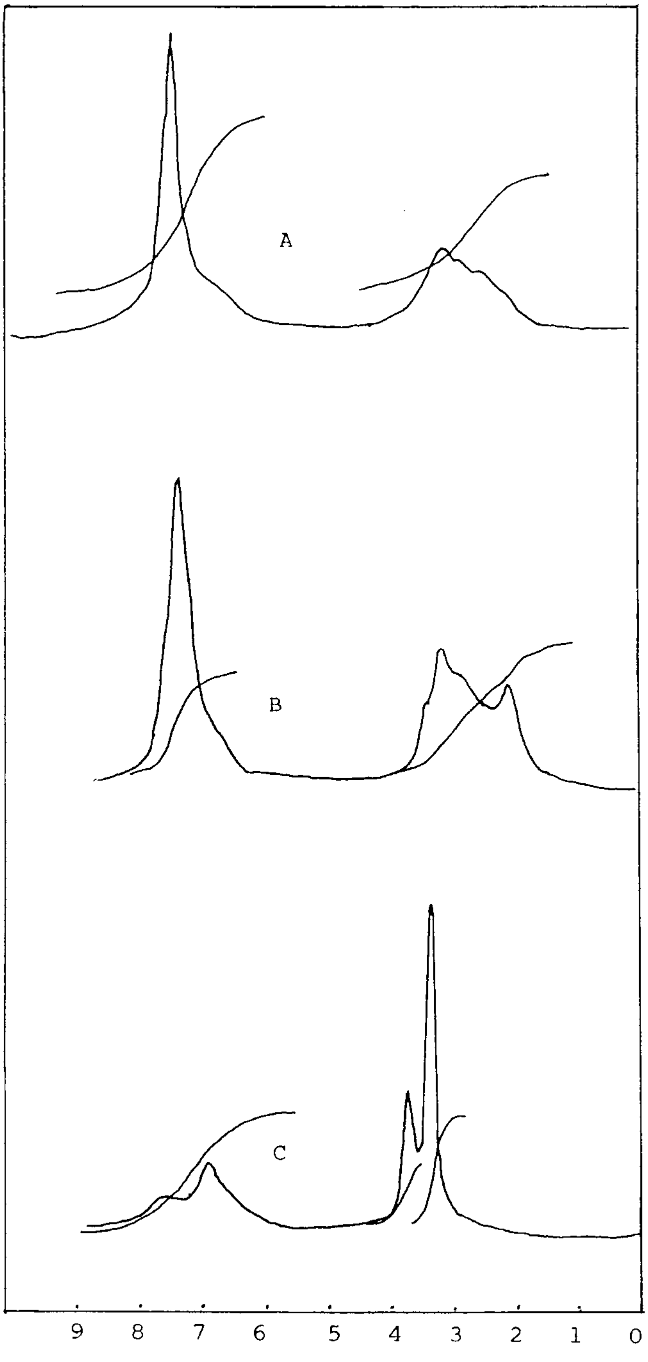


FIG. 2. The ^{1}H-NMR spectra of poly(4-hydroxy-1,6-heptadiyne) derivatives. (A) Poly(4-hydroxy-4-phenyl-1,6-heptadiyne). (B) Poly{4-hydroxy-4-(4′-methylphenyl)-1,6-heptadiyne}. (C) Poly{4-hydroxy-4-(4′-methoxyphenyl)-1,6-heptadiyne}.

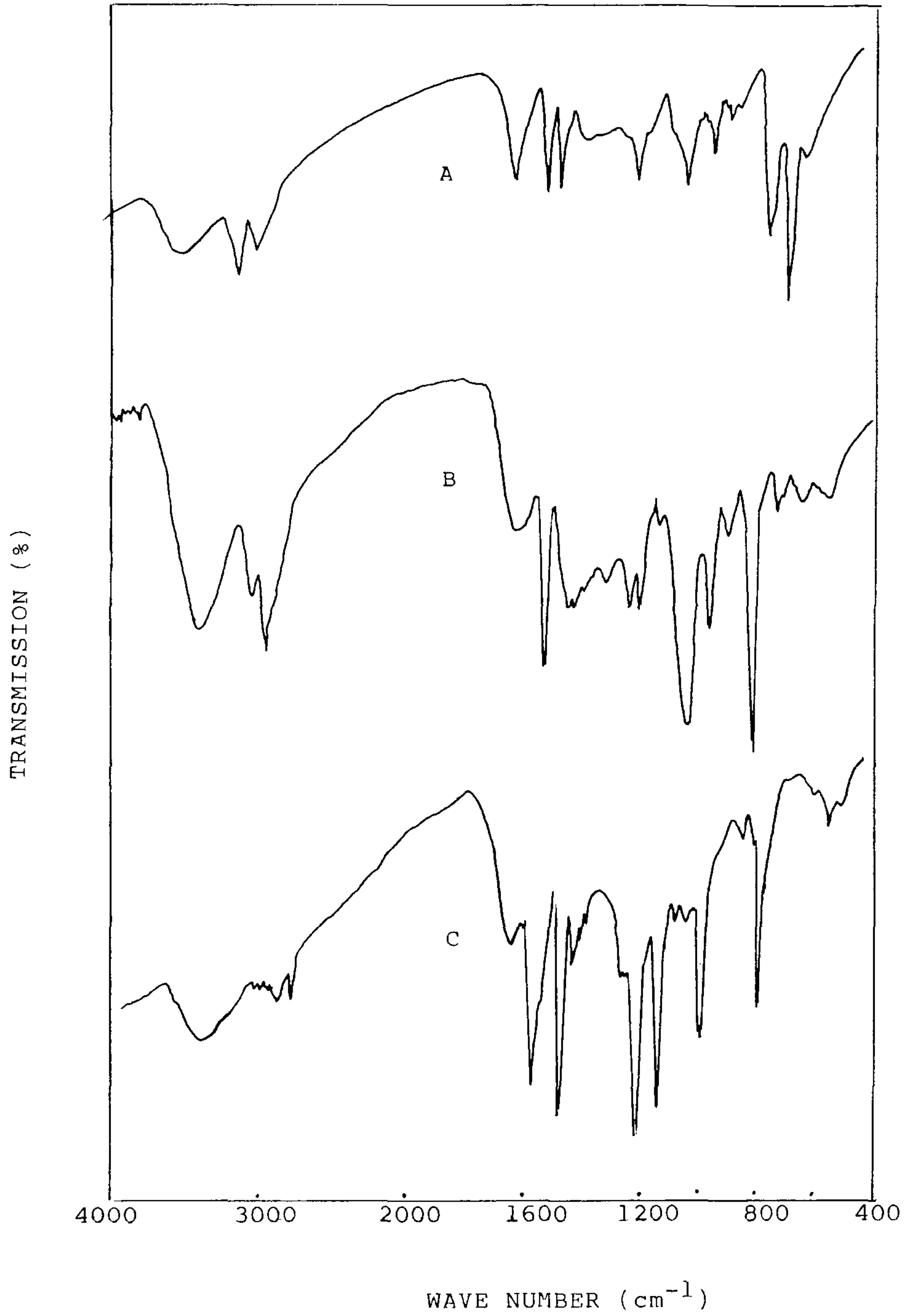


FIG. 3. The IR spectra of poly(4-hydroxy-1,6-heptadiyne) derivatives. (A) Poly(4-hydroxy-4-phenyl-1,6-heptadiyne). (B) Poly{4-hydroxy-4-(*p*-methylphenyl)-1,6-heptadiyne}. (C) Poly{4-hydroxy-4-(*p*-methoxyphenyl)-1,6-heptadiyne}.

TABLE 3. Elemental Analysis of Poly(4-Hydroxy-1,6-heptadiyne) Derivatives

Polymer	Calculated (found) C	H	O	Catalyst residues (Mo) in polymer
Poly(HPHD)[a]	84.78 (84.42)	6.52 (6.29)	8.70 (8.86)	0 (0.43)
Poly(HMHD)[a]	84.85 (84.68)	7.07 (6.86)	8.08 (8.14)	0 (0.32)
Poly(HMOHD)[b]	78.51 (78.18)	6.54 (6.16)	14.95 (15.23)	0 (0.48)

[a] Polymerization was carried out 60°C for 24 hours by $MoCl_5$. Initial monomer concentration $[M_0]$ was 1.0 M.

[b] Polymerization was carried out by $MoCl_5$ at 30°C for 24 hours. Initial monomer concentration $[M_0]$ was 0.125 M.

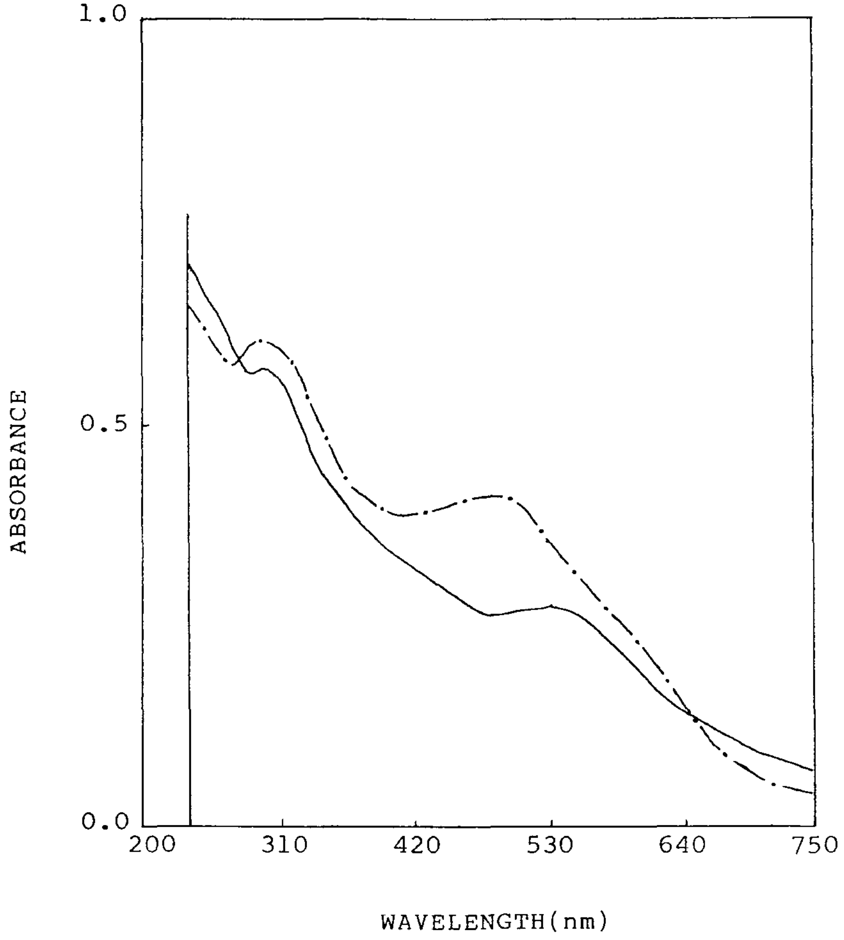


FIG. 4. The UV-visible spectra of poly(4-hydroxy-4-phenyl-1,6-heptadiyne) and poly[4-hydroxy-4-(4′-methylphenyl)-1,6-heptadiyne]. (—) Poly(HPHD). (– · –) Poly(HMHD).

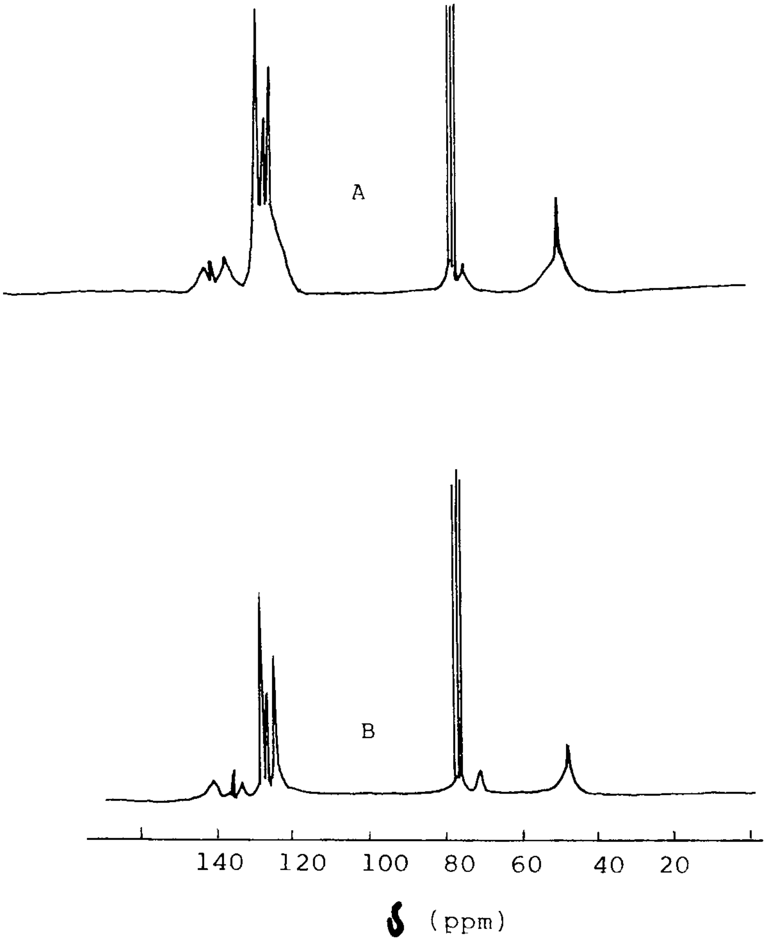


FIG. 5. ^{13}C-NMR spectra of poly(4-hydroxy-4-phenyl-1,6-heptadiyne) and poly[4-hydroxy-4-(*p*-methylphenyl)-1,6-heptadiyne]. (A) Poly(HPHD). (B) Poly(HMHD).

TABLE 4. The Number-Average Molecular Weights (M_n) and Inherent Viscosities [η] of Poly(4-Hydroxy-1,6-heptadiyne) Derivatives

Expt.	Polymer	$M_n \times 10^3$ [a]	[η], [b] dL/g
1	Poly(HPHD) [c]	21	0.18
2	Poly(HMHD) [c]	25	0.202
3	Poly(HMOHD) [d]	–	0.103

[a] Determined by GPC with polystyrene standards.

[b] Measured in DMSO at 35°C.

[c] Polymerization was carried out 60°C for 24 hours by $MoCl_5$. Initial monomer concentration [M_0] was 1.0 M.

[d] Polymerization was carried out by $MoCl_5$ at 30°C for 24 hours. Initial monomer concentration [M_0] was 0.125 M.

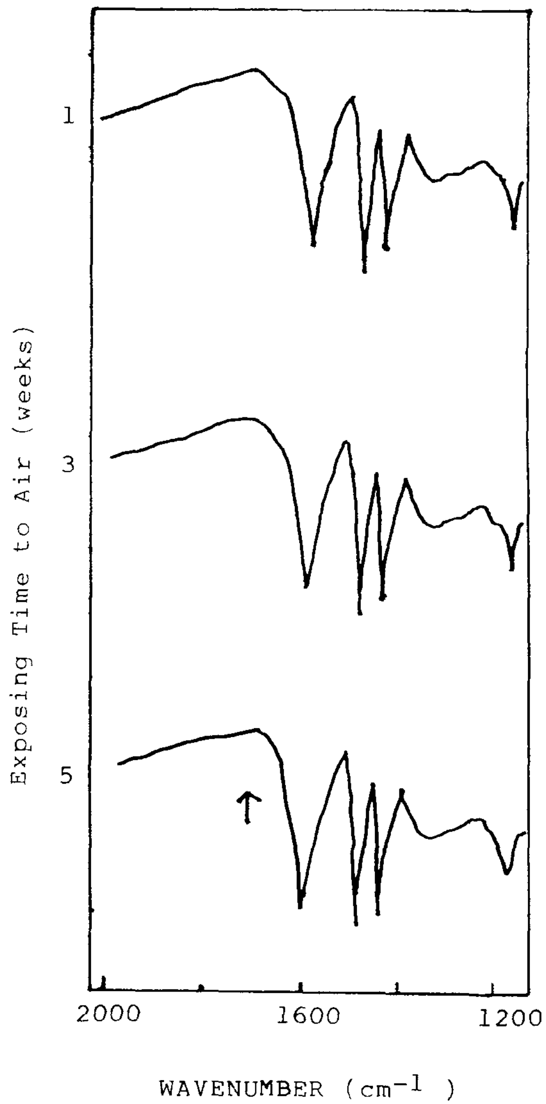


FIG. 6. IR spectrum for oxidation stability to air at room temperature of poly(4-hydroxy-4-phenyl-1,6-heptadiyne).

drogen stretching nor the carbon—carbon triple bond stretching band presented in the IR spectra of the monomers. Instead, the carbon—carbon double bond stretching band at 1600–1650 cm^{-1} indicates highly conjugated unsaturation. The elemental analysis data are listed in Table 3. The values of elemental analysis for poly(4-hydroxy-1,6-heptadiyne) derivatives, prepared by $MoCl_5$, rigorously excluding oxygen and analyzed immediately after drying under vacuum, agreed with the calculated values with a small deviation. The UV-visible spectra of poly(HPHD) and poly(HMHD) were obtained in chloroform (Fig. 4). A characteristic peak of conju-

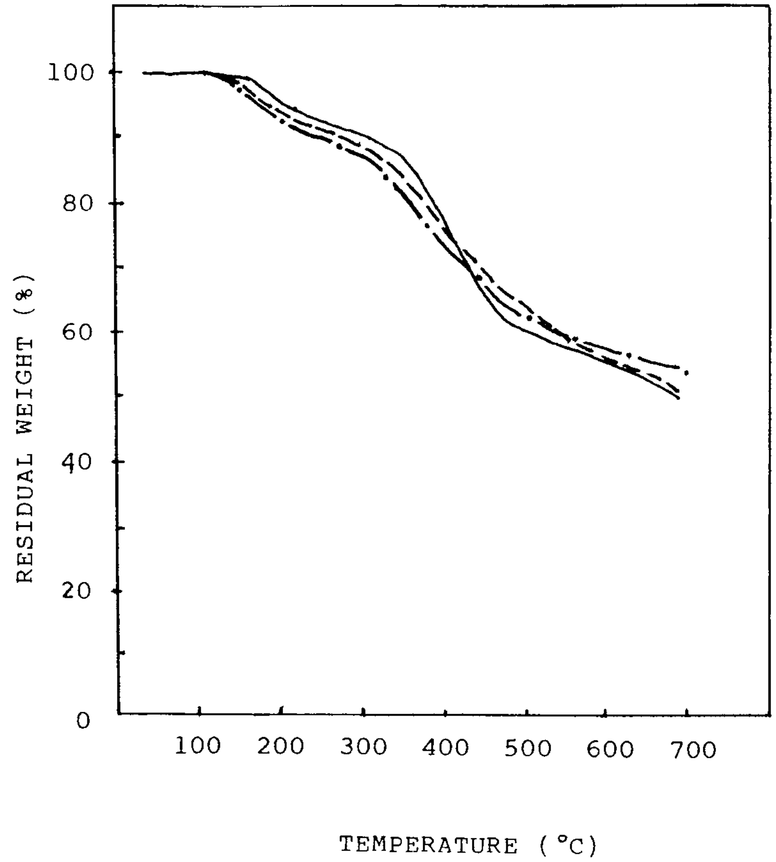


FIG. 7. TGA thermograms of poly(4-hydroxy-1,6-heptadiyne) derivatives. (——) Poly(HPHD). (- - -) Poly(HMHD). (— · —) Poly(HMOHD).

gated polyenes, broad $\pi \rightarrow \pi^*$ absorption with maximum absorption at 500 nm which was absent in monomers, appeared in the visible region (300–700 nm). In the ^{13}C-NMR spectra (Fig. 5), the peaks at 130 and 140 ppm are due to the conjugated carbons of the polymer backbone.

Table 4 presents number-average molecular weights (M_n) and inherent viscosities [η] of poly(4-hydroxy-1,6-heptadiyne) derivatives obtained by $MoCl_5$ catalyst. The M_ns of poly(HPHD) and poly(HMHD) containing bulky aromatic substituents at the 4-position are 20,000–30,000, although that of poly(4-hydroxy-1,6-heptadiyne) only reaches several thousand [3]. However, poly(HMOHD) has a low viscosity. It is supposed that the propagating polymer species are precipitated because polymerization solvents such as chlorobenzene and dioxane are poor solvents for high molecular weight poly(HMOHD).

To study air oxidation stability, poly(4-hydroxy-1,6-heptadiyne) was exposed to air at room temperature for 1 month. There was no identification of air oxidation, such as a new carbonyl band in the IR spectrum (Fig. 6).

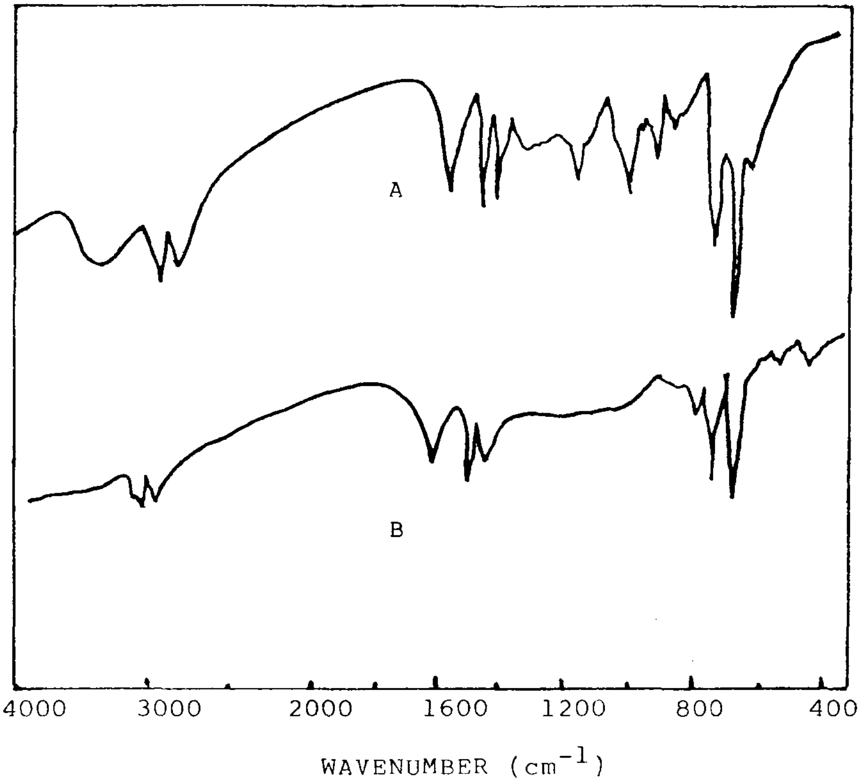


FIG. 8. IR spectra of poly(4-hydroxy-4-phenyl-1,6-heptadiyne) (A) and thermal dehydrated poly(4-hydroxy-4-phenyl-1,6-heptadiyne) (B).

Figure 7 shows the TGA thermograms of poly(4-hydroxy-1,6-heptadiyne) derivatives. The TGA curve of poly(HPHD) indicates that the retained weight is 99% of the original weight at 110°C, 90% at 260°C, and 47% at 600°C. The TGA curve of poly(HMOHD) shows that the retained weight is 99% of its original weight at 110°C, 90% at 240°C, and 57% at 600°C. These values indicate that the thermal stability of poly(4-hydroxy-1,6-heptadiyne) derivatives is poly(HMOHD) < poly(HMHD) < poly(HPHD). These results suggest that the weight loss of 10–13% at about 200°C is caused by thermal dehydration, and thermal dehydration of poly(HMOHD) with a good electron-donating substituent is more favorable than those of poly(HPHD) and poly(HMHD). The IR spectrum of polymer after heat treatment at 200°C for 5 hours under a nitrogen atmosphere agrees with this suggestion. The spectrum shows no absorption bands at 3500 and 1100–1050 cm^{-1} which can be assigned to O—H and C—O stretching bands, respectively (Fig. 8).

In the present study we found that poly(4-hydroxy-1,6-heptadiyne) derivatives containing a hydroxy functional group and a bulky aromatic substituent have better solubility and higher molecular weight than polyacetylene derivatives containing a hydroxy functional group [3, 11].

CONCLUSION

In this paper we described the synthesis and properties of poly(4-hydroxy-1,6-heptadiyne) derivatives containing a hydroxy functional group and a bulky aromatic substituent. From spectroscopic data, the resulting polymers possess polyene structures with cyclic recurring units in the polymer backbone. The resulting polymers were thermally and oxidatively more stable and had higher number-average molecular weights (M_n) than the corresponding 4-hydroxy-1,6-heptadiyne derivatives containing aliphatic substituents.

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