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Cyclopolymerization of 4,4-diphenoxy-1,6-heptadiyne by transition metal catalysts

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SUMMARY

Cyclopolymerization was carried out by various catalyst systems. $MoCl_5$-based catalyst systems are more effective for the polymerization of 4,4-diphenoxy-1,6-heptadiyne than WCl_6-based catalyst systems. Polymerization of 4,4-diphenoxy-1,6-heptadiyne leads to soluble, purple colored polymer with number average molecular weight ($\overline{Mn}$) of $3.6x10^4$-$5.2x10^4$. ^1H- and ^{13}C-MNR, IR,and UV-visible spectra of the resulting polymer indicated that poly(4,4-diphenoxy-1,6-heptadiyne) possesses a polyene structure presumably with cyclic recurring units in the polymer backbone. Poly(4,4-diphenoxy-1,6-heptadiyne) had good thermal and oxidative stability, and good solubility in organic solvents. The electrical conductivity of iodine-doped polymer was 10^{-3}-10^{-2} S/cm.

INTRODUCTION

Recently, many polymers have been synthesized from substituted acetylenes by use of transition metal catalysts (1). Unlike polyacetylene, these substituted polyacetylenes undergo neither oxidation nor molecular weight decrease in air at room temperature (2) because their main chains have twisted conformation owing to their substitutents. In our previous work, the polymerization of nonconjugated diynes such as dipropargyl silanes (3), 4,4-diphenyl-1,6-heptadiyne (4), and dipropargyl malonate derivatives (5,6) have been studied. The present article deals with the polymerization of 4,4-diphenoxy-1,6-heptadiyne (DPHD), an α,ω-diyne by transition metal catalysts. The structure and physical properties, (e.g., thermal and oxidative stability, electrical properties) of the resulting polymers were studied.

EXPERIMENTAL

Materials. Diphenyl carbonate (Polyscience Inc) and phosphorous pentachloride (Fluka AG) were used without further purification. Propargyl bromide was dried and distilled by recommended procedures (4). Tungsten (IV) and molybdenium (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-NMR spectra were recorded on a Varian FT-80A spectrometer. ^{13}C-NMR spectra were taken on Varian FT-80A and Bruker AM-200 spectrometers. Infrared (IR) spectra were measured on a Perkin-Elmer model 267 grating spectrometer using potassium bromide pellets. UV-visible spectra were obtained with a Beckmann DU-6 spectrophotometer. The number average molecular weights ($\overline{Mn}$) of the polymers were measured by means of GPC 150C Waters using a calibration curves for polystyrene standards. Thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere at a heating rate of 10 °C/min up to 500 °C with a Perkin-Elmer thermal analyzer. Electrical conductivities were measured by 4-point probe DC-method with a Hewelett-Packard 6261A power supply and Keithly 485 picoammeter.

Preparation of monomer, 4,4-diphenoxy-1,6-heptadiyne (DPHD).

Scheme I outlines the synthesis of the monomer (II). Diphenoxydichloromethane (I) was prepared as follows. Diphenyl carbonate (21.4 g, 0.1 mol) and phosphorous pentachloride (31.2 g, 0.15 mol) were mixed in a round-bottomed flask equipped with distillation apparatus. The mixture was heated at 210 °C without a solvent in an oil bath. During the reaction, the side product, $POCl_3$ is eliminated by distillation. After about 30 h, the crude diphenoxydichloromethane (I) was distilled [95 % yield, b.p. 180 °C/0.1 mmHg]. ^{13}C-NMR ($CDCl_3$): 132, 131.6, 129, 126.2, 121 ppm, ^{1}H-NMR: 7.2 ppm (s)

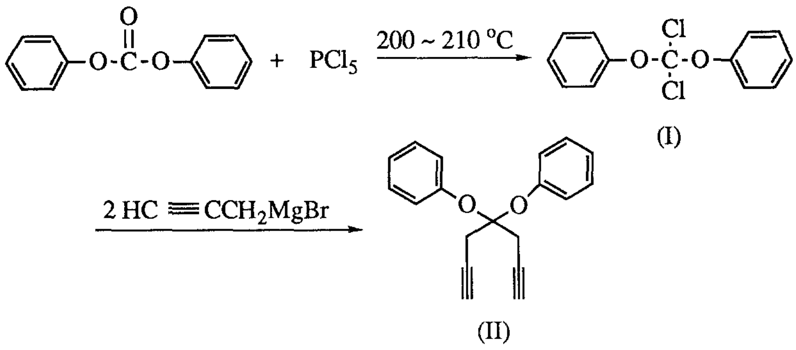
Grignard reagent prepared from 0.25 mol of magnesium turnings (6 g) and 0.3 mol of propargyl bromide (44.2 g) was added to the solution of diphenoxydichloromethane (0.1 mol, 27.2 g) in 100 ml diethyl ether by cannula for 1 h at 0 °C.

After the reaction mixture was stirred at room temperature for 24 h, it was quenched with saturated aqueous NH_4Cl solution and extracted with diethyl ether. The crude 4,4-diphenoxy-1,6-heptadiyne (II) was purified by distillation followed by recrystallization from pentane [yield 50 % b.p. 115 °C/ 0.1 mmHg , m.p: 47.5 °C, white needle-like crystal].

Polymerization. The polymerization was carried out with $MoCl_5$- and WCl_6-based catalyst systems (7). Scheme II outlines the polymerization of monomer with transition metal catalysts.

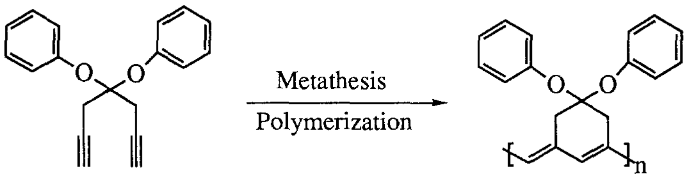
Results and Discussion The polymerization of 4,4-diphenoxy-1,6-heptadiyne, which contains a ketal functional group, was carried out by various catalyst systems, the results of which are shown in Table I. $MoCl_5$-based catalyst systems are more effective for the polymerization of DPHD than WCl_6-based ones. Similar results were found in the polymerization of dipropargyl derivativies (3,8,9) although opposite results were found in the polymerization of mono-substituted acetylene (1, (a)).

Scheme I



$(n\text{-}Bu)_4Sn$ has been an excellent cocatalyst for the polymerization of substituted acetylenes. Also, $(n\text{-}Bu)_4Sn$ exhibited cocatalyst activity compared with $EtAlCl_2$ for the polymerization of DPHD by $MoCl_5$. However, $EtAlCl_2$, an organoaluminum cocatalyst, is especially effective for the polymerization of DPHD by WCl_6. These results coincide with that of polymerization of 4,4-diphenyl-1,6-heptadiyne (4). The solvent effect on the polymerization of DPHD was also investigated.

Scheme II



Catalyst : $MoCl_5$, WCl_6
Cocatalyst : $EtAlCl_2$, $(n\text{-}Bu)_4Sn$

High polymer yields were achieved with aromatic hydrocarbons such as chlorobenzene and toluene. Further, polymerization proceeded quantitatively also in oxygen-containing solvents such as THF. Aromatic hydrocarbons and oxygen-containing solvents are good solvents for both catalysts and poly(DPHD). The result is different from that of polymerization of 4,4-diphenyl-1,6-heptadiyne (4) but is similar to that of dipropargylcarbinol which has a hydroxy functional group (8).

The time dependence of polymer yield in the polymerization of DPHD by $MoCl_5$ was also investigated. The polymerization proceeded rapidly within 6 h to reach 90 % yield and the quantitative yield was reached after 12 h, while the polymerization of 4,4-diphenyl-1,6-heptadiyne proceeded slowly and the quantitative yield was reached after 25 h in the same condition (4). Therefore, DPHD monomer is more reactive in polymerization than 4,4-

diphenyl-1,6-heptadiyne.

Table I. Polymerization of 4,4-diphenoxy-1,6-heptadiyne by Various Catalyst Systems (7)

Exp. No.	Catalyst System (mole ratio)	Polymer Yield (%)	$Mn/10^{4,a}$
1	$MoCl_5$	95	5.2
2	$MoCl_5$ — $EtAlCl_2$ (1:2)	80	4.5
3	$MoCl_5$ — $EtAlCl_2$ (1:4)	85	4.3
4	$MoCl_5$ — $(n\text{-}Bu)_4Sn$ (1:2)	90	5.0
5	$MoCl_5$ — $(n\text{-}Bu)_4Sn$ (1:4)	91	4.8
6	WCl_6	5	—
7	WCl_6 — $EtAlCl_2$ (1:2)	20	—
8	WCl_6 — $EtAlCl_2$ (1:4)	45	3.6
9	WCl_6 — $(n\text{-}Bu)_4Sn$ (1:2)	17	—
10	WCl_6 — $(n\text{-}Bu)_4Sn$ (1:4)	20	—

[a] Values were obtained by GPC analysis with polystyrene standards calibration.

The ^{1}H-NMR spectra of DPHD and poly(DPHD) are shown in Figure 1. The broad peaks which are assignable to the hydrogen of the conjugated double bond appeared at 6.7-7.4 ppm along with the phenyl protons and the allylic protons of poly(DPHD) at 2.8-4.0 ppm. Figure 2 shows the IR spectra of DPHD and poly(DPHD). The IR spectrum of the poly(DPHD) showed neither the acetylenic carbon-hydrogen stretching nor the carbon-carbon triple bond stretching observed in the IR spectrum of the monomer. The band characteristic of conjugated -C=C- sequences unfortunately can not be clearly identified, due to the interference in the region of 1590~1660 cm^{-1} of benzene ring absorption band dominating the weight of the molecule. Figure 3 exhibits the ^{13}C-NMR spectra of DPHD and poly(DPHD). While acetylenic carbon peaks at 82 and 69 ppm were not present, carbon peaks due to the conjugated double bond were observed at 125-130 ppm. The peak of the methylene carbon adjacent to the polyene backbone has shifted from 30 ppm in the monomer to 48 ppm in the polymer.

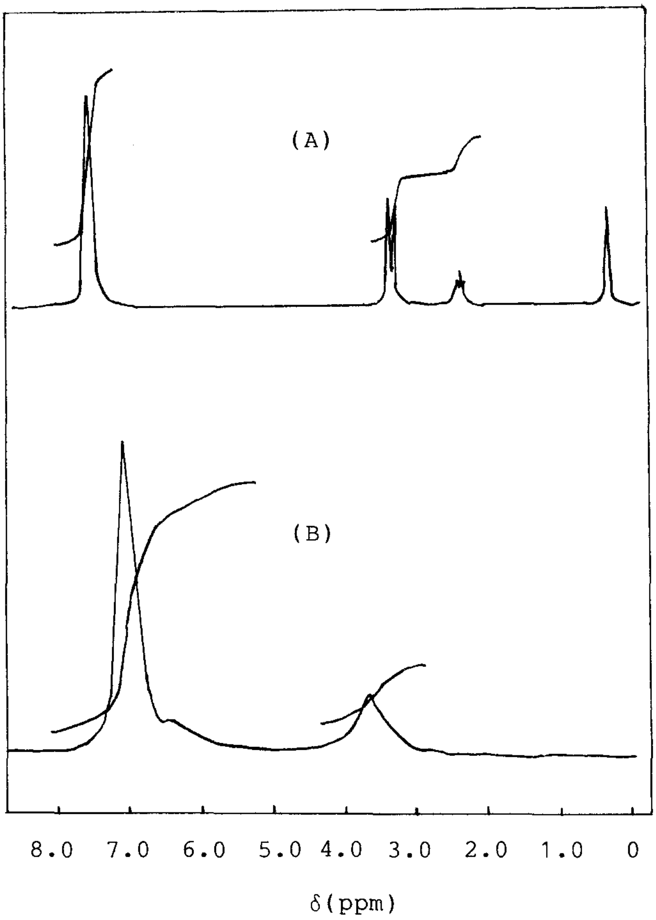


Figure 1. ^{1}H-NMR spectra of 4,4-diphenoxy-1,6-heptadiyne (A) and poly(4,4-diphenoxy-1,6-heptadiyne) (B).

The UV-visible spectrum of poly(DPHD) were obtained in 1,2-dichloroethane. A broad π-π^* transition characteristic of conjugated polymers appears at the visible region (λmax= 540, ε= 2700). The number average molecular weights ($\overline{Mn}$) of poly(DPHD) are in the range of 3.6×10^4-5.2×10^4 and inherent viscosity [η] of poly(DPHD) with $\overline{Mn}$=52000 is 0.68 dL/g at 25 °C in THF. The resulting polymers were completly soluble in various organic solvents such as chloroform, benzene and 1,4-dioxane except for polar protic and nonpolar solvents such as methanol and n-hexane. From the above results, it is proposed that poly(DPHD) possesses a polyene structure, with cyclic recurring unit. TGA suggests that the polymer is stable up to 175 °C. Poly(DPHD) retained 99 % of its original weight at 180

°C and 55 % at 500 °C.

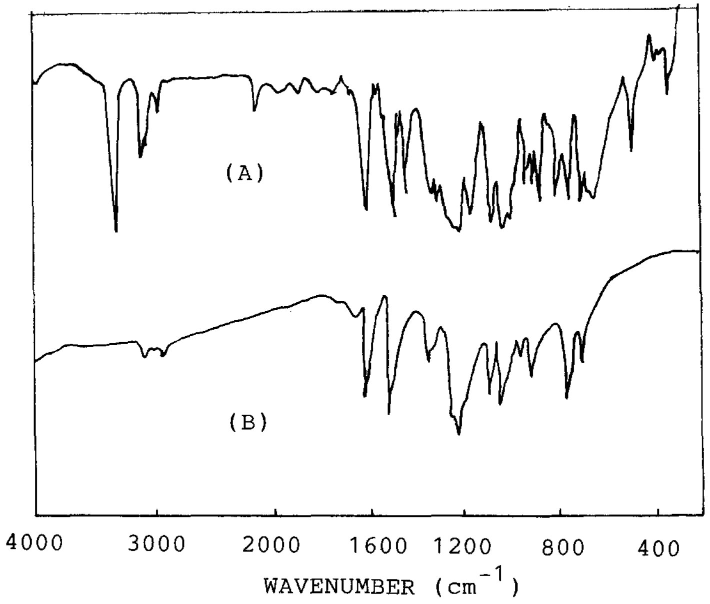


Figure 2. IR spectra of 4,4-diphenoxy-1,6-heptadiyne (A) and poly(4,4-diphenoxy-1,6-hetadiyne) (B).

When poly(DPHD) was exposed to air at room temperature for 2 months, there was no indication of air oxidation such as new carbonyl band by oxidation of conjugated backbone in IR spectrum (Figure 4). These indicate that poly(DPHD) with a ketal functional group has good thermal and oxidative stability.

When a pressed pellet of the polymer was doped by exposure to iodine vapor in vacuo, the electrical conductivity of the doped poly(DPHD) $[(C_{19}H_{16}O_2)_1 (I_2)_{0.47}]$ was 2.0x 10^{-2} S/cm. The maximum electrical conductivity of iodine doped poly(DPHD) is higher than that of iodine-doped poly(4,4-diphenyl-1.6-heptadiyne) (4) (10^{-4} S/cm).

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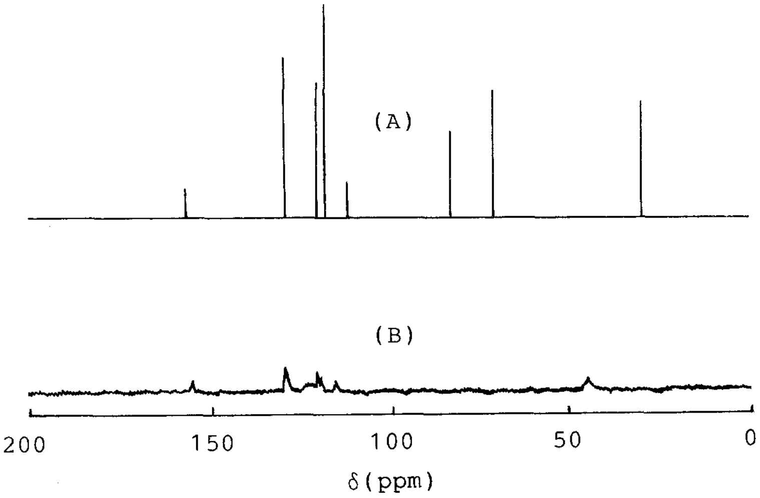

Figure 3. ^{13}C-NMR spectra of 4,4-diphenoxy-1,6-heptadiyne) (A) and poly(4,4-diphenoxy-1,6-heptadiyne) (B).

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7. Polymerization. A solution of $MoCl_5$ (0.073 ml, 0.2 M chlorobenzene solution) is added to a solution of DPHD (0.2 g) and chlorobenzene (7.3 ml, $[M]_o = 0.1$) at room temperature. The polymerization was carried out at 60 °C for 24 h, and the polymerization was terminated by adding a small amount of methanol. The resulting polymer was precipitated with a large excess of diethyl ether. Polymer yield was determined by gravimetry.

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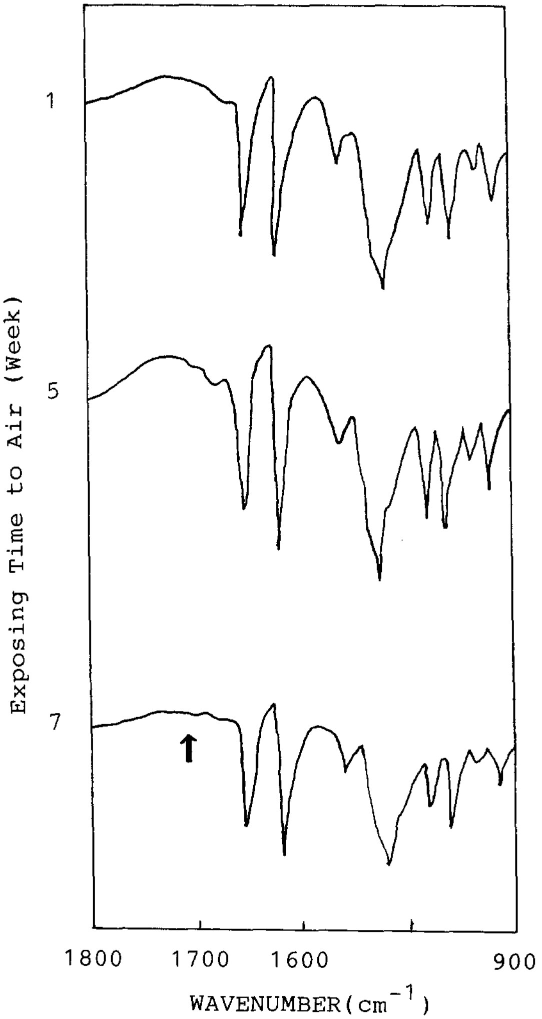

Figure 4. Oxidation stability of air at room temperature of poly(4,4-diphenoxy-1,6-heptadiyne).

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