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A NOVEL CLASS OF CONJUGATED POLYACETYLENES: SYNTHESIS OF POLY(1,4-DIPROPARGYLOXY-2-BUTYNE) BY DOUBLE RING FORMING CYCLOPOLYMERIZATION

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ABSTRACT

A novel type of polyacetylene with double cyclic structures was synthesized by the double ring forming polymerization of 1,4-dipropargyloxy-2-butyne using transition metal catalysts. It was found that $MoCl_5$-based catalysts were very effective for the polymerization of linearly nonconjugated triacetylene monomer. The resulting polymer exhibited partial solubility in organic solvents such as DMSO, DMF and NMP. The structure of the products were confirmed by IR, UV-visible, and ^1H- and ^{13}C NMR spectroscopy. The polymers obtained were found to be amorphous and showed thermal stability up to 160 ^0C.

INTRODUCTION

Polyacetylenes have been the subject of intensive research due to their interesting electronic and optical properties [1-5]. Many of the workers have developed the routes to polyacetylenes synthesis through obtaining free standing thin film using Ziegler-Natta catalyst [1] or substituted polyacetylenes using Mo, W halide based catalysts [6-8]. Other classes of polyacetylenes have also been developed through the cyclopolymerization of 1,6-heptadiynes or dipropargyl derivatives with Ziegler-Natta catalysts [9, 10] or transition metal catalysts [11-14]. Especially, poly(1,6-

heptadiyne)s having substituents at the 4-position exhibited remarkably improved solubility in common organic solvents, long-term stability toward air oxidation and higher average conjugation length. However, the polymerization of nonconjugated triacetylenes which can yield a new type of substituted polyacetylene having two cyclic recurring unit has not been investigated so far.

In this paper, we report on the synthesis of novel class of polyacetylene with double cyclic recurring unit by double ring forming polymerization of 1,4-dipropargyloxy-2-butyne (DPOB). In addition, the characterization and physical properties of the resulting products are also discussed.

EXPERIMENTAL

Monomer (1, 4-Dipropargyloxy-2-butyne, DPOB)

A two-phase system composed of propargyl bromide (17 g, 0.12 mol) in hexane (80 mL) and 2-butyne-1,4-diol (4.3 g, 0.05 mol), sodium hydroxide (40 g, 1.0 mol), and 1 g of tetrabutylammonium hydrogen sulfate in water (80 mL) was stirred overnight at room temperature and heated to reflux under stirring for 0.5 hr. After the reaction system was cooled to room temperature, water (100 mL) was added, and the organic layer was extracted three times with hexane (30 mL each). The product was isolated by evaporating the solvent after drying the solution with anhydrous magnesium sulfate. The crude product was fractionally distilled under vacuo to yield 2.5 g (31 %) of colorless liquid, bp 66 ^{0}C/10 mmHg.; ^{1}H NMR (CDCl$_3$) δ 2.41 (t, J=2.3, 2H), 4.12 (t, J=2.2, 4H), 4.18 (d, J=2.3, 4H) ; ^{13}C NMR (CDCl$_3$) δ 56.1, 56.3 (-CH$_2$OCH$_2$-), 74.9 (HC≡), 78.6 (-C≡CH), 81.8 (-C≡C-). IR (cm^{-1}); 2117 (HC≡C), 3283 (≡C-H). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.08; H, 6.22. Found: C, 74.07; H, 6.20.

Materials

Tungsten (VI) and molybdenum (V) chloride (Aldrich Chem. Co., resublimed 99.9 %) were used without further purification. Palladium (II) chloride, tetrabutyltin, and ethylaluminum dichloride (Aldrich Chem. Co.) were used without further purification. All solvents were used after purification according to conventional methods. Special care was taken to ensure complete removal of moisture and oxygen.

Polymerization

A polymerization ampule equipped with a rubber septum was flushed with dry nitrogen. Injections of catalyst solution and monomer were done by means of hypodermic syringes. A typical polymerization procedure was as follows : In a 20 mL ampule containing 6.95 mL of dioxane were injected a mixture of MoCl$_5$ (0.2 M, 0.4 mL, 0.08 mmol) and EtAlCl$_2$ (1 M, 0.32 mL, 0.32 mmol) and 0.33 g (2 mmol) of DPOB ([M]$_0$ = 0.25 M). After standing at 80 °C for 24 h, 5 mL of methanol were added, and the resulting polymer solution was precipitated into a large excess methanol. The precipitated polymer was filtered from the solution and dried under vacuum at 50 °C for 24 hr.

Instruments

^{1}H- and ^{13}C-NMR spectra were recorded with the use of a Bruker AM-300 spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as the internal standard. FTIR spectra were measured with neat oils or KBr pellets on a Bomem MB-100 spectrometer, and frequencies are given in reciprocal centimeters. A Shimadzu UV-3100S spectrometer was used for UV-visible spectral data. Elemental analysis was performed with a Perkin-Elmer 240DS elemental analyzer. Thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyzer under nitrogen at a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Polymerization

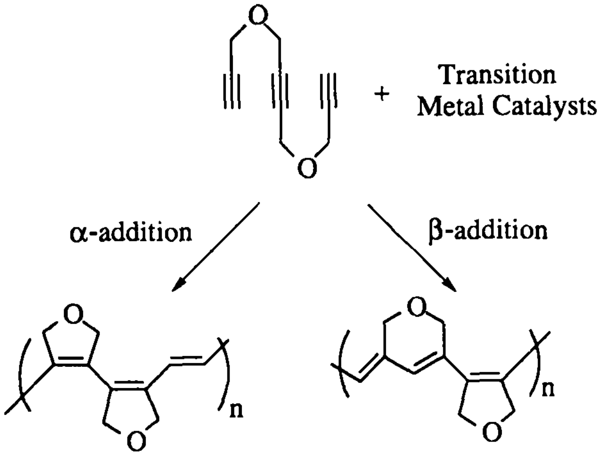
Scheme 1 outlines the double cyclopolymerization of the linearly nonconjugated triacetylene monomer.

The polymerization of DPOB was carried out with various transition metal catalysts, and the results are summerized in Table 1. Mo-based catalysts were found to be very effective for the polymerization of DPOB. Similar results were also observed in the polymerizarion of dipropargyl ether derivatives [11, 15]. As shown in Table 1, the polymerization by $MoCl_5$ associated with cocatalysts gives slightly lower yields than that of $MoCl_5$ alone. On the other hand, WCl_6 alone and WCl_6-based catalysts are less effective than $MoCl_5$-based catalysts for the polymerization of DPOB giving only trace yields. $PdCl_2$ polymerized DPOB to give poly(DPOB) in a yield of 42 %. Poly(DPOB)s obtained with most catalysts were brown or dark-brown. In general, unsubstituted poly(dipropargyl) derivatives such as poly(dipropargyl ether) [11], poly(1.6-heptadiyne) [9,10], and poly(dipropagyl sulfide) [12] are insoluble in any of the organic solvents. The insolubility of these polymers may be caused by the somewhat cross-linking of polymer chain and/or the chain rigidity of conjugated polymer backbone. Surprisingly, we found that the solubility of the resulting polymer was dependent on the initial monomer concentration and catalyst amount used. Poly(DPOB) obtained by $MoCl_5$ catalyst of M/C = 25 and $[M]_0 = 0.25$ was partially soluble in organic solvents such as DMSO, DMF, and NMP, and the soluble portion of poly(DPOB) was less than 35 % of the polymer yield. Poly(DPOB) obtained by the other conditions were insoluble in any of the organic solvents.

Polymer Structure and Properties

Polymerized products of 1,4-dipropargyloxy-2-butyne were characterized by various instrumental methods. Figure 1 shows the FTIR spectra of DPOB and poly(DPOB). The FTIR spectrum of the monomer clearly shows the bands due to the acetylenic carbon-hydrogen stretching band at 3283 cm^{-1} and terminal carbon-carbon triple bond stretching band at 2117 cm^{-1}. After polymerization, a dramatic change appears in the FTIR spectrum. The bands at 3283 and 2117 cm^{-1} due to the acetylenic group completely disappear in the polymer. Instead, the carbon-carbon double bond stretching band in the polymer backbone is observed at about 1625 cm^{-1}. The peak at about 3400 cm^{-1} was deduced to be due to the absorbed moisture and/or the catalyst residues. Similar phenomena were observed in the IR spectra of various polyacetylene derivatives [11-13].

The solid state CPMAS ^{13}C NMR spectrum of the poly(DPOB) is shown in Figure 2. The sharp peaks of the terminal (at 56.1ppm) and internal (at 56.3 ppm) methylene carbon atoms adjacent to the oxygen atom in the DPOB shift to a broad peak centered at 75 ppm in the poly(DOPB), which is the allylic methylene carbon



Scheme 1. Double Ring Forming Cyclopolymerization

TABLE 1.
Polymerization of 1,4-dipropargyloxy-2-butyne (DPOB)[a]

Exp. no.	Catalyst System[b] (mole ratio)	M/C[c]	$[M]_0$[d]	solvent	Polymer yield[e] (%)	color
1	$MoCl_5$	50	1.0	dioxane	94	black
2	$MoCl_5$	50	0.25	CB[f]	100	dark-brown
3	$MoCl_5$	25	0.25	dioxane	98	brown
4	$MoCl_5$-$EtAlCl_2$ (1: 4)	50	0.5	dioxane	79	dark-brown
5	$MoCl_5$-n-Bu_4Sn (1 : 4)	50	0.5	dioxane	80	dark-brown
6	WCl_6-$EtAlCl_2$ (1 : 4)	25	1	dioxane	trace	
7	WCl_6-n-Bu_4Sn (1 : 4)	25	1	dioxane	trace	
8	$PdCl_2$	15	0.5	DMF	42	brown

[a] Polymerization was carried out at 80 °C for 24 hr. [b]The mixture of catalyst and cocatalyst in chlorobenzene was aged at 30 °C for 15 min before use. [c]Mole ratio of monomer to catalyst. [d]Initial monomer concentration ($[M]_0$). [e]Methanol-insoluble polymer yield. [f]Chlorobenzene

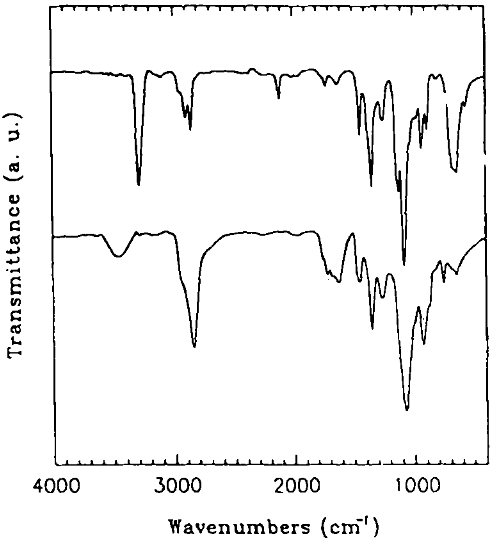


Fig. 1. FTIR spectra of DPOB (A) and poly(DPOB) (B) in neat oil and KBr pellet, respectively. (sample; no. 3 in Table 1).

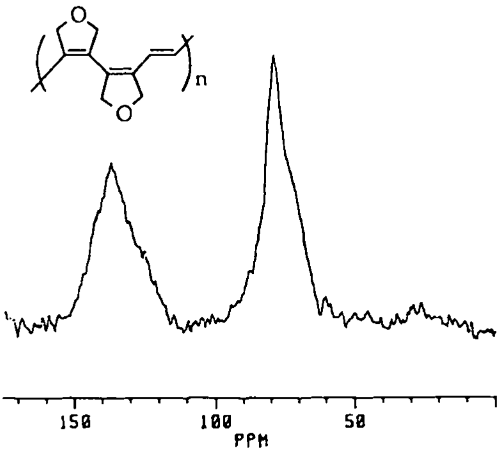


Fig. 2. CPMAS ^{13}C NMR spectrum of the poly(DPOB). (sample; no. 3 in Table 1)

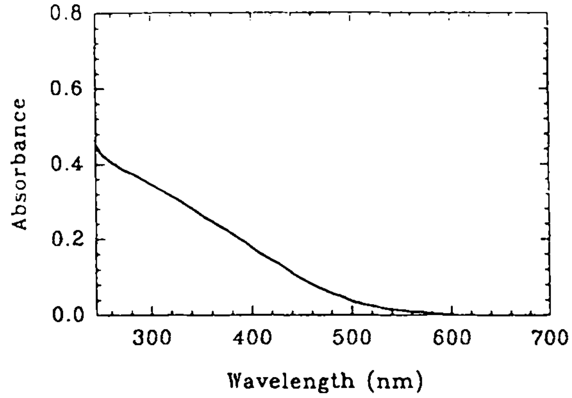


Fig. 3. UV-visible spectrum of the soluble poly(DPOB) in DMSO solution.

peaks. In addition, the sharp peaks of the terminal (at 74.9 and 78.6 ppm) and internal (at 81.8 ppm) acetylenic carbon shift to a broad peak at the region of 120 ~ 150 ppm in the poly(DPOB), which is the olefinic carbon peak of the polymer backbone. It indicates that both sorts of acetylenes, terminal and internal, participate in the polymerization which leads to the π-conjugated olefinic carbon of the polymer backbone. Soluble poly(DPOB) are characterized by ^{1}H NMR analysis. The newly appeared broad peaks at 3.5 - 5.0 ppm are due to the allylic methylene protons adjacent to the oxygen atom. The peaks at 6.1 and 7.2 ppm, which were absent in the NMR spectrum of the monomer, are assigned to the vinyl protons of the conjugated polymer backbone.

The UV-visible spectrum of the soluble poly(DPOB) was obtained in DMSO (Figure 3). The absorption spectrum of the polymer showed a characteristic absorption of the conjugated polymer, the $\pi-\pi^*$ absorption at a long wavelength (up to 600 nm). From the above spectral data and cyclopolymerization mechanism [15], it is proposed that the polymer structure is a twice cyclized form as described in scheme 1.

It has been reported that the poly(1,6-heptadiyne)s with cyclic conjugated double bonds has both five and six membered ring structure with a certain ratio, which should depend on the polymerization conditions and the kinds of catalysts used [15]. In the case of nonconjugated triacetylene system, however, a five membered ring in the repeat units is always produced regardless of α- or β-addition due to the cyclization mechanism. In the recent study on the cyclopolymerization of the 1,6-heptadiynes having bulky substituent at the 4-position, dominantly five membered cyclic rings were obtained by the $MoCl_5$ catalysts [16].

The thermal stability of the resulting polymer was evaluated by thermogravimetric analysis (TGA) under nitrogen atomosphere. It shows that poly(DPOB) retained 96.2 % of its original weight at 162 ^{0}C and 53 % at 600 ^{0}C, which is similar to simple poly(dipropargyl ether) [11]. Poly(DPOB) appeared to be amorphous when examined by X-ray diffraction.

CONCLUSIONS

From this reseach, a novel type of polyacetylene with double cyclic structure was prepared by the double ring-forming polymerization. The enhenced catalytic activity of $MoCl_5$-based catalysts was thought to be due to the activation of catalyst by oxygen atom of monomer. From the spectral data, it was found that both sorts of acetylenes, terminal and internal, participate in the polymerization to yield a new type of polyacetylene. It was concluded that the present poly(DPOB) having a five-membered ring in the repeat units is always produced regardless of α- or β-addition polymerization mechanism. The present double ring forming cyclopolymerization method may also be applied to the 1,6,11-dodecatriynes having bulky substituent at 4,10-position, producing the double cyclopolymers having well defined five membered cyclic polyene structure in the polymer backbone. Further works on the synthesis of soluble poly(1,6,11-dodecatriyne) derivatives are now in progress.

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