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SYNTHESIS AND CHARACTERIZATION OF POLY(2,2-DIPROPARGYL-1,3-PROPYLENE BENZALDEHYDE ACETAL) CONTAINING A BULKY ACETAL STRUCTURE

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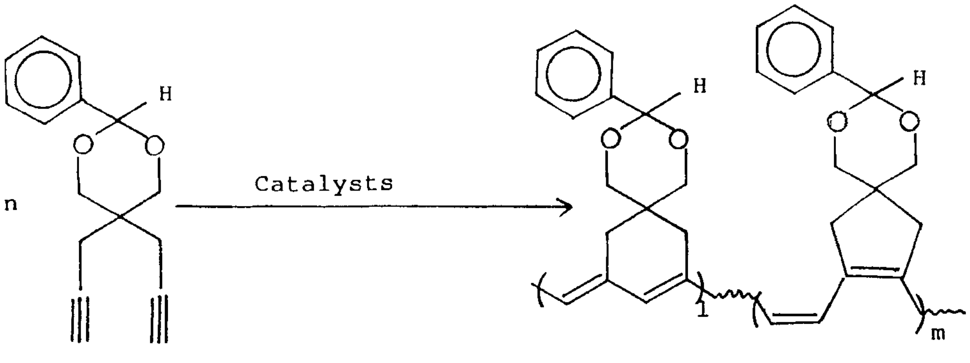
ABSTRACT

Poly(2,2-dipropargyl-1,3-propylene benzaldehyde acetal) (PDPBA), a cyclopolymer containing a bulky acetal functional group, was prepared with transition metal catalysts. $MoCl_5$ was found to be the most effective catalyst, and any cocatalyst effect was hardly observed. Polymerization was quantitatively carried out under mild conditions (30°C, $M_0 = 0.125$) with $MoCl_5$-based catalysts. The structure and physical properties of the resulting polymer were investigated. The spectral data indicated that the polymer contains alternating double and single bonds along the polymer backbone and a cyclic recurring unit with spiro acetal group. The polymer was completely soluble in common organic solvents. The M_n value of the polymer was in the 70,000 to 80,000 range relative to polystyrene standards by GPC. In addition, the polymer possessed good thermal and oxidative stability. The electrical conductivity of the undoped polymer was 10^{-12} S/cm.

INTRODUCTION

There have been many studies on the polymerization of various substituted acetylenes by transition metal catalysts [1]. Recently, Gibson et al. reported the synthesis of cyclic polyene, poly(1,6-heptadiyne), by cyclopolymerization of 1,6-heptadiyne using the Ziegler–Natta catalyst, but the resulting polymer was insoluble in any organic solvents and unstable to air oxidation [2, 3]. In our previous work it was found that $MoCl_5$- and WCl_6-based catalyst systems are very effective for the cyclopolymerization of nonconjugated diyne derivatives, which give polymers soluble in organic solvents and stable to air oxidation [4–9]. However, there has been no report on the cyclopolymerization of 1,6-heptadiyne derivatives with a bulky acetal functional group which is expected to be easily cyclopolymerized. The present article deals with the cyclopolymerization of 2,2-dipropargyl-1,3-propylene benzaldehyde acetal using $MoCl_5$- and WCl_6-based catalysts. The characterization and physical properties of the resulting polymer are discussed.



SCHEME 1.

TABLE 1. Polymerization of DPBA by Transition Metal Catalysts[a]

Experimental	Catalyst system,[b] mole ratio in parentheses	Polymer yield, %	$\overline{M}_n \times 10^{-4}$
1	$MoCl_5$	99	7.2
2	$MoCl_5 \cdot (n\text{-}Bu)_4Sn$ (1:2)	95	7.5
3	$MoCl_5 \cdot Ph_4Sn$ (1:2)	93	6.8
4	$MoCl_5 \cdot Et_2AlCl$ (1:2)	78[c]	–
5	$MoCl_5 \cdot EtAlCl_2$ (1:2)	85[c]	–
6	WCl_6	0	–
7	$WCl_6 \cdot (n\text{-}Bu)_4Sn$ (1:2)	0	–
8	$WCl_6 \cdot Ph_4Sn$ (1:2)	0	–
9	$WCl_6 \cdot Et_2AlCl$ (1:2)	10	–
10	$WCl_6 \cdot EtAlCl_2$ (1:2)	40[c]	–

[a] Polymerization was carried out at 30°C for 24 hours. The initial monomer concentration $[M]_0$ was 0.125 M, and the monomer to catalyst mole ratio was 50.

[b] Mixture of catalyst and cocatalyst in chlorobenzene was aged at 30°C for 15 minutes before use as a cocatalyst.

[c] Crosslinked polymer.

EXPERIMENTAL

Materials

$LiAlH_4$, diethyl malonate, and benzaldehyde (Aldrich Chemicals) were used without further purification. Propargyl bromide (Aldrich Chemicals, 80 wt% solution in toluene) was dried over calcium hydride and fractionally distilled by recommended procedures [4-9]. Tungsten(VI) and molybdenum(V) chloride (Aldrich Chemicals, resublimed, 99+ %) were used without further purification. Tetraphenyltin (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride. Tetrabutyltin was distilled under reduced pressure. Organoaluminum compounds (Aldrich Chemicals, 25% solution in hexane) such as Et_2AlCl and $EtAlCl_2$ were used as received. All solvents were purified in the conventional manners.

Preparation of 2,2-Dipropargyl-1,3-propylene Benzaldehyde Acetal (DPBA)

Diethyl dipropargylmalonate, the starting compound, was prepared as described in the literature [7]. A solution of 24 g (0.1 mol) dipropargyl malonate in 50 mL dry ether was added dropwise to dry ether (200 mL) containing 4.4 g (0.1 mol) $LiAlH_4$ at a rate such as to produce gentle reflux. The reaction was completed by refluxing for 2 hours. The excess hydride was destroyed by the addition of ethyl acetate. The ether layer was separated after extraction with ether, and the crude product was recrystallized from hexane, yielding 4,4-bis(hydroxymethyl)-1,6-heptadiyne (85%, mp 85°C). DPBA was prepared by refluxing the benzene solution of 4,4-bis(hydroxymethyl)-1,6-heptadiyne (15 g, 0.1 mol) and benzaldehyde (14 g,

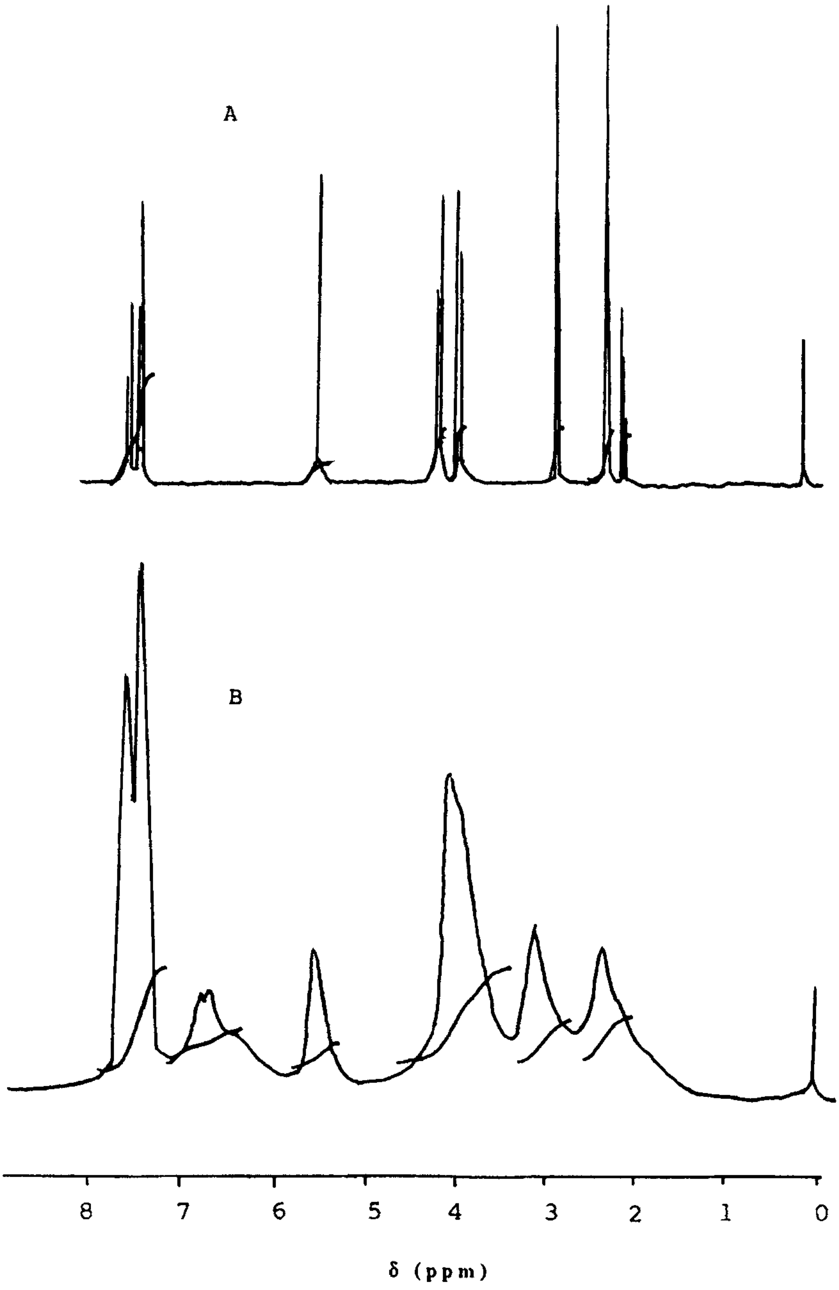


FIG. 1. ^{1}H-NMR spectra of DPBA (A) and poly(DPBA) (B).

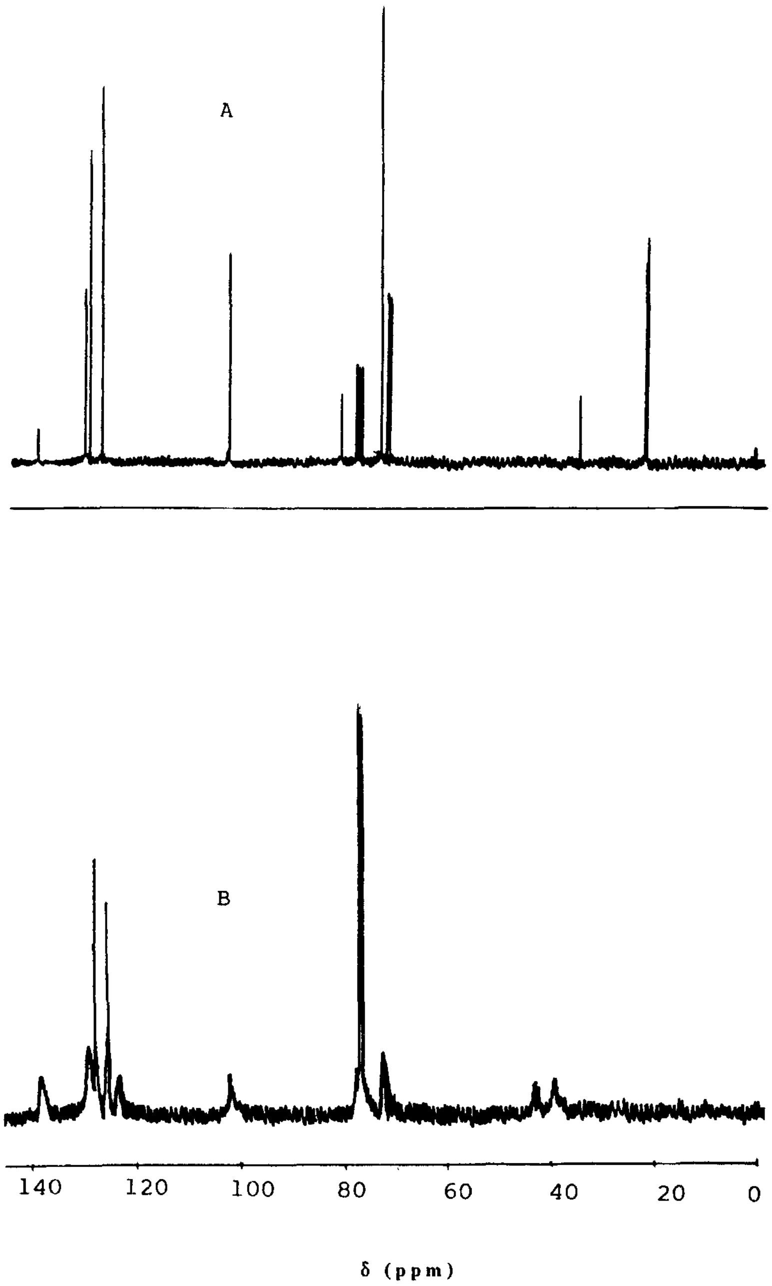


FIG. 2. ^{13}C-NMR spectra of DPBA (A) and poly(DPBA) (B).

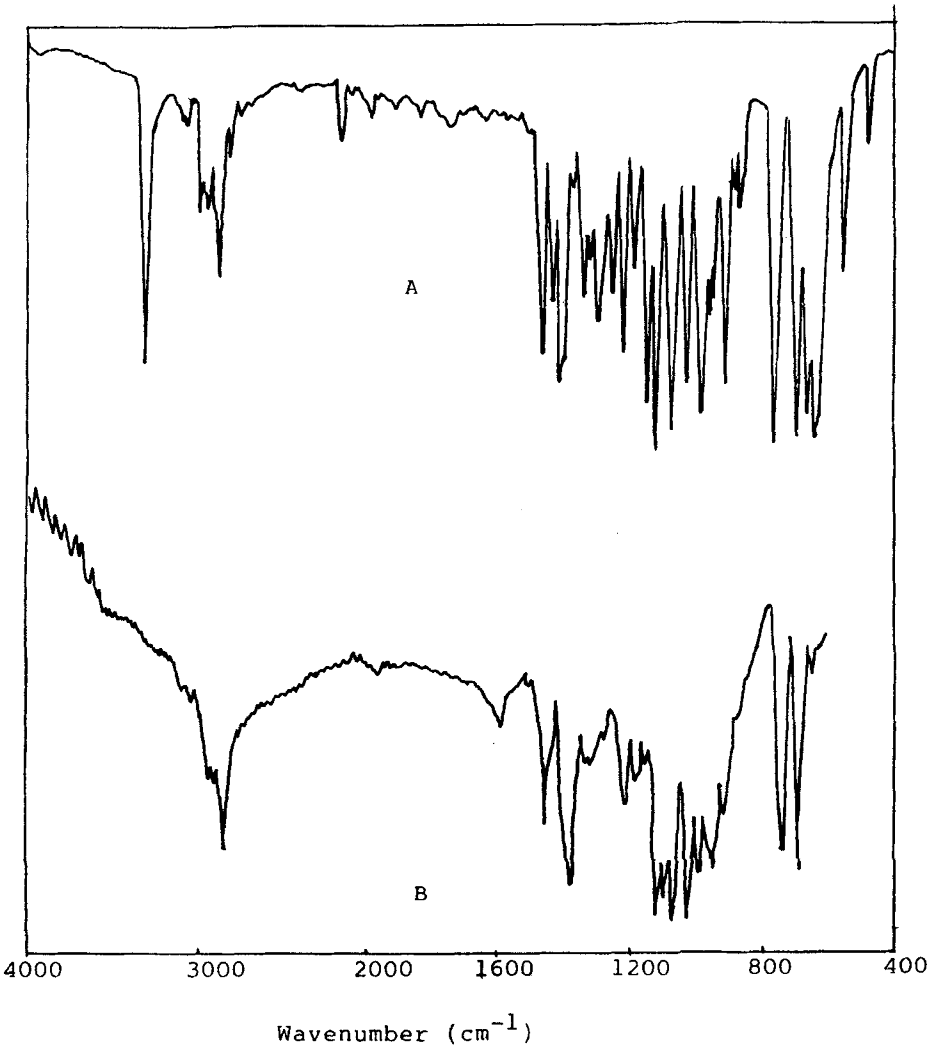


FIG. 3. IR spectra of DPBA (A) and poly(DPBA) (B) in KBr pellets.

0.13 mol) in the presence of a catalytic amount of *p*-toluene sulfonic acid in a flask with a barette trap for 12 hours. Benzene was evaporated after the reaction, and the resulting mixture was extracted with ether. After evaporation of the solvent, the residue was recrystallized in hexane to give the monomer (mp: 54°C; yield 27 g, 93%).

Polymerization

Catalyst preparation and polymerization were carried out under a dry nitrogen atmosphere as described in Refs. 4–9. Transition metal halides and organometallic compounds were dissolved to make a 0.2-M solution in each solvent before use.

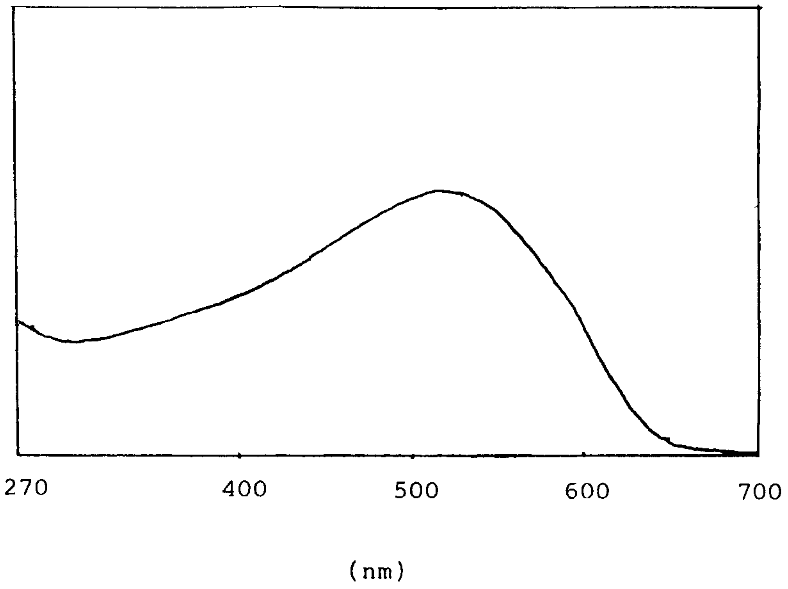


FIG. 4. UV-Vis spectrum of poly(DPBA) in $CHCl_3$.

TABLE 2. Solubility Behavior of Poly(DPBA)

Solvent	Solubility[a]
Benzene	+ +
Chlorobenzene	+ +
Chloroform	+ +
Dichloromethane	+ +
Carbon tetrachloride	+ −
Hexane	− −
1,4-Dioxane	+ +
Tetrahydrofurane	+ +
Ether	− −
Acetone	− −
Ethyl acetate	− −
N,*N*-Dimethylformamide	+ −
Methanol	− −
Formic acid	− −

[a] + + = soluble, + − = partially soluble, − − = insoluble

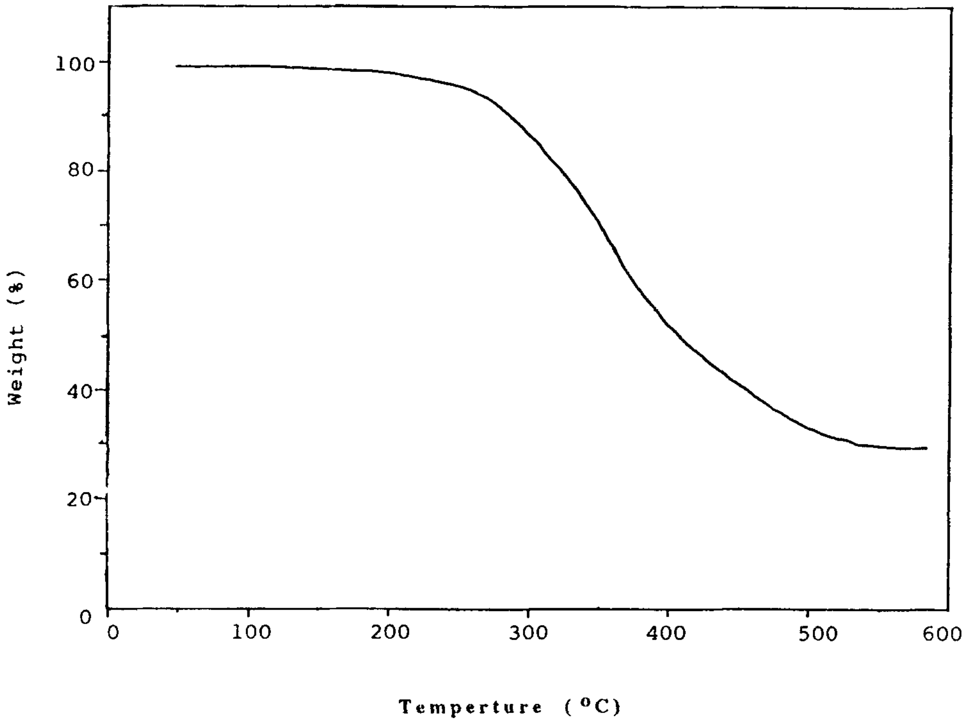


FIG. 5. TGA thermogram of poly(DPBA).

The typical polymerization procedure used is as follows: A catalyst solution was injected into the monomer solution. After the mixture was heated at 30°C for 24 hours, polymerization was quenched 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.

Instruments

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AM-200 spectrometer. Infrared spectra were taken on a Perkin-Elmer model 267 grating spectrometer using potassium bromide pellets. UV-Visible spectra were obtained with a Cary 17 spectrometer with an Aminco-XY recorder. The number-average molecular weights of the polymer ($\overline{M}_n$) were measured by means of a GPC-150 C Waters using calibration curves for polystyrene. Thermogravimetric analysis (TGA) was measured under a nitrogen atmosphere at a heating rate of 10°C/min up to 600°C with a TGA Perkin-Elmer.

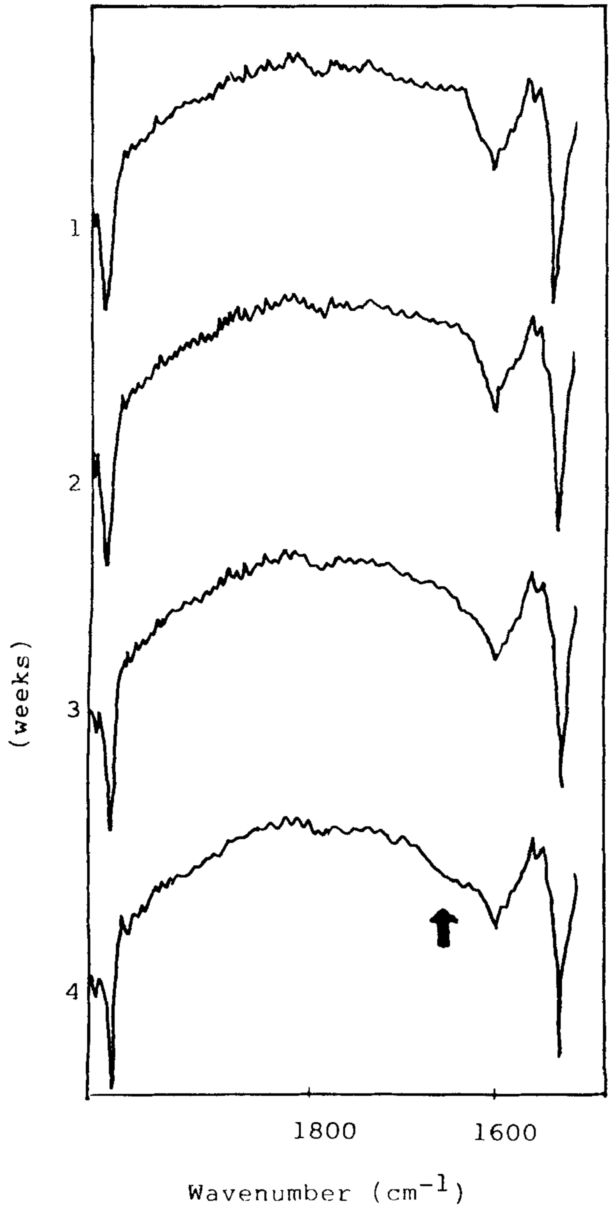


FIG. 6. Oxidative stability of poly(DPBA) to air at room temperature.

RESULTS AND DISCUSSION

Scheme 1 outlines the cyclopolymerization of monomer with transition metal catalysts. The results for the polymerization of monomer by various catalyst systems are listed in Table 1. It was found that the polymerizability of DPBA was very high, and polymerization was carried out in mild condition even at 30°C, $[M]_0 = 0.125$. These facts afford a remarkable contrast with the cyclopolymerizations of other 1,6-heptadiyne derivatives which were carried out at 60°C [2, 4–6]. $MoCl_5$-based catalyst systems are more effective for the polymerization of monomer than WCl_6-based ones. Similar results were found in the polymerization of 1,6-heptadiyne derivatives [4–9], although opposite results were found in the polymerization of monosubstituted acetylene [10, 11]. The polymer yield with WCl_6-based catalysts was larger than those with WCl_6 alone. $EtAlCl_2$ exhibited the highest cocatalyst activity. These results are consistent with the cyclopolymerization of other 1,6-heptadiyne derivatives [4, 5].

To investigate the effect of polymerization solvents on polymerizability, we polymerized monomers in various solvents. It was reported that the most suitable solvents for polymerization by transition metal chloride-based catalysts are aromatic hydrocarbons, especially toluene and chlorobenzene [4]. In our study, high polymer yields were also obtained in the aromatic hydrocarbon benzene.

The polymer structure was identified by ^1H- and ^{13}C-NMR, IR, and UV-Vis spectroscopies. Figure 1 shows the ^1H-NMR spectra of DPBA and poly(DPBA). In the ^1H-NMR spectrum of poly(DPBA), the acetylenic proton peak at 2.0 ppm disappeared and a new vinyl proton peak at 6.2–7.0 ppm along with the phenyl protons appeared. The ^{13}C-NMR spectra of DPBA and poly(DPBA) are shown in Fig. 2. Acetylenic carbon peaks, which should have appeared at 72 and 80 ppm, disappeared in the polymer. Instead, the carbon peak of conjugated double bond appeared at 123 and 130 ppm. The peak of methylene carbon adjacent to the polymer backbone shifted from 23 to 43 ppm on polymerization. Figure 3 shows the IR spectra of DPBA and poly(DPBA). The IR spectrum of poly(DPBA) showed neither the acetylenic carbon—hydrogen stretching band nor the stretching band of carbon—carbon triple bond stretching presented in the IR spectrum of the monomer at 3300 and 2150 cm^{-1}, respectively. On the other hand, the stretching band at 1600–1650 cm^{-1} showed up. It indicated the polymer has a highly conjugated cyclic polymer backbone. The UV-Vis spectrum of poly(DPBA) were obtained in chloroform (Fig. 4). A broad π-π^* transition characteristic of conjugated polymers appeared at the visible region ($\lambda_{max} = 520$ nm, $\epsilon = 5837$). The number-average molecular weights (M_n) of poly(DPBA) are in the 70,000 to 80,000 range. The polymer was completely soluble in various organic solvents such as chloroform, THF, and 1,4-dioxane, and it could be easily cast on glass plates to give a black, shiny thin film. It was, however, insoluble in *n*-hexane, acetone, diethyl ether, and ethyl acetate (Table 2). The solubility behavior is comparable to that of poly(dipropargyl isopropylidene malonate) with spiro group, which was partially soluble because of a crosslinking portion [12]. From the above spectral and solubility data, it is proposed that the polymer structure is a cyclized form as described in Scheme 1 [13].

The TGA data suggest that the polymer is stable up to 230°C. Poly(DPBA) retained 97 and 50% of its original weight at 230 and 420°C, respectively (Fig. 5). The oxidative stability of poly(DPBA) to air was examined by checking the appearance of new peaks of the carbonyl groups formed by air oxidation in the infrared spectra for 4 successive weeks. The present polymer showed no notable carbonyl peak (at ca. 1700 cm^{-1}) even after exposure to air for 3 weeks (Fig. 6). This indicated that poly(DPBA) with spiro acetal functional groups has good thermal and oxidative stability.

The electrical conductivity of the undoped polymer was 10^{-12} S/cm.

The fairly good thermal and oxidative stability and the solubility of the present polymer, which has a rigid main chain and bulky spiro acetal side groups, are notable characteristics. We are now attempting to prepare a gas permeable membrane by film casting.

CONCLUSION

For this article we prepared poly(2,2-dipropargyl-1,3-propylene benzaldehyde acetal) containing a bulky spiro structure by transition metal catalysts. Polymerization was quantitatively carried out in mild condition (30°C, $[M]_0 = 0.125$) by $MoCl_5$-based catalysts. The obtained polymer was completely soluble in common organic solvents, and stable to thermal and air oxidation. The electrical conductivity of undoped polymer was 10^{-12} S/cm.

ACKNOWLEDGMENTS

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