

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

## Polymerization of 1-Ethynyl-1-Cyclohexanol by Transition Metal Catalysts

Yeong-Soon Gal<sup>a</sup>

<sup>a</sup> Agency for Defense Development, Taejon, Korea

**To cite this Article** Gal, Yeong-Soon(1994) 'Polymerization of 1-Ethynyl-1-Cyclohexanol by Transition Metal Catalysts', *Journal of Macromolecular Science, Part A*, 31: 6, 703 – 714

**To link to this Article:** DOI: 10.1080/10601329409349749

**URL:** <http://dx.doi.org/10.1080/10601329409349749>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# POLYMERIZATION OF 1-ETHYNYL-1-CYCLOHEXANOL BY TRANSITION METAL CATALYSTS

YEONG-SOON GAL

Agency for Defense Development  
4-4-5, P.O. Box 35, Yuseong 305-600, Taejon, Korea

## ABSTRACT

The polymerization of 1-ethynyl-1-cyclohexanol (ECHO) was carried out by various transition metal catalysts. The Mo- and W-based catalysts gave a relatively low yield of polymer ( $\leq 32\%$ ). The catalytic activity of Mo-based catalysts was greater than that of W-based catalysts.  $\text{PdCl}_2$  was a very effective catalyst for the present polymerization and gave a high yield of polymer.  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  and  $\text{PtCl}_2$  were also found to be effective catalysts. The structure of the resulting poly(ECHO) was identified by various instrumental methods as a conjugated polyene structure having an  $\alpha$ -hydroxycyclohexyl substituent. The poly(ECHO)s were mostly light-brown powders and completely soluble in various organic solvents such as chloroform, chlorobenzene, benzene, DMSO, and THF. Thermal and morphological properties were also studied.

## INTRODUCTION

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

The polymerization of the propargyl derivative, which is a monosubstituted acetylene, is scarce and restricted to propargyl halides [15], propargyl ethers [15], dipropargyl ether [16], and propiolic acid [17].

In recent years we have reported the polymerization of propargyl halides [18, 19], ethers [20], and amines [21], and the cyclopolymerization of dipropargyl derivatives such as dipropargyl ether [22], sulfide [23], silanes [24], germaniums [25], and diphenylmethane [26].

The polymerization of 2-propyn-1-ol, which has a hydroxy functional group, is carried out by  $\text{PdCl}_2$  [15],  $\text{NiI}_2(\text{Ph}_3\text{P})_2$  [27],  $\text{Ni}(\text{NCS})(\text{C}\equiv\text{CR})(\text{Ph}_3\text{P})_2$  [27],  $\gamma$ -rays [28], plasma [29], etc. We have also reported a systematic study on the polymerization of 2-propyn-1-ol by various Mo- and W-based catalysts [30]. However, the poly(2-propyn-1-ol) obtained was insoluble in any organic solvent. Recently we prepared such soluble poly(2-propyn-1-ol) homologues as poly(3-butyn-2-ol), poly(1-octyn-3-ol), and poly(2-phenyl-3-butyn-2-ol) by introducing a substituent at the methylene carbon of 2-propyn-1-ol [31].

A systematic study on the polymerization of ECHO has not been reported. The copolymerization of ECHO with cyclopentadiene in xylene at 200–300°C was reported [32]. Dimerization of ECHO was carried out using nickel [33] and rhodium [34] metal complex catalysts. The trimerization and oligomerization of ECHO by organometallic complexes of nickel were reported by some research groups [35–38]. In recent years the solid-state polymerization of ECHO was carried out by irradiation in a Co-60  $\gamma$ -ray source at a dose rate of 0.06 Mrad/h in a benzene solution or in the solid state. The polymerization gave almost 80–90% polymer yield whereas in the solid state there was about 50% conversion [39]. However, in this polymerization the polymerization time was very long (about 4000 hours) and the products at lower conversions were mixtures of trimer, oligomers, and polymer.

The present paper reports a facile synthesis of poly(ECHO) in high yield by Pd-, Pt-, Mo-, and W-based catalysts, and the characterization of the resulting poly(ECHO).

## EXPERIMENTAL

### Materials

ECHO (Aldrich Chemicals, 99%) was used after fractional distillation.  $\text{MoCl}_5$ ,  $\text{MoCl}_4$ , and  $\text{WCl}_6$  (Aldrich Chemicals, resublimed, 99+ %) were used as received. Tetraphenyltin (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride.  $\text{EtAlCl}_2$  (Aldrich Chemicals, 1.8 M solution in toluene) was used as received.  $\text{PdCl}_2$  (Aldrich Chemicals, 99.995%) and  $\text{PtCl}_2$  (Strem) were used without further purification.  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  was prepared by a reported method [40]. All polymerization solvents were analytical grade materials. They were dried with appropriate drying agents and fractionally distilled.

### Preparation of Catalyst Systems

All procedures for catalyst system preparation were carried out under a dry nitrogen atmosphere because the active species are sensitive to moisture or oxygen.  $\text{MoCl}_5$ ,  $\text{MoCl}_4$ , and  $\text{WCl}_6$  were dissolved in chlorobenzene as 0.1 and 0.2 M solutions before use.  $\text{PdCl}_2$ ,  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ ,  $\text{PtCl}_2$ , and  $\text{Ph}_4\text{Sn}$  were added as powder in the polymerization ampule.

## Polymerization Procedures

A polymerization ampule equipped with rubber septum was flushed with dry nitrogen. Injections of catalyst solution and monomer were done by means of hypodermic syringes from which air and moisture had been carefully excluded.

### Polymerization of ECHO by $\text{MoCl}_5$ - $\text{EtAlCl}_2$ (1:2)

A catalyst solution was prepared by mixing  $\text{MoCl}_5$  (0.425 mL of 0.2 M chlorobenzene solution, 0.0805 mmol),  $\text{EtAlCl}_2$  (0.850 mL of 0.2 M chlorobenzene solution, 0.161 mmol), and chlorobenzene (0.925 mL,  $[\text{M}]_0 = 1.5$ ) and aged by keeping it at 30°C for 15 minutes. To this solution was added ECHO (0.5g, 4.026 mmol) at room temperature. The polymerization was carried out at 80°C for 24 hours. The polymerization was stopped by adding a small amount of methanol. The solvents (chlorobenzene, methanol) were removed by vacuum evaporation below a temperature of 50°C. A cosolvent (DMF/ethanol, volume ratio 3/1) was added to this sample. The resulting polymer solution was precipitated in excess distilled water. The polymer was filtered from the solution and dried under vacuum at 40°C for 24 hours. The polymer yield was 30%.

### Polymerization of ECHO by $\text{PdCl}_2$

$\text{PdCl}_2$  (0.024 g, 0.134 mmol) was dissolved in DMF (4.86 mL,  $[\text{M}]_0 = 0.75$ ) at 90°C. ECHO (0.5 g, 4.026 mmol) was added to this catalyst solution. After a given polymerization time (24 hours), 10 mL cosolvent (DMF/ethanol, volume ratio 3/1)

TABLE 1. Polymerization of ECHO by Mo- and W-Based Catalysts<sup>a</sup>

Experiment	Catalyst system <sup>b</sup> (mole ratio)	Polymer yield, <sup>c</sup> %	$\overline{M}_n$ <sup>d</sup>
1	$\text{MoCl}_5$	10	—
2	$\text{MoCl}_5$ - $\text{EtAlCl}_2$ (1:2)	30	2410
3	$\text{MoCl}_5$ - $\text{Ph}_4\text{Sn}$ (1:1)	27	2120
4	$\text{MoCl}_4$	13	—
5	$\text{MoCl}_4$ - $\text{EtAlCl}_2$ (1:2)	32	2750
6	$\text{WCl}_6$	5	—
7	$\text{WCl}_6$ - $\text{Ph}_4\text{Sn}$ (1:1)	16	—
8	$\text{WCl}_6$ - $\text{EtAlCl}_2$ (1:2)	11	—

<sup>a</sup>Polymerization was carried out for 24 hours at 80°C in chlorobenzene. The monomer-to-catalyst mole ratio (M/C) and initial monomer concentration ( $[\text{M}]_0$ ) were 50 and 1.5 M, respectively.

<sup>b</sup>Mixture of catalyst and cocatalyst was aged at 30°C for 15 minutes before use.

<sup>c</sup>Water-insoluble polymer.

<sup>d</sup>Measured by means of Waters GPC-510 using calibration curves for polystyrene.

was added and the polymer solution was precipitated in excess distilled water. The polymer was filtered from the solution and dried under vacuum at 40°C for 24 hours. The polymer yield was 93%.

### Instruments and Measurement

NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ) spectra were recorded on a Bruker AM-200 spectrometer in  $\text{CDCl}_3$ , 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 (UV)-visible spectra were obtained using a Shimadzu UV-3100s spectrophotometer in chloroform. The average molecular weights of the polymers were measured with a Waters GPC-510 using calibration curves for polystyrene. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere at a heating rate of 10°C/min up to 700°C with a DuPont 1090 Analyzer. X-ray diffraction patterns of polymer samples were obtained on a Rigaku Geigerflex x-ray diffractometer equipped with a Wahrus flat-plate camera using Ni-filtered  $\text{CuK}_\alpha$  radiation at a scan speed of 4°/min.

## RESULTS AND DISCUSSION

The polymerization of ECHO was carried out by various transition metal catalysts.

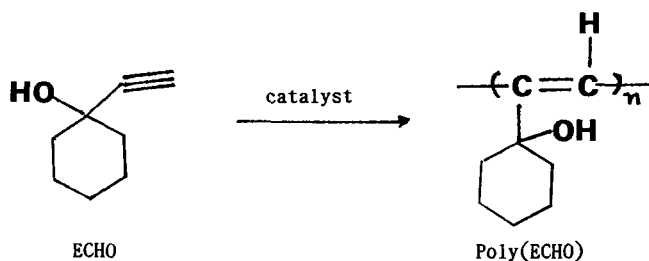


Table 1 shows the results for the polymerization of ECHO by Mo- and W-based catalysts. The polymer yields were relatively low. The catalytic activities of Mo-based catalysts were found to be greater than those of W-based catalysts. This result is consistent with those for the polymerization of propargyl derivatives having oxygen atom such as 2-propyn-1-ol [31], alkyl propargyl ether [20], dipropargyl ether [22], and phenyl propargyl ether [41]. The molybdenum chloride-EtAlCl<sub>2</sub> catalyst system polymerized ECHO to give a moderate yield of poly(ECHO). The catalytic activity of  $\text{MoCl}_4$  was similar with that of  $\text{MoCl}_5$ . The number-average molecular weights ( $\overline{M}_n$ ) of poly(ECHO) obtained by Mo-based catalysts were relatively low ( $<\overline{M}_n = 3000$ ).

Table 2 shows the results for the polymerization of ECHO by  $\text{PdCl}_2$ ,  $(\text{Ph}_3\text{P})_2\text{-PdCl}_2$ , and  $\text{PtCl}_2$ . In general, the polymer yields were greater than those obtained by Mo- and W-based catalysts. The polymerization proceeded well in such solvents as DMF, DMSO, nitrobenzene, and 1,4-dioxane to give a high yield of polymer. As the initial monomer concentration ( $[\text{M}]_0$ ) was increased from 0.5 to 1.0 (Experiments 2, 3, and 4), the polymer yield also increased, from 91% at  $[\text{M}]_0 = 0.5$  to 98% at  $[\text{M}]_0 = 1.0$ .  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  also polymerized ECHO to give a moderate yield

TABLE 2. Polymerization of ECHO by Pd- and Pt-Based Catalysts<sup>a</sup>

Experiment	Catalyst	M/C <sup>b</sup> (mole ratio)	[M] <sub>0</sub> <sup>c</sup>	Solvent	Temperature, °C	Polymer yield, %	$\overline{M}_n$ <sup>e</sup>
1	PdCl <sub>2</sub>	50	0.75	DMF	90	66	1810
2	PdCl <sub>2</sub>	30	0.75	DMF	90	93	2350
3	PdCl <sub>2</sub>	30	0.5	DMF	90	91	2370
4	PdCl <sub>2</sub>	30	1.0	DMF	90	98	2240
5	PdCl <sub>2</sub>	30	0.75	Nitrobenzene	90	87	650
6	PdCl <sub>2</sub>	30	0.75	1,4-Dioxane	90	79	1930
7	PdCl <sub>2</sub>	30	0.75	DMSO	90	99	1120
8	PdCl <sub>2</sub>	30	0.75	EtOH	60	27	1840
9	PdCl <sub>2</sub>	30	0.75	HCO <sub>2</sub> H	90	0	—
10	(Ph <sub>3</sub> P) <sub>2</sub> PdCl <sub>2</sub>	30	0.75	DMF	90	50	910
11	PtCl <sub>2</sub>	30	0.75	DMF	90	71	1270

<sup>a</sup>Polymerization was carried out for 24 hours.<sup>b</sup>Monomer-to-catalyst mole ratio.<sup>c</sup>Initial monomer concentration (M).<sup>d</sup>Water-insoluble polymer.<sup>e</sup>Measured by means of a Waters GPC-150C using calibration curves for polystyrene.

(50%) of polymer.  $\text{PtCl}_2$  was also found to be effective for the present polymerization of ECHO. The number-average molecular weights ( $\overline{M}_n$ ) of poly(ECHO) prepared by Pd and Pt chlorides were in the range from 910 to 2370. In most cases the GPC chromatograms were unimodal. This indicates that the present polymer samples do not contain the dimer or trimer of ECHO.

The structure of poly(ECHO) was characterized by various instrumental methods such as NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ), IR, and UV-visible spectroscopies. Figure 1 shows the  $^1\text{H}$ -NMR spectrum of poly(ECHO) prepared by  $\text{PdCl}_2$  in DMF. The peaks at 5.5–6.5 ppm are due to the vinyl protons on the polymer backbone and the hydroxy protons. There are also methylene protons at 1.3–2.8 ppm.

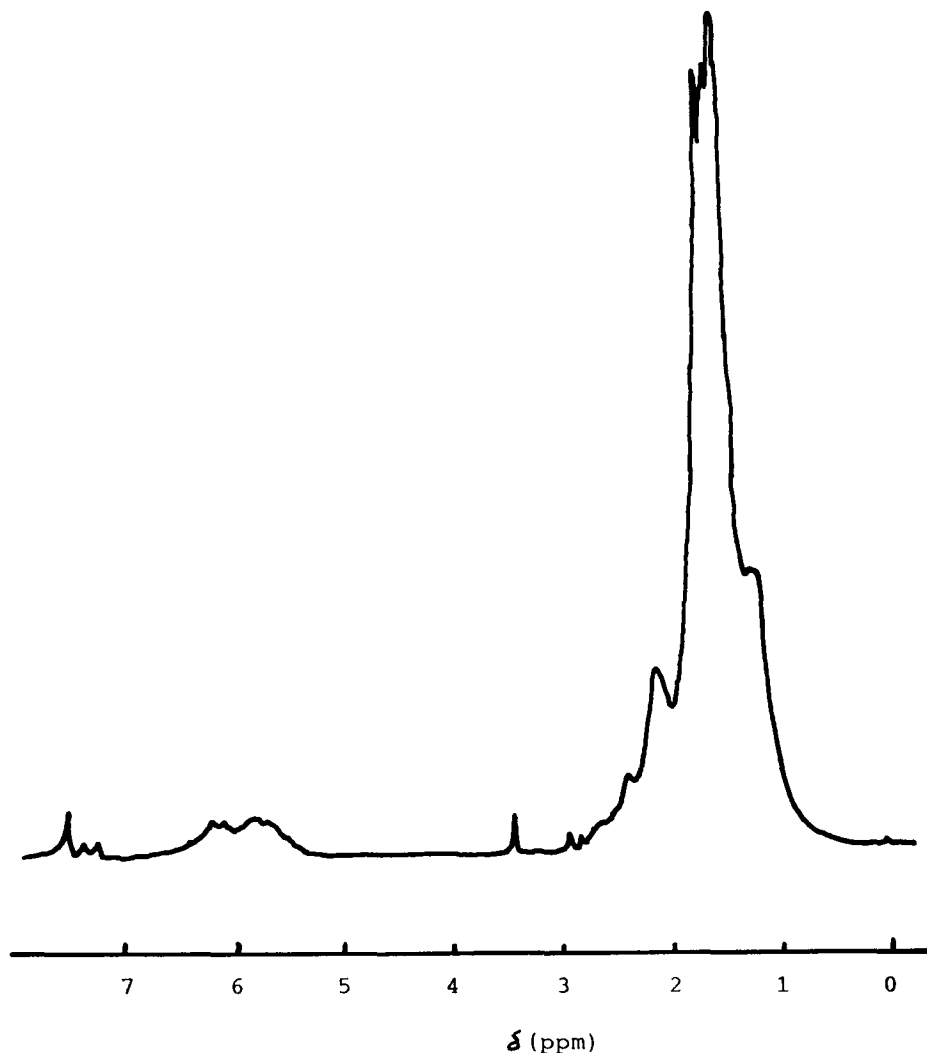


FIG. 1.  $^1\text{H}$ -NMR spectrum of poly(ECHO) in  $\text{CDCl}_3$ .

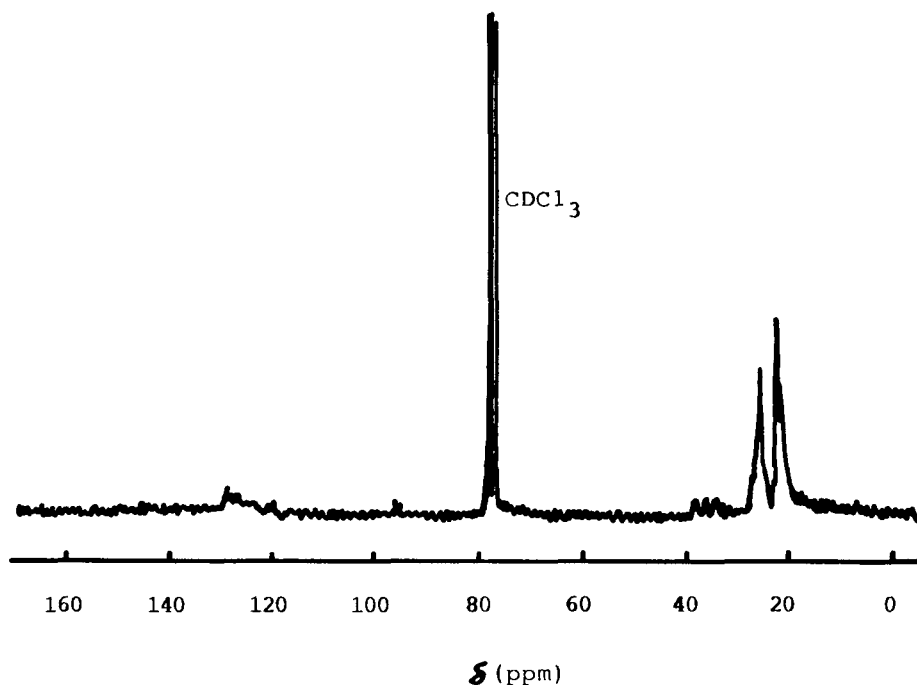


FIG. 2.  $^{13}\text{C}$ -NMR spectrum of poly(ECHO) in  $\text{CDCl}_3$ .

Figure 2 shows the  $^{13}\text{C}$ -NMR spectrum of poly(ECHO) prepared by  $\text{PdCl}_2$ . It shows the presence of olefinic carbons in the polymer backbone at 125–135 ppm and methylene carbon peaks at 15–40 ppm.

Figure 3 shows the IR spectra of ECHO and poly(ECHO) in a KBr pellet. The IR spectrum of poly(ECHO) showed neither the acetylenic hydrogen ( $3306\text{ cm}^{-1}$ ) nor the carbon-carbon triple bond stretching ( $2110\text{ cm}^{-1}$ ) presented in the IR spectrum of ECHO. Instead, the carbon-carbon double bond stretching frequency at about  $1660\text{ cm}^{-1}$  indicates a highly conjugated unsaturation.

The UV-visible spectrum (Fig. 4) of poly(ECHO) was recorded in chloroform. It shows a characteristic absorption peak of conjugated polymer,  $\pi \rightarrow \pi^*$  absorption at a long wavelength (up to 600 nm). The intensity of the absorption peak at longer wavelength was greater than that of poly(ECHO) prepared by the irradiation of a Co-60  $\gamma$ -ray source [39]. The increased intensity at longer wavelength was due to the increased molecular weight of the present poly(ECHO). The spectral properties of poly(ECHO)s prepared by Mo-based catalysts were similar to those of poly(ECHO) prepared by  $\text{PdCl}_2$ , regardless of the polymerization conditions.

These spectral data indicate that the present poly(ECHO)s have a conjugated polyene structure having an  $\alpha$ -hydroxycyclohexyl substituent.

Solubility tests of poly(ECHO)s were performed for powder sample in excess solvent. Poly(ECHO) was completely soluble in various organic solvents such as chloroform, 1,1,1-trichloroethane, chlorobenzene, benzene, ethanol, DMSO, and



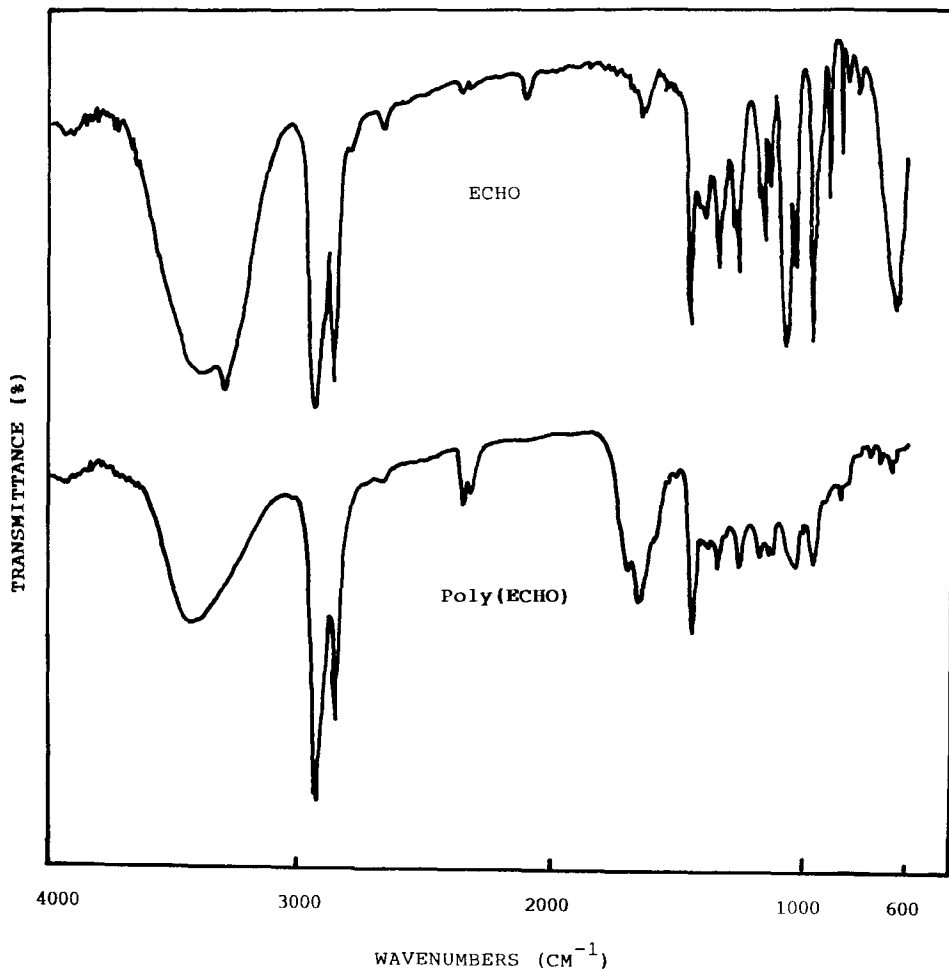


FIG. 3. FT-IR spectra of ECHO and poly(ECHO) in KBr pellet.

THF but insoluble in *n*-hexane and water. The resulting poly(ECHO) was mostly a light-brown powder.

Figure 5 shows the TGA thermogram of poly(ECHO). This polymer shows a gradual weight loss from the initial low temperature. This may be due to the absorbed moisture and organic residues in the polymer. This thermogram shows that poly(ECHO) retains 91% of its original weight at 200°C, 80% at 270°C, 40% at 390°C, and 19% at 500°C.

The morphology of the resulting poly(ECHO) was also investigated by x-ray diffraction analysis (Fig. 6). The data of x-ray diffraction analysis are as follows:  $2\theta(\Delta 2\theta/2\theta) = 8.5(1.29), 17.2(0.59)$ . 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 [42], the present poly(ECHO) is amorphous.

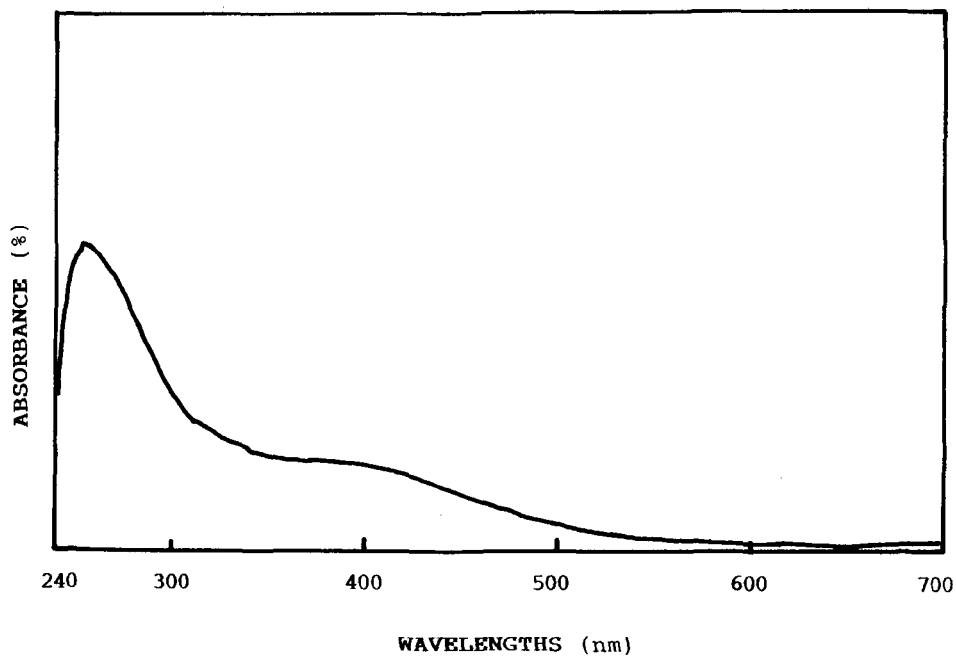
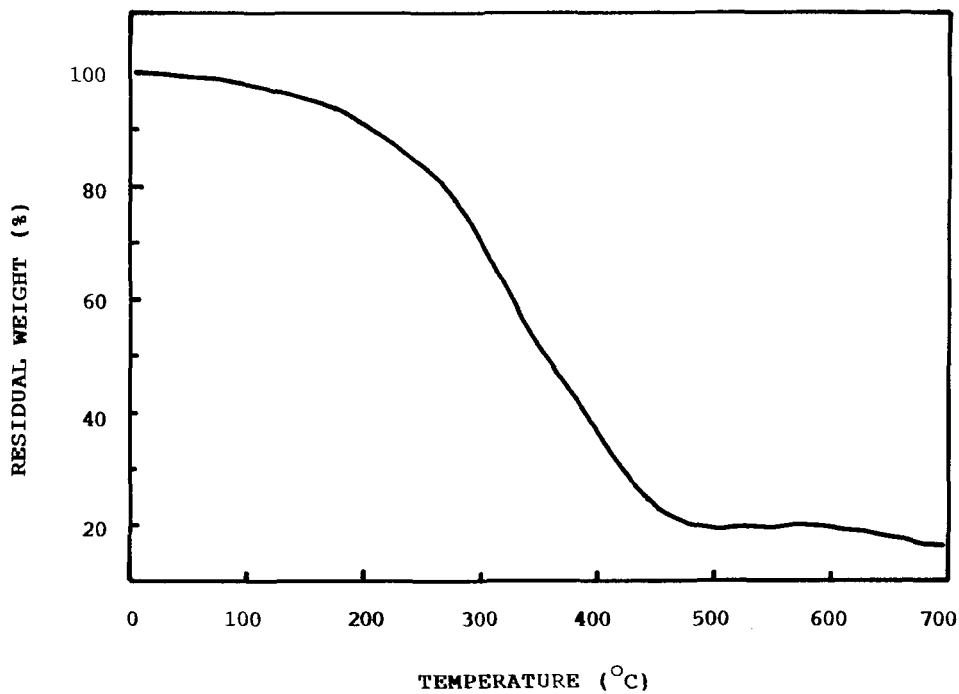
FIG. 4. UV-visible spectrum of poly(ECHO) in CHCl<sub>3</sub>.

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

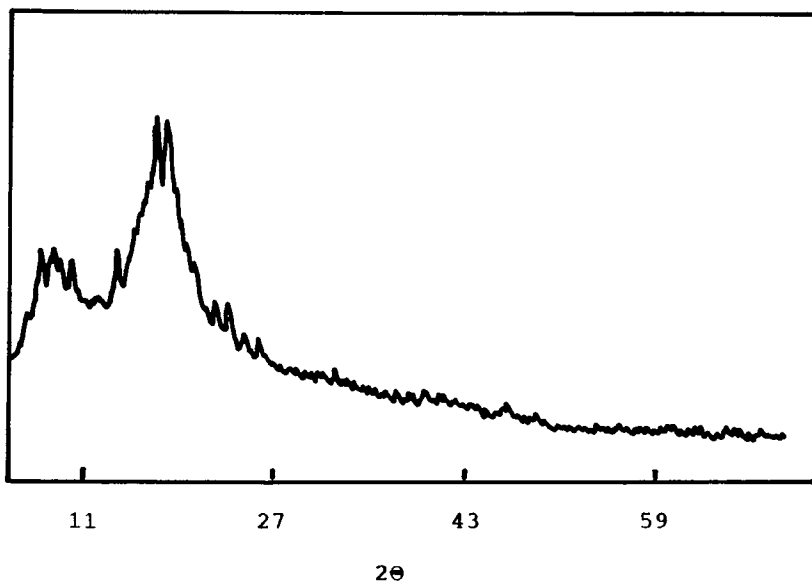


FIG. 6. X-ray diffractogram of poly(ECHO).

## CONCLUSIONS

Interesting results for the polymerization of ECHO having a hydroxy functional group were presented in this paper. The catalytic activity of Mo-based catalysts was greater than that of W-based catalysts.  $\text{PdCl}_2$  polymerized ECHO effectively in various solvents to give a high yield of polymer.  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  and  $\text{PtCl}_2$  were also found to be effective catalysts. It was concluded from various instrumental analyses that the present poly(ECHO) has a conjugated polymer backbone having an  $\alpha$ -hydroxycyclohexyl substituent. Poly(ECHO) was completely soluble in chloroform, ethanol, DMSO, and THF but insoluble in *n*-hexane and water. The data of x-ray analysis showed that poly(ECHO) is amorphous.

## REFERENCES

- [1] M. G. Chauser, Yu. M. Rodionov, V. M. Misin, and M. I. Cherkashin, *Russ. Chem. Rev.*, **45**, 348 (1976).
- [2] H. W. Gibson, *Handbook of Conducting Polymers*, Vol. I (T. A. Skotheim, Ed.), Dekker, New York, 1986, p. 405.
- [3] A. Camus, V. Faruffini, A. Furlani, N. Marsich, G. Ortaggi, R. Paolesse, and M. V. Russo, *Appl. Organomet. Chem.*, **2**, 533 (1988).
- [4] K. C. Wallace, A. H. Liu, W. M. Davis, and R. R. Schrock, *Organometallics*, **8**, 644 (1990).
- [5] Y. S. Gal and S. K. Choi, *Polymer (Korea)*, **13**, 188 (1989).
- [6] H. Kita, T. Takamoto, K. Tanaka, and K-I. Okamoto, *Polym. Bull.*, **20**, 349 (1988).

- [7] B-Z. Tang, T. Masuda, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 1261 (1989).
- [8] Y. Nagase, S. Mori, and K. Matsui, *J. Appl. Polym. Sci.*, **37**, 1259 (1989).
- [9] Y. Nagase, K. Sugimoto, Y. Takamura, and K. Matsui, *Ibid.*, **43**, 1227 (1991).
- [10] S. H. Jin, S. H. Kim, H. N. Cho, and S. K. Choi, *Macromolecules*, **24**, 6040 (1991).
- [11] S. H. Jin, S. J. Choi, W. S. Ahn, H. N. Cho, and S. K. Choi, *Ibid.*, **26**, In Press.
- [12] T. Higashimura, B-Z. Tang, T. Masuda, H. Yamaoka, and T. Matsuyama, *Polym. J.*, **17**, 393 (1985).
- [13] B-Z. Tang, T. Masuda, T. Higashimura, and H. Yamaoka, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 1197 (1989).
- [14] Y. Mujje, Z. Jian, L. Aibing, S. Zhiquan, Z. Mingjian, and L. Senhao, *Ibid.*, **27**, 3829 (1989).
- [15] L. A. Akopyan, S. G. Grigoryan, G. A. Zhamkochyan, and S. G. Matsoyan, *Vysokomol. Soedin., Ser. A*, **17**, 2517 (1975).
- [16] L. A. Akopyan, G. V. Ambartsummyan, E. V. Ovakimyan, and S. G. Matsoyan, *Ibid.*, **19**, 271 (1977).
- [17] T. Masuda, M. Kawai, and T. Higashimura, *Polymer*, **23**, 744 (1982).
- [18] W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Bull. Korean Chem. Soc.*, **9**, 328 (1988).
- [19] W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Polymer (Korea)*, **12**, 729 (1988).
- [20] W. C. Lee, M. W. Huh, Y. S. Gal, and S. K. Choi, *Ibid.*, **13**, 520 (1989).
- [21] Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 2657 (1992).
- [22] Y. S. Gal and S. K. Choi, *Polymer (Korea)*, **11**, 563 (1987).
- [23] Y. S. Gal and S. K. Choi, *J. Polym. Sci., Polym. Lett. Ed.*, **26**, 115 (1988).
- [24] Y. H. Kim, Y. S. Gal, E. Y. Kim, and S. K. Choi, *Macromolecules*, **21**, 1991 (1988).
- [25] O. K. Cho, Y. H. Kim, K. Y. Choi, and S. K. Choi, *Ibid.*, **23**, 12 (1990).
- [26] M. S. Jang, S. K. Kwon, and S. K. Choi, *Ibid.*, **23**, 4135 (1990).
- [27] A. Furlani, M. V. Russo, P. Carusi, S. Licocchia, E. Leoni, and G. Valenti, *Gazz. Chim. Ital.*, **113**, 671 (1983).
- [28] S. Okamura and K. Hayashi, Japan 7886 (1986); *Chem. Abstr.*, **59**, 7671h.
- [29] K. Yoshimura, T. Kitade, K. Kitamura, and K. Hozumi, *J. Appl. Polym. Sci.*, **38**, 1011 (1989).
- [30] M. G. Voronkov, V. B. Pukhnarevich, S. P. Sushchinskaya, V. Z. Annenkova, V. M. Annenkova, and N. J. Andreeva, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 43 (1980).
- [31] Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *Polymer (Korea)*, **16**, 597 (1992).
- [32] R. Hoene (BASF A.G.), German Offen. DE3,017,619 (C/.Co 8F 232/06), (November 12, 1981).
- [33] H. J. Schmit and H. Singer, *J. Organomet. Chem.*, **153**, 165 (1978).
- [34] L. A. Akopyan, S. G. Grigoryan, G. A. Chukhadzhyan, and S. G. Matsoyan, *Zh. Org. Khim.*, **9**, 2004 (1973).

- [35] F. Hockemeyer and P. August, German Offen. DE 2,654,893 (B05D-005/08).
- [36] R. E. Kittle and G. M. Ronk, German Offen. 2,631,299 (C08L-083/04).
- [37] P. Carusi, A. Furlani, and L. Suber, *Congr. Naz. Chim. Inorg. (Atti)*, 13th, p. 334 (1980); *Chem. Abstr.*, 95(9), 79535w.
- [38] P. Carusi, G. Cerichelli, A. Furlani, M. V. Ruso, and L. Suber, *Appl. Organomet. Chem.*, 1, 555 (1987).
- [39] A. Usanmaz and N. Kizilirmak, *J. Macromol. Sci. – Pure Appl. Chem.*, A29, 1175 (1992).
- [40] H. M. Colguhoun, J. Holton, D. J. Thompson, and M. V. Twigg, *New Pathway for Organic Synthesis*, Plenum Press, New York, 1984, p. 383.
- [41] W. C. Lee, Y. S. Gal, M. S. Ryoo, S. H. Han, and S. K. Choi, *Polymer (Korea)*, 15, 283 (1991).
- [42] T. Masuda and T. Higashimura, *Acc. Chem. Res.*, 17, 51 (1984).

Received July 16, 1993

Revision received September 7, 1993