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Polymerization of *p*-Chlorophenyl Propargyl Ether by Molybdenum- and Tungsten- Based Catalysts

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The Polymerization of *p*-chlorophenyl propargyl ether (CPE) was carried out using various transition metal catalysts. The catalytic activity of MoCl₅-based catalysts was greater than that of WCl₆-based catalysts. MoCl₅ alone and MoCl₅-cocatalyst systems polymerized CPE very effectively to give a high yield of poly(CPE). In most cases, the polymer yield was quantitative and the average molecular weight (\bar{M}_n) was in the range of 9,000 and 17,000. The NMR, IR, UV-visible spectra indicated that the present poly(CPE) has a linear conjugated polyene structure having *p*-chlorophenyl oxymethylene substituent. The poly(CPE) was mostly dark-brown colored powder and was completely soluble in various organic solvents such as chloroform, methylene chloride, THF, chlorobenzene, etc. The X-ray diffraction analysis indicated that the present poly(CPE) is amorphous.

Introduction

The polymerization of acetylene and its derivatives is one of the fundamental methods for the synthesis of polymers with a conjugated system, which can be used as organic semiconductors.^{1,2} Polyacetylene has been the simplest conjugated organic conducting polymer, of which a rapidly increasing interest is being aroused in recent years, since the discovery of the high electric conductivity of the doped polyacetylene was found in 1977.³ A number of studies for the polymerization of acetylene have been discussed on the synthesis method, structure properties correlations, electric and optical properties, and various cells application for practical purpose.⁴⁻⁶

However, polyacetylene was insoluble in any organic solvent and unstable to air oxidation. To solve these drawback, various mono- and disubstituted acetylene derivatives were

synthesized and polymerized.^{7,8}

A few study on the polymerization of propargyl derivatives, such as propargyl halide,⁹ phenyl propargyl ether,⁹ dipropargyl ether,¹⁰ etc., those are monosubstituted acetylenes, has been published.

In recent years we have reported the polymerization of propargyl halides,^{11,12} propargyl ethers,¹³ and propargyl amines¹⁴ and the cyclopolymerization of dipropargyl derivatives such as dipropargyl ether,¹⁵ dipropargyl diphenylmethane,¹⁶ dipropargylsilanes,¹⁷ dipropargylgermaniums, etc. And also the polymerization of phenyl and para-substituted phenyl (substituent=OMe, CN) propargyl ethers was carried out and the physical properties of the resulting polymers were characterized.^{19,20} However, in these polymerizations, the polymer yield and the molecular weight were relatively low. In some cases, a small amount of insoluble polymer was also produced.

Now we report on the high polymer yield on the polymerization of *p*-chlorophenyl propargyl ether (CPE) by molybdenum- and tungsten-based catalysts and the relatively high molecular weights of the resulting poly (CPE). The thermal and physical properties of poly (CPE) were also described.

Experimental

Materials. Propargyl bromide (Aldrich Chemicals., 80 wt.% solution in toluene) was dried with calcium hydride and distilled. 4-chlorophenol (Aldrich Chemicals., 99+%) was used as received. MoCl_5 and WCl_6 (Aldrich Chemicals., resublimed, 99+%) and EtAlCl_2 (Aldrich Chemicals., 1.8 M solution in toluene) were used without further purification. Tetra-butyltin was distilled under reduced pressure. All polymerization solvents were analytical grade materials. They were dried with appropriate drying agent and fractionally distilled.

Instruments and Measurement. NMR (^1H - and ^{13}C -) spectra were recorded on a Bruker AM-300 spectrometer and chemical shifts were reported in ppm units with tetramethylsilane as internal standard. Infrared spectra were taken on a Bomem MB-100 spectrometer. UV-visible spectra were recorded on a Shimadzu UV-3100S spectrometer in THF. The average molecular weights of polymers were measured by means of GPC-510 of Waters with a calibration curves using polystyrene standard. Thermogravimetric analysis (TGA) were performed under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ with Dupont 951 Thermogravimetric Analyzer. X-ray diffraction patterns of polymer samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Wahren flat-plate camera using Ni-filtered $\text{Cu-K}\alpha$ radiation at a scan speed of $4^\circ/\text{min}$.

Preparation of CPE. In the three neck flask equipped with an additional funnel for solid delivery, a stirrer, and a thermometer, 64.3 g (0.5 mol) of *p*-chlorophenol, 77 g (0.65 mol) of propargyl bromide, and 400 ml of ethanol were added. Then finely powdered KOH (24 g, 0.6 mol) was added over a period of 30 min to the vigorously stirred mixture. After addition, the mixture was heated under reflux for 2 hrs. The mixture was then cooled and 500 ml of ice-water was added. The layer was separated and the aqueous layer was extracted one time with a small amount of ethyl ether. The extract and the organic layer were combined, washed with water and dried over magnesium sulfate. The volatile compounds were removed on the rotary evaporator. The remaining liquid was distilled quickly at a reduced pressure through a 40 cm Vigreux column. CPE was obtained in 95% yield, b.p. $100^\circ\text{C}/0.1\text{ mmHg}$.

$^1\text{H-NMR}$ (δ , ppm, Figure 1): 7.2 (2H), 6.9 (2H), 4.6 (2H), 2.5 (1H).

$^{13}\text{C-NMR}$ (δ , ppm, Figure 2): 156.1, 129.3, 126.5, 116.2, 76.4, 75.8, 56.0.

IR (wavenumbers, cm^{-1} , Figure 3): 3293, 2920, 2124, 1568, 1480, 1288, 1227, 1022.

Polymerization Procedures. All procedures for the preparation of catalyst solutions and polymerizations were carried out under dry nitrogen atmosphere because the active species are sensitive to moisture or oxygen. Transition metal catalysts and organoaluminum compounds were dissolved in chlorobenzene and adjusted concentrations to 0.05, 0.1 and 0.2 M solution before use. A polymerization ampule

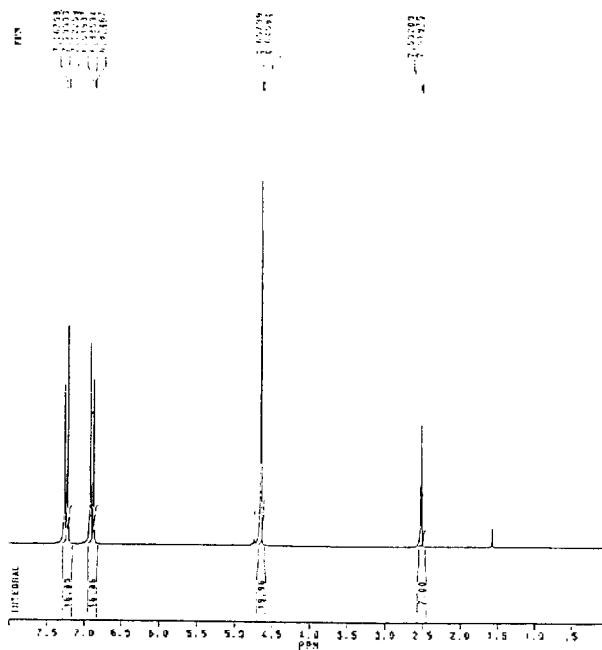


Figure 1. $^1\text{H-NMR}$ spectrum of CPE in CDCl_3 .

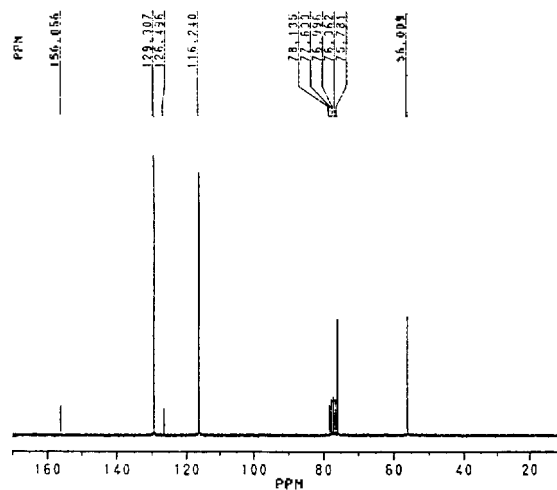


Figure 2. $^{13}\text{C-NMR}$ spectrum of CPE in CDCl_3 .

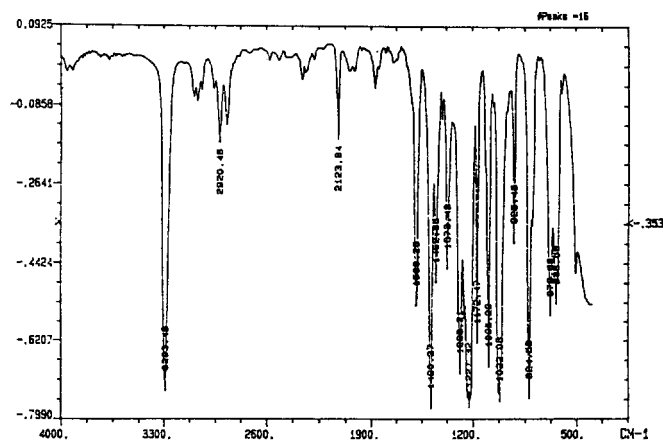


Figure 3. IR spectrum of CPE in KBr pellet.

Table 1. Polymerization of *p*-Chlorophenyl Propargyl Ether by MoCl₅-Based Catalysts.^a

Experiment No.	Catalyst System ^b (mole ratio)	[M] ₀ ^c	M/C ^d	P.Y. ^e (%)	\bar{M}_n ^f
1	MoCl ₅	0.5	50	100	14,800
2	MoCl ₅	1.0	50	100	14,000
3	MoCl ₅	1.0	100	95	17,000
4	MoCl ₅	0.5	100	76	—
5	MoCl ₅ -EtAlCl ₂ (1 : 4)	0.5	100	90	9,000
5	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn(1 : 4)	0.5	100	100	12,300
5	MoCl ₅ -Ph ₄ Sn(1 : 2)	0.5	100	98	12,000

^aPolymerization was carried out at 60°C for 24 h in chlorobenzene. ^bMixture of catalyst and cocatalyst was aged at 30°C for 15 min before use as catalyst. ^cInitial monomer concentration (M). ^dMonomer to catalyst mole ratio. ^e*n*-Hexane insoluble polymer. ^fValues were obtained by GPC analysis with the calibration using polystyrene standards.

equipped with rubber septum was flushed with purified nitrogen.

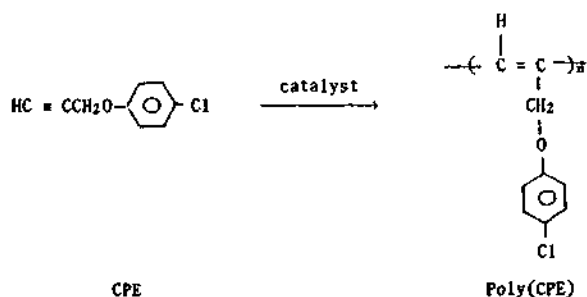
Injections of catalyst solution and monomer into ampules were done by means of hypodermic-syringes from which air and moisture were carefully excluded. After a given polymerization time, the polymer solution was dissolved in chloroform and the polymer was precipitated from excess *n*-hexane. The polymer was filtered and dried under vacuum at 40°C for 24 hrs. The polymer yield was calculated by gravimetry.

Polymerization of CPE by MoCl₅. A solution of MoCl₅ (1.2 ml 0.05 M chlorobenzene solution, 0.06 mmol) and chlorobenzene (4.32 ml) is prepared. To this solution is added CPE (0.5 g, 3.001 mmol) at room temperature (initial monomer concentration of CPE in the system, [M]₀=0.5). The polymerization was carried out at 60°C for 24 hrs. Yield of polymer was 95%, \bar{M}_n =17,000.

Polymerization of CPE by MoCl₅-EtAlCl₂(1 : 4). A catalyst solution is prepared by mixing MoCl₅ (0.6 ml 0.05 M chlorobenzene solution, 0.03 mmol), EtAlCl₂ (0.6 ml 0.2 M chlorobenzene solution, 0.12 mmol), and chlorobenzene (4.32 ml) and aged by keeping at 30°C for 15 min. To this solution is added CPE (0.5 g, 3.001 mmol) at room temperature ([M]₀=0.5). The polymerization carried out at 60°C for 24 hrs. Yield of polymer was 100%, \bar{M}_n =9,000.

Results and Discussion

The Polymerization of CPE, a propargyl derivative, was carried out at various reaction conditions.

**Table 2.** Polymerization of *p*-Chlorophenyl Propargyl Ether by WCl₆-Based Catalysts.^a

Experiment No.	Catalyst System ^b (mole ratio)	P.Y. ^c (%)	\bar{M}_n ^d
1	WCl ₆	32	—
2	WCl ₆ -EtAlCl ₂ (1 : 4)	5	—
3	WCl ₆ -(<i>n</i> -Bu) ₄ Sn(1 : 4)	43	4,500
4	WCl ₆ -Ph ₄ Sn(1 : 2)	40	3,800

^aPolymerization was carried out at 60°C for 24 h in chlorobenzene. Initial monomer concentration ([M]₀) and monomer to catalyst mole ratio were 0.5 and 100, respectively. ^bMixture of catalyst and cocatalyst was aged at 30°C for 15 min before use as catalyst. ^c*n*-Hexane insoluble polymer. ^dValues were obtained by GPC analysis with the calibration using polystyrene standards.

Because Mo-based catalyst system was known to be effective for the polymerization of oxygen-containing acetylene monomers such as propiolic acid,²¹ 2-propyn-1-ol,²² dipropargyl ether,¹⁵ etc., Mo-based catalyst systems were selected and tested for the polymerization of CPE. Table 1 shows the results for the polymerization of CPE by Mo-based catalysts.

MoCl₅ alone polymerized CPE very effectively to give high yield of poly(CPE). The polymer yield was quantitative when [M]₀ and CPE to MoCl₅ mole ratio were 1 M and 50, respectively. It has been known that the addition of a small amount of reducing agents such as Ph₄Sn and *n*-Bu₄Sn increases the polymer yield and molecular weight in the case of MoCl₅-catalyzed polymerization of 2-ethynylthiophene²³ and 2-ethynylfuran.²⁴ Another cocatalyst, EtAlCl₂, which was also reported as very effective cocatalyst for the polymerization of 2-ethynylpyridine when it is combined with MoCl₅²⁵ was also used in the present polymerization. It turned out that the catalyst system consisted with MoCl₅ and organotin or organoaluminum compounds, also effectively polymerized CPE to give poly(CPE) in high yield. The high catalytic activity of MoCl₅ alone and MoCl₅-cocatalyst was thought to be due to the activation of MoCl₅ by CPE containing oxygen atom. The average molecular weight (\bar{M}_n) were in the range of 9,000 and 17,000. These molecular weights of the present poly(CPE) were greater than those of other similar polymers from *para*-substituted phenyl (substituent = OMe, CN) propargyl ethers.^{19,20}

Table 2 shows the results for the polymerization of CPE by WCl₆-based catalysts. In general, it was found that the catalytic activity of WCl₆-based catalysts was lower in comparison to that of MoCl₅-based catalysts. This result is consistent with those for the polymerization of some propargyl ethers such as alkyl propargyl ether,²⁶ phenyl propargyl ether,¹⁹ and dipropargyl ether.¹⁵ Similar results were obtained in the present case, WCl₆ alone polymerized CPE to give a moderate yield of polymer. Organotin compounds such as (*n*-Bu)₄Sn and Ph₄Sn as cocatalysts of WCl₆ slightly increased the polymer yield in the polymerization of CPE. EtAlCl₂ seems to decrease the catalytic activity of WCl₆ as can be seen at Table 2.

The structure of poly(CPE) was characterized by NMR (¹H- and ¹³C-), IR, and UV-visible spectroscopies. Figure 4

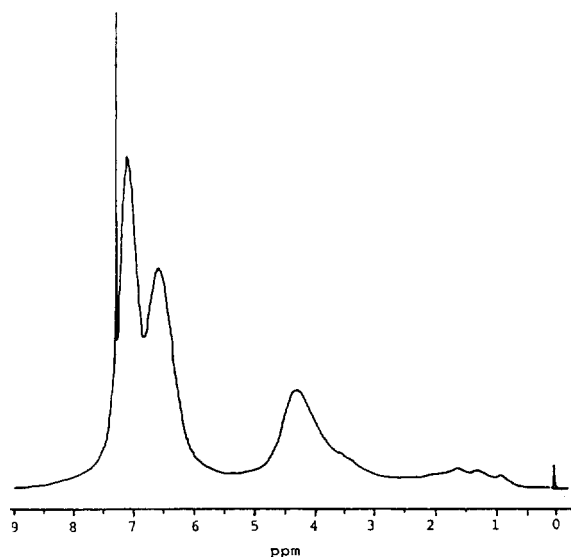


Figure 4. ¹H-NMR spectrum of poly(CPE) in CDCl₃.

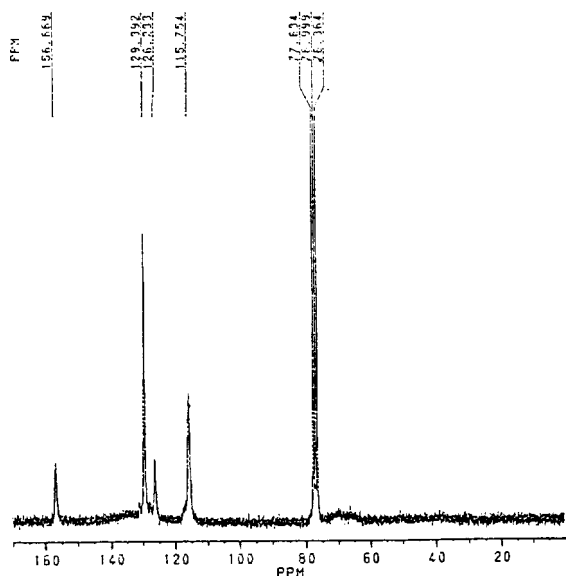


Figure 5. ¹³C-NMR spectrum of poly(CPE) in CDCl₃.

shows the ¹H-NMR spectrum of poly(CPE). It exhibits the phenyl and vinyl protons at 5.5-7.5 ppm and the methylene protons at 2.8-5.0 ppm.

The ¹³C-NMR spectrum (Figure 5) of poly(CPE) shows the presence of the olefinic carbons in the polymer backbone at 135 ppm, and shows the disappearance of the acetylenic carbons that were seen at 75.8 and 78.1 ppm in the ¹³C-NMR spectrum of CPE. The methylene carbon peak shifted from 56 ppm for CPE to 70 ppm for poly(CPE).

The IR spectrum (Figure 6) of poly(CPE) showed neither acetylenic hydrogen stretching (3293 cm⁻¹) nor the carbon-carbon triple bond stretching (2124 cm⁻¹) which were attributed to CPE. On the other hand, the carbon-carbon double bond stretching frequency at 1600 cm⁻¹ was observed and indicates that there is a highly conjugated unsaturation of poly(CPE). The absorption peaks at 821 cm⁻¹ and 1232 cm⁻¹ are due to C-O-C stretching and the CH out-of-plane defor-

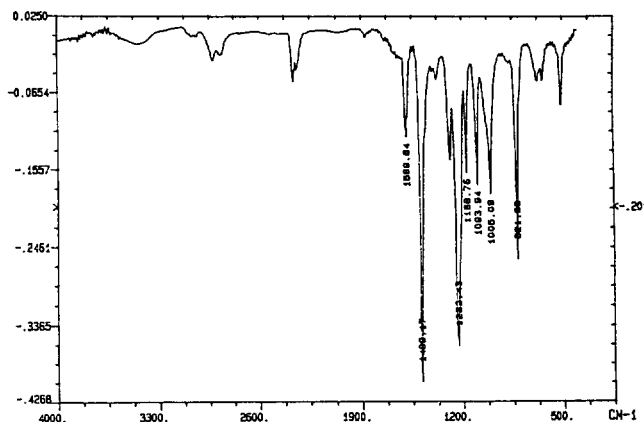


Figure 6. IR spectrum of poly(CPE) in KBr pellet.

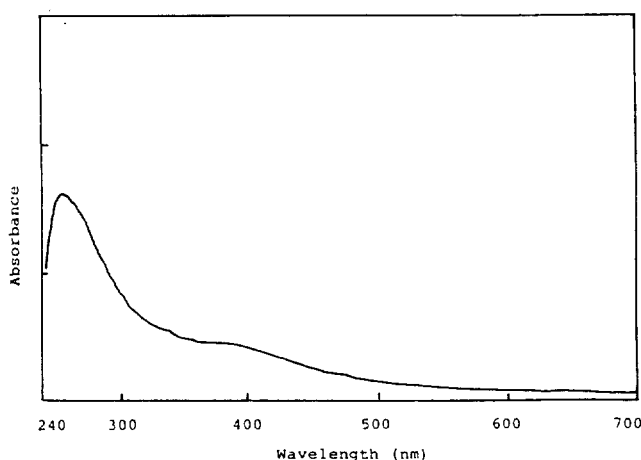


Figure 7. UV-visible spectrum of poly(CPE) in chloroform.

mation of *p*-substituted benzene, respectively.²⁷

The UV-visible spectrum (Figure 7) of poly(CPE) was recorded in chloroform. A characteristic peak of conjugated polymer appeared in the visible region, which is originated from the $\pi \rightarrow \pi^*$ transition of conjugated backbone. The intensity of absorption peak at longer wavelengths was greater than those of poly(phenyl propargyl ether) and its homologues.^{19,20} This was thought to be due to the increased molecular weight of the present poly(CPE) in comparison to those of poly(phenyl propargyl ether) and its homologues. These spectral data indicate the present poly(CPE) to have a conjugated polyene structure containing *p*-chlorophenyl oxymethylene substituent.

Poly(CPE) was completely soluble in various organic solvents such as chloroform, methylene chloride, THF, chlorobenzene, benzene, etc., but insoluble in *n*-hexane, ethyl ether, acetone, etc. The poly(CPE) was mostly dark brown colored powder.

Figure 8 shows the TGA thermogram of poly(CPE). The poly(CPE) is thermally stable up to 170°C and decomposes above this temperature. It shows that poly(CPE) retains 95% of its original weight at 195°C, 50% at 412°C, 30% at 493, and 4% at 700°C.

The X-ray diffraction analysis (Figure 9) of poly(CPE) was carried out. The data of X-ray diffraction analysis shows that 2θ and $\Delta 2\theta/2\theta$ are 19.0 and 0.44, respectively. Because the

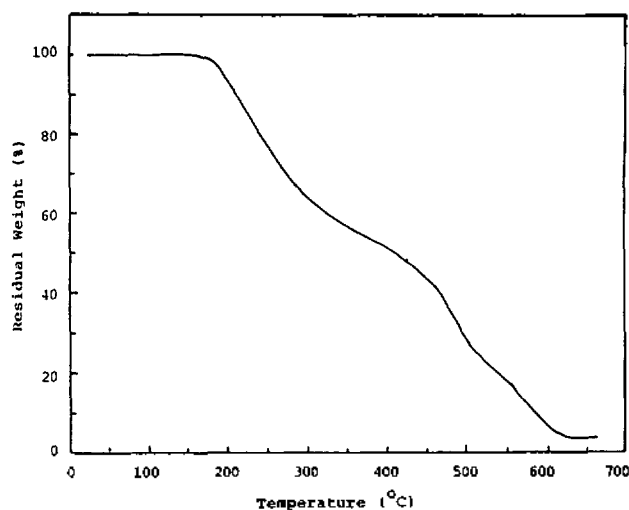


Figure 8. TGA thermogram of poly(CPE).

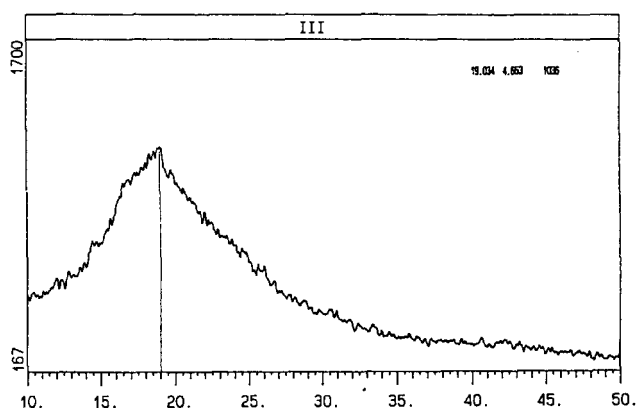


Figure 9. X-ray diffractogram of poly(CPE).

peak in diffraction pattern is broad, and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35,⁸ it can be concluded that the present poly(CPE) is amorphous.

Conclusions

The Polymerization behaviors of a propargyl derivative, CPE, were studied by various transition metal catalysts and the characterization of resulting polymer was also carried out by various instrumental methods. The catalytic activity of MoCl_5 -based catalysts was greater than that of WCl_6 -based catalysts. The higher catalytic activity of MoCl_5 alone and MoCl_5 -cocatalyst was thought to be due to the activation of MoCl_5 by monomer containing oxygen atom. The polymer yield was high and the molecular weights were greater than those of its similar homologues. It can be concluded that the resulting poly(CPE) have a conjugated polyene backbone structure containing *p*-chlorophenyl oxymethylene substituent by various instrumental methods. Poly(CPE) was mostly dark-brown colored powder and was completely soluble in various organic solvents such as chloroform, methylene chloride, THF, chlorobenzene etc., but insoluble in *n*-hexane, ethyl ether, acetone, etc.

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