

폴리(프로파길 페닐 에테르)의 합성과 그 특성에 관한 연구

이원철·갈영순*·류문삼*·한성호**·최삼권**

경북산업대학 섬유공학과 · *국방과학연구소 · **한국과학기술원 화학과

(1991년 1월 15일 접수)

Synthesis and Properties of Poly(phenyl propargyl ether)

Won-Chul Lee, Yeong-Soon Gal*, Moon-Sam Ryoo*, Sung-Ho Han**, and Sam-Kwon Choi**

Department of Textile Engineering, Kyungpook Sanup University, Taegu 701-702, Korea

*Agency for Defense Development, P. O. Box 35, Taejeon 300-600, Korea.

**Department of Chemistry, Korea Advanced Institute of Science and Technology,

P. O. Box 150, Cheongryang, Seoul 130-650, Korea

(Received January 15, 1991)

요약 :여러가지 전이금속촉매를 사용하여 프로파길 페닐 에테르(PPE)를 중합시켰다. MoCl_5 계 촉매가 WCl_6 계 촉매보다 훨씬 더 효과적이었으며 MoCl_5 를 사용한 PPE의 중합에서 $(n\text{-Bu})_4\text{Sn}$ 이 매우 우수한 조촉매로 밝혀졌다. 본 중합에 적합한 용매는 1,2-디클로로에탄, 톨루엔, 클로로벤젠 등이었으며 NMR, IR, UV-visible 분광분석에 의해 합성한 중합체의 구조를 분석한 결과 공액 폴리엔 구조를 가지고 있음을 알 수 있었다. 폴리(PPE)는 벤젠, 클로로벤젠, 클로로포름과 같은 방향성 및 할로젠이 포함된 탄화수소 용매에는 완전히 녹는 반면 메탄올, 개미산, 헥산 등에는 용해하지 않았다. 열중량분석 결과 폴리(PPE)는 200°C 까지 안정함을 알 수 있었다.

Abstract : The polymerization of propargyl phenyl ether(PPE) was carried out by various transition metal catalysts. MoCl_5 -based catalysts were more effective than WCl_6 -based catalysts. $(n\text{-Bu})_4\text{Sn}$ was found to be very effective cocatalyst for the polymerization of PPE by MoCl_5 . It was found that 1,2-dichloroethane, toluene, chlorobenzene are good solvents for this polymerization. The resulting poly(propargyl phenyl ether)[poly(PPE)] structure was identified by NMR, IR, UV-visible spectroscopies to have highly conjugated polyene structure. The poly(PPE) was completely soluble in aromatic and halogenated hydrocarbons such as benzene, chlorobenzene, and chloroform, but insoluble in methanol, formic acid, and hexane. The poly(PPE) was thermally stable up to 200°C .

INTRODUCTION

The synthesis and study of the properties of polymers having conjugated double bonds and heteroatoms(sulfur, nitrogen, oxygen, and metal

atoms) in the conjugated polymer chain is a very promising direction of development in the chemistry of high molecular weight polymer.¹⁻⁴ A characteristic feature of such polymers is as follows.⁵⁻⁷ (a) conductivity(semiconductivity), (b) paramag-

netism, (c) migration and transfer of energy, (d) color, (e) chemical reactivity and complex formation ability. Because of these unique properties, polyene-based polymers seems promising as specialty polymer materials, which might have unique and useful functions. A number of substituted acetylenes such as phenylacetylene,⁸ 2-ethynylacetylene,⁹ 2-ethynylfuran,¹⁰ t-butylacetylene,¹¹ etc. are polymerized by various transition metal catalysts.

However, there have been a few study for the polymerization of propargyl derivatives¹² and the polymers from propargyl derivatives such as propargyl bromide, propargyl chloride, and propargyl alcohol are mostly insoluble in any organic solvents.^{13,14} In recent years, we reported firstly the synthesis of soluble poly(propargyl bromide) and poly(propargyl chloride) by using $\text{TiCl}_4\text{-EtAlCl}_2$ catalyst systems.^{15,16} And also we used the W- and Mo-based catalyst systems, which were very effective for the cyclopolymerization of dipropargyl derivatives.¹⁷⁻¹⁹

The present article deals with the polymerization of PPE and the characterization of the resulting poly(PPE).

EXPERIMENTAL

Materials

Propargyl bromide (Aldrich Chemicals., 80 wt % solution in toluene) was dried over calcium hydride and fractionally distilled. Phenol (Janssen Chimica, 99%) and potassium hydroxide (Janssen Chimica) were used as received. Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemicals., resublimed, 99+ %) were used without further purification. Tetrabutyltin (Aldrich Chemicals., tech., 93%), ethylaluminum dichloride (Aldrich Chemicals., 25 wt % (1.8 M) solution in toluene), and palladium(II) chloride (Aldrich Chemicals., 99.995%) were used as received. All polymerization solvents were dried with a propiate drying agent and fractionally distilled before use.

Instruments

¹H-NMR spectra were recorded on a Varian FT

T-80A NMR spectrometer. Infrared spectra were taken on a BOMEN's MB 100 spectrometer using a potassium bromide pellets. UV-visible spectra were obtained with a Cary spectrophotometer. Number- and weight average molecular weights of poly(PPE) were measured by means of GPC-150C of Waters using a calibration curves for polystyrene. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10°C/min up to 800°C with a Perkin Elmer TGS-1 thermobalance.

Preparation of PPE

In the three-neck flask, which is equipped with an additional funnel for solid, a stirrer, and a thermometer, 47g (0.5 mol) of phenol, 77g (0.65 mol) of propargyl bromide and 400ml of ethanol were added. Then machined powdered KOH (0.6mol) was added in 30 min to the vigorously stirred mixture. After the addition the mixture was heated under reflux for 2 hr. The mixture was then cooled and 500 ml of ice-water added. The layers were separated and the aqueous layer extracted one time with a small amount of ethyl ether. Extract and main portion were combined, washed with water and dried over magnesium sulfate. PPE was obtained in a yield 75%, bp. 80°C/20mmHg.

¹H-NMR (Fig. 1, A, δ , ppm) : 2.7(1H), 4.8(2H), 7.0~7.7(5H). IR (Fig. 1, B, wavenumber, cm^{-1}) : 3288($\equiv\text{C-H}$ stretching), 2122($\text{C}\equiv\text{C}$ stretching).

Polymerization

All polymerizations were carried out under dry nitrogen atmosphere because the active species of the catalysts are very sensitive to oxygen and moisture. Catalyst solution consisting of two components (e. g., WCl_6 and EtAlCl_2) were aged at 30°C for 15 min before use to activate the catalysts. A typical polymerization procedure is as follows : In a 20ml ampoule equipped with rubber septum, 3.04ml of 0.05M MoCl_5 solution, 0.76ml of 0.2M (n-Bu)₄ Sn solution, and 2.8ml chlorobenzene were injected. After aging at 30°C for 15min, 1.0g of PPE was injected to this catalyst solution. After standing at 60°C for 24hr, the polymerization was terminated with a small amount of methanol.

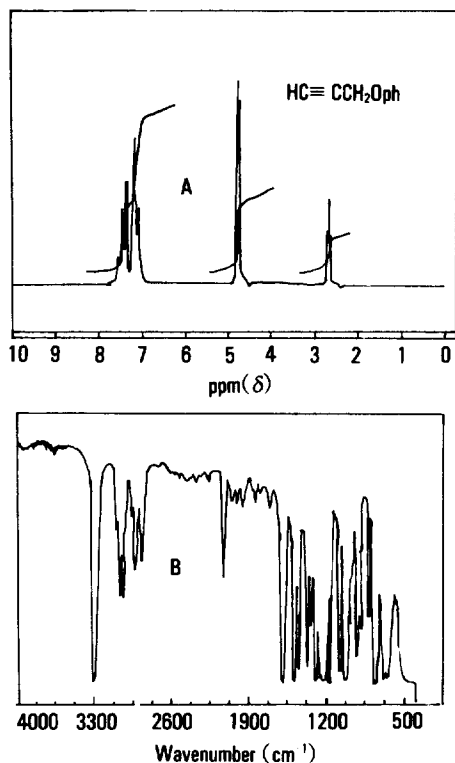


Fig. 1. ^1H -NMR(A) and IR spectra(B) of phenyl propargyl ether(PPE).

Then, 10 ml of chloroform was added, and the polymer was isolated by precipitation into a large excess of methanol. The precipitated polymer was filtered from the solution and dried under vacuum at 40°C for 24hr. The polymer yield was calculated by gravimetry.

RESULTS AND DISCUSSION

Polymerization

The polymerization of PPE were carried out with various transition metal-based catalysts.

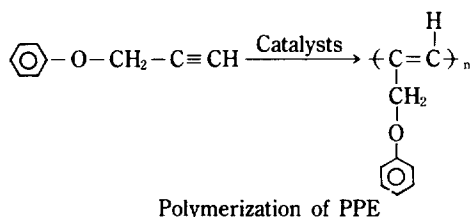


Table 1. Polymerization of Phenyl Propargyl Ether (PPE) by Various Transition Metal Catalysts^a

Exp. No.	Catalyst System ^b (mole ratio)	$[\text{M}]_0^c$	Polymer Yield(%) ^d
1	MoCl_5	1.0	52
2	$\text{MoCl}_5\text{-EtAlCl}_2(1:1)$	1.0	10
3	$\text{MoCl}_5\text{-EtAlCl}_2(1:1)$	2.0	18
4	$\text{MoCl}_5\text{-(n-Bu)}_4\text{Sn}(1:1)$	1.0	72
5	$\text{MoCl}_5\text{-(n-Bu)}_4\text{Sn}(1:1)$	2.0	86
6	WCl_6	1.0	5
7	$\text{WCl}_6\text{-EtAlCl}_2(1:1)$	1.0	5
8	$\text{WCl}_6\text{-(n-Bu)}_4\text{Sn}(1:1)$	1.0	10
9	PdCl_2^e	1.0	30

^a Polymerization was carried out at 60°C for 24 hr in $\text{ClCH}_2\text{CH}_2\text{Cl}$.

^b Mixture of catalyst and cocatalyst in $\text{ClCH}_2\text{CH}_2\text{Cl}$ and chlorobenzene was aged at 30°C for 15 min.

^c Initial monomer concentration(M).

^d Methanol insoluble polymer.

^e Polymerization was carried out at 90°C for 24 hrs in DMF.

Table 1 shows the results for the polymerization of PPE by various transition metal catalysts. MoCl_5 alone gives some moderate yield of polymer. EtAlCl_2 , which was very effective cocatalyst in the polymerization of 2-ethynylpyridine²⁰ and propargyl chloride¹⁵ even decreased the polymer yield. However $(\text{n-Bu})_4\text{Sn}$ was found to be very effective cocatalyst for this polymerization. In general WCl_6 alone and WCl_6 -based catalysts were less effective than MoCl_5 -based catalysts. PdCl_2 polymerized PPE to give poly(PPE) in the yield of 30%.

Fig.2 shows the time dependence curve in the polymerization of PPE by $\text{MoCl}_5\text{-(n-Bu)}_4\text{Sn}$. The polymerization was proceeded rapidly within 2 hr to the extent of about 50% and then polymerization was proceeded more slowly.

Table 2 shows the solvent effect for the polymerization of PPE by MoCl_5 at 60°C . It was found that 1,2-dichloroethane, toluene, and chlorobenzene are good solvents for this polymerization. On the other hand, dioxane and monoglyme were found to be poor solvent.

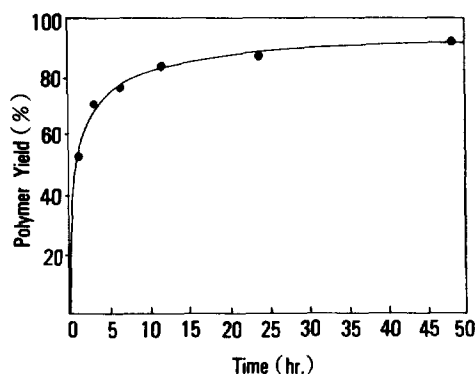


Fig. 2. Time dependence curve in the polymerization of phenyl propargyl ether by MoCl_5 -(*n*-Bu) $_4$ Sn at 60 °C, $[\text{M}]_0=2.0$, M/C(monomer to catalyst mole ratio) = 50.

Table 2. Solvent Effect in the Polymerization of Phenyl Propargyl Ether(PPE)^a

Exp.No.	Solvent	$[\text{M}]_0^b$	Polymer Yield(%) ^c
1	$\text{ClCH}_2\text{CH}_2\text{Cl}$	1.0	52
2	$\text{ClCH}_2\text{CH}_2\text{Cl}$	2.0	80
3	Toluene	1.0	48
4	Toluene	2.0	78
5	Chlorobenzene	1.0	46
6	Chlorobenzene	2.0	66
7	Monoglyme	1.0	0
8	Monoglyme	2.0	5
9	Dioxane	1.0	8
10	Dioxane	2.0	17
11	Ethyl acetate	1.0	48
12	Ethyl acetate	2.0	50

^a Polymerization was carried out by MoCl_5 at 60°C for 24 hrs. Monomer to catalyst mole ratio(M/C) was 50.

^b Initial monomer concentration(M).

^c Methanol insoluble polymer.

Polymer Structure

The structure of poly(PPE) was characterized by NMR, IR, and UV-visible spectroscopy. Fig. 3 shows the ^1H -NMR and IR spectra of poly(PPE). ^1H -NMR spectrum shows the aromatic and vinyl protons at 6.3~7.7 ppm, and it also shows methy-

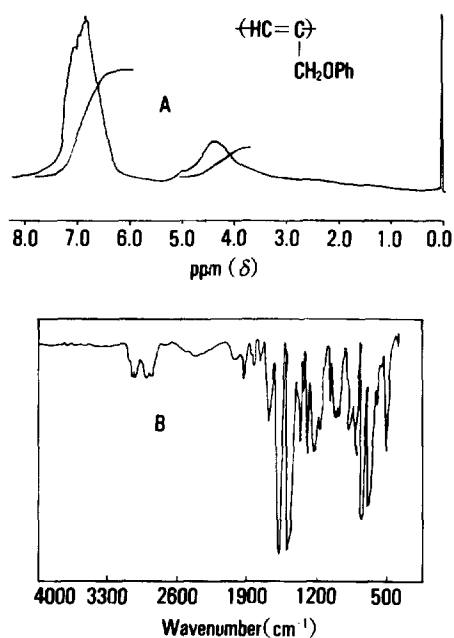


Fig. 3. ^1H -NMR(A) and IR spectra(B) of Poly(phenyl propargyl ether).

lene protons at 3.5~5.2 ppm. The IR spectrum of poly(PPE) shows neither acetylenic carbon-hydrogen stretching frequency nor carbon-carbon triple bond stretching frequency.

Fig. 4 shows the UV-visible spectra of PPE and poly(PPE) in 1,2-dichloroethane. A characteristic peak of conjugated polymer appeared in visible region in the case of poly(PPE). From these observations, it is concluded that the present poly(PPE) have a highly conjugated structure.

Physical Properties

Poly(propargyl ethers) having aliphatic substituents such as methyl, ethyl, propyl, *n*-butyl, and tetrahydrofuryl substituent were mostly insoluble in any organic solvent except for the polymers prepared by PdCl_2 . These insolubility of poly(propargyl ethers) prepared by W- and Mo-based catalysts is assumed to be due to the crosslinking of active allyl protons in polymers by catalysts or other factors. However, the present poly(PPE) was completely soluble in aromatic and halogenated hydrocarbons such as benzene, chlorobenzene,

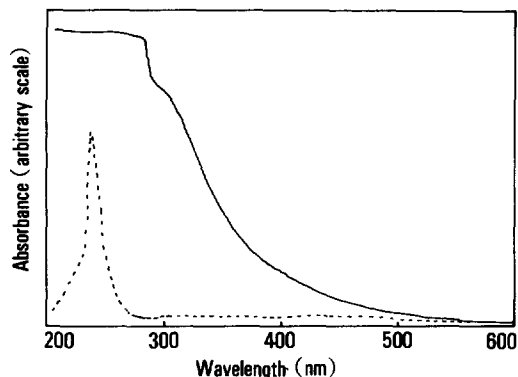


Fig. 4. UV-Visible spectra of phenyl propargyl ether (-----) and poly(phenyl propargyl ether) (—) in 1,2-dichloroethane.

Table 3. Molecular Weights of Poly(phenyl propargyl ether)^a

Sample	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
1-4	3,200	10,600	3.3
1-5	5,700	14,800	2.6
2-2	3,600	11,700	3.3
2-4	5,800	16,400	2.8
2-5	2,800	7,400	2.6

^a Molecular weights were measured by GPC using calibration curves for polystyrene in tetrahydrofuran solution.

^b a : table number, b : experiment number.

chloroform, etc., but insoluble in methanol, formic acid, and hexanes. The poly(PPE) prepared by W- and Mo-based catalysts was brown and dark-red powder whereas the poly(PPE) prepared by PdCl_2 has black color.

Table 3 shows the number- and average molecular weights of some poly(PPE). In general, the average molecular weights ($\bar{M}_n=2,700\sim5,800$, $\bar{M}_w=7,400\sim16,400$) were relatively low. The polydispersity (\bar{M}_w/\bar{M}_n) was in the range of 2.6 and 3.3.

Fig. 5 shows the TGA thermogram of poly(PPE). The poly(PPE) is thermally stable up to 200°C and decomposes above this temperature. It shows that poly(PPE) retained 95% of its original

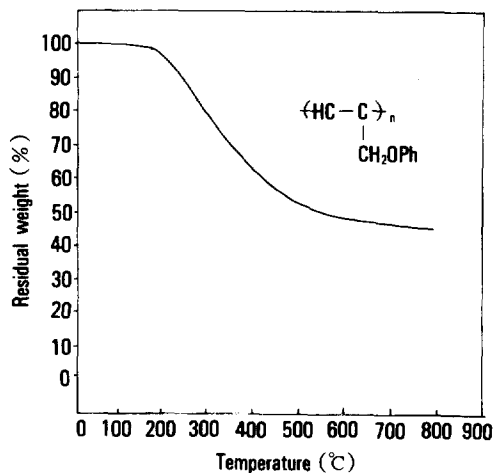


Fig. 5. TGA Curve of Poly(phenyl propargyl ether).

weight at 225°C, 70% at 360°C, 50% at 560°C, and 46% at 800°C.

Further works on the electrical and morphological properties of poly(PPE) are in progress.

Acknowledgement : This work was partly supported by the Korea Science and Engineering Foundations.

REFERENCES

1. Y. M. Paushkin, T. P. Vishnyakova, S. A. Nisova, A. F. Lunin, O. Y. Omarov, Y. Y. Markov, F. F. Machus, I. A. Golubera, L. S. Polak, I. I. Patalakh, V. A. Stychenko, and T. A. Sokolinskaya, *J. Polym. Sci. A-1*, **5**, 1203 (1967).
2. G. E. Wnek, J. C. W. Chien, F. E. Karasz, and C. P. Lillya, *Polymer*, **20**, 1441 (1979).
3. E. T. Kang, A. P. Bhatt, E. Villaroel, W. A. Anderson, and P. Ehrlich, *J. Polym. Sci. Polym. Lett. Ed.*, **20**, 143 (1982).
4. C. Camus, V. Faruffini, A. Furlani, N. Marsich, G. Ortaggi, R. Paolesse, and M. V. Russo, *Appl. Organomet. Chem.*, **2**, 533 (1988).
5. T. Masuda and T. Higashimura, *Acc. Chem. Res.*, **17**, 51 (1984).
6. C. I. Simionescu and V. Percec, *Prog. Polym. Sci.*, **8**, 133 (1982).

7. G. Wegner, *Angew. Chem., Int. Ed. Engl.*, **20**, 361 (1981).
8. T. Masuda, K. I. Hasegawa, and T. Higashimura, *Macromolecules*, **7**, 728 (1974).
9. Y. S. Gal, H. N. Cho, and S. K. Choi, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 2021 (1986).
10. Y. S. Gal, H. N. Cho, and S. K. Choi, *Polymer (Korea)*, **10**, 688 (1986).
11. Y. Okano, T. Masuda, and T. Higashimura, *Polymer J.*, **14**, 477 (1982).
12. M. G. Chauser, Yu. M. Rodionov, V. M. Misin, and M. I. Cherkashin, *Russ. Chem. Rev.*, **45**, 348 (1976).
13. A. Furlani, M. V. Russo, P. Carusi, S. Licoccia, E. Leoni, and G. G. Valenti, *Gazz. Chim. Ital.*, **113**, 671 (1983).
14. 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**, 53 (1980).
15. W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Bull. Korean Chem. Soc.*, **9**, 328 (1988).
16. W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Polymer(Korea)*, **12**, 720 (1988).
17. Y. S. Gal and S. K. Choi, *J. Polym. Sci. Polym. Lett. Ed.*, **26**, 115 (1988).
18. Y. H. Kim, Y. S. Gal, U. Y. Kim, and S. K. Choi, *Macromolecules*, **21**, 1991 (1988).
19. M. S. Ryoo, W. C. Lee, and S. K. Choi, *Macromolecules*, **23**, 3029 (1990).
20. Y. S. Gal, H. N. Cho, S. K. Kwon, and S. K. Choi, *Polymer(Korea)*, **12**, 30 (1988).
21. W. C. Lee, M. W. Huh, Y. S. Gal, and S. K. Choi, *Polymer(Korea)*, **13**, 5220 (1989).