

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 ACETYLENE DERIVATIVES BY METALLOCENE CATALYSTS: POLYMERIZATION OF PHENYLACETYLENE BY BIS(CYCLOPENTADIENYL)MOLYBDENUM DICHLORIDE-BASED CATALYST SYSTEM

Yeong-Soon Gal<sup>a</sup>; Won-Chul Lee<sup>b</sup>; Sung-Ho Jin<sup>c</sup>; Hyong-Jong Lee; Sang-Yul Kim<sup>d</sup>; Dong-Won Kim<sup>e</sup>; Jang-Myoun Ko<sup>e</sup>; Jong-Han Chun<sup>e</sup>

<sup>a</sup> Polymer Chemistry Laboratory, College of General Education, Kyungil University, Kyungsangbuk-Do, Korea <sup>b</sup> Department of Textiles and Fashion, Fashion Kyungil University, Kyungsangbuk-Do, Korea <sup>c</sup> Division of Science Education, Pusan National University, Pusan, Korea <sup>d</sup> Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon, Korea <sup>e</sup> Department of Industrial Chemistry, Taejon National University of Technology, Taejon, Korea

Online publication date: 28 February 2001

**To cite this Article** Gal, Yeong-Soon , Lee, Won-Chul , Jin, Sung-Ho , Lee, Hyong-Jong , Kim, Sang-Yul , Kim, Dong-Won , Ko, Jang-Myoun and Chun, Jong-Han(2001) 'POLYMERIZATION OF ACETYLENE DERIVATIVES BY METALLOCENE CATALYSTS: POLYMERIZATION OF PHENYLACETYLENE BY BIS(CYCLOPENTADIENYL)MOLYBDENUM DICHLORIDE-BASED CATALYST SYSTEM', *Journal of Macromolecular Science, Part A*, 38: 3, 263 – 279

**To link to this Article:** DOI: 10.1081/MA-100103348

**URL:** <http://dx.doi.org/10.1081/MA-100103348>

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 ACETYLENE  
DERIVATIVES BY METALLOCENE  
CATALYSTS: POLYMERIZATION OF  
PHENYLACETYLENE BY  
BIS(CYCLOPENTADIENYL)MOLYBDENUM  
DICHLORIDE-BASED CATALYST SYSTEM**

**Yeong-Soon Gal,<sup>1,\*</sup> Won-Chul Lee,<sup>2</sup> Sung-Ho Jin,<sup>3</sup> Hyong-Jong  
Lee,<sup>4</sup> Sang-Yul Kim,<sup>5</sup> Dong-Won Kim,<sup>6</sup> Jang-Myoun Ko,<sup>6</sup> and  
Jong-Han Chun<sup>6</sup>**

<sup>1</sup>Polymer Chemistry Laboratory, College of General Education,  
Kyungil University, Kyongsangbuk-Do, Korea

<sup>2</sup>Department of Textiles and Fashion, Fashion Kyungil University,  
Hayang 712-701, Kyongsangbuk-Do, Korea

<sup>3</sup>Division of Science Education, Pusan National University,  
Pusan 609-735, Korea

<sup>4</sup>Zenphotronics, Rm 303, K-MAC BLD., 104-11 Moonji-Dong,  
Yusong-Gu, Taejon 305-380, Korea

<sup>5</sup>Department of Chemistry, Korea Advanced Institute of Science and  
Technology, Taejon 305-701, Korea

<sup>6</sup>Department of Industrial Chemistry, Taejon National University of  
Technology, Yusong-Gu, Taejon 305-719, Korea

**ABSTRACT**

Bis(cyclopentadienyl)molybdenum dichloride-based catalyst systems were used for the polymerization of phenylacetylene. The bis(cyclopentadienyl)molybdenum-based catalyst systems were found to be effective for the polymerization of phenylacetylene to give a relatively high yield of polymer.  $\text{EtAlCl}_2$  showed high cocatalytic activity for the polymerization of phenylacetylene by  $\text{Cp}_2\text{MoCl}_2$ . The polymerization behaviors were studied according

---

\*Corresponding author. E-mail: ysgal@bear.kyungil.ac.kr

to such reaction variables as monomer to catalyst mole ratio, initial monomer concentration, polymerization temperature, time, etc. The polymer structure was characterized by various instrumental methods to be the conjugated polymer backbone structure having phenyl substituents. The resulting poly(PA)s were generally light-brown powders and soluble in common organic solvents. The physical and thermal properties of the resulting poly(phenylacetylene) were also investigated.

*Key Words:* Phenylacetylene; Metallocene catalyst bis(cyclopentadienyl)molybdenum dichloride; Conjugated polymer.

## INTRODUCTION

Conjugated polymers from acetylene derivatives have potential as organic semiconductors (1–4), membranes for gas separation and for liquid-mixture separation (5–7). Also, as materials for enantioseparation of racemates by high-performance liquid chromatography (8), as a side-chain liquid crystal (9), as materials for chemical sensors (10,11), as materials for nonlinear optical property (18–21), and for photoluminescence and electroluminescence properties (15–18).

The Mo- and W-based catalysts have been used as the catalyst system for the polymerization of acetylene derivatives having various functionality (3,19–21). In particular, Mo-based catalyst systems have been known to be effective for the polymerization of substituted acetylenes containing some polar functional groups, such as hydroxy (22,23), carboxylic acid (24), ester (25), and ethers (26). In recent years, it was reported that a novel molybdenum oxytetrachloride ( $\text{MoOCl}_4$ )-based catalyst ( $\text{MoOCl}_4$ - $\text{Et}_3\text{Al}$ - $\text{EtOH}$ ,  $\text{MoOCl}_4$ - $\text{Et}_2\text{Zn}$ - $\text{EtOH}$ ) induces the living polymerization of *o*-(trifluoromethyl)phenylacetylene (27,28).

The polymerization of phenylacetylene, a typical acetylene derivative, has been carried out by various initiator systems (19,29). We have also reported the polymerization of phenylacetylene by  $\text{MoCl}_5$ /2-propyn-1-ol homologues (30,31) and  $\text{Mo}(\text{OEt})_5$ - $\text{EtAlCl}_2$  catalyst system (32).

Group IV metallocene catalysts, such as  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{Cp}_2\text{ZrCl}_2$ , and  $\text{Cp}_2\text{HfCl}_2/\text{R}_x\text{AlCl}_{3-x}$  have been applied for the polymerization of acetylene derivatives (33). To our knowledge, there have been no reports on the studies for the polymerization of acetylene derivatives using bis(cyclopentadienyl)molybdenum dichloride ( $\text{Cp}_2\text{MoCl}_2$ )-based metallocene catalysts. In our previous communication, we reported the attempted polymerization of phenylacetylene by  $\text{Cp}_2\text{MoCl}_2$ -organoaluminium compound-based catalyst (34).

The present article reports the full accounts on the catalytic activity of  $\text{Cp}_2\text{MoCl}_2$ -based catalyst for the polymerization of phenylacetylene and the characterization of the resulting poly(phenylacetylene).

## EXPERIMENTAL

### Instrumentation

Nuclear magnetic resonance (NMR) ( $^1\text{H}$ - and  $^{13}\text{C}$ -) spectra were recorded on a Bruker AM-200 spectrometer in  $\text{CDCl}_3$ , and chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. Infrared (IR) spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. Elemental analyses were performed with Perkin-Elmer 240DS Elemental Analyzer. The molecular weights of polymers were determined in tetrahydrofuran (THF) solvent with a Waters GPC-150C calibrated with polystyrene standards. Ultraviolet (UV)-visible spectra were taken on a JASCO V-530 spectrophotometer in THF solvent. Thermogravimetry (TGA) was performed under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$  up to  $700^\circ\text{C}$  with a DuPont 2200 thermogravimetric analyzer. DSC thermograms were taken on a DuPont 910 differential scanning calorimeter under nitrogen atmosphere at a scanning rate of  $10^\circ\text{C}/\text{min}$ .

### Materials

Bis(cyclopentadienyl)molybdenum dichloride ( $\text{Cp}_2\text{MoCl}_2$ , Aldrich Chemicals, 98%) was used as received. Organoaluminium compounds such as  $\text{Et}_3\text{Al}$ ,  $\text{Et}_2\text{AlCl}$ ,  $\text{EtAlCl}_2$  (Aldrich Chemicals, 25 wt% solution in toluene) were also used without further purification. Phenylacetylene (PA, Aldrich Chemicals, 98%) was dried with calcium hydride and fractionally distilled.  $\text{Ph}_4\text{Sn}$  (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride.  $\text{Me}_4\text{Sn}$  (Aldrich Chemicals, 95%) was dried with calcium hydride and distilled. The analytical grade solvents were dried with an appropriate drying agent and fractionally distilled.

### Polymerization of Phenylacetylene by $\text{Cp}_2\text{MoCl}_2$ - $\text{EtAlCl}_2$ Catalyst System

$\text{Cp}_2\text{MoCl}_2$  (0.029 g, 0.098 mmol) and chlorobenzene (0.69 mL,  $[\text{M}]_0$ ) are introduced to the polymerization ampule, flushed with dry nitrogen, and then equipped with rubber septum. This catalyst solution was aged at  $30^\circ\text{C}$  for 15 min after the addition of  $\text{EtAlCl}_2$  (1.224 mL 0.4M chlorobenzene solution, 0.49 mmol) to the solution. To this solution, 0.5 g (4.90 mmol) of PA is injected. After standing at  $80^\circ\text{C}$  for 24 h, the polymerization was stopped by adding a small amount of methanol. The resulting polymer was dissolved in chloroform, followed by precipitation with excess methanol. The precipitated polymers were filtered from the solution and dried to constant a weight under vacuum at  $40^\circ\text{C}$  for 24 h. The polymer yield was calculated by gravimetry.

## RESULTS AND DISCUSSION

The polymerization of PA by MoCl<sub>5</sub> and Cp<sub>2</sub>MoCl<sub>2</sub>-based catalyst systems was carried out under various reaction conditions.

Table 1 shows the general scope for the polymerization of phenylacetylene by molybdenum-based catalysts. MoCl<sub>5</sub> alone, which was very effective catalysts for the polymerization of some acetylene derivatives carrying heteroatom (24,35) polymerized PA to give poly(PA) in 21% yield. Cp<sub>2</sub>MoCl<sub>2</sub> itself was tested for this polymerization of PA; however, it did not give any polymeric product. Cp<sub>2</sub>MoCl<sub>2</sub> itself was mostly insoluble in the polymerization solvents (aromatic hydrocarbons such as benzene, toluene, and chlorobenzene). The inactivity of Cp<sub>2</sub>MoCl<sub>2</sub> itself for the polymerization of PA was assumed to be mainly due to the poor solubility of Cp<sub>2</sub>MoCl<sub>2</sub> catalyst to the polymerization solvent.

The activation of Cp<sub>2</sub>MoCl<sub>2</sub> catalyst was attempted by the addition of organoaluminium compounds, as known in the polymerization case of PA by Cp<sub>2</sub>HfCl<sub>2</sub> (33). The addition of organoaluminium compounds such as Et<sub>3</sub>Al, Et<sub>2</sub>AlCl, and EtAlCl<sub>2</sub> to the Cp<sub>2</sub>MoCl<sub>2</sub> chlorobenzene solution made the catalyst

**Table 1.** Polymerization of Phenylacetylene by MoCl<sub>5</sub> and Cp<sub>2</sub>MoCl<sub>2</sub>-Based Catalysts<sup>a</sup>

Exp.No	Catalyst System (Mol ratio) <sup>b</sup>	Polymer Yield (%) <sup>c</sup>	M <sub>n</sub> <sup>d</sup>
1	MoCl <sub>5</sub>	21	3820
2	Cp <sub>2</sub> MoCl <sub>2</sub>	0	-
3	Cp <sub>2</sub> MoCl <sub>2</sub> -Ph <sub>4</sub> Sn (1:1)	trace	-
4	Cp <sub>2</sub> MoCl <sub>2</sub> -Me <sub>4</sub> Sn (1:2)	trace	-
5	Cp <sub>2</sub> MoCl <sub>2</sub> -EtAlCl <sub>2</sub> (1:3)	77	4280
6	Cp <sub>2</sub> MoCl <sub>2</sub> - Et <sub>2</sub> AlCl (1:3)	36	3880
7	Cp <sub>2</sub> MoCl <sub>2</sub> - Et <sub>3</sub> Al (1:3)	21	3250

<sup>a</sup>The polymerization was carried out at 80°C for 24 h in chlorobenzene. M:C and initial monomer concentration ([M]<sub>0</sub>) were 50 and 2.0M, respectively.

<sup>b</sup>The mixture of Cp<sub>2</sub>MoCl<sub>2</sub> and organoaluminium compound was aged for 15 min at 30°C before use.

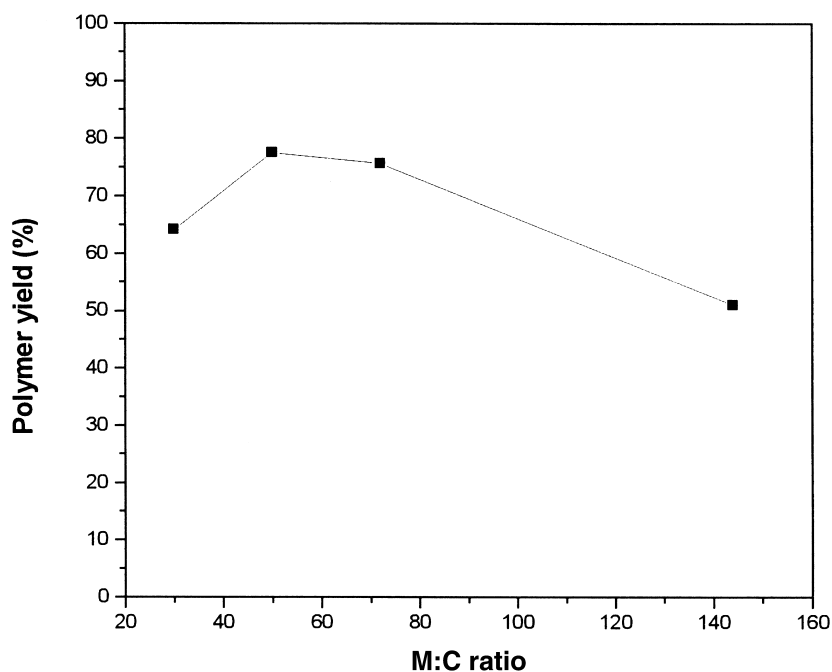
<sup>c</sup>Methanol-insoluble polymer acid yield.

<sup>d</sup>Determined by GPC analysis with polystyrene standards.

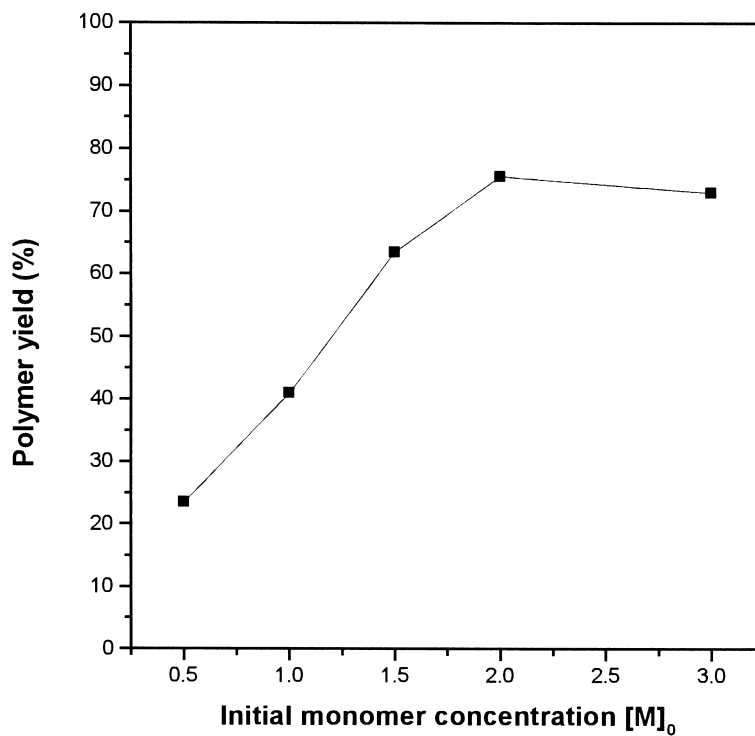
solution into dark-purple suspension phase. The catalyst system composed of  $\text{Cp}_2\text{MoCl}_2$  and  $\text{EtAlCl}_2$  increased the polymer yield from 0% to 87%.  $\text{Et}_2\text{AlCl}$  and  $\text{Et}_3\text{Al}$  also showed some cocatalytic activities for the polymerization of PA by  $\text{Cp}_2\text{MoCl}_2$ , although the polymer yields were lower than that when  $\text{EtAlCl}_2$  was used as cocatalyst. However, organotin compounds, such as  $\text{Ph}_4\text{Sn}$  and  $\text{Me}_4\text{Sn}$ , did not show any cocatalytic activity for this polymerization by  $\text{Cp}_2\text{MoCl}_2$ . The reason was assumed to be due to the insufficient activation of  $\text{Cp}_2\text{MoCl}_2$  by organotin compounds.  $\text{EtAlCl}_2$  itself was tested for the polymerization of PA in order to check the possibility of cationic polymerization of PA with  $\text{EtAlCl}_2$ . However, only light-yellow oligomeric products were obtained. This fact revealed that the present polymerization of PA with  $\text{Cp}_2\text{MoCl}_2$ - $\text{EtAlCl}_2$  catalyst system proceed in classical metathesis polymerization mechanism via metallacyclobutene intermediate.

The effect of monomer to catalyst mole ratio (M:C) for the polymerization of PA by  $\text{Cp}_2\text{MoCl}_2$ - $\text{EtAlCl}_2$  catalyst system is depicted in Figure 1. The best polymerization result was obtained when the M:C is 50. Even in the case of high M:C value (M:C = 144), the poly(PA) was obtained in 51% yield.

The effect of initial monomer concentration ( $[\text{M}]_0$ ) for this polymerization was tested in the range of 0.5 to 3.0 M. The results are shown in Figure 2. In general, the polymer yield increased as the  $[\text{M}]_0$  increased. However, slightly insolu-



**Figure 1.** The effect of monomer to catalyst mole ratio (M/C) for the polymerization of PA by  $\text{Cp}_2\text{MoCl}_2$ - $\text{EtAlCl}_2$  catalyst system.



**Figure 2.** The effect of initial monomer concentration ( $[M]_0$ ) for the polymerization of PA by  $Cp_2MoCl_2$ - $EtAlCl_2$  catalyst system.

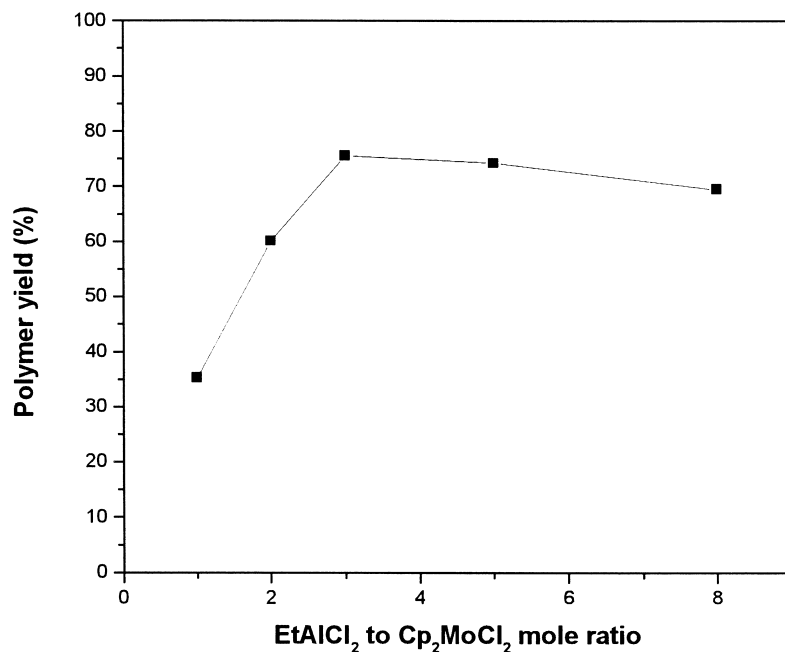
ble products were obtained in the case of high initial monomer concentration ( $[M]_0 = 3.0$ ).

Figure 3 shows the effect of cocatalyst to catalyst mole ratio (the mole ratio of  $EtAlCl_2$  to  $Cp_2MoCl_2$ , cocat:cat) for the polymerization of PA by  $Cp_2MoCl_2$ - $EtAlCl_2$  catalyst system. The polymer yield was increased up to 3 of the cocat/cat mole ratio and then, the polymer yields were slightly decreased. The polymer yield was 69%, even in the case of the cocatalyst/catalyst, mole ratio is 8.

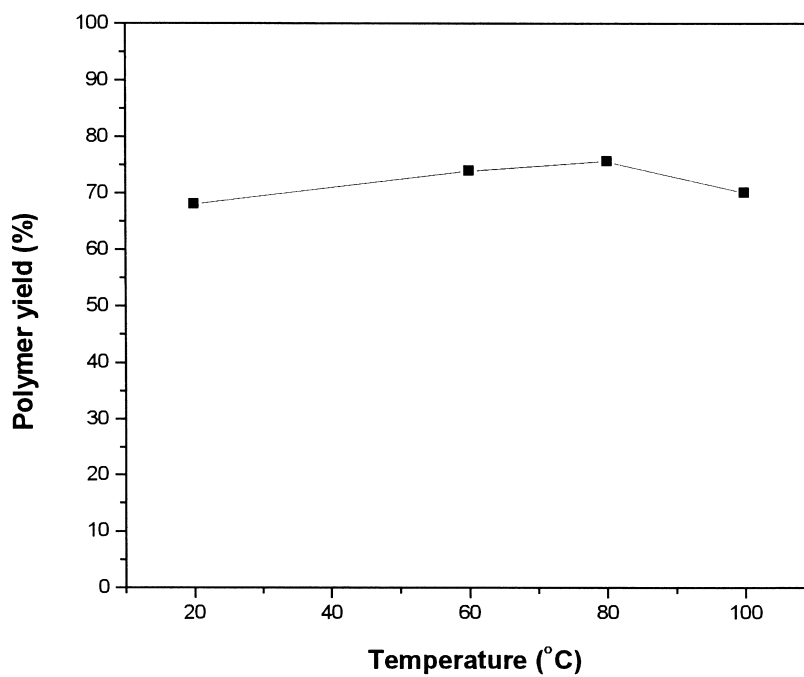
The effect of reaction temperature was also tested in the temperature range of 20°C to 100°C. As shown in Figure 4, it was found that this polymerization proceeded well at a wide temperature ranges to give high polymer yield (68–76%).

The polymer yields according to the polymerization time were consecutively calculated (Fig. 5). This polymerization proceeded well within the first 30 min, accompanying some mild exothermic reaction. As the polymerization time increased, the polymer yield also slightly increased to 3 h, and then plateaus.

The polymer structure of the resulting poly(PA) was characterized by elemental analyses, NMR ( $^1H$ - and  $^{13}C$ -), IR, and UV-visible spectroscopies. The elemental analysis data of reprecipitated poly(PA) agreed with the theoretical value: Calcd.: for  $(C_8H_6)_n$ : C, 94.08%; H, 5.92% Found: C, 93.26%; H, 5.62%.

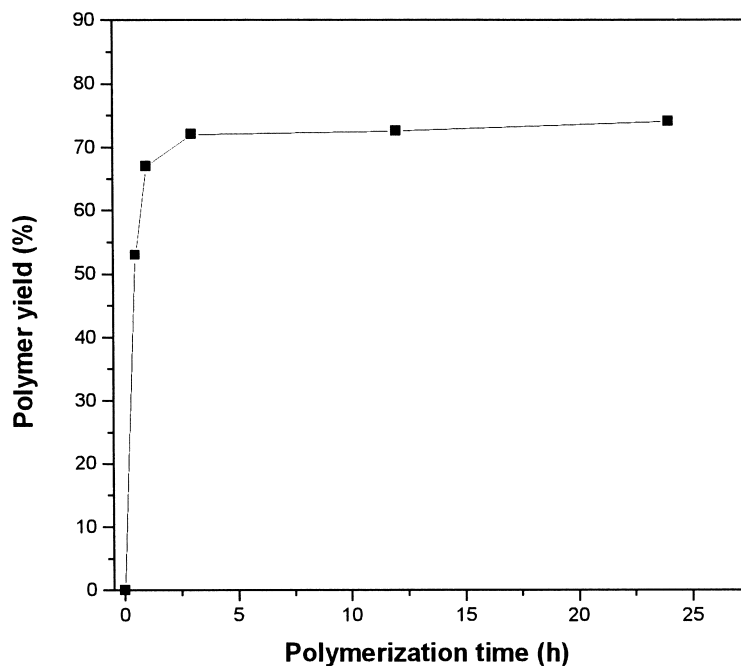


*Figure 3.* The effect of EtAlCl<sub>2</sub> to Cp<sub>2</sub>MoCl<sub>2</sub> mole ratio for the polymerization of PA by Cp<sub>2</sub>MoCl<sub>2</sub>-EtAlCl<sub>2</sub> catalyst system.



*Figure 4.* The effect of polymerization temperature for the polymerization of PA by Cp<sub>2</sub>MoCl<sub>2</sub>-EtAlCl<sub>2</sub> catalyst system.



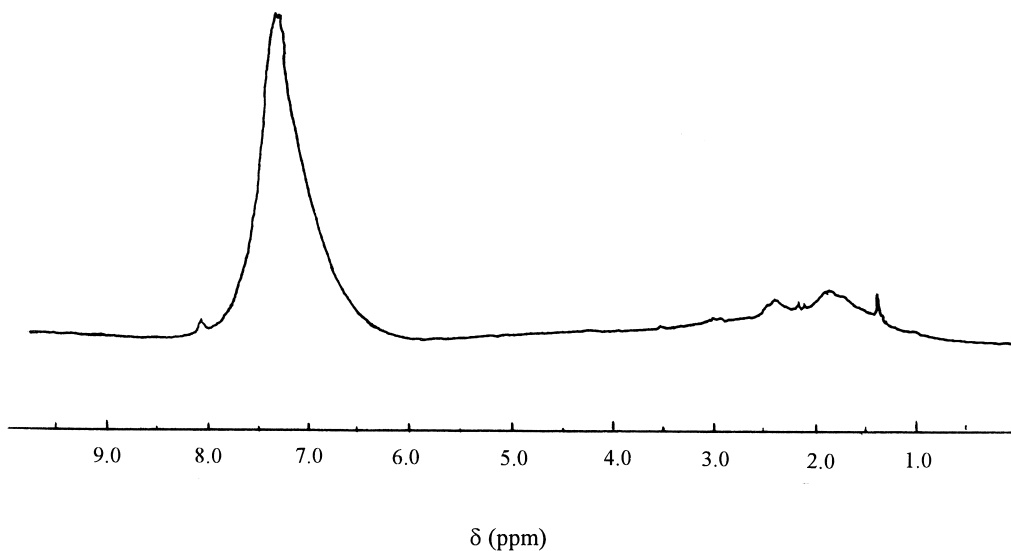


**Figure 5.** The effect of the polymerization time for the polymerization of PA by  $\text{Cp}_2\text{MoCl}_2$ - $\text{EtAlCl}_2$  catalyst system.

Figure 6 shows the proton NMR ( $^1\text{H}$ -NMR) spectrum of poly(PA) prepared by  $\text{Cp}_2\text{MoCl}_2$ - $\text{EtAlCl}_2$  catalyst system. The broad peak at 6.0 to 8.0 ppm originated from the protons of aromatic phenyl substituent and the vinyl protons of conjugated polymer backbone. Moreover, the present NMR spectrum also shows some distinct and wide resonance peaks at 1.0 to 3.5 ppm, which cannot be seen at the NMR spectrum of ideal poly(PA). The peak at aliphatic proton regions was found to be more intense than those of poly(PA)s prepared by  $\text{MoCl}_5$ - $\text{HC}\equiv\text{CCH}_2\text{OH}$  catalyst system (36). This signals may be due to the a low content of aliphatic (methyl, ethyl) protons, which arise from the initiation step (migration insertion of monomer into the metal-alkyl bond).

Figure 7 shows the  $^{13}\text{C}$ -NMR spectrum of poly(PA) in  $\text{CDCl}_3$ . The chemical shift of the carbons on the phenyl substituent was observed at 120 to 132 ppm, whereas those of the carbons on the conjugated double bond of the polymer backbone were observed at 133 to 155 ppm.

Figure 8 shows the IR spectra of poly(PA) prepared by  $\text{Cp}_2\text{MoCl}_2$ - $\text{EtAlCl}_2$  catalyst system. In the IR spectrum of poly(PA), it did not show the acetylenic  $\text{C}\equiv\text{C}$  bond stretching frequency and the acetylenic  $\equiv\text{C-H}$  stretching frequency. Instead, the  $\text{C}=\text{C}$  stretching frequency peak of conjugated polymer backbone at  $1598\text{ cm}^{-1}$  became more intense than those of PA. It shows the aromatic  $=\text{C-H}$



**Figure 6.** <sup>1</sup>H-NMR spectrum of poly(PA) prepared by Cp<sub>2</sub>MoCl<sub>2</sub>-EtAlCl<sub>2</sub> catalyst system.

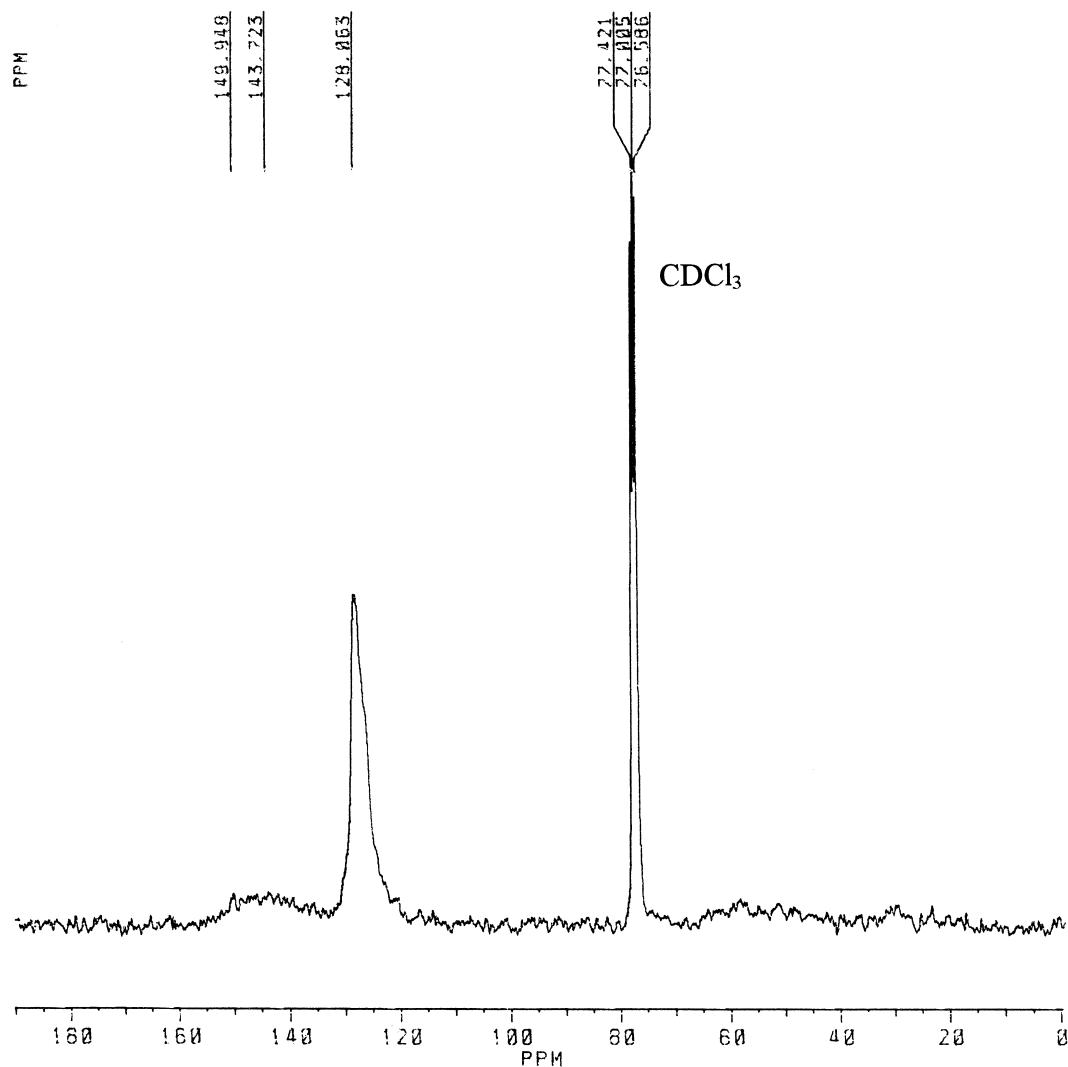
stretching frequencies of phenyl substituents at 3021 and 3055 cm<sup>-1</sup>. And, it also shows the aliphatic C-H stretching frequencies at 2937 and 2963 cm<sup>-1</sup>, which the presence of aliphatic moiety was confirmed by <sup>1</sup>H-NMR spectroscopy. The absorption frequencies at 757 and 698 cm<sup>-1</sup> are due the C-H out-of-plane deformation of monosubstituted benzene.

The UV-visible spectrum of poly(PA) prepared by Cp<sub>2</sub>MoCl<sub>2</sub>-EtAlCl<sub>2</sub> catalyst system also showed a characteristic peak of conjugated polymer, a wide broad π→π\* absorption up to 500 nm.

These spectral data indicate that the resulting poly(PA) have a conjugated polymer backbone system carrying pendant phenyl substituents.

The resulting poly(PA)s were generally light-brown powders. The solubility test was performed for powdery samples in excess solvent. The poly(PA)s were completely soluble in THF, chloroform, benzene, chlorobenzene, and but insoluble in methanol, ethyl ether, and *n*-hexane. The number average molecular weights ( $M_n$ ) and the polydispersities ( $M_w/M_n$ ) of the resulting poly(PA)s were in the range of 2960-4280 and 1.72-2.48, respectively, depending on the polymerization conditions.

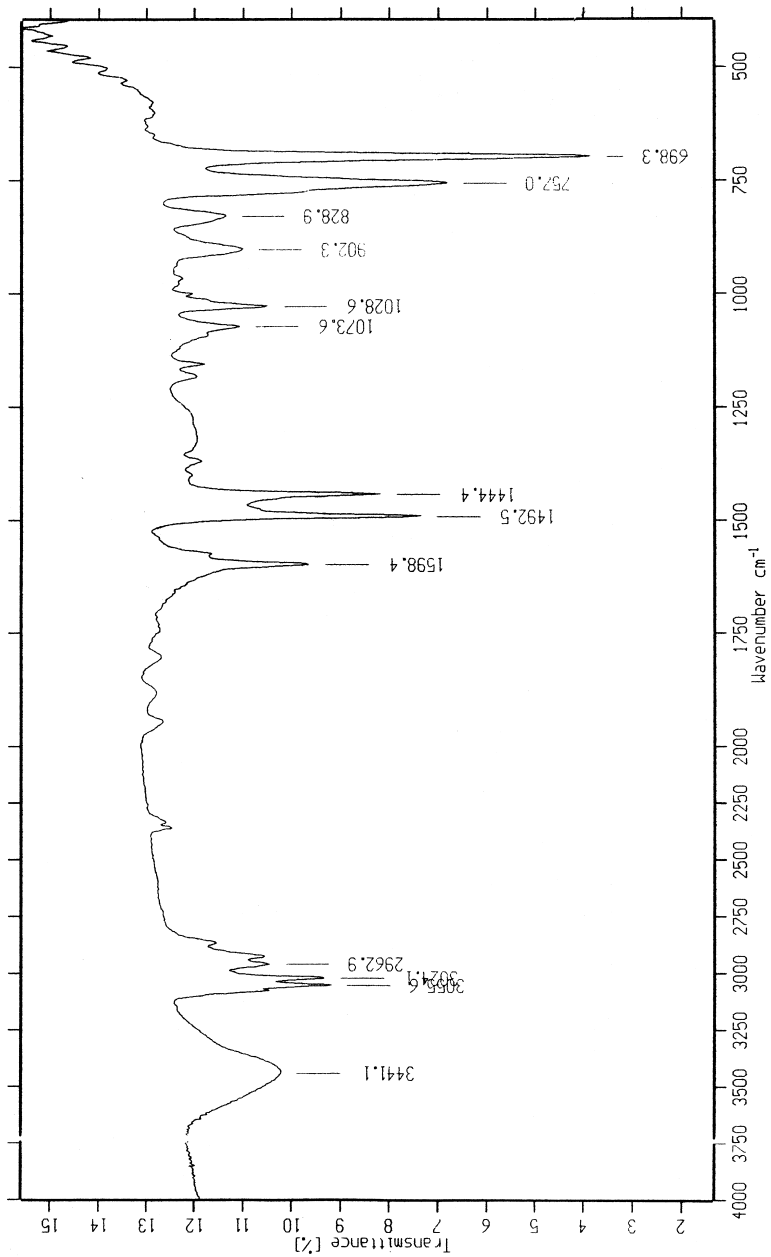
The TGA thermogram (Fig. 9) of poly(PA) was also measured under nitrogen atmosphere. This thermogram shows an abrupt weight loss after 340°C, which is originated from the thermal decomposition and the crosslinking of the present polymer system. The slight weight loss at low temperature (200°C) is due to the absorbed moisture and/or organic residues in the polymer (37). The poly(PA)



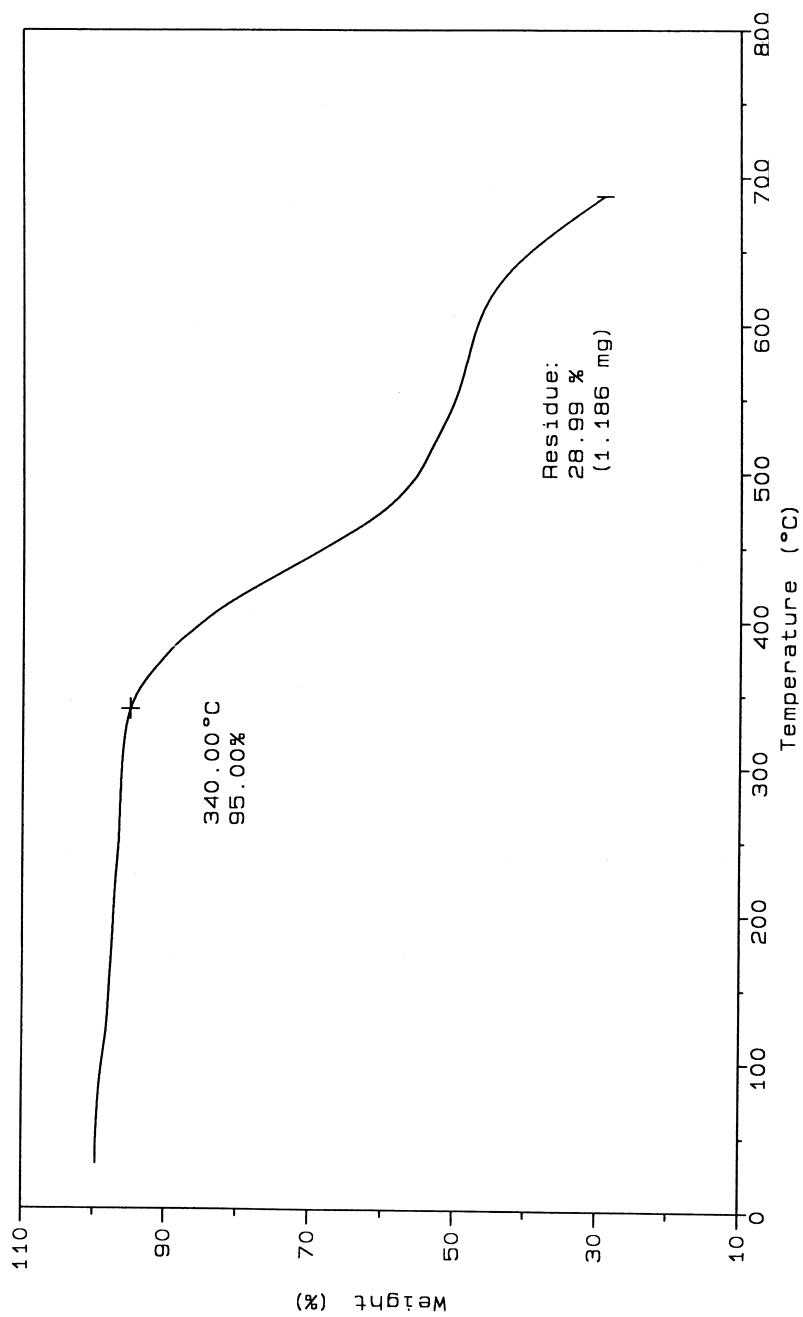
**Figure 7.**  $^{13}\text{C}$ -NMR spectrum of poly(PA) prepared by  $\text{Cp}_2\text{MoCl}_2$ - $\text{EtAlCl}_2$  catalyst system.

retains 97.5% of its original weight at 200°C, 96.5% at 300°C, 90.0% at 382°C, 80.0 at 421°C, 50.0% at 57°C, and 29.0% at 690°C.

Figure 10 shows the DSC thermogram of poly(PA) prepared by  $\text{Cp}_2\text{MoCl}_2$ - $\text{EtAlCl}_2$  catalyst system. This polymer did not show the characteristic glass-transition temperature ( $T_g$ ) peak as like with those of other similar conjugated polymers (38, 39). The exothermic peak starting at about 210.5°C and 238.3°C is due to the conformational isomerization of the polymer system (40, 41).



**Figure 8.** IR spectrum of poly(PA) prepared by  $\text{Cp}_2\text{MoCl}_2\text{-EtAlCl}_2$  catalyst system.



**Figure 9.** TGA thermogram of poly(PA) prepared by  $\text{Cp}_2\text{MoCl}_2\text{-EtAlCl}_2$  catalyst system.

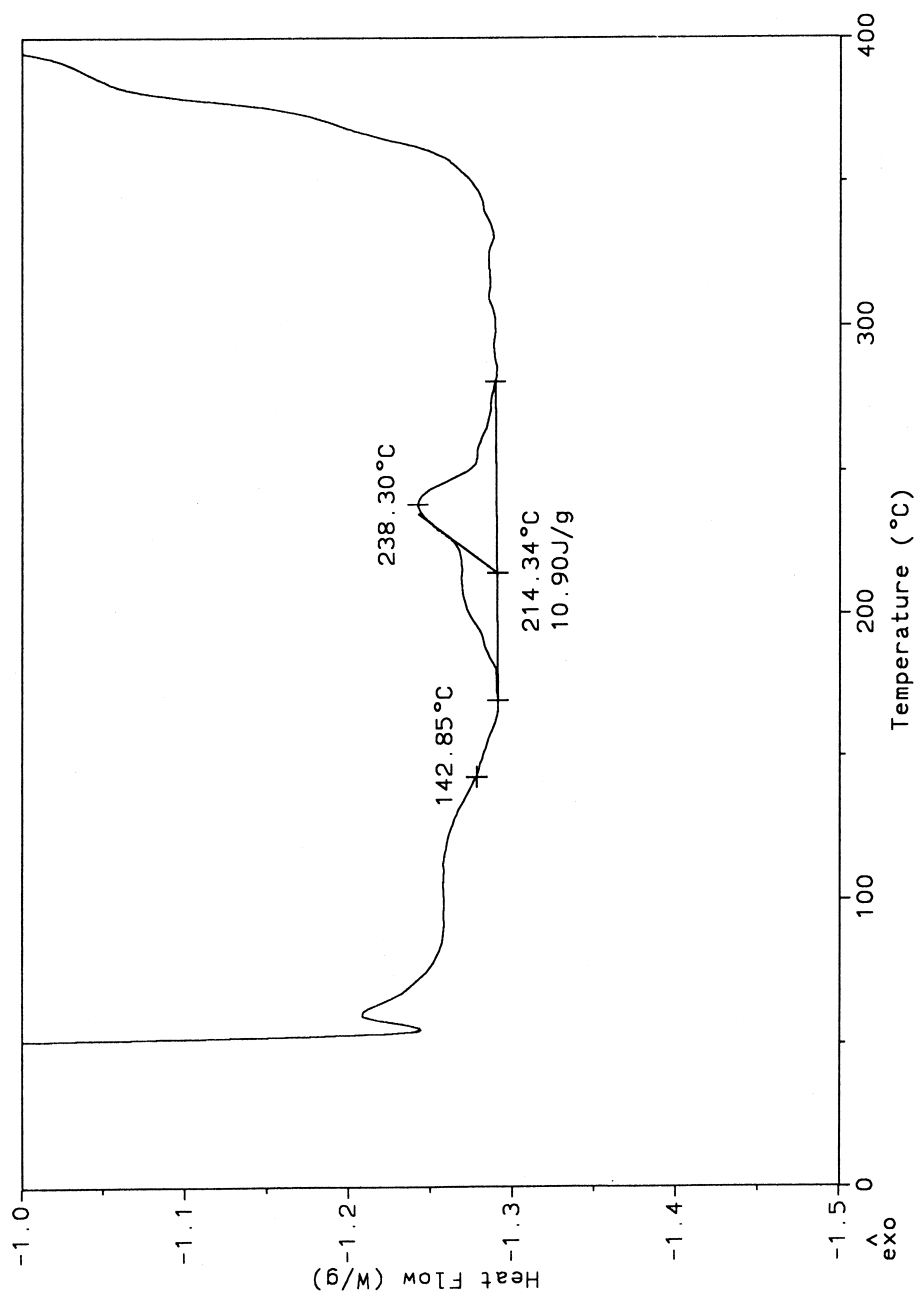


Figure 10. DSC thermogram of poly(PA) prepared by  $\text{Cp}_2\text{MoCl}_2\text{-EtAlCl}_2$  catalyst system.

## CONCLUSION

The present article summarized the polymerization behaviors of PA with new metallocene-based catalyst, Cp<sub>2</sub>MoCl<sub>2</sub>-organoaluminium compounds. This catalyst system was found to be very effective for the polymerization of PA. The addition of organoaluminium compounds made the insoluble Cp<sub>2</sub>MoCl<sub>2</sub> catalyst into an activated suspension catalyst solution. The chemical structure of resulting poly(PA) was characterized by various instrumental methods to have conjugated polymer backbone system having phenyl substituents. Cp<sub>2</sub>MoCl<sub>2</sub>-organoaluminium compound catalyst may be applied to the polymerization of other functional acetylene derivatives.

## ACKNOWLEDGMENTS

This work was supported by the Korea Science and Engineering Foundations (KOSEF) through the Advanced Material Research Center for Better Environment at Taejon National University of Technology.

## REFERENCES

1. Gal, Y.S.; Jung, B.; Choi, S.K. Electrical Conductivity of Poly(2-ethynylthiophene) and Poly(2-ethynylfuran) Doped with Electron Acceptors. *J. Appl. Polym. Sci.* **1991**, *42*, 1793–1797.
2. Tabata, M.; Sone, T.; Sadahiro, Y. Precise Synthesis of Monosubstituted Polyacetylenes Using Rh Complex Catalysts. Control of Solid Structure and Conjugation Length. *Macromol. Chem. Phys.* **1999**, *200* (2), 265–282.
3. Choi, S.K.; Gal, Y.S.; Jin, S.H.; Kim, H.K. Poly(1,6-heptadiyne)-Based Materials by Metathesis Polymerization. *Chem. Rev.* **2000**, *100* (4), 1645–1681.
4. Seo, I.K.; Park, Y.T.; Kim, Y.R. Synthesis and Properties of Conjugated Polycarbosilanes with 1,4-Bis(thiophene or phenylene)-buta-1,3-diyne. *Bull. Korean Chem. Soc.* **1999**, *20* (6), 677–682.
5. Tsuchihara, K.; Masuda, T.; Higashimura, T. Tractable Silicon-Containing Poly(diphenylacetylene): Their Synthesis and High Gas Permeability. *J. Am. Chem. Soc.* **1991**, *113*, 8548–8549.
6. Nagai, K.; Higuchi, A.; Nakagawa, T. Gas Permeation and Sorption in Brominated Poly(1-trimethyl-1-propyne) Membrane. *J. Appl. Polym. Sci.* **1994**, *54*, 1353–1361.
7. Toy, L.G.; Nagai, K.; Freeman, B.D.; Pinnau, I.; He, Z.; Masuda, T.; Teraguchi, M.; Yampolskii, Yu. M. Pure-Gas and Vapor Permeation and Sorption Properties of Poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene] (PTMSDA). *Macromolecules* **2000**, *33*, 2516–2524.

8. Yashima, E.; Matsushima, T.; Nimura, T.; Okamoto, Y. Enantioseparation on Optically Active Stereoregular Polyphenylacetylene Derivatives as Chiral Stationary Phases for HPLC. *Korea Polym. J.* **1996**, *4* (2), 139–146.
9. Choi, S.K.; Lee, J.H.; Kang, S.J.; Jin, S.H. Side-Chain Liquid-Crystalline Poly(1,6-heptadiyne)s and Other Side-Chain Liquid-Crystalline Polyacetylenes. *Prog. Polym. Sci.* **1997**, *22*, 693–734.
10. Bearzotti, A.; D'Amico, A.; Furlani, A.; Iucci, G.; Russo, M.V. Fast Humidity Response of a Metal Halide-Doped Novel Polymer. *Sens. Actuators, B.* **1992**, *7*, 451–454.
11. Furlani, A.; Iucci, G.; Russo, M.V.; Bearzotti, A.; D'Amico, A. Iodine Doped Polyphenylacetylene Thin Film as Humidity Sensor. *Sens. Actuators, B.* **1992**, *8*, 123–126.
12. Samuel, D.W.; Ledoux, I.; Dhenaut, C.; Zyss, J.; Fox, H.H.; Schrock, R.R.; Silbey, R.J. Saturation of Cubic Optical Nonlinearity in Long-Chain Polyene Oligomers. *Science* **1994**, *265*, 1070–1072.
13. Halvorson, C.; Hays, A.; Kraabel, B.; Wu, R.; Wudl, F.; Heeger, A.J. A 160-Femtosecond Optical Image Processor Based on a Conjugated Polymer. *Science* **1994**, *265*, 1215–1216.
14. Lee, H.J.; Won, Y.H.; Kang, S.J.; Choi, S.K.; Kim, H.K. Synthesis and Characterization of NLO Chromophores Bearing Poly(1,6-heptadiyne)s for Electro-Optic Application. *J. Polym. Sci. Polym. Chem. Ed.* **1996**, *34*, 2333–2340.
15. Tada, K.; Hidayat, H.; Hirohata, M.; Teraguchi, M.; Masuda, T.; Yoshino, K. Optical Properties and Blue and Green Electroluminescence in Soluble Disubstituted Acetylene Polymers. *Jpn. J. Appl. Phys.* **1996**, *35*, L1138–L1141.
16. Gal, Y.S.; Lee, S.S.; Bae, J.S.; Kim, B.S.; Jang, S.H.; Jin, S.H. Synthesis and Optical Properties of Poly[6'-(N-carbazolyl)hexyl-2-ethynylpyridinium bromide]. *Bull. Korean Chem. Soc.* **1999**, *20* (4), 451–455.
17. Gal, Y.S.; Lee, W.C.; Lee, S.J.; Park, J.W.; Ko, J.M.; Chun, J.H. Synthesis and Electro-Optical Properties of Poly(2-ethynylpyridinium tosylate) Having Propargyl Side Chain. *J. Macromol. Sci.—Pure Appl. Chem.* **1999**, *A36(10)*, 1503–1519.
18. Gal, Y.S.; Lee, W.C.; Lee, S.S.; Bae, J.S.; Kim, B.S.; Jang, S.H.; Jin, S.H.; Park, J.W. Synthesis and Optical Properties of Poly(2-ethynylpyridinium bromide) Having Glycidyl Functionality. *Korea Polym. J.* **2000**, *8(3)*, 131–136.
19. Masuda, T.; Higashimura, T. Polyacetylenes with Substituents: Their Synthesis and Properties. *Adv. Polym. Sci.* **1987**, *81*, 121–165.
20. Choi, S.K.; Lee, J.H.; Kim, H.K. A New Class of Multifunctional Poly(1,6-heptadiyne)-Based Materials by Metathesis Polymerization. *Macromol. Symp.* **1997**, *118*, 67–72.
21. Schattenmann, F.J.; Schrock, R.R. Soluble, Highly Conjugated Polyenes via the Molybdenum-Catalyzed Copolymerization of Acetylene and Diethyl Dipropargylmalonate. *Macromolecules* **1996**, *29*, 8990–8991.
22. Gal, Y.S. Polymerization of 1-Ethynyl-1-cyclohexanol by Transition Metal Catalysts. *J. Macromol. Sci.—Pure Appl. Chem.* **1994**, *A31(6)*, 703–714.
23. Gal, Y.S.; Lee, W.C.; Jin, S.H.; Lee, H.J. Polymerization of 3-Ethynylphenol by Transition Metal Catalysts. *Korea Polym. J.* **2000**, *8*, *in press*.



24. Masuda, T.; Kawai, M.; Higashimura, T. Polymerization of Propiolic Acid and Its Derivatives Catalyzed by  $\text{MoCl}_5$ . *Polymer* **1982**, *23*, 744–747.
25. Ryoo, M.S.; Lee, W.C.; Choi, S. K. Cyclopolymerization of Diethyl Dipropargylmalonate by Transition Metal Catalysts. *Macromolecules* **1990**, *23*, 3029–3031.
26. Lee, W.C.; Seo, J.H.; Gal, Y.S.; Jin, S.H.; Choi, S.K. Polymerization of *p*-Chlorophenyl Propargyl Ether by Molybdenum- and Tungsten-Based Catalysts. *Bull. Korean Chem. Soc.* **1993**, *14*, 708–712.
27. Hayano, S.; Masuda, T. Living Polymerization of Substituted Acetylenes by a Novel Ternary Catalyst,  $\text{MoOCl}_4\text{-Et}_2\text{Zn-EtOH}$ . *Macromol. Chem. Phys.* **1997**, *198*, 3041–3049.
28. Kaneshiro, H.; Hayano, S.; Masuda, T. Living Polymerization of [*o*-(Trifluoromethyl)phenyl]acetylene by a New Catalyst System,  $\text{MoOCl}_4\text{-Et}_3\text{Al-EtOH}$  (1:1:4). *Macromol. Chem. Phys.* **1999**, *200*, 113–117.
29. Kunzler, J.; Percec, V. Living Polymerization of Aryl Substituted Acetylenes by  $\text{MoCl}_5$  and  $\text{WCl}_6$  Based Initiators: The Ortho Phenyl Substituent Effect. *J. Polym. Sci. Polym. Chem. Ed.* **1990**, *28*, 1221–1236.
30. Gal, Y.S.; Jung, B.; Lee, W.C.; Choi, S.K. Polymerization of Phenylacetylene by Molybdenum Pentachloride/2-Propyn-1-ol Catalyst Systems. *Bull. Korean Chem. Soc.* **1993**, *14* (2), 171–172.
31. Gal, Y.S.; Jung, B.; Lee, W.C.; Choi, S.K. The Effect of Polar Acetylenic Derivatives as Activator on the Polymerization of Phenylacetylene by  $\text{MoCl}_5$ . *Polym. (Korea)*. **1994**, *18*(1), 130–133.
32. Gal, Y.S.; Jung, B.; Cho, H.N.; Lee, W.C.; Choi, S.K. Polymerization of Acetylene Derivatives by Transition Metal Alkoxides. *Bull. Korean Chem. Soc.* **1992**, *13*(1), 4–5.
33. Siskos, M.G.; Bokaris, E.P.; Zarkadis, A.K.; Kyriakakou, G. Polymerization of Phenylacetylene by Hafnocene Dichloride/ $\text{R}_x\text{AlCl}_{3-x}$  Catalytic Systems. *Eur. Polym. J.* **1992**, *28*(9), 1127–1130.
34. Gal, Y.S. Polymerization of Phenylacetylene by Molybdocene Dichloride-Organaluminium Compound Catalyst System. *Eur. Polym. J.* **2000**, *36*, 2059–2062.
35. Gal, Y.S.; Jung, B.; Lee, W.C.; Choi, S.K. Polymerization of 2-Propyn-1-ol by Transition Metal Catalysts. *Polym. (Korea)* **1992**, *16*(5), 597–603.
36. Gal, Y.S.; Jung, B.; Lee, W.C.; Choi, S.K. The Effect of 2-Propyn-1-ol on the Polymerization of Phenylacetylene by  $\text{MoCl}_5$ . *Polym. (Korea)* **1993**, *17*(4), 365–371.
37. Gal, Y.S.; Jung, B.; Lee, W.C.; Lee, H.J.; Choi, S.K. Polymerization of Phosphorus-Containing Acetylenes. 3. Polymerization of Triethyl -Propargylphosphonoacetate by Transition Metal Catalysts. *Macromolecules* **1995**, *28*, 2086–2088.
38. Lee, W.C.; Gal, Y.S.; Kim, S.H.; Jin, S.H.; Jang, S.H.; Choi, S.K. Polymerization of 4-Hydroxy-*N*-propargylpiperidine by Transition Metal Catalysts. *J. Macromol. Sci.—Pure Appl. Chem.* **1999**, *A36*(4), 531–547.
39. Jeon, S. J.; Shim, S. C.; Cho, C. S.; Kim, T. J.; Gal, Y. S. Catalytic Cyclopolymerization and Copolymerization of 1,6-Heptadiynes by  $\text{Mo(CO)}_6$ . *J. Polym. Sci. Polym. Chem. Ed.* **2000**, *38*, 2663–2670.
40. Simionescu, C.I.; Dumitrescu, S.; Percec, V. The Polymerization of Acetylene Derivatives. XXV. Synthesis and Properties of Isomeric Poly(-ethynynaphthalene). *Polym. J.* **1976**, *8*(2), 139–149.

41. Simionescu, C.I.; Percec, V.; Dumitrescu, S. Polymerization of Acetylene Derivatives. XXX. Isomers of Polyphenylacetylene. *J. Polym. Sci. Polym. Chem. Ed.* **1977**, *15*, 2497–2509.

Received May 30, 2000

Revision received September 22, 2000