Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

CYCLOPOLYMERIZATION OF DIPROPARGYL DERIVATIVES BY Cp_2MoCl_2-$EtAlCl_2$ CATALYST SYSTEM

Yeong-Soon Gal[a]; Sung-Ho Jin[b]; Sung-Hyun Kim[c]; Hyung-Jong Lee; Kwang-Nak Koh[d]; Sung-Hoon Kim[e]; Dong-Won Kim[f]; Jang-Myoun Ko[f]; Jong-Han Chun[f]; Sang-Yul Kim[g]
[a] College of General Education, Polymer Chemistry Laboratory, Kyungil University, Hayang, Kyungsangbuk-Do, Korea [b] Department of Chemistry Education, Pusan National University, Pusan, Korea [c] Advanced Materials Research Institute, Taejon, Korea [d] Department of Chemical Engineering, Kyungpook National University, Daegu, Korea [e] Department of Dyeing and Finishing, Kyungpook National University, Daegu, Korea [f] Department of Industrial Chemistry, Hanbat National University, Yusong-Gu, Taejon, Korea [g] Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon, Korea

To cite this Article Gal, Yeong-Soon , Jin, Sung-Ho , Kim, Sung-Hyun , Lee, Hyung-Jong , Koh, Kwang-Nak , Kim, Sung-Hoon , Kim, Dong-Won , Ko, Jang-Myoun , Chun, Jong-Han and Kim, Sang-Yul(2002) 'CYCLOPOLYMERIZATION OF DIPROPARGYL DERIVATIVES BY Cp_2MoCl_2-$EtAlCl_2$ CATALYST SYSTEM', Journal of Macromolecular Science, Part A, 39: 3, 237 — 249

To link to this Article: DOI: 10.1081/MA-120013263

URL: http://dx.doi.org/10.1081/MA-120013263

J. MACROMOL. SCI.—PURE APPL. CHEM., A39(3), 237–249 (2002)

NOTE

CYCLOPOLYMERIZATION OF DIPROPARGYL DERIVATIVES BY Cp_2MoCl_2-$EtAlCl_2$ CATALYST SYSTEM

**Yeong-Soon Gal,[1],* Sung-Ho Jin,[2] Sung-Hyun Kim,[3]
Hyung-Jong Lee,[4] Kwang-Nak Koh,[5] Sung-Hoon Kim,[6]
Dong-Won Kim,[7] Jang-Myoun Ko,[7] Jong-Han Chun,[7]
and Sang-Yul Kim[8]**

[1]Polymer Chemistry Laboratory, College of General Education,
Kyungil University, Hayang 712-701, Kyungsangbuk-Do, Korea
[2]Department of Chemistry Education, Pusan National University,
Pusan 609-735, Korea
[3]Advanced Materials Research Institute, LG Chem,
Taejon, 305-380, Korea
[4]ZEN PHOTONICS Co., Ltd., 104-11 Moonji-dong,
Taejon, 306-230, Korea
[5]Department of Chemical Engineering and [6]Department of Dyeing
and Finishing, Kyungpook National University, Daegu 702-701,
Korea
[7]Department of Industrial Chemistry, Hanbat National University,
Yusong-Gu, Taejon 305-719, Korea
[8]Department of Chemistry, Korea Advanced Institute of Science
and Technology, Taejon 305-701, Korea

ABSTRACT

A Cp_2MoCl_2-$EtAlCl_2$ catalyst system was used for the cyclopolymerization of various dipropargyl derivatives having different functionalities. These catalyst systems were found to be very effective for the polymerization of some dipropargyl monomers to give a relatively high yield of polymer. The polymerization behaviors were strongly dependent

---

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

on the functionalities of dipropargyl monomers. The polymerization of such dipropargyl monomers as 1,6-heptadiyne, diphenyldipropargyl methane, diethyldipropargyl malonate, etc. proceeded well to give a quantitative yield, whereas this catalyst system was found to be less effective for the polymerization of dipropargyl monomers having perfluoroalkyl groups and quaternary ammonium salts. The polymer structure of the resulting polymers was characterized by various instrumental methods such as NMR, IR, and UV-visible spectroscopies to have a conjugated polyene backbone system with cyclic recurring units. The portion of 5- and 6-membered rings of the present conjugated cyclopolymer were also discussed.

Key Words: Cyclopolymerization; Dipropargyl derivatives; Polyacetylene; Bis(cyclopentadienyl)molybdenum dichloride; Conjugated polymers

INTRODUCTION

During the past four decades, a large effort has produced a wide range of mono-and disubstituted polyacetylenes with various pendant groups [1–3]. Conjugated polymers obtained from acetylene derivatives have potential as organic semiconductors [4–6], membranes for gas separation and for liquid-mixture separation [7–9], materials for enantioseparation of racemates by high performance liquid chromatograpy [10, 11], a side-chain liquid crystal [1, 12], materials for chemical sensors [13, 14], as materials for nonlinear optical property [15–17], and for photoluminescence and electroluminescence properties [18–21].

Various catalyst systems have been used as the catalyst system for the polymerization of acetylene derivatives having functionalities [1–3, 22–24]. The Mo-based catalyst systems have been known to be effective for the polymerization of substituted acetylenes containing some polar functional groups such as hydroxy [25, 26], carboxylic acid and ester [27, 28], and ethers [29]. In recent years, it was reported that a novel molybdenum oxytetrachloride ($MoOCl_4$)-based catalyst ($MoOCl_4$-Et_3Al-EtOH, $MoOCl_4$-Et_2Zn-EtOH) induces the living polymerization of *o*-(trifluoromethyl)-phenylacetylene [30, 31].

Group IV metallocene catalysts such as Cp_2TiCl_2, Cp_2ZrCl_2, and Cp_2HfCl_2/R_xAlCl_{3-x} have been applied for the polymerization of acetylene derivatives [32]. We first used the bis(cyclopentadienyl)molybdenum dichloride (Cp_2MoCl_2)-based metallocene catalysts for the polymerization of phenylacetylene [33, 34]. The Cp_2MoCl_2-$EtAlCl_2$ catalyst system were found to be effective for the polymerization of phenylacetylene to give a relatively high yield of polymer. The Cp_2MoCl_2 was relatively stable to air conditions, thus easier to handle than the other molybdenum chlorides such $MoCl_4$, $MoCl_5$, and $MoOCl_4$.

Now we used this Cp_2MoCl_2 catalyst system for other acetylenic monomers, especially dipropargyl derivatives, which can be cyclopolymerized to give a conjugated polymer having cyclic recurring units.

The present article reports on the polymerization behaviors of various dipropargyl monomers with Cp_2MoCl_2-based catalysts and the characterization of the resulting conjugated cyclopolymers.

EXPERIMENTAL

Materials

Cp_2MoCl_2 (Aldrich Chemicals, 98%) and Organoaluminium compounds such as Et_3Al, Et_2AlCl, $EtAlCl_2$ (Aldrich Chemicals., 25 wt% solution in toluene) were used without further purification. 1,6-Heptadiyne (Farchan Laboratories) and tripropargylamine (Aldrich Chemicals, 98%) were dried with calcium hydride and distilled. Ph_4Sn (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride. Me_4Sn (Aldrich Chemicals, 95%) was dried with calcium hydride and distilled. The analytical grade solvents were dried with an appropriate drying agent and fractionally distilled.

Monomers

Diethyl dipropargylmalonate (DEDPM) was prepared by the reaction of propargyl bromide and the sodium ethoxide solution of diethyl malonate as described in the literature [28]. Diphenyldipropargylmethane was prepared by the Grignard reaction [35]. The other dipropargyl monomers were synthesized by reaction of the corresponding functional alcohols with dipropargylmalonyl chloride or dipropargylacetyl chloride in the presence of triethylamine or pyridine as solvent. Details of the synthesis and characterization of the monomers have already been reported [3, 36].

Polymerization of DEDPM by Cp_2MoCl_2-$EtAlCl_2$ Catalyst System

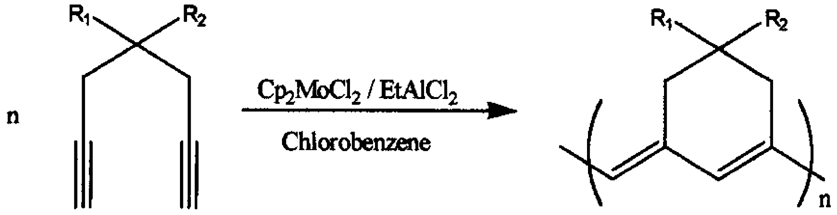
Cp_2MoCl_2 (24.32 mg, 0.082 mmol) and chlorobenzene (4.12 mL, $[M]_0$: 0.8 M) are introduced to the polymerization ampoule, flushed with dry nitrogen, then equipped with a rubber septum. This catalyst solution was aged at 30°C for 15 minutes after the addition of $EtAlCl_2$ (0.41 mL 0.4 M chlorobenzene solution, 0.16 mmol). To this solution, 1.0 g (4.1 mmol) of DEDPM is injected. In a short time, the polymerization solution changed to a red color and the solution viscosity was gradually increased. After standing at 80°C for 24 hours, 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 weight under vacuum at 40°C for 24 hours. The polymer yield was 98%.

Instruments

NMR (^{1}H- and ^{13}C-) spectra of polymers were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in $CDCl_3$ and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. UV-visible spectra were placed in chloroform on a JASCO V-530 spectrophotometer.

RESULTS AND DISCUSSION

The cyclopolymerization of dipropargyl monomers by Cp_2MoCl_2-based catalyst systems was carried out as follows (Sch. 1):



Scheme 1.

Cp_2MoCl_2 itself was tested for the cyclopolymerization of DEDPM. However, Cp_2MoCl_2 did not give any polymeric product. Cp_2MoCl_2 itself was mostly insoluble in the polymerization solvent (chlorobenzene). The inactivity of Cp_2MoCl_2 itself for the polymerization of DEDPM was assumed to be mainly due to the poor solubility of Cp_2MoCl_2 catalyst to the polymerization solvent.

In our previous works [33, 34], we found that the addition of organoaluminium compounds such as Et_3Al, Et_2AlCl, and $EtAlCl_2$ to Cp_2MoCl_2 catalyst made the catalyst solution into a dark-purple suspension phase, and this catalyst solution obtained from Cp_2MoCl_2 and organoaluminium compound polymerized phenylacetylene effectively to give a high yield of polymer.

In the present cyclopolymerization of dipropargyl monomers, we used this binary catalyst system composed of Cp_2MoCl_2 and organoaluminium compounds. In the polymerization of DEDPM by Cp_2MoCl_2, the other organoaluminium compounds such as Et_2AlCl and Et_3Al showed lower co-catalytic activities than that of $EtAlCl_2$. Thus the $EtAlCl_2$ was selected as a typical cocatalyst for the cyclopolymerization of dipropargyl monomers. The organotin compounds such as Ph_4Sn and Me_4Sn, which showed some co-catalytic activity for the polymerization of acetylene derivatives by $MoCl_5$ and WCl_6 [37, 38] were also used as a cocatalyst. However these organotin compounds did not show any cocatalytic activity for this polymerization by Cp_2MoCl_2. The reason was assumed to be due to the insufficient activation of Cp_2MoCl_2 by organotin compounds.

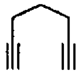
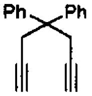
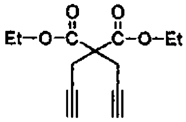
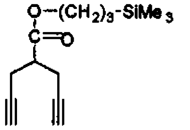
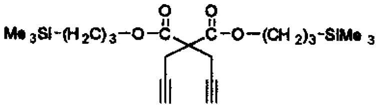
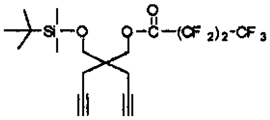
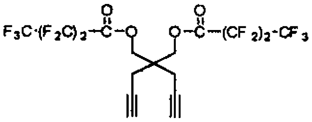
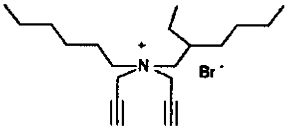
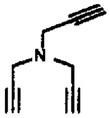
Table 1 shows the results for the polymerization of dipropargyl monomers having different functionalities by Cp_2MoCl_2-$EtAlCl_2$ catalyst system. The polymerization of DEDPM by Cp_2MoCl_2-$EtAlCl_2$ catalyst proceeded well to give a high yield of polymer. The polymerzation solution changed into a red color and the solution viscosity was gradually increased as soon as the DEDPM was added to the catalyst solution. The polymerization behaviors of diphenyldipropargylmethane and dipropargyl monomers carrying trimethylsilyl groups (exp. no. 4, 5) were similar with that of DEDPM. The polymer yields were generally quantitative. In the polymerization of 1,6-heptadiyne, the polymerization solution changed into red color and the solution viscosity was quickly increased as soon as this monomer was injected to the Cp_2MoCl_2-$EtAlCl_2$ solution. This polymerization seemed to proceed in a homogeneous manner. However, the precipitated poly(1,6-heptadiyne) was insoluble in any organic solvent though the polymer yield was quantitative.

The catalytic activity of the Cp_2MoCl_2-$EtAlCl_2$ catalyst system were found to be very low for the polymerization of dipropargyl monomers having perfluoroalkyl groups and quaternary ammonium salt. This phenomenon may be explained by the catalytic poisoning effect of the Cp_2MoCl_2-$EtAlCl_2$ catalyst system by these functional groups although the exact reason is not fully understood in the present time.

This Cp_2MoCl_2-$EtAlCl_2$ catalyst system was also applied for the polymerization of tripropargylamine (exp. no. 9). The polymerization of tripropargylamine gave the corresponding polymer in relatively low yield (35%). In particular, the poly(tripropargylamine) was a black powder and insoluble in any organic solvents. The molecular weights of the polymers obtained by Cp_2MoCl_2-$EtAlCl_2$ catalyst system were in the range of 16,500–27,000, depending on the monomers. These values are relatively lower than those of the same polymers obtained by $MoCl_5$ or $Mo(CO)_6$ catalyst [3, 36, 39–41].

$EtAlCl_2$ itself was also tested for the polymerization of DEDPM in order to check the possibility of cationic polymerization of dipropargyl monomers with EtAlCl2. However, any polymeric product was not obtained.

Table 1. Cyclopolymerization of Dipropargyl Monomers by Cp_2MoCl_2-$EtAlCl_2$ Catalyst Systems

Exp. No	Monom	Polymer Yield ^{b}(%)	M_n^{c}
1		98	insoluble
2		95	16,500
3		98	27,000
4		99	22,100
5		95	25,600
6		10	–
7		0	–
8		0	–
9		35	insoluble

[a] Polymerization was carried out in chlorobenzene at 80°C for 24 hours. Initial monomer concentration ($[M]_o$) and monomer to catalyst mole ratio (M/C) were 0.8 M and 50, respectively; The mixture of Cp_2MoCl_2 and $EtAlCl_2$ solution was aged at 30°C for 15 minutes before use; [b] Methanol-insoluble yield; [c] Determined by GPC analysis with polystyrene standards.

This fact revealed that the present polymerization of dipropargyl monomers with Cp_2MoCl_2-$EtAlCl_2$ catalyst system proceed in classical metathesis polymerization mechanism via metallacyclobutene intermediate though the exact mechanism is not fully understood.

The solubility tests were performed for the powdery samples in a large excess of solvents. The poly(DEDPM) prepared by Cp_2MoCl_2-$EtAlCl_2$ catalyst system was soluble in methylene chloride, chloroform, THF, ethyl acetate, and DMF, but insoluble in ethyl ether, hexanes, methanol, toluene, etc. The other three homologues (exp. no. 2, 4, 5) were also soluble in halogenated and aromatic hydrocarbons such as methylene chloride, chloroform, chlorobenzene, and toluene. On the other hand, the poly(1,6-heptadiyne) and poly(tripropargylamine) were insoluble in any organic solvents although the polymerization solution seems to be homogeneous during the polymerization of 1,6-heptadiyne. The insolubility of poly(1,6-heptadiyne) and poly(tripropargylamine) was thought to be the cross-linking reaction by the activated allyl protons of the resulting polymers [42–44].

The chemical structure of the resulting polymers were characterized by NMR (^{1}H- and ^{13}C-), IR, and UV-visible spectroscopies. Figure 1 shows the FT-IR spectrum of poly(DEDPM) in KBr pellet. This spectrum did not show any absorption at the acetylenic ≡C-H stretching frequencies ($3310\,cm^{-1}$) and the acetylenic C≡C stretching frequencies. Figure 2 shows the ^{1}H-NMR spectrum of a typical poly(DEDPM) in $CDCl_3$. The peaks at 5.6–7.2 ppm, which are assigned to the vinyl protons of con-

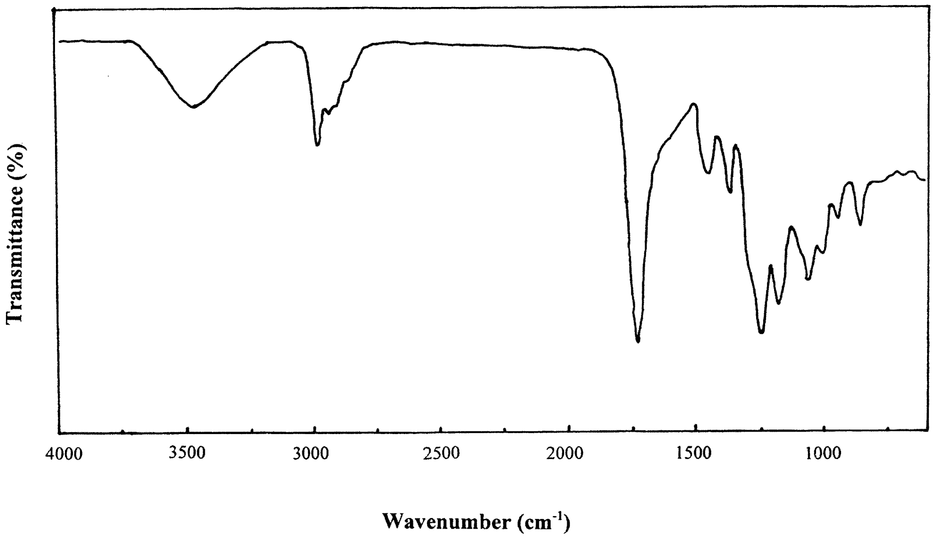


Figure 1. FT-IR spectrum of poly(DEDPM) prepared by Cp_2MoCl_2-$EtAlCl_2$ catalyst system (KBr pellet).

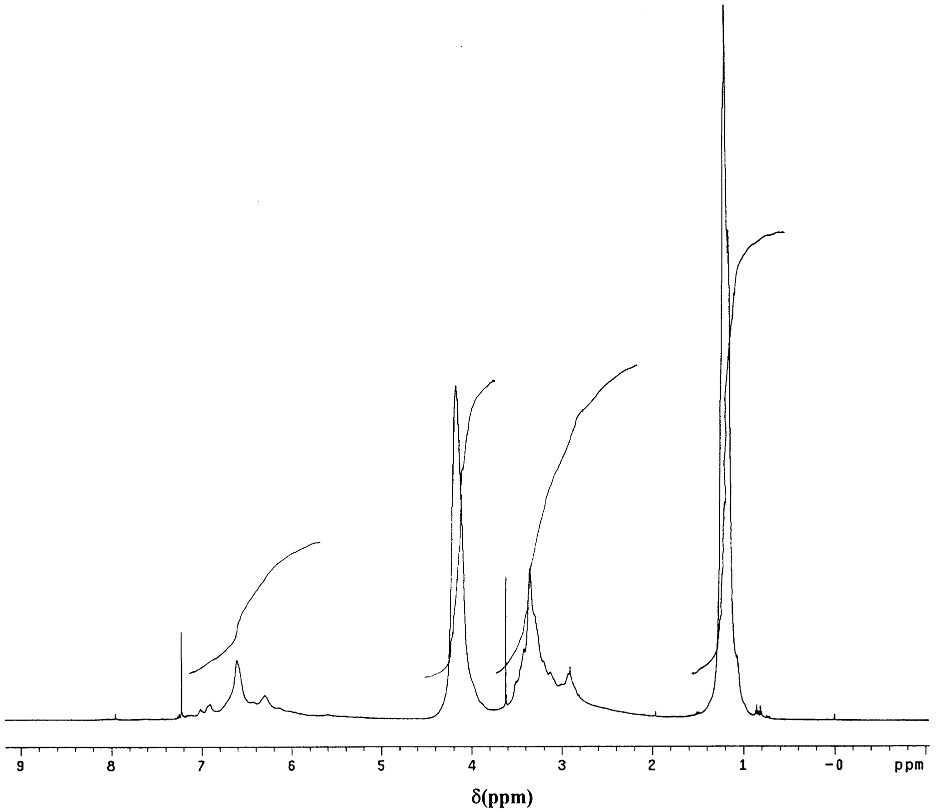


Figure 2. ^{1}H-NMR spectrum of poly(DEDPM) prepared by Cp_2MoCl_2-$EtAlCl_2$ catalyst system (solvent: $CDCl_3$).

jugated double bonds, were newly observed. The peaks at the 2.6–3.6 ppm and the 4.2 ppm are due to the methylene protons adjacent to the conjugated carbons and the methylene protons of ethyl groups, respectively. From peak shapes at 2.6–3.6 ppm, it was anticipated that more complicated microstructures besides the ideal six-membered structure are presented.

Figure 3 shows the ^{13}C-NMR spectrum of poly(DEDPM) in $CDCl_3$. This spectrum did not show any acetylenic carbon peaks, which was seen at 72.9 and 79.6 ppm in the ^{13}C-NMR spectrum of DEDPM monomer. Instead, the carbon peaks of conjugated polyene backbone appeared recently at 123 and 136 ppm. More information on the polymer microstructure was obtained from the resonance of the quaternary carbon atoms [45]. It was reported that the two clusters of resonances for the quaternary carbon atoms in poly(DEDPM) can be assigned to quaternary carbons in five-membered rings

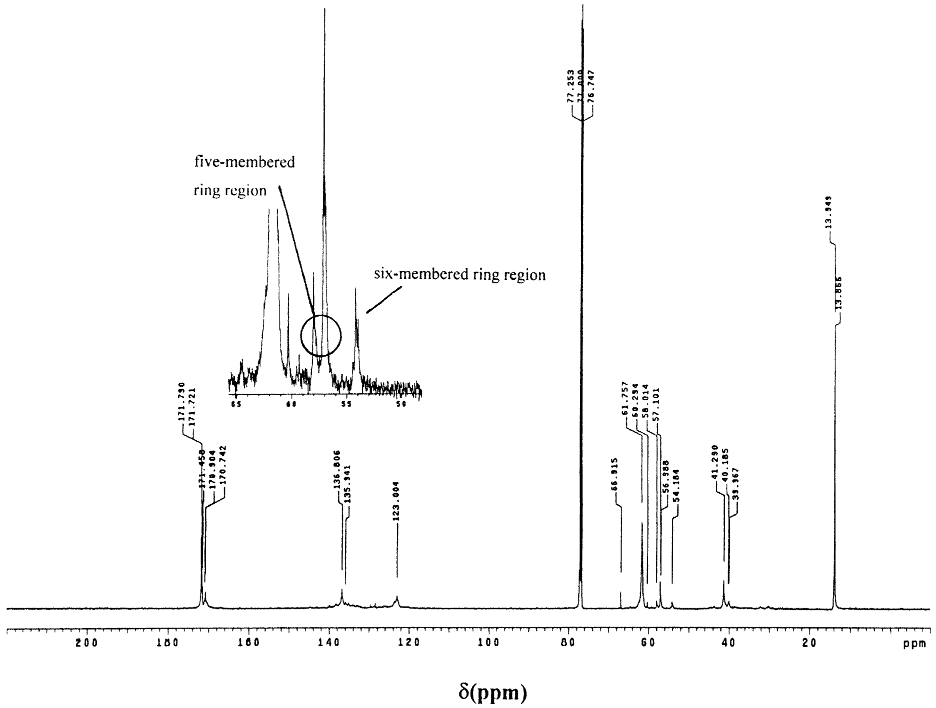


Figure 3. ^{13}C-NMR spectrum of poly(DEDPM) prepared by Cp_2MoCl_2-$EtAlCl_2$ catalyst system (solvent: $CDCl_3$).

(57–58 ppm), and in six-membered rings (54–55 ppm), respectively [45]. As shown in this figure, there are relatively small peaks at 54.18 ppm, which may correspond to the quaternary carbon atoms of six-membered rings moieties. On the other hand, some characteristic peaks at 57.10 and 58.01 ppm, which are due to the quaternary carbon atoms of five-membered rings moieties were extensively observed. From these observations, it was judged that the present poly(DEDPM) was consistent with a mixture of five and six-membered ring moieties and the extent of five-membered ring moiety was higher than that of five-membered ring moiety. The two allylic methylene carbon peaks at 40.19 and 41.29 ppm can be ascribed to the carbons in different local environments within the polymer chain and/or to the presence of cis/trans isomerism in the double bond formed between monomer ring units.

Figure 4 shows the UV-visible spectrum of the resulting poly(DEDPM) in chloroform. A characteristic peak of the conjugated polymer, broad $\Pi \rightarrow \Pi^*$ transitions which are absent in monomer, appeared at longer wavelength up to 675 nm (λ_{max}: 532 nm).

These spectral data indicated that the present poly(DEDPM) have a conjugated polyene backbone structure with cyclic recurring units.

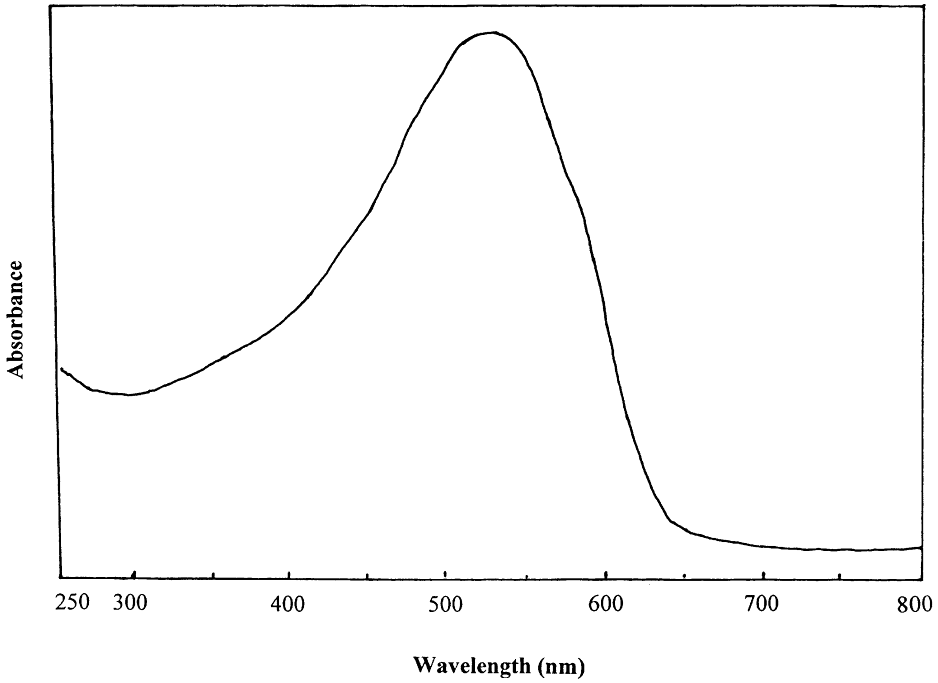


Figure 4. UV-visible spectrum of poly(DEDPM) prepared by Cp_2MoCl_2-$EtAlCl_2$ catalyst system (solvent: chloroform).

CONCLUSION

In this study, we used the Cp_2MoCl_2-$EtAlCl_2$ catalyst system for the ring forming polymerization of dipropargyl monomers carrying various functionalities. This catalyst system was found to be effective for the cyclopolymerization of some dipropargyl derivatives. It was thought that the addition of organoaluminium compounds made the insoluble Cp_2MoCl_2 catalyst into an activated suspension catalyst solution. These Cp_2MoCl_2-organoaluminium compound catalyst systems may be applied to the polymerization of other functional acetylenic and vinyl monomers. The polymer structure of the resulting polymers was characterized by various instrumental methods such as NMR, IR, and UV-visible spectroscopies to have a conjugated polyene backbone system with cyclic recurring units.

ACKNOWLEDGMENTS

This work was supported by grant No. 2000-2-30800-001-3 from the Basic Research Program of the Korea Science & Engineering Foundation (KOSEF).

REFERENCES

1. 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.
2. Masuda, T. in Catalysis in Precision Polymerization, Kobayashi, S., Ed., Chapter 2.4, Wiley: Chichester, 1997.
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*, 1645–1681.
4. Gal, Y.S.; Choi, S.K. Electrical Conductivity and Spectral Properties of Iodine-Doped Poly(2-ethynylpyridine). J. Appl. Polym. Sci. **1993**, *50*, 601–606.
5. Tabata, M.; Sone, T.; Sadahiro, Y. Precise Synthesis of Monosubstituted Polyacetylenes Using Rh Complex Catalysts. Control of Solid Structure and π-Conjugation Length. *Macromol*. Chem. Phys. **1999**, *200* (2), 265–282.
6. Lee, C.W.; Rhee, H.W.; Kim, C.; Gong, M.S. Chemiluminescent Properties of Fluorene- and Carbazole-Containing Fluorophores. Bull. Korean Chem. Soc. **2000**, *21* (7), 701–704.
7. 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.
8. 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.
9. 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.
10. Yashima, E.; Matsushima, T.; Nimura, T.; Okamoto, Y. Enantioseparation on Optically Active Stereoregular Polyphenylacetylene Derivatives as Chiral Stationary Phases for HPLC. Korea Polymer J. **1996**, *4* (2), 139–146.
11. Aoki, T.; Shinohara, K.-I.; Kaneko, T.; Oikawa, E. Enantioselective Permeation of Various Racemates Through an Optically Active Poly{1-[dimethyl(10-pinanyl)silyl]-1-propyne Membrane. Macromolecules **1996**, *29*, 4192–4198.
12. Jin, S.H.; Kang, S.W.; Park, J.G.; Lee, J.C.; Choi, K.S. Synthesis and Characterization of New Thermotropic Side-Chain Liquid Crystal Polymers Containing 1,6-Heptadiyne Backbone. Journ. Mac. Sci.-Pure & Appl. Chem. **1995**, *A32*, 455–466.
13. Bearzotti, A.; D'Amico, A.; Furlani, A.; Iucci, G.; Russo, M.V. Fast Humidity Response of a Metal Halide-Doped Novel Polymer. Sensors and Actuators B **1992**, *7*, 451–454.
14. Furlani, A.; Iucci, G.; Russo, M.V.; Bearzotti, A.; D'Amico, A. Iodine Doped Polyphenylacetylene Thin Film as Humidity Sensor. Sensors and Actuators B **1992**, *8*, 123–126.
15. 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.

16. Halvorson, C.; Hays, A.; Kraabel, B.; Wu, R.; Wudl, F.; Heeger, A.J. A160 Femtosecond Optical Image Processor Based on a Conjugated Polymer. Science **1994**, *265*, 1215–1216.
17. 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.: Part A: Polym. Chem. **1996**, *34*, 2333–2340.
18. 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*, L1138–1141.
19. 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.
20. Gal, Y.S.; Lee, W.C.; Kim, S.Y.; Park, J.W.; Jin, S.H.; Koh, K.N.; Kim, S.H. Synthesis and Properties of Poly(2-ethynylpyridinium Bromide) Having Propargyl Side Chains. J. Polym. Sci.: Part A: Polym. Chem. **2001**, *39*, 3151–3158.
21. 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-ethynylpyridinum Bromide) Having Glycidyl Functionality. Korea Polymer J. **2000**, *8* (3), 131–136.
22. Masuda, T.; Higashimura, T. Polyacetylenes with Substituents: Their Synthesis and Properties. Adv. Polym. Sci. **1987**, *81*, 121–165.
23. 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.
24. 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.
25. Gal, Y.S. Polymerization of 1-Ethynyl-1-cyclohexanol by Transition Metal Catalysts. Journ. Mac. Sci.-Pure & Appl. Chem. **1994**, *A31* (6), 703–714.
26. Gal, Y.S.; Lee, W.C.; Jin, S.H.; Lee, H.J. Polymerization of 3-Ethynylphenol by Transition Metal Catalysts. Korea Polymer J. **2000**, *8*, 231–237.
27. Masuda, T.; Kawai, M.; Higashimura, T. Polymerization of Propiolic Acid and its Derivatives Catalyzed by MoCl5. Polymer **1982**, *23*, 744–747.
28. Ryoo, M.S.; Lee, W.C.; Choi, S.K. Cyclopolymerization of Diethyl Dipropargylmalonate by Transition Metal Catalysts. Macromolecules **1990**, *23*, 3029–3031.
29. 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.
30. Hayano, S.; Masuda, T. Living Polymerization of Substituted Acetylenes by a Novel Ternary Catalyst, $MoOCl_4$-Et_2Zn-EtOH. Macromol. Chem. Phys. **1997**, *198*, 3041–3049.
31. Kaneshiro, H.; Hayano, S.; Masuda, T. Living Polymerization of [o-(Trifluoromethyl)phenyl]acetylene by a New Catalyst System, $MoOCl_4$-Et_3Al-EtOH (1:1:4). Macromol. Chem. Phys. **1999**, *200*, 113–117.
32. Siskos, M.G.; Bokaris, E.P.; Zarkadis, A.K.; Kyriakakou, G. Polymerization of Phenylacetylene by Hafnocene Dichloride/R_xAlCl_{3-x} Catalytic Systems. Eur. Polym. J. **1992**, *28* (9), 1127–1130.

33. Gal, Y.S. Polymerization of Phenylacetylene by Molybdocene Dichloride-Organoaluminium Compound Catalyst System. Eur. Polym. J. **2000**, *36*, 2059–2062.
34. Gal, Y.S.; Lee, W.C.; Jin, S.H.; Lee, H.J.; Kim, S.Y.; Kim, D.W.; Ko, J.M.; Chun, J.H. Polymerization of Acetylene Derivatives by Metallocene Catalysts: Polymerization of Phenylacetylene by Bis(cyclopentadienyl)molybdenum Dichloride-Based Catalyst System. Journ. Mac. Sci., Pure & Appl. Chem. **2001**, *A38*(3), 263–279.
35. Jang, M.S.; Kwon, S.K.; Choi, S.K. Cyclopolymerization of Diphenyldipropargylmethane by Transition Metal Catalysts. Macromolecules **1990**, *23*, 4135–4140.
36. Kim, S.H.; Kim, Y.H.; Cho, H.N.; Kwon, S.K.; Kim, H.K.; Choi, S.K. Unusual Optical Absorption Behavior, Polymer Structure, and Air Stability of Poly(1,6-heptadiyne)s with Substituents at the 4-Position. *Macromolecules* **1996**, *29*, 5422–5426.
37. Gal, Y.S.; Cho, H.N.; Choi, S.K. Polymerization of 2-Ethynylthiophene by WCl6- and MoCl5-Based Catalysts, J. Polym. Sci.: Part A: Polym. Chem. **1986**, *24*, 2021–2025.
38. Gal, Y.S.; Jung, B.; Lee, W.C.; Lee, H.J.; Choi, S.K. Polymerization of Phosphorus-Containing Acetylenes. 3. Polymerization of Triethyl a-Propargylphosphonoacetate by Transition Metal Catalysts. Macromolecules **1995**, *28*, 2086–2088.
39. Jeon, S.J.; Shim, S.C.; Cho, C.S.; Kim, T.J.; Gal, Y.S. $Mo(CO)_6$-Catalyzed Cyclopolymerization of Diethyl Dipropargylmalonate to Give a Polyene Containing Only Five-Membered Rings. J. Polym. Sci. Polym. Chem. Ed. **1999**, *37*, 877–880.
40. Jeon, S.J.; Shim, S.C.; Cho, C.S.; Kim, T.J.; Gal, Y.S. Catalytic Cyclopolymerization and Copolymerization of 1,6-Heptadiynes by $Mo(CO)_6$. J. Polym. Sci.: Part A: Polym. Chem. **2000**, *38*, 2663–2670.
41. Jeon, S.J.; Shim, S.C.; Cho, C.S.; Kim, T.J.; Gal, Y.S. Catalytic Cyclopolymerization and Copolymerization of Diethyl Dipropargylmalonate by (toluene)-$Mo(CO)_3$. Bull. Korean Chem. Soc. **2000**, *21*, 980–984.
42. Gal, Y.S.; Lee, W.C.; Gui, T.L.; Jin, S.H.; Koh, K.N.; Kim, S.H.; Kim, D.W.; Ko, J.M.; Chun, J.H. Cyclopolymerization of 1,6-Heptadiyne by Molybdenum and Tungsten-Based Catalysts. Korea Polymer J. **2001**, *7*, 220–227.
43. Gal, Y.S.; Lee, W.C.; Choi, S.K.; Kim, Y.C.; Jung, B. Polymerization of Tripropargylamine by Transition Metal Catalysts and Molecular Structure of Poly(tripropargylamine). *Eur. Polym. J.* **1996**, *32*, 579–585.
44. Gal, Y.S.; Lee, W.C.; Kim, S.H.; Lee, S.S.; Jwa, S.T.; Park, S.H. Double Ring-Forming Cyclopolymerization of Tripropargylammonium Salts by Transition Metal Catalysts. Journ. Mac. Sci., Pure & Appl. Chem. **1999**, *A36*(3), 429–448.
45. Fox, H.H.; Wolf, M.O.; O'Dell, R.; Lin, B.L.; Schrock, R.R.; Wrighton, M.S. Living Cyclopolymerization of 1,6-Heptadiyne Derivatives Using Well-Defined Alkylidene Complexes: Polymerization Mechanism, Polymer Structure, and Polymer Properties. J. Am. Chem. Soc. **1994**, *116*, 2827–2843.

Received June 10, 2001
Revision received September 30, 2001

Downloaded At: 11:56 24 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081MA120013263