

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 Phenylacetylene by Molybdenum (V) Chloride Activated by Acetylene Compounds

Yeong-Soon Gal^a

^a Polymer Chemistry Laboratory, College of General Education, Kyungpook Sanup University, Hayang, Kyungsangbuk-Do, Korea

To cite this Article Gal, Yeong-Soon(1997) 'Polymerization of Phenylacetylene by Molybdenum (V) Chloride Activated by Acetylene Compounds', *Journal of Macromolecular Science, Part A*, 34: 2, 377 – 381

To link to this Article: DOI: 10.1080/10601329708014963

URL: <http://dx.doi.org/10.1080/10601329708014963>

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 PHENYLACETYLENE BY MOLYBDENUM (V) CHLORIDE ACTIVATED BY ACETYLENE COMPOUNDS

Yeong-Soon Gal

Polymer Chemistry Laboratory, College of General Education, Kyungpook Sanup
University, Hayang 712-701, Kyungsangbuk-Do, Korea

ABSTRACT

The activating effect of acetylenic compounds for the polymerization of phenylacetylene by molybdenum (V) chloride. The alkyl and aromatic terminal acetylenes were found to activate the MoCl_5 for the polymerization of phenylacetylene. The terminal acetylenes having acidic hydrogen (functional group: carboxylic acid, hydroxy) also activate the MoCl_5 catalysts. On the other hand, the polymerization of phenylacetylene using MoCl_5 -acetylenic amines did not proceed.

INTRODUCTION

Tungsten and molybdenum-based catalyst systems have been used for the olefin metathesis and ring-opening polymerization of cycloolefins [1-3]. And it was also found that these catalyst systems were very effective for the polymerization of some acetylene derivatives such as phenylacetylene [4,5], β -naphthylacetylene [6], 2-ethynylthiophene [7], 4-phenyl-1-butyne[8], etc. The molybdenum(V) chloride-based catalysts were found to be very effective for the polymerization of oxygen atom-containing acetylene derivatives such as propilic acid [9], methyl

propiolate [9], and acetylenic alcohols [10-12]. We have also found that some acetylene derivatives such as dipropargyl ether [13], 2-propyn-1-ol [14,15], and diethyl dipropargylmalonate [16], are easily polymerized by molybdenum chloride to give a quantitative yield of polymer. In recent years, we reported that the acetylenic alcohol compounds activate the molybdenum chloride for the polymerization of some acetylene derivatives [17,18]. On the other hand, these acetylenic alcohols rather deactivate the W-based catalyst systems.

The hydrogens in terminal alkynes are relatively acidic. Acetylene itself has a pKa of about 25. It is a far weaker acid than water or the alcohols (pKa 16-19), but it is much more acidic than ammonia (pKa 35).

It was thought that the high catalytic activity of tungsten and molybdenum chlorides for the polymerization of some acetylene derivatives is originated by the activation of transition metal chlorides by the terminal acetylenic functions.

Now we report an activating effect of some representative acetylenic compounds in the polymerization of phenylacetylene by molybdenum (V) chloride.

EXPERIMENTAL

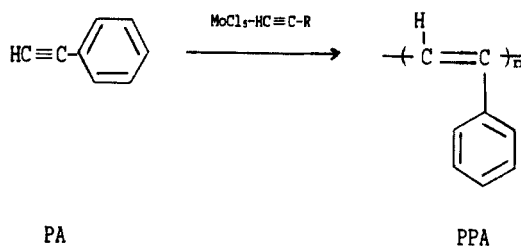
Acetylene compounds were received from Aldrich Chemicals. They were dried with appropriate drying agent and fractionally distilled. MoCl₅ (Aldrich Chemicals., resublimed, 99.9+%) was used as 0.1 M solution, whereas the acetylenic compounds were dissolved as 0.2 M solution.

A polymerization ampule equipped with rubber septum was flushed with dry nitrogen. The catalyst solution containing acetylenic compounds was aged for 15 min. at 20°C before use. Injections of MoCl₅ solution and monomer were done by means of hypodermic syringes from which air and moisture had been carefully excluded. After a given time of polymerization, the polymerization was stopped by adding a small amount of methanol. In general, the resulting polymer was dissolved in chloroform, followed by precipitation with excess methanol from the solution and dried to a constant weight under vacuum at 40°C for 24 hrs. The polymer yield was calculated by gravimetry.

RESULTS AND DISCUSSION

The polymerization of phenylacetylene was carried out by the molybdenum (V) chloride activated with the acetylenic compounds as follows (Scheme I).

Table 1 shows the activating effect of acetylenic compounds for the polymerization of phenylacetylene by molybdenum (V) chloride. In fact, the Mo-based catalysts were found to be less effective for the polymerization of phenylacetylene than that of W-based catalysts, whereas WCl₆ itself gave a high



Scheme I. Polymerization of Phenylacetylene

TABLE I
Polymerization of Phenylacetylene by Molybdenum (V) Chloride Activated
with Acetylenic Compounds.^a

Exp. No.	Catalyst System	Polymer Yield(%) ^b	\bar{M}_n^c
1	MoCl ₅	34	6850
2	MoCl ₅ -HC≡C(CH ₂) ₃ CH ₃	69	5730
3	MoCl ₅ -HC≡C-	72	6970
4	MoCl ₅ -HC≡C-	53	7500
5	MoCl ₅ -(HC≡CCH ₂) ₂ CH ₂	67	10300
6	MoCl ₅ -HC≡CCO ₂ H	57	5170
7	MoCl ₅ -HC≡CCH ₂ OH	58	7200
8	MoCl ₅ -HC≡CCH ₂ NH ₂	trace	-
9	MoCl ₅ -HC≡CC(Et) ₂ NH ₂	0	-

^aPolymerization was carried out at 60°C in chlorobenzene for 24 hrs. Initial monomer concentration ([M]₀) and monomer to catalyst mole ratio were 1.0M and 50, respectively. ^bMethanol-insoluble polymer. ^cMeasured by means of a Waters GPC-150C using the calibration curves for polystyrenes.

polymer yield (≥80%) and relatively high molecular weight (> 10000). The polymerization of phenylacetylene by molybdenum(V) chloride activated by acetylenic compounds was carried out at 60°C in chlorobenzene for 24 hrs. MoCl₅ itself gives a moderate yield of polymer (34%). In the most cases using the terminal acetylenic compounds besides the acetylenic amines, the polymer yields were increased. When 1-hexyne (alkylacetylene, R= n-butyl) is used, the polymer

yield and number average molecular weight were 69% and 5730, respectively. Aromatic acetylenes (substituent= phenyl, 2-thienyl) also activate the polymerization of phenylacetylene using molybdenum(V) chloride. The activating effect of phenylacetylene was found to be somewhat greater than that of 2-ethynylthiophene. This indicates that the sulfur atom of 2-ethynylthiophene slightly coordinate with molybdenum(V) chloride. When the 1,6-heptadiyne having two terminal acetylene functional groups in the same compound was used, the polymerization was also well proceeded to give a high polymer yield (67%) and the resulting polymers were found to have mostly high molecular weight.

The most high molecular weight of polyphenylacetylene obtained by the catalyst system of $\text{MoCl}_5\text{-(HC}\equiv\text{CCH}_2)_2\text{CH}_2$ was thought to be caused by the highly activating effect of 1,6-heptadiyne and/or the slightly cross-linkable products by difunctional compounds.

The terminal acetylenes having acidic hydrogen (ex., carboxylic acid, hydroxy) were also tested for the present polymerization (exp. no. 6, 7). The propiolic acid⁹ and 2-propyn-1-ol¹⁵ had been known to be easily polymerized by molybdenum(V) chloride itself after having some induction period to give a high polymer yield. It had been explained that the monomer is polymerized by the molybdenum(V) chloride activated by the monomer itself. In the present polymerization, the molybdenum(V) chloride activated by propiolic acid or 2-propyn-1-ol can also polymerize phenylacetylene to give a relatively high polymer yield. However the polymerization of phenylacetylene using MoCl_5 -acetylenic amines (exp. no. 8, 9) failed to polymerize to give no polymers.

The resulting polyphenylacetylenes obtained by MoCl_5 -acetylenic compounds were mostly yellow or brown powder according to the polymerization conditions. They were mostly soluble in aromatic and halogenated hydrocarbons such as chloroform, benzene, CCl_4 , etc.

REFERENCES

1. K. J. Ivin, *Olefin Metathesis*, Academic Press, London, 1983.
2. V. Dragutan, A. T. Balaban, and M. Dimonie, *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-olefins*, John Wiley & Sons, New York, 1985.
3. V. C. Gibson, *Adv. Mater.*, **6**, 37 (1994).
4. T. Masuda, K-I. Hasegawa, and T. Higashimura, *Macromolecules*, **7**, 728 (1974).
5. M. G. Voronkov, V. B. Pukhnarevich, S. P. Suschinskara, V. Z. Annenkova, V. M. Annenkova, and N. J. Andreeva, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 53 (1980).
6. T. Ohtori, T. Masuda, and T. Higashimura, *Polymer J.*, **11**, 805 (1979).
7. Y. S. Gal, H. N. Cho, and S. K. Choi, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 2021 (1986).
8. S. Y. Oh, F. Oguri, K. Akagi, and H. Shirakawa, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 781 (1993).

9. T. Masuda, M. Kawai, and T. Higashimura, *Polymer*, 23, 744 (1982).
10. L. A. Akopyan, S. G. Grigoryan, Sh. T. Yegurtdzhyan, and S. G. Matsoyan, *Vysokomol. Soedin. (A)*, 17, 1072 (1975).
11. L. A. Akopyan, S. G. Grigoryan, G. A. Zhamkochyan, and S. G. Matsoyan, *Vysokomol. Soedin. (A)*, 17, 2517 (1975).
12. 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).
13. Y. S. Gal and S. K. Choi, *Polymer (Korea)*, 11, 563 (1987).
14. W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Polymer (Korea)*, 12, 720 (1988).
15. Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *Polymer (Korea)*, 14, 597 (1992).
16. M. S. Jang, S. K. Kwon, and S. K. Choi, *Macromolecules*, 23, 4135 (1990).
17. Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *Bull. Korean Chem. Soc.*, 14, 171 (1993).
18. Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *Polymer (Korea)*, 18, 130 (1994).