This article was downloaded by:
On: *25 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 Acrylamide and Copolymerization with Acrylonitrile with AIEt$_3$-Hexamethyl Phosphoric Acid Triamide Complex

Akira Akimoto[a]
[a] Central Research Laboratory, Toyo Soda Manufacturing Co., Ltd., Shinnanyo-shi, Yamaguchi-ken, Japan

To cite this Article Akimoto, Akira(1974) 'Polymerization of Acrylamide and Copolymerization with Acrylonitrile with AIEt$_3$-Hexamethyl Phosphoric Acid Triamide Complex', Journal of Macromolecular Science, Part A, 8: 7, 1261 — 1271
To link to this Article: DOI: 10.1080/00222337408068629
URL: http://dx.doi.org/10.1080/00222337408068629

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.

J. MACROMOL SCI.—CHEM., A8(7), pp. 1261-1271 (1974)

Polymerization of Acrylamide and Copolymerization with Acrylonitrile with $AlEt_3$-Hexamethyl Phosphoric Acid Triamide Complex

AKIRA AKIMOTO

Central Research Laboratory
Toyo Soda Manufacturing Co., Ltd.
Shinnanyo-shi, Yamaguchi-ken, Japan

Downloaded At: 09:57 25 January 2011

ABSTRACT

The polymerization of acrylamide and its copolymerization with acrylonitrile were investigated with $AlEt_3$ and $AlEt_3$-hexamethyl phosphoric acid triamide. $AlEt_3$ initiates the polymerization of acrylamide. The addition of hexamethyl phosphoric acid triamide greatly influences the yields of methanol-insoluble polymer, η_{sp}/c, and the structure of polymer. Vinyl polymerization is dominant with $AlEt_3$ in the presence of hexamethyl phosphoric acid triamide. On copolymerization of acrylamide with acrylonitrile, the acrylonitrile content in the copolymer increased with the addition of hexamethyl phosphoric acid triamide on $AlEt_3$.

Copyright © 1975 by Marcel Dekker, Inc. All Rights Reserved. Neither this work nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

INTRODUCTION

Breslow [1] first reported that the polymerization of acrylamide (AcAm) in the presence of alkali catalysts such as alkali metal alkoxide does not give a vinyl-type polymer, poly(AcAm), but gives poly(β-alanine); there occurs a so-called polymerization with hydrogen migration. Later, many other authors studied the effective catalysts for the polymerization of acrylamide with hydrogen migration, such as Grignard reagents [2, 3], metal alkoxides [4], n-BuLi [3], and lithium benzophenone ketyl [5].

Two different initiation mechanisms are proposed for the sodium alkoxide initiated polymerization. Breslow et al. [1] reported that the predominating initiation reaction may comply with reaction scheme

$$CH_2=CHCONH_2 + B^{\ominus} \rightleftharpoons CH_2=CHCONH^{\ominus} + BH \qquad (1)$$

The second initiation mechanism was proposed by Ogata [6] who concluded that the nucleophilic attack at the β-carbon atom to carbonyl must be the initiation step of the polymerization reaction:

$$CH_2=CHCONH_2 + B^{\ominus} \rightleftharpoons BCH_2\overset{\ominus}{C}HCONH_2 \rightleftharpoons BCH_2CH_2CON\overset{\ominus}{H} \qquad (2)$$

Tani et al. reported that the initiation reaction of AcAm polymerization may well be discussed by considering the different actions of sodium methoxide and sodium t-butoxide toward AcAm [7].

In a previous paper the author reported the effect of hexamethyl phosphoric acid triamide (HMPA) on the rate of polymerization in the $AlEt_3$ initiated-copolymerization of epichlorhydrin with methyl methacrylate (MMA) [8]. Furthermore, the catalytic behavior of the $AlEt_3$-HMPA complex is known to be peculiar to the copolymerization of MMA with acrylonitrile (AN) [9].

The present work reports the results obtained by polymerizing AcAm and by copolymerizing AcAm with AN initiated with both $AlEt_3$ catalyst and the $AlEt_3$-HMPA complex catalyst.

EXPERIMENTAL

Materials

AcAm and other methyl substituent derivatives were commercially supplied. AcAm was recrystallized from chloroform each time before polymerization; in some cases the monomer was purified by sublimation in vacuo before use. AN and the solvents used were purified by

Downloaded At: 09:57 25 January 2011

conventional methods. $AlEt_3$ was purified by distillation under reduced pressure and was stored as a normal solution in toluene. HMPA was dried over calcium hydride, vacumm distilled, and stored as a normal solution in toluene.

Polymerization Procedure

All experiments were performed in a glass tube which was filled in a dry box with dry monomer, solvent, and catalyst; in all cases phenyl-β-naphthylamine (PBNA) was added as an inhibitor of free-radical polymerization. The tube was then evacuated, sealed in a nitrogen atmosphere, and kept at 80° C. At the end of each polymerization there was a solid white product on the walls of the reaction tube. After a given time of reaction, the polymerization mixture was poured into methanol containing a small amount of hydrochloric acid. The methanol-insoluble polymer was glass-filtered, washed, and dried under vacuum.

Characterization of Polymer

Poly(AcAm) obtained with $AlEt_3$ alone and the $AlEt_3$-HMPA complex contains two kinds of polymer; that is, a transition polymer and a vinyl polymer. The fraction of these units in the polymer was conveniently determined from the optical density of the IR spectrum of a secondary amide group in the polymer [10]. The D-values in Table 1, 2, and 3 show the ratio of $D_{1535\ cm^{-1}}$ to $D_{1660\ cm^{-1}}$. The monomer content of the copolymer of AcAm with AN was also determined by means of IR spectroscopy using the ratio of the optical density of $D_{2260\ cm^{-1}}$ to $D_{1660\ cm^{-1}}$, as shown by the D'-values in Table 5 and in Fig. 4 [11]. Elemental analyses for carbon and nitrogen were also carried out on most of the copolymers, but reproducibility was poor. Polymer viscosities were measured by an Ostwald viscometer in 1% formic acid solution at 30° C.

RESULTS AND DISCUSSION

In an anionic polymerization of polar vinyl monomers such as MMA and AN, the catalytic activity of AlR_3 is known to be enhanced in the presence of a Lewis base [12]. In a previous paper [9] the author suggested that the $AlEt_3$-HMPA complex initiates the anionic polymerization of MMA and AN at 80°C. It is expected that in the case of AcAm the anionic vinyl polymerization selectively occurs through the

Downloaded At: 09:57 25 January 2011

TABLE 1. Polymerization of AcAm Initiated by $AlEt_3$ and $AlEt_3$-HMPA Complex[a]

Expt. No.	$AlEt_3$ (mole %)[b]	HMPA (mole %)[b]	Methanol insoluble polymer (%)	η_{sp}/c	D-value
1	1	-	7.0	0.17	0.16
2	2	-	17.4	0.17	0.15
3	3	-	24.0	0.20	0.14
4	5	-	29.5	0.18	0.14
5	1	1	12.3	0.35	0.10
6	2	2	23.7	0.32	0.09
7	3	3	29.9	0.37	0.07
8	5	5	39.4	0.35	0.10

[a] AcAm, 0.035 mole; PBNA, 0.05 g; toluene, 20 ml; polymerization for 20 hr.

[b] On monomer.

Downloaded At: 09:57 25 January 2011

formation of the complex. Therefore the effect of HMPA was further investigated in the polymerization of AcAm with $AlEt_3$.

Table 1 shows the results of the polymerization of AcAm obtained with the $AlEt_3$-HMPA complex at the various catalyst concentrations together with the results of polymerization with the corresponding concentrations of $AlEt_3$ alone. The yields of methanol-insoluble polymer, η_{sp}/c, and D-value were compared. $AlEt_3$ showed fairly good catalyst activity for the polymerization of AcAm. The values of η_{sp}/c of the polymer obtained have a maximum value at about 3 mole % catalyst concentration in this condition, while D-values were constant in the 0.14 and 0.16 range in spite of $AlEt_3$ concentrations. These results coincide with that of polymerization with n-BuLi as a catalyst [10]. The increase of polymer yields did not influence the structure of poly(AcAm).

It is well known that poly(β-alanine) was produced by polymerization with hydrogen migration catalyzed by a strong base, while the vinyl polymer was obtained by a weak basic catalyst [4]. It is likely that vinyl polymerization may take precedence when $AlEt_3$ is used among weak bases.

At each concentration of $AlEt_3$ the addition of HMPA increased the yield of poly(AcAm). The presence of HMPA leads to a marked increase

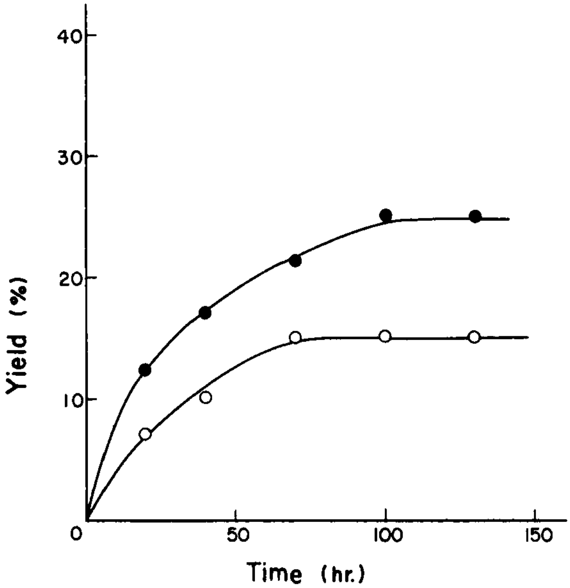

FIG. 1. Plot of percent yield of methanol-insoluble polymer vs time: (●) $AlEt_3$-HMPA; (○) $AlEt_3$. AcAm, 0.035 mole; $AlEt_3$, 1 mole % (on monomer); HMPA/$AlEt_3$ = 1.0/1.0 (molar ratio); PBNA, 0.05 g; and toluene, 20 ml.

Downloaded At: 09:57 25 January 2011

in the molecular weight of poly(AcAm), while the D-value becomes lower.

Figure 1 shows a typical plot of percentage yield of methanol-insoluble polymer against time. There is a fall in yield of about 25 and 15% with $AlEt_3$-HMPA complex and $AlEt_3$ alone, respectively. In every instance the $AlEt_3$-HMPA complex shows the higher catalytic activity.

Figure 2 presents the solution viscosity (η_{sp}/c) of polymer obtained in Fig. 1. The η_{sp}/c of the polymer obtained with the $AlEt_3$-HMPA complex is always a higher value than that of the polymer obtained with $AlEt_3$. η_{sp}/c gradually becomes larger as polymerization proceeds. This is probably due to both the living polymerization of this system and the internal reaction between the resulted polymers.

Fig. 3 shows the D-values of the polymer with both catalysts. The D-value of the polymer with the $AlEt_3$-HMPA complex is always lower than that of polymer with $AlEt_3$. All D-values are rather constant, in spite of the yields.

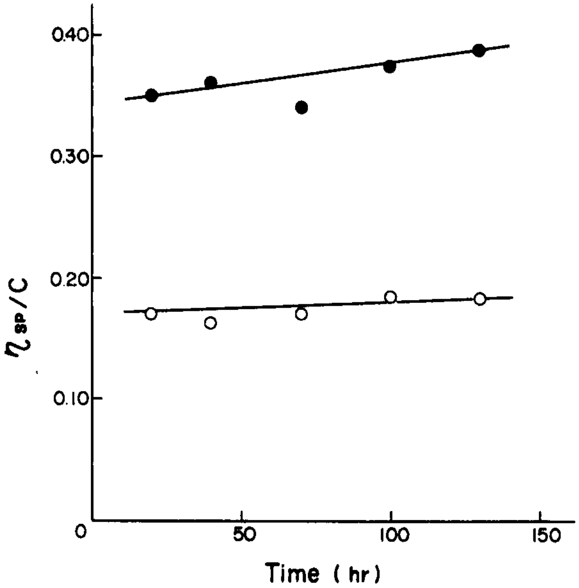

FIG. 2. Plot of η_{sp}/c vs time: (●) $AlEt_3$-HMPA; (○) $AlEt_3$.

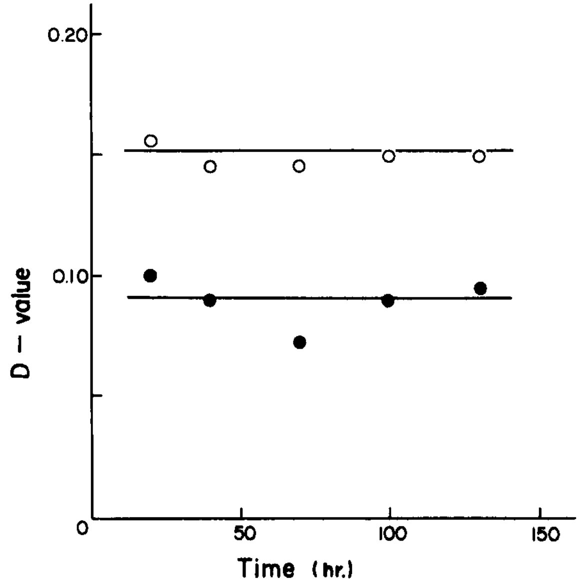

FIG. 3. Plot of D-value vs time: (●) $AlEt_3$-HMPA; (○) $AlEt_3$.

Downloaded At: 09:57 25 January 2011

At a constant $AlEt_3$ content, the addition of HMPA increases the yields of methanol-insoluble polymer of AcAm as the molar ratio of HMPA to $AlEt_3$ is increased, and the rate of polymerization flattens out as the ratio is equal to or greater than 1 (Table 2). Higher molecular weight polymers of AcAm were obtained by increasing the molar ratio, while the D-value was gradually reduced. These results suggest that the new formation of the complex reflects the polymerization of AcAm. It seems that HMPA forms the stable complex and prevents polymerization with hydrogen migration. The polymerization of AcAm with this complex catalyst is of the coordinate anionic type.

TABLE 2. Effect of HMPA on the Polymerization of AcAm with $AlEt_3$[a]

Expt. No.	$HMPA/AlEt_3$ molar ratio	Methanol insoluble polymer (%)	η_{sp}/c	D-value
1	0.0/1.0	7.0	0.17	0.16
9	0.5/1.0	8.6	0.20	0.12
5	1.0/1.0	12.3	0.35	0.10
10	2.0/1.0	12.0	0.35	0.09

[a] AcAm, 0.035 mole/ $AlEt_3$, 1 mole % (on monomer); PBNA, 0.05 g; toluene, 20 ml; polymerization for 20 hr.

Downloaded At: 09:57 25 January 2011

In an anionic polymerization, polar solvents such as dioxane and pyridine solvate the countercation in the propagation moiety, and the concentration of the free propagating anion is increased with a corresponding increase in the rate of polymerization. However, the results observed in Table 3 show a constant rate of polymerization in dioxane and in pyridine. These results are quite different from those with n-BuLi [3]. The fact that the activating propagation end is not a free anion nor a solvent separated ion-pair supports selective vinyl polymerization with the $AlEt_3$-HMPA complex.

Table 4 presents the results of the polymerization of AcAm and methyl substituent derivatives of AcAm with the complex catalyst system.

The complex shows lower catalytic activity toward methacrylamide and N,N-dimethylacrylamide such as is found with n-BuLi [13, 14]. However, this catalyst shows no catalytic activity toward crotonamide. It seems that the steric hindrance of this monomer limits the approach of the catalytic active site.

TABLE 3. Polymerization of AcAm in Various Solvents[a]

Expt. No.	Solvent	Methanol insoluble polymer (%)	η_{sp}/c	D-value
5	Toluene	12.3	0.35	0.10
11	Dioxane	15.2	0.32	0.07
12	Pyridine	12.0	0.32	0.07

[a] AcAm, 0.035 mole; $AlEt_3$, 1 mole % (on monomer); HMPA/$AlEt_3$ = 1.0/1.0 (molar ratio); PBNA, 0.05 g; solvent, 20 ml; polymerization for 20 hr.

TABLE 4. Polymerization of AcAm and Its Methyl Substituent Derivatives with the $AlEt_3$-HMPA Complex[a]

Expt. No.	Monomer	Methanol insoluble polymer	
		Yield (%)	η_{sp}/c
13	Acrylamide	17.4	0.36
14	Methacrylamide	3.8	0.25
15	Crotonamide	0.0	-
16	N,N-Dimethylacrylamide	10.3	0.23

[a] Monomer, 0.035 mole; $AlEt_3$, 1 mole % (on monomer); HMPA/$AlEt_3$ = 1.0/1.0 (molar ratio); PBNA, 0.05 g; toluene, 20 ml; polymerization for 40 hr.

Downloaded At: 09:57 25 January 2011

Table 5 presents the results of the copolymerization of AcAm with AN initiated by both catalysts. The rate of copolymerization with the complex catalyst is higher than that with $AlEt_3$ alone at all monomer compositions, and the η_{sp}/c of the copolymer is low. Figure 4 shows the dependence of the D'-value of the copolymer on the molar ratio of AN to AcAm. The AN content in copolymers increased with the complex catalyst as compared with $AlEt_3$.

Downloaded At: 09:57 25 January 2011

TABLE 5. Copolymerization of AcAm with AN Catalyzed by Both $AlEt_3$ and the $AlEt_3$-HMPA Complex[a]

Expt. No.	Monomer feed		Catalyst system		Mathanol insoluble polymer		
	AcAm (mole %)	AN (mole %)	$AlEt_3$[b] (mole %)	HMPA[b] (mole %)	Yield (%)	η_{sp}/c[c]	D'-value
17	79	21	2.0	-	3.2	-	0.028
18	58	42	2.0	-	1.7	0.049	0.083
19	38	62	2.0	-	1.6	-	0.100
20	79	21	2.0	2.0	5.5	-	0.038
21	58	42	2.0	2.0	3.0	0.056	0.099
22	38	62	2.0	2.0	3.1	-	0.120

[a] Total monomer, 0.035 mole; PBNA, 0.05 g; toluene, 20 ml; polymerization for 20 hr.

[b] On total monomer mixture.

[c] Measured in 1% N,N-dimethylformamide solution at 30°C.

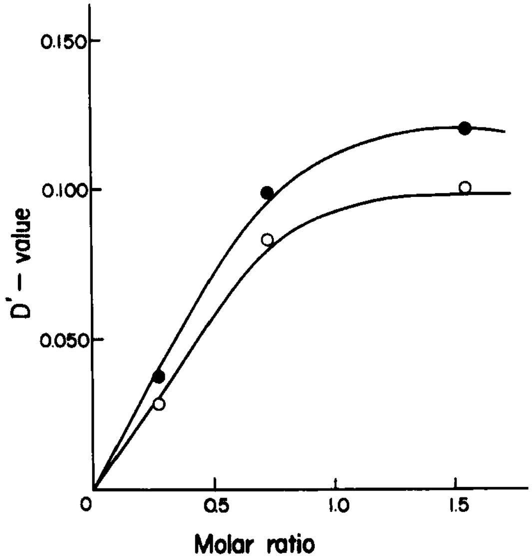

FIG. 4. Plot of D'-value vs molar ratio of AN to AcAm: (●) $AlEt_3$-HMPA; (○) $AlEt_3$.

Downloaded At: 09:57 25 January 2011

ACKNOWLEDGMENTS

The author wishes to thank Dr. Y. Kosaka and Mr. S. Imura for their encouragement and valuable discussions.

REFERENCES

[1] D. S. Breslow, G. E. Hulse, and A. S. Matlack, J. Amer. Chem. Soc., 79, 3760 (1957).

[2] N. Ogata, J. Polym. Sci., 46, 271 (1960).

[3] H. Nakayama, T. Higashimura, and S. Okamura, Kobunshi Kagaku, 23, 537 (1966).

[4] S. Okamura, T. Higashimura, and T. Senō, Ibid., 20, 364 (1963).

[5] A. Leoni, S. Franco, and G. Polla, J. Polym. Sci., A-1, 6, 3187 (1968).

[6] N. Ogata, Makromol. Chem., 40, 55 (1960).

[7] H. Tani, N. Oguni, and T. Araki, Ibid., 76, 82 (1964).

[8] A. Akimoto, J. Macromol. Sci.—Chem., A-7, 1339 (1973).

[9] A. Akimoto and T. Okada, Ibid., A-7, 1555 (1973).

[10] H. Nakayama, T. Higashimura, and S. Okamura, Kobunshi Kagaku, 23, 433 (1966).

[11] K. Ito, K. Baba, and Y. Yamashita, Kogyo Kagaku Zasshi, 68, 703 (1965).
[12] M. Ikeda, T. Hirano, and T. Tsuruta, Makromol. Chem., 150, 127 (1971).
[13] H. Nakayama, T. Higashimura, and S. Okamura, Kobunshi Kagaku, 24, 296 (1967).
[14] K. Butler, P. R. Thomas, and G. Jylex, J. Polym. Sci., 48, 357 (1960).

Accepted by editor April 30, 1974
Received for publication June 10, 1974

Downloaded At: 09:57 25 January 2011