

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 *N, N*-Dimethylaminopropyl-Acrylamide Through Hydrogen Transfer Induced by the Propagation of the Polyacrolein Anion

Natsuki Yamashita^a; Atsuhito Tadokoro^b; Eiichiozu Toshihisa Maeshima^b; Ion C. Baianu^c; Lun-Shin Wei^a

^a Department of Food Science, University of Illinois, Urbana, Illinois ^b Department of Applied Chemistry, Faculty of Science and Engineering Kinki University, Higashi-Osaka, Japan ^c Physical Chemistry and NMR Laboratories, University of Illinois, Urbana, Illinois

To cite this Article Yamashita, Natsuki , Tadokoro, Atsuhito , Maeshima, Eiichiozu Toshihisa , Baianu, Ion C. and Wei, Lun-Shin(1987) 'Polymerization of *N, N*-Dimethylaminopropyl-Acrylamide Through Hydrogen Transfer Induced by the Propagation of the Polyacrolein Anion', *Journal of Macromolecular Science, Part A*, 24: 10, 1223 — 1239

To link to this Article: DOI: 10.1080/00222338708076941

URL: <http://dx.doi.org/10.1080/00222338708076941>

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 *N,N*-DIMETHYLAMINOPROPYL-ACRYLAMIDE THROUGH HYDROGEN TRANSFER INDUCED BY THE PROPAGATION OF THE POLYACROLEIN ANION

NATSUKI YAMASHITA

Department of Food Science
University of Illinois
Urbana, Illinois 61801

ATSUHITO TADOKORO, EIICHI OZU, and TOSHIHISA MAESHIMA

Department of Applied Chemistry
Faculty of Science and Engineering
Kinki University
3-4-1 Kowakae, Higashi-Osaka, 577 Japan

ION C. BAIANU

Physical Chemistry and NMR Laboratories
University of Illinois
Urbana, Illinois 61801

LUN-SHIN WEI

Department of Food Science
University of Illinois
Urbana, Illinois 61801

ABSTRACT

The anionic polymerization of acrolein (AL) with *N,N*-dimethylamino-propylacrylamide (DMAPA) in the presence of water was investigated in tetrahydrofuran, benzene, and ethanol at 0°C in a nitrogen atmosphere. The resulting polymers were found to be essentially vinyl poly-

mers with one DMAPA attached and an aldehyde side chain. From observations of the polymerization process by ^1H NMR, we find that polymerization was initiated by the hydroxyl anion formed in the thermodynamic equilibrium between the amine of DMAPA and water. The hydrogen transfer reaction of DMAPA was caused by the propagating poly-AL anion. On the other hand, the monomer reactivity ratios and the Q_2-e_2 values of DMAPA were determined by the free-radical copolymerization of styrene (St, M_1) with DMAPA and AIBN as initiator.

INTRODUCTION

In earlier reports [1, 2] we described how acrolein (AL) and methyl vinyl ketone could be homopolymerized by a mixture of amine and water below room temperature. Kinetic investigations revealed that the polymerization was initiated by the hydroxyl anion formed in the thermodynamic equilibrium between amine and water. The anionic polymerization of AL [3], methyl vinyl ketone [3], methyl methacrylate [4, 5], and acrylamide [6] in the presence of imidazole has also been reported previously in detail. This polymerization was found to be initiated by a thermodynamic equilibrium between the imidazole and an initial adduct of imidazole and the monomer in the initial polymerization step.

We have also reported the anionic copolymerizations of AL with acrylamide and its derivatives in the presence of a mixture of pyridine and water or an imidazole catalyst [6, 7]. In this case the copolymerization of AL with methacrylamide readily yielded a typical vinyl copolymer; however, *N,N*-dimethylacrylamide was not copolymerized because of its poor anionic polymerizability ($e = -0.45$). It is interesting to note that the acrylamide copolymerizes with AL through a hydrogen transfer reaction from the poly-AL anion. This observation may be explained by the interactions between a propagating poly-AL anion (carbanion) and an amide group, and between a carbonyl and an amide group.

In recent years, *N,N*-dimethylaminopropylacrylamide (DMAPA), which is an acrylamide derivative with an amide and an amine group, has become well known as an important agent for practical applications [8-13]. This report provides strong evidence for the hydrogen transfer polymerization of DMAPA induced by the propagating poly-AL anion.

EXPERIMENTAL

Materials

Acrolein (AL) and methyl vinyl ketone (MVK) were prepared as described in previous papers [14, 15]. Styrene (St), tetrahydrofuran (THF), benzene, dioxane, ethanol, and *n*-hexane were purified by conventional methods [16]. *N,N*-Dimethylaminopropylacrylamide (DMAPA) was purified by vacuum distillation at 103°C/0.01 torr (lit. bp 117°C/2 torr [12, 13]) with hydroquinone and calcium hydride. The purities of these monomers and solvents were confirmed by gas chromatography as well as by IR and NMR spectroscopy. 2,2'-Azobisisobutyronitrile (AIBN) was used as a radical initiator, and imidazole (Im) was used as an anionic catalyst after recrystallization from benzene [16]. *n*-Butyllithium (*n*-BuLi) was used directly as a typical anionic catalyst.

Polymerization Methods

Free-radical copolymerization of St (M_1) with DMAPA in benzene by AIBN at 60°C was carried out in a sealed tube. The required amounts of the monomers, the initiator, and the solvent were placed in a tube. After degassing by repeated freezing and thawing cycles, the tube was sealed. The radical copolymerization was stopped at the 10% conversion level. The reaction mixture was poured into a large amount of *n*-hexane to precipitate at 45°C; the precipitate was then filtered and dried in vacuum to constant weight.

The radical copolymerization of MVK (M_1) with SMAPA in dioxane by AIBN at 60°C was carried out similarly to the above procedure. The reaction mixture was poured into a large amount of ether, then the copolymer was filtered off and dried in vacuum to constant weight.

The monomer-copolymer composition curves, the monomer reactivity ratios (r_1 and r_2), and the $Q-e$ values of the Alfrey-Price equation [17] were calculated on a microcomputer by using a program for analyzing copolymer composition [18].

The anionic polymerization in THF and ethanol at 0°C under nitrogen was carried out as described in the preceding papers [1, 3, 6].

Analyses

Elementary analysis of polymers was performed with a Yanaco CHN Cor-der MT-2. IR spectra were recorded with a KBr disk with a Nihon-bunkou

IRA-2 spectrophotometer. $^1\text{H-NMR}$ spectra were recorded at 90 MHz in THF-d8 with a Hitachi-Perkin Elmer Model 25 cw spectrometer. The viscosity of the polymers was determined in methanol at 25°C with an Ostward viscometer. The intrinsic viscosity, $[\eta]$, was determined from the specific viscosity, η_{sp}/c , as described in Ref. 19.

RESULTS AND DISCUSSION

Copolymerization Parameters of DMAPA

The copolymerization parameters of DMAPA for the radical copolymerization with St and MVK were investigated. No data are available in the literature for this reaction. Radical copolymerizations of St (M_1) and DMAPA in benzene at 60°C were carried out with AIBN (Table 1). These polymers, obtained as white powders, were soluble in acetone, methanol, benzene, THF, and water.

The IR spectra of the copolymers in KBr disks have several characteristic absorption bands of poly-St: $-\text{C}_6\text{H}_5$ at 3030, 2850, 760, and 690 cm^{-1} . The absorption bands of the $-\text{CONH}-$ (amide II) group of the DMAPA unit were observed at 1650 and 1530 cm^{-1} ; the bands of the $=\text{N}-\text{CH}_3$ group were observed at 1380 and 1240 cm^{-1} . However, the bands of the vinyl group (expected to occur at 990 and 910 cm^{-1}) were not present in the IR spectra. The intrinsic viscosity of the DMAPA homopolymer was obtained in methanol at 25°C and found to be 0.422 dL/g [19]. The melting points of copolymers were in the range $36\text{-}120^\circ\text{C}$.

The reactivity ratios were determined to be $r_1 = 1.63$ and $r_2 = 0.45$. The monomer-copolymer composition curves are summarized in Fig. 1; the experimental values fall on the calculated curve. The radical copolymerizations of MVK (M_1) with the DMAPA in dioxane at 60°C are reported in Table 2. These polymers, obtained as white or pale-yellow powders, were soluble in acetone, methanol, dioxane, benzene, THF, and water. The IR spectra of the copolymers have several characteristic absorption bands: the $-\text{CH}_2-$ chain at $3000\text{-}2890\text{ cm}^{-1}$, the $=\text{C}=\text{O}$ group at $1710\text{-}1690\text{ cm}^{-1}$, the $-\text{COCH}_3$ group at 1350 cm^{-1} (based on the poly-MVK unit), the $-\text{CONH}-$ group at 1650 and 1530 cm^{-1} , and the $=\text{N}-\text{CH}_3$ group at 1380 and 1240 cm^{-1} (based on the poly-DMAPA unit). The melting points of the copolymers in this system were in the range $65\text{-}120^\circ\text{C}$.

The monomer reactivity ratios were found to be $r_1 = 1.18$ and $r_2 = 0.39$. The corresponding monomer-copolymer composition curves are also shown

TABLE 1. Copolymerization of St (M_1) with DMAPA (M_2)^a

St charged, mol%	Polymerization time, min	Conversion, %	Nitrogen in polymer, %	Incorporated St, mol%
0	20	49.2	17.3	0
20	190	13.9	13.4	33.5
30	122	9.4	11.6	45.3
40	130	7.7	10.0	54.2
50	152	8.8	8.1	64.5
60	232	5.9	6.5	72.5
70	245	8.4	4.9	80.1
80	240	2.9	3.2	87.5
100	420	13.0	0	100

^aCopolymerization conditions: Total monomers, 1.0 mol/L; AIBN, 0.02 mol/L; solvent, benzene; temperature, 60°C.

in Fig. 1. The Q - e values were determined from the above results (Table 3). The e_2 value of DMAPA is smaller than the values of other monomers such as acrylamide, methacrylamide, and *N,N*-dimethylacrylamide, i.e., this is a typical example of a nonconjugated monomer. It can be inferred from our e values that the anionic polymerizability of this monomer is relatively low compared to other monomers.

Anionic Copolymerizability of AL and DMAPA

The anionic polymerizability of DMAPA unexpectedly gave a negative e value (-0.26) for the electron-accepting monomer. We have already reported the hydrogen transfer polymerization of acrylamide induced by the propagation of the poly-AL anion [6, 7], as well as the interaction between the carbonyl group and the amide group in the polymerization reaction [8-11]. The latter reactivity depends on the structure of the amide group rather than on the value of the pK_a or the group polarity. In order to examine this point, several anionic copolymerizations were carried out in THF, benzene, and

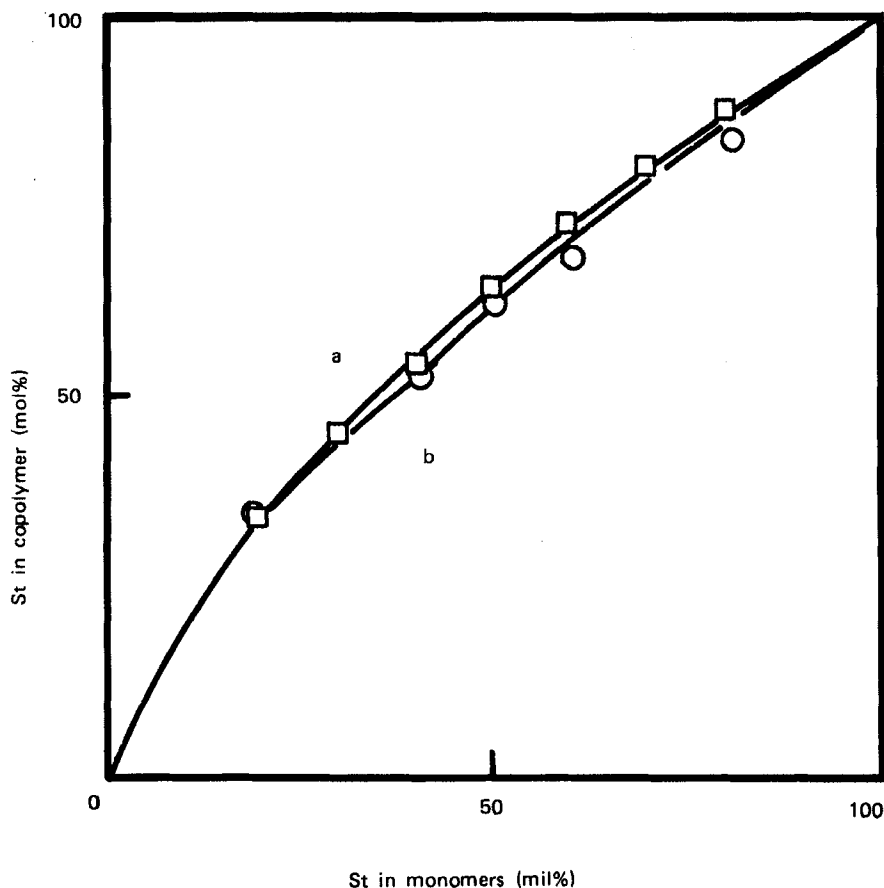


FIG. 1. Monomer-copolymer composition curves. a: St-DMAPA system. b: MVK-DMAPA system.

ethanol under various conditions (Table 4). It was found that DMAPA did not have appreciable anionic homo- and copolymerizabilities in the presence of *n*-BuLi and imidazole. We have also reported the anionic polymerization of AL in the presence of a mixture of amine and water [1, 14, 15]. Kinetic investigations revealed that the hydroxyl anion was formed as a result of a thermodynamic equilibrium between amine and water. Therefore, the polymerizability of AL in the presence of DMAPA and water was investigated in THF

TABLE 2. Copolymerization of MVK(M_1) with DMAPA (M_2)^a

MVK charged, mol%	Polymerization time, min	Conversion, %	Nitrogen in polymer, %	Incorporated MVK, mol%
0	30	6.4	0	0
20	313	9.2	5.4	33.7
40	315	7.5	9.1	52.6
50	315	7.9	10.3	61.9
60	277	7.4	12.0	68.6
80	315	8.6	14.6	83.7
100	315	9.7	17.5	100

^aCopolymerization conditions: Total monomers, 0.75 mol/L; AIBN, 0.002 mol/L; solvent, dioxane; temperature, 60°C.

and ethanol at 0°C without a catalyst (Table 5). The addition of water initiated the polymerization reaction; the reactivity increased with the amount of water added. The tendency of instantaneous polymerization with a large amount of water added was indicated in previous papers [1, 14, 15]. No polymerization took place, of course, in the absence of water (Table 4).

Poly-AL is converted into an insoluble and infusible polymer by intramolecular cyclization and/or intermolecular crosslinking of the side chains [1, 20]. The poly-AL has an adsorptive capacity which depends on the interactions between the carbonyl groups [20]. To further investigate this point,

TABLE 3. Copolymerization Parameters^a

M_1	r_1	r_2	$r_1 \cdot r_2$	Q_2	e_2
St	1.63	0.46	0.75	0.40	-0.26
MVK	1.18	0.38	0.46	0.32	-0.24

^a Q and e for acrylamide derivatives: Acrylamide, 1.18 and 1.30; methacrylamide, 0.59 and -0.88; *N,N*-dimethyl acrylamide, 0.53 and -0.54.

TABLE 4. Anionic Homo- and Copolymerizabilities of Al (M_1) and DMAPA (M_2)^a

Catalyst	Solvent	Monomers charged, mol%		Temperature, °C	Time, h	Conversion, %
		M_1	M_2			
<i>n</i> -BuLi ^b	THF	0	100	0	140	0
		80	20	0	41	36.0
Im ^c	THF	0	100	30	141	0
		50	50	30	141	3.1
		100	0	30	141	41.9
None	Benzene	45	55	0	72	0
	Ethanol	45	55	0	72	0
	THF	45	55	0	72	0

^aPolymerization conditions: Total monomers, 2.0 mol/L; atmosphere, nitrogen gas. Nitrogen content of the polymer in all cases was 0%.

^b*n*-Butyllithium, 1.95 mmol/L [4].

^cImidazole, 100 mmol/L [5].

purified polymer fractions were obtained by using the separation procedures indicated in Fig. 2.

The purified polymers, white or pale-yellow powders, were generally insoluble in organic solvents. It is interesting to note that the results of the elemental analyses indicate the presence of nitrogen in the polymer (Table 5). The IR spectrum (Fig. 3c) has several characteristic absorption bands of poly-AL [1, 20], such as the $-\text{CH}_2-$ chain ($3000\text{--}2900\text{ cm}^{-1}$) and the $=\text{C}=\text{O}$ group ($1720\text{--}1680\text{ cm}^{-1}$). The absorption bands of poly-DMAPA, such as those of the $-\text{CONHR}$ and $-\text{CONH}-$ groups observed at $1680\text{--}1640$, 1350 , and 1240 cm^{-1} , indicate the presence of several poly-DMAPA units in the polymer. The absorption bands of the vinyl group were also present at 980 and 935 cm^{-1} . These observations clearly suggest a chain transfer reaction between the poly-AL and DMAPA [6, 7].

TABLE 5. Polymerization of AL in the Presence of DMAPA and Water at 0°C^a

Solvent	Volume of added water, mL	Conversion, %	Nitrogen in polymer, %
Ethanol ^b	0	0	0
	3.2	0	0
	5.6	7.7	1.44
	9.6	9.4	1.69
	11.2	d	—
THF ^c	0	0	0
	1.4	44.6	0.59
	2.7	54.9	0.81
	3.2	d	—
	5.6	d	—

^aPolymerization conditions: Total volume, 20 mL; time, 26 h; atmosphere, nitrogen gas.

^bMonomer: AL, 0.75 mol/L.

^cMonomers: AL, 0.75 mol/L; DMAPA, 0.61 mol/L.

^dExplosive, instantaneous reaction.

Observations of the Initial Polymerization Step by ¹H NMR

As previously described, structural analyses of the insoluble poly-AL are difficult by classical or standard procedures. In order to investigate the polymerization mechanism of AL with DMAPA, several mixtures of the monomers in H₂O/D₂O and THF-d₈ were examined by ¹H NMR, as described previously [3, 4].

A mixture of both monomers did not react or polymerize without water (Figs. 4a and 5a). This result agrees very well with the results in Table 1. On the other hand, the OH proton signal from water usually occurs at 4.7 ppm, but in our samples the signal from the hydroxyl proton of H₂O occurred near 3.4 ppm (Fig. 4). We attribute this downfield shift to the interactions between the monomer and water. It was also interesting that the proton peak at 3.4

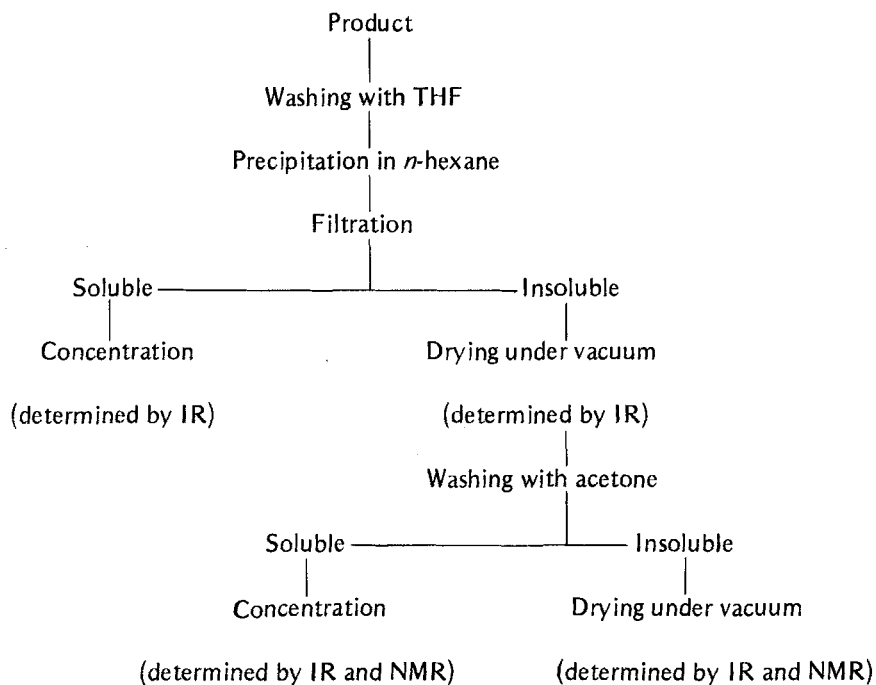


FIG. 2. Separation procedures for polymers.

ppm shifted gradually downfield with increasing reaction time (Figs. 4c and d). The proton signal near 3.9 ppm shifted downfield upon addition of D_2O , and the peak at 3.3 ppm from DMAPA showed evidence of multiplicity (Figs. 5a, b, and c). On the other hand, the vinyl group peak at 6.3-6.6 ppm of AL decreased in a stepwise manner with the reaction time, whereas the peak from the vinyl groups at 5.4-5.6 ppm did not change (Figs. 5a and c). These data are summarized in Table 6. The proton peaks from the aldehyde groups of AL at 9.6-9.8 ppm decreased as a result of the reaction (Figs. 5a, b, and c), consistent with intramolecular cyclization or intermolecular crosslinking of the aldehyde groups in the AL monomer or in the polymer [3, 20].

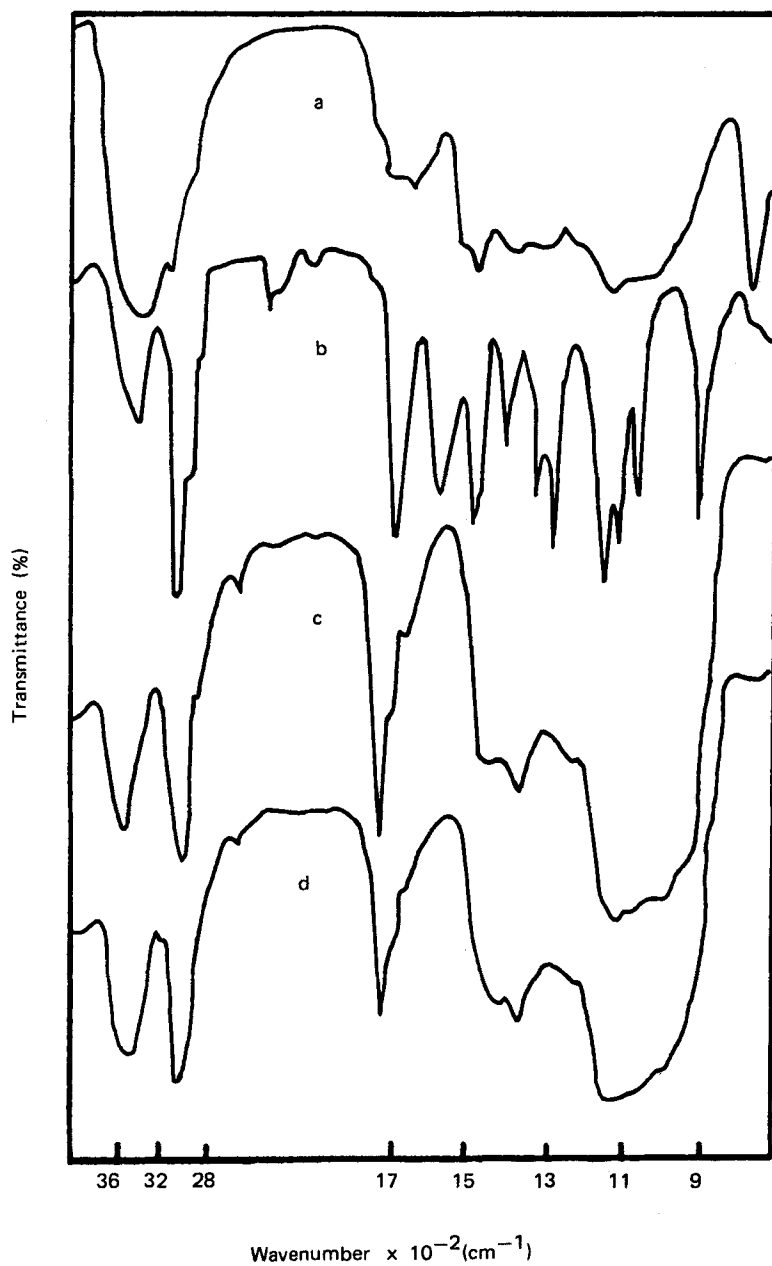


FIG. 3. IR spectra of polymers in a KBr disk. a: AL homopolymer. b: DMAPA homopolymer. c and d: AL-DMAPA polymer.

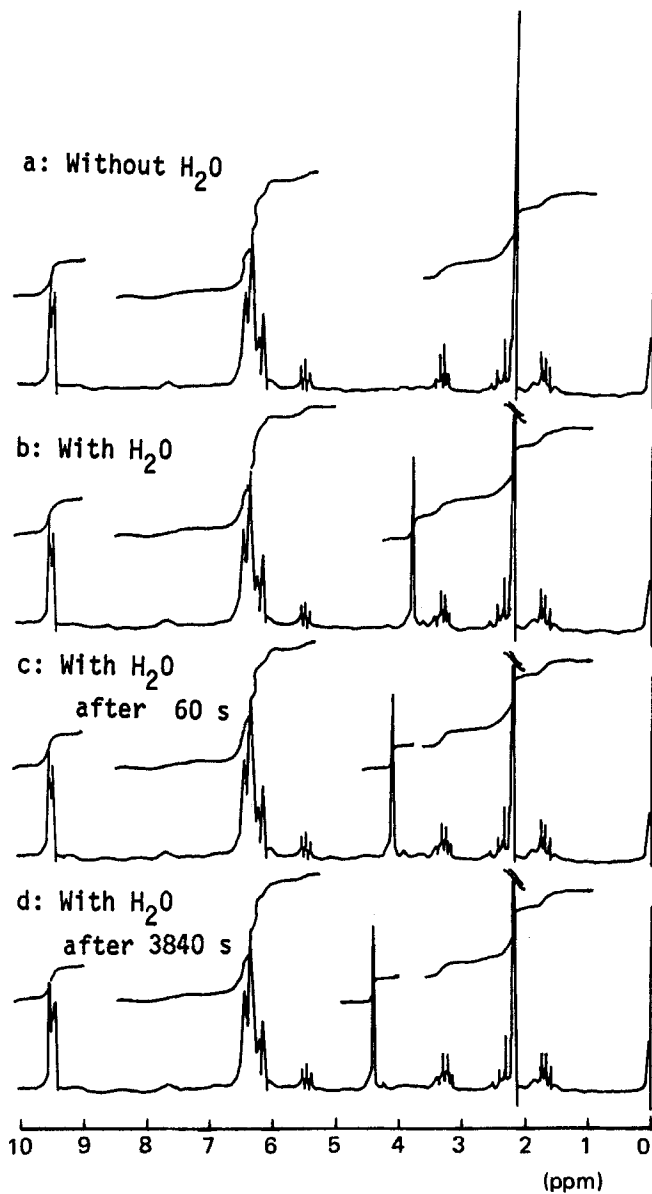


FIG. 4. $^1\text{H-NMR}$ spectra for the polymerization reaction of the AL-DMAPA system with water in THF-d_8 .

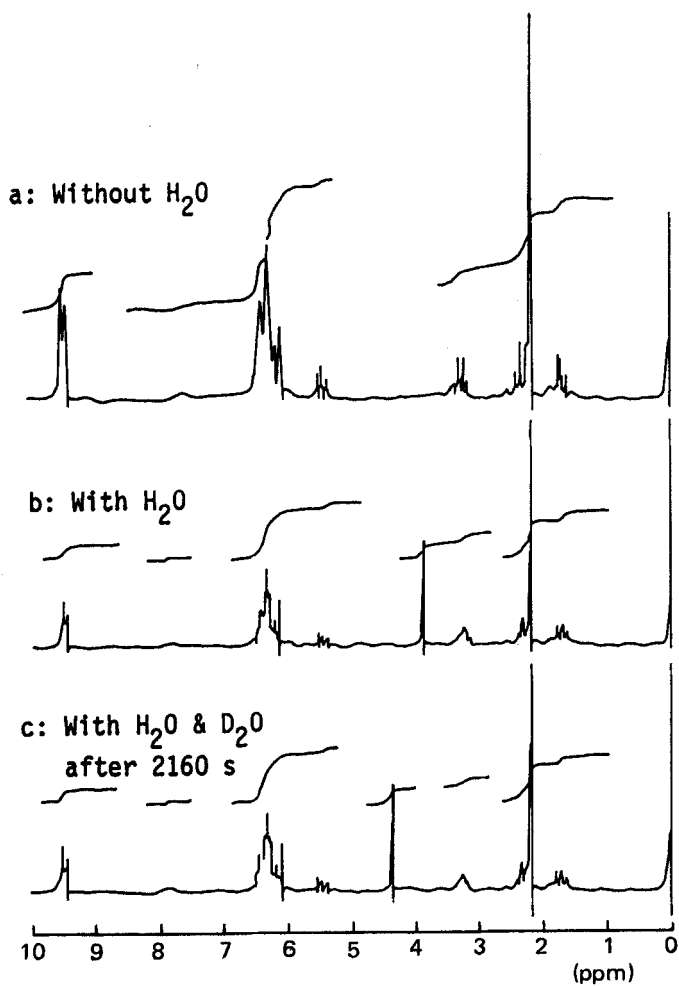


FIG. 5. ¹H-NMR spectra for the polymerization reaction of the AL-DMAPA system with H₂O and D₂O in THF-d₈.

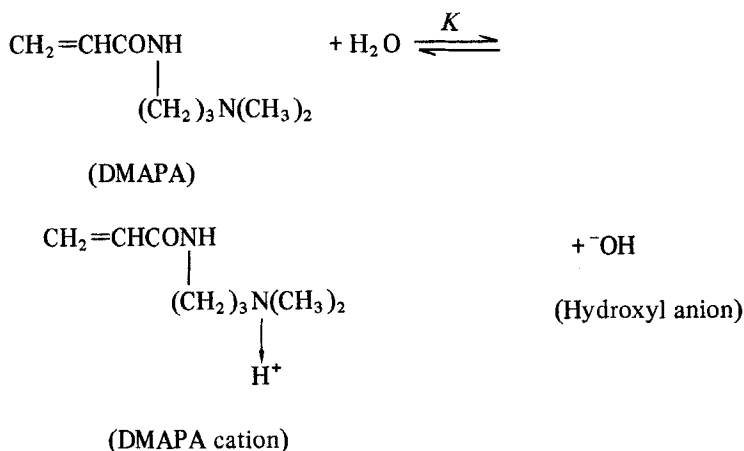
TABLE 6. $^1\text{H-NMR}$ Chemical Shift Data for the Polymerization of DMAPA Induced by AL

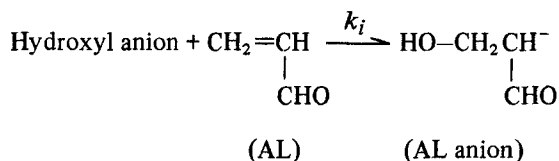
Reaction time, min	Vinyl group of AL, ppm	Vinyl group of DMAPA, ppm	H_2O , ppm
—	6.3-6.6 (8, m)	5.4-5.6 (1, q), 6.1-6.3 (2, q)	—
2	6.3-6.6 (8, m)	5.4-5.6 (1, q), 6.1-6.3 (2, q)	3.9 (2, s)
18	6.3-6.6 (6, m)	5.4-5.6 (1, q), 6.1-6.3 (2, q)	4.0 (2, s)
36	6.3-6.6 (6, m)	5.4-5.6 (1, q), 6.1-6.3 (2, q)	4.1 (2, s)
74	6.3-6.6 (4, m)	5.4-5.6 (1, q), 6.1-6.3 (2, q)	3.9-4.3 (2, b)
151	6.3-6.6 (1, m)	5.4-5.6 (1, q), 6.1-6.3 (2, q)	3.9-4.3 (-, b)
240	6.3-6.6 (1, m)	5.4-5.6 (1, q), 6.1-6.3 (2, q)	3.8-4.5 (-, b)

POLYMERIZATION MECHANISMS

Based on the above observations, the following explanation is put forward. The polymerization of AL is initiated by the reversible equilibrium between the DMAPA monomer and water.

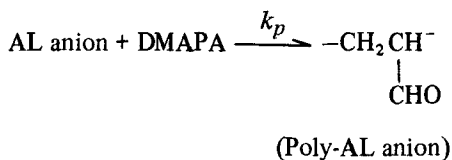
Initiation:





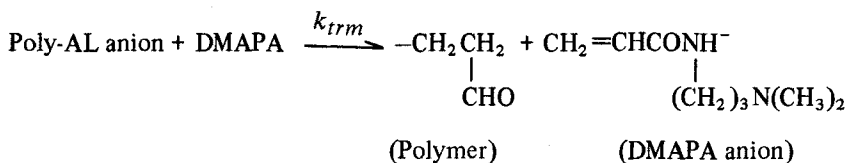
This initiation mechanism was considered in detail in previous papers [1, 14, 15] for the polymerization of AL induced by a mixture of triethylamine and water. DMAPA could not be ionically polymerized by this hydroxyl group, as shown in Figs. 4 and 5, because this monomer has an e_2 value of -0.26 (Table 3).

Propagation:

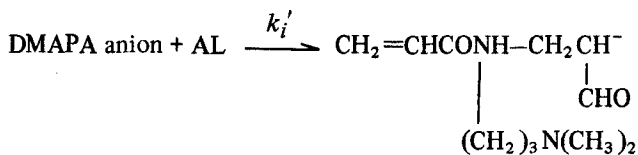


In previous reports [6, 7] we showed that the hydrogen transfer polymerization of acrylamide with AL occurs in the presence of a mixture of amine and water or of imidazole. The same mechanism may also operate for the polymerization reactions discussed above. The hydrogen transfer mechanism of the polymerization of DMAPA with the poly-AL propagating anion may therefore be considered to be as follows.

Termination and Chain Transfer:



Re-initiation:



CONCLUSIONS

DMAPA serves as an initiator of the anionic polymerization, as a counterion on the propagation step, as a chain transfer agent, and as a terminator. The investigations of the hydrogen transfer mechanism of DMAPA induced by the AL and poly-AL anions were reviewed, and it became evident that more kinetic work by different approaches is necessary and that the analysis of the new polymers formed requires new techniques.

REFERENCES

- [1] N. Yamashita, H. Inoue, and T. Maeshima, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2739 (1979).
- [2] N. Yamashita, H. Sumitomo, and T. Maeshima, *Kogyo Kagaku Zasshi*, **71**, 1723 (1968).
- [3] N. Yamashita, S. Morita, and T. Maeshima, *J. Macromol. Sci.—Chem.*, **A12(9)**, 1261 (1978).
- [4] S. Morita, H. Inoue, N. Yamashita, and T. Maeshima, *Ibid.*, **A16(5)**, 1003 (1981).
- [5] N. Yamashita, H. Tanaka, S. Deguchi, T. Maeshima, and L. S. Wei, *Ibid.*, **24(9)**, 0000 (1987).
- [6] S. Morita, K. Ikezawa, H. Inoue, N. Yamashita, and T. Maeshima, *Ibid.*, **A17(9)**, 1495 (1982).
- [7] N. Yamashita, K. Ikezawa, Y. Yamamoto, H. Kinugasa, and T. Maeshima, *Ibid.*, **A21(5)**, 291 (1984).
- [8] N. Yamashita, K. Ikezawa, S. Ayukawa, and T. Maeshima, *Ibid.*, **A21(5)**, 615 (1984).
- [9] E. Ozu, T. Mitsuta, K. Ikezawa, N. Yamashita, and T. Maeshima, *Nihon Kagaku Kaishi*, **1986(9)**, 1252 (1986).
- [10] N. Yamashita, S. Morita, M. Nishino, and T. Maeshima, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 239 (1983).
- [11] N. Yamashita, N. Omori, Y. Koumi, and T. Maeshima, *Nihon Kagaku Kaishi*, **1985(4)**, 776 (1985).
- [12] Sanyo Chemical Industries Ltd., Japanese Patent 58 49,410 (1983).
- [13] Arakawa Chemical Industries Ltd., Japanese Patent 56 60,095 (1983).
- [14] N. Yamashita et al., *Kogyo Kagaku Zasshi*, **74**, 2153 (1971).
- [15] N. Yamashita et al., *Ibid.*, **74**, 2367 (1971).
- [16] T. Otsu and M. Kinoshita (eds.), *Experimental Methods of Polymer Syn-*

theses, Kagaku Dojin, Kyoto, Japan, 1975; The Society of Polymer Science Japan (ed.), *Syntheses of Monomers*, Kyoritsu Syuppan, Tokyo, Japan, 1958.

- [17] J. Alfrey and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).
- [18] K. Endo (ed.), "The Analyzing Programs for Copolymer Composition by Microcomputer," *Kagaku*, **40**(12), 1 (1985).
- [19] J. Brandrup and E. H. Immergut (eds.), *Polymer Handbook*, 2nd ed., Wiley, New York, 1974.
- [20] R. C. Schulz (ed.), "Acrolein Polymers" in *The Encyclopedia of Polymer Science and Engineering*, Vol. 1, 2nd ed., Wiley, New York, 1985.

Received January 27, 1987

Revision received March 16, 1987