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

Preparation and Thermal Decomposition of Cyclic Azoamidinium Salts as Water-Soluble Radical Initiators for Polymerization over A Wide Temperature Range

Hirotoshi Fujie[a]; Kazuo Shiraki[a]; Tsutomu Miyagawa[a]; Noriaki Minamii[a]; Bunichiro Yamada[b]; Takayuki Otsu[b]
[a] Wako Pure Chemical Industries, Ltd., Osaka, Japan [b] Department of Applied Chemistry, Faculty of Engineering Osaka City University Sugimoto, Osaka, Japan

To cite this Article Fujie, Hirotoshi , Shiraki, Kazuo , Miyagawa, Tsutomu , Minamii, Noriaki , Yamada, Bunichiro and Otsu, Takayuki(1992) 'Preparation and Thermal Decomposition of Cyclic Azoamidinium Salts as Water-Soluble Radical Initiators for Polymerization over A Wide Temperature Range', Journal of Macromolecular Science, Part A, 29: 9, 741 — 751

To link to this Article: DOI: 10.1080/10601329208054113

URL: http://dx.doi.org/10.1080/10601329208054113

J.M.S.—PURE APPL. CHEM., A29(9), pp. 741–751 (1992)

PREPARATION AND THERMAL DECOMPOSITION OF CYCLIC AZOAMIDINIUM SALTS AS WATER-SOLUBLE RADICAL INITIATORS FOR POLYMERIZATION OVER A WIDE TEMPERATURE RANGE

HIROTOSHI FUJIE, KAZUO SHIRAKI, TSUTOMU MIYAGAWA,
and NORIAKI MINAMII

Wako Pure Chemical Industries, Ltd.
Doshomachi, Chuo-ku, Osaka 541, Japan

BUNICHIRO YAMADA and TAKAYUKI OTSU*

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

ABSTRACT

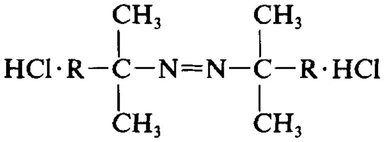
A series of cyclic azoamidinium chlorides as water-soluble initiators were prepared by reactions of the iminoether derived from 2,2′-azobisisobutyronitrile with substituted alkylene diamines. The first-order rate constants for the decomposition of the azoamidinium salts varied from 0.59×10^{-5} to 14.1×10^{-5} s^{-1} with the ring size and the alkyl substitution of the ring. Decomposition of 2,2′-azobis[2-(imidazoline-2-yl)propane] dihydrochloride was found to be accelerated by alkyl substitution on the imidazolinium ring. However, the azoamidinium compounds having larger rings, 2,2′-azobis[2-(3,4,5-trihydropyrimidine-2-yl)propane] dihydrochloride and 2,2′-azobis[2-(4,5,6,7-tetrahydro-1*H*-1,3-diazepine-2-yl)propane] dihydrochloride, decomposed at a slower rate than the unsubstituted azobis[2-(imidazoline-2-yl)-propane] dihydrochloride. These new initiators were found to be capable of initiating radical polymerizations of acrylamide and vinyl acetate.

INTRODUCTION

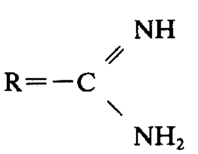
Aliphatic azo compounds and various types of peroxides have been employed as initiators of radical polymerization [1]. The azo initiators feature unimolecular decomposition which produces pairs of carbon-centered radicals, and the decomposition rates are usually affected by the solvent to a small extent. 2,2′-Azobisisobutyronitrile (AIBN), 2,2′-azobis-2,4-dimethylvaleronitrile (AVN), and 1,1′-azobiscyclohexane-1-carbonitrile (ACN) are commercially available azo initiators. The decomposition of AIBN at 60°C is as fast as that of AVN and ACN at 44 and 78°C, respectively [1]. Consequently, we can initiate polymerization at an acceptable rate over a wide temperature range by using AIBN, AVN, ACN, and other azo initiators. However, these initiators are soluble in organic solvents and insoluble in water.

Only a few water-soluble azo initiators, such as 4,4′-azobis-4-cyanopentanoic acid (ACP) and azobis(2-amidinopropane) dihydrochloride (*1*), have been commercially available. If water-soluble azo initiators with different decomposition rates were available, they could be conveniently utilized for radical polymerization in aqueous media. From such a point of view, we synthesized a series of cyclic azoamidinium salts (AZAM's) to employ as initiators for polymerization. The AZAM's synthesized are 2,2′-azobis[2-(imidazoline-2-yl)propane] dihydrochloride and its substituents (*2a*–*2e* and *3a*–*3f*), 2,2′-azobis[2-(3,4,5-trihydropyrimidine-2-yl)-propane] dihydrochloride and its substituent (*4a*–*4b*), and 2,2′-azobis[2-(4,5,6,7-tetrahydro-1*H*-1,3-diazepine-2-yl)propane] dihydrochloride (*5*).

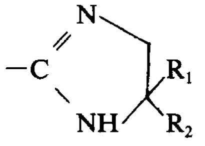
Although decomposition of *1* and polymerization initiated with *1* have been studied [2–5], its substituents, *2*, *3*, *4*, and *5* (except for *2a*), have neither been prepared nor used as initiators. Among AZAM's, *2a* has been prepared by Hammond et al. [2] who used it as a precursor of the azoamidinium nitrate. The initiators prepared and employed for the polymerization are as follows:



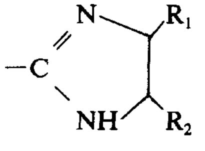
$$\mathrm{HCl\cdot R-\overset{CH_3}{\underset{CH_3}{C}}-N{=}N-\overset{CH_3}{\underset{CH_3}{C}}-R\cdot HCl}$$



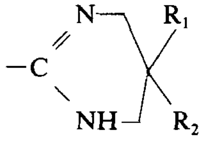
1



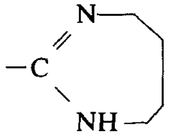
2a, $R_1 = R_2 = H$; *2b*, $R_1 = CH_3$, $R_2 = H$, *2c*, $R_1 = R_2 = CH_3$; *2d*, $R_1 = CH_3$, $R_2 = C_2H_5$; *2e*, $R_1 = CH_3$, $R_2 = CH_2CH(CH_3)_2$



3a, $R_1 = R_2 = CH_3$; *3b*, $R_1 = CH_3$, $R_2 = C_2H_5$; *3c*, $R_1 = CH_3$, $R_2 = CH(CH_3)_2$; *3d*, $R_1 = CH_3$, $R_2 = CH_2\text{-}CH(CH_3)_2$; *3e*, $R_1 = C_2H_5$, $R_2 = n\text{-}C_3H_7$; *3f*, $R_1 = n\text{-}C_3H_7$, $R_2 = n\text{-}C_4H_9$



4a, $R_1 = R_2 = H$; *4b*, $R_1 = R_2 = CH_3$

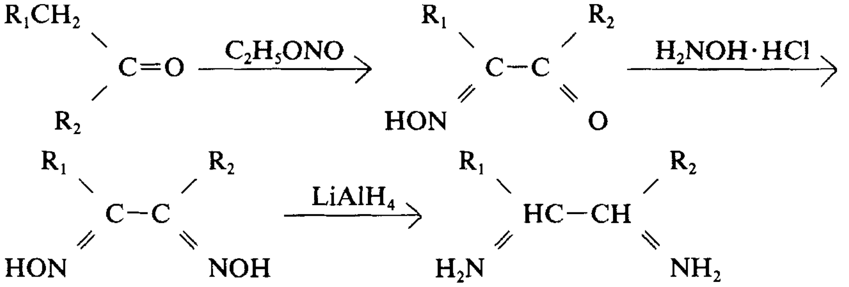


5

EXPERIMENTAL

Materials

1,1-Dialkyl-1,2-ethylenediamines were prepared by reduction of α,α-dialkyl-α-aminonitriles [6] with lithium aluminum hydride. 1,2-Dialkyl-1,2-ethylenediamines were prepared by reduction of 1,2-dialkylglyoxime with lithium aluminum hydride according to the following sequence of reactions:



The azomidines and their salts were prepared in 60–70% yields by reactions of the iminoether derived from AIBN [7] with the corresponding diamines. All the initiators synthesized are water soluble and were recrystallized from water. Formation of the desired AZAM's were verified by ^1H- and ^{13}C-NMR spectroscopy.

Spectroscopy

The NMR spectra were recorded on JEOL GSX-270 and JEOL 60QX spectrometers. Deuterium oxide was used as solvent.

Thermal Decomposition

Thermal decomposition of AZAM was monitored by optical density at 360 nm due to the azo group in 1 wt% solution with a Shimadzu UV160 spectrophotometer. The decomposition rate constant (k_d) was obtained as the slope of the first-order plot.

Polymerization

Acrylamide (AcAm) and vinyl acetate (VAc) were polymerized after recrystallization from methanol and distillation under reduced pressure, respectively. Polymerizations of AcAm in water and VAc in methanol in 1-L flasks were induced with AZAM and *1* in aqueous and methanol media, respectively. The polymerizations were followed gravimetrically. Aliquots were withdrawn from the polymerization mixture at appropriate time intervals and were precipitated in acetone and *n*-hexane, respectively, and the percentage conversion was calculated from the weight of the polymer. Inherent viscosities, η_{inh} (dL/g), of poly(AcAm) and poly(VAc) were measured at 25°C in aqueous (0.03 g/dL) and methanol solutions (0.5 g/dL), respectively, by using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Decomposition Rate Constant

Figure 1 shows the ^{1}H-NMR spectrum of *2a*. The other AZAM's exhibited the signals of the methyl group bound to the quaternary carbon adjacent to the azo group and the methylene or methyne group in the ring at the chemical shifts close to those in Fig. 1. The ^{13}C-NMR spectra of *2a* and *5* in Fig. 2 also show the signals due to the methyl group bound to the quaternary carbon whose resonances are observed in these spectra, the methylene group bound to the nitrogen, and the C=N group. In addition to these resonances, the signals due to the respective

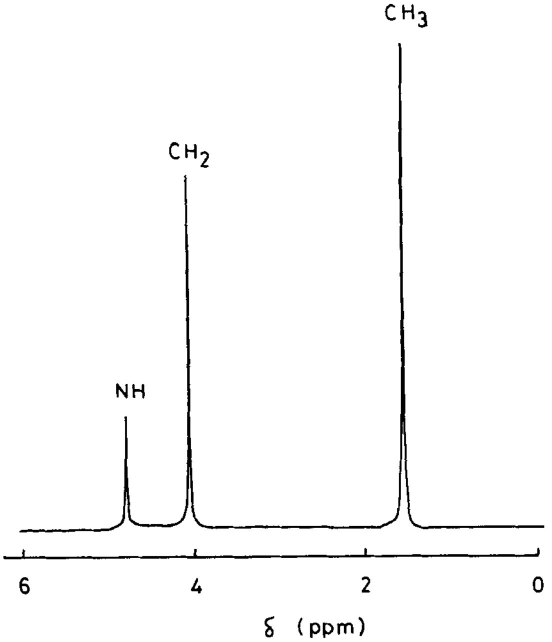


FIG. 1. ^{1}H-NMR spectrum of *2a*.

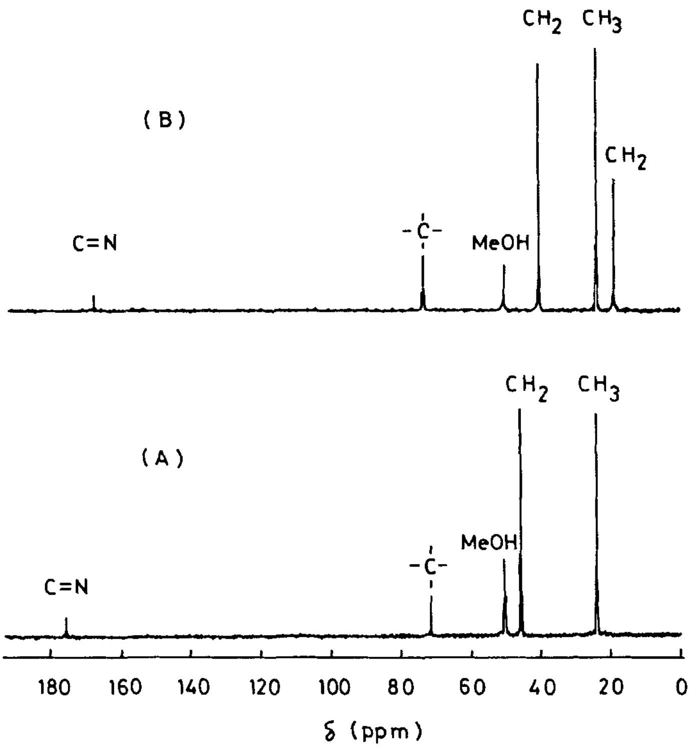


FIG. 2. ^{13}C-NMR spectra of *2a* (A) and *5* (B).

substituents and methylenes or methyne group involved in the ring verified AZAM's structures.

The k_d values for the decomposition of AZAM's were determined by the first-order plot using the change in the optical density at 360 nm. Figure 3 illustrates a decrease in the optical density with time, and the first-order plot for *2c* is shown in Fig. 4 as an example. The k_d values obtained in water and methanol are summarized in Table 1 together with those for some free amidines in methanol. The cyclic AZAM's decompose about 10 times faster in water than do the corresponding free amidines in methanol. The amidinium group is considered to stabilize the incipient radical to a greater extent than does the amidine group.

Figure 5 presents plots of the half-life period versus temperature to give linear relationships for ACP, *1*, *2a*, *3e*, and *4a*. Apparently, *2a* and *3e* decompose faster than the conventional water-soluble initiators, ACP and *1*. The half-life period of 500 min, which is an appropriate decomposition rate for an initiator, is estimated for *3e*, *2a*, *1*, *4a*, and ACP to be 37, 47, 58, 61, and 71 °C, respectively, indicating that they can conveniently be used over this temperature range.

While repulsion of the positive charge might play a significant role for the faster decomposition of AZAM, a considerable contribution of the charge repulsion to the homolysis of *1* has been ruled out [2]. Dougherty has pointed out that the activation parameters for the decomposition of *1* in water are quite similar to those of the decomposition of AIBN [3]. The similar decomposition rate constants for

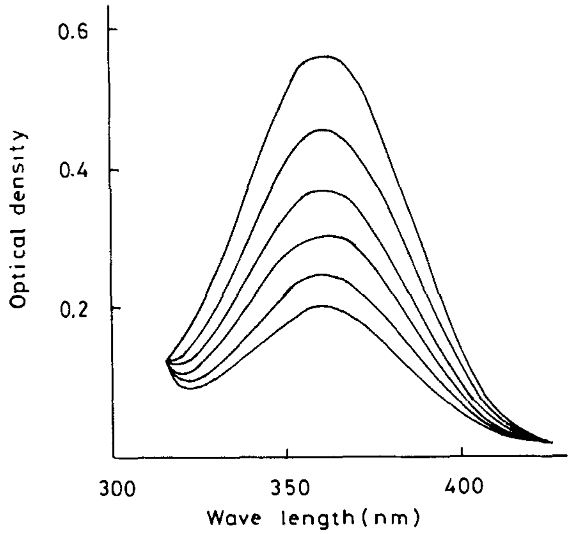


FIG. 3. Decrease in the optical density over the range from 310 to 430 nm by decomposition of *2c*.

most AZAM's and *1*, both in methanol and in water (compared in Fig. 6), as well as the small solvent effect on the decomposition of *1* reported by Hammond and Neuman [2], are also evidence of a minor contribution of the charge interaction.

When we compare the "cyclic" compound *2a* with the "noncyclic" homologue *1*, the k_d value of the former is 5 times larger than that of the latter. Moreover, the decomposition of *2a* was found to be further accelerated by 5,5- or 4,5-dialkyl substitution (*2b*-*2e* and *3a*-*3f*). Among the AZAM's examined, *3e* decomposed at

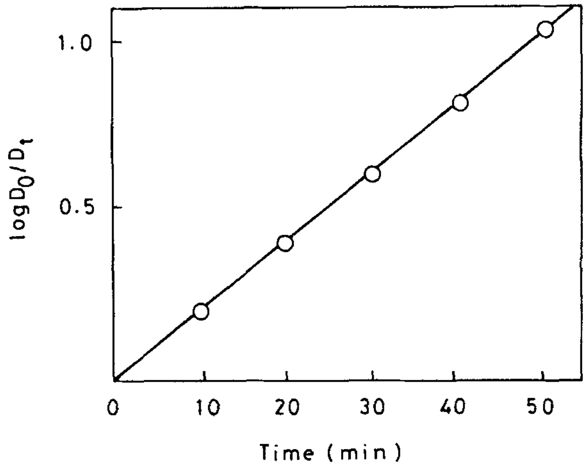
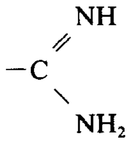
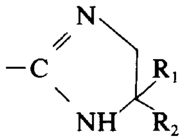
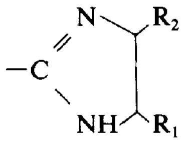
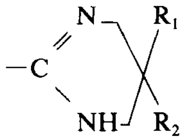
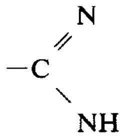


FIG. 4. First-order kinetic plot for decomposition of *2c*: D_0 and D_t denote the initial optical density and the optical density after decomposition for *t* min, respectively.

TABLE 1. The Values of K_d for AZAM and Azoamidine at 50°C

No.	R	R_1	R_2	$k_d \times 10^5, s^{-1}$ H_2O	$k_d \times 10^5, s^{-1}$ CH_3OH	$k_d \times 10^{5,a} s^{-1}$, CH_3OH
1	 $-C(=NH)NH_2$	—	—	0.81	1.45	—
2a		H	H	4.02	4.83	0.47
2b		CH_3	H	6.73	7.48	1.23
2c		CH_3	CH_3	9.30	9.55	0.93
2d		CH_3	C_2H_5	7.38	6.80	—
2e		CH_3	$CH_2CH(CH_3)_2$	7.08	5.54	—
3a		CH_3	CH_3	8.94	9.21	—
3b		CH_3	C_2H_5	11.0	9.48	—
3c		CH_3	$CH(CH_3)_2$	10.1	7.72	—
3d		CH_3	$CH_2CH(CH_3)_2$	9.78	7.72	—
3e		C_2H_5	n-C_3H_7	14.1	10.6	—
3f		n-C_3H_7	n-C_4H_9	13.3	9.75	—
4a		H	H	0.59	0.78	0.11
4b		CH_3	CH_3	0.79	0.80	0.09
5	 $-C(=N)NH$	H	H	1.04	1.23	—

[a] k_d for azoamidine.

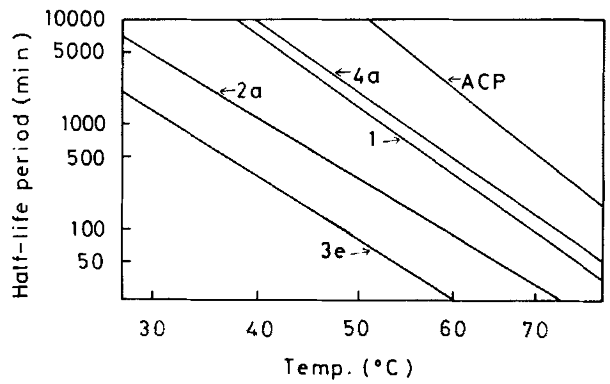


FIG. 5. Dependence of half-life period of AZAM's and ACP on temperature.

the fastest rate in water at 50°C, $k_d = 14.1 \times 10^{-5}\ s^{-1}$, which is greater than that of AIBN by a factor of 15.5. The seven-membered cyclic AZAM *5* decomposed slightly faster than *1*. However, the k_d values for two types of the six-membered cyclic AZAM's, *4a* and *4b*, in water, 0.59×10^{-5} and $0.79 \times 10^{-5}\ s^{-1}$, are smaller than that for *1*, $0.81 \times 10^{-5}\ s^{-1}$.

Among the initiators synthesized, *2a–2e* exhibited almost the same k_d values in water and methanol as shown in Fig. 6. However, the decompositions of the series of *3*, except for *3a*, in water are apparently faster than those for the decompositions in methanol. This tendency suggests that the faster decompositions of *2b–2e* and *3a–3f* than of *2a* could not be interpreted by a common factor.

Since decomposition rates of azoalkanes have been known to correlate fairly well with the stabilization energy of the radical formed [8], the five-membered imidazolium ring, which is preferable to the planar structure, could stabilize the incipient radical by a resonance effect. The most favorable angle of N—C—N for stabilization of the primary radical is expected to be ca. 120°, which could be too large for an inner angle of the five-membered ring. Repulsion between the alkyl groups on the 5-carbon of the ring in *2b–2f* could result in an alkyl-C-alkyl angle greater than 109.5°, leading to a decrease in the $CH_2—C—CH_2$ angle in the imidazolinium ring. Consequently, the N—C—N angle could increase and approach 120°, and acceleration by 5,5-dialkyl substitution could be observed.

Furthermore, the dialkyl substitution on the 4- and 5-carbons in *3a–3f* can extend the C—C bond to decrease the internal strain of the planar imidazolium

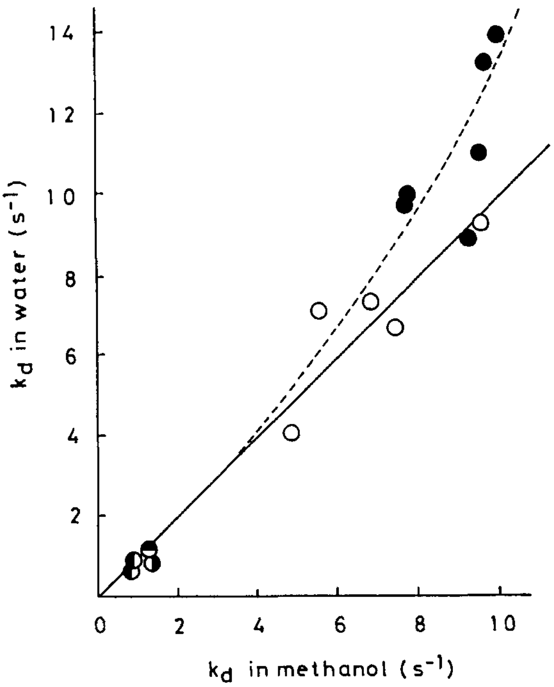


FIG. 6. Comparison of k_d of AZAM's in water with that in methanol at 50°C: (◑) *1*; (○) *2*; (●) *3*; (◐) *4*; (◒) *5*.

ring. These two factors seem to increase the k_d value in the series of *2* and *3*, unless the large alkyl groups disturb the coplanarity. The observed changes in k_d values by ring size and alkyl substitution suggest that the coplanarity closely relating to the resonance stabilization of the incipient radical is the most significant factor for fast decomposition.

Polymerization

AZAM's were used for polymerization of AcAm and VAc. Figure 7 depicts conversion-time plots for the polymerizations of AcAm in water at 50°C. As expected from the faster decomposition of *2a* and *2c*, polymerization was faster with *2a* and *2c* than with *1*, *4a*, and *5*.

Since the AZAM's used were sparingly soluble in methanol, we polymerized VAc in methanol and the time-conversion plots are shown in Fig. 8. A quite similar tendency in the polymerization rate of VAc to the AcAm polymerization rate was observed except for the polymerizations initiated with *1* and *5*, because the values of k_d for *1* in water and methanol are smaller and greater than those for *5* in the respective solvents, as shown in Table 1.

These findings indicate that the overall rates of polymerization increase with an increase in the k_d value in each solvent. Furthermore, the polymerization rates were confirmed to be proportional to the square root of the initiator concentration as expected from the standard kinetics of radical polymerization.

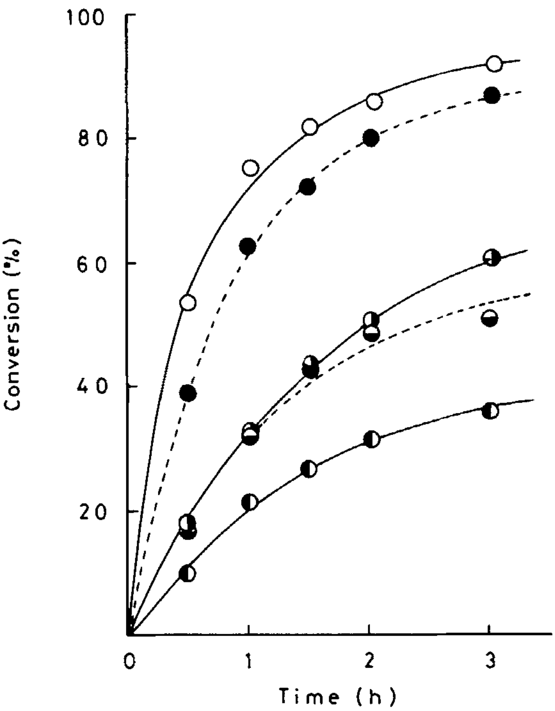


FIG. 7. Polymerization of AcAm in water (5 wt%) initiated with various AZAM's (5.8×10^{-5} mol/L) at 50°C: (◒) *1*; (●) *2a*; (○) *2c*; (◐) *4a*; (◑) *5*.

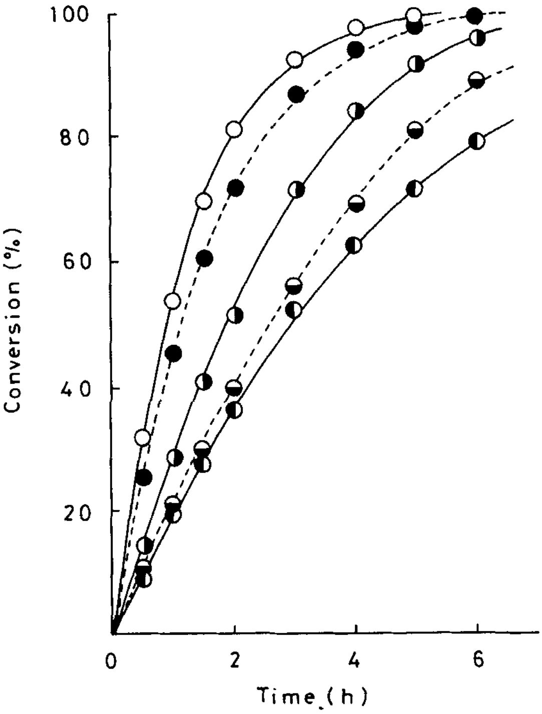


FIG. 8. Polymerization of VAc in methanol (50 vol%) initiated with various AZAM's (1.7×10^{-3} mol/L) at 50°C: (◒) *1*; (●) *2a*; (○) *2c*; (◐) *4a*; (◑) *5*.

Consider the relationship between the molecular weight of the polymer and the initiation rate; η_{inh} (dL/g), of the polymers was measured (shown in Table 2). A decrease in the value of k_d in water resulted in an increase in the viscosity of poly(AcAm); an initiator with faster decomposition brought about a polymer of lower molecular weight. These findings also confirm that polymerizations with AZAM's proceed through a radical chain mechanism. However, the η_{inh} of poly-

TABLE 2. η_{inh} of Poly(AcAm) and Poly(VAc) Prepared by Using AZAM

	$k_d \times 10^5$, s^{-1}		η_{inh}, dL/g	
Initiator	Water	Methanol	Poly(AcAm)[a]	Poly(VAc)[b]
1	0.81	1.45	12.54	0.36
2a	4.02	4.83	9.90	0.34
2c	9.30	9.55	9.06	0.34
4a	0.59	0.78	13.21	0.39
5	1.04	1.23	12.51	0.37

[a] Aqueous solution (0.03 g/dL) at 25°C.
[b] Methanol solution (0.5 g/dL) at 25°C.

(VAc) changed only slightly with the k_d value, probably due to the considerable chain transfer to the monomer and polymer [9].

CONCLUSION

Water-soluble initiators which can be used over a wide temperature range were prepared by structural modification in AZAM. Synthesized AZAM's possess a sufficient initiating activity, and their half-life period of 500 min, which could be sufficiently fast for an initiator for radical polymerization, is estimated to be from 35 to 60°C, depending on the ring size and the alkyl substitution.

REFERENCES

[1] J. C. Masson, "Decomposition Rates of Organic Free Radical Initiators," in *Polymer Handbook*, 3rd ed. (J. Brandrup and E. H. Immergut, eds.), Wiley, New York, 1989, p. II/1.

[2] G. S. Hammond and R. C. Neuman Jr., *J. Am. Chem. Soc., 85*, 1501 (1963).

[3] T. J. Dougherty, *Ibid., 83*, 4849 (1961).

[4] K. Ito, *J. Polym. Sci., Polym. Chem. Ed., 11*, 1673 (1973).

[5] N. Minamii, B. Yamada, and T. Otsu, *Mem. Fac. Eng., Osaka City Univ., 28*, 101 (1987).

[6] M. Freifelder and R. B. Hasbrouck, *J. Am. Chem. Soc., 82*, 696 (1960).

[7] J. Thiele and K. Heuser, *Justus Liebigs Ann. Chem., 290*, 1 (1896).

[8] J. W. Timberlake, "Azoalkane Decompositions as Measures of Radical Substituent Effects," in *Substituent Effects in Radical Chemistry* (H. G. Viehe, Z. Janousek, and R. Merényi, eds.), Reidel, 1986, p. 271.

[9] K. Hatada, Y. Terawaki, T. Kitayama, M. Kamachi, and M. Tamaki, *Polym. Bull., 4*, 451 (1981).

Received January 24, 1992