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

MECHANISTIC STUDY ON POLYMERIZATION OF ACRYLAMIDE INDUCED BY CYCLOHEXANONE BASED ON THE INTERACTION BETWEEN THE CARBONYL AND AMIDE GROUPS

Xu-Dong Zhong[a]; Manabu Ishifune[a]; Natsuki Yamashita
[a] Department of Applied Chemistry, Kinki University, Osaka, Japan

To cite this Article Zhong, Xu-Dong , Ishifune, Manabu and Yamashita, Natsuki(1999) 'MECHANISTIC STUDY ON POLYMERIZATION OF ACRYLAMIDE INDUCED BY CYCLOHEXANONE BASED ON THE INTERACTION BETWEEN THE CARBONYL AND AMIDE GROUPS', Journal of Macromolecular Science, Part A, 36: 2, 275 — 286

To link to this Article: DOI: 10.1081/MA-100101530

URL: http://dx.doi.org/10.1081/MA-100101530

J.M.S.—PURE APPL. CHEM., A36(2), pp. 275–286 (1999)

MECHANISTIC STUDY ON POLYMERIZATION OF ACRYLAMIDE INDUCED BY CYCLOHEXANONE BASED ON THE INTERACTION BETWEEN THE CARBONYL AND AMIDE GROUPS

Xu-Dong Zhong, Manabu Ishifune, and Natsuki Yamashita[*]
Department of Applied Chemistry
Kinki University
3-4-1 Kowakae, Higashi-Osaka
Osaka 577-8502, Japan

Key Words: Acrylamide, *N,N*-dimethylacrylamide, Cyclohexanone, 2,6-Dimethylcyclohexanone, Carbonyl-amide Interaction

ABSTRACT

Homopolymerization of acrylamide (AAm) initiated with cyclohexanone (CHn) was carried out in THF at 75°C under argon atmosphere. It was found that the rate of polymerization (Rp) can be expressed by $Rp = k[AAm]^{1.6}[CHn]^{0.6}$. The polymerization was confirmed to proceed through a radical-initiated mechanism from the resulting polymerization equation. The effects of temperature of the Rp were discussed in the temperature range of 70-80°C. The overall activation energy (Ea) was estimated to be 138.9 kJ/mol. 2,6-Dimethylcyclohexnone (DMCHn) was also applied instead of CHn. The acceleration effect of DMCHn on the polymerization was higher than that of CHn in the case of AAm, but was lower in the case of methyl methacrylate under the same conditions. No effect of CHn on the polymerization of *N,N*-dimethylacrylamide was found under these conditions. The participation of $-NH_2$ in the complexation of a monomer with CHn is proposed to induce this radical polymerization.

---

[*] Author to whom correspondence should be addressed.

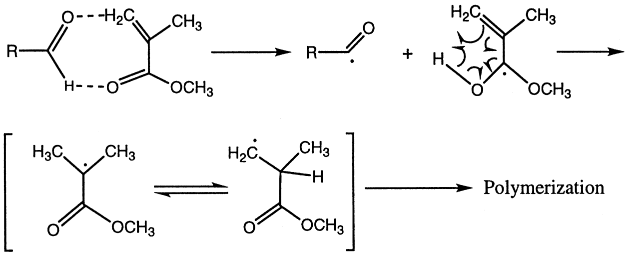
www.dekker.com

INTRODUCTION

Radical polymerization of several polar vinyl monomers in the presence of an active acidic hydrogen atom containing compound (e.g., aldehydes, ketones, etc.) has been the subject of many publications [1-8]. As shown in Scheme 1, the mechanism of the reaction involving transfer of the hydrogen radical abstracted from these compounds to the monomer, was originally proposed by M. Imoto. [3-5]. They found the poly(acrolein-co-styrene) [9] and poly(methyl vinyl ketone-co-styrene) [10] can initiate the radical polymerization of methyl methacrylate (MMA). When the -CHO group of poly(acrolein-co-styrene) was hydrogenated with $NaBH_4$ to the CH_2OH group, the initiation ability of poly(acrolein-co-styrene) was lost. It was concluded that the active center of poly(acrolein-co-styrene) was the -CHO group.

Subsequently, M. Imoto also reported that not only macromolecular aldehyde compounds, such as poly(formylstyrene) [11] and poly(4-formyl-2-methoxy phenyl methylacrylate), [3] but also low-molecular aldehyde of vanillin [3] or benzaldehyde [4] could initiate the radical polymerization of MMA and many other vinyl monomers [5]. A similar type of interaction between MMA and cyclohexanone (CHn) molecules has been proposed by A. Kaim [6], which resulted in the generation of radicals in the polymerization system.

Furthermore, A. Kaim has reported the polymerization of MMA initiated with CHn [7, 12] and other ketones (such as cyclopentanone, cycloheptanone, acetylacetone, etc.) [13], the copolymerization of MMA with styrene [14] and acrylamide (AAm) [15], the copolymerization of AAm with styrene in the presence of CHn [16]. In their literature [6], several polar vinyl monomers (including acrylamide, *N-tert*-butyl acrylamide and *N-tert*-amylacrylamide) were



Scheme 1

confirmed to be initiated with CHn in dioxane at 75°C. The interesting fact is that the highest polymer conversion among many polar vinyl monomers was obtained for AAm. The reason for this result, however, was not clarified in later reports.

In our laboratory, it has been reported [17-20] that the polymerization of acrolein and methyl vinyl ketone (MVK) could be initiated with poly(AAm), and also the polymerization of AAm could be initiated with poly(MVK) in THF or methanol. Interaction between the carbonyl group and the amide group was considered to induce this polymerization. Thus, we suggest that in the case of the polymerization of AAm initiated with CHn, the mechanism of polymerization is quite different from the case of MMA. The present paper deals in detail with the mechanism of the polymerization of AAm initiated with CHn based on the relationship between Rp and concentration of the monomer or initiator in THF. Also, the polymerization of *N,N*-dimethylacrylamide in the presence of CHn, and the polymerization of MMA in the presence of CHn and 2,6-dimethylcyclohexanone, were discussed, comparing the case of AAm.

EXPERIMENTAL

Materials

Acrylamide (AAm) was recrystallized twice from benzene. *N,N*-dimethylacrylamide (DMAAm) and methyl methacrylate (MMA) were distilled under reduced pressure in the presence of hydroquinone as a radical inhibitor under a dry oxygen-free nitrogen stream before use. Cyclohexanone (CHn) and 2,6-dimetylcyclohexanone (DMCHn) were distilled twice under reduced pressure, and under a dry oxygen-free nitrogen stream. Tetrahydrofuran (THF) was purified by the conventional method [20].

Polymerization Method

All polymerizations were carried out with no irradiation (light-shielded condition). The measured amounts of monomers and THF were placed in a glass ampoule under argon. The ampoule was degassed by repeating freeze-evacuate-thaw cycles three times, and sealed under argon. The reaction was carried out in a water bath which was maintained at constant temperature (75°C). After the specified polymerization time, the reaction was stopped by placing the ampoule in an ice-water bath. The polymerization mixture was poured into a large amount of diethyl ether, and the resulting precipitate was filtered and dried to constant weight in a vacuum oven at room temperature. The crude polymer was purified by reprecipitation from water into THF. The structure of the resulting poly(AAm) was estimated by IR, ^{1}H NMR, and ^{13}C NMR spectra.

Analyses

IR spectra were recorded with a Perkin-Elmer 1760-X FT-IR. ^{1}H NMR, and ^{13}C NMR spectra were recorded by a Nippon-Denshi JNM-FX200 (270) and a JNM-GX500 instrument, respectively.

RESULTS AND DISCUSSION

Effect of Concentration of the Monomer and Initiator on the Polymerization of AAm

Homopolymerization of AAm in the presence of CHn was carried out in THF at 75°C. The time-conversion curves for polymerization of AAm initiated by CHn were presented in Figures 1 and 2. The AAm monomer was smoothly polymerized in the presence of CHn. No homopolymerization of AAm was found in the absence of CHn under the same conditions. All polymerizations of AAm initiated with CHn were inhibited by adding a small amount of a radical inhibitor (hydroquinone). The polymerization yield increased with increase of the concentration of the monomer and CHn in THF at 75°C. In Figure 1, the amount of AAm was varied in the concentration range of 0.5-1.5 mol/L by keeping the concentration of CHn constant at [CHn] = 0.4 mol/L. Figure 2 shows the conversion of

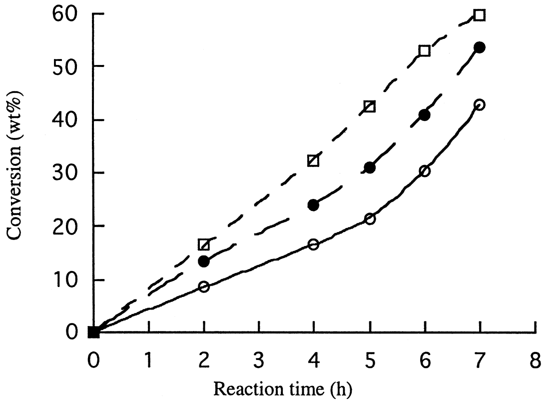


Figure 1. Time-conversion curves of the polymerization of AAm initiated with the CHn in THF at 75°C under argon. [CHn] = 0.4 mol/L; (○) [AAm] = 0.5 mol/L; (●) [AAm] = 1.0 mol/L; (□) [AAm] = 1.5 mol/L.

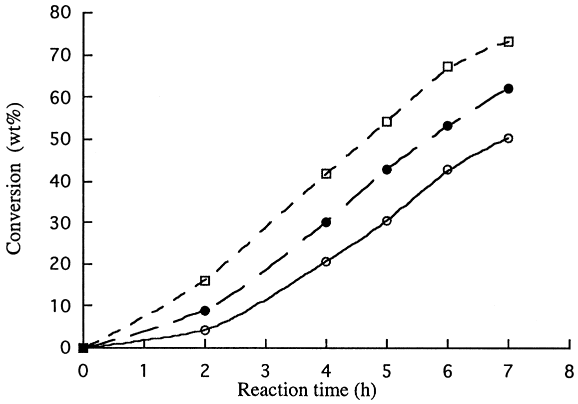


Figure 2. Time-conversion curves of the polymerization of AAm initiated with the CHn in THF at 75°C under argon. [AAm] = 1.0 mol/L; (○) [CHn] = 0.2 mol/L; (●) [CHn] = 0.6 mol/L; (□) [CHn] = 1.0 mol/L.

AAm initiated with various amounts of CHn. The concentration of CHn was varied in the concentration range of 0.2-1.0 mol/L by keeping the concentration of AAm constant at [AAm] = 1.0 mol/L.

Reaction Order with Respect to AAm and CHn

From the straight lines in the initial reaction step, the overall rate of polymerization, Rp (overall), can be calculated. The rate of polymerization (Rp) of AAm initiated with CHn was calculated by the method used by T. Ouchi [5] to estimate the kinetic equation for the polymerization of AAm initiated with CHn, because no thermal polymerization of AAm in the absence of CHn occurred under these conditions, Rp (thermal) = 0. Thus, Rp of AAm initiated with CHn is equal to Rp(overall) according to Equation 1:

$$R^2p = R^2p_{(overall)} - R^2p_{(thermal)} \tag{1}$$

By taking into account, the postulated radical mechanism of polymerization initiated with CHn, we can express Rp by Equation (2):

$$Rp = k[AAm]^m\,[CHn]^n \tag{2}$$

The relationships between Rp and [AAm] or [CHn] are presented in Figure 3. The slopes *m* and *n* were calculated by the method of least squares for 1.6 and 0.6, respectively. Correlation factors for linear regression are for the calculated

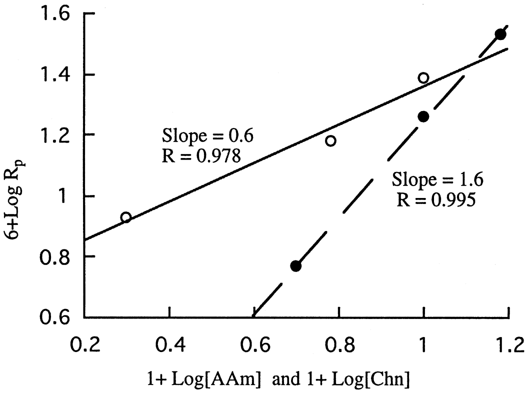
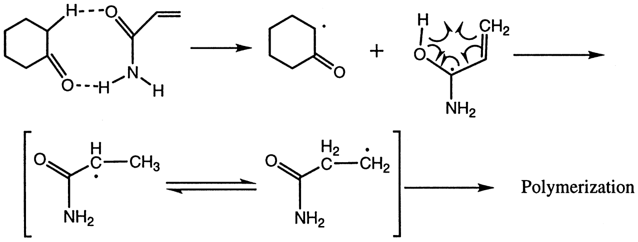


Figure 3. Relationship between the Rp and the monomer or initiator concentration in THF at 75°C. (●) [AAm] = 0.5,1.0,1.5 mol/L and [CHn] = 0.4 mol/L; (○) [CHn] = 0.2, 0.6, 1.0 mol/L and [AAm] = 1.0 mol/L.

values *m* and *n* with 0.995 and 0.978. Thus, the Rp of AAm initiated with CHn can be formulated with approximation (Equation 3):

$$Rp = k[AAm]^{1.6}\,[CHn]^{0.6} \tag{3}$$

As expected, this is different from the result of MMA initiated with CHn in dioxane by A. Kaim [7]. In Kaim's report, the Rp of MMA initiated with CHn was proportional to the concentration of the monomer and to the square root of the concentration of the initiator ($Rp = k[MMA][CHn]^{0.5}$). For this reason, Equation (3) can substantiate our view that the radical polymerization of AAm initiated with CHn is quite different from the case of MMA. As shown in Scheme 2, we suggest that the oxygen atom in the carbonyl group of CHn preferentially forms a complex with the hydrogen atom of $-NH_2$ in the amide group through a hydrogen bridge. This hydrogen bridge is assumed to raise the reactivity of the vinyl monomer itself. The fact that the Rp of AAm initiated with CHn exhibits 1.6 order and 0.6 order depending on the monomer and initiator, respectively, can be explained as follows according to the theory of T. Otsu [21]; the radical resource of initiation and propagation is first from the formation of a complex for CHn with AAm molecules, combining with a hydrogen bond between the carbonyl and amide groups, and the termination of polymerization is disproportional termination. A similar result has also been reported by T. Ouchi [5]. In the investigation of polymerization MMA initiated with benzaldehyde and another



Scheme 2

aldehyde (RCHO), the rate equation was found to be Rp $= k[MMA]^{1.5}$ $[RCHO]^{0.5}$.

Proof of the Radical Mechanism

That the polymerization of AAm initiated with CHn proceeds through a radical mechanism can be confirmed by two methods: (a) complete inhibition of polym-erization by adding a small amount of a radical inhibitor (hydroquinone), and (b) copolymerization of AAm with styrene to calculate the values of r_1(0.62) and r_2 (0.67) [16]. On the other hand, the spectra of IR, ^{1}H NMR and ^{13}C NMR for poly(AAm) obtained from the polymerization initiated with CHn are the same as the spectra for the case of using a conventional radical initiator (AIBN). From these facts, it is confirmed that the polymerization of AAm initiated with CHn proceeds through a radical mechanism.

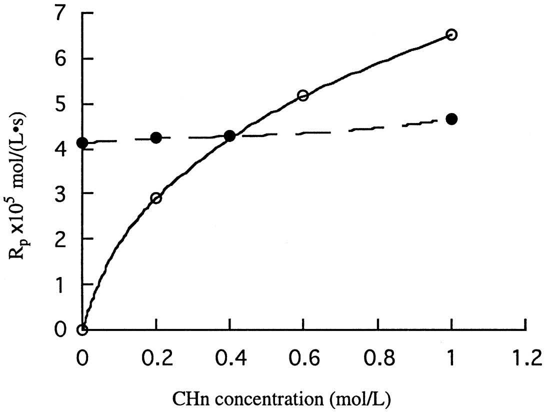


Figure 4. Relationship curves between the R_P and the concentration of CHn in the homopolymerization of AAm and DMAAm in THF at 75°C under argon.
(○) Polymerization of the AAm initiated with Chn.
(●) Polymerization of the DMAAm initiated with CHn.

Effect of CHn on the Polymerization of AAm and DMAAm

In order to investigate the participation of the -NH_2 group in complexation of the AAm monomer with CHn, the polymerization of DMAAm was also carried out in the presence of CHn in THF at 75°C. As shown in Figure 4, no acceleration of CHn on the Rp of DMAAm was found under the same conditions compared with AAm. This result can be explained by the fact that the DMAAm monomer, in which two hydrogen atoms on the amide group were replaced with methyl groups, does not form an adequate complex with CHn, therefore, the reactivity of the DMAAm monomer or the corresponding radical is unchanged (originally thermal polymerizability) in this environment. It shows good agreement with our concept described above.

Effect of CHn and DMCHn on the Polymerization of AAm and MMA

It is known that when the C-atom is attached to the electron-withdrawing atom or group, such as an oxygen atom or a carbonyl group, any hydrogen attached to the carbon becomes weakly acidic. Organic compounds with this type of hydrogen atoms undergo many ionic reactions, e.g., the metalation reaction. Simultaneously, the same hydrogen atoms are the most reactive ones in various radical reactions. It was shown for CHn that the hydrogen atom on the α-position of the carbon atoms was radically abstracted [22-23]. The mechanism of the initiation reaction involving transfer of the hydrogen radical abstracted from the active compound to the monomer was originally proposed by Ouchi *et al.* [5] for the polymerization of MMA initiated with aldehydes (RCHO). A similar type of interaction between MMA and CHn molecules has also been proposed by A.

TABLE 1. Polymerizations[a] of AAm in the Presence of the CHn and DMCHn in THF

Run	AAm, (mol/L)	Initiator	Temperature, (°C)	Reaction time, (h)	yield, %
1	1.0	–	75	4.0	0
2	1.0	CHn	75	2.5	6.2
3	1.0	CHn	80	2.5	15.0
4	1.0	DMCHn	75	2.5	10.7
5	1.0	DMCHn	80	2.5	17.1

[a] Polymerization conditions: [Initiator] = 0.4 mol/L; under argon atmosphere; no irradiation.

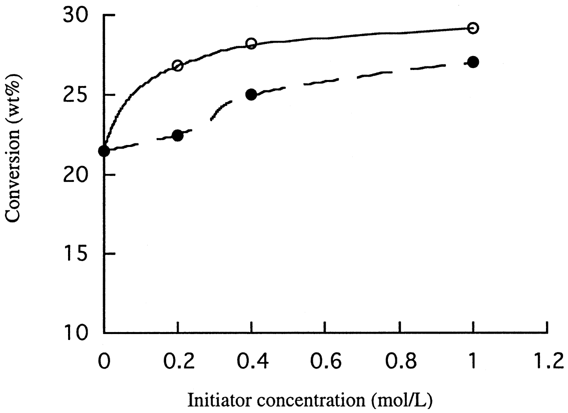


Figure 5. Relationship between the conversion of the polymerization of MMA and the initiator concentration in THF at 75°C under argon.
(○) Polymerization of NMA initiated with the CHn.
(●) Polymerization of MMA initiated with the DMCHn.

Kaim [6]. In the polymerization of MMA initiated with CHn, the hydrogen atoms in the α-position of CHn molecules are suggested to play an important role in generation of radicals which initiate the polymerization.

In order to investigate the effect of the hydrogen atom in the α-position of CHn on the Rp of AAm, DMCHn was used as an initiator for comparison with the case of CHn. The results are summarized in Table 1 and Figure 5. The yield of polymerization initiated with DMCHn is higher than that of CHn in the case of AAm, but is lower in the MMA system. The substitution of two hydrogen atoms in the α-position with methyl groups increased the electron density of carbonyl group, and promoted the complexation of the carbonyl group with -NH_2, which induced the generation of radicals in this system. The hydrogen bonding ability of ketones to the amide group also affects the AAm monomer association [24] and consequently, disturbs the keto/enol equilibrium of AAm [25], which raises vinyl bond activity in this system. In the case of MMA, there are not these additional acceleration effects, and the steric hindrance of the methyl groups on the 2,6-position predominates. The mechanism of polymerization of AAm initiated with CHn can be proposed as shown in Scheme 2.

Effect of Temperature on the Rp of AAm Initiated with CHn

The influence of temperature on the Rp of AAm in a temperature range of 70-80°C was also studied. The calculated Rp values were correlated with the

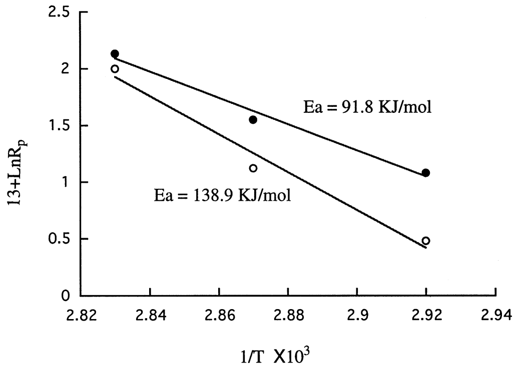


Figure 6. Relationship between the LnRp and the I/T for the polymerization of AAm initiated with the CHn and DMCHn in THF under argon in a temperature range of 70-80°C. [AAm] = 1.0 mol/L;
(○) initiated with the CHn, [CHn] = 0.4 mol/L, Ea = 138.9 KJ/mol, R = 0.988.
(●) initiated with the DMCHn, [DMCHn] = 0.4 mol/L, Ea = 91.8 KJ/mol, R = 0.992.

reciprocals of the polymerization temperature. Figure 6 is an Arrhenius plot which shows that the relationship between LnRp and 1/T in a temperature range of 70-80°C forms a curved line for the polymerization of AAm initiated with CHn and DMCHn. From the slope of the line (70-80°C) the overall activation energy (Ea) was calculated as 138.9 KJ/mol, 91.8 KJ/mol for CHn and DMCHn, respectively. A comparison of the results obtained with the values of Ea for the polymerization of MMA initiated with aldehyde (Ea = 36-37 KJ/mol) or Poly(vinyl alcohol) (Ea = 85-89 KJ/mol)[5, 26] and cyclohexanone (Ea = 137 KJ/mol) [7] shows that the Ea of the polymerization initiated with an abstracted H-atom depends strongly on the initiators.

CONCLUSION

The Rp for AAm initiated with CHn in THF can be concluded as Rp = $k[AAm]^{1.6}[CHn]^{0.6}$. The polymerization of AAm was suggested to proceed by the radical-initiated mechanism from the resulting equation. The acceleration effect of DMCHn on the polymerization was higher than that of CHn in the case of AAm, but was lower in the case of methyl methacrylate in THF at 75°C. No effect of CHn was found in the polymerization of *N,N*-dimethylacrylamide. The overall activation energy (Ea) of the polymerization of AAm was estimated to be 138.9 kJ/mol and 91.8 KJ/mol for CHn and DMCHn, respectively, in the temperature range of 70-80°C. It can be assumed that the radical to induce the initiation of AAm is preferentially generated from the AAm monomer itself which is activated by the hydrogen bonding interaction between the amide group and the carbonyl group of ketone.

REFERENCES

[1] K. Kubushiro, K. Takemoto, and M. Imoto, *Makromol. Chem., 120*, 39 (1968).
[2] T. Sato, M. Metsugi, and T. Otsu, *Ibid*., *180*, 1175 (1979).
[3] M. Imoto, T. Maede, and T. Ouchi, *Chem. Lett.*, 153 (1978).
[4] M. Imoto, T. Maede, and T. Ouchi, *J. Polym. Sci., Polym. Chem. Ed*., *17*, 385 (1979).
[5] T. Ouchi, N. Murayama, and M. Imoto, *Bull. Chem. Soc. Jpn*., *53*, 748 (1980).
[6] A. Kaim, *J. Polym. Sci., Polym. Lett. Ed*., *22*, 203 (1984).
[7] A. Kaim, *J. Polym. Sci., Polym. Chem. Ed*., *22*, 1891 (1984).
[8] A. Kaim, *J. Polym. Mater*., *3*, 73 (1986).
[9] M. Imoto, M. Oishi, and T. Ouchi*, Makromol. Chem*., *175*, 2219 (1974).
[10] M. Imoto, M. Oishi, and T. Ouchi, *Makromol. Chem*., *176*, 3289 (1975).
[11] M. Imoto, T. Meada, N. Murayamia, and T. Ouchi, *Chem. Lett.,* 729 (1979).
[12] A. Kaim, *J. Mac. Sci., Pure & Appl. Chem., A 33(1)*, 53 (1996).
[13] A. Kaim, *J. Polym. Mater*., *3*, 73 (1986).
[14] M. Munsif Ali Talpur and A. Kaim, *J. Mac. Sci., Pure & Appl. Chem., A 31*(5), 535 (1994).
[15] M. Munsif Ali Talpur, P. Oracz, and A. Kaim, *Polymer*, *Vol. 37, No. 28*, 4149 (1996).
[16] M. Munsif Ali Talpur and A. Kaim, *J. Mac. Sci., Pure & Appl. Chem*., *A 32 (2)*, 241 (1995).
[17] S. Morita, H. Inoue, N. Yamashita, and T. Maeshima*, J. Sci. and Technol. Kinki Univ.,* 1657 (1981).
[18] N. Yamashita, K. Ikezawa, S. Ayukawa, and T. Maeshima, *J. Mac. Sci. - Chem., A 21(5)*, 615 (1984).
[19] T. Tsuneka, M. Ishifune, and N. Yamashita, *Ibid., A 31(9)*, 1169 (1994).
[20] T. Otsu and M. Kinoshita, Eds., *Experimental Method of Polymer Syntheses*, Kagaku DouJin, Kyoto, Japan, 1991.

[21] T. Otsu, *Chemistry of Macromolecular Syntheses*, Kagaku DouJin, Kyoto, Japan, 1981.

[22] A. Singh and G. R. Freeman, *Can. J. Chem.*, *42*, 1869 (1964).

[23] R. Srinivasan, *Advan. Photochem.*, *4*, 123 (1966).

[24] M. Jacob, G. Smets, and F. Deschryver, *J. Polym. Sci., Polym. Lett. Ed.*, *10*, 669 (1972).

[25] L. M. Minsk, C. Kotlarchik, and R. S. Darlak, *J. Polym. Sci., Polym. Chem. Ed.*, *11*, 353 (1973).

[26] M. Imoto, K. Takemoto, and T. Otsuki, *Makromol. Chem., 104*, 244 (1967).

Received June 10, 1998
Revision received September 15, 1998

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 13:28 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/101081MA100101530