Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Preparation of Amidoxime-Fiber Adsorbents Based on Poly(Methacrylonitrile) for Recovery of Uranium from Seawater

Nalan Kabay[a]
[a] INSTITUTE OF NUCLEAR SCIENCES EGE UNIVERSITY, BORNOVA, IZMIR, TURKEY

To cite this Article Kabay, Nalan(1994) 'Preparation of Amidoxime-Fiber Adsorbents Based on Poly(Methacrylonitrile) for Recovery of Uranium from Seawater', Separation Science and Technology, 29: 3, 375 — 384
To link to this Article: DOI: 10.1080/01496399408002489
URL: http://dx.doi.org/10.1080/01496399408002489

SEPARATION SCIENCE AND TECHNOLOGY, **29**(3), pp. 375–384, 1994

Preparation of Amidoxime-Fiber Adsorbents Based on Poly(Methacrylonitrile) for Recovery of Uranium from Seawater*

NALAN KABAY
INSTITUTE OF NUCLEAR SCIENCES
EGE UNIVERSITY
35100 BORNOVA, IZMIR, TURKEY

ABSTRACT

Polymerization of methacrylonitrile was performed with anionic initiators as reported in the literature. The molecular weight of the polymer produced using BuLi as initiator at 0 ± 2°C was on the order of 10^5. Maximum conversion was 97% with BuLi initiator. For comparison, methacrylonitrile was polymerized with diethylmagnesium in dioxane at 70°C. High-molecular weight polymers with 50–60% conversions were produced by diethylmagnesium initiator. The polymethacrylonitrile obtained by BuLi initiator was used for the fiber production process. The conversion of nitrile was performed by treatment with 3% NH_2OH in MeOH at 80°C. The amidoxime-fiber adsorbent gave a large adsorption rate, such as 176 μg of U/g of adsorbent/day, in a batchwise seawater adsorption test.

INTRODUCTION

The chelating resins containing amidoxime groups have been shown to be most effective for the recovery of uranium from seawater. A polymeric adsorbent containing amidoxime groups may be prepared in various shapes by different procedures. One of these is the preparation of spherical amidoxime resins from poly(acrylonitrile-*co*-divinylbenzene) beads as widely used by Egawa et al. and other researchers (1–14).

Poly(acrylonitrile)-based fibrous adsorbents containing amidoxime groups have also been shown to be useful in the recovery of uranium from

---

* Dedicated to Prof. Iwao Tabushi.

seawater because of their high adsorption capacity and rapid adsorption rate (15). The fibrous adsorbents, however, have been found to have poor mechanical stability when they are contacted with alkali due to hydrolysis of the remaining cyano groups into hydrophilic acidic groups and a decrease in mechanical strength (16). Recently, radiation-induced grafting was found to be a convenient method to produce a more stable fibrous adsorbent (16–19). Saito et al. suggested a novel adsorption system using amidoxime hollow fibers prepared by radiation-induced grafting of acrylonitrile onto polyethylene hollow fiber and subsequent chemical conversions. Hollow fibers have been found to be easier to handle and to be resistant during the passage of seawater (20–23). Kobuke et al. reported on a composite fiber adsorbent which exhibited superior adsorption characteristics (24, 25).

The objective of this study was to compare various routes for the synthesis of poly(methacrylonitrile) leading to the preparation of amidoxime-fiber adsorbents and to determine their ability with regard to the recovery of uranium from seawater.

EXPERIMENTAL

Materials

The chemicals were products of Wako Junyaku and Nakarai Kagaku Chemical, and they were purified in the same manner described in the literature. Methacrylonitrile was purified by refluxing with CaH_2 for 7 hours followed by distillation under reduced pressure. Petroleum ether was refluxed with $LiAlH_4$ for 7 hours and then distilled before use. Ethyl ether was washed with 10% $NaHSO_3$. After successive washings with a saturated NaCl solution containing a small amount of concentrated H_2SO_4 and two portions of saturated NaCl, ether was left over $MgSO_4$ overnight, refluxed with metallic sodium, and then distilled before use. Ethyl bromide was washed with concentrated H_2SO_4. After successive washings with distilled water, 5% $NaHSO_3$ solution, and distilled water, ethyl bromide was left over $CaCl_2$ overnight. It was refluxed with CaH_2 and then distilled. Dioxane was distilled, followed by refluxing with metallic sodium. BuLi was used directly without further purification. Liquid reagents were transferred with hypodermic syringes. Other solvents and reagents were generally used without further purification. The commercial sample of MAN/6DVB/20 ED/300P copolymer beads was supplied by Mitsubishi Kasei Co.

Apparatus

Infrared spectra were recorded by using a Hitachi 260-50 infrared spectrometer. The colorimetric determination of uranium was performed using a highly sensitive Union Giken SM-401 spectrophotometer.

Synthesis of Poly(methacrylonitrile) Using BuLi as Initiator

The polymerization was performed in a three-necked flask, connected with vacuum and nitrogen inlet as described by Feit et al. (26). For Runs 1–5 in Table 1, methacrylonitrile (7.5 mL) was added dropwise to a solution of BuLi (1.44 mL) in petroleum ether (40 mL). The reaction mixture was stirred for 60 minutes at 0 ± 2°C under N_2 atmosphere. After reaction, the polymerization mixture was added to a 5% HCl solution to stop the polymerization. The product was collected by filtration, washed with distilled water, and then dried under vacuum at 45°C.

Poly(methacrylonitrile) was also synthesized by changing the addition order of reagents (Run 6 in Table 1). In that case, BuLi (1.44 mL) was added to a solution of methacrylonitrile (7.5 mL) in petroleum ether (40 mL).

Synthesis of Poly(methacrylonitrile) Using Diethylmagnesium as Initiator

Diethylmagnesium (Et_2Mg) was prepared as described in the literature (27). Polymerization was performed following the method described by Joh et al. (28). Polymerization of methacrylonitrile was carried out using

TABLE 1
Polymerization of Methacrylonitrile by BuLi as Initiator[a]

Run	[MAN] (mol/L)	[MAN]/[BuLi]	Yield (%)	[μ]	$\overline{M}_w$
1	1.916	39.1	64.1	1.14	1.19×10^5
2	1.916	39.1	78.3	1.48	1.30×10^5
3	1.916	39.1	90.0	1.54	1.40×10^5
4	1.916	39.1	97.1	1.45	1.25×10^5
5	1.916	39.1	85.2	1.31	1.03×10^5
6	1.916	39.1	78.0	0.84	4.40×10^4

[a] Total concentration of BuLi, 0.049 mol/L; polymerization temperature, Runs 1–5: 0 ± 2°C; and Run 6: −70°C.

a three-necked flask equipped with a condenser, nitrogen inlet, dropping funnel, and stirrer. Methacrylonitrile (7.5 mL) was added dropwise to a suspension of diethylmagnesium (1.3 mL) in dioxane (40 mL) with stirring and allowed to polymerize at 70°C for 4 hours. After that, the product was poured into methanol containing about 5% HCl solution to stop the polymerization. The polymer was filtered off, washed with methanol, and dried under vacuum at 45°C to give 3 g of product, corresponding to 50% conversion (Run 1 in Table 2). In the case of Run 2 (Table 2), methacrylonitrile (7.5 mL) was added dropwise to a suspension of diethylmagnesium (1.32 mL) in dioxane (67.5 mL) by stirring. The polymerization was completed after 12.5 hours. The product was filtered off, washed with MeOH, and dried under vacuum at 45°C to provide 3.6 g of product (conversion, 60%).

Viscosity Measurements

Viscosities were determined in dichloroacetic acid as described in the literature (26, 29). The following equation was used to determine intrinsic viscosities by measuring the viscosity of the polymer solution at one concentration (0.1 g/100 mL):

$$\mu = \mu_0 \times e^{[\mu]C}$$

where μ_0, μ, and $[\mu]$ are the viscosity of the solvent, viscosity of the polymer solution, and the intrinsic viscosity, respectively, and C is the concentration of the polymer solution in g/100 mL. Molecular weight (M) was calculated by using the equation of Joh et al. (29):

$$[\mu] = 3.24 \times 10^{-3} M^{0.520}$$

Preparation of Fiber Adsorbents

The finely powdered polymers synthesized using BuLi as initiator were used to produce fiber materials. The production of fiber materials was performed by Toray Industries Inc.

TABLE 2
Polymerization of Methacrylonitrile by Et_2Mg as Initiator[a]

Run	$[Et_2Mg]$ (mol/L)	Dioxane (mL)	Conversion (%)	$[\mu]$	$\overline{M}_w$
1	0.0316	40	50	4.34	1.03×10^6
2	0.0316	40	60	5.00	1.36×10^6

[a] Polymerization: 70°C, 4 hours, N_2 atmosphere; methacrylonitrile, 7.5 mL.

A solution of KOH in MeOH (7.88 g KOH in 61 mL MeOH) was added dropwise to a methanolic hydroxylamine hydrochloride solution (10.43 g $NH_2OH{\cdot}HCl$ in 104 mL MeOH). After the mixture was stirred with a magnetic stirrer, the KCl precipitated was filtered off. Functionalization of poly(methacrylonitrile) fibers was carried out with 3% NH_2OH in methanol. The reaction mixture was gently refluxed and then filtered, washed with methanol and dried under vacuum at 45°C. The conversion of the nitrile to the amidoxime was shown by the disappearance of CN absorption at 2235 cm^{-1} on the IR spectra.

Adsorption Tests

The fiber adsorbent (50 mg) was immersed in 10 mL of 1 M NaOH for 6, 12, 24, 48, and 96 hours. After alkaline treatment, the sample was neutralized by 0.1 M HCl, added gradually. Complete neutralization was confirmed by no further pH change in the neutral pH range. The fiber adsorbent was washed with deionized water. The alkali-treated fiber adsorbent was immersed in 5 L of natural seawater thermostated at 25 ± 0.05°C. The seawater was swirled at a constant speed (180–200 rpm) by a poly(tetrafluoroethylene) blade driven by a mechanical stirrer. After 24 hours of immersion, the fiber was filtered off and washed with deionized water. The elution of uranium was performed by immersing the fiber adsorbent into 10 mL of 1 M HCl (3×) for 1 hour. The spectrophotometric determination of uranium was based on the U-Arsenazo III complex. The absorbance of the solution was measured at 665 nm wavelength.

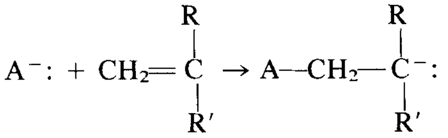
RESULTS AND DISCUSSION

Synthesis of Poly(methacrylonitrile)

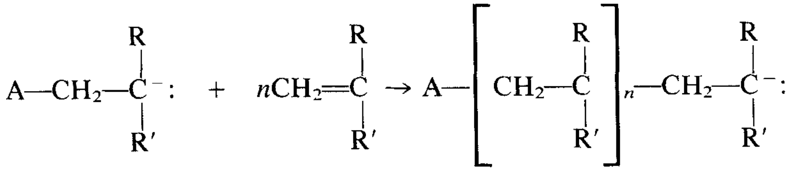
A different approach for preparing the amidoxime adsorbents used for the recovery of uranium from seawater is to use poly(methacrylonitrile) as the base polymer. It is known that acrylonitrile is more easily attacked by nucleophiles at both the nitrile group and the double bond, and is a more reactive dienophile (30). With this in mind, it was considered that unlike poly(acrylonitrile)-based adsorbents, poly(methacrylonitrile)-based ones are more stable, with little site deterioration during alkaline treatment.

Ionic polymerization of methacrylonitrile has been successfully used with anionic initiators in inert solvents, as reported in the literature (30). The highly electronegative cyano group of methacrylonitrile makes nucleophilic attack easy. It has been reported by Beaman (31) that methacrylonitrile polymerizes rapidly even at temperatures as low as −75°C because this monomer contains no α-hydrogen atom which could cause chain termination and subsequent branching from the newly formed active center.

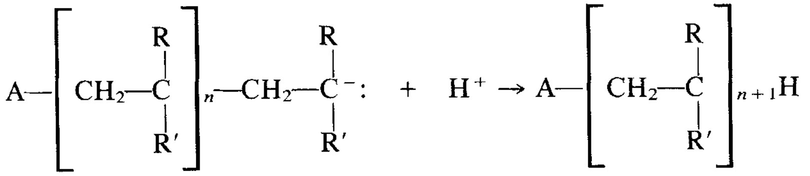
The mechanism of base-induced polymerization is given as follows (31):



$$A^{-}: + CH_2{=}\underset{R'}{\overset{R}{\underset{|}{\overset{|}{C}}}} \rightarrow A{-}CH_2{-}\underset{R'}{\overset{R}{\underset{|}{\overset{|}{C}}}}{}^{-}: \tag{1}$$



$$A{-}CH_2{-}\underset{R'}{\overset{R}{\underset{|}{\overset{|}{C}}}}{}^{-}: + nCH_2{=}\underset{R'}{\overset{R}{\underset{|}{\overset{|}{C}}}} \rightarrow A{-}\left[CH_2{-}\underset{R'}{\overset{R}{\underset{|}{\overset{|}{C}}}}\right]_n{-}CH_2{-}\underset{R'}{\overset{R}{\underset{|}{\overset{|}{C}}}}{}^{-}: \tag{2}$$



$$A{-}\left[CH_2{-}\underset{R'}{\overset{R}{\underset{|}{\overset{|}{C}}}}\right]_n{-}CH_2{-}\underset{R'}{\overset{R}{\underset{|}{\overset{|}{C}}}}{}^{-}: + H^{+} \rightarrow A{-}\left[CH_2{-}\underset{R'}{\overset{R}{\underset{|}{\overset{|}{C}}}}\right]_{n+1}H \tag{3}$$

where A^{-}: is the initiating negative group, R is an electron-withdrawing group, and R′ is H or some other substituent. Termination reaction (3) may occur in various manners, such as elimination of A^{-}:.

Overberger et al. studied the mechanism of initiation in the lithium–ammonia–methacrylonitrile system (32). The use of quaternary ammonium hydroxides as catalysts for the polymerization of methacrylonitrile was investigated by Zilkha et al. (33). The anionic homogeneous polymerization of methacrylonitrile by alcoholic solutions of alkali metal alkoxides in dimethylformamide was studied by Feit et al. (34). The same authors investigated the mechanism of anionic heterogeneous polymerization of methacrylonitrile by butyllithium (26). They concluded that the absence of a chain transfer reaction in the case of methacrylonitrile, due to the α-methyl group in this monomer, will lead to a high-molecular-weight polymer. With this in mind, we have used butyllithium for the anionic polymerization of methacrylonitrile.

Following the experimental work by Feit et al. (26), the conditions employed for the anionic polymerization of methacrylonitrile by butyllithium as initiator were chosen to allow a maximum degree of stereoregularity and a high molecular weight. A number of polymethacrylonitriles have been synthesized by employing different addition orders of reagents at various stirring speeds. The results are summarized in Table 1. The polymers for Runs 1–5 were synthesized by adding the monomer solution to the initiator solution and swirling the polymerization mixture at various speeds. The polymerization temperature was kept at 0 ± 2°C. The highest conversion occurred with the highest swirling speed. However, this was not sufficient to enhance the intrinsic viscosity and the molecular weight. The polymerization for Run 6 was performed by adding the initiator solution to the monomer and keeping the temperature at −70°C. As shown in Table 1, conversion of the Run 6 polymerization was 78%. However, some decreases in intrinsic viscosity and molecular weight were obtained. It is noted in the literature that the molecular weight remains practically constant when the polymerization temperature is varied from −30 to +10°C. The results show that polymers with higher molecular weights are obtained when the monomer is added to the initiator at 0 ± 2°C.

The stereospecific polymerization of methacrylonitrile with diethylmagnesium was studied in detail by Joh et al. (28). It was noted that the intrinsic viscosity, stereoregularity, and molecular weight of the polymer were higher when dioxane was used as a solvent during polymerization. Although conversion was low, the polymer obtained in dioxane had a higher stereoregularity and molecular weight than those obtained in hydrocarbon solvents (28).

For comparison, poly(methacrylonitrile) was synthesized using diethylmagnesium as initiator according to a literature procedure (28). Polymerization for Runs 1,2 in Table 2 was performed with various stirring speeds. The molecular weights were very similar in both cases. The conversions were in the 50–60% range. According to the literature, conversion was 37% when dioxane was used as the solvent. However, the molecular weights were very similar to the value given in the literature.

Preparation of Fiber Adsorbent

The fiber material was produced from the poly(methacrylonitrile) synthesized with butyllithium as initiator at 0 ± 2°C. The functionalization was performed using 3% NH_2OH in MeOH at 80°C. The conversion of the nitrile to the amidoxime functionality was indicated by the disappearance of CN absorption at 2235 cm^{-1} in the IR spectra. The main absorptions at 3200–3400, 1625, and 925 cm^{-1}, which are due to —OH, $>C{=}N$—, and $=N{-}O$— of amidoxime groups, respectively, were also observed in the IR spectra of fiber adsorbents.

Adsorption Characteristics of the Fiber Adsorbent

Figure 1 shows the adsorption profile obtained by 1-day adsorption from 5 L of natural seawater by using 50 mg of the fiber adsorbent in a batch system at 25°C as a function of alkaline treatment time. The fiber adsorbents were treated with 1 M NaOH for 6, 12, 24, 48, and 96 hours, respectively. As shown in Fig. 1, the adsorption rate of uranium was increased by the alkaline treatment. After 48 hours of alkaline treatment, the best adsorption rate obtained was 176 μg of U/g of adsorbent/day. As explained in the literature (9, 11, 35, 36), alkaline treatment enhances the potential for much faster adsorption characteristics. It is believed that both the physical structure in the swollen state and the chemical structure due to alkaline treatment contributed to the high performance achieved. For comparison, adsorption data were obtained by using spherical amidoxime resins derived from the copolymer beads of methacrylonitrile (commercial sample, MAN/6DVB/20 ED/300P). As shown in Table 3, the adsorption rates were lower than those obtained by fiber adsorbent. This implies that the crosslinked MAN/6DVB/20 ED/300P-based spherical amidoxime resins swell less than the fiber adsorbents due to their relatively high intrinsic hydrophobicity. The adsorption rate of spherical amidoxime resins increased in a manner similar to alkaline treatment, although the adsorption values fluctuated. These fluctuations may be due to a discrepancy in the kinetic behavior of spherical amidoxime resins during the adsorption period.

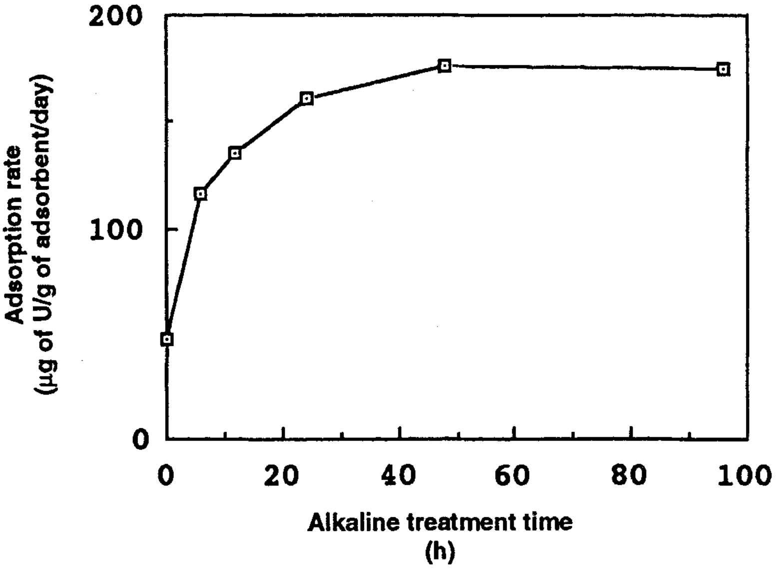


FIG. 1 Effect of alkaline treatment on the adsorption rate of uranium from seawater by fiber adsorbent.

TABLE 3
Effect of Alkaline Treatment on the Uptake of Uranium from Seawater by MAN/6DVB/20 ED/300P-Based Chelating Resin

Alkaline treatment time (h)[a]	μg U[b]	Adsorption rate (μg of U/g of adsorbent/day)
0	2.15	43.0
12	4.91	98.2
24	4.53	90.6
48	4.15	83.0
96	5.10	102.0

[a] 1 M NaOH.
[b] Values are based on 50 mg of adsorbent (before alkaline treament).

CONCLUSION

Although an adsorption rate as high as 176 μg of U/g of adsorbent/day was achieved, this value is lower than an economically feasible value such as 500 μg of U/g of adsorbent/day. However, the results are encouraging enough to justify further study in the preparation of poly(methacylonitrile)-based fiber adsorbents for the recovery of uranium from seawater. The results suggest that in optimizing the adsorption characteristics of poly(methacrylonitrile)-based fiber adsorbents, a basic requirement exist in terms of the improvement of physical and chemical properties, and that these factors should be carefully balanced against capacity requirements.

ACKNOWLEDGMENTS

This research was performed in Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Japan. The author thanks Prof. Y. Kobuke for his help during this study.

REFERENCES

1. H. Egawa and H. Harada, *Nippon Kagaku Kaishi*, p. 958 (1979).
2. H. Egawa, H. Harada, and T. Nonaka, *Ibid.*, p. 1767 (1980).
3. H. Egawa, H. Harada, and T. Shuto, *Ibid.*, p. 1773 (1980).
4. H. J. Schenk, L. Astheimer, E. G. Witte, and K. Schwochau, *Sep. Sci. Technol.*, *17*, 1293 (1982).
5. L. Astheimer, H. J. Schenk, E. G. Witte, and K. Schwochau, *Ibid.*, *18*, 307 (1983).
6. H. Egawa, M. Nakayama, T. Nonaka, and E. Sugihara, *J. Appl. Polym. Sci.*, *33*, 1993 (1987).

7. H. Egawa, M. Nakayama, T. Nonaka, H. Yamamoto, and K. Uemura, *Ibid.*, *34*, 1557 (1987).
8. M. Nakayama, K. Uemura, T. Nonaka, and H. Egawa, *Ibid.*, *36*, 1617 (1988).
9. H. Egawa, N. Kabay, S. Saigo, T. Nonaka, and T. Shuto, *Bull. Soc. Sea Water Sci. Jpn.*, *45*, 324 (1991).
10. H. Egawa, T. Nonaka, and S. Abe, *J. Appl. Polym. Sci.*, *45*, 837 (1992).
11. H. Egawa, N. Kabay, T. Shuto, and A. Jyo, *Ibid.*, *46*, 129 (1992).
12. H. Egawa, N. Kabay, T. Shuto, and A. Jyo, *Ind. Eng. Chem. Res.*, *32*, 540 (1993).
13. H. Egawa, N. Kabay, T. Shuto, and A. Jyo, *Ibid.*, *32*, 709 (1993).
14. N. Kabay and H. Egawa, *Sep. Sci. Technol.*, *28*, 1985 (1993).
15. S. Katoh, K. Sugasaka, K. Sakane, N. Takai, H. Takahashi, Y. Umezawa, and K. Itagaki, *Nippon Kagaku Kaishi*, p. 1455 (1982).
16. H. Omichi, A. Katakai, T. Sugo, and J. Okamoto, *Sep. Sci. Technol.*, *20*, 163 (1985).
17. H. Omichi, A. Katakai, T. Sugo, and J. Okamoto, *Ibid.*, *21*, 563 (1986).
18. H. Omichi, A. Katakai, T. Sugo, J. Okamoto, S. Katoh, K. Sakane, K. Sugasaka, and T. Itagaki, *Ibid.*, *22*, 1313 (1987).
19. N. Kabay, A. Katakai, T. Sugo, and H. Egawa, *J. Appl. Polym. Sci.*, *49*, 599 (1993).
20. K. Saito, K. Uezu, T. Hori, S. Furusaki, T. Sugo, and J. Okamoto, *AIChE J.*, *34*, 411 (1988).
21. K. Uezu, K. Saito, T. Hori, S. Furusaki, T. Sugo, and J. Okamoto, *Nippon Genshiryoku Gakkaishi*, *30*, 359 (1988).
22. K. Saito, T. Yamaguchi, K. Uezu, S. Furusaki, T. Sugo, and J. Okamoto, *J. Appl. Polym. Sci.*, *39*, 2153 (1990).
23. T. Takeda, K. Saito, K. Uezu, S. Furusaki, T. Sugo, and J. Okamoto, *Ind. Eng. Chem. Res.*, *30*, 185 (1991).
24. Y. Kobuke, I. Tabushi, T. Aoki, T. Kamishi, and I. Hagiwara, *Ibid.*, *27*, 1461 (1988).
25. Y. Kobuke, T. Aoki, H. Tanaka, and I. Tabushi, *Ibid.*, *29*, 1662 (1990).
26. B. Feit, E. Heller, and A. Zilkha, *J. Polym. Sci.*, *Part A-1*, *4*, 1151 (1966).
27. R. C. Houston and A. H. Agett, *J. Org. Chem.*, *6*, 123 (1941).
28. Y. Joh, Y. Kotake, T. Yoshihara, F. Ide, and K. Nakatsuka, *J. Polym. Sci.*, *Part A-1*, *5*, 605 (1967).
29. Y. Joh, Y. Kotake, T. Yoshimura, F. Ide, and K. Nakatsuka, *Ibid.*, *5*, 53 (1967).
30. *Encyclopedia of Polymer Science and Technology*, *15*, 319 (1971).
31. R. G. Beaman, *J. Am. Chem. Soc.*, *70*, 3115 (1948).
32. C. G. Overberger, E. M. Pearce, and N. Mayes, *J. Polym. Sci.*, *34*, 109 (1959).
33. A. Zilkha, B. Feit, and M. Frankel, *Ibid.*, *49*, 231 (1961).
34. B. Feit, J. Wallach, and A. Zilkha, *Ibid.*, *Part A-1*, *2*, 4743 (1964).
35. Y. Kobuke, H. Tanaka, and H. Ogoshi, *Polym. J.*, *22*, 179 (1990).
36. H. Egawa, N. Kabay, T. Nonaka, and T. Shuto, *Bull. Soc. Sea Water Sci. Jpn.*, *45*, 87 (1991).

Received by editor June 10, 1993