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

Synthesis, Characterization, and Polymerization of New Hydroxyethyl Methacrylate Containing Cyclobutane Ring

Mehmet Coşkun[a]; Kadir Demirelli[a]; Misir A. Ahmetzade[a]
[a] Department of Chemistry, Faculty of Science and Arts University of Firat Elazig, Turkey

To cite this Article Coşkun, Mehmet , Demirelli, Kadir and Ahmetzade, Misir A.(1997) 'Synthesis, Characterization, and Polymerization of New Hydroxyethyl Methacrylate Containing Cyclobutane Ring', Journal of Macromolecular Science, Part A, 34: 3, 429 — 438
To link to this Article: DOI: 10.1080/10601329708014970
URL: http://dx.doi.org/10.1080/10601329708014970

J.M.S.—PURE APPL. CHEM., A34(3), pp. 429–438 (1997)

SYNTHESIS, CHARACTERIZATION, AND POLYMERIZATION OF NEW HYDROXYETHYL METHACRYLATE CONTAINING CYCLOBUTANE RING

MEHMET COŞKUN, KADIR DEMIRELLI, and
MISIR A. AHMETZADE

Department of Chemistry
Faculty of Science and Arts
University of Firat
Elaziğ, Turkey

ABSTRACT

2-(3-Chloro-3-methylcyclobutyl)-2-hydroxyethyl methacrylate was prepared from the reaction of methacrylic acid with the oxirane compound obtained from the chlorhydrin formed in the cyclization of 1-chloro-2, 3-epoxy-5-methyl-5-hexene. This is a new methacrylate ester. Polymerization of this monomer was carried out in 1,4-dioxane solution at 60°C using benzoyl peroxide as the initiator. Activation energy for the polymerization was found to be 7.33 kcal/mol from experiments done at three different temperature. Weight-average molecular weight of the polymer obtained at 60°C was determined to be 67,572 by the GPC technique. The DSC curve showed a glass transition at 83°C. Infrared, proton, and carbon-13 nuclear magnetic resonance techniques were used in characterization of the monomer and its homopolymer. The TGA curve of the polymer was investigated by comparing it with that of poly(2-hydroxyethyl methacrylate).

INTRODUCTION

2-Hydroxyethyl methacrylate (HEMA) is a monomer having numerous applications. Poly(2-hydroxyethyl methacrylate), poly(HEMA), has found a wide range of biomedical applications including hydrogel, hemodialysis, membranes, contact lenses, and a variety of other related and potential uses [1–3]. The copolymers of this monomer with some other monomers are also used in applications as mentioned above [4–6]. A review has been published on 2-hydroxyethyl methacrylate monomer and its homo and copolymers in recent years [7]. Chemical modifications on the hydroxyl group of HEMA, and poly(HEMA) and its copolymers are a synthetic route for the preparation of new functional methacrylate esters [8–12]. Moreover, polymers with the cyclobutane ring in their side or main chains, which show a positive-type photoresist property, were prepared from α-truxillate [13], β- or δ-truxinates [14], or α or β-truxillate [15]. 1,3-Disubstituted cyclobutanes also show some biological activities [16–18].

This article reports the synthesis of a new hydroxyethyl methacrylate monomer which contains the cyclobutane ring, and of its polymer, and their characterization by infrared, ^{1}H and ^{13}C-NMR, and thermal analysis techniques. Since the polymer being discussed has the 2-hydroxyethyl group in its side chain, its thermal properties are compared with those of poly(HEMA).

EXPERIMENTAL

Materials

Diethyl ether, toluene, 1,4-dioxane, *n*-hexane (Aldrich), and anhydrous $AlCl_3$ (Riedel) were used as received. Dichloromethane was dried over $MgSO_4$ before use. 1-Chloro-2,3-epoxy-5-methyl-5-hexene (**1**) was prepared from 2,3-dichlor propanal and 2-methyl propen via the method given by Sadikzade et al. [19] of the Institute of Polymeric Materials, Academy of Sciences of Azerbaidzhan, to us.

Preparation of 1-Chloro-1-methyl-3-(2-chloro-1-hydroxyethyl) cyclobutane (2)

A 250-mL four-necked flask was fitted with a condenser and a stirrer, an addition funnel, and a thermometer. Dichloromethane (150 mL) and 15 g (112 mmol) anhydrous $AlCl_3$ were introduced into the flask, and dried HCl gas was passed through the mixture with stirring at about -5°C for 20 minutes. Then 15 g (102 mmol) of **1** was added dropwise to the mixture and the temperature was increased above $+5$°C. The reaction content was stirred at room temperature for a further 40 minutes. The mixture was poured into crushed ice with HCl. The organic layer was washed several times with water and dried over $MgSO_4$. After removing dichloromethane, **2** was distilled under vacuum. Yield: 63%. Physical data: bp 126°C (at 10 mmHg), $d_4^{20} = 1.1993$, $n_4^{20} = 1.4920$.

FT-IR: 3542 cm^{-1} (free OH), 3420 cm^{-1} (O—H), 3000–2850 (C—H), 695 cm^{-1} (C—Cl, in $-CH_2Cl$), 770 cm^{-1} (C—Cl on cyclobutane).

^{1}H-NMR ($CDCl_3$ δ ppm): 3.8 (dt, 1H, $J = 3.5$, Hz, $J = 7.0$ Hz, —CHO—), 3.5 (m, 2H, $-CH_2Cl$), 2.2–2.9 (m, 5H cyclobutane ring protons), 1.75 (s, 3H, $-CH_3$).

^{13}C-NMR ($CDCl_3$, δ ppm): 74.4 (C—O), 67.3 (C—Cl, quaterner), 62.3 (C—Cl, methylene), 40.9–42.4 (methylene in cylobutane), 32.2 (—CH— in cyclobutane), 30.7; 31.6 ($-CH_3$).

Synthesis of 1-Chloro-1-methyl-3-epoxyethyl Cyclobutane (3)

3 was obtained from the reaction of 2 with KOH via a method reported in the literature [20]. Yield: 70%, d_4^{20} = 1.1425, n_4^{20} = 1.4774, bp 83°C (at 10 mmHg).

FT-IR: 770 cm^{-1} (C—Cl on cyclobutane), 776 cm^{-1} (epoxide, C—H bending vibration), 850 cm^{-1} (epoxide, asymmetric ring stretching), 1250 cm^{-1} (epoxide, symmetric ring stretching), 3043 cm^{-1} (epoxide, C—H stretching).

^{1}H-NMR (δ ppm): 1.63; 1.70 ($-CH_3$), 2.2–2.7 (cyclobutane ring protons), 2.7; 3.1 (epoxide ring protons).

^{13}C-NMR (δ ppm): 31.4; 31.7 ($-CH_3$), 32.6; 34.0 (—CH— in cyclobutane), 41.0–44.3 (methylene carbons in cyclobutane), 47.2; 47.4 ($-CH_2-$ in epoxide ring), 54.9; 55.4 (—CH— in epoxide ring), 64.3 (C—Cl, quaterner carbon).

Synthesis of 2-(3-Chloro-3-methylcyclobutyl)-2-hydroxyethyl methacrylate (CBHEMA) (monomer) (4)

The monomer was prepared via the method given for the epoxy-carboxy reactions [21, 22]. For this purpose, 7.2 g (49 mmol) of 3 and 8.3 g (97 mmol) of methacrylic acid were stirred in 50 mL toluene at 85–90°C in a reflux condenser for 28 hours in the presence of 1.6 mL pyridine and 100 ppm hydroquinone as catalyst and inhibitor, respectively. Then the solution was cooled to room temperature and neutralized with a 5% KOH solution. The organic layer was washed with water several times, and the water layer was washed with diethyl ether a few times. The organic layers were collected and dried over anhydrous $MgSO_4$ overnight. Toluene was evaporated, and the residue was distilled at 130°C at 5 mmHg to give colorless liquid 4. Yield: 56%, d_4^{20} = 1.0940, n_4^{20} = 1.4797.

Characteristic FT-IR bands: 770 cm^{-1}, 920 cm^{-1}, 1171 cm^{-1}, 1295 cm^{-1}, 1640 cm^{-1}, 1718 cm^{-1}, 3040 cm^{-1}, and 3453 cm^{-1}.

^{1}H-NMR (δ ppm): 6.1 and 5.6 (CH_2=), 4.2–3.8 ($OCH_2CH(OH)$), 2.2–2.7 (cyclobutane ring protons), 1.92 (=C—CH_3), 1.72 ($-CH_3$ on cyclobutane ring).

^{13}C-NMR (δ ppm): 169.5 (C=O), 137.9 (CH_2=C—), 128.3; 128.2 (CH_2=C—), 79.4, 75.0, 74.0 (OCH_2—), 69.4, 69.0 (CH—OH), 65.0, 64.5, 64.1 (C—Cl), 44.3, 44.2, 44.1, 43.0 (CH_2 in cyclobutane), 34.3, 33.2 (CH in cyclobutane), 32.7, 32.6, 31.0 ($-CH_3$ on cyclobutane), 20.3 (=C—CH_3).

Polymerization of 4

4 was freed from inhibitor by washing with dilute KOH solution followed by distilled water, and then drying over anhydrous $MgSO_4$. Appropriate amounts of 4 and 1,4-dioxane and benzoyl peroxide (0.2% of the weight of the monomer) were placed in a reaction tube and purged with Ar for 10 minutes. The sealed tube was kept at 60°C for 16 hours. The reaction contents were poured dropwise into a large excess of *n*-hexane. Poly[2-(3-chloro-3-methylcyclobutyl)-2-hydroxyethyl meth-

acrylate] [poly(CBHEMA)] was purified by reprecipitation with *n*-hexane from 1,4-dioxane solution and finally dried under vacuum (conversion 75%).

Characterization Techniques

Infrared (IR) analysis was performed using a Mattson 1000 FT-IR spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded at 25°C with $CDCl_3$ as solvent and using a Varian-Gemini 200 MHz spectrometer. Thermal data were obtained using a Shimadzu DSC-50 instrument and a TG-50 thermobalance.

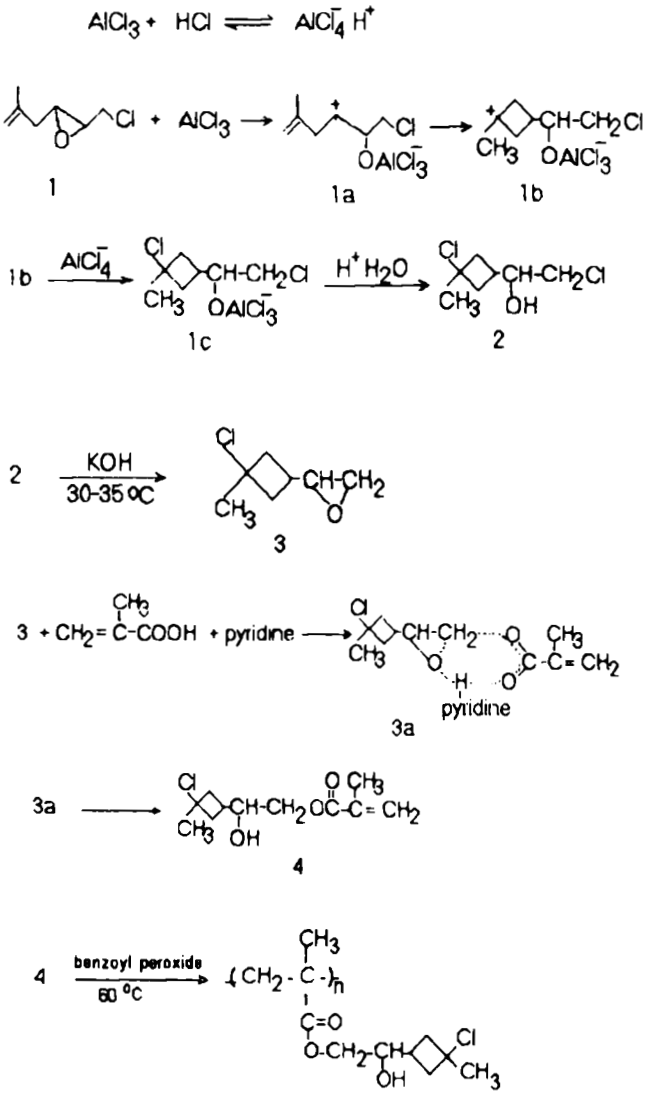
The solubility parameter of the polymer was estimated from the solubility test using 1,4-dioxane as solvent and using *n*-hexane and ethyl alcohol–*n*-hexane as nonsolvents. The density of the polymer was determined in a mixture of ethyl alcohol and formic acid using the floatation method. The limiting viscosity number was determined in 1,4-dioxane at 25°C. The average molecular weight of the polymer was measured by the GPC technique using polystyrene as a standard.

RESULTS AND DISCUSSION

When aromatic alkylation of benzene or toluene with 1-chlor-2,3-epoxy-5-methyl-5-hexene (**1**) was carried out in presence of anhydrous $AlCl_3$ by Ahmedov et al. [23, 24], **2** was obtained as a side product of the reaction. The mechanism of formation of this side product was based on the synthesis of **2**.

As shown in Scheme 1, we propose a new route for 2-hydroxyethyl methacrylate (HEMA) containing cyclobutane ring and chlorin. The homoallylic cation (**1a**) is formed from the oxirane (**1**) and aluminum chloride. It then undergoes cyclization to the methylcyclobutyl cation (**1b**) [23], and **1b** takes Cl- from $AlCl_4^-$. Hydrolysis of **1c** gives **2**. When aromatics such as benzene or toluene are present in the reaction media instead of $AlCl_4^-$ or HCl (excess), **1b** is mainly used in aromatic alkylation [23]. The small amount of $AlCl_4^-$ or HCl which is formed from $AlCl_3$ and a little moisture in the reaction media help to produce **2** as a side product [23, 24]. The reaction of methacrylic acid with the oxirane (**3**) is a carboxy-epoxy reaction. Mechanisms of this kind of reaction have been given for some epoxy compounds and some carboxylic acids in the presence of a base as a catalyst [21, 22]. According to the mechanism adapted from the literature, the epoxide, methacrylic acid, and pyridine give monomer **4** over a cyclic complex (**3a**). The yields of the reactions in Scheme 1 are of medium quantity (56–70%).

During polymerization, the bands at 920, 1640, and 3040 cm^{-1} which concern double bonds, disappeared. The C=O stretching shifted from 1718 to 1735 cm^{-1} by conjugation in the FT-IR spectrum of the monomer (Fig. 1). Poly(CBHEMA) also shows bands at 3452 cm^{-1} (broad) for —OH, at 1273 cm^{-1} for asymmetric stretching of C—O—C, and at 770 cm^{-1} for C—Cl. The ^{1}H- and ^{13}C-NMR spectra of the polymer are shown in Figs. 2 and 3, respectively. The signals at 3.2–4.2 ppm are assigned to $OCH_2CH(OH)$—. The signals of cyclobutane ring protons are at 2.0–2.8 ppm. The signals of methylene protons in the polymer backbone and of methyl protons on the cyclobutane ring are at 1.5–1.9 ppm. The signals at 0.8–1.2 ppm are due to methyl protons on the polymer backbone.



SCHEME 1. Synthesis of the monomer.

^{13}C-NMR assignments of the polymer, δ ppm = 179.7-179.3 (C=O), 78.7-74.0 (OCH_2), 70.0-69.0 (CHOH), 64.7-64.1 (C—Cl, quaterner), 54.0, 56.0, 48.2-47.0 (CH_2 in polymer backbone), 48.2, 48.0, 47.6, 47.5, 47.2, 47.0 (quaterner carbon in polymer backbone), 45.3-43.2 (CH_2 in cyclobutane ring), 34.4; 33.2 (CH—, in cyclobutane ring), 32.5-32.0 (CH_3 on cyclobutane), and 20.3-22.2 (CH_3 on polymer backbone).

Plots of percent conversion versus time are given in Fig. 4 for the polymerization of CBHEMA at 60, 70, and 80°C in the presence of benzoyl peroxide in sealed tubes. The percent conversion was calculated from the calibration curve based on the band at 1640 cm^{-1} in the FT-IR spectrum of the monomer. The activation

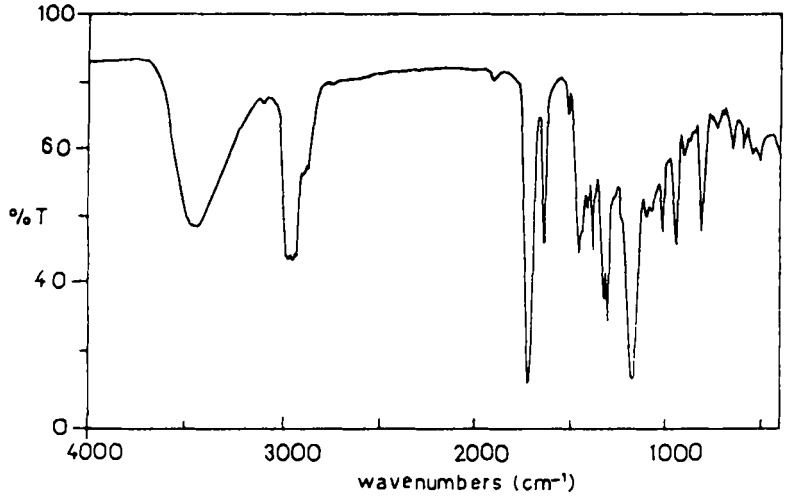


FIG. 1. FT-IR spectrum of the CBHEMA monomer.

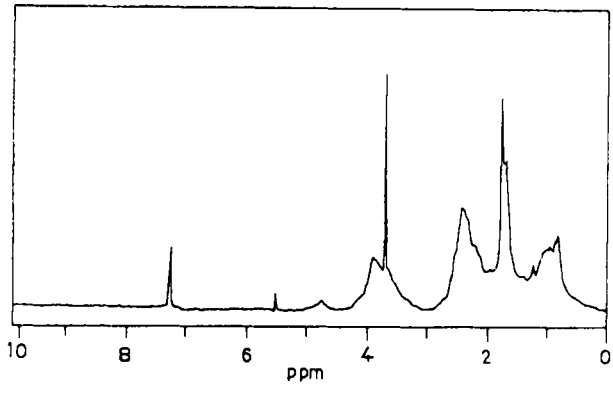


FIG. 2. ^{1}H-NMR spectrum of poly(CBHEMA).

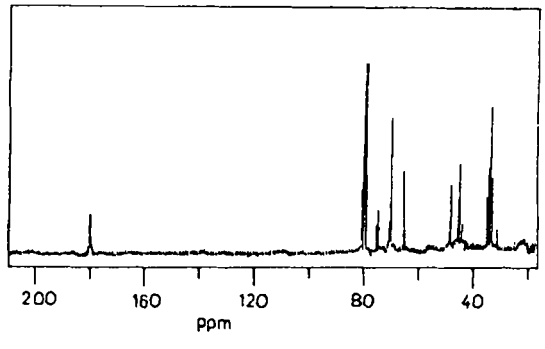


FIG. 3. ^{13}C-NMR spectrum of poly(CBHEMA).

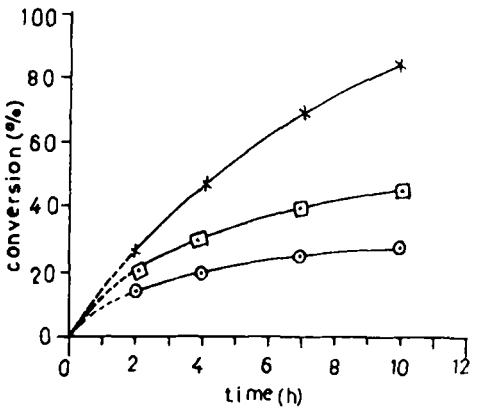


FIG. 4. Plots of % conversion vs time for polymerization of CBHEMA at 60°C (⊙), 70°C (⊡), and 80°C (×). Solvent, 1,4-dioxane; [CBHEMA], 0.8 mol/L.

energy of the polymerization was estimated at 7.33 kcal/mol using data given in Fig. 4. The glass transition temperature, chlorine content, solubility parameter, and density of poly(CBHEMA) are shown in Table 1. The glass transition temperature (from the DSC thermogram) reported for the polymer is the midpoint of the glass transition region. The glass transition temperature for poly(HEMA) obtained from radical polymerization at 60°C was reported as 100°C [25]. Poly(CBHEMA) has a glass transition temperature (T_g = 83°C) lower than that of poly(HEMA). The cyclobutyl group in the side chain of CBHEMA units probably decreases intermolecular hydrogen bondings, and thus poly(CBHEMA) has more flexible molecules than does poly(HEMA). This means that poly(CBHEMA) has a higher free volume and a lower glass transition temperature than does poly(HEMA).

The limiting viscosity number of the polymer was measured as 1.08 dL/g in 1,4-dioxane at 25°C. The weight-average molecular weight of the polymer was determined as 67,572 (polydispersity = 4.8) by GPC using polystyrene and tetrahydrofurane (THF) as the standard and solvent, respectively. The GPC profile showed a unimodal elution curve (Fig. 5). This indicates that any reaction apart from the normal addition reaction of the double bond was not carried out during polymerization. The polydispersity index showed that the molecular weight distribution was fairly wide.

The TGA curve of poly(CBHEMA) is shown in Fig. 6 as compared with that of poly(HEMA). The degradation of poly(CBHEMA) occurred in three stages. The first stage, in which HCl elimination mainly occurs, was observed at 155–240°C with 18% weight loss. The second stage decomposition commences at 240–495°C

TABLE 1. Some Properties of Poly(CBHEMA)

	T_g, °C	Cl%, by weight	δ, $cal^{1/2} \cdot cm^{-3/2}$	d, g/cm^3
Poly(CBHEMA)	83	16.2 (calcd. 15.3)	9.8	1.150

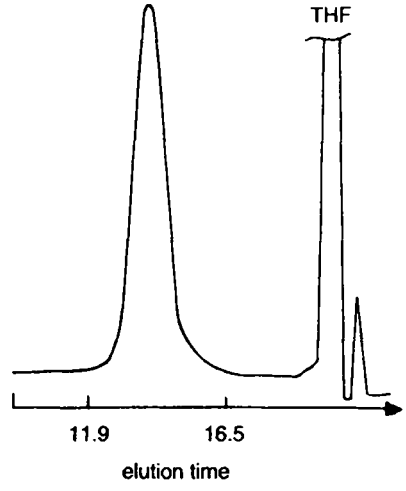


FIG. 5. GPC curve of poly(CBHEMA).

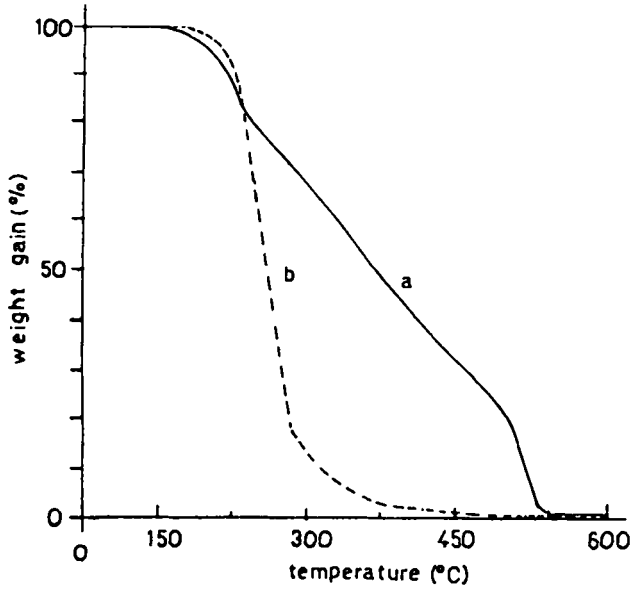


FIG. 6. TGA curves of (a) poly(CBHEMA) and (b) poly(HEMA).

with 59% weight loss. The third stage happens at 495–545°C with 22% weight loss. About 1% residue was left at 545°C. The residue at 240°C was insoluble in many solvents. This shows that crosslinking is also an important reaction during HCl elimination. Decomposition of poly(HEMA) prepared under the same conditions with poly(CBHEMA) occurred in a single stage (Fig. 6, Curve b). Monomer evolution, which is evidence of depolymerization, was superior to crosslinking in the degradation of poly(HEMA) [26].

ACKNOWLEDGMENT

The authors thank the Firat University Research Fund for financial support to this project (Project FÜNAF-193).

REFERENCES

[1] H. Mori, O. Wakisaka, A. Hirao, and S. Nakahama, *Macromol. Chem. Phys., 195*, 3213 (1994).
[2] O. Wichterle and D. Lim, *Nature, 185*, 117 (1960).
[3] J. D. Andrade, *Hydrogels for Medical and Related Applications* (ACS Symp. Ser. *31*), American Chemical Society, Washington, D.C., 1976.
[4] O. Wichterle, *Encycl. Polym. Sci. Technol., 15*, 273 (1972).
[5] M. Miyata, S. Senda, and K. Takemoto, *Macromol. Chem., 185*, 647 (1984).
[6] M. F. Refojo, *Encycl. Chem. Technol., 6*, (1976).
[7] J. P. Montheard, M. Chatzopoulos, and D. Chappard, *J. Macromol. Sci. – Rev. Macromol. Chem. Phys., C32*(1), 1 (1992).
[8] K. Fisher and C. D. Eisenbach, *Macromol. Chem., Rapid Commun., 9*, 503 (1988).
[9] W. A. Feld, D. W. Bombick, and L. L. Friar, *J. Polym. Sci., Polym. Chem. Ed., 20*, 263 (1982).
[10] K. Ishihare, N. Muramoto, T. Lida, and I. Shineshara, *Polym. Bull., 7*, 457 (1982).
[11] S. Sevcik, J. Stamberg, and P. Schmidt, *J. Polym. Sci., Part C, 16*, 821 (1967).
[12] T. Nishikubo, T. Isawa, I. Imagawa, and K. Kobayashi, *J. Polym. Sci., Polym. Chem. Ed., 19*, 2795 (1981).
[13] (a) S. Caccamese, P. Maravigna, G. Montaudo, A. Recca, and E. Scamporrino, *Ibid., 17*, 1463 (1979). (b) J. A. Moore and A. Dasheff, *Chem. Mater., 1*, 163 (1988).
[14] (a) S. Caccamese, P. Maraviigna, G. Montauda, A. Recca, and E. Scamporrino, *J. Polym. Chem., Polym. Chem. Ed., 16*, 3125 (1978). (b) P. Maravigna, G. Montaudo, A. Recca, E. Scamporrino, G. G. Aloibi, and U. Mazzucato, *J. Polym. Sci., Polym. Lett. Ed., 18*, 5 (1980).
[15] (a) T. Iizawa, T. Miyaji, and T. Nishikubo, *J. Polym. Sci., Polym. Chem. Ed., 26*, 2941 (1988). (b) T. Nishikubo, T. Iizawa, Y. Shiozaki, and T. Koito, *Polym. Sci., Part A: Polym. Chem., 30*, 449 (1992).
[16] E. Roger, C. J. Pierre, V. Pualette, G. Gerard, J. P. Chapat, and G. Robert, *Eur. J. Med. Chem. – Chim. Ther., 12*(6), 501 (1977).
[17] G. Gerard, *Ibid., 14*(6), 493 (1979).
[18] M. A. Ahmedov, I. M. Ahmedov, R. A. Akhundov, R. R. Kostikov, D. A. Piriyeva, and I. K. Sardarov, USSR Patent 1,777,322 A1 (1992).
[19] S. I. Sadikzade, M. A. Ahmedov, and G. H. Memedov, *J. Org. Chem., USSR, 9*(1), 66 (1973).
[20] R. R. Ahmedov, K. Kyazimov, I. I. Viladimirova, and O. G. Kasimova, *Azer. Khim. Zh., 6*, 85 (1980).
[21] P. J. Madec and E. Marechal, *Macromol. Chem., 184*, 323 (1983).

[22] B. Boutevin, Y. Pietrasanta, and J. P. Parisi, *Ibid., 188*, 1621 (1987).
[23] M. A. Ahmedov, Z. G. Mustafayeva, I. M. Ahmedov, and R. R. Kostikov, *Zh. Org. Khim., 27*(7), 1434 (1991).
[24] M. A. Ahmedov, M. Coşkun, E. Özdemir, and I. M. Ahmedov, *Kimya 94, X. Ulusal Kimya Kongresi, Bursa, 19–21 Eylül 1994*, p. 318.
[25] G. A. Russell, P. A. Hiltner, D. E. Gregonic, A. C. Visser, and J. D. Andrade, *J. Polym. Sci., Polym. Phys. Ed., 18*, 1271 (1980).
[26] J. Razga and J. Petranek, *J. Eur. Polym. J., 11*, 805 (1975).

Received February 25, 1996
Revision received July 9, 1996