Polymer Bulletin 36, 157–164 (1996)

Polymer Bulletin

Synthesis and characterization of poly(2-methylaziridine)

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Received: 26 July 1995/Revised version: 18 September 1995/Accepted: 26 September 1995

SUMMARY

The cationic polymerization of 2-methylaziridine using boron trifluoride etherate as initiator at different monomer/initiator ratios, temperatures, solvents, and times of polymerization was carried out. The effect of these variables on the polymerization yield and viscosity of the polymers was studied. All the polymers were characterized by elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy, thermogravimetric analyses and differential scanning calorimetry.

INTRODUCTION

It is well known that poly(ethyleneimine) derivates produced by the ring-opening cationic polymerization of N- or C- substituted ethyleneimine have highly branched structures (1-4). Some N-alkylethyleneimines are converted into the corresponding 1,4-dialkylpiperazines with yields as high as 95% when treated with hydrohalic acids (5-7). Goethals et al. (8-10) have studied the polymerization of N-tert-butylaziridine which proceeds under certain conditions as "temporally living". Velichkova et al. (11) have synthesized poly(N-tert-butylaziridine)s with different functional end-groups. On the other hand, N-(hydroxyethyl)ethyleneimine was homopolymerized by BF_3Et_2O (12) and their chelation properties were studied using Liquid-Phase Polymer-Based Retention (LPR) (13).

Other syntheses of ethyleneimine and some derivatives have also been reported (14-16). These poly(alkyleneimine)s can be easily modified by polymer analogous reactions showing metal ion complexation properties (17-18). This paper refers to the cationic polymerization of 2-methylaziridine (MAz) using the BF_3Et_2O as initiator under different experimental conditions. The goal was to investigate the influence of polymerization variables such as concentration of initiator, polarity of solvent, time, and temperature on the molecular mass and conversion, and the thermal behaviour.

EXPERIMENTAL PART

Materials: Solvents, dichloromethane, N,N-dimethylformamide, acetonitrile, methanol and diethylether were purified according to the literature (19). 2-Methylaziridine (MAz) monomer (Aldrich) was purified by distillation under N_2. Boron trifluoride etherate (Merck) was distilled previously.

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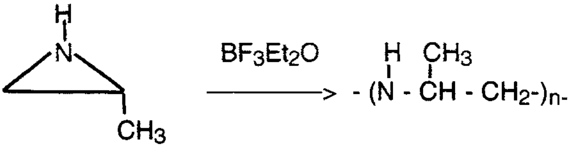
Polymerizations: All polymerizations were carried out in a closed tube (50 cm^3 capacity) in a nitrogen atmosphere. The initiator (1-5 mol%) was added at the required temperature and the polymerization was continued for a determined time. The polymers were isolated by pouring the reaction mixture into an excess of diethylether and decantation. To purify the polymer, it was dissolved in methanol and precipitated three times in diethyl ether; then it was dried in vacuum to constant weight. The polymers are rubbery products.

Measurements: FT-IR spectra were recorded on a Bruker IFS-48 spectrophotometer. ^1H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC 250 spectrometer. The viscosity was determined with an Ostwald Viscometer thermostated at 30.0°C ± 0.1 using CH_3OH as solvent. The thermogravimetric and differential scanning calorimetry analyses were carried out using a Simultaneous Thermal Analyser STA 625. Sample (1.416 mg) was heated in a platinum sample holder between 25°C and 550°C at 10°C min^{-1} under nitrogen atmosphere.

RESULTS AND DISCUSSION

2-Methylaziridine was also polymerized previously through N-benzyl phtalimide derivative as thermal initiator giving poly(propyleneimine) with Mn = 1000-3000 (20). Isotactic and atactic propyleneimine were prepared by the polymerization of L- and DL-4-methyl-2-oxazoline, respectively, using dimethylsulfate as initiator (21).

The polymerization of MAz initiated by BF_3Et_2O was investigated. The reaction conditions and results are summarized in Table 1.



All the polymers were gummy or viscous oils. They were insoluble in water and soluble in $CHCl_3$ and DMSO. Analysis: Calculated for (C_3H_7N); C, 63.16; H, 12.28; N, 24.56. Found: C, 63.21; H, 12.31; N, 24.50.

The polymerization yield in CH_3CN for all concentrations of BF_3Et_2O studied (1-5 mol%) depended on temperature and time. At 24 h and 70°C the polymerization reaction is quantitative. There is an effect of the dielectric constant of the solvents (acetonitrile, dimethylformamide, 1,2-dichloroethane) on the yield and viscosity. The most polar solvents increased the yield and viscosity.

The viscosity of MAz polymers obtained in acetonitrile decreased compared to those obtained by bulk polymerization.

Figures 1 and 2 show time-conversion and temperature-conversion curves, respectively. The reaction became slower later and did not show an induction period. On the other hand, as the temperature increases the conversion increases up to 100% at 70°C.

Table 1. Data of the polymerization of 2-methylaziridine (MAz).

Polymer N°	BF_3Et_2O[a] (mol%)	Solvent (5 ml)	Time (h)	Temp. (°C)	Yield (g)	Yield (%)	[η][b] ($dl \cdot g^{-1}$)
1	1	CH_3CN	24	70	1.14	100	0.044
2	2	CH_3CN	24	70	1.14	100	0.068
3	3	CH_3CN	24	70	1.14	100	0.075
4	4	CH_3CN	24	70	1.14	100	0.095
5	5	CH_3CN	24	70	1.14	100	0.103
6	1	CH_3CN	24	40	0.24	21	0.010
7	1	CH_3CN	24	50	0.27	23	0.024
8	1	CH_3CN	24	60	0.38	34	0.033
9	1	CH_3CN	3	70	0.12	11	0.009
10	1	CH_3CN	6	70	0.24	21	0.012
11	1	CH_3CN	15	70	0.39	44	0.036
12	1	CH_3CN	30	70	1.12	98	0.038
13	1	CH_3CN	35	70	1.11	97	0.040
14	1	DMF	24	70	1.14	100	0.043
15	1	$ClCH_2CH_2Cl$	24	70	0.77	65	0.033
16	1	none	24	70	1.14	100	0.057

a) With respect to monomer concentration

b) Determined in methanol at 30.0±0.1°C.

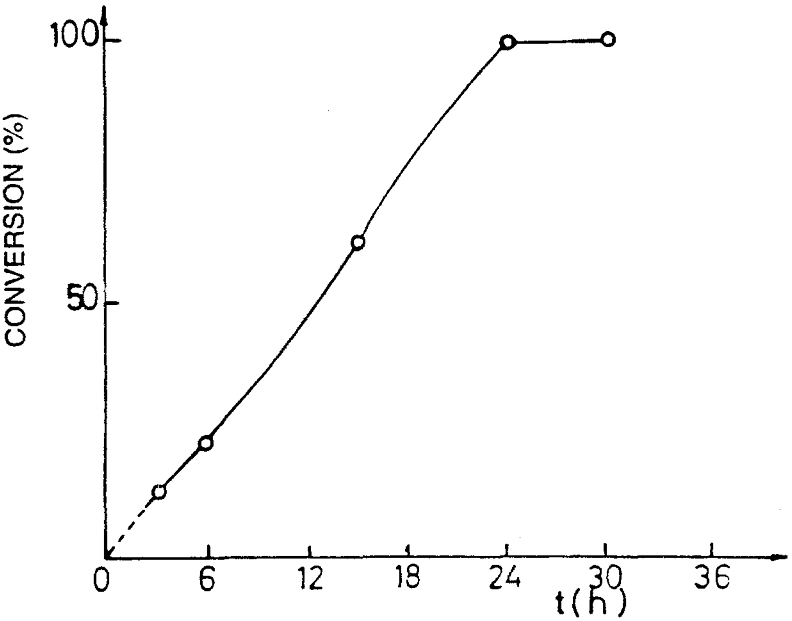


Figure 1. Time/conversion curve in the polymerization of 2-methylaziridine (MAz) with BF_3Et_2O, 1 mol% in acetonitrile at 70°C.

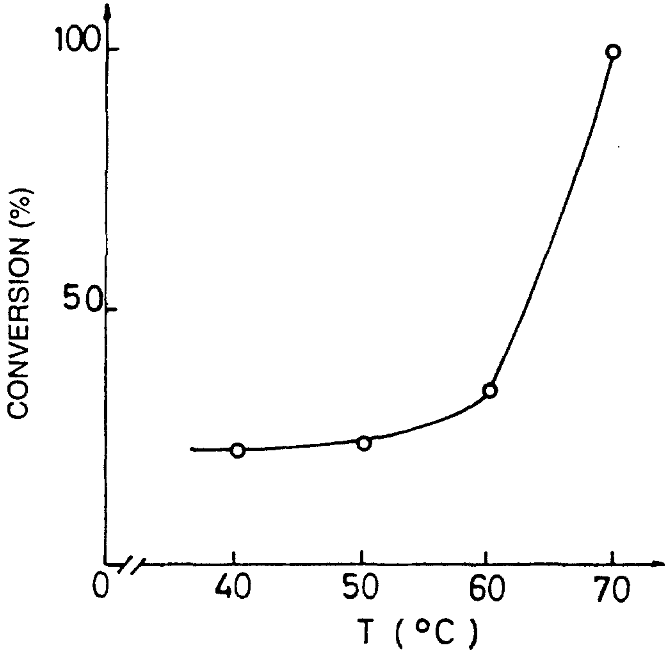


Figure 2. Temperature-conversion curve in the polymerization of 2-methylaziridine (MAz) with BF_3Et_2O, 1 mol% in acetonitrile by 24 h.

The structure of MAz polymers (C_3H_7N) was determined by FT-IR, ^1H-NMR and ^{13}C-NMR spectroscopy. The FT-IR spectrum of the polymer showed absorption bands at 3289 cm^{-1} (ν_{N-H}), 2965 (ν_{C-H}), 1457 (δ_{CH_2}), and 1216 (ν_{C-N}) (see Figure 3).

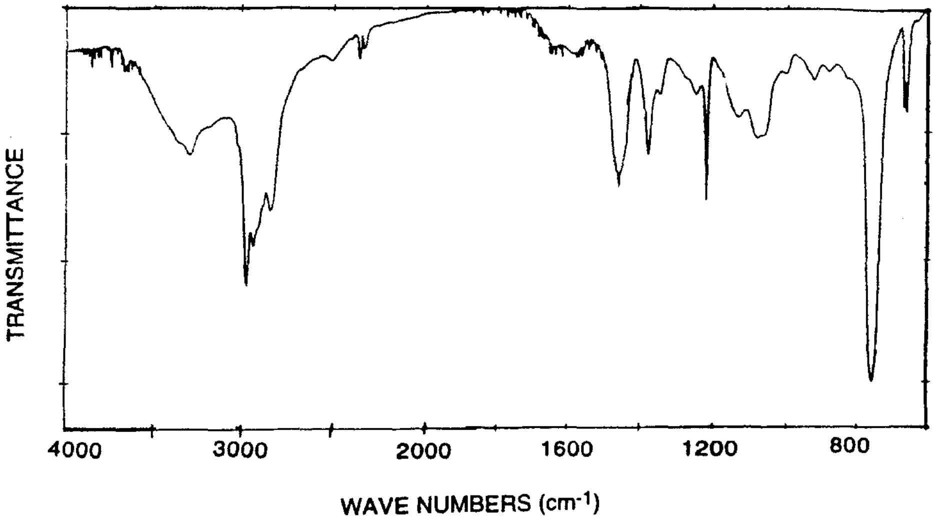


Figure 3. FT-IR spectrum (KBr) of MAz polymer sample 1.

Figure 4 shows the ^{1}H-NMR spectrum of the MAz polymer at 70°C in acetonitrile (see Table 1, polymer 1). It shows the expected signals: **a** at $\delta = 1.05$ ppm attributed to methyl protons; the broad signal **b** between $\delta = 2.10$ and 2.67 ppm assigned to methylene and methyne protons and the signal **c** at $\delta = 7.35$ corresponds to the solvent $CHCl_3/CDCl_3$.

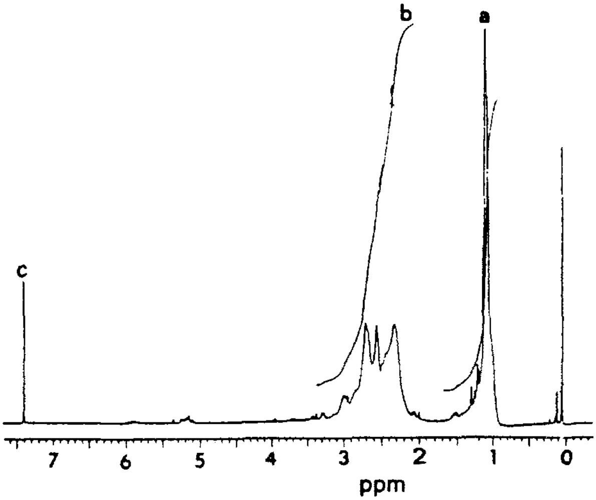


Figure 4. ^{1}H-NMR spectrum of MAz polymer sample 1 (250 MHz, D_2O room temperature and TMS).

The ^{13}C-NMR spectrum shows broad signals at $\delta = 21.69$ (CH_3), at $\delta = 47.16$-57.49 ppm corresponding to methylene and methyne carbons and 77.2 ppm the signal of the solvent $CHCl_3/CDCl_3$ (see Figure 5).

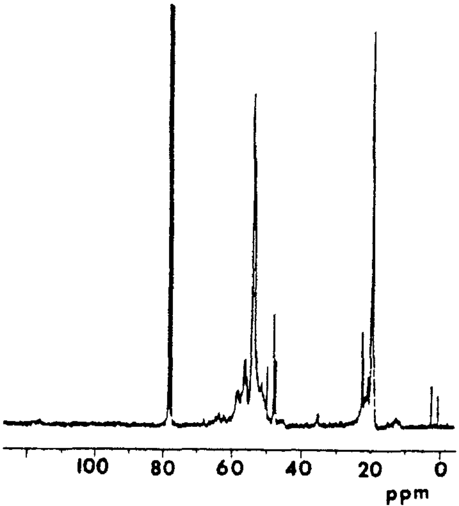


Figure 5. ^{13}C-NMR spectrum of MAz polymer sample 1 (62.6 MHz, $CDCl_3$, room temperature, TMS).

With respect to the polymerization mechanism, it is known that the basic aziridines are not reactive towards nucleophilic compounds unless the nitrogen has been quaternized, protonated or has formed a Lewis acid adduct. The polymerization initiated with boron trifluoride diethyl etherate propagates mainly by nucleophilic attack of the free aziridine at methylene carbon of the aziridinium cation.

Poly(2-methylaziridine) is very stable up to 200°C and it degrades continuously in one stage (see Figure 6).

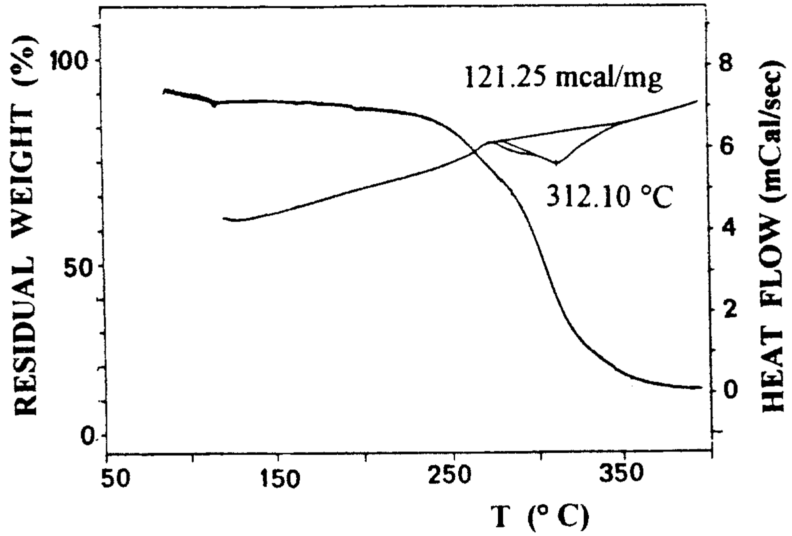


Figure 6. TG-DSC trace for the MAz polymer, sample 1. (Heating rate: 10°C min^{-1}, weight sample: 1.416 mg, nitrogen atmosphere).

The thermal decomposition kinetics of the thermogravimetric weight-loss can be described by the following equation:

$$-\frac{d\alpha}{dt} = K_n (1-\alpha)^n$$

where α is the fraction of the sample weight reacted at time t, n is the reaction order, and K_n is the specific rate. The reaction rate $d\alpha/dt$ was calculated using a differential technique which considers the heating rate and uses the temperatures vs. sample weight-fraction data (22). The activation energy Ea was calculated according to the equation:

$$\beta = \ln\left[-\frac{d\alpha/dt}{v(1-\alpha)^n}\right] = \ln A - \frac{Ea}{RT}$$

and using a linear multiple regression program by plotting β vs. 1/T (see Figure 7).

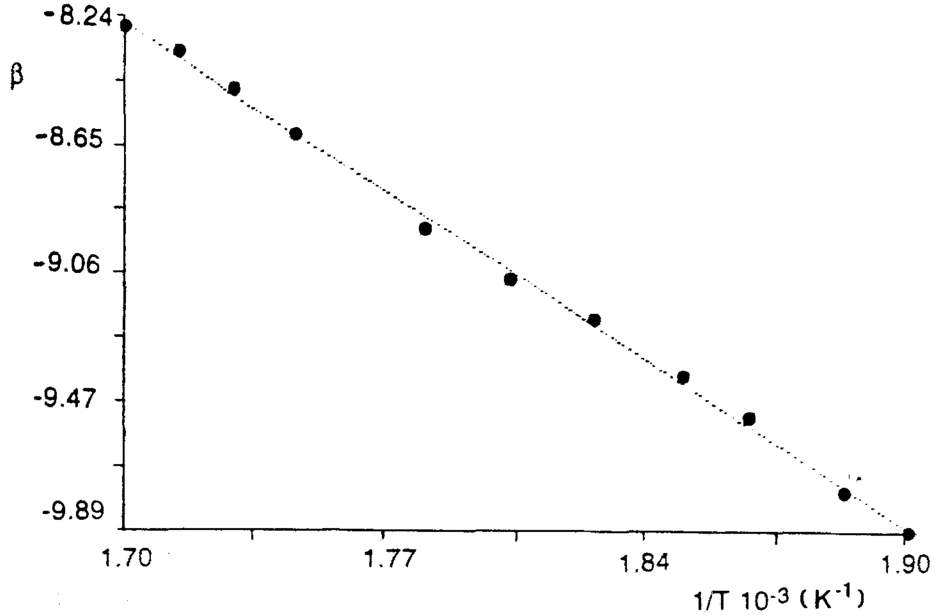


Figure 7. Arrhenius plot for the thermal degradation of MAz polymer, sample 1.

The linear relationship obtained indicated that the thermal degradation reaction is of 0 order . The coefficient of linear correlation was 0.998.

ACKNOWLEDGEMENTS

The authors thank FONDECYT (Grant 1951104) and Dirección de Investigación, Universidad de Concepción.

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