Polymer Bulletin 23, 571–576 (1990)

Polymer Bulletin

Cationic polymerization of 2,4,4-trimethyl-2-oxazoline

B. L. Rivas and M. Zapata

Polímeros, Departamento de Química, Facultad de Ciencias, Universidad de Concepción,
Casilla 3-C, Concepción, Chile

SUMMARY

The cationic homopolymerization of 2,4,4-trimethyl -2-oxazoline using BF_3Et_2O as initiator at different initiator concentrations, temperatures, times and solvents of polymerization were carried out. The effect of these variables on the polymerization yield and viscosity of the polymers were studied. Polymers were characterized by IR, ^1H NMR and ^{13}C NMR which support that the polymerization reaction occurs by ring opening of oxazoline through oxazolinium intermediates.

INTRODUCTION

Cationic (1-8) and zwitterion (9-12) ring-opening polymerization of 2-oxazolines have received considerable attention. Cationic ring-polymerization of 2-oxazolines is a convenient method to prepare poly(N-acetylethyleneimine)s. It is induced by alkylsulphonates, alkyl halides or Lewis acids, which proceeds via oxazolinium species, which can easily terminated by various nucleophiles (13). Therefore, the utilization of this advantage is possible to perform a versatile production of block, graft copolymers (1) and macromers (14) of 2-oxazolines. On the other hand, by basic hydrolisis of poly(N-acetylethyleneimine)s is possible to obtain linear poly(ethyleneimine) which is a very useful polymer support (8,15).

We have reported the cationic polymerization of 2-oxazoline derivatives (7,8) that occurs by ring opening nucleophilic attack on the C-5 of the oxazoline ring. This paper report an extension of this work to the polymerization of 2,4,4-trimethyl-2-oxazoline.

EXPERIMENTAL PART

Materials: Solvents, CH_3CN, DMF, CH_3OH, $ClCH_2CH_2Cl$, diethylether were purified in an usual manner (16). 2,4,4-trimethyl-2-oxazoline TMOX, (Aldrich Chem. Co.) was purified by distillation under N_2.

Polymerization: For bulk polymerization, the monomer was placed in a polymerization tube under nitrogen and then reacted at the desired temperature. BF_3Et_2O was added at 1.0 mol%. Acetonitrile, DMF, $ClCH_2CH_2Cl$ were used as solvents in solution polymerization and these were carried out under nitrogen at different temperatures, initiatior concentrations. Polymers from solution and bulk polymerization were isolated and purified pouring the reaction mixture in an excess of diethylether to precipitate the polymer. The diethylether was separated by decantation and the polymer washed with ether, CH_3CN, filtered and then dried in vacuum oven at 30°C.

Measurements: The IR spectra were recorded on a Perkin Elmer spectrophotometer Model 577. The ^1H NMR were recorded on a Varian XL-100 spectrometer (100 MHz) using solutions in $CDCl_3$ with TMS as internal standard. Natural abundance ^{13}C NMR were recorded at 36°C on a Varian CFT spectrometer (20 MHz). Proton and ^{13}C NMR chemical shifts are reported in ppm downfield from internal standard, TMS. The viscosity of polymers was determined with an Ostwald viscometer, thermostated at 30.0±0.1°C, using methanol as solvent.

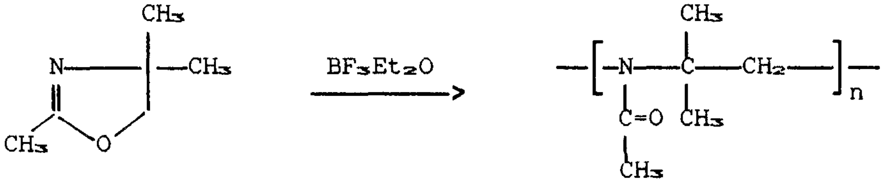
RESULTS AND DISCUSSION

Cyclic iminoethers are well known to undergo cationic ring-opening polymerization with various comonomers (17). It is also stablished that the polymerization occurs by ionic or covalent propagating species. Therefore, the nature of the propagation is influenced by various factors e.g, the nucleophilicity of monomer and the counter-anion, the substituents of monomers,polarity of solvent, polymerization time.

Usually the polymerization of oxazolines involves substituents in 2-position.

Nevertheless, the polymerization reaction occurs by attack of the nitrogen (from oxazoline) on the CH_2-O (5-position) of the oxazolinium species, has been reported previously, the polymerization of 5-methyl-2-oxazoline initiated by MeI (18).

Now, we describe the ring-opening polymerization of 2,4,4-trimethyl-2-oxazoline at different experimental conditions.



1 2

The conditions and results of the polymerization reaction are summarized in Table 1.

Table 1. Conditions and results of solution and bulk polymerization of 2,4,4-trimethyl-2-oxazoline.

Polymer (N°)	BF_3Et_2O (mol%)	Temp. (°C)	Solvent (10 ml)	Time (h)	Yield (%)	$[\eta]$ $(dl\cdot g^{-1})$
1	1	70	CH_3CN	24	35	0.040
2	2	70	CH_3CN	24	36	0.041
3	3	70	CH_3CN	24	46	0.042
4	4	70	CH_3CN	24	50	0.045
5	5	70	CH_3CN	24	54	0.048
6	1	50	CH_3CN	24	16	0.026
7	1	60	CH_3CN	24	22	0.037
8	1	80	CH_3CN	24	47	0.035
9	1	70	CH_3CN	48	43	0.046
10	1	70	CH_3CN	55	54	0.051
11	1	70	CH_3CN	72	72	0.065
12	1	70	DMF	24	46	0.068
13	1	70	$ClCH_2CH_2Cl$	24	31	0.058
14	1	70	Bulk	24	100	0.044

All the polymers are soluble in water, DMSO, $CHCl_3$, methanol. The polymerization yield as well as the viscosity increase by increasing the initiator concentration, the time and polymerization temperature. A 100% polymerization yield was obtained only in bulk polymerization (polymer 14). On the other hand, the solution polymerization in the more polar solvents, CH_3CN, DMF produces polymers with higher viscosity and polymerization yield than that polymerization carried out in $ClCH_2CH_2Cl$.

Characterization of Polymer: The TMOX polymer was characterized by elemental analyses, IR, ^1H NMR and

^{13}C NMR spectroscopy. The elemental analyses (Found: C, 63.68; H,9.68; N,12.37) was in agreement with the calculated (C,63.72; H,9.73; N,12.39). The infrared spectrum of the TMOX polymer, showed among other signals, absorption bands at 2960, 2930, 2870 (C-H); 1650 (C=O, amide) and 1245 (C-N) cm^{-1} in agreement with those of structure 2.

Fig 1. shows ^{1}H NMR spectrum of the TMOX polymer prepared at 70°C in CH_3CN (see Table 1, polymer 1)

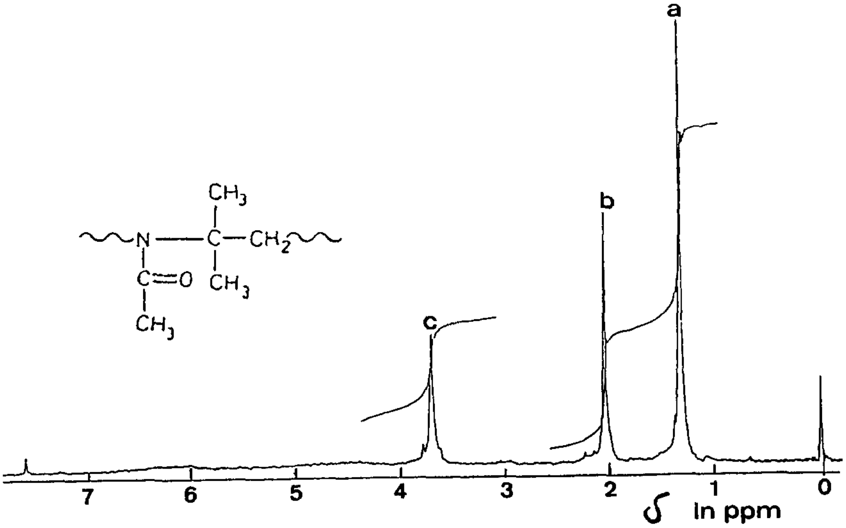


Figure 1. ^{1}H NMR spectrum of TMOX polymer sample 1 (100 MHz, $CDCl_3$, internal standard: TMS)

The proton NMR spectrum shows the three expected signals. The signal **a** at δ=1.20 was attributed to the methyl protons (6H); signal **b** at δ=2.05 was assigned to the methyl protons (3H) attached to carbonyl group and signal **c** at δ=3.60 (2H) was ascribed to the methylene protons attached to nitrogen.

Figure 2. shows the ^{13}C NMR spectrum of TMOX polymer (solution polymerization at 70°C) with various signals assigned as follows: signal at δ=23.74 corresponds to methyl carbons attached to carbon of the main chain; signal at δ=36.97 was assigned to methyl carbon attached to carbonyl group; signal at δ=54.34 was attributed to the quaternary carbon of the main chain; the signal at δ=67.59 was assigned to methylene carbon, and the signal at δ=169.64 ppm was ascribed to the carbonyl carbon. This assignment was corroborated by an off-resonance spectrum. It shows that the signal at δ=23.74 appeared as quartet; the signal at δ=36.97 as singlet and the signal at δ=67.59 ppm as triplet.

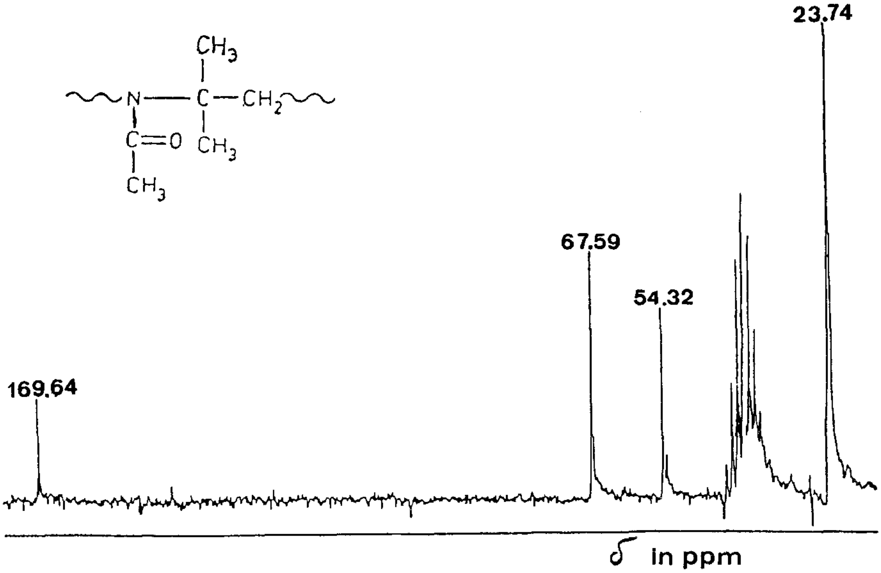
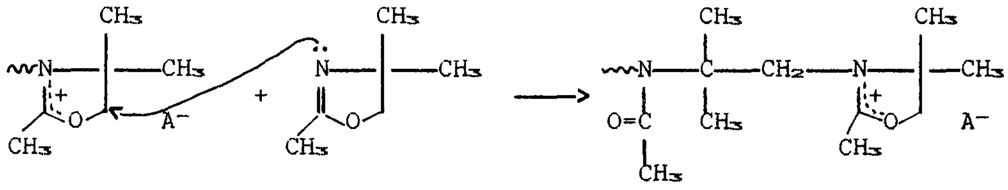


Figure 2. ^{13}C NMR spectrum of TMOX polymer sample 1 (20 MHz, DMSO-d$_6$, TMS, 36°C)

Polymerization mechanism: Our results indicate the similarity with other oxazoline polymerizations. The polymerization reaction involves nucleophilic ring opening by attack of nitrogen to cleave the CH_2-O bond of the oxazoline ring.



The polymerization would proceed by the stepwise mechanism as evidencied by the increase in molecular weight with increasing reaction time (see Table 1)

TMOX polymerization produces polymers with lower rates than that other oxazolines due to steric hindrance (19,20)

REFERENCES

1.- S.Kobayashi, T.Igarashi, Y.Moriuchi and T.Saegusa Macromolecules,19, 535 (1986).
2.- S.Kobayashi, N.Shimizu and T.Saegusa, Polym.Bull. (Berlin),11, 247 (1984).
3.- P.A.Gunatillake, G.Odian and D.A.Tomalia, Macromolecules,20, 247 (1984).
4.- C.I.Simionescu, G.David and M.Grigoras, Eur.Polym. J,23,689 (1987).
5.- T.Saegusa and S.Kobayashi, Makromol.Chem.Makromol Symp.1,23 (1986).
6.- S.Kobayashi, S.Iijima, T.Igaroshi and T.Saegusa, Macromolecules,20, 1729 (1987).
7.- B.L.Rivas and S.I.Ananías, Polym.Bull.(Berlin),18, 189 (1987).
8.- J.Bartulín, B.L.Rivas, M.T.Rodriguez and U.Angne, Makromol.Chem.,183, 2935 (1982).
9.- T.Saegusa, Angew.Chem.Int.Ed.Engl.,16, 862 (1977).
10.- G.Odian and P.A.Gunatillake, Macromolecules,18, 605 (1985).
11.- B.L.Rivas, G.S.Canessa, and S.A.Pooley, Makromol. Chem.,187, 71 (1986).
12.- C.I.Simionescu, M.Grigoras, E.Bîcu and G.Onofrei, Polym. Bull.(Berlin),14, 79 (1985).
13.- S.Kobayashi, T.Mizutani and T.Saegusa, Makromol. Chem., 185, 441 (1984).
14.- S.Kobayashi, E.Masuda, S.Shoda and Y. Shimano, Macromolecules, 22, 2878 (1989).
15.- T.Saegusa, H.Ikeda and H.Fujii, Macromolecules,5, 108 (1972).
16.- "ORGANIKUM" VEB Deutscher Verlag der Wissenschaften, Berlin (1972).
17.- T.Saegusa and S.Kobayashi, Encycl. Polym. Sci. Technol. Supp 6, 21, 220 (1976).
18.- S.Kobayashi, K.Marikawa, N.Shimizu and T.Saegusa, Polym.Bull.(Berlin),11, 253 (1984).
19.- B.L.Rivas, Ph.D.Thesis, University of Concepción (1980).
20.- T.Saegusa, H.Ikeda and H.Fujii, Polym.J.,3, 35 (1972).

Accepted April 3, 1990 K