

Ring opening polymerization of 2-ethyl-2-oxazoline

B. L. Rivas and S. I. Ananías

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

SUMMARY

Cationic ring opening polymerization of 2-ethyl-2-oxazoline using boron trifluoride etherate as initiator at different concentrations was carried out. It was performed in bulk and in solution. The effect of the temperature and solvent polymerization on the yield and viscosity was also studied. All the polymers were characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy.

INTRODUCTION

Cyclic iminoethers are well known to undergo cationic ring opening polymerization with various initiators(1). Resulting polymers of poly(N-acylalkyleneimines) from the isomerization polymerization of cyclic iminoethers are good starting polymers leading to linear poly(alkyleneimines) (2-3), functional polymers which are used as support in polymer-analogous reactions (4-7).

Saegusa and coworkers (8-9), Tomalia and coworkers (10), Levy and coworkers (11-12) and Goethals (13) among other authors have published about ring opening polymerization of oxazoline and oxazine derivatives.

The present paper describes the ring opening polymerization of 2-ethyl-2-oxazoline by boron trifluoride etherate, BF_3OEt_2 and the temperature and solvent effect on the reactivity.

EXPERIMENTAL PART

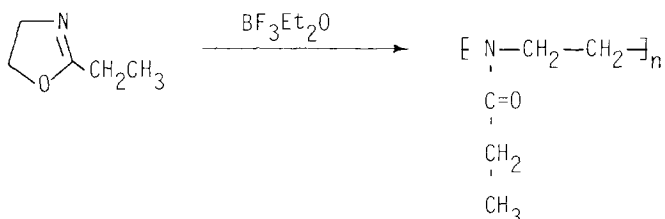
Materials: 2-Ethyl-2-oxazoline (Aldrich Chem.Co.) was purified by distillation from KOH. Acetonitrile, 1,2-dichloroethane, nitrobenzene, toluene were purified according to usual methods (14). BF_3OEt_2 (Merck) was distilled.

Polymerizations: Solution polymerization were carried out under nitrogen. The initiator was added to 0.1 mole of 2-ethyl-2-oxazoline dissolved in 20 ml acetonitrile. The reaction proceeded at a given temperature for a definite period. The polymers were precipitated in ethyl ether, filtered and dried in vacuum over phosphorus pentoxide. The elemental analyses for all polymers was practically the same. For example, for polymer 3: $(\text{C}_5\text{H}_9\text{NO})_n$ (99,04) Calc. C: 60.63; H: 9.08; N: 14.13
Exp. C: 60.58; H: 9.11; N: 14.13

Measurements: IR, ^1H NMR, ^{13}C NMR spectra were recorded on a Perkin Elmer 577 infrared spectrometer, a Bruker AW-80 and Varian XL-100 spectrometer respectively. The chemical shifts were reported relative to internal TMS. The viscosity from dimethylformamide was measured at 30°C with an Ostwald viscometer.

RESULTS AND DISCUSSION

It is known that cationic homopolymerization of cyclic iminoethers produces poly(N-acylalkyleneimines). We have reported previously the homopolymerization of 2-methyl-2-oxazoline under different experimental conditions (15). Now we report the cationic ring opening polymerization of 2-ethyl-2-oxazoline using $\text{BF}_3\text{Et}_2\text{O}$ as initiator.



This reaction was carried out at different concentrations of initiator in solution and in bulk. (see Table 1).

Table 1.- Polymerization of 2-ethyl-2-oxazoline with $\text{BF}_3\text{Et}_2\text{O}$ as initiator at 70°C and 24 h.

Polymer Sample Number	Initiator Concentration (mol%)	Solvent	Yield (%)	$[\eta]$ (dl/g)
1	0.5	CH_3CN	96.7	0.84
2	1.0	CH_3CN	100.0	0.83
3	2.0	CH_3CN	100.0	0.80
4	3.0	CH_3CN	100.0	0.76
5	4.0	CH_3CN	100.0	0.77
6	1.0	bulk	95.6	0.86

The polymerization yield for all concentrations of initiator studied was greater than 95% and there is not a significant influence of the initiator concentration on the yield. The intrinsic viscosity decreases as the initiator concentration increases.

Furthermore, Tables 2 and 3 show the effect of the dielectric constant of solvent (acetonitrile, benzene, toluene, 1,2-dichloroethane) and the temperature on the yield and polymer viscosity.

Table 2.- Effect of the temperature on solution polymerization reaction (CH_3CN) of 2-ethyl-2-oxazoline using $\text{BF}_3\text{Et}_2\text{O}$ (1 mol%) as initiator for 24 h.

Polymer Sample number	Polym.Temp. ($^{\circ}\text{C}$)	Yield (%)	$[\eta]$ (dl/g)
7	40	20.0	0.50
8	50	29.0	0.61
9	60	80.0	0.67
10	70	100.0	0.83
11	80	100.0	1.08

The data in table 2 show that an increase in polymerization temperature increases the yield. The viscosity increases from 0.50 up to 1.08 as the polymerization temperature increases from 40°C to 80°C .

Table 3.- Effect of the polymerization solvent on the reaction of 2-ethyl-2-oxazoline at 70°C , for 24 h using $\text{BF}_3\text{Et}_2\text{O}$ (1 mol %) as initiator.

Polymer Sample number	Solvent	ξ^{a}	Yield (%)	$[\eta]$ (dl/g)
12	toluene	2.37g	68.6	0.95
13	1,2-dichloroethane	10.65	100.0	0.91
14	nitrobenzene	35.74	100.0	0.92
15	acetonitrile	37.50	100.0	0.83

a) Dielectric constant at 20°C except for toluene (25°C)

The lowest yield is obtained in toluene as solvent. The other solvents that have greater dielectric constants gave 100% yields.

All the polymers were characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy.

The IR spectrum (KBr) shows among other absorption bands, a band at 1630 cm^{-1} corresponding to $\nu_{\text{C=O}}$ (amide).

The ^1H NMR spectrum (80 MHz, DCCl_3 , TMS) shows signals at $\delta=1.05$ ($-\text{CH}_3$), $\delta=2.50$ (attributed to methylene protons of the lateral chain) and $\delta=3.48$ ppm (assigned to methylene protons of the backbone) (see Fig. 1).

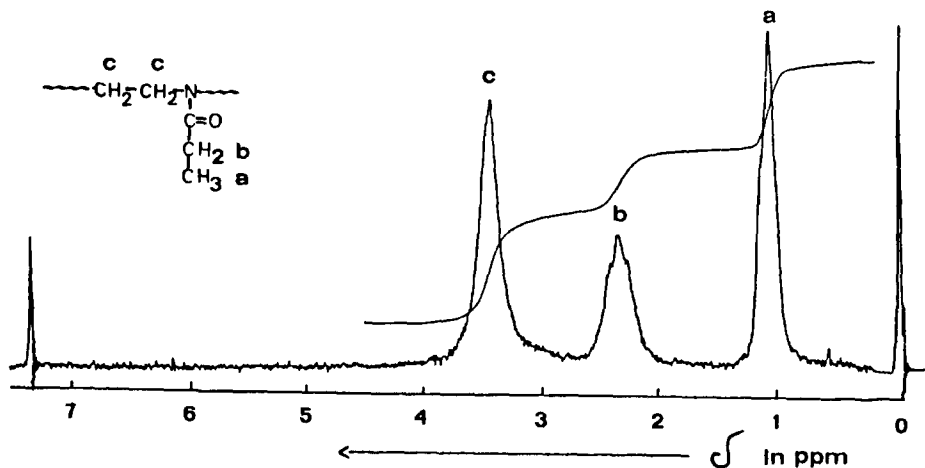


Fig.1 ^1H NMR spectrum of poly(N-propionyliminoethylene), sample 2. (80 MHz, DCCl_3 , room temperature; internal standard: TMS).

The ^{13}C NMR spectrum of poly(N-propionylethyleneimine) should exhibit four signals. However, seven signals were observed: $\delta=9.33$ assigned to methyl carbon; at $\delta=25.85$ attributed to the methylene carbon of the pendant group. Between 43.0 and 46.2 ppm there is a broad signal and is possible to assign at least three signals at $\delta=43.67$, 45.48, 46.11 ppm assigned to the methylene carbons of the backbone. Finally at low field is possible to see signals at $\delta=173.58$ and 174.20 ppm attributed to the carbonyl carbon. The signal at $\delta=77.20$ corresponds to the solvent carbon ($\text{HCCl}_3/\text{DCCl}_3$ mixture). (see Fig.2).

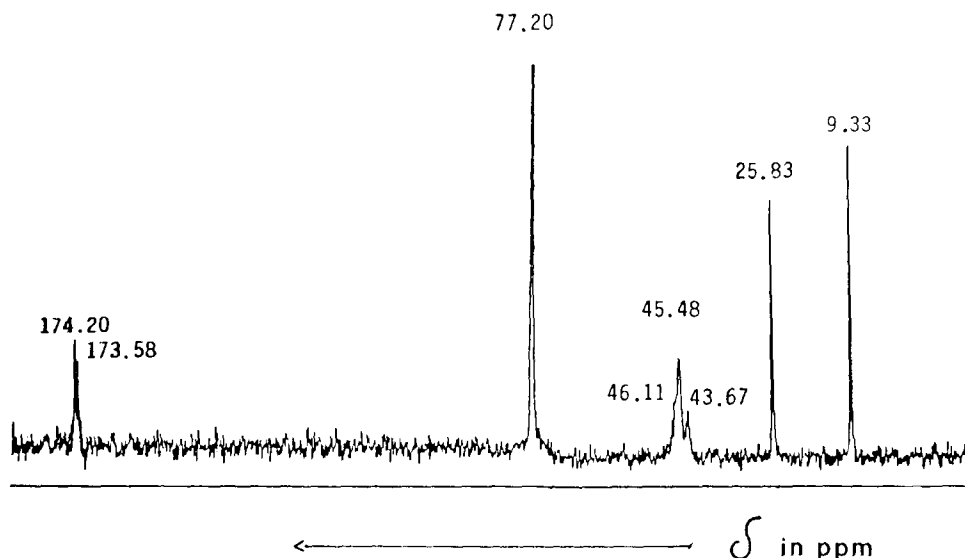


Fig. 2. ^{13}C NMR spectrum of poly(N-propionyliminoethylene), sample 2. (20 MHz, DCCl_3 , room temperature; internal standard: TMS).

Signal splitting was also observed with other polymers such as poly(N-formylethyleneimine)(16), poly(N-acetyleneimine)(15), and poly-(N-formylpropyleneimine)(17). This splitting may be due to restricted rotation of the amide bond $-\text{N}-\text{C}=\text{O}$ giving syn and anti isomers.

In respect to the initiation mechanism, it would be similar to other oxazoline derivatives (11) i.e., involving coordination of initiator on the nitrogen atom and forming an oxazolinium ion. The only nucleophile in the medium is the nitrogen atom of the other monomer; this monomer attacks, the oxazolinium ion and produces an oxazolinium ion on the incoming monomer. Tomalia et al. (11) founded evidences for this mechanism by ^1H NMR. Activation of this position in the monomer-initiator complex is expected to deshield these protons with respect to the monomer. In effect, the ^1H -NMR for both compounds recorded under the same conditions showed that these protons were deshielded with respect to the monomer, with a chemical shift difference of 0.52 ppm.

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