

Synthesis and characterization of poly(*N*-propionyl)iminoethylene

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SUMMARY

The cationic polymerization of 2-ethyl-2-oxazoline using CH_3I 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. The poly(*N*-propionyl)iminoethylene was hydrolyzed in acid medium obtaining a linear poly(ethyleneimine) (PEI). All the polymers were characterized by elemental analysis, IR, ^1H NMR, and ^{13}C NMR spectroscopy.

INTRODUCTION

It is well known that poly(ethyleneimine) produced by the ring-opening cationic polymerization of ethyleneimine has a highly branched structure (1-3) and normally it is accompanied by side reactions such as a reaction between the growing species and the amino group of the produced polymer chain. In some cases cyclic oligomers are also produced. Therefore, the cationic (4-14) and zwitterionic polymerization (15-20) of 2-oxazolines have received considerable attention, particularly the homopolymerization which is induced by alkyl sulfonates or Lewis acids. Subsequently, the linear poly(ethyleneimine) which is a very useful polymer support (21-23) is obtained by basic or acid hydrolysis of poly(*N*-acyl) iminoethylene.

The present paper reports the cationic polymerization of 2-ethyl-2-oxazoline by methyl iodide under different experimental conditions.

EXPERIMENTAL PART

Materials : Solvents were purified in the usual manner (24). 2-Ethyl-2-oxazoline, ETOX (Aldrich Chem. Co.) was purified by distillation from NaOH under N_2 .

Polymerization : When solvent and ETOX were admixed in a flask tube under nitrogen atmosphere at a polymerization temperature, e.g. 70°C , the polymerization commenced. The reaction mixture was poured into ether to precipitate the polymeric product, which was then isolated by centrifugation and dried in vacuo.

Hydrolysis of poly(*N*-propionyl)iminoethylene : Poly (ETOX). An aqueous solution of poly(ETOX) was refluxed with 6N HCl in 24 h under a continuous stream of nitrogen. PEI \cdot HCl was dissolved in water, reprecipitated in acetone, and filtered under vacuum.

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Measurements : The IR spectra were recorded on a Perkin Elmer spectrophotometer Model 577. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrophotometer. Proton and ^{13}C NMR were reported in ppm downfield from internal standard. The viscosity was determined with an Ostwald viscometer, thermostated at $30.0^\circ\text{C} \pm 0.1$ using methanol as solvent.

RESULTS AND DISCUSSION

Cyclic iminoethers are highly nucleophilic monomers, second only to cyclic amines. It is also established that the polymerization occurs by ionic or covalent species. Therefore, the nature of propagation is influenced by several factors e.g. the substituent of monomer, nucleophilicity of monomer and the counter-ion, polarity of solvent.

Now we report the ring-opening polymerization of 2-ethyl-2-oxazoline under different experimental conditions by using the electrophilic initiator methyl iodide.

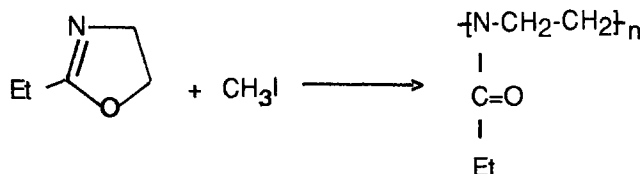


Table 1. Polymerization of 2-ethyl-2-oxazoline with CH_3I as initiator.

Polymer N ^o	CH_3I (mol%)	Solvent (5 ml)	Time (h)	Temp. ($^\circ\text{C}$)	Yield (%)	$[\eta]$ (dl/g)
1	0.5	CH_3CN	24	70	96	0.074
2	1.0	CH_3CN	24	70	100	0.069
3	2.0	CH_3CN	24	70	100	0.037
4	3.0	CH_3CN	24	70	100	0.024
5	4.0	CH_3CN	24	70	100	0.020
6	1.0	Bulk	24	70	100	0.085
7	1.0	DMF	24	70	88	0.057
8	1.0	$\text{ClCH}_2\text{CH}_2\text{Cl}$	24	70	69	0.042
9	1.0	Toluene	24	70	28	0.015
10	1.0	CH_3CN	24	40	30	0.037
11	1.0	CH_3CN	24	50	44	0.050
12	1.0	CH_3CN	24	60	66	0.061
13	1.0	CH_3CN	24	80	100	0.075
14	1.0	CH_3CN	2	70	34	0.018
15	1.0	CH_3CN	7	70	45	0.025
16	1.0	CH_3CN	14	70	60	0.038
17	1.0	CH_3CN	30	70	100	0.078

The polymerization yields in CH_3CN for all concentrations of initiator studied (0.5-4.0 mol %) was greater than 95%. At 24 h and 70°C the polymerization reaction is quantitative. There is an effect of the dielectric constant of solvent (acetonitrile, dimethylformamide, toluene, 1,2-dichloroethane) on the yield and polymer viscosity. The most polar solvent produces a polymer with the highest yield and viscosity. An increase in polymerization temperature and time increases the yield and the viscosity.

Characterization of Polymer : The ETOX polymer was characterized by elemental analysis, IR, ^1H NMR, and ^{13}C NMR spectroscopy. Anal. Calcd. for $(\text{C}_5\text{H}_9\text{NO})_n$: C, 60.60; H, 9.09; N, 14.14; Found: C, 60.39; H, 9.06; N, 13.99. The infrared spectrum of these ETOX polymers shows among other signals, absorption bands at 1960, 2930, 2870 (C-H); at 1640 (C=O, amide) and 1240 cm^{-1} (C-N).

The proton NMR spectrum shows the three expected signals. The signal **a** at $\delta = 1.11\text{ ppm}$ was ascribed to methyl protons (3H); the signal **b** at $\delta = 2.34\text{ ppm}$ was assigned to methylene protons from the propionyl group (2H) and the signal **c** at $\delta = 3.50\text{ ppm}$ was attributed to methylene protons of the main chain (4H) (see Fig. 1).

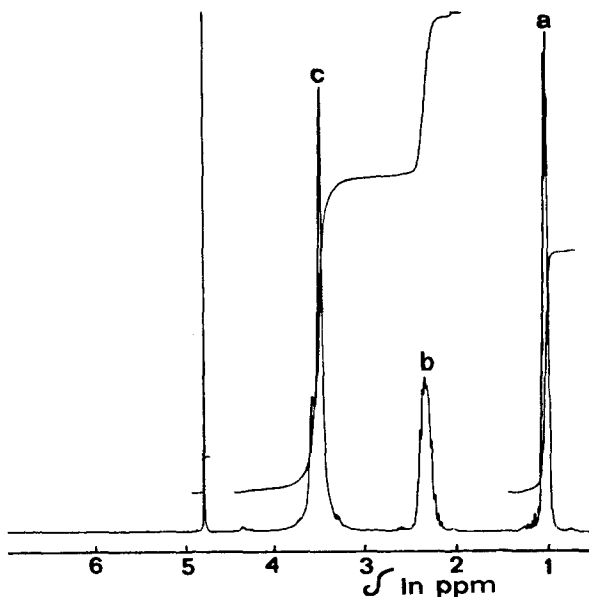


Figure 1. ^1H NMR spectrum of ETOX polymer sample 1 (250 MHz, D_2O , room temperature, TMS as internal standard).

The ^{13}C NMR spectrum presents four signals. The signal **a** at $\delta = 11.72\text{ ppm}$ (CH_3); signal **b** at $\delta = 28.44\text{ ppm}$ ($\text{CH}_2\text{-C=O}$); signal **c** between 45.54 ppm and 49.11 ppm ($\text{CH}_2\text{-N-}$) and signal **d** at $\delta = 180.24\text{ ppm}$ (C=O) (see Fig. 2).

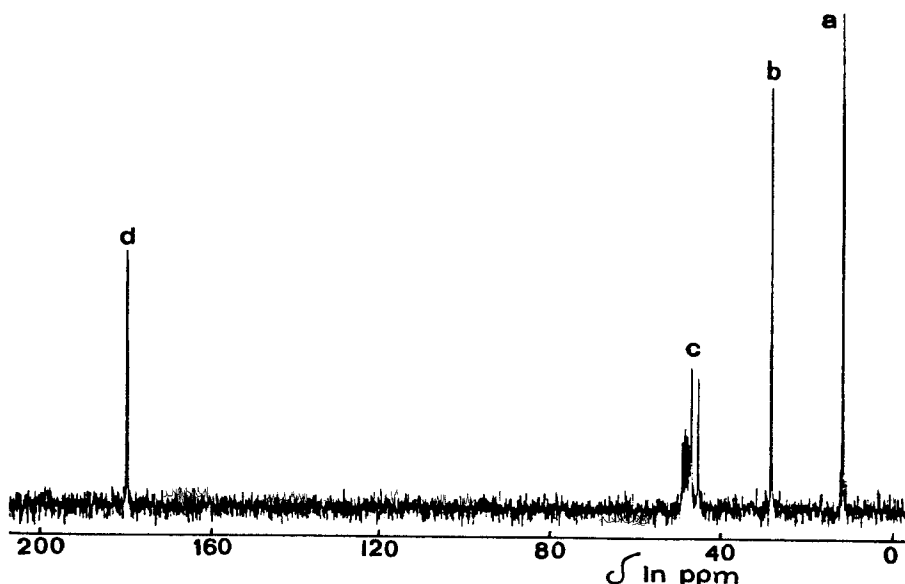


Figure 2. ^{13}C NMR spectrum of ETOX polymer sample 1 (D_2O , room temperature, TMS as internal standard).

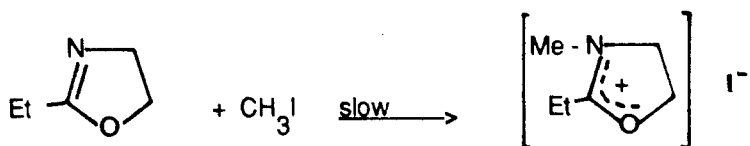
Due to the presence of a doublet for methyl protons and two signals for carbonyl group it is possible to conclude from ^1H NMR and ^{13}C NMR spectra that poly(N-propionyl)iminoethylene undergoes hindered rotation about the amide bond. Similar behaviour was previously observed for other poly(N-acyl)iminoethylenes (25,26).

The subsequent acid hydrolysis of poly(N-propionyl)iminoethylene produced a linear poly(ethyleneimine) almost quantitatively. The linear poly(ethyleneimine) showed the usual spectroscopic and solubility properties (25).

Polymerization Mechanism : 2-Ethyl-2-oxazoline polymerizes cationically by opening of the O-alkyl bond in the immonium cation, which is attacked by the most nucleophilic N-atom of the monomer involving ionic and covalent species according to the scheme shown on the next page.

Initiation involves the reaction between ETOX and CH_3I and yields an unstable intermediate of oxazolinium iodide **3**; the formation of this species is the rate determining step. The propagation step is the successive reaction of ETOX with covalent species **5** and **6**, which occurs through intermediates **3** and **5**.

Initiation:

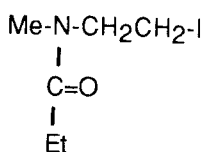


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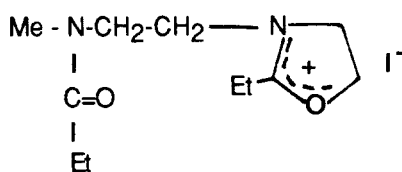
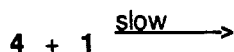
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$\xrightarrow{\text{fast}}$

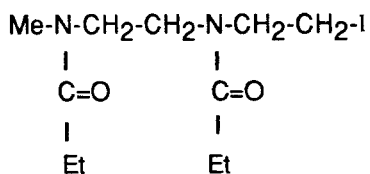
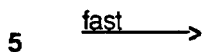


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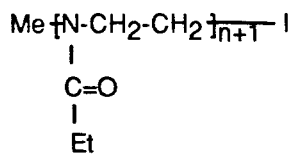
Propagation:



5



6



7

REFERENCES

1. W.G. Barb, (1955) *J.Chem.Soc.* 2654, 2577.
2. G.D. Jones, A.N. Langsjoen, M.M.C. Neuman and J.L. Zamlefer, (1974) *J.Org.Chem.* 9:125.
3. C.R. Dick and G.E. Ham, (1970) *J.Macromol.Sci.Chem.*, A4: 1301.
4. T. Saegusa and S. Kobayashi, (1986) *Makromol.Chem. Makromol.Symp.* 1:23.
5. T. Saegusa, (1972) *Macromolecules*, 5: 372.
6. S. Kobayashi, T. Igarashi, Y. Moriuchi and T. Saegusa, (1986) *Macromolecules*, 19: 535.
7. S. Kobayashi, N. Shimazu and T. Saegusa, (1984) *Polym. Bull.* 11:247.
8. S. Kobayashi, S. Iijima, T. Igaroshi and T. Saegusa, (1987) *Macromolecules*, 20:1730.
9. S. Kobayashi, H. Uyama, and Y. Narita, (1990) *Macromolecules*, 23:353.
10. S. Kobayashi, E. Masuda, S. Shoda and Y. Shimano, (1989) *Macromolecules*, 22:2878.
11. P.A. Gunatillake, G. Odian and D.A. Tomalia, (1987) *Macromolecules*, 20:2356.
12. B.L. Rivas and S.I. Ananías, (1987) *Polym.Bull.* 18:189.
13. B.L. Rivas and M. Zapata, (1990) *Polym.Bull.* 23:571.
14. C.I. Simionescu, G. David and M. Grigoras, (1987) *Eur.Polym.J.* 23:689.
15. T. Saegusa, (1977) *Angew.Chem.Int.Ed.Engl.* 16:862.
16. T. Saegusa, H. Ikeda and H. Fujii, (1972) *Macromolecules*, 5:354.
17. G. Odian and p.A. Gunatillake, (1985) *Macromolecules*, 18:605.
18. S.I. Simionescu, M. Grigoras, E. Bicu and G. Onofrei, (1985) *Polym.Bull.* 14:79.
19. B.L. Rivas, G.S. Canessa and S.A. Pooley, (1986) *Makromol.Chem.* 187:71.
20. B.L. Rivas and G. del C. Pizarro, (1989) *Eur.Polym.J.* 25:1227.
21. J. Bartulín and B.L. Rivas, (1981) *Makromol.Chem., Rapid Commun.* 2:375.
22. E. Bayer, B.Ya. Spivakov and K.E. Geckeler, (1985) *Polym.Bull.* 13:305.
23. C.G. Overberger and Y. Inaki, (1979) *J.Polym.Sci., Polym.Chem.Ed.* 17:1739.
24. "Organikum", VEB Deutscher Verlag der Wissenschaften, Berlin (1972).
25. J. Bartulín, B.L. Rivas, M. Rodríguez and U. Angne, (1982) *Makromol.Chem.* 183:2935.
26. K.J. Ivin, L.C. Kuan-Essig, E.D. Lille and P. Watt, (1976) *Polymer*, 17:656.