

Preparation and Characterization of Cyclic Polyesters from Ring-Chain Reactions of Poly(oxyepichlorhydrin oxymaloyl)

Mohammed Issam Ferrahi, Mohammed Belbachir

Laboratoire de Chimie des Polymères, Département de Chimie, Faculté des Sciences, Université d'Oran Es-Sènia BP No. 1524 El M'Naouar, 31000 Oran, Algeria

Received 2 January 2006; accepted 24 February 2006

DOI 10.1002/app.24429

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, the synthesis and characterization of cyclic polyesters of poly(oxyepichlorhydrin oxymaloyl) from a ring-chain reaction induced by "Maghnite," an acid-exchanged montmorillonite as acid solid cocatalyst (Mag-H^+), is described. Maghnite is already used as catalyst for polymerization of many vinylic and heterocyclic monomers [Belbachir, U.S. Pat. 066969.0101 (2001)]. The reactions were monitored by gel permeation chroma-

tography and $^1\text{H-NMR}$ spectroscopy and the existence of cyclic species was proven. The effect of the amount of catalyst on yield and molecular weight of polymer was studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1240–1243, 2006

Key words: anhydride; maghnite; montmorillonite; maleic; epichlorhydrin

INTRODUCTION

Montmorillonites, a class of inexpensive and noncorrosive solid acids, have been used as efficient catalysts for organic reactions.¹ Montmorillonite catalysts are easily recovered and reused.^{2–29} In continuation of our studies on environmentally benign methods using solid supports, we report that acid-exchanged montmorillonite (Mag-H^+) is a novel, efficient solid catalyst for the synthesis of cyclic polyesters from ring-chain reaction of poly(oxyepichlorhydrin oxymaloyl) (Scheme 1).

In contrast to the more usually used catalyst, Mag-H^+ can be easily separated from the polymer and regenerated by heating to a temperature above 100°C. The effect of the relative amounts of Mag-H^+ has been discussed.

EXPERIMENTAL

Materials

The preparation of the "Maghnite- H^+ 0.25M" (Mag-H) was carried out by using a method similar to that described by Belbachir et al.²⁵ Epichlorhydrin (99%),

maleic anhydride (99%), ethanol (99%), and acetone (99%) were used as received.

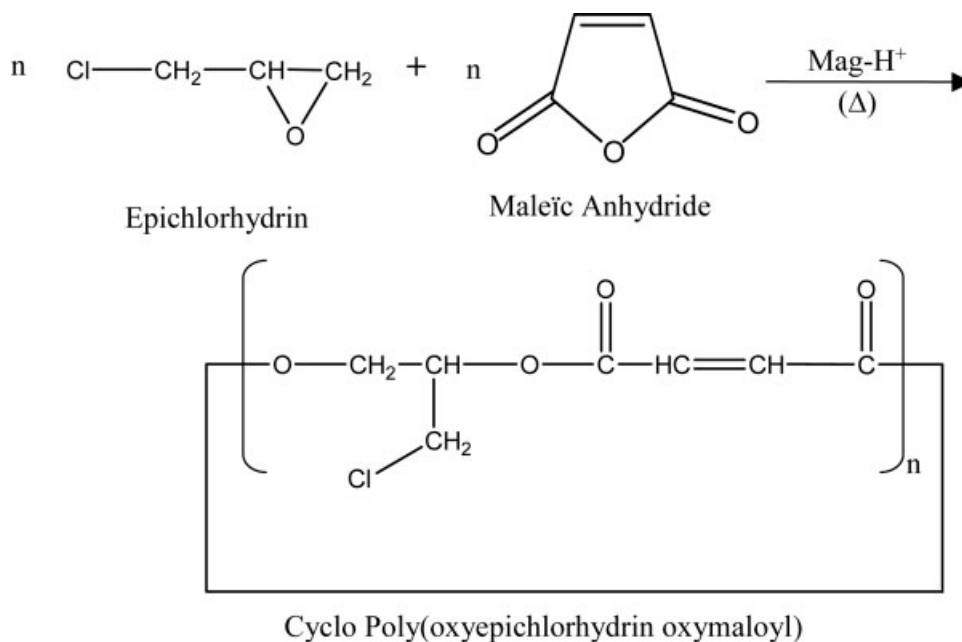
Procedure and polymer characterization

Polymerizations were carried out in stirred flasks at 40°C. The catalyst was dried in a muffle at 120°C overnight and then transferred to a vacuum desiccator containing P_2O_5 . After cooling to room temperature under vacuum, the mineral was added to the epichlorhydrin (10.64 mol/L) and maleic anhydride (8.54 mol/L) mixture preliminary kept in stirred flask at 40°C. At the required time, an aliquot of the reaction mixture was then taken in such manner as to exclude any clay mineral and slowly added to ethanol with stirring. The precipitated polymer was filtered off and dried under vacuum and weighed. The polymers were redissolved in acetone and precipitated into ethanol for characterization and molecular weight measurement.

Molecular weights were determined by a Waters high-pressure GPC instrument (Model 6000A Pump) having a series of ultra-Styrigel columns (100, 500, 103, 104, 105 Å), a differential refractometer 2401, and a UV absorbance detector Model 440. The flow rate of tetrahydrofuran was 1 mL/min. The calibration curve was made with well-fractionated poly(oxybutylene oxymaleoyl) standards.

$^1\text{H-NMR}$ spectra were recorded on an AM 300 FT Bruker instrument using deuterated acetone as solvent, and tetramethylsilane as internal standard.

Correspondence to: M.I. Ferrahi (mohammed.ferrahi@caramail.com).



Scheme 1 Synthesis of cyclic poly(oxyepichlorhydrin oxymaloyl) by Mag-H⁺ catalyst.

RESULTS AND DISCUSSION

Polymerization and product characterization

The results of bulk polycondensation experiments of 10.64M epichlorhydrin with 8.54M maleic anhydride induced by Maghnite-H⁺ 0.25M are reported in Table I. For all these experiments, the temperature was kept constant at 40°C for 6 h (Table I).

Effect of the amount of Mag-H on the polymerization

We can see from Table I that the yield increases as the proportion of Maghnite-H⁺ 0.25M increases (experiments 1, 2, 3). Table II shows the effect of the amount of Mag-H on the polymerization yield. Indeed, by using various amounts of Mag-H (2.5%, 5%, and 10% by weight), the polymerization was carried out in bulk at 40°C. The polymerization yield

increased with the amount of Mag-H, thus clearly showing the effect of Mag-H as a catalyst. This phenomenon is probably the result of an increase in the number of "initiating active sites" responsible of inducing polymerization, a number that is prorate to the amount of catalyst used a reaction (Table II).

Characterization of products

An investigation by 300 MHz ¹H-NMR spectroscopy was devoted to the analysis of the polymer from experiment 3 in Table I (Fig. 1).

According to the work published by Hamilton and Semlyen³⁰ and Vivas and Contreras,³¹ the 300 MHz ¹H-NMR spectra (in deuterated acetone, Fig. 1) showed four sets of peaks, corresponding to the chloride methylene groups at 3.62 ppm, the β-methylene groups at 3.75 ppm, the α-methylene groups at

TABLE I
Polycondensation of Epichlorhydrin with Maleic Anhydride Induced by Maghnite-H⁺ 0.25M

Experiment	Maghnite-H ⁺ 0.25M (%)	Yield (%)	M _n	M _w	M _w /M _n
1	10	47.15	732	3582	4.89
2	5	36.72	821	4363	5.31
3	2.5	21.67	914	4971	5.44

TABLE II
Yields with Time for 10.64 mol/L of Epichlorhydrin and 8.54 mol/L of Maleic Anhydride

Amount of Maghnite-H ⁺ 0.25M (%)	Yield (%)					
	1 h	2 h	3 h	4 h	5 h	6 h
2.5	10.43	12.62	15.36	17.86	19.64	21.67
5	15.3	19.9	25.57	28.73	32.75	36.72
10	23.52	27.52	32.67	37.45	42.83	47.15

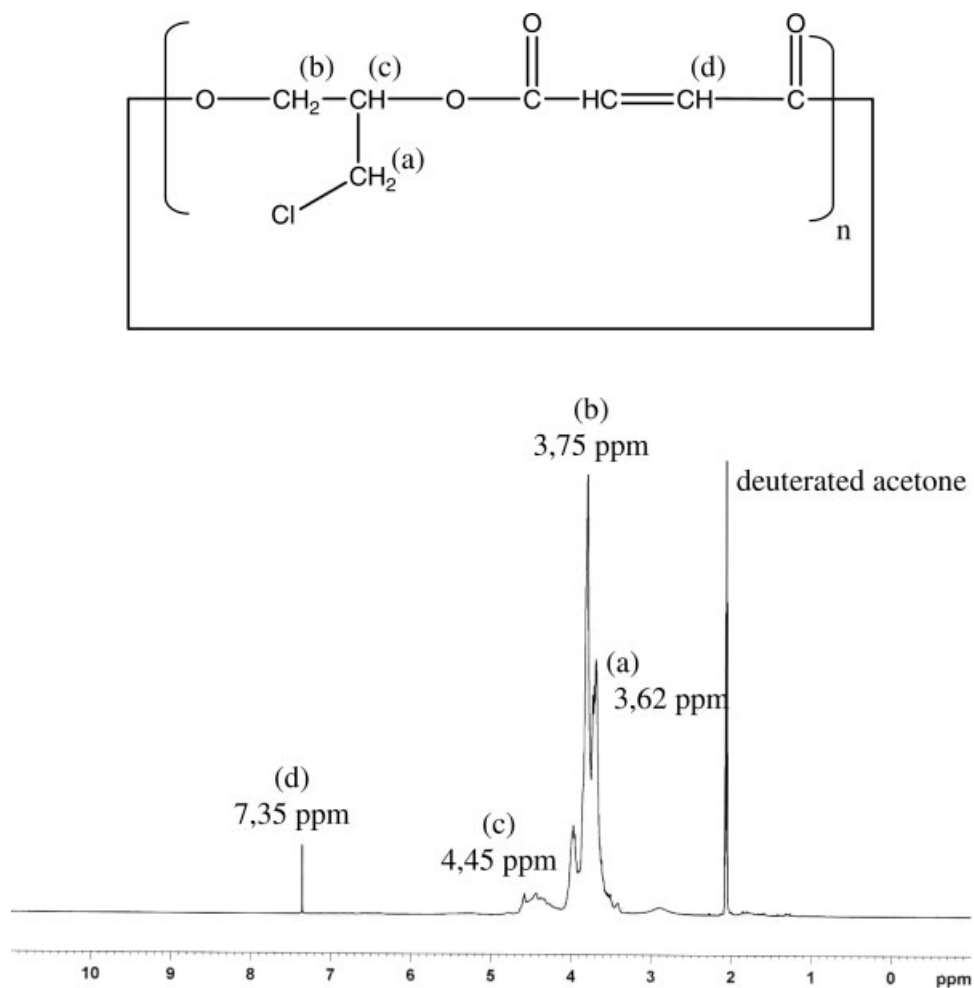


Figure 1 ¹H-NMR spectra of the cyclic poly(oxyepichlorhydrine oxymaloyl) product of experiment 3 in Table I in deuterated acetone.

4.45 ppm, and the ethylene groups at 7.35 ppm, respectively.

CONCLUSIONS

In conclusion, we have found that acid-exchanged maghnite is effective as acidic catalyst for the preparation of cyclic polyesters of poly(oxyepichlorhydrine oxymaloyl). The catalytic activity of this catalyst, measured by the yield and the molecular weight of the formed polymer, depends on the proportion of catalyst in the reaction medium. The polymerization proceeds smoothly by a very simple procedure, and a simple filtration is sufficient to recover the catalyst.

References

1. Belbachir, M. U.S. Pat. 066969.0101 (2001).
2. Aldridge, L. P.; McLaughlin, J. R.; Pope, C. G. *J Catal* 1973, 30, 409.
3. Forni, L. *Catal Rev* 1973, 8, 65.
4. Fripiat, J. J.; Gastuche, M. C.; Richard, R. B. *J Phys Chem* 1962, 66, 806.
5. Theng, B. K. G. *Dev Sedimentol* 1982, 35, 197.
6. Kowalska, M.; Cock, D. L. *Chemosphere* 1998, 36, 547.
7. Evangetou, V. P.; Marsi, M.; Vandiviere, M. M. *Plant Soil* 1999, 213, 63.
8. Kwon, O. Y.; Park, K. W.; Jeong, S. Y. *Bull Kor Chem Soc* 2001, 22, 678.
9. Moeke, W. Süd-Chemie AG, Munich, West Germany, 1974; p 365.
10. Ballantine, J. A.; Davies, M.; O'Neil, R. M.; Patel, I.; Purnell, J. H.; Williams, K. J.; Thomas, J. M. *J Mol Catal* 1984, 26, 57.
11. Lee, D. G.; Nomeldin, N. *Tetrahedron Lett* 1981, 22, 4889.
12. Chiang, C. S.; McKillop, A.; Taylor, E. C.; White, J. F. *J Am Chem Soc* 1976, 98, 6750.
13. Coenélis, A.; Laszlo, P. *Synthesis* 1985, 909.
14. Ballantine, J. A.; Puenell, J. H.; Thomas, J. M. *J Mol Catal* 1984, 26, 157.
15. Hojabri, F. *J Appl Chem Biotechnol* 1971, 21, 87.
16. Yahyaoui, A.; Belbachir, M.; Hachemaoui, A. *Int J Mol Sci* 2003, 4, 572.
17. Thomas, C. L.; Hickey, J.; Stecker, G. *Ind Eng Chem* 1950, 42, 866.
18. Kaplan, H. U.S. Pat. 3,287,422 (1966).
19. Hojabri, F. *J Appl Chem Biotechnol* 1971, 21, 87.

20. Ballantine, J. A.; Davies, M.; Purnell, H. *JCS Chem Comm* 1981, 427.
21. Odian, G. *La Polymerisation: Principles et Applications*; Ed Technica: New York, 1994; p 222.
22. Breen, C.; Madejová, J.; Komadel, P. *J Mater Chem* 1995, 5, 496.
23. Farmer, V. C. In *Infrared Spectra of Minerals*; Farmer, V. C., Ed.; Mineralogical Society: London, 1974; p 331.
24. Moeke, H. H. W. In *Infrared Spectra of Minerals*; Farmer, V. C., Ed.; Mineralogical Society: London, 1974; p 365.
25. Madejová, J.; Bednàniková, E.; Komadel, P.; Cícel, B. In *Proceedings of the 11th Conference on Chemistry of Minerals and Petroleum*, Ceske Budějovica, 1990; Konta, J., Ed.; Charles University: Prague, 1993; p 267.
26. Belbachir, M.; Bensaoula, A. U.S. Pat. 6,274,527 B1 (2001).
27. Ferrahi, M. I.; Belbachir, M. *Int J Mol Sci* 2003, 4, 312.
28. Ferrahi, M. I.; Belbachir, M. *J Polym Res* 2005, 12, 4, 167.
29. Ferrahi, M. I.; Belbachir, M. *Molécules* 2004, 9, 968.
30. Hamilton, S. C.; Semlyen, J. A. *Polymer* 1997, 38, 1685.
31. Vivas, M.; Contreras, J. *Eur Polym J* 2003, 39, 43.