

# Telechelic of Poly (Propylene Oxide) Catalyzed by Maghnite-H<sup>+</sup>

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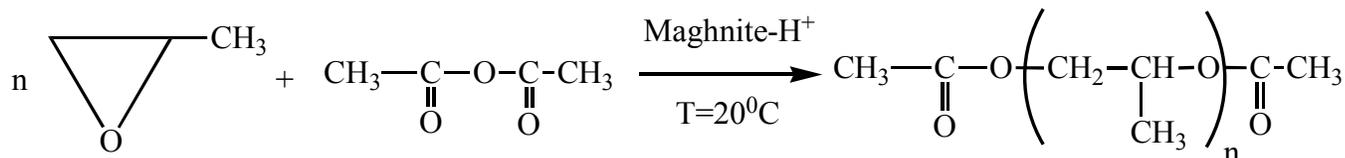
**Abstract:** Telechelic poly (propylene oxide) (PPO) bismacromonomers bearing methyl Acetate end groups, were prepared by cationic ring-opening polymerization of propylene oxide (PO), in the presence of Acetic anhydride, catalyzed by Maghnite-H<sup>+</sup> (Mag-H<sup>+</sup>), in bulk. Mag-H<sup>+</sup> is a montmorillonite sheet silicate clay which was exchanged with protons.

The influence of the amount of acetic anhydride and the reaction time on The polymerisation yield and molecular weight were studied. The products have been characterized by Nuclear magnetic resonance (<sup>1</sup>H-NMR).

**Keywords:** Maghnite-H<sup>+</sup>, poly (propylene oxide), macromonomers, cationic polymerization.

## INTRODUCTION

Propylene oxide can be polymerized by a variety of catalysts to produce polymers of high or low molecular weight and of crystalline or amorphous character [1,2]. Macromonomers are linear macromolecules carrying polymerisable functions at one or two chain ends [3,4].



The preparation of graft copolymers by use of macromonomers has been extensively investigated. This method provides an excellent means of designing graft copolymers of controlled structure [5-8].

Recently, an Algerian proton exchangeable montmorillonite clay called Mag-H<sup>+</sup>, a new initiator, was used as catalyst for cationic polymerization of a number of vinylic and heterocyclic monomers [9-12].

In the present work, we present a new approach to design telechelic poly(propylene oxide) in one shot, namely by the polymerization of propylene oxide in the presence of acetic anhydride catalyzed by Mag-H<sup>+</sup>. This catalyst can be easily separated from the polymer.

The effect of different synthesis parameters, such as the amount of acetic anhydride and the reaction time, are discussed.

## EXPERIMENTAL

### Materials

Propylene oxide (Aldrich) were dried over calcium hydride and distilled.

Acetic Anhydride was distilled under acetate sodium hydride, under reduced pressure.

The montmorillonite-H<sup>+</sup> (Mag-H<sup>+</sup>) was prepared.

### Instrumentation

The chemical structure of the products, <sup>1</sup>H-NMR was used (BRUKER 300 AVANCE) with tetramethylsilane as the internal reference.

The viscosimetric molecular weight (M<sub>v</sub>) was also calculated from the intrinsic viscosity measured in acetone at 25°C, with capillary viscosimeter, viscolgic TI-1, version 3-1 Semantec, by the following Mark-Houwink equation

$$[\eta] = 7.5510^{-2} (M_v)^{0.56}$$

### Purification of the Products

The purification of polymers were carried out by dissolving the product in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and filtering to eliminate the Mag-H<sup>+</sup>. Then, dichloromethane was removed by evaporation.

## RESULTS AND DISCUSSION

### Characterization of Products

Telechelic of PPO obtained by ring opening polymerisation of PO in the presence of acetic anhydride catalyzed by Mag-H<sup>+</sup>, each acetate group being linked to the

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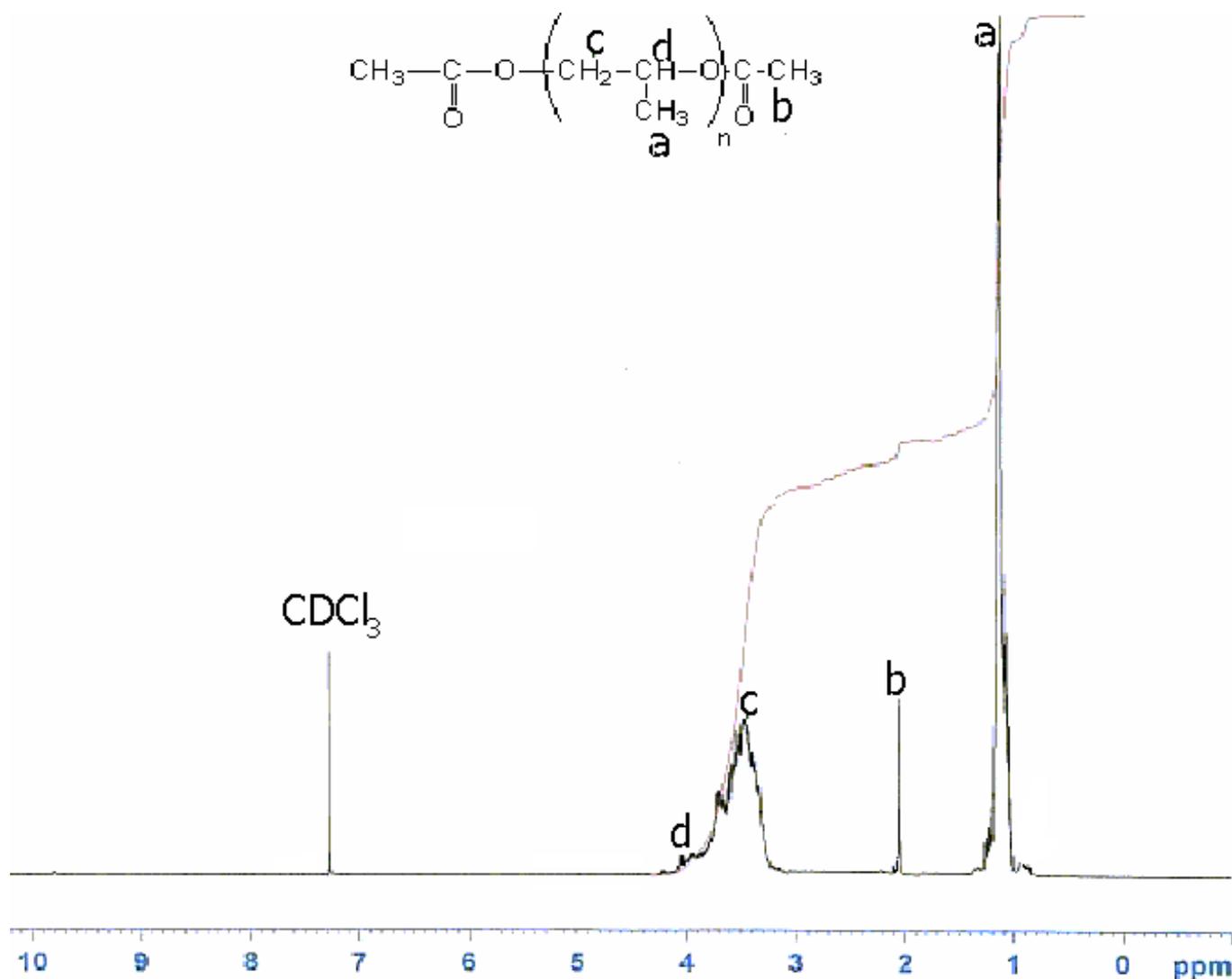


Fig. (1). <sup>1</sup>H-RMN spectrum (300MHz) of Poly (propylene oxide) in CDCl<sub>3</sub>.

polymer chain–end by an ester function. The acetate end group are clearly visible in the <sup>1</sup>H-NMR spectrum of telechelic PPO as shown in Fig. (1).

In <sup>1</sup>H-NMR spectroscopy 300MHz (solvent CDCl<sub>3</sub>) (Fig. 1) consist of four sets of peaks corresponding to the methyl groups (a) at 1.11 ppm, the α methylene groups (c, d) at 3.30-3.69 and the methyl groups of the main chain (b) at 2.05 ppm of ester.

#### Effect of the Proportion of Acetic Anhydride on the Polymerization

The data in Table 1 shows that the yield increases as the proportion of acetic anhydride increases. This result is due to a multiplication of the active centers. However, the molecular weight increases when the proportion of acetic anhydride is reduced. This result is due to an increase in the number of methyl groups at the extremities of the chains that block the growth of polymer chains.

Table 1. Average Molecular Weight and Yields with AA of PPO: for 1g of Mag-H<sup>+</sup> (g), PO (5 g, 0.086 mole), Time = 8h, Temperature= 20°C

AA (% by Weight)	Yield (%)	M <sub>v</sub> (g/mole)
1	60	8700
2	67	7650
4	71	7250
6	74	6450
8	78	5400
10	81	3750

AA: Acetic anhydride.

M<sub>v</sub>: Viscosity average molecular weight.

**CONCLUSION**

On the basis of the results obtained during this investigation, the following conclusions have been drawn:

- Activation of Maghnite with H<sub>2</sub>SO<sub>4</sub> can be done to increase the bentonite activity.
- Acid-exchanged Maghnite is effective as an acidic catalyst for the synthesis of PPO telechelic.
- The yield and the viscosity average molecular weight of synthesized telechelic PPO depend on both the amount of acetic anhydride.

**REFERENCES**

- [1] Pierre, L.E.St. Polyalkylene oxide and other polyethers. *Polyethers Part I*, **1963**, *13*, 130-140.
- [2] Furukawa, J.T.; Saegusa, T. Polymerization of Aldehydes and Oxides. *Polyethers Part II*, **1963**, *44*.
- [3] Rempp, P.; Franta, E. Advance synthesis and cationic polymerization of bicyclo orthoester-based poly( $\epsilon$ -caprolactone) macromonomer and depolymerization of the obtained graft copolymer. *Polym. Sci.*, **1984**, *1*, 58.
- [4] Chujo, Y.; Yamashita, Y. In Synthesis of an original poly(vinylidene fluoride-co-hexafluoropropylene)-g-perfluoropolyether graft copolymer, telechelic polymers: synthesis and application; Goethals, E.J., Ed.; CRC: Boca-Raton, **1989**, 163.
- [5] Kobayashi, S.; Kaku, M.; Mizutani, T.; Saegusa, T. Poly(ethylene oxide) macromonomers. *Polym. Bull.*, **1983**, *9*, 169.
- [6] Tsukahara, Y.; Ito, K.; Tsai, H.; Yamashita, Y. Investigation of the end groups of prepolymers/macromonomers prepared by radical chain transfer reaction. *J. Polym. Sci.*, **1989**, *27*, 1099.
- [7] Percec, V.; Wang, J. H. Synthesis of oligo(oxyethylene) methacrylate-ended Poly(*n*-hexyl isocyanate) rodlike macromonomers and their radical copolymerization behavior with methyl methacrylate. *Macromol. Symp.*, **1992**, *54*, 561.
- [8] Gnanou, Y.; Lutz, P. The influence of total monomer concentration on the "reactivity" of  $\omega$ -(*p*-vinylbenzyl ether) macromonomers of poly(2,6-dimethyl-1,4-phenylene oxide) determined from radical copolymerization experiments with butyl methacrylate. *Makromol. Chem.*, **1989**, *190*, 577.
- [9] Belbachir, M.; Bensaoula, A. Maghnite-H<sup>+</sup>, an ecocatalyst for cationic polymerization A.US Patent. **2001**, 6274527B1.
- [10] Harrane, A.; Meghabar, R.; Belbachir, M. Cationic ring opening polymerization of glycolide catalysed by a montmorillonite clay catalyst. *Int. J. Mol. Sci.*, **2002**, *3*, 790.
- [11] Ferrahi, M. I.; Belbachir, M. Polycondensation of tetrahydrofuran with phthalic anhydride induced by a proton exchanged montmorillonite clay. *Int. J. Mol. Sci.*, **2003**, *4*, 312.
- [12] Affaf, M.; Meghabar, R.; Belbachir, M. Maghnite-H<sup>+</sup>, an ecocatalyst for cationic polymerization of N-vinyl-2-pyrrolidone, *Polymer*, **2003**, *44*, 4097.

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