Cyclic polyesters prepared by poly(oxypropylene oxymaloyl) ring-chain reactions

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Abstract. The synthesis of cyclic polyesters of poly(oxypropylene oxymaloyl) from a ring-chain reaction was carried out at 40°C with 'Maghnite' an acid exchanged montmorillonite as acid solid ecocatalyst (Mag-H⁺). 'Maghnite' is already used as catalyst for polymerization of many vinylic and heterocyclic monomers [1]. The effect of amount of catalyst on yield and molecular weight of polymer was studied.

A typical reaction product was analyzed by gel permeation chromatography (GPC) as well as by nuclear magnetic resonance spectroscopy (¹H-NMR) and the existence of cyclic species was proven.

Keywords: polymer synthesis, molecular engineering, maleic anhydride, maghnite, montmorillonite, oxypropylene

1. Introduction

As clay catalysts, montmorillonites a class of inexpensive and non-corrosive solid acids, have been used as efficient catalysts for organic reactions. Montmorillonite catalysts are easily recovered and reused [2–8]. In continuation of our studies on environmentally bening methods using solid supports, we report that acid-exchanged montmoril-

lonite (Mag-H⁺) is a novel, efficient solid catalyst for the synthesis of cyclic polyesters from ring-chain reaction of poly(oxypropylene oxymaloyl) 'Figure 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⁺ was discussed.

Figure 1. Synthesis of Cyclo Poly(oxypropylene oxymaloyl) by Mag-H⁺ catalyst

2. Experimental

2.1. Materials

1) 'Maghnite-H⁺ 0.25M': The preparation of the Mag-H was carried out by using a method similar to that described by Belbachir and al. [1]. Indeed, the raw-Maghnite (20 g) was crushed for 20 min using a Prolabo ceramic balls grinder. It was then dried by baking at 105°C for 2 h. The Maghnite was then weighed and placed in an Erlenmeyer flask together with 500 ml of distilled water. The

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Maghnite/water mixture was stirred using a magnetic stirrer and combined with sulfuric acid, until saturation was achieved over 2 days at room temperature, the mineral was washed with water until it became sulfate free and then dried at 150°C.

The concentration 0.25M of sulfuric acid treatment solution was used to prepare ‘Maghnite-H⁺ 0.25M’.

2) Propylene oxide (99%), Maleic anhydride (99%), Ethanol (99%) and Acetone (99%) were used as received.

2.2. Procedure and Polymer characterization

Polymerizations were carried out in stirred flasks at 40°C. The catalyst was dried in a muffle at 120°C over night and then transferred to a vacuum desiccator containing P₂O₅. After cooling to room temperature under vacuum, the mineral was added to the Propylene oxide (10.85 mol/l), 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 serie 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 (THF) was 1 ml/min. The calibration curve was made with well-fractionated Poly(oxybutylene oxymaleoyl) standards.

¹H-NMR spectra were recorded on an AM 300 FT Bruker instrument using deuterated acetone as solvent, and tetramethylsilane (TMS) as internal standard.

3. Results and Discussion

3.1. Polymerization and Product Characterization

The results of bulk polycondensation experiments of 10.85 M Propylene oxide with 8.54 M maleic anhydride induced by ‘Maghnite-H⁺ 0.25M’ are

Table 1. Polycondensation of Propylene oxide with maleic anhydride induced by ‘Maghnite-H⁺ 0.25M’

Experiment	‘Maghnite-H ⁺ 0.25M’ [%]	Yield [%]	M _n	M _w	M _w /M _n
1	15	50.2	549	1825	3.32
2	10	42.7	641	2971	4.63
3	5	31.5	735	3758	5.11
4	2.5	17.2	823	4685	5.69

reported in Table 1. For all these experiments the temperature was kept constant at 40°C for 6 hours.

3.2. Effect of the amount of Mag-H on the polymerization

We can see from Table 1 that the yield increases as the proportion of ‘Maghnite-H⁺ 0.25M’ increases. However the molecular weight decreases (experiments 1, 2, 3, 4). Table 2 shows the effect of the amount of Mag-H on the polymerization yield. Indeed, using various amounts of Mag-H: 2.5, 5, 10 and 15% 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 prorata to the amount of catalyst used a reaction.

3.3. Characterization of products

An investigation was devoted to the analysis of the polymer from experiment 4 in Table 1 by 300 MHz ¹H-NMR spectroscopy (Figure 2).

According to the work published by Hamilton and Semlyen [9] and Vivas and Contreras [10] the 300 MHz ¹H-NMR spectra (in deuterated acetone, Figure 2) showed four sets of peaks, corresponding to the methyl group at 1.45 ppm, the β methylene

Table 2. Yields with time for 10.85 mol/L of Propylene oxide, 8.54 mol/L of maleic anhydride, the amounts of Maghnite-H⁺ 0.25M were: a) 2.5%, b) 5%, c) 10%, d) 15%

Yields [%]	Time [hours]					
	1	2	3	4	5	6
a	8.5	10.8	12.7	13.5	15.2	17.2
b	12.5	16.7	21.6	24.8	28.4	31.5
c	21.7	24.5	28.7	32.8	37.2	42.7
d	27.8	30.5	34.3	39.9	46.2	50.2

Figure 2. ^1H -NMR spectra of the cyclic poly(oxypropylene oxymaleoyl) product of experiment 4 in Table 1

groups at 3.65 ppm, the α methylene groups at 4.25 ppm, and the ethylene groups at 7.75 ppm, respectively.

4. Conclusions

The present work shows that the preparation of cyclic polyesters of poly(oxypropylene oxymaleoyl) can be induced in heterogenous phase by proton exchanged montmorillonite clay called Maghnite (Mag-H^+). 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, cyclic polyesters of poly(oxypropylene oxymaleoyl) was produced by a very simple procedure, just by filtering, the clay

can be separated from the reaction mixture, and acidic clay is inexpensive, stable and non corrosive.

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