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One Step For The Preparation Of Cyclic Polyesters Of Poly (Oxybutylene Oxyphthaleoyl)



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ABSTRACT

The present study shows the synthesis of cyclic oligomers of poly (oxybutylene oxyphthaleoyl) from the polycondensation of the tetrahydrofuran with phthalic anhydride using the Maghnite-H⁺ (Mag-H) as catalyst. Temperature is varied between 20 and 120°C. The effects of reaction temperature, amount of Maghnite-H⁺ and reaction time on the yield and the molecular weight are investigated. The results indicate that the polymerization rate increases with increasing the proportion of catalyst. © 2006 Trade Science Inc. - INDIA

KEYWORDS

Anhydride;
Maghnite;
Montmorillonite;
Tetrahydrofuran.

INTRODUCTION

Montmorillonites have both bronsted and Lewis acid sites and when exchanged with cations having a high charges density, as protons, produce highly-active catalysts for acid-catalysed reactions^[2-5]. Inceralated organic molecules are mobile and can be highly polarized when situated in the space between the charged clay layers. These exchanged montmorillonites have been successfully used as catalysts for the reactions

of polymerization^[4].

In the present work cyclic oligomers of poly (oxybutylene oxyphthaleoyl) were prepared successfully and cleanly. It is usually prepared from butandiol and phthalic anhydride at high temperature until 210°C^[6]. One of the biggest problems with this reaction has been the diol. In this respect, it is even more interesting to use tetrahydrofuran as a source of an oxybutylene part in the polymer. This method allow also to conduct the polymerization at room temperature.

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The purpose of this paper is also to study the polycondensation and examines the catalytic activity of an Algerian proton exchanged montmorillonite clay called 'Maghnite'^[7-15] a new non-toxic catalyst^[15] Mag-H can be easily separated from the polymer product and regenerated by heating to a temperature above 100°C^[15]. The effect of some factors such as the amount of the Mag-H, and effect of temperature are discussed.

EXPERIMENTAL

Materials

- 1) "Maghnite-H⁺xM": The preparation of the magH was carried out by using a method similar to that described by belbachir and al.^[15]. Indeed, the raw-maghnite(20g) was crushed for 20min using a prolabo ceramic balls grinder. It was then dried by baking at 105°C for 2h. The Maghnite was then weighed and placed in an Erlenmeyer flask together with 500ml of distilled water. The 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 concentrations 0.05M, 0.10M, 0.15M, 0.20M, 0.25M, 0.30M and 0.35M of sulfuric acid treatment solutions were used to prepare 'Maghnite-H⁺0.05M', 'Maghnite-H⁺ 0.10M', 'Maghnite-H⁺ 0.15M', 'Maghnite-H⁺ 0.20M', 'MaghniteH⁺ 0.25M', 'Maghnite-H⁺ 0.30M' and 'Maghnite-H⁺ 0.35M' respectively.
- 2) Tetrahydrofuran(THF 99%) was used as received.
- 3) Phthalic anhydride(99%) was used as received.
- 4) Ethanol(99%) was used as received.

Procedure and polymer characterization

Polymerizations were carried out in stirred flasks. 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 tetrahydrofuran(10.75mol/l) and phthalic anhydride (5.67mol/l) mixture preliminary kept in stirred flask. 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 THF 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, 105A°), a differential refractometer 2401 and a UV absorbance detector model 440. The flow rate of tetrahydrofuran(THF) was 1ml/min. The calibration curve was made with well-fractionated poly(oxybutylene oxyphthaleoyl) standards.

¹HNMR spectra were run in acetone deutere on an AM 300FT Bruker spectrometer using tetramethylsilane(TMS) as internal standard.

RESULTS AND DISCUSSION

Catalyst structure

The elementary analysis of the selected samples obtained using XRF and yields obtained from the reaction of 1g of each sample with 10.75mol/l of THF and 5.67mol/l of phthalic anhydride during 6 hours in a bulk at 40°C are as settled in the following TABLE 1.

It is necessary to report that the best value of yield was obtained with 'Maghnite-H⁺ 0.25M', for this reason we kept this sample to study the effect of catalyst and acetic anhydride proportions on polymerization. Acid treatment of 'Raw-Maghnite' cause reduction in octahedral content(Al₂O₃) resulted in an increase in the proportion of silica(SiO₂) observed.

Polymerization and products characterization

TABLE 2 shows the experimental results for the polycondensation of THF 10.75M with phthalic anhydride 8.43M induced by 'Maghnite-H⁺ 0.25M' proceed in bulk at different temperatures. It was found that Maghnite-H⁺ by itself possesses good activity as catalyst for the polycondensation. The extent and the degree of polymerization reach maximum values around 40-60°C. On the other hand, with the increase in the reaction temperature above

TABLE 1: Elementary compositions of protons exchanged samples 'Maghnite-H⁺'

sample	Compositions wt%											Yield%
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	As	PF*	
Raw-Maghnite	63.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	0.05	11	00
Mag-H 0.05M	70.75	14.67	1.05	0.30	1.01	0.49	0.78	0.16	0.75	0.04	10	5.32
Mag-H 0.10M	71.00	14.60	1.00	0.30	0.98	0.39	0.78	0.16	0.55	0.04	10.2	11.64
Mag-H 0.15M	71.58	14.45	0.95	0.29	0.91	0.35	0.77	0.15	0.42	0.03	10.1	17.38
Mag-H 0.20M	71.65	14.20	0.80	0.28	0.85	0.30	0.77	0.15	0.39	0.01	10.6	20.75
Mag-H 0.25M	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	0.01	11	36.82
Mag-H 0.30M	73.20	13.85	0.70	0.27	0.78	0.20	0.76	0.13	0.31	0.02	9.78	29.17
Mag-H 0.35M	75.31	13.52	0.71	0.26	0.78	0.18	0.75	0.13	0.32	0.01	8.03	24.35

*PF : Pert in Fire

TABLE 2: Effect of reaction temperature on the polymerization

T(°C)	Yield (%)	M _v ×10 ^{-3a}	M _w /M _n ^b
20	53.17	2.38	1.32
40	74.65	2.75	1.54
60	74.71	4.23	1.86
80	71.25	4.95	2.13
100	65.37	3.28	1.15
120	58.46	1.95	1.08

[THF]=10.75mol/l; [PA]= 6.57 mol/l; 5% of Maghnite-H⁺ 0.25M. Reaction time=8 hours.^aDetermined in acetone at 25°C.^bFrom gpc, measured in THF at 40°C.

80°C the molecular weight and the yield of the obtained polymers decrease progressively suggesting the possible occurrence of thermal degradation.

Effect of the amount of Mag-H on the polymerization

The effect of the amount of Maghnite-H⁺ on the polymerization was examined (TABLE 3). It can be noted that the yield increases with increasing "Maghnite-H⁺ 0.25M" proportion. TABLE 3 shows the effect of the amount of Mag-H on the polymerization rate. Indeed, using various amounts of Mag-H, 2.5, 5 and 10% by weight, the polymerization was carried in bulk at 40°C. The polymerization rate increases with the amount of Mag-H, in which the effect of Mag-H as a catalyst is clearly shown. This phenomena is probably the result of number of 'initiating active sites' responsible of inducing polymerization, this number is prorata to the catalyst amount used in reaction.

Polymerization using 5% of Maghnite-H⁺ 0.25M was carried in bulk at 80°C and the reaction

TABLE 3: Polymerization using different amount of Maghnite-H⁺

Maghnite-H ⁺ 0.25M (%)	Yield (%)	M _v ×10 ^{-3a}	M _w /M _n ^b
2.5	38.45	4.32	1.73
5	74.65	2.75	1.54
10	87.34	1.29	1.25

[THF]=10.75mol/l; [PA]= 6.57 mol/l.

Reaction time=8 hours.

^aDetermined in acetone at 25°C.^bFrom gpc, measured in THF at 40°CTABLE 4: Kinetic evolution of polycondensation of THF with Phthalic anhydride catalyzed by Maghnite-H⁺ 0.25M

Time(h)	Yield(%)	M _v ×10 ^{-3a}	M _w /M _n ^b
2	3.58	2.52	1.23
3	6.56	2.65	1.21
4	12.53	2.79	1.18
5	45.68	2.93	1.35
6	68.63	4.86	1.29
8	80.27	5.37	2.47

[THF]=10.75mol/l; [PA]= 6.57 mol/l; 5% of Maghnite-H⁺ 0.25M.^aDetermined in acetone at 25°C.^bFrom gpc, measured in THF at 40°C

was monitored at various times. The results are given in TABLE 4 shows the evolution of the yield and the molecular weight of the polymer with reaction time. The molecular weight increases with polymerization time. On the other hand, the yield increases with the time and it can be noted that initially the polymerization proceeds very slowly; this can be considered as an induction period(4h). At the end of this period. the polymerization process becomes faster.

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Characterization of products

An investigation was devoted to the analysis of the polymer by $^1\text{H-NMR}$ spectroscopy at 300MHz (TABLE 5).

According to the work published by S.C.Hamilton and J.A.Semlyen^[16], M.Vivas and J.Contreras^[17], $^1\text{H-NMR}$ spectroscopy at 300 MHz (Solvent

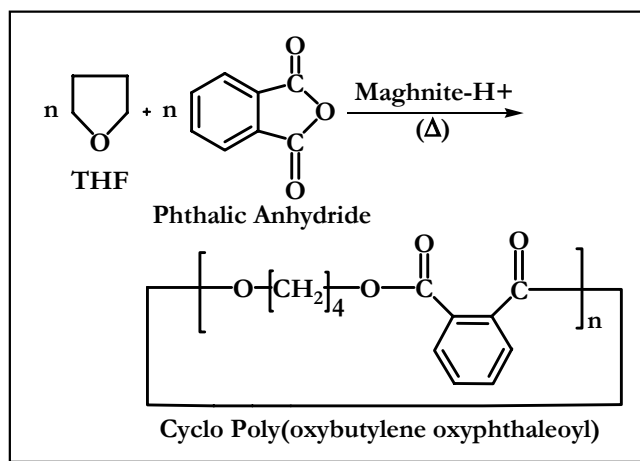
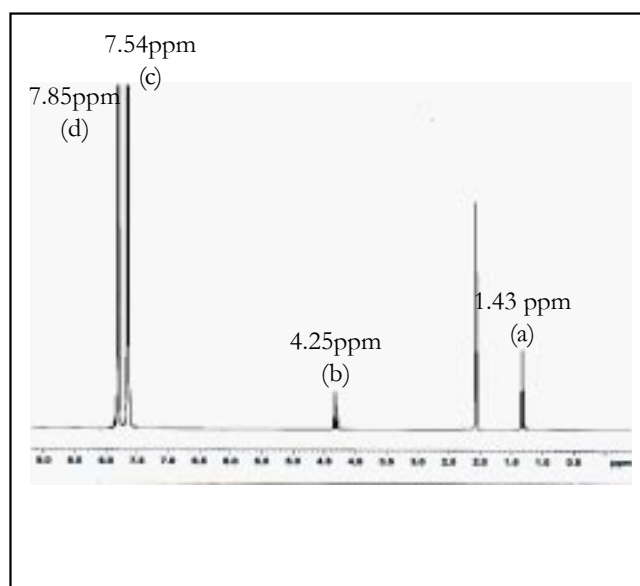
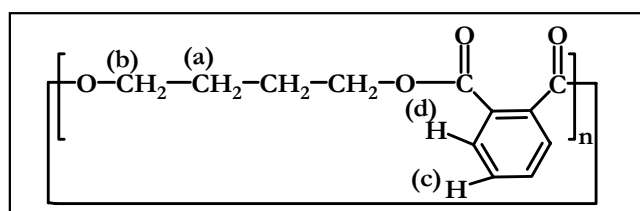


TABLE 5: Results of products analysis by $^1\text{H-NMR}$ spectroscopy

Proton type	(a)	(b)	(c)	(d)
δ in ppm	1.43	4.25	7.54	7.85



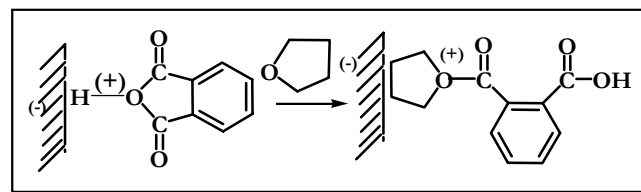
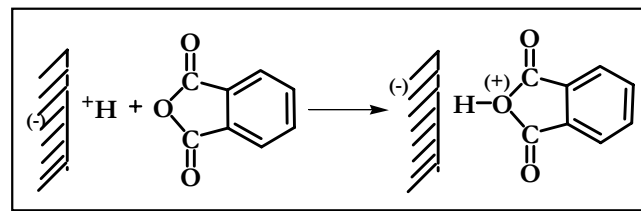
acetone deutere) showed different peaks, the β methylene groups at 1.43ppm, the α methylene groups at 4.25ppm, and phenyl groups at 7.54ppm and 7.85ppm. the peak at 2.09ppm is attributable to solvent(acetone one deutere)

Mechanism of the reaction

Polycondensations proceed by successive reactions between the functional groups of the reagents. According to the foregoing discussion and the results of product analysis, we may suggest the mechanism below for the resulting reaction of polymerization induced by 'Maghnite-H 0.25M'.

Protons carried by montmorillonite sheets of 'H-Maghnite 0.25M' induced the polymerization, these montmorillonite sheets take place as counter-anions.

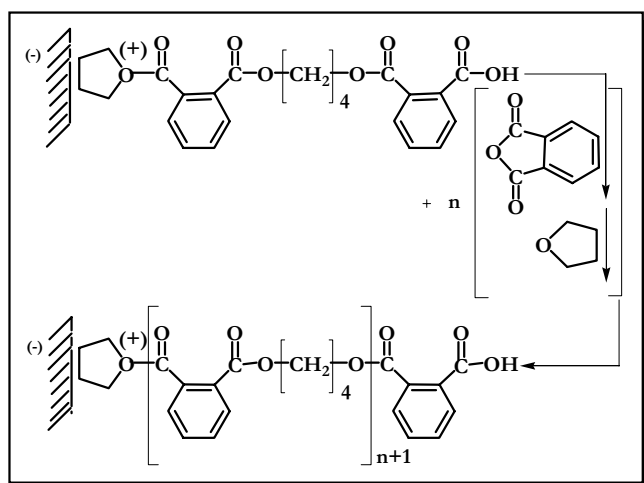
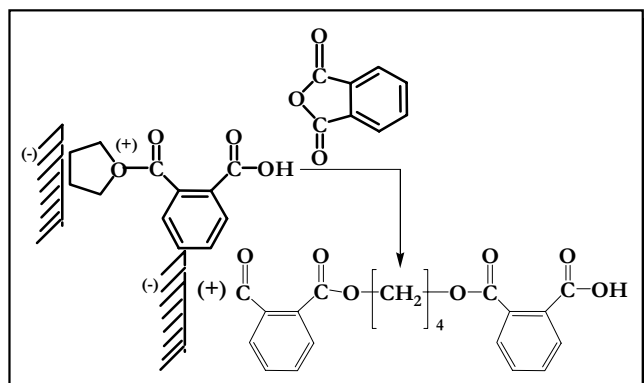
The first stage is the protonation of phthalic



anhydride. then a molecule of THF attacks in a nucleophilic way protonic phthalic anhydride.

The formed ions oxonium take place in the vicinity of the counter-anion carried by montmorillonite sheets, then there is a nucleophilic attack of the oxygen of phthalic anhydride on the carbon located in alpha of oxygen charge carrier positive of the chains in growth.

The next stage is a nucleophilic attack of the oxygen of the THF on carbon-cation of the chains in growth. then we have a successive additions of the phthalic anhydride suivue of the THF the last stage will be a nucleophilic attack of the oxygen of the phthalic acid pattern formed in the first stage which results from the protonation of maleïc anhydride on the carbon located in alpha of oxygen charge carrier positive of the chains in growth which gives cyclic polyester of poly(oxybutylene oxyphthaloyl).

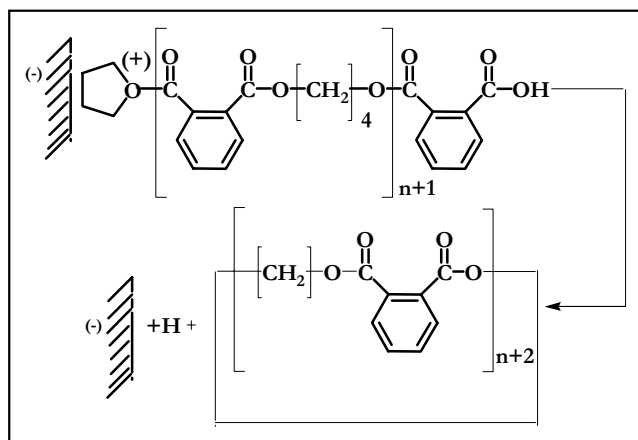
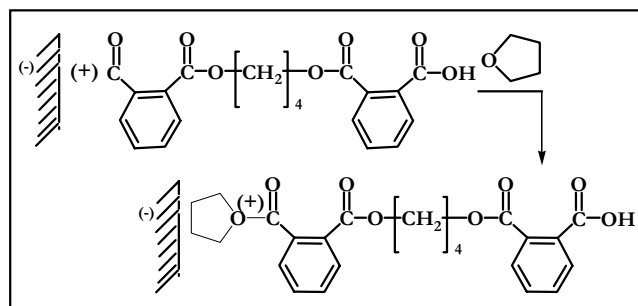


CONCLUSION

We have shown that Maghnite 0.25M treated in an acid medium catalyses the polymerization of the tetrahydrofuran with phthalic anhydride to prepare cyclic oligomers of poly(oxybutylene oxyphthaloyl). It were produced by a very simple procedure. Through simple filtering the clay can be separated from the reaction mixtures. Moreover this acidic clay is inexpensive, stable and non corrosive.

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