

# One-Step Synthesis of Bis-Macromonomers of Poly(1,3-dioxolane) Catalyzed by Maghnite-H<sup>+</sup>

Fatiha Reguieg,<sup>1</sup> Nabahat Sahli,<sup>1</sup> Mohamed Belbachir,<sup>1</sup> Pierre J. Lutz<sup>2</sup>

<sup>1</sup>Laboratoire de Chimie des Polymères, Université d'Oran, 3100 Oran, Algeria

<sup>2</sup>Institut Charles Sadron, UPR 22, F-67083 Strasbourg, France

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**ABSTRACT:** Telechelic poly(1,3-dioxolane) (PDXL) bis-macromonomers bearing methyl methacrylate end groups were prepared by cationic ring-opening polymerization of 1,3-dioxolane (DXL), in the presence of methacrylic anhydride, catalyzed by Maghnite-H<sup>+</sup> (Mag-H<sup>+</sup>), in bulk and in solution. Maghnite is a montmorillonite sheet silicate clay, which exchanged with protons to produce Mag-H<sup>+</sup>. The influence of the amount of Mag-H<sup>+</sup>, monomer (DXL), and

methacrylic anhydride on monomer conversion was studied. The polymerization yield and the molecular weight of  $\alpha,\omega$ -bis-unsaturated PDXLs prepared depend on the amount of Mag-H<sup>+</sup> used and the reaction time. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3147–3152, 2006

**Key words:** Maghnite; Maghnite-H<sup>+</sup>; poly(1,3-dioxolane); macromonomers; cationic polymerization

## INTRODUCTION

Macromonomers are linear macromolecules carrying polymerizable functions at one or two chain ends.<sup>1,2</sup> Numerous examples of macromonomer synthesis by different polymerization processes and extensive studies on their copolymerization behavior have been reported.<sup>3–6</sup> Nevertheless, the cationic initiators and catalysts used for these synthesis are expensive and often toxic either because of side-products or heavy metals such as antimony, chromium, mercury, etc. Frequently, these initiators require high pressure and very high or very low temperature to achieve controlled polymerization. Therefore, the presence of toxic impurities precludes the use of the polymers prepared in biomedical applications.

Recently, an algerian proton exchanged montmorillonite clay called Maghnite-H<sup>+</sup> (Mag-H<sup>+</sup>), a new non-toxic cationic initiator, was used as catalyst for cationic polymerization of a number of vinylic and heterocyclic monomers.<sup>7–10</sup>

In the present work, we present a new approach to design telechelic poly(1,3-dioxolane) (PDXL) bis-macromonomers in one shot, namely by the polymerization of 1,3-dioxolane (DXL) in the presence of methacrylic anhydride and catalyzed by Mag-H<sup>+</sup>. This catalyst can be easily separated from the polymer

product and regenerated by heating at a temperature above 100°C.<sup>7</sup>

The effects of different synthesis parameters, such as the amount of Mag-H<sup>+</sup>, monomer, methacrylic anhydride, are discussed, together with the mechanism of polymerization.

## EXPERIMENTAL

### Reagents

(DXL) (96%), methacrylic anhydride (94%), tetrahydrofuran (THF) (99%), dichloromethane, and ethanol (98%) were purchased from Aldrich and used as received.

### Preparation of Mag-H<sup>+</sup>

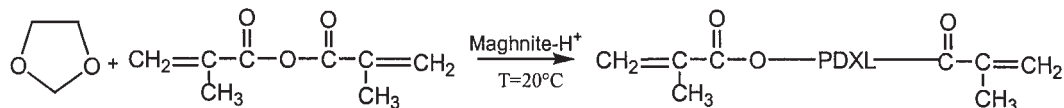
Pristine Maghnite is activated with a sulfuric acid solution to give a Maghnite exchanged with protons, called Mag-H<sup>+</sup>. In an Erlenmeyer flask, crushed raw Maghnite (30 g) was dispersed in a volume of distilled water (120 mL). The mixture was stirred using a magnetic stirrer for 2 h at room temperature. Then, a solution of sulfuric acid 0.5M (100 mL) was added. The solution thus obtained was maintained for two days under stirring, then the mineral was filtered off and washed several times with distilled water upto pH 7. After filtration, the Mag-H<sup>+</sup> was dried in an oven for 24 h, at 105°C and was then crushed.

### Instrumentation

To determine the chemical structure of the products, <sup>1</sup>H-NMR was used (BRUKER 300 AVANCE), with

Correspondence to: P. J. Lutz (lutz@ics.u\_strasbg.fr).

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**Scheme 1** Schematic representation of the synthesis of a  $\alpha,\omega$ -unsaturated PDXL macromonomer.

tetramethylsilane as the internal reference. The double bond content was obtained by UV spectroscopy (UV/visible Shimadzu 2101 PC apparatus) in acetonitrile ( $\lambda_{\text{max}}$  (nm) = 206; reference, ethyl methacrylate;  $\epsilon$  = 8511;  $\lambda$  (nm) = 206). The molecular weight of the synthesized PDXL was determined in THF by Size Exclusion Chromatography (SEC), using poly(ethylene oxide glycol) (POEG) samples as standards for calibration. It has been shown<sup>5,6</sup> that calibration with POEG or PDXL samples gave the same values of  $M_n$ . The viscosimetric molecular weight ( $M_v$ ) was also calculated from the intrinsic viscosity measured in THF at 25°C, with a capillary viscosimeter, viscoligic TL1, version 3-1 Semantec, by the following Mark-Houwink equation

$$[\eta] = 17 \times 10^{-3} (M_v)^{0.73}$$

### Synthesis of PDXL bis-macromonomer

The functionalization of DXL with methacrylic anhydride in the presence of Mag-H<sup>+</sup> as a catalyst was carried out by cationic ring-opening polymerization in bulk and in solution under different conditions to study the effects of different synthesis parameters (Scheme 1).

#### Synthesis of PDXL bis-macromonomers in bulk

Each mixture was prepared with a weighted quantity of Mag-H<sup>+</sup> dried just before use for 1 h in a drying oven at 100°C. DXL (10.6 g, 0.143 mol) and methacrylic anhydride (1.1 g,  $7.15 \times 10^{-3}$  mol), were mixed, and various amounts of Mag-H<sup>+</sup> (1, 2.7, 4, 6, 10 and 20 (wt %) were added. The reaction was carried out at 20°C under dry nitrogen for 1 h.

#### Synthesis of PDXL bis-macromonomer in solution

Three mixtures were prepared, each composed of 21.2 g DXL (0.286 mol) and 0.58 g of Mag-H<sup>+</sup> (2.7% by weight), using various quantities of methacrylic anhydride (0.0143, 0.0143, and 0.0228 mol), respectively. To each mixture, 20, 10, and 10 mL of CH<sub>2</sub>Cl<sub>2</sub> were added, respectively. The reaction mixtures were stirred for 45–315 min, at 20°C under dry nitrogen.

### Purification of the products

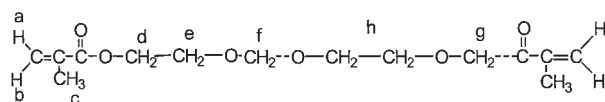
Purification and removal of unreacted monomer and low molecular weight polymers were carried out by dissolving the product in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and filtering to eliminate the Mag-H<sup>+</sup>. Then, dichloromethane was removed by evaporation, the sample was redissolved in THF, and the PDXL solution was precipitated in cold ethanol. The precipitated polymer was filtered and dried under vacuum. It was finally kept in refrigerator until use.

## RESULTS AND DISCUSSION

### Structural analysis

Bis-macromonomers of PDXL were obtained by ring-opening polymerization of DXL in the presence of methacrylic anhydride by Mag-H<sup>+</sup>; each methacrylate group being linked to the polymer chain-end by an ester function.

The methacrylate end groups are clearly visible in the <sup>1</sup>H-NMR spectrum of  $\alpha,\omega$ -bis-unsaturated PDXLs, as shown in Figure 1. The presence of the unsaturated end group was also determined by UV analysis made in acetonitrile.



### Effect of the amount of Mag-H<sup>+</sup>

Table I shows the weight-average molecular weight ( $M_w$ ) and the number-average molecular weight ( $M_n$ ) determined by SEC and by UV, the molecular weight distribution ( $I$ ), the viscosimetric molecular weight ( $M_v$ ), and the polymerization yields of the  $\alpha,\omega$ -bis-unsaturated PDXL prepared.

First, we note that the value of the number-average molecular weight determined either by SEC or by UV is in good agreement when using 2.7 wt % of Mag-H<sup>+</sup>. Therefore, it can be concluded that the synthetic method used is efficient to access PDXL macromonomers almost quantitatively fitted with methacrylate end groups.

As shown in Table I, when the amount of Mag-H<sup>+</sup> used was 2.7 wt %, the highest rate of functionalization observed was around 87%. However, the use of a

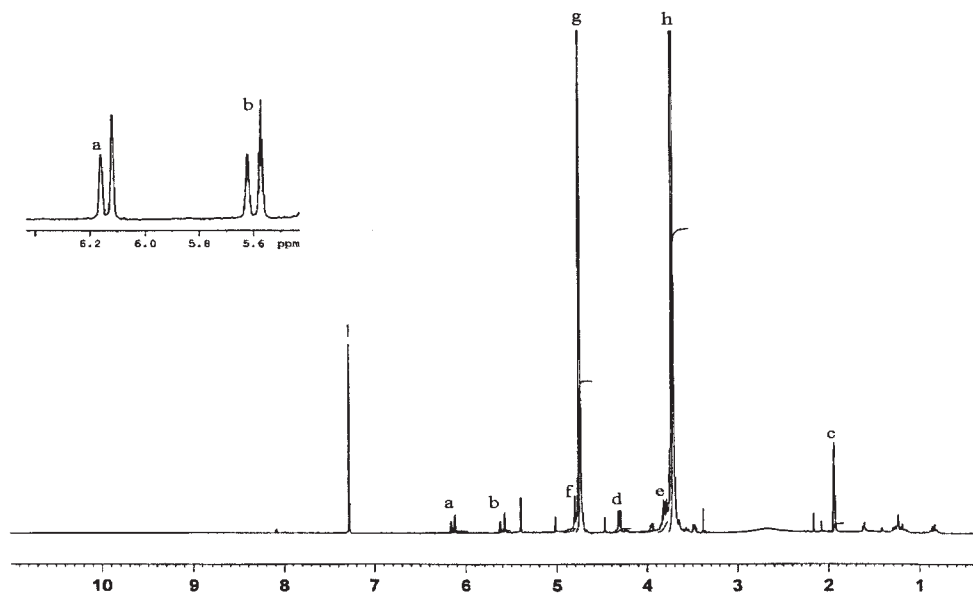


Figure 1  $^1\text{H-NMR}$  spectrum (300 MHz) of  $\alpha,\omega$ -bis-unsaturated PDXL (solvent,  $\text{CDCl}_3$ )

higher amount of  $\text{Mag-H}^+$  causes a certain lowering of the rate of functionalization, i.e., close to 65%. Apparently, because of its increased concentration, the catalyst attacks the acetal groups of PDXL, causing the destruction of some double bonds, as it has been demonstrated earlier.<sup>3,6</sup>

Second, it was found that the polymerization yields, which are defined as (amount of monomer converted/initial amount of monomer) $\times 100$ , were in the range 12–8 wt %. As shown in Figure 2, a yield of 85 wt % was reached for 2.7 wt % of  $\text{Mag-H}^+$ , and the use of a lower or higher amount of clay caused a decrease of the yield of the reaction.

Third, the number-average molecular weight of PDXL synthesized with different amounts of catalyst, obtained by SEC, are given in Figure 3. It is observed that within the range tested (2.7–10 wt %), the molec-

ular weights are remarkably constant, close to  $5000 \text{ g mol}^{-1}$ .

#### Effect of reaction time

Figures 4 and 5 show, respectively, the yield and viscosity-average molecular weight of the synthesized  $\alpha,\omega$ -bis-unsaturated PDXL plotted against the reaction time for different amounts of DXL and methacrylic anhydride on the same basis as in Table II. An optimum reaction time that gave samples with the highest molecular weight and yield was observed, in all cases.

In the early stages of the reaction (90 min), the polymerization was slow and the yield was between 22.2 and 33.5 wt %, and then it accelerated sharply to reach a maximum of 92.4 wt % in 315 min (Fig. 4).

TABLE I  
Molecular Characteristics of  $\alpha,\omega$ -bis-Unsaturated PDXL Macromonomers Synthesized in Bulk

Mag- $\text{H}^+$ (%)	$M_w^a$	$M_n^b$	$M_n^c$	$I^d$	$M_v^e$	Amount of double bonds <sup>f</sup> (%)	Yield (%)
1	—	—	5030	—	4700	20	12
2.7	7200	4500	5200	1.6	4900	87	85
4	7300	4550	—	1.6	5000	—	70
6	8400	4600	7100	1.82	5500	65	66
10	8500	5500	7800	1.54	6800	75	53
20	6900	4500	7300	1.53	5500	62	62

All molecular weights are expressed in  $\text{g mol}^{-1}$ .

<sup>a</sup> Weight-average molecular weight determined by SEC.

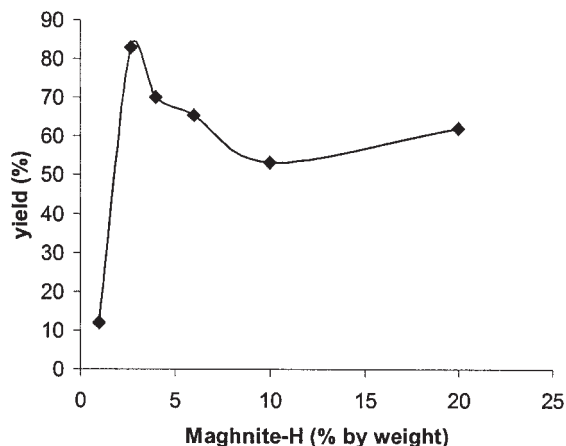
<sup>b</sup> Number-average molecular weight determined by SEC.

<sup>c</sup> Number-average molecular weight determined by UV.

<sup>d</sup> Polydispersity index.

<sup>e</sup> Viscosity-average molecular weight.

<sup>f</sup> Amount of double bonds measured by UV (in acetonitrile).

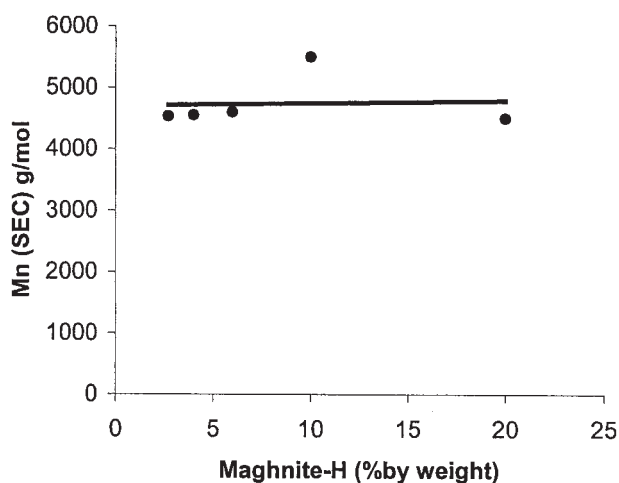


**Figure 2** Effect of the amount of Mag-H<sup>+</sup> on the yield of  $\alpha,\omega$ -bis-unsaturated PDXL.

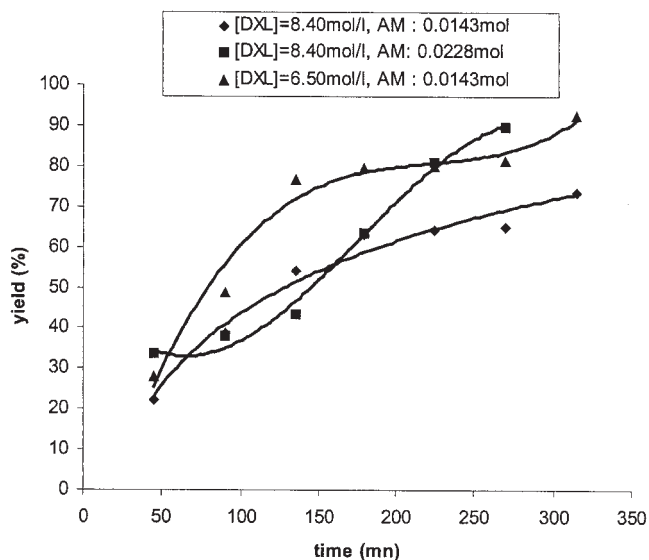
It was also observed that the viscosity-average molecular weight ( $M_v$ ) decreased significantly with increasing polymerization time (Fig. 5): indeed, relatively high molecular weights are formed at first, which then gradually decreases. This means that the yield may increase and, at the same time, the average molecular weight decreases. These observations are explained in terms of either depolymerization or transfer.

#### Effect of dioxolane and methacrylic anhydride contents

According to Figures 4 and 5, synthesis of  $\alpha,\omega$ -bis-unsaturated PDXL with different amounts of DXL and methacrylic anhydride showed similar profiles, although the molecular weights and yields of the compounds were different.



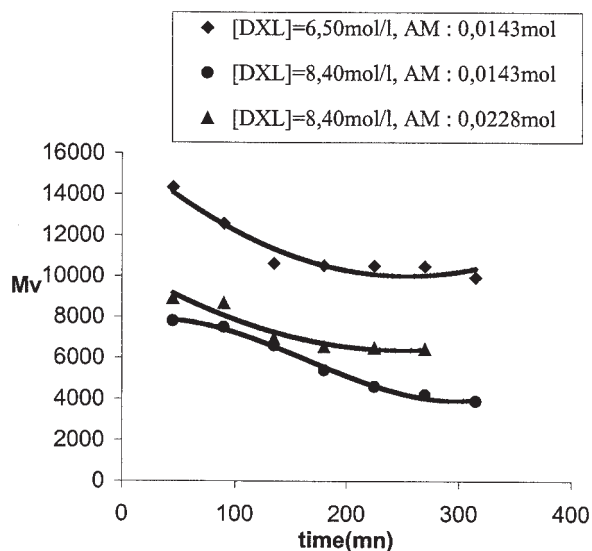
**Figure 3** Effect of the amount of Mag-H<sup>+</sup> on the number-average molecular weight of  $\alpha,\omega$ -bis-unsaturated PDXL



**Figure 4** Effect of the reaction time upon the conversion of DXL.

When the concentration of DXL is increased, the yield of the product decreases, and the average molecular weight determined by viscosity measurement decreases. This means that the growing reaction proceeds faster when using a small monomer concentration.

The polymerization with 0.0228 mol of methacrylic anhydride gave higher molecular weights than with 0.0143 mol, but a high yield (about 87 wt %) was achieved in 270 min in the first case, while in the second case high yield (70 wt %) was achieved in 315 min.



**Figure 5** Effect of the reaction time upon the viscosimetric molecular weight of the PDXL  $\alpha,\omega$ -bis-unsaturated.

**TABLE II**  
Average Molecular Weights and Yields of  $\alpha,\omega$ -bis-  
Unsaturated PDXL Synthesized in Dichloromethane  
(Maghnite-H<sup>+</sup>, 2.7 % by weight; T = 20°C)

[DXL] <sup>a</sup> (mol/L)	AM <sup>b</sup> (mol)	T (min)	<i>M<sub>v</sub></i> <sup>c</sup>	Yield (%)
6.50	0.0143	45	14,400	28.0
		90	12,600	48.9
		135	10,600	76.8
		180	10,500	79.6
		225	10,500	80.1
		270	10,500	81.2
8.40	0.0143	45	7,800	22.2
		90	7,500	38.6
		135	6,600	54.3
		180	5,400	63.2
		225	4,600	64.0
		270	4,200	64.8
8.40	0.0228	45	8,900	33.5
		90	8,680	38.0
		135	6,950	43.4
		180	6,550	63.6
		225	6,500	81.0
		270	6,430	89.6

<sup>a</sup> 1,3-Dioxolane.

<sup>b</sup> Methacrylic anhydride.

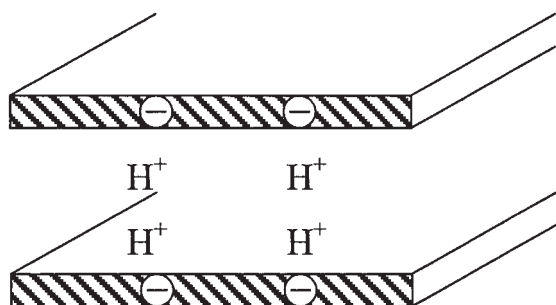
<sup>c</sup> Viscosimetric average molecular weight.

### Mechanism of polymerization

Mag-H<sup>+</sup> is a proton-exchanged montmorillonite sheet silicate clay. The montmorillonite lattice is composed of layers made up of two silica tetrahedral sheets with a central alumina octahedral sheet.<sup>7</sup> The protons carried by Mag-H<sup>+</sup> in the interlayer space induce cationic polymerization, and the montmorillonite sheets play the role of counter-anions (Scheme 2).

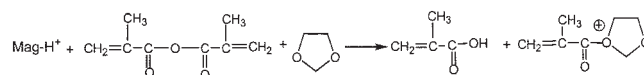
DXL, which is an heterocyclic monomer containing an acetal function, polymerizes only cationically, according to the following three steps:

1. Initiation: The first step in the polymerization of DXL with methacrylic anhydride is the protona-

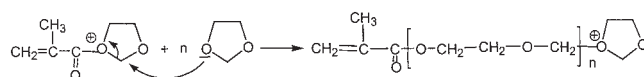


Scheme 2 Schematic representation of Mag-H<sup>+</sup>

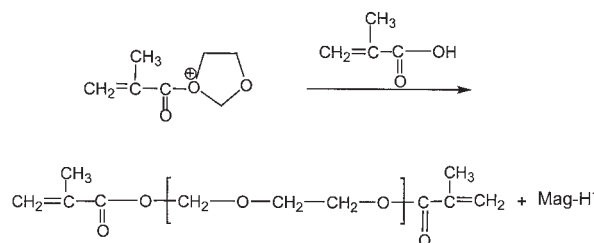
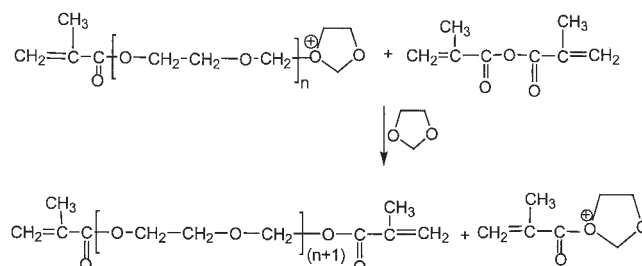
tion of methacrylic anhydride by the Mag-H<sup>+</sup>. Then, initiation occurs through formation of a secondary oxonium ion derived from the monomer.



2. Propagation: The propagation takes place through nucleophilic attack of oxygen onto a carbon of the oxonium ion.



3. Termination and chain transfer:



### 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 PDXL bis-macromonomers.
- We investigated the reaction conditions for polymerization of DXL with methacrylic anhydride. The yield and the molecular weight of the synthesized  $\alpha,\omega$ -bis-unsaturated PDXL depend on both the amount of Mag-H<sup>+</sup> used and the reaction time. The optimum reaction conditions for the synthesis of PDXL bis-macromonomers were defined as: 2.7 wt % of Mag-H<sup>+</sup>, 5% by molar concentration of methacrylic anhydride, and reaction time 1 h.
- Further work is under investigation to use these macromonomers for the synthesis, directly in water, of degradable hydrogels

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