

# Maghnite-H<sup>+</sup> as a Cationic Catalyst in the Synthesis of Poly(1,3-dioxolane) and $\alpha,\omega$ -Methacryloyloxy-Poly(1,3-dioxolane)

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**ABSTRACT:** The polymerization of 1,3-dioxolane catalyzed by Maghnite-H<sup>+</sup> (Mag-H<sup>+</sup>), a montmorillonite sheet silicate clay exchanged with protons, was investigated. The cationic ring-opening polymerization of 1,3-dioxolane was initiated by Mag-H<sup>+</sup> at different temperatures (20, 30, 50, and 70°C) in bulk and in a solvent (dichloromethane). The effects of the amount of Mag-H<sup>+</sup> and the temperature were studied. The polymerization rate and the average molecular weights increased with an increase in the temperature and the proportion of the catalyst. These results indicated the

cationic nature of the polymerization and suggested that the polymerization was initiated by proton addition to the monomer from Mag-H<sup>+</sup>. Moreover, we used a simple method, in one step in bulk and in solution at room temperature (20°C), to prepare a telechelic bismacromonomer:  $\alpha,\omega$ -bisunsaturated poly(1,3-dioxolane). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 78–82, 2006

**Key words:** cationic polymerization; clay; telechelics

## INTRODUCTION

Over the past years, the polymerization of cyclic acetal has attracted much attention, its mechanism has been studied,<sup>1</sup> and it is now possible to control the synthesis of poly(1,3-dioxolane) (PDXL) and to prepare it with a controlled molecular weight.<sup>2</sup> There is a diversity of applications, such as films for packaging materials, binders, molded materials, film casting, plastic bags, controlled drug release, and bioseparation. Indeed, PDXL with functional groups is more interesting because it is used in the preparation of hydrogels,<sup>3–6</sup> which are suitable materials for numerous biomedical applications. Among the different ways of preparing such hydrogels, the homopolymerization of hydrophilic, bifunctional macromonomers, such as bifunctional poly(ethylene oxide),<sup>7,8</sup>  $\alpha,\omega$ -methacryloyloxy-PDXL,<sup>6,9</sup> and  $\alpha,\omega$ -acryloyloxy-PDXL,<sup>10–12</sup> represents a good approach. However, the latter macromonomers are synthesized by traditional methods in two steps: first, a diol such as ethylene glycol and classic initiators (Lewis acids) are used to prepare PDXL with hydroxyl groups at both chain ends,<sup>13</sup> and

in the second step,  $\alpha,\omega$ -methacryloyloxy-PDXL or  $\alpha,\omega$ -acryloyloxy-PDXL is prepared by the reaction of hydroxylated PDXL with methacrylic or acrylic acid.<sup>14</sup> Therefore, this process costs more and uses toxic catalysts that cannot be separated from the polymer.

We propose in this article a new method of preparing  $\alpha,\omega$ -methacryloyloxy-PDXL that is done in only one step. Indeed, to produce PDXL and  $\alpha,\omega$ -methacryloyloxy-PDXL, we use Maghnite-H<sup>+</sup> (Mag-H<sup>+</sup>), a new nontoxic cationic initiator of heterocyclic monomers<sup>15–22</sup> and vinyl monomers.<sup>23,24</sup> Mag-H<sup>+</sup> can be easily separated from the polymer and regenerated.<sup>15</sup> The effects of some factors, such as the amount of Mag-H<sup>+</sup>, the temperature, and the mechanism of polymerization, are discussed.

## EXPERIMENTAL

### Reagents

1,3-Dioxolane (1,3-DXL), methacrylic anhydride, anhydride acetic, and all solvents were purchased from Aldrich (France). 1,3-DXL and all solvents were purified by the usual methods, and methacrylic anhydride was distilled under reduced pressure before use.

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

The preparation of Mag-H<sup>+</sup> was carried out with a method similar to that described by Belbachir and Bensaoula.<sup>15</sup> Indeed, raw Mag-H<sup>+</sup> (20 g) was crushed

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Scheme 1

for 20 min with a Prolabo ceramic balls grinder (France). It was then dried through baking at 105°C for 2 h. Mag-H<sup>+</sup> was then weighed and placed in an Erlenmeyer flask together with 500 mL of distilled water. The Mag-H<sup>+</sup>/water mixture was stirred with a magnetic stirrer and combined with 0.25M sulfuric acid until saturation was achieved over 2 days at room temperature; the mineral was washed with water until it was sulfate-free and was dried at 150°C.

### Synthesis of PDXL

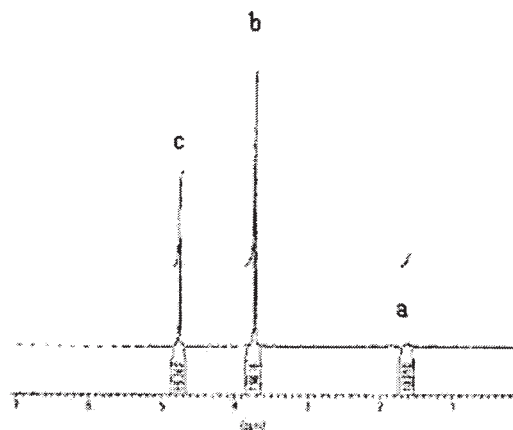
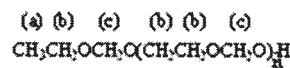
The polymerization of 1,3-DXL was carried out in bulk in a heterogeneous system. A mixture was prepared with 10 g of 1,3-DXL and 0.1 g of Mag-H<sup>+</sup> and was introduced into a 100-mL flask. The mixture was then stirred at 20°C with a magnetic stirrer under dry nitrogen. After 5 h, a quantity of dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was added, and the content was dried in vacuo to eliminate Mag-H<sup>+</sup>. A quantity of the solvent evaporated; afterwards, the product was precipitated in methanol at 0°C.

The resulting PDXL samples were characterized by size exclusion chromatography (SEC) for molar mass determination and by <sup>1</sup>H-NMR (AC 200NS, Bruker, France) and IR spectroscopy (FTIR Genesis, Mattson, UK).

### Synthesis of the PDXL bismacromonomer

Into a 100-mL flask that contained a quantity of 1,3-DXL were added methacrylic anhydride and Mag-H<sup>+</sup>, and the mixture was stirred in CH<sub>2</sub>Cl<sub>2</sub> at 20°C and under dry nitrogen with a magnetic stirrer. After 3 h, a quantity of CH<sub>2</sub>Cl<sub>2</sub> was added to the mixture, which was filtered and precipitated in ethanol at -70°C.

The macromonomer was then submitted to characterization by SEC for molar mass determination and by <sup>1</sup>H-NMR and IR spectroscopy. The SEC experiments were conducted on a Waters Associates apparatus with a Waters 401 refractive-index detector. Four microstyragel columns were used (30 cm long and 1

Figure 1 <sup>1</sup>H-NMR (200 MHz) spectrum of PDXL in CDCl<sub>3</sub>.

cm in diameter). The eluent was tetrahydrofuran (elution speed = 1 mL/min), and polyethylenoxide (PEO) standards were used for calibration.

## RESULTS AND DISCUSSION

### Polymerization of 1,3-DXL

The ring-opening polymerizations of heterocyclic monomers such as 1,3-DXL are initiated by Lewis acids, protic acid, and so forth. Recently, Ferrahi and Belbachir<sup>16</sup> and Ouis et al.<sup>21</sup> polymerized tetrahydrofuran, and Yahiaoui et al.<sup>18</sup> and Harrane et al.<sup>22</sup> polymerized propylene oxide and ε-caprolactone, respectively, with Mag-H<sup>+</sup> as an initiator. Indeed, the first part of this work concerns the synthesis of PDXL with Mag-H<sup>+</sup>. The ring-opening polymerization of 1,3-DXL was carried out in bulk and CH<sub>2</sub>Cl<sub>2</sub> in the presence of Mag-H<sup>+</sup> powder (heterogeneous system) at 20°C (Scheme 1 and Table I). The proof for this ring-opening polymerization mechanism was obtained by <sup>1</sup>H-

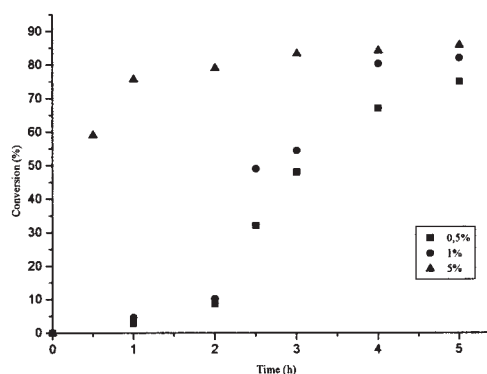
Figure 2 Effect of the amount of the catalyst on the polymerization of 1,3-DXL (75.15 mol/L 1,3-DXL, 20°C, and CH<sub>2</sub>Cl<sub>2</sub>).

TABLE I  
Experimental Results of the 1,3-DXL Polymerization

$m_{\text{DXL}}$ (g)	$m_{\text{clay}}$ (g)	$\rho$ (%)	$M_w$	$M_n$	$I$
10	0.1	82	3270	2156	1.5

$m$ , mass;  $w$ , weight;  $\rho$ , yield (%);  $I$ , polydispersity index ( $M_w/M_n$ ).

**TABLE II**  
Average Molecular Weights and Polydispersity Index (*I*)  
Values Determined by SEC

Mag-H <sup>+</sup> (%)	Yield (%)	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	<i>I</i> <sup>a</sup>
0.5	75	6,274	20,542	3.27
1	82	6,522	14,100	2.16
5	85.8	5,922	12,601	2.13

1,3-DXL: 75.15 mol/L, 20°C, CH<sub>2</sub>Cl<sub>2</sub>.

<sup>a</sup> *M<sub>w</sub>*/*M<sub>n</sub>*.

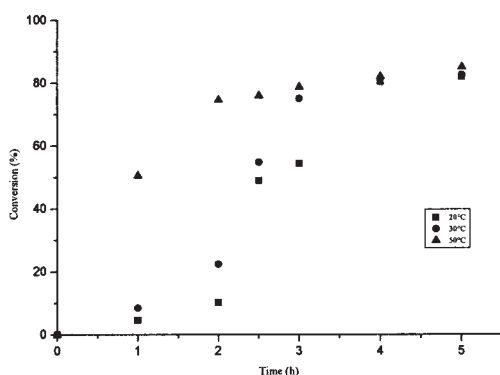
NMR spectroscopy (Fig. 1). IR spectroscopy exhibited two bands at 2935 and 2807 cm<sup>-1</sup> corresponding to methylene and a strong band at 3590 cm<sup>-1</sup> corresponding to hydroxy groups.

#### Effect of the amount of mag-H<sup>+</sup> on the polymerization

Figure 1 and Table II show the effects of the amount of Mag-H<sup>+</sup> (0.5, 1, and 5%) on the polymerization rate of 1,3-DXL and on the molecular weight of PDXL. The polymerization rate and molar mass increased with an increasing amount of Mag-H<sup>+</sup>. Therefore, the effect of Mag-H<sup>+</sup> as a cationic ring-opening polymerization initiator of 1,3-DXL was clearly shown.

#### Effect of the temperature on the polymerization

In the presence of Mag-H<sup>+</sup>, the cationic ring-opening of PDXL was carried out in CH<sub>2</sub>Cl<sub>2</sub> at 20, 30, and 50°C, and the effect of temperature on the polymerization was examined. The results are shown in Figure 3 and Table III. The rate of polymerization and weight-average molecular weight (*M<sub>w</sub>*) increased with the temperature. Tsubokawa<sup>25</sup> found similar results in the cationic ring-opening polymerization of 1,3-DXL initiated by CO<sup>+</sup>CLO<sub>4</sub> groups on carbon black.



**Figure 3** Effect of the temperature on the polymerization of PDXL catalyzed by Mag-H<sup>+</sup> (0.1 g; 75.15 mol/L 1,3-DXL and CH<sub>2</sub>Cl<sub>2</sub>).

**TABLE III**  
Average Molecular Weights Polydispersity Index (*I*)  
Values Determined by SEC

Temperature (°C)	Yield (%)	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	<i>I</i> <sup>a</sup>
20	82	2156	3270	1.52
30	82.6	2990	6590	2.20
50	85	4770	8950	1.87

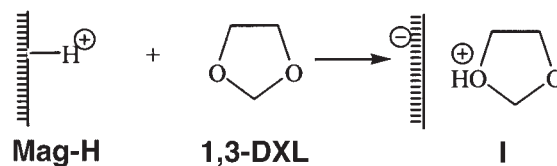
Mag-H: 0.1 g; 1,3-DXL: 75.15 mol/L, CH<sub>2</sub>Cl<sub>2</sub>.

<sup>a</sup> *M<sub>w</sub>*/*M<sub>n</sub>*.

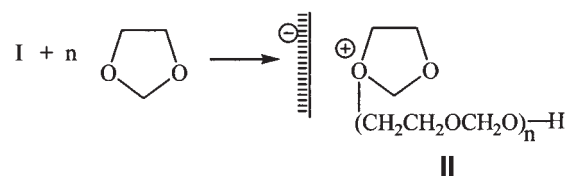
#### Mechanism of the polymerization

The polymerization of 1,3-DXL is considered to be initiated only through a cationic path. Protons carried by Mag-H<sup>+</sup> initiate the cationic polymerization of 1,3-DXL, and Mag-H<sup>+</sup> acts as a counterion. Propagation and termination then take place by the conventional cationic mechanism.

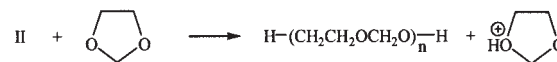
Scheme 2 presents the initiation. The initiation is



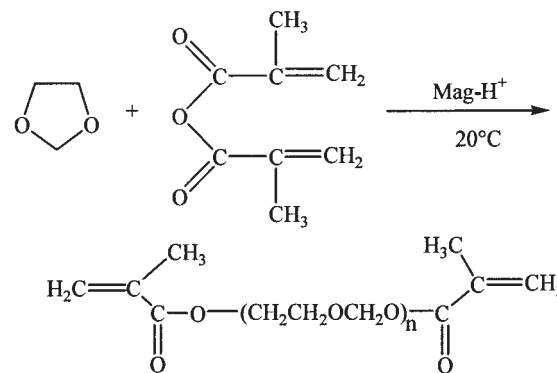
Scheme 2



Scheme 3



Scheme 4



Scheme 5

TABLE IV  
Experimental Results of the Preparation of PDXL  
Bismacromonomers

$m_{\text{DXL}}$ (g)	$m_{\text{TDA}}$ (g)	$m_{\text{AM}}$ (g)	$V_{\text{CH}_2\text{Cl}_2}$ (mL)	$M_n$ (UV)	$M_n$ (SEC)	$M_w$ (SEC)	$I$
30	0.72	0.5	0	3,000	3,565	8,695	2.4
30	0.72	0.5	30	7,200	6,019	12,326	2.0

$m$ , mass;  $w$ , weight;  $V_{\text{CH}_2\text{Cl}_2}$  is volume (mL);  $I$ , polydispersity index ( $M_w/M_n$ ).

conducted between the initiator and the first molecule of the monomer to form the active species. Scheme 3 shows the propagation, and Scheme 4 presents the termination.

### Synthesis of $\alpha,\omega$ -bisunsaturated PDXL

1,3-DXL can be polymerized to form dihydroxylated telechelic polymers, whose end groups can be reacted with monomers to form PDXL bismacromonomers. Indeed, Franta et al.<sup>6</sup> synthesized  $\alpha,\omega$ -methacryloyloxy-PDXL by adding methacrylic acid to hydroxylated PDXL, and Du et al.<sup>12</sup> synthesized PDXL bismacromonomers by two methods: the acrylation of dihydroxylated PDXL with acrylic acid and the addition of 2-hydroxyethylmethacrylate as a transfer agent during the polymerization. In this work, we propose a new method to prepare PDXL bismacromonomers in one step with Mag-H<sup>+</sup> as an initiator and by the addition of methacrylic anhydride as a transfer agent to the cationic polymerization system (Scheme 5). The cationic polymerization was carried out in bulk and in  $\text{CH}_2\text{Cl}_2$ , as shown in Table III.

<sup>1</sup>H-NMR spectroscopy was used for end-group identification, as shown in Figure 4. The double-bond content was also obtained by UV spectroscopy in acetonitrile (UV 2101 PC, Shimadzu, Japan; maximum

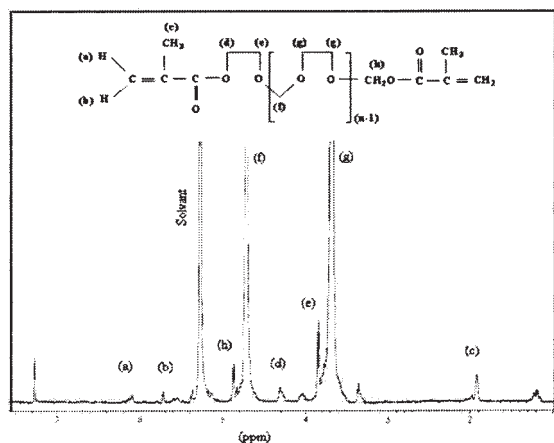
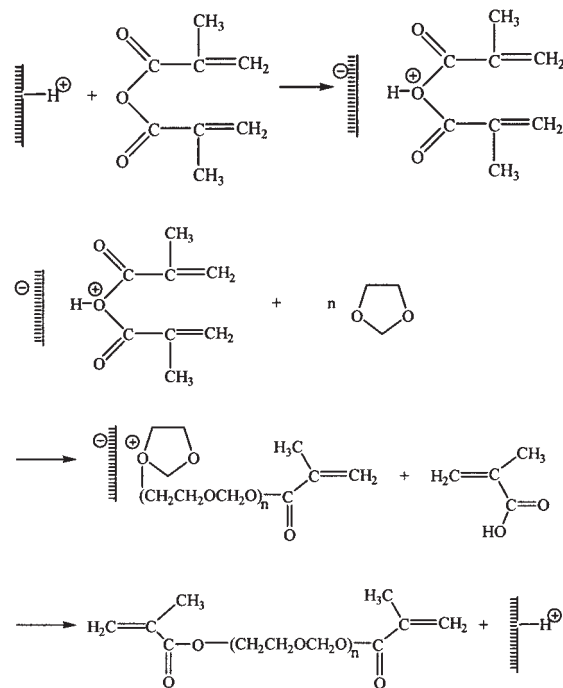


Figure 4 <sup>1</sup>H-NMR (200 MHz) spectrum of  $\alpha,\omega$ -methacryloyloxy-PDXL in  $\text{CDCl}_3$ .



Scheme 6

wavelength = 200 nm, extinction coefficient = 8511 L mol<sup>-1</sup> cm<sup>-1</sup>, reference = ethyl methacrylate).

The IR spectrum exhibited a strong band at 1720 cm<sup>-1</sup> corresponding to a carbonyl ester.

The number-average molecular weights ( $M_n$ 's) of the PDXL bismacromonomers are given in Table IV. The values measured by SEC and UV spectroscopy are in good agreement.

### Synthesis mechanism of $\alpha,\omega$ -methacryloyloxy-PDXL

Methacrylic anhydride acts as a transfer agent, and then the chain-transfer step proceeds to give  $\alpha,\omega$ -bisunsaturated PDXL (Scheme 6).

## CONCLUSIONS

The cationic polymerization of 1,3-DXL was initiated by Mag-H<sup>+</sup> powder in a heterogeneous phase. The polymerization was considered to be initiated by proton addition from Mag-H<sup>+</sup> to the monomer, and propagation proceeded with Mag-H<sup>+</sup> as a counter-ion.

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