Macromol. Symp. **2006**, 245–246, 1–4 DOI: 10.1002/masy.200651301

Maghnite, a Green Catalyst for Cationic Polymerization of Vinylic and Cyclic Monomers

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Summary: Maghnite-H is a nontoxic catalyst for cationic polymerization of vinylic and heterocyclic monomers. This catalyst is issued from the proton exchange of Algerian montmorillonite clay. One application of this catalyst is to produce polydioxolane derivatives. The polymerization of 1,3-dioxolane catalyzed by Maghnite-H; (Mag-H), was investigated. The cationic ring-opening polymerization of 1,3-dioxolane was initiated by Mag-H at different temperatures (20, 30, 50, and 70 °C) in bulk and in a solvent (dichloromethane). The effects of the amount of Mag-H 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. Moreover, we used a simple method, in one step in bulk and in solution at room temperature (20 °C), to prepare a telechelic bismacromonomer: bis-unsaturated poly(1,3-dioxolane).

Keywords: 1,3-dioxolane; catalyst; Maghnite-H; poly(1,3-dioxolane)

Introduction

Over the past years, the polymerization of cyclic acetal has attracted much attention, its mechanism has been studied,[1] and it is now possible to control the synthesis of poly(1,3-dioxolane) (PDXL) and to prepare it with a controlled molecular weight.[2] 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,[3–6] 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),[7,8] methacryloyloxy-PDXL,[6,9] and acryloyloxy-PDXL,[10–12] 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[13] and in the second step methacryloyloxy-PDXL or acryloyloxy-PDXL is prepared by the reaction of hydroxylation PDXL with methacrylic or acrylic acid.[14]

We propose in this article a new method of preparing methacryloyloxy-PDXL that is done in only one step. Indeed, to produce PDXL and methacryloyloxy-PDXL, we use Maghnite-H (Mag-H), a new nontoxic cationic initiator of heterocyclic monomers[15–22] and vinyl monomers.[23,24] Mag-H can be easily separated from the polymer and regenerated.[15]

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[16] and Ouis et al.[21] polymerized tetrahydrofuran, and Yahiaoui et al.[18] and Harrane

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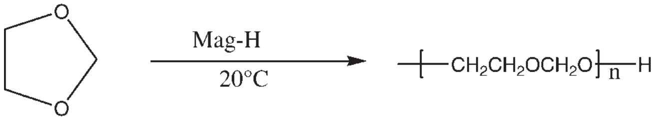


Scheme 1.

et al.[22] polymerized propylene oxide and caprolactone, respectively, with Mag-H as an initiator. Indeed, the first part of this work concerns the synthesis of PDXL with Mag-H. The ring-opening polymerization of 1,3-DXL was carried out in bulk and CH_2Cl_2 in the presence of Mag-H powder (heterogeneous system) at 20 °C (Scheme 1 and Table 1). The proof for this ring-opening polymerization mechanism was obtained by ^{1}H- NMR spectroscopy (Figure 1). IR spectroscopy exhibited two bands at 2935 and 2807 cm^{-1} corresponding to methylene and a strong band at 3590 cm^{-1} corresponding to hydroxy groups.

Table 1.
Experimental Results of the 1,3-DXL Polymerization.

m_{DXL}	m_{clay}	Conv%	Mw	Mn	Mw/Mn
10	0.1	82	3270	2156	1.5

Table 2 shows the effects of the amount of Mag-H (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. Therefore, the effect of Mag-H as a cationic ring-opening polymerization initiator of 1,3-DXL was clearly shown.

In the presence of Mag-H, the cationic ring opening of PDXL was carried out in CH_2Cl_2 at 20, 30, and 50 °C, and the effect of temperature on the polymerization was examined. The results are shown in Table 3. The rate of polymerization and weight average molecular weight (M_w) increased with the temperature. Tsubokawa[25] found similar

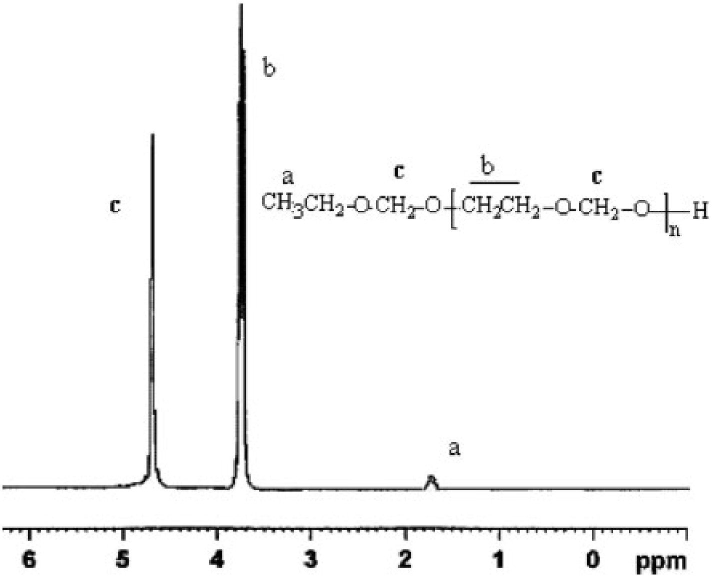


Figure 1.
1 H-NMR (200 MHz) spectrum of PDXL in $CDCl_3$.

Table 2.
Average Molecular Weights and Polydispersity Index (I)Values Determined by SEC.

Mag-H(%)	Conv%	Mn	Mw	Mw/Mn
0.5	75	6274	20542	3.27
1	82	6522	14100	2.16
5	85.8	5922	12601	2.13

Table 3.
Average Molecular Weights Polydispersity Index (I) Values Determined by SEC.

Temperature °C	Conv%	Mn	Mw	Mw/Mn
20	82	2156	3270	1.52
30	82.6	2990	6590	2.20
50	85	4770	8950	1.87

results in the cationic ring-opening polymerization of 1,3-DXL initiated by $COClO_4$ groups on carbon black.

Synthesis of 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.[6] synthesized methacryloyloxy-PDXL by adding methacrylic acid to hydroxylated PDXL, and Du et al.[12] 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 as an initiator and by the addition of methacrylic anhydride as a transfer agent to the cationic polymerization system (Scheme 2). The cationic polymerization was carried out in bulk and in CH_2Cl_2, as shown in Table 4.

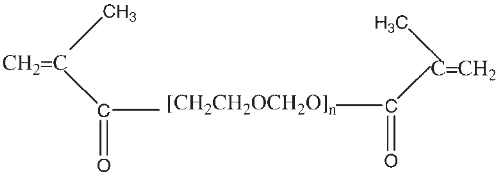
^{1}H-NMR spectroscopy was used for end-group identification. The double-bond content was also obtained by UV spectroscopy in acetonitrile. The IR spectrum exhibited a strong band at 1720 cm^{-1} corresponding to a carbonyl ester. The number average molecular weights (Mn's) of the PDXL bismacromonomers are given in Table 4. The values measured by SEC and UV spectroscopy are in good agreement.

Conclusion

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

Table 4.
Experimental Results of the Preparation of PDXL Bismacromonomers.

m_{DXL}(g)	m_{clay}(g)	m_{Am}(g)	VCH_2Cl_2	Mn(SEC)	Mw(SEC)	Mw/Mn
30	0.72	0.5	0	3565	8695	2.4
30	0.72	0.5	30	6019	12326	2.0



Scheme 2.

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