

CATIONIC RING-OPENING POLYMERIZATION OF TETRAHYDROFURAN WITH KEGGIN-TYPE HETEROPOLYCOMPOUNDS AS SOLID ACID CATALYSTS*

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Abstract Three Keggin-type heteropolyanions, namely $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$, $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ were prepared and tested in the ring-opening polymerization reaction of tetrahydrofuran. The effects of the counter-cation (H^+ , NH_4^+) and the peripheral atoms (Mo, W) on the polymerization were investigated. It has been found that when the protons of $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ were replaced by the ammonium cations the polymerization rate decreased dramatically. Whereas, when the peripheral atoms (Mo) were replaced by their homologous (W), the polymerization rate increased twofold. As for the viscosity average molecular weight (M_v) of polymer products, it was found that the high molecular weight (7930) was obtained by using $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$. The molecular weight (M_v) obtained by $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ was 6470 and 6810, respectively.

Keywords: Tetrahydrofuran; Heteropoly compounds; Ring opening polymerization; Cyclic ether; Solid acid.

INTRODUCTION

The ring-opening polymerization of cyclic monomers is a useful method to prepare new polymers of novel structure especially microstructure controlled copolymers that are otherwise difficult to obtain by conventional polymerization methods. Thus, wide varieties of organic compounds have been exploited as possible monomers to secure polymers of novel structures *via* ring-opening polymerization. Among cationically polymerizable compounds, cyclic ethers are of major interest in the field of polymer chemistry, because polyethers produced by polymerization possess the high polarisability and flexibility of their main chain.

Among cyclic monomers, the polymerization of tetrahydrofuran has been the subject of a large number of papers^[1–6]. The polymerization could be initiated by electrophilic agents such as Brønsted acids (HCl , H_2SO_4 , HClO_4 , *etc.*) and also by Lewis acids (AlCl_3 , $\text{BF}_3\cdot\text{OEt}_2$, TiCl_4 , *etc.*). However, the protonic acid catalysts used are very noxious, corrosive and expensive, and the Lewis acids required great amount. Increasing environmental concerns in recent years call for a more effective catalytic process. In this regard, studies have been made in the development of solid acids to replace aggressive and dangerous homogeneous acid to overcome the problem of separating the catalyst from the products and from the disposal of solid/liquid waste. Solid Brønsted acids with super acidic character, such as Keggin-type heteropolyacids have been used as efficient catalysts for a variety of organic reactions. Due to their unique combination of acid-base and redox properties, they have been used successfully as catalysts in both homogeneous and heterogeneous media^[7–11]. During the last decades various

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research groups have found that heteropolyacids are suitable initiators for cationic polymerization of tetrahydrofuran^[12–19]. Izumi *et al.*^[19] found that 12-tungstophosphoric acid was more active than HClO_4 in the polymerization of THF.

This paper deals with the ring opening polymerization of tetrahydrofuran (THF) catalyzed by Keggin-type heteropolycompounds. Bulk polymerization reactions were performed at room temperature using $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$, and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ as catalysts. The effects of the counter-cation (H^+ , NH_4^+) and the peripheral atoms (Mo, W) on the bulk polymerization reactions were investigated.

EXPERIMENTAL

Preparation of the Catalysts

$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ were prepared in a classical way as described in the literature^[21]. $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ was prepared using the following procedure: the compound is precipitated by adding slowly the stoichiometric required amount of ortho-phosphoric acid (H_3PO_4 85%) and perchloric acid (HClO_4 70%) to an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. The Keggin-type anion $\text{PMo}_{12}\text{O}_{40}^{3-}$ is formed in solution at acid conditions, and the insoluble ammonium 12-molybdophosphate salt is immediately precipitated.

Catalysts Characterization

The Keggin structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$, and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ was checked by means of infrared (IR) spectroscopy. The number of protons, ammonium cations and water molecules in the heteropolycompounds was checked by means of thermogravimetry (TGA). IR spectra were recorded with an infrared spectrometer GENESIS II-FTIR ($4000\text{--}400\text{ cm}^{-1}$) as KBr pellets. Thermogravimetric analysis (TGA) was carried out on a PERKIN-ELMER TGA instrument with a heating rate of 5 K/min in flowing N_2 .

Procedure and Polymer Characterization

THF polymerization experiments were carried out in a stirred flask at 20°C. Typically, a fixed amount of catalyst was added to the mixture of THF (10 mL) and acetic anhydride (2 mL) under stirring. It was found that the polymerization did not occur without anhydride acetic. Polymerization was terminated with the addition of saturated NaOH aqueous solution and then stirred for 5 min. At the end of the reaction, the precipitated polymer was filtrated off, and then dissolved in butanone. After removing the catalyst by filtration, the polymer was precipitated in methanol for characterization and molecular weight measurements.

Molecular weights were determined by measurement of viscosity. The inherent viscosity of poly(THF) obtained was measured in tetrahydrofuran solutions at 25°C by using an Ubbelohde type viscometer. The viscosity average molecular weight (M_v) was calculated by the following equation: $[\eta] = 2 \times 10^{-4} M_v^{0.65}$. $^1\text{H-NMR}$ spectra were recorded on a Bruker Avance 400 MHz spectrophotometer with 5 mm NMR tubes using deuterated acetone- D_6 as solvent. Differential scanning calorimeter (DSC) model DSC-60 made by Shimadzu was utilized here. The specimens weigh about 12 mg each. Each specimen was placed in aluminum pans. The pan was placed in the DSC's oven in air at atmospheric pressure. Specimens were heated at a constant heating rate of 5 K/min to 150°C. The specimen was held there for 5 min then cooled at 5 K/min to room temperature.

RESULTS AND DISCUSSION

Characterization of Catalysts

Infrared spectra

The spectra of the catalysts used, are shown in Fig. 1. The IR spectra have been assigned according to Refs. [20, 21]. The main characteristic features of the Keggin structure are observed at $1080\text{--}1060\text{ cm}^{-1}$ ($\nu_{\text{as}} \text{P}=\text{O}_a$), $990\text{--}960\text{ cm}^{-1}$ ($\nu_{\text{as}} \text{Mo}=\text{O}_d$), $900\text{--}870\text{ cm}^{-1}$ ($\nu_a \text{Mo}=\text{O}_d-\text{Mo}$) and $810\text{--}760\text{ cm}^{-1}$ ($\nu_{\text{as}} \text{Mo}=\text{O}_c-\text{Mo}$), respectively. Besides the above characteristic frequencies of the heteropolyanion, there are a broad band at 3212 cm^{-1} and a sharp band at 1414 cm^{-1} , which are the feature absorption of NH_4^+ groups, these results indicate the formation of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ ^[20].

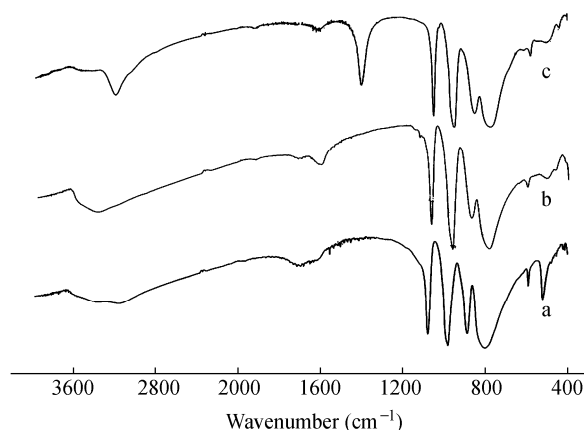


Fig. 1 IR spectra of (a) $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$, (b) $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ and (c) $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$

Thermogravimetric analysis

The number of hydrogen atoms, ammonium cations and water molecules in the heteropolycompounds can be determined by thermogravimetric analysis by the loss of weight as soon as the temperature is increased. The obtained results suggest the following chemical formulae: $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$, and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$. The TG results are consistent with published results^[22, 23].

Polymerization Reaction

Polymer product characterization

In order to investigate the activity of the heteropolyacids and the ammonium salt catalysts for the polymerization of THF, we carried out the bulk polymerization over $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$. The results showed that these three solid acid catalysts could induce the ring opening polymerization of tetrahydrofuran as evidenced by ^1H -NMR (Fig. 2 and Table 1) and IR spectra (Fig. 3).

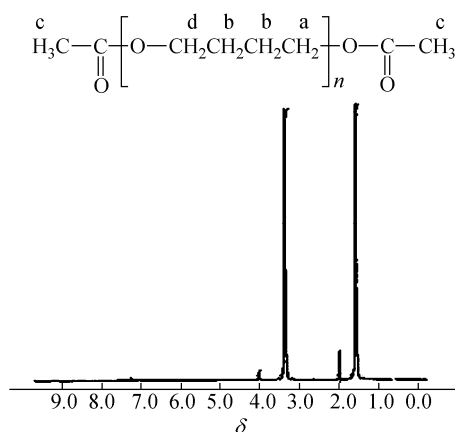


Fig. 2 ^1H -NMR spectrum of poly(THF) in CD_3OCD_3

Table 1. Chemical shift of polymer protons

Proton type	a	b	c	d
δ	4	1.57	2	3.39

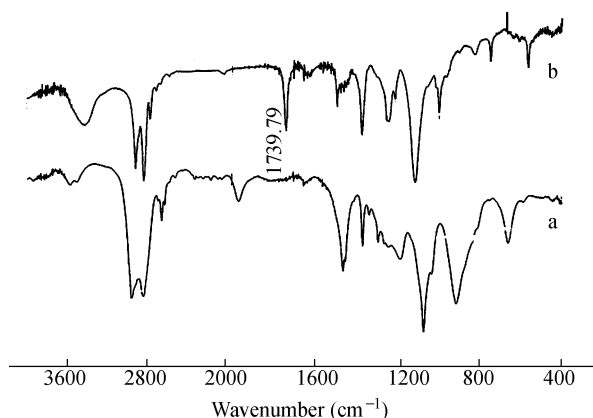
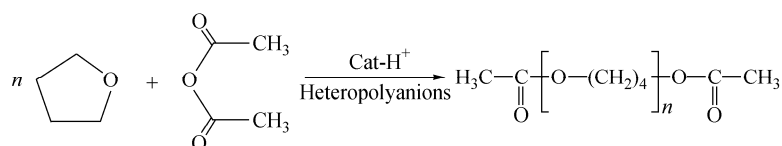


Fig. 3 Infrared spectra of initial samples of (a) monomer THF and (b) poly(THF)

The IR spectrum is depicted in Fig. 3. It can be seen from this result that the band at 1739.79 cm^{-1} is assigned to the carbonyl of the ester^[24] in the polymer obtained according to the following reaction.



Catalysts reactivity

The reactivity of these prepared catalysts in the polymerization of tetrahydrofuran was depicted in Fig. 4. When the polymerization was catalyzed by $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$, the results showed that the conversion increased with time, and then a decline of the conversion was observed. A possible explanation is probably related to that a depolymerization had occurred. In fact, it was observed at longer reaction times a decrease in the viscosity of the polymer. The maximum yield (50.5%) was obtained at 4 h. When the protons of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$ were replaced by ammonium cations (NH_4^+), the ammonium salt obtained $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot 4\text{H}_2\text{O}$, showed a dramatic decrease in the polymerization rate. In fact, no measurable yields were observed before 12 h of reaction time. Thus to obtain significant conversions, we carried out the polymerization for 60 h. The maximum yield (53.1%) was obtained at 60 h. As for the peripheral atoms, the results showed that when the Mo addenda atoms were replaced by their homologous W atoms, an increase of the polymerization rate was observed. However, like that what was observed in the case of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$, a decline of the conversion was observed. It worth noting

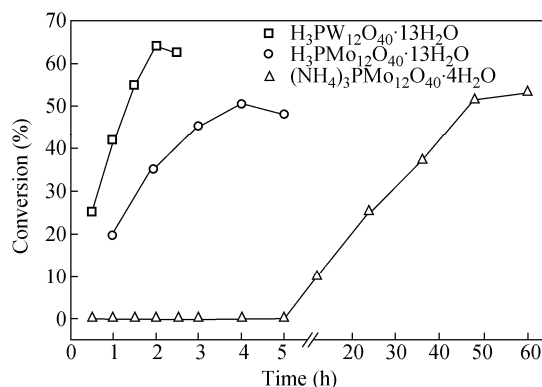


Fig. 4 Effect of the reaction time on the polymer yield of the polymerization catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$ and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot 4\text{H}_2\text{O}$

that when the reaction was catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$ the maximum value of the polymer yield (63.9%) was obtained at only 2 h. Additionally, this yield was the highest among those obtained by these tested catalysts.

The effect of the counter-cation and the peripheral atoms on the conversion and on the polymer properties was also investigated. The results are reported in Table 2 and Fig. 5. It can be seen that the molecular weight of the polytetrahydrofuran obtained by the use of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$ as catalyst has the highest value. The polymerization yield and the molecular weight (7930, 6470 and 6810) of poly(THF) obtained are directly proportional to the acidity strength of the heteropolyacids ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O} > \text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O} > (\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot 4\text{H}_2\text{O}$ ^[25]). Thus, this result suggests that strong Brønsted acidity is suitable for the ring opening polymerization of cyclic ethers. Figure 5 shows the DSC thermograms of the polytetrahydrofuran obtained with these three catalysts. Comparison of thermograms indicates that the melting temperature (T_m) increases with the increase of the acidity strength of the catalysts. The results are in agreement with those obtained for the average molecular weight (M_v).

Table 2. Effect of the counter-cation and the peripheral atoms on the viscosimetric average molecular weight (M_v) and on the conversion

Catalyst	$\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$	$(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot 4\text{H}_2\text{O}$	$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$
M_v	6470	6810	7930
Yield (%)	50.5	53.1	63.9
Time (h)	4	60	2

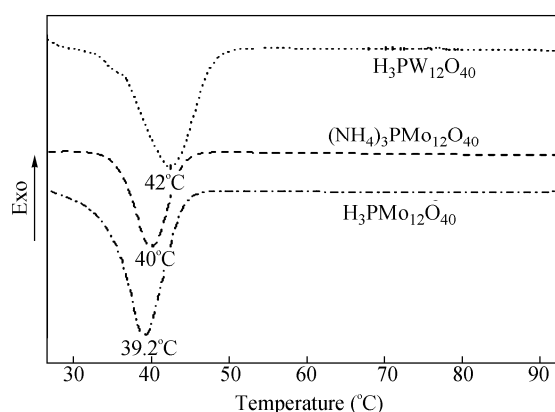


Fig. 5 Effect of the counter-cation and the peripheral atoms on the melting temperature of poly(THF)

CONCLUSIONS

Bulk polymerization of THF was performed using $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$, $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot 4\text{H}_2\text{O}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$. The results showed that $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$ was the effective catalyst for the ring opening polymerization reaction owing to its strong Brønsted acidity. It can be considered as the suitable catalyst for preparing poly(THF) as a soft segment for thermoplastic elastomers. The use of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as a solid acid catalyst, instead of the usual soluble inorganic acids, is a contribution to reduction of waste. In fact, a simple filtration is sufficient to recover the catalyst.

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