

Article

Reactivity of Heteropolymolybdates and Heteropolytungstates in the Cationic Polymerization of Styrene

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Abstract: The two heteropolyacids $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, and their homologous salts $(NH_4)_3PW_{12}O_{40}$, and $(NH_4)_3PMo_{12}O_{40}$ were prepared and tested in the cationic polymerization of styrene. The results showed that the heteropolytungstates were more reactive than the heteropolymolybdates. It has been found that the yield and the viscosity average molecular weight (M_v) of polystyrene are directly proportional to the acidity strength of the heteropolyanions ($H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > (NH_4)_3PW_{12}O_{40} > (NH_4)_3PMo_{12}O_{40}$). The highest yield (68.0%) and M_v (7,930) were obtained by using $H_3PW_{12}O_{40}$. In addition, $H_3PW_{12}O_{40}$ polymerized the styrene under mild conditions and was recyclable, and could behave as a truly heterogeneous catalyst.

Keywords: heteropoly compounds; cationic polymerization; polystyrene; solid acid

1. Introduction

Modern chemical industry necessitates much more efficient usage of energy and resources, in order to minimize the undesirable environmental impact, competing with the rapidly growing population. In this context solid acid catalysts have attracted much attention in organic synthesis owing to their easy work-up procedures, easy filtration, and minimization of cost and waste generation due to reuse and recycling of these compounds [1]. The advantages of heterogeneous catalysts over homogeneous ones include stability (towards air and moisture), lack of corrosion, ease of handling, recovery and regeneration. Among the heterogeneous catalysts used, numerous works have reported the application of heteropolyanions as new materials in various fields.

Heteropolyanions are oxoclusters of transition metals such as W and Mo. They are discrete species, insoluble in non-polar solvents but highly soluble in polar ones without structure change. Due to their unique combination of acid-base and redox properties these kinds of solids have been used successfully as solid catalysts in their acidic or their salt form for acid and redox catalyzed reactions in both homogeneous and heterogeneous media [2–7]. Because of their stronger acidity, they generally exhibit higher catalytic activity than conventional acids, such as sulfuric and nitric acids [8–10]. Recently heteropolyanions had been introduced into the field of polymer science [11–15]. Chen *et al.* [11] have studied the polymerization of styrene over 12-molybdophosphoric acid. To the best knowledge of the authors, other heteropolyanions with much stronger acidity, namely 12-tungstophosphoric acid were not investigated. Thus, in this paper, the investigation was extended to a series of heteropoly compounds having W and Mo as added atoms and we have attempted to compare the reactivity between W and Mo in the cationic polymerization of styrene. It is worth noting that Mo and W heteropolyoxoanions have attracted much attention in the area of catalytic reactions [3,12].

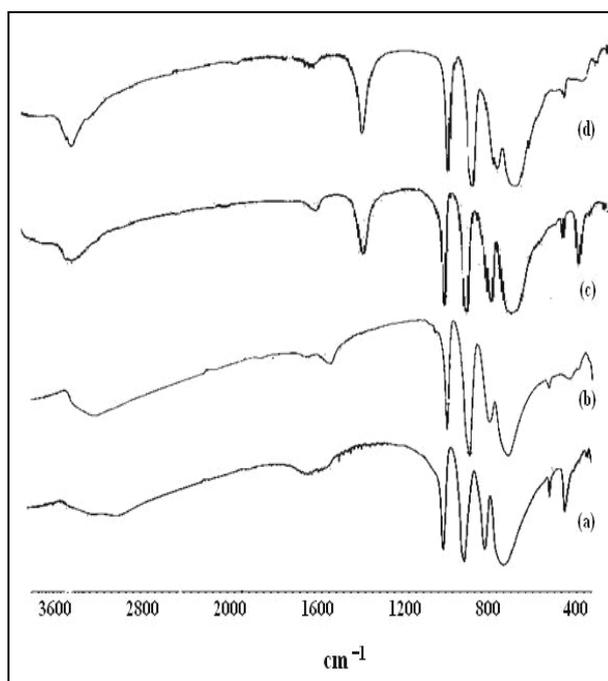
2. Results and Discussion

2.1. Catalyst characterization

2.1.1. Infrared spectra

The spectra of the catalysts used are shown in Figure 1. The IR spectra have been assigned according to [16,17]. The main characteristic features of the Keggin structure are observed at $1,080\text{--}1,060\text{ cm}^{-1}$ ($\nu_{\text{as}}\text{ P-O}_a$), at $990\text{--}960\text{ cm}^{-1}$ ($\nu_{\text{as}}\text{ M-O}_d$), at $900\text{--}870\text{ cm}^{-1}$ ($\nu_a\text{ M-O}_d\text{-M}$), and at $810\text{--}760\text{ cm}^{-1}$ ($\nu_{\text{as}}\text{ M-O}_c\text{-M}$), respectively ($\text{M} = \text{W}$ or Mo).

Figure 1. IR spectra of: a) $\text{H}_3\text{PW}_{12}\text{O}_{40}$; b) $\text{H}_3\text{PMo}_{12}\text{O}_{40}$; c) $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$; d) $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$.

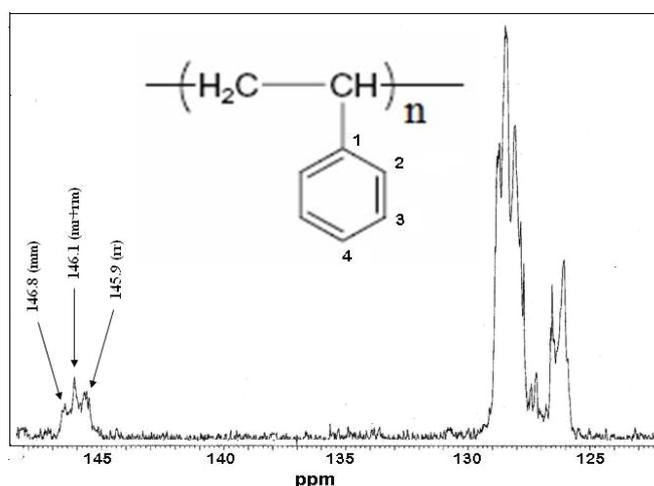


Besides the above characteristic frequencies of the heteropolyanions, in spectra c) and d) there is a broad band at $3,212\text{ cm}^{-1}$, and a sharp band at $1,414\text{ cm}^{-1}$, which are characteristic absorptions of the NH_4^+ group, which indicates the formation of the ammonium salts $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ [16].

2.1.2. Characterization of the polymer product

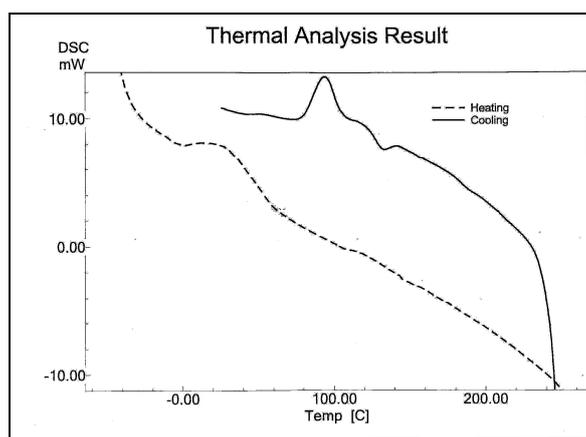
The results showed that these four solid acid catalysts induced the polymerization of styrene, as evidenced by ^{13}C -NMR (Figure 2).

Figure 2. 100 MHz ^{13}C -NMR spectrum in CDCl_3 of polystyrene obtained with $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst.



The analysis of the ^{13}C -NMR spectra showed the signals of aliphatic carbon atoms at 40.4 and 43.8 ppm and signals corresponding to the *meta*, *ortho* and *para* carbon atoms of the aromatic ring in the region between 125.5 and 128.0 ppm. The aromatic C_1 -carbons gave three signals at 145.3, 145.7 and 146.1 ppm attributed to the (rr), (mr + rm) and (mm) diads, respectively, according to [18]. It was found that this kind of catalyst essentially gave a mixture of diads (mr + rm) (65–70%), rr (20–25%) and a small quantity of diad mm (10–15 %).

Figure 3. The DSC thermograms of polystyrene material obtained at $20\text{ }^\circ\text{C}/\text{min}$ heating and cooling rate.



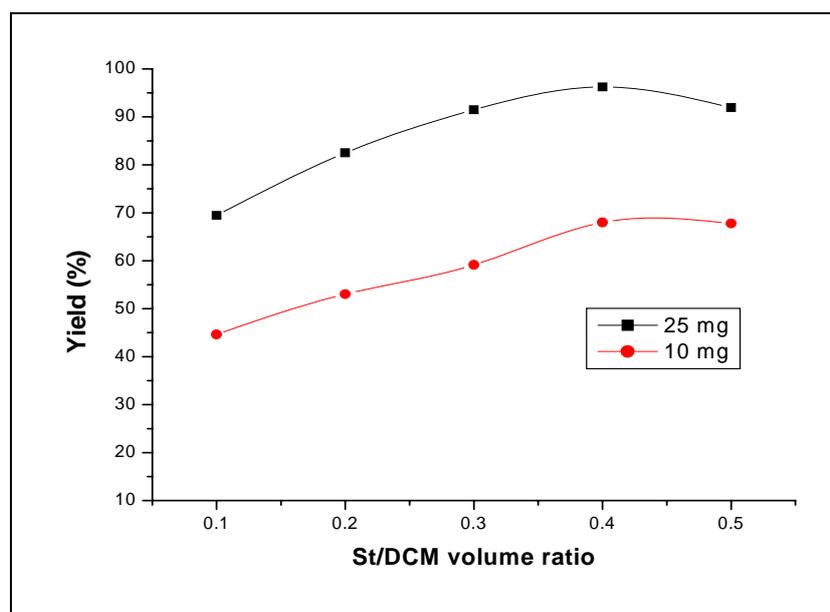
Differential scanning calorimetry studies characterized further these polystyrene materials. Figure 3 shows a glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) at 58.2 °C, 149.9 °C, and 94.5 °C respectively.

2.2. Catalyst reactivity

2.2.1. Effect of the styrene/DCM ratio

Since the bulk polymerization of styrene was rapidly stopped and the magnetic bar could not stir, we decided to perform the polymerization reactions in a solvent. The styrene polymerization reactions were thus carried out in dichloromethane (DCM) in the presence of $H_3PW_{12}O_{40}$ as catalyst in order to examine the effect of the solvent ratio on the catalytic properties of the catalyst and therefore select the suitable St/solvent ratio. The polymerization reactions were catalyzed by 10 mg and 25 mg of $H_3PW_{12}O_{40}$. The results are shown in Figure 4. It can be seen from this figure that for both catalyst amounts, the best yield was obtained for the volume ratio St/DCM = 0.4.

Figure 4. Effect of St/DCM volume ratio on styrene polymerization using $H_3PW_{12}O_{40}$ catalyst. Reaction conditions : T = 25 °C; catalyst amount 10 mg and 25 mg; reaction time 160 min.



2.2.2. Reactivity of W and Mo in the heteropolyacids

Figure 5 shows the effect of the reaction time on the yields. It can be seen from the figure that the yields increased linearly for both heteropolyacids. During all the time of the polymerization, the yield of the 12-tungstophosphoric acid reaction remained higher than that obtained with 12-molybdophosphoric acid. The yields obtained at 5 h of reaction time with $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ are 68.0% and 45.0% respectively. The average molecular weights obtained also at this reaction time are 9,250 and 5,560, respectively. As $H_3PW_{12}O_{40}$ has stronger acidity than that of $H_3PMo_{12}O_{40}$, these results suggest that strength acidity of the catalyst play an important role for the formation and the physical properties of polystyrene ($H_3PW_{12}O_{40} > H_3PMo_{12}O_{40}$ [7]). Figure 6 shows the yield of

polystyrene obtained for various amounts for both catalysts, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. It can be seen from this figure that both catalysts have remarkably the same tendency; however, the 12-tungstophosphoric acid (W as added atom) gives a higher yield than that of 12-molybdophosphoric acid (Mo as added atoms). For low catalyst amounts, one can see that the gap in the yield values between the two catalysts is high, whereas for higher amounts, the gap decreased.

Figure 5. Effect of the reaction time on the styrene polymerization (in dichloromethane) over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalysts. Polymerization was carried out at 25 °C using 10 mg of catalyst.

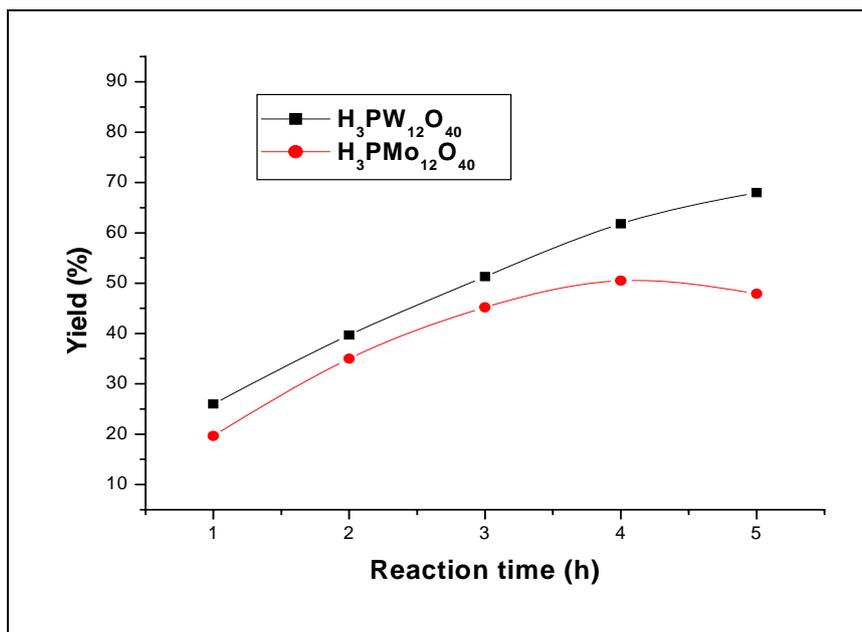
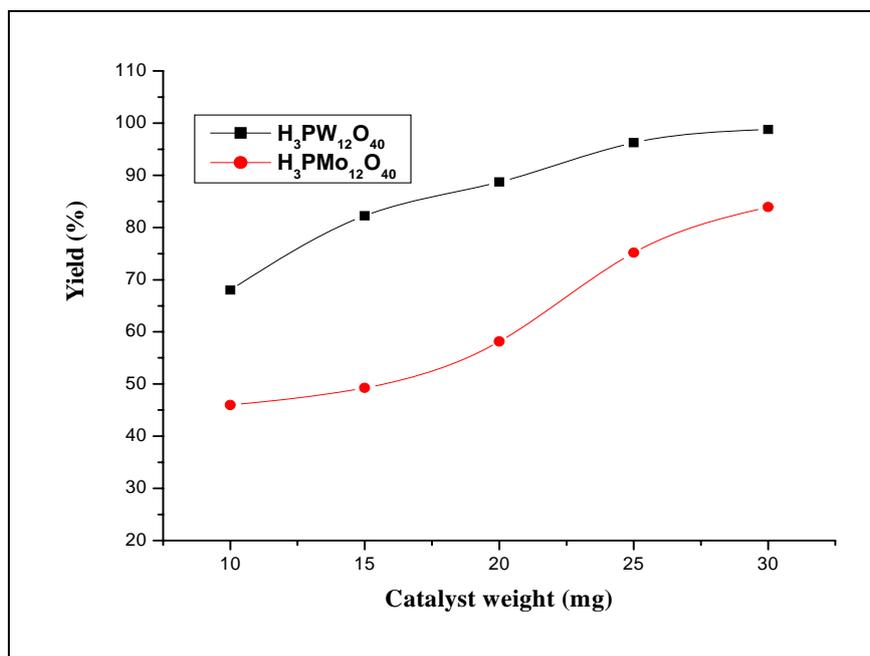


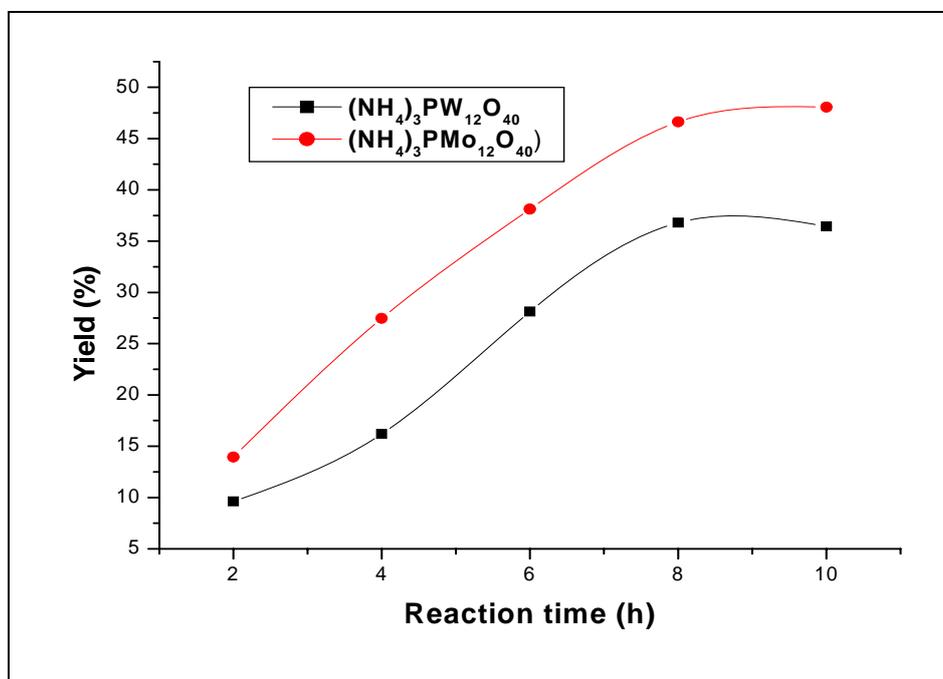
Figure 6. Effect of the amount of catalyst on styrene polymerization (in dichloromethane) using $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalysts. Polymerization was carried out at 25 °C during 5 h.



2.2.3. Reactivity of W and Mo in ammonium salts

The effect of the reaction time on the polymerization was shown in Figure 7. When the protons of the heteropolyacids were replaced by ammonium cations (NH_4^+), the obtained ammonium salts showed a dramatic decrease in the polymerization rate. In fact, no measurable yields were observed before 2 h of reaction time for both solids. Thus to obtain significant conversions, we carried out the polymerization for 12 h. Like their homologous heteropolyacids, the results showed that when the W atoms were replaced by their homologous Mo atoms, a decrease of the polymerization rate was observed.

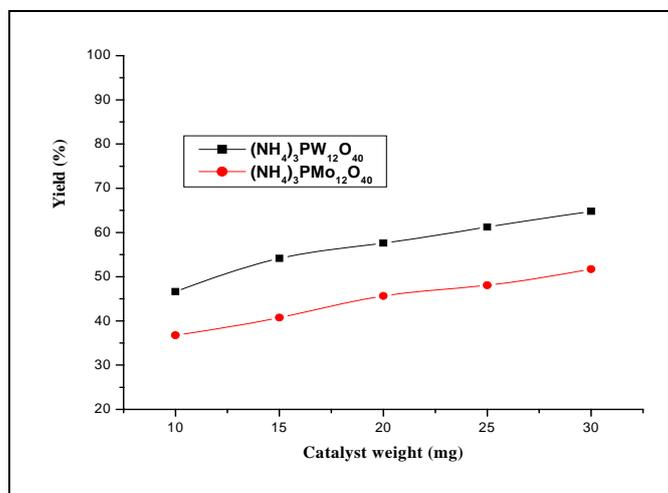
Figure 7. Effect of the reaction time on the styrene polymerization (in dichloromethane) using $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ catalysts. Polymerization was carried out at 25 °C using 10 mg of catalyst.



The yields obtained at 12 h of reaction time with $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ are 48.1% and 36.8%, respectively. The average molecular weights obtained at this reaction time are 5,657 and 4,095, respectively. As the acidity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is stronger than that of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, these results suggest that strength acidity of the catalyst play an important role for the formation and the physical properties of polystyrene. The effect of the catalyst amount on the polymerization was depicted in Figure 8. The results show that for both catalysts the yields have remarkably the same tendency; however, the ammonium salt containing the W atoms presents a slight higher conversion than that containing the Mo ones.

If we take into account the yields obtained for 5 hours of polymerization with this series of catalysts; $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (68.0 %), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (45.0%), $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ (33.1%), and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ (22.6%) we can see that the reactivity is directly proportional to the acidity strength of the heteropolyanions ($\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_3\text{PMo}_{12}\text{O}_{40} > (\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} > (\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ [7]). Thus, this result indicates that strong Brønsted acidity is suitable for the cationic polymerization of styrene.

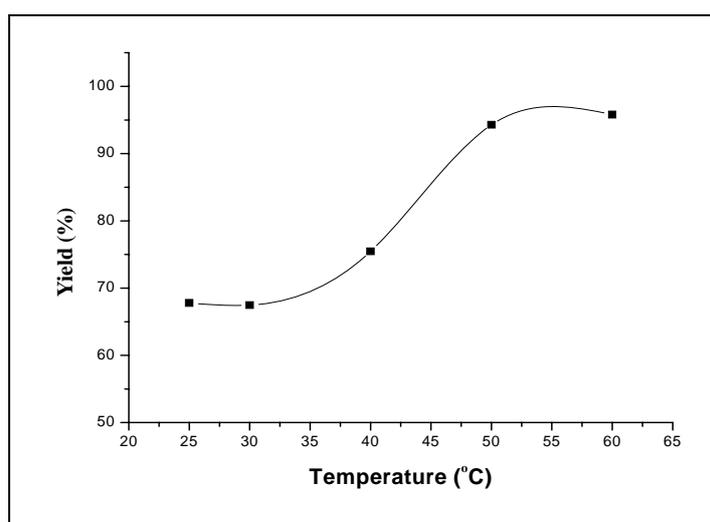
Figure 8. Effect of the amount of catalyst on styrene polymerization (in dichloromethane) using $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ catalysts. Polymerization was carried out at 25 °C during 12 h.



2.2.4. Effect of reaction temperature

The effect of the polymerization temperature on the conversion was examined by keeping the composition of the St/DCM = 0.4. The results are shown in Figure 9. It can be seen from this figure that the rate of polymerization increases with the increase in temperature. The yield increases rapidly from 67.8% to 95.3% when the temperature increases from 25 °C to 50 °C. Then after, it remains stable at about 95.8% when the temperature increases from 50 to 60 °C.

Figure 9. Influence of the reaction temperature on the polymerization of styrene. Polymerization was carried out in dichloromethane (St/DCM (volume ratio) = 0.4.) using 0.025 g of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst.

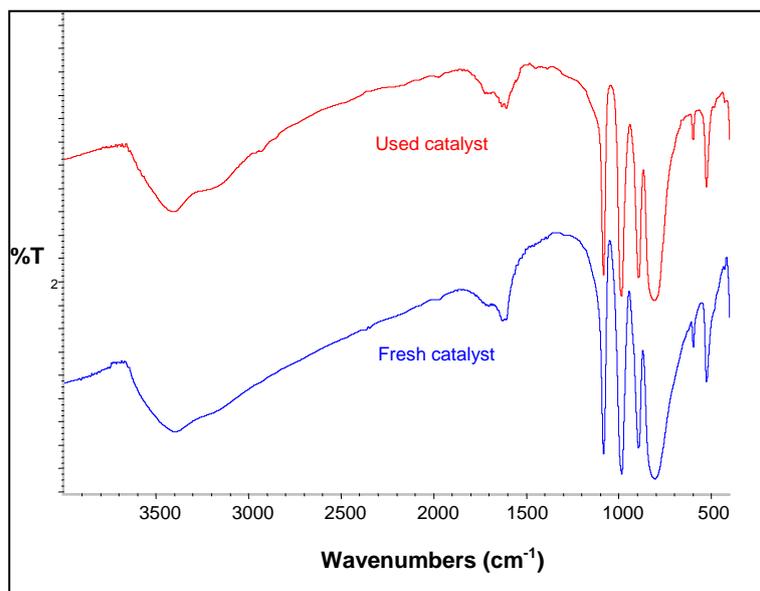


2.2.5. Catalyst recycling

Much effort has been devoted not only to the development of superior catalysts but also to finding ways to enable their repeated use. In order to investigate this possibility for $\text{H}_3\text{PW}_{12}\text{O}_{40}$, this latter was

separated from the reaction mixture by filtration after the reaction, regenerated by washing with cyclohexane for five times, dried at 150 over night, and used again in a fresh reaction. The IR spectra of the fresh and recycled catalyst are shown in Figure 10. It can be seen from the figure that the Keggin structure of the catalyst did not change. The regenerated catalyst was used for the recycling study under the same reaction conditions. When the reaction was carried out at 60 °C by the fresh and the used catalyst, the yield obtained is 95.8% and 72.1%, respectively. This result confirms the recyclable applicability of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ for the polymerization of styrene.

Figure 10. FTIR spectra of fresh and used $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts.



3. Experimental

3.1. Preparation of the catalysts

$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ (abbreviated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$) were prepared in a classical way as described in the literature [16]. $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ (abbreviated $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$) were prepared from their homologous acids using the following procedure: the compound is precipitated by adding slowly the stoichiometric required amount of ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$ to an aqueous solution of $\text{H}_3\text{PM}_{12}\text{O}_{40}$ ($\text{M}=\text{W}; \text{Mo}$). The insoluble ammonium salt is immediately precipitated. Then after the salt was filtered off, washed with water and dried overnight at 120 °C.

3.2. Procedure of polymerization

The bulk polymerizations of styrene were carried out in a stirred flask at 25 °C for a definite time. Typically, a fixed amount of catalyst was added to 10 mL of styrene and 4 mL of dichloromethane under stirring. The polymerization was quenched by the addition of saturated NaOH aqueous solution. The resulting precipitated polymer was filtered off, then dissolved in butanone to removing the catalyst, which is insoluble in butanone. The recovered polymer was precipitated into aqueous ethanol

solution, filtrated off, dried at 40–50 °C under vacuum, and weighed. Then, the polymer was purified by dissolving it in chloroform and precipitation into ethanol for characterization.

Catalysts and polymers characterization

The Keggin structure of the prepared heteropolyanions was checked by infrared (IR) spectroscopy. IR spectra were recorded with a GENESIS II- FTIR (4000–400 cm^{-1}) infrared spectrometer as KBr pellets. ^{13}C -NMR spectra were recorded on a Jeol ECLIPSE 400 MHz spectrophotometer using tetramethylsilane (TMS) as external reference. The chemical shifts are given in ppm. The glass transition temperature of the pure components was measured with a DSC (Setaram Labsys DSC 16), previously calibrated with indium, at 20 °C/min rate. The samples of 10–15 mg were preheated to 200 °C under nitrogen atmosphere and kept at that temperature for 10 min to ensure total elimination of solvent. The data were collected from the second and third scan. No degradation phenomenon of PS was observed in all thermograms. The glass transition temperature was taken as the midpoint in the heat capacity. Molecular weights were determined by measurement of viscosity. Inherent viscosity of poly(styrene) obtained were measured in toluene solution at 25 °C by using an Ubbelohde type viscometer. The viscosity average molecular weight (M_v) was calculated by the following equation: $[\eta] = 9.77 \times 10^{-3} \cdot M_v^{0.73}$ [19].

4. Conclusions

The polymerization of styrene in dichloromethane was performed using $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$, and $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ as catalysts. It has been found that the catalysts containing W were more reactive than those containing Mo. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was the most effective catalyst in terms of yield and M_v due to its stronger Brønsted acidity. The use of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as a heterogeneous solid acid catalyst, instead of the usual soluble inorganic acids, is a contribution to a reduction of waste. In fact, this latter can polymerize styrene under mild conditions and a simple filtration is sufficient to recover the catalyst which can be reused.

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Sample Availability: Samples of the compounds are available from the authors.

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