Research Article

Keggin-Type Heteropolyacid for Ring-Opening Polymerization of Cyclohexene Oxide: Molecular Weight Control

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Polymerization of 1,2-cyclohexene oxide (CHO) in dichloromethane was catalyzed by 12-tungstophosphoric acid ($H_3PW_{12}O_{40} \cdot 13H_2O$) as a super solid acid. The effect of polymerization parameters such as reaction time, temperature, and catalyst amount was investigated. The effect of acetic anhydride as a ring-opening agent was also investigated. The resulting poly(1,2-cyclohexene oxide) (PCHO) was characterized by Fourier transform infrared (FTIR), nuclear magnetic resonance spectroscopy (^{1}HNMR), gel-permeation chromatography (GPC), and differential scanning calorimetry (DSC). It has been found that the PCHO prepared over $H_3PW_{12}O_{40} \cdot 13H_2O$ has a stereoregularity higher than that prepared over clay and Aluminium alkoxide catalysts. The T_g value obtained is due to the microstructure but not to molecular weight. The yield and the molecular weight of the polymer depend strongly on the reaction conditions. Molecular weights can be readily controlled by changing reaction temperature, reaction time, and catalyst amount. Contrary to most polymerization reactions, the molecular weight increases with the temperature increase. Addition of acetic anhydride to the reaction medium increased the yield threefold.

1. Introduction

Due to their high polarizability and flexibility, polyethers constitute a very important soft segment for producing thermoplastic elastomers. Many of these polymers have been synthesized by ring-opening polymerization (ROP) of cyclic ether monomers [1]. Among cyclic monomers' ring-opening polymerization that of cyclohexene oxide (epoxide) into polycyclohexene oxide (polyether) has been the subject of a large number of papers [2–5]. This is due to the fact that cyclohexene oxide (CHO) polymers are useful materials. In fact, they are used in the synthesis of various alicyclic target materials including pesticides, pharmaceuticals, perfumery, and dyestuffs. ROP of cyclic ethers could be initiated by electrophilic agents such as Brønsted acids (HCl, H_2SO_4, $HClO_4$, etc.) and Lewis acids ($AlCl_3$, BF_3OEt_2, $TiCl_4$, etc.). However, the protonic acid catalysts used are corrosive and not recoverable, and the Lewis acids required great amount to achieve acceptable polymer yields. Because of increasing

environmental concerns in recent years, a more effective catalytic process has been sought. In this respect, researchers have conducted studies on the development of solid acids so that aggressive and dangerous homogeneous acids can be replaced to overcome the problem of separating the catalysts from the products and from the disposal of solid/liquid waste. Solid Brønsted acids with super acidic character, such as the Keggin-type heteropolyacids, are known as highly active catalysts [6–8]. Due to their strong acidity, these "super acids" catalyze various reactions much more effectively than the conventional protonic acids [9, 10]. In recent years, heteropolyacids have been used as catalysts to induce the polymerization of various monomers such as cyclic ethers, styrene, acetals, polyalcohols, and lactones [11–13]. In a previous paper [14] we have reported the polymerization of tetrahydrofuran catalyzed by a series of heteropolyacids. It has been found that $H_3PW_{12}O_{40}$ was the efficient catalyst of the series of heteropolyacids tested. This fact prompted us to investigate the cationic ring-opening polymerization of CHO

by this catalyst. The effect of reaction temperature, reaction time, catalyst amount, and acetic anhydride proportion on the polymerization was investigated.

2. Materials and Methods

2.1. Catalyst Preparation. $H_3PW_{12}O_{40}$ was prepared according to a now well-known method [15]; that is, 100 g of $Na_2WO_4·2H_2O$ was dissolved in 100 mL of warm distilled water and then successively 85% H_3PO_4 (5 mL) and 37.5% HCl (22 mL) were added slowly to the solution. The mixture was concentrated to three quarters of its initial volume by heating and then after that it was cooled to room temperature. The cooled mixture was extracted with diethyl ether in hydrochloric acid medium. The product formed with ether, which settled down at the bottom, was separated from the aqueous phase. The white crystals of $H_3PW_{12}O_{40}·13H_2O$ were dried at room temperature.

2.2. Polymerization Procedure. Polymerization reactions of CHO were carried out in dichloromethane in a glass reactor fitted with a condenser. The temperature of the reactor was adjusted by a heating jacket. Typically, a fixed amount of $H_3PW_{12}O_{40}$ as catalyst was added to CHO (10 mL) and dichloromethane (4 mL) mixture under stirring at a desired temperature. Polymerization was terminated with addition of a saturated NaOH aqueous solution and still stirred for 5 min. At the end of the reaction, the resulting PCHO polymer was precipitated in methanol and then filtrated off for characterization and molecular weight measurements.

2.3. Catalyst and Polymer Characterization. The Keggin structure of the catalyst ($H_3PW_{12}O_{40}$) was checked by means of FTIR. IR spectrum was recorded with an infrared spectrometer GENESIS II FTIR (4000–400 cm^{-1}) as KBr pellets.

The polymer was characterized by using FTIR spectroscopy, NMR spectroscopy, differential scanning calorimeter (DSC), and molecular weight measurements. ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrophotometer using 5 mm NMR tubes using deuterated acetone-D6 as solvent. DSC model DSC-60 made by Shimadzu was utilized here. The specimens weigh about 12 mg each. Each specimen was placed in aluminum pan. The pan was placed in the DSC's oven in air at atmospheric pressure. Specimens were heated at a constant heating rate of 5°C/min to 300°C. Molecular weight measurements were determined by means of a HT-GPC, Model 430, Viscotek, Houston, TX, USA, gel-permeation chromatograph (GPC) with CLM6210 column.

3. Results and Discussion

3.1. Characterization of the Catalyst. Infrared spectrum of 12-tungstophosphoric acid, $H_3PW_{12}O_{40}·13H_2O$ (abbreviated as $H_3PW_{12}O_{40}$), is shown in Figure 1. According to [16], the main characteristic features of the Keggin structure observed at 1080–1060 cm^{-1} (ν_{as} P-O$_a$), at 990–960 cm^{-1} (ν_{as} Mo-O$_d$),

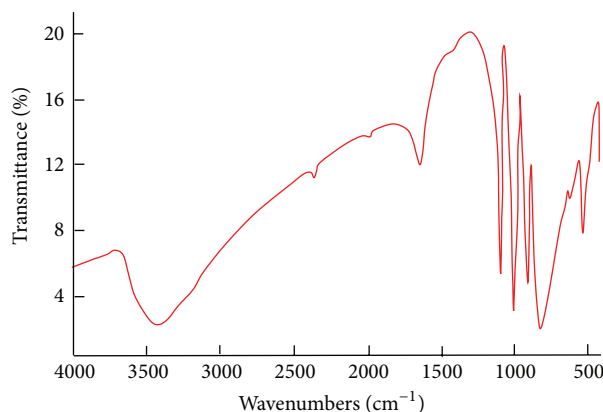FIGURE 1: IR spectrum of $H_3PW_{12}O_{40}$.
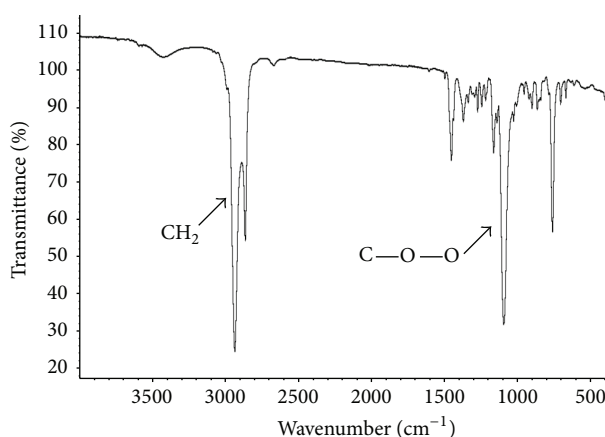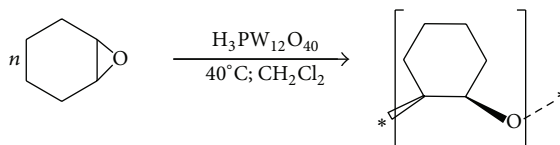

FIGURE 2: IR spectrum of poly(CHO). Polymerization catalyzed by 0.2 g of $H_3PW_{12}O_{40}$ at 40°C during 3 hours in CH_2Cl_2.

at 900–870 cm^{-1} (ν_a Mo-O$_d$-Mo), and at 810–760 cm^{-1} (ν_{as} Mo-O$_c$-Mo) were obtained.

3.2. Polymer Characterization. The cationic ring-opening polymerization of cyclohexene oxide was catalyzed by $H_3PW_{12}O_{40}$ solid super acid catalyst in dichloromethane at 40°C (Scheme 1).

The IR spectrum of PCHO is shown in Figure 2. The bands present at 2932 (γ_{as} CH$_2$), 2859 (γ_s CH$_2$, γ CH), 1449 (δ CH$_2$), 1366 (δ CH$_2$), 1158, 1090 (C-O-C antisymmetric stretching), 895, 850, and 756 (δ CH out-of-plane). These assignments for PCHO agree well with those of Yahiaoui et al. [2] and Suga and Aoyama [17] for the PCHO prepared with an acid-exchanged montmorillonite clay catalyst.

Figure 3 shows different peaks, the methylene groups (cyclohexane CH$_2$-) at 1.0–2.0 ppm, and methine groups (CH$_2$-CHO) at 3.2–3.6 ppm. The signal of the methine protons appears in the form of two peaks (3.28 and 3.33 ppm), which we attribute, respectively, to triads isotactic (mm) and heterotactic (mr and rm). These assignments for PCHO agree well with those of Ling et al. [5] for the PCHO prepared over recyclable scandium triflate in room temperature ionic liquid catalyst.

SCHEME 1: Reaction scheme for the synthesis of PCHO by ring-opening polymerization of CHO over $H_3PW_{12}O_{40}$ catalyst.
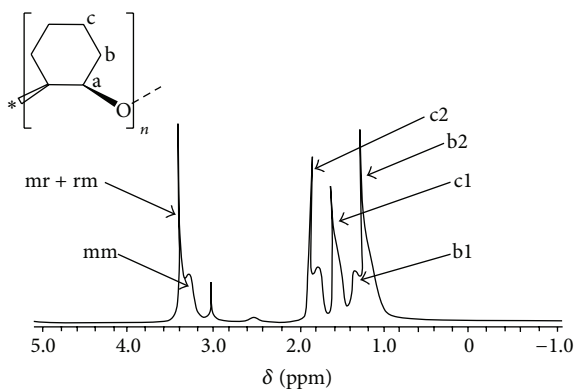

FIGURE 3: ^{1}HNMR spectrum of PCHO. Polymerization catalyzed by 0.2 g of $H_3PW_{12}O_{40} \cdot 13H_2O$ at 40°C during 3 hours in CH_2Cl_2.
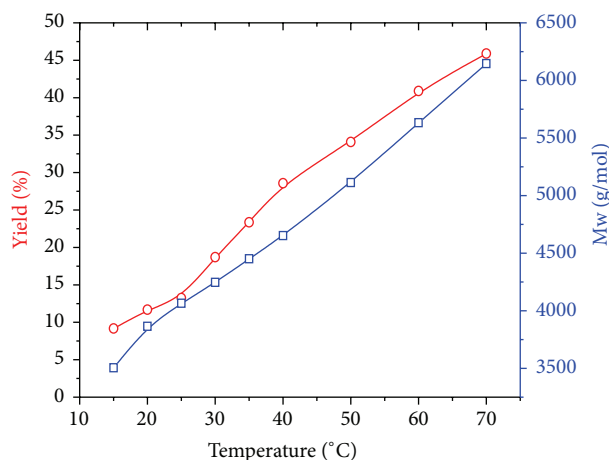

FIGURE 4: Yield and Mw of PCHO as a function of reaction temperature. Polymerization catalyzed by 0.2 g of $H_3PW_{12}O_{40}$ during 3 hours in CH_2Cl_2.

FIGURE 5: Typical DSC thermograms of the prepared PCHO obtained at a heating rate of 20°C/min. Polymerization catalyzed by 0.2 g of $H_3PW_{12}O_{40}$ during 3 hours in CH_2Cl_2.

3.3. Effect of Reaction Temperature.

The effect of the reaction temperature on the yield, molecular weight, and T_g of the PCHO was investigated. The reactions were carried out in a temperature ranging from 15°C to 70°C in dichloromethane solvent. Figure 4 shows the effect of the temperature on the yield and on the molecular weight. It can be seen that both the yield and the molecular weight increased with the increase of the temperature. This result is in agreement with that reported in the literature [2]. The increase of the yield with temperature is an expected result but the increase of the molecular weight is unexpected. In fact, in most polymerization reactions, the molecular weight decreases
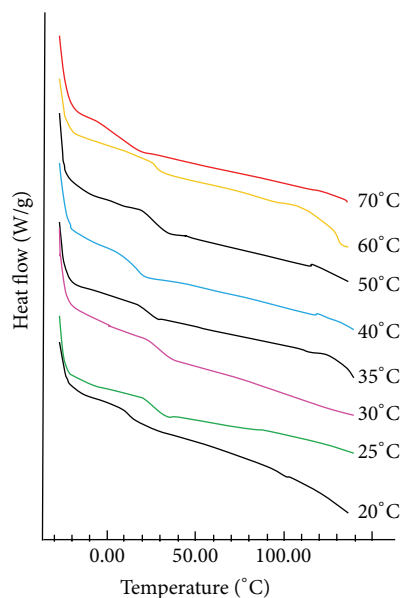
with the increase of the temperature owing to the fact that the temperature accelerates the rate of chain transfer reactions which in turn decreases the molecular weight [18]. In the case of CHO polymerization, the increase of the molecular weight can be explained by the fact that the HO- group bound to a rigid cyclohexene ring cannot approach sufficiently close to the oxygen atom to allow for the interchange reaction [19].

The effect of the temperature reaction on the PCHO T_g is shown in Figure 5. It can be seen that the T_g values are ranging between 23 and 37°C. These T_g values are different from that observed by Yahiaoui et al. (T_g = 75.23°C) over a clay catalyst [2]. As for the PCHO prepared by Zevaco et al. over Aluminium alkoxides catalyst [20], the authors reported that they have not observed a clear glass transition temperature but a broad endotherm between 66 and 100°C (max at 70°C) which they have attributed to a melting point of their resulting polymer. The difference in the T_g value between our polymer and that of Yahiaoui et al. and Zevaco et al. might be due to the difference in the microstructure of the prepared polymer. Indeed, our PCHO which was prepared by a super acid (Keggin heteropolyacid) has a different stereoregularity than that prepared by these authors. In fact, the ^{1}H NMR spectrum of our PCHO showed only two peaks (3.28 and 3.33 ppm) for the signals of the methine
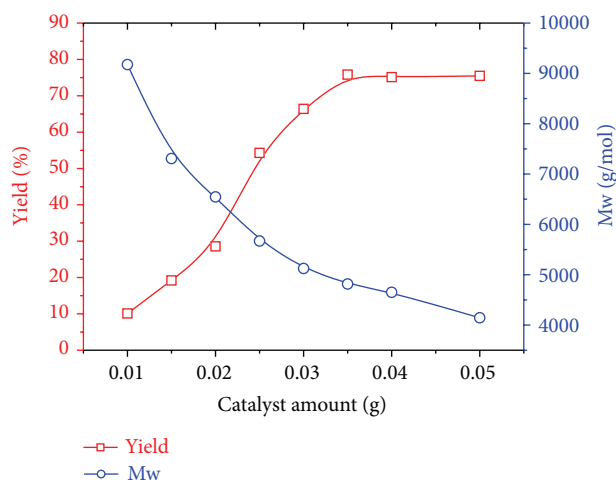
FIGURE 6: Effect of catalyst amount on the molecular weight and yield for the polymerization of CHO in CH_2Cl_2 at 40°C over $H_3PW_{12}O_{40}$.

FIGURE 7: Effect of reaction time on the conversion and molecular weight of PCHO in CH_2Cl_2 at 40°C over $H_3PW_{12}O_{40}$.

protons which we have attributed, respectively, to triads isotactic (mm) and heterotactic (mr and rm) whereas the NMR of the PCHO prepared by Yahiaoui et al. [2] and Zevaco et al. [20] showed three peaks (3.3, 3.4, and 3.5 ppm) and (3.66, 3.78, and 3.88 ppm), respectively, which they attribute, respectively, to triads isotactic (mm), heterotactic (mr and rm), and syndiotactic (rr).

3.4. Effect of Catalyst Amount. To investigate the effect of the amount of catalyst on the polymerization yield and molecular weight, we carried out the polymerization reaction of CHO (10 mL) in dichloromethane (4 mL) at 40°C during 3 hours. The results obtained are reported in Figure 6. It can be seen that the polymer yield increases as the mass of the catalyst increases, whereas the molecular weight decreases. The highest molecular weight (9100 g mol^{-1}) was obtained for the lowest amount used of catalyst (10 mg). The inverse proportionality between the molecular weight and the amount of catalyst can be explained by the fact that when the amount of the catalyst increased, the number of initiating active responsible sites (H^+) for inducing polymerization increased and consequently the number of chains increased which is obviously at the expense of the length of the chains. The decrease in molecular weight might be due also to the increase in water which increased with the increase of catalyst amount.

3.5. The Effect of Reaction Time. Effect of reaction time on the yield and the molecular weight of the polymer were examined. The polymerization reactions were catalyzed by 0.02 g of catalyst at 40°C in dichloromethane solvent. The results (Figure 7) show that both the yield and molecular weight of the polymer increase with increasing reaction time. The increase of the yield and the molecular weight was rapid for short reaction times whereas for long time reactions a slight variation is observed. A yield of 64% and a molecular
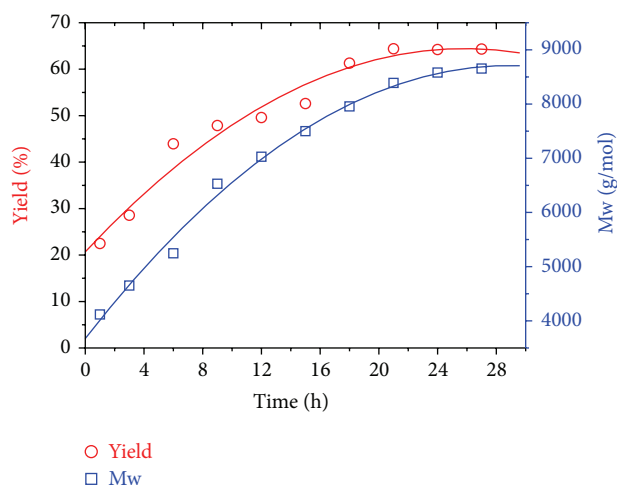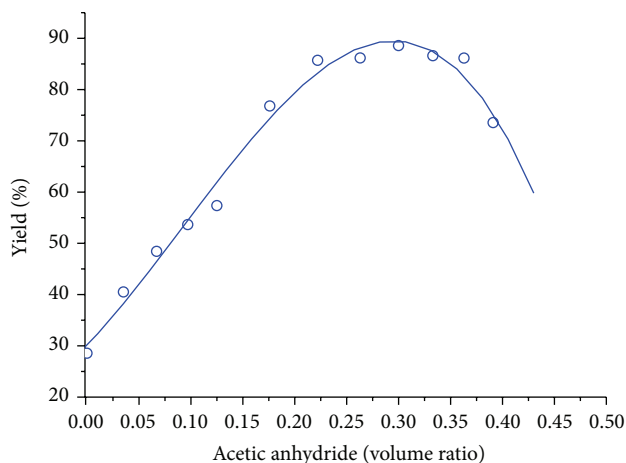

FIGURE 8: Effect of acetic anhydride proportion on PCHO yield. Reaction conditions: $T = 40$°C; reaction time = 3 h.

weight of 8300 g mol^{-1} are reached after 21 hours of reaction. The stagnation of the molecular mass may be due to the fact that, at higher yields and higher molecular weights, the viscosity of the medium increased and therefore the reaction became kinetically slow. So there was a stagnation of the molecular weight and yield.

3.6. Effect of Acetic Anhydride Proportion. Acetic anhydride has been used for the ring-opening of many heterocyclic compounds and it has been found that the yield of the polymer depends on its used proportion [21–23]. That is why we have tried to study its effect on the ring-opening of CHO. To achieve this, different volumes are added to the solution CHO/CH_2Cl_2. The reactions were carried out at 40°C for three hours. The results obtained (Figure 8) showed that the yield of the polymer depends strongly on the acetic anhydride proportion. In fact, when the volume ratio varies from 0 to

Initiation

$$(CH_3CO)_2O + H_3PW_{12}O_{40} \longrightarrow \left[CH_3\overset{\oplus}{C}O\right]\left[H_2PW_{12}O_{40}^{\ominus}\right] + CH_3COOH$$

Propagation

Termination
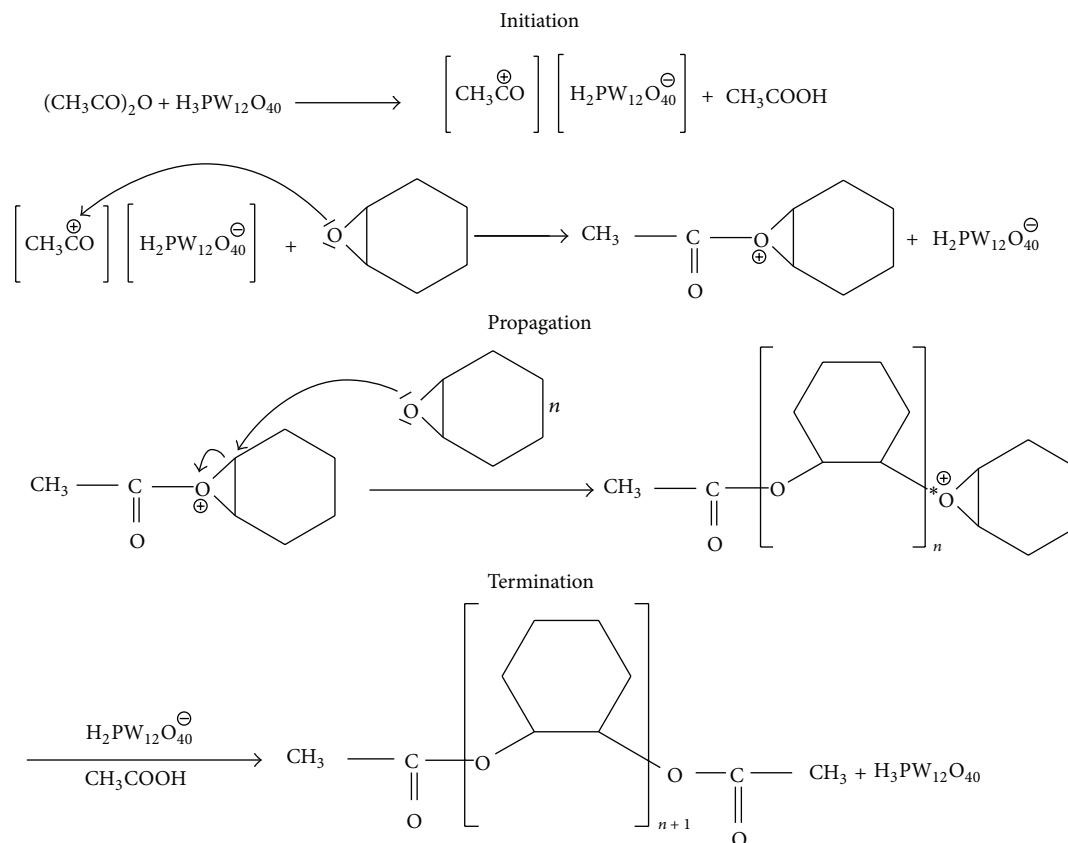
SCHEME 2: Mechanism for the ring-opening polymerization of cyclohexene oxide in the presence of acetic anhydride over $H_3PW_{12}O_{40}$ catalyst.

0.30, the yield increased by 20% to 60%. This shows that the initial value has tripled. When the volume ratio of the acetic anhydride added is beyond 0.3, the yield decreased. The decrease of the yield at high acetic anhydride volume ratio might be due to consumption of heteropolyacid protons by the acetic anhydride leading to acetic acid (a weak acid) or to an increase in the number of methyl groups at the extremities of the chains that block the growth of polymer chains. In fact, large addition of acetic anhydride to the mixture creates chain ends unable to take part in polymerization.

3.7. Polymerization Mechanism. The ring-opening polymerization of PCHO can be achieved by addition of acetic anhydride via a cationic pathway. According to the obtained results, we propose a cationic mechanism for the polymerization initiated by protons provided by $H_3PW_{12}O_{40}$ (Scheme 2). *Initiation.* The first stage is the protonation of acetic anhydride by $H_3PW_{12}O_{40}$, leading to the formation of acetyl polyoxometalate salt. Then there is a nucleophilic attack of the oxygen of cyclohexene oxide on the carbon atom of the acetyl species. The formed oxonium ion undergoes a nucleophilic attack on the carbon by the oxygen of the cyclohexene oxide of the chains in growth. *Propagation.* In this stage, the protonated oxonium ion undergoes a nucleophilic

attack by a molecule of cyclohexene oxide. *Termination.* The last stage is a nucleophilic attack of the oxygen of the acetic acid formed in the first stage on the carbon in alpha of positively charged oxygen of the chains in growth.

4. Conclusions

From the results it can be concluded that Keggin-type heteropolyacid ($H_3PW_{12}O_{40}$) is an effective catalyst of the ring-opening polymerization of cyclohexene oxide owing to its strong Brønsted acidity.

The microstructure of the resulting PCHO is different from that prepared over clay and alumina alkoxide catalysts. The low T_g value of the PCHO is due to the microstructure but not to molecular weight. Contrary to most polymerization reactions, the molecular weight and the yield increase with the increase of the temperature.

The decrease in the molecular weight with the increase of the amount of catalyst might be due to the increase of the amount of water which increased with the increase of catalyst amount or to the increase of the number of initiating active sites (H^+) which increases the number of chains at the expense of the length of the chains.

Controlled low molecular weight of the PCHO over $H_3PW_{12}O_{40}$ can find various applications. It can be used for preparing soft segments for thermoplastic elastomers.

The use of $H_3PW_{12}O_{40}$ as a solid acid catalyst instead of the usual soluble inorganic acids is a contribution to a reduction of waste.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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