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Synthesis, Characterization and Catalytic Polymerization of *N*-Methyl Imidazolium Phosphotungstic Catalyst

Dianyu Chen *, Zhaoyi Deng, Xiaoqin Liu and Rong Wang

Jiangsu Key Laboratory of Advanced Functional Materials, Department of Chemistry and Materials Engineering, Changshu Institute of Technology, Changshu 215500, China; E-Mails: d1170351808@163.com (Z.D.); lxq2124@163.com (X.L.); wr2833@sina.com (R.W.)

* Author to whom correspondence should be addressed; E-Mail: chendy@cslg.edu.cn; Tel.: +86-512-5225-1842.

Abstract: *N*-methyl imidazolium phosphotungstic salt has been synthesized and used as a special catalyst for photopolymerization of vinyl monomers. This is a fast and smooth reaction, and high molecular weight polymers with narrow polydispersity are obtained within 60 min. The compound was structurally characterized by elemental analysis, IR spectroscopy, and ^{1}H NMR spectroscopy. The electrochemical property is determined on a CHI 660 electrochemistry workstation. The polymerization initiated by *N*-methyl imidazolium phosphotungstic salt showed controlling characteristics, the catalyst can be easily isolated from polymer product, and reused for at least 10 times.

Keywords: *N*-methyl imidazolium phosphotungstic salt; electrochemical; catalytic polymerization; recoverable

1. Introduction

Heteropoly acids (HPAs) have attracted significant attention because of their high acidity and favorable redox properties [1–8]. Among different HPAs, Keggin type (such as phosphotungstic acid) are well known and widely studied compounds for various catalytic applications, such as Friedel-Craft's alky-lation, acylation, oxidation, hydration of alkenes, esterification, transesterification, and carbonylation [9–14].

Heteropoly acids (HPAs) and compounds were firstly employed in our research group to initiate styrene for polymerization [15,16], which was the only polymerization example for vinyl monomers.

Styrene polymerization initiated by HPA was excellent, and followed cationic polymerization theory [15]. However, the reaction carried out so rapidly that it disadvantaged both experimental research and plant application. This limited the use of a wide range of vinyl monomers in polymerization. As such it requires a suitable method to address the problem of HPA-mediated cationic polymerization. One of the best methods was selecting a suitable ligand to stabilize the active center during polymerization.

In present paper, *N*-methyl imidazolium was used for modifying the stability of phosphotungstic acid (PTA). The compound was structurally characterized by elemental analysis, IR spectroscopy, and ^{1}H NMR spectroscopy. The electrochemical property was determined on a CHI 660 electrochemistry workstation. The catalysis activity was studied in photopolymerization of vinyl monomers.

2. Results and Discussion

2.1. IR Analysis

Figure 1 shows the FT-IR spectra of the as-prepared catalysts: $H_3PW_{12}O_{40}$ (a); $[(C_3H_3)N_2CH_3]_3$ $(PW_{12}O_{40})$ (b); the catalyst after one cycle of polymerization (c); and the catalyst after 10 cycles of polymerization (d). Over a range of 800–1100 cm^{-1}, the absorption bands around 1080, 985, 896, and 804 cm^{-1}, corresponding to the four characteristic skeletal vibrations of the Keggin oxoanions, were observed in the FT-IR spectra of sample (a). These absorption bands are attributed to the vibrations of $\upsilon as(P–O_a)$, $\upsilon as(W=O_d)$, and $\upsilon as(W–O_b–W)$ in corner-shared octahedra, and $\upsilon as(W–O_c–W)$ in edge-shared octahedra, respectively [17–19]. For the FT-IR spectrum of the samples from (b) to (d), the absorption band at 1080 cm^{-1} is attributed to the vibration of $\upsilon as(P–O_a)$, the absorption bands of $\upsilon as(W=O_d)$, $\upsilon as(W–O_b–W)$, and $\upsilon as(W–O_c–W)$ shift to 984 (for b, 982 for c, and 982 for d), 894 (for b, 898 for c, and 896 for d), and 811 (for b, 820 for c, and 808 for d) cm^{-1}. These shifts indicate the changes of the bond length and bond angle. Compared with the spectra of sample (a), high similarity was found in these bands of samples (b) to (d), which indicated that the Keggin structure was not destroyed after modified by *N*-methyl imidazolium and, secondly, no change was found during the catalysis polymerization. The possible reason of these band changes is that the MoO_6 octahedra of the polyanions were distorted in some degrees because of the influence of the *N*-methyl imidazolium cations.
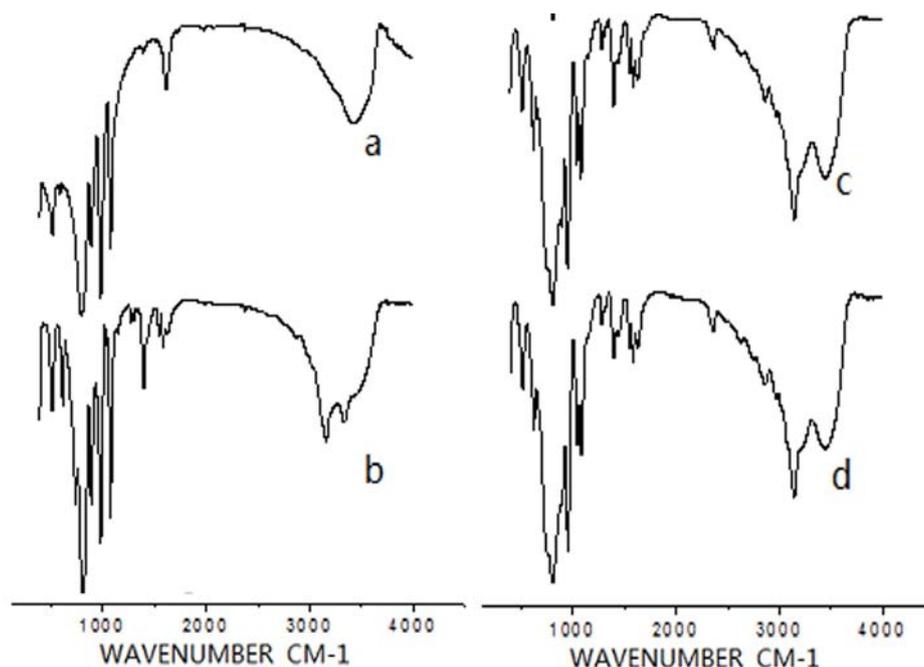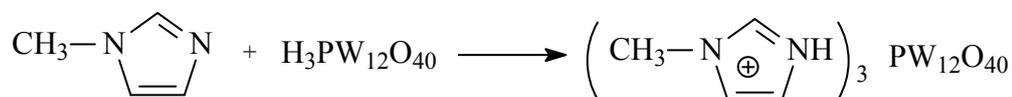
Figure 1. IR analysis. (**a**) phosphotungstic acid; (**b**) *N*-methyl imidazolium phosphotungstic salt; (**c**) the catalyst after one cycle of polymerization; and (**d**), the catalyst after 10 cycles of polymerization.

2.2. ^1H NMR Analysis

From Figure 2a, the peak at 5.416 ppm was attributed to the protons in phosphotungstic acid, and the peak at 2.475 ppm was attributed to the solvent of CD_3COCD_3. That is, all of the protons in phosphotungstic acid were in the same chemical environments. Figure 2b shows the ^1H NMR spectrum of *N*-methyl imidazolium phosphotungstic salt, the peak at 5.416 ppm disappeared, and four new peaks appeared: 8.83 ppm was attributed to C^2H, 7.61 ppm and 7.55 ppm were attributed to C^4H and C^5H, and 3.78 ppm was attributed to C^6H_3 (see the formula in Figure 2), which might indicate that the protons in phosphotungstic acid had transferred from phosphotungstic acid to the N atom of *N*-methyl imidazolium unit. The possible reaction process was deduced as follows:

$$CH_3-N \diagup\!\!\!\diagdown N \; + \; H_3PW_{12}O_{40} \longrightarrow \left(CH_3-N\underset{\oplus}{\diagup\!\!\!\diagdown} NH \right)_3 \; PW_{12}O_{40}$$

After catalytic polymerization (Figure 2c,d), the four peaks in Figure 2b were shifted to 8.63, 7.53, 7.43, and 3.82 ppm (8.60, 7.52, 7.42 and 3.81 in Figure 2c,d) separately. The same result as the IR analysis was obtained; that is, *N*-methyl imidazolium phosphotungstic salt had a stable structure, and could be reused several times.
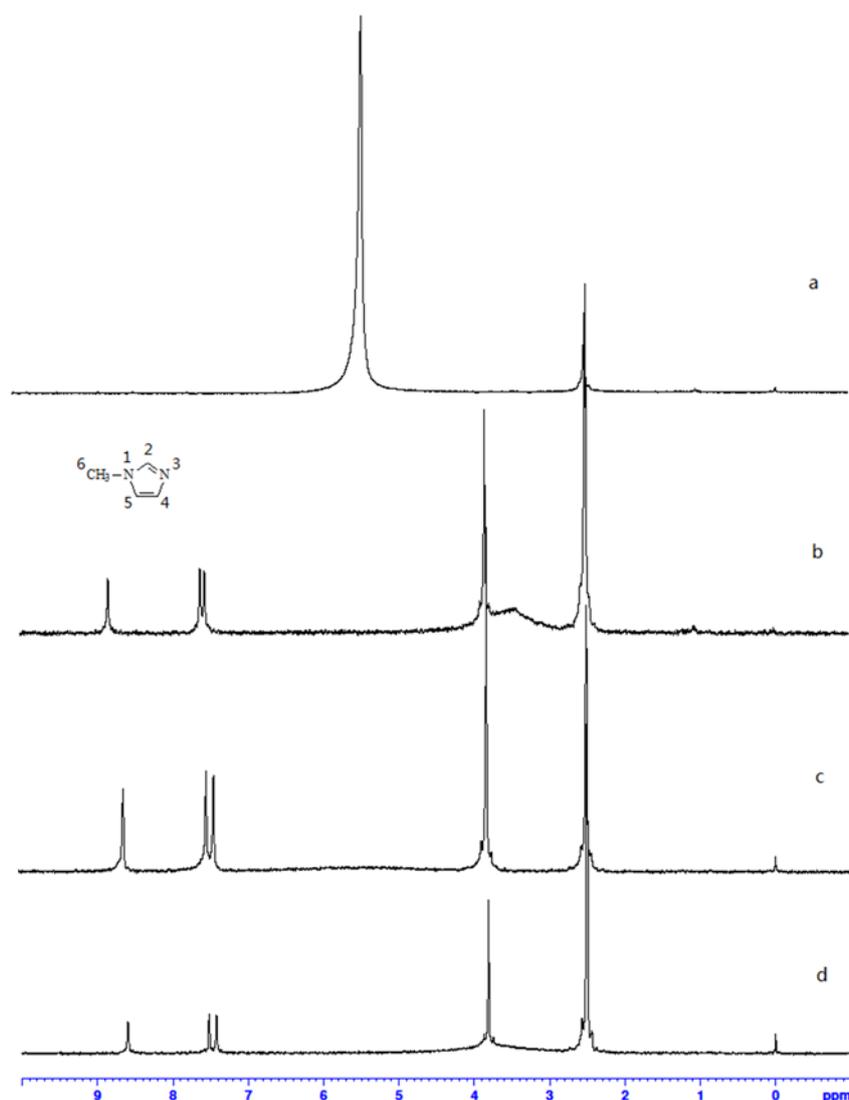
Figure 2. ^{1}H NMR spectra. (**a**) phosphotungstic acid; (**b**) *N*-methyl imidazolium phosphotungstic salt; (**c**) the catalyst after one cycle of polymerization; (**d**) the catalyst after 10 cycles of polymerization.

2.3. Electro-Chemical Property Analysis

Figure 3 showed cyclic voltammograms (CVs) of the aimed product in 0.5 M buffer solution of HAc-NaAc with a different scan rate. Redox potential was shown at 1.08 and 0.57 when the scan rate was selected as 100 mV/s. With an increase of the scan rate, the oxidation peak potential shifted more positively and the reduction potential shifted more negatively, while the peak currents increased linearly with an increase of the square of the scan rate (inset A). This revealed that the electrochemical behavior of the complex chemsorbed on the surface of the ligands showing a diffusion-confined redox process [20].

Additionally, the electrode modified by the complex had high stability. In 0.5 M buffer solution of HAc-NaAc and potential range of −0.4–1.6 V, the peak currents had no weakening after scanning 300 times, and even laying aside for two months. This indicated the potential application in both the chemical sensor and recovery catalyst.
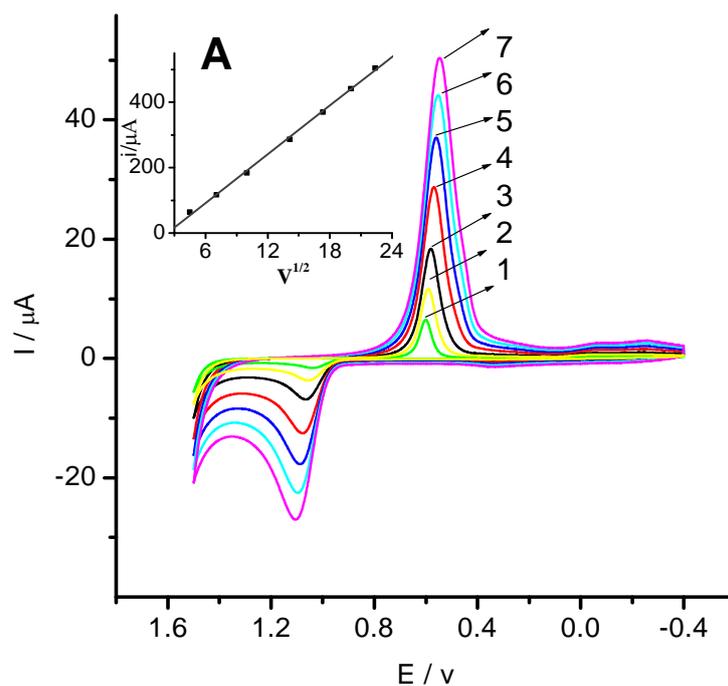
Figure 3. Cyclic voltammograms of gold/complex electrode (solid line) in a 0.5 M buffer solution of HAc-NaAc. 1–7: 20, 50, 100, 200, 300, 400, and 500 mV·s^{-1} (from inside to outside). Inset (**A**): the variation of cathodic peak current with scan rate.

2.4. Catalytic Activity

Polymerizations of styrene with this catalyst proceed readily under a 359 nm light radiation for 60 min at room temperature. This is a fast and smooth reaction when compared to the polymerization initiated by phosphotungstic acid [15]. The increase in rate is manifested by a lowering of molecular weight from 5464 to 1304, and broadening of the polydispersity from 1.21 to 3.11, which is ascribed to the chain transfer reaction [21]. These observations led us to lower the reaction temperature and radiation power, in an attempt to avoid an excessive chain transfer reaction. Polymerization proceeds efficiently at Reaction 3, reaching 73% conversion after 60 min at 20 °C and 300 W power. When the molar ratio of monomer to catalyst was doubled from 50 to 100, an approximate doubling of the Mn is observed (Reactions 3 and 9, Table 1), as would be expected for a controlling polymerization.

Styrene, vinyl acetate, methyl methacrylate, and butyl acrylate were used, as representative of the vinyl monomers, for the photopolymerization initiated by *N*-methyl imidazolium phosphotungstic salt (Reactions 3, 10, 11, and 12, Table 1). All reactions at 20 °C and 300 W showed very good catalytic activity. This, taken together with the relatively narrow PDI values and high Mn of the products, indicated that the polymerization shows controlled characteristics. Figure 4 showed the evolution of Mn as a function of [M]/[Cat] for Reaction 3, 10, 11, and 12, which increased linearly, again as would be expected for controlling polymerization.

Table 1. Final molecular weight and conversion data for the polymers synthesized in this work.

Reaction [a]	Temperature/°C	Time/min	Power/W	Conversion/% [b]	Mn [c]	PDI [c]
1 [d]	20	40	300	63	4531	1.26
2 [d]	20	50	300	70	4917	1.23
3 [d]	20	60	300	72	5464	1.21
4 [d]	30	60	300	65	5006	1.62
5 [d]	40	60	300	43	3564	1.67
6 [d]	50	60	300	16	2833	2.16
7 [d]	20	60	500	65	4654	2.23
8 [d]	20	60	800	58	1303	3.11
9 [d,*]	20	120	300	58	11437	1.31
10 [e]	20	60	300	75	7407	1.27
11 [f]	20	60	300	59	7689	1.21
12 [g]	20	60	300	68	8230	1.54

[a] All reactions carried were 50% *v/v* in acetone. [b] Conversion from integration of ^{1}HNMR. [c] Determined using PL GPC-50 against polystyrene standards. Vinyl monomer: [d] styrene; [e] vinyl acetate; [f] methyl methacrylate; [g] butyl carylate. [monomer]/[catalyst]: [d] 50:1; [d,*] 100:1.
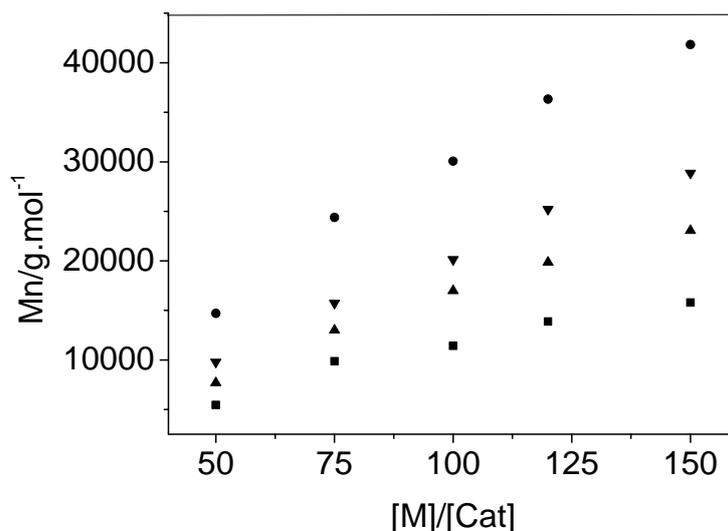

Figure 4. Evolution of molar mass with [M]/[Cat] for polymerization; (■) polystyrene, (●) poly(vinyl acetate), (▲) poly(methyl methacrylate), and (▼) poly(butyl acrylate).

N-methyl imidazolium phosphotungstic salt is insoluble with most of organic solvents, such as acetone, toluene, and so on, which allows easy isolation of the catalyst from the polymerization system for potential reuse. After 10 cycles of reuse in styrene polymerization (see Figure 5), catalyst recovery is up to 92.4%, molecular weight and polydispersity of polystyrene retained a stable level (Mn changed randomly between 8194 and 10695, PDI changed randomly between 1.15 and 1.67), which indicated that *N*-methyl imidazolium phosphotungstic salt was a recovery catalyst, and could be used repeatedly 10 times, at least.
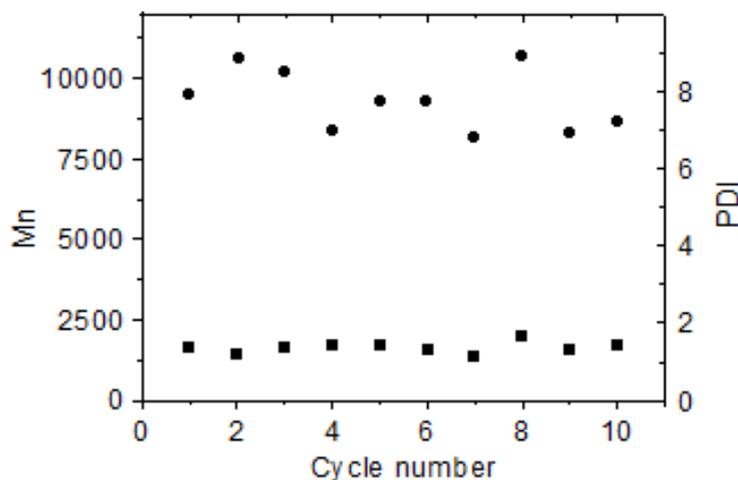
Figure 5. The recovery results of the catalyst. ●, Mn; ■, PDI.

3. Experimental Section

3.1. Materials and Instruments

All chemicals purchased were of reagent grade and used without further purification. The elemental analyses for C, H, and N were performed with an EA1110-CHNS elemental analyzer (CARLO-ERBA, ERBA, Italy). The IR spectra were obtained on a NICOLET380 spectrum (THERMO, Waltham, MA, USA) using KBr disks in the range 4000–400 cm^{-1}. ^{1}H NMR spectra were recorded on a BRUKER Avance DPX 300MHz spectrometer (BRUKER, Tucson, AZ, USA). Polymerization was performed in a XPA-1 photochemical reactor (Xujiang, Nanjing, China), with a 300 W Hg light source, and the rolling rate was 20 rpm, the wavelength of the radiation light was selected as 365 nm. Molecular weight and molecular weight distribution of the polymers were measured by PL GPC 50 (AGILENT, Cheshire, UK) at 25 °C using THF as eluent against polystyrene standards, flow rate: 1 mL/min, sample concentration: 1 mg/mL.

3.2. Catalyst Preparation

$H_3PW_{12}O_{40} \cdot 16.5H_2O$ of 6.35 g (0.002 mol) was dissolved in 24 mL of ethanol and heated at 40 °C for 30 min under stirring. Then, 0.49 g of $[(C_3H_3)N_2CH_3]$ (0.006 mol) in ethanol (58 mL) was added to the solution dropwise under stirring. The solution was stirred continuously for 8 h. The resultant precipitate was filtered and washed with ethanol. After drying in a vacuum oven at 30 °C for 12 h, a white powder catalyst was obtained. Yield: 77.8% (based on W). Anal. Calcd for $C_{12}H_{18}N_6O_{40}PW_{12}$: C: 4.59; N: 2.68; H: 0.57%. Found: C: 4.62; N: 2.61; H: 0.62%.

3.3. Electrochemical Property Determination

All electrochemical measurements were carried out on a CHI 660 electrochemistry workstation (Chenghua, Shanghai, China). A three-electrode setup was employed for the electrochemical studies, gold (Au) was utilized as the working electrode, modified with the complex acetone solution. A platinum disk was used as the counter electrode, and the reference electrode was a saturated calomel reference

electrode (SCE). Before being used, the oxidized gold working electrode surfaces were generated by applying 2.0 V *vs.* SCE for 90 s in 2 M NaOH solution.

3.4. Typical Polymerization Process

The catalytic activity test of *N*-methyl imidazolium phosphotungstic salt was performed as follows: $[(C_3H_3)N_2CH_3]_3(PW_{12}O_{40})$ of 0.31 g (0.1 mmol) was mixed with 10 g of acetone in a quartz reaction tube, stirred by magnetic power. Dry nitrogen was input for about 20 min to eliminate the effect of possible air, and then 0.10 g (10 mmol) of styrene was added. The polymerization was performed on a XPA-1 photochemical reactor, with 300 W Hg light source and the rolling rate was 20 rpm, the wavelength of the radiation light was selected as 365 nm. The polymerization was terminated by addition of acidic methanol, the polymer product was precipitated into 50 mL methanol, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight. The catalyst was filtered and washed three times with acetone, and then dried in vacuum at 80 °C for reuse.

Gel permeation chromatography (GPC) analyses of polymer samples were carried out at 25 °C using THF as eluent on a Polymer Laboratory-50 instrument and calibrated using monodispersed polystyrene standards at a flow rate of 1.0 mL/min. Number-average molecular weight and polydispersity of polymers were given relative to PS standards.

4. Conclusions

In summary, *N*-methyl imidazolium phosphotungstic salt was an excellent catalyst for the polymerization of vinyl monomers. Polymerizations showed controlled characteristics, and the catalyst could be isolated easily and reused for at least 10 times.

Author Contributions

Dianyu Chen conceived and designed the experiments; Zhaoyi Deng performed the experiments; Zhaoyi Deng and XiaoqinLiu characterized the catalyst; Xiaoqin Liu determined electrochemical property; Rong Wang operated GPC and obtained Mn and PDI of the polymer product.

Conflicts of Interest

The authors declare no conflicts of interest.

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