



A new catalyst of 12-molybdophosphoric acid for cationic polymerization of styrene: activity and mechanism studies

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Abstract

A new and efficient catalyst of 12-molybdophosphoric acid was employed in this paper for styrene cationic polymerization. The characteristic polymerization was so efficient that in less than 20 min the monomer conversion was up to 84%, and the polymer product yield was obtained 74.66%. In order to acknowledge this new catalysis reaction, special techniques of infrared spectroscopy (IR), nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction (XRD), and X-ray photoelectronic energy spectroscopy (XPS) were used in this paper, and it showed that the crystal structure of the heteropoly anion was not destroyed during reaction, and the protons dissociating in catalyst played important role in polymerization. Finally the possible mechanism was put forward as electron coordination-cationic polymerized reaction theory. In this theory, the aimed catalyst played three important roles as: oxidation agent, polymerization initiator, and the operate anion of the growing cationic center.

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1. Introduction

12-Molybdophosphoric acid, with the crystal structure of Keggin style [1], molecular of $H_3PMo_{12}O_{40}$, was one kind of the widely applied catalytic species with high catalysis efficiency [2,3]. Until now, 12-molybdophosphoric acid had been employed widely as organic reaction catalyst in the fields of both homogeneous and heterogeneous reactions [4–9]. Furthermore, 12-molybdophosphoric acid and its derivatives were found great latencies in the fields of electricity [10], magnetism [11], medicine [12] and the like.

In recent 20 years, 12-molybdophosphoric acid had also been introduced into polymerization of oxygen heterocycle compounds such as tetrahydrofuran and so on. In these reactions, the aimed catalyst acted as polymerization initiator, and the reaction mechanism was accepted commonly as cationic polymerization [13–17]. But the deficiency was still present, that was, all of the monomers studied before were limited into cyclic ethers, acetals, polyalcohols and lactones, but not to any others more, and the mechanism was not found in public literatures.

In present paper, the catalysis of 12-molybdophosphoric acid was used for cationic polymerization of styrene, the efficiency of this catalyst was studied, and the possible mechanism of electron

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coordination-cationic polymer reaction theory was put forward.

2. Experimental procedure

2.1. Pretreatment of styrene

Before polymerization, the monomer of styrene, provided by Lanzhou Petro-Chemical Research Institute (Lanzhou, China), was pretreated as following process: washed with 5% of sodium hydroxide and distilled water, then dried in the presence of calcium chloride, and distilled with vacuum of 0.08 and temperature of 60 °C.

2.2. Pretreatment of 12-molybdophosphoric acid

In order to eliminate the effect of water, which could cause electron transfer in 12-molybdophosphoric acid, the catalyst, provided by Shanghai Chemical Reagent Plant (China), was pretreated at 150 °C for 10 h before use.

2.3. Intermediate preparation

Reaction intermediate was the important component to study the polymerization mechanism, in this paper, the reaction intermediate was obtained by following operations: small amount of 12-molybdophosphoric acid was placed in a dried vacuum tube, and steam of styrene was passed continuously in to the vacuum tube at room temperature until the color of catalyst turned from yellow to blue.

2.4. Typical procedure

The procedure was performed with 12-molybdophosphoric acid as the catalyst in a flask at ice salt bath (about -6°C). Ten milliliters of styrene and 20 ml of dichloromethane were added into the flask, stirred with magnetic power. Ten minutes later, 20 mg of 12-molybdophosphoric acid and very small amount of tetrabutylammonium fluoride and titanium tetrachloride was added. As the solubility of 12-molybdophosphoric acid in CH_2Cl_2 and styrene was very limited, the solution at beginning was not homogeneous, and the initiating step was very slow.

But once the color was evidenced from the initially yellow to blue (which was predicated of initiating beginning), polymerization was taken place, with temperature increasing. After polymerization, the sample product was filtered by reprecipitation twice from CH_2Cl_2 solution to excess ethanol, and dried in vacuum until all small molecules of alcohol and styrene were discarded off. The polymer was isolated as blue power.

2.5. Characterization techniques

Catalyst, intermediate and polymer product were characterized by the techniques of infrared spectroscopy (IR), nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction (XRD), and X-ray photoelectronic energy spectroscopy (XPS). Polymer products molecular weight was tested by gel permeate chromatography (GPC).

GPC was recorded by Waters 150C/GPC (Waters, USA). Infrared spectrums in the $400\text{--}4000\text{ cm}^{-1}$ were recorded on a Perkin-Elmer 1710 Fourier Transform spectrometer. NMR spectrum was recorded on Varian FT-80A spectrometer. The X-ray diffraction spectrum of the sample was recorded on a Rigaku D MAX III VC, Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5404\text{ \AA}$). XPS measurements were performed with a PHI-5702 XPS/AES spectrometer, using the $\text{Mg K}\alpha$ X-ray source (1253.6 eV) and a pass energy of 29.35 eV. The reference energy was the C 1s signal at 284.6 eV.

3. Results and discussion

3.1. The catalysis efficiency of 12-molybdophosphoric acid in polymerization

Styrene polymerization initiated by 12-molybdophosphoric acid was accompanied with temperature variation. After 9 min induction period, the reaction temperature increased sharply from -6°C to the maximum of 26°C , then decreased down without a pause (summarized in Fig. 1). The temperature inflexions were recorded as a, b, c, d, e, f, and g, respectively, and relevant results were summarized in Table 1. At the highest temperature spot (only 20 min), monomer conversion was up to 84%, and the polymer yield to 74.66%. At the same time, although Mn of all of the

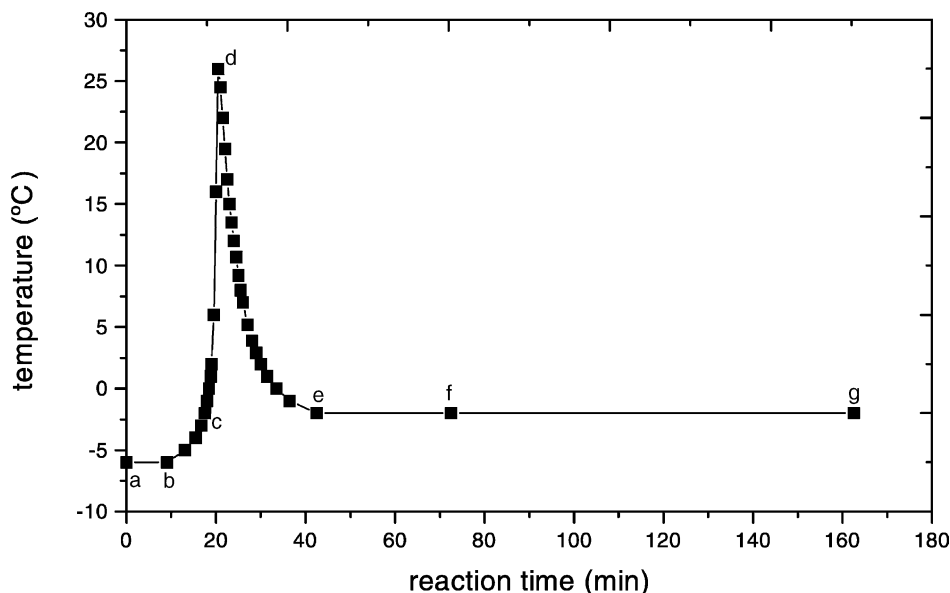


Fig. 1. The relationship of temperature with reaction time.

polymer products was not very large, polydispersity were narrow, that is, the aimed catalyst had the function to stabilize the active center when styrene polymerized, which will be discussed later. In summary, the catalyst for this polymerization is very efficient.

3.2. Characterization

3.2.1. IR characterization

From the IR spectrum of the catalyst of 12-molybdophosphoric acid (Fig. 2a), the band at 1064 cm^{-1} was attributed to the asymmetric stretching vibration of the central PO_4 tetrahedron ($\text{Vas}(\text{P}-\text{O})$), and the band at 962 cm^{-1} , to a stretching vibration of Mo

$=\text{O}_t$ ($\text{Vas}(\text{Mo}=\text{O})$), where O_t was the terminal oxygen. The other two bands, at 869 and 768 cm^{-1} , were assigned to the stretching vibration of the $\text{Mo}-\text{O}_c-\text{Mo}$ bridges between corner shared MoO_6 octahedra ($\text{Vas}(\text{Mo}-\text{O}-\text{Mo})$), and to the stretching vibration of the $\text{Mo}-\text{O}_e-\text{Mo}$ bridges between edge shared MoO_6 octahedra ($\text{Vas}(\text{Mo}-\text{O}-\text{Mo})$), respectively. And these four bands were the characteristic IR bands for 12-molybdophosphoric acid structure [18–20].

Comparing with the bands change discussed above for Fig. 2a, although the styrene IR bands were obvious in reaction intermediate and polymer product (see Fig. 2b and c), the corresponding catalyst bands

Table 1
Relationship of monomer conversion with reaction time

	Inflection						
	a	b	c	d	e	f	g
Time (min)	0	9	16	20	42.5	72.5	162.5
Conv. (%)	0	12.57	32.73	84.00	88.82	91.14	94.78
Yield (%)	0	11.23	30.90	74.66	82.82	89.91	93.30
Mn (10^3)	–	6.55	7.57	7.68	5.88	4.45	6.87
<i>D</i>	–	2.58	2.60	2.65	2.70	2.62	2.39

Conv. is the monomer conversion, Mn is the number average molecular weight, and *D* is the polydispersity of the polymer product.

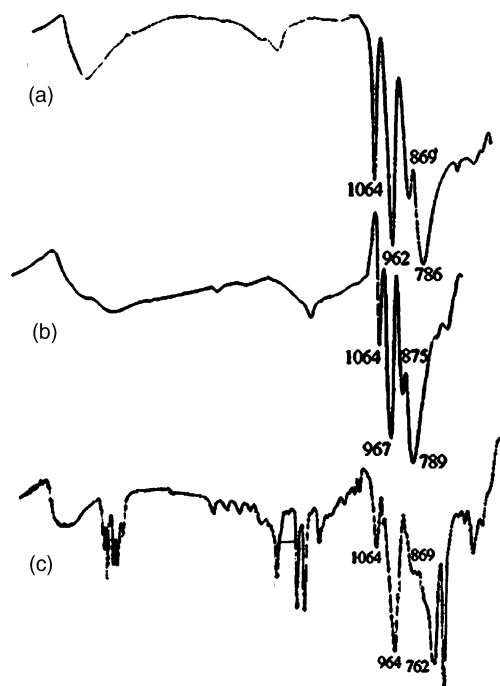


Fig. 2. The IR spectrum: (a) about 12-molybdophosphoric acid before reaction; (b) about 12-molybdophosphoric acid adsorbed styrene; (c) about the polymer produced.

were still appeared between 600 and 1100 cm^{-1} . It could be concluded that the crystal structure of 12-molybdophosphoric acid was not destroyed during polymerization.

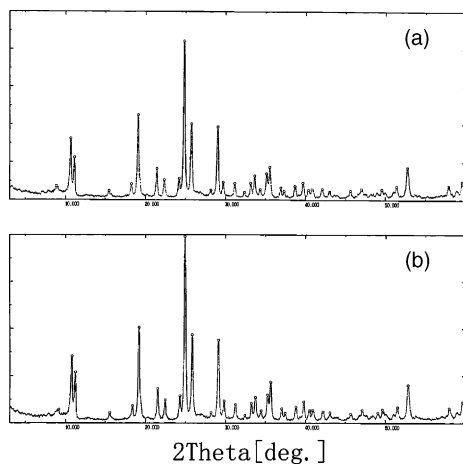


Fig. 3. The X-ray diffraction spectrum of the samples: (a) about 12-molybdophosphoric acid; (b) about the reaction intermediate.

3.2.2. XRD characterization

Fig. 3 showed that both the catalyst and the intermediate had the same X-ray diffraction intensity changes within the theta of 0 – 30 . That was, the crystal structure of the heteropoly anion was not destroyed during reaction, which was also proved by IR spectrums studied above.

3.2.3. ^1H NMR characterization

As discussed before [6–8], dissociate protons in 12-molybdophosphoric acid was divided into two kinds: hydrogen bonding to bridge oxygen and to end oxygen, and which was very active in catalysis. ^1H NMR (in Fig. 4) showed that before polymerization, chemical shift of proton was majorly contributed

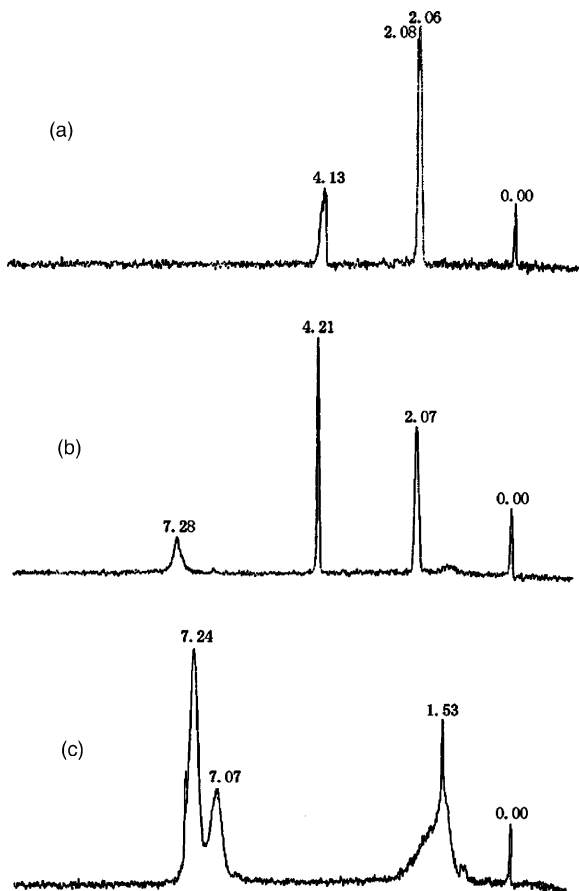


Fig. 4. Nuclear magnetic resonance (NMR) spectroscopy: (a) 12-molybdophosphoric acid; (b) reaction intermediate; (c) the polymer product.

at 2.06 ppm, which was attributed to the chemical structure of bridge oxygen of Mo–O(H)–Mo (including Mo–O_c(H)–Mo and Mo–O_e(H)–Mo); but very small peak intensity was appeared at 4.13 ppm, which was attributed to the structure of end oxygen of Mo–O(H). After adsorption of styrene, the proton at bridge oxygen shifted quickly to end oxygen (peak intensity was increased at 2.06 ppm, and decreased at 4.21 ppm). But for the polymer product, the bands at 2.07 and 4.21 ppm were all disappeared, that was, the protons were all taken part into the polymerization. It was indicated that the proton in catalyst of 12-molybdophosphoric acid was active, easily to transfer from bridge oxygen to end oxygen, and played important role in polymerization procession.

3.2.4. XPS characterization

The surface chemical composition of the catalyst and polymer product was analyzed by X-ray photoelectron spectroscopy. From the results in Table 2, two peaks appear for the original Mo was appeared, and the area ratio was 2:3, bonding energy was 232.8 and 236.1 eV, which indicated that the Mo in

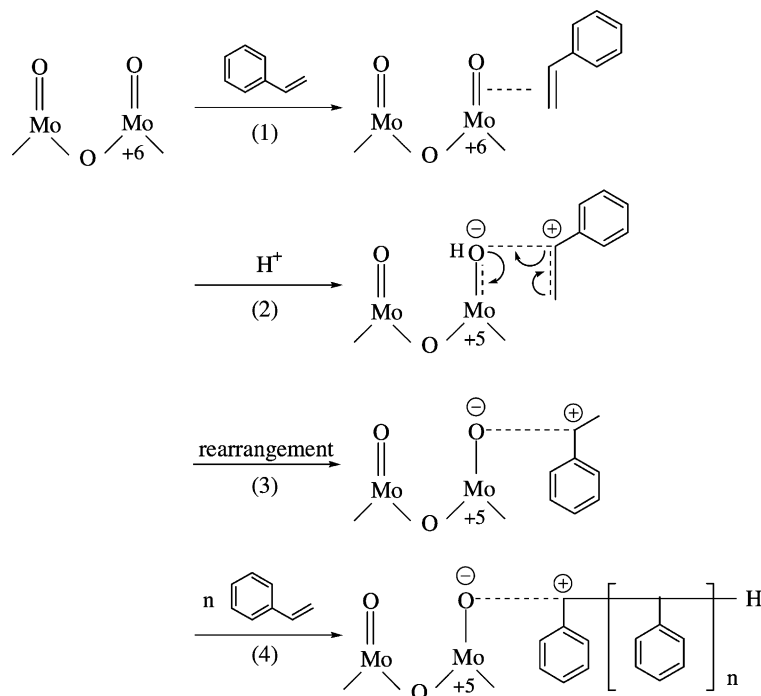
Table 2

The XPS results of the catalyst of 12-molybdophosphoric acid and the polymer product

Atom	12-Molybdophosphoric acid	The polymer product
Mo 3d	232.8, 236.1	231.0 (Mo ⁵⁺ 3d5/2), 234.5 (Mo ⁵⁺ 3d3/2), 233.8 (Mo ⁶⁺ 3d5/2), 237.4 (Mo ⁶⁺ 3d3/2)
O 1s	530.8, 532.3	532.4, 533.8
C 1s	286.3, 284.6 ^a	285.7, 284.6

^a Refers to C 1s reference energy.

12-molybdophosphoric acid was lying in the state of Mo⁶⁺ [21]. But after polymerization, the peaks were splitted into fours as 231.0 eV (Mo⁵⁺ 3d5/2), 233.8 eV (Mo⁶⁺ 3d5/2), 234.5 eV (Mo⁵⁺ 3d3/2) and 237.4 eV (Mo⁶⁺ 3d3/2), which indicated that part of Mo⁶⁺ was reduced to Mo⁵⁺. It might be caused by accepting electrons from styrene monomer, and expressed as the color change from yellow to blue during polymerization. Part of O 1s at 530.8 and 532.3 eV was shifted up 1.5–532.4 and 533.8 eV, and part of C 1s at 286.3 eV



Scheme 1. Reaction mechanism of styrene polymerization caused by 12-molybdophosphoric acid.

was shifted down 0.6–285.7 eV, which could be indicated that the electron was deviated from C and lean to O, and the weak force of the cationic active center might be formed between the atoms of C and O.

3.3. Possible mechanism deduction

As discussed above, the possible styrene polymerization mechanism would be described as **Scheme 1**. Where, in step 1, the monomer molecular of styrene was adsorbed on the surface of the catalyst, 12-molybdophosphoric acid. In step 2, electron coordination was formed between these molecules by electron transfer, and proton in 12-molybdophosphoric acid was shifted quickly from bridge oxygen to end oxygen. This step was an oxygenation reaction step, in the catalyst of 12-molybdophosphoric acid, Mo^{6+} was changed partly into Mo^{5+} , with color changed from yellow to blue. Step 3 was the initiating step in styrene polymerization. The cationic active center was formed in this step by electron and proton rearrangement. Step 4 was the chain-increasing step, and in this step, polystyrene was produced.

4. Conclusion

12-Molybdophosphoric acid was an efficient catalyst for styrene cationic polymerization, and which followed the reaction mechanism of electron coordination-cationic polymerizing theory. In this theory, the aimed catalyst played three important roles as: election capture, polymerization initiator, and the operate anion of the growing cationic center.

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