



Dual role study of 12-molybdophosphoric acid on styrene polymerization

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Received 7 May 2003; received in revised form 4 July 2003; accepted 7 July 2003

Abstract

12-Molybdophosphoric acid (12-MPA) was studied in present paper as a special polymerized catalyst with a dual catalytic role of initiation and inhibition. Dilatometry results indicated that 12-MPA played its inhibition function in free radical polymerization of styrene initiated by AIBN, although we had reported the initiation role not long ago. 12-MPA inhibition mechanism was put forward by ESR spectrum as redox reaction between additive of 12-MPA and initiator of AIBN, which was supported by IR, TG/DTA and GC-MS studies. Thus, the dual role of 12-MPA in styrene polymerization was put forward, that is, 12-MPA played as cationic polymerization initiator when it alone in styrene, but as inhibitor when existed together with AIBN. In the condition of the latter, an excessive problem was discussed, e.g. if part of AIBN remained after oxidation, styrene would be polymerized following free radical mechanism, but the reaction rate was slower than that without 12-MPA (12-MPA was expressed as inhibitor); on the contrary, if the residual reagent was 12-MPA after redox, styrene polymerization would still take place, but styrene would be polymerized following cationic mechanism.

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Keywords: 12-Molybdophosphoric acid; Styrene; Polymerization; Catalysis; Dual role

1. Introduction

Catalysis by 12-molybdophosphoric acid (12-MPA), an important kind of heteropoly acid catalysts, and related polyoxometalate compounds were a field of increasing importance [1–6]. 12-MPA had several advantages as catalyst that made it economically and environmentally attractive [1]. On the other hand, 12-MPA had a very strong capability approaching the superacid region; furthermore, they were efficient oxidants, exhibiting fast, reversible multi-electron redox transformations under rather mild condition [7–9]. Until now, 12-MPA was widely employed for both fundamental and applied researches.

In recent several years, besides the use for acid and redox catalyst, 12-MPA had been introduced into the field of polymer science and engineering. Monomers such as cyclic ethers, acetals, polyalcohols and lactones were polymerized

in the presence of 12-MPA [10–14]. Not long ago, we reported it as a new catalyst for cationic polymerization of styrene [15], and the reaction mechanism was put forward at the same time. It seemed that 12-MPA was a typical initiator for styrene polymerization.

But about 15 years ago, Khakhinov et al. [16] had reported the reverse view that 12-MPA played its inhibition role in free radical polymerization of (meth)acrylate and its relative. And this view was very coincident to the strong oxidation property of 12-MPA [18]. Therefore, another problem that what was the role of 12-MPA played in polymerization was put forward.

Since the initiation function had been reported by us [15], in this paper, the research was emphasized on the other function of the dual role of 12-MPA. Dilatometry was firstly introduced in present paper to characterize the inhibition effect of 12-MPA on styrene polymerization when AIBN existed. At the same time, ESR, IR, TG and GC-MS were employed to explain the reason of inhibition, that is, when alone in styrene polymerization system, 12-MPA could initiate styrene cationic polymerization; but once it existed with the free radical initiator of AIBN, AIBN would be partially

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consumed by redox with 12-MPA, and the catalyst of 12-MPA would be exhibited as inhibitor.

2. Experimental

2.1. Materials and apparatus

Styrene came from Lanzhou Petrochemical Complexes (Lanzhou, China), and was purified by distillation before use. 12-MPA was purchased from Beijing Chemical Plant (Beijing, China), and used immediately without purification. 2,2'-Azobis (isobutyronitrile) (AIBN) was recrystallized from ethanol for twice before use. The other reagents were all analysis grade.

Dilatometer was prepared with 1 mm capillary diameter, and 14 ml reaction trough cubage. ESR spectra were recorded on Bruker ER 200D-SRC electron paramagnetic resonator (Germany), with modulate frequency of 100 KHz, microwave frequency of 9.44 GHz, time constant of 0.5 s and intensity of magnetic field as 200–3380 G in the detecting, the radical stabilizing reagent was selected as (*tert*-C₄H₉)NO.

IR spectra was recorded on Nicolet AVATAR 360 infrared spectrometer (Germany), UV spectra was recorded on Shimadzu UV-240 ultraviolet spectrometer (Japan), and the TG/DTA was operated on ZPY-2P thermal analysis apparatus (Shanghai, China) with temperature-rising rate of 10 °C min⁻¹. GC-MS was operated on Finnigan Trance DSQ GC/MS 2000, using stretch quartz capillary column (Ptx-5ms, 15 m × 0.25 mm i.d.), ion source of EI, temperature was rising from 18 to 300 °C.

2.2. Operation of the dilatometer

Before polymerization, the monomer of styrene is pre-treated as following process: washed by 5% of sodium hydroxide and distilled water, then dried in the presence of calcium chloride for 24 h, and distilled with vacuum of 0.08 and the temperature of 60 °C.

Small amount of the 12-MPA and 20 mg of AIBN are dissolved in 20 ml styrene, and 14 ml complex solution is removed into dilatometer, and started to polymerize in constant temperature trough with temperature of 60 °C, record the solution line in dilatometer with different time.

2.3. Reaction of 12-MPA and AIBN

In a 25 ml rockered flask, 25 mg 12-MPA was added into the access AIBN dichloromethane solution. Stirred the solution steadily, and rising the temperature slowly up to 40 °C. Stopped the reaction after 2 h later, filtrated the catalyst from reaction solution, and dried in vacuum. IR, UV and TGA were employed for detect catalyst change, GC-MS for solution component monitoring.

3. Results and discussion

3.1. Inhibition function in free radical polymerization determined by dilatometer

As discussed before, 12-MPA was an efficient catalyst with strong oxidation properties, and large capability for capturing electrons. Just for this character of oxidation, 12-MPA was thought ordinarily to be deleterious to free radical reaction, including free radical polymerization of styrene. In order to understand the function of 12-MPA in free radical polymerization quantitatively, method of dilatometry was employed in this paper for determining 12-MPA effect on styrene's free radical polymerization.

As we all known, the rate of free radical polymerization has been provided, that is

$$R_p = K_p[M] \left(\frac{fK_d[I]}{K_t} \right)^{1/2} \quad (1)$$

where R_p is the overall rate of polymerization, K_d the rate constant for the initiator dissociation, K_p the rate constant for propagation step, K_t the rate constant for termination step, $[I]$ the concentration of the initiator species, $[M]$ the overall monomer concentration added, and f is the molar fraction of initiator radicals formed which actually add to monomer and initiate polymerization.

After a series of deduction [17], Eq. (1) would be converted to

$$R_p = \frac{[M]d_2r}{V_0(d_2 - d_1)} \frac{\Delta h}{\Delta t} \quad (2)$$

where Δh is the height change at any time Δt , d_1 the density of monomer, d_2 the density of polymer, V_0 the initial volume of dilatometer, and r is the cross-radius of the capillary in dilatometer. For

$$\frac{[M]d_2S}{V_0(d_2 - d_1)} = K \quad (3)$$

where K is a constant for this experiment, and is defined here as the overall polymerization rate constant, and S is the cross-area of the capillary. That was, Eq. (2) could be summarized as

$$R_p = K \frac{\Delta h}{\Delta t} \quad (4)$$

Eq. (4) is the basis of dilatometry determination, for $d_1 = 0.8712 \text{ g ml}^{-1}$, $d_2 = 1.050 \text{ g ml}^{-1}$, $V_0 = 14 \text{ ml}$, $[M] = 8.377 \text{ mol l}^{-1}$, $S = 2.04 \times 10^{-2} \text{ cm}^2$, so $K = 7.174 \times 10^2 \text{ mol (l min)}^{-1}$.

In this experiment, different concentration of 12-MPA effect on styrene free radical polymerization was shown in Fig. 1. It was obviously that 12-MPA with different concentration in solution did restrain the free radical polymerization of styrene (slope of the line in Fig. 1 slowing down), and as 12-MPA concentration increased, polymerization rate fell in some degrees (Table 1).

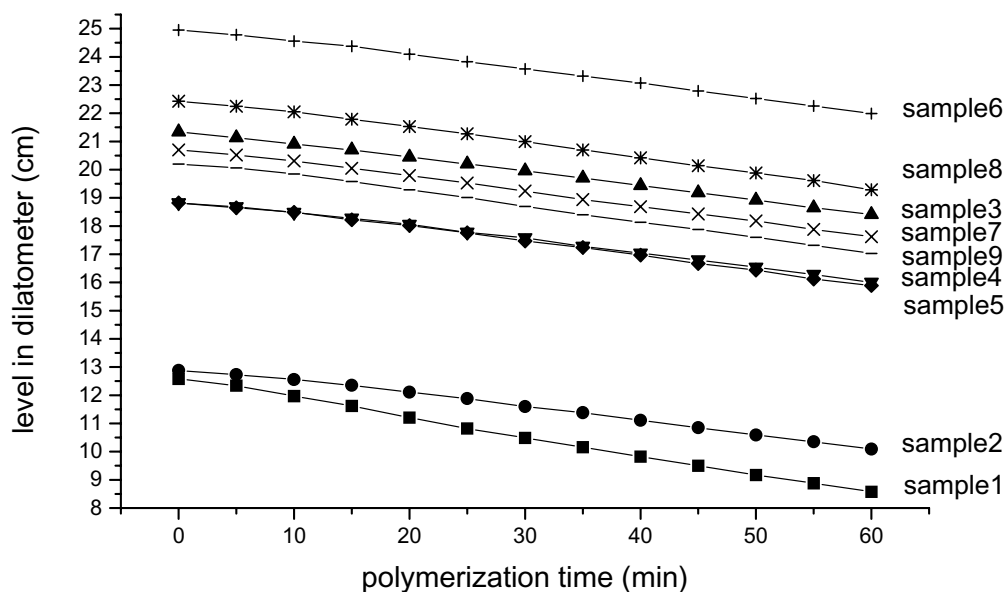


Fig. 1. Effect of 12-MPA on polymerization by dilatometer, where samples 1–9 were corresponding to the 12-MPA concentration of 0, 0.108, 0.0756, 0.0529, 0.0370, 0.0260, 0.0182, 0.0127 and 0.0094 mg ml⁻¹, respectively.

In order to understand this effect more clearly, the kinetic study was carried out. After regression, relationship of the polymerization rate changes and the concentration of 12-MPA could be obtained as

$$\log \Delta R_p = -0.67 + 0.16 \log[H] \quad (5)$$

Eq. (5) could be easily converted to $\Delta R_p = 0.21 \times [H]^{0.16}$, $[H]$ is the molar concentration of 12-MPA. That was, the decreased polymerization rate caused by 12-MPA was direct proportion to $[H]^{0.16}$.

Apparently, 12-MPA did play inhibition function in free radical polymerization initiated by AIBN. But its effect on polymerization was not so remarkable to the theoretical estimation [16], the reason of which, by our consideration, would be contributed to the limited solubility of 12-MPA in styrene.

3.2. Dual role deduction

In order to know the inhibition process of 12-MPA in free radical polymerization of styrene with AIBN, the characterization method of ESR was employed.

Comparing with decomposition ESR spectra of *tert*-C₄H₉NO (Fig. 2a) AIBN/*tert*-C₄H₉NO (Fig. 2b) and styrene/*tert*-C₄H₉NO (Fig. 2c), the ESR spectra of styrene/AIBN/*tert*-C₄H₉NO (Fig. 2d) would be simply contributed to the composition complex spectra of AIBN and styrene. But the band was broadened than the above three, the reason of which would be considered as cooperation of several different composition radicals. But for the styrene/AIBN/12-MPA/*tert*-C₄H₉NO (Fig. 2d), as 12-MPA added, most of the radical formed during reaction was captured and did not appear in spectra, and which would be considered for the reason 12-MPA restraining styrene radical polymerization.

In a word, the inhibition function of 12-MPA in free radical polymerization initiated by AIBN, in great degrees, owned to the free radical capturing of 12-MPA during reactions.

3.3. Reaction between 12-MPA and AIBN

For the dual role of initiation function of AIBN and radical capturing property of 12-MPA, a hypothesis was proposed.

Table 1
Calculation results from Fig. 1

[H] (mg ml ⁻¹)	log[H]	$\Delta h/\Delta t$ (cm min ⁻¹)	R_p (mol min ⁻¹)	ΔR_p (mol min ⁻¹)	log ΔR_p
0		-0.0685	-0.4837	0	
0.108	-0.966	-0.0478	-0.3389	0.1448	-0.839
0.0756	-1.119	-0.0495	-0.3510	0.1327	-0.877
0.0529	-1.276	-0.0480	-0.3404	0.1433	-0.844
0.0370	-1.432	-0.0502	-0.3560	0.1277	-0.894
0.0260	-1.585	-0.0504	-0.3574	0.1263	-0.899
0.0182	-1.740	-0.0526	-0.3730	0.1107	-0.956
0.0127	-1.896	-0.0532	-0.3772	0.1065	-0.973
0.0094	-2.027	-0.0547	-0.3879	0.0958	-1.018

[H] is the mole concentration of 12-MPA in styrene.

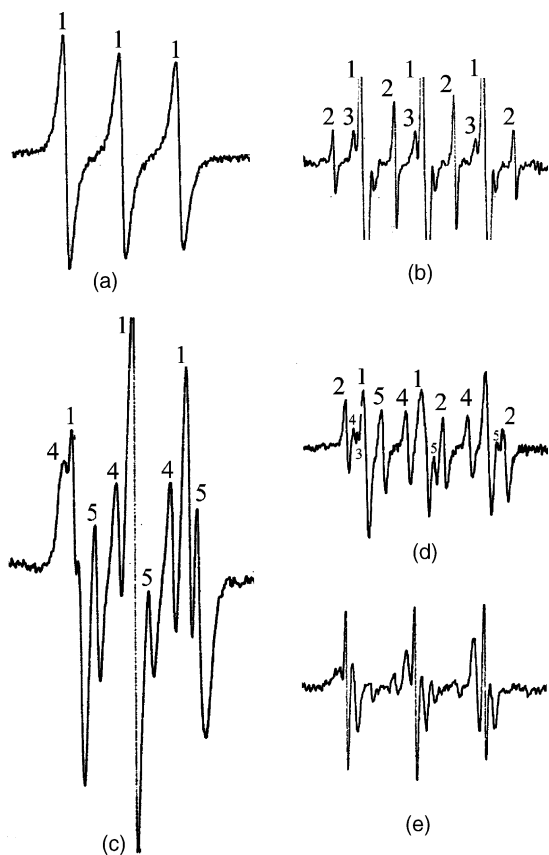


Fig. 2. 12-MPA effect on styrene radical polymerization by ESR spectra at 60°, where (a) the radical capture reagent of *iso*-C₄H₉NO; (b) AIBN; (c) St; (d) AIBN and St; (e) AIBN, 12-MPA and St.

That was, in the polymerization system, the first reaction would be taken place with great possibility between 12-MPA and AIBN, and the interaction result determined the polymerization property. The hypothesis was proved as follows.

After reaction, AIBN was decomposed partially into smaller molecules; and at the same time, 12-MPA was reduced, and the color was changed from yellow to blue, which was suggested part of Mo in 12-MPA was reduced from +6 valence to +5 or even to +4 [15,20]. In Fig. 3, although the catalyst crystalline structure did not change (characteristic IR bands of Keggin structure at 3379, 1599, 1064, 962, 870, and 782 cm⁻¹ [20]), but the new bands appeared between 1700 and 1600, 1600–1100 and <700 cm⁻¹ fields, was the proofs of decomposed products of AIBN, and the reduced products was adsorbed on 12-MPA surface by coordinated bond [18,19]. Once these coordinated bond positions were all saturated by reduced molecular, 12-MPA would lose his oxidation properties.

Furthermore, studies by TG/DTA analysis (Fig. 4) showed that there did have any small molecules loaded on the catalyst surface of 12-MPA by chemical bond ($H = 100.81 \text{ J g}^{-1}$). If all of these small molecules were regarded as 2-cyano-propene (the primary reduced product of AIBN), according to the loss weight ratio of 8.7%, there were ap-

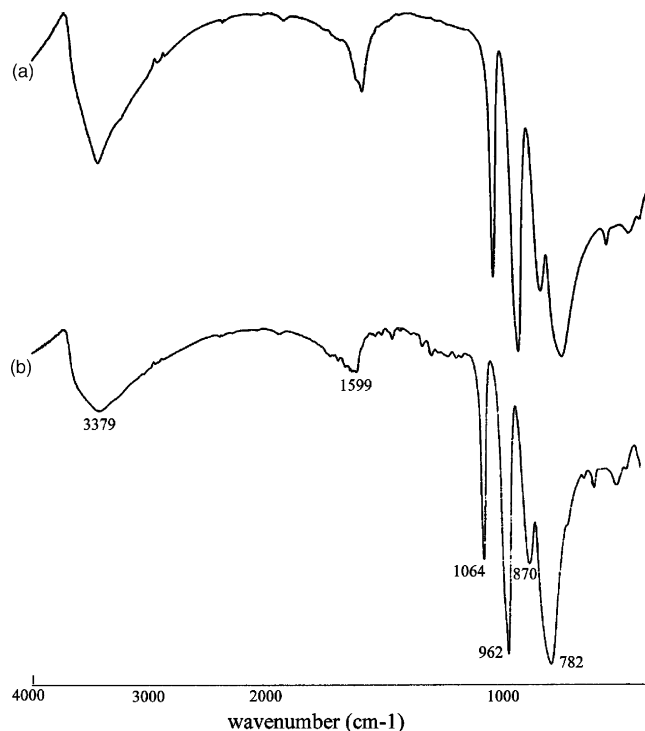


Fig. 3. IR spectra of 12-MPA catalyst, where (a) the pure 12-MPA; (b) the 12-MPA after reaction with AIBN.

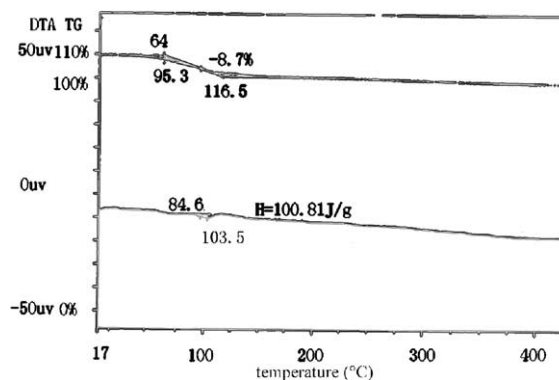
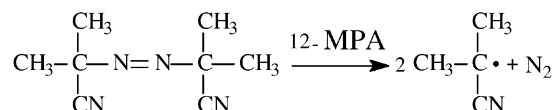


Fig. 4. TG/DTA spectra of 12-MPA after reaction with AIBN.

proximate 2.5 mol small molecules on 1 mol 12-MPA, and almost to 12-MPA saturated absorbability (theoretical value is 3) [21].

GC-MS results showed that despite AIBN unreacted with 12-MPA, the fractional compounds in reaction solution were found as 2-cyano-propenyl radical, 2-cyano-propene, 2-cyano-propane, and 1-vinyl-*N*-heterocyclopropane. It was distinctly that all of these small molecules were the derivatives of 2-cyano-propenyl radical. So, the decomposing equation of AIBN with 12-MPA would be expressed as



4. Conclusion

Summarily, 12-MPA played its dual role in styrene polymerization at different reaction conditions. Firstly, 12-MPA would initiate styrene cationic polymerization when it alone in styrene. Secondly, in the free radical polymerization of styrene initiated by AIBN, 12-MPA would react with AIBN in priority, and if AIBN is the excessive reagent, styrene would polymerized as free radical mechanism, and 12-MPA played its inhibition in this polymerization system; if 12-MPA was excess, 12-MPA was the polymerization initiator and would initiate styrene for cationic polymerization.

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