

# Polymerization of Methyl Methacrylate Catalyzed by Macromolecule–Copper (II) Complex in Sodium Sulfite Aqueous System

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**ABSTRACT:** Vinyl polymerization initiated by a copper complex immobilized on a novel polymer and characterization has been studied. Monomer, 4-aldehyde-3-hydroxy phenyl acrylate (Ahpa), and its homopolymer, poly(4-aldehyde-3-hydroxy phenyl acrylate) (PAhpa), were synthesized and characterized using IR, elemental analysis, <sup>1</sup>H NMR, TOF MS, etc. The side chain of the polymer can further coordinate with transition metal ions. Its polymeric Cu(II) complex in Na<sub>2</sub>SO<sub>3</sub> system is proved to be another useful catalyst in polymerization of methyl methacrylate (MMA) at room temperature. The obtained poly(methyl methacrylate)

(PMMA) is similar to those determined by conventional free radical polymerization at the same conditions. Moreover, the catalytic mechanism studied was a "Coordination Hydrogen-Transfer" process, which is different from that of CuCl<sub>2</sub>/Na<sub>2</sub>SO<sub>3</sub> system, but analogous with that of PVAm-Cu(II)/Na<sub>2</sub>SO<sub>3</sub> (PVAm = polyvinylamine) system, was speculated and testified. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1285–1290, 2007

**Key words:** macromolecule–metal complexes; radical polymerization; catalyst; cupric complex

## INTRODUCTION

Synthetic macromolecule–metal complexes (MMC) have been investigated intensively as catalysts for practical use because they are more reactive than the corresponding monomeric analogues because of the specificity induced by the macromolecular matrix.<sup>1–4</sup> For example, it was found that immobilization of titanium, molybdenum, and neodymium on the polymer support resulted in an increase of catalytic activity in polymerization of olefins,<sup>5</sup> alkynes,<sup>6</sup> and dienes.<sup>7</sup> Nowadays, polymerizations using efficient MMC systems under mild and environmental-friendly conditions are attracted considerable attention.<sup>8,9</sup> However, the mechanism of polymerization initiated using MMC is rarely studied. In our previous report,<sup>9,10</sup> a Cu(II) complex, PVAm–Cu(II)/Na<sub>2</sub>SO<sub>3</sub> (PVAm = polyvinylamine) system, was used in the polymerization of MMA for its good catalytic property and moderate reaction condition. More interestingly, the mechanism of

polymerization is not the traditional reduction–oxidation mechanism as in CuCl<sub>2</sub>/Na<sub>2</sub>SO<sub>3</sub> system, but the coordination of PVAm and Cu(II) that initiates the polymerization. Based on this result, we attempt to design and synthesis different monomers containing different coordination atoms. Their corresponding polymers as ligands can coordinate transition metal ions to form MMCs. Our interest is focused on the catalytic property of those MMCs in polymerization of vinyl monomers. By comparing the different coordinate ability of polymer ligands, we can study and compare their polymerization mechanisms. It may be important for better designing practical MMCs with higher catalytic property.

This study deals with a monomer, 4-aldehyde-3-hydroxy phenyl acrylate (Ahpa), and its homopolymer, poly(4-aldehyde-3-hydroxy phenyl acrylate) (PAhpa), which is thermally stable and its side chain can coordinate with Cu(II) ions. This polymeric Cu(II) complex in Na<sub>2</sub>SO<sub>3</sub> system is proved to be another useful catalyst in polymerization of MMA at room temperature. However, its catalytic mechanism is also studied, includes a hydrogen-transfer coordination (HTC) process analogous with that of PVAm–Cu(II)/Na<sub>2</sub>SO<sub>3</sub> system.

## EXPERIMENTAL

### Materials

Benzoyl peroxide (BPO) purchased from Beijing chemical reagents company was recrystallized from chloro-

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form/methanol mixture, 2,4-dihydroxybenzaldehyde (Acros) was recrystallized from ethanol/water mixture. Acryloyl chloride (Merck, analytical grade) was used as received. Dimethylformamide (DMF), copper chloride, ammonia, and anhydrous sodium sulfite were all purchased from Shanghai Chemical Reagent, and MMA (China Medical (group) Shanghai Chemical Reagent) was purified by the usual procedures and stored in a refrigerator. Tetrahydrofuran (THF) and triethylamine (TEA) from Shanghai Chemical Reagent were distilled after refluxing with sodium.

### Synthesis of monomer, Ahpa

2,4-Dihydroxybenzaldehyde (6.9 g, 0.05 mol), TEA (6.8 mL, 0.05 mol), and hydroquinone (3 g) were mixed in THF (500 mL) at  $-5^{\circ}\text{C}$  and acryloyl chloride (4.5 mL in quantum satis of THF) was dropwisely added. A byproduct, quaternary ammonium salt, was formed after 3 h, and filtered off. A small amount of *p*-hydroxyl anisole was then added to the filtrate. THF was evaporated under vacuum to obtain an oil product, which was dissolved in ethyl ether, washed with distilled water, dried over anhydrous sodium sulfate, and cooled in a refrigerator. The final white block crystals were recrystallized from ethanol/water mixture. Yield: 65.6% (6.3 g).

$^1\text{H}$  NMR: 6.06–6.09 (1H, d), 6.28–6.35 (1H, q), 6.62–6.66 (1H, d), 6.81 (1H, s), 6.83–6.85 (1H, d), 7.58–7.60 (1H, d), 9.86 (1H, s), and 11.24 (1H, s). TOF-MS (EI): 192.04 (100%), 137.04 (41.65%), 78.02 (16.41), 63.00 (16.45), 62.02 (7.86). Anal. Calcd for  $\text{C}_{10}\text{H}_8\text{O}_4$ : C, 62.50; H, 4.20; O, 33.30. Found: C, 62.45; H, 4.17; O, 33.38. IR ( $\text{cm}^{-1}$ ): 1149, 1659, 1744, 3102, 3400. Melting point:  $32^{\circ}\text{C}$ .

### Polymerization of Ahpa

The polymerization of Ahpa (10 g) by using BPO (0.5 g) as initiator in THF solution (100 mL) was processed under nitrogen for 15 min at room temperature, and then refluxed for 8 h under nitrogen atmosphere. Excessive methanol was added and the precipitated PAhpa was filtered, washed with methanol, and purified by precipitated from methanol and chloroform. The final product was dried in vacuum at  $50^{\circ}\text{C}$  for constant weight.

$^1\text{H}$ -NMR: 11.19 ppm (aromatic-OH), 9.81 ppm (aldehyde), 6.72 and 7.52 ppm (aromatic protons), 1.67–2.62 ppm (methylene and methine protons).  $M_n = 3.26 \times 10^4$ ,  $M_w = 7.59 \times 10^4$ . The polydispersity index for PAhpa is 2.33.

### Preparation of PAhpa–Copper (II) complex

PAhpa (1 g) was dissolved in 60 mL of DMF and ammonia was added to adjust the pH value at 7–8. Copper (II) chloride (22 g in 100 mL water solution) was

dropwisely added to the DMF solution under stirring. The mixture was kept overnight at room temperature. The complex PAhpa–Cu(II) was precipitated and filtered, washed with DMF, acetone, and distilled water to remove excessive ligand and copper chloride respectively. The existence of chloride in washed water solution was determined by  $\text{AgNO}_3$  aqueous solution. The complex was dried in vacuum at  $60^{\circ}\text{C}$  for constant weight, grinding into 80–100 mesh. It does not dissolve in water and common organic solvents and the amount of copper in the complex estimated by titrimetric procedure is 2.93 mmol/g.

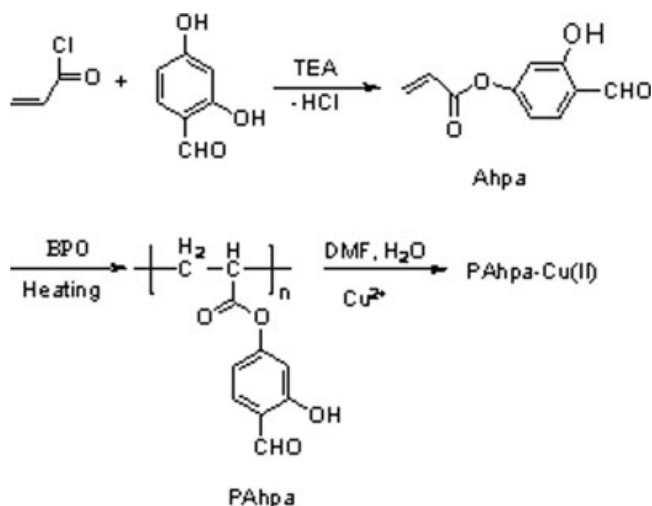
### Preparation and purification of PMMA

Proper quantities of sodium sulfite, distilled water, and PAhpa–Cu(II) were put together into a vessel at expectant temperature under nitrogen atmosphere. MMA was quickly added and the polymerization was processed. After certain intervals of reaction time, the polymerizations were quenched by adding diphenylpicrylhydrazyl (DPPH, 0.1 g). The precipitated polymers were filtered, washed with methanol, dried *in vacuo* at  $50^{\circ}\text{C}$  and the conversions were calculated. The obtained polymers were purified by dissolving in THF and subsequent precipitation into methanol and a little dilute hydrochloric acid. The purified products were dried in vacuum again at  $50^{\circ}\text{C}$  for constant weight.

The polymerizations of other monomers such as styrene (St), butyl acrylate (BA), ethyl acrylate (EA), ethyl methacrylate (EMA), butyl methacrylate (BMA), octyl methacrylate (OMA), and lauryl methacrylate (LMA) with PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$  system in aqueous solution were carried out similar to that of MMA. EMA together with BMA are polymerized in a low yield, while no other polymer products were obtained even reaction time exceeded for 48 h.

### Measurements

Copper content in the polymeric metal complex was estimated by using a titrimetric procedure after decomposing. In other words, aqueous hydrochloric acid was used to destroy the complex structure first, then the well-known iodimetry method was used to calculate the copper content in the filtrate.<sup>11</sup> The weight average molecular weight ( $M_w$ ), number average molecular weight ( $M_n$ ), and polydispersity index of PAhpa and PMMA were determined by gel permeation chromatography (Waters 1515) using THF and calibrated with polystyrene standards. FTIR spectra of PAhpa and its metal complex were recorded on a Mangna 550 spectrophotometer, using KBr pellet method.  $^1\text{H}$  NMR spectrum of Ahpa, PAhpa, and PMMA were recorded on an Inova spectrometer operating at 400 MHz and 298 K, using  $\text{CDCl}_3$  as solvent



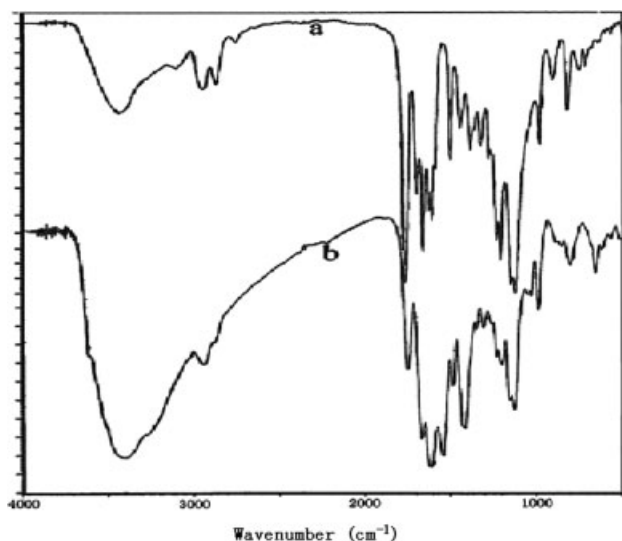
**Scheme 1** Synthesis scheme of PAhpa and PAhpa-Cu(II) complex.

with a sample concentration of 4% (w/v) and tetramethylsilane (TMS) as an internal reference. Element analysis was obtained using Carlo Erba-MOD1106 instrument. Mass spectrum was recorded on a Macro-mass TOF MS instrument. Thermogravimetric analysis was carried out on a Perkin-Elmer TGA7 thermobalance at a heating rate of  $20^\circ\text{C min}^{-1}$  under nitrogen.

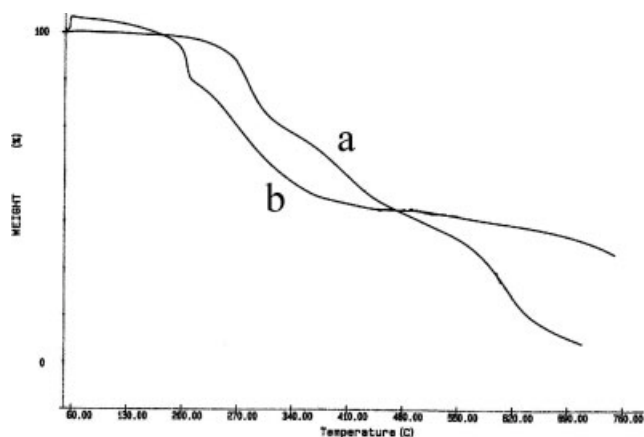
## RESULTS AND DISCUSSION

### Characterizations of PAhpa and its Cu(II) complex

Scheme 1 shows the preparations of PAhpa and its Cu(II) complex. PAhpa is characterized by H NMR, FTIR, and thermal analysis.



**Figure 1** FTIR spectra of PAhpa (a) and PAhpa-Cu(II) (b).



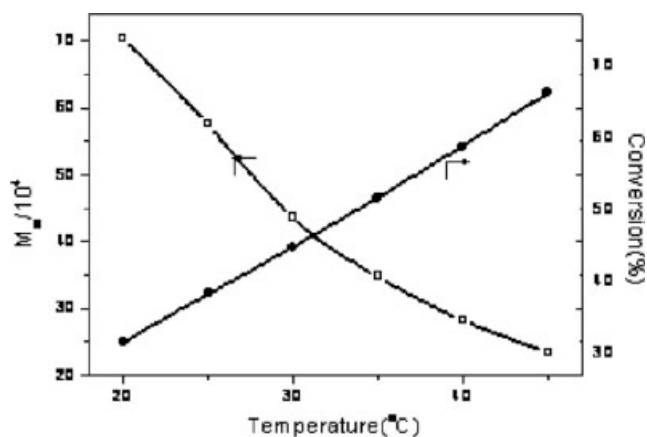
**Figure 2** TGA curves of PAhpa (a) and PAhpa-Cu(II) (b) (1 mg, heating rate:  $20^\circ\text{C/min}$ ).

The FTIR spectra of PAhpa (a) and PAhpa-Cu(II) (b) are shown in Figure 1. PAhpa exhibits absorption band at  $1762$  and  $1320\text{ cm}^{-1}$ , which ascribe to the carbonyl group and C—O stretching vibration of ester, respectively, while these bands shift to  $1749$  and  $1304\text{ cm}^{-1}$ , respectively, in the complex. This indicates that copper atoms coordinate with polymer ligands by the oxygen atoms. In addition, the complex shows a broad absorption band of  $\text{H}_2\text{O}$  molecule in the region around  $3400\text{ cm}^{-1}$ . It may be attributed to the coordinated  $\text{H}_2\text{O}$  molecule because the absorption band remains after the complex was heated at  $110^\circ\text{C}$  for 2 h.

Figure 2 shows the TGA curves of PAhpa (a) and PAhpa-Cu(II) complex (b). The thermal decomposition behaviors of PAhpa and its Cu(II) complex are different. PAhpa starts to lose its weight at  $144^\circ\text{C}$  while PAhpa-Cu(II) at  $155^\circ\text{C}$  with obvious loss of solvent weight. In addition, PAhpa decomposes almost 100% at  $700^\circ\text{C}$ ; however, the remnant of Cu(II) complex is 44.1% at  $735^\circ\text{C}$ . The above results together with titrimetric procedure all verified the coordination of copper ion and PAhpa. However, the precise structure or coordination geometry of Cu(II) ion is difficult to be revealed. Moreover, it is unavoidable that the curl and twist of macromolecules may cause the unsaturated coordination of copper ion.

### Characterizations of polymerization of MMA

The initiating activities of PAhpa-Cu(II)/ $\text{Na}_2\text{SO}_3$  system are investigated under different temperatures firstly. Conversions of MMA and number average molecular weights of PMMA at different temperatures are shown in Figure 3. The results infer that the catalytic efficiency is largely influenced by temperature. With reaction temperature increasing, the conversion of MMA increases straightly while the  $M_w$  of PMMA decreased obviously. For example, the weight average molecular weight is  $7.0 \times 10^5\text{ g/mol}$  at  $20^\circ\text{C}$  but

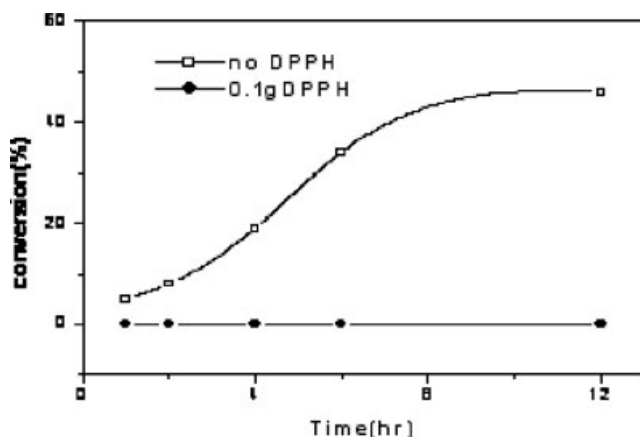


**Figure 3** Relationship of initiating ability and temperature (catalyst: 40 mg;  $\text{Na}_2\text{SO}_3$ : 50 mg;  $\text{H}_2\text{O}$ : 50 mL; MMA: 1 g; time: 12 h.; pH: 7).

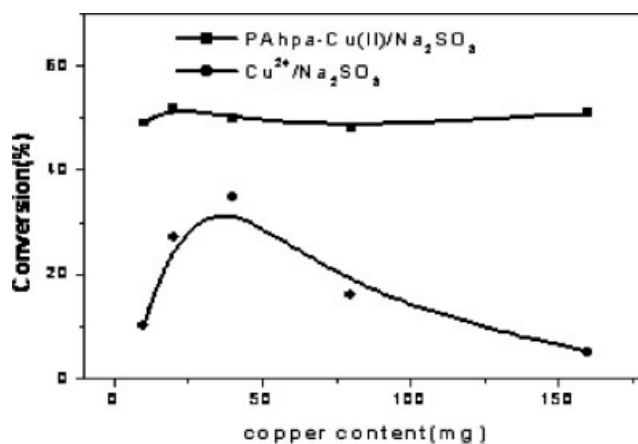
decreases to  $2.3 \times 10^5$  g/mol at  $45^\circ\text{C}$ . On the other hand, with reaction temperature increasing from 20 to  $45^\circ\text{C}$ , the conversion of monomer increases from 31 to 66%. The polydispersity index of PMMA is about 3–4. The tacticity of PMMA initiated by the system of PAhpa–Cu(II) and sodium sulfite were determined using  $^1\text{H}$  NMR spectroscopy. The values of 6.31% (mm), 35.77% (mr), and 57.92% (rr) are similar to those determined by conventional free radical polymerization at the same conditions.

### Study of radical mechanism

A free radical scavenger, DPPH (0.1 g), was added into the catalytic system; the polymerization was then inhibited completely (Fig. 4). The polymerization is proved to accord with a free radical mechanism. It can also explain that the  $M_w$  of PMMA decreases with increase in the temperature. In a free radical polymerization, the  $M_w$  decreases with increase in the concen-



**Figure 4** Inhibition of polymerization by DPPH (MMA: 1 g; catalyst: 40 mg;  $\text{Na}_2\text{SO}_3$ : 50 mg;  $\text{H}_2\text{O}$ : 50 mL; temperature:  $30^\circ\text{C}$ ; pH = 7).



**Figure 5** Effects of copper content on the monomer conversion in  $\text{CuCl}_2/\text{Na}_2\text{SO}_3$  system and PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$  system ( $\text{Na}_2\text{SO}_3$ : 50 mg;  $\text{H}_2\text{O}$ : 50 mL; MMA: 1 g; time: 12 h; temperature:  $30^\circ\text{C}$ ; pH = 7).

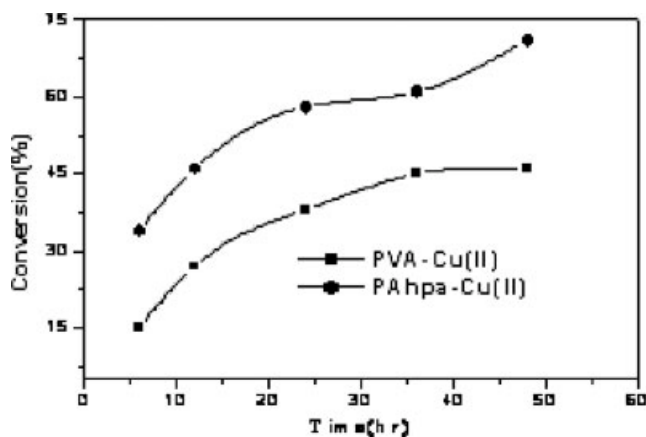
tration of radicals. However, it is still unclear where the free radicals come from. So, it is necessary to study the initiation mechanism of the polymerization in this PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$  system.

### Comparison between polymerizations of MMA catalyzed by PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$ and by $\text{CuCl}_2/\text{Na}_2\text{SO}_3$

First, two different systems, PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$  system and  $\text{CuCl}_2/\text{Na}_2\text{SO}_3$  system, are studied to better understand the initiation mechanism of the polymerization. As shown in Figure 5, the conversion of PMMA was affected by concentration of cupric in  $\text{Cu}^{2+}/\text{Na}_2\text{SO}_3$  system significantly, while the influence is minor by use of PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$  system. Furthermore, PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$  system shows more effective catalytic activity in MMA polymerization and the monomer conversion is higher under the similar conditions. The polymerization mechanism in PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$  system is obviously different from that of  $\text{CuCl}_2/\text{Na}_2\text{SO}_3$  system, reduction–oxidation mechanism.<sup>9,10</sup> Is the polymerization mechanism similar to that of PVA–Cu(II)/ $\text{Na}_2\text{SO}_3$  system, a “Coordination Hydrogen-Transfer” process?

### Comparison between polymerizations of MMA catalyzed by PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$ and by PVA–Cu(II)/ $\text{Na}_2\text{SO}_3$

Second, we compare the polymerization of MMA in PVA–Cu(II)/ $\text{Na}_2\text{SO}_3$  (PVA = polyvinyl alcohol) system<sup>12</sup> and PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$  system. Conversions of MMA in both systems are increased with reaction time, which are presented in Figure 6. This indicates that they have similar catalytic behavior. However, polymerization in PAhpa–Cu(II)/ $\text{Na}_2\text{SO}_3$  system shows higher initiating activities than in PVA–



**Figure 6** Effects of time on the conversion of monomer initiated by PVA-Cu(II)/Na<sub>2</sub>SO<sub>3</sub> and PAhpa-Cu(II)/Na<sub>2</sub>SO<sub>3</sub> (catalyst: 40 mg; Na<sub>2</sub>SO<sub>3</sub>: 50 mg; H<sub>2</sub>O: 50 mL; MMA: 1 g; temperature: 30°C; pH: 7).

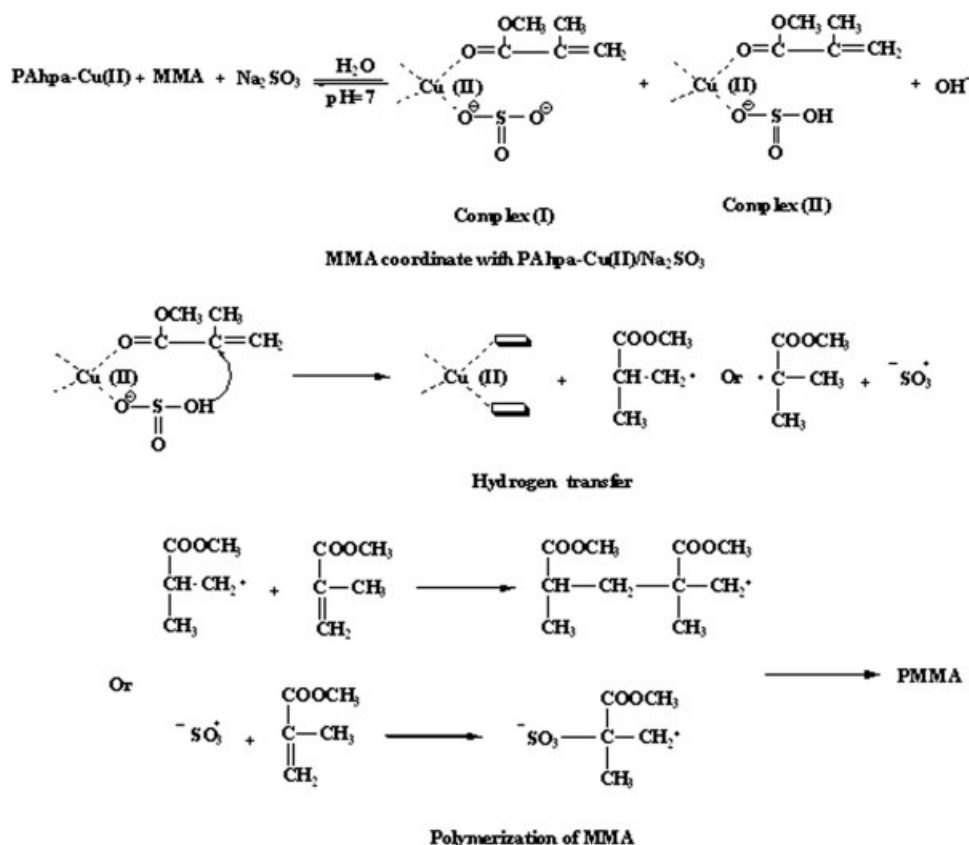
Cu(II)/Na<sub>2</sub>SO<sub>3</sub> system. For example, the conversion of MMA polymerized by PAhpa-Cu(II)/Na<sub>2</sub>SO<sub>3</sub> system is 25% larger than that by PVA-Cu(II)/Na<sub>2</sub>SO<sub>3</sub> system at 50°C.

**Proposed initiation mechanism**

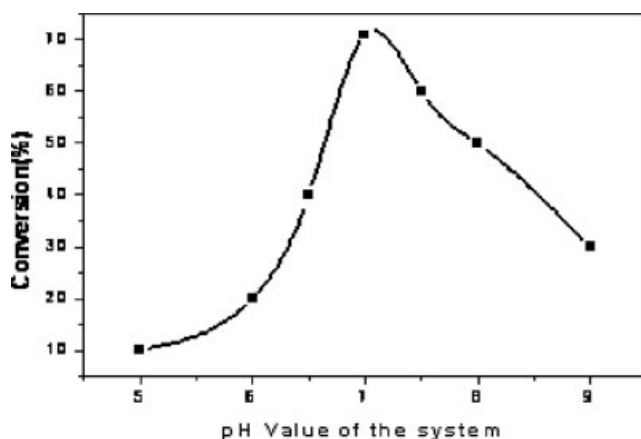
Based on previous studies,<sup>9,10</sup> we propose a possible three-step initiation mechanism (Scheme 2): first, the

oxygen atoms of HSO<sub>3</sub><sup>-</sup> and carbonyl of MMA monomer which are stronger electron donors can substitute coordinated H<sub>2</sub>O or occupy the uncoordinated sites of Cu(II) ions (Step 1). Second, MMA and HSO<sub>3</sub><sup>-</sup> can be further activated on the surface of PAhpa-Cu(II) and free radicals are obtained from the process of hydrogen transfer (Step 2), and then initiate the polymerization of MMA, which diffused from oil phase to water phase and activated on the PAhpa-Cu(II) surface (Step 3). Therefore, the PAhpa-Cu(II) catalyzes MMA polymerization in a coordination way.

To confirm the proposed mechanism, we carry out the polymerizations of MMA initiated by PAhpa-Cu(II)/Na<sub>2</sub>SO<sub>3</sub> system with various pH values. As shown in Figure 7, it is clear that the catalytic activity is influenced by pH values greatly. When pH value is 7, the conversion of MMA reaches the highest (71%). The result is also similar to that found in the MMA polymerization with PVAm-Cu(II)/Na<sub>2</sub>SO<sub>3</sub> system (highest conversion is 62% at pH = 7). Because the concentration of HSO<sub>3</sub><sup>-</sup> is dominated at this pH value (according to theoretical calculation, the concentrations of [H<sub>2</sub>SO<sub>3</sub>], [HSO<sub>3</sub><sup>-</sup>], and [SO<sub>3</sub><sup>2-</sup>] are 4.11 × 10<sup>-8</sup>, 4.38 × 10<sup>-3</sup>, 2.27 × 10<sup>-3</sup> mol/L, respectively, Formulae 1 and 2), it also implies that HSO<sub>3</sub><sup>-</sup> produced from sodium sulfite by second-order hydrolysis plays an important role in this polymerization. The experiment of dye partition further verifies the exist-



**Scheme 2** Proposed initiation mechanism for polymerization of MMA.

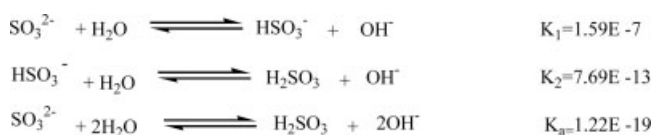


**Figure 7** Relationship between conversions of monomer and pH of the system (catalyst: 40 mg; Na<sub>2</sub>SO<sub>3</sub>: 50 mg; H<sub>2</sub>O: 50 mL; MMA: 1 g; temperature: 30°C; time: 48 h).

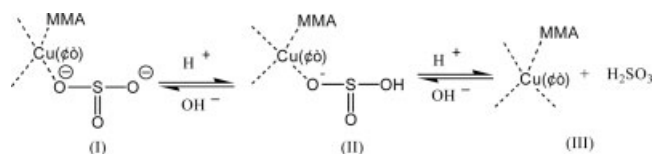
tence of SO<sub>3</sub><sup>-</sup> as end group in PMMA. So we conclude that HSO<sub>3</sub><sup>-</sup> was one of the active species and source of primary radicals.

Besides that of MMA, polymerization of other monomers such as St, BA, EA, EMA, BMA, OMA, and LMA were also made. The results show that only MMA polymerized with the PAhpa-Cu(II)/Na<sub>2</sub>SO<sub>3</sub> system in a high conversion, EMA together with BMA are polymerized in a low yield, while St, BA, EA, OMA, and LMA cannot be polymerized completely. The reason that St cannot be polymerized is its non-coordination atoms. Although BA and EA have carbonyl oxygen atom, they are lack of donor methyl group on double bond and the double bond is hard to be polarized. For EMA, BMA, OMA, and LMA, there are electron-donating methyl group and coordinating atom oxygen, they can polymerize to some degree. However, with increasing of ester chain, the hindering effect escalates and initiation efficiency declines. So in the four monomers, EMA and BMA can be polymerized in a low yield while OMA and LMA cannot be polymerized.

That is, MMA forms a particular HTC with PAhpa-Cu(II) and sodium sulfite, so the system of PAhpa-Cu(II)/sodium sulfite is able to initiate polymerization of MMA in heterogeneous solution in the presence of



**Formula 1.** Hydrolysis equilibrium equations of sodium sulfite.



**Formula 2.** Coordination equilibrium of the system under different pH values.

water in a coordination-hydrogen-transfer mechanism.

## CONCLUSIONS

Monomer, Ahpa, and its homopolymer, PAhpa, were synthesized and characterized. Its polymeric Cu(II) complex in Na<sub>2</sub>SO<sub>3</sub> system is proved to be another useful catalyst in polymerization of MMA at room temperature. It shows better initiation activity than the corresponding low molecular catalyst; the largest conversion of monomer could reach 71%, when the highest weight average molecular weight achieved is  $7.0 \times 10^5$ .

The catalytic mechanism was also studied includes a HTC process, analogous with that of PVAm-Cu(II)/Na<sub>2</sub>SO<sub>3</sub> system and a process of "Coordination Hydrogen-Transfer" was involved in the initiation. It is compared with previously reported the PVAm/Na<sub>2</sub>SO<sub>3</sub> system applied in the homopolymerization and copolymerization of MMA, that belong to this family of catalyst.

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