# Catalytic function of cross-linked polyvinylamine–Cu(II) complexes for polymerization of methyl methacrylate

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## Abstract

Polymer–metal complexes (PMC) catalyst was synthesized by cross-linked polyvinylamine (PVAm) with Cu(II). It has been found that PVAm–Cu(II)/sodium sulphite ($Na_2SO_3$) system can use as initiator for polymerization of methyl methacrylate (MMA). The overall polymerization rate can be expressed as $R_p = k[MMA]^{1.4}[Na_2SO_3]^{0.5}[PVAm-Cu(II)]^0$. $E_a = 61.3\,KJ\,mol^{-1}$. The influences on conversion of polymerization and molecular weight of polymerization of MMA have been investigated with compared to that of polymerization initiated by $Cu^{2+}/Na_2SO_3$ system. Mw of PMMA initiated by PVAm–Cu(II)/$Na_2SO_3$ system can reach 1240000. It has been observed that the influences of constitute of PVAm–Cu(II) have impact on the activity in polymerization of MMA. The polymerization is preceded by free radical, and primary radicals are formed by the process of "complexation-hydron transformation" between PVAm–Cu(II)/$Na_2SO_3$/MMA system.
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*Keywords:* Radical polymerization; Polyvinylamine; PMC; Catalyst; Cupric ion

## 1. Introduction

A great attention has been paid to the advantages such as recycle and the ease of separation and purification of PMC catalyst. Many work have investigated widely in organic reaction, and the study of PMC catalyst in polymerization has been concerned in recent years [1–5]. Tamio Nishimura used nylon-3-Cu(II)/urea system as initiator for of methyl methacrylate (MMA); [6] Keiichi Krmura used vinyl alcohol copolymer-supported cupric ion/$CCl_4$ system for polymerization [7,8]. The major problems encountered in above polymerization were critical reactive condition and low conversion of polymerization. Yang Chaoxong found cupric ion supported over polypropylene-graft poly-carboxylate/sodium sulphite system could use as initiator for polymerization of MMA, and reaction condition was moderate; [9] however, the report did not discuss in terms of conversion of polymerization, molecular weight of polymerization of MMA and the influence of constitute of polymer-supported catalyst on polymerization. In the present study, we chose PVAm–Cu(II)/$Na_2SO_3$ system as

initiator for polymerization of MMA. We extensively discuss the rate of polymerization of MMA, the influences on conversion of polymerization and molecular weight of polymerization of MMA with compared to that of polymerization initiated by $Cu^{2+}/Na_2SO_3$ system. Compared to the homogeneous system of $Cu^{2+}/Na_2SO_3$, the inhomogeneous PVAm–Cu(II) system can be easily separated from the polymer product, which is environmentally valuable because the coordinated Cu(II) would not become pollutant while the hydrophile $Cu^{2+}$ is harmful to environment. The PVAm–Cu(II) catalyzes MMA polymerization in a different mechanism from the $Cu^{2+}/Na_2SO_3$ does and the former's activity is higher and gives higher monomer conversion.

## 2. Experimental

### 2.1. Materials

Methyl methacrylate was purified as described in [10] before polymerization, the redistilled monomer was under reduced pressure, and the fraction boiling at 312 K (70 mmHg) was collected. Sodium sulphite and cupric sulphate were all analytically pure grade.

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## 2.2. Preparation of PVAm–Cu(II)

Cross-linked PVAm synthesized as described previously was added to a solution of cupric sulphate [11]. The mixture was stirred for 2 h, then filtered off, washed with deionized water to the absence of cupric ion, and dried under vacuum at 323 K for 24 h.

The amount of cupric in the PVAm–Cu(II) was determined by complex metric titration after ignition. EA 1110 element analyzer measured N, H and C elements in PVAm–Cu(II). The IR absorption spectra of the PVAm and its cupric complex were taken in KBr pellets with a Mangna-550 infrared spectrophotometer, and Perkin-Elmer thermal analyzer measured TG curve of PVAm and PVAm–Cu(II).

## 2.3. Polymerization procedure and analysis of polymer

Appropriate quantities of MMA, cupric sulphate or PVAm–Cu(II) (equal mole cupric ion) and ketone were placed in the reaction vessel through pure nitrogen for protection, and maintained at the desired temperature by a thermostat. The requisite quantity of sodium sulphite solution was quickly introduced and the polymerization was allowed to continue. After a specified interval of time, further polymerization was quenched by the addition of an excess of 2,2-diphenyl-1-picrylhydrazyl (DPPH) solution. The polymers were then precipitated, filtered and refined. The polymer obtained dried under vacuum below 313 K to constant weight. The rate of polymerization ($R_p$) was calculated gravimetrically [12].

The structure and tacticity of polymers were analyzed by $^1$H INOVA 400 Hz NMR spectrometer at 298 K [13]. Weight-average molecular weights and the molecular weight distribution of obtained polymer were determined by GPC. GPC experiments were conducted in THF at 298 K, using Waters 1515 gel permeation chromatograph.

The structure of coordination was analyzed through photoelectron spectroscopy (type: NP-1, Shenyang).

## 3. Results and discussion

### 3.1. Characteristics of polymer-supported cupric complex

The infrared absorption spectra changes are observed upon PVAm and PVAm–Cu(II). Fig. 1 shows the absorption peaks of the PVAm are 3514, 2021, 1666, 1404, 652 cm$^{-1}$, the PVAm–Cu(II) are 3514, 2021, 1692, 1397, 876, 602 cm$^{-1}$. The spectrum of PVAm–Cu(II) presents a decrease in the peak intensity of 3514, 2021 cm$^{-1}$ whereas the absorption peak 1666 cm$^{-1}$ in PVAm spectrum shifts to 1692 cm$^{-1}$. All changes suggest the bond between –NH$_2$ and Cu(II) are formed in PVAm–Cu(II).
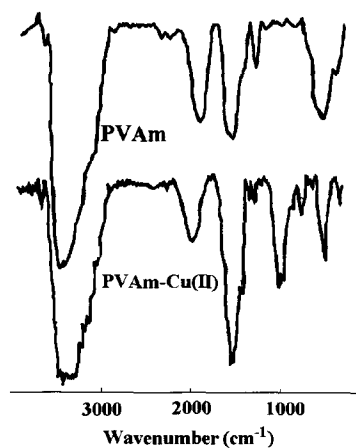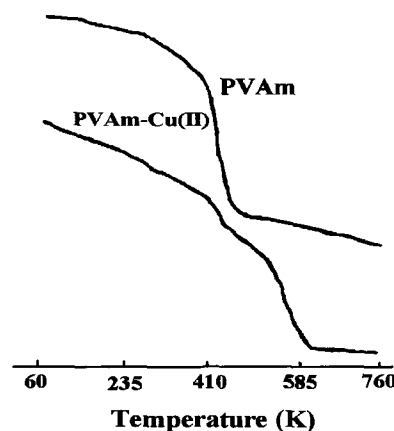


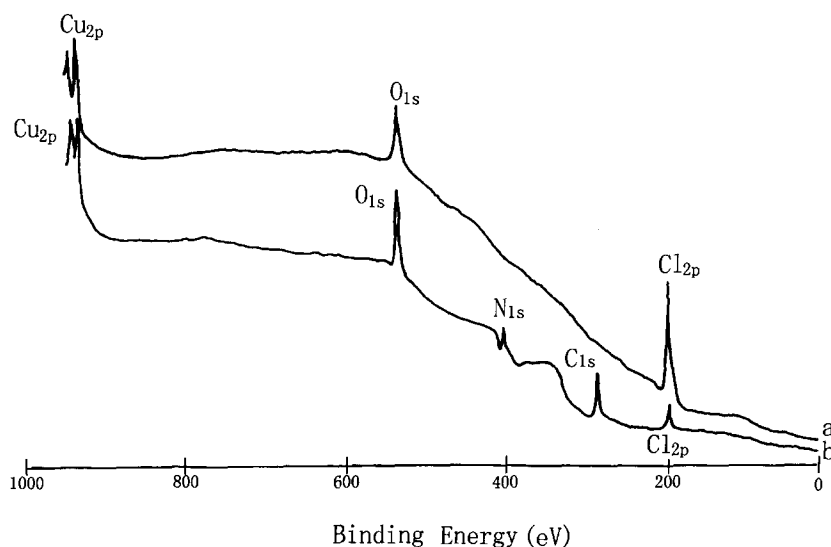Fig. 1. IR spectra.



Fig. 2. TG curves.

The TG curves are different between PVAm and PVAm–Cu(II). Fig. 2 shows PVAm loss weight 56.27% in 325–480 K while PVAm–Cu(II) 23.90%. With compared to PVAm curve, TG curve of PVAm–Cu(II) show the process of losing weight is mild. This present PVAm–Cu(II) has more thermo-stable than that of PVAm.

XPS of PVAm, CuCl$_2$ and PVAm–Cu( II ) showed in Fig. 3. From this figure, it is displayed that all the elements of the PVAm–Cu(II) were inspected expect H. Inner electron's binding energy of relative atoms showed in Table 1.
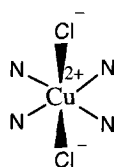
After coordination, electron's binding energy of N$_{1s}$ (405.10 eV) was greater than the one before coordination (400.4 eV). Based on this test result and the valence-bond theory [14], it can be considered that Cu(II) accepted lone

Table 1
Electron binding energy (eV) of XPS Cu(II)–PVAm

| Sample | O$_{1s}$ | Cl$_{2p}$ | N$_{1s}$ | Cu$_{2p}$$^{2+}$ | |
|---|---|---|---|---|---|
| | | | | 2p$_{3/2}$ | 2p$_{1/2}$ |
| PVAm | 531.6 | | 400.4 | | |
| CuCl$_2$·2H$_2$O | | 199.8 | | 934.2 | 954.6 |
| PVAm–CuCl$_2$ | 531.6 | 198.8 | 405.1 | 932.6 | 953.3 |

Fig. 3. XPS spectra of (a) CuCl$_2$·2H$_2$O; (b) PVAm–Cu(II).

electron pair of N and O on the chain of PVAm and during the coordination electric charge transferred as N → Cu. According to Table 1, the Cl⁻ electron's binding energy of Cl$_{2p}$ of coordination was less than that of CuCl$_2$·2H$_2$O by 1 eV, because coordination between Cu$^{2+}$ and N of polymer caused electron of N partly transfer to Cu$^{2+}$, which increased electric charge of Cl atom and decreased electron's binding energy of Cl$_{2p}$ of the coordination. According to the test and analysis of XPS, the surrounding space of Cu$^{2+}$ was partly occupied by Cl⁻, which was a action of electrostatic attraction. So we may confer that structure (the described structure just relatively indicated the way N atoms bond to Cu$^{2+}$, not intended to show a planar structure of four N atoms) of the complex might be
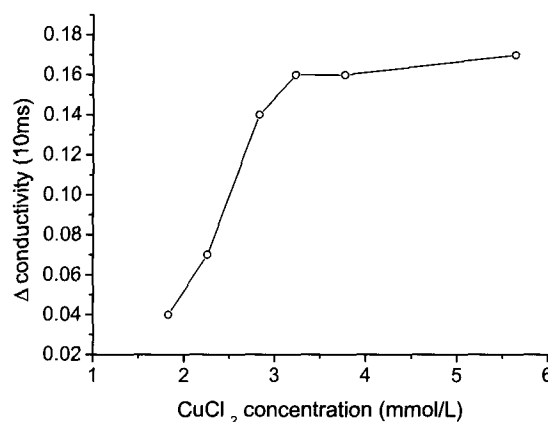


The ratio of coordination of Cu$^{2+}$ and N on PVAm is roughly measured, through electric conductivity comparison between a series of CuCl$_2$ aqueous solutions and corresponding Cu–PVAm solutions. The result was showed in Table 2



Fig. 4. Difference of electric conductivity between CuCl$_2$ aqueous solution and corresponding PVAm–Cu(II) solution.

and Fig. 4. When Cu$^{2+}$ concentration is about 32.3 mmol l$^{-1}$ and the corresponding ratio of N/Cu is about 3.5, the difference of electric conductivities varied slightly with Cu$^{2+}$ concentration increasing.

Since the curl and intertwist of macromolecule, Cu(II) cannot completely coordination with N atom of PVAm unit chain. So it could be roughly inferred that in complex of PVAm–Cu(II), the ratio of N/Cu is about 4 [15].
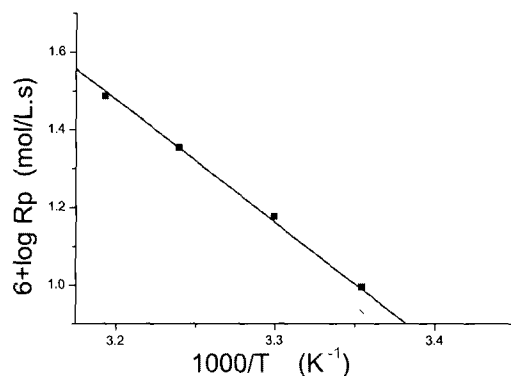
Table 2
Difference of electric conductivity of CuCl$_2$ aqueous solution and PVAm–Cu solution

| Sample | Group A | | | Group B | | $K_a$–$K_b$ (10 ms) |
|---|---|---|---|---|---|---|
| | CuCl$_2$ (mmol l$^{-1}$) | $K_a$ (10 ms) | Mass of PVAm (g) | Ratio of Cu$^{2+}$/N | $K_b$ (10 ms) | |
| 1 | 18.3 | 31.4 | 1 | 1:6 | 31.0 | 0.4 |
| 2 | 22.6 | 36.4 | 1 | 1:5 | 35.7 | 0.7 |
| 3 | 28.3 | 44.2 | 1 | 1:4 | 43.4 | 0.8 |
| 4 | 32.3 | 50.6 | 1 | 1:3.5 | 49.0 | 1.6 |
| 5 | 37.7 | 54.9 | 1 | 1:3.0 | 53.3 | 1.6 |
| 6 | 56.5 | 84.3 | 1 | 1:2 | 82.6 | 1.7 |

$K_a$, electric conductivity of CuCl$_2$ aqueous solution; $K_b$, electric conductivity of PVAm–Cu(II) solution.

Fig. 5. The influence of reactive temperature on rate of polymerization MMA.

### 3.2. Kinetic study of the polymerization of MMA by using the PVAm–Cu(II)/Na₂SO₃ catalytic system

The polymerization of MMA with PVAm–Cu(II)/Na₂SO₃ system has been kinetically investigated in ketone solution. Fig. 5 shows the rate of polymerization versus $1/T$ was calculated. The $R_p$ values were put in Arrhenius equation and overall activation energies $(E_a)$ were estimated, $E_a = 61.3\,KJ\,mol^{-1}$. Compared with the overall activation energy $(E_a = 101.6\,KJ\,mol^{-1})$ which estimated under the condition of polymerization of MMA initiated by cupric ion/sodium sulphite [16], the result show PVAm–Cu(II)/Na₂SO₃ system decreases the overall activation energy.

Fig. 6 shows the relationship between $R_p$ and the MMA concentration at 303 K when the concentration of sodium sulphite was fixed at $4.74\,mmol\,l^{-1}$. $R_p$ is proportional to the 1.4 power of the monomer concentration, suggesting that the monomer participates in the initiation process.

Fig. 7 presents the dependence of $R_p$ on the concentration of sodium sulphite at 303 K at a fixed MMA concentration $(0.2\,mol\,l^{-1})$. $R_p$ increases in proportion to the 0.50 power of concentration of sodium sulphite, indicating that the polymerization involves the usual bimolecular termination between polymer radicals. This result suggests that sodium sulphite and PVAm–Cu(II) form a complex with a high stability constant that can produce initiating radicals.
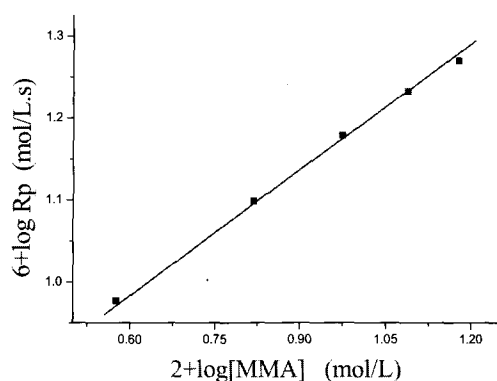


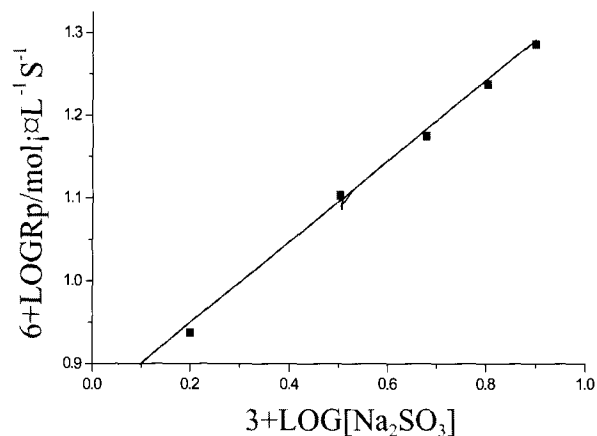Fig. 6. The influence of concentration of on rate of polymerization.



Fig. 7. The influence of concentration of Na₂SO₃ on rate of polymerization.

Fig. 8 presents the relationship between conversion of polymerization of MMA and the weight of PVAm–Cu(II) when the concentration of sodium sulphite was fixed at $4.74\,mmol\,l^{-1}$ and the MMA concentration was fixed at $0.2\,mol\,l^{-1}$ at 303 K. The weight of PVAm–Cu(II) has no influence on conversion of polymerization of MMA. Therefore, $R_p$ is proportional to the 0 power of the weight of PVAm–Cu(II).

From the aforementioned results, the following kinetic expression is obtained for the present polymerization:

$$R_p = k[MMA]^{1.4}[Na_2SO_3]^{0.5}[PVAm-Cu(II)]^0$$

### 3.3. The influences of the conversion, molecular weight and polydispersity of polymerization of MMA

The conversion of PMMA was calculated after 12 h polymerization of MMA at 303 K. Fig. 9 shows the conversion of polymerization of MMA initiated by $Cu^{2+}/Na_2SO_3$ system is lower than that of by PVAm–Cu(II)/Na₂SO₃ system at a fixed MMA concentration $(0.2\,mol\,l^{-1})$. Fig. 10
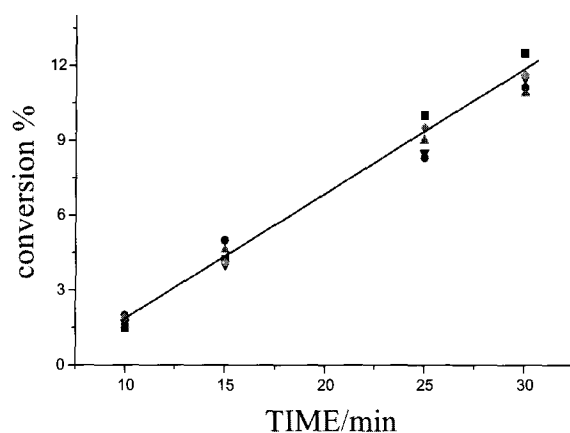


Fig. 8. The influence of amount of P–Cu(II) on conversion of PMMA: (●) 30 mg; (◆) 25 mg; (▼) 20 mg; (▲) 10 mg; (■) 5 mg.
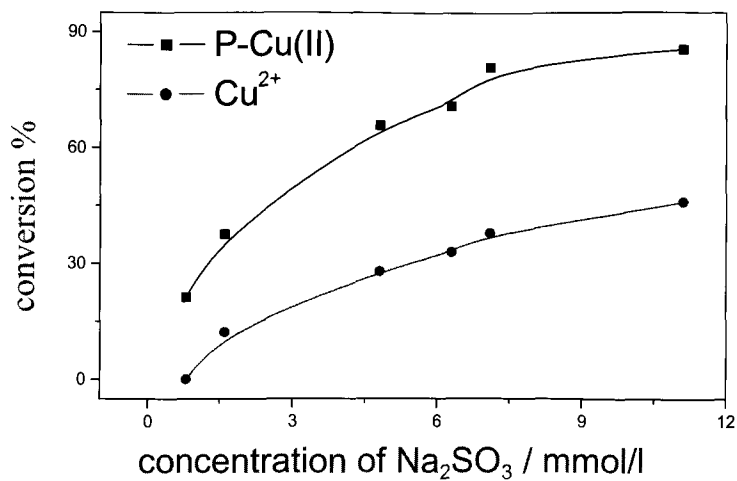
Fig. 9. The influence of concentration of Na$_2$SO$_3$ on conversion of PMMA.
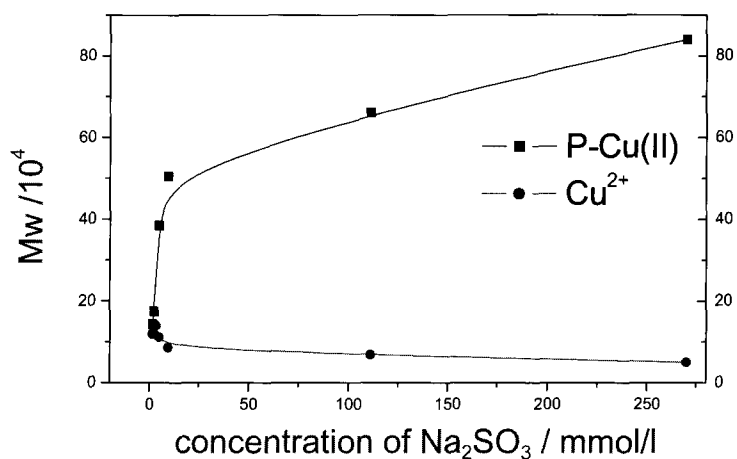


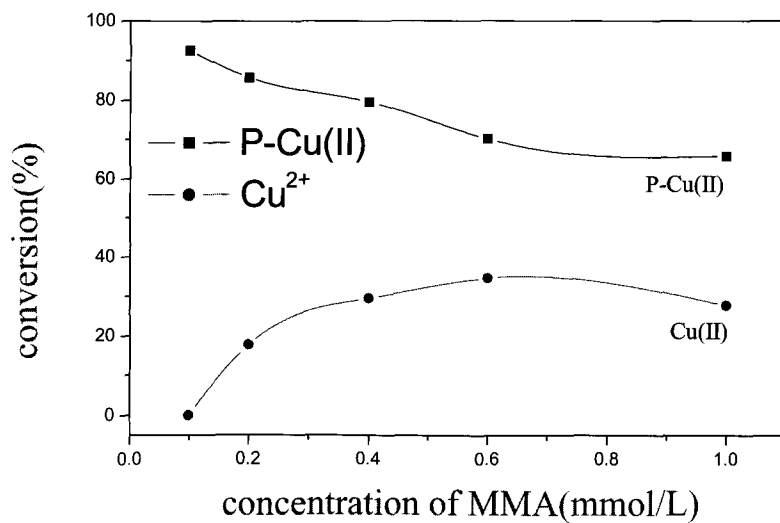Fig. 10. The influence of NaSO$_3$ concentration on $\bar{M}_w$.



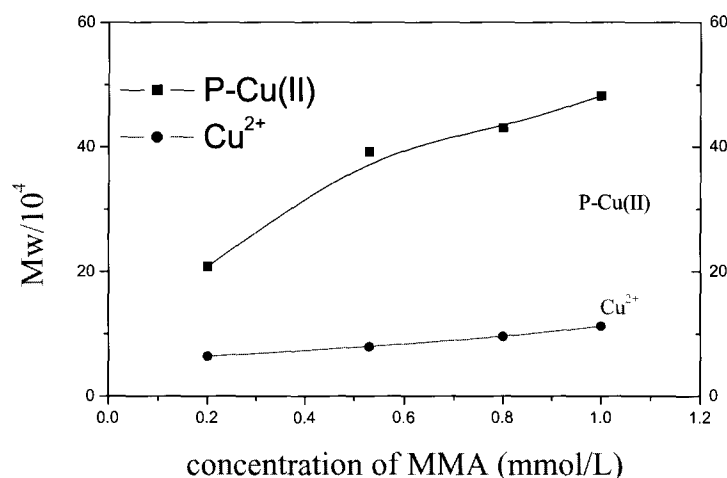Fig. 11. Influence of concentration of MMA on MMA conversion.

Fig. 12. Then influence of concentration of MMA on $\bar{M}_w$.

shows PMMA initiated by $Cu^{2+}/Na_2SO_3$ system have lower weight-average molecular weight $(M_w)$ than that of by PVAm–Cu(II)/Na$_2$SO$_3$ system at a fixed MMA concentration $(0.2\,mol\,l^{-1})$. The $M_w$ of PMMA initiated by $Cu^{2+}/Na_2SO_3$ system is 140,000 when sodium sulphite concentration is $3\,mmol\,l^{-1}$. The $\bar{M}_w$ of PMMA initiated by PVAm–Cu(II)/Na$_2$SO$_3$ system increases while sodium sulphite concentration increases; the $M_w$ is 1,240,000 if the sodium sulphite concentration is $0.360\,mol\,l^{-1}$. The result shows initiation the mechanism of PMMA initiated by PVAm–Cu(II)/Na$_2$SO$_3$ system is different from that of initiated by $Cu^{2+}/Na_2SO_3$ system.

Fig. 11 presents the influences of monomer concentration on conversion of PMMA. The conversion of PMMA initiated by PVAm–Cu(II)/Na$_2$SO$_3$ system decreases when the monomer concentration increases; while the conversion of PMMA initiated by $Cu^{2+}/Na_2SO_3$ system has a peak conversion of PMMA which reaches 34.8%. Fig. 12 presents the obviously influence of monomer concentration on $\bar{M}_w$. The result suggest PVAm–Cu(II)/Na$_2$SO$_3$ system has dif-

ferent process of catalyst and the efficiencies of catalyst is better than that of $Cu^{2+}/Na_2SO_3$ system.

Fig. 13 shows PVAm–Cu(II) has no influence on conversion of PMMA while $Cu^{2+}$ has a peak conversion of PMMA, which reaches 41%. The optimum mole ratio of $Cu^{2+}$ and sodium sulphite is 1:3. Fig. 14 shows the $Cu^{2+}$ has influence on $\bar{M}_w$ of PMMA, but the PVAm–Cu(II) has no influence on $M_w$ of PMMA. The results show chelated cupric ion, i.e. PVAm–Cu(II) has different function of initiation from cupric ion.

The polydispersity $(\bar{M}_w/\bar{M}_n)$ of PMMA which initiated either by PVAm–Cu(II)/Na$_2$SO$_3$ system or $Cu^{2+}/Na_2SO_3$ system values of 3.0 are similar to those of conventional radical polymerization of MMA [17].

### 3.4. Proposed initiation mechanism for polymerization of MMA

Compared to Cu(II)–PVAm/Na$_2$SO$_3$ system, CuCl$_2$/Na$_2$SO$_3$ and cupric isobutyrate/Na$_2$SO$_3$ system were tested to
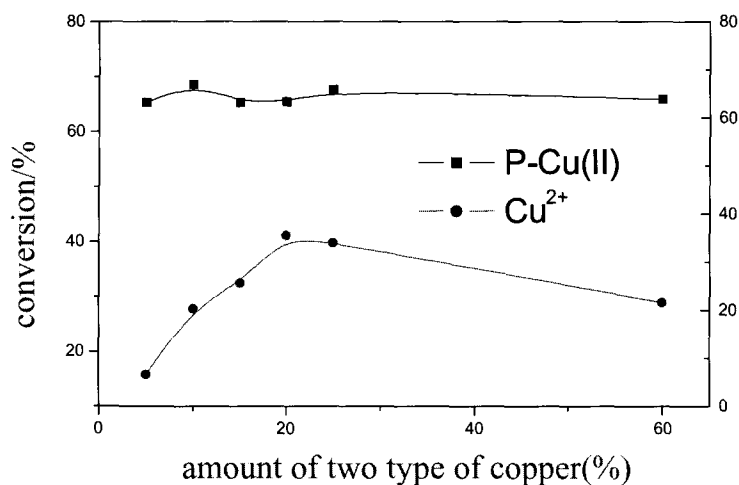


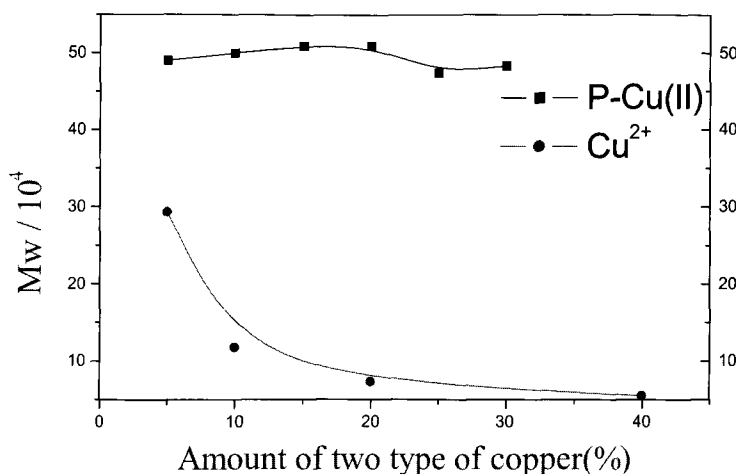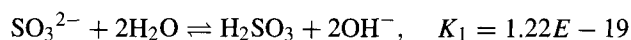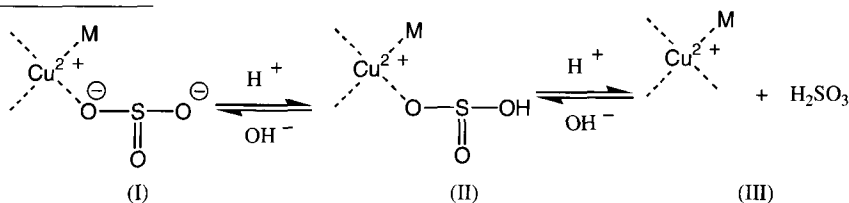Fig. 13. The influence of amount of two type of cupric ion on conversion of PMMA.

Fig. 14. The influence of amount of two type of cupric ion on $M_w$ of PMMA.

initiate MMA polymerization. During the initiation step, the colour of $CuCl_2/Na_2SO_3$ and cupric isobutyrate/$Na_2SO_3$ changed from blue to reseda, which is an obvious evidence $Cu^{2+}$ was deduced into $Cu^+$. While PVAm–Cu(II)/$Na_2SO_3$ did not take any change in colour, that is, the PVAm–Cu(II) catalyzed MMA polymerization in a different mechanism from the $CuCl_2/Na_2SO_3$ and cupric isobutyrate/$Na_2SO_3$ did.

Besides MMA, other monomers such as styrene, butyl methacrylate, butyl acrylate, were also tested. Styrene cannot be catalyzed to polymerization even when water solution's pH v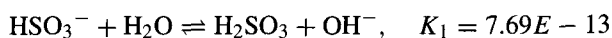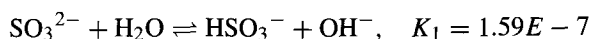alue is 7, because styrene does not have unbonding lone-pair electron and cannot coordinate with PVAm–Cu(II). Other acrylate monomers cannot be polymerized because there is lack of donor methyl on double bond and the double bond could not be polarized, although there are carbonyl oxygen, which disable them to coordinate with Cu(II). Whether active species could come into being depends on the structure of monomers, so PVAm–Cu(II)/$Na_2SO_3$ might catalyze MMA polymerization in a different mechanism from the oxidation–reduction mechanism.

In process of initiation, PVAm–Cu(II) supplied space for active species coming into being. In the catalysis system, $Na_2SO_3$ acts as initiator and the source of primary free radicals. The pH value of $Na_2SO_3$'s water solution (0.1 g $Na_2SO_3$ solved in 350 g water) is 7, which implies existence of secondary hydrolysis equilibrium of $Na_2SO_3$ in water solution.

$$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-, \quad K_1 = 1.59E - 7$$

$$HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-, \quad K_1 = 7.69E - 13$$

$$SO_3^{2-} + 2H_2O \rightleftharpoons H_2SO_3 + 2OH^-, \quad K_1 = 1.22E - 19$$

Calculation indicates, when $Na_2SO_3$'s hydrolysis is one-stage, the solution's pH value is about 9.3, while when the hydrolysis is mainly in the secondary way the pH value is about 6.9. Based on the pH value, the ion concentration could be calculated. $[H_2SO_3] = 4.11E - 5\,mmol\,l^{-1}$, $[SO_3^{2-}] = 2.27\,mmol\,l^{-1}$, $[HSO_3^-] = 4.38\,mmol\,l^{-1}$. That is to say, $Na_2SO_3$ mainly exists as $HSO_3^-$, secondly as $SO_3^{2-}$ in the initiation process showed as following an equilibrium is maintained with varied pH value.



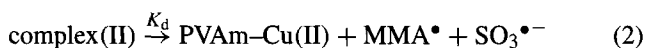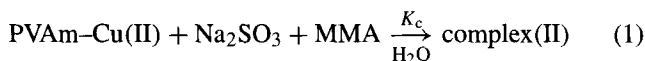When the pH is approximately 7, $SO_3^{2-}$ coordinates with PVAm–Cu(II) as (II), by which primary radicals come into being.

When MMA added to PVAm–Cu(II)/$Na_2SO_3$ system at the presence of water, monomer,$HSO_3^-$ and $SO_3^{2-}$ all coordinated to $Cu^{2+}$. The reaction between $HSO_3^-$ and monomer was the most important step in initiation process, which could be accelerated when monomer and $HSO_3^-$ both coordinated to central Cu. Concentration of $HSO_3^-$, which strongly depends on the solution pH value, was pivotal to initiation process. When pH value of solution was adjusted by hydrochloric acid to about 3 or lower, MMA could not be catalyzed to polymerization since in acid solution $Na_2SO_3$ is turned into $H_2SO_3$ or $SO_2$ and the concentration of $HSO_3^-$ is very low, which decreased even cut off the primary free radical source. While the solution pH value is adjusted to 8 by NaOH, according to the calculation, $[H_2SO_3] = 2.77\,mmol\,l^{-1}$, $[SO_3^{2-}] = 2.27\,mmol\,l^{-1}$, $[HSO_3^-] = 0.36\,mmol\,l^{-1}$ and the system could catalyze the MMA polymerization with MMA yield lower than

50%. Only when $Na_2SO_3$ solution pH value is 7, the yield of PMMA could be the highest. When $Na_2SO_3$ water solution was at higher or lower pH value, PMMA yield may considerably decrease.
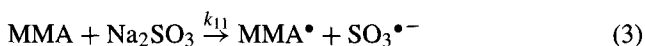
Monomer and $HSO_3^-$ were both activated by the positive charge on central $Cu^{2+}$ and the H of $HSO_3^-$ transferred to monomer, by which primary radical came into being.

$Na_2SO_3$ was one of the initiation species since terminal group $SO_3^-$ was detected by Dye-partition method [18]. Because the polymerization rate did not relate to use level of PVAm–Cu(II) and monomer was also one of the reactant in initiation step, we deduced a complexation-H transfer mechanism. In the process of hydrogen transfer, by which the radicals come into being, the carbon bonding to fewer H is the prior destination of H transfer [19].

Coordination of monomer with PVAm–Cu(II)/$Na_2SO_3$:

$$PVAm–Cu(II) + Na_2SO_3 + MMA \xrightarrow[H_2O]{K_c} complex(II) \quad (1)$$

$$complex(II) \xrightarrow{K_d} PVAm–Cu(II) + MMA^\bullet + SO_3^{\bullet-} \quad (2)$$

from the formulation (1) and (2), following formulations could be inferred:

$$MMA + Na_2SO_3 \xrightarrow{k_{11}} MMA^\bullet + SO_3^{\bullet-} \quad (3)$$

$$SO_3^{\bullet-} + MMA \xrightarrow{k_{12}} O_3SMMA^\bullet \quad (4)$$

(3) is the rate controlling step, so initiation rate could be formulated as follows:

$$R_i = K_{11}[MMA][Na_2SO_3] = K_cK_d[MMA][Na_2SO_3]$$

The propagation rate is

$$R_p = k_p[MMA][MMA^\bullet] \quad (5)$$

According to Deb and Mecyerhoff [20], termination of this polymerization was in a diradical way. That is

$$R_t = k_t[MMA^\bullet]^2 \quad (6)$$

Table 3
Stereoregularity of PMMA catalyzed by $Cu^{2+}$ and P–Cu(II)

| Type of copper | $Cu^{2+}$ | P–Cu(II) | | |
|---|---|---|---|---|
| | | No. 2 | No. 4 | No. 10 |
| Microstructure of PMMA (triade) | | | | |
| mm | 0.04 | 0.03 | 0.04 | 0.04 |
| mr | 0.32 | 0.34 | 0.31 | 0.32 |
| rr | 0.64 | 0.63 | 0.65 | 0.64 |

according to the hypothesis of radical stable state, $R_i = R_t$, so

$$[MMA^\bullet] = \left[\frac{k_ck_d}{k_t}\right]^{1/2} [MMA]^{1/2}[Na_2SO_3]^{1/2} \quad (7)$$

When $[MMA^\bullet]$ in Eq. (5) was substituted by Eq. (7), Eq. (5) could be formulated as follows:

$$R_p = K_p\left[\frac{K_cK_d}{K_t}\right]^{1/2} [MMA]^{3/2}[Na_2SO_3]^{1/2}$$

The rate formulation above is similar to the experimental result

$$R_p = K[MMA]^{1.4}[Na_2SO_3]^{1/2}$$

and so the hydrogen transfer mechanism is acceptable.

### 3.5. The tacticities of PMMA

The tacticities of PMMA formed in polymerization with either PVAm–Cu(II)/$Na_2SO_3$ system or $Cu^{2+}$/$Na_2SO_3$ system at 303 K were determined to be mm = 3–4%, mr = 31–34%, and rr = 63–65% by $^1$H NMR spectroscopy. Similar results are also reported for conventional radical polymerization of MMA (Table 3) [21].

### 3.6. Influence of the constitution of PVAm–Cu(II) on the catalytic activity

In order to find out the relationship between the constitution and the catalytic activity of PVAm–Cu(II), three

Table 4
The influence of $-NH_2/Cu^{2+}$ ratio on catalysis of MMA

| Run no. | Cross-linking level (%) | $-NH_2/-CONH_2$ (mol mmol$^{-1}$) | $-NH_2$ (mmol g$^{-1}$) | Bound metal (mmol g$^{-1}$) | $-NH_2/Cu^{2+}$ (mmol mmol$^{-1}$) | Conversion (%) | $M_w/10^4$ |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 68:32 | 6.325 | 1.965 | 3.2 | 53.8 | 35.7 |
| 2 | | | 8.453 | 1.654 | 5.1 | 62.1 | 45.6 |
| 3 | | | 9.432 | 1.342 | 7.0 | 56.8 | 33.9 |
| 4 | 5 | 47:53 | 8.837 | 1.732 | 5.1 | 70.7 | 55.5 |
| 5 | | | 9.872 | 1.432 | 6.9 | 65.3 | 35.9 |
| 6 | | | 10.540 | 1.034 | 10.2 | 54.6 | 28.6 |
| 7 | | 34:66 | 10.350 | 1.543 | 6.7 | 63.2 | 34.6 |
| 8 | | | 11.654 | 1.153 | 10.1 | 56.3 | 26.4 |
| 9 | | | 12.342 | 0.878 | 14.1 | 45.6 | 23.2 |
| 10 | 10 | 44:56 | 8.437 | 1.668 | 5.0 | 65.7 | 48.2 |
| 11 | | | 10.432 | 1.346 | 7.7 | 60.1 | 32.7 |
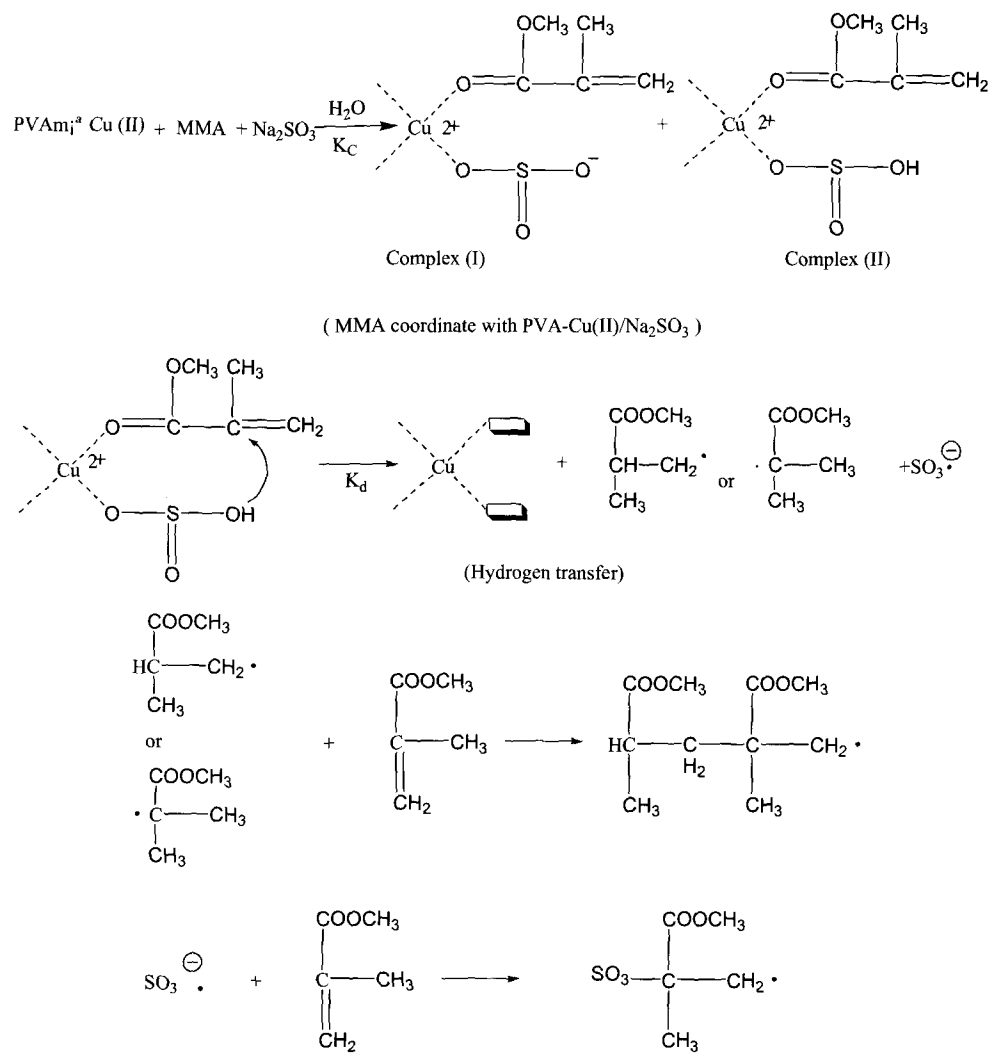
Fig. 15. Suggested mechanism of initiation.

different cross-linking level of PVAm were synthesized. It is clear from the results in Table 1 that no matter how cross-linking level, the catalyst activity was optimum as long as the –NH$_2$/Cu(II) was about 5.1. This may indicate environment of cupric ion in PVAm–Cu(II) is favourable for the formation of active centres. Among the group, no. 4 shows the conversion of PMMA reached 70.7% and $M_w$ of polymerization of MMA is 555,000 (reactive temperature 303 K). From Table 4, it is clear the function of –NH$_2$/Cu(II) plays an important role in the initiation (Fig. 15).

## 4. Conclusion

1. The monomer play a part in the production of free radicals, overall activation energies is 61.3 KJ mol$^{-1}$, and overall polymerization rate can been expressed as $R_p = k[MMA]^{1.4}[Na_2SO_3]^{0.5}[PVAm–Cu(II)]^0$.

2. The conversion of PMMA and Mw of PMMA initiated by PVAm–Cu(II)/Na$_2$SO$_3$ system are higher than that of Cu$^{2+}$/Na$_2$SO$_3$ system, while there is no influence on steroregularity of PMMA initiated either by PVAm–Cu(II)/Na$_2$SO$_3$ system or by Cu$^{2+}$/Na$_2$SO$_3$ system.

3. There has obviously influence of –NH$_2$/Cu(II) in the PVAm–Cu(II) on the polymerization of MMA. The optimum ratio of –NH$_2$/Cu(II) is 5.1.

4. With compared to initiation of Cu$^{2+}$/Na$_2$SO$_3$ system, the PMMA initiated by PVAm–Cu(II)/Na$_2$SO$_3$ system is easier of separation and purification.

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