

Polystyrene copper(II) complex containing azacrown ether functional groups as catalyst for room-temperature polymerization of MMA

Jianmei Lu^{a,b,*}, Qingfeng Xu^a, Yuanqing Xu^a, Najun Li^a, Yesu Guo^a

^a Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Suzhou University, 1 Shizi St. Suzhou 215006, Jiangsu, China

^b Jiangsu Polytechnic University, Changzhou 213016, Jiangsu, China

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Abstract

A polymeric copper complex PS–DCTACE–Cu(II) including cross-linked polystyrene as ligand, whose surface was modified by dicarbonyl tetraza-crown ether groups, was prepared and characterized. It was utilized as a heterogeneous catalyst for methyl methacrylate (MMA) polymerization in Na₂SO₃ aqueous solution at ambient temperature. The monomer conversion was high and reaction condition was mild. Moreover, the catalyst had good mechanical property and was very easy to be recycled from the reaction system. The polymerization mechanism was also proposed and confirmed by corresponding detections. The polymerization proceeded through a free radical way, in which the radicals were formed by the process of ‘chloridion leaving-hydrogen transfer’ in this PS–DCTACE–Cu(II)/Na₂SO₃/MMA system.

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1. Introduction

Polymeric metal complexes (PMC) are currently attracting considerable attention for a variety of applications, including development in nuclear chemistry, organic synthesis, wastewater treatment [1–6]. In particular, some polymeric transition metal complexes have shown unique properties in free radical polymerizations because of the specificity induced by the polymer matrix. For example, polymerizations initiated by polymeric metal complexes are usually heterogeneous reactions, in which the product is easier to be separated from the system and the catalysts can be recycled and reused. Although previous studies show earlier PMC need rigorous conditions and the conversion of monomer was low, progresses devoted to improving the reaction condition and monomer conversion have been made in our lab and others [7–9]. For instance,

we once chose a PVAm–Cu(II)/Na₂SO₃ system (polyvinylamine, PVAm) as initiator for MMA homopolymerization and copolymerization. The polymerizations were moderate and environmental friendly. The mechanism of polymerization was also pretty interesting and different from that of CuCl₂/Na₂SO₃ system (reduction–oxidation mechanism). It was unsaturated coordination of Cu(II) in the polymeric complex due to the curl and intertwist of macromolecule that catalyze the MMA polymerization. In this system, polymerizations were initiated by free radicals, which were generated from a process of ‘complexation-hydrogen transfer’. However, the amorphous catalyst powder had very poor mechanical property and was difficult to separate from reaction system after continuous stirring. In addition, using of excessive organic solvent make the extraction more complicated.

Based on the previous research, we keep interests in obtaining other analogous complexes as practicable polymeric catalysts. Herein, we choose surface-modified cross-linked polystyrene (with a diameter of 1 mm) as poly-

* Corresponding author. Tel.: +86 512 65112621; fax: +86 512 65224783.
E-mail address: lujm@suda.edu.cn (J. Lu).

meric ligand. Dicarboxyl tetraza-crown ether functional groups are fixed on the surface to obtain a coordination-saturated Cu(II) complex, in which four N atoms from a tetraza-crown ether group can pick up a Cu(II) ion steadily. However, could such a complex with saturated coordination number catalyze the polymerization of MMA, and how it works? With the question in mind, we prepared this kind of cross-linked polystyrene and studied the catalysis of its Cu(II) complex for MMA polymerization. The polystyrene and its Cu(II) complex could not dissolve in common water and organic solvents. By utilizing the heterogeneous PS–DCTACE–Cu(II)/Na₂SO₃ aqueous system, the polymerization of MMA was proceeded at room temperature with better monomer conversion (82%). The obtained PMMA can dissolve in organic solvents and the catalyst can be easily recycled by filtrate. More importantly, we found that the mechanical property of the catalyst increased greatly. Its shape was preserved much better than those of other amorphous analogues. Moreover, in this PS–DCTACE–Cu(II)/Na₂SO₃ system, a new catalytic mechanism—‘chloridion leaving-hydrogen transfer’—was also proposed and studied herein.

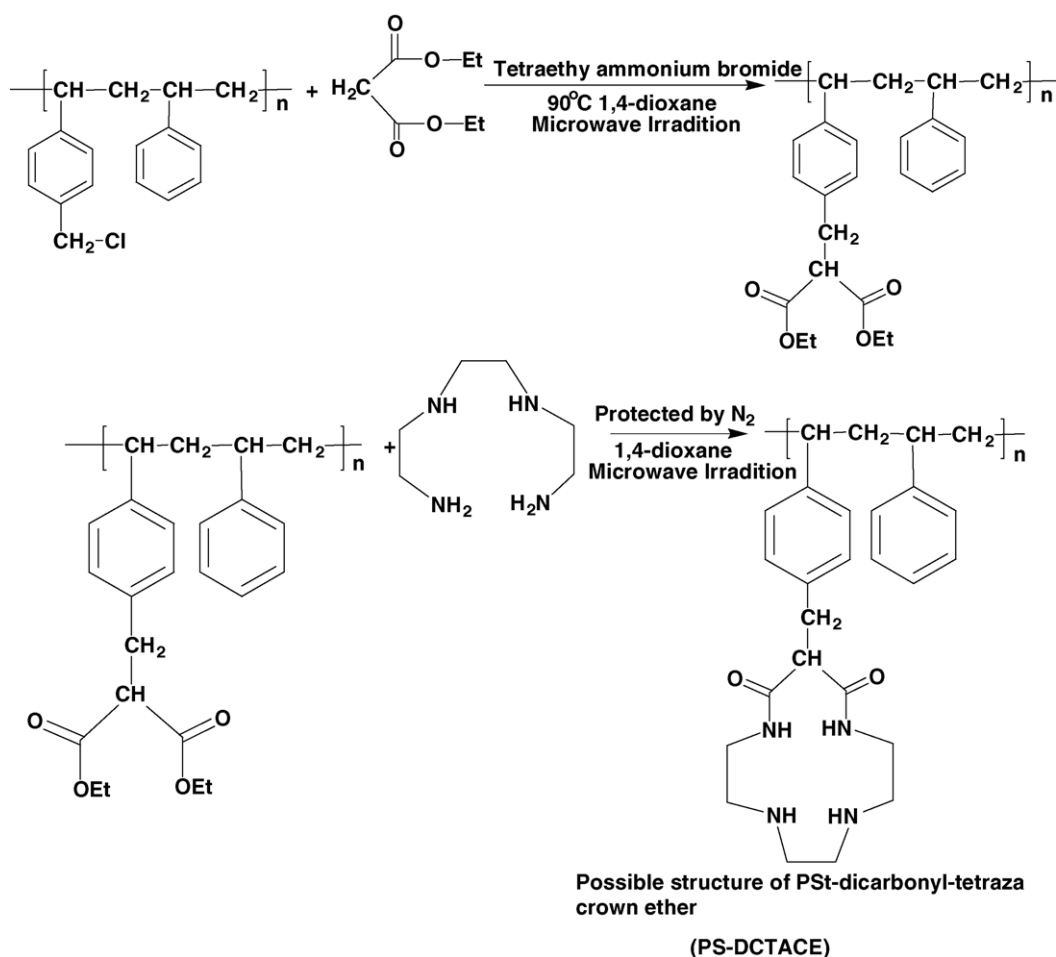
2. Experimental

2.1. Materials

Methyl methacrylate (MMA), methyl acrylate (MA), styrene (ST) and butyl acrylate (BA) were purified before polymerization [10] while styrene was purified as described in reference [11]. Chloromethylation cross-linked polystyrene (small ball with a diameter of 1 mm, cross-linked degree is 3.5% and chlorine content is 18%), diethyl malonate, triethylene tetramine, sodium sulfite and cupric dichloride were used as received without further purification.

2.2. Preparation of PS–DCTACE and PS–DCTACE–Cu(II)

The synthesis of the cross-linked polystyrene, onto whose surface was fixed with dicarboxyl tetraza-crown ether groups (dicarboxyl tetraza-crown ether polystyrene, PS–DCTACE) was depicted in Scheme 1. Polystyrene–diether malonate (PS–DEM) was obtained by treatment of chloromethylation cross-linked polystyrene in 1,4-dioxane with diethyl malonate and KOH aqueous solution under microwave radi-



Scheme 1. Synthesis process of PS–DCTACE.

ation. The product was washed with acetone, deionized water and dried in vacuo. Triethylenetetramine was then reacted with the PS-DEM under microwave radiation to form the cross-linked polymer PS-DCTACE. IR (KBr) of PS-DCTACE: (3414, 2850, 1645 (C=O), 1500, 1092, 652 cm^{-1}); the N content in PS-DCTACE was 8.87% and the benzyl chloride conversion to dicarbonyl-tetraza crown ether was 31.6%.

Polymeric complex PS-DCTACE-Cu(II) was obtained by the reaction of PS-DCTACE and cupric dichloride. The mixture was stirred overnight and filtered. The final product was washed with deionized water to remove excessive cupric ion and dried in vacuum. IR (KBr) of PS-DCTACE-Cu(II): 3447, 2894, 2810, 1637 (C=O), 1480, 1100, 630 cm^{-1} . The copper content in the complex was determined by HITACHI 180-80 atomic absorption spectroscopy. The coordination style of the cupric was determined by X-ray photoelectron spectroscopy (XPS) and electric conductivity.

2.3. Polymerization procedure and analysis of polymer

The polymerization of MMA with PS-DCTACE-Cu(II)/ Na_2SO_3 system has been investigated at room temperature. The mixture of MMA, PS-DCTACE-Cu(II) and sodium sulfite with appropriate ratios was added into aqueous solution (50 mL) under nitrogen. The polymerization was terminated by adding 2,2-diphenyl-1-picrylhydrazyl solution (DPPH). PMMA was precipitated, filtered and dried under vacuum till the weigh is a constant. Weight-average molecular weights and the molecule weight distributions of the products were determined by Waters 1515 gel permeation chromatograph GPC. GPC experiments were conducted in tetrahydrofuran (THF) solution at 298 K with polystyrene as reference.

The polymerizations of other monomers such as styrene, butyl acrylate and methyl acrylate with PS-DCTACE-Cu(II)/ Na_2SO_3 system in aqueous solution were carried out similar with that of MMA polymerization. However, no polymer product was obtained even reaction time exceeded 24 h.

3. Results and discussion

3.1. Characteristics of PS-DCTACE

3.1.1. Solid-state NMR spectra

The solid-state ^{13}C NMR of PS-DCTACE spectrum is shown in Fig. 1. It reveals the structure of tetraza-crown ether connecting with the cross-linked polymer. The resonances at 49.4–55.0 and 180.4 ppm are very similar with those found in the organic compound 1,4,7,10-tetraaza-cyclotridecane-11,13-dione. Thus, we speculate that the side chain of PS-DCTACE has analogous structure with that of 1,4,7,10-tetraaza-cyclotridecane-11,13-dione.

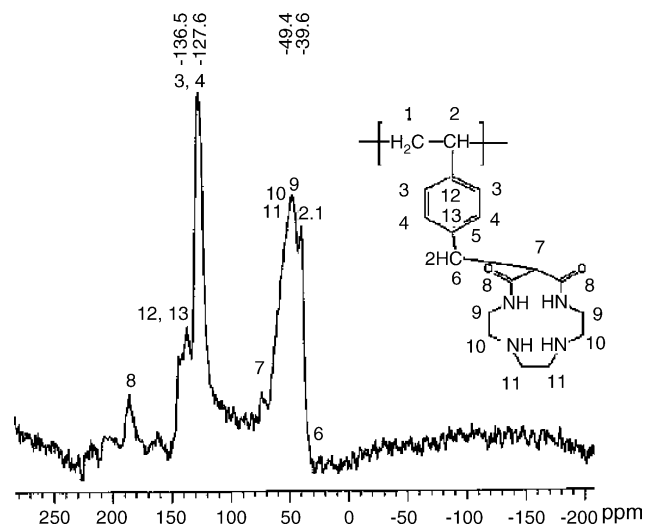


Fig. 1. 300 MHz solid-state ^{13}C CP NMR spectra of PS-DCTACE.

3.2. Characteristics of complex PS-DCTACE-Cu(II)

3.2.1. XPS spectra

The inner electrons' binding energies of PS-DCTACE-Cu(II) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ are shown in Table 1, respectively.

Table 1 show that Cu^{2+} ions coordinate with the functional groups fixed on the surface of polymer. For example, the binding energy of $\text{Cu}2p_{3/2}$, $\text{Cu}2p_{1/2}$ in PS-DCTACE-Cu(II) are 1.8 and 2.3 eV, respectively, less than those of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (934.2 and 954.6 eV). The electron's binding energy of N 1s (401.0 eV) in Cu(II) complex is larger 1.1 eV than that in PS-DCTACE. These obvious differences describe that Cu ions are coordinated with N atoms from the functional group DCTACE. The result is similar with that observed in the PVAm-Cu(II) complex [9]. It is worthy noting that another binding energy of Cu at 942.6 eV in PS-DCTACE-Cu(II) complex is low-energy shifted and its strength is obviously decreased compared with that of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Fig. 2). It infers that Cu(II) in the complex might adopt a low-spin state and the coordination number of Cu(II) in the PS-DCTACE-Cu(II) is 6, four N atoms from a tetraza-crown ether group and two Cl^- anions [12]. In addition, Cl^- electron's binding energy of $\text{Cl}2p$ of PS-DCTACE-Cu(II) is 1 eV less than that of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, which indicates that the interaction between Cl^- and Cu(II) is weakened.

Table 1

Electron binding energy (eV) of XPS of PS-DCTACE and PS-DCTACE-Cu(II)

Sample	Cl_{2p}	N_{1s}	Cu_{2p}^{2+}		
			Master peak		Shoulder peak
			$2p_{3/2}$	$2p_{1/2}$	
PS-DCTACE		399.6			
$\text{CuCl}_2 \cdot \text{H}_2\text{O}$	199.2		934.2	954.6	945.1
PS-DCTACE-Cu(II)	198.1	401.0	932.4	952.3	942.6 (weak)

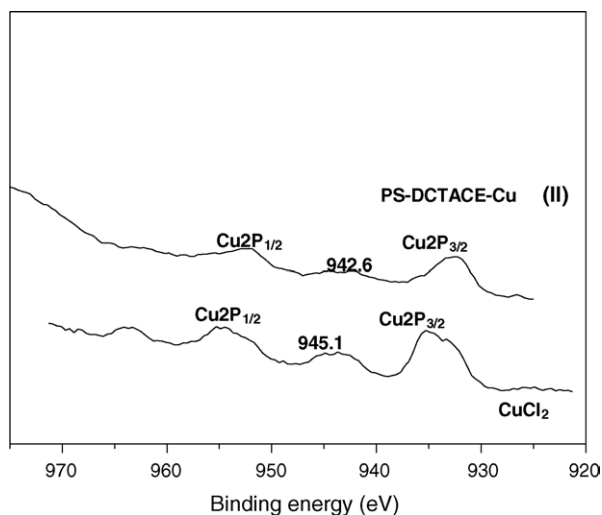


Fig. 2. XPS spectra of PS-DCTACE-Cu(II) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

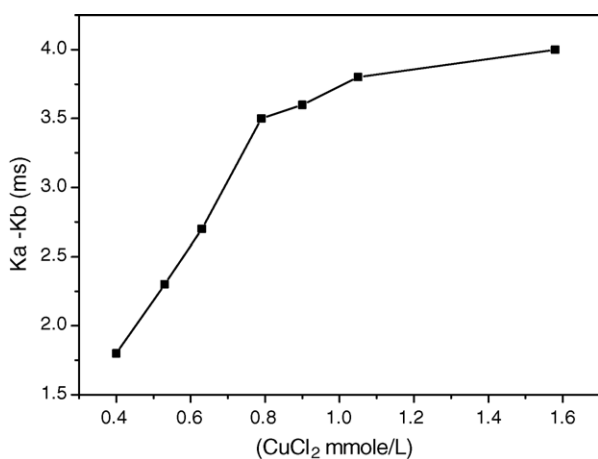


Fig. 3. Difference of electric conductivity between CuCl_2 aqueous solution and corresponding PVA m -Cu(II) solution.

3.2.2. Electric conductivity

The coordination number of Cu(II) is further measured by electric conductivity with comparison of CuCl_2 aqueous solutions and corresponding PS-DCTACE-Cu(II) solutions. The results are shown in Table 2 and Fig. 3. According to Table 2, electric conductivity almost keeps a constant after the concentration of Cu(II) is about 7.9 mmol/L and the cor-

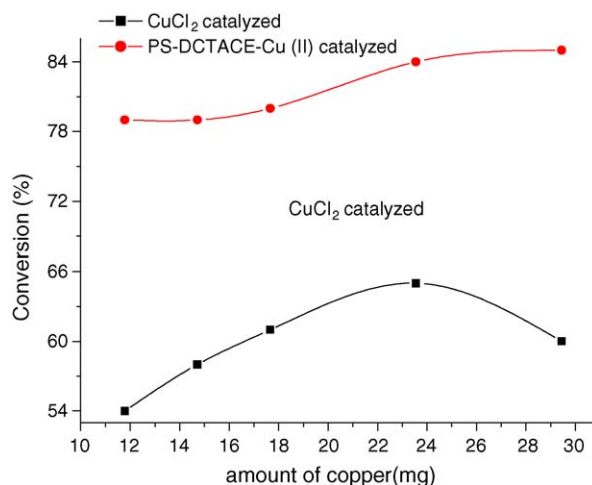


Fig. 4. The effects of amount of coordinated Cu^{2+} and Cu^{2+} on monomer conversion (reaction time 4 h; temperature 29 °C).

responding ratio of N/Cu is about 4.0. Thus, we speculate that the ratio of N/Cu is about 4 [13].

3.3. Proposed mechanism for polymerization of MMA

3.3.1. Comparison of the polymerization of MMA catalyzed by copper(II) and PS-DCTACE-Cu(II) complex

The polymerization of MMA can be initiated by PS-DCTACE-Cu(II) with the existence of Na_2SO_3 solution even at room temperature, while PS-DCTACE-Cu(II) shows no catalytic property to MMA polymerization with absence of Na_2SO_3 aqueous solution. Obviously, Na_2SO_3 plays an important role in the process of polymerization. In order to better understand the mechanism of the polymerization of MMA, two different systems: PS-DCTACE-Cu(II)/ Na_2SO_3 system and CuCl_2 / Na_2SO_3 system are studied firstly. As shown in Fig. 4, the MMA conversion was influenced by concentration of cupric in $\text{Cu}^{2+}/\text{Na}_2\text{SO}_3$ system significantly, while the influence is minor by use of PS-DCTACE-Cu(II)/ Na_2SO_3 system. On the other hand, PS-DCTACE-Cu(II)/ Na_2SO_3 system shows more effective catalytic activity in MMA polymerization and the monomer conversion is higher under the similar conditions. Thus, we speculate that the polymerization mechanism in

Table 2

Difference of electric conductivity between CuCl_2 aqueous solution and corresponding PS-DCTACE-Cu(II)/ Na_2SO_3 system

Group A			Group B			$K_a - K_b$ (10 ms)
Sample	CuCl_2 (mmol/L)	K_a (10 ms)	Mass of PS-DCTACE (g)	Ratio of Cu/N	K_b (10 ms)	
1	4.0	0.78	0.5	1:8.0	0.60	0.18
2	5.3	0.98	0.5	1:6.0	0.75	0.23
3	6.3	1.20	0.5	1:5.0	0.93	0.27
4	7.9	1.50	0.5	1:4.0	1.15	0.35
5	9.0	1.69	0.5	1:3.5	1.32	0.37
6	10.5	1.93	0.5	1:3.0	1.51	0.42
7	15.8	2.85	0.5	1:2.0	2.41	0.44

PS–DCTACE–Cu(II)/Na₂SO₃ system may be different from that in CuCl₂/Na₂SO₃ system (reduction–oxidation mechanism).

3.3.2. Polymerization in different pH value with PS–DCTACE–Cu(II)/Na₂SO₃ system

The reactivity of PS–DCTACE–Cu(II)/Na₂SO₃ system at different pH value is investigated in order to confirm the primary radicals involved in the polymerization.

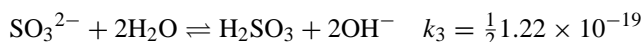
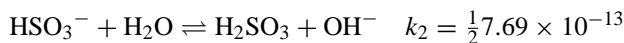
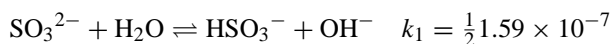


Fig. 5 shows the monomer conversion at different pH value. The conversion is promoted at the beginning with the pH value increasing. However, the highest conversion (62%) is reached at pH=7, but decreases greatly after that. The result is similar with that found in the MMA polymerization by use of PVAm–Cu(II)/Na₂SO₃ system. It implies that HSO₃[−] participates in this polymerization because the concentration of HSO₃[−] is dominated at this pH value (according to theoretical calculation, the concentrations of H₂SO₃, HSO₃[−] and SO₃^{2−} are 4.11 × 10^{−8} mol/L, 4.38 × 10^{−3} mol/L, 2.27 × 10^{−3} mol/L, respectively, at pH=7). We consider that the oxygen atoms of HSO₃[−] and carbonyl of MMA monomer may coordinate with Cu(II) when the Cl[−] anions dissociate from the complex, so that MMA and HSO₃[−] can be activated by the complexation. H free radical is dissociated from the activated HSO₃[−], initiating the polymerization of MMA. Therefore, the PS–DCTACE–Cu(II) catalyzes MMA polymerization in a coordination way. In addition, the existence of SO₃[−] as end group in PMMA was verified through dye partition [14], which further indicated that HSO₃[−] was one of the active species and source of primary radicals.

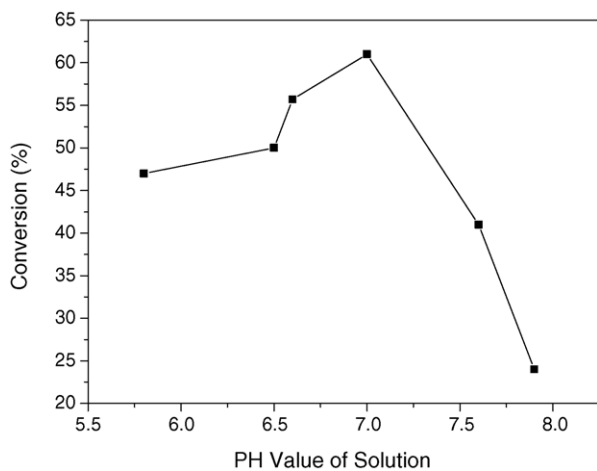


Fig. 5. The relationship of monomer conversion and pH value (reaction time 3 h).

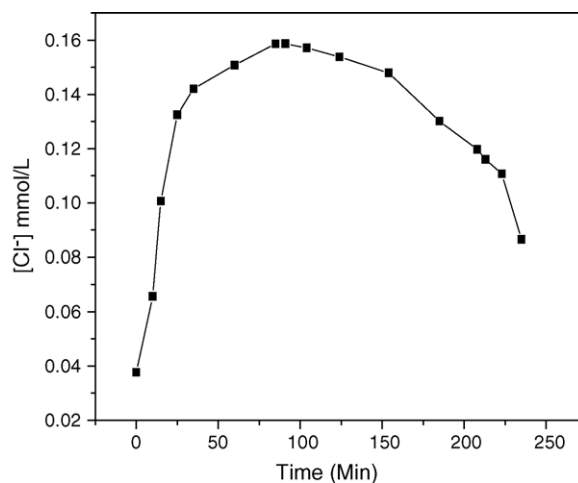


Fig. 6. The relationship of time with concentration of chloridion.

3.3.3. Chloridion detection in the polymerization

A chloridion selective electrode was applied in determining the concentrations of free Cl[−] ions ([Cl[−]]) in this system and the relationship of polymerization time with [Cl[−]] is shown in Fig. 6. It depicts that during the polymerization, [Cl[−]] increases significantly at first half an hour, and then decreases gradually after a certain period (about 100 min). As the stronger donor atoms, oxygen atoms from MMA and HSO₃[−], can substitute for the Cl[−] ions at first, free chlorides enter into the solution and the correspondent [Cl[−]] increases. When the polymerization was initiated, Cu(II) coordinate free Cl[−] again with MMA and HSO₃[−] leaving. So, the chloridion detection shows free [Cl[−]] is obviously reduced. The variation of [Cl[−]] verifies that it is the process ‘chloridion leaving–hydrogen transfer’ that initiates the polymerization.

3.3.4. Polymerizations of other monomers with PS–DCTACE–Cu(II) aqueous system

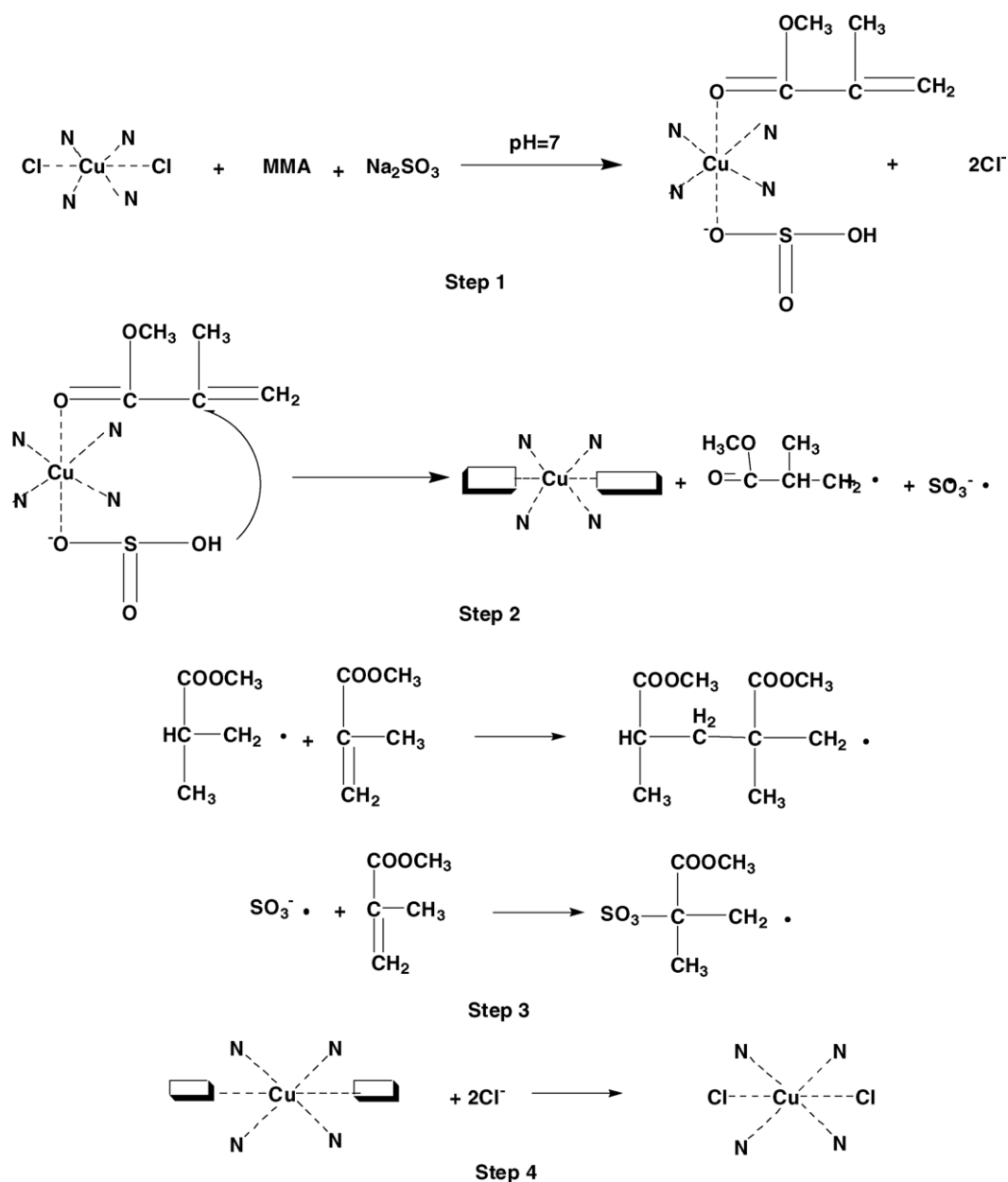
According to our previous research [8], we suspect that the PS–DCTACE–Cu(II)/Na₂SO₃ system has special catalysis for MMA polymerization. So, it was utilized to catalyze the polymerization of styrene, butyl acrylate, methyl acrylate and MMA, respectively, at room temperature. The results show that only PMMA was obtained in 29% conversion and the other monomers cannot be catalyzed in this system. It is reasonable that the mentioned monomers except MMA cannot be polymerized in this system [8]. Due to lack of lone-pair electrons, styrene could not coordinate with PS–DCTACE–Cu(II) so that the polymerization cannot be proceeded. Other acrylate monomers cannot be catalyzed because lack of donor methyl on double bond (BA) or the double bond difficult to be polarized (Table 3). That is, because MMA has donor methyl on double bond and can coordinate with Cu(II) ion by oxygen atom, it is easy to be initiated by the PS–DCTACE–Cu(II)/Na₂SO₃ system.

Table 3
Comparison of polymerization of four type monomers

Monomer	Weight (g)	Temperature (°C)	Reaction time (h)	Conversion (%)
MMA	1	23	1	29
MA	1	23	1	0
ST	1	23	1	0
BA	1	23	1	0

According to all above experiments, we therefore propose a novel mechanism (Scheme 2), which is different from those applied in $\text{CuCl}_2/\text{Na}_2\text{SO}_3$ system and $\text{PVAm-Cu(II)/Na}_2\text{SO}_3$ system. It is a four-step process. Firstly, the leaving of Cl^-

results in the coordination vacancy around the Cu(II) ion so that HSO_3^- and carbonyl of MMA can be activated by coordinating with Cu(II) (step 1). Secondly, the activated HSO_3^- can provide H free radicals to initiate the polymerization (step 2). In the catalysis system, Na_2SO_3 acts as initiator and the source of primary free radicals. Terminal SO_3 group was detected in the polymer by dye-partition and further manifest that SO_3^- is one of the reactive species (step 3). However, when the polymerization is initiated, the HSO_3^- and carbonyl of MMA dissociate with Cu(II) and Cl^- ions return to the former coordination sites (step 4). That is, the process 'chloridion leaving-hydrogen transfer' that initiates the polymerisation.



Scheme 2. Speculated mechanism of MMA polymerization in $\text{PS-DCTACE-Cu(II)/Na}_2\text{SO}_3$ system.

Table 4

Property of PMMA obtained in PS–DCTACE–Cu(II)/Na₂SO₃ system (reaction temperature: 20 °C)

Reaction time (h)	Mw (average)	Polydispersity	Conversion (%)
2	92,570	2.037	34.8
4	140,132	3.638	42
5	181,834	3.907	47
9	720,730	5.018	65
12	974,542	4.480	78

3.4. Polymerization of MMA in PS–DCTACE–Cu(II)/Na₂SO₃ system

The average molecular weight (Mw), polydispersity and yield of PMMA obtained in PS–DCTACE–Cu(II)/Na₂SO₃ system at 20 °C were listed in Table 4. As presented in Table 4, obtained PMMA has higher monomer conversion as well as higher molecular weight. It is concluded that PS–DCTACE–Cu(II)/Na₂SO₃ system may be a good catalyst in polymerization of MMA without steric conditions. Experiments also show, even at room temperature, the molecular weight of PMMA can be reached at almost 1 million with monomer conversion of 82% after 12 h.

4. Conclusions

A surface-modified polystyrene, PS–DCTACE and its Cu(II) complex (PS–DCTACE–Cu(II)) were synthesized and characterized by spectroscopy. The Cu(II) ion was coordinated in a saturated way, two chlorides and four N atoms from a tetraza-crown group, which was determined by XPS and electric conductivity. The title complex can initiate the polymerization of MMA with existence of Na₂SO₃ in high monomer conversion and high molecular weight in moderate condition. More importantly, the mechanical property of the catalyst increased greatly. Its shape was preserved much better than those of other amorphous analogues and easier to be

recycled. The mechanism of the polymerization was different from that of CuCl₂/Na₂SO₃ system (reduction–oxidation mechanism). It is verified that a process of ‘Cl[−] leaving–H transferring’ was involved in the initiation. It is compared with previously reported the PVAm/Na₂SO₃ system applied in the homopolymerization and copolymerization of MMA, that belong to this family of catalyst.

Acknowledgements

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