

# Rapid Homogeneous Preparation of Cellulose Graft Copolymer in BMIMCl Under Microwave Irradiation

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Received 12 January 2010; accepted 14 March 2010

DOI 10.1002/app.32451

Published online 19 May 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Acrylic acid(AA) was grafted onto cellulose in homogeneous media by using ammonium persulfate as an initiator in the presence of *N,N'*-methylenebisacrylamide as a crosslinker under microwave (MW) irradiation. The powerful and highly efficient direct solvent, 1-butyl-3-methylimidazolium chloride ionic liquid was used as the solvent for the dissolution of cellulose and the media for the homogeneous graft polymerization of AA onto cellulose. The use of MW resulted in a drastic reduction of reaction time: 3 min irradiation was sufficient, compared with 30 min to 5 h, as conventional heating was used. Investigation was con-

ducted on the effect of reaction parameters, such as monomer concentration, crosslinker dosage, exposure temperature and exposure time. The structure of the graft copolymer was confirmed by IR spectrum, thermogravimetric analyzer, and scanning electron microscope. The results show that the MW irradiation method can increase the reaction rate. And the graft copolymer is also an effective metal ion adsorbent. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 399–404, 2010

**Key words:** cellulose; graft copolymerization; ionic liquids; microwave; acrylic acid

## INTRODUCTION

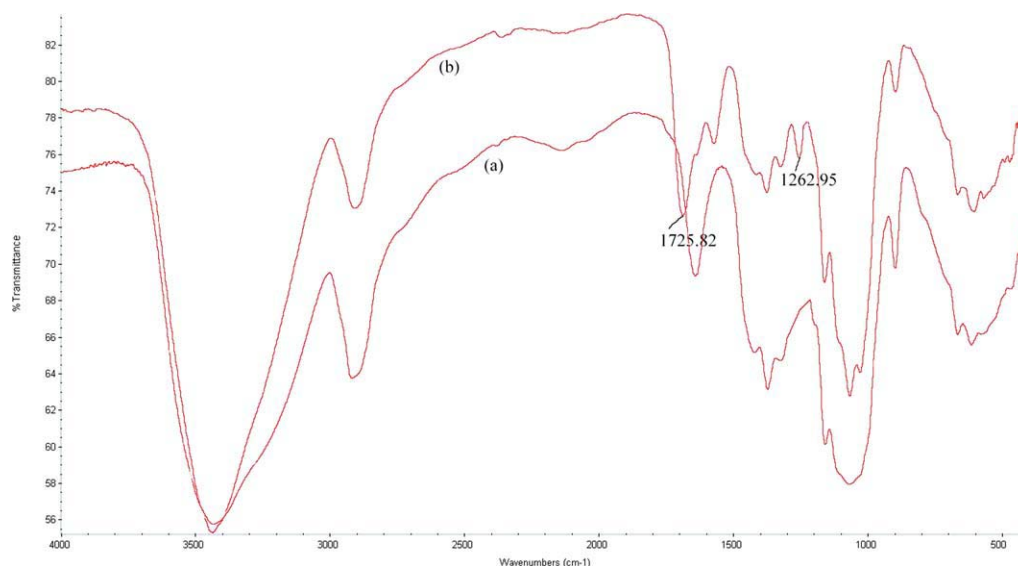
Because of increasing environmental awareness and diminishing petroleum-based resources,<sup>1</sup> there is a growing desire to develop new materials derived from renewable resources via green processing. The replacement of synthetic polymers with biosourced materials is one such area of particular interest. Cellulose, as one of the most abundant natural resources, offers a wide range of desirable properties including biological compatibility, relatively resistance to most chemical attack, and benign decomposition products, thus, economically and environmentally sustainable cellulose-based materials are in tremendous demand. Cellulose can be chemically modified to possess new functional groups. One of the chemical methods is to graft vinyl functional monomers onto glucose rings using radical polymerization systems. Conventionally vinyl monomers are grafted onto cellulose using various redox systems carried out by conductive heating with an external heat source(e.g., an oil-bath or heating mantle).<sup>2–4</sup> This is a comparatively slow (usually takes 1 to 5 h) and inefficient method for transferring energy into the system since it depends on convection currents and on the thermal conductivity of various materials that must be penetrated, and generally results in the

temperature of the reaction vessel being higher than that of the reaction mixture. Microwave (MW) irradiation<sup>5–8</sup> using the commercial MW oven as efficient thermal energy has received increasing interest in organic synthesis due to the remarkable enhancement of the rates of some organic reactions over conventional reaction.<sup>9,10</sup> MW energy can be directly and uniformly absorbed throughout the entire volume of an object, causing it to heat up evenly and rapidly.<sup>11</sup> It results into almost instantaneous ‘in core’ heating of materials in a homogeneous and selective manner. Recently under MW conditions, grafting of acrylamide and acrylonitrile on to guar gum and polyacrylonitrile<sup>12</sup> on to chitosan could be achieved in a very short reaction time in the absence of any redox initiator/catalyst.

Ionic liquids (ILs), the good solvents<sup>13</sup> and reaction media<sup>3</sup> of cellulose, due to their good properties including low melting points, wide liquid ranges, and lack of vapor pressure have received increasing interest around the world. Meanwhile, ILs was excellent MW absorbing agents due to their high ionic conductivity and polarizability, thus leading to a high heating rate and a significantly shortened reaction time.

In this work, the graft copolymerization of acrylic acid (AA) with cellulose using an IL 1-*N*-butyl-3-methylimidazolium chloride (BMIMCl) as a reaction medium was achieved in good yield for short reaction time under MW irradiation. Moreover, the obtained graft copolymers were also tested for their adsorption ability for Cu<sup>2+</sup> ions.

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**Figure 1** FTIR spectra of the native cellulose (a) and its graft copolymer (b).

## EXPERIMENTAL

### Materials and equipment

Cotton linter (cellulose, CE) was used as received. The ionic liquids (IL) 1-*N*-butyl-3-methylimidazolium chloride (BMIMCl, mp. 73°C), was purchased from Henan Lihua Pharmaceutical; All the other reagents were of analytical grade and used as received. IR spectra were recorded on a Spectrum GX Infrared Spectrophotometer (California, USA) using KBr pellets. Thermal stability of samples was examined on a TGA 500 thermogravimetric analyzer (Delaware, USA) in N<sub>2</sub> atmosphere. Scanning electron microscope (SEM) images of cellulose and graft copolymers were obtained by a FEI-QUANTA200 scanning electron micrograph machine (Amsterdam, Holland).

**Microwave instrumentation.** Multimode reactor: ETHOS Synth Lab station (Ethos start, Milestone). The multimode MW has a twin magnetron (2 × 800 W, 2.45 GHz) with a maximum delivered power of 1000 W in 10 W increments (pulsed irradiation). Built-in magnetic stirring (Teflon-coated stirring bar) was used in all operations. During experiments, time, temperature, and power were measured with the “easy WAVE” software package. The temperature was measured throughout the reaction and evaluated by an infrared detector, which indicated the surface temperature.

### MW cellulose solubilization

Dissolution of cellulose was performed using the cellulose without any pretreatment. The cellulose samples were added to the molten ILs (BMIMCl) in one-neck glass flask and irradiated in the MW oven at desired

temperature for a few minutes under magnetic stirring. ILs were heated with exceptional efficiency by MWs<sup>14</sup> and care should be taken to avoid excess localized heating that could induce cellulose pyrolysis

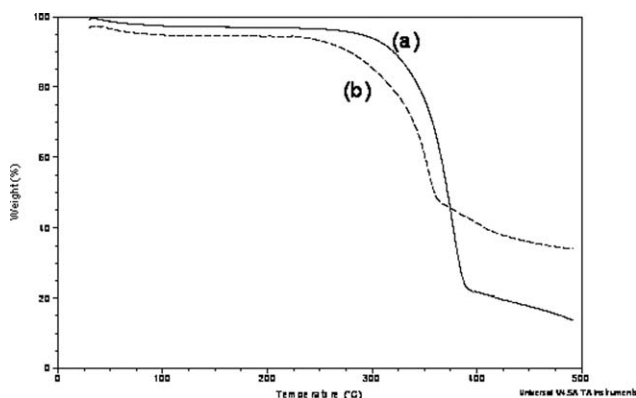
### Homogeneous graft of cellulose with AA under MW irradiation

Following complete dissolution of the cellulose, a solution of ammonium persulfate (APS) in DMSO, the initiator, was added; after magnetic stirring in MW oven for a few seconds, a predetermined volume of partially neutralized AA and a predetermined volume of *N,N'*-methylenebisacrylamide (MBA) in DMSO solution, the crosslinker, were added to the solution, respectively, the mixture was magnetic stirring and irradiated in the oven at desired temperature for required time. To compare with the MW method, the traditional heating method is used that let the reactor continue to place in the thermostated oil bath at 60°C to react for 2 h. After completing reaction, the flask was removed from oven and cooled to room temperature. The product was isolated by precipitation into excess deionized water, filtered, and washed several times, and then washed with a mixture of ethanol to remove the unreacted monomer. Finally, the grafted sample was extracted with acetone in a soxhlet apparatus for 24 h to dissolve all the homopolymer.

Grafting percentage and grafting efficiency were calculated according to the following equations:

$$\text{Grafting percentage (GP\%)} = (W_2 - W_0)/W_0 \times 100;$$

$$\text{Grafting efficiency (GE\%)} = (W_2 - W_0)/W_1 \times 100,$$



**Figure 2** TGA of native cellulose (a) and grafted cellulose (b).

where  $W_0$ ,  $W_1$ , and  $W_2$  are the weight of the raw cellulose, the graft copolymer, and the AA, respectively.

### Adsorption ability for $\text{Cu}^{2+}$ ions

Sorption experiments were conducted in a conical flask and equilibrated using a shaker. Then, 50 mL of 500 mg/L  $\text{Cu}^{2+}$  (pH was adjust to 5) ion solutions were placed in flasks and equilibrated with 0.1 g of graft copolymers at room temperature. After 2 h of shaking, the solutions were filtered, and the filtrates were analyzed using a GBC model 902 double beam atomic absorbance spectrophotometer (Victoria, Australia). The results were reported in terms of the amount of metal ions absorbed per gram of the graft copolymer.

## RESULTS AND DISCUSSION

### Characterization of the graft copolymer

#### FTIR spectra

Figure 1 shows the FTIR spectra of the native cellulose(a) and its graft copolymer (b)samples. The peaks at  $1725$  and  $1262\text{ cm}^{-1}$  correspond to the  $\text{—C=O}$  group and  $\text{C—O}$  group of the AA, respectively, which confirmed the introduction of the AA side chain into the CE backbone by graft copolymerization.

#### Thermogravimetric analyzer

As seen in Figure 2, the thermal decomposition of CE [Fig. 2(a)] occurs at  $270^\circ\text{C}$  and undergoes two stages. In the first stage, the weight of loss continues up to  $390^\circ\text{C}$  during which there is 72% weight loss. The second stage starts at  $390^\circ\text{C}$ , and a residue of 13 wt % remains after heating CE to  $500^\circ\text{C}$ . When CE is grafted with AA under MW heating, the thermal stability [Fig. 2(b)] is decreased slightly. Grafted cellulose underwent its first and major decomposition step at  $230^\circ\text{C}$ , where 56 wt % of its weight was lost. The second degradation step occurred at  $360^\circ\text{C}$ ,

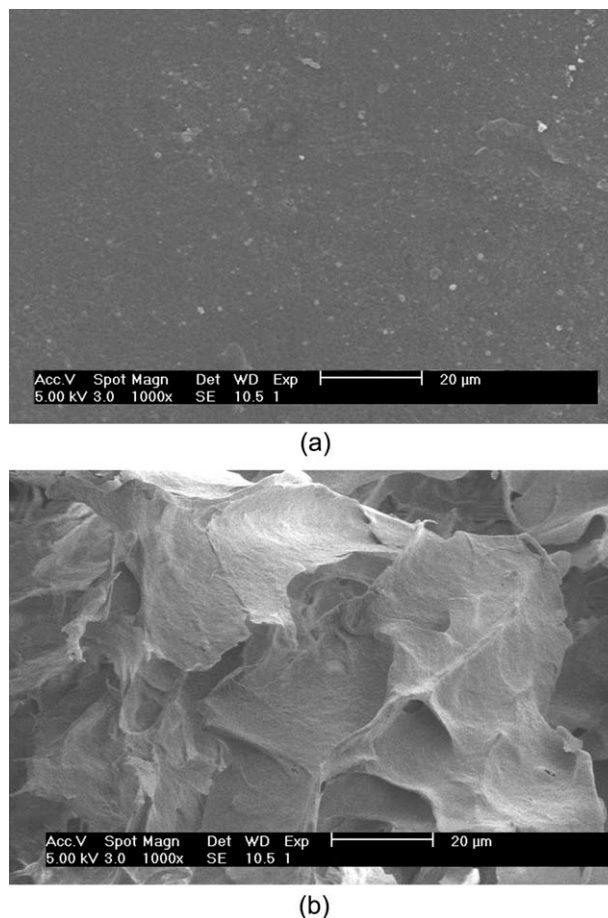
leaving a residue of 34 wt % as the temperature reached  $500^\circ\text{C}$ . Above  $375^\circ\text{C}$ , the grafted cellulose shows higher stability than cellulose.

### Scanning electron microscope

SEM pictures of the cellulose [Fig. 3(a)] and the grafted cellulose [Fig. 3(b)] also confirm grafting whereby a distinguished change is observed in the surface morphology after grafting. The smooth surface of the cellulose is lost after grafting and the fluffy morphology is clearly observed.

### Optimization of the reaction conditions

The optimal conditions of the grafting reaction was selected from the orthogonal tests. Five independent variables: amount of monomer, AA (g/g CE), amount of initiator, APS (g/g CE), dosage of cross-linker, MBA (g/g CE), reaction temperature, and reaction time were chosen, each at four levels. The investigated variables and their test levels are listed in Table I. Reference to the experimental design theory, the orthogonal array  $L_{16}(4^5)$  was selected to arrange the test program. The  $\text{Cu}^{2+}$  ions adsorption



**Figure 3** SEM of native cellulose (a) and grafted cellulose (b).

**TABLE I**  
Factors and Levels

Factors	Levels			
	1	2	3	4
A Monomer amount (g/g CE)	1	2	3	4
B Initiator dosage (g/g CE)	0	0.05	0.1	0.2
C Crosslinker dosage (g/g CE)	0.01	0.05	0.1	0.2
D Reaction temperature (°C)	20	40	60	80
E Reaction time (min)	3	5	10	20

of the grafting copolymer was a criterion of each test. The test results are listed in Table II.

The order of influence of each variable on the metal ion adsorption appears to be  $D > A > B > C > E$ . Thus, the reaction temperature has the greatest influence and the reaction time has the smallest influence. The optimum level of each variable is A-2, B-3, C-2, D-4, E-1. Therefore, the optimum reaction conditions were as follows: amount of monomer, 2 g/g CE; dosage of initiator, 0.1 g/g CE dosage of crosslinker, 0.05 g/g CE; reaction temperature, 80°C, and reaction time, 3 min. Under these conditions (No.17), the copolymer has the adsorption ability of 172.2 mg/g for  $\text{Cu}^{2+}$  ions.

The result obtained by the conventional heating method<sup>15</sup> was also given in Table II, and it can be seen that the adsorption ability of 174.8 mg/g for  $\text{Cu}^{2+}$  ions was achieved in 120 min at 60°C using the thermostated oil bath. This means the MW irradiation can greatly enhance the reaction rate compared with the traditional heating method.

#### Effect of monomer

The grafting percentage (*GP*) was found to increase with an increase in the initial mass ratio of monomer to cellulose and then level off (Fig. 4), which could be due to the greater availability of the monomer molecules in the proximity of the cellulose increasing the chance of the molecular collision and hence grafting. The continuous decrease of grafting efficiency (*GE*) with an increase in monomer amount and the level off of *GP* with further increase in monomer amount may be associated with the fact that increasing numbers of monomer molecules led to an increase of the likelihood of homopolymerization versus graft copolymerization.<sup>16</sup>

#### Effect of initiator

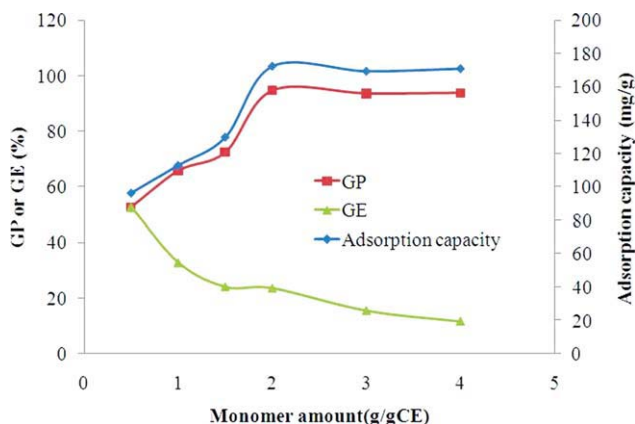
The effect of initiator on the graft copolymerization was shown in Figure 5 as other reaction variables are maintained constant. The figure shows that the AA can be grafted onto cellulose even no initiator was added under MW irradiation. Mechanism of the formation of the free radicals under MW irradiation can be explained as Singh's report.<sup>17</sup> The dielectric heating of MW results in bond breaking of —OH groups on cellulose to create radical sites at oxygen atom. Further MWs are also reported to have special effects<sup>18</sup> of lowering of Gibbs energy of activation of the reactions and in view of the above two effects, a plausible free radicals mechanism for the grafting under the MW irradiation has been proposed. In presence of radical initiator,

**TABLE II**  
Result of Orthogonal Experiments

Experiment No.	A (g/g CE)	B (g/g CE)	C (g/g CE)	D (°C)	E (min)	Adsorption capacity (mg/g)
1	1	0	0.01	20	3	67.5
2	1	0.01	0.05	40	5	75.6
3	1	0.05	0.1	60	10	94.6
4	1	0.1	0.2	80	20	111.5
5	2	0	0.05	60	20	131.6
6	2	0.01	0.01	80	10	169.2
7	2	0.05	0.2	20	5	106.8
8	2	0.1	0.1	40	3	110.1
9	3	0	0.1	80	5	96.6
10	3	0.01	0.2	60	3	81.5
11	3	0.05	0.01	40	20	98.1
12	3	0.1	0.05	20	10	72.9
13	4	0	0.2	40	10	36.6
14	4	0.01	0.1	20	20	45.8
15	4	0.05	0.05	80	3	160.5
16	4	0.1	0.01	60	5	96.7
$k_1$	87.30	83.08	107.86	73.25	104.90	
$k_2$	129.42	93.02	110.15	80.10	93.92	
$k_3$	87.28	115.00	86.78	101.10	93.32	
$k_4$	84.90	97.80	84.10	134.45	96.75	
R	44.52	31.92	26.05	61.20	11.58	
17 <sup>a</sup>	2	0.05	0.05	80	3	172.2
18 <sup>b</sup>	4	0.1	0.05	60	120	174.8

<sup>a</sup> experiment conducted under the optimal conditions select from orthogonal experiments.

<sup>b</sup> experiment conducted under traditional heating.

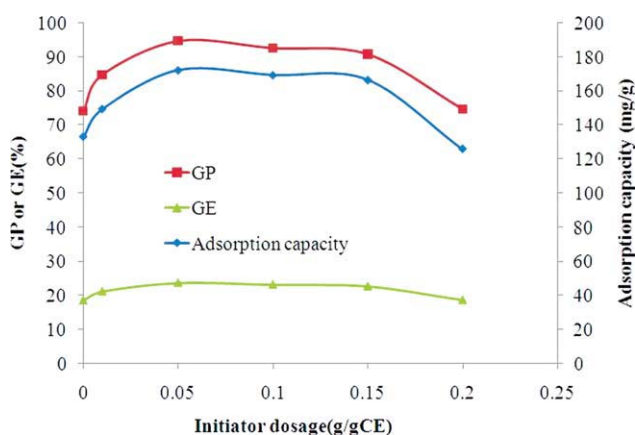


**Figure 4** Effect of monomer amount on grafting. Initiator dosage, 0.05 (g/g CE), crosslink dosage, 0.05 g/g CE, reaction time, 3 min and reaction temperature, 60°C.

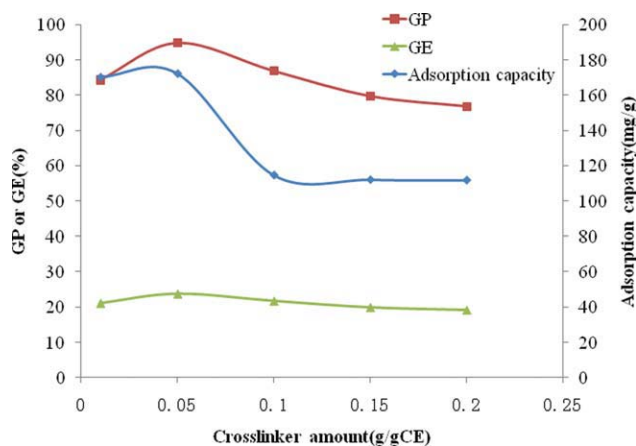
both *GP* and *GE* show an increase at first, followed by a decrease with an increase in the initiator dosage. The increase of *GP* may be ascribed to the increase of macroradicals generated by increasing levels of radical initiator on the glucose unit of cellulose, and therefore, more available sites of cellulose to react with AA. When the mass ratio of APS to cellulose was increased by more than 0.05 (g/g), the concentration of persulfate radicals increased and consequently initiated more of the homopolymerization of AA, which resulted in a decrease in both *GP* and *GE*.

#### Effect of crosslinker

Crosslinks have to be present in the copolymer to prevent dissolution of the hydrophilic polymer chains in an aqueous environment. The overall crosslink density of the final product was controlled by the efficiency of crosslinker incorporation. Figure 6 shows the effect of amount of MBA crosslinker used on grafting reaction whereas other reaction variables were kept constant. The results indicate that, with the increase of amount of



**Figure 5** Effect of initiator dosage on grafting. Monomer amount, 2 g/g CE, crosslink dosage, 0.05 g/g CE, reaction time, 3 min, and reaction temperature, 60°C.



**Figure 6** Effect of crosslinker on grafting. Monomer amount, 2 g/g CE, initiator dosage, 0.05 g/g CE, reaction time, 3 min and temperature, 60°C.

crosslinker, *GP* and *GE* increase firstly and decrease slightly when the amount of crosslinker exceeds 0.05 g/g CE. As for the  $\text{Cu}^{2+}$  adsorption capacity of the product, it increases when the amount of crosslinker is below 0.05 g/g CE. However, it decreases remarkably when the amount of crosslinker exceeds 0.05 g/g CE. This is because higher crosslinker concentration produce more crosslinked points in polymeric chains and increases the extent of crosslinking of the polymer network, which results in less swelling when it is brought into contact with the solvent. The similar observations have been reported and explained in the literature.<sup>19,20</sup> Therefore, the more proper amount of the crosslinker should be 0.05 g/g CE and *GP*, *GE*, and adsorption capacity of the graft copolymer are 94.7%, 23.7%, and 172.2 mg/g, respectively.

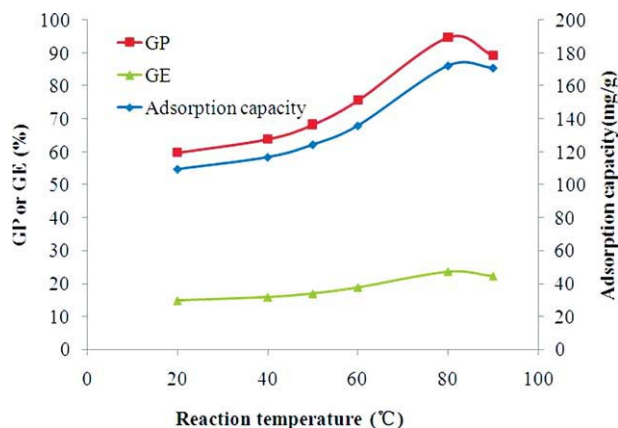
#### Effect of temperature

Figure 7 shows that both *GP* and *GE* reached a maximum at 80°C. The reaction between the hydroxyl groups of cellulose and APS did not progress readily when the reaction temperature was too low. A higher temperature was helpful in increasing the bimolecular collisions for APS and cellulose, which led to the increase of cellulose macroradicals, and therefore enhanced the graft copolymerization of AA onto cellulose. On the other hand, *GP* and *GE* decreased with a further increase in temperature, probably due to the enhanced possibilities of termination and chain transfer at a relatively higher reaction temperature.<sup>21</sup>

#### Graft mechanism

ILs was excellent MW-absorbing agents, thus leading to a high heating rate and a significantly shortened reaction time.

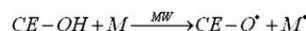
In presence of radical initiator, the sulphate ion radicals ( $\text{SO}_4^-$ ), which are well known as chain



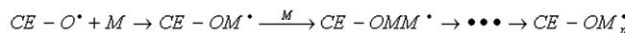
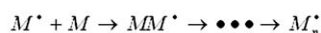
**Figure 7** Effect of temperature on grafting. Monomer amount, 2 g/g CE, initiator dosage, 0.05 g/g CE, crosslink dosage, 0.05 g/g CE, reaction time, 3 min.

carriers,<sup>22</sup> may initiate graft copolymerization by H abstraction from cellulose back bone. As no radical initiator is added, the grafting observed could be initiated by the generation of the free radicals under the influence of the MWs that can be explained as follows: Cellulose is a large molecule with many —OH groups. In the absence of any initiator, the dielectric heating will involve rapid energy transfer from these groups to neighboring molecules (AA), as it is not possible to store the energy in a specific part of the molecule. The dielectric heating results in bond breaking creating radical sites at oxygen atom. Further MWs are also reported to have special effects<sup>18</sup> of lowering of Gibbs energy of activation of the reactions and in view of the above two effects, a plausible free radicals mechanism for the grafting under the MW irradiation has been proposed. O—H bonds at cellulose absorb MW energy and will cleave generating monomer free radical and macro radical (Scheme 1).

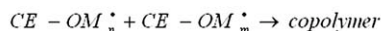
#### Initiation



#### Propogation



#### Termination



**Scheme 1** Mechanism under microwave irradiation. Where CE stands for cellulose, M stands for AA, MW stands for microwave.

## CONCLUSIONS

The graft copolymerization of AA onto cellulose was successfully conducted by MW irradiation, using APS as an initiator and MBA as a crosslinker. High grafting percentage of AA was achieved in rather short time under MW irradiation, compared to the conventional heating method. The optimum reaction conditions were as follows: amount of monomer, 2 g/g CE; dosage of initiator, 0.1 g/g CE; dosage of crosslinker, 0.05 g/g CE; reaction temperature, 80°C; and reaction time, 3 min. Under these conditions, the copolymer has the adsorption ability of 172.2 mg/g for Cu<sup>2+</sup> ions. The copolymer was confirmed by the characterization of FTIR, TGA, and SEM. The grafted cellulose so obtained using MW irradiation was an efficient adsorbent for Cu<sup>2+</sup> ions thus showing its potential in removal of metal ions from waste and natural water.

The research was financially supported by Program for Changjiang Scholars and Innovative Research Team in University (IRT0552) and Fund of China Post Doctor (20070410238).

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