

# Preparation and Characterization of Crosslinked Glyoxalated Polyacrylamide Paper-Strengthening Agent

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**ABSTRACT:** To obtain additives that could simultaneously increase the dry strength and wet strength of paper sheets, we synthesized a series of crosslinked cationic glyoxalated polyacrylamide (GPAM) resins by using acrylamide (AM), 2-methacryloxyethyl trimethyl ammonium chloride (DMC), *N*-methylolacrylamide (NMA), 2-mercaptoethanol, and glyoxal as the main materials. GPAM demonstrated excellent properties and had a good strengthening ability under the following polymerization conditions: dosage of AM = 55 wt %, dosage of the cationic monomer DMC = 5.5 wt %, dosage of the crosslinking monomer NMA = 8.0 wt %, dosage of chain-transfer agent 2-mercaptoethanol = 1.0 wt %, dosage of glyoxal = 30 wt %, and charge of the initiator (ammonium persulfate/sodium bisulfite = 1 : 2) = 0.5 wt %. The products

were characterized by Fourier transform infrared spectroscopy, <sup>1</sup>H-NMR, size exclusion chromatography, and Ubbelohde viscometry. The copolymers with a viscosity-average molecular weight of approximately 26,000 and a polydispersity index of 1.460 had a much better strengthening ability. When these GPAM resins were used as paper-strengthening agents, the mechanical strength of the paper was remarkably enhanced, and the dry and wet tensile indices of the handsheets increased by 24.6 and 381%, respectively, compared with those of handsheets without GPAM. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**Key words:** copolymers; crosslinking; networks; polymer synthesis and characterization; radical polymerization

## INTRODUCTION

In recent years, the Chinese pulp and paper industry has become a booming development, but there has been a huge shortage of pulping resources. Therefore, more and more secondary fibers, fillers, and high-yield pulps have been applied in this industry; this has resulted in a deterioration of the paper-strength properties. The strength properties of paper are extremely important for manufacturers and end users and in recycling.<sup>1–3</sup> Moreover, several paper grades, such as tissue paper, paper towels, and a few printing and writing papers, rely heavily on these two properties, the dry strength and wet strength.<sup>4</sup> Novel papermaking additives clearly need

to be developed to meet the demand for more cost-effective strengthening agents.

Paper-strength properties can be improved by the addition of strengthening agents to the fiber suspensions at the wet end of papermaking. The charge density, molecular weight (MW), and molecular structure of an additive affect its strengthening ability.<sup>5</sup> Crosslinked polymers, an innovative class of strengthening agents, are obtained by the interconnecting of molecular chains together.<sup>6</sup> Because of the special structure of these novel polymers, their solution viscosity is lower compared with traditional linear polymers. The extended chain conformation of network polymers has made them a recent object of much research interest worldwide.<sup>7</sup> When crosslinked polymers are applied, the macromolecular chains of fiber–fiber interactions can be intertwined, and a considerably better network structure in the paper sheets is formed; this limits movement among the fibers.<sup>8,9</sup> Research has also shown that the strengthening ability of network polymers is superior to that of traditional linear polymers. However, data on the use of crosslinked polymers as strengthening agents at the wet end of papermaking remains limited.

Glyoxal, which contains two merged aldehyde groups, has very active chemical properties. It produces a hemiacetal structure via a reaction between

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the aldehyde group and the hydroxyl groups in cellulose in the papermaking process; this reduces the expansion and deformation of rewetted paper sheets.<sup>10</sup> Therefore, glyoxal helps to significantly improve the wet tensile strength of paper. Yuan et al.<sup>11</sup> obtained a similar product, which had a poor stability, low monomer conversion, and low MW because of the great difference in the reactivity ratio between diallyldimethylammonium chloride (DADMAC) and acrylamide (AM). In this study, 2-methacryloxyethyl trimethyl ammonium chloride (DMC) was used instead of DADMAC as cationic monomer; this greatly improved the properties of the products. We obtained a higher MW, a higher positive charge density, an excellent storage stability, and better strengthening ability. Moreover, the copolymerization became much easier to control.

In this study, *N*-methylolacrylamide (NMA) and 2-mercaptoethanol were used as additives to modify the structure of the polymer. Crosslinked glyoxalated polyacrylamide (GPAM) polymers, which have the combined advantages of crosslinked polymers and glyoxal, were synthesized with glyoxal as the crosslinker. In addition, the synthesized GPAM resins were used as strengthening agents in the wet end of the papermaking process to determine the strengthening ability of the copolymers. The results demonstrate that the GPAM resins not only remarkably improved the dry strength of paper sheets but also significantly enhanced their wet strength. The copolymers were characterized with respect to their average MW and molecular structure.

## EXPERIMENTAL

### Materials

The AM monomer (commercially available) was purchased from Hengju Chemical Group (Beijing, China), and the molecular-structure-modified monomers 2-mercaptoethanol [analytical reagent (AR) grade] and NMA (AR grade) were purchased from Wonderful Chemicals Co., Ltd. (Zibo, Shandong Province, China) and were used without further purification. The cationic monomer DMC was purchased from Xinghuo Chemical Industries, Ltd. (Yantai, Shandong Province, China) as a 78% aqueous solution and was used as received. All catalysts, including ammonium persulfate (AR grade), sodium bisulfite (AR grade), ethanol (AR grade), acetone (AR grade), and glyoxal (AR grade) were purchased from Jiangtian Chemical Co., Ltd. (Tianjin, China) and were used without further purification. The nitrogen used was a high-purity grade. The pulp stock, consisting of de-inked pulp, bleached chemithermomechanical pulp, bleached hardwood kraft pulp, and bleached softwood kraft pulp at a 25 : 25 :

35 : 15 weight ratio, was provided by a local pulp and paper mill company.

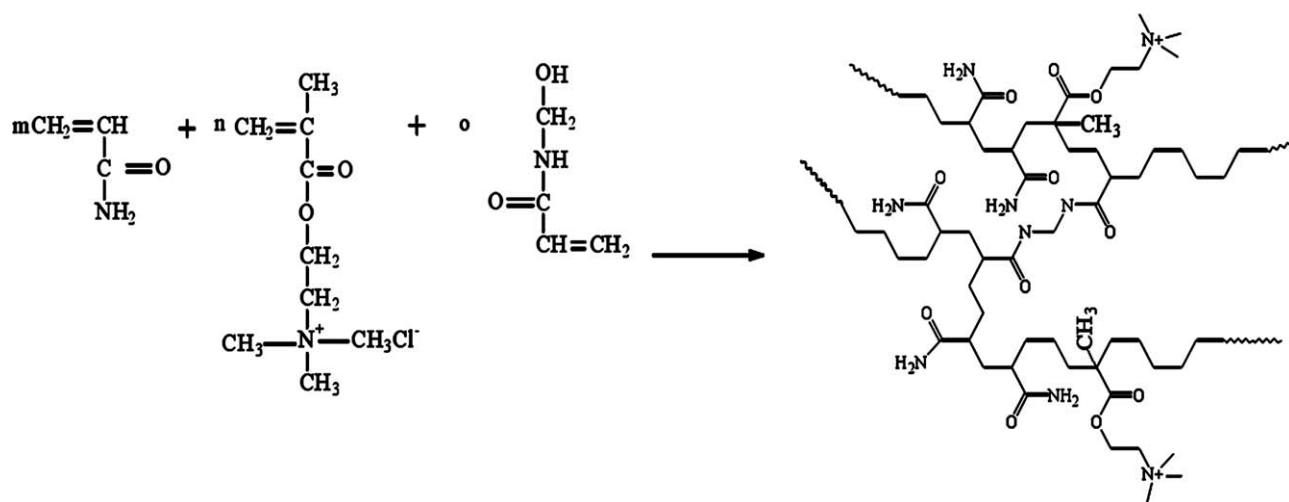
### Preparation of cationic GPAM

Deionized water, 27 g of AM, 2.7 g of DMC, 3.9 g of NMA, and 0.49 g of 2-mercaptoethanol were mixed together in a suitable 150-mL beaker. An amount of 20% of the mixed monomers was added to a suitable 250-mL flask equipped with a stirring apparatus, a thermometer, a nitrogen inlet tube, and a reflux condenser; the flask was then placed in a water bath. After the mixture was purged with N<sub>2</sub> under controlled temperature conditions, the polymerization was initiated by the injection of 20% of the 0.245 g of water-soluble initiator (ammonium persulfate/sodium bisulfite = 1 : 2) into the system. Stirring was done at 65°C for 30 min. The residual mixed monomers were continuously added dropwise within 105 min, and the residual initiator (ammonium persulfate/sodium bisulfite = 1 : 2) was added within 120 min. During this procedure, the ammonium persulfate and sodium bisulfite were added separately with two devices. After all of the chemicals were added, stirring was maintained at 65°C for 30 min, and the crosslinked Cationic Polyacrylamide was obtained (Scheme 1). The temperature was lowered to 60°C, and 14.7 g of glyoxal solution was subsequently added to the CPAM aqueous solution. Stirring was maintained at 60°C for 140 min, after which GPAM was obtained (Scheme 2).

### Characterization

We precipitated both the CPAM (obtained in the first step) and GPAM (the final product) by pouring the polymer solution into a large quantity of ethanol and then washing with acetone. This process was repeated several times to remove the homopolymers and unreacted monomers. The purified samples were then vacuum-dried to a constant weight at 40°C.

The Fourier transform infrared (FTIR) spectra of the CPAM and GPAM in KBr pellets (1%) were recorded with an FTIR-650 spectrophotometer (Gangdong, Co., Ltd. Tianjin, China) operating between 4000 and 400 cm<sup>-1</sup>. The <sup>1</sup>H-NMR (600-MHz) spectra of CPAM and GPAM were obtained with a Bruker AV-600 spectrometer (Karlsruhe, Germany) at an operating temperature of 25°C with D<sub>2</sub>O as a solvent. The values for the number-average molecular weights ( $M_n$ 's) and weight-average molecular weights ( $M_w$ 's) of CPAM and GPAM were determined by size exclusion chromatography (SEC) with a DAWNEOS-Optilab rEX (Wyatt) equipped with a high performance liquid chromatography (HPLC) pump (Waters) and two columns, OHpak SB-804 (10 μm) 8.0 × 300 mm<sup>2</sup> and OHpak SB-802.5 (10 μm) 8.0 × 300 mm<sup>2</sup> (Shodex, Japan). The eluent phases used were a 0.1M sodium



Scheme 1 Synthesis of the crosslinked CPAM.

nitrate solution and a 0.02% sodium azide solution, respectively. The flow rate was 0.5 mL/min, and the operating temperature was 40°C. The inherent viscosities ( $[\eta]$ 's) were obtained with a concentration of 8 g/L in a 1 mol/L NaCl aqueous solution at 30°C with an Ubbelohde suspended-level viscometer. The MW of the GPAM sample was calculated according to the Mark-Houwink equation ( $[\eta] = 4.74 \times 10^{-3} MW^{0.8}$ ).<sup>12</sup>

The storage stability was obtained by observation of how long the solution took to gel while standing at 25°C. For the mechanical stability measurements, 100 mL of the GPAM solution was placed into a special container, and stirring proceeded at 6096 rpm for 10 min. Then, the strengthening ability of the solution was measured to determine the mechanical stability. For pH stability measurements, 50 mL of GPAM solution was placed separately into two test tubes, and we added 5 mL of HCl (1 mol/L) and 5 mL of KOH (1 mol/L), respectively. The test tubes were allowed to stand for 24 h, and then, their strengthening ability was determined through use in paper making. The solubility of the resultant GPAM was tested with water. A sample (10 g) of GPAM was added to a volumetric flask (100 mL) containing water, and the solubility was observed.<sup>13</sup>

#### Paper making with cationic GPAM

The mixed pulp stock was disintegrated with a Sweden disintegrator (Shanghai, China) in 25°C water for 5 min. The pulp concentration and pH value were adjusted to 0.55% and 7.0, respectively. Subsequently, 0.3% (solid content based on the oven-dried pulp) of self-made GPAM was added to the mixed pulp furnish, and the mixture was stirred for 5 min. Laboratory sheets with a grammage of approximately 60 g/m<sup>2</sup> were prepared in a conventional sheet former according to TAPPI standards. The wet webs were vacuum-dried at 95°C for 6 min.

#### Evaluation of the paper-strength properties

The handsheets were conditioned at  $23 \pm 1^\circ\text{C}$  and  $50\% \pm 2\%$  relative humidity according to TAPPI T402. The dry tensile and wet tensile strengths were measured in accordance with TAPPI T 494 and TAPPI T 456, respectively, with Lorentzen & Wettre tensile testers. During the wet strength measurement, the soaking time for the 15-mm-wide specimen strips in deionized water was set to 10 min, and excess water was removed from the strips with blotters. The wet strips were then immediately subjected to tensile strength measurement with a span of 10 cm. The wet tensile strength was expressed as the wet strength index according to the method for measuring the dry tensile strength of paper samples.

## RESULTS AND DISCUSSION

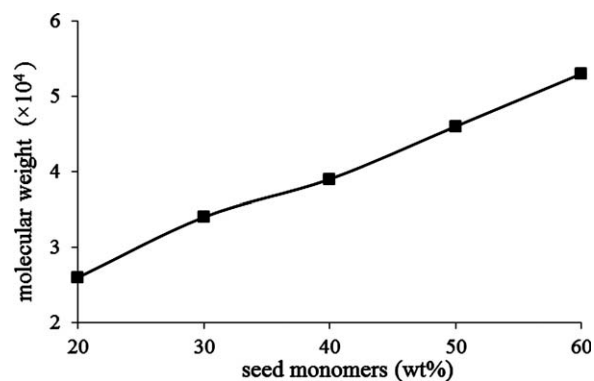
#### Effects of the GPAM preparation conditions on the MW and strengthening ability of GPAM

##### Seed monomer dosage

The rate of living free-radical polymerization is very fast. When the raw materials are all added at once, the heat release is very strong because of the self-acceleration of the reaction; this, in turn, leads to the reaction easily getting out of control.<sup>13</sup> In this study,



Scheme 2 Reaction between the glyoxal and amide groups on the CPAM backbone.

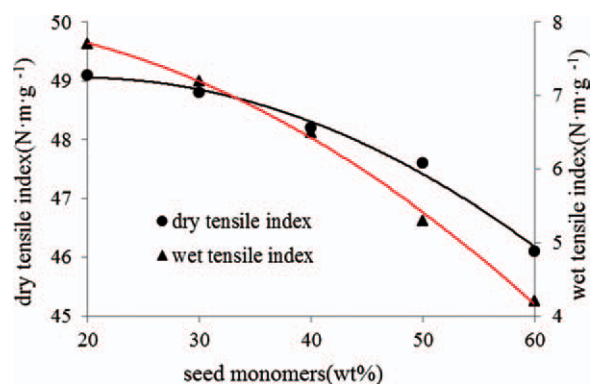


**Figure 1** Effect of the seed monomer dosage on the MW of GPAM.

the reaction was carried out through a semicontinuous seeded aqueous polymerization, which had a stable and weak heat release.<sup>14</sup> The distribution of MW of the obtained polymers was much narrower; this improved the stability of GPAM. During the utilization procedure, the adsorption effect on the fiber surface was also enhanced.

As illustrated in Figure 1, the MW of GPAM increased with increasing levels of seed monomers. This pattern was attributed to the increases in the seed monomers and copolymerization rate, which in turn, led to rapid increases in the polymer MW. The MW of GPAM and its distribution affected the polymer properties and the strengthening ability greatly. In general, the narrow MW distributions resulted in an excellent strengthening ability.

As shown in Figure 2, the mechanical strength of the sheets decreased with increasing dosage of seed monomers. The maximum dry tensile index and wet tensile index of the seed monomers at 20 wt % were 49.1 and 7.7 N m/g, respectively. The strength properties of the handsheets began to diminish as the amount of seed monomers was continuously increased. This may have been due to the relation-



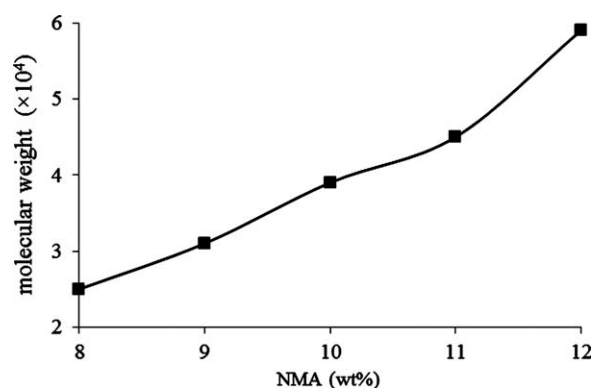
**Figure 2** Effect of the seed monomer dosage on the strengthening ability of GPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

ship between the polymerization rate and the quantity of the seed monomers. When the amount of seed monomers was increased, more monomers reacted in the first stage; this, in turn, accelerated the reaction speed. Moreover, the final products had larger MWs with increasing seed monomer dosage; this resulted in fewer molecules per unit of polymer and, consequently, decreased the strengthening ability of GPAM. When the seed monomer dosage was 20%, the reaction process was stable; this resulted in a suitable MW of obtained GPAM. As such, a seed monomer dosage of 20% was determined to be the optimum condition.

#### NMA dosage

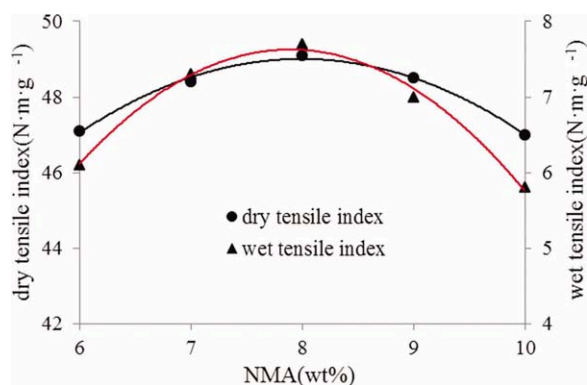
In the copolymerization, crosslinking monomers were always introduced to form a multiple-dimensional network structure. In this study, NMA was used as the crosslinking monomer to obtain the crosslinked GPAM. Moreover, the methylene crosslinking bonds were formed through the condensation reaction of  $-\text{NHCH}_2\text{OH}$  groups in NMA. With GPAM as the strengthening agent in papermaking, the methylene crosslinking bonds reacted with the hydroxyl groups in cellulose, bearing the substantial film on the fibers' surface and, thereby, enhancing the interfiber bond strength and the strength properties of the sheets.<sup>15</sup>

The dosage of NMA used was essential to the reaction system because of its crosslinking character. As shown in Figure 3, the MW of GPAM increased with increasing NMA dosage. NMA had a very active chemical character as it contained a hydroxymethyl group. More linear chains were, therefore, crosslinked together when the NMA dosage was high; this led to a rapidly increasing MW and distribution. According to the Flory–Huggins equation,<sup>16</sup> the crosslinking reaction rate was slow when the dosage of NMA was low; this resulted in a



**Figure 3** Effect of the NMA dosage on the MW of GPAM.





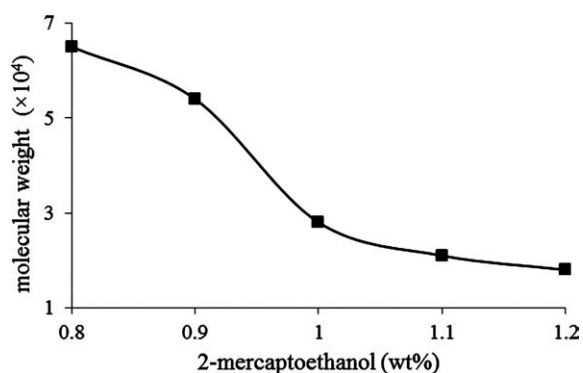
**Figure 4** Effect of the NMA dosage on the strengthening ability of GPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

diminished polymer crosslinking density and, ultimately, a low MW for GPAM.

Figure 4 demonstrates that the dry strength and wet strength of the paper initially increased but then decreased during later stages. Increased NMA dosage led to a higher polymer crosslinking density and a better polymer network structure. Thus, when GPAM was applied to the wet end of the papermaking process, the combination among the fibers was considerably improved; this enhanced the strength of the sheets. However, when the NMA dosage was beyond 10 wt %, the MW was higher than desired, and some gel particles were detected on the surface of the sheets. This negatively affected the paper's formation and smoothness. Consequently, the strengthening ability of the polymer was very poor and even disappeared. The optimized dosage was obtained with 8 wt % NMA.

#### 2-Mercaptoethanol dosage

In this study, 2-mercaptoethanol was chosen as the chain-transfer agent. It was used to control the MWs of the polymers and increase the quantity of pendant amide groups on their backbone. GPAM was obtained by the reaction between pendant amide groups and



**Figure 5** Effect of the 2-mercaptoethanol dosage on the MW of GPAM.

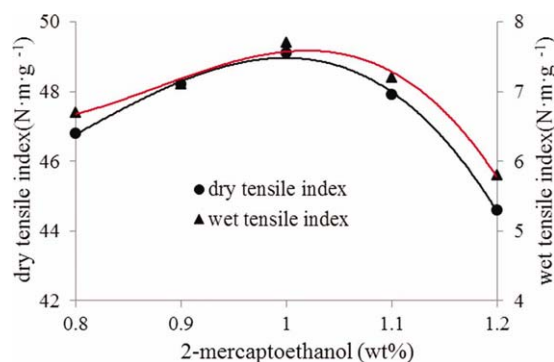
glyoxal. Therefore, the 2-mercaptoethanol dosage had critical effects on the polymer properties, including the storage stability and mechanical stability; this, thereby, affected the strengthening ability of GPAM.

As shown in Figure 5, the MW of GPAM decreased with increasing 2-mercaptoethanol dosage. When the 2-mercaptoethanol dosage was larger than 1.2 wt %, the MW of GPAM was changed very little because large quantity of mercaptan free radicals were generated by more living free radicals reacting with 2-mercaptoethanol instead of initiating polymerization. On the contrary,  $[\eta]$  and MW of the polymers were large when the 2-mercaptoethanol dosage was low because there were more living free radicals to initiate the polymerization.

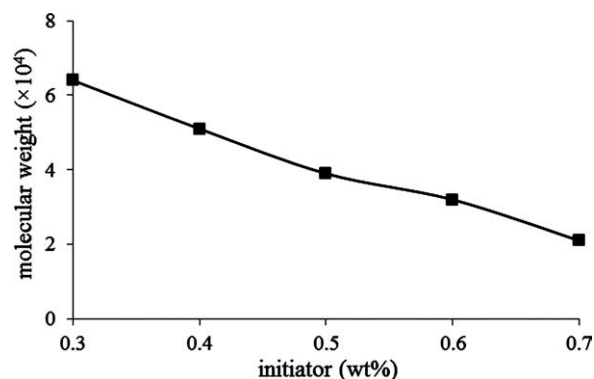
Figure 6 demonstrates that with increasing 2-mercaptoethanol dosage, the dry strength and wet strength of the paper first increased and then decreased at later stages. The fact that the molecular size of the polymer made it more suitable for use as a paper-strengthening agent because of the increased 2-mercaptoethanol dosage (from 0.8 to 1.0%) explained this phenomenon. In summary, with increased 2-mercaptoethanol dosage, the molecular size and crosslinking density of the polymer more appropriately improved the interfiber strength bonds of the paper. However, when the dosage of 2-mercaptoethanol exceeded 1.0%, the MW was lower than desired, and the amount of residual monomers increased. The molecular sizes were too small to improve the paper strength. Therefore, the optimized dosage of 2-mercaptoethanol obtained was 1.0 wt %.

#### Initiator dosage

Research has shown that the type and dosage of initiator had critical effects on the performance of the polymers. In this study, ammonium persulfate and sodium hydrogen sulfite were used together as the redox initiator.



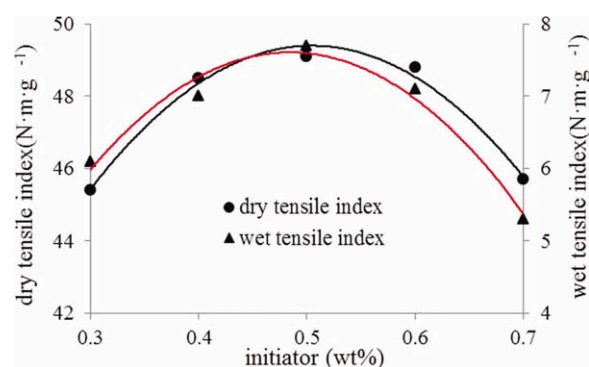
**Figure 6** Effect of the 2-mercaptoethanol dosage on the strengthening ability of GPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



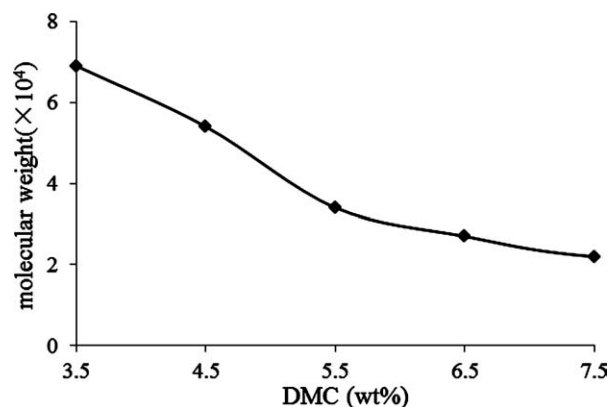
**Figure 7** Effect of the initiator dosage on the MW of GPAM.

As Figure 7 shows, with increasing initiator dosage, the MW of the obtained GPAM decreased. The *kinetic chain length* of a radical chain polymerization is defined as the average number of monomer molecules consumed per each radical that initiates a polymer chain. It is proportional to either the radical concentration or the polymerization rate.<sup>17</sup> Hence, increasing the polymerization rate and initiator dosage in the free-radical polymerization led to smaller sized polymer molecules. On the contrary, when the initiator dosage was low and few free radicals were generated in the reaction system, the termination reaction between radicals decreased, which in turn, led us to obtain polymers with higher MWs. Moreover, the polymerization rate was slow; this resulted from few free radicals and resulted in the low monomer conversion and bad polymer stability.

Figure 8 shows that the dry strength and wet strength of the handsheets initially increased but subsequently decreased after GPAM was added as the initiator dosage increased from 0.5 to 0.7%. This phenomenon was attributed to the fact that the MWs of polymers were higher when the initiator was lower; in addition, the polymerization was not completed. In addition, with increased initiator dosage, the molecular size of the obtained polymer



**Figure 8** Effect of the initiator dosage on the strengthening ability of GPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



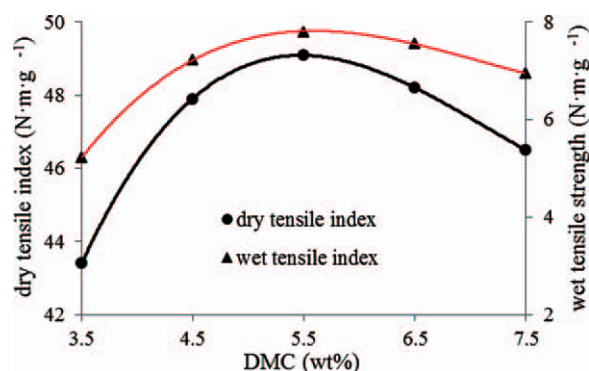
**Figure 9** Effect of the DMC dosage on the MW of GPAM.

became increasingly appropriate for GPAM to qualify as a paper-strengthening agent. However, when the dosage of initiator was larger than 0.5%, an increasing number of living radicals were generated. As a result, the molecular size of GPAM too small to have good strengthening ability. In consequence, the optimum initiator dosage was 0.5 wt %.

#### DMC dosage

The type of cationic monomer has critical effects of the reaction process and polymers' MWs. In copolymerization, the reactivity ratios of AM and DMC were 0.25 and 1.71, respectively. However, when it came to DADMAC and AM, the reactivity ratios were 6.40–7.54 and 0.05–0.58, respectively.<sup>18</sup> In this study, DMC was chosen as the cationic monomer. As shown in Figure 9, with increasing DMC dosage, the MW of the obtained GPAM decreased. The reasons were that the DMC activeness was much lower than that of AM,<sup>19,20</sup> DMC could not carry on the full copolymerization with AM, and the product included massive residual DMC monomer, so the MW decreased.

Figure 10 demonstrates that the dry strength and wet strength of the paper initially increased but then



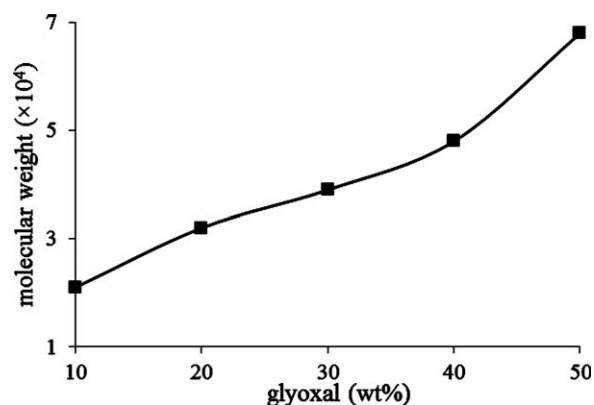
**Figure 10** Effect of the DMC dosage on the strengthening ability of GPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

decreased during later stages. This phenomenon was attributed to the fact that the MWs of the polymers were higher when the DMC dosage was lower. In addition, with increased DMC dosage, the molecular size of the obtained polymer became increasingly appropriate for GPAM to be used as a paper-strengthening agent. However, when the dosage of initiator was larger than 5.5%, an increasing quantity of residual DMC monomer was left in GPAM; in addition, the polymerization was not completed. As a result, the molecular size of GPAM was too small to have a good strengthening ability. In consequence, the optimum initiator dosage was 0.5 wt %.

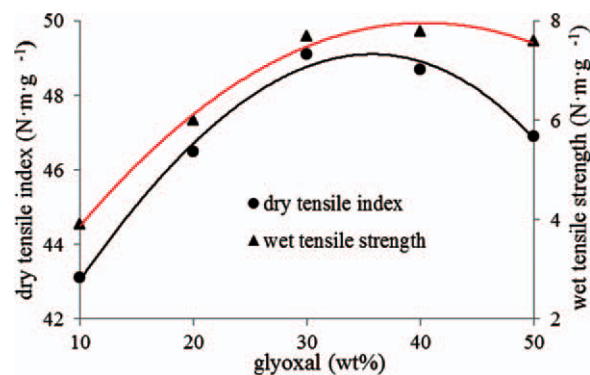
### Glyoxal dosage

The dosage of glyoxal used had critical effects on the properties and strengthening ability of GPAM. As shown in Figure 11, with increasing glyoxal dosage, the MW of the obtained GPAM increased. Glyoxal has a very active chemical character, as it contains two aldehyde groups. More pendant amide groups, therefore, reacted with the aldehyde groups, and more molecules were crosslinked together when the glyoxal dosage was high; this resulted in an increased polymer crosslinking density. Meanwhile, the reaction became much more difficult to control. On the contrary, the crosslinking reaction rate was slow, and the number of amide groups participating in the reaction was small when the dosage of glyoxal was low; this resulted in a diminished polymer crosslinking density and, ultimately, a low MW for GPAM.

Figure 12 demonstrates that the dry strength and wet strength of paper initially increased but then decreased during later stages. An increased glyoxal dosage led to more pendant aldehyde groups in the polymer; thus, when GPAM was applied to the wet end of the papermaking process, the aldehyde groups reacted with hydroxyl groups in cellulose, bearing an aldol condensation structure with cova-



**Figure 11** Effect of the glyoxal dosage on the MW of GPAM.



**Figure 12** Effect of the glyoxal dosage on the strengthening ability of GPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

lent bond and, thereby, enhancing the dry strength of the sheets. In addition, when the handsheets were rewetted, the aldol condensation structure still blocked the hydrogen-bonding area in the paper to retain its strength and, thus, the wet strength increased. However, excessive free glyoxal also caused severe embrittlement of paper, whose folding characteristic were significantly affected. Yellowing and curling problems also developed.<sup>20</sup>

In contrast, when the dosage of glyoxal was low, the molecular sizes of the generated molecules became too small to improve the interfiber bonding strength of the paper. Excellent strength properties of the handsheets were observed for the handsheets when the dosage was 30 wt %. Much deliberation, hence, identified this rate as the optimum glyoxal dosage by weight.

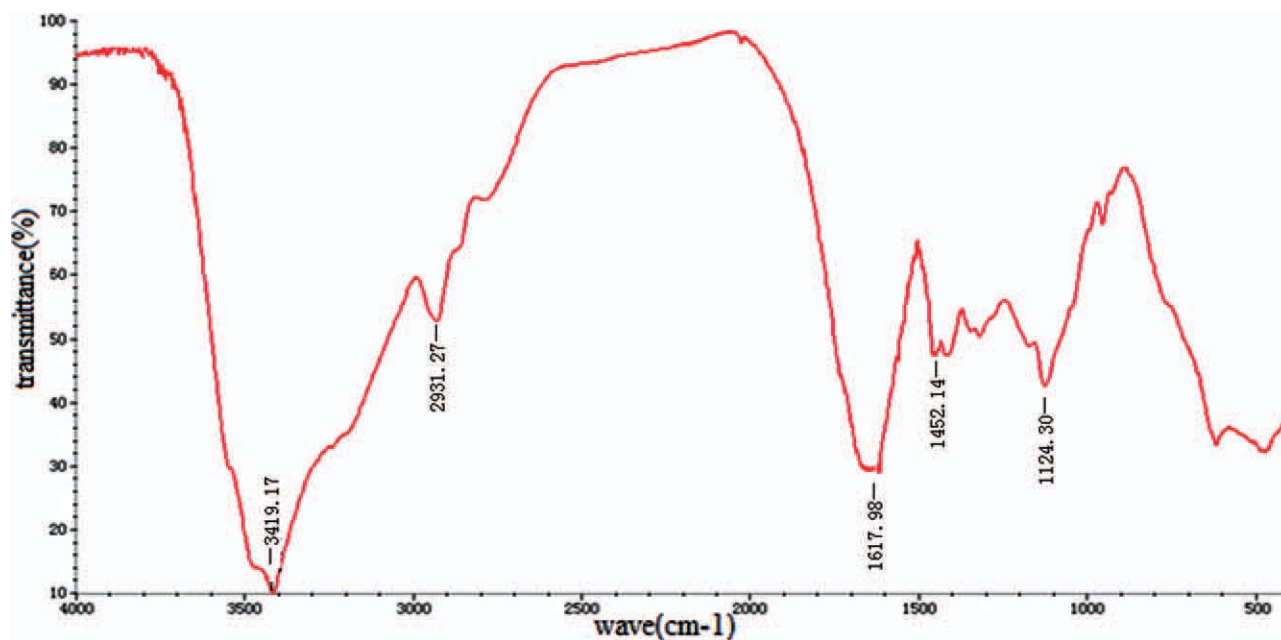
### Properties and characterization of GPAM

The properties of GPAM, prepared under the optimum conditions, were investigated, and the results are shown in Table I. The aqueous solution demonstrated excellent performance in the laboratory studies.

Figure 13 shows the infrared absorption spectrum of CPAM washed with ethanol and acetone. The stretching vibration absorption peak of the amide group (N—H) was  $3419.17 \text{ cm}^{-1}$ , the characteristic absorption peak of methyl ( $-\text{CH}_3$ ) in  $-\text{N}+(\text{CH}_3)_3$

**TABLE I**  
Physicochemical Properties of the Experimental GPAM

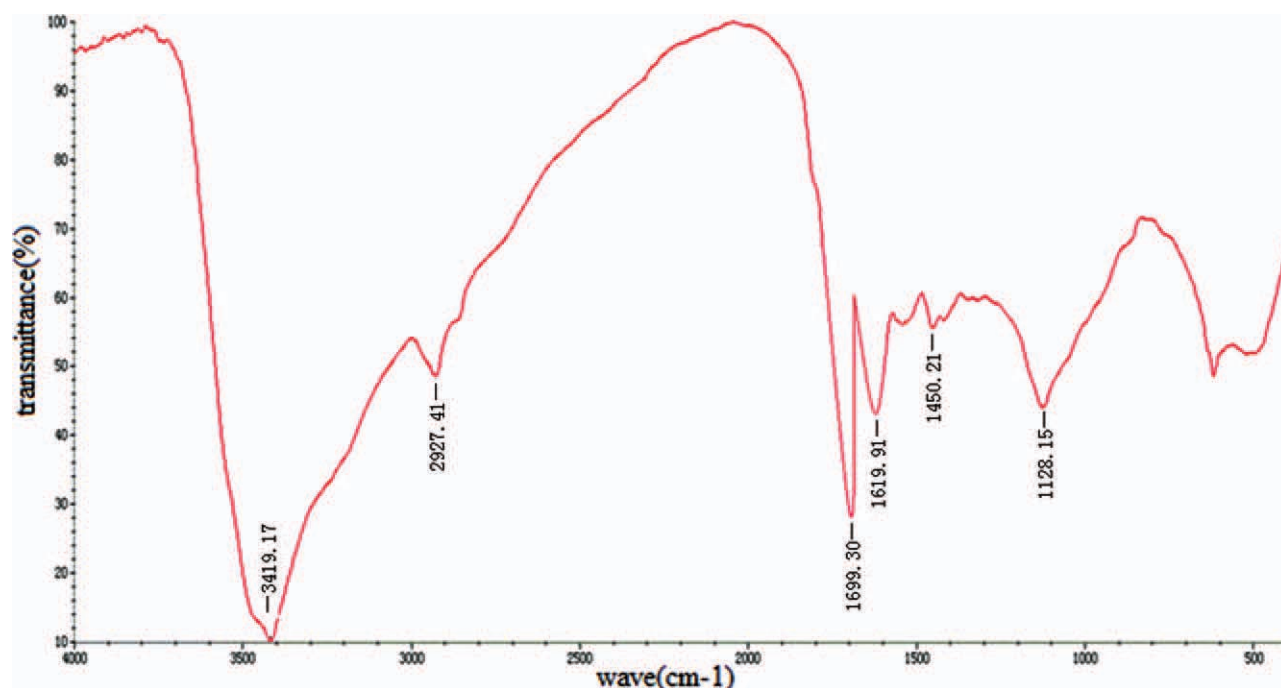
Property	
Appearance	Transparent
Water solubility	Instant
Solid content	About 10%
pH stability	3–4.5
MW	$2.1\text{--}5.6 \times 10^4$
Mechanical stability	Stable
Storage stability	Stable over 60 days
Dilution stability	Stable



**Figure 13** FTIR spectrum of CPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

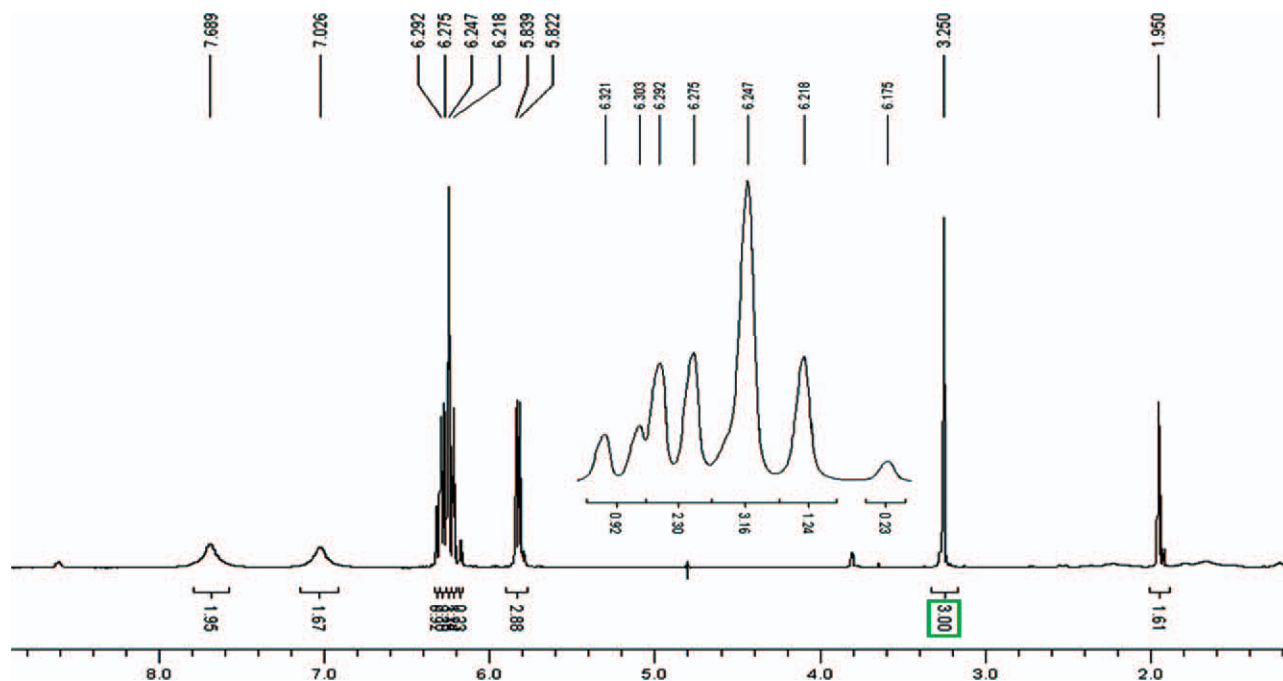
was  $2931.27\text{ cm}^{-1}$ , the characteristic absorption peak of carbonyl (C=O) in the amide group was  $1617.98\text{ cm}^{-1}$ , the bending vibration absorption peak of methylene ( $-\text{CH}_2-$ ) in  $-\text{CH}_2-\text{N}+(\text{CH}_3)_3$  was  $1452.14\text{ cm}^{-1}$ , and the absorption peak of pentatomic heterocyclic compounds was  $1124.30\text{ cm}^{-1}$ . These FTIR data indicate that the CPAM included AM and DMC organic functional groups and had a network structure.

Figure 14 represents the FTIR spectrum of GPAM as characterized by FTIR spectroscopy. The specific adsorption peaks of the main functional groups of GPAM were almost the same as those of CPAM. The only difference between the two was the characteristic absorption peak of carbonyl (C=O) in the aldehyde group of GPAM ( $1699.30\text{ cm}^{-1}$ ). The FTIR spectrum of GPAM confirmed its



**Figure 14** FTIR spectrum of GPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





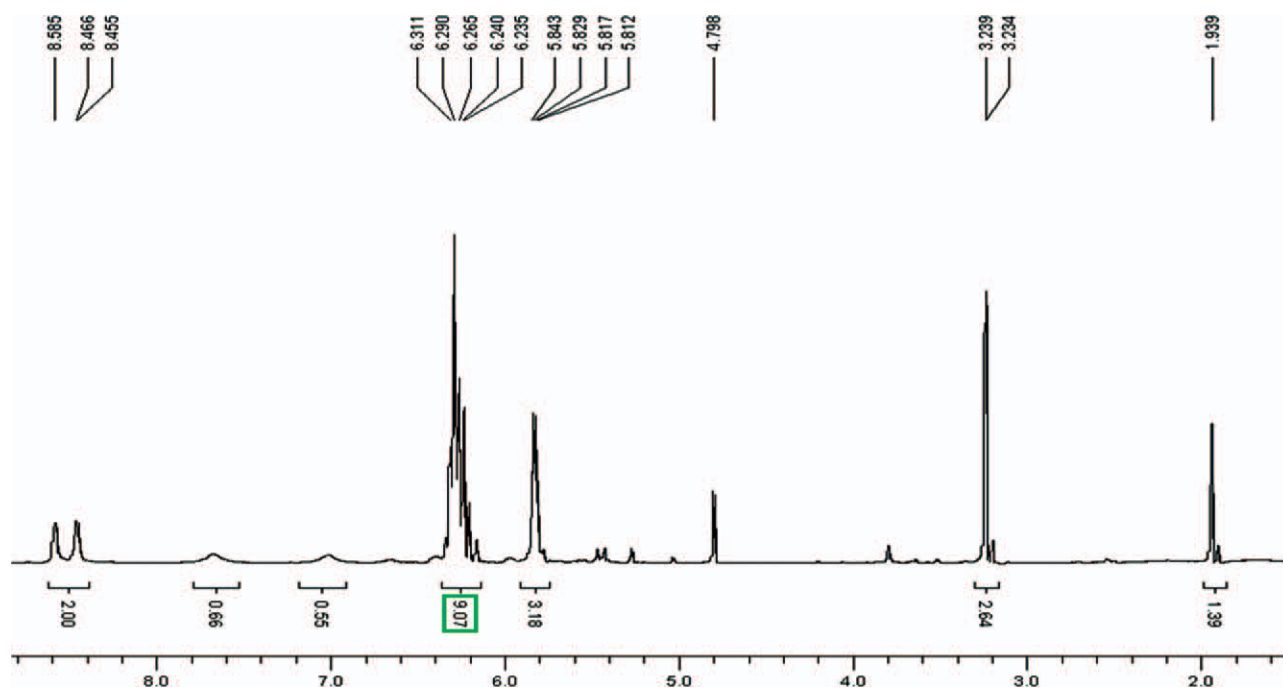
**Figure 15**  $^1\text{H-NMR}$  spectrum of CPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

network structure and that modified copolymerization had occurred.

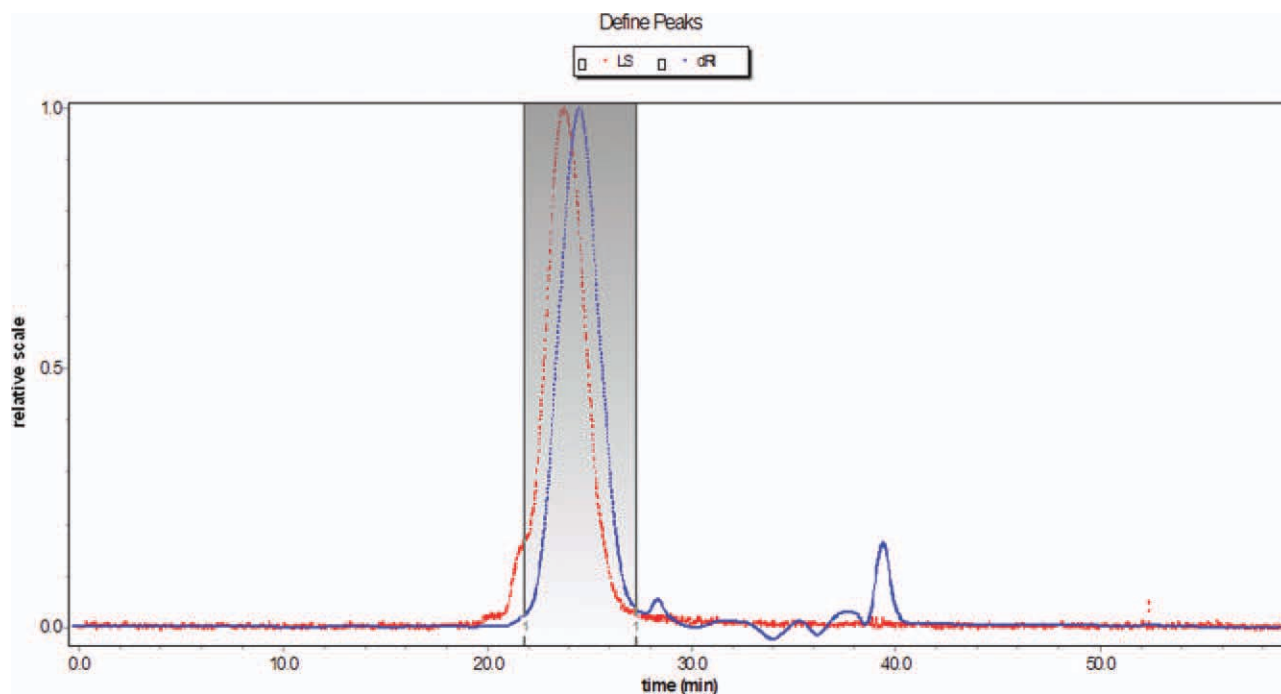
Figure 15 illustrates the  $^1\text{H-NMR}$  spectrum of CPAM, which showed that the resonance at 1.950 ppm was attributable to the methyl group of DMC. The resonance at 3.250 ppm was attributed to the methyl group in the quaternary amine. The broad peaks from 5.822 to 5.839 ppm accounted for

the propenyl group of the substituents and all the protons of AM. The broad peaks from 6.218 to 6.292 ppm came from the substituents of DMC. The chemical shifts at 7.026 and 7.689 ppm were assigned to amide groups of AM. These data verified that the copolymerization between AM and DMC occurred.

To confirm that glyoxal was grafted on the backbone of CPAM,  $^1\text{H-NMR}$  spectrum of GPAM was



**Figure 16**  $^1\text{H-NMR}$  spectrum of GPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

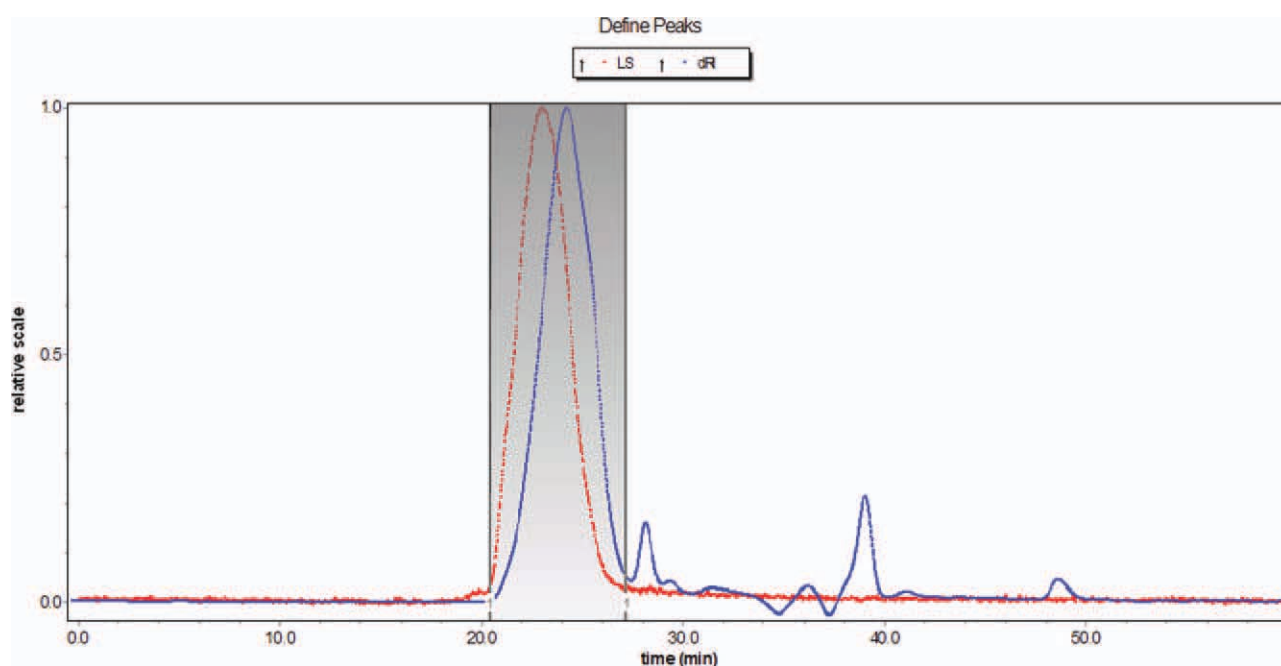


**Figure 17** SEC spectrum of CPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

used. Figure 16 presents the  $^1\text{H-NMR}$  spectrum of GPAM. Compared with the  $^1\text{H-NMR}$  spectrum of CPAM, two new peaks at 8.455 and 8.585 ppm, which were assigned to the aldehyde group of glyoxal, were observed in GPAM in addition to the expected signals for the block copolymer. The results

demonstrate that the monomer glyoxal was successfully grafted onto CPAM.

The values for  $M_n$  and  $M_w$  were determined by SEC with polystyrene standards; the molecular weight was 300,000 g/mol, with a polydispersity index equal to 1.401. Figure 17 presents the SEC



**Figure 18** SEC spectrum of GPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE II**  
Physical Properties of the Paper after the Addition of Different Strengthening Agents

Strengthening agent	Basic weight	Tensile index (N m/g)	Tensile index increased ratio (%)	Rewet tensile index (N m/g)	Tensile index increased ratio (%)
CPAM	62.7	45.6	15.7	2.5	56.2
PAE	62.9	44.7	13.4	6.1	281
GPAM	62.7	49.1	24.6	7.7	381
Control	61.7	39.4	0	1.6	0

The dosage of self-made GPAM was 0.3% (solid content based on the oven-dried pulp), and the dosages of commercial CPAM and PAE were both 0.5% (solid content based on the oven-dried pulp).

curves of CPAM. The  $M_n$  and  $M_w$  values of CPAM were 16,060 and 21,697, respectively, and the polydispersity index was 1.351. Figure 18 presents the SEC curves of GPAM. The  $M_n$  and  $M_w$  values of GPAM were 18,180 and 26,550, respectively, and the polydispersity index was 1.460. These results show that the GPAM resins, with a relatively molar mass distribution, were obtained by synthesis in two stages.

### Strengthening ability of GPAM

GPAM aqueous solutions were prepared under the optimum conditions, and the strengthening ability of GPAM was analyzed (Table II). Traditional cationic PAM<sup>21</sup> and polyamidoamine-epichlorohydrin (PAE),<sup>22</sup> which were provided by a local mill, were also evaluated.

The dry and wet tensile indices of cultural paper increased by 24.6 and 381%, respectively, compared with control, after the GPAM resin was added to the pulp furnish (Table II). Moreover, the obtained GPAM resin had a much better strengthening ability than the commercial strengthening agents (traditional cationic polyacrylamide and PAE). Particularly, the GPAM resin was found to have suitable high-yield pulp and secondary fibers, which have both been increasingly used recently, because the network structure of the obtained GPAM improved the smoothness and formation of the paper.

### CONCLUSIONS

The crosslinked GPAM strengthening agent demonstrated excellent performance and strengthening ability under the following conditions: seed monomer dosage = 20 wt %, NMA dosage = 8.0 wt %, 2-mercaptoethanol dosage = 1.0 wt %, initiator dosage = 0.5 wt %, and glyoxal dosage = 30 wt %. Its MW was approximately 26,000, and it had a narrow distribution. Both the dry and wet tensile strengths of the pa-

per significantly improved after GPAM was added. When the GPAM dosage was 0.3% (solid content based on the oven-dried pulp), the dry and wet tensile indices of the cultural paper increased by 24.6 and 381%, respectively, compared to those of the paper without GPAM. Compared with commercial products (CPAM and PAE), the synthesized GPAM had a much better strengthening ability. It clearly improved the dry strength of the paper and enhanced its wet strength; these results indicate that GPAM resin has great potential for wide applications.

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