

# Novel Biodegradable Flocculating Agents Prepared by Grafting Polyacrylamide to Konjac

Chenxin Xie,<sup>1,2</sup> Yujun Feng,<sup>1</sup> Weiping Cao,<sup>1</sup> Houkai Teng,<sup>2</sup> Jufeng Li,<sup>3</sup> Zhiyong Lu<sup>1</sup>

<sup>1</sup>Center for Macromolecular Sciences, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, People's Republic of China

<sup>2</sup>National Research Center of Industrial Water Treatment Engineering and Technology, CNOOC Tianjin Chemical Research and Design Institute, Tianjin 300131, People's Republic of China

<sup>3</sup>Health Safety and Environmental Monitoring Center, Research Institute of Safety and Environmental Technologies (RISET), China National Petroleum Corporation (CNPC), No. 8, Zhi Xin West Road, Beijing 100083, People's Republic of China

Received 2 January 2008; accepted 9 August 2008

DOI 10.1002/app.29198

Published online 25 November 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Grafting copolymers of polyacrylamide (PAM) with Konjac gum (KGM) have been synthesized using ceric-ion-induced initiation technique. The copolymers were characterized using several instrumental techniques, including infrared (IR) spectroscopy, elementary analysis, scanning electron microscopy (SEM), size exclusion chromatography (SEC) analysis, and intrinsic viscosity to confirm the success of grafting. The flocculation performance of graft copolymers was characterized by two methods. One was to study the relationship between the flocculants doses in kaolin suspension and the supernatant transmittance, and the other is to examine the time dependence of sediment height of kaolin suspensions. It was

found that the graft copolymer is better than KGM and pure PAM. Biodegradation behavior was testified by monitoring the decay of relative viscosities, and approved by KGM ether bonds breaking in IR spectra and the molecule weight reduction in SEC analysis. The results indicate that the grafted KGM copolymers have improved both, flocculation performance and better biodegradable properties than the unmodified parent KGM and pure PAM. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2527–2536, 2009

**Key words:** graft copolymerization; Konjac; biodegradation; flocculants; polyacrylamide

## INTRODUCTION

Flocculating agents, or flocculants, are the important components which cause flocculation, a process of bringing together small particles to form larger particles by adding minute quantities of chemicals in water treatment.<sup>1</sup> Normally, flocculants are classified into inorganic and organic categories. Though the inorganic flocculants (also called coagulants) with multivalent metals like Aluminum and Iron are widely employed, organic flocculants based on acrylamide (AM)-based polymers, like polyacrylamide (PAM) and its derivatives, are generally more effective than their inorganic counterparts as they possess the advantages, such as low dose, ease in handling, no interference with pH of the suspensions and larger floc-forming capability.<sup>1</sup> However, the associ-

ated unreacted acrylamide monomers resided in synthetic polymers have been proved to be carcinogenic,<sup>2</sup> though the synthetic polymers themselves are nontoxic.<sup>3</sup> It is well-known that AM-based polymers show the properties of thermal, photo, biological, and chemical degradation,<sup>4,5</sup> but the lack of self-degradable characteristic presents another major drawback of the organic flocculants, which will result in "secondary pollution" for the environment.

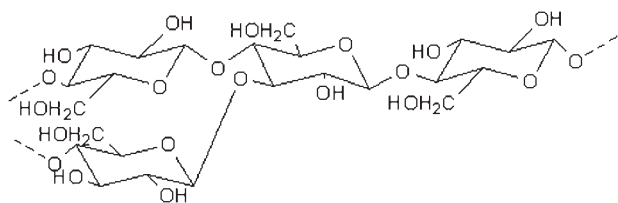
To obviate these limitations of PAM polymers, "green" flocculants have been appealed to minimize the postpollution for the environment. These environmentally-friendly materials are normally prepared by modification of polysaccharides with water-soluble polymers, combining the merits of high-flocculation efficiency from synthetic polymers and self-degradability from natural macromolecules, and they have gained increased interest from both academic community and industrial field. Singh's team has successively investigated various natural products by grafting PAM to polysaccharides, such as guar gum,<sup>6</sup> xanthan gum,<sup>7</sup> sodium alginate,<sup>8</sup> carboxymethyl cellulose,<sup>9</sup> amylose,<sup>10</sup> dextran<sup>11</sup> and glycogen,<sup>12</sup> etc. Khalil et al.<sup>13–16</sup> have also developed a series of starch derivatives used as flocculants and chelating agents to remove heavy metals. Compared

Correspondence to: Y. Feng (yjfeng@cioc.ac.cn).

Contract grant sponsor: Sichuan Provincial Scientific Research Foundation; contract grant number: 2008JY0002.

Contract grant sponsor: Guangdong Provincial Scientific Research Foundation; contract grant number: 2005A30402002.

Contract grant sponsor: Chinese Academy of Sciences.



**Figure 1** The structural representation of Konjac glucomannan.

with the parent polysaccharides, the “tailored” derivatives show higher flocculation efficiency owing to the greater approachability of the dangling flexible PAM chains to the contaminant particles of the suspensions. Although the biodegradability was frequently emphasized, little information has been documented except that enzyme-induced degradation<sup>17</sup> was occasionally reported.

In our laboratory, an attempt has been made to develop novel biodegradable flocculants possessing both improved flocculability and real self-degradability. Konjac glucomannan (KGM), a polysaccharide extracted from tubers of *Amorphophallus* Konjac plants, was chosen to be the parent macromolecules as it is conveniently available in China and Southeast Asia where it is widely planted in mountain or hilly areas. Normally, Konjac has been used as food and food additives, because of its excellent biocompatibility and biodegradable activity, and its derivatives have been extensively applied in drug delivery,<sup>18–20</sup> films and membranes, coating materials, emulsifiers and surfactants,<sup>21,22</sup> etc. In the physical point of view, the solubility of KGM in water is low and its aqueous solution is very viscous, but it can hold a large amount of water and form a strong gel in the presence of alkali.<sup>23,24</sup> As shown in Figure 1, KGM consists of  $\beta$ -(1 $\rightarrow$ 4)-linked-D-mannose and D-glucose residues as the main chain with branches through  $\beta$ -(1 $\rightarrow$ 6)-glucose units.<sup>25</sup> In a molar ratio of 1.6 : 1 with branching of 8% degree,<sup>26</sup> KGM has an average molecular weight of 0.67 to 1.9 million.<sup>23,27</sup> Because of its high molecular weight and biodegradability,<sup>28</sup> it is possible to modify KGM through the O–H bond in its molecule architecture by grafting functionality to form a novel family of flocculants. But unfortunately, to the best of our knowledge, there are few reports to date on the utilization of modified Konjacs as flocculants.

In a previous article, we reported the phosphate-esterification product of Konjac as flocculation agents that possess both flocculability and biodegradability.<sup>29</sup> However, anionic polymers like these esterified products have been seldom utilized as flocculants. Therefore, ongoing pursuit on “tailoring” Konjac via grafting nonionic or cationic water-soluble monomer onto its backbone has been continued in our laboratory. Presented in this work are the

results to graft a nonionic water-soluble monomer, acrylamide, to Konjac, including synthesis, characterization, and the examination of flocculation and biodegradation properties as well.

## EXPERIMENTAL

### Materials

Konjac gum (120–200 mesh) was purchased from Root Co. (Chengdu, China) without further treatment. The effective KGM content in the powder is approximate to 95%. Acrylamide (AM) (99.5%) was bought from Changjiu Agri-Scientific Co. (Nanchang, China). Ceric ammonium nitrate (CAN) (AR), acetone, EDTA (AR), kaolin (Guangxi Xilong, China) are all commercial products and used as received. The water used in this work was doubly distilled, and nitrogen has the purity of 99.999%.

Homopolymer, PAM, with molecular weight of around 2 million was synthesized via free-radical aqueous solution polymerization in our laboratory as a counterpart in comparison with the grafted products in structural characterization, flocculation performance.

### Graft copolymerization

Grafting copolymerization was carried out in a three-neck flask by the ceric-ion induced initiation process.<sup>30,31</sup> The typical synthesis procedure is as follows: 1.0 g Konjac gum was dissolved in 125 mL distilled water with constant stirring and bubbling of a stream of nitrogen for about 1 h. The desired quantity of AM was dissolved in 50 mL of distilled water and mixed with the Konjac gum solution. The solution was then purged with nitrogen for 30 min. At this stage, 25 mL CAN solution and 0.073 g EDTA which was used for chelating the trace heavy metals in both monomer and Konjac gum were added. The reaction was allowed to continue for 5 h, after which it was terminated by adding a saturated solution of hydroquinone. The reaction temperature was maintained at  $60 \pm 1^\circ\text{C}$ . At the end of the reaction, the polymer was precipitated by adding an excess of acetone. It was then dried in a vacuum oven until constant weight was obtained. The synthesis parameters are depicted in Table I.

### Characterization

#### Infrared spectroscopy

The infrared (IR) spectra of the KGM, PAM, KGM-g-PAM1, and KGM-g-PAM1b which was the purified product of the biodegraded residue of KGM-g-PAM1, were registered in solid state using a KBr pellet method in the transmittance mode. A Nicolet

**TABLE I**  
**Synthesis Parameters of Graft Copolymerization**

Polymer	Feed ratio			Product		$[\eta]$ (mL · g <sup>-1</sup> )
	Konjac (g)	AM (mol)	CAN ( $\times 10^4$ mol)	$X_{\text{PAM}}$ (%)	Conversion <sup>a</sup> (%)	
KGM-g-PAM1	1.0	0.12	1.875	84.51	81.5	389.1
KGM-g-PAM2	1.0	0.12	2.500	90.40	82.5	346.5
KGM-g-PAM3	1.0	0.12	5.000	98.60	82.6	269.6
KGM-g-PAM4	1.0	0.08	1.875	83.52	77.4	341.0
KGM-g-PAM5	1.0	0.18	1.875	92.94	84.5	449.1
KGM-g-PAM6	1.0	0.24	1.875	95.40	87.3	465.3

<sup>a</sup> Conversion is determined gravitationally: [39] conversion = [(weight of grafted copolymer – weight of polysaccharide)/amount of acrylamide]  $\times 100$ .

MX-1E IR spectrophotometer was used to record the IR spectra in the scanning range of 4000 to 400 cm<sup>-1</sup>.

#### Elementary analysis

The elementary analysis of all the samples, namely, KGM and their grafted copolymers were done using a Carlo Erba 1106 Elemental Analyzer. Considering only four elements, i.e., C, H, O, and N are resided in AM, three of them, C, H and, N, were measured in this work, by which PAM content in the grafted polymers can be determined sufficiently through the characteristic “N” content (Table II).

#### Scanning electron microscopy (SEM) observation

KGM, KGM-g-PAM1, and KGM-g-PAM1b were used for SEM analysis to compare their bulk morphology with an AMRY-1000B scanning electron microscope. The samples were gold-coated and a magnification of 2000–4000 times was obtained.

#### Size exclusion chromatography analysis

Size exclusion chromatography (SEC) analysis was performed to compare the changes of molecular

weight (MW) and molecular weight distribution (MWD) of KGM, KGM-g-PAM1, and KGM-g-PAM1b. The analysis was conducted using a Water 515 liquid chromatograph instrument connected with a Waters 2410 refractive index detector. The gel permeation column was linear ultrahydrogel (7.8  $\times$  300 mm), and the solvent used was distilled water. Polymer standards of Dextran were used from NICPBP (National Institute for the Control of Pharmaceutical and Biological Products). The samples were dissolved in 0.1M NaCl solution and analyzed at a flow rate of 0.8 mL min<sup>-1</sup>.

#### Intrinsic viscosity measurement

Intrinsic viscosities of polymers were measured with the “five-spot” dilution method using an Ubbelohde viscometer (constant: 0.00705) at 30  $\pm$  0.1°C. The solvent used was distilled water.

#### Flocculation efficiency

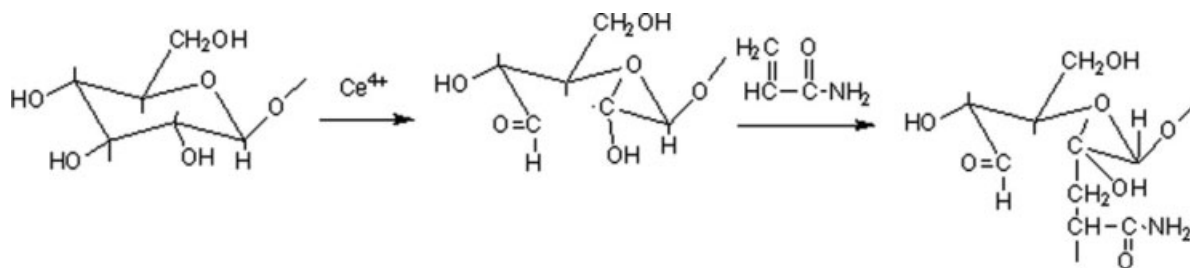
Flocculation performance of the polymers was examined firstly by using the well-accepted Jar tests<sup>32</sup>: Six beakers of 1% (w/v) kaolin aqueous suspension were used for flocculation studies. Immediately after the addition of the polymer flocculants, all the suspensions were stirred at a constant speed of 75 rpm for 2 min, followed by a slow agitation at 25 rpm for 5 min. The flocs were then allowed to settle down for 2 min. At the end of the settling period, the transmission of supernatant liquid at 670 nm was measured using a UV-VIS spectrometer (HITACHI-U2010). The dose of flocculants was varied in the range of 0.1 to 3 ppm.

The flocculation characteristics were also further confirmed by column settling method.<sup>33</sup> The flocculation studies were carried out in 5% kaolin suspension with the help of a 100-mL stoppered graduated cylinder. First, the kaolin suspension was put into the cylinder and then the polymer solution was added. The final polymer concentration in the suspension was kept at 1 ppm. The cylinder was then

**TABLE II**  
**The Elementary Analysis Results of Konjac and Grafting Products**

Polymer	Measured value			Theoretical value
	C%	H%	N%	N% <sup>a</sup>
Konjac	39.96	6.19	0.12	0.00
KGM-g-PAM 1	46.69	7.29	15.54	17.31
KGM-g-PAM 2	46.78	7.37	15.70	17.46
KGM-g-PAM 3	47.05	7.41	15.80	17.62
KGM-g-PAM 4	45.53	7.00	14.69	16.30
KGM-g-PAM 5	47.39	7.20	16.16	18.18
KGM-g-PAM 6	46.35	7.13	16.23	18.57

<sup>a</sup> Theoretical value of N% = the weight of acrylamide in feed ratio  $\times$  percent of N in acrylamide  $\times$  the conversion in Table I/the weight of KGM-g-PAM copolymer.



**Scheme 1** The mechanism route for grafting PAM onto Konjac.

inverted 20 times for thorough mixing. After the cylinder was set upright, the height of sediment was measured over time interval.

### Biodegradation monitoring

The change of relative viscosity ( $\eta_r$ ), the ratio of polymer solution flow time to that of solvent, water, was used to monitor biodegradability.  $\eta_r$  was measured by using a capillary glass tube at certain intervals of time over the entire test. All the viscosity measurements were conducted at 30°C when bacterial activity is at a maximum.<sup>17</sup> After 190 h of biodegradation test, the  $\eta_r$  was nearly unchanged and humus was found in the solution, which impeded further measurement.

## RESULTS AND DISCUSSION

### Synthesis and characterization

#### Synthesis

A number of methods, such as catalyst-,  $\gamma$ -ray radiation-,<sup>34,35</sup> microwave radiation-induced initiation,<sup>36</sup> are available for initiating grafting sites on a polysaccharide backbone. However, the ceric-ion-induced redox initiation method<sup>30,31</sup> has been proved to be the most preferable. Listed in Table I are the synthesis parameters for the KGM-based grafted copolymers prepared by Ce(IV) initiation. Two series of grafted copolymers have been synthesized by grafting PAM onto Konjac gum. During the preparation of the first series of polymers, KGM-g-PAM1, KGM-g-PAM2, and KGM-g-PAM3, the initiator concentration varied but the concentrations of KGM and AM were kept constant; whereas for the second series of polymers, KGM-g-PAM4, KGM-g-PAM5, KGM-g-PAM6, and KGM-g-PAM1, AM concentration was varied at fixed KGM and initiator concentrations.

In a grafting process, the avoidance of production and elimination of homopolymer could be the most important concerns. Homopolymer is inevitably produced according to the mechanism of ceric-ion-induced initiation technique, and it is reported<sup>9,31,34,37,38</sup> that the homopolymer could be removed by using Soxhlet extraction with a mixture

of special solvents. Solvents used in these reports, such as a mixture of ethylene glycol and acetic acid (60 : 40, vol : vol)<sup>31</sup> or a mixture of formamide and acetic acid (1 : 1, vol : vol)<sup>38</sup> were followed in our work to remove homopolymers. But eventually, no change of copolymer amount has been observed indicating that no compounds have been removed from the grafted products. This is probably because of the fact that the ceric-ion-induced method initiates free-radical sites exclusively on the polysaccharide backbone, thus preventing from the formation of homopolymer.<sup>39,40</sup> Owen and Shen<sup>41</sup> found that high concentration of AM always resulted in homopolymerization, but when AM is less than 2.0M, and nitric acid and CAN are less than 1.2 and 0.1M, homopolymer would not be produced in the graft copolymerization. In our experiment, AM content is between 0.4 and 1.2M, and CAN content is much less than 0.1M when no nitric acid was used. Therefore, it is anticipated that no homopolymer would be produced in the graft of PAM on KGM backbone.

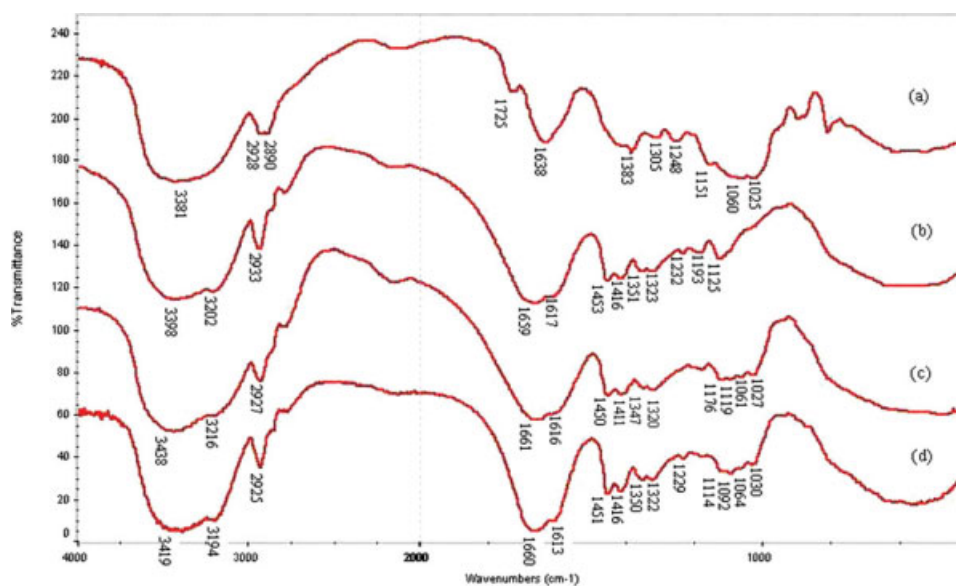
It is believed<sup>42,43</sup> that the mechanism of ceric-ion initiated graft copolymerization is decomposing and generating free-radical sites on the polysaccharide skeleton. Listed in Scheme 1 is the suggested reaction path for the graft reaction of KGM:

The average number of grafting sites per backbone of the polysaccharide molecule depends on the ratio of the concentration of Ce(IV) to that of Konjac. A relatively low concentration of catalyst will initiate few grafting sites, resulting in longer PAM chains against shorter PAM chains at higher concentration. This is reflected in their corresponding intrinsic viscosity ( $[\eta]$ ) values (Table I).

#### Structural, morphological, and molecular weight characterizations

Figure 2 compares IR spectra of KGM, PAM, KGM-g-PAM1, and KGM-g-PAM1b. In the IR spectra of KGM, the peaks at 895 and 810  $\text{cm}^{-1}$  are the characteristic absorption bands of mannose residues in the polysaccharides.<sup>44</sup> The broad band at 3381  $\text{cm}^{-1}$  is because of the stretching mode of the O—H groups. An intense band at 1725  $\text{cm}^{-1}$  is assigned to the first overtone of the O—H bending vibration.<sup>45</sup> The





**Figure 2** Comparison of IR spectra of (a) KGM, (b) PAM, (c) KGM-g-PAM1, and (d) KGM-g-PAM1b. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

absorption band at  $1636\text{ cm}^{-1}$  is the intramolecular hydrogen bonds. The band at  $1151\text{ cm}^{-1}$  is assigned to C—O stretching, and the band at  $1248\text{ cm}^{-1}$  is the fragment of  $\text{CH}_2\text{OH}$ . The bands at 1060, 1305, 1383, 2890, and  $2928\text{ cm}^{-1}$  are resulted from C—H stretching. The band at  $1025\text{ cm}^{-1}$  contributes to the stretching vibration of C—O.<sup>46</sup>

In the case of grafted copolymer KGM-g-PAM, the peaks at 3438 and  $3216\text{ cm}^{-1}$  are attributed to the overlap of  $-\text{NH}_2$  stretching band of amide group and O—H stretching band. The bands around 1661 and  $1616\text{ cm}^{-1}$  are attributed to amide-I (C=O stretching) and amide-II (N—H bending) of the amide group in PAM. The C—N stretching bands appear at 1450, 1411, 1347, and  $1320\text{ cm}^{-1}$ . The bands in PAM at  $1232\text{ cm}^{-1}$  disappeared in KGM-g-PAM as the C—N bands vanished in  $\text{NHC}=\text{O}$ . The bands at 1176, 1119, 1061, and  $1027\text{ cm}^{-1}$  are still remaining in KGM-g-PAM as the C—O—C stretch. The absence of the peak at  $1725\text{ cm}^{-1}$  of KGM is indicative of breaking of O—H.

The IR spectrum of the biodegraded product, KGM-g-PAM1, has the similar peaks as those in KGM-g-PAM except the band at  $1229\text{ cm}^{-1}$ . This is due to the peaks of C—O—C are too strong to show the  $\text{NHC}=\text{O}$  band, but the biodegradation cut the ether bonds because the ether bonds are the preferable degraded sites in the polysaccharide backbone.<sup>47</sup> As a result, the peak at  $1229\text{ cm}^{-1}$  appeared in the IR spectrum of KGM-g-PAM1b owing to the broken bonds.

It shows in the elementary analysis (Table II) that the “N” element content has been changed largely when grafted PAM onto KGM. However, the negligible amount of nitrogen in KGM may be the trace quantities of unisolated proteins in the polysaccha-

rides. It has been found that there is a considerable percentage of nitrogen in the grafted polymer chains. In the series of grafted copolymers based on KGM, the variation in the nitrogen content is not significant. The higher percentage of nitrogen may be due to the increased PAM content in the grafted copolymer, which is also owing to the higher moles of AM in the reaction feed. KGM-g-PAM4 has the smallest percentage of nitrogen, which has lowest PAM content compared to other graft copolymers in the series. The theoretical value of N% is similar to that found in the measurement.

From the measured “N” content, the weight fraction of the grafted PAM,  $X_{\text{PAM}}$  in the copolymer can be calculated via the following equations:

$$W_{\text{PAM}} = N_{\text{copolymer}}\% / (14/71) \quad (1)$$

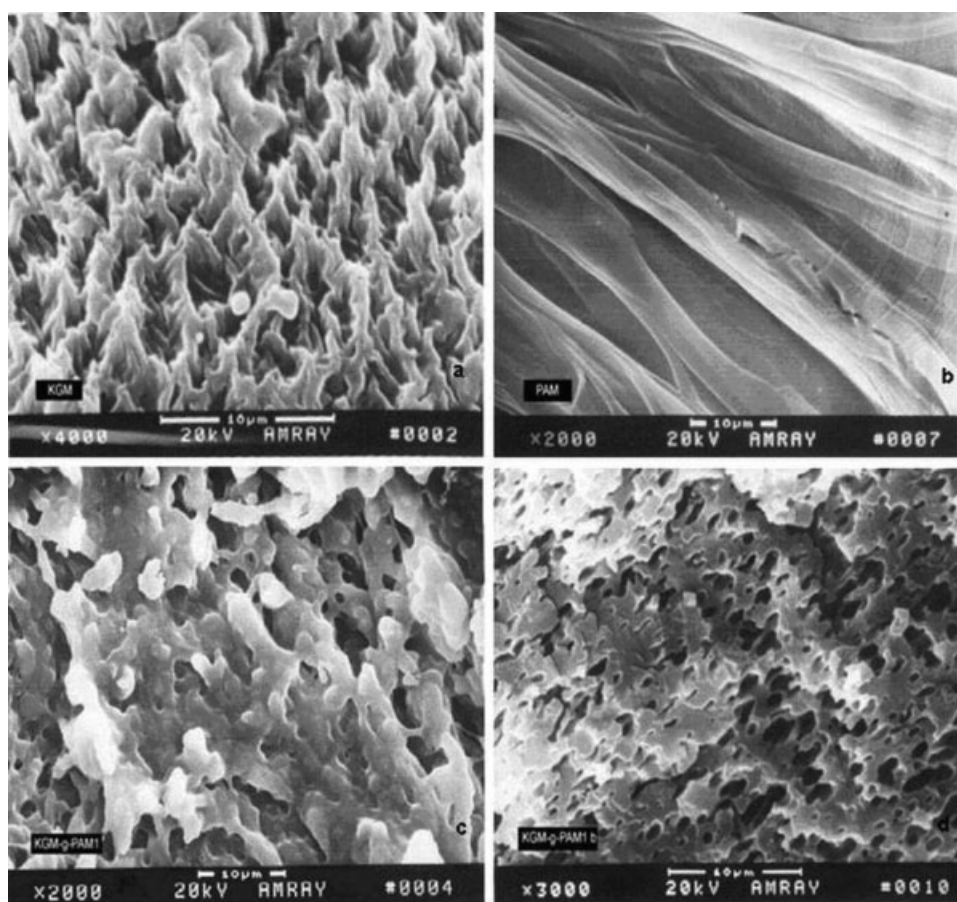
$$C_{\text{PAM}}\% = 36 \times N_{\text{copolymer}}\% / 14 \quad (2)$$

$$C_{\text{KGM}}\% = C_{\text{copolymer}}\% - C_{\text{PAM}}\% \quad (3)$$

$$W_{\text{KGM}} = C_{\text{KGM}}\% / C_{\text{copolymer}}\% \quad (4)$$

$$X_{\text{PAM}} = W_{\text{PAM}} / (W_{\text{PAM}} + W_{\text{KGM}}) \quad (5)$$

where  $W_{\text{PAM}}$ ,  $W_{\text{KGM}}$  stand for PAM and KGM contents in the grafted copolymers;  $C_{\text{PAM}}$  and  $C_{\text{KGM}}$  refer to the theoretical value of element “carbon” content in PAM and KGM, respectively;  $C_{\text{copolymer}}$  and  $N_{\text{copolymer}}$  represent the measured values of “carbon” and “nitrogen” contents in copolymer; “14” and “71” are the atom weight of element “N” and molecular weight of AM.



**Figure 3** Scanning electron micrographs of (a) Konjac, (b) PAM, (c) KGM-g-PAM1, and (d) KGM-g-PAM1b.

Difference in polymer bulk morphology observed by SEM can gain insight into the structural information of the products. Exhibited in Figure 3 are the bulk morphologies of KGM, PAM, KGM-g-PAM1, and KGM-g-PAM1b. Apparent differences can be evidenced between the parent KGM, PAM and the grafted product, KGM-g-PAM1: the regular sharply “forest” structure of KGM is lost after grafting, and the “melted” structure of KGM-g-PAM1 also differs from the “strip” structure of PAM. These differences in bulk morphology of the unmodified parent, grafted product and PAM confirm the success of grafting copolymerization. The difference between KGM-g-PAM1 and biodegraded residue, KGM-g-PAM1b, will be discussed later.

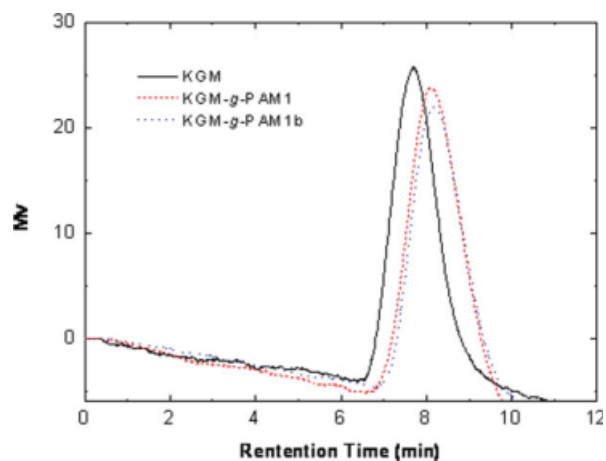
SEC is a convenient process to analyze polymer’s MW and MWD. The aim to use SEC in this study is

to compare the changes of MW and MWD for the unmodified polymer, the grafted polymer, and the biodegraded polymer, so as to further verify the success of graft copolymerization and biodegradation.

As shown in Table III, the MW of KGM is about 2 million whereas KGM-g-PAM1 and KGM-g-PAM1b are only 0.92 and 0.78 million, respectively, which corresponds to the different retention time in SEC analysis (Fig. 4). These molecular weight differences were probably resulted from the solubility difference between the unmodified parent KGM and grafted KGM-g-PAM1: microgel resided in KGM solution may lead to higher MW, which was also confirmed in Figure 9 (see the “Biodegradation studies” section) where much larger relative viscosity,  $\eta_r$ , was witnessed, while homogeneous aqueous solution of KGM-g-PAM1 enables its MW to be precisely

**TABLE III**  
The SEC Results of Konjac, KGM-g-PAM1, and its Biodegradation Products KGM-g-PAM1b

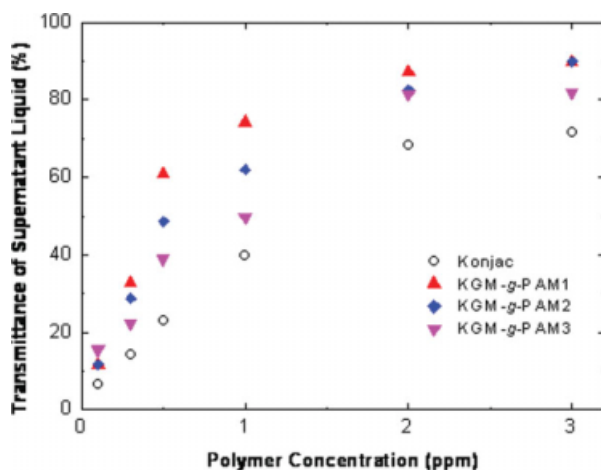
Polymer	Retention time (min)	MP ( $\times 10^{-6} \text{ g} \cdot \text{mol}^{-1}$ )	MW ( $\times 10^{-6} \text{ g} \cdot \text{mol}^{-1}$ )	Mn ( $\times 10^{-6} \text{ g} \cdot \text{mol}^{-1}$ )	Polydispersity	$[\eta]$ ( $\text{mL} \cdot \text{g}^{-1}$ )
Konjac	7.707	1.49	2.04	0.78	2.62	—
KGM-g-PAM1	8.121	0.68	0.92	0.31	2.95	389.1
KGM-g-PAM1b	8.171	0.62	0.78	0.29	2.64	—



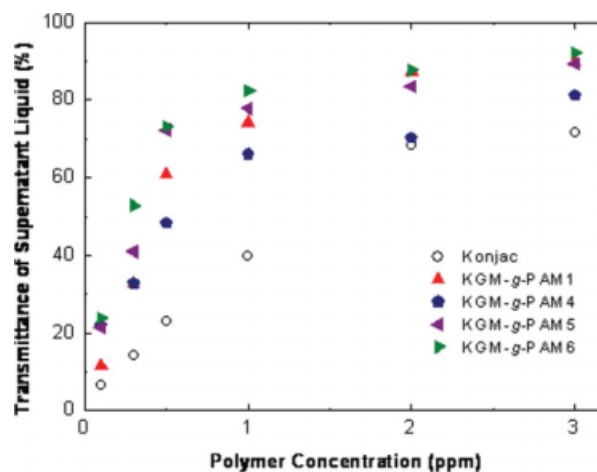
**Figure 4** SEC analysis of (a) Konjac, (b) KGM-g-PAM1, and (c) KGM-g-PAM1b. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

determined. Similar results between the unmodified and grafted guar gum were also reported elsewhere.<sup>17</sup>

Intrinsic viscosities,  $[\eta]$ , of all the grafted copolymers are also reported in Table I. Intrinsic viscosity of a polymer is indicative of its hydrodynamic volume in solution, which depends on its molecular weight, structure, nature of the solvent as well as the temperature of the medium. For two polymers with approximately similar molecular weight, the branched polymer has lower hydrodynamic volume compared to its linear counterpart and thus has lower intrinsic viscosity value. Furthermore, the longer the branching, the higher the intrinsic viscosity and vice versa. The intrinsic viscosity of a polymer, although greatly dependent on its molecular weight,



**Figure 5** Transmittance of supernatant liquid varies against flocculant dose in kaolin suspension (1%) for the unmodified Konjac and grafted products prepared at different initiator concentration. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 6** Transmittance of supernatant liquid varies against flocculant dose in kaolin suspension (1%) for the unmodified Konjac and grafted products prepared at different AM content. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

is also significantly influenced by the structure of the polymer in solution.<sup>48</sup> When the CAN concentration increased in the feed ratio, the length of PAM chains was reduced, because a greater number of free radical sites were created by the higher concentration of CAN. In the case of a series of grafted copolymers with the same backbone, the longer the grafted chains, the higher the hydrodynamic volume and hence, the intrinsic viscosity.

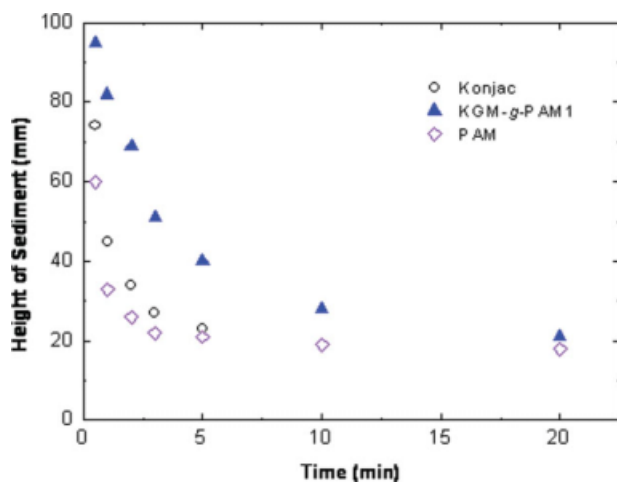
The series of grafted copolymers consist of KGM-g-PAM1, KGM-g-PAM2, and KGM-g-PAM3, which were prepared by varying Ce(IV) concentration at fixed KGM and AM loadings. In this series, a decrease occurred in  $[\eta]$  values with increasing Ce(IV) level. This implies that the number of grafting sites increase with the augment of Ce(IV) concentration and the length of grafted chain decreases when the point of grafted chain increases.

Another series of graft copolymers include KGM-g-PAM1, KGM-g-PAM4, KGM-g-PAM5 and KGM-g-PAM6 that were synthesized by varying AM concentration while keeping Ce(IV) and KGM levels constant. In this series,  $[\eta]$  increases upon increasing AM content, indicating the length of grafted PAM chains is increased.

### Flocculation studies

The flocculation performance is firstly explained in terms of the transmittance of the supernatant liquid. The higher the transmittance, the better the flocculating agent is. Both Figures 5 and 6 compared the transmittance changes of the supernatant liquid versus polymer concentration in the case of all grafted copolymers and KGM. Among the first series of





**Figure 7** Variation of the sediment height versus time for kaolin suspensions (1%) flocculated by the unmodified Konjac, grafted product KGM-g-PAM1, and PAM at polymer concentration of 1 ppm. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

grafted copolymers, KGM-g-PAM1, KGM-g-PAM2, and KGM-g-PAM3, higher flocculation efficiency was found for the polymer with higher  $[\eta]$  values. But among another series of grafted copolymers, KGM-g-PAM1, KGM-g-PAM4, KGM-g-PAM5, and KGM-g-PAM6, KGM-g-PAM6 is slightly more efficient. These results can be further verified by the shorter sedimentation time and larger flocs with KGM-g-PAM1 and KGM-g-PAM6 compared with their analogies.

Figures 7 and 8 compared the transmittance of the supernatant liquid and the speed of sediments among KGM, KGM-g-PAM1, and PAM, respectively. As described in the experimental section, the homopolymer reference, PAM, was synthesized in our laboratory and its molecule weight is close to 2 million. It shows the grafted product, KGM-g-PAM1, has better flocculation efficiency than PAM and the parent KGM. The increased flocculability of the grafted products is due to their greater approachability to the contaminants, which could be the result of the spreading effect of the dangling grafted PAM chains on the rigid polysaccharide backbone.

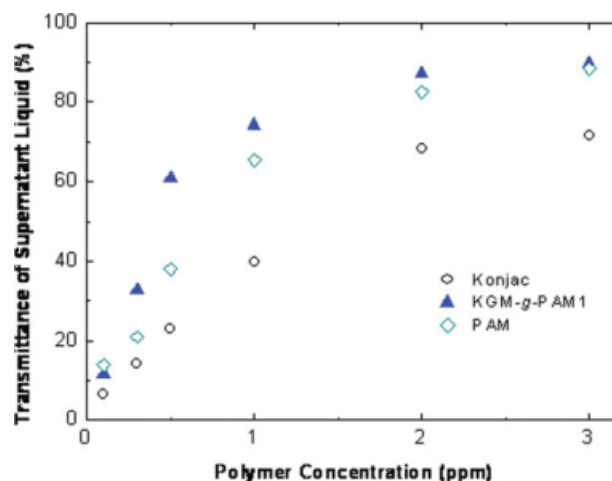
It is well-known that bridging is one of the major flocculation mechanisms of polymeric flocculants. The mechanism is particularly favored when long-chain polymers which do not have a high level of charges are used.<sup>49</sup> Essentially, the nonionic polymer increases the size of the flocs by interaction with the floc surface,<sup>50</sup> and bridging then occurs when the adsorbed chains interact with another floc in the same way.

To create effective bridging, there must be sufficient polymeric chains, which extend far enough

from the particle surface to attach to other particles. In bridging flocculation, macromolecule configurations and lengths play important roles.<sup>51</sup> When the long-chain polymer molecules are adsorbed on the particles' surface, they tend to form loops and extend some distance from the particle surface into the aqueous phase.<sup>52</sup> Their ends also dangle and get adsorbed on the surface of another particle, forming a bridge between the particles. As there are no ionic groups in Konjac gum, its flocculability apparently arrives from bridging mechanism.

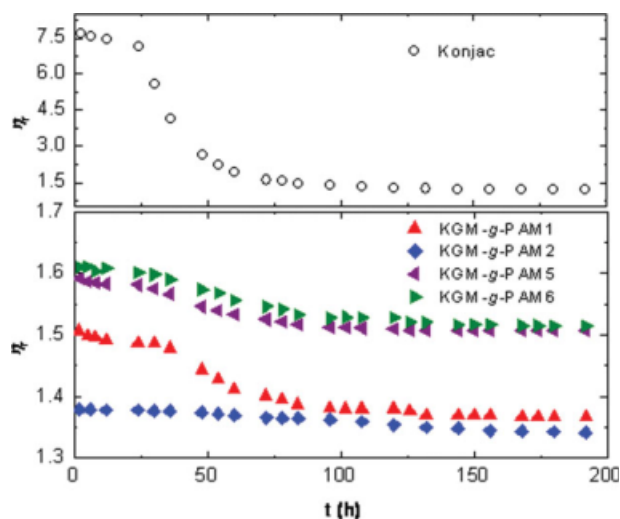
The bridging takes place by adsorption of a polymer molecule at more than one site on a particle or at sites from different particles. They tend to form loops and extend aqueous phase when the long-chain polymer molecules are adsorbed on the surface of particles. Their ends also dangle and get adsorbed on the surface of another particle forming a bridge between the particles. For effective bridging to occur, the length of polymer chains should be long so they can extend from one particle surface to another. Hence, as seen Figures 5 and 6, the polymers with longer chains would be more effective than those with shorter chains.

The product's  $X_{\text{PAM}}$  did not influence the effect of flocculation, which means that it's not the content but the chain length of PAM plays the major role for flocculation. On the other hand, increasing ceric-ion concentration resulted in the augment of the grafted points but decreased the length of PAM chains. The more dangling but shorter PAM chains make bridging worse because of the reduction of the adsorbing particle ability. The increase of the AM concentration also leads to the increasing of the length of the PAM



**Figure 8** Comparative transmittance of supernatant varies against flocculants dose in kaolin suspension (1%) for the unmodified Konjac, modified product KGM-g-PAM1, and PAM. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]





**Figure 9**  $\eta_r$  versus time for unmodified and modified Konjacs to monitor the biodegradation ( $T = 30^\circ\text{C}$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

chains, and the longer the chains, the more effective of the flocculating performance is.

### Biodegradation studies

The biodegradation of polysaccharide proceeds mainly through hydrolysis and oxidation. There are many factors governing biodegradability, such as temperature, UV, moisture level, oxygen, and nutrients.<sup>17</sup> In this test, the factors which influence biodegradability were controlled. The test temperature was controlled at  $30^\circ\text{C}$ , and UV, moisture level, oxygen, and nutrients were also controlled in the common room condition. Hydroxy, hydroperoxide, and carboxyl groups were formed during degradation, and this may lead to increased hydrophobicity, which can cause biodegradation. Though their structures are different because PAM has been incorporated, the grafted copolymers still show the biodegradability like their parent polymer, Konjac gum, and the biodegradation still took place on ether chains in KGM, which can be verified by IR in Figure 2.

Biodegradation can also be examined by monitoring the decay of  $\eta_r$ , the ratio of viscosity of polymer solution to that of solvent, water, at certain intervals of time over the entire test.<sup>39</sup> The test of biodegradation did not stopped until 190 h when humus generates. Figure 9 compares variation tendency of  $\eta_r$  for the four KGM-g-PAM representatives, as well as their unmodified parent Konjac gum.

At the very beginning,  $\eta_r$  of KGM-g-PAM products is all lower than that of Konjac gum. This was due to the undissolved microgel found in Konjac solution<sup>27</sup> while grafted products are completely dis-

solved. This notable distinctness makes the different  $\eta_r$  of the grafted products and the ungrafted Konjac.

As time proceeded, decay of  $\eta_r$  was evidenced for both the modified and unmodified products. Nevertheless, much sharper decrease for the parent Konjac was witnessed. When times reached 80 h,  $\eta_r$  of Konjac decreased from 7.5 to 1.5. In such a process, viscosity loss is as high as 80%. But in the same time interval, viscosity losses for KGM-g-PAM1, KGM-g-PAM2, KGM-g-PAM5, and KGM-g-PAM6 are only 8.0%, 1.5%, 5.0%, and 5.6% respectively. The interesting thing one may find is that the degradation for all the products, including the unmodified, mainly occurs between the time interval 30 to 80 h, out of which  $\eta_r$  was nearly unchanged. This implies not only the optimum degradation time for Konjac gum is just in such a period, but the main depolymerization occurs in polysaccharide skeleton other than PAM chain.

From Figure 9, one can also find the viscosity loss of KGM-g-PAM2 is less than that of KGM-g-PAM1, but KGM-g-PAM6 resembles KGM-g-PAM5. This may results from the more grafted points in KGM-g-PAM2 than in KGM-g-PAM1. More grafted points make more PAM chains which reside in the aqueous solution, leading to higher viscosity left. Although same grafted points are anticipated for KGM-g-PAM1, KGM-g-PAM5, and KGM-g-PAM6 because of the same amount of initiator used in their grafting reaction (Table I), larger MWs owing to higher AM level in feed ratio were obtained for the latter two products. This suggests that longer PAM chains were grafted in KGM-g-PAM5 and KGM-g-PAM6 than in KGM-g-PAM1. Therefore, the left longer PAM chains for KGM-g-PAM5 and KGM-g-PAM6 resulted in lower viscosity losses. As KGM-g-PAM5 and KGM-g-PAM6 have similar MW (Table I), their viscosity losses are also very close.

The biodegradation can be further approved by the SEM observations where the degraded residue, KGM-g-PAM1b, is observed as unrich, porous form that has been changed from the continuous "melting" structure in KGM-g-PAM1 (Fig. 3). The porous structure is inclining to the configuration of left grafted products, in which KGM has been partly degraded, and the grafted PAM chains were still attached to the degraded KGM residue, leading to some "holes" evidenced in the SEM micrograph.

Biodegradation can also be further confirmed by the changes of MW and MWD of the grafted polymer before and after degradation. As shown in Figure 4 and Table III, MW of KGM-g-PAM1 reduces from 0.92 million to 0.77 million after depolymerization, revealing the biodegradation happened. In the same way, the biodegradation of KGM-g-PAM1 led the polydispersity of the degraded product, KGM-g-PAM1b, to fall to 2.64. These all demonstrated

that the products of KGM-g-PAM1 biodegraded successfully.

### CONCLUSIONS

“Green” flocculants with both good flocculation efficiency and biodegradability are the pursuit of the water treatment industry. These products inherit the good performance but overcome the drawbacks such as toxicity and “secondary pollution” of traditional flocculants.

This article is one part of our series work focusing on biodegradable flocculants based on KGM polysaccharide. From the above experimental studies, the grafted products show both improved flocculation efficiency and biodegradability compared to parent Konjac and the homopolymer, PAM. Among the grafted products, those containing long chain PAM perform better than the short chain and multiple grafted ones in the flocculating test. Although the degradability of the products with long chain PAM is worse than the short chain ones and so are the multiple grafted ones. A real “green” flocculant should possess flocculability and biodegradability simultaneously. Based on such a criterion, KGM-g-PAM1 in this work would be the optimized product among the grafted KGM family.

### References

1. Bratby, J. Coagulation and Flocculation. Uplands Press: London, 1980.
2. Rice, J. M. *Mutat Res* 2005, 580, 3.
3. Seybold, C. A. *Commun Soil Sci Plant Anal* 1994, 25, 2171.
4. Marcus, J. C.; Greg, G. Q. *Chem Rev* 2002, 102, 3067.
5. Sorbie, K. S. *Polymer-Improved Oil Recovery*. CRC Press: Boca Raton, 1991.
6. Nayak, B. R.; Singh, R. P. *Polym Int* 2001, 50, 875.
7. Adhikary, P.; Singh, R. P. *J Appl Polym Sci* 2004, 94, 1411.
8. Tripathy, T.; Singh, R. P. *J Appl Polym Sci* 2001, 81, 3296.
9. Biswal, D. R.; Singh, R. P. *Carbohydr Polym* 2004, 57, 379.
10. Karmakar, N. C.; Singh, R. P. *Colloids Surf A* 1997, 133, 119.
11. Krishnamoorthi, S.; Singh, R. P. *Carbohydr Polym* 2007, 69, 371.
12. Pal, S.; Mal, D.; Singh, R. P. *Colloids Surf A* 2006, 289, 193.
13. Khalil, M. I. *Starch/Stärke* 2001, 53, 35.
14. Khalil, M. I.; Aly, A. A. *Starch/Stärke* 2001, 53, 84.
15. Khalil, M. I.; Aly, A. A. *Starch/Stärke* 2002, 54, 132.
16. Khalil, M. I.; Farag, S. *J Appl Polym Sci* 1998, 69, 45.
17. Singh, R. P.; Karmakar, G. P.; Rath, S. K. *Polym Eng Sci* 2000, 40, 46.
18. Du, J.; Sun, R.; Xiong, C. *Macromol Rapid Comm* 2004, 25, 954.
19. Wang, K.; He, Z. *Int J Pharm* 2002, 244, 117.
20. Pathak, C. P.; Barman, S. P.; Philbrook, M. C. 2003, US Pat 6,639,014.
21. Zhang, Y. Q.; Xie, B. *J Carbohydr Polym* 2005, 60, 27.
22. Li, B.; Xie, B. *J Carbohydr Polym* 2006, 64, 510.
23. Chen, L. G.; Zhuo, R. X. *Polymer* 2005, 46, 6274.
24. Yoshimura, M.; Nishinari, K. *Food Hydrocolloids* 1999, 13, 227.
25. Katsuraya, K.; Okuyama, K. *Carbohydr Polym* 2003, 53, 183.
26. Kato, K.; Matsuda, K. *Agr Biol Chem* 1969, 33, 1446.
27. Maeda, M.; Shimahara, H. *Agric Biol Chem* 1980, 44, 245.
28. Chen, L. G.; Zhuo, R. X. *Polymer* 2005, 46, 6274.
29. Xie, C.; Feng, Y.; Cao, W.; Lu, Z.; Xia, Y. *Carbohydr Polym* 2007, 67, 566.
30. David, W. J.; Samuel, M. H. *Chem Rev* 2001, 101, 3245.
31. Varma, I. K.; Singh, O. P.; Sandle, N. K. *Macromol Mater Eng* 1993, 119, 183.
32. Pal, S.; Mal, D.; Singh, R. P. *Carbohydr Polym* 2005, 59, 417.
33. Biswal, D. R.; Singh, R. P. *J Appl Polym Sci* 2004, 94, 1480.
34. Wang, J. P.; Chen, Y. Z.; Ge, X. W. *Chemosphere* 2007, 66, 1752.
35. Jayashree, B.; Virendra, K.; Bhardwaj, Y. K. *Radiat Phys Chem* 2007, 76, 1624.
36. Singh, V.; Tiwari, A.; Tripathi, D. N.; Rashmi, S. *Polymer* 2006, 47, 254.
37. Udaya, D. T.; Tejraj, M. A. *J Controlled Release* 2004, 95, 567.
38. Fanta, G. F. In: *Block and Graft Copolymerization*, Vol. 1; Ceresa, R. J., Ed. Wiley: New York, 1973.
39. McCormick, C. L.; Park, L. S. *J Polym Sci Polym Chem Ed* 1981, 19, 2229.
40. Pottenger, C. R.; Johnson, D. C. *J Polym Sci* 1970, 3, 301.
41. Owen, D. R.; Shen, T. C. In: *Structure-Solubility Relationship in Polymers*; Harris, F. W.; Seymour, R. P. Eds.; Academic Press: New York, 1977.
42. Pottenger, C. R.; Johnson, D. C. *J Polym Sci* 1971, 8, 301.
43. Reyes, Z.; Rist, C. E.; Russel, C. R. *J Polym Sci* 1966, 4, 1031.
44. Xiao, C. B.; Liu, C. H. *J Appl Polym Sci* 2004, 93, 1868.
45. Chiu, H. C.; Hsiue, T.; Chen, W. Y. *Polymer* 2004, 45, 1627.
46. Zhang, H.; Nisinari, K. *Biopolymers* 2001, 59, 38.
47. Satyanarayana, D.; Chatterji, P. R. *Macromol Chem Phys* 1993, 33, 349.
48. Bruno V. *Polymer Chemistry*. Springer-Verlag: New York, 1973, p 516.
49. Bolto, B. A. *Prog Polym Sci* 1995, 20, 987.
50. Stoll, S.; Buffle, J. *J Colloid Interf Sci* 1996, 180, 548.
51. Singh, R. P.; Tripathy, T.; Karmakar, G. P. *Curr Sci* 2000, 78, 798.
52. Jayasekara, R.; Harding, I. *J Polym Environ* 2005, 13, 231.