

# Preparation and Retention of Poly(ethylene oxide)-Grafted Cationic Polyacrylamide Microparticles

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**ABSTRACT:** Novel microparticles of poly(ethylene oxide) (PEO)-grafted cationic polyacrylamide were prepared through the free-radical tetrapolymerization of acrylamide, acryloyloxyethyl trimethylammonium chloride (DAC), PEO macromonomer, and *N,N'*-methylene bisacrylamide in an inverse microemulsion. The effects of the DAC content and the PEO chain length and content on the diameter and

distribution of the microparticles were studied. Highly effective retention aids were obtained in retention experiments with fibers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 359–363, 2006

**Key words:** PEO-grafted cationic polyacrylamide microparticle; tetrapolymerization; retention

## INTRODUCTION

In the last several years, many new flocculation systems that are superior to traditional linear polymers have been developed. One of the technical innovations in industry is the use of microparticle flocculation systems to improve solid waste removal in wastewater treatment and fine solid retention in papermaking.<sup>1–7</sup> For example, a microparticle flocculant system, by effectively retaining suspended and dissolved solids, can create a more open and uniform sheet structure in paper.

Much of the literature on microparticle applications in the papermaking industry concerns anionic microparticles in conjunction with a high-molecular-weight cationic polymer.<sup>8–11</sup> Anionic colloidal silica with cationic starch and anionic montmorillonite with cationic polyacrylamide are typical microparticle flocculant systems. In principle, cationic microparticles should be more effective because of negatively charged fiber fines and waste solids; therefore, cationic polymeric microparticles have recently become a hot spot of study.<sup>12</sup> Ono and Deng<sup>13</sup> reported synthetic cationic polymeric microparticles with a range of particle sizes and charge densities prepared by inverse microemulsion polymerization. Xiao et al.<sup>14</sup> also reported a synergistic effect of cationic polymer microparticles and

anionic polymers on fine clay. Experimental results showed that a cationic polymer microparticle can flocculate fine particles of clay; however, a two-component system consisting of cationic polymer microparticles and an anionic polymer can produce substantially higher levels of flocculation than either component alone.

In this study, cationic polyacrylamide microparticles with side chains of poly(ethylene oxide) (PEO) were synthesized via the inverse microemulsion tetrapolymerization of acrylamide (AM), acryloyloxyethyl trimethylammonium chloride (DAC), PEO macromonomer (PEO-A), and *N,N'*-methylene bisacrylamide (MBA). For the PEO-grafted cationic polyacrylamide microparticles as monocomponent retention aids (or flocculants) in papermaking, in comparison with other retention systems, the first pass retention ( $r_{pu}$ ) was high.

## EXPERIMENTAL

### Materials

AM, obtained from Jiaozuo Duoshengduo Chemical Co., Ltd. (Jiaozuo, China), was recrystallized from acetone. Technical-grade DAC and 2,2'-azobis(2-amidinopropen) dihydrochloride (AIBA) from Green Chemical Co., Ltd. (Guangzhou, China), were used without further purification. MBA was provided by Merck-Schuchardt Co. (Munich, Germany). Gasoline was purchased from the market and washed with concentrated H<sub>2</sub>SO<sub>4</sub> and NaOH solutions. Span 80 and Tween 80, obtained from Shanghai Chemical Reagent Co. (Shanghai, China), were used as supplied. Other

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TABLE I  
Polymerization Recipes and Properties of Microparticles

Designation	AM, DAC, PEO-A, MBA monomer feed ratio (wt %)	Conversion (wt %)	Mean particle size (nm)	Polydispersity index
M-0	95.19:0.00:0.96:3.85	81.3	52.3	0.473
M-1	92.97:2.22:0.96:3.85	81.2	58.3	0.562
M-2	90.75:4.44:0.96:3.85	75.8	62.4	0.587
M-3	86.31:8.88:0.96:3.85	62.9	75.2	0.643
M-4	81.03:14.16:0.96:3.85	57.6	90.0	0.652
M-5	77.43:17.76:0.96:3.85	53.5	102.3	0.661
M-6	88.24:8.88:0.96:1.92	68.3	83.5	0.650
M-7	82.46:8.88:0.96:7.70	86.5	49.7	0.541
M-8	87.27:8.88:0.00:3.85	52.9	110.3	0.654
M-9	86.79:8.88:0.48:3.85	53.6	94.2	0.646
M-10	85.35:8.88:1.92:3.85	67.2	59.4	0.625
M-11	83.43:8.88:3.84:3.85	71.4	51.1	0.572
M-12	79.59:8.88:7.68:3.85	77.4	45.5	0.517
M-13 <sup>a</sup>	83.43:8.88:3.84:3.85	83.1	56.8	0.640
M-14 <sup>b</sup>	83.43:8.88:3.84:3.85	57.4	92.7	0.673
M-15 <sup>c</sup>	83.43:8.88:3.84:3.85	52.8	119.6	0.698
M-16 <sup>d</sup>	83.43:8.88:3.84:3.85	50.2	128.9	0.731

<sup>a</sup>  $M_{r,PEO-A} = 400$ .

<sup>b</sup>  $M_{r,PEO-A} = 600$ .

<sup>c</sup>  $M_{r,PEO-A} = 1500$ .

<sup>d</sup>  $M_{r,PEO-A} = 2000$ . Other  $M_{r,PEO-A} = 1000$ .

reagents were guarantee reagent (GR)-grade and were used as received.

PEO [relative molecular mass ( $M_r$ ) = 400, 600, 1000, 1500, or 2000] was prepared by the method reported by She et al.<sup>15</sup>

### Preparation of the PEO-grafted cationic polyacrylamide microparticles (PCPMs)

The inverse microemulsion tetrapolymerization of AM, DAC, PEO-A, and MBA was carried out at 43°C with a 100-mL, three-necked, round-bottom flask fitted with a condenser and a magnetic stirrer under nitrogen. DAC, PEO-A, and MBA were dissolved in an aqueous solution of AM to an appropriate concentration, The required amounts of Span 80 and Tween 80, dissolved in gasoline, were put in a reactor, and a water phase was added to attain a water/oil ratio of 1:3 (v/v). The mixture was stirred vigorously for 30 min; after 5 min of purging with nitrogen, the reactor was immersed in a water bath thermostated at 43°C, and an initiator solution was added to start the polymerization. After a total of 5 h of polymerization with stirring, the microemulsion was taken out from the reactor. The resulting product was precipitated in acetone, washed, and vacuum-dried at 50°C to a constant weight. The weight ratio of the dried product to the initial reactants represented the conversion (wt %).

### Characterization of the tetrapolymer

Fourier transform infrared (FTIR) spectra of the tetrapolymer (KBr pellet) were recorded with a Nicolet

760 FTIR spectrometer (Madison, WI, USA) in the 500–4000-cm<sup>-1</sup> range. The particle size distribution of the tetrapolymer microemulsion was determined by a Malvern Autosizer Lo-C particle diameter distribution measuring appliance (Malvern, UK) with a laser of 670 nm at 23°C.

$r_{pu}$  of the tetrapolymer microemulsion was measured as follows. The test was operated according to a manual papermaking process flow with a 12.2-g jet needle pulp. After pulp was put into the papermaking machinery, the required amount of 0.1% PCPM was added to the pulp. Then, a manual papermaking test was carried out.  $r_{pu}$  was calculated with the following formula:

$$r_{pu} = \frac{m_{pa}}{m_{pu}} \times 100\%$$

where  $m_{pa}$  is the dry mass of the paper and  $m_{pu}$  is the absolute dry mass of the pulp.

## RESULTS AND DISCUSSION

### Tetrapolymerization

The inverse microemulsion tetrapolymerization of AM, DAC, PEO-A, and MBA at various monomer feed ratios was carried out under the following conditions: water/oil = 1:3 (v/v), [monomer]<sub>total</sub> = 40 wt % (in the water phase), [AIBA] = 0.15 wt % (in the water phase), and [Span 80 + Tween 80] = 25 wt % (in the oil phase).

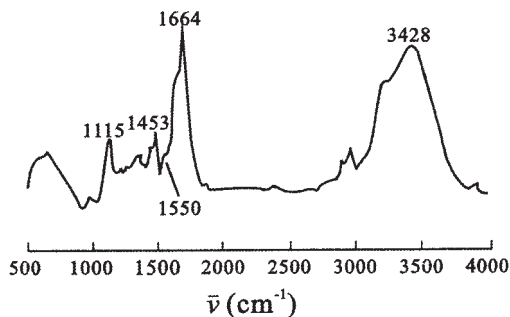


Figure 1 FTIR spectrum of sample M-3.

Table I shows the polymerization recipes and properties of the microparticles. The effect of the comonomer composition on the polymerization conversion and the properties of the microparticles can be analyzed with Table I.

The effect of the DAC content in the initial monomer feed on the microemulsion particle size and distribution can be seen in Table I (M-0, M-1, M-2, M-3, M-4, and M-5). The mean particle size and polydispersity index both increased with increasing DAC content in the initial monomer feed. This was due to the increasing system hydrophile-lipophile balance (HLB) value when the DAC content in the monomer feed increased; this resulted in decreasing microemulsion stability, which produced particle interagglutination. Sparnacci et al.<sup>16</sup> also found this phenomenon while preparing polyacrylamide microparticles. We suppose that a high cationic monomer concentration could prolong the particle coring period and widen the particle distribution.

The effects of the PEO-A content in the monomer feed on the microemulsion particle diameter and size distribution are shown in Table I (M-8, M-9, M-10, M-11, and M-12). The mean particle size and polydispersity index both decreased with increasing PEO-A content in the monomer feed. Kim et al.<sup>17</sup> stated that PEO-A is a comonomer and a space stabilizer in polymerization. With increasing PEO-A content in the comonomer, the stability of the polymeric system increased, so the microemulsion particle diameter became small and the particle size distribution became narrow. However, when the monomer composition of the feed was the same (Table I, M-11, M-13, M-14, M-15, and M-16), the mean particle size and polydispersity index both increased with an increase in  $M_r$  of PEO-A. A probable interpretation is that the PEO-grafted chain covered the cationic electrocharge placed on the microparticle surface and reduced repulsive interactions among the microemulsion particles. In addition, wrapping the connection of the PEO-grafted chain among the microparticles could also produce microemulsion agglutination, and the longer the PEO-A molecular chain was, the larger the interaction was.

Table I (M-6, M-3, and M-7) also presents the experimental results of the effect of the MBA composition in the feed on the microemulsion particle size and distribution. The mean particle size and polydispersity index both decreased with increasing MBA content. On the one hand, MBA had additional emulsification because the molecular structure of MBA is similar to that of AM; on the other hand, the crosslinking degree of the microparticle was raised with an increase in MBA, and this produced microparticle tightness, so the microparticle diameter decreased.

Figure 1 shows the FTIR spectrum of sample M-3; the absorbance at 1664 and 3428  $\text{cm}^{-1}$ , attributed to the amide group ( $-\text{CONH}_2$ ) absorption, was present in  $-\text{AM}-$  units. Similarly, the absorbances at 1453 [ $-\text{N}^+(\text{CH}_3)_3$ ], 1115 ( $-\text{CH}_2-\text{O}-\text{CH}_2-$ ), and 1550  $\text{cm}^{-1}$  ( $-\text{NH}-\text{CH}_2-\text{NH}-$ ) were characteristic peaks for  $-\text{DAC}-$ ,  $-\text{PEO-A}-$ , and  $-\text{MBA}-$  units, respectively.

### PCPM retention

Figure 2 shows the effect of the PCPM (M-4, M-9, and M-10) dosage on the pulp  $r_{\text{pu}}$  value. When the microparticle dosage was lower than 0.2% (relative  $m_{\text{pu}}$ ), the rates of retention increased sharply with increasing PCPM dosage. However, when the microparticle dosage was higher than 0.2%, the rates of retention slowly decreased with an increase in the PCPM dosage. This was because only if the microparticle aid was adequate for adsorption-bridging flocculation could the floc units be tightly formed among the suspended colloidal particles. Nevertheless, if the microparticle dosage was too high, the bridge formation was difficult, and this was due to the reduction of particle surface adsorption sites. Moreover, if once the microparticle dosage surpassed the maximum value at 0.2%, the  $\zeta$  potential of the floc units was larger than zero, and this made the negatively charged floc units be-

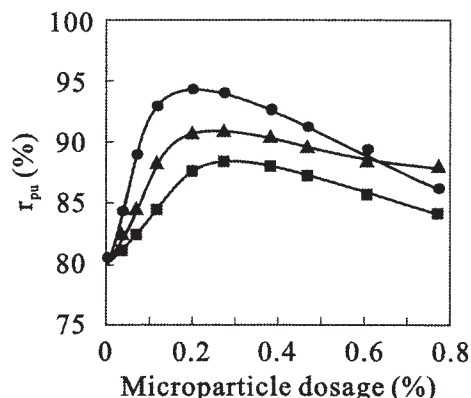
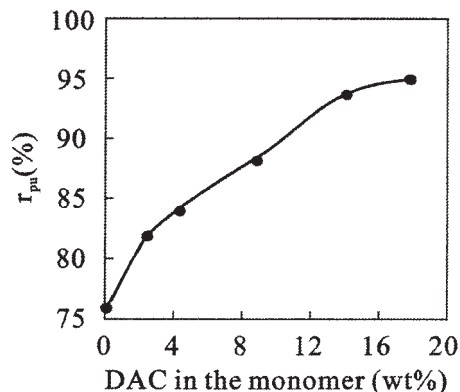


Figure 2 Effect of the microparticle dosage on the pulp  $r_{\text{pu}}$  value: (●) M-4, (■) M-9, and (▲) M-10.



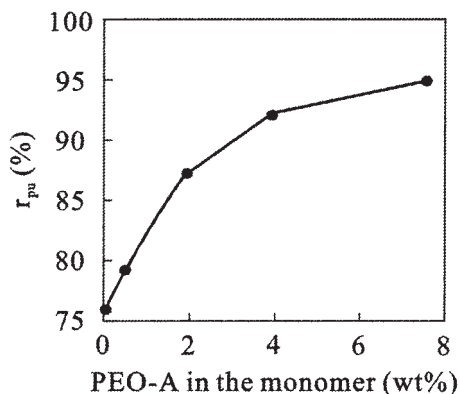
**Figure 3** Effect of the DAC content on the pulp  $r_{pu}$  value [feed composition = 0.96 wt % PEO-A and 3.85 wt % MBA; microparticle dosage = 0.2% (relative  $m_{pu}$ )].

come positively charged, resulting in a reduction of the retention effect because of the repulsive interactions among the positively charged floc units.

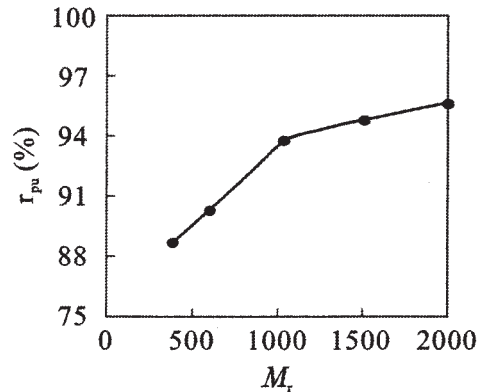
The effect of the DAC content in the initial monomer feed on the pulp  $r_{pu}$  value is shown in Figure 3. The rate of retention increased with increasing DAC content when it was below 14% and then achieved a critical value of 95%. Because the pulp fiber was negatively charged,<sup>18</sup> the cationic groups of the microparticles could bring about electrostatic adsorption with pulp fibers, and thus the rate of retention increased obviously with an increase in the DAC content.

The change in  $r_{pu}$  value of the pulp with the PEO-A content in the initial monomer feed is shown in Figure 4. The pulp retention rate increased with increasing PEO-A content. When the PEO-A content was greater than 3.84%, the pulp retention rate rose 16% more than that of blank pulp because the increasing PEO-A chain density of the microparticles caused more effective bridging flocculation.

The effect of the PEO-A  $M_r$  value on the pulp  $r_{pu}$  value is shown in Figure 5. The microparticle retention



**Figure 4** Effect of the PEO-A ( $M_r = 1000$ ) content on the pulp  $r_{pu}$  value [feed composition = 8.88 wt % DAC and 3.85 wt % MBA; microparticle dosage = 0.2% (relative  $m_{pu}$ )].



**Figure 5** Effect of the PEO-A  $M_r$  value on the pulp  $r_{pu}$  value [feed composition = 3.84 wt % PEO-A, 8.88 wt % DAC, and 3.85 wt % MBA; microparticle dosage = 0.2% (relative  $m_{pu}$ )].

rate increased with increasing PEO-A  $M_r$ . According to the basic principle of PEO flocculation,<sup>19</sup> the flocculability of PEO-A improved with increasing PEO chain length, so the high PEO-A  $M_r$  value of PCPM increased the pulp fine retention accordingly.

#### Retention mechanism of PCPM

On the basis of the experimental results, we considered a mechanism for the retention of PCPMs with pulp fibers. The large amount of surface-active cations of PCPMs could be combined into hard aggregation with pulp fibers in various modes. The positively charged groups contained in the particles could produce electrostatic adsorption with negatively charged pulp fibers; the ionic bond energy was 214–334 kJ/mol.<sup>20</sup> During the papermaking process, the PEO-grafted chain of PCPM reached out from the particle surface and formed a net-shaped structure through a bridging action of the hydrogen bond between the ether bond of the PEO chain and pulp fibers, and thus the pulp  $r_{pu}$  value was improved.

#### CONCLUSIONS

Crosslinked PCPMs were prepared by inverse microemulsion tetrapolymerization, with a particle size of 45–130 nm and a distribution index of 0.47–0.74. FTIR measurements demonstrated that the prepared microparticles were composed of chain units of AM, DAC, PEO-A, and MBA.

Tetrapolymers containing more than 14% DAC and more than 4% PEO-A ( $M_r \geq 1000$ ) in the initial monomer feed were highly effective microemulsion retention aids for pulp fibers. The pulp  $r_{pu}$  value was improved by the synergetic effect of the ionic bond and hydrogen-bonded action between the microparticles and paper fibers.

**References**

1. Wågberg, L.; Eriksson, J. *Chem Eng J* 2000, 80, 51.
2. Ovenden, C.; Xiao, H. *Colloids Surf A* 2002, 197, 225.
3. Spengler, J. F.; Coakley, W. T. *Langmuir* 2003, 19, 3635.
4. Covarrubias, R. M.; Kessler, B.; Magee, K. *Pulp Pap* 2003, 77, 40.
5. Gruber, E.; Muller, P. *Tappi J* 2004, 3, 17.
6. Isermann, R.; Blum, R.; Champ, S.; Esser, A. *Int Paperworld IPW* 2004, 1, 26.
7. Brouillette, F.; Morneau, D.; Chabot, B.; Daneault, C. *App J* 2005, 58, 47.
8. Staffan, W.; Peter, S.; Göran, D.; Per, S.; Ann, S. *J Colloid Interface Sci* 1992, 151, 178.
9. Lars, W.; Mirjam, B.; Inger, Å.; Agen, S. *Tappi J* 1996, 79, 157.
10. Gibbs, A.; Xiao, H.; Deng, Y.; Pelton, R. *Tappi J* 1997, 80, 163.
11. Liu, W.; Ni, Y.; Xiao, H. *J Pulp Pap Sci* 2003, 29, 145.
12. Zegui, Y.; Yulin, D. *Chem Eng J* 2000, 80, 31.
13. Ono, H.; Deng, Y. *J Colloid Interface Sci* 1997, 188, 183.
14. Xiao, H.; Liu, Z.; Wisenan, N. *J Colloid Interface Sci* 1999, 216, 409.
15. She, N.; Peng, X.; Shen, J. *Petrochem Technol* 2003, 32, 216.
16. Sparnacci, K.; Tondelli, L.; Laus, M. *J Polym Sci Part A: Polym Chem* 2000, 38, 3347.
17. Kim, K. S.; Cho, S. H.; Kim, Y. J. *Polym J* 1993, 25, 847.
18. Liu, W. *Papermaking Chem* 2000, 3, 18.
19. Xiao, H.; Pelton, R.; Hamielec, A. *Tappi J* 1996, 79, 129.
20. Shen, Y. *Preparation and Mechanism of Papermaking Chemical*; Light Industry: Beijing, 1999.