

Cationic Polystyrene Spheres for Removal of Anionic Contaminants in White Water of Papermaking

He Xiao,¹ Beihai He,^{1,2} Liying Qian,¹ Junrong Li¹

¹State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China 510641

²National Engineering Research Center of Papermaking & Pollution Control, South China University of Technology, Guangzhou, China 510641

Correspondence to: J. Li (E-mail: ppljrr@163.com)

ABSTRACT: In a paper mill's water circuit, normal runnability of the paper machine is often disturbed due to the buildup of dissolved and colloidal substances (DCS). Contaminant adsorption on a solid adsorbent in a fluidized bed reactor has been applied for white water treatment. In the present study, polystyrene (PS) spheres were firstly acylated by acryloyl chloride, then poly(methacryloxyethyl-trimethyl ammonium chloride) (PMAC) was grafted onto the acylated PS spheres, induced by surface-initiated free-radical polymerization. Fourier transform infrared spectroscopy, thermal gravimetric analysis, and scanning electron microscopy were used to characterize the changes of PS spheres in chemical structures and surface morphology. The results showed that acylated PS spheres could be easily grafted with PMAC in 53.83% weight increase. Polyelectrolyte loading of PS spheres reached up to 1.72 mmol/g. The resulted cationic modified PS spheres could effectively decrease the cationic demand in white water and it still maintained high performance after operating repeatedly for 10 batches. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 10.1002/app.41379.

KEYWORDS: applications; polystyrene; radical polymerization; resins; synthesis and processing

Received 19 April 2014; accepted 7 August 2014

DOI: 10.1002/app.41379

INTRODUCTION

Dissolved and colloidal substances (DCS) in a papermaking system continuously accumulate with increasing utilization of recycling white water. Besides the dissolved anionic substances there is a variety of insoluble hydrophobic substances mainly coming from the raw materials, wood extractives, coating additives, adhesives, etc.¹ Accumulation of these substances lead to many serious problems, such as poor runnability of the paper machine, inefficiency of chemicals, and poor physical properties of the paper produced.^{2–4} DCS generally have anionic characters and are referred to “anionic trash” since they can form polyelectrolyte complexes with added cationic chemicals.

Current available technologies to control detrimental substances are based on chemical treatments mostly. The use of highly cationic polymers is a common possibility to remove DCS by fixing the DCS onto the fibers.^{5–7} However, the fixed DCS in the fiber mat may still impair machine runnability, especially in the press section and drying section.^{8,9} Other treatment technologies such as biological enzyme^{10,11} and membrane filtration treatment^{12,13} have been proposed, but adaptability and costs have restricted implementations in mills.

In recent years, there is growing interest in using ion exchange resins to resolve these problems in paper mills and cardboard industries.^{14,15} Adsorption of contaminants from process water with some suitable adsorbents in a fluidized bed reactor has been proposed to allow papermaking operations under high-cycle operations of whitewater. Gel-type ion exchange resin (Amberlite IRA-67) can adsorb poly-galacturonic acid 19 mg/g and rosin acid 45 mg/g, respectively.¹⁶ In the meanwhile, to lower the costs, inorganic modified materials have been also used as adsorbents in a fluidized bed reactor.^{17–19} Calcined Mg/Al hydrotalcite compounds can adsorb rosin acid 434.78 mg/g at 323 K corresponding to Langmuir adsorption principle.²⁰ Although these adsorbents used for removal of DCS material are very effective, the adsorption capacity and pH adaptability often limit their application.²¹ So, it is critical to improve adsorption capacity, adsorption efficiency, and operation stability in exploitation of a new kind of adsorption materials.

Regarding ion exchange resins, it is known that polystyrene (PS) spheres are widely used as the matrix material because they are cheap, accessible, and they have high mechanical strength.^{22,23} However, the cationic or anionic groups on the surface of traditional ion exchange resins are short molecular

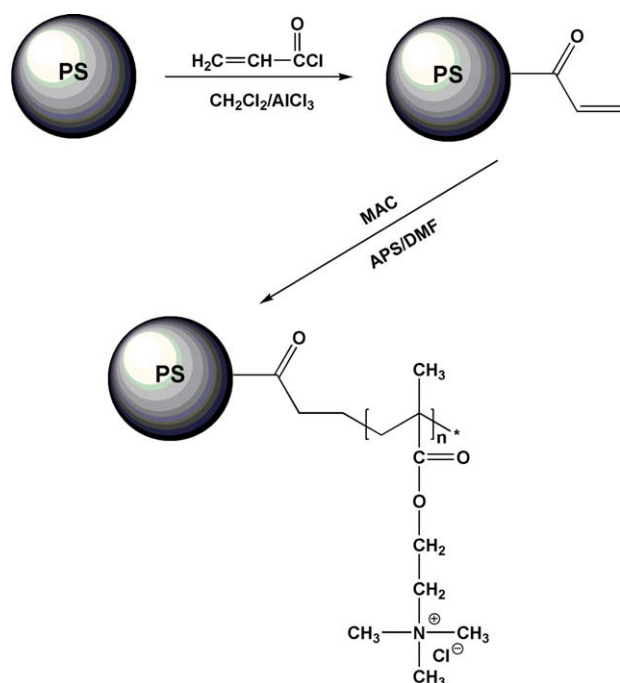


Figure 1. The preparation process of cationic PS spheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chains, such as tertiary amine, quaternary ammonium, sulfonic, and carboxyl groups. In the present study, we intended to decorate the spheres surface with a fibrous polymer. Therefore, PS spheres were firstly acylated by acryloyl chloride and then grafted with poly(methacryloxyethyltrimethyl ammonium chloride) (PMAC) brushes, using surface-initiated free-radical polymerization (Figure 1). Surface-initiated parameters (e.g., solvent, PS/MAC mass ratio, MAC concentration, initiator concentration) were optimized to evaluate the results of cationic polyelectrolyte binding on the PS spheres. Finally, capability of the adsorbents such as cationic demand reduction and reusability were investigated.

EXPERIMENTAL

Materials

Dichloromethane was dried with calcium hydride (CaH_2) overnight and distilled before use. Anhydrous aluminum chloride, *N,N*-dimethyl formamide and ammonium persulfate were purchased from Aladdin Industrial. Acryloyl chloride and methacryloxyethyltrimethyl ammonium chloride (MAC) were purchased from J&K Scientific Co. Crosslinked PS spheres (50–100 mesh) were kindly supported by Zhejiang Zhengguang Industrial Co., China. White water was obtained from Yueyang Paper Co., China.

Acylation of PS Spheres

PS spheres were successively purified by tetrahydrofuran, distilled water, ethanol before use. The synthesis procedure was referred to a previously published method.²⁴ Briefly, 0.26 g of purified PS spheres were suspended in 5 g of anhydrous dichloromethane and 0.68 g of acryloyl chloride was added drop wise. Then, 0.73 g of anhydrous aluminum chloride was followed by batch-wise addition with continuous stirring. The reaction solution was stirred at 30°C for 4 h and thrown into substantial distilled water

to quench the reaction. Finally, the crude product was successively washed by ethanol, dilute hydrochloric acid (volume ratio 1 : 100), and distilled water for 30 min. The purified product was vacuum-dried at 50°C for 24 h to constant weight, which was collected as yellowish sphere beads.

Cationization of PS Spheres

Acylated PS spheres grafting with PMAC were carried out in a glass reactor. About 0.2 g of acylated PS spheres were suspended in 8.1 g of *N,N*-dimethyl formamide and swelled for 12 h. After this period, the initiator ammonium persulfate (APS, 3 mg) was injected into the flask to initiate the free-radical polymerization, followed by drop-wise addition of MAC (4 g) with continuous stirring at 60°C for 4 h. Then the reaction was continuously warmed at 80°C for 3 h. The crude products were washed by distilled water for 30 min to remove homo-polymer of MAC. After being vacuum-dried at 50°C for 24 h to constant weight, the final product in the form of yellowish sphere bead surrounded with transparency polymeric gel was obtained. Weight increase was evaluated by the following equation:

$$\Delta W\% = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

where ΔW is the weight increase of acylated PS spheres, W_2 is the weight of cationic PS spheres, W_1 is the weight of acylated PS spheres.

Characterization of Cationic PS Spheres

The Fourier transform infrared spectroscopy (FTIR) spectra of various PS spheres in KBr pellets were recorded by NEXUS 670 (Thermo Nicolet, USA), operating between 4000 cm^{-1} and 400 cm^{-1} . The thermal stabilities of PS spheres, acylated and cationic PS spheres were evaluated using thermal gravimetric analysis (TGA, Q500, TA, USA). Samples were heated in an aluminum crucible to 700°C at a heating rate of 10 °C/min while the apparatus was continually flushed with nitrogen at a flow rate of 25 mL/min. The surface morphologies of cationic PS spheres were observed using a scanning electron microscope (SEM, EVO18, ZEISS, Germany). Element analyses of cationic PS spheres were investigated by elemental analyzer (Vario EL cube, Elementar, Germany), and polyelectrolyte loading was calculated by the following equation:

$$X_c = \frac{N\%}{14} \quad (2)$$

where X_c (mmol/g) is the polyelectrolyte loading of PS spheres, $N\%$ is Nitrogen content of cationic PS spheres, 14 is Nitrogen relative molecular mass.

Batch Test and Application of Cationic PS Spheres

The application experiments were carried out in 50-mL beaker by mixing 20 mL white water and 0.2 g cationic PS spheres with magnetic stirring in the water bath. After adsorption, the supernatant of the mixture was analyzed using a particle charge detector (PCD-04, Mütek, Germany) with a standard 0.001N poly(diallyl dimethyl ammonium chloride) (poly-DADMAC). The recycling capabilities of cationic PS spheres were evaluated by repeating adsorption/elution experiments. Elution conditions were as follows: 1 mol/L sodium hydroxide as an eluant at room temperature for 10 min.

Table I. Effect of Solvent on Process of Grafting Reaction (PS/MAC Mass ratio 1 : 19.5, MAC Concentration 40 wt %, Initiator Concentration 0.1 wt %)

	Methanol	THF	DMSO	Toluene	DMF	H ₂ O
Weight increase (%)	10.15	19.45	17.05	-15.8	41.55	-0.85
Polyelectrolyte loading (mmol/g)	1.06	1.2	1.29	0.14	1.64	0.67

RESULTS AND DISCUSSION

Optimization of Preparing Cationic PS Spheres Conditions

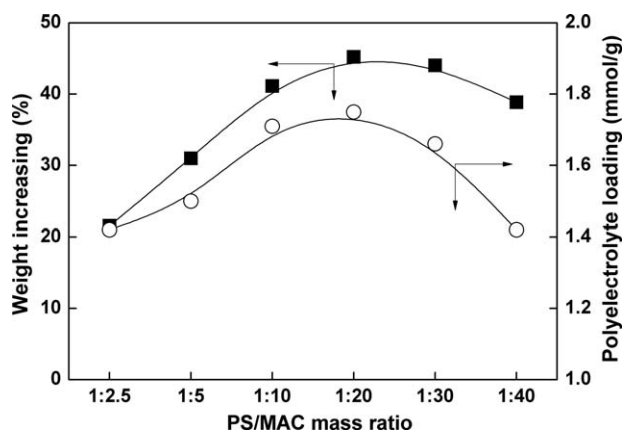
Effect of Solvent on Preparation of Cationic PS Spheres.

PMAC was grafted onto acylated PS spheres by free-radical polymerization. This procedure gave “hair like” polymers in which grafted chains were linked to PS spheres with hydrophilic molecular chains. Before doing so, the active double bond was introduced to the surface of PS spheres by acylation reaction of acryloyl chloride. Then the PMAC was grafted onto the PS spheres through two-phase free-radical polymerization, where monomers (MAC) were initiated and growing on the solid substrates from the reaction solution. The method belongs to “grafting from” technology which provides better control of the chain densities and assembled polymer chains on the surface.²⁵

Hydrophobic acetylated PS spheres are difficult to graft by hydrophilic cationic monomer (MAC) directly, therefore, the selection of an appropriate solvent is very important for grafting reaction smoothly. In this study, weight increase of grafted products as well as polyelectrolyte loading was used to reflect the results of grafting reaction indirectly.

We performed comparative studies on six kinds of reaction medium and the results are shown in Table I. It was clear that the changes of weight increase and polyelectrolyte loading were consistent in the six solvents. Toluene performed the worst and DMF was the best, which brought 41.55% weight increase and 1.64 mmol/g polyelectrolyte loading. So, in this thesis, if no special instructions are given, all the reaction solvent is DMF.

Effect of PS/MAC Mass Ratio on Preparation of Cationic PS Spheres. Figure 2 shows the effects of PS/MAC mass ratio on the preparation of cationic PS spheres. With the increase of MAC dosage, more and more MAC monomer would be grafted onto the surface of PS spheres. When the PS/MAC mass ratio

**Figure 2.** Effect of PS/MAC mass ratio on process of grafting reaction (MAC concentration 40 wt %, initiator concentration 0.1 wt %).

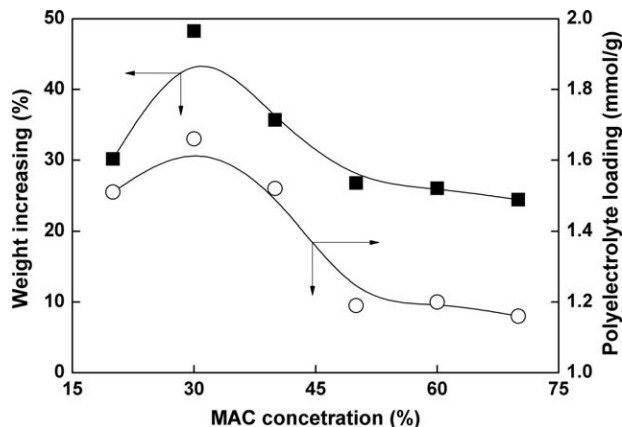
was 1 : 20, both weight increase and polyelectrolyte loading reached to the highest point, 45.21% and 1.75 mmol/g, respectively. However, when the PS/MAC mass ratio was larger than 1 : 20, homo-polymerization was faster than grafting reaction and so, the weight increase and polyelectrolyte loading decreased.

Effect of MAC Concentration on Preparation of Cationic PS Spheres.

MAC concentration was also one of the most important factors on grafting reaction of PS spheres. From the Figure 3, it could be seen that with the increase of MAC concentration, the weight increase and polyelectrolyte loading increase at first and then decrease. When the concentration of MAC was 30%, weight increase and polyelectrolyte loading were 48.27% and 1.66 mmol/g, respectively. When the concentration of MAC was at high level, homo-polymerization of MAC was accelerated too fast, causing lower poly-MAC bonding onto the PS. On the other hand, the higher MAC concentration means the fewer amounts of DMF in polymerization system and so the PS spheres could not be swelled well enough to graft reaction.

Effect of Initiator Concentration on Preparation of Cationic PS Spheres.

From Figure 4, it was shown that with the increase of initiator concentration, weight increase and polyelectrolyte loading increased quickly at first and then decreased gradually. At low level of initiator concentration, the initiator efficiency and polymerization rate decreased due to the “cage effect.”²⁶ With the increase of initiator concentration, the intermolecular collision probability of initial free radicals with MAC monomers increased. Meanwhile, the more acylated PS spheres were initiated, the more polyelectrolyte had a chance to be grafted onto PS spheres. Appropriate initiator concentration was 0.075 wt % in which PS spheres could graft 1.72 mmol/g polyelectrolyte with 53.83% weight increase. But overdose initiator could generate too many free radicals and increased the termination rate,

**Figure 3.** Effect of MAC concentration on process of grafting reaction (PS/MAC mass ratio 1 : 20, initiator concentration 0.1 wt %).

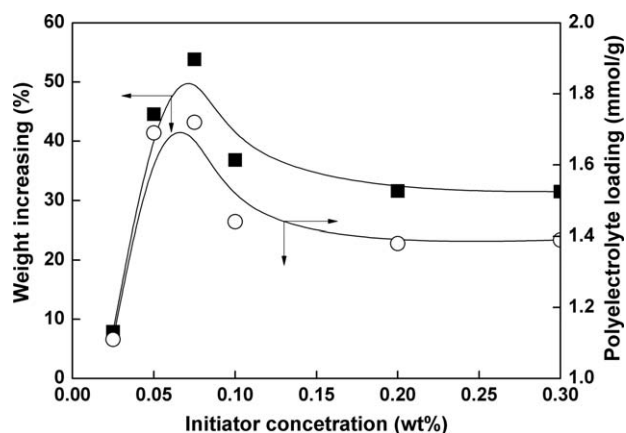


Figure 4. Effect of initiator concentration on process of grafting reaction (PS/MAC mass ratio 1 : 20, MAC concentration 30 wt %).

which resulted in low weight increase and polyelectrolyte loading of cationic PS spheres.

Characterization of Cationic PS Spheres

Figure 5 shows the FTIR spectra of PS spheres and modified PS spheres. Wavenumber 1681 cm^{-1} shows a characteristic stretching vibration peak of carbonyl group ($-\text{C}=\text{O}$). The peaks at 1416 cm^{-1} and 983 cm^{-1} are representative of a deformation vibration of vinyl indicating that acryloyl chloride has been grafted onto the PS spheres. The peaks at 1726 cm^{-1} and 954 cm^{-1} should be assigned to ester carbonyl group

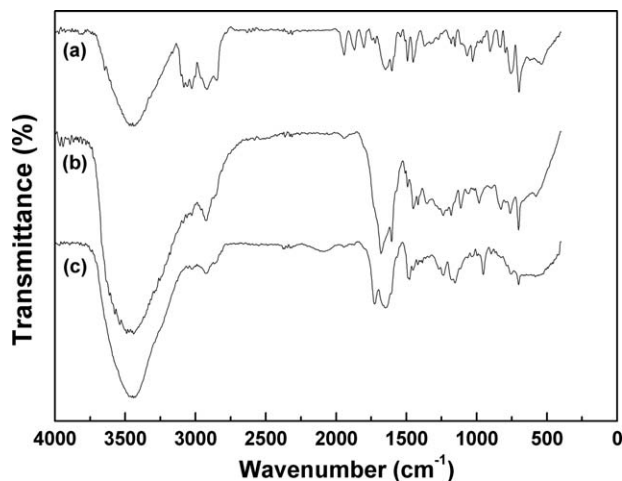


Figure 5. FTIR spectra of PS spheres (a), acylated PS spheres (b), and cationic PS spheres (c).

($\text{O}=\text{C}-\text{O}$) stretching vibration and quaternary ammonium salt characteristic absorption from the MAC unit, respectively.

Thermal gravimetric analysis of PS spheres and the modified ones was conducted with TGA. Figure 6 gives the thermal gravimetric (TG) and derivative TG curves for three kinds of PS spheres with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ under a nitrogen atmosphere. For PS spheres, thermal degradation occurred in one distinct stage, and the maximum value of the peak (which characterizes the degradation of crosslinked PS), appeared at

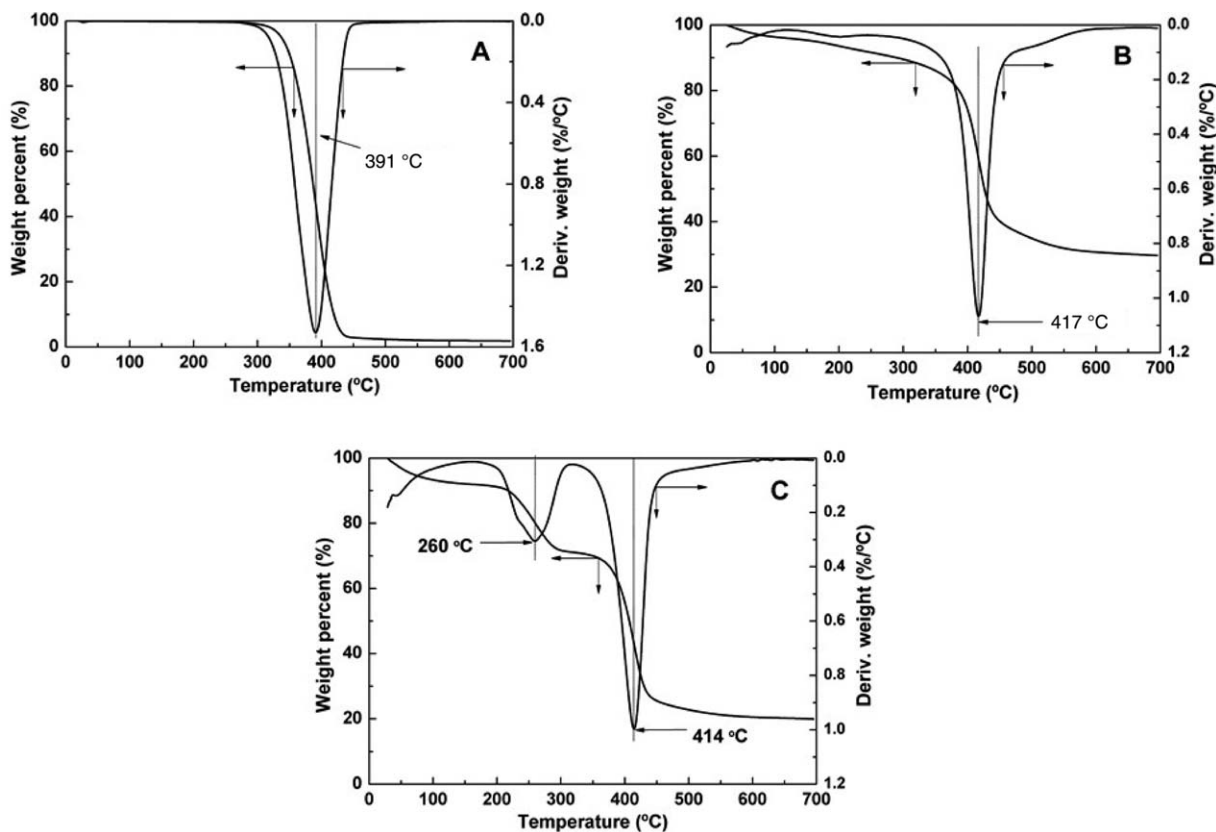


Figure 6. TGA of PS spheres (A), acylated PS spheres (B), and cationic PS spheres (C).

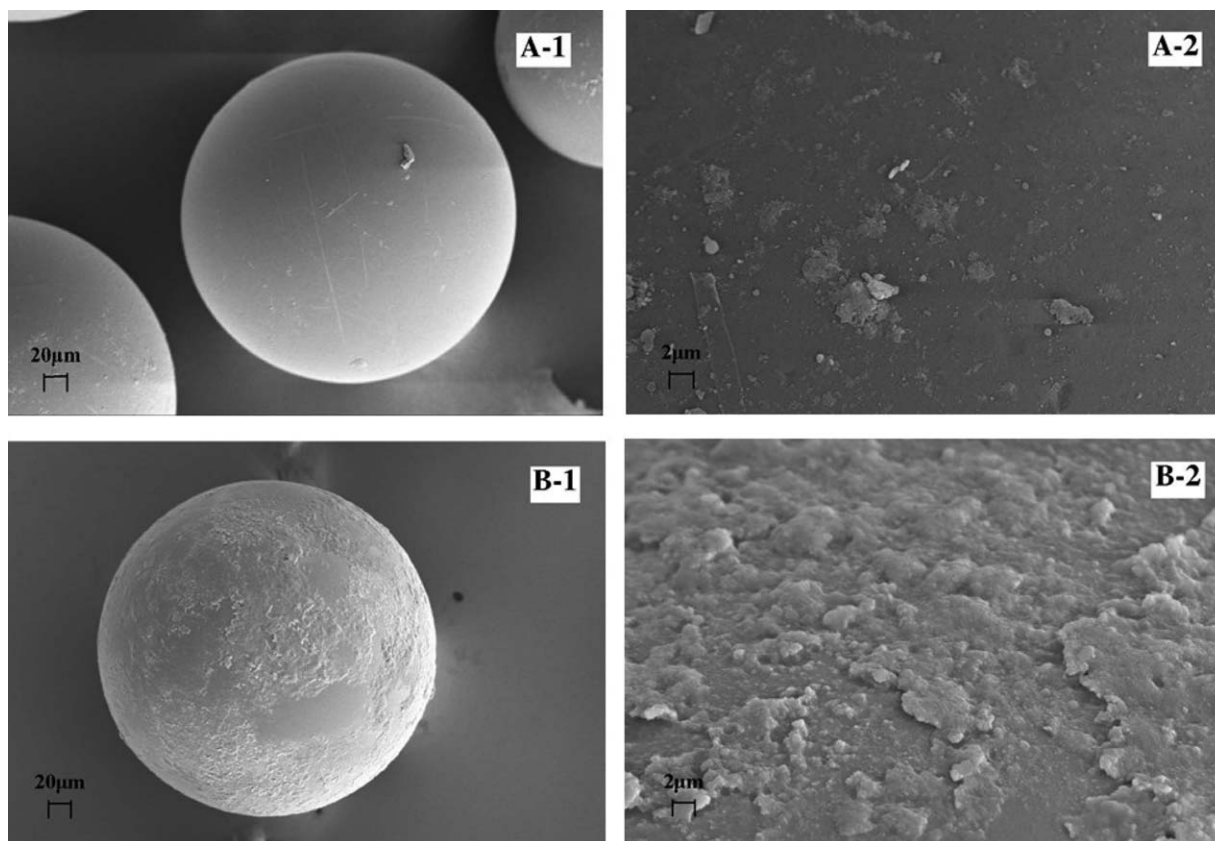


Figure 7. SEM images of PS spheres (A-1 and A-2) and cationic PS spheres (B-1 and B-2).

391°C. For acylated PS spheres, the maximum value of the peak appeared at 417°C because some benzene rings of PS had been substituted by acryloyl chloride. For cationic PS spheres, two peaks appeared in derivative TG curves, the main peak at 414°C corresponded to the degradation of the PS spheres core, and the shoulder peak around 260°C corresponded to the degradation of the linear PMAC layer.

SEM images of PS spheres and cationic PS spheres are displayed in Figure 7. Appearances of two kinds of spheres were very uni-

form, and the surface of cationic PS spheres became a little rougher after surface-grafting reaction, which meant the PMAC was well grafted onto the surface of PS spheres.

Application of Cationic PS Spheres to Control DCS in White Water

The cationic demand was determined by colloidal titration using standard polymer solutions of poly-DADMAC (cationic). As shown in Figure 8, effects of treating time and temperature on the removal of DCS were evaluated when the cationic PS

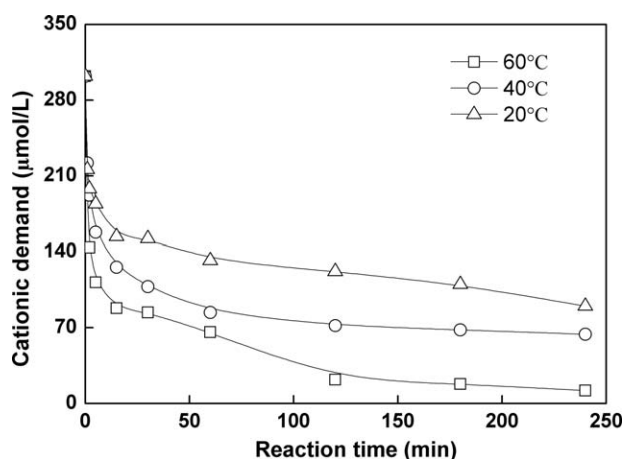


Figure 8. Effect of treating time and temperature on the removal of DCS (sorbent amount 10 g/L).

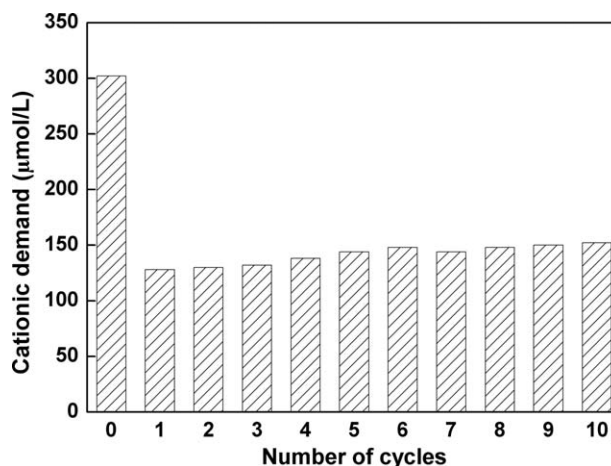


Figure 9. Reusability of cationic PS spheres (adsorbent amount 10 g/L, treating for 15 min at 40°C).

spheres amount was 10 g/L. The curves showed that the cationic demand decreased dramatically at the beginning of the minutes. That's to say, the resulting cationic PS spheres are very efficient to remove the anionic trash of papermaking white water. Furthermore, the removal efficiency of cationic PS spheres improved by increase temperature due to the molecular motion in the system. This molecular motion may be accelerated with the increase of temperature and the macromolecule of PMAC grafted on PS surface could stretch thoroughly, resulting in catching more anionic trash. On the other hand, DCS, especially, dissolved substances have better diffusion at higher temperature or longer contact time. Thus, more DCS were easily adsorbed onto the cationic PS.

The reusability is an important parameter related to the application potential of adsorption technology. In this study, anionic substances adsorbed onto the cationic PS spheres can be easily exchanged by hydroxide ion in order to recover adsorption capacity of cationic PS spheres. As seen from Figure 9, the resulted PS spheres were used for ten cycles. Cationic demand in white water had been still reduced above 50% after ten batches. Their treatment performance for white water was not obviously reduced. This shows that the cationic PS spheres prepared here have very good repeated performance and are very suitable for industrial applications. Moreover, it is believed that it can be recycled for many times, regarding with its chemical structure.

CONCLUSIONS

The aim of this article is to develop a solid adsorbent designed for adsorption of anionic contaminants from white water in papermaking. The cationic PMAC was grafted on the surface of PS spheres by two-steps surface-initiated radical polymerization successfully. Excellent product was obtained under the conditions as follows: the solvent DMF, PS/MAC mass ratio 1 : 20, MAC concentration 30 wt % and initiator concentration 0.075 wt %. The resulted cationic PS spheres could adapt to different temperature of white water and exhibited a very good performance in lowering cationic demand of white water as well as a good reusability.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the State Key Laboratory of Pulp and Paper Engineering Fund (No.201114), the National Natural Science Foundation of China (Grant No. 31200457), the Fundamental Research Funds for the Central Universities (2013ZZ0072) for financial support.

REFERENCES

1. Miao, Q.; Huang, L.; Chen, L. *Bioresources* **2013**, *8*, 1431.
2. Francis, D. W.; Ouchi, M. D. *J. Pulp Pap. Sci.* **2001**, *27*, 289.

3. Whipple, W. L.; Maltesh, C. *J. Colloid Interface Sci.* **2002**, *256*, 33.
4. Rundlöf, M.; Eriksson, M.; Ström, H.; Wågberg, L. *Cellulose* **2002**, *9*, 127.
5. Wågberg, L.; Ondaral, S.; Enarsson, L. *Ind. Eng. Chem. Res.* **2007**, *46*, 2212.
6. McLean, D. S.; Stack, K. R.; Richardson, D. E. *Appita J.* **2010**, *63*, 199.
7. Wågberg, L.; Asell, I. *Colloid Surf. A* **1995**, *104*, 169.
8. Carre, B.; Brun, J.; Galland, G. *Pulp Pap. Canada* **1998**, *99*, 75.
9. Hassler, T. *Tappi J.* **1988**, *71*, 195.
10. Liu, K.; Zhao, G.; He, B.; Chen, L.; Huang, L. *Bioresour. Technol.* **2012**, *123*, 616.
11. Wu, R.; He, B.; Zhao, G.; Qian, L.; Li, X. *Carbohydr. Polym.* **2013**, *97*, 523.
12. Nuortila-Jokinen, J.; Mnttri, M.; Huuhilo, T.; Kallioinen, M.; Nyström, M. *Water Sci. Technol.* **2004**, *50*, 217.
13. Pizzichini, M.; Russo, C.; Meo, C. D. *Desalination* **2005**, *178*, 351.
14. Kratochuil, D.; Bratty, M. (Bioteq Environmental Technologies Inc.). U.S. Pat. 8,551,340 (**2013**).
15. Richardson, D.; Murray, B.; Blom, L. In 64th Appita Annual Conference and Exhibition, Melbourne, Australia, April 18–21, 2010; Carlton, Vic.; Appita Inc., **2010**, p 129.
16. Vallerand, R.; Daneault, C.; Chabot, B. *J. Pulp Pap. Sci.* **2010**, *36*, 22.
17. Oulanti, L.; Daneault, C.; Chabot, B. *Chem. Eng. J.* **2012**, *209*, 28.
18. Huang, L.; Xiao, H.; Ni, Y. *Sep. Purif. Technol.* **2006**, *49*, 264.
19. Loranger, E.; Daneault, C.; Chabot, B. *Chem. Eng. J.* **2010**, *160*, 671.
20. Yang, D.; Song, Z.; Qian, X. *Ind. Eng. Chem. Res.* **2013**, *52*, 6956.
21. Ozer, O.; Ince, A.; Karagoz, B.; Bicak, N. *Desalination* **2013**, *309*, 141.
22. Veverka, P.; Jerabek, K. *React. Funct. Polym.* **1999**, *41*, 21.
23. Pan, B.; Xiong, Y.; Li, A.; Chen, J.; Zhang, Q.; Jin, X. *React. Funct. Polym.* **2002**, *53*, 63.
24. Zhou, Y.; Wei, R.; Liu, X.; Zhang, X. *Chin. J. Process Eng.* **2007**, *7*, 1050.
25. Prucker, O.; Ruhe, J. *Macromolecules* **1998**, *31*, 592.
26. Pan, Z. In Polymer Chemistry (enhanced version); Chemical Industry Press: Beijing, **2007**; Chapter 3, p 78.