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ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · FEBRUARY 2009

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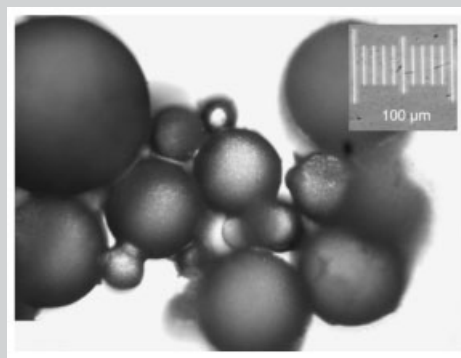
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**Summary:** Novel crosslinked porous particles based on the ionic copolymer of 1,1,3,3-tetramethylguanidine acrylate (TMGA) and *N,N*-methylenebisacrylamide (MBA) were prepared via an inverse suspension polymerization using cyclohexane as continuous phase and Span 60 as the dispersant. The SO<sub>2</sub> absorption–desorption properties of the P(TMGA-*co*-MBA) particles were studied for the first time. The particles showed excellent SO<sub>2</sub> absorption properties: high capacity and rate. These absorption properties, as well as the particle volume, shape, and morphology, remained unchanged during the SO<sub>2</sub> absorption–desorption cycles. The material appeared to be a good candidate as SO<sub>2</sub> absorbent for fuel gas desulfurization (FGD) and purification of other SO<sub>2</sub>-containing gases.



Optical microscope image of the P(TMGA-*co*-MBA) porous particles.

# Preparation and SO<sub>2</sub> Absorption/Desorption Properties of Crosslinked Poly(1,1,3,3-Tetramethylguanidine Acrylate) Porous Particles

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Received: August 14, 2006; Revised: September 14, 2006; Accepted: September 14, 2006; DOI: 10.1002/marc.200600563

**Keywords:** adsorption; crosslinking; inverse suspension polymerization; ionomers; porous polymer particle

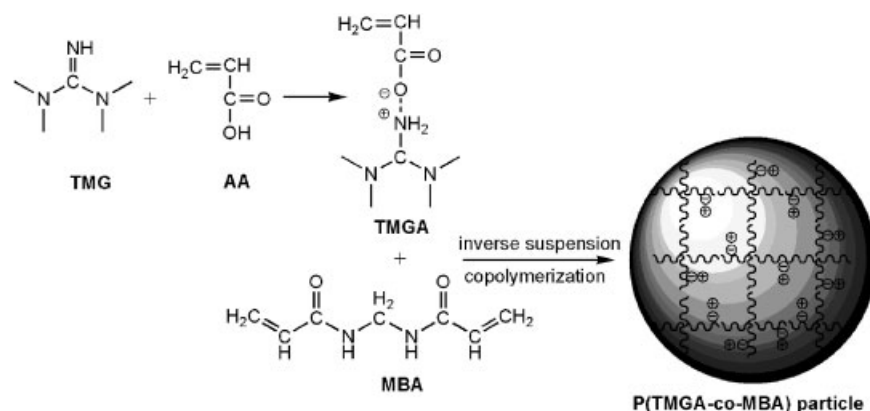
## Introduction

Ionic liquids (ILs) <sup>[1–7]</sup> and IL polymers <sup>[8,9]</sup> have been reported to be able to dissolve or absorb some gases that include CO<sub>2</sub>, <sup>[1–5,8]</sup> ethylene, <sup>[5,6]</sup> ethane, <sup>[6]</sup> SO<sub>2</sub>, <sup>[7]</sup> etc. especially at high pressures. This characteristic of ILs and IL polymers provides a new opportunity for gas separation and purification. Among these gases, the separation and purification of SO<sub>2</sub> is of particular interest because the SO<sub>2</sub> emission from fossil-fuel combustion has become one of the major air pollutants. Selective absorption and desorption of SO<sub>2</sub> may find applications in fuel gas desulfurization (FGD) and purification of other SO<sub>2</sub>-containing gases.

Recently, Han et al. found that 1,1,3,3-tetramethylguanidine lactate (TMGL), a new IL, is able to absorb SO<sub>2</sub> from

a simulated fuel gas with high absorption capacity and high selectivity. <sup>[7]</sup> However, high viscosity and other inherent disadvantages of the wet desulfurization with liquid SO<sub>2</sub> absorbent make ILs inferior to solid absorbents used for dry desulfurization. Solid polymeric absorbents are therefore more attractive in practice than their liquid counterparts.

In our previous study, <sup>[10]</sup> poly(1,1,3,3-tetramethylguanidine acrylate) (PTMGA), a novel ionic polymer, was synthesized via the free radical polymerization of 1,1,3,3-tetramethylguanidine acrylate (TMGA) in an aqueous solution. It has been found that PTMGA can absorb SO<sub>2</sub> with high selectivity, high capacity, and rapid rate. With a good desorption behavior, the materials can also be reused in SO<sub>2</sub> absorption–desorption cycles. However, the water-



Scheme 1. Synthesis of crosslinked P(TMGA-co-MBA) particles via inverse suspension copolymerization of TMGA and MBA.

soluble PTMGA samples experienced volume shrinkage and shape deformation during the cycling. To solve this problem, we directly synthesized crosslinked porous copolymer particles via an inverse suspension copolymerization of TMGA with *N,N*-methylenebisacrylamide (MBA). The copolymer P(TMGA-co-MBA) was characterized and its SO<sub>2</sub> absorption properties were examined. This new material appeared to be much better in terms of stability and more practical polymeric SO<sub>2</sub> absorbent.

## Experimental Part

### Materials

Acrylic acid (AA) (C.P., Sinopharm Chemical Reagent Co., Ltd., China) was distilled under vacuum prior to use. 1,1,3,3-Tetramethylguanidine (TMG) ( $\geq 99.2\%$ , Zibo Senjie Chemical Auxiliary Co., Ltd., China), MBA (J&K Chemical Co., Ltd., China), cyclohexane, Span 60, and potassium persulfate (KPS) were used as received. Sulfur dioxide (SO<sub>2</sub>,  $\geq 98.0\%$ ) was purchased from Hangzhou Jingong Special Gas Co. Ltd. and used as received. 1,1,3,3-Tetramethylguanidine acrylate (TMGA, **3**) was synthesized via a direct neutralization of TMG (**1**) and AA (**2**) at 25 °C, as described previously.<sup>[10]</sup>

### Synthesis of Crosslinked Porous P(TMGA-co-MBA) Particles

Crosslinked porous P(TMGA-co-MBA) particles were synthesized via an inverse suspension copolymerization of TMGA and MBA with cyclohexane as oil phase and Span 60 as dispersant. Cyclohexane and Span 60 were added to a four-neck flask equipped with a thermometer, condenser, stirrer, and N<sub>2</sub> inlet. The solution was stirred under N<sub>2</sub> for half an hour. A mixture of TMGA and MBA as well as an aqueous solution of KPS were then added during a period of 15 min through a dropping funnel. The suspension thus formed was heated to 70 °C and reacted for 8 h. Upon the completion of the reaction, the solvent was removed and the polymer particles were collected, washed with methanol, and vacuum-dried at 70 °C until a constant weight was reached. The dry copolymer particle samples were stored in a desiccator prior to the SO<sub>2</sub> absorption and characterization.

### SO<sub>2</sub> Absorption and Desorption

The SO<sub>2</sub> absorption and desorption experiments were conducted as previously described.<sup>[10]</sup> For example, 10 g of the dry copolymer particles were charged to a U-shaped glass tube. Before SO<sub>2</sub> absorption, the sample was pretreated as follows: degassed and further dried under vacuum at 70 °C for 1 h,

Table 1. Conditions and results of the inverse suspension copolymerization of TMGA and MBA.

Run	$M^{\text{a)}$	O/W <sup>b)</sup>	KPS <sup>c)</sup>	MBA <sup>c)</sup>	Span 60 <sup>c)</sup>	$T$	$r$	$t$	Yield
	%		%	%	%	°C	rpm	h	%
1	72	4/1	1	2	1	65	550	8	83.2
2	60	4/1	1	2	1	70	550	8	91.6
3	50	4/1	0.5	2	1	70	550	8	92.7

<sup>a)</sup> Weight percent of monomer in the aqueous phase.

<sup>b)</sup> Volume ratio of oil phase versus water/aqueous phase.

<sup>c)</sup> Weight percent based on the monomer mixture.

preheated to a predetermined temperature in a water bath, and then filled with nitrogen. The SO<sub>2</sub> gas from a gas cylinder was passed through a gas washing bottle filled with concentrated sulfuric acid to remove traces of water vapor, and entered into an aqueous solution of sodium hydroxide before venting. When the flow rate became stable (about 80 mL · min<sup>-1</sup>), SO<sub>2</sub> gas entered into the U-tube at a stable flow rate. Residual SO<sub>2</sub> flowed out of the U-tube and was collected by the NaOH aqueous solution. At a predetermined time, the SO<sub>2</sub> flew through a bypass and the U-tube was carefully removed from the system, sealed immediately, and then weighed with an electronic balance to determine the amount of SO<sub>2</sub> absorbed. The U-tube was then connected to the system again and the above operations were repeated until the U-tube reached a constant weight. The molar ratio (*R*) of absorbed SO<sub>2</sub> molecule to TMGA monomer unit in the copolymer is used as an index to quantify the absorption amount.

For the SO<sub>2</sub> desorption, the U-tube charged with the SO<sub>2</sub>-absorbed copolymer particles was first immersed in a water bath and heated to a set temperature. It was then vacuumed (~80 mmHg). At a given time, it was filled with nitrogen and then removed and weighed. The same operations were repeated until the weight of the U-tube leveled off.

### Characterization

The particle morphology was investigated by scanning electron microscopy (SEM, SEMJSM-100×). The sample was coated with gold using a sputter-coater and was then observed at 20 kV. The particle size distribution was determined with LS-230 Coulter particle size analyzer. Cyclohexane was used as the measurement medium. The pore size distributions and porosities of the copolymer particles were measured with a mercury intrusion method (PoreMaster-60, Quantachrome Co.).

## Results and Discussion

### Preparation and Characterization of Crosslinked Porous P(TMGA-co-MBA) Particles

Because both TMGA and PTMGA are very hydrophilic, the crosslinked copolymer of TMGA was synthesized via an inverse suspension copolymerization using water-soluble MBA as a crosslinking comonomer, as shown in Scheme 1. Cyclohexane was employed as the dispersion medium, and Span 60 that has an HLB value of 4.7 was used as the dispersant. Table 1 summarizes the polymerization conditions. Three samples were prepared with high yields. Unlike the previously synthesized water-soluble PTMGA homopolymer products, the crosslinked copolymer particles obtained in this work were swellable but no longer soluble in water. The swelling ratio was about 76 g water per gram polymer.

Figure 1 shows the P(TMGA-co-MBA) particle morphology. The optical microscope image [Figure 1(A)] indicated that spherical particles were readily formed in the inverse suspension copolymerization. The SEM image

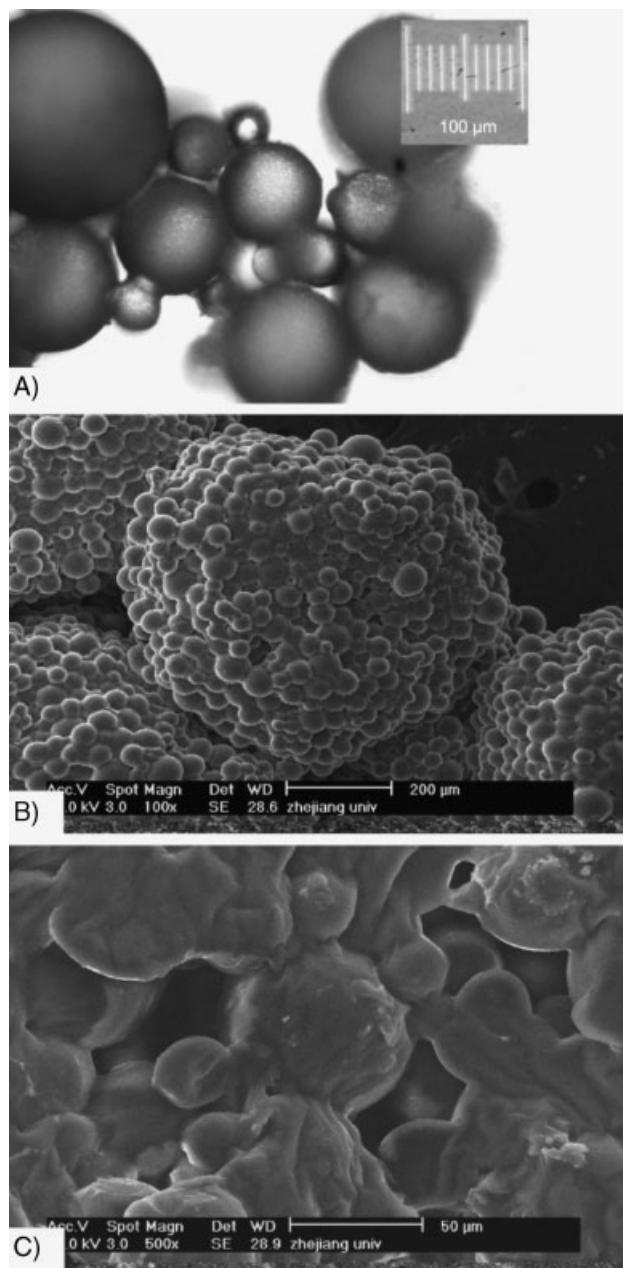


Figure 1. Optical microscope image of the P(TMGA-co-MBA) porous particles (A); SEM images of the particle surface (B) and a section (C) of the surface.

of the particle surface [Figure 1(B)] revealed that the macroscopic particles were composed of many smaller spherical subparticles. There were micropores formed at the interstitial spaces between adjacent subparticles [Figure 1(C)]. The subparticles were solid and no pores were observed. This result suggests that the subparticles were coagulated during the polymerization to form the macroscopic porous particles.

The particle size distributions of all the three samples were broad, as shown in Figure 2(A). The particle size increased with the monomer concentration in the aqueous

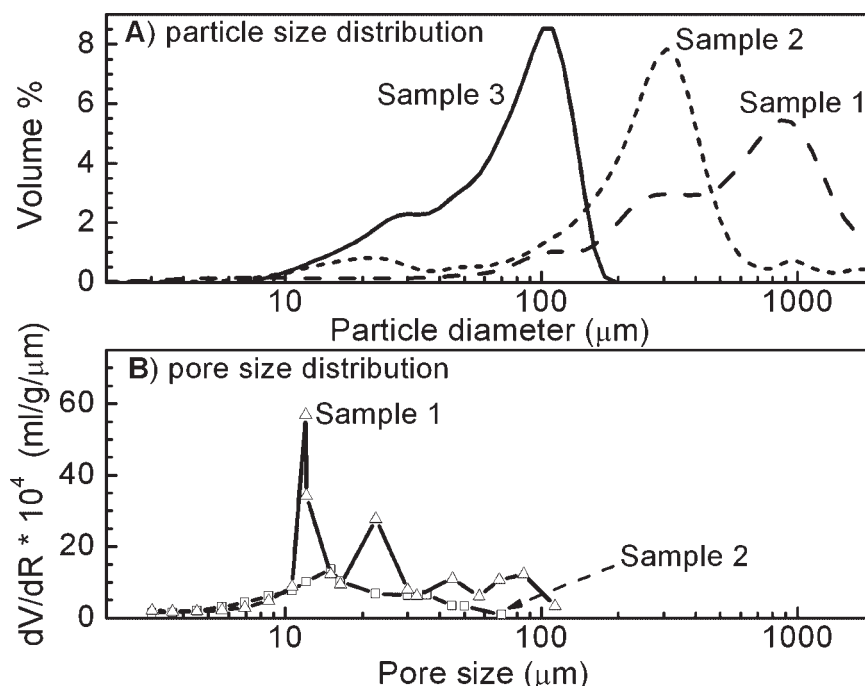


Figure 2. The particle size distributions (A) and pore size distributions (B) of the P(TMGA-co-MBA) samples prepared by an inverse suspension polymerization.

phase. The volume-average particle sizes were 457, 212, and 68  $\mu\text{m}$  for Samples 1, 2, and 3, respectively. The difference in the particle sizes may be resulted from the viscosity of the aqueous phase. Due to the high viscosity of the IL monomer TMGA, the aqueous phase (dispersed phase) with high monomer concentration was more viscous and became more difficult to disperse. Therefore, the sizes of the dispersed phases increased and so did the sizes of the coagulated macroscopic particles.

The pore size distributions of the macroscopic particles were measured by a mercury intrusion method, as shown in Figure 2(B). The apparent porosities were estimated to be 43 and 39% for Samples 1 and 2, respectively. Both interstitial spaces between the macroscopic particles and those between the subparticles contributed to the porosity. As the particle size distributions were very broad, the separate contributions of the two kinds of pores could not be clearly identified in Figure 1 and 2. However, based on the fact that a broad size distribution particle product has a porosity  $<26\%$  (note: packing monodispersed spheres yields a porosity of 26%), the true porosities inside the macroscopic particles of Samples 1 and 2 are estimated to be  $>17\%$  and  $>13\%$ , respectively. Both samples have an almost equal specific surface area of  $230 \text{ m}^2 \cdot \text{g}^{-1}$ .

#### *SO<sub>2</sub> Absorption/Desorption of P(TMGA-co-MBA) Particles*

The crosslinked P(TMGA-co-MBA) copolymer particles exhibited the  $\text{SO}_2$  absorption/desorption properties

comparable to the uncrosslinked PTMGA counterparts. However, the PTMGA materials shrank after the  $\text{SO}_2$  absorption, as shown in Figure 3(A) and 3(B). In contrast, the crosslinked particles kept their morphology unchanged, as shown in Figure 3(C) and 3(D). This is clearly advantageous in applications particularly when multiple absorption/desorption cycles are applied. This suggests that the plasticization effect of the absorbed  $\text{SO}_2$  (ref.<sup>[10]</sup>) was significantly weakened when the polymer was crosslinked.

Figure 3 also shows the change of color before and after the  $\text{SO}_2$  absorption. The fresh P(TMGA-co-MBA) materials were white spherical particles. When  $\text{SO}_2$  gas flowed through the U-tube, the color turned yellow quickly, and then gradually became orange, indicating chemical absorption occurred as previously described.<sup>[10]</sup> The fresh PTMGA materials were white to light yellow powder. It turned orange to red when  $\text{SO}_2$  was absorbed.

The crosslinked P(TMGA-co-MBA) particles were evaluated for the absorption-desorption cycles. Figure 4 shows the absorption/desorption kinetics in two cycles. The absorption was conducted at  $50^\circ\text{C}$  under atmospheric pressure. The desorption was at  $90^\circ\text{C}$  under vacuum. The absorption rate was high with an equilibrium absorption capacity ( $R_{\text{eq1}} = 1.35$ ) reached in less than 2 h. The desorption rate was slower with a lower equilibrium capacity ( $R_{\text{eq2}} = 0.52$ ) reached in over 3 h. In the desorption process, the color changed from orange to light yellow. The color did not return to the original white because some residual  $\text{SO}_2$  content ( $R_{\text{eq2}}$ ) remained at  $90^\circ\text{C}$ . In the subsequent cycles, the color repeated between orange and light yellow. The



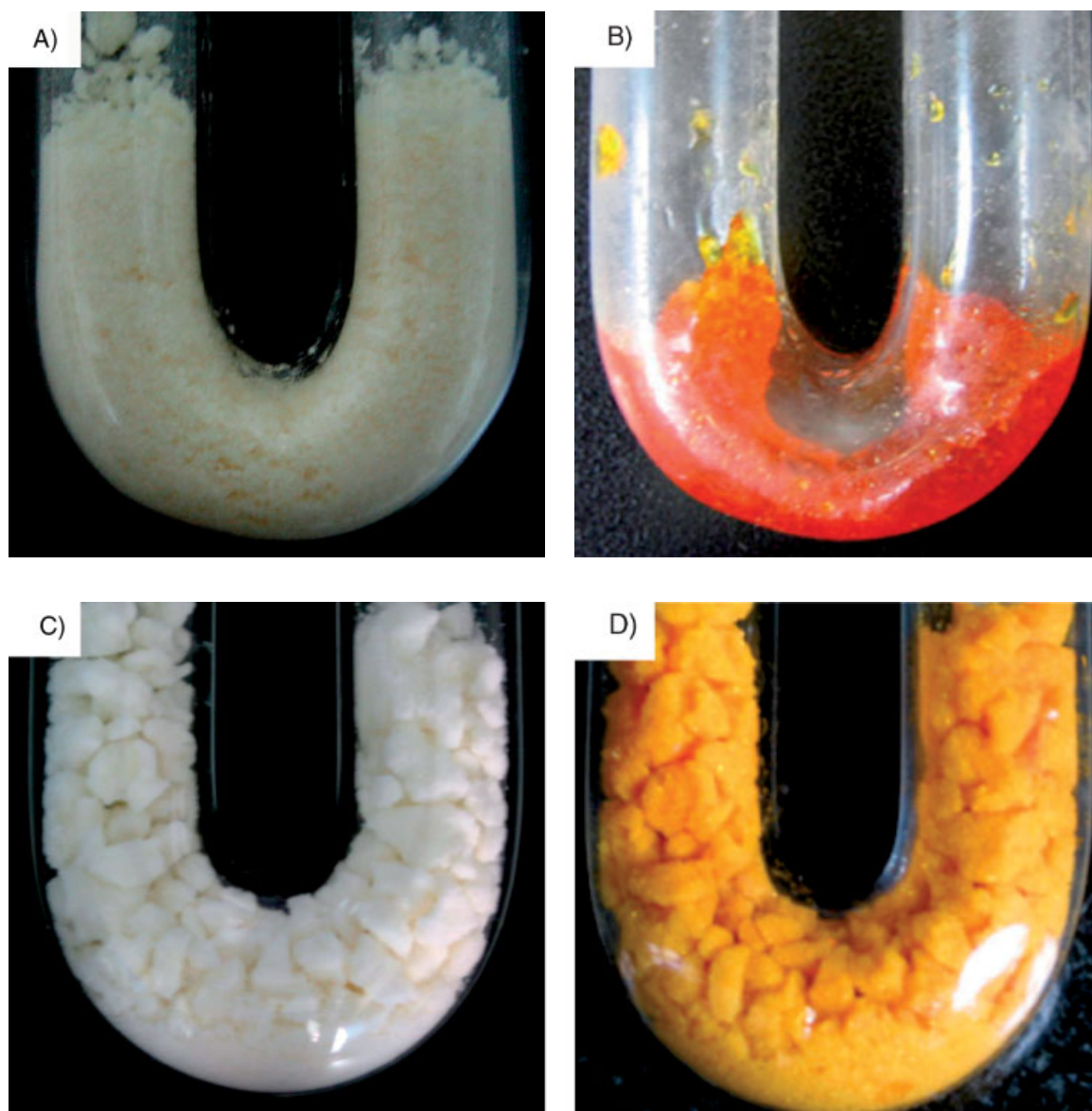


Figure 3. The appearance of PTMGA and P(TMGA-*co*-MBA) particles before and after SO<sub>2</sub> absorption (absorbed at 50 °C). (A) PTMGA, before absorption; (B) PTMGA, after absorption; (C) P(TMGA-*co*-MBA), before absorption; (D) P(TMGA-*co*-MBA), after absorption.

crosslinked polymer absorbent was stable and kept its absorption and desorption properties unchanged. In one cycle, 0.83 mol SO<sub>2</sub> per mol TMGA unit, i.e., 0.26 g SO<sub>2</sub> per gram P(TMGA-*co*-MBA) was removed.

The crosslinked P(TMGA-*co*-MBA) has higher equilibrium absorption capacities under the same conditions than its PTMGA counterpart ( $R_{eq1} = 1.15$  for PTMGA<sup>[10]</sup>). This enhanced absorption may be attributed to an increase in the surface area due to the porous structure of the crosslinked particles. As a result, the desorption became relatively difficult with a slower rate and higher content of the residual SO<sub>2</sub> ( $R_{eq2} = 0.35$  for PTMGA<sup>[10]</sup>). However, the SO<sub>2</sub>

amount removed in one absorption/desorption cycle was almost the same for the crosslinked copolymer and the linear homopolymer.

## Conclusion

Crosslinked P(TMGA-*co*-MBA) porous particles were directly synthesized via an inverse suspension copolymerization of TMGA and MBA using cyclohexane as the continuous phase and Span 60 as the dispersant. The materials exhibited excellent SO<sub>2</sub> absorption properties and

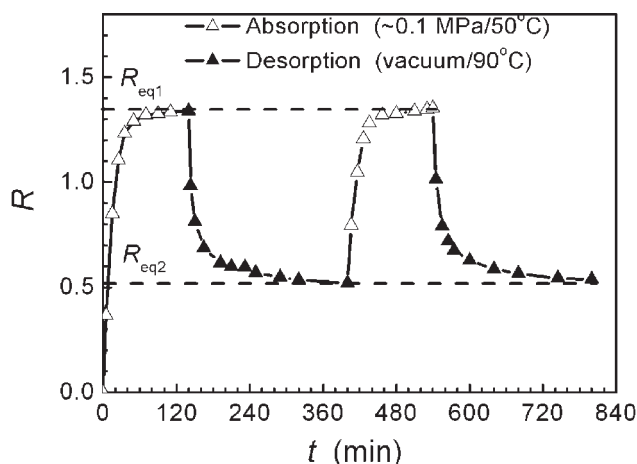


Figure 4.  $\text{SO}_2$  absorption-desorption cycles of the P(TMGA-co-MBA) particles.  $R$  is the molar ratio of  $\text{SO}_2$  absorbed to TMGA unit. In each cycle,  $\text{SO}_2$  was first absorbed at  $50^\circ\text{C}$  under atmospheric pressure and then desorbed at  $90^\circ\text{C}$  under vacuum.

could be reused in the  $\text{SO}_2$  absorption-desorption cycles. Compared to the linear water-soluble PTMGA, the cross-linked P(TMGA-co-MBA) was no longer soluble in water and kept the particle morphology (shape and volume) and the  $\text{SO}_2$  absorption properties unchanged during the  $\text{SO}_2$  absorption/desorption cycles. Such products are more stable and useful in applications as polymeric  $\text{SO}_2$  absorbent.

**Acknowledgements:** We thank NSFC (20304012, 20428605), the Prior Special Fund of National Basic Research Program of China (2004CCA05500) and the Natural Science Foundation of Zhejiang Province (No. Y404084) for financial supports. S. Zhu also thanks the JB program of NSFC and the CJC Program of Chinese Ministry of Education as well as Zhejiang University for supporting the collaboration.

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