Synthesis and SO2Absorption/Desorption Properties of Poly(1,1,3,3-tetramethylguanidine acrylate)

4 AUTHORS, INCLUDING:

Linbo Wu
Zhejiang University
48 PUBLICATIONS 1,111 CITATIONS

Shiping Zhu
McMaster University
333 PUBLICATIONS 7,997 CITATIONS

Synthesis and SO$_2$ Absorption/Desorption Properties of Poly(1,1,3,3-tetramethylguanidine acrylate)

Dong An,[†] Linbo Wu,*,[†] Bo-Geng Li,*,[†] and Shiping Zhu[‡]

State Key Laboratory of Polymer Reaction Engineering, Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China, and Department of Chemical Engineering and Department of Materials Science and Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada

ABSTRACT: A novel ionic polymer, poly(1,1,3,3-tetramethylguanidine acrylate) (PTMGA), was synthesized, and its SO$_2$ absorption and desorption properties were studied for the first time. 1,1,3,3-Tetramethylguanidine acrylate, a polymerizable ionic liquid (IL), was first prepared via neutralization of 1,1,3,3-tetramethylguanidine and acrylic acid. PTMGA was then synthesized via free radical polymerization of TMGA. The polymer adsorbed SO$_2$ with high selectivity, capacity, and rate. The absorption capacity and rate of PTMGA were significantly higher than the monomer. The SO$_2$ absorbed at a relatively low temperature was effectively desorbed at higher temperatures and/or under vacuum. The absorption/desorption process could be repeatedly operated, and thus the polymer was reused. Under a typical operation condition, about 0.3 g of SO$_2$ per gram of polymer was separated in each cycle. The PTMGA material showed a good potential as solid-state SO$_2$ absorbent for applications in purification of SO$_2$-containing gas such as fuel gas desulfurization.

Introduction

Ionic liquids (ILs) have many special properties that include extremely low vapor pressure, high thermal and chemical stability, and excellent solvent power for organic and inorganic compounds.[1] Most ILs are nonflammable and lowly toxic. As an alternative to volatile organic compounds (VOCs) and metallic catalysts, ILs have been extensively investigated as green media for separation and organic catalysts for reaction.[1−3] In addition, it has been reported that ILs can dissolve or absorb some gases such as CO$_2$,[4−9] ethylene,[8,9] ethane,[9] etc., especially at high pressure. This characteristic of ILs provides a new opportunity for gas separation and purification.

Recently, Han et al. synthesized ionic liquids based on 1,1,3,3-tetramethylguanidine (TMG) by directly neutralizing TMG with acids[10] and found that 1,1,3,3-tetramethylguanidine lactate (TMGL) was able to absorb SO$_2$ from a simulated fuel gas with high absorption capacity and selectivity.[11] Riisager et al. also reported the SO$_2$ absorption behaviors of other ILs.[12] Selective absorption and desorption of SO$_2$ by ILs may find applications in treatment of SO$_2$-containing gases such as fuel gas desulfurization (FGD).[11,12] This may provide a new opportunity for air cleaning considering that SO$_2$ emission from fossil-fuel combustion is one of the major air pollutants.

It has been reported that the CO$_2$ absorption capacity of some ILs can be significantly enhanced when the ILs are converted to corresponding polymers.[13] In addition, the high viscosity and other inherent disadvantages such as large investment and high operation cost of wet desulfurization make ILs inferior to solid absorbents used for dry desulfurization. Solid-state polymeric absorbents may be more attractive in practicability than their liquid counterparts. In this study, we synthesize 1,1,3,3-tetramethylguanidine acrylate (TMGA) by simple neutralization

* Corresponding authors. Linbo Wu: Tel +86-571-87952631; Fax +86-571-87951612. Bo-Geng Li: Tel +86-571-87952623; Fax +86-571-87952623.
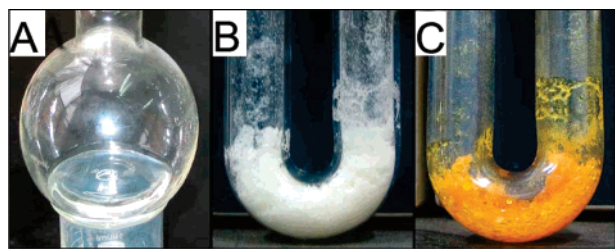† Zhejiang University.
‡ McMaster University.

Scheme 1. Synthesis of TMGA (3) and PTMGA (4) Using TMG (1) and AA (2) as Starting Materials and Possible Chemical Absorption Mechanism of PTMGA
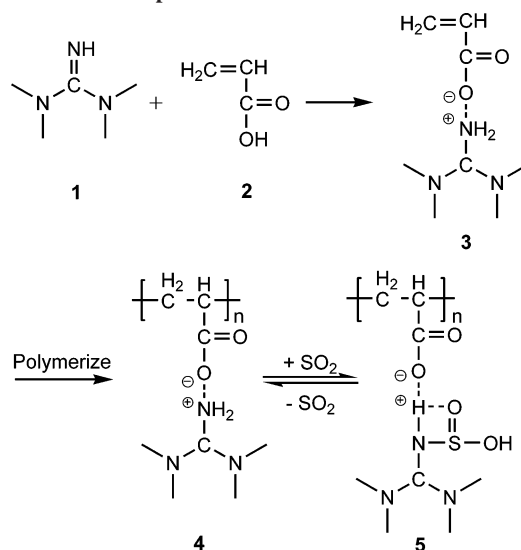
of TMG with acrylic acid and polymerize the IL monomer via the free radical mechanism to its corresponding ionic polymer, poly(1,1,3,3-tetramethylguanidine acrylate) (PTMGA) (see Scheme 1). Our objective is to investigate the SO$_2$ absorption and desorption properties of PTMGA. We attempt to develop a novel polymeric absorbent for SO$_2$ purification with high selectivity, capacity, and rate.

Experimental Section

Materials. Acrylic acid (AA, C.P., Sinopharm Chemical Reagent Co., Ltd., China) was distilled under vacuum prier to use. 1,1,3,3-Tetramethylguanidine (TMG, ≥99.2%, Zibo Senjie Chemical Auxiliary Co., Ltd, China) and potassium persulfate (KPS, ≥99.5%, Yixing Second Chemical Reagent Factory, China) were used without further purification. Sulfur dioxide (SO$_2$, ≥98.0%), oxygen (O$_2$, ≥99.99%), hydrogen (H$_2$, ≥99.99%), nitrogen (N$_2$, ≥99.5%),
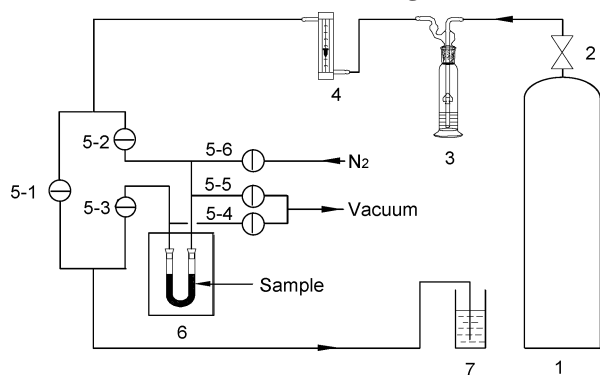
Figure 1. Appearance of (A) monomer TMGA, (B) polymer PTMGA, and (C) SO₂-saturated PTMGA sample (absorbed at 50 °C).

Scheme 2. Experimental Apparatus for Gas Absorption and Desorption of PTMGA and TMGA: 1, Gas Cylinder; 2, Reducing Valve; 3, Dryer; 4, Rotary Flowmeter; 5-1 to 5-6, Valves; 6, Paraffin Bath; 7, Gas Outlet (Adsorbed by NaOH Solution before Venting)

and carbon dioxide (CO₂, ≥99.995%) were all purchased from Hangzhou Jingong Special Gas Co. Ltd. and used as received.

Synthesis of TMGA. 1,1,3,3-Tetramethylguanidine acrylate (TMGA, **3**) was synthesized via direct neutralization of TMG (**1**) and acrylic acid (**2**) under nitrogen atmosphere (see Scheme 1). TMG (46.69 g, 0.4 mol) and H₂O (100 mL) were first added to a dried 250 mL three-neck flask. The flask was equipped with a reflux condenser and magnetic stirrer and was immersed in a thermostatically controlled water bath (25 °C). Acrylic acid (28.88 g, 0.4 mol) was then added dropwise in 30 min. The reaction was continued at room temperature for 4 h, and the reaction mixture was then vacuum-distilled at 70 °C to remove water and unreacted TMG and AA. Finally, a colorless, transparent and hygroscopic TMGA liquid (see Figure 1A) was produced with a yield of 97%. FTIR: C−H in −CH₃ (2953.2 cm⁻¹), CH₃−N (2816.0 cm⁻¹), C−N (1085.5 cm⁻¹), N−H (3277.9, 3107, 1646.8 cm⁻¹), C=O (1720 cm⁻¹), and C=N (1608.9 cm⁻¹).

Synthesis of PTMGA. Poly(1,1,3,3-tetramethylguanidine acrylate) (PTMGA, **4**) was synthesized via free radical polymerization of TMGA. Potassium persulfate (KPS, 0.7 wt % based on the monomer) was added to the prepared aqueous solution of TMGA. The polymerization was carried out at 80 °C for 6 h under nitrogen protection. At the end of polymerization, a few drops of 1,4-dihydroxybenzene aqueous solution (0.3 wt % based on the monomer) were added as inhibitor. The resulting mixture was distilled under vacuum at 70 °C over 12 h. The PTMGA sample was collected with a yield of 86%. The solid was crushed and stored in a desiccator prior to use. ¹H NMR (500 MHz, (CD₃)₂SO, δ: ppm): 2.50 (1H, −CH−), 2.76 (s, 12H, N−CH₃), 5.75(2H, =NH₂). FTIR: C−H in CH₃ (2949.2 cm⁻¹), CH₃−N (2803.7 cm⁻¹), C−N (1037.5 cm⁻¹), N−H (3282.0, 3114.5, 1648.9 cm⁻¹), C=O (1720.2 cm⁻¹), C=N (1609.7 cm⁻¹).

SO₂ Absorption and Desorption. Scheme 2 shows the SO₂ absorption and desorption apparatus. For SO₂ absorption, 10 g of dried PTMGA powder was charged to a U-shaped glass tube (80 mm high and 15 mm in diameter). Valves 5-1, 5-2, 5-3, and 5-6 were closed, and valves 5-4 and 5-5 were opened. The sample was degassed and further dried under vacuum at 70 °C for 1 h before

it was preheated to a predetermined absorption temperature. Valves 5-4 and 5-5 were then closed, and valve 5-6 was opened to fill the U-tube with nitrogen. After the nitrogen pressure reached an atmospheric pressure (regulated by valve 5-2 if needed), valve 5-6 was closed. Valves 2 and 5-1 were opened one after another. The SO₂ gas from a gas cylinder passed through a gas washing bottle filled with concentrated sulfuric acid to remove trace water vapor and entered into an aqueous solution of sodium hydroxide before venting. When the SO₂ gas flow rate became stable (about 80 mL/min), valve 5-1 was closed and at the same time valves 5-2 and 5-3 were opened. The SO₂ gas entered into the U-tube at a stable flow rate. Residual SO₂ flowed out of the U-tube and was collected by the NaOH aqueous solution. At a predetermined time, valve 5-1 was opened and valves 5-2 and 5-3 were closed. The U-tube was carefully removed from the system, sealed immediately, and then weighed with an electronic balance (100 g in capacity and 0.1 mg in sensitivity) to determine the amount of SO₂ 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 absorptions of other gases were conducted following the same procedure.

For SO₂ desorption, the U-tube charged with the SO₂-absorbed PTMGA was connected to the system. All the valves were closed before the U-tube was heated to a given temperature. Valves 5-4 and 5-5 were then opened to start the SO₂ desorption process (under vacuum ~80 mmHg). At a given time, valves 5-4 and 5-5 were closed, and valve 5-6 was opened to fill the U-tube with nitrogen. The U-tube was then removed and weighed. The same operations were repeated until the weight of the U-tube leveled off.

Characterization. The molecular weight distribution of PTMGA was measured at 30 °C by gel permeation chromatography (GPC, Waters 2690/2410) equipped with three poly(ethylene glycol) (PEG) columns (Ultrahydrogel column: 120 7.8 × 300 mm, 500 7.8 × 300 mm, and 1000 7.8 × 300 mm) and a Waters 2410 refractive index detector. The eluent (0.8 mL/min) was an aqueous solution of NaNO₃ (0.1 M). The glass transition temperature (T_g) and melting point (T_m) of PTMGA were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-7 thermal analyzer. The heating rate was of 20 °C/min, and the determination of T_g and T_m was based on the second scan. Thermogravimetric analysis (TGA) of PTMGA was conducted on a Perkin-Elmer Instrument Pyris 1 TGA under nitrogen with a heating rate of 10 °C/min. The FTIR spectra of TMGA, PTMGA, and SO₂-absorbed PTMGA were measured on a Nicolet 5700 infrared spectrometer. The ¹H NMR spectra of PTMGA and SO₂-adsorbed PTMGA were recorded on an Advance DMX 500 (500 MHz) spectrometer using (CD₃)₂SO as solvent and tetramethylsilane (TMS) as an internal reference.

Results and Discussion

Synthesis and Thermal Properties of PTMGA. TMGA was a colorless, transparent, hygroscopic, and polymerizable ionic liquid with a melting point of −20.1 °C (Figure 1A). It was SO₂-absorbable itself. However, it is very viscous (13.6 Pa·s at 25 °C), and its viscosity increased in the absorption process. We are more interested in its polymer as a solid absorbent material. TMGA is readily polymerized to obtain PTMGA in bulk or aqueous solution via free radical mechanism. A yield of 86.0% was obtained in an aqueous solution polymerization with potassium persulfate (KPS) as initiator. The sample has a weight-average molecular weight 18 000 g mol⁻¹ and a polydispersity 1.73. The material is a white solid (see Figure 1B) and is strongly hygroscopic and water-soluble.

As a polymeric absorbent, it must be thermally stable to endure the operation temperature of gas absorption and desorption. Figure 2A shows the DSC curve of PTMGA. It has a glass transition temperature (T_g) of 93.5 °C. The onset temperature of glass transition is 86 °C. Figure 2B shows the result of thermogravimetric analysis (TGA). A weight loss of about 9%
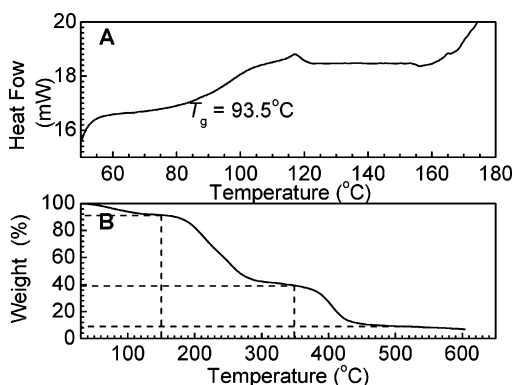
Figure 2. (A) DSC and (B) TGA curves of PTMGA. The heating rates were 20 °C/min (DSC) and 10 °C/min (TGA).
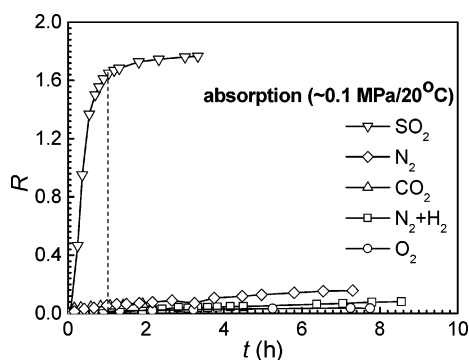

Figure 3. Absorption behaviors of PTMGA for various gases (SO_2, N_2, CO_2, $N_2 + H_2$, O_2) at 20 °C and under atmospheric pressure.

Figure 4. (A) SO_2 absorption of PTMGA under atmospheric pressure (~0.1 MPa) followed by (B) SO_2 desorption under vacuum at the same temperature. Four absorption/desorption temperatures are 20, 50, 75, and 90 °C.

Figure 5. Desorption of SO_2-saturated PTMGA (absorbed at atmospheric pressure and 50 °C) under atmospheric pressure and at high temperatures: 125 and 140 °C.

at the early stage was observed because PTMGA is very hygroscopic. The polymer is stable up to 150 °C. An obvious weight loss was observed at >170 °C. The weight reached a plateau at about 350 °C and further decreased at >370 °C. The final residue above 480 °C was 9%. The weight losses at the two plateaus were 52% and 30%, respectively. We attributed the former to the cleavage of the ionic bond between carboxyl anion and 1,1,3,3-tetramethylguanidine cation and the latter to the pyrolysis of polymer backbone. This hypothesis was validated by the FTIR spectrum of a PTMGA sample heated to 350 °C and by its lack of SO_2 absorption capacity (see Supporting Information). On the basis of its thermal properties, PTMGA may be a good candidate for SO_2 absorption at temperature lower than 90 °C.

SO_2 Absorption. The experiments on gas absorption were carried out under atmospheric pressure (~0.1 MPa) and at various temperatures. Various gases that include SO_2, N_2, CO_2, $N_2 + H_2$, and O_2 were tested. The color of PTMGA material in the U-tube changed from white to orange upon exposure to SO_2 gas at 50 °C, as shown in Figure 1C. In addition, the PTMGA powder collapsed and its volume shrunk to some extent. This may be caused by a plasticization effect of absorbed SO_2 on the polymer. The weight of the material increased and eventually leveled off in the SO_2 absorption. However, the changes in weight were not obvious in the absorption of other gases. The molar ratio (R) of absorbed gas molecule to TMGA monomer unit in the polymer is used as an index to quantify the absorption amount. As shown in Figure 3, the polymer is very selective toward SO_2 absorption. The SO_2 absorption process was rapid and soon reached an equilibrium capacity (R_{eq1}) of 1.75. In contrast, the absorptions of other gases were much slower and their capacities were lower than 0.15.

Temperature has a strong effect on the SO_2 absorption property of PTMGA. The colors of SO_2-saturated PTMGA
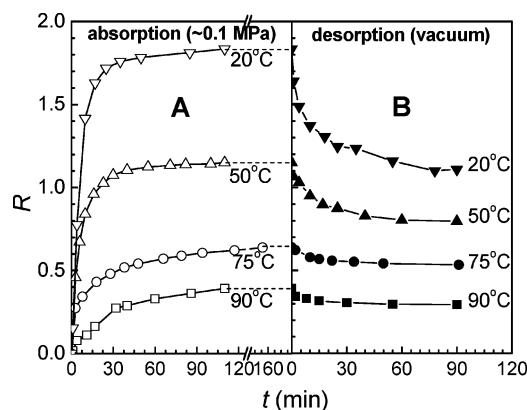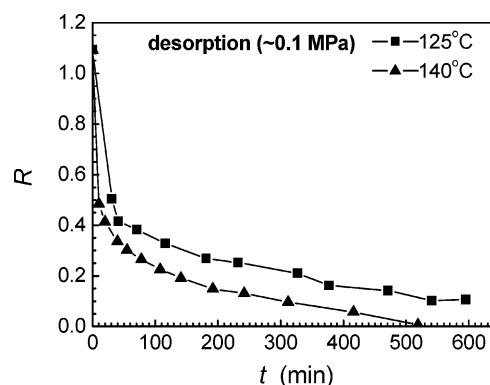
samples were different at different temperatures: orange at 20 and 50 °C, yellow at 70 °C, and light yellow at 90 °C. As shown in Figure 4A, a high equilibrium absorption capacity (R_{eq1}) and a high absorption rate were observed at room temperature, but the capacity and rate decreased significantly with temperature. The R_{eq1} value reached 1.80 (i.e., 0.62 g of SO_2/g of polymer) at 20 °C but reduced to 0.39 (0.13 g of SO_2/g of polymer) at 90 °C. This result shows that high temperature is not a favorable condition for SO_2 absorption using the PTMGA material. However, it may be advantageous to absorb SO_2 at low temperature and regenerate the absorbent through desorption at high temperature.

SO_2 Desorption. The SO_2 molecules absorbed at low temperature were readily desorbed at high temperature. The higher the temperature, the more complete the SO_2 desorption. A complete desorption was achieved at 140 °C, as shown in Figure 5. However, the desorption rate was low under an atmospheric pressure. It took 8−10 h to reach the desorption equilibrium even at 125−140 °C. Moreover, the polymer material softened at temperature higher than its T_g. An alternative approach is to desorb SO_2 under a reduced pressure (or vacuum). The amount of absorption decreased gradually to another lower equilibrium value (R_{eq2}), as shown in Figure 4B. This result suggests that the pressure has an important influence on the desorption rate. The desorption process at a reduced pressure is driven by the diffusion of SO_2 molecules from polymer particle surface to gas phase.

Four PTMGA samples saturated with SO_2 at 50 °C and under atmospheric pressure were subject to vacuum at temperatures ranging from 50 to 110 °C. Figure 6 shows the results. The
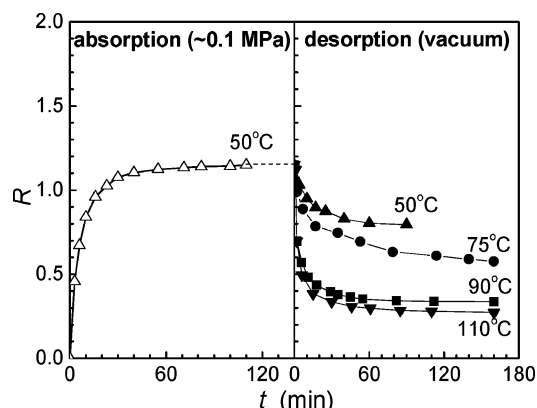
Figure 6. Desorption of SO_2-saturated PTMGAs (absorbed under atmospheric pressure and at 50 °C) under vacuum and at various temperatures: 50, 75, 90, and 110 °C.
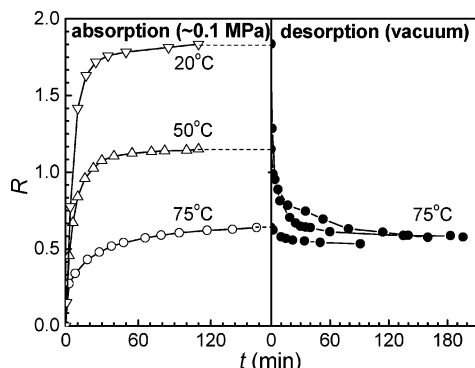

Figure 7. Desorption under vacuum and at 75 °C of three SO_2-saturated PTMGAs containing SO_2 absorbed under atmospheric pressure and at various temperatures: 20, 50, and 75 °C.

SO_2 amount decreased gradually with time and leveled off at a final equilibrium value (R_{eq2}). The SO_2 absorbed at a relatively low temperature can be partially but effectively removed under vacuum at higher temperature. Under this combined condition of elevating temperature and reducing pressure, the desorption was more complete and the rate was higher than that of elevating temperature or reducing pressure alone. The R value decreased from the original R_{eq1} 1.16 to the final R_{eq2} 0.79 at 50 °C and to 0.27 at 110 °C. However, the time required to reach R_{eq2} appeared to be independent of the desorption temperature. It took about 1 h to reach the equilibrium R_{eq2}. In the desorption process, the color of the polymer material was lightened to various extents depending on desorption temperature. It turned light yellow at 90 and 110 °C.

In another desorption experiment, three PTMGA samples saturated with SO_2 at 20, 50, and 75 °C were vacuumized at 75 °C. Similar desorption kinetics were observed as shown in Figure 7. The R_{eq2} value reached the same level of 0.56 ± 0.03 in 1 h for all the samples. It suggests that the R_{eq2} is independent of the absorption condition and is determined only by the desorption condition. Both absorption and desorption are equilibrium processes that are determined only by thermodynamic state, namely, temperature and pressure. Change in the state results in a new equilibrium. The rate of desorption is determined by the extent of change of the state, i.e., the differences of temperature and pressure. Both temperature and pressure play important roles in desorption.

The equilibrium absorption capacities R_{eq1} and R_{eq2} at atmospheric pressure and under vacuum are plotted as a function of temperature in Figure 8. The data obtained under the same conditions were averaged, and the standard errors were provided.
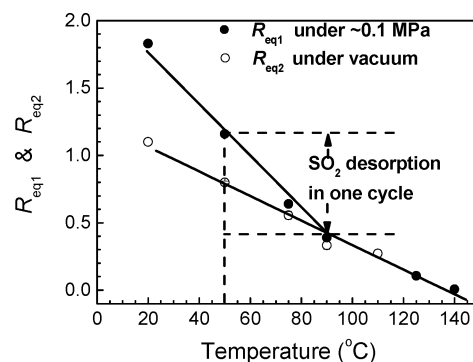

Figure 8. Influence of temperature on the SO_2 absorption: filled circle, absorption under atmospheric pressure; empty circle, absorption under vacuum (i.e., the residual SO_2 after desorption under vacuum).
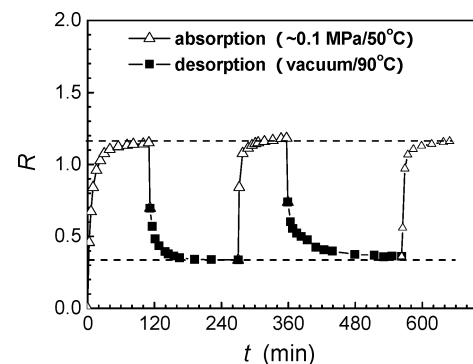

Figure 9. Absorption−desorption cycles of PTMGA. In each cycle, SO_2 is absorbed under atmospheric pressure and at 50 °C and desorbed under vacuum and at 90 °C.
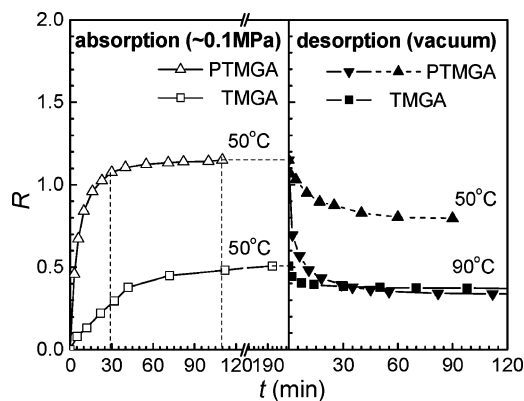

Figure 10. Comparison of SO_2 absorption and desorption behaviors of the monomer TMGA and the polymer PTMGA.

Both R_{eq1} and R_{eq2} decreased linearly with temperature from 20 to 90 °C. At temperature higher than 90 °C, R_{eq1} and R_{eq2} became equal and followed a single $R-T$ line. The absolute R_{eq2} was mainly determined by temperature while the difference $R_{eq1} - R_{eq2}$ was determined by the pressure change. They both decreased with an increase in temperature. The contribution from pressure became negligible when temperature was >90 °C.

SO₂ Absorption/Desorption Cycles. The polymer absorbent can be reused in absorption−desorption cycles. The operation conditions for a required desorption ability can be designed using Figure 8. Figure 9 shows the kinetics of absorption−desorption cycles (absorption at 50 °C and desorption at 90 °C). Both absorption and desorption rates were high, and the equilibrium absorption capacities (R_{eq1} and R_{eq2}) were reached in 1 or 2 h. In the first cycle, the fresh polymer changed its color from white
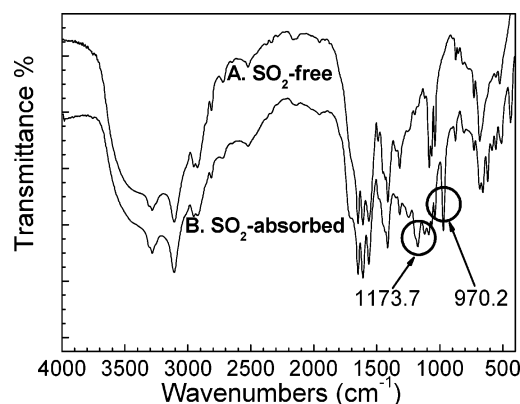
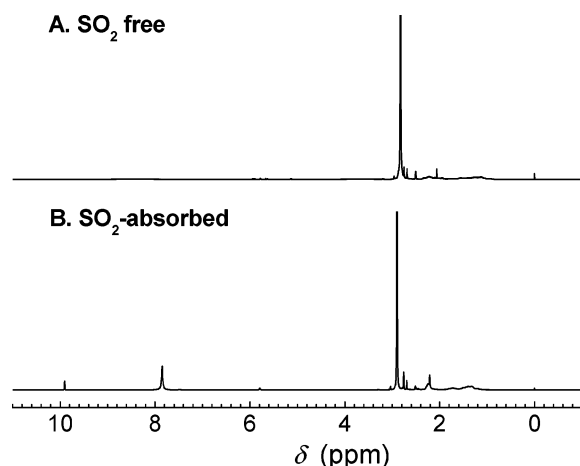**Figure 11.** FTIR spectra of (A) SO_2-free and (B) SO_2-absorbed PTMGA.

Figure 12. ^1H NMR spectra of (A) SO_2-free and (B) SO_2-absorbed PTMGA.

to orange during the absorption process and changed to light yellow during the desorption process. The color did not return to white because some residual SO_2 remained at 90 °C. In the subsequent cycles, the color repeated between orange and light yellow. The R_{eq1} was 1.15 at 50 °C and the R_{eq2} 0.35 at 90 °C. In one cycle, 0.8 mol of SO_2 per mole TMGA unit; i.e., 0.27 g of SO_2 per gram of PTMGA was removed. The PTMGA absorbent was stable and kept its absorption and desorption properties unchanged, as shown in Figure 9.

Comparison between PTMGA and TMGA. The absorption and desorption behaviors of the polymer and the monomer absorbents were compared. Figure 10 shows absorption at 50 °C under atmospheric pressure and desorption at 90 °C under vacuum. The equilibrium absorption capacity of the polymer is twice as high as the monomer. The absorption rate of the former is also more rapid. Similar enhancement has reported for CO_2 absorption using poly(ionic liquid)s.[13,14] When the SO_2-satuated polymer and monomer were desorbed at 90 °C under vacuum, the desorption amount of the monomer was also lower than that of the polymer. The SO_2 absorption capacity of PTMGA is higher than TMG lactate[11] but comparable to $[TMGB_2]$ $[BTA]$.[12]

Mechanism of SO_2 Absorption. Han et al. reported that TMGL absorbed SO_2 both chemically and physically.[11] However, it is interesting that Riisager et al. in a very recent paper found physical absorption only with the ionic liquids they investigated.[12] For our PTMGA polymer, the physical absorption does occur and plays an important role because the absorption capacity at room temperature is much higher than one SO_2 per TMGA unit, i.e., the maximum capacity of chemical absorption.

At the same time, chemical interaction between the TMG moiety and SO_2 was also observed in both FTIR and ^1H NMR spectra of SO_2-free and SO_2-absorbed samples. In the FTIR spectra shown in Figure 11, the common peaks for both samples are C—H in —CH_3 (2953.2 cm^{-1}), CH_3—N (2816.0 cm^{-1}), C—N (1085.5 cm^{-1}), N—H (3277.9, 3107, 1646.8 cm^{-1}), C=O (1720 cm^{-1}), and C=N (1608.9 cm^{-1}). In addition, two new peaks appeared at 1173.7 and 970.2 cm^{-1} in the SO_2-absorbed sample. This suggests that there existed chemical interactions between SO_2 molecule and amine moiety of the polymer. These two extra absorption peaks are attributed to the extension vibration of the S=O and S—O group, respectively. In the ^1H NMR spectra (Figure 12), two new resonances were observed at 7.86 and 9.91 ppm for the SO_2-absorbed polymer. They are attributed to the formation of S=O···H and S—O—H bonds. A piece of additional information is the change of color during absorption that indicates chemical reactions. We therefore believe the coexistence of both chemical and physical absorption mechanisms in our system.

In summary, a novel ionic polymer PTMGA was synthesized via free radical polymerization of a polymerizable ionic liquid monomer TMGA, and its SO_2 absorption and desorption properties were studied for the first time. It is shown that PTMGA is able to absorb SO_2 with high selectivity, capacity, and rate. The polymer absorption capacity and rate are significantly higher than the monomer. The absorption temperature and pressure have a strong influence on the absorption and desorption behaviors. Low temperature favors high absorption capacity. Therefore, SO_2 absorbed at low temperature can be effectively desorbed at high temperature and/or under vacuum. The polymer material is stable and can be reused in the absorption/desorption cycles. In a typical operation, about 0.3 g of SO_2 per gram of polymer can be removed in each cycle. Our work has demonstrated that the ionic polymer has high selectivity, capacity, rate, and reusability in SO_2 absorption and separation. The material appears to have good potential in applications as a solid-state SO_2 absorbent in FGD and other fields that require purification of SO_2-containing gases.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2083.
(2) Sheldon, R. *Chem. Commun.* **2001**, *23*, 2399−2407.
(3) Kubisa, P. *Prog. Polym. Sci.* **2004**, *29*, 3−12.
(4) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 5300−5308.
(5) Kamps, A. P.-S.; Tuma, D.; Xia, J. Z.; Maurer, G. *J. Chem. Eng. Data* **2003**, *48*, 746−749.
(6) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, Jr., J. H. *J. Am. Chem. Soc.* **2002**, *124*, 926−927.
(7) Scovazzo, P.; Camper, D.; Kieft, J.; Poshusta, J.; Koval, C.; Noble, R. *Ind. Eng. Chem. Res.* **2004**, *43*, 6855−6860.
(8) Camper, D.; Scovazzo, P.; Koval, C.; Noble, R. *Ind. Eng. Chem. Res.* **2004**, *43*, 3049−3054.
(9) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2002**, *106*, 7315−7320.

(10) Gao, H. X.; Han, B. X.; Li, J. C.; Jiang, T.; Liu, Z. M.; Wu, W. Z.; Chang, Y. H.; Zhang, J. *Synth. Commn.* **2004**, *34*, 3083−3089.

(11) Wu, W. Z.; Han, B. X.; Gao, H. X.; Liu, Z. M.; Jiang, T.; Huang, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 2415−2417.

(12) Huang, J.; Riisager, H.; Wasserscheid, P.; Fehrmann, R. *Chem. Commun.* **2006***, 38*, 4027−4029.

(13) Tang, J. B.; Sun, W. L.; Tang, H. D.; Radosz, M.; Shen, Y. Q. *Macromolecules* **2005**, *38*, 2037−2039.

(14) Tang, H. D.; Tang, J. B.; Ding, S. J.; Radosz, M.; Shen, Y. Q. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1432−1443.