

Effect of Crosslinked Structure on SO₂ Gas Sorption Properties in Amino-Functional Copolymers

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ABSTRACT: SO₂ gas sorption properties were examined for poly(styrene-co-chloromethyl styrene) functionalized with *N,N*-dimethyl-1,3-propanediamine (DMPDA). The DMPDA-functional copolymers were prepared under various reaction conditions. Two types of SO₂ sorption behaviors were observed for these DMPDA-functional copolymers: SO₂ sorption capacity was very high irrespective of slow sorption/desorption rates (type I), and the sorption/desorption rates were very fast while SO₂ sorption capacity was small (type II). Fourier transform infrared analysis and dielectric loss measurement revealed that the type II sorption behavior was obtained for the highly crosslinked

DMPDA-functional copolymers. The degree of crosslinking was affected by both the solvent used to react DMPDA with the copolymer and the percent conversion of the chloromethyl styrene group. It was confirmed that DMPDA-functional copolymers having a highly crosslinked structure are suitable materials in quartz crystal microbalance (QCM)-type polymeric SO₂ gas sensors. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2982–2987, 2003

Key words: adsorption; crosslinking; functionalization of polymers; sensors

INTRODUCTION

Many studies on the development of practical SO₂ gas sensors have been reported. Most of these utilize ceramics such as stabilized zirconia,¹ other solid electrolytes,^{2–5} or metal oxides^{6,7} for the sensing materials. In contrast, only a few reports have appeared on polymeric materials as sensing materials.^{8–13} It is well known that SO₂ a strong Lewis acid gas, is absorbed by the basic amino group, and most reports on polymeric SO₂ sensors have utilized amino-functional compounds as sensor coatings.^{9–13} However, each of these had one or more shortcomings, such as slow response, high detection limit, high operating temperature, low selectivity, and/or lack of long-term stability. Our previous investigation showed that amino-functional poly(styrene-co-chloromethyl styrene) derivatives containing siloxane oligomer provided fast response and good recovery around room temperature (50°C).¹⁴ Nevertheless, it has also become apparent that, for the practical use of these copolymers, further enhancement of their sensitivity and reduction of their response time are necessary. Toward these ends, we have been studying the optimization of the conditions needed to prepare the amino-functional copolymers as the sensor coatings. In this article, we investigated the effects of different preparation condi-

tions and of the resulting crosslinked structures of the amino-functional copolymers on SO₂ sorption.

EXPERIMENTAL

Synthesis of DMPDA-functional St-CMSt copolymers

A *N,N*-dimethyl-1,3-propanediamine (DMPDA)-functional styrene-co-chloromethyl styrene (St-CMSt) polymer was synthesized according to the literature.¹⁵ First, the St-CMSt copolymer was synthesized. The CMSt mole fraction in the copolymer determined by elemental analysis was 0.21 in this study. Then, 0.5 mol/L of St-CMSt copolymer was reacted with 1.0 mol/L of DMPDA. The alkylation reaction to produce aminated copolymers was performed in four different solvents: toluene, (*o*-*m*-*p*-)xylene, tetrahydrofuran, and 1,4-dioxane under a nitrogen purge. Various reaction times (within 2 h) were allowed at room temperature, resulting in DMPDA-functional copolymers having different amino contents dissolved in solvent. The procedures of the synthesis were described in detail previously.¹⁴ The possible chemical structure of the prepared DMPDA-functional copolymers is shown in Figure 1. In this figure, structure (A) shows the unreacted chloromethyl styrene, (B) and (C) show pendant amine groups that arose from the reaction of one of the two amines of DMPDA with the chloromethyl styrene group, and (D) shows the crosslinked structure that arose from the reaction of both amines of DMPDA with the chloromethyl styrene group.

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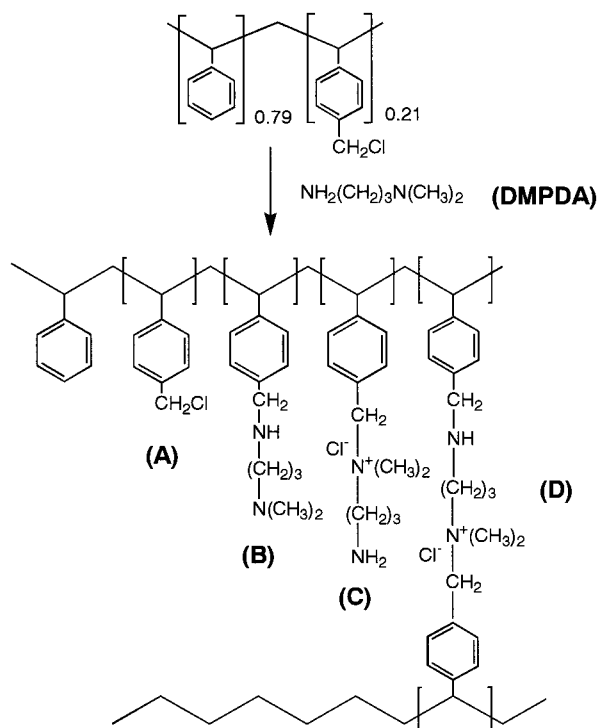


Figure 1 Chemical structure of a DMPDA-functional copolymer.

Preparation of devices for measurements

For the measurement of SO_2 sorption properties of the DMPDA-functional copolymer films, a quartz crystal microbalance (QCM)-type device was prepared as follows. The solution of DMPDA-functional copolymer was spin coated on an AT-cut quartz crystal (4 MHz resonant frequency) with a silver electrode on each side. The film was then postheated at 80°C for 2 h under vacuum to evaporate the unreacted monomer and the solvent. The thickness of the film was around $2\ \mu\text{m}$ for all measuring devices. Figure 2(a) illustrates the QCM-type device.

A sandwich-type device [Fig. 2(b)] was also prepared for the dielectric loss measurement as follows. The solution of DMPDA-functional copolymer was spin coated on a 4-in. alumina substrate with a Pt thin film lower electrode. After postheating at 80°C for 2 h under vacuum, a gold upper electrode was deposited by vacuum evaporation.

Measurements

The film-coated quartz crystal was placed in a thermostated small vessel. After the steady frequency had been obtained in N_2 atmosphere, the time-dependent oscillation frequency was recorded during exposure to the film for 50 ppm of SO_2 diluted with N_2 for 60 min; then the atmosphere was turned back to N_2 . Each sample gas was allowed to flow over the sensor at a rate of $50\ \text{cm}^3/\text{min}$. The variation in the resonant frequency of the crystal

was measured with a universal counter (Advantest, TR 5822, Tokyo, Japan). The underlying principle of QCM is based on changes Δf (Hz) in the fundamental oscillation frequency f_0 upon mass changes on the crystal surface. The linear relationship between the mass added onto the crystal surface and the change in its frequency can be derived from the Sauerbrey equation^{16,17}:

$$\Delta f = C f_0^2 \Delta m / A \quad (1)$$

where C is the constant, A is the surface area (cm^2) of crystal, and Δm is the mass change (g).

The sandwich-type device was set in a measuring cell, and the dielectric loss was measured at 1 kHz from room temperature to 350°C in N_2 atmosphere using an LCR meter (Yokogawa Hewlett-Packard, 4277A, Tokyo, Japan).

An infrared (IR) spectrum of the sample was obtained by using a Fourier transform infrared spectrometer (FTIR, JASCO 300E).

RESULTS AND DISCUSSION

SO_2 sorption properties of DMPDA-functional copolymers

SO_2 sorption properties were measured for the DMPDA-functional copolymers prepared at various

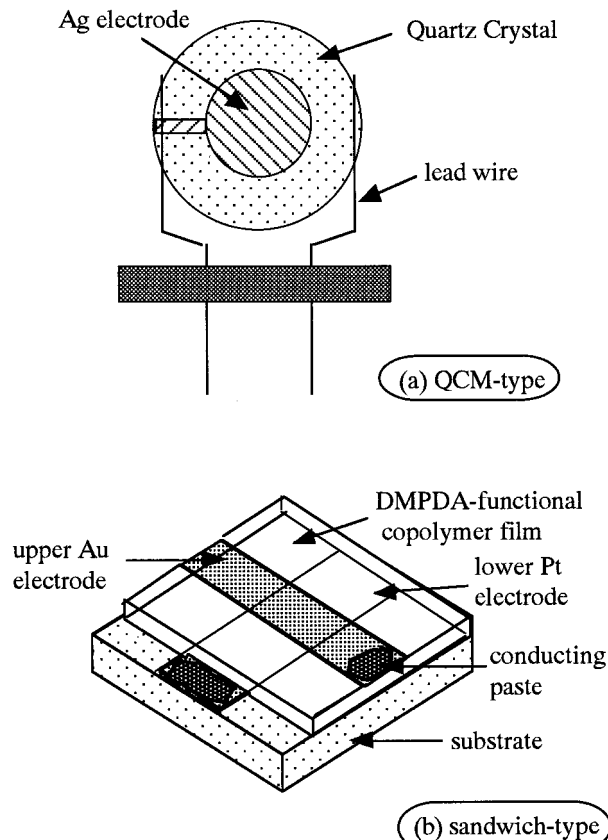


Figure 2 Illustrations of (a) QCM-type and (b) sandwich-type devices.

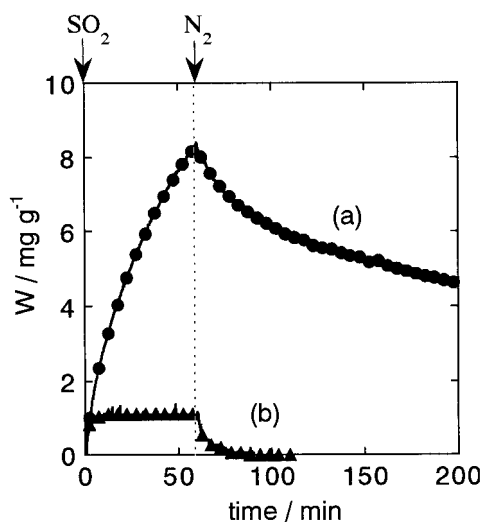


Figure 3 Two typical SO_2 sorption/desorption responses of DMPDA-functional copolymer films measured for 50 ppm SO_2 at 50°C . (a) type I (film prepared in tetrahydrofuran solution) and (b) type II (film prepared in toluene solution).

conditions. The amount of sorbed SO_2 (W) in the copolymer was calculated by eq. (2), which was derived from eq. (1):

$$W = \{(f_N - f_s)/(f_0 - f_N)\} \times 1000. \quad (2)$$

where f_0 , f_N , and f_s are the frequency of the fundamental oscillation (uncoated crystal), that of the film-coated crystal measured in N_2 atmosphere, and that of the film-coated crystal measured in SO_2 atmosphere, respectively. In this equation, $f_N - f_s$ is the frequency shift due to the SO_2 sorption and $f_0 - f_N$ is that due to the film coating. Consequently, W is equivalent to the SO_2 sorption capacity per unit mass of the DMPDA-functional copolymer film. In this study, W increased by exposure to SO_2 gas for all films. Since reference runs for St-CMSt copolymer without amine functionality did not show SO_2 sorption, it was confirmed that the introduced amine groups acted as strong SO_2 adsorption sites. Interestingly, SO_2 sorption responses obtained for the DMPDA-functional copolymers prepared at various conditions were divided roughly into two types. The first type (type I) represents high SO_2 sorption ability, while it takes a long time to reach the equilibrium value, as illustrated in Figure 3(a). Furthermore, with this type, the SO_2 desorption rate was also very slow, and desorption was observed to be incomplete even 140 min after the introduction of N_2 . The second type (type II), illustrated in Figure 3(b), had fast sorption and desorption rates, while the SO_2 sorption ability was small. Interestingly, all the DMPDA-functional copolymers prepared in toluene or xylene solution showed type II SO_2 sorption/desorption responses. On the other hand, the type I

responses were observed for some of the films prepared in tetrahydrofuran or 1,4-dioxane solution.

Structural characterization of DMPDA-functional copolymers

Beckman et al. reported that the amine-acid gas adduct formed principally at the pendant amine group, whereas the linkage amine group had a negligible effect on gas sorption; these phenomena were attributed to the low nucleophilic strength and the steric hindrance induced by the aliphatic substituents.¹⁸ Consequently, to enhance gas sorption capacity, St-CMSt copolymer is normally reacted in the presence of a large excess of diamine (more than 100 times) in order to prevent a crosslinked formation.^{14,18} In our present case, however, the molar ratio of DMPDA to chloromethyl styrene was no more than 10. At this point it is reasonable to attribute the two different SO_2 sorption responses shown in Figure 3 to the difference in the crosslinked structure of the DMPDA-functional copolymer films. Thus, FTIR analysis was designed to investigate the structure of the prepared films. The FTIR spectra of all films indicated the formation of an amino-functional product, as evidenced by the medium intensity centered at 3400 cm^{-1} (primary or secondary N—H stretch) and the characteristic C—N stretch band at $1120\text{--}1110\text{ cm}^{-1}$. To estimate the primary or secondary amine content in the DMPDA-functional copolymers, we chose the peak of the out-of-plane vibration of phenyl ring at 757 cm^{-1} as the internal standard and adopted the peak height method. The relative peak height at 3400 cm^{-1} [RH(3400)] to the peak height at 757 cm^{-1} described by eq. (3) may be correlated to the pendant primary or the linkage secondary amine content in the DMPDA-functional copolymers:

$$\text{RH}(3400) = H_a(3400\text{ cm}^{-1})/H_a(757\text{ cm}^{-1}) \quad (3)$$

The percent conversion (%C) of the chlorine group to the amino group was also calculated from the change in the peak height at 1260 cm^{-1} , which is assigned to the rocking vibration of the C—Cl bond relative to the peak height at 757 cm^{-1} as follows:

$$\%C = \{1 - [H_a(1260\text{ cm}^{-1})/H_a(757\text{ cm}^{-1})]/[H_0(1260\text{ cm}^{-1})/H_0(757\text{ cm}^{-1})]\} \times 100 \quad (4)$$

where H_a and H_0 mean the peak height at the indicated wave number for the DMPDA-functional copolymers and the St-CMSt copolymer without amine functionality, respectively. It is noted here that the calculated %C arose from structures (B)–(D) in Figure 1. The relationship between RH(3400) and %C is shown in Figure 4 for the DMPDA-functional copoly-

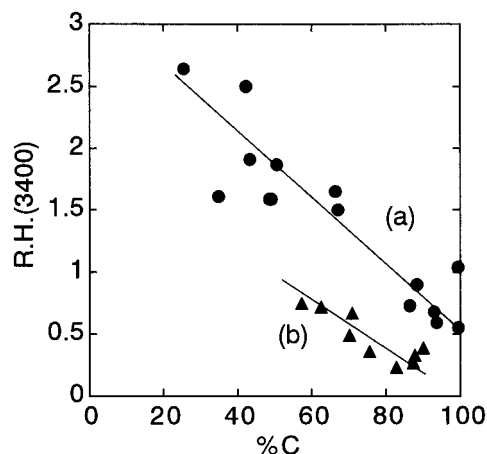


Figure 4 Relationship between RH (3400) and %C: (a) film was prepared in tetrahydrofuran solution and (b) film was prepared in toluene solution.

mer films prepared in tetrahydrofuran and in toluene solutions. It is observed that the value of RH(3400) decreases with an increase in %C for both cases. If the alkylation reaction of diamine occurs only in the form of structure (B) and/or (C), the primary or secondary amine content becomes the increasing function of %C. The present unexpected result suggests that the crosslinked structure (D) increases and the primary content decreases with %C [the secondary amine content is the same in either case of structure (B) and D]. Furthermore, the fact that the film prepared in toluene solution has a lower RH(3400) value, especially at the lower %C value, means that the crosslinked structure forms easily. The result obtained for the film prepared in 1,4-dioxane solution displayed a trend similar to that of the film prepared in tetrahydrofuran solution, while that for the film prepared in xylene solution was similar to that for the film prepared in toluene solution.

Dielectric relaxation measurement supported the above IR analysis. It is known that the dielectric relaxation of a polymer arises from the segment motion of the main chain and the side chain. If the crosslinked structure forms, the segment motion of these chains seems to be depressed. Figure 5 shows the temperature dependence of $\tan\delta$ spectra at 1 kHz for two films having the lower %C values, one prepared in tetrahydrofuran and the other prepared in toluene solution. The two films show two different relaxations, labeled α and β in order of decreasing temperature. The α relaxation, which corresponds to the relaxation of the polymer main chain, starts at 130–150°C and peaks at 160–180°C. The β relaxation, which starts at $\approx 70^\circ\text{C}$ and peaks at $\approx 110^\circ\text{C}$, may reflect the relaxation of the side chain [the pendant amine group shown in Figure 1(B) and (C)]. It is observed that the values of $\tan\delta$ at both peaks are very high for the film prepared in tetrahydrofuran solution, while those values are very

low for the film prepared in toluene solution. This result substantiates the result of FTIR, and leads to the conclusion that the major structures of the film prepared in tetrahydrofuran (or 1,4-dioxane) solution at lower %C value are the structures (B) and (C). Then, the ratio of the structure (D) increases as the reaction proceeds. On the other hand, DMPDA-functional copolymers prepared in toluene (or xylene) solution have predominantly the crosslinked structure (D) even at lower %C.

At the present stage, the effect of solvent on the reaction mechanism is not clear. One possible explanation is as follows. Toluene and xylene are nonpolar solvents and their solubility parameter values are 8.9 and 8.8, respectively.¹⁹ On the other hand, tetrahydrofuran and 1,4-dioxane are moderately polar solvents and their solubility parameters are 9.1 and 10.0, respectively. These differences in the nature of solvents could affect the degree of the chain swelling (expansion) of the polymer in each solvent and resulted in the difference in the extent of the crosslinking.

Effect of crosslinked structure on SO₂ sorption

The relationship between SO₂ sorption capacity and RH(3400) was examined as shown in Figure 6. Since an almost linear relationship was obtained, it was confirmed that the pendant primary amine group played a role as a major SO₂ adsorption site and SO₂ adsorption on the pendant tertiary amine group was relatively small. Figure 7 illustrates the relationship between SO₂ sorption ability and %C. This relationship indicates that the crosslinked structure clearly affects the SO₂ sorption capacity. For example, the amount of SO₂ sorption decreases with an increase in the value of %C for the films prepared in tetrahydrofuran (or 1,4-dioxane) solution. This is because the

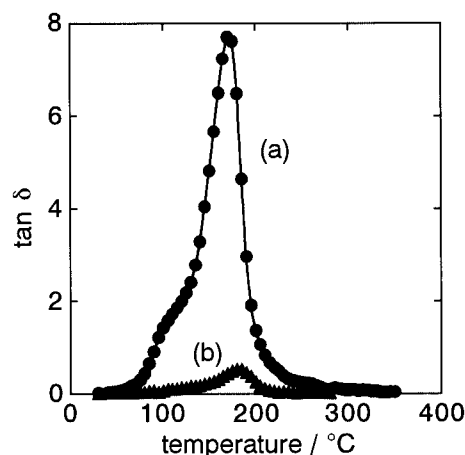


Figure 5 Typical dielectric relaxation spectra for the DMPDA-functional copolymers measured at 1 kHz; symbols are the same as those in Figure 4.

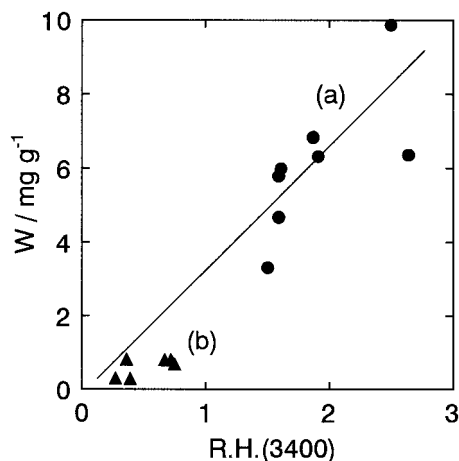


Figure 6 Relationship between SO_2 sorption capacity measured for 50 ppm SO_2 at 50°C and R.H.(3400); symbols are the same as those in Figure 4.

pendant primary amine group as an active SO_2 adsorption site was diminished as the crosslinked formation with %C proceeded, as mentioned above. In addition, the decrement of SO_2 sorption with %C means the linkage secondary amine and the linkage ammonium salts have small effect on SO_2 adsorption, as well as the pendant tertiary amine group, due to the low nucleophilic strength and/or the steric hindrance. It should be noted here that the type I sorption behavior was obtained for the films having lower %C, that is, having insufficient crosslinked structures. When a film has a highly crosslinked structure at higher %C, even if the film was prepared in tetrahydrofuran (or 1,4-dioxane) solution, the SO_2 sorption behaved as type II. On the other hand, for the films prepared in toluene (or xylene) solution, the SO_2 sorption capacity is low and almost independent of %C. In this case, the crosslinked structure formed preferen-

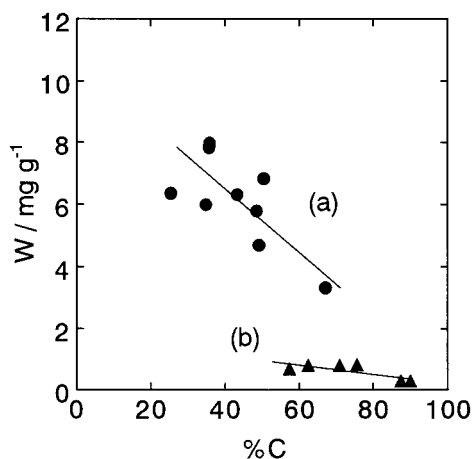


Figure 7 Relationship between SO_2 sorption capacity measured for 50 ppm SO_2 at 50°C and %C; symbols are the same as those in Figure 4.

TABLE I
Sensing Characteristics of DMPDA-Functional Copolymer Films for 50 ppm SO_2

Sorption type of the film	Measuring temp. ($^\circ\text{C}$)	Sensitivity (mg g^{-1})	Response time (min)	Recovery (%)
Type I ^a	90	1.5	60	83
Type II ^b	50	1.1	8	100

^a Film was prepared in tetrahydrofuran solution.

^b Film was prepared in toluene solution.

tially even at lower %C. As a result, all films prepared in toluene (or xylene) solution showed Type II sorption behavior.

The reason why type II sorption/desorption rates were fast can be explained as follows. The diffusion of penetrants in polymers is a function of the polymer chain packing (or cohesive energy density). In the case of the DMPDA-functional linear polymers, a strong electronic donor-acceptor interaction between the phenyl and amine groups, indicating tight chain packing, is easily expected. The introduction of a crosslinked structure in such a tightly packed polymer may play a role as a spacer and enhance the free volume. Consequently, the sorption and desorption rates exceed those of linear polymers.

Application for SO_2 sensors

By utilizing the present DMPDA-functional copolymers as sensor coatings, it is possible to fabricate the QCM-type SO_2 gas sensors. For practical gas sensors, important characteristics include the fast response time (fast sorption/desorption) and the good recovery (complete desorption) as well as the high sensitivity (high gas sorption capacity). As shown in Figure 2(a), the response time of the film showing type I behavior was very slow and the recovery was invariably poor. Diffusion for gas-polymer systems is a kinetic parameter that depends on the temperature. To reduce the response time and improve the recovery, the measuring temperature was raised from 50 to 90°C . The results were compared with those of the film showing type II sorption behavior obtained at 50°C [shown in Fig. 2(b)] and summarized in table I. While the sensitivity of the film showing type I sorption decreased with an increase in the measuring temperature, the response time decreased significantly and the recovery (complete desorption = 100%) was also improved as expected. However, these values were still insufficient for practical use of the sensor. From these results, it was confirmed that a highly crosslinked film showing type II SO_2 sorption behavior was suitable for use as a SO_2 gas sensor material. Moreover, the sensor is operable near room temperature.

CONCLUSION

The SO₂ sorption properties of DMPDA-functional St-CMSt copolymers were examined. Two different types of sorption behavior were observed. Type I sorption behavior was characterized by the high SO₂ sorption ability and slow sorption/desorption rates, and type II was characterized by the low sorption ability and fast sorption/desorption rates. FTIR analysis and dielectric measurement revealed that the difference in the sorption behavior arose from the difference in the crosslinked structure. Type II sorption was obtained when a highly crosslinked structure was formed. We showed herein that DMPDA-functional copolymers having highly crosslinked structures can serve to prepare a practical coating for the QCM-type SO₂ sensor.

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