

Toluene-Vapor Sorption of Chemically Modified Methyl Methacrylate-*co*-Chloromethyl Styrene Copolymers with *N,N*-Dimethyl-1,3-Propanediamine Measured with a Quartz Crystal Microbalance

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ABSTRACT: The sorption properties of toluene vapor were measured for methyl methacrylate (MMA)-*co*-chloromethyl styrene (CMSt) copolymers chemically modified with *N,N*-dimethyl-1,3-propanediamine (DMPDA) to develop a novel quartz crystal microbalance toluene-vapor sensor coating. The influence of the structure of the comonomer, the composition of the copolymer, and the film thickness on the toluene sorption properties were investigated. The modified MMA-CMSt copolymers were capable of large, fast, and reversible sorption versus the

modified styrene-CMSt copolymers. The largest sorption capacity was obtained for MMA-CMSt-DMPDA with a 96 mol % CMSt concentration. These behaviors were explained by a combination of the plasticization of the copolymers by the introduction of bulky DMPDA at lower CMSt concentrations and the formation of a loosely cross-linked structure at higher CMSt concentrations. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1086–1093, 2009

Key words: adsorption; functionalization of polymers; sensors

INTRODUCTION

The monitoring of volatile organic compounds such as benzene, toluene, and xylene has become a necessary task because of regulations in many countries of the world. Although current monitoring methods (i.e., gas chromatography and infrared spectroscopy) have high sensitivity, they are expensive and are not used for real-time measurements. An attractive alternative is the use of real-time sensors that can be placed *in situ*, reducing the need for sample collection and expensive off-site analyses. One possible device is a resonant sensor, in which the sorption of the target molecules from the environment in an appropriate chemically sensitive material produces a shift of the resonance frequency.^{1–10} One problem, however, is that a single sensor device cannot be a selective and sensitive volatile organic compound sensor because individual sensors respond to various degrees to widely different analytes. Thus, chemical sensor arrays have attracted significant interest for the purpose of analyzing volatile analytes.^{11–13} However, because the accuracy, selectivity,

and sensitivity of computed results for given samples are determined by the individual sensor responses within a sensor set, the development of a sensor coating and a selective and sensitive sensor device are still much needed in the design of practical sensor arrays.

We have been studying gas sorption properties of chemically modified copolymers, using the quartz crystal microbalance (QCM) technique for basic research concerning the selection of appropriate polymer coatings for gas sensor applications.^{14–17} These materials show considerable promise and have several advantages. First, their chemical structures are readily modified, and this enables custom-designed materials with specific selectivity to target analytes. Second, unlike semiconducting metal oxide sensors, the sensing operation can occur at room temperature, and this lowers the power consumption requirements. In a previous report, we proposed novel QCM-type toluene-vapor sensor coatings based on a styrene (St)-*co*-chloromethyl styrene (CMSt) copolymer.¹⁸ In that study, it was shown that the copolymer, chemically modified with some diamines, had a larger toluene-vapor sorption capacity, a faster rate of sorption, and excellent reversibility versus conventional polymer coatings such as polystyrene and poly(dimethyl siloxane). Among those diamines used as modifiers, *N,N*-

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dimethyl-1,3-propanediamine (DMPDA) showed the most relevant characteristics. However, its sensing characteristics are not necessarily satisfactory for practical use. For further improvement of the sensing properties, in this study, we prepared a chemically modified methyl methacrylate (MMA)-*co*-CMSt copolymer with DMPDA. The modified copolymer was coated onto a piezoelectric quartz crystal, and its toluene-vapor sorption properties were measured. Specifically, we examined the effects of the structure of the comonomer, the composition of the copolymer, and the film thickness on the toluene-vapor sorption properties.

EXPERIMENTAL

Synthesis of chemically modified MMA-*co*-CMSt copolymers with DMPDA

A chemically modified MMA-*co*-CMSt copolymer with DMPDA (MMA-CMSt-DMPDA) was synthesized according to the method described in a previous report.¹⁸ First, the MMA-*co*-CMSt copolymer precursor (MMA-CMSt) was synthesized in a toluene solution via free-radical polymerization initiated by azobisisobutyronitrile. The CMSt concentration (C_{CMSt}) values of the copolymer precursor were varied by changes in the mixing ratio of MMA and CMSt in the solution and determined by elemental analysis. The C_{CMSt} values of all the prepared copolymer precursors in this study and their designations are shown in Table I.

Each MMA-CMSt was modified chemically by an alkylation reaction using DMPDA. The alkylation reaction was performed at room temperature according to the literature,¹⁸⁻²⁰ except for the reaction time, which was several minutes in this experiment. The reaction scheme and a possible chemical structure of the prepared copolymers (MMA-CMSt-DMPDA) are shown in Figure 1.

Toluene-vapor sorption measurement

Each MMA-CMSt-DMPDA solution was spin-coated on one side of an AT-cut quartz crystal (4-MHz resonant frequency) having a silver electrode on both sides. The film was then postheated at 80°C under reduced pressure for 2 h. The film was assumed to be homogeneous with a uniform thickness. The thickness was varied by changes in the rotational speed of the spin coater and was estimated on the basis of the frequency shift (Δf) after postheating in dry N₂ with the Sauerbrey equation (described later) under the assumption that the density of all films was 1 g/cm³. This estimation was valid for this MMA-CMSt-DMPDA because the viscoelastic contribution to Δf was negligible, as mentioned later.

TABLE I
 C_{CMSt} Values of the Prepared Copolymer Precursors

Comonomer	C_{CMSt}	Designation
—	100	MMA(0)-CMSt(100)
MMA	96	MMA(4)-CMSt(96)
MMA	70	MMA(30)-CMSt(70)
MMA	45	MMA(55)-CMSt(45)
MMA	26	MMA(74)-CMSt(26)
St	20	St(80)-CMSt(20)
St	46	St(54)-CMSt(46)

C_{CMSt} is the molar percentage of CMSt in the copolymer as determined by elemental analysis.

The setup used to measure the toluene-vapor sorption and the measuring procedure are described in detail in the previous article.¹⁸ In this study, the sorption properties of toluene vapor were measured at the maximum concentration allowed by our experimental setup, which was 540 ppm. Except for the measurement of the damping of the oscillator [expressed by the resistance (R)], the variation in the resonant frequency of the quartz crystal was measured with a frequency counter (TR 5822, Advantest, Tokyo, Japan). R was measured with a QCM system (QCM-934, Seiko EG&G, Matsudo, Japan). All measurements were performed at 30°C.

The underlying principle of QCM is based on Δf (Hz) in the fundamental oscillation frequency (f_0) upon mass changes [Δm (g)] 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:²¹

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

where C is a constant and A is the surface area (cm²) of the crystal. The Sauerbrey equation assumes that the added mass is uniformly distributed in a rigid thin film. When the viscoelastic effects of the film coating are significant, the gravimetric interpretation is inaccurate.^{22,23} The deviations from the Sauerbrey relation are accompanied by increasing damping of the oscillator, which is expressed by R . Consequently, R is a helpful indicator of viscoelastic contributions.²² In this study, R was almost constant after the film deposition and during the toluene-vapor sorption/desorption process for all modified copolymers tested. This result suggests that the linear relationship between the mass of sorbed toluene vapor and the measured Δf value can be expected to hold in this study.

Characterization of the chemically modified copolymers

The glass-transition temperatures (T_g 's) were evaluated with a Pyris 1 differential scanning calorimeter (Perkin Elmer Japan Co., Ltd., Yokohama, Japan) at a heating rate of 40°C/min under a nitrogen atmosphere.

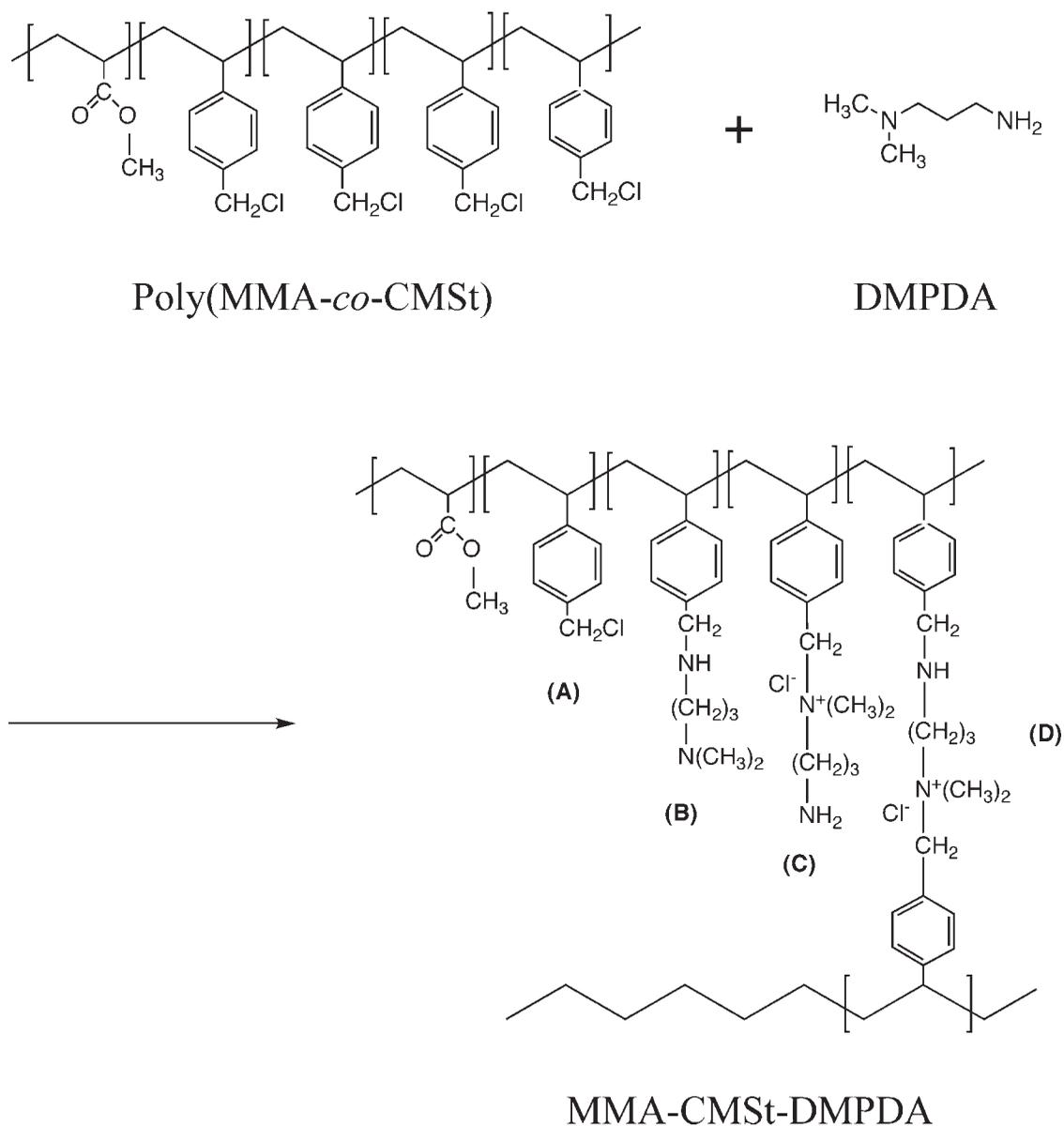


Figure 1 Reaction of MMA-*co*-CMSt copolymer (Poly(MMA-*co*-CMSt) with *N,N*-dimethyl-1,3-propane diamine (DMPDA) and chemical structure of the prepared MMA-CMSt-DMPDA.

The dielectric loss measurement was performed as follows. First, a sandwich-type device was prepared. The device was set in a measuring cell, and the dielectric loss was measured at 5 kHz from room temperature to 240°C at a heating rate of 3°C/min in an N₂ atmosphere with an LCR meter (4277A, Yokogawa Hewlett-Packard, Tokyo, Japan). Details of the measurement have been described elsewhere.¹⁴

RESULTS AND DISCUSSION

Toluene-vapor sorption/desorption response of MMA-CMSt-DMPDA

A typical toluene-vapor sorption/desorption response obtained for MMA-CMSt-DMPDA is shown

in Figure 2. After a steady frequency had been obtained in a dry N₂ atmosphere, 540 ppm toluene vapor was introduced into the measuring vessel. The time at which the toluene vapor was introduced was defined as 0 min. Then, the time dependence of $\Delta f [f(\text{N}_2) - f(\text{toluene})]$ was recorded while the film was exposed to toluene vapor for 60 min, where $f(\text{N}_2)$ and $f(\text{toluene})$ are the frequencies obtained in a dry N₂ and 540 ppm toluene vapor, respectively. As Figure 2 shows, oscillation frequency decreased as a result of the exposure of the film to toluene vapor; this resulted in a positive value of Δf . This Δf value is directly related to the sorption of toluene vapor, as mentioned in the Experimental section. Figure 2 also shows the recovery (desorption process) of the

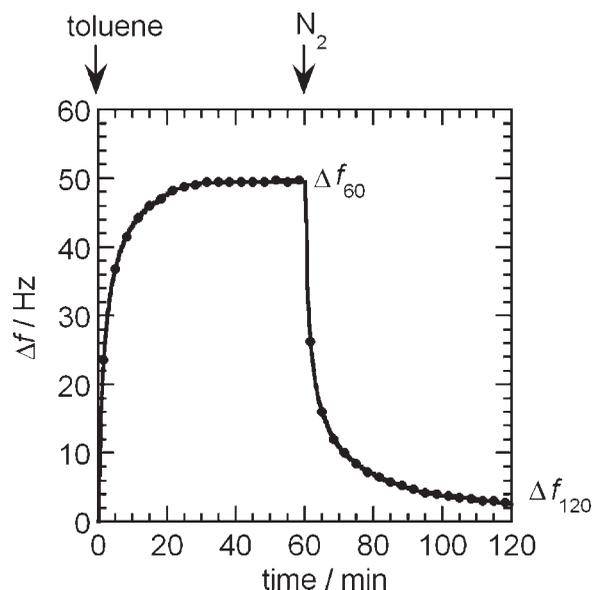


Figure 2 Typical toluene-vapor sorption/desorption response for MMA-CMSt-DMPDA on exposure to 540 ppm of toluene vapor measured at 30°C.

response. After the film was exposed to toluene vapor for 60 min, the atmosphere was turned back to dry N₂, and this resulted in the recovery of Δf toward the original value. For the comparison of toluene-vapor sorption/desorption responses hereafter, several response properties were defined as follows. Δf_{60} is the frequency shift obtained after 60 min of exposure to toluene vapor. The 80% response time (t_{80}) is the length of time necessary to reach 80% of the final value of sorption (Δf_{60}). R as a value representing the recovery (complete desorption = 100%) is estimated according to eq. (2):

$$R = [(\Delta f_{60} - \Delta f_{120}) / \Delta f_{60}] \times 100 \quad (2)$$

where Δf_{120} is the frequency shift obtained after 60 min of re-exposure to dry N₂.

Effects of the structure of the comonomer

Figure 3 shows the toluene-vapor sorption/desorption responses for MMA(74)-CMSt(26)-DMPDA as well as the previously reported results for St(80)-CMSt(20)-DMPDA and St(80)-CMSt(20) for comparison.¹⁸ The designations for these coatings are shown in Table I. So that we could examine the effect of the comonomer, the C_{CMSt} values of all the copolymers were similar, and the film thicknesses of all the copolymers were made uniform at about 2 μm . As Figure 3 shows, the introduction of DMPDA into the copolymer precursor yielded a large value of Δf . The modified MMA-CMSt also showed improved toluene-vapor sorption/desorption kinetics. The copolymerization of CMSt with MMA yielded a larger Δf

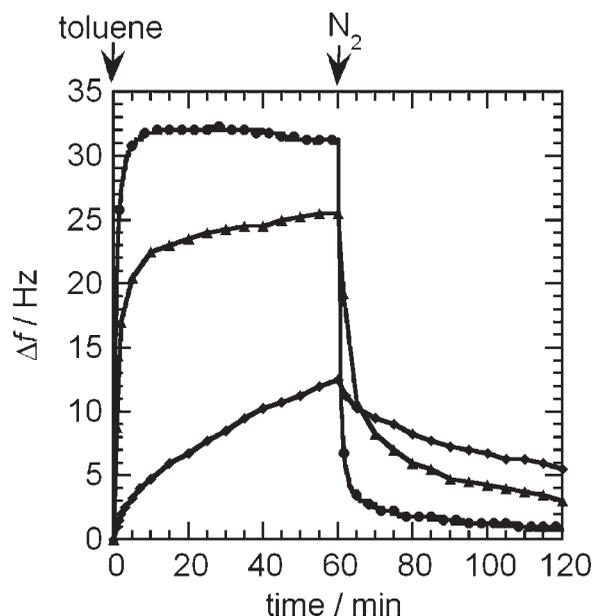


Figure 3 Toluene-vapor sorption/desorption responses for the modified copolymers on exposure to 540 ppm of toluene vapor measured at 30°C: (●) MMA(74)-CMSt(26)-DMPDA, (▲) St(80)-CMSt(20)-DMPDA, and (◆) St(80)-CMSt(20).

value and a faster rate of sorption versus copolymerization with St, as summarized in Table II.

Effects of the composition of the copolymers

Figure 4 shows the sorption/desorption responses for MMA-CMSt-DMPDA samples with different copolymer compositions but the same film thickness (ca. 1.6 μm). Significant differences in the toluene-vapor sorption capacity due to differences in the C_{CMSt} values can be observed. The largest sorption capacity was obtained for MMA-CMSt-DMPDA having a C_{CMSt} value of 96 mol %. The sorption/desorption kinetics also showed a high C_{CMSt} dependence, as summarized in Table III. These behaviors are related to the variation of T_g discussed in a later section.

Effects of the film thickness

Figure 5 shows the dependence of the Δf_{60} value on the film thickness. Δf_{60} increased linearly with

TABLE II
Sorption/Desorption Properties of the Chemically Modified Copolymers Consisting of Different Comonomers

	Δf_{60} (Hz)	t_{80} (min)	R (%)
MMA(74)-CMSt(26)-DMPDA	32	2	98
St(80)-CMSt(20)-DMPDA	25	5	94
St(80)-CMSt(20) precursor	13	40	56

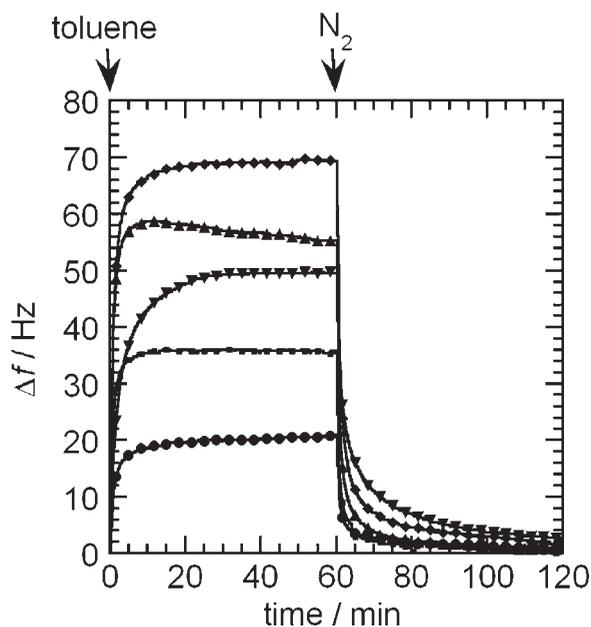


Figure 4 Toluene-vapor sorption/desorption responses for MMA-CMSt-DMPDAs with different copolymer compositions on exposure to 540 ppm of toluene vapor measured at 30°C: (●) MMA(74)-CMSt(26)-DMPDA, (■) MMA(55)-CMSt(45)-DMPDA, (▲) MMA(30)-CMSt(70)-DMPDA, (◆) MMA(4)-CMSt(96)-DMPDA, and (▼) MMA(0)-CMSt(100)-DMPDA.

increases in the film thickness for all MMA-CMSt-DMPDA coatings. These results suggest that both easy diffusion and homogeneous sorption of toluene vapor occurred in the bulk of these films. Furthermore, the slope became larger with all of the C_{CMSt} values except for MMA(0)-CMSt(100)-DMPDA, and this is in agreement with the result for the maximum Δf_{60} value at $C_{\text{CMSt}} = 96$ mol %, as shown in Figure 4. On the other hand, the thickness dependence of Δf_{60} observed for St-CMSt-DMPDA was very small. Furthermore, St(54)-CMSt(46)-DMPDA showed a decrease in the slope rather than an increase, although C_{CMSt} was higher than that for St(80)-CMSt(20)-DMPDA. These behaviors demonstrate depressed vapor diffusion for the modified St-CMSt copolymers, and this is indicative of the formation of an unfavorable rigid structure by a crosslinking reaction.¹⁸ As a result, a sensitivity of MMA-CMSt-DMPDA 5 times greater than that of St-CMSt-

TABLE III
Sorption/Desorption Properties of MMA-CMSt-DMPDAs with Different Copolymer Compositions

	Δf_{60} (Hz)	t_{80} (min)	R (%)
MMA(0)-CMSt(100)-DMPDA	50	7	95
MMA(4)-CMSt(96)-DMPDA	70	2	98
MMA(30)-CMSt(70)-DMPDA	59	2	99
MMA(55)-CMSt(45)-DMPDA	36	2	100
MMA(74)-CMSt(26)-DMPDA	21	4	95

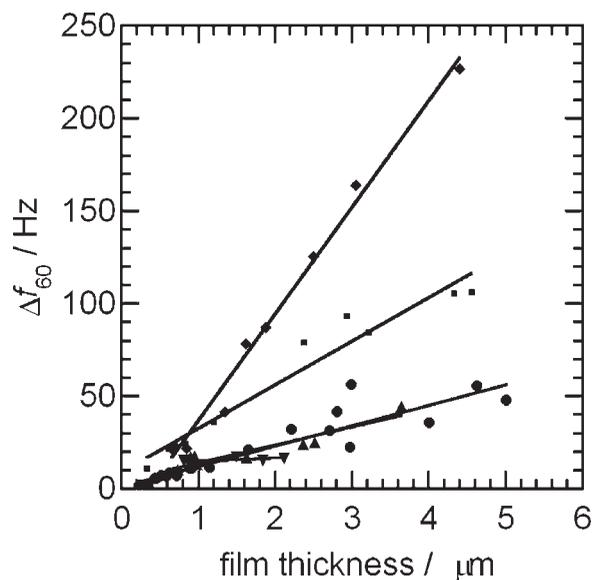


Figure 5 Dependence of Δf_{60} on the film thickness for MMA-CMSt-DMPDA and St-CMSt-DMPDA measured at 30°C: (●) MMA(74)-CMSt(26)-DMPDA, (■) MMA(55)-CMSt(45)-DMPDA, (◆) MMA(4)-CMSt(96)-DMPDA, (▲) St(80)-CMSt(20)-DMPDA, and (▼) St(54)-CMSt(46)-DMPDA.

DMPDA was achieved. The largest sensitivity obtained in this study was 2.4 ppm/Hz ($\Delta f_{60} = 227$ Hz for 540 ppm toluene vapor), which was obtained for MMA(4)-CMSt(96)-DMPDA with a 4.3- μm film thickness.

Discussion of the sorption behavior of MMA-CMSt-DMPDA

It is important to understand the sorption/desorption behaviors taking place in the modified copolymers. First, the percentage conversion (%C) of CMSt was calculated by elemental analysis. The results are summarized in Table IV. The value of %C decreased with an increase in C_{CMSt} in the copolymer. The steric hindrance of CMSt reacting with DMPDA may prevent the reaction of other adjacent CMSt groups. With the %C values, the concentration of CMSt that reacted with DMPDA in the copolymer ($C_{\text{CMSt-DMPDA}}$) was estimated with eq. (3) and is summarized in Table IV:

TABLE IV
%C of CMSt and $C_{\text{CMSt-DMPDA}}$ Values of MMA-CMSt-DMPDAs

	%C	$C_{\text{CMSt-DMPDA}}$
MMA(0)-CMSt(100)-DMPDA	51	51
MMA(4)-CMSt(96)-DMPDA	77	74
MMA(30)-CMSt(70)-DMPDA	76	53
MMA(55)-CMSt(45)-DMPDA	81	36
MMA(74)-CMSt(26)-DMPDA	94	25

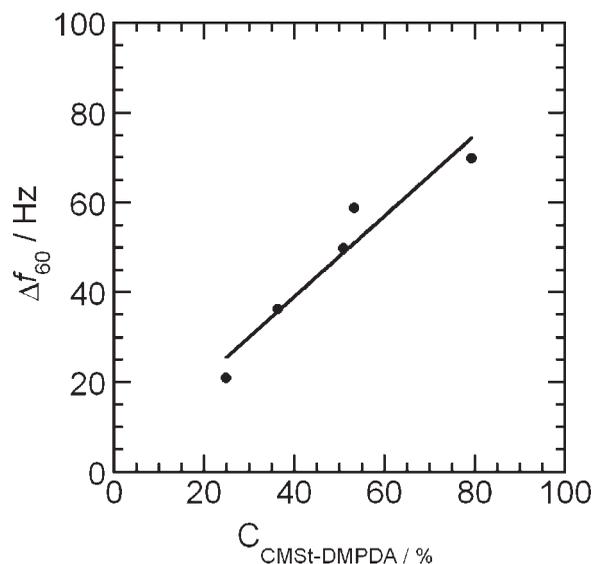


Figure 6 Relationship between Δf_{60} shown in Figure 4 and $C_{\text{CMSt-DMPDA}}$ measured at 30°C.

$$C_{\text{CMSt-DMPDA}} = \%C \times (C_{\text{CMSt}}/100) \quad (3)$$

The relationship between Δf_{60} , included in Figure 4, and $C_{\text{CMSt-DMPDA}}$ is illustrated in Figure 6. Δf_{60} increased linearly with $C_{\text{CMSt-DMPDA}}$. This result indicates that the introduced DMPDAs played an important role in the toluene-vapor sorption behavior of the modified MMA-CMSt copolymers. The possibility that the introduced amino groups could act as adsorption sites is low because it was confirmed previously for modified St-CMSt that the difference in the structure of the terminal amino groups did not affect the toluene-vapor sorption capacity.¹⁸

T_g was measured for MMA-CMSt precursors by differential scanning calorimetry (DSC). Because only a single T_g was observed, these copolymer precursors seemed to be predominantly of the random type within the sensitivity limits of the thermal analysis technique. The T_g values were found to vary linearly with C_{CMSt} , as shown in Figure 7. This behavior is similar to that observed for St-CMSt random copolymers,²⁰ but the T_g 's of MMA-CMSt became higher because of the substitution of MMA for St. T_g was also measured for various compositions of MMA-CMSt-DMPDAs, as shown in Figure 7. MMA(0)-CMSt(100)-DMPDA did not show any thermal transition from room temperature to 200°C. As can be seen, the introduced bulky DMPDAs acted to plasticize the copolymer, lowering the T_g 's in comparison with that of the MMA-CMSt precursors at the same value of C_{CMSt} . It is interesting that T_g had its minimum at $C_{\text{CMSt}} = 87$ mol %. Beckman et al.²⁰ obtained similar results for St-CMSt-Ethyl-enediamine. In that study, the minimum was observed at $C_{\text{CMSt}} = 40$ mol %; they speculated that

this unusual behavior was due to a loss of chain mobility caused by strong electronic donor-acceptor interactions between the phenyl and amine groups. The substitution of MMA for St in this study may have removed this effect and resulted in the further reduction of T_g at higher C_{CMSt} values. The possible origin of the minimum shown in this plot is discussed later on the basis of dielectric relaxation spectroscopy (DRS) measurements. It is well known that the diffusion coefficient of gas molecules in polymers increases with a decrease in T_g . Consequently, the observed large and linear film thickness dependence of Δf_{60} even at higher C_{CMSt} values in Figure 5 can be rationalized by the fact that the toluene molecule diffusion coefficient goes through a maximum around $C_{\text{CMSt}} = 87$ mol %. However, Δf_{60} of MMA(4)-CMSt(96)-DMPDA exhibited its maximum value regardless of the increase in T_g . It should be recognized that the sorption behavior of gases in glassy polymers has been successfully described by the dual-mode sorption model.²⁴⁻²⁷ The model is based on the principle of two sites: (1) a site for dissolution according to Henry's law and (2) a site for adsorbed molecules according to Langmuir's law in the frozen microvoids (holes) of the glassy polymer. The microvoids within glassy polymers are known to be closely related to gas sorption and diffusion.²⁸ In general, the number of microvoids increases with T_g , and this may result in the maximum of the sorption capacity occurring at $C_{\text{CMSt}} = 96$ mol %.

The DRS method is a technique potentially capable of probing molecular motion. The technique is more sensitive to the glass transition than DSC scans.²⁹ In DRS, the highest temperature peak (α relaxation) is generally related to the large-scale,

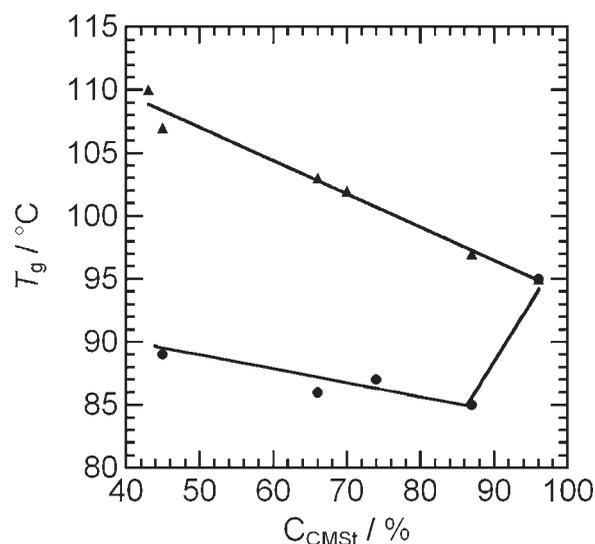


Figure 7 T_g values of the copolymers determined from DSC: (●) MMA-CMSt-DMPDA and (▲) MMA-CMSt precursor.

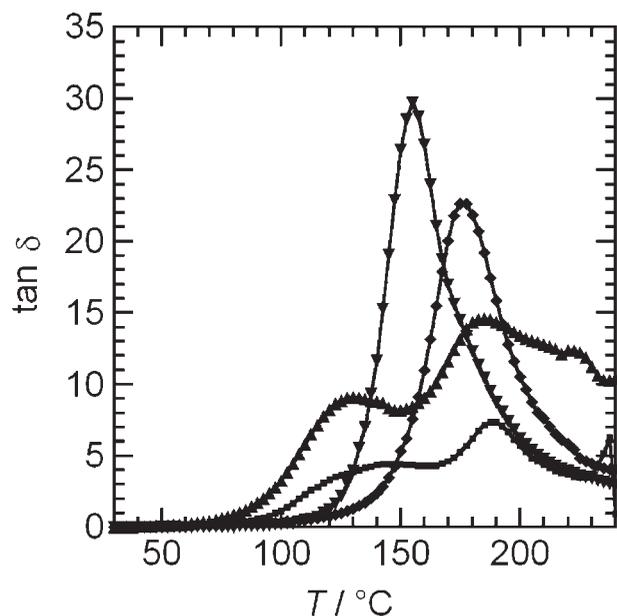


Figure 8 Isochronal plots of $\tan \delta$ versus temperature (T) at 5 kHz for MMA–CMSt–DMPDA: (■) MMA(55)–CMSt(45)–DMPDA, (▲) MMA(30)–CMSt(70)–DMPDA, (◆) MMA(4)–CMSt(96)–DMPDA, and (▼) MMA(0)–CMSt(100)–DMPDA.

cooperative Brownian motion of the main chains associated with the glass transition. However, it is generally found that the T_g related to the DRS maxima will be higher than the T_g measured by DSC, and the dielectric relaxation peak shifts to higher temperatures with increasing frequency.³⁰ At temperatures below the α relaxation, the mobility of the polymer chain is reduced, and sub- T_g relaxations (β relaxations) in the glassy state can be observed. This relaxation includes local motion of dipoles in the main chains, motion of side chains, and local reorganization within side chains. Figure 8 shows the temperature dependence of $\tan \delta$ spectra obtained at 5 kHz for various compositions of MMA–CMSt–DMPDAs. The spectra for MMA(55)–CMSt(45)–DMPDA and MMA(30)–CMSt(70)–DMPDA show two main relaxation processes. An increase in the magnitude of α and β peaks occurred with an increase in C_{CMSt} , that is, with an increase in $C_{\text{CMSt-DMPDA}}$. This result indicates that DMPDAs plasticized the copolymer and increased the chain mobility, in agreement with the results of DSC. On the other hand, the modified copolymers with high C_{CMSt} values showed somewhat more complex behavior. The β peak was found to shift to higher temperatures and to overlap with the α peak and thus was inseparable from the α relaxation. This peak shift seemed to be a manifestation of the physical restriction imposed by the formation of a crosslinked structure (D) in Figure 1 on the molecular segmental mobility of the side chains having structures B and/

or C. The formation of the crosslinked structure seemed to produce greater values of T_g for MMA(4)–CMSt(96)–DMPDA, as shown in Figure 7. The formation of the crosslinked structure was also confirmed for modified St–CMSt copolymers previously.¹⁸ However, in these modified MMA–CMSt copolymers, the finding that the magnitude of the loss peak in Figure 8 was still high and that no other T_g 's at higher temperatures were observed by DSC indicated that the ratio of the crosslinked structure in the structures of the copolymers shown in Figure 1 was not large. This result can be attributed to the short reaction time for alkylation, as described in the Experimental section. We confirmed that a longer reaction time resulted in the gelation and rapid reduction of the vapor sorption capacity.

CONCLUSIONS

The toluene-vapor sorption properties of chemically modified copolymers were examined with a QCM technique. The effects of the comonomers, copolymer composition, and film thickness were evaluated. The results demonstrated that the sorption properties were a function of the composition of the copolymers.

MMA–CMSt copolymers modified with DMPDA were capable of large, fast, and reversible toluene-vapor sorption. This behavior was explained by the combination of the plasticization of the copolymers achieved by the introduction of bulky DMPDAs at lower C_{CMSt} values and the formation of a loosely crosslinked structure at higher C_{CMSt} values. As a result, a sensitivity of MMA–CMSt–DMPDA 5 times greater than that of St–CMSt–DMPDA was achieved. The sensitivity obtained for MMA–CMSt–DMPDA with 96 mol % CMSt and a 4.3- μm film thickness was 2.4 ppm/Hz. This sensitivity was comparable to that obtained in other studies.^{8–10}

These results also suggest that copolymers with an optimized composition may offer an interesting approach to constructing large libraries of chemically diverse polymeric sensors. These classes of copolymers are easily synthesized and can be customized for specific chemicals by the use of suitable modifiers.^{14,15,17} Furthermore, polymeric materials have flexibility in detector design beyond just QCM, such as the surface acoustic wave (SAW) or chemiresistor-based approach using copolymer/carbon black composite films; this flexibility will make it possible to obtain further sensitivity enhancement. The approach should be suitable for a variety of implementations in gas sensors and/or electronic noses.

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