Effects of Organic Groups on Structure and Viscoelastic Properties of Organic−Inorganic Polysiloxane Hybrid System

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The structure and viscoelastic properties of an organic−inorganic hybrid system composed of an organically modified polysiloxane network were examined, and the influence of organic groups on elastic-modulus variation by heat treatment was studied. The increase in the number of phenyl (Ph) groups per silicon decelerates the increase in elastic modulus; the substitution of the Ph group for a methyl (Me) group accelerates it. The system basically consists of $R_{4-m}Si[O-]_{m/2}$ units, where R is the organic group. The ^{29}Si magic-angle spinning (MAS) NMR and gel permeation chromatography (GPC) measurements classified the structure related with the viscoelastic behavior into two factors: the number of bridging oxygens and the distribution of molecular weight. The elastic modulus was expressed by these structural factors through a simple empirical formula, irrespective of the type and number of the organic groups. The effects of the organic groups on the variation in elastic modulus by heat treatment were found to work mostly only through the molecular-weight change, and such effects can be controlled by the type or the number of organic groups.

I. Introduction

Low-melting glass, which generally has a softening temperature, T_S, below 600 °C, is indispensable to semiconductor devices and instruments for various purposes (used as seals, insulation, etc).[1] One method for lowering the T_S is to reduce the number of cross linkages that constitute the network structure, and lead (Pb) has often been introduced into the glass network to realize this because of the smaller coordination number and weaker bonding of Pb−O vs Si−O.[2] However, Pb-free materials are strongly desired from the viewpoint of environmental pollutions. Thus, low-melting glass composed of organic−inorganic hybrid systems has recently become a promising candidate for such a breakthrough.[3,4] Furthermore, the application of this type of hybrid glass in photonic devices is expected, because the existence of both organic and inorganic parts in a system promotes the doping of dyes and transition metals.[5] Photothermal fine-processing with low energy can be realized by taking advantage of the low T_S and dopant receptivity.[6] The fundamental properties of the hybrid glass, that is, the relationship between the structure and viscoelastic properties, should be clarified for the applications. In particular, the role of organic groups in polycondensation cannot be ignored for controlling the softening behavior.

The present low-melting glass consists of a polysiloxane network and organic functional groups, $R_{4-m}Si[O-]_{m/2}$, where R is the phenyl (Ph) or methyl (Me) group and m is the number of oxygens required to bridge a silicon; in other words, it is the bridging-oxygen number per silicon. The softening behavior is strongly connected to the number of Si−O bonds in the polysiloxane network.[7−10] The viscosity of sodalime-silicate glass, which is a typical inorganic network-forming system, decreases with an increase in the sodium concentration,[7] because sodium may terminate the Si−O bond and consequently reduce the number of bridging oxygens. In addition, m is expected to be a primary factor that dominates the softening behavior in the present hybrid system, and its control is considered an effective way to design the viscoelastic property. In other words, m can be controlled by changing the number of network terminators, that is, the organic groups on silicon. Apart from these molecular structures, the effect of the interaction between the molecules, namely, the intermolecular entanglement, should not be ignored for discussing the relationship between the structure and the softening behavior in the hybrid system. It has been reported that the effect of the interaction depends on molecular size.[11,13] For example, the elastic moduli of materials composed of normal molecular chains such as polystyrene, polydimethylsiloxane, etc. increase monotonically with an increase in the molecular weight, and furthermore, the rubbery state appears above a certain value of the molecular weight.

The organic-modified polysiloxane system exhibits a complex structure, that is, the distribution of the molecules composed of a three-dimensional siloxane network and organic groups as a network terminator. The organic groups have been reported to change the T_S,[12] but how the organic groups affect the softening behavior on a microscopic level has not yet been elucidated, which hinders the design of the thermomechanical property. In the present study, we attempted to consistently relate the viscoelastic property to the structure, and the organic-group effects on the relationship were then examined by classifying the effect into two types: (i) the increase in the number of

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organic groups per silicon (the *number* effect of substituents) and (ii) the substitution for different organic groups (the *kind* effect of substituents). A Ph group was introduced to examine (i), because of its large volume as compared with a unit of siloxane bonding. The Ph and Me groups have differences in the molecular weight and chemical properties, and in order to approach (ii), the Ph groups were substituted for the Me groups in order to keep the total number of these organic groups constant.

II. Experimental

As mentioned in the previous section, monophenyltriethoxysilane (PhSi(OEt)$_3$), diphenyldiethoxysilane (Ph$_2$Si(OEt)$_2$), and monomethyltriethoxysilane (MeSi(OEt)$_3$) were used as starting solutions for the sol−gel reaction, and two types of samples, $(1 - x)$PhSi[O-]$_{3/2}$:xPh$_2$Si[O-]$_{2/2}$ and $(1 - y)$PhSi[O-]$_{3/2}$:yMeSi[O-]$_{3/2}$, were prepared for studying the substituent effects (i) and (ii), respectively, where x and y are the mixture ratios of the starting materials. A mixture of ethanol, water, and hydrochloric acid was added dropwise to a mixture of PhSi(OEt)$_3$ and ethanol. After the solution was stirred for 3 h at room temperature in air, a mixture of Ph$_2$Si(OEt)$_2$ or MeSi(OEt)$_3$ with ethanol was added dropwise to it. Next, ammonia was added to the solution after stirring it for another 3 h. The solution gelled after being stirred for a couple of days at room temperature in air. The gel then became a glassy transparent solid by heat treatment for 1 day at 110 °C in air. In order to remove the NH$_4$Cl microcrystals, the bulk samples were crushed into powder and then rinsed with water and dried for 1 h at 110 °C in a decompression chamber. The samples prepared by the aforementioned procedure were further heat-treated at 200 °C in air, and the structure and viscoelastic properties were then examined after the heat treatments for the prescribed durations, as mentioned below.

The measurements of the dynamic shear modulus were carried out using a rheometer (UBM Co., Ltd., Model Rheosol G-2000). A dynamic torsion was applied to a sample sandwiched between the two parallel plates of appropriate diameter with a clearance of 1 mm, and the stress in response was detected. The absolute error of the system was evaluated using silicone oil (Nippon Grease Co., Ltd., JS160000), which has been registered as a standard in code d'indexation des materiaux de reference (COMAR), and the value measured by the present apparatus was then found to agree with the certified value within a range of ±10%. The measurements were carried out at frequencies ranging from 10^{-3} to 10 Hz and at temperatures from 20 to 200 °C. The duration required for the measurements was reduced as little as possible in order to avoid an undesirable structural change at a high temperature during the measurements. Furthermore, to confirm the extent of such an undesirable change, the last measurement was always carried out at the same temperature where the initial measurement was performed, and then the difference in these results was found to be less than 10%. The elastic modulus as a function of frequency can be regarded as being equivalent to that as a function of temperature.[14] This is referred to as thermorheological simplicity[15] and has been verified experimentally for many glass forming materials.[16−18] By following this simplicity in the present study, the elastic-modulus spectra obtained at various temperatures were shifted along the frequency axis in order to superpose on the spectrum at 100 °C.

Structural information relevant to the viscoelastic property was obtained through nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC).

The bonding state around silicon was examined using ^{29}Si MAS NMR (Chemagnetics, Model CMX-400), where the measurement was performed at a spin rate of 3 kHz and a pulse delay of 240 s at room temperature. The chemical shift of the apparatus was calibrated before every measurement using polydimethylsilane as the present standard sample whose peak location of −31 ppm has been determined by tetramethylsilane. The spectra were deconvoluted into the attributed Gaussian peaks and are described in detail in the next section. From their peak areas, the number of bridging oxygens per silicon was estimated and discussed as an indicator of the dimensionality of the polysiloxane network or, in other words, the intramolecular structure.

Other than the bridging-oxygen number, the molecular weight was taken into account. In order to obtain the spatial distribution of the molecular weight, which is considered to strongly influence the interaction between the molecules, the samples dissolved in tetrahydrofuran (THF) eluent were examined using the GPC apparatus (Tosoh Co., Ltd., Model RI-8000). Single-dispersed polydimethylsiloxane (PDMS) standards with three different molecular weights were measured for the calibration and the standards were supplied commercially by Aldrich.

III. Results

Figure 1a−c shows the imaginary parts of the elastic moduli, $G''(\omega)$, of the samples with $x = y = 0$, $x = 0.3$, and $y = 0.3$, respectively. $G''(\omega)$ increases gradually by heat treatment, indicating that the system is in the middle of polycondensation, which was confirmed by the NMR and GPC measurements as described later. The solid lines show linear fittings to the plots on a log−log scale. The result that $G'' \propto \omega$ corresponds to the so-called Newtonian flow. With an increase in the number of Ph$_2$Si[O-]$_2$ units per silicon, x, the increase in G'' by the heat treatment is decelerated and the slope of the spectrum is maintained at unity. On the other hand, the increase in G'' is accelerated with an increase in the number of the substitution of PhSi[O-]$_3$ units for MeSi[O-]$_3$ units, y, and the slope of the spectrum decreases by heat treatment for an extended duration, which implies that structural viscosity appears.

In the present study, G'' at $\omega = 1$ rad/s, which is denoted as G''_u, was selected to quantify the change in the viscoelastic property by heat treatment. The values of G''_u at various x and y are plotted against the heat-treatment duration in Figure 2a. The increase in G''_u by heat treatment is suppressed systematically with an increase in x and is enhanced with an increase in y, although the data are scattered at $t = 0$ min. The solid and broken lines are linear fits, and their slopes, which are approximately regarded as the rate of the increase in G''_u by heat treatment, are plotted against x and y in Figure 2b. The slope simply decreases and increases with an increase in x and y, respectively.

The bridging-oxygen number, m, is a physical quantity to characterize the spatial dimensionality of the polysiloxane network well and was determined by the ^{29}Si MAS NMR. Figure 3a−c shows the NMR spectra at $x = y = 0$, $x = 0.3$, and $y = 0.3$, respectively. As indicated by the broken curves, the measured spectra were deconvoluted into the attributed Gaussian peaks. The spectra can be basically classified into two peak groups, T and D, which are produced from silicon exhibiting three and two oxygens around it, respectively.[19−22] The T_R^k peak originates from the state where a silicon has one nonreactive organic group, R (= Ph or Me), k bridging oxygens, and $(3 - k)$ nonbridging oxygens with reactive groups such as ethoxy and hydroxyl.[20,21] The D_R^k peak is caused by the state
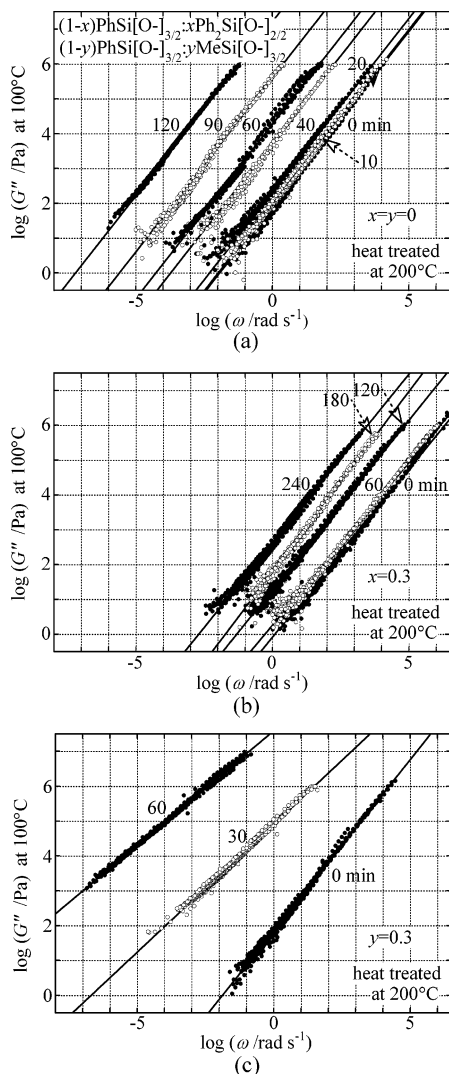
Figure 1. Elastic-modulus spectra after various heat-treatment durations at 200 °C for (a) $x = y = 0$, (b) $x = 0.3$, and (c) $y = 0.3$. The spectra measured at various temperatures between 20 and 200 °C were shifted along the ω-axis to superpose on the spectrum at 100 °C. Solid lines are linear fittings in the log−log scale.

where a silicon has two R, k bridging oxygens, and $(2 - k)$ nonbridging oxygens with the reactive groups.[20] The D_{cycl} peak has been reported to originate from hexaphenylcyclosiloxane.[22] From these peak areas, the bridging-oxygen number spatially averaged over the entire volume in the sample, $\langle m \rangle$, was estimated, and the values at various x and y are shown as a function of the heat-treatment time in Figure 4a. The values of $\langle m \rangle$ for $(1 - x)\text{PhSi[O-]}_{3/2}:x\text{Ph}_2\text{Si[O-]}_{2/2}$ and $(1 - y)\text{PhSi[O-}]_{3/2}:y\text{MeSi[O-]}_{3/2}$ systems are expected to change toward $(3 - x)$ and 3, respectively, as the polycondensation ideally progresses. The extent of the reaction, γ, defined as the ratio of $\langle m \rangle$ during the reaction in progress to $\langle m \rangle$ predicted by complete polycondensation, was estimated and is plotted against heat-treatment duration in Figure 4b. The increase in $\langle m \rangle$ and γ by heat treatment tends to be discouraged with an increase in x. This tendency roughly agrees with the results that the increase in G'' by heat treatment is suppressed by an increase in x (see Figure 2a). On the other hand, the increase in $\langle m \rangle$ and γ was not found to change systematically with an increase in y. This is not sufficient to explain the reason why the increase in G'' is enhanced by an increase in y. Another structural factor should be regarded in order to consistently explain the origin of the increase in G'' by heat treatment.
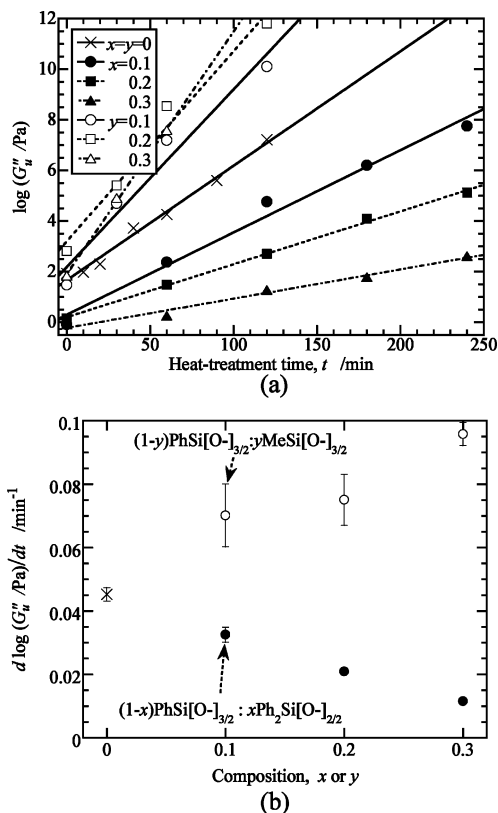

Figure 2. The influences of the amount of organic groups, x and y, on the increase in elastic modulus at $\omega = 1$ rad/s, G''_u: (a) shows G''_u at various x and y against the duration of heat treatment at 200 °C, where solid and dotted lines are linear fittings; (b) shows the rate of increase in log G''_u by heat treatment, corresponding to the slopes of the fitted lines shown in Figure 2a, against x and y.

The molecular weight, M, is strongly related to the viscoelastic property of many organic polymers.[11] In the present study, M was examined along with the bridging-oxygen number. The distributions of M at $x = y = 0$, $x = 0.3$, and $y = 0.3$, which were detected by GPC, are shown in Figure 5a−c, respectively. M increases as its distribution extends by heat treatment, and such an increase is decelerated and accelerated by increasing x and y, respectively. The weight average of the M distribution, $\langle M \rangle$, was employed as an indicator of the M distribution in the present study, although the complex distribution cannot be completely quantified by $\langle M \rangle$. The values of $\langle M \rangle$ at various x and y are plotted against the heat-treatment time in Figure 6a. The slopes of the fitted lines, as shown by solid lines, are approximately the degree of how rapidly the molecular size increases by heat treatment. Figure 6b shows the slopes as functions of x and y. The increase in $\langle M \rangle$ by heat treatment is discouraged and encouraged with an increase in x and y, respectively, which is similar to the behavior in the elastic-modulus change.

IV. Discussion

The present study focuses on the manner in which the organic functional groups influence the changes in the structure and viscoelastic properties by heat treatment. The two characteristic functional groups, Ph and Me groups, were selected for investigating the effects of (i) and (ii) as described in the Introduction. In the case of the $(1 - x)\text{PhSi[O-]}_{3/2}:x\text{Ph}_2\text{Si[O-}]_{2/2}$ system, the influence of the Ph-group numbers on the viscoelastic and structural changes by varying x, that is, the *number* effect of substituents, was examined. In the case of the

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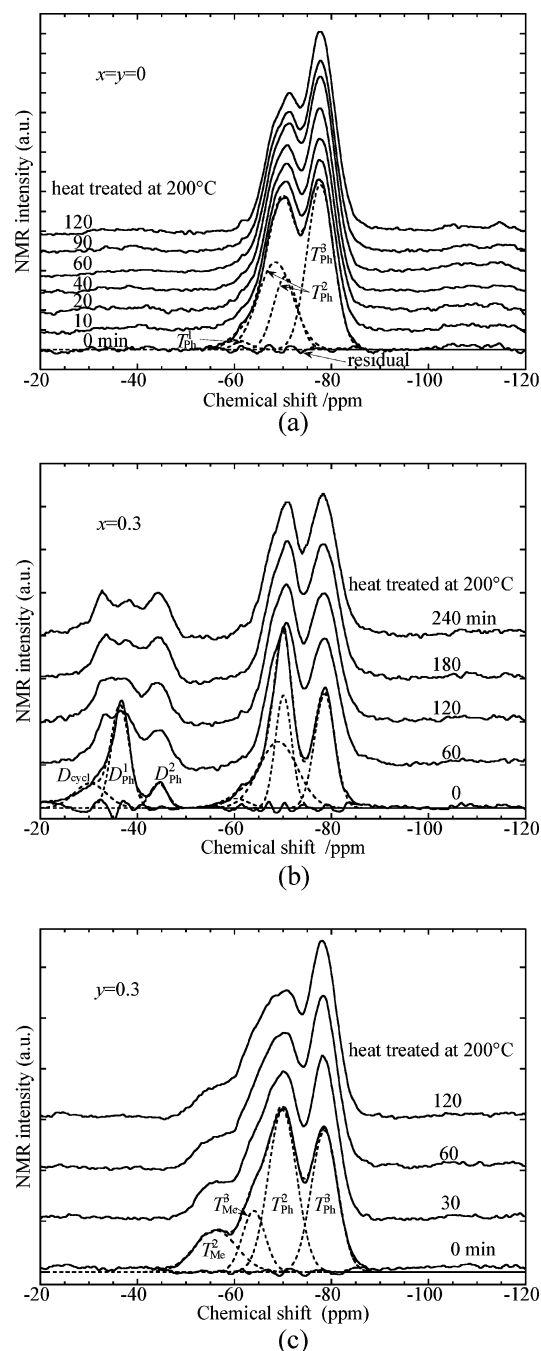*J. Phys. Chem. B, Vol. 111, No. 5, 2007* **985**

Figure 3. ^{29}Si MAS NMR spectra at (a) $x = y = 0$, (b) $x = 0.3$, and (c) $y = 0.3$ after various heat-treatment times. The spectra were deconvoluted into Gaussian peaks as shown by the broken curves, where the respective peaks are attributed as noted in the text.

$(1 - y)$PhSi[O-]$_{3/2}$:yMeSi[O-]$_{3/2}$ system, by changing y, the substitution of Ph groups for Me groups can be varied while maintaining the total number of these functional groups as a constant, and thus, the Ph-group effect was compared with the Me-group effect, namely, the *kind* effect of the substituents.

The NMR and GPC results suggest that the present materials exhibit a complex structure, that is, the distribution of various-sized molecules possessing a wide-ranging number of bridging oxygens per silicon. The intermolecular linkages among the distributed molecules are regarded as sufficiently weak to be snapped by the THF as the GPC eluent. Figure 7 shows an indicator of the molecular size, $\langle M \rangle$, plotted against the extent of the reaction, γ, and the inset shows the relationship between the bridging-oxygen number, $\langle m \rangle$, and γ. Because γ was
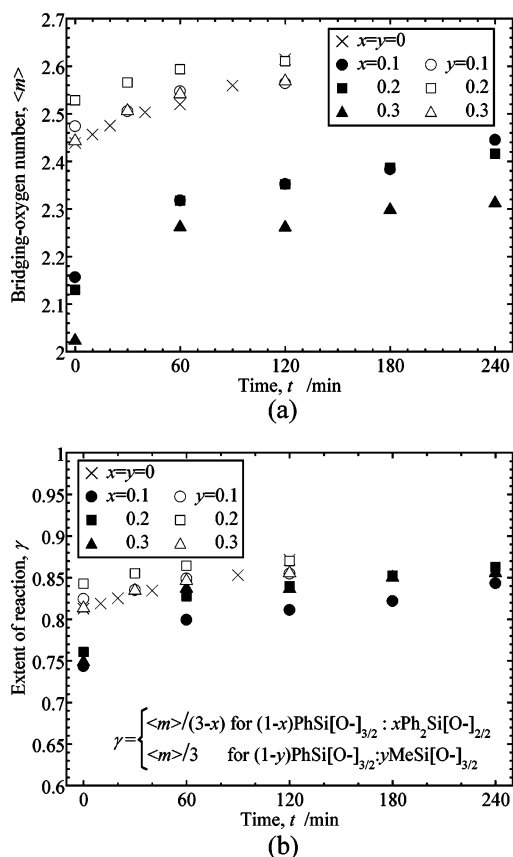

Figure 4. The number of bridging oxygens, $\langle m \rangle$, and the extent of reaction, γ, as functions of heat-treatment durations: (a) shows $\langle m \rangle$, which was estimated from the deconvoluted peak areas, at various x and y (the values for $(1 - x)$PhSi[O-]$_{3/2}$:xPh$_2$Si[O-]$_{2/2}$ and $(1 - y)$-PhSi[O-]$_{3/2}$:yMeSi[O-]$_{3/2}$ systems approach $(3 - x)$ and 3 with the progress in the heat treatment); (b) shows γ at various x and y, where γ was estimated from $\langle m \rangle$ and it approaches unity after the polycondensation is ideally completed.

estimated from the quantities $\langle m \rangle$, x, and y, as described in the previous section, $\langle m \rangle$ changes along the dotted lines with an increase in γ as shown in the inset. $\langle M \rangle$ increases exponentially with an increase in γ, and the manner of the increase does not appear to vary systematically with a variation in x and y. Because the properties of sol−gel products are generally sensitive to the reaction conditions with regard to humidity, time for gelation, etc., such delicate experiments are speculated to hinder the systematic data.

Figure 8a shows a plot of G''_u as a function of $\langle m \rangle$ and $\langle M \rangle$ in order to examine the relationship between structure and the elastic properties. G''_u increases monotonically with an increase in $\langle m \rangle$ and $\log\langle M \rangle$, and such an increase is independent of the values of x and y. To quantify the relationship empirically, a planar fitting, which is the simplest formula, was presently attempted for all the data, as shown by a meshed plane and is expressed by

$$\log G''_u = (-34.47 \pm 3.14) + (9.06 \pm 1.39)\langle m \rangle + (3.83 \pm 0.45) \log \langle M \rangle \quad (1)$$

Figure 8b shows the plot viewed along the cross lines of the fitted plane with the $\langle m \rangle - \log\langle M \rangle$ plane in Figure 8a, where the solid line is a cross-section profile of the fitted plane. All the data are along the fitted plane. The coefficients of $\langle m \rangle$ and $\log\langle M \rangle$, as shown in the abscissa in Figure 8b, correspond to the degree of how strongly $\langle m \rangle$ and $\langle M \rangle$ contribute to the increase in G''_u, respectively. Nonzero coefficients of $\langle m \rangle$ and $\log\langle M \rangle$
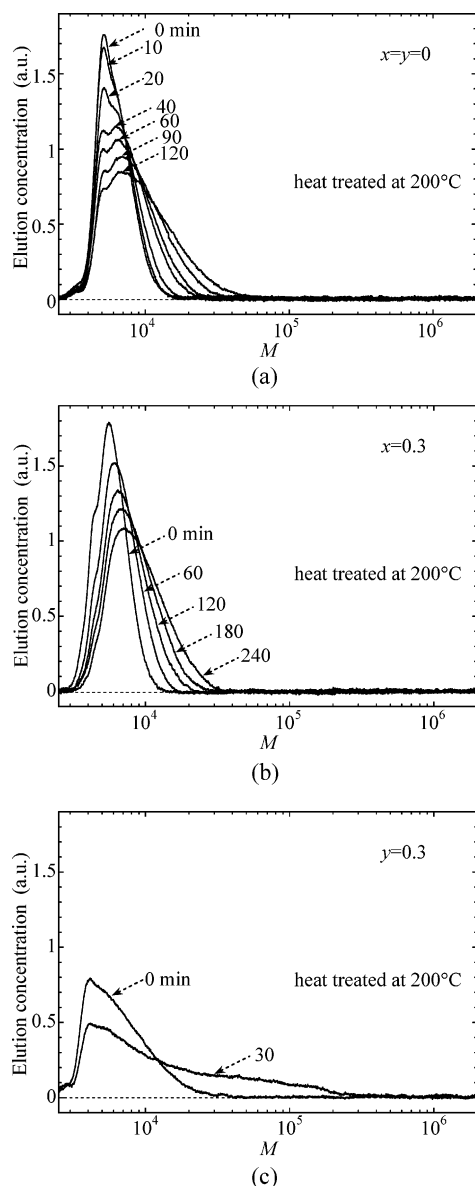
(a)

(b)

(c)

Figure 5. Distributions of molecular weights at (a) $x = y = 0$, (b) $x = 0.3$, and (c) $y = 0.3$ after various heat-treatment durations at 200 °C.

indicate that both the bridging-oxygen number and the molecular-size distribution influence the viscoelastic property. From the viewpoint of material design, the planar fitting suggests that the elastic modulus can be flexible and simply controlled by varying $\langle m \rangle$ and $\langle M \rangle$.

Other than the value of the elastic modulus, the frequency dependence in the elastic-modulus spectrum is important for characterizing the viscoelastic property. In the present study, the slopes of the linear fittings shown by solid lines in Figure 1 are regarded as ω dependence of G'' and are discussed. Figure 9 shows the slopes, $\mathrm{d}(\log G'')/\mathrm{d}(\log \omega)$, against $\langle m \rangle$ and log-$\langle M \rangle$. The slope retains a constant value around unity at a small value of $\langle M \rangle$, and it tends to decrease gradually with an increase in $\log\langle M \rangle$, and then it falls critically down to a value around 0.7 when $\log\langle M \rangle$ exceeds 4.8, although it appears to be insensitive to the change in $\langle m \rangle$, as shown in the inset. Although the viscoelastic behavior with a slope of unity corresponds to the Newtonian flow, the decrease in the slope indicates that the structural viscosity, or rubbery state, appears. In many organic polymers, the rubbery state has been found to appear with an increase in the molecular weight above a certain critical value,
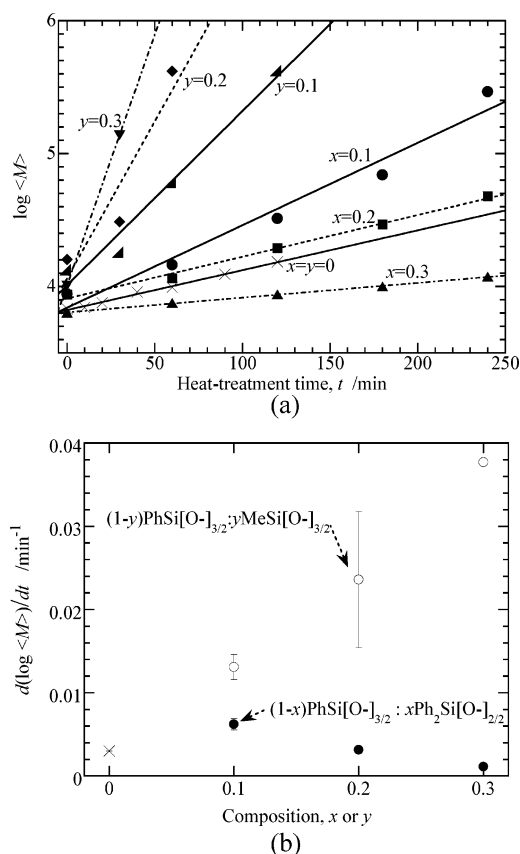

(a)

(b)

Figure 6. The influence of organic groups on the increase in molecular weight by heat treatment at 200 °C. Part a shows the weight average of molecular-weight distribution, $\langle M \rangle$, presently defined as an indicator of the increase in M and estimated from the data in Figure 5. Note that solid and broken lines are linear fittings. The rate of the increase in $\langle M \rangle$ by heat treatment, $\mathrm{d}(\log \langle M \rangle)/\mathrm{d}t$, which is the slope of the fitted lines shown in Figure 6a, is plotted as a function of x and y in (b).
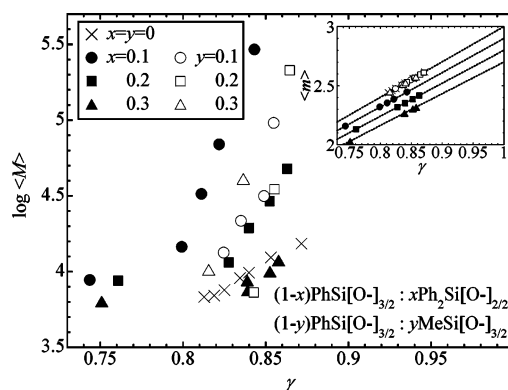

Figure 7. The relationship between $\langle M \rangle$ and the extent of reaction, γ, at various x and y. The inset shows the relationship between $\langle m \rangle$ and γ, where the data change along dotted lines.

and it originates from the strong intermolecular interaction, or entanglement.[11] The appearance of a rubbery state in the present system is similar to that in many other organic polymers.

The functions of the organic groups in the changes in structure and viscoelastic properties are summarized as follows:

(1) The increase in the elastic modulus by heat treatment is decelerated with an increase in the number of Ph groups per silicon (*number* effect of substituents).

(2) It is accelerated with an increase in the substitution number of Ph for Me groups (*kind* effect of substituents).

(3) The number of bridging oxygens gradually increases by

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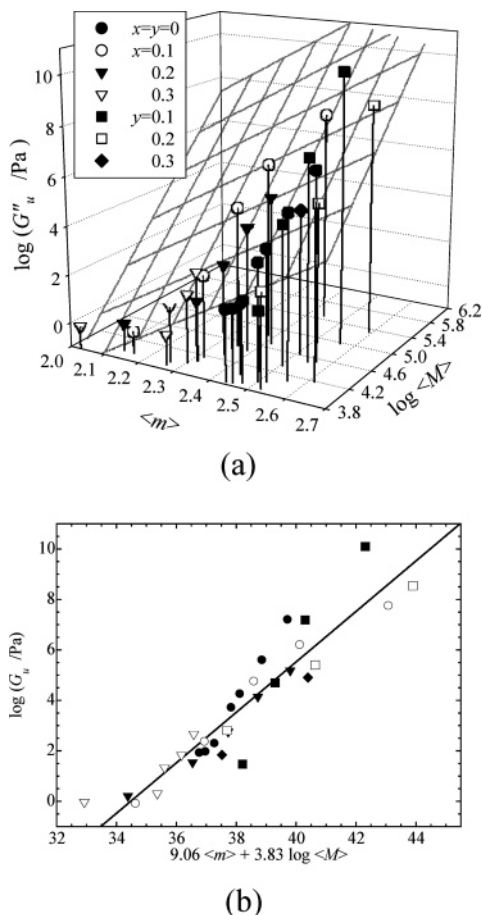*J. Phys. Chem. B, Vol. 111, No. 5, 2007* **987**

(a)

(b)

Figure 8. The relationship between the elastic modulus, the average number of bridging oxygens, and the weight average of the molecular-weight distribution, G''_u, $\langle m \rangle$, and $\langle M \rangle$, respectively, at various x and y: (a) meshed plane is a planar fitting of all the present data, whose formula is expressed in eq 1; (b) shows the plot viewed along the cross lines of the fitted plane with the $\langle m \rangle - \log \langle M \rangle$ plane in Figure 8a, where the solid line is a cross-section profile of the fitted plane and expressed by in eq 1.
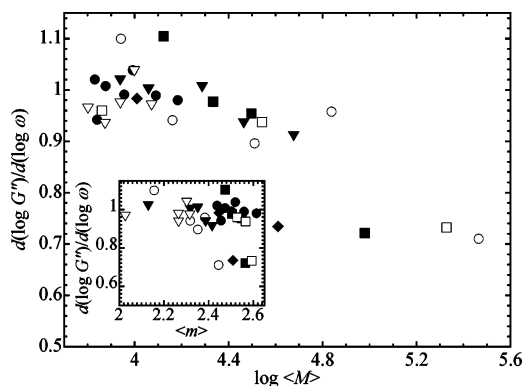

Figure 9. The frequency dependences of elastic moduli for all the present samples, which are slopes of the fitted lines in Figure 1, as a function of the weight average of the molecular-weight distribution. The inset shows the value against the average number of bridging oxygens.

the heat treatment, and organic groups have no significant influence on the manner of the increase within the measurement accuracy.

(4) The spatial distribution of the molecular size extends exponentially toward a large value with the progress in polycondensation. The increase in the molecular size is discouraged by increasing the Ph-group number per silicon; it is

encouraged by increasing the substitution number of Ph groups for Me groups.

(5) The elastic modulus approximately increases linearly with an increase in the bridging-oxygen number and the molecular size, and this linear relationship is irrespective of the type and the amount of the present organic groups.

(6) The appearance of the rubbery state depends more strongly on the molecular weight rather than the bridging-oxygen number.

Summaries 1−5 lead to the consideration that both of the changes in the bridging-oxygen number and the molecular weight contribute to the increase in the elastic modulus by heat treatment; however, the manner of such an increase is influenced by the organic functional groups mainly through a change in the molecular weight.

Two simple systems, $(1 - x)\text{PhSi}[\text{O-}]_{3/2}:x\text{Ph}_2\text{Si}[\text{O-}]_{2/2}$ and $(1 - y)\text{PhSi}[\text{O-}]_{3/2}:y\text{MeSi}[\text{O-}]_{3/2}$, were presently selected from the many types of polysiloxane materials, and then the number and kind effects of the substituents on the change in the viscoelastic property by heat treatment were severally studied. This fundamental information is essential to predict the softening behavior of the more-complicated organic-modified polysiloxane systems. For example, the softening temperature, T_S, of $(1 - z)\text{PhSi}[\text{O-}]_{3/2}:z\text{Ph}_2\text{Si}[\text{O-}]_{2/2}$ and $(1 - z)\text{PhSi}[\text{O-}]_{3/2}:z\text{Si}[\text{O-}]_{4/2}$ systems at various z after extended heat-treatment, was measured by thermomechanical analysis.[12] According to this paper, T_S increases and decreases with an increase in z in the respective systems. This behavior in T_S against z is explained by summary 1; that is, the Ph-group numbers increase and decrease with an increase in z in the former and the latter systems, respectively. In this paper, T_S of the $(1 - z)\text{PhSi}[\text{O-}]_{3/2}:z\text{Me}_2 \text{Si}[\text{O-}]_{2/2}$ system was also compared with that of the $(1 - z)\text{PhSi}[\text{O-}]_{3/2}:z\text{Ph}_2\text{Si}[\text{O-}]_{2/2}$ system. The T_S of both systems was reported to decrease with an increase in z, which is consistent with summary 1; that is, the number of organic groups in both the systems increases with an increase in z. Furthermore, the rate of the decrease in T_S per z for the $(1 - z)\text{PhSi}[\text{O-}]_{3/2}:z\text{Me}_2 \text{Si}[\text{O-}]_{2/2}$ system was reported to be smaller than that for the $(1 - z)\text{PhSi}[\text{O-}]_{3/2}:z\text{Ph}_2\text{Si}[\text{O-}]_{2/2}$ system. The former system possesses both the number and the kind effects of the substituents; only the number effect exists in the latter system. From summaries 1 and 2, the existence of two effects in the former system can be simply considered to weaken each other.

V. Conclusion

The relationship between the structure and the viscoelastic properties and the influences of the organic groups on the relationship were investigated. Two types of organic-group effects were studied, that is, the number and kind effects of the substituents. An increase in phenyl-group numbers per silicon decelerates the increase in the elastic modulus by heat treatment; the increase in the substitution number of the phenyl groups for the methyl groups accelerates it. According to the NMR and GPC results, the organic−inorganic hybrid material possesses a complex structure, the distribution of various-sized molecules with a polysiloxane network structure with various spatial-dimensionalities. This structure was classified into two quantities: average number of bridging oxygens and the molecular-weight distribution. The elastic modulus was then well expressed by a simple formula of these two structural factors. The viscoelastic property is strongly related with both the structural factors, and the relationship does not depend on the organic groups. However, the organic groups influence the change in the elastic modulus by heat treatment mainly through

the change in the molecular weight, and such effects can be controlled by the type or the amount of organic groups.

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