# Preparation of Phenyl-modified Siloxane Glasses with Softening Temperature Controlled by Rapid Heat Treatment (RHT)

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Thermosoftening phenylpolysiloxane glasses with controlled softening temperature have been obtained by a heat treatment at temperatures close to the decomposition temperature of organic component for several minutes, which we call a rapid heat treatment (RHT). Precursor glasses for RHT should be silanol-free, which were prepared by polycondensation of fully hydrolyzed small oligomers. The softening temperature ($T_s$) and weight-average molecular weight ($M_w$) of the obtained glasses could be controlled by the RHT at 400–500 °C for 5 min. The decrease of the molecular weight through the rearrangement of siloxane network was responsible for a decrease of the softening temperature by RHT.

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It was reported that the extent of polycondensation of $PhSiO_{3/2}$ siloxane was increased by a prolonged heat treatment (e.g., at 200 °C for 200 h), resulting in the disappearance of the thermosoftening property.[1,2] On the other hand, $(1-x)$-$PhSiO_{3/2}$–$xPh_2SiO_{2/2}$ glasses retained the thermosoftening property even after prolonged heating because of the lower crosslinking density.[2–5] It was also possible to eliminate all silanol groups in the siloxane melt by heating the obtained gel at 250 °C for 1 h under reduced pressure, resulting in a complete polycondensation. However, so far, it has been very difficult to control the $T_s$ of the obtained glass. It can be explained by a large distribution of molecular weight as a result of successive polymerization of siloxane oligomers which is hardly controlled. Accordingly, the purpose of this study is to control the $T_s$ and $M_w$ of the glasses by a post treatment of the obtained siloxane such as a rapid heat treatment (RHT) in which the obtained siloxane was heat treated for a several minutes at high temperatures very close to the decomposition temperature of organic functional groups of organosiloxane.

$0.8PhSiO_{3/2}$–$0.2Ph_2SiO_{2/2}$ glass was prepared by the method reported in ref 4, followed by the RHT as mentioned below. The composition of the starting solutions was given by phenyltriethoxysilane (PhTES):diethoxydiphenylsilane (DEDPhS):ethanol:water:acetic acid catalyst, 0.8:0.2:10:50:0.1 in molar ratio. The sol was prepared by mixing PhTES, ethanol, water, and acetic acid under stirring at room temperature. The mixed solution was heated at 60 °C for an hour in an open system. After DEDPhS was added to it, the sol was heated at 60 °C for 2 h. A glass melt was then obtained by further concentration and polycondensation at 150 °C for 5 h. Subsequently, the phenyl-modified polysiloxane glass underwent complete polycondensation at 250 °C for 1 h under reduced pressure. The phenyl-modified polysiloxane glass (2 g) in powder form was then put into a preheated furnace at 400–525 °C, and left for 5–15 min under atmospheric pressure (RHT). Molecular weight of the obtained siloxane was estimated by GPC. The elution time was converted to molecular weight using an analytical curve obtained by polydiphenyl siloxane of known molecular weight.

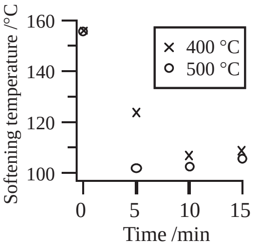

**Figure 1.** $T$s of $0.8PhSiO_{3/2}$–$0.2Ph_2SiO_{2/2}$ after RHT at 400 and 500 °C for 0, 5, 10, and 15 min.

Figure 1 shows the change of $T_s$ with the different RHT duration. $T_s$ decreased with increasing RHT duration until 10 and 5 min for RHT at 400 and 500 °C, respectively. Then, the $T_s$ increased with the duration. The thermosoftening property finally disappeared by prolonged heat treatment at these temperatures. Hereafter, the RHT treatment was carried out for 5 min duration. Colorless, yellow-discolored glasses and brown foam material were obtained by RHT at 400–475, 500–525, and 550 °C, respectively. The $T_s$ of the glasses after RHT was stable against the prolonged heat-treatment. For example, the $T_s$ (=103 °C) of $0.8PhSiO_{3/2}$–$0.2Ph_2SiO_{2/2}$ glass after RHT at 500 °C remained unchanged even after heating at 200 °C for 100 h.

Figure 2 shows the GPC curves of the siloxane glasses before and after RHT at 400 and 500 °C. It is very interesting to mention that the $M_w$ of the glasses after RHT decreased as compared with the precursor glass obtained by a reduced heat treatment at 250 °C. Thus, it is clear that the rearrangement, such as dissociation and recombination, of siloxane network did occur under RHT. The $^{29}Si$ NMR spectra of the obtained glasses after reduced-pressure heating and RHT at 400 °C are shown in Figure 3 (left-hand side). $D^2$ and $T^3$ were observed in the spectra,

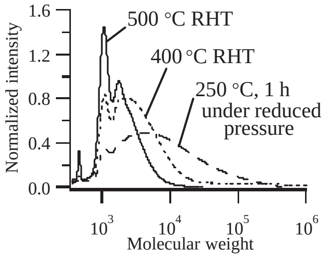

**Figure 2.** GPC curves of $0.8PhSiO_{3/2}$–$0.2Ph_2SiO_{2/2}$ after various post heat treatments.

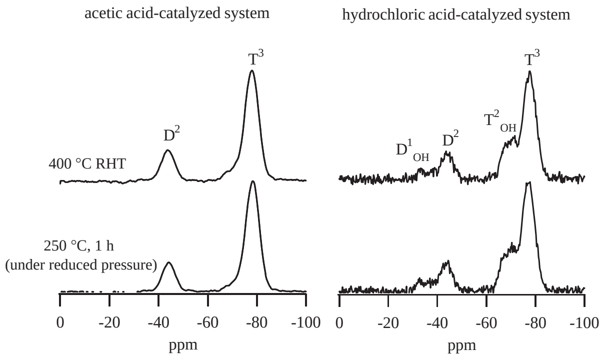

**Figure 3.** $^{29}$Si NMR spectra of $0.8PhSiO_{3/2}$–$0.2Ph_2SiO_{2/2}$ after heating at 250 °C under reduced pressure and RHT.

**Table 1.** $T_s$, $M_w$, and $P$ of $0.8PhSiO_{3/2}$–$0.2Ph_2SiO_{2/2}$ after various post heat-treatments

| Heating conditions | $T_s$/°C | $M_w$ | $P$ |
|---|---|---|---|
| 150 °C, 5 h | 47 | 2,700 | 2.0 |
| 250 °C, 1 h under reduced pressure | 156 | 65,500 | 2.8 |
| 400 °C RHT | 124 | 7,800 | 2.8 |
| 500 °C RHT | 103 | 3,500 | 2.8 |
| 525 °C RHT | 122 | 8,100 | 2.8 |

suggesting the complete polycondensation both before and after RHT.[6–8] Thus, we can say that siloxane bond was dissociated by thermally induced molecular motion and was quickly recombined each other to form smaller molecules. The $T_s$, $M_w$, and the extent of polycondensation ($P$) of $0.8PhSiO_{3/2}$–$0.2Ph_2SiO_{2/2}$ are shown in Table 1. Because of the complete polycondensation, $M_w$ and $P$ were increased largely by the reduced-pressure heating. $T_s$, $M_w$ decreased with increasing RHT temperature in the range of 400–500 °C, although their values increased with increasing RHT temperature over 500 °C. In the case of RHT at 525 °C, the $T_s$ as well as $M_w$ did not decrease, which is probably due to the oxidation of the phenyl group. Actually, estimated glass composition from $^{29}$Si NMR spectrum after RHT at 525 °C was $0.82PhSiO_{3/2}$–$0.18Ph_2SiO_{2/2}$. Therefore, the decrease of phenyl content in the glass (especially in the D unit) was confirmed.

It should be noted here that the decrease of $T_s$ by RHT was only observed for the silanol-free siloxane glasses, which can be obtained by reduced heat treatment of siloxane gel prepared from acetic acid-catalyzed system. Only the increase of $T_s$ was observed for hydrochloric acid-catalyzed system by RHT ($T_s$' of the samples after RHT at 400 and 500 °C are 142 and 175 °C, respectively). In the case of the glass containing residual OH groups prepared from hydrochloric acid-catalyzed system, RHT was not effective in controlling the $T_s$ and $M_w$. In hydrochloric acid-catalyzed system, $D^1{}_{OH}$ and $T^2{}_{OH}$ which include OH group were observed even after RHT as shown in Figure 3 (right-hand side). This is probably because free volume and network flexibility were given to the glass matrix by introduction of such isolated OH groups. Therefore, it is considered that the rearrangement of siloxane bonds leads to the formation of three-dimensionally developed network structure. It is required in order to realize the complete polycondensation that the sol composition (acid catalyst and water content) has to be selected in such a way that the hydrolysis and polycondensation occur independently.

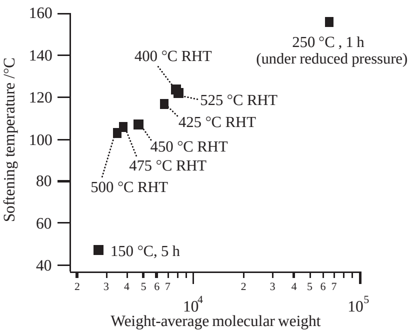

**Figure 4.** Correlation between $M_w$ and $T_s$ of $0.8PhSiO_{3/2}$–$0.2Ph_2SiO_{2/2}$ after various post heat-treatments.

The breaking of siloxane bonds is known to depend on the number of Si atoms in the siloxane ring, in other words, the siloxane ring size.[9–11] In the case of $0.8PhSiO_{3/2}$–$0.2Ph_2SiO_{2/2}$ glass, the strain of the siloxane ring is considered to be larger than that of silica because of the presence of bulky phenyl groups in a crowded state. It was observed for the glasses obtained by RHT that the decrease of the $T_s$ by RHT is considered to be caused by thermal breaking of the siloxane bonds and rearrangement of the siloxane structure. The absorption bands due to siloxane bonds around 1000–1080 cm$^{-1}$ decreased after 400–525 °C RHT. In the IR spectrometry of silica glass, the lower wavenumber region in the absorption bands due to the siloxane bonds (1000–1130 cm$^{-1}$) is assigned to smaller siloxane rings.[12] This result suggests the breaking of small siloxane rings and the generation of larger ones.[12] The detailed analysis of rearrangement of siloxane network will be discussed in the forth coming paper.

The plots of the $T_s$ and $M_w$ of obtained glasses for various post heat treatments are shown in Figure 4. The $T_s$ and $M_w$ were low when heated at 150 °C because the degree of condensation $P$ was not so high. A linear relationship between them was observed for the samples after RHT at 400–500 °C. Therefore, the $T_s$ of the glasses obtained by RHT primarily depend on their $M_w$. $T_s$ can be also changed by changing RHT duration as shown in Figure 1.

In conclusion, silanol-free thermosoftening phenyl polysiloxane glasses were obtained by heating at 250 °C for an hour under reduced pressure and RHT at 400–500 °C for 5 min. Furthermore, the $T_s$ could be controlled by the RHT temperature without changing the glass composition.

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