Effect of Thermal Conditions on the Cluster Formation of Sulfonated Polystyrene Ionomers

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The effect of thermal conditions on the clustering of sulfonated polystyrene ionomers was investigated. It was found that when the zinc-sulfonated ionomer was dried above a matrix glass transition temperature ($T_g$), the cluster $T_n$ was observed at ca. 310 °C, which is ca. 45 °C higher than that for the ionomer dried below the matrix $T_g$. This difference is believed to be the result of an increase in ion mobility at higher temperatures, which improves the multiplet formation and clustering; thus the cluster $T_n$ increases. In the lithium ionomer case, however, the increase in the cluster $T_n$ was ca. 6 °C upon annealing. From the results, it was suggested that in the zinc ionomer, the zinc ion is soft and divalent, which results in weaker interactions in multiplets, and thus decreases the stability of the multiplets. Therefore, the thermal effect is more significant for the zinc ionomers than for the lithium ionomers.

Introduction

Ionomers are usually known as polymers containing less than ca. 15 mol % of ionic groups along nonionic backbone chains.1 One of the interesting characteristics of polystyrene-based ionomers is the presence of two glass transitions (Tg's) in certain ion contents. The glass transition at lower temperature is called a matrix glass transition, whereas that at a higher temperature is known as a cluster $T_g$. Polystyrene ionomers also show the ionic peak in the small-angle X-ray scattering (SAXS) profile. In order to explain this behavior qualitatively, Eisenberg et al. proposed Eisenberg-Hird-Moore (EHM) model of random ionomer.2 According to the EHM model, ionic groups having high dielectric constant phase-separate from the matrix of low dielectric constant, and those ionic groups form ionic aggregates, called multiplets,3 owing to the ionic interactions between the ionic groups. Now, the multiplets act as points which reduce the mobility of chains surrounding the multiplet. If the ion content is low, the size of the reduced mobility area is so small that the area including the multiplet cannot have its own glass transition. When the ion content increases, the number of the multiplets increases. If the ion concentration is high, the regions of the reduced mobility start to overlap. The overlapping regions are now called clusters, and the regions show their own $T_g$ at higher temperatures than the matrix $T_g$. In the model, Eisenberg et al. described that the multiplets in the cluster phase act as scattering centers and that thus the SAXS peak represents the average intermultiplet distances.

It has been known that the cluster formation can be affected by various experimental conditions,1,4-7 among which, in the present study we focus on the thermal conditions. At this point, it will be useful to review some of previous findings. In the case of sulfonated polystyrene ionomers, Galambos et al.8 found that, when Mn²⁺ neutralized sulfonated polystyrene (6.7 mol% of ions) sample was cast from the mixed solvent of THF and water (9/1 v/v), no SAXS peak was observed. However, when the sample was heated, the ionomer started to show a SAXS peak, and the intensity of the SAXS peak increased with increasing temperature. They suggested that at high temperatures water molecules were removed from the sample, and that the scattering center started to form. Connolly9 studied the effect of thermal treatment on the mechanical properties of a polystyrene ionomer containing 2.5 mol% of sodium sulfonate. He found that tan $\delta$ peak positions shifted to higher temperatures upon annealing, but that annealing temperature did not change significantly the tan $\delta$ peak positions. Furthermore, Hara et al.10 also investigated the annealing effect on the mechanical properties of a sulfonate polystyrene ionomer containing 2.5 mol% of ions. They reported that the annealing of the ionomer sample at 200 °C for 24 hours induced a weak cluster $T_g$ at ca. 210 °C. However, the results reported for the sulfonate ionomers so far are rather scattered, and thus one can conclude only as far as the thermal treatment affects the clustering.

In the case of carboxylate system, Kim and Eisenberg studied systematically the effect of thermal treatment and humidity on the cluster formation in poly(styrene-co-sodium methacrylate) (3.4 mol% of ionic groups).11 They found that the cluster $T_n$ of the thermally treated sample (at 220 °C for 3 days) was ca. 10 °C higher than that of an ionomer without annealing. In addition, the cluster $T_n$ of the ionomer containing 0.04 wt% of water was ca. 9 °C lower than that of a well-dried sample. They postulated that the polar water molecules could reside in multiplets and weaken the interactions between ionic groups in the multiplets. As a result, the ionic groups can hop at relatively lower temperatures than in the well-dried sample, and thus the cluster $T_n$ decreases.

From the above findings, one can ask the following questions. First of all, how strong would be the thermal effect on the clustering of an ionomer having higher ion contents? If the properties of ionomers are changed by the thermal treatment, the ionomers of a high ion content will show a

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more profound effect. Secondly and especially, how strong is the effect of thermal treatment on the cluster formation in sulfonate ionomers? In the sulfonate ionomers, as one can expect, the ionic interactions are stronger than those in the carboxylate ionomers; thus the thermal influence may be more significant for the sulfonate than for the carboxylate.

In the present study, we investigated the effect of thermal treatment on the cluster formation of a sulfonated polystyrene ionomer (10.7 mol% of ions) neutralized with Zn$^{2+}$. We chose the zinc acetate to neutralize the ionomer, since one can find the zinc cation as a counterion in some of commercialized ionomers. In addition, to compare the thermal effect on the properties of an ionomer neutralized with a divalent cation to that of an ionomer neutralized with a monovalent ion, we also prepared lithium-sulfonated polystyrene ionomers. In order to study the thermal effect systematically, we dried and annealed ionomers at two different temperatures for two different periods of time, and we investigated the dynamic mechanical behavior of ionomers.

**Experimental**

**Sample Preparation.** High molecular weight polystyrene (MW=ca. 500,000) was prepared by bulk free radical polymerization. Sulfonic acid groups were introduced into the polystyrene by a sulfonation method slightly modified from Makowski et al.$^5$. The sulfonation level was ca. 10.7 mol%. The acid form sample in benzene/methanol (9/1 v/v) was neutralized with methanolic lithium hydroxide and zinc acetate. The solution was freeze-dried and then dried further under vacuum at 120 °C for one day and five days or at 190 °C for one day, depending on the experimental condition. In order to prepare for dynamic mechanical property measurements, the samples were compression molded in a mold at 280 °C with pressure of 25 MPa for five minutes. The pressure was slowly released, and the mold was slowly cooled to below the matrix $T_c$. The samples were removed from the mold and annealed under vacuum at 120 or 190 °C for one or five days, depending on the designed condition. The dimensions of the molded sample were ca. 2.5×7×30 mm. The various thermal conditions for drying and annealing are listed in Table 1.

**Dynamic Mechanical Thermal Analysis (DMTA).** A Polymer Laboratories DMTA Mark II was utilized for the measurement of the mechanical properties of ionomers. For each sample, the storage moduli ($E'$) and loss tangent (tan δ) were obtained in a dual cantilever bending mode as a function of temperature at a heating rate of 1 °C/min. The experiments were performed at five frequencies (0.3, 1, 3, 10, and 30 Hz).

**Data Analysis.** Activation energies for the matrix and cluster glass transitions were calculated using an Arrhenius plot of log frequency against inverse peak temperature.

**Results and Discussion**

Figure 1 shows the storage modulus ($E'$) and loss tangent (tan δ) values as a function of temperature at 1 Hz of a zinc neutralized ionomer dried and annealed at 120 °C for one day (120-D1-120-A1) and an ionomer dried at 190 °C and annealed at 120 °C for one day (190-D1-120-A1). At this point, it should be mentioned that 120 °C is lower than the matrix $T_c$ of ionomer but is thought to be high enough to dry the sample; the temperature of 190 °C is below the thermal decomposition temperature of ionomers (i.e., >300 °C) and is in between the matrix $T_c$ and the cluster $T_g$ of the ionomer. At 190 °C, the polymer chains in the matrix phase can have some degree of mobility. In the storage modulus curves, one sees as a function of temperature the glassy region, the glass transition of the matrix phase, the "ionic plateau", the glass transition of clusters, and the rubbery "plateau". It is seen that the storage modulus values of the two ionomers are similar up to ca. 150 °C. However, above

![Figure 1. Storage modulus ($E'$) and loss tangent (tan δ) measured as a function of temperature at 1 Hz for the 120-D1-120-A1 and 190-D1-120-A1 ionomers.](image-url)
that temperature the modulus curves of the two ionomers diverge. For example, at 250 °C, the storage modulus of the 120-D1-120-A1 is ca. $4.0 \times 10^9$ Pa, while that of the 190-D1-120-A1 is $1.5 \times 10^7$ Pa. In the tan δ curves, there are two peaks; the one at the lower temperature is caused by the glass transition of the matrix phase, whereas the other, at higher temperature, is owing to the cluster $T'_g$; the aspects were discussed elsewhere.\textsuperscript{13,14} Figure 1 also shows that the matrix $T'_g$ peaks at ca. 160 °C are similar in positions and sizes, but that the position of the cluster $T'_g$ peak maximum of the 190-D1-120-A1 sample (i.e. cluster $T'_g$ at ca. 310 °C) is ca. 45 °C higher than that of the 120-D1-120-A1 sample (i.e. cluster $T'_g$ at ca. 265 °C). The temperatures of tan δ peak maxima at 1 Hz are listed in Table 2.

From Kim and Eisenberg's study mentioned above,\textsuperscript{11} it can be thought that the difference in the cluster $T'_g$ of the present study is simply owing to the polar plasticization effect by the presence of water molecules. Thus, we will consider the polar plasticization effect first. At this point, it should be noted that the possible presence of water molecules can be investigated by using such methods as spectroscopy techniques. However, our main aim is to find the answer to the question of the presence of the water molecules in multiplets by DMTA experiments under well-designed experimental conditions.

It was expected that, if we dried samples for a longer period of time, we could eliminate more water molecules from the samples. Thus, we dried a sample at 120 °C for the extended period of five days before molding and annealed it at the same temperature for one day after molding (120-D5-120-A1). We also prepared one more sample which was dried at 120 °C for one day and annealed for five days (120-D1-120-A5) in order to avoid the possible moisture absorption during the molding process. Figure 2 shows the mechanical properties of these two samples as well as those of the 120-D1-120-A1 sample. It is seen that the storage moduli of these three samples are similar. In the loss tangent curves, one also sees a little change in the shape of the curves. The matrix $T'_g$ peaks for the samples dried or annealed for five days are rather lower at similar temperature positions than that of the ionomer dried for one day, whereas the cluster $T'_g$ peaks for the samples thermally treated for five days are slightly higher than that of the 120-D1-120-A1 sample. The positions of cluster $T'_g$ peak maximum of three ionomers are similar at 265±4 °C. From this result, it can be concluded that the effect of longer drying time on the ionomer properties is minor, and that the difference in the cluster $T'_g$ in Figure 1 does not come from the polar plasticization.

One question arises from the above results; the difference in the cluster $T'_g$ values in Figure 1 may be owing to drying temperature not to drying time. In an attempt to answer, we dried the sample at 190 °C for one day and then stored it

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Sample & Matrix $T'_g$ (°C) & Cluster $T'_g$ (°C) &  \\
\hline
zinc ionomers & & &  \\
120-D1-120-A1 & 168 & 266 &  \\
120-D1-120-A5 & 172 & 257 &  \\
120-D5-120-A1 & 166 & 265 &  \\
190-D1-120-A1 & 168 & 312 &  \\
(190-D1-5)-120-D1-120-A1 & 169 & 311 &  \\
lithium ionomers & & &  \\
Li-120-D1-120-A1 & 169 & 317 &  \\
Li-190-D1-190-A1 & 164 & 323 &  \\
\hline
\end{tabular}
\caption{Temperatures of tan δ peak maxima}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Storage moduli (E') and loss tangent (tan δ) measured as a function of temperature at 1 Hz for the 120-D1-120-A1, 120-D5-120-A1, and 190-D1-120-A5 ionomers.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Storage moduli (E') and loss tangent (tan δ) measured as a function of temperature at 1 Hz for the 190-D1-120-A1 and (190-D1-5)-120-D1-120-A1 ionomers.}
\end{figure}
under ambient conditions to allow the sample to absorb the moisture as much as possible. Subsequently, we dried the sample again at 120 °C for one day, molded it, and annealed it at 120 °C for one day [(190-D1-5)-120-D1-120-A1]. Shown in Figure 3 are the results of the mechanical property measurements of the (190-D1-5)-120-D1-120-A1 and the 190-D1-120-A1 samples. If the difference in the cluster \( T_g \)'s in Figure 1 is solely owing to the different drying temperature, the (190-D1-5)-120-D1-120-A1 sample should show curves similar to those of the 120-D1-120-A1 ionomer. However, in Figure 3, it is seen that the properties of the (190-D1-5)-120-D1-120-A1 ionomer are very much similar to those of the 190-D1-120-A1 sample. This result implies that the annealing effect is operative here. If the ionomer is dried at higher temperatures, not only can water molecules be removed, but also the polymer chain can have a high enough mobility that improves the multiplet formation and clustering. The improved multiplet formation naturally results in the more clustering and more rigid multiplet, and thus the cluster \( T_g \) increases. Table 3 shows apparent activation energies for the glass transition of the matrix and cluster phases. The activation energies for the matrix \( T_g \) of ionomers treated at 120 °C are somewhat higher than those of ionomers treated at 190 °C, whereas those for the cluster \( T_g \) of the 120 °C ionomers are lower than those of the 190 °C ionomers. From the findings, it can be suggested that the thermal treatment of the samples at two different temperatures induces two different morphologies in this ionomer system.

As the next stage, in order to investigate the effect of types of cation on the clustering, we prepared samples neutralized with alkali metal ion, i.e. Li⁺. Figure 4 shows the storage modulus and loss tangent curves of lithium samples dried and annealed at 120 (Li-120-D1-120-A1) and 190 °C (Li-190-D1-190-A1). The storage modulus curves appear to be similar, but the cluster \( T_g \) peak position for the Li-190-D1-190-A1 sample is ca. 6 °C higher than for the Li-120-D1-120-A1 sample. This result is similar to that of Kim and Eisenberg's study, in which they found that the increase in the cluster \( T_g \) of the poly(styrene-co-sodium methacrylate) ionomer by annealing is 10 °C. In Figures 4 and 5, we can also find that the cluster \( T_g \) in the zinc ionomer increases by 45 °C, whereas the increase is only 6 °C in the lithium ionomer. This difference may be owing to the nature of transition metal zinc ion; the zinc ion as a soft cation has weaker ionic interactions in the multiplets than does an alkali metal ion. Furthermore, in the case of the ionomer neutralized with a divalent cation, i.e. Zn²⁺, which needs two amionic groups for electroneutrality, the ion groups experience a more steric influence than in the ionomers neutralized with alkali metal ions when they form multiplets. Therefore, in the case of zinc-neutralized sample, the ion groups are rather loosely bound in the multiplets, and thus the thermal effect is significant.

**Conclusions**

The effect of the thermal treatment of poly(styrene-co-zinc styrenesulfonate) ionomer on the cluster \( T_g \) was investigated. If the sample was dried below the matrix \( T_g \), the length of drying time did not change the position of the cluster \( T_g \), which means that the degree of dryness does not strongly affect the cluster formation of ionomers. However, when the sample was dried above the matrix \( T_g \), it was observed that the cluster \( T_g \) increased by ca. 45 °C. This implies that at high temperatures the mobility of the chain increases and that new multiplets and more rigid multiplets can form; as a result, cluster glass transition temperature increases.

It was also found that in the lithium-neutralized sample the effect of the thermal treatment was much weaker than in the zinc sample. This finding can be explained by the fact that the zinc cation is a soft and divalent cation, resulting in weaker ionic interactions in the multiplets; thus the stability of zinc-sulfonate multiplets can be affected more strongly by the thermal conditions.

**References**

Synthesis and Fungicidal Activity of 1-[(1H-1,2,4-triazol-1-yl)alkyl]-1-silacyclopentanes

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A series of six-membered ring organosilicon compounds, 1-aryl-1-[(1H-1,2,4-triazol-1-yl)alkyl]-1-silacyclopentanes 3a-c, have been synthesized by four-step reactions starting from 1-(chloroalkyl)trichlorosilanes. Their fungicidal activities were tested in vitro for ten fungi and in vivo assay for four fungi occurring in rice, barley, tomato, and etc. and compared with the flusilazole. Especially, 1-p-fluorophenyl-1-[(1H-1,2,4-triazol-1-yl)alkyl]-1-silacyclopentanes (3a, alkyl=methyl; 3b, alkyl=ethyl) showed good fungicidal activity with broad spectrum close to the flusilazole in in vivo assay.

Introduction

Much attention has been paid to a synthetic approach, which can modify organic compounds with good biological activity to new silicon-introduced compounds in agrochemicals. Several modified organosilicon compounds have shown superior biological activities to the original organic compounds. Since it was found that especially bis(4-fluorophenyl)methyl(1H-1,2,4-triazol-1-yl)methylsilane known as flusilazole was effective in control of a broad spectrum of plant diseases in 1985, this is now one of the leading agricultural fungicides in silicon-based biological compounds. Many organosilicon compounds with the triazole group as an active site were then patented as good fungicides. The biological activity of these compounds is dependent on substituents on silicon at organosilicon compounds with triazolyl group and on the space length between silicon and the triazolyl group. Generally the organosilicon compounds containing both a p-substituted phenyl group and a triazolylmethyl group on the silicon atom, have shown good biological activities. The potency of biological activity was found to be increased in the broad spectrum for fungi, as the space length between the silicon and triazole is decreased to methylene from propylene. In a series of compounds, the structures of which p-fluorophenyl and (triadizol)ethylmethyl group on the silicon atom are best for the fungicidal activity. Based on literatures on these subjects, we synthesized the modified 1-aryl-1-[(1H-1,2,4-triazol-1-yl)alkyl]-1-silacyclopeptanes which were cyclized with butylene instead of both groups, methyl and p-fluorophenyl group, on the silicon of flusilazole. These compounds show good biological activities comparable to the flusilazole. In the expansion of this series, we wish to report the synthesis and the biological activity of six-membered ring compounds, 1-aryl-1-[(1H-1,2,4-triazol-1-yl)alkyl]-1-silacyclopentanes 3a-c, and compared with five-membered ring compounds.

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