Effect of poly(propylene oxide) segment size on structure-property relationships in elastomeric ionene

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The dynamic mechanical, thermal scanning, stress-strain and water sorption behaviours of the elastomeric ionene consisting of ionene and poly(propylene oxide) (PPO) segments are studied. The effect of PPO segment size on the microphase-separated structure in this material is described by the change of dynamic mechanical and thermal relaxation temperatures. The mixing of the PPO segment into the ionene segment domain increases with decrease of PPO segment size and reduces the crosslinking effect of the ionene segment domain, which leads to an increase in hysteresis for loading in this material. The number of equilibrium sorbed water molecules per ionene segment increases with increase in the purity of the ionene segment domain.

Keywords Elastomeric ionene; poly(propyleneoxide); mechanical properties; thermal properties; microphase-separated structure; water sorption

INTRODUCTION

Introducing ions into polymeric materials alters the supermolecular structure of polymers through ion-ion interaction and/or ion-polymer dipole interaction, and consequently affects many chemical and physical properties. A series of recent studies has been devoted to elucidating the structure-property relationships in ion-containing polymers¹. As a result, the ion-containing polymers have found a wide range of applications.

The majority of the studies of ion-containing polymers were performed on the properties and supermolecular structure of so-called ionomers; copolymers composed of a non-polar monomer such as $styrene^{2-5}$ and ethylene⁶⁻⁹ and an ionic monomer. In these ionomers, the ions aggregate to form ionic multiplets acting as transient crosslinks at low ion concentration, whereas at higher concentrations more extensive aggregation is encountered, leading to the formation of ionic clusters. These clusters, in turn, act not only as crosslinks but also as reinforcing filler, giving the sample some of the properties of phase-separated systems such as some block copolymers or partially crystalline materials. The formation of the ionic clusters is influenced by the dielectric constants of the host polymers $^{2,10-12}$, and the higher the dielectric constant the higher is the ion concentration at which the onset of clustering takes place. On the contrary, many kinds of ions can dissolve in polar polymers¹²⁻¹⁵ such as poly(propylene oxide)(PPO) up to a high concentration without forming ionic clusters, which leads to the enhancement of glass transition temperature and melt viscosity of the host polymer. In both cases, ion-ion interaction and/or ion-polymer dipole interaction influence(s) the structure and property of the ion-containing polymers.

Ionenes are one of the ionic polymers, with quaternary nitrogen atoms in the main chain. Many ionene structures have been synthesized¹, since Rembaum *et al.*¹⁶ first

reported them. Only a few investigations^{17,18}, however, have been reported on their physical properties, since they are very hard, brittle materials and highly hygroscopic. Some reports^{19–21} have been concerned with the mechanical properties of elastomeric ionenes based on polybutadiene, a kind of rubber-based ionomer containing cationic units. However, these ionomers have a three-dimensional crosslinked structure and the structure–property relationships in the elastomeric ionenes have not up to now been clarified.

We have studied the preparation of the linear elastomeric ionene characterized by alternating structure of PPO and ionene segments, and have carried out an application to an electrically conducting polymer^{22,23}. It is of considerable interest to explore the structureproperty correlations, directing attention to the microphase structure, since the ionic segment exists between the polar PPO segments which can dissolve ions up to a high concentration^{12,15}. In this study, the structure-property relationships in linear elastomeric ionenes prepared as a function of the PPO segment size were studied by means of dynamic mechanical, thermal scanning and stress-strain measurements. Especially, the effect of PPO segment size on the microphase-separated structure of the materials was noticed. Furthermore, the influence of water sorption on the mechanical properties was investigated.

EXPERIMENTAL

Materials

The elastomeric ionenes were prepared by the same procedure as reported earlier²², so only brief details are given here. The molecular weight of PPO lay between 420 and 2880. The dimethylamino-terminated prepolymer was prepared by reacting PPO with 2,4-tolylenediisocyanate and N,N-dimethylaminoethanol,

Table 1 Characterization of elastomeric ionene

Designation	PPO segment (mol.wt)	lonene segment (wt%)	Elemental analyses (%)				
				С	Н	N	[η] * (dl g ^{—1})
E1-1	440	73.2	Calcd	51.4	6.76	7.15	0.236
			Found	48.4	6.71	6.80	
EI-2	1160	49.6	Calcd	54.9	7.95	4.83	0.165
			Found	53.2	8.19	4.67	
EI-3	2020	36.1	Calcd	56.8	8.62	3.51	0.221
			Found	55.6	8.94	3.29	
EI-4	2880	28.4	Calcd	57.9	9.00	2.79	0.259
			Found	55.6	9.17	2.76	

* [η] values represent A values of Fuoss and Strauss equation: $\eta_{sp}/C = A/(1 + B\sqrt{C})$ at 25°C in methanol



successively. The prepolymer was converted into the alkylbromide-terminated prepolymer by reacting with 1,5-dibromopentane. The alkylbromide-terminated prepolymer was extended by 4,4'-bipyridil using the Menschutkin reaction in methanol at 60°C for 180 h, in order to obtain the elastomeric ionene. The elastomeric ionene obtained was purified by precipitation using diethylether. Characterization of the elastomeric ionenes is presented in *Table 1* with the chemical structure of the sample. The elastomeric ionene is characterized by the alternating structure of the rigid ionene segment and the flexible PPO segment. The structure of the ionene segment is constant in all the samples, so the composition of the ionene segment decreases with the increase of PPO segment size.

All the samples used in various measurements were prepared as films of thickness of the order of 10^{-2} cm by solvent casting. The elastomeric ionene was dissolved in methanol, cast onto a clean Teflon substrate and the solvent allowed to evaporate slowly at room temperature. The films were then vacuum-dried at 50°C for 72 h. Film EI-1 was too brittle to measure the dynamic mechanical and stress–strain behaviour. These measurements were carried out for EI-2, EI-3 and EI-4.

Dynamic mechanical measurements

A direct-reading dynamic viscoelastometer (Toyo Measuring Instrument Co.) was employed to make dynamic mechanical measurements at 10 Hz for temperatures from -100° to 100° C under a dry nitrogen atmosphere. The rate of temperature change was maintained at 2° C min⁻¹. The film dimensions were about 5 mm × 20 mm.

Thermal analyses

Differential scanning calorimetry (d.s.c.) measurements were performed using a Rigaku Denki TG-DSC 8085 at a programmed heating rate of 20° C min⁻¹. The sample weight was 10–20 mg. The glass transition temperature (T_g) was located as the point of intersection of the baseline with the extrapolated sloping portion of the thermogram resulting from the baseline shift which is experienced during this transition. Wide-angle X-ray diffraction pattern measurements

Wide-angle X-ray diffraction patterns were measured with a Rigaku Denki D-3F diffractometer using a Cu target.

Stress-strain measurements

Stress-strain measurements were carried out at a strain rate of $1\% \text{ s}^{-1}$ with a Shimazu DSS-500 autograph using a 5 kg load cell. Hysteresis measurements were made by loading and unloading the strip specimens at constant crosshead speed to an increasing strain level at each cycle. The percentage hysteresis for a given cycle is calculated by the ratio of the area bounded by the loading-unloading curves to the total area under the loading curve.

Water sorption

The sorption kinetic measurements were made by letting samples dry in the atmosphere with 50% relative humidity at room temperature and recording their weights periodically. The water content

water content (%) =
$$\frac{\text{weight of water}}{\text{weight of dry sample}} \times 100$$

was calculated by measuring the total weight after the preweighed sample had been sealed.

RESULTS AND DISCUSSION

Microphase-separated structure of constituent segments

The storage modulus (E') vs. temperature curves of EI-2, EI-3 and EI-4 are shown in *Figure 1*. Two mechanical relaxations were observed in all the samples. The first relaxation temperature (T_1) was at -60° to -40° C, and the second one (T_2) was at 20° to 70° C. In the higher temperature region than the second relaxation, the samples gradually became fluid. EI-3 and EI-4 were found to be a thermoplastic elastomer having an E' value of about 10^7 Pa for the temperature range from about -50° to 70° C. Corresponding to the change in E', two loss peaks were observed in the loss modulus (E'') vs. temperature curves, as shown in *Figure 2*. These



Figure 1 Temperature dependence of storage modulus (E') of elastomeric ionenes at 10 Hz



Figure 2 Temperature dependence of loss modulus (E'') of elastomeric ionenes at 10 Hz

observations are similar to the characteristic behaviour of two-phase systems such as block or graft copolymers composed of two dissimilar segments, and ionomers crosslinked with metal ions forming ionic multiplet or ionic cluster structure. The E' value in the rubbery plateau region increased with decrease of PPO segment size, that is, increase of the weight fraction of the ionene segment. This indicates that the ionene segment and the PPO segment form a two-phase system in the elastomeric ionene, since PPO and ionene are known to be in rubbery and glassy states¹⁸ at ambient temperatures, respectively. Not only the composition of the ionene segment but also the continuity and the purity of the ionene segment phase seem to be responsible for the level of the rubbery plateau region. T_1 and T_2 obtained in the dynamic mechanical measurements shifted to lower and higher temperature with increase of PPO segment size, respectively. This is discussed in the following section.

The d.s.c. curves for the elastomeric ionenes and PPO are shown in Figure 3. An endotherm was observed in the region -80° to 100° C for all the elastomeric ionenes. The endotherm temperatures are consistent with T_1 in the dynamic mechanical measurements. Considering that T_q of PPO is about -70° C, the T₁ relaxation is attributed to micro-Brownian motion of the PPO main chain caused by the glass transition of the PPO segments. The d.s.c. curves did not show an apparent endotherm corresponding to the T_2 relaxation in the dynamic mechanical measurements. However, the T_2 relaxation seems to be caused by the glass transition of the ionene segment, since the wide-angle $(2\theta = 5-40^{\circ})$ X-ray diffraction patterns of the elastomeric ionene did not show any apparent diffraction peaks assignable to microcrystallinity of the ionene segment and the sample gradually became fluid at temperatures higher than the T_2 relaxation. T_a of the ionene homopolymer could not be detected from d.s.c. measurement, and it was too brittle to use the dynamic viscoelastometer. Tsutsui et al.¹⁸ have reported that T_a 's of (m,n) ionene, whose m and n numbers ranged from 2 to 10, lay between 90° and 140°C from a torsional braid analysis. Furthermore, it has been reported^{17,18} that T_g of (m,n) ionene decreased greatly by addition of a small amount of plasticizers such as glycerine and water. There is a chemical structural difference between the ionene segment in this study and the (m,n) ionenes. However, T_g of ionomers are known to be influenced mainly by the ratio of ion charge (q) to the inter-ion distance between cation and anion at closest approach (a). Cations are ammonium ions, anions are



Figure 3 Differential scanning calorimetry curves of elastomeric ionenes and poly(propylene oxide) (PPO)



Figure 4 Relation between weight fraction of ionene segment in elastomeric ionene (W_i) and relaxation temperatures from dynamic mechanical measurement (\bigcirc, \bigcirc) and d.s.c. (\triangle) : open circles correspond to low relaxation temperatures (T_1) and closed circles correspond to high relaxation temperatures (T_2)

bromine ions, and inter-cation spacings are similar in these two systems. This means that the q/a ratio is similar in the ionene segment in this study and the (m,n) ionenes. So, the effect of the chemical structural difference on T_a may be neglected. It is true that the T_2 relaxation temperature is lower than the reported T_g values of the (m,n) ionenes. However, considering the small ionene segment size and the plasticizing of the ionene segment by the PPO segment, which is discussed in the following, it is plausible that the T_2 relaxation is assigned to the glass transition of the ionene segment. The reason why the endotherm corresponding to the glass transition of the ionene segment was not observed is as follows. The ionene segment begins micro-Brownian motion with increasing temperature, the transition is very broad and occurs continuously rather than over a narrow temperature range. The broadness of the transition can be confirmed by the broad absorption peak of E'' values, corresponding to the T_2 relaxation, in Figure 2. A similar result had been obtained in the transition of the ionic clusters in styrenesodium methacrylate copolymers⁴. From these results, it is obvious that a microphase-separated structure of the constituent segments is formed. Regions rich in the ionene segment and regions rich in the PPO segment exist in the elastomeric ionene.

Change in microstructure with PPO segment size

The relaxation temperatures obtained from the dynamic mechanical measurements and the thermal analyses are shown in *Figure 4* as a function of the weight fraction of the ionene segment in the elastomeric ionene (W_f) . T_1 increased and T_2 decreased with increase of W_f , respectively. This tendency is explained by the advance of intermixing between the PPO segment phase and the ionene segment phase with decrease of the PPO segment

size. In the elastomeric ionenes, the aggregation of the rigid ionene segment is controlled by the PPO segment size, since the PPO segment with low T_g has flexibility of the main chain. So, the degree of phase separation of the ionene segment from the PPO segment decreases with decrease of the PPO segment size. It was reported^{12,15} that PPO with electron-donating ether oxygen in the main chain could dissolve many inorganic salts and that this dissolution raised the T_a of the polymer through ionpolymer dipole interaction. Considering these investigations, the dissolution of the ionene segment into the PPO segment domain raises T_g of the PPO segment, which is advanced by the decrease of the PPO segment size. At the same time, the penetration of the PPO segment into the ionene segment domain is advanced by the decrease of the PPO segment size. This penetration increases the distance between ions in the ionene segment domain and decreases T_a of the ionene segment. Therefore, it is found that the intermixing between the PPO segment phase and the ionene segment phase is the major factor for the behaviour observed in Figure 4.

Effect of microstructure on stress-strain behaviour

The stress-strain curves for EI-2, EI-3 and EI-4 are shown in *Figure 5*. EI-1 was hard, brittle material. On the other hand, EI-2, EI-3 and EI-4 were ductile or elastomeric materials, showing elongation to break of about 80%. The tensile modulus decreased with increase of the PPO segment size. The apparent yield point was observed in EI-2. These results are characteristic of a change from the continuous hard ionene segment phase to the continuous soft PPO segment phase in the two-phase system. EI-1 is expected to form the continuous ionene segment phase because of the high W_f value. For EI-2, EI-3 and EI-4, since the W_f value is lower than 50% and the elongation to break is about 80%, a continuous PPO segment phase in which the ionene segment domain is dispersed is formed.



Figure 5 Stress-strain curves of elastomeric ionenes (strain rate = $1\% s^{-1}$)



Figure 6 Stress-strain curves for successively increasing cyclic deformation of EI-2



Figure 7 Percentage hysteresis as a function of strain in elastomeric ionenes

The hysteresis behaviour for EI-2 is shown in Figure 6. It was clear that the extent of the permanent set increased at a greater strain level, and a large amount of hysteresis was observed. Hysteresis corresponds to the heat build-up under cyclic loading and is characterized by the morphology of a material²⁴. In the elastomeric ionenes EI-2, EI-3 and EI-4, the ionene segment domain disperses in the continuous PPO segments. So the mixing of the PPO segment into the ionene segment domain increases the hysteresis. Thus, the hysteresis properties are very sensitive to phase mixing and domain morphology²⁴. The percentage hysteresis as a function of strain for EI-2, EI-3 and EI-4 is shown in Figure 7. The percentage hysteresis of EI-2, EI-3 and EI-4 was about 50, 30 and 20%, respectively. These values increased in the order of EI-4, EI-3 and EI-2. This result shows that the mixing of the PPO segment into the ionene segment domain increases with decrease of the PPO segment size. Consequently, the distances between ions increases, which lowers the crosslinking effect of the ionene segment domain, and chain slippage is able to occur easily. These phenomena are consistent with the results described in *Figure 4*.

Water sorption

The sorption kinetic curves for water in the elastomeric ionenes are shown in *Figure 8*. The water content increased with time and reached equilibrium after about 15 h in all the samples. The equilibrium water content increased with decrease of PPO segment size and was very high compared with PPO. Therefore, water sorption occurs mainly in the ionene segment domain, and increase of the equilibrium water content with decrease of the PPO segment size is attributed to the rise of the W_f value. The equilibrium water content and the number of equilibrium sorbed water molecules per ionene segment are summarized in *Table 2*. This number of water molecules is calculated by subtracting the amount of equilibrium sorbed water in PPO from that in the elastomeric ionene.



Figure 8 Sorption kinetic curves for water in elastomeric ionenes and poly(propylene oxide) (PPO) at room temperature and 50% relative humidity: EI-1, \bigcirc ; EI-2, \triangle ; EI-3, \square ; EI-4, \bigtriangledown ; PPO, \blacksquare

Table 2 Equilibrium water content in elastomeric ionene and the number of sorbed water molecules per ionene segment at room temperature and 50% relative humidity

Designation	Water content (%)	H₂O molecules per ionene segment
EI-1	8.35	7.0
EI-2	7.65	9.2
EI-3	6.65	10.6
EI-4	5.60	11.0
PPO	0.88	_



Figure 9 Stress-strain curves of elastomeric ionenes at water content of 2% (strain rate = $1\% \text{ s}^{-1}$)

The number of sorbed water molecules per ionene segment decreased with decrease of the PPO segment size. As described above, the mixing of the PPO segment into the ionene segment domain increases with decrease of the PPO segment size. It is considered that the penetrating PPO segments solvate the ionic sites and occupy the solvation sites of each ion. If the N⁺ atoms are assumed to be solvated by water molecules, the number of sorbed water molecules per N⁺ atom is 1.8 for EI-1, 2.3 for EI-2, 2.7 for EI-3, and 2.8 for EI-4, respectively. Since water molecules are sorbed to the ionic sites which are not solvated by the PPO segment, the number of sorbed water molecules decreases with decrease of the PPO segment size.

The stress-strain curves for the elastomeric ionenes whose water content is 2% are shown in Figure 9. Compared with the dry samples in Figure 5, the tensile modulus and tensile strength were reduced greatly in all the wet samples. Especially, the modulus and the strength of EI-2 in the wet state were the lowest, whereas its modulus and its strength in the dry state were the highest. It has been reported¹⁸ that T_g of ionene was reduced abnormally by absorbing a little water. So, in the elastomeric ionenes, a little sorbed water swells the hard ionene segment domain and greatly decreases its modulus, which leads to the decrease of the modulus and tensile strength of the materials. In EI-2, the effect of water sorption on the tensile properties is emphasized particularly because the W_f value is high and the purity of the ionene segment domain is low.

The hysteresis behaviour of the same wet samples is shown in *Figure 10*. Compared with the dry samples in *Figure 7*, the hydteresis value of EI-2 changed from 50% to 80%, while these values of EI-3 and EI-4 were about 20– 30% and were similar to the values of the dry samples. In EI-3 and EI-4, water sorption into the ionene segment domain seems to have little influence on the crosslinking effect of the ionene segment domain, whereas the water sorption somewhat reduces the modulus of the domain. Therefore, it may be considered that the hysteresis



Figure 10 Percentage hysteresis as a function of strain in elastomeric ionenes at water content of 2%

behaviour of the wet elastomeric ionenes is influenced by the purity of the ionene segment domain in the dry state. In EI-2, the crosslinking effect decreased greatly by water sorption, because of the low purity of the ionene segment domain.

CONCLUSION

The elastomeric ionene, a block copolymer consisting of flexible PPO segment with various segment sizes and hard ionene segment with constant segment size, forms a microphase-separated structure of the constituent segments. The hard ionene segment domain segregated from the PPO segment has a crosslinking effect in the materials. The elastomeric ionene whose W_f value is about 30-40% is obtained as a thermoplastic elastomer.

The microphase-separated structure changes with PPO segment size, and this change is attributed to the mixing of the PPO segment phase and the ionene segment phase. The degree of phase mixing increases with decrease of the PPO segment size. The dissolution of the ionene segment into the PPO segment domain increases T_g of the PPO segment. On the other hand, the penetration of the PPO segment into the ionene segment domain increases the inter-ion distance between cation and anion and decreases T_g of the ionene segment. Purity of the ionene segment domain has a strong influence on the hysteresis behaviour of the elastomeric ionenes. The percentage hysteresis increases greatly with decrease of purity.

Water sorption occurs mainly in the ionene segment domain. The number of equilibrium sorbed water molecules per ionene segment is affected by the purity of the ionene segment domain, and this number reduces with a decrease in purity. Water sorption somewhat decreases the modulus of the ionene segment domain, which leads to a decrease in the modulus of the materials.

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