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The development of the ionic microphase in sulfonated poly(ethylene-*co*-propylene-*co*-ethylidene norbornene) ionomers during physical aging above T_g

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Abstract

The effect of physical aging above T_g on ionic aggregation in the zinc salt of sulfonated poly(ethylene-*co*-propylene-*co*-ethylidene norbornene) ionomer was investigated by differential scanning calorimetry (DSC), small angle X-ray scattering (SAXS), and dynamic mechanical thermal analysis (DMTA). The time-dependent development of a high temperature DSC endotherm and a high temperature tan δ relaxation were attributed to the dynamics of microphase separation of ionic aggregates. That conclusion was confirmed by the concurrent growth of a SAXS peak corresponding to the ionic microphase. The aging process at 25 °C occurred over a period of about 1 month, even though the ionomer was ca. 70 °C above T_g, where segmental mobility of the polymer is expected to be high. The kinetics of aging were dependent on temperature; a maximum in the rate of ionic aggregate formation occurred between 10 and 45 °C. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ionomer; Physical aging; Sulfonated poly(ethylene-*co*-propylene-*co*-ethylidene norbornene) ionomer

1. Introduction

Physical aging refers to the time-dependent changes in the thermodynamic properties of polymers that are not in an equilibrium state [1]; this phenomenon is usually important in polymer glasses, i.e. at temperatures below T_g. Because ionomers are microphase separated polymers, the non-polar continuous phase and the ionic microphase may exhibit separate glass transitions, and, in fact, high-temperature mechanical and dielectric relaxations that are usually observed in ionomers have been attributed to a glass transition of the ionic aggregates [2–4]. One might presume, therefore, that the ionomer melt between the lower T_g of the continuous, non-polar phase and the higher T_g of the ionic aggregates is likely to be a non-equilibrium state, similar to a glass, due to the restricted mobility of the chain segments that are bound to the ions within the ionic microphase. As with glass-forming materials, when an ionomer is cooled at a finite rate from elevated temperature, there may be a characteristic temperature, e.g. T_g of the ionic aggregates, below which the chains lack sufficient mobility to achieve their equilibrium conformation during the cooling experiment. As a consequence, physical aging may take place, even when the polymer is above the matrix T_g due to changes in the chain conformations and/or the ionic microstructure as the system progresses towards its equilibrium state.

Whereas, there is a relatively large literature on the physical aging of glassy materials, few studies have considered the physical aging of microphase separated polymers, and particularly, ionomers [5–9]. Sulfonated poly(ethylene-*co*-*ran*-propylene-*co*-*ran*-ethylidene norbornene) ionomers (SEPDM) are thermoplastic elastomers with properties at ambient temperature similar to those of covalently cross-linked EPDM, even at very low levels of metal sulfonate groups, e.g. 30 mequiv. phr (per hundred parts rubber) [10–14]. Association of the metal sulfonate groups provides strong physical cross-links at ambient temperature, but the ionomer becomes thermoplastic at elevated temperatures due to weakening of the intermolecular associations, which permits melt processing [12,13]. SEPDM is a particularly attractive ionomer to use for studying physical aging. Because it is prepared by a simple post-sulfonation of EPDM, direct comparisons between the ionomer and the parent, non-ionic polymer are possible, and because the ionic microstructure disappears above ca. 190 °C [8], which is presumably the ionic phase T_g.

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The matrix T_{g} of the SEPDM is ca. −45 °C, so that at ambient temperatures the ionomer is ca. 70 °C above T_{g}, where relaxation of the non-ionic polymer should be rapid. However, Mauer et al. [7] observed an endothermic peak at ca. 150 °C in differential scanning calorimeter (DSC) thermograms of SEPDM undergoing physical aging at room temperature, and the magnitude of the endotherm depended on the ionic species concentration and time. Those authors suggested that the DSC endotherm, as well as multiple inflections observed by thermomechanical analysis (TMA) of the aged ionomers, were due to changes in the aggregation of the ionic species, though they presented no direct evidence for this in their paper. More recently, Jackson et al. [8] reported a temperature-resolved small angle X-ray scattering (SAXS) study of SEPDM and compositions of the ionomers containing a zinc-stearate plasticizer that suggests a non-equilibrium ionic microstructure is produced when the ionomer is cooled from above the ionic phase T_{g}.

Changes in the thermodynamic state, i.e. physical aging, of an ionomer should be manifested in its thermal properties, which is consistent with the DSC results reported by Mauer et al. [7]. But, the question remains as to whether physical aging of an ionomer is accompanied by changes in the ionic microstructure, or as with glasses, simply changes in the chain conformation. Since it is the ionic microstructure that is responsible for the interesting and desirable properties of ionomers, this question has important implications with regard to the long-time stability of the physical, mechanical and transport properties of ionomers, as well as the more academic problem of how microstructure develops in self-assembling materials. The objective of the research reported in this paper was to determine if physical aging of an ionomer above T_{g} involved changes in the microphase-separated ionic aggregates and, if so, to learn something about the kinetics of that process.

2. Experimental section

A zinc salt of SEPDM, Zn-SEPDM, containing 30 mequiv. phr of zinc sulfonate groups was supplied by Exxon Research and Engineering Co. (Annandale, NJ). The composition of the parent EPDM was 55% ethylene, 40% propylene, and 5% ethylidene norbornene. The ionomer was prepared by sulfonating the EPDM with acetyl sulfate and converting the product to the zinc salt by neutralization of the sulfonated polymer with zinc acetate [15]. Samples were compression molded into ca. 0.6 mm thick films at ca. 180 °C. Some samples were tested soon after compression molding (the aging time for these is hereafter denoted as 30 min) and the rest were aged isothermally at −15, 10, 25 or 45 °C in an air-convection oven for times ranging from 1 to 30 days.

DSC thermograms were obtained with a TA Instruments DSC, model 2920. Encapsulated samples, ~10 mg, were heated in a nitrogen atmosphere from −100 to 350 °C at a heating rate of 20 °C/min. The samples were only used once and then discarded, because of degradation above 300 °C.

Dynamic mechanical behavior was characterized from −110 to 200 °C with a TA Instruments dynamic mechanical analyzer (DMTA), model 2980, using a tensile fixture, a heating rate of 5 °C/min and a frequency of 1 Hz. The specimens had a gauge length of ca. 20 mm and a cross-section of ca. 3.5 mm^2.

Wide-angle X-ray diffraction (WAXD) data were obtained with a Bruker D5005 X-ray diffractometer. A scintillation counter detector and Cu K_α radiation were used. The diffraction intensity was measured at a scanning rate of 1°/min over a range of scattering angle, $2\theta = 5$–45°. SAXS data were obtained on aged films at room temperature using a Rigaku rotating anode (40 kV accelerating voltage; 100 mA current) and a Bruker SAXS instrument that included a 2-dimensional Hi-Star detector. Cu K_α radiation was used with a Ni-filter and pinhole collimation. Data were obtained over a scattering vector range of $q = 0.5$–$3.5\ \mathrm{nm}^{-1}$ ($q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle and $\lambda = 0.1542$ nm was the X-ray wavelength).

3. Results and discussion

3.1. Effect of physical aging time on the ionic microstructure of Zn-SEPDM

The effect of aging time on the DSC thermograms of Zn-SEPDM aged at 25 °C is shown in Fig. 1. For aging times greater than 5 days, a distinct, but broad endotherm was observed between ca. 100 and 190 °C, which is consistent with the DSC results reported by Mauer et al. for similar ionomers [7]. For aging times of 5, 15, and 30 days, the enthalpy changes associated with the endotherm were 6.3,

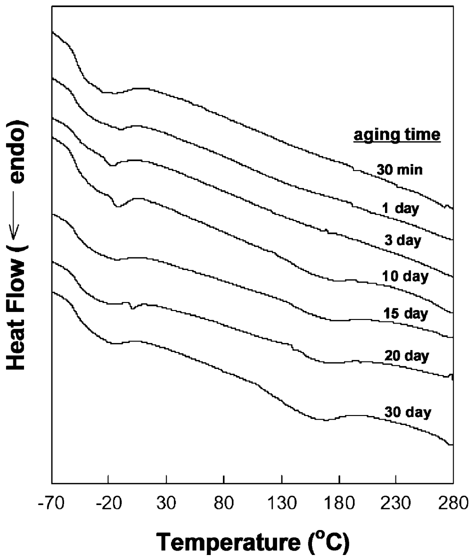


Fig. 1. DSC thermograms of Zn-SEPDM for various aging times at 25 °C.

19.6 and 30.5 J/g, respectively; the increasing enthalpy relaxation is consistent with a lowering of the sample's specific enthalpy during physical aging at 25 °C [1].

The major question addressed in the discussion that follows is whether that enthalpy change is also associated with either the formation or relaxation of an ionic microphase. Although DSC cannot provide direct evidence of the presence or absence of an ionic microphase, it is instructive to note that the endotherm terminated at ca. 190 °C, which is the same temperature at which Jackson et al. [8] reported that a peak in the SAXS of Zn-SEPDM disappeared. Although the exact details of the spatial and geometric arrangement of the ions in the ionic aggregates of ionomers has remained elusive despite nearly 30 years of investigation, it is generally agreed that the peak observed in the SAXS of ionomers, which corresponds to a Bragg spacing of ca. 2–6 nm and is often referred to as the 'ionomer peak', is due to microphase-separation of ion-rich aggregates [4,9]. The temperature coincidence of the DSC endotherm and the SAXS peak suggests a connection between the DSC and SAXS information. Jackson et al. [8] attributed the disappearance of the SAXS at 190 °C for Zn-SEPDM to an 'order–disorder transition' of the ionic microphase. Therefore, the enthalpy relaxation observed by DSC during physical aging following cooling of the material from elevated temperature may indeed correspond to the formation and growth of the ionic microphase as proposed by Mauer et al. [7].

Some may question the use of the term 'order–disorder transition', which describes a first-order transition, such as the thermally reversible change of a block copolymer from a mesophase to a disordered liquid. The ionomer microstructure is characterized by a size scale that is an order of magnitude smaller than that of block copolymers, and the degree of order is much less, as evidenced by only the single, broad peak that is observed by SAXS. Still, the ionic aggregate microstructure is thermally reversible [8], though the disordering occurs over a wide range of temperatures. In that respect, however, the transition may be similar to the melting of semi-crystalline polymers, where the melting endotherms observed by DSC can be quite broad as a result of different sized crystals and the impurities represented by the crystallite surface. The surface area/volume ratio for an ionic aggregate is expected to be large compared with polymer crystals or block copolymer mesophases, and as a result, a 'real' sample may exhibit a broad temperature range over which disordering occurs. As with polymer crystallites, however, the breadth of the transition observed experimentally does not preclude that it is a first-order thermodynamic transition.

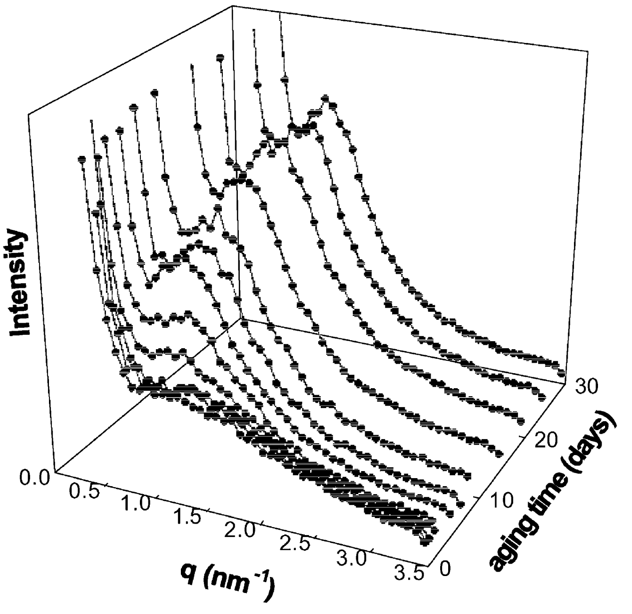


Fig. 2. SAXS data for Zn-SEPDM for various aging times at 25 °C.

Fig. 2 shows the SAXS data for the Zn-SEPDM as a function of aging time at 25 °C. For aging times of 30 min–2 days, the scattering patterns showed a high intensity upturn at low q and a broad, weak shoulder at higher q. The intensity upturn at low q is commonly observed in the scattering pattern from ionomers and attributed to a heterogeneous distribution of the ionic species in the polymer [14,16]. The shoulder is probably actually a weak, diffuse ionic peak that indicates either that the ionic aggregates were not completely destroyed during the compression molding process, which is likely since the temperature used was below 190 °C, or that some microphase separation of the ionic aggregates occurred during the cooling and/or aging processes. For the Zn-SEPDM specimens aged for 3–30 day at 25 °C, a distinct peak appeared in the scattering pattern between ca. $q = 0.7 - 2.2\ \mathrm{nm}^{-1}$, which corresponds to a characteristic size, d, in real space ($d = 2\pi/q$) of 2.9–9.0 nm. The maximum in the scattering peak was at ca. $q = 1.0\ \mathrm{nm}^{-1}$ ($d = 6.3\ \mu\mathrm{m}$), and the scattering intensity increased with increasing aging time up to ca. 20 days, after which the scattering pattern did not change. The increase of the scattering intensity with aging time is due to the development of the ionomer microstructure. As the scattering peak developed in the first 3–5 days of aging, the maximum intensity moved slightly to lower q, indicating a larger characteristic size, and the peak became sharper. The shape and breadth of the peak did not change significantly after 5 days aging, which indicates that the details of the aggregate structure did not change appreciably with longer aging times, though the concentration of aggregates did increase with aging from 5–30 days, as evident by the increasing intensity during that period. The time-dependence of the SAXS intensity is qualitatively similar to that of the endotherm observed by DSC; both suggest the growth of the ionic aggregate structure during physical aging.

A number of models of the ionic aggregates have been proposed to describe the SAXS data of ionomers [17].

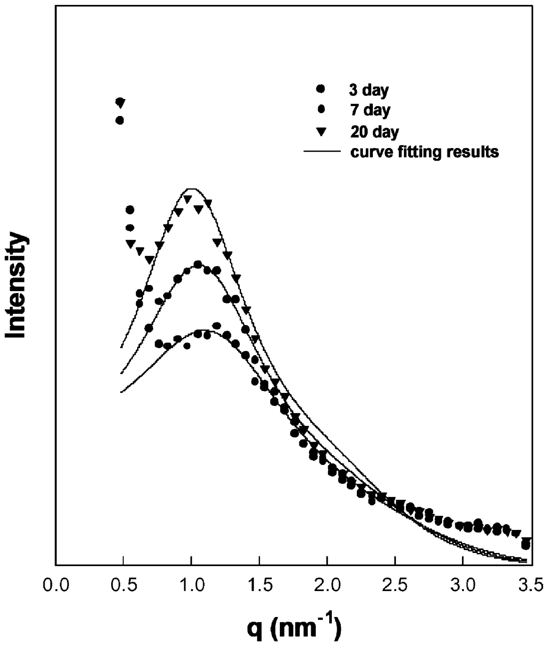
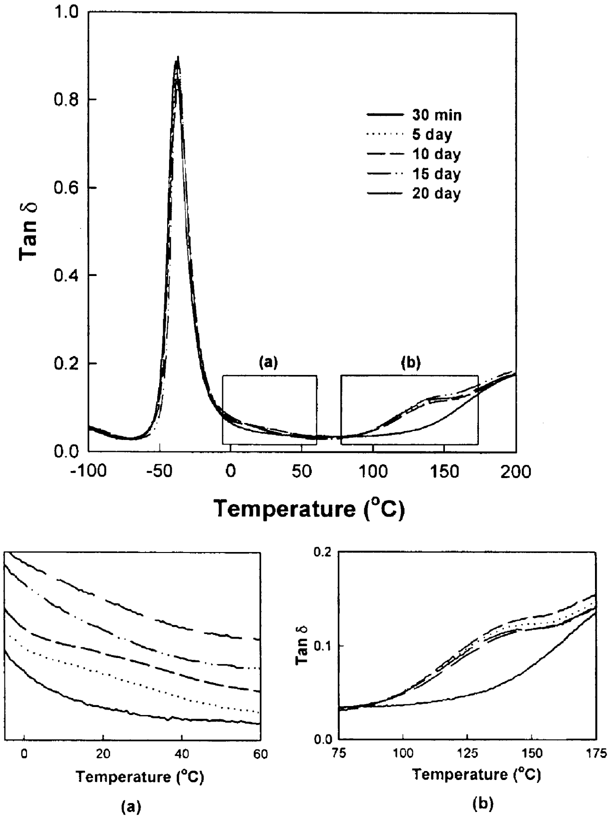


Fig. 3. Least squares fits (solid curves) of Eq. (1) to SAXS data for Zn-SEPDM aged for various times at 25 °C.



(a) (b)

Fig. 4. Loss tangent (tan δ) versus temperature for Zn-SEPDM at various aging times at 25 °C. Inserts show expanded scale for two temperature intervals above T_g of the elastomer.

While none of the models capture all of the features of the SAXS patterns and none is universally accepted, it is still instructive to use model fits to compare the SAXS data obtained for different aging times of the same specimen, see Fig. 2. The intermolecular interference model of Yarusso and Cooper [18] does a relatively good job at fitting the position and shape of the SAXS ionomer peak, though it does not fit the intensity upturn at low q. Their modified hard sphere model for the ionic aggregates gives the following equation for the scattering intensity.

$$I(q) = I_e(q)V\frac{1}{V_p}V_1^2k\rho_1^2\Phi^2(qR_1)\frac{1}{1+(8V_{ca}/V_p)\varepsilon\Phi(2qR_{ca})} \qquad (1)$$

where

$$V_{ca} = \frac{4}{3}\pi R_{ca}^3; \qquad V_1 = \frac{4}{3}\pi R_1^3; \qquad\qquad (2)$$
$$\Phi(x) = \frac{3(\sin x - x\cos x)}{x^3}$$

and q is the magnitude of the scattering wavevector. $I_e(q)$ is the scattering intensity from an electron, $I(q)$ is the experimental scattering intensity, V_p is the average system volume per particle, V is the volume of the sample illuminated by the X-ray beam, ρ_i is the electron density difference between the matrix and ionic aggregate, ε is a constant very close to one, R_i is the radius of the ionic aggregate, and $2R_{ca}$ is the distance of closest approach between two ionic aggregates.

Non-linear least squares fits of Eq. (1) to the time-dependent SAXS data, treating R_i, $2R_{ca}$, V_p and $I_eV\rho_i$ as adjustable parameters, are shown in Fig. 3. The diameter of the ionic aggregates, $2R_i$, for 3, 7, and 20 days were 2.22, 2.28, and 2.34 nm, respectively, indicating that the size of the ionic aggregates remained essentially constant, or perhaps increased slightly, during physical aging. Agarwal and Prestridge [19] observed large domains, ~500–1000 nm in SEPDM using transmission electron microscopy (TEM), but the large features they observed may have been due to either overlap of multiple domains in thick sections or the presence of excess zinc acetate used for the neutralization. Another TEM evaluation of SEPDM ionomers by Handlin et al. [20] detected domains with diameters of 2–3 nm, which is similar to the R_i values calculated from the SAXS data in Fig. 3.

The Yarusso–Cooper model assumes hard-sphere ionic aggregates with liquid-like order and which have a distance of closest approach, $2R_{ca}$, due to a sheath of bulk polymer that surrounds the aggregate. The $2R_{ca}$ values determined from the model fits of the SAXS data for 3, 7 and 20 days were 4.36, 4.80 and 5.27 nm, respectively. $2R_{ca}$ is expected to be most sensitive to the conformation of the polymer chains attached to the ionic groups in the aggregates, and the changing $2R_{ca}$ is consistent with the concept of a non-equilibrium state for the ionomer and the progression of the chain conformation towards equilibrium. One might reasonably expect the conformation of the chain to become more compact with time, since physical aging usually involves a densification of the bulk polymer, which should decrease R_{ca}—opposite the trend in the calculated values. Physical aging of the polymer chain, however, is usually observed below T_g, whereas in the present case the physical aging occurred above T_g where one might expect the unperturbed chain to quickly achieve equilibrium. In this case, however, physical aging involved the redistribution of the ionic species into the ionic aggregates, and it is not clear a priori how that should affect the conformation of the polymer backbone. Although the size of the aggregates did not change with time, the concentration of the aggregates increased, and the R_{ca} results suggest that the increasing volume fraction of aggregates produced an expansion of the chain as the ionic groups not initially part of an aggregate diffuse together to form new ionic aggregates. While that explanation is speculative, it may explain in part the conflicting reports of how ionic aggregation affects the chain conformation of ionomers [21–23]. Both chain expansion and no change in the coil dimensions of sulfonated ionomers have been reported, and perhaps the contradictory observations are due to non-equilibrium effects. The aging results reported herein suggest that measurements of the chain dimensions, e.g. by small angle neutron scattering, during physical aging of an ionomer above T_g may provide some insight into the question of how ionic aggregation affects the chain size and reconcile the conflicting experimental results.

The effect of physical aging of Zn-SEPDM on the dynamic mechanical behavior is shown in Fig. 4. The peak in tan δ at -38 °C represents the glass transition of the polymer, and neither the shape of the peak, nor T_g changed appreciably with aging time. However, a broad peak in tan δ developed between ca. 95 and 165 °C with increasing aging time. That temperature range was similar to that of the peak in the DSC endotherms that also developed during the same time period, and it is likely that both events had the same origin. Furthermore, the kinetics of the development of the DSC endotherm and the tan δ peak were similar to that for the development of the SAXS peak, which leads to the conclusion that the high temperature events seen by DSC and DMTA correspond to an order–disorder transition of the ionic aggregates in Zn-SEPDM. The development of the DSC and DMTA peaks with aging time at 25 °C tracks the formation and growth of the ionic aggregate microstructure.

In a study of the plasticization of Zn-SEPDM containing higher ethylene concentration (75 wt%) than used in the present study (55 wt%), Kurian et al. [25] reported a dynamic mechanical transition at about 119 °C that they attributed to the melting of a crystalline phase of polyethylene blocks. Although the parent EPDM used for the present study and the Zn-SEPDM were reported to have no measurable crystallinity [9,24], WAXD measurements were made to rule out crystallinity as the origin of the high temperature DSC endotherm and the peak in tan δ. WAXD data for the Zn-SEPDM ionomer after compression molding and after physical aging at 25 °C for 30 days showed no evidence of crystallinity. The WAXD pattern for the ionomer was similar to that obtained for the parent EPDM, showing only an amorphous halo centered at $2\theta = 19°$. The pattern did not change noticeably with aging time.

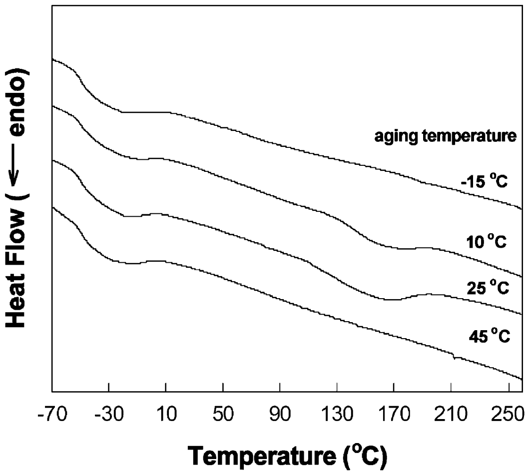


Fig. 5. DSC thermograms for Zn-SEPDM after 30 days aging at various temperatures.

3.2. *Effect of aging temperature on ionic aggregation*

The effect of aging temperature on the development of the ionic microstructure of Zn-SEPDM is shown in Figs. 5–7. DSC thermograms for Zn-SEPDM aged at -15, 10, 25, and 45 °C for 30 days are shown in Fig. 5. A high temperature endotherm between 100 and 190 °C developed in the samples aged at 10 and 25 °C, but it was not evident in the samples aged at -15 and 45 °C. The enthalpy associated with that endotherm was greater for the material aged at 25 °C than at 10 °C. These results indicate that the kinetics of the formation of ionic aggregates was sensitive to

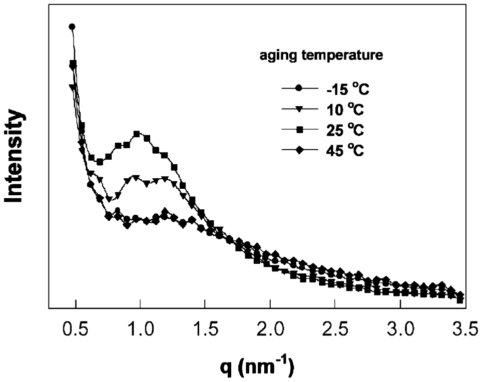


Fig. 6. SAXS data for Zn-SEPDM after 30 days aging at various temperatures.

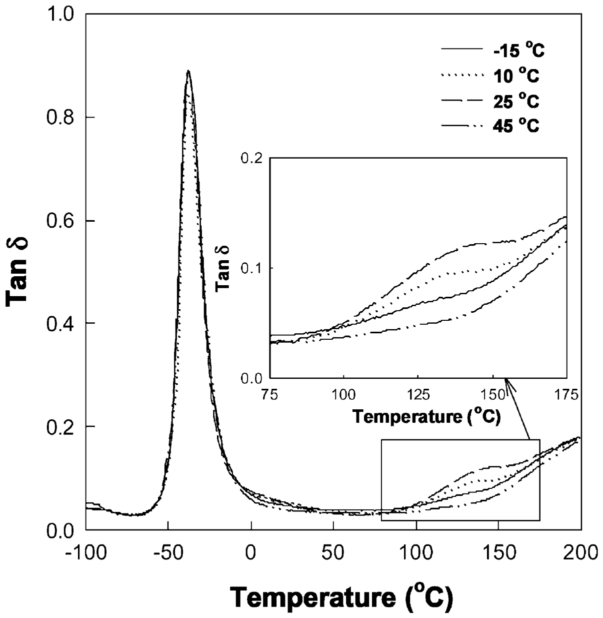


Fig. 7. Loss tangent (tan δ)) versus temperature for Zn-SEPDM after 30 days aging at various temperatures.

temperature and the most rapid growth rate occurred between 10 and 45 °C, probably near 25 °C.

The SAXS and tan δ curves for the same samples, Figs. 6 and 7, respectively, are consistent with the DSC results. When the aging was done at -15 or 45 °C, no noticeable SAXS ionic peak or high temperature tan δ peak were observed. Both features, however, developed when the ionomer was aged at l0 and 25 °C, with the latter showing the largest effect.

The maximum in the rate of the ionic aggregate formation between 10 and 45 °C is somewhat puzzling in that all the temperatures considered (-15–45 °C) were well above T_g for the polymer backbone and far below the order–disorder transition for the ionic microstructure. The explanation may involve a competition between the dipole–dipole interactions that promote ionic aggregation and the elastic forces of the polymer chains that oppose ionic aggregation [26]. Higher temperatures promote molecular mobility of the chain, which favor diffusion of the ionic groups and promote aggregation. However, as the temperature increases, the elastic forces in the rubber also increase, which may inhibit formation of the aggregates. A more detailed study of the relaxation behavior of the ionomer in the -10 and 45 °C temperature interval is needed to better assess what is clearly a rather complex temperature dependence of the aging kinetics.

Another feature of the tan δ data obtained during physical aging at 25 °C, see Fig. 4, warrants comment. The data for the temperature interval in the region from ca. 0 to 60 °C, which is just above the peak for the glass transition, are replotted in one of the enlargements included in Fig. 4. A distinct increase in the magnitude of tan δ occurred in that temperature interval as the aging time increased. Although the origin of this cannot be ascertained from these data, it is most likely associated with changes in the mobility of the polymer backbone. When the ionomer is initially cooled from the melt, and before the aggregate microstructure fully develops, the ion-pairs not located within ionic aggregates associate within the hydrocarbon-rich phase due to dipole–dipole interactions. Although the physical crosslinks formed by the associations of the ionic groups dispersed in the rubber phase restrict the mobility of the chain segments immediately attached to the ionic groups, the mobility of the rest of the chain should be essentially unaffected. As the ionic groups associate into larger, microphase-separated ionic aggregates, more chain segments are affected as the chain packs around and/or within the aggregates to accommodate the ionic associations. This increases the volume fraction of chain segments with restricted mobility [3,27] and which effectively have a higher T_g. The maximum in the tan δ peak increased by ~1 °C during

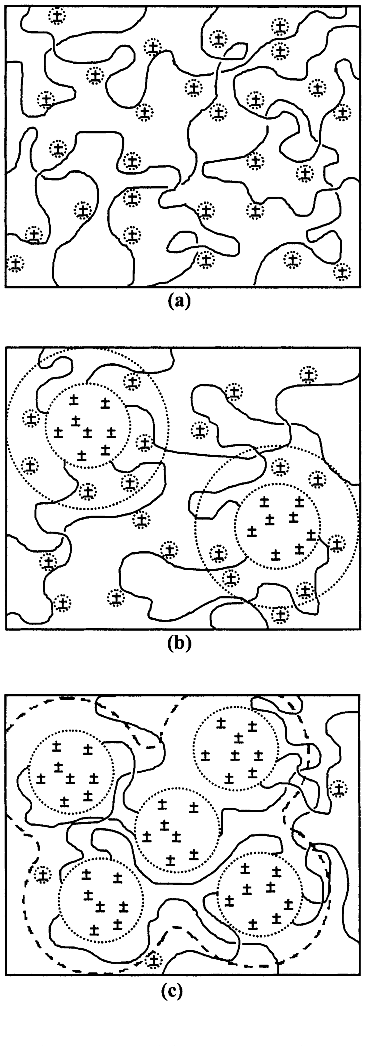


Fig. 8. Schematic illustration of ionic aggregation process in the Zn-SEPDM with aging time: (a) soon after compression molding; (b) aging times of 3–20 days; (c) aging time of over 20 days.

physical aging, and that small effect is probably a consequence of the very low ionic group concentration in this ionomer -30 mequiv. phr corresponds to roughly one sulfonate group per 200 backbone carbon atoms.

3.3. Kinetics of ionic aggregation in Zn-SEPDM

The physical aging results for Zn-SEPDM may arbitrarily be divided into four time periods: (i) immediately following quenching from the melt, (ii) the first couple of days after cooling from the melt, (iii) ca. 3–20 days and (iv) greater than 20 days. During melt processing, the ionic domain structure that is present in the as-received, well-aged elastomer crumb is destroyed by the high temperature and stresses. The ionic groups, however, are still associated as simple multiplets due to the strong dipole–dipole interactions, and this is responsible for the high viscosity of the melt. Herein, multiplets are defined as associated ionic groups that are distributed within the rubber matrix and do not constitute a separate microphase. Presumably, the kinetics of the ionic aggregation is slower than the cooling rate from the melt, so that the quenched microstructure of the cooled elastomer is more or less the same as that in the melt, see Fig. 8(a). Either no or relatively little microphase separation of the ionic aggregates occurred following the quench from the melt.

For a couple of days following the compression molding of the ionomer, the microstructure consisted primarily of multiplets. During this time period, no high temperature endotherm was observed in the DSC thermograms and only a very weak, diffuse ionomer peak was seen by SAXS, which may have been due to ionic aggregates that were not destroyed by processing below the aggregate order–disorder temperature.

The ionic aggregate microstructure represents the equilibrium state for an ionomer, and as a consequence, the multiplets coalesced into larger ionic aggregates. The ionic aggregates produce the ionomer peak in the SAXS, and the dissociation of the ionic aggregates at elevated temperature produce the high temperature endotherm in the DSC thermograms and the high temperature relaxation observed by DMTA. After about 3 days, the concentration of ionic aggregates became sufficiently high so that those three features were detected. The most significant growth of the ionic microstructure occurred during the physical aging period of 3–20 days. What is most significant about that result is that at room temperature, the polymer was ~70 °C above T_g of the elastomer, and the chain segments should have liquid-like mobility. Yet, the approach to equilibrium was still a very slow process.

The physical aging for the ionic microstructure involves a complex competition between the polar forces that favor ionic aggregation and elastic forces that oppose ordering. Because the ionic groups are bonded to the chain, the hydrocarbon chain must either participate in the aggregate structure or form a corona around the aggregates in which the chain segments have restricted mobility compared with the chain segments far removed from the ionic aggregates [27]. The cartoon in Fig. 8(b) is a schematic of one possible organization of the ionic microstructure; the dotted line surrounding the ionic aggregates denotes a region of restricted mobility of the hydrocarbon chain. Also, note that at this stage, there still may be ionic groups dispersed in the matrix as multiplets.

After about 20 days of physical aging, the DSC thermograms, the SAXS profiles and the dynamic mechanical behavior did not change appreciably with time. At that point, the microstructure may have achieved equilibrium, as shown in Fig. 8(c) in which nearly all of the ionic groups have diffused into ionic aggregates and the region of restricted mobility overlaps the different ionic aggregates and constitutes all or nearly all of the material. An alternative explanation is that equilibrium was not yet achieved, but that the kinetics of new aggregate formation became too slow to observe any additional changes in the timeframe of these experiments. The mobility of the chain segments should decrease with aging time as the volume fraction of chains within the region of restricted mobility increases.

3.4. Physical aging of glassy ionomers

The physical aging results described above for SEPDM were conducted above the T_g of the elastomer, where segmental motion is likely to be relatively facile. Nevertheless, the ionic microstructure did not rapidly achieve equilibrium, which is evident from the time-dependent thermal, mechanical and scattering properties. An obvious next question is what happens with ionomers aged below the matrix T_g. Previously, we reported the development of a DSC endotherm below T_g for sulfonated polystyrene (SPS) ionomers annealed at ca. 90 °C below T_g for up to 3

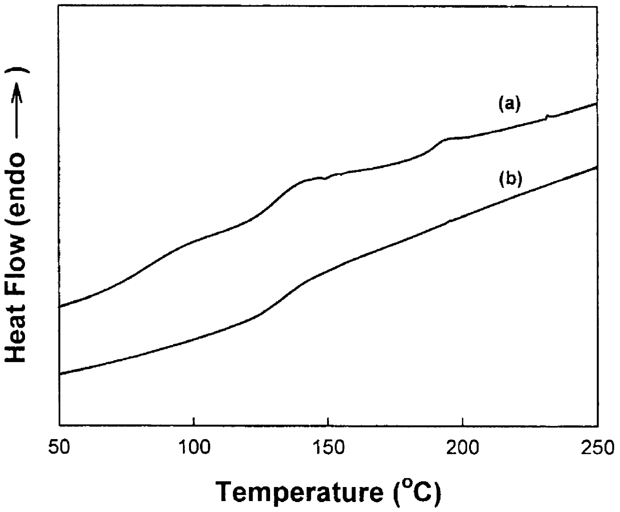


Fig. 9. DSC heating thermograms (40 °C/min) of 6.8 Zn-SPS: (a) after physical aging at room temperature for >4 years and (b) after cooling rapidly from the melt following thermogram (a).

months [28]. In that study, no new thermal transitions were observed in the DSC thermograms above T_g and a subsequent SAXS study of SPS samples aged at ca. 90 °C below T_g for up to 2 months revealed no changes in the ionic microstructure [29]. In that case, the origin of the DSC endotherm below T_g was probably a consequence of physical aging of the polystyrene phase.

One would expect the kinetics of any microstructural changes during physical aging below T_g, e.g. SPS at room temperature, to be much slower than for physical aging above T_g, as with the SEPDM elastomers described above. The observations of the ionic microstructure changes in SEPDM and their rather slow kinetics persuaded us to look for evidence of microstructural changes in SPS samples that were aged for much longer times than used previously in Refs. [28] and [29]. Fig. 9 shows the DSC heating thermogram of a compression molded film of a zinc salt of SPS with 6.8 mol% sulfonation (6.8 ZnSPS) that was stored in a sealed jar in our laboratory for over 4 years. Physical aging at room temperature, which was ca. 90 °C below T_g produced a high temperature endotherm above T_g at ca. 190 °C. However, the heating endotherm immediately following the cooling of the sample from the melt did not exhibit the high temperature endotherm. It is unlikely that the origin of the 190 °C endotherm was absorbed water, since hydration equilibrium in these ionomers is achieved within days and the DSC endotherm was not observed in experiments in which the ionomers were aged for up to 3 months [28]. It is tempting to attribute the endotherm in Fig. 9 to changes in the ionic microstructure similar to what was reported above for SEPDM, but it is also precarious to draw such a conclusion based on this single experiment. This result, however, suggests that the physical aging of the microstructure of glassy ionomers may occur, albeit very slowly. More work is needed to confirm that hypothesis, though the apparent requirement of aging times of several years is not particularly convenient.

4. Conclusions

The results reported in this paper have several ramifications with regard to ionomer technology, as well as more fundamental questions concerning the structure–property relationships of ionomers. From a practical perspective, the demonstration of the non-equilibrium nature of the ionic microstructure suggests that the mechanical, dielectric and transport properties of ionomers may also undergo significant time-dependent changes. This report focused on the physical aging of ionomers above T_g and as such, it is particularly relevant to elastomeric ionomers, such as commercial poly(ethylene-*co*-*ran*-methacrylic (acrylic) acid) ionomers. For those ionomers, physical aging may also be influenced by the presence of crystallinity. The preliminary data presented for the SPS ionomer aged below T_g suggest that the ionic microstructure of ionomer glasses may also be susceptible to changes during physical aging, though at a much slower rate than for elastomeric ionomers.

The non-equilibrium aspect of ionomer microstructure, as demonstrated by this research, needs to be better appreciated by those investigating the structure and properties of ionomers. Clearly, substantial aging effects will exacerbate attempts at forming universal, or even definitive, conclusions as to the nature of these materials, and all studies need to be framed within the context of probing a moving target. This is something that has long been recognized by scientists studying polymer glasses, which can exhibit substantial physical aging effects. As a result, any useful investigation of ionomers requires a careful documentation of the thermal history of the samples. A more far-reaching conjecture is that other phase-separated polymers, and especially microphase separated materials such as block copolymers and nanocomposites where the interphase volumes are likely to be large, may also exhibit physical aging effects above the T_g of one of the components.

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References

[1] Struik LCE. Physical aging in amorphous polymers and other materials. New York: Elsevier, 1978.
[2] Eisenberg A, King M. Ion-containing polymers. New York: Academic Press, 1977.
[3] Eisenberg A, Kim JS. Introduction to ionomers. New York: Wiley-Interscience, 1998.
[4] Fitzgerald JJ, Weiss RA. J Macromol Sci, Rev Macromol Chem Phys 1988;C28:99.
[5] Weiss RA. J Polym Sci, Polym Phys Ed 1982;20:65.
[6] Kohzaki M, Tsujita Y, Takizawa A, Kinoshita T. J Appl Polym Sci 1987;33:2393.
[7] Maurer JJ, Harvey GD, Agarwal PK. J Polym Sci, Polym Phys Ed 1990;28:1443.
[8] Jackson OA, Koberstein JT, Weiss RA. J Polym Sci, Polym Phys Ed 1999;37:3141.
[9] Galambos AF, Stockton WB, Koberstein JT, Sen A, Weiss RA, Russell TP. Macromolecules 1987;20:3091.
[10] MacKnight WJ, Lundberg RD. Rubber Chem Technol 1984;57:652.
[11] Paeglis AU, O'Shea FX. Rubber Chem Technol 1988;61:223.
[12] Dasgupta AM, David DJ, Misra A. J Appl Polym Sci 1992;44:1213.
[13] Agarwal PK, Makowski HS, Lundberg RD. Macromolecules 1980;13:1679.
[14] Agarwal PK, Lundberg RD. Macromolecules 1984;17:1928.
[15] Makowski HS, Lundberg RD, Westerman L, Bock J. In: Eisenberg A, editor. Ions in Polymers. Advances in Chemistry Series 187. Washington, DC: American Chemical Society. 1980. p. 3.
[16] Register RA, Ding YS, Foucart M, Jerome R, Hubbard SR, Hodgson

KO, Cooper SL. In: Utracki LA, Weiss RA, editors. Multiphase polymers: blends and ionomers, Advances in chemistry. Series no. 395. Washington, DC: American Chemical Society, 1989. p. 420.

[17] Grady BP, Cooper SL. In: Tant MR, Mauritz KA, Wilkes GL, editors. Ionomers. New York: Van Nostrand Reinhold, 1997. Chapter 2.

[18] Yarusso DJ, Cooper SL. Macromolecules 1982;15:136.

[19] Agarwal PK, Prestridge EB. Polymer 1983;24:487.

[20] Handlin DL, MacKnight WJ, Thomas EL. Macromolecules 1981;14:795.

[21] Earnest TR, Higgins JS, Handlin DL, MacKnight WJ. Macromolecules 1981;14:192.

[22] Register RA, Pruckmayr G, Cooper SL. Macromolecules 1990;23:3023.

[23] Visser SA, Cooper SL. Macromolecules 1991;24:2576.

[24] Mauer JJ. In: Turi EA, editor. Thermal characterization of polymeric materials. New York: Academic Press, 1981. Chapter 6.

[25] Kurian T, Khastgir D, De PP, Tripathy DK, De SK, Peiffer DG. Polymer 1996;37:413.

[26] Eisenberg A. Macromolecules 1970;3:147.

[27] Eisenberg A, Hird B, Moore RB. Macromolecules 1990;23:4098.

[28] Weiss RA. J Polym Sci, Polym Phys Ed 1982;20:65.

[29] Weiss RA, Lefelar JA. Polymer 1986;27:3.