Selective Plasticization of the Ionic Domains in a Segmented Thermoplastic Ionene Cationomer

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SYNOPSIS

The use of zinc stearate as an ionic plasticizer has been demonstrated to function effectively in a segmented ionene cationomer thereby permitting its melt processability. The ionene polymer is prepared by reacting dimethylamino-terminated polytetramethylene oxide (PTMO) oligomers with various benzyl dihalide compounds, leading to a segmented cationomer. Since the unplasticized ionene polymer undergoes degradation near the softening temperature (ca. 180°C), an ionic plasticizer was incorporated as a means of lowering the softening temperature to prevent degradation and permit melt processability. Zinc stearate was utilized in this study as it has been demonstrated to function well in other ionomers (essentially anionomers) in this capacity. Through the utilization of melt rheological and solid-state morphological investigations, it has been clearly shown that zinc stearate will function effectively as an ionic plasticizer in these quite different ionomer materials by lowering the softening temperature to ca. 120°C, thereby permitting melt processability. In addition, due to the crystallization of the zinc stearate following cooling, this same species also serves to enhance the mechanical properties in the solid state.

INTRODUCTION

Ionomers are generally classified as polymers that contain less than 15 mol % of the ionizable moieties.[1] The ionic interactions present in these materials provide an additional means of controlling polymer structure and properties. In random ionomers, the ionic groups are located randomly along the polymeric backbone, resulting in a network structure that is rather poorly defined. Another approach is to synthesize ionomers where the ionic groups are placed at well-defined locations such as in the telechelic ionomers or "segmented ionomers"—an example of the latter being the segmented ionene polymers. These specific systems will be addressed within this paper.

Although there have been several approaches taken to synthesize ionene-based polymers, the route utilized in the present study is that of the Menshutkin reaction as shown in Scheme 1, which illustrates the reaction of dimethyl amino-terminated polytetramethylene oxide oligomers (PTMO) with benzyl dihalide compounds.[2]

In the case of the specific material discussed in this paper, the halogen counterion was bromine and
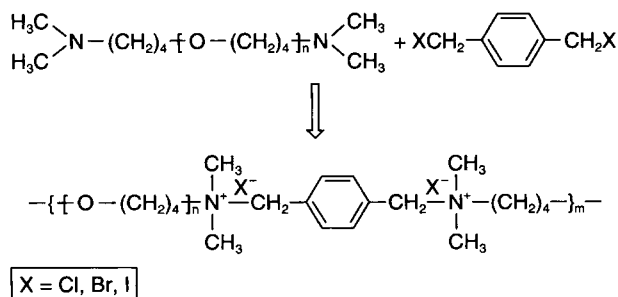
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Scheme 1

the molecular weight of the PTMO segment was 1400 g/mol. This sample will be designated as IB-NS-14. Based on the above chemistry, it was initially *anticipated* that at the higher processing temperatures the PTMO-based elastomeric ionomer would dequaternize rapidly (without any side reactions) to give a readily processable syrup of lower molecular weight oligomeric diamines and oligomeric alkyl dihalides. However, on cooling, these lower molecular weight reactants would hopefully rapidly requaternize to its original higher molecular weight, providing a useful solid material. Initial tests fell far short of this ideal scenario when thermally processed near their softening point (ca. 150–180°C), with significant loss of both ultimate tensile strength and elongation. This was due in part to the irreversible loss in molecular weight as noted by Leir and Stark.[2] Therefore, in order for these materials to be considered thermoplastic, there is a need to identify a suitable additive so that the softening temperature can be lowered (without any change in the chemistry of the system, i.e., retaining the overall molecular weight of the parent material), thus facilitating thermal processing.

Conventionally, the role of a plasticizer has often been viewed as increasing the free volume available to the polymer segments, thereby lowering both the T_g and the melt viscosity of the polymer. Some of the desired features of such conventional plasticizers are compatibility with the matrix polymer and being nonvolatile or of low vapor pressure at the processing temperatures and, more importantly, they should not adversely affect the mechanical and/or chemical properties of the matrix resin.[3]

Lundberg et al.[4] showed that there are essentially two very different types of plasticizers that can be used to plasticize ionomers: those that uniformly increase the free volume of the backbone ("backbone plasticizers") and those that act selectively to diminish the interchain association of the ionic groups on the polymer chain ("ionic plasticizer"). The latter class of plasticizers are more effective at lowering the melt viscosity of ionomers than are the former ones. Lundberg et al.[4] demonstrated that it is possible to selectively plasticize either the ion-rich phase or the nonpolar hydrocarbon phase of sulfonated polystyrene (SPS) ionomers. Specifically, dioctyl pthalate (DOP) performed essentially as a backbone plasticizer, whereas glycerol—a polar additive—selectively plasticized the ionic groups. As an example, Figure 1 illustrates the differences in the resulting melt viscosity using the two types of plasticizers. For example, the addition of only 3.5 wt % glycerol was required to reduce the melt viscosity from 3.2
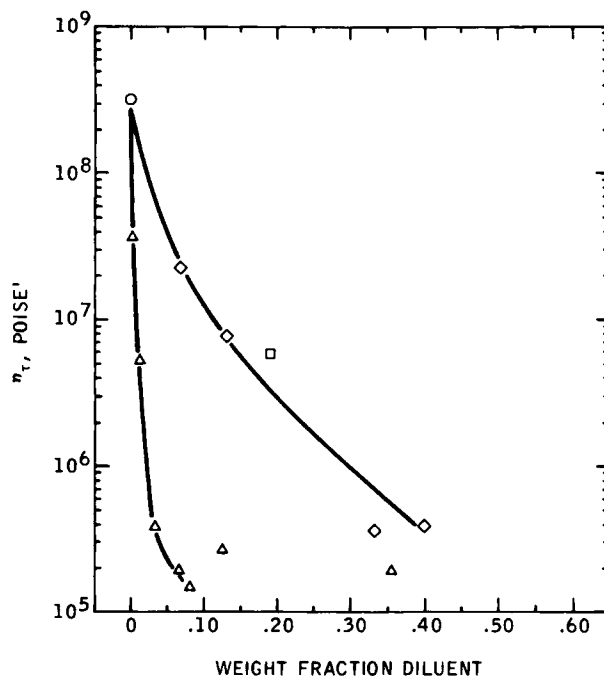

Figure 1 Melt viscosity of 1.78 mol % Na–SPS vs. weight fraction of diluent: (O) base resin; (◇) base resin + DOP; (△) base resin + glycerol. From Lundberg et al.[4]

× 10^8 poise to 4 × 10^5 poise, whereas 40 wt % of DOP was required to achieve the same effect at the same temperature (220°C) and shear rate. This difference was attributed to the differences in the plasticization mechanisms of the two plasticizers; glycerol preferentially solvates (or shields) the ionic interactions of the metal sulfonate groups in the ionic domains, whereas DOP plasticizes the polymer backbone by lowering T_g.[4] Though glycerol dramatically reduces the melt viscosity of the ionomer, it has very little influence on T_g. On the other hand, DOP reduces the melt viscosity by lowering the T_g of the backbone material. This type of behavior is typical of a conventional plasticizer. Lundberg et al.[4] have demonstrated that by a judicious combination of both plasticization approaches using lightly sulfonated polystyrene, it is possible to prepare a flexible polymer similar to plasticized poly(vinyl chloride).

Duvdevani et al.[5] suggested that some polar additives could weaken or destroy the ionic interactions (responsible for network formation) at melt processing temperatures but would allow reestablishment of the ionic interactions at the use temperatures. One convenient way of shielding the ionic interactions is by using a polar additive that is highly crystalline in nature, such as zinc stearate. Upon

melting, zinc stearate shields the ionic interactions, resulting in a significant reduction in the melt viscosity in ionomers. Upon cooling, due to the strong tendency for zinc stearate to recrystallize below the melting point, there is sufficient driving force for the zinc stearate to migrate out of the ionic domains. This enables reformation of the ionic interactions, which results in the reestablishment of the ionic network.[5]

The principles of selective plasticization were also applied by Makowski and Lundberg[3] to a number of sulfonated EPDM (S-EPDM) systems using stearic acid and its metal derivatives. Addition of stearic acid resulted in a significant reduction of the melt viscosity of these systems. However, the tensile properties were adversely affected at 70°C (while an improvement was observed at 25°C) along with an increase in water uptake. In contrast, incorporation of 30–90 mequiv/100 g polymer of zinc stearate showed a remarkable improvement in tensile properties at both 25 and 70°C accompanied by a drastic reduction in melt viscosity. The improvement in mechanical properties was primarily due to microphase separation of zinc stearate into small crystallites (less than 5000 Å in size) that function as a reinforcing filler. Also, materials incorporated with zinc stearate showed a reduction in water absorption.[5]

Agarwal et al.[6] proposed that zinc stearate above its melting point solvates or "dissolves" the ionic interactions, permitting the flow of polymer segments at high temperatures. With the ionic interactions shielded, a structure very similar to amorphous high molecular weight polymers results where the polymer chain segments are free to undergo coordinated deformation at elevated temperatures. Another explanation that has been given is that the ionic plasticizers improve flow by promoting ionic bond interchange during deformation. The authors, however, were unable to distinguish between the two proposed mechanisms.

Recently, Weiss et al.[7] examined sodium-neutralized sulfonated polystyrene ionomers using dynamic mechanical analysis. They reported that DOP lowered the T_g of the backbone polymer and shifted the entire modulus versus temperature curve to lower temperatures, typical of a conventional plasticizer. However, no significant differences in the DMA curves (both G' and G'' curves) were observed. But glycerol substantially decreased the softening temperature while having little or no effect on the T_g of the backbone. The rubbery plateau and the high-temperature loss peak was also found to disappear with glycerol addition. These results clearly

support the preferential plasticization of the two phases of an ionomer by polar and nonpolar diluents as suggested earlier by Lundberg et al.[4]

In another study, Weiss et al.[8] utilized real-time small-angle and wide-angle X-ray scattering to study the temperature-dependent microstructure of zinc stearate plasticized sulfonated EPDM. Near 100°C, they observed the development of a peak around 4.5 nm that disappears above 120°C. They assigned this small-angle scattering peak to the formation of ionic clusters at elevated temperatures. This is likely incorrect because a scattering peak of crystalline zinc stearate in the small angle region occurs ca. 4.5 nm. However, it is surprising as to why they do not observe the zinc stearate scattering peak at lower temperatures even with a zinc stearate loading level of up to 30 phr.

It has been clearly shown in the literature that by judicious selection of a polar additive one can effectively control the nature of ion interactions in ionomeric materials. The *objective* of the present study was therefore to identify a suitable additive that would lower the softening temperature so that the segmented ionene materials (cationomers) can be thermally processed without significant loss of their excellent elastomeric bulk properties[9] and, hence, allow them to be considered as a thermoplastic elastomer.

EXPERIMENTAL

Materials

The ionene polymers investigated in our study were synthesized by Leir and Stark based on the reaction of α,ω-bis(dimethylamino) polytetramethylene oxide with 1,4 dibromo-p-xylene. Details regarding the synthesis of these novel ionene polymers have already been reported.[2] The average molecular weight of the PTMO segments in the ionene polymer used in this study was 1400 g/mol.

Determination of the overall molecular weight of these ionene polymers was difficult due to the strong tendency of the ionic groups to interact with the GPC column. Hence, only inherent viscosity (I.V.) data are available for these materials. The I.V. values obtained suggest that all of the ionene materials prepared were of reasonably high molecular weight.[2]

Film Preparation

The plasticized ionene samples were prepared by adding predetermined amounts of zinc stearate

powder to a chloroform solution of the ionene and stirred until a uniform suspension was obtained. The resulting suspension was poured into a Teflon boat. Aluminum foil was placed over the boat to control the rate of evaporation of the solvent. The solution casting process was carried out at ambient conditions. The resulting film, which was opaque in appearance, was later compression molded at 130°C for 2 min, and an *uniform clear film* was obtained that was utilized for further characterization.

Mechanical Properties

The tensile studies were conducted using an Instron Model 1122. Dog-bone samples measuring 10 mm in length (gauge) and 2.8 mm in width were tested at a crosshead speed of 50 mm per minute.

Dynamic Mechanical Analysis

The dynamic mechanical analysis (DMA) of the samples were carried out in an Autovibron Visco-elastometer (Model DDV-II-C) (IMASS) that operates in a tensile mode. The dynamic storage modulus, E', the loss modulus, E'', and the loss tangent, tan δ, were obtained at a heating rate of 2°C per minute. The different parameters were determined as a function of temperature (from -150°C to 200°C) at a frequency of 11 Hz.

Thermal Analysis

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-4 at a scan rate of 20°C per minute. The DSC experiments were performed under a nitrogen atmosphere.

Wide-Angle X-Ray Scattering

The wide-angle experiments were conducted with a Phillips table-top X-ray generator model PW1170 equipped with a standard vacuum-sealed Warhus photographic pinhole camera. To study the presence of strain-induced crystallinity, the samples were stretched to the desired amount and clamped in a rigid sample holder and mounted within the Warhus camera.

Scanning Electron Microscopy

A Cambridge Stereoscan 200 scanning electron microscope (SEM) with a secondary electron detector was used to obtain micrographs of fractured surfaces. These surfaces were prepared by breaking the sam-

ples that had been cooled in liquid nitrogen for 15–25 min. Specimen surfaces were sputter-coated with a 150 Å layer of gold.

Rheological Measurements

The rheological measurements were conducted on a Rheometrics mechanical spectrometer (Model RMS-800) under a nitrogen atmosphere. The parallel plate (2.5 cm diameter) geometry was used for all the experiments. Frequency-sweep measurements were performed in the dynamic oscillatory mode at a constant strain of 7%. Cooling experiments were conducted in the dynamic oscillatory mode at a frequency of 10 rad/s and at a strain of 7%. The jump strain experiments were performed using an initial strain of 50% (or 0.5 strain units). In this experiment, the material is strained quickly to a given level and the torque is monitored as a function of time. The stress relaxation, $\sigma(t)$, and the relaxation modulus, $G(t)$, is obtained from the observed torque values.

RESULTS AND DISCUSSION

Preliminary Investigation

In a prior report on related ionene systems, Leir and Stark[2] observed that considerable degradation took place when the ionene materials were thermally processed above its softening point of about 170–180°C. To study the processability of the unplasticized ionene polymer, IB-NS-14 was compression molded at 180°C for 5 min and quickly quenched to ambient conditions. Later, the sample was thermally annealed at 70°C under vacuum. Sections of this material were removed at frequent intervals to perform the tensile experiments. Figure 2(a) shows the stress-strain behavior of the material as a function of the annealing time *subsequent* to compression molding. The figure shows only a part of the stress-strain profile for the sample that was *not* compression molded (notice the arrow in curve E). The complete stress-strain profile of this as-cast sample is shown later in Figure 4(a). Details regarding the complete deformation profile of this material will be discussed later. For all further discussions, this sample will serve as a reference or control material.

All samples that underwent the 180°C thermal treatment (compression molding) exhibited very poor mechanical properties (i.e., low modulus, low ultimate tensile strength, and ultimate elongation). In fact, immediately after compression molding, the material was tacky in nature. Specifically, the ulti-
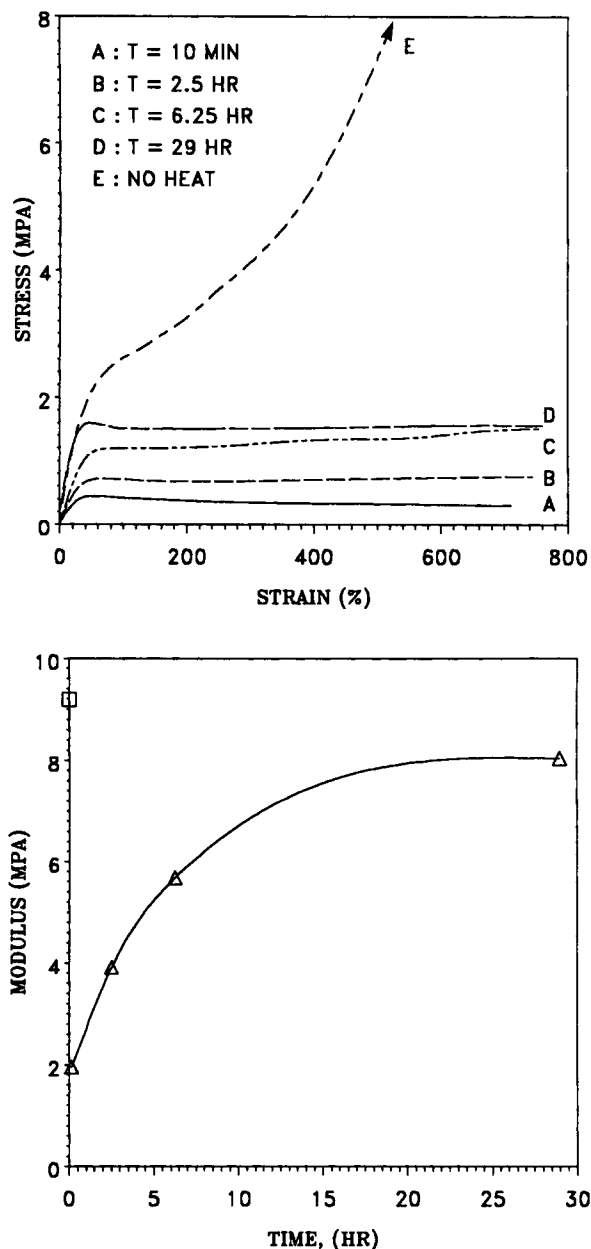
Figure 2   Effect of thermal cycling at 180°C for sample IB-NS-14: (a) stress-elongation behavior, (b) modulus recovery (□ = untreated; △ = thermally treated).

mate tensile strength and ultimate elongation of the reference material that *had not* undergone thermal treatment was ca. 14 MPa and 1300%, respectively. However, some of the other ionene materials that we had studied earlier (but not addressed in this paper) exhibited ultimate tensile strengths between 30 and 40 MPa and elongations up to 1200%.[9] For the IB-NS-14 samples that underwent the thermal treatment, the tensile strength recovered from ca. 0.4 MPa after a 10 min annealing period (curve A)

to ca. 1.6 MPa when annealed for 29 h (curve D); however, no significant improvement in the ultimate elongation is observed (ca. 750% for curves A–D). Based on the earlier work of Leir and Stark,[2] it was speculated that extensive degradation had occurred. To substantiate this speculation, inherent viscosity (I.V.) measurements (which are indicative of the overall molecular weight) were conducted. Table I shows the inherent viscosity values obtained from the IB-NS-14 samples that were thermally treated at 180°C for different lengths of time. A considerable decrease in the I.V. of the material was observed with time (from 0.43 to 0.17, a 60% decrease when the heat treatment time was 22 min). This indicates that significant lowering of the overall molecular weight occurred in these ionene materials at the elevated temperature. Although the details of the origin of this degradation was not addressed, it is clearly evident that this ionene polymer in the neat form cannot be thermally processed without loss of material properties and therefore cannot function as a thermoplastic elastomer.

Figure 2(b) shows the effect of annealing time (at 70°C) on modulus of the material that underwent the 180°C thermal treatment. Notice that the modulus of the *untreated* sample was ca. 9.2 MPa. For the thermally treated samples, the modulus of the material significantly recovered with time (ca. 8.2 MPa in 29 h). The observed recovery for the modulus is presumably due to the requaternization of the ionene segments that aggregate to form the ionic domains.

Based on this ionene chemistry (recall Scheme I), it is expected that the ionene polymer partially reverts to the initial reactants near the softening point of the ionene segments. Leir and Stark[2] speculated that on cooling, however, the requaternization reaction in the solid state may be slow. Also, if degradation of the PTMO segments occurred, the overall functionality for the Menshutkin reaction of the dimethyl amino-terminated PTMO would become

Table I   I.V. Measurements of Sample IB-NS-14 as a Function of Time Following Thermal Treatment

Time (min)	I.V.[a] (dL/0.4 g in CHCl₃)
0[b]	0.43
14	0.23
22	0.17

[a] At room temperature.
[b] Material was not compression molded.

less than two. In step-growth polymerization, a functionality very close to two is essential for obtaining reasonably high molecular weight polymer. Both the above mechanisms could significantly lower the overall molecular weight of the resulting polymer, which may be the reason for the poor properties exhibited by these materials. Also, the modulus of the material recovers significantly with annealing time (at 70°C), which is believed to be primarily due to the requaternization of some of the ionene segments. This again supports the earlier speculation that the PTMO segments in the material may have also degraded somewhat when heated to elevated temperature. *It was anticipated that by lowering the softening temperature of the ionene polymer through the use of an ionic plasticizer, loss of molecular weight could be averted.*

It was shown earlier that the electrostatic interactions of the ionic moieties in the ionene segments are responsible for the excellent network character of these ionene polymers.[9] Therefore, it is probable that if an additive were to shield the ionic interactions of the ionene polymer at the processing temperature the material properties (especially the melt viscosity) would approach that of the backbone chain (i.e., PTMO segments with no ionic interactions). As discussed earlier, zinc stearate is an effective plasticizer of the ionic domains in sulfonated EPDM ionomers, resulting in a lowering of the softening temperature. However, the question remained in our case as to the efficiency of zinc stearate as an ionic plasticizer in the ionene systems—a cationomer, whereas the former system was an anionomer.

Effect of Zinc Stearate Incorporation on Properties

Dynamic Mechanical Properties

Figure 3 shows the dynamic mechanical spectra of the IB-NS-14 polymer as a function of the zinc stearate loading level, from 0 to 60 phr (parts per hundred resin). Recall that the 0 phr material was solution cast and did not have any prior heat treatment. The dynamic mechanical spectra exhibit four main transitions. The tan δ data has been plotted on a logarithmic scale so that subtle changes in the transitions can be clearly distinguished. The transition occurring at $-120°C$, which is designated as γ, is seen in all the samples and arises from rotation of the methylene sequences in the PTMO backbone.[10] The intensity of this transition decreases with increasing zinc stearate loading level, possibly because of some partial restrictions placed on the
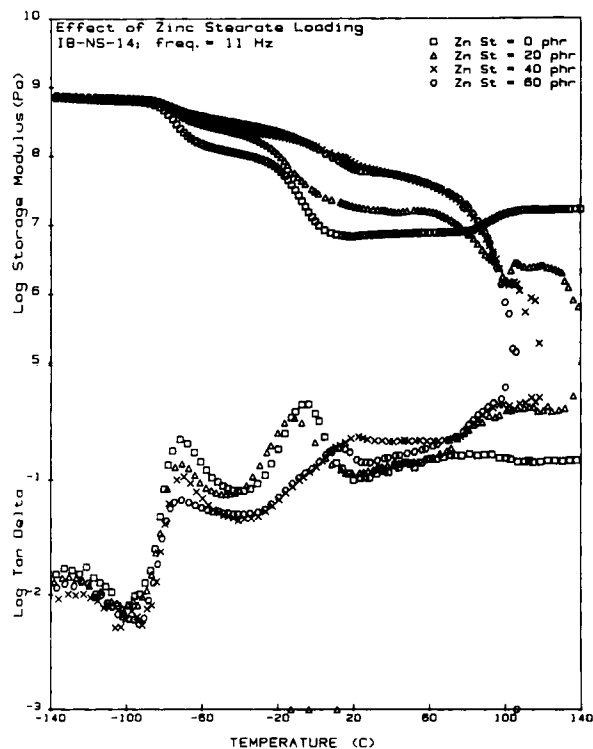

Figure 3 Dynamic mechanical analysis of IB-NS-14 samples—some containing zinc stearate: (a) E' curves; (b) tan δ curves.

relaxation process of the methylene sequences by the zinc stearate crystallites present within the polymer matrix but also due to a lower volume fraction of polymer.

A second transition, attributed to the glass transition of the PTMO segments and designated as α_g, occurs around $-70°C$. As the data illustrate, the location of the glass transition peak is nearly the same for all samples. This is a characteristic feature of ionic plasticizers where the T_g of the backbone material is not significantly affected. As with the γ transition, the intensity of the tan δ peak (α_g) decreased with increasing zinc stearate loading. The reason for this occurrence is the same as that observed for the γ transition. Beyond the glass transition temperature, the modulus of the plasticized materials is greater than is the unplasticized ionene polymer due to the presence of zinc stearate that is crystalline at these temperatures and acts as a reinforcing filler.

A third transition, designated as α_c, is related to the general crystallization and melting behavior of the PTMO soft segment—the latter process occurs at ca. 0°C. The reason for the decreasing modulus extending from nearly -70 to 25°C is undoubtedly due to the initial softening of the amorphous PTMO

in conjunction with the melting of PTMO crystallites. However, in the plasticized samples, two types of crystallites are expected to be present: PTMO and zinc stearate. Within the plasticized samples, a distinct α_c transition is observed only in the 20 phr sample, while the high concentration of the zinc stearate crystallites masks any signs of melting of the PTMO crystallites in the 40 and 60 phr samples.

In the temperature range between 0 and 70°C, the modulus of the material increases with increasing zinc stearate loading levels. This is not surprising since it has been reported in the literature that zinc stearate acts as a reinforcing filler below its melting point ($T_m = 124$°C).[11] However, in the *unplasticized material* above 70°C, the storage modulus surprisingly increases with temperature. The reason for this occurrence is due to a crystallization ordering mechanism of the ionene segments above 70°C,[12] which becomes less distinct when the ionene segment content is lower, i.e., at higher PTMO molecular weight segments.

As shown in an earlier work relating to these ionene materials, a fourth transition occurs ca. 180°C, at which point the *unplasticized* materials displayed significant softening, due to the loss of association of the ionic moieties.[9] With the addition of zinc stearate, the softening temperature is lowered to ca. 120°C due to the plasticization effect of the zinc stearate, which is distinctly evident in the 60 phr sample. *It is clearly seen that on incorporation of zinc stearate the softening temperature of the ionene polymer is significantly reduced, which is the main objective in this study.* In the discussion that follows, the effect of the incorporation of zinc stearate on the physical and morphological properties will be discussed.

Mechanical Properties

Figure 4(a) shows the effect of zinc stearate loading on the stress-strain behavior of the ionene polymer with PTMO segment molecular weight of 1400 (IB-NS-14) at ambient conditions. All the plasticized materials were compression molded at 130°C for 5 min. From Figure 4(a), it is observed that only a small reduction in the ultimate tensile strength is observed with increasing levels of zinc stearate loading (from 15 to 12 MPa with the addition of 60 phr zinc stearate). At strains greater than 500%, the tensile strength is particularly enhanced by the strain-induced crystallization of the PTMO segments.[9] This effect is seen in the 0 and 20 phr materials in Figure 4(a). The ultimate elongation decreases slightly, from 1300% to 1000%, due to zinc
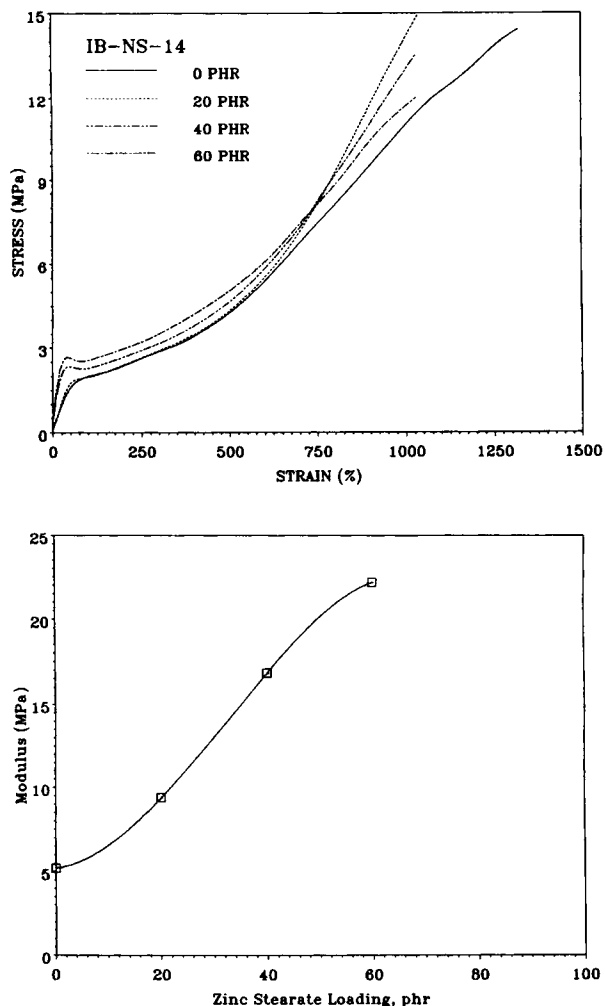

Figure 4 Effect of zinc stearate loading level on the mechanical properties of the IB-NS-14 samples: (a) stress-elongation behavior; (b) modulus.

stearate incorporation. It is speculated that "ion hopping," which tends to provide higher elongations in ionomers (and usually accents permanent set or hysteresis), is severely restricted with zinc stearate incorporation.[13] This may be the cause for the reduction in the ultimate elongation. In addition, a distinct yield behavior is observed in the 40 and 60 phr materials, but is absent in the 0 and 20 phr materials. The yielding behavior is often typical of filled systems. In Figure 4(b), the modulus of the material is plotted as a function of zinc stearate loading. As expected, the modulus increased with increasing levels of zinc stearate. Hence, it is seen that the addition of zinc stearate does not greatly alter the mechanical properties of the parent ionene polymer. The ultimate tensile strength and the ultimate elongation decrease slightly, but an improvement in the

modulus of the material is observed with increased loading levels as expected.

Structure and Morphology

Wide-Angle X-Ray Scattering (WAXS)

As stated earlier, zinc stearate is a polar crystalline material at ambient conditions. Figure 5 depicts the wide-angle X-ray scattering pattern for the industrial-grade zinc stearate that had been pressed into a film at 130°C. The diffraction rings seen in the pattern are very sharp, resulting from the zinc stearate crystallites. Figure 6 depicts the ambient temperature wide-angle X-ray scattering patterns of the unplasticized sample along with the plasticized sample with 40 phr zinc stearate. The 20 and 60 phr samples also show a similar behavior. The absence of crystalline rings in the unplasticized sample [Fig. 6(a)] is indicative of the material being amorphous in nature. Though it has been reported that higher molecular weight PTMO segments crystallize at
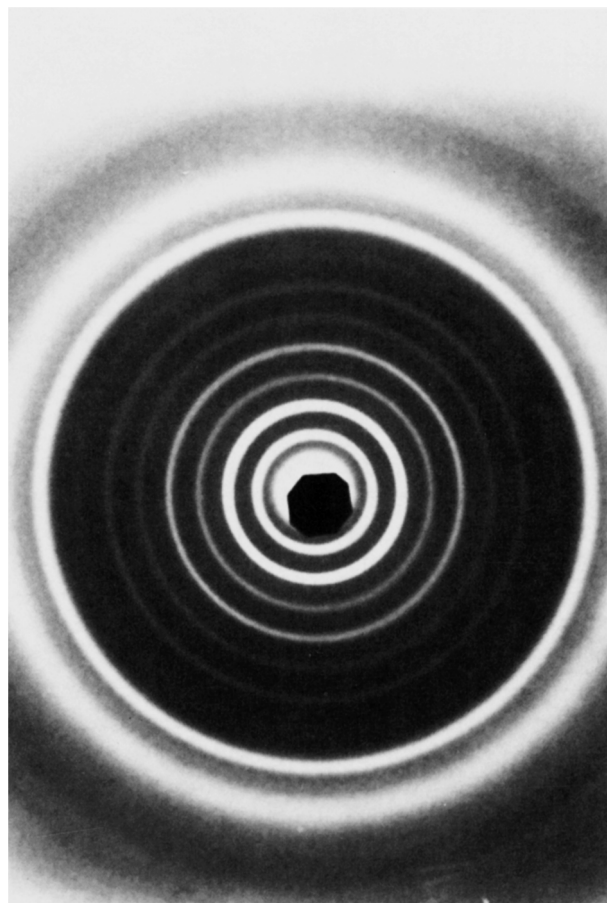
Figure 5   WAXS pattern of industrial-grade zinc stearate (pressed at 130°C).

ambient conditions, Feng[14] has shown that PTMO segments in these ionene materials can crystallize at ambient conditions only when the PTMO segment molecular weight exceeds 3000 g/mol. Therefore, it is expected that the material would be amorphous with the PTMO segment molecular weight being 1400 g/mol.

Distinct diffraction rings, similar to those of the zinc stearate powder, are seen in all the plasticized samples [Fig. 6(b)]. A similar observation was also made in zinc stearate plasticized sulfonated EDPM systems studied earlier in this laboratory.[11] This suggests that the zinc stearate in the ionene polymer is crystalline at ambient conditions. In addition, no azimuthal dependence in the WAXS pattern is observed in Figure 6(b), which indicates that these crystallites are randomly oriented in the polymer matrix. On stretching the samples, however, considerable orientation of the zinc crystallites occur. The orientation of the zinc stearate crystallites can be inferred from the presence of a high degree of azimuthal dependence in the WAXS patterns, seen in Figure 6(c). On the release of the applied stress, some degree of azimuthal dependence is still observed [Fig. 6(d)], indicating that the orientation instilled by the applied stress is not completely lost. With increasing zinc stearate loading, the number and/or the size of the crystallites increases. This, of course, is likely responsible for the observed increase in the modulus with increasing zinc stearate loading. Based only on the WAXS results, no conclusion can be made regarding the size and the distribution of the crystallites in the plasticized materials.

Scanning Electron Microscopy (SEM) of Fracture Surfaces

Scanning electron microscopy (SEM) was used in an attempt to determine if zinc stearate had phase separated from the ionene polymer. In Figure 7, SEM micrographs of the fractured surfaces of both unplasticized and plasticized samples are shown at nearly the same magnification of ca. 1100X. Interestingly, the surface texture of the unplasticized polymer is very different from those that contain zinc stearate but no distinct crystallites can be seen. The edges of the fractured surface of the unplasticized sample [Fig. 7(a)] are rather smooth, whereas those containing zinc stearate are quite rough. In Figure 7(b) and (c), where the zinc stearate loading level is 20 and 40 phr, respectively, no distinct regions of aggregation of the zinc stearate particles were noticed in the entire viewing region of the sam-
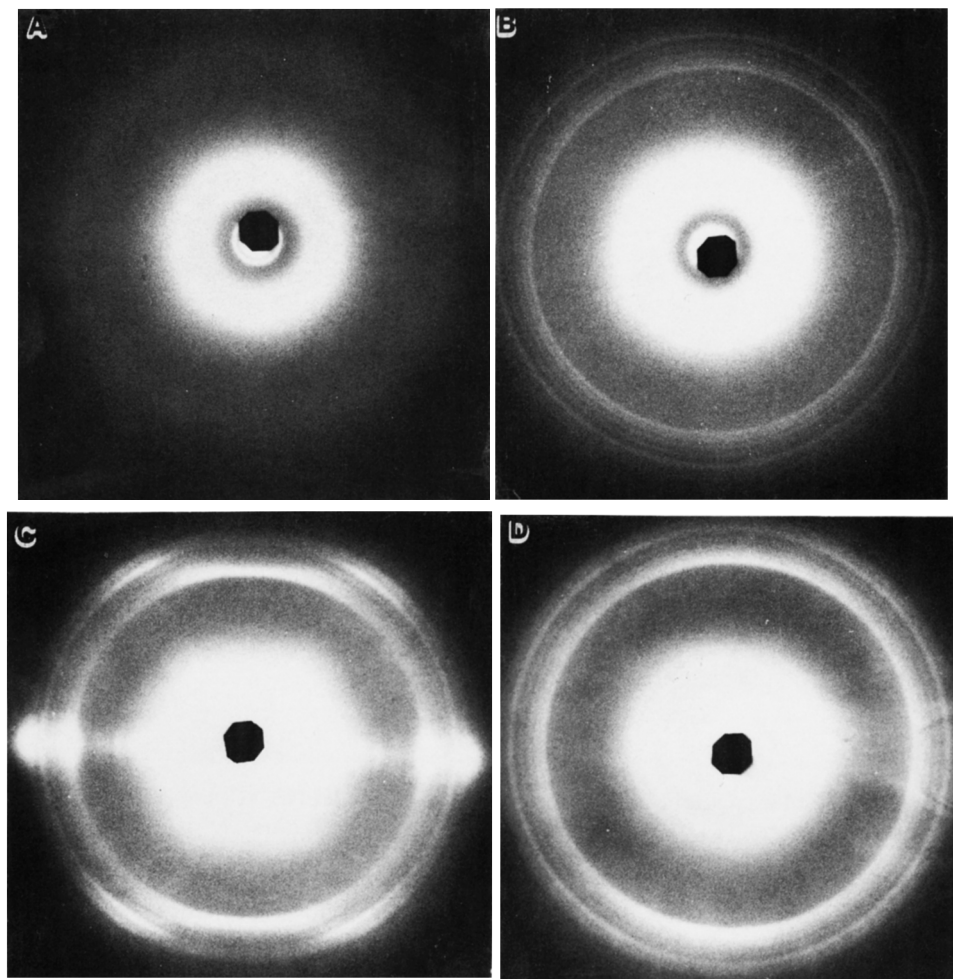
Figure 6   WAXS patterns of the IB-NS-14 samples: (a) 0 phr, (b) 40 phr—ambient, (c) 40 phr—stretched (λ = 7), (d) 40 phr (after release of the applied stress).

ples. However, in the 60 phr sample [Fig. 7(d)], some small aggregates with an average aggregate size of 2 μm (microns) were observed at higher magnification [see Fig. 8(a)]. These aggregates morphologically appear to be highly crystalline and are believed to be due to zinc stearate aggregates, based on the similarity between its structure and that present in the industrial-grade zinc stearate powder. Figure 8(a) shows a higher magnification (18K×) of one of these aggregates. For comparison, a similar magnification SEM micrograph of the zinc stearate powder used in this study is shown in Figure 8(b). The morphological features of the aggregate in the 60 phr material is clearly similar in structure to that the zinc stearate powder with an average size of ca. 4 μm.

Readdressing the fracture surfaces of the plasticized ionene, Figure 9 shows a higher magnification of a representative region for samples containing 20

and 40 phr of zinc stearate. The micrograph to the right (9b) represents a 4× magnification of the highlighted region on the left. Even at such high magnification, no aggregation is observed, which indicates that zinc stearate is very compatible with the ionene polymer up to a loading level of 40 phr. The term "compatible" has been used here to imply that zinc stearate does not migrate (or bloom) to the surface. Because of its polar nature, zinc stearate is expected to be distributed preferentially near the ionic domains. From the micrographs in Figure 7, it can be seen that the fractured surface area of the plasticized samples is very much higher than in the unplasticized sample. This indicates that a higher fracture energy may be required to create the additional surface area. Based on this information, it is speculated that the fractured toughness of the plasticized materials might well be higher than for the parent ionene polymer. Of course, the fracture
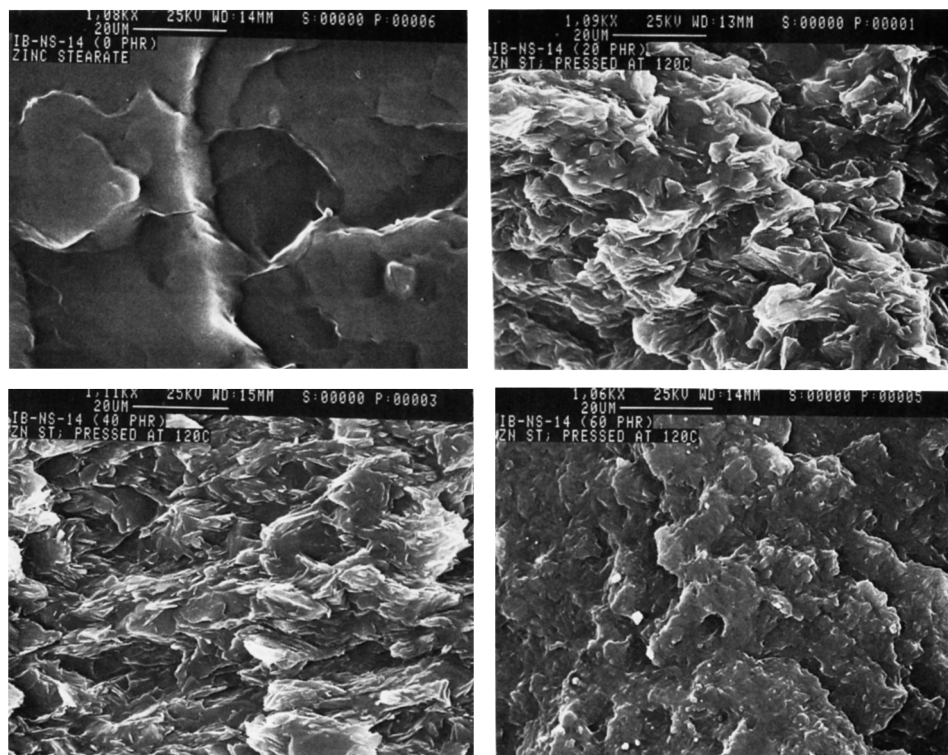
Figure 7 SEM micrographs of fractured surfaces of the IB-NS-14 samples—some containing zinc stearate: (a) 0 phr, (b) 20 phr, (c) 40 phr, (d) 60 phr.

behavior in the filled samples is greatly altered on account of zinc stearate incorporation, which leads to the creation of the additional surface area. However, no further studies have been conducted to quantify the nature of the fracture toughness due to zinc stearate incorporation.

Thermal Properties

Figure 10 shows a differential scanning calorimetry (DSC) scan of an industrial-grade zinc stearate and the unplasticized ionene polymer. A sharp endothermic peak is observed in Figure 10(a) at ca. 124°C that is due to the melting of the zinc stearate crystallites. This melting point is in good agreement with the reported values of zinc stearate in the literature.[15] Figure 10(b) shows the DSC scan of the *unplasticized* ionene polymer. An endothermic peak is observed at ca. 173°C. From TGA measurements, the onset of the weight loss also occurs near this temperature. Hence, the endothermic peak may be due to the weakening of the ionic interactions in the polymer and, more specifically, to the onset of degradation in the ionene segments.

Figure 11 shows the effect of zinc stearate incorporation on the melting transitions in the plasticized

sample with 60 phr zinc stearate. The sample was scanned in the temperature range between 50 to 130°C at a rate of 20°C per minute. Curve 1 represents the initial scan of the solution cast sample. The sample was then cooled slowly at 1.5°C per minute (which is the cooling rate utilized in the cooling experiment in the dynamic melt studies) to ambient conditions and later rescanned at 20°C per minute (curve 2). In curve 1, an endothermic peak is observed at ca. 106°C, resulting from the melting of the zinc stearate crystallites. Recall that the endothermic peak for the zinc stearate powder occurs at ca. 124°C. A considerable depression (about 18°C) in the melting point of zinc stearate is observed when incorporated in the ionene polymer. The depression in the melting point was also observed in the plasticized "anionomeric" EPDM systems studied earlier by Duvdevani et al.[5] It is speculated that some of the ionene segments likely form nucleation sites for the crystallization of zinc stearate. A depression in the melting point is also expected due to the presence of the ionene matrix material that likely also limits the size of the crystal growth.

On visual examination, it was observed that the zinc stearate, even at a loading of 60 phr, was very
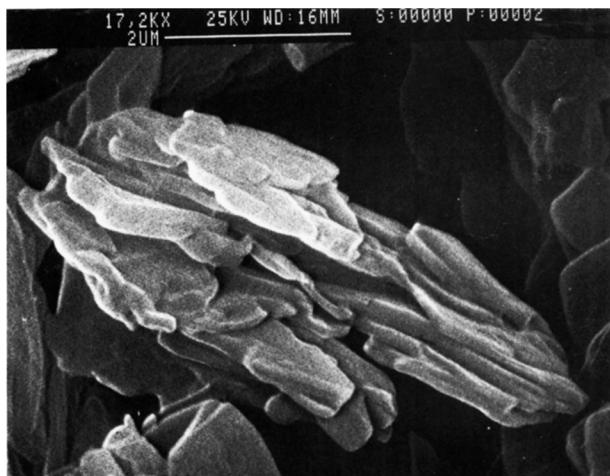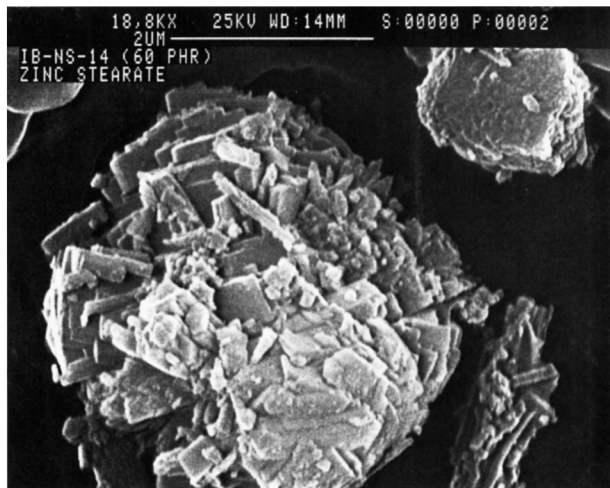
melting point of stearic acid may have likely shifted to somewhat higher temperatures, causing the observance of the shoulder at ca. 80–85°C. The slow cooling process provides ample time for both zinc stearate and stearic acid to form separate crystals. Therefore, on rescanning, a distinct endothermic peak is observed at ca. 71°C, which is in good agreement with the reported values for the melting point of stearic acid crystallites. This observation at least supports the earlier speculation that the presence of stearic acid is responsible for the shoulder near 80–85°C.

Rheological Properties

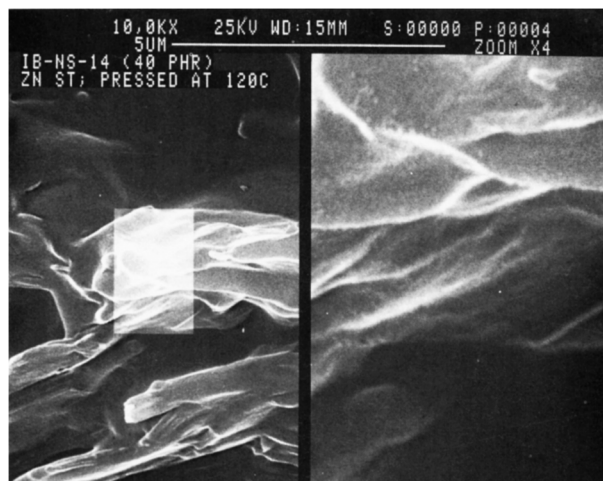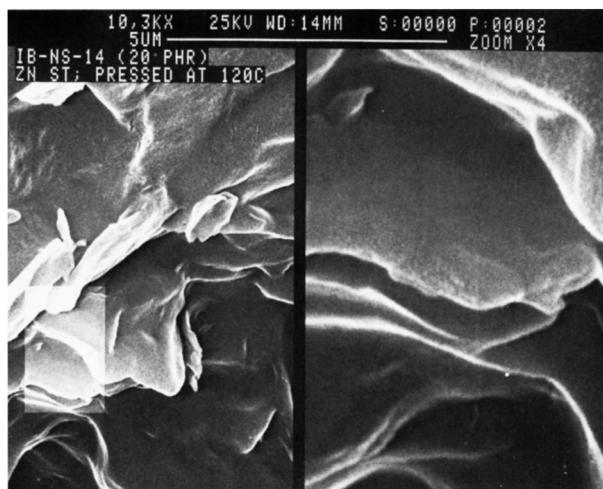The main purpose in incorporating zinc stearate was to lower the softening temperatures of the ionene

Figure 8 SEM micrographs of zinc stearate aggregates: (a) plasticized sample (60 phr); (b) zinc stearate powder.

compatible with the ionene polymer and exhibited no signs of "blooming" occurring to the surface, although at the high loading, some zinc stearate crystals seemed to be within the matrix as discussed earlier. The melting peak of zinc stearate crystallites, however, broadens considerably when the plasticizer is incorporated in the ionene polymer. This can be attributed to the presence of impurities in the zinc stearate crystallites and also to a distribution in their size. A distinct shoulder is also observed in curve 1 around 80–85°C. In industrial-grade zinc stearate, stearic acid is a main contaminant. During the slow solvent casting process, both zinc stearate and stearic acid may have cocrystallized together at ambient conditions. The literature suggests that the melting point of stearic acid is ca. 70°C.[15] It is speculated that due to the cocrystallization process the

Figure 9 Fractures surfaces of zinc stearate plasticized samples: (a) 20 phr; (b) 40 phr; Magnification = 18K×.
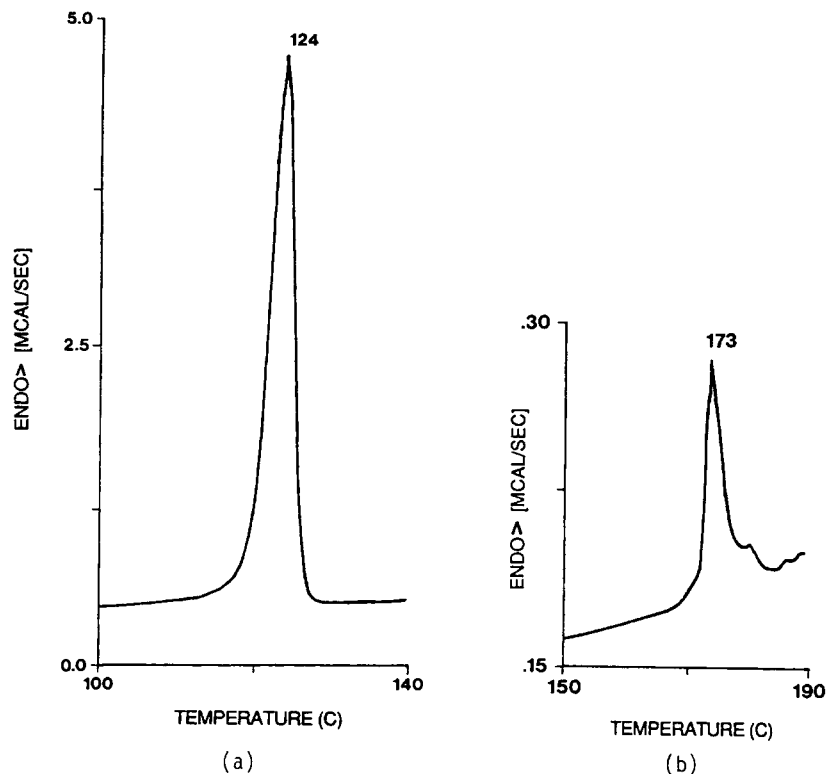
Figure 10 DSC scan of (a) industrial-grade zinc stearate and (b) unplasticized IB–NS-14 (scan rate = 20°C/min).
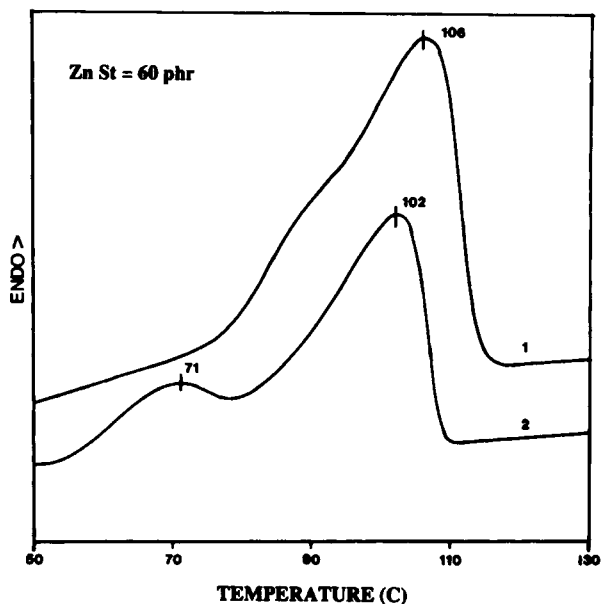

Figure 11 Effect of zinc stearate incorporation on thermal transitions for a 60 phr zinc stearate containing sample; curve 1 represents the initial scan of the solvent cast sample, and curve 2 represents a rescan of the same sample after cooling it at 1.5°C/min to room temperature (23°C).

polymer so that the material could be thermally processed. It was discussed earlier that above its melting point zinc stearate shields the ionic interactions lowering not only the softening temperature but also the melt viscosity. To verify this, dynamic mechanical measurements in the melt were conducted on a Rheometrics mechanical spectrometer (RMS) to determine the effect of zinc stearate incorporation on the melt properties of the ionene polymer. From dynamic mechanical analysis (recall Fig. 3), it was observed that the plasticized samples essentially soften ca. 120°C. Therefore, the melt studies for the plasticized samples were conducted at 120°C. In addition, the melt studies for the unplasticized polymer was conducted at 180°C, which is near its softening temperature. For purposes of comparison with the plasticized samples, the unplasticized samples could not be tested at 120°C because it was still a solid at that temperature.

The frequency-sweep measurements of the plasticized samples and the unplasticized samples are shown in Figure 12. Notice that the shape of the 0 phr sample (curve A) is very different from the general shape of the plasticized samples (curves B–D). It is speculated that considerable degradation of the
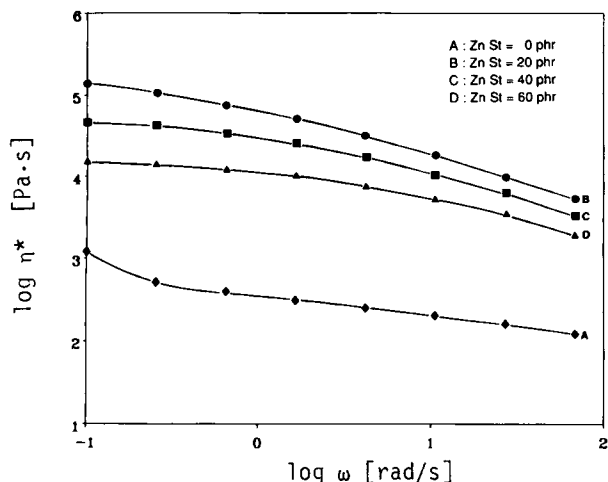
Figure 12 Effect of zinc stearate incorporation on the melt viscosity (at 120°C) of the IB-NS-14 ionene polymer.

ionene polymer occurs during the duration of the experiment ($\sim$ 15 min) and which is responsible for the observed behavior.

Specifically, from the time-sweep measurements conducted initially on this sample, η^* decreases by almost an order of magnitude for the 0 phr sample in ca. 15 min. This clearly supports the speculation that considerable degradation occurs in the unplasticized material at 180°C. Though the data on the plasticized material is of no considerable significance due to the occurrence of degradation, it nevertheless

serves somewhat as a reference material for *comparison* with the plasticized samples.

The dynamic melt viscosity of the plasticized samples decreases with increasing levels of zinc stearate loading. It is expected that with increasing zinc stearate loading more of the ionic domains are shielded, which would, in effect, reduce the ionic cross-link density in the system and lower the melt viscosity of the medium. In addition, zinc stearate, being an ionic plasticizer, also plasticizes the ionic domains. All the plasticized samples show typical shear thinning behavior, which is a characteristic feature of all thermoplastic materials.

Figure 13 depicts the location of the crossover frequency as a function of zinc stearate loading. The crossover frequency corresponds to that frequency where the ratio $G''/G' = 1$ (or tan $\delta = 1$). The crossover frequency for the unplasticized material does not appear within the frequency range studied, but, as stated earlier, the data from the 0 phr material is of little significance due to the occurrence of its degradation. For the plasticized samples, the crossover frequency shifts to higher frequencies with increasing zinc stearate loading, as expected. The shift to the higher frequencies is indicative of shorter relaxation times in the material, which may be due to a reduction in the apparent ionic cross-link density and also due to the plasticization of the ionic domains by zinc stearate. This further confirms the earlier speculation that a higher level of plasticization occurs with increasing zinc stearate loading.
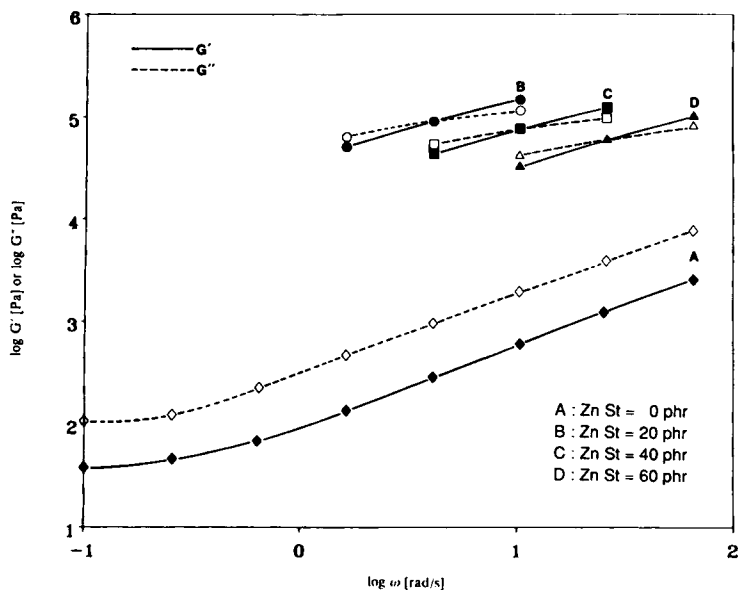

Figure 13 Location of the crossover frequency (at 120°C) for the IB-NS-14 zinc stearate plasticized samples.

To understand the relaxation behavior of the ionene polymer as a function of zinc stearate loading level, the well-known "jump strain" experiment in the melt was attempted (experimental details discussed earlier). For reasons given earlier, all the plasticized samples were tested at 120°C, and the unplasticized sample (0 phr) was tested at 180°C. The results of the jump strain experiment is shown in Figure 14. The relaxation modulus data, $G(t)$, is plotted on a semilog scale in Figure 14(a) and on a log–log plot in Figure 14(b). In Figure 14(a), it is seen that the material relaxes faster with increasing zinc stearate loading. At low zinc stearate loading, it is speculated that small amounts are incorporated in each of the ionic domains, which would, in effect, plasticize the ionic domains to a certain extent. With the increasing zinc stearate loading, the ionic domains are further plasticized, and, therefore, the
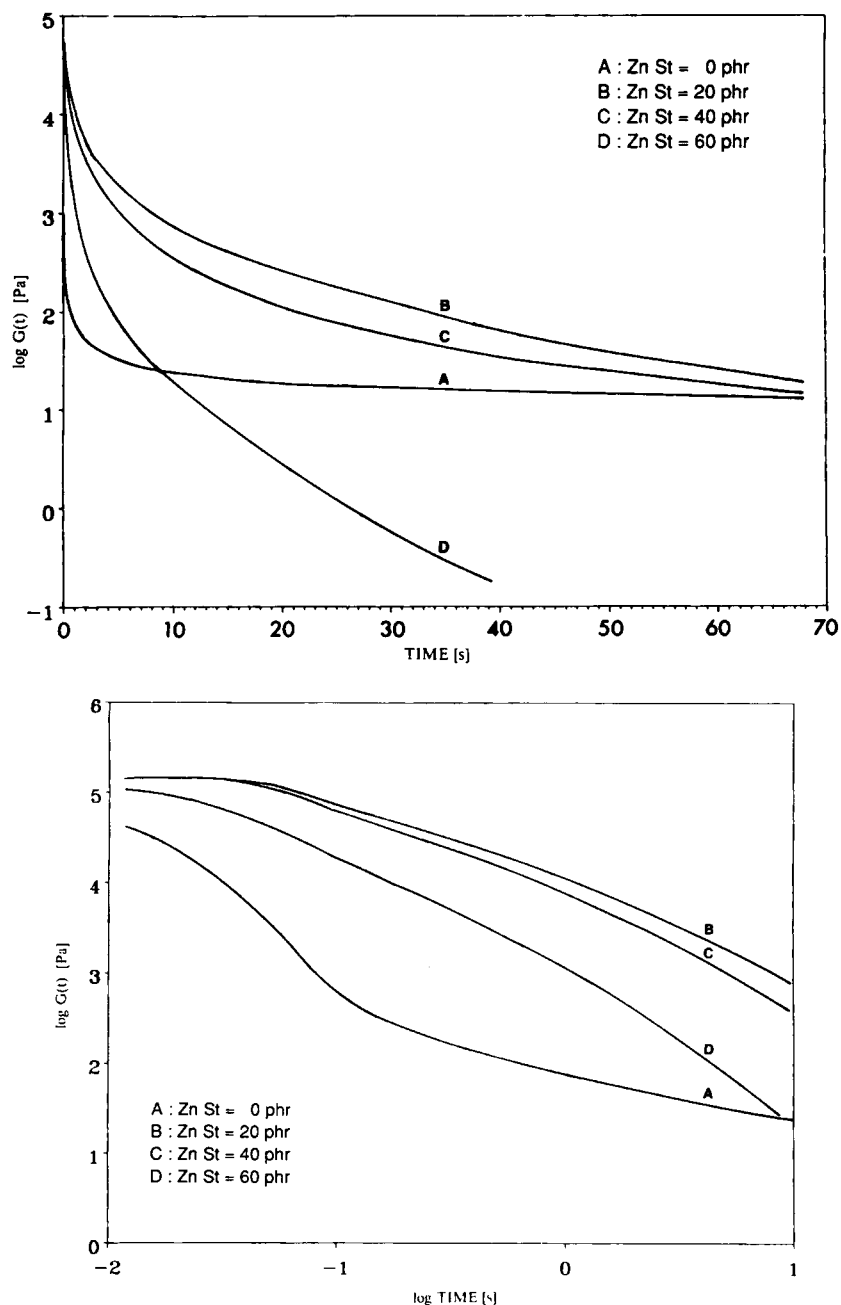

Figure 14 Results of the jump strain experiment at 120°C; initial strain = 50%: (a) semilog scale; (b) log–log scale.

material relaxes faster or in a shorter time scale with increasing plasticizer content. It is expected that zinc stearate will not only shield the ionic interactions in the system but will also plasticize the ionic domains, and, hence, it functions in a dual role.

All the applied stress is essentially relaxed in the unplasticized material (curve A) since after the degradation process the material likely contains only much lower molecular weight segments of the original polymer. Also, the relaxation time decreases considerably with temperature (recall that the 0 phr material was tested at 180°C). The log–log scale in Figure 14(b) serves to expand the time scales at shorter time intervals. The response time of the RMS instrument is ca. 0.03 s, and therefore any data below this time is not expected to be of any significance. It is clearly seen that the relaxation process is accelerated with increasing zinc stearate loading. However, an apparent residual stress is observed even after 70 s in all the plasticized samples except the 60 phr material. This is an interesting observation. Based on the SEM analysis, it was expected that all the ionic domains would have been plasticized at least at a loading level of level of 40 phr. At present, no explanation is provided for this reproducibly observed behavior.

Nonisothermal cooling experiments were conducted to determine the temperature at which the structure of the material is regained as a result of zinc stearate crystallization. It was expected that there would be a considerable increase in the viscosity of the material when the zinc stearate begins to crystallize. Therefore, the melt viscosity was monitored as a function of cooling temperature (Fig. 15). The 60 phr sample was heated to 130°C, and the material was cooled at 1.5°C/min, until the torque values exceeded the acceptable range. While cooling from 130°C, a gradual increase in the viscosity was observed, which is essentially caused by the decreasing temperature. On further cooling, a considerable increase in the melt viscosity was observed with the onset being at ca. 63°C. This is due to the crystallization of zinc stearate. The technique of differential scanning calorimetry (DSC) was also used to confirm that zinc stearate was indeed responsible for the observed behavior. In the DSC experiment, the sample was heated to 130°C and then also cooled at a controlled rate of 1.5°C/min (the same as in the RMS). As expected, the onset for an exotherm was observed at the supercooling temperature of ca. 63°C with the peak located at ca. 56°C. This observation clearly supports the earlier speculation that the structure being formed at ca. 63°C is due to zinc stearate crystallization. Based on this information, this ionene material (or related ionene systems) can now be processed at 120°C with an added ionic plasticizer using an appropriate mold temperature to favor zinc stearate crystallization.

CONCLUSIONS

This study has shown that the strong ionic cross-links, which are responsible for the excellent me-
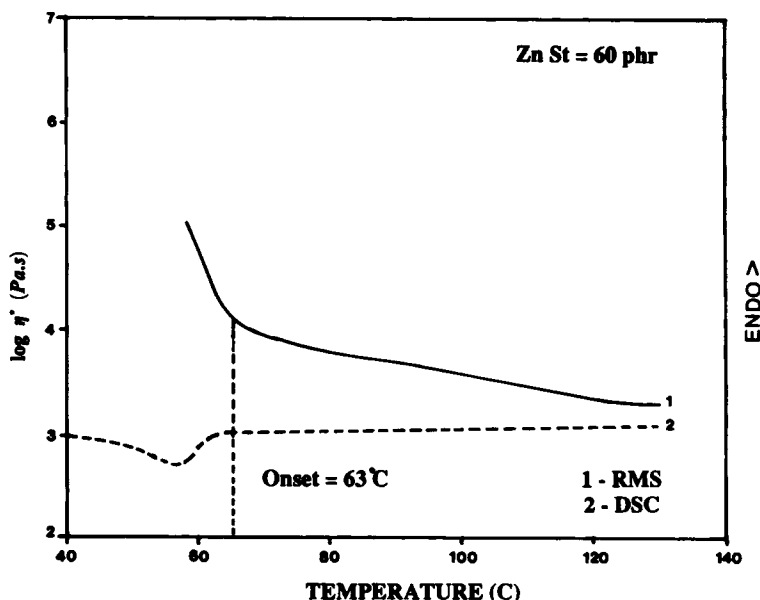

Figure 15   Nonisothermal cooling profiles of IB-NS-14 with 60 phr zinc stearate.

chanical properties at ambient conditions in segmented ionene polymers (based on benzyl dihalide with PTMO as the soft segment), can be controlled with the use of a suitable polar additive, such as zinc stearate. The mechanical properties of the host ionene polymer are not adversely affected with the zinc stearate addition. The additive is very "compatible" with the ionene "cationomer," even up to the loading level of 60 phr. In addition, the softening temperature and the melt viscosity are significantly reduced with zinc stearate addition. By appropriate selection of zinc stearate loading, the segmented ionene polymers can now be thermally processed without problems of degradation or major loss of properties.

REFERENCES

1. A. D. Wilson and H. J. Prosser, Eds., *Developments in Ionic Polymers-1*, ACS Symp. No. 302, American Chemical Society, Washington, DC, 1986.
2. C. M. Leir and J. E. Stark, *J. Appl. Polym. Sci.*, **37**, 1535 (1989).
3. H. S. Makowski and R. D. Lundberg, in *Ions in Polymers*, A. Eisenberg, Ed., Adv. Chem. Ser., 187, American Chemical Society, Washington, DC, 1980, Chap. 3.
4. R. D. Lundberg, H. S. Makowski, and M. L. Westerman, in *Ions in Polymers*, A. Eisenberg, Ed., Adv. Chem. Ser. 187, American Chemical Society, Washington, DC, 1980, Chap. 5.
5. I. Duvdevani, R. D. Lundberg, C. Wood-Lordova, and G. L. Wilkes, in *Coulombic Interactions in Macromolecular System*, A. Eisenberg and F. E. Bailey, Eds., ACS Symp. Ser. 302, American Chemical Society, Washington, DC, 1986, p. 184.
6. P. K. Agarwal, H. S. Makowski, and R. D. Lundberg, *Macromolecules*, **13**, 1679 (1980).
7. J. J. Fitzgerald, D. Kim, and R. A. Weiss, *J. Polym. Sci. Polym. Lett. Ed.*, **24**, 263 (1986).
8. R. A. Weiss, A. Sen, A. F. Galambos, and J. T. Koberstein, *Polym. Mater. Sci. Eng.*, **59**, 176 (1988).
9. D. Feng, L. N. Venkateshwaran, G. L. Wilkes, J. E. Stark, and C. M. Leir, *J. Appl. Polym. Sci.*, **37**, 1549 (1989).
10. A. H. Willbourn, *Trans. Faraday Soc.*, **54**, 717 (1958).
11. C. B. Wood, Masters Thesis, Department of Chemical Engineering, Virginia Polytechnic Institute & State University, March, 1982.
12. D. Feng, personal communication.
13. M. Hara and A. Eisenberg, *Macromolecules*, to appear.
14. D. Feng, Ph.D. Dissertation, Department of Chemical Engineering, Virginia Polytechnic Institute & State University, April, 1989.
15. R. D. Lundberg and H. S. Makowski, in *Ions in Polymers*, A. Eisenberg, Ed., Adv. Chem. Ser., 187, American Chemical Society, Washington, DC, 1980, Chap. 2.