Ionic Naphthalene Thermotropic Copolyesters: Divalent Salts and Tensile Mechanical Properties

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ABSTRACT: Novel ionic naphthalene thermotropic polymers (NTPs), based on wholly aromatic copolyesters, were synthesized, and their tensile mechanical properties were investigated. These ionic NTPs, containing 1 mol % ionic groups with divalent metal counterions (Ba, Ca, Mg, and Zn), exhibited thermotropic liquid crystallinity. Among them, the Ca salt NTP maintained a high molecular weight and exhibited excellent thermal and mechanical properties. Systematic comparison was made among nonionic NTP, ionic NTP (Na salt), and ionic NTP (Ca salt), since they possessed similar molecular weights and since their film specimens were made under similar processing conditions. Ionic NTP with monovalent Na ions showed a moderate increase in tensile modulus and strength over nonionic NTP. However, ionic NTP with divalent Ca ions showed a significant increase: i.e., 76% increase in modulus and 147% increase in strength. An increase in tensile properties arises from enhanced lateral support, via ionic bonds (cross-links), between highly aligned NTP chains. Ionic cross-links can effectively enhance tensile properties of the LCPs, unlike covalent cross-links, which are less effective. This arises from the nondirectional nature of ionic bonds, which makes the bonds thermally labile; thus chains aligned under elongational flow at high processing temperature are reinforced effectively upon cooling. Tensile fracture surface morphologies of ionic NTPs were also investigated as a function of counterion.

Introduction

Main-chain thermotropic liquid crystalline polymers (TLCPs) have attracted much attention for their unique properties, such as excellent tensile and thermal properties, good chemical resistance, and ease of processing. However, there are drawbacks that prevent them from more extensive use. One is poor transverse and compressive strengths in contrast to very high axial strength. Another is poor miscibility and adhesion with other polymers, when LCPs and conventional polymers are blended.[1−3] Both problems basically arise from weak intermolecular interactions either in a TLCP itself or in a TLCP/polymer blend.[1,2]

Various approaches have been used to develop TLCPs with improved transverse and compressive strengths with only marginal success.[4] One approach to accomplish this is to enhance interchain interactions of LCP molecules via chemical cross-linking.[1,2,4] However, only a moderate improvement, if any, of fiber axial compressive strength has been achieved with a decrease, usually a substantial loss, in tensile properties.[2,4] This is also true for fibers made from random coil polymers.[2] Heat treatment of TLCPs may increase tensile strength by raising the molecular weight of the polymers, but the transverse properties are essentially the same.[5,6] Thus, a major challenge is to enhance transverse/compressive properties of LCPs without sacrificing desirable tensile properties.[2]

We are currently developing ionic TLCPs by introducing ionic groups (and ionic bonds) into LCP chains to obtain better tensile and compressive properties.[7−9] It is known that strong ionic interactions (bonds) between polymer chains can significantly enhance mechanical properties, which include compressive strength, as demonstrated for flexible ionomers.[10−12] In ionic polymers, polymer chains are ionically cross-linked through nondirectional ionic bonds, which are strong but are thermally labile.[11] Thus, unlike chemically cross-linked polymers, they melt upon heating and re-form upon cooling. Our preliminary results have indicated that both tensile and compressive properties are enhanced in ionic NTPs,[8] in which ionic groups (ionic bonds) are incorporated into NTP chains.

In the previous work,[7] we synthesized and characterized novel ionic NTPs (Na salt) based on wholly aromatic polyesters, which were made by random copolymerization of 1,4-hydroxybenzoic acid (HBA), 6,2-hydroxynaphthoic acid (HNA), and ionic comonomer sodium 5-sulfoisophthalate (SSI). All the ionic NTPs (Na salt) had fiber-forming molecular weights and exhibited liquid crystallinity with nematic mesophase texture over a wide temperature range, without showing a transition to an isotropic phase at least up to 380 °C. Detailed discussion about the ion content effect on thermal properties, optical textures, and fracture morphology of these ionic NTPs is found elsewhere.[7]

In this study, we prepared ionic NTPs containing various divalent metal ions (Mg, Ca, Zn, Ba) in an attempt to achieve more effective enhancement in mechanical properties than was previously noted in synthesized ionic NTP with monovalent Na ions. It is well-known for ion-containing polymers that replacement of a monovalent ion, such as Na^+, with a divalent one, such as Ca^{2+}, significantly enhances mechanical properties by strengthening the ionic bonds, insofar as metal ions are restricted to IA and IIA elements.[12] For

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example, both tensile and fatigue properties of sulfonated polystyrene ionomers (Ca salt) were found to be much better than those of Na salts.[12] In another example, it was found that, in a Ca-salt PMMA ionomer of 0.8 mol % ion content, shear deformation was developed in addition to crazing, whereas in a Na-salt PMMA ionomer of the same ionic content, deformation occurred only by crazing, as in PMMA.[13] Such a change in deformation modes usually leads to better mechanical properties.[12] These data are explained as arising from stronger ionic bonds formed in the divalent Ca salt than in the monovalent Na salt. Thus, we may anticipate finding better mechanical properties for ionic NTPs with divalent ions.

In addition to characterization and morphological studies of ionic NTPs, their tensile properties were investigated. For comparison, tests were also conducted for a nonionic NTP and an ionic NTP with Na ions. It was found that the introduction of ionic bonds improved mechanical properties in the transverse direction, which is a drawback of LCPs.[1,6,14] Moreover, unlike chemical cross-linking or other modifications known to LCPs,[4] ionic cross-linking significantly enhanced tensile properties along the chain direction. In addition, the effects of the nature of the counterion on the tensile properties and tensile fracture morphology and a possible molecular mechanism of tensile failure are discussed.

Experimental Section

Preparation of Ionic NTPs. All the ionic NTP samples were prepared according to the method described previously.[7] To prepare ionic NTPs that contain divalent metal ions, metal ions were introduced into the ionic comonomers by in-situ cation exchange during the heating process of reaction mixtures: i.e., divalent metal acetate was added to three base monomers, 4-hydroxybenzonic acid (HBA), 6-hydroxy-2-naphthoic acid (HNA), and sodium 5-sulfoisophthalate (SSI), in the beginning of the reaction.

In this work, an excess amount (15 mol %) of acetate was added to ensure complete exchange of cations. We also performed the following separate experiment to confirm complete cation exchange: first, ionic monomer SSI was mixed with calcium acetate, and after purification of the resultant monomer, chemical analysis of the monomer was conducted, which confirmed complete cation exchange. In the synthesis of ionic NTP, sodium acetate produced was removed in the final stage of the polymer preparation; i.e., after the reaction was completed, the resulting polymer was ground into powder and washed with methanol and acetone, respectively; thus the sodium acetate and unreacted monomers were removed during this process. All the ionic NTPs with divalent metal ions had the same composition, i.e., 73 mol % HBA, 26 mol % HNA, and 1 mol % SSI.

Viscosity. Viscosity measurements of ionic NTP polymers were conducted with a capillary viscometer at 0.1 wt % concentration in a solvent mixture, pentafluorophenol (PFP)/hexafluoro-2-propanol (HFIP) (50/50 v/v), at 25 °C.[5] The inherent viscosity (IV) value was determined by the following equation: $\mathrm{IV} = \ln(\eta_{\mathrm{rel}})/c$, where c is the polymer concentration and η_{rel} is the relative viscosity, which is the ratio of the flow times of the polymer solution and the pure mixed solvent.

Differential Scanning Calorimetry (DSC). Thermal transitions of NTP polymers were studied with DSC using a TA Instrument thermal analyst (2100/910). Samples of 5–10 mg were examined at a heating rate of 20 °C/min, followed by cooling to ambient temperature under a nitrogen atmosphere, to determine the melting and crystallization temperatures (T_m and T_c). The T_m and T_c values are determined from peak temperatures of the melting endotherm and crystallization exotherm on DSC thermograms.

Thermogravimetric Analysis (TGA). TGA measurements were conducted with a TA Instrument (2100/951). Powder samples of ca. 15 mg were tested at a heating rate of 10 °C/min under a nitrogen atmosphere.

Tensile Tests. Tensile tests were conducted on thin film specimens, with a Minimat Materials Tester (Polymer Laboratories), according to the ASTM Standard (D882-91). The cross-head speed used was 0.1 mm/min. Films were melt extruded with Micro-Melt extruder (Hoechst Celanese) having a film die of 0.005 in. thickness and 0.250 in. width, cooled at ambient temperature, and then collected with a wind-up roll at a take-up speed of 5–12 m/min. Film thickness was measured with a micrometer at the various points of the film, and an average value, usually in the range of 10–40 μm, was used. At least five specimens were tested for each sample at room temperature and average values were used for analysis. The tensile modulus was determined from the initial slope of the stress–strain curve, and both the tensile strength and maximum strain were those at the break point (ultimate properties).

Dynamic Mechanical Thermal Analysis (DMTA). Since glass transition temperatures were not detected by DSC for both nonionic and low ionic content NTP samples,[7] DMTA was used: this method is more sensitive to smaller structure. Specimens of 10 mm length and 3.0 mm width were cut from melt-extruded films. A TA instrument (DMA983) was used for tensile testing with a fixed frequency mode of 0.1 Hz. All the measurements were conducted at an amplitude of 0.10 mm and a heating rate of 4 °C/min.

Scanning Electron Microscopy (SEM). Tensile-fractured specimens of both the nonionic and ionic NTPs were examined with SEM. After being mounted on a stub with conducting double-sided carbon tape, specimens were coated with gold for 4 min in a sputter coater (Polaron, SEM coating unit E 5100). The specimens were then examined with a scanning electron microscope (Amray 1200 C) operating at 30 kV, and images were recorded directly from the cathode ray tube on Polaroid 55 films.

Polarizing Light Microscopy (PLM). To examine the liquid crystalline structure of ionic NTP samples, polarizing light microscopy was used. Micrographs were taken with a polarized light microscope, Olympus (BH-2), with Polaroid 59 color films at room temperature. Two types of film specimens were used: one was made through in-situ melting between two glass slides on a hot stage (Mettler F52), and the other was made from melt extrusion.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR was used to identify sulfonate groups that were incorporated into ionic NTP chains. Thin film specimens made by melt extrusion were used for IR measurements. IR spectra were collected with an average scan of 25 at a resolution of 2 cm^{-1} in a transmission mode with an ATI Mattson spectrometer (Genesis Series FTIR).

Results and Discussion

Characterization and Thermal Properties of Ionic NTPs with Divalent Metal Ions. To check if sulfonate groups were properly incorporated into NTPs, FTIR analysis was used. A major difference between an ionic NTP and a nonionic NTP is that the former contains ionic sulfonate groups and the latter does not. The S–O stretching mode, which normally lies in 600–700 cm^{-1} for organic sulfonates,[15] is used to identify sulfonate groups of ionic NTPs. The IR spectra in the range of 500–850 cm^{-1} are compared between (a) nonionic NTP and (b) 1 mol % ionic NTP (Ca salt) in Figure 1. Although no S–O stretching mode is seen in the nonionic NTP, such a mode is clearly identified at 646 cm^{-1} for the 1 mol % ionic NTP (Ca salt). Only a relatively weak band is seen due to the low ionic (sulfonate group) content of the polymer. This is consistent with the previous result on 1 mol % ionic NTP

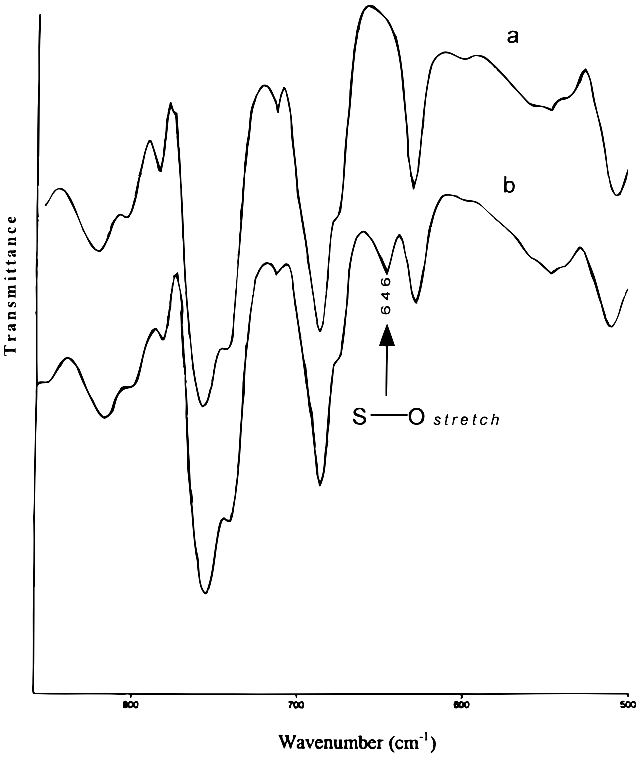

Figure 1. IR spectra for (a) nonionic NTP and (b) 1 mol % ionic NTP (Ca salt) in the range of 500−850 cm^{-1}.

(Na salt), in which only a weak band was observed at 647 cm^{-1}.[7] FTIR results clearly indicate successful incorporation of ionic (sulfonate) groups into the NTP chains.

To investigate the effect of counterion on thermal properties, DSC and TGA measurements were conducted on ionic NTPs. DSC was used to study primary transitions, such as melting (i.e., transition from three-dimensional solid crystal to nematic liquid melt), crystallization, and glass transition. All the DSC measurements were conducted on as-made polymers.

Figure 2 shows both heating and cooling curves in the DSC thermograms, plotted on the same scale of the heat flow, to show the changes associated with the change in the counterion. No glass transitions were detected by DSC, in good agreement with the previous DSC results on nonionic NTP and ionic NTPs (Na salt) of low ionic content (1 and 2 mol %).[7] Table 1 lists transition temperatures (T_m and T_c), the heat of fusion (ΔH_m), and the heat of crystallization (ΔH_c), which were determined from the thermograms. Although ΔH_c values show only small differences for different divalent counterions, there are large differences in the ΔH_m values. This is because ΔH_m is sensitive to the state of crystalline samples, such as the size and the perfection of crystalline structure, and thermal histrory,[16] and because the state of crystals is influenced by a counterion, whereas ΔH_c is less sensitive, since crystallization upon cooling occurs from the melt under the same cooling conditions (via DSC scanning).

Figure 3 shows how the crystallization temperature changes with the ionic radius of the divalent ion (group IIA metal ions). Zn data are excluded from this plot, since Zn is a transition metal ion (group IIB) and is not expected to follow a simple rule of ionic bonds.[11] Figure 3 clearly indicates that the T_c decreases as the ionic radius decreases. It is expected that the ionic interactions between a sulfonate group and a cation increase with a decrease in the cation size, since the interionic distance becomes smaller.[10,11] As a result of stronger interchain ionic interactions, which still exist in the melt, the melt viscosity increases and segmental mobility of polymer chains for spatial arrangement during crystallization is reduced. This leads to larger supercooling[17] and therefore lowers the crystallization temperature. Such an explanation is also used to understand the large amount of supercooling observed for a crystalline ionomer, poly(ethylene-*co*-sodium methacrylate).[18,19]

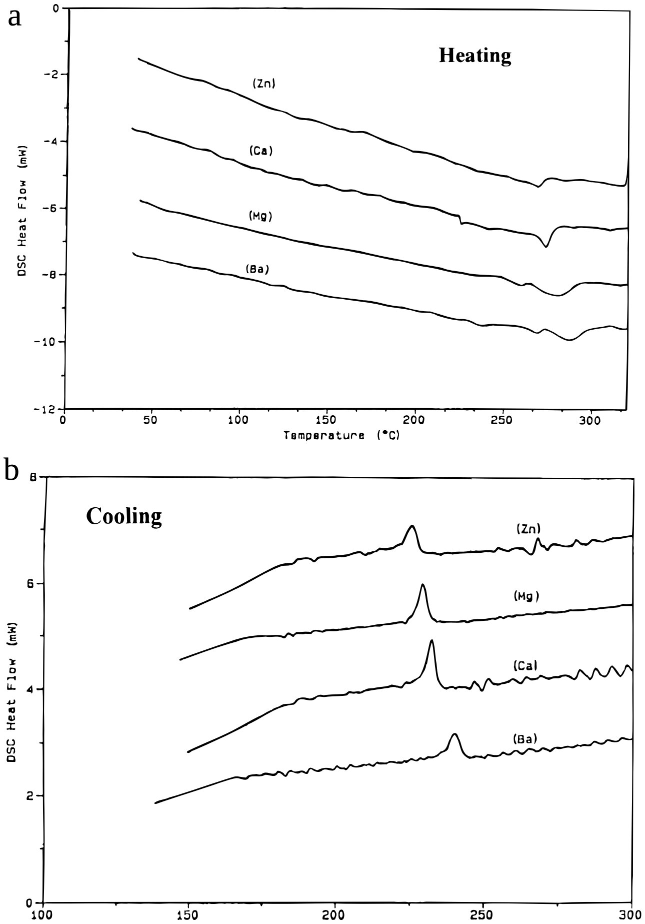

Figure 2. DSC thermograms of 1 mol % ionic NTPs with various divalent ions (Mg, Ca, Ba, Zn): (a) heating curves; (b) cooling curves.

Table 1. DSC Results of 1 mol % Ionic NTPs with Divalent Cations

cation	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)
Mg^{2+}	279	229	2.84	2.44
Ca^{2+}	273	232	1.77	3.15
Ba^{2+}	287	240	1.68	2.64
Zn^{2+}	267	226	0.75	2.37

Thermal stability of the ionic NTPs containing divalent ions was examined by thermogravimetric analysis (TGA). All the ionic NTPs investigated were thermally stable (i.e., no weight loss) up to at least ca. 380 °C, a temperature far above the melting temperatures. Our previous TGA result on ionic NTP (Na salt) also showed that the onset temperature, where two tangential lines in TGA curves intersect, was around 380 °C.[7] Figure 4 shows a typical TGA curve for the best sample among those studied, i.e., ionic NTP (Ca salt) of 1 mol %, which reveals excellent thermal stability up to ca. 500 °C. It

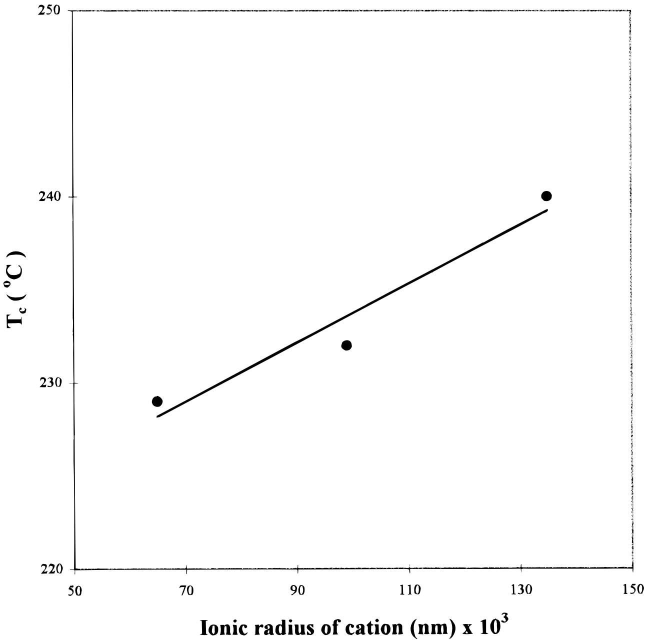

Figure 3. Crystallization temperature vs counterion ionic radius of ionic NTPs with various divalent ions (Mg, Ca, Ba). A line is drawn simply to guide the eye.

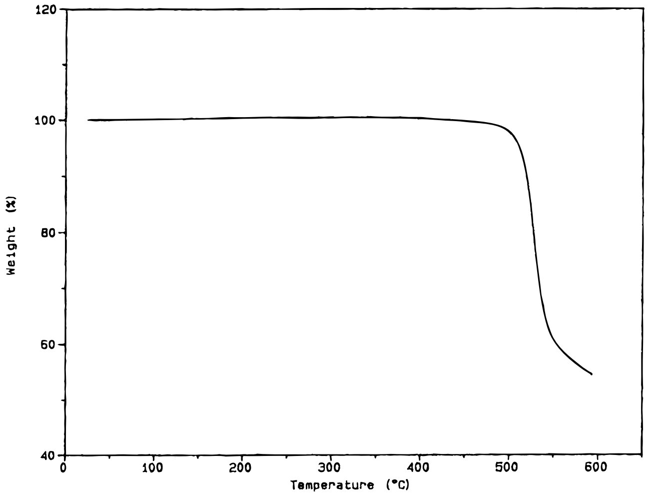

Figure 4. TGA curve of 1 mol % ionic NTP (Ca salt).

should be stressed that this polymer also exhibits excellent tensile properties, as will be discussed.

Finally, it should be added that all the melt-extruded films of ionic NTPs (divalent salts) revealed nematic liquid crystalline structure; i.e., they exhibited extensive birefringence with threaded texture in a fine scale under crossed polarizers (pictures not shown). The birefringence pattern is similar to that observed for ionic NTPs (Na-salt).[7]

Effect of Counterion on Tensile Mechanical Properties. It has been reported for conventional ion-containing polymers (ionomers) that the nature of the counterion can influence mechanical properties, with the effectiveness depending on the type of ionomer.[12] Thus, it is of interest to investigate the effect of counterion on the mechanical properties of ionic NTP.

Table 2 summarizes the tensile properties of 1 mol % ionic NTP as well as nonionic NTP. Although Na and Ca salts show better tensile properties than nonionic NTP, Mg and Zn salts show decreased tensile properties. To understand this, the inherent viscosity (IV) was also measured for these samples, and these IV values are listed in Table 2. It has been reported that the tensile strength of NTP fibers depends on the molecular weight, which increases with an increase in the IV value.[6] Note that Mg and Zn salts have significantly lower IV values than Na or Ca salt and the nonionic NTP. Hence, the poor tensile properties of ionic NTP with Mg or Zn are attributed to a lower molecular weight. The preferable IV values to achieve good mechanical properties and processability are reported to be 4.5−5.5 for NTP type polymers.[20] For the Ba salt, the IV value was also low and only brittle nonuniform films were produced from melt extrusion, which were not suitable for tensile tests. The reason why lower molecular weights were obtained for the ionic NTPs with Mg, Ba, and Zn ions is not clear. One possible explanation for the Mg and Zn salts is that these ions have considerable tendency to covalently bond.[21] Also, since Ba ion has a large ionic radius, and presumably the ion size effect in solution[21] favors ionic aggregation, this would prevent polymer chain growth during copolymerization. It was also observed that the Ba salt was more difficult to dissolve than other ionic NTPs in Table 2.

Table 2. Tensile Properties of Nonionic and 1 mol % Ionic NTP Films[a] as Well as Inherent Viscosity

cation	(nonionic)	Na^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	Zn^{2+}
tensile modulus (GPa)	13.3	14.9	16.4	23.4		10.0
tensile strength (MPa)	142	162	106	351		86
max. strain (%)	1.27	1.22	0.61	1.59		0.85
IV (dL/g)	5.12	5.66	2.50	4.83	2.24	3.88

[a] Film takeup speed at 5 m/min with a thickness of 30−40 μm.

Since comparable molecular weights were obtained for the nonionic NTP, the ionic NTP (Na salt), and the ionic NTP (Ca salt), as seen in Table 2, reasonable comparison of tensile properties can be made for these polymers. It is seen from Table 2 that the tensile properties increase in the order nonionic NTP < ionic NTP (Na salt) < ionic NTP (Ca salt). Comparing with the nonionic NTP, the modulus of the Na salt increases by 12%, the strength by 14%, and the strain to fracture by − 4%, respectively. For the Ca salt, enhancement is much more significant: comparing with the nonionic NTP, the modulus increases by 76%, the strength by 147%, and the strain to fracture by 25%. This increase is more significant when we consider the fact that the Ca salt has the smallest molecular weight (IV) value among these three polymers. These results clearly demonstrate that introducing even a small amount of ionic groups (1 mol %) into NTP chains enhances tensile properties. More importantly, great enhancement is achieved when Ca salt is used as the metal ion. Significant increases in mechanical properties by replacing a counterion from a monovalent ion (group IA) to a divalent one (group IIA) are well-known for ionomers, since divalent ions form stronger and more stable ionic bonds than monovalent ions.[10,11,22]

The difference in the strength of interchain interactions may also be seen in the change of T_g values. As already mentioned in the Experimental Section, glass transitions of these NTPs were not detected by DSC, but they are detected by DMTA. DMTA curves are shown in Figure 5, where T_g values were determined as the maximum peak positions of the loss modulus (E'') curves: i.e., 83.7 °C for the nonionic NTP, 93.3 °C for the Na salt, and 102.0 °C for the Ca salt, respectively. The T_g value of the Na salt is in good agreement with

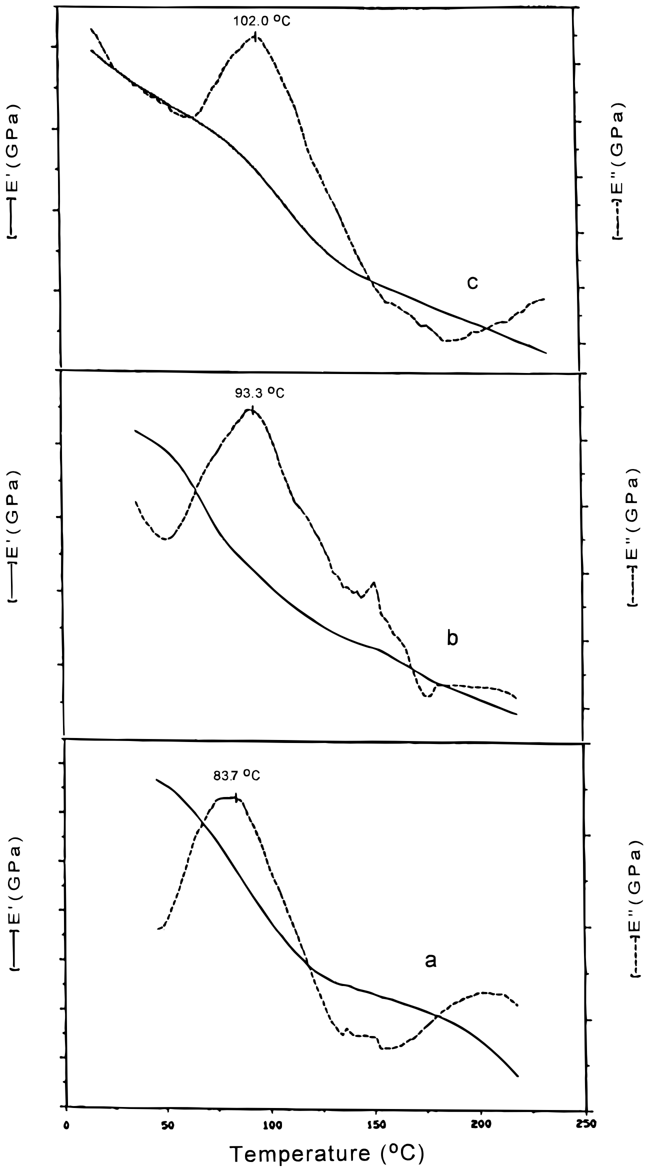

Figure 5. Storage modulus (E') and loss modulus (E'') vs temperature for (a) nonionic NTP, (b) 1 mol % ionic NTP (Na salt), and (c) 1 mol % ionic NTP (Ca salt). T_g values taken from peak positions are also indicated.

those of ionic NTPs (Na salt) having 5–10 mol % ionic contents, determined by DSC, i.e., a 92–96 °C range, which showed little difference with ionic content due to the balance between ionic bonds and flexibility incorporated into the chain.[7] The increase in the T_g seen in Figure 5 is due to enhanced intermolecular interactions through ionic bonds; as the interchain interaction increases, segmental mobility of the chains becomes more restricted, and as a results, the T_g rises.[10,11] Thus, our T_g results indicate that the interchain interaction increases in the order nonionic NTP < ionic NTP (Na salt) < ionic NTP (Ca salt). Similar T_g increases associated with the change of counterion from nonionic to monovalent Na salt, and to divalent Ca salt, were reported elsewhere. For example, the T_g of the poly(phosphoric acid) is −10 °C, which increases to 285 °C for the Na salt and 520 °C for the Ca salt.[23]

Calundann and Jaffe reported that tensile properties of nonionic NTP extrudates were a strong function of molecular parameters, such as polymer molecular weight and molecular orientation.[5] We can provide an additional molecular parameter to control (or enhance) tensile properties; i.e., *strong, but thermally labile ionic bonds*, as seen for ionic NTPs. Figure 6 shows typical stress–strain curves for a nonionic NTP, an ionic NTP (Na salt), and an ionic NTP (Ca salt). The initial slope of the stress–strain curve increases, reflecting an increase in tensile modulus (stiffness), in the order nonionic NTP < the Na salt < the Ca salt. Figure 6 also indicates that the NTP polymer becomes stronger and tougher, i.e., more energy is needed to break the sample, upon the change of counterion. It was also found for the ionic NTP (Ca salt) that a further increase in the already highest modulus and tensile strength among ionic NTPs synthesized in this laboratory could be achieved by using a higher takeup speed in the melt extrusion, as shown in Figure 7. This is due to higher molecular orientation resulting from higher drawdown speed.[5]

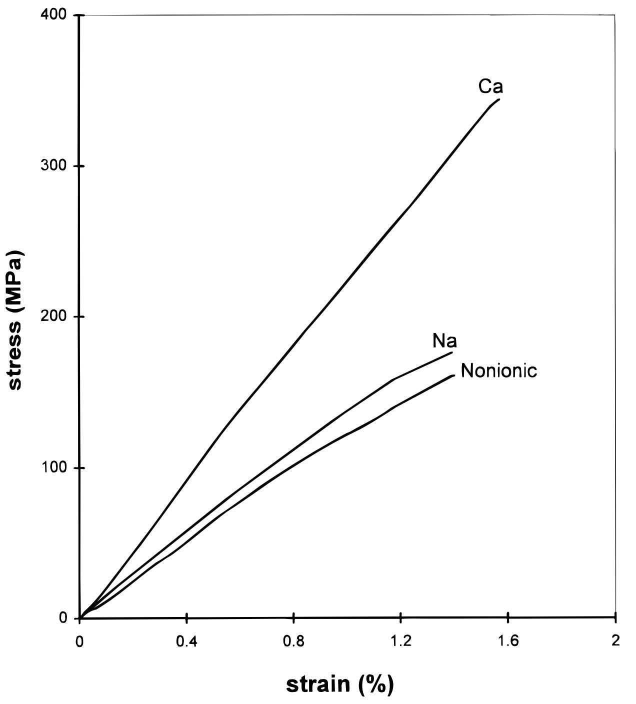

Figure 6. Typical stress–strain curves for film samples of nonionic NTP, 1 mol % ionic NTP (Na salt), and 1 mol % ionic NTP (Ca salt). The film takeup speed in melt extrusion is 5 m/min.

Our tensile results on ionic NTPs may be compared with the theoretical prediction based on the highly oriented LCP fibers.[6] This theory is based on the idea that the load transfer between polymer chains is through intermolecular interaction, which acts in a manner similar to the shear stress in short-fiber composites (e.g., a shear lag model). The model has been successful in describing quantitatively the strength of nonionic NTP fibers.[6] According to this model, when the local interchain load exceeds a critical value, the interchain bonding breaks, which leads to fibrillation. The model predicts that any process that increases the shear strength, thus intermolecular bonding, will also increase the fiber strength.[6] Our data generally confirm this prediction: since interchain interaction is greatly enhanced with ionic bonds, especially those with divalent Ca ionic cross-links, the strength increases significantly. It should also be added that the enhanced shear strength is also expected to increase the compressive

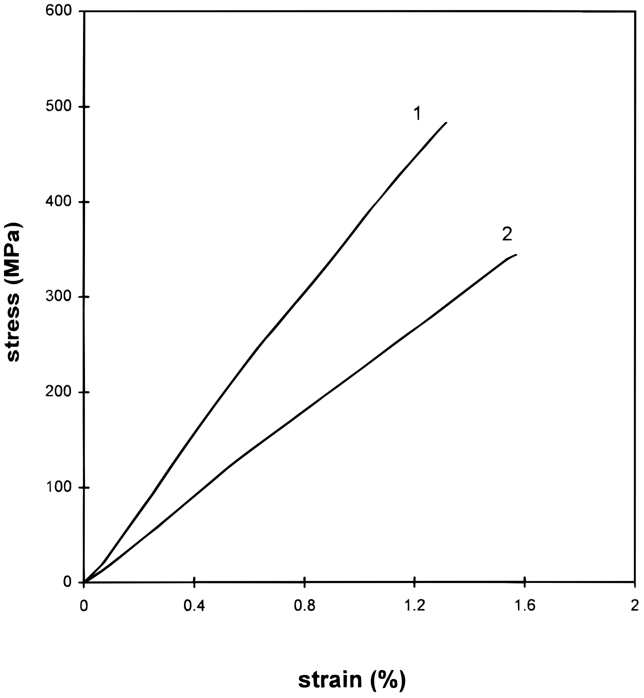

Figure 7. Typical stress−strain curves for 1 mol % ionic NTP (Ca salt) films with different takeup speeds: (1) 12 m/min; (2) 5 m/min.

strength of fibers.[1] This is also observed in our experiments.[8,9]

Although the degree of molecular orientation may be different to some extent for these NTPs, it does not diminish our conclusion on the important role of ionic bonds in enhancing mechanical properties. It is expected that the degree of orientation of ionic NTPs is lower than that of nonionic NTP. This is because the introduction of kinked units (with ionic groups) into NTP chains opposes the mesogenicity of the polymer by reducing the persistence length and thus effective axial ratio and because the ionic interactions between the ionic NTP chains can increase the melt viscosity and thus the internal friction under flow. As a consequence, polymer chains are less likely to align along the applied force field (elongational flow). This was shown in our previous studies of ionic NTP (Na salt) by polarizing optical microscopy.[7] Therefore, the significant improvement in tensile properties observed for ionic NTPs is explained as arising from increased lateral interactions via ionic bonds, which surpasses the negative effect via some ordering loss.

Effect of Counterion on Tensile Fracture Morphology and Failure Mechanisms. The effect of counterion on the fracture surface morphology of tensile specimens was investigated with SEM. Representative samples were chosen from the tensile-tested specimens for SEM study. Figure 8 shows SEM micrographs of the tensile fracture surfaces of extruded films. A clear dependence of fracture behavior on the counterion is noted. First, the nonionic NTP film failed at relatively localized random locations between the grips and showed a nonfibrillar structure (Figure 8a). Although fibrillar textures have been commonly observed for drawn TLCP extrudates, especially for those of high molecular weight,[25] this sample (nonionic NTP) did not show fibrillation. This is probably due to a relatively low molecular weight of the polymer in a practically useful molecular weight range. The surface of the film is more pleated along the transverse direction, with only a uniform hairlike texture. Second, the ionic NTP (Na salt) film failed at less localized random locations between the grips and showed a tendency of more resistance to fracture perpendicular to the extension direction with a trace of fibril structure (Figure 8b). This may indicate that the additional ionic interactions between the polymer chains provide more resistance to being pleated along the transverse direction of the entire gauge length. The ionic interactions can contribute to better transverse properties[8,9] in addition to better axial tensile properties, as shown in this work. A coarse skin surface with irregularly woody texture, revealed in Figure 8, was also observed for manually drawn fibers.[7]

Finally, the ionic NTP (Ca salt) films revealed a distinct failure mode from that of the nonionic NTP and the ionic NTP (Na salt), as viewed vertically to the film's long axis in Figure 8c,d: i.e., no distinct localized fracturing was observed and the films failed by splitting into continuous narrow strips along the extension direction with some fibrillar connections between these strips. Turek and Simon[24] studied the SEM tensile fracture surface morphologies of nonionic NTP extrudates produced from different dies, and they observed different failure modes, which they attributed to different levels of orientation of the NTP chains. Likewise, it is of interest to understand the unique mode of failure of the ionic NTP (Ca salt).

As already described, film samples were produced under the similar processing conditions for the nonionic NTP, the Na salt, and the Ca salt, and these have similar molecular weights (similar IV values); yet, the ionic NTP (Ca salt) shows much higher tensile properties than the others do. The excellent tensile mechanical properties and a distinct mode of tensile failure should be attributed to the stronger interchain ionic bonds of this polymer. The divalent Ca ion can form strong ionic cross-links between the ionic NTP chains. The ionic cross-links may be broken (or weakened) upon melting at high temperatures and re-formed after chain alignment by elongational flow during extrusion, as schematically shown by Figure 9a. The re-formed ionic cross-links in the highly aligned film may have the effect of "lengthening" the rigid NTP chains by ionic association, which may also contribute to the higher tensile properties and distinct failure mode. As reported for nonionic NTP polymers,[5,6,25] higher molecular weight polymers have higher tensile properties and stronger tendency to develop fibrillar structures. A simple picture of partial debonding of ionic cross-links in the ionic NTP during tensile deformation is schematically shown by Figure 9b.

We have shown that ionic bonds are very effective in improving mechanical properties of LCPs, whereas covalent bonds are reported to be less effective.[1,2,4] It is well-known that polymers with ionic cross-links are re-formed upon heating but those with covalent cross-links are not. This is because ionic bonds are nondirectional and thus easier to re-form upon cooling after melting,[11] while covalent bonds are highly directional, and thus more difficult to re-form, in addition to the possibility of degradation. In the case of liquid crystalline polymers, ionic bonds (cross-links) are broken (or weakened) at high processing temperature, and after chains are aligned under elongational flow field, ionic bonds are re-formed upon cooling (see Figure 9a). Thus, ionic bonds are re-formed after the proper chain align-

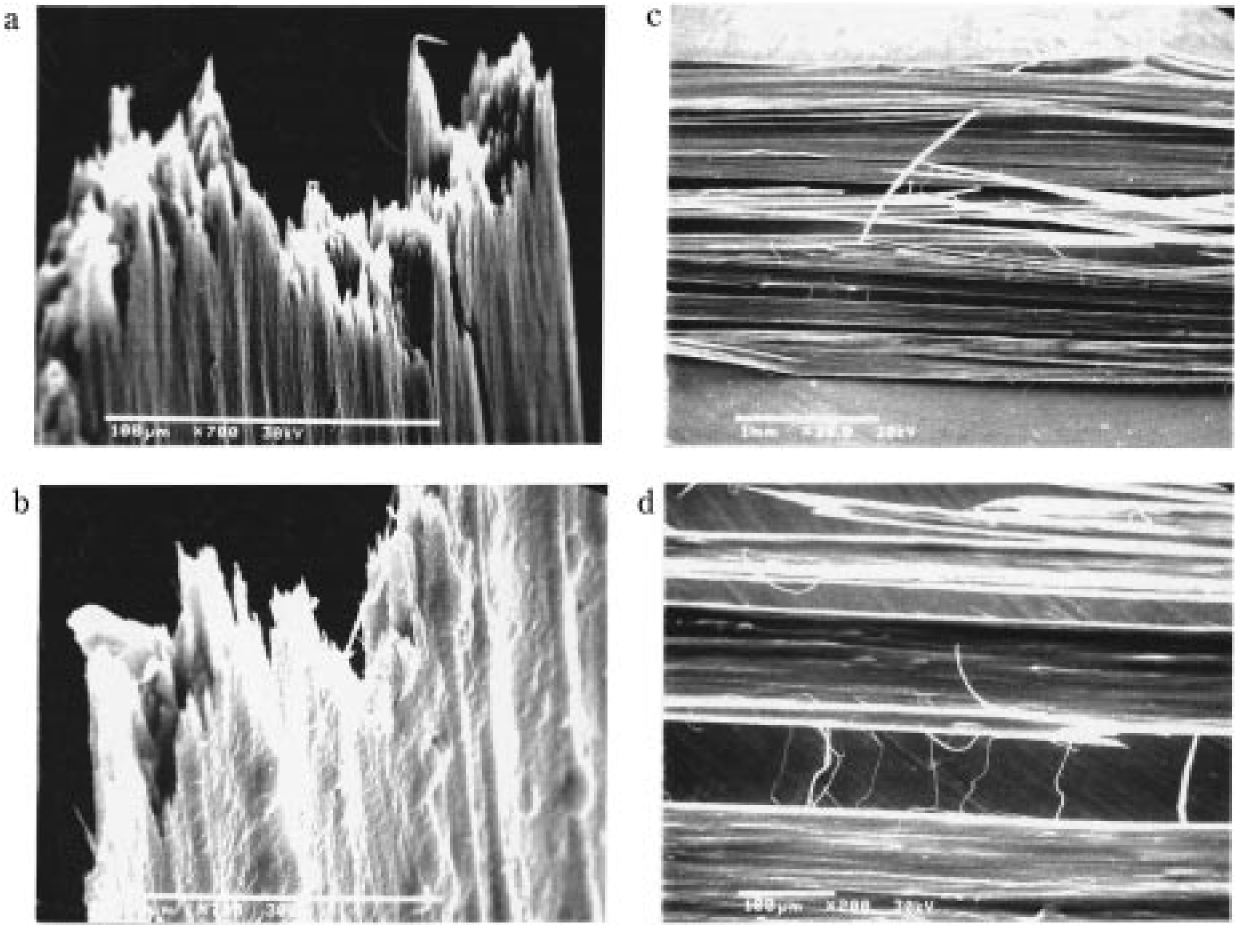

Figure 8. SEM micrographs of tensile fracture surfaces: (a) nonionic NTP; (b) 1 mol % ionic NTP (Na salt); (c) and (d): 1 mol % ionic NTP (Ca salt).

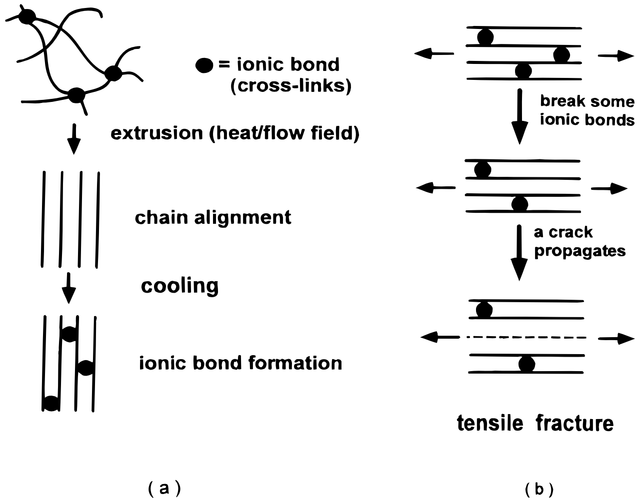

Figure 9. Schematic illustration showing (a) chain alignment and ionic bond formation during melt extrusion of ionic NTP and (b) partial debonding and fracture during tensile testing.

ment. In contrast, although covalent bonds may be introduced via thermally induced cross-linking reactions after chain alignment, this does not necessarily proceed in an ideal fashion. For example, it was reported that thermal reaction led to undesirable side reactions and that the temperature for the cross-linking reaction was too low for good molecular orientation.[4] Therefore, incorporation of ionic bonds is a promising approach to enhance mechanical properties of LCPs.

Conclusions

Novel ionic NTPs that contain a small amount of ionic groups (1 mol %) with divalent metal ions (Mg, Ca, Ba, Zn) have been prepared. All of the ionic NTPs prepared exhibit thermotropic liquid crystallinity. Among them, ionic NTP having a divalent Ca ion retains a high molecular weight and exhibits excellent thermal stability and mechanical properties. Ionic NTPs containing other divalent ions (Mg, Ba, and Zn) tend to have lower molecular weights, which may arise from complex chemistry and aggregation of the ionic monomers during polymerization.

Ionic NTP (Na salt) shows a moderate increase in tensile modulus and strength over nonionic NTP. However, ionic NTP with divalent Ca ions shows a significant increase in these properties: 76% increase in modulus and 147% in strength. An increase in tensile properties arises from stronger lateral support, via ionic bonds (cross-links), in highly aligned NTP chains. The interchain interaction is especially greatly enhanced with a divalent Ca ion, which allows a higher tensile load to be transferred between finite length chains without causing chain breakage. Unlike covalent cross-links, which usually reduce tensile properties of LCPs, ionic cross-links can effectively enhance tensile properties. This arises from the nondirectional nature of ionic bonds, which makes these bonds thermally labile; thus aligned chains are reinforced effectively upon cooling.

Ionic interactions also exert significant influence on tensile fracture surface morphology. Nonionic NTP reveals relatively uniform fracture surface morphology with hairlike texture pleated along the transverse direction. Ionic NTP (Na salt) film seems more ductile and more resistant to fracture along the transverse direction presumably due to interchain ionic interactions. A distinct tensile fracture is observed for ionic NTP (Ca salt) film: films split into continuous parallel strips along the extension direction with some fibril connections between these strips. Stronger ionic cross-links due to presence of divalent Ca ions between aligned chains may have the effect of "lengthening" the aligned NTP chains, which may be responsible for more homogeneous parallel fracture over the entire film under higher tensile load.

We have demonstrated effective enhancement in tensile properties via ionic bonds, especially useful for divalent Ca salts. We also observed an increase in compressive properties of ionic NTPs. This is achieved by introducing only a fraction of ionic groups (e.g., 1 mol %). Thus, incorporation of ionic bonds into LCPs is a promising approach for improving compressive (and transverse) properties without sacrificing excellent tensile properties. Coupled with the advantage of ionic bonds for being thermally labile and reprocessable, ionic bonds can be used to develop novel polymeric materials whose intermolecular interactions can be reinforced via ionic bonds.

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