

# Ionic Naphthalene Thermotropic Copolyesters: Enhanced Compressive Properties of Fibers

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**ABSTRACT:** Compressive properties of fibers made from ionic naphthalene thermotropic polymers (NTPs) were investigated. These (main-chain) thermotropic liquid crystalline polymers (LCPs) are wholly aromatic copolyesters, which contain 1 mol % ionic groups with either monovalent Na ion or divalent Ca ion. The SEM observations of kink band formation on both a single knotted fiber and a deformed fiber under axial compression in a composite suggest enhanced compressive properties for the ionic NTP fibers as compared with nonionic NTP fibers. It is believed that the enhancement of the compressive properties is due to the presence of strong lateral ionic bonds in the ionic NTP fibers, which provide interlinks both between molecules and between supermolecular domains. Tensile strength values of the ionic NTP fibers are slightly higher than those of the nonionic NTP fibers, even though the take-up speed, and thus the molecular orientation, is lower for the ionic NTP than for the nonionic NTP. This reflects the beneficial effect of ionic bonds in enhancing tensile properties.

## Introduction

Main-chain liquid crystalline polymers (LCPs)<sup>1–4</sup> contain inherently rigid units, thereby forming a highly “extended chain” morphology, leading to remarkable mechanical properties and thermal stability. There are two major LCP types: one is lyotropic LCP, e.g., Kevlar based on poly(*p*-phenyleneterephthalamide) (PPTA),<sup>5</sup> which forms liquid crystalline structure with a diluent (in solution); another is thermotropic LCP, e.g., Vectra based on wholly aromatic polyester,<sup>6</sup> which forms liquid crystalline structure upon heating. While the lyotropic LCP can be fabricated only in fibers or films, the thermotropic LCP can be made into a three-dimensional structure by conventional processing, such as injection molding. This makes thermotropic LCP a unique material for a wide range of applications.<sup>7,8</sup>

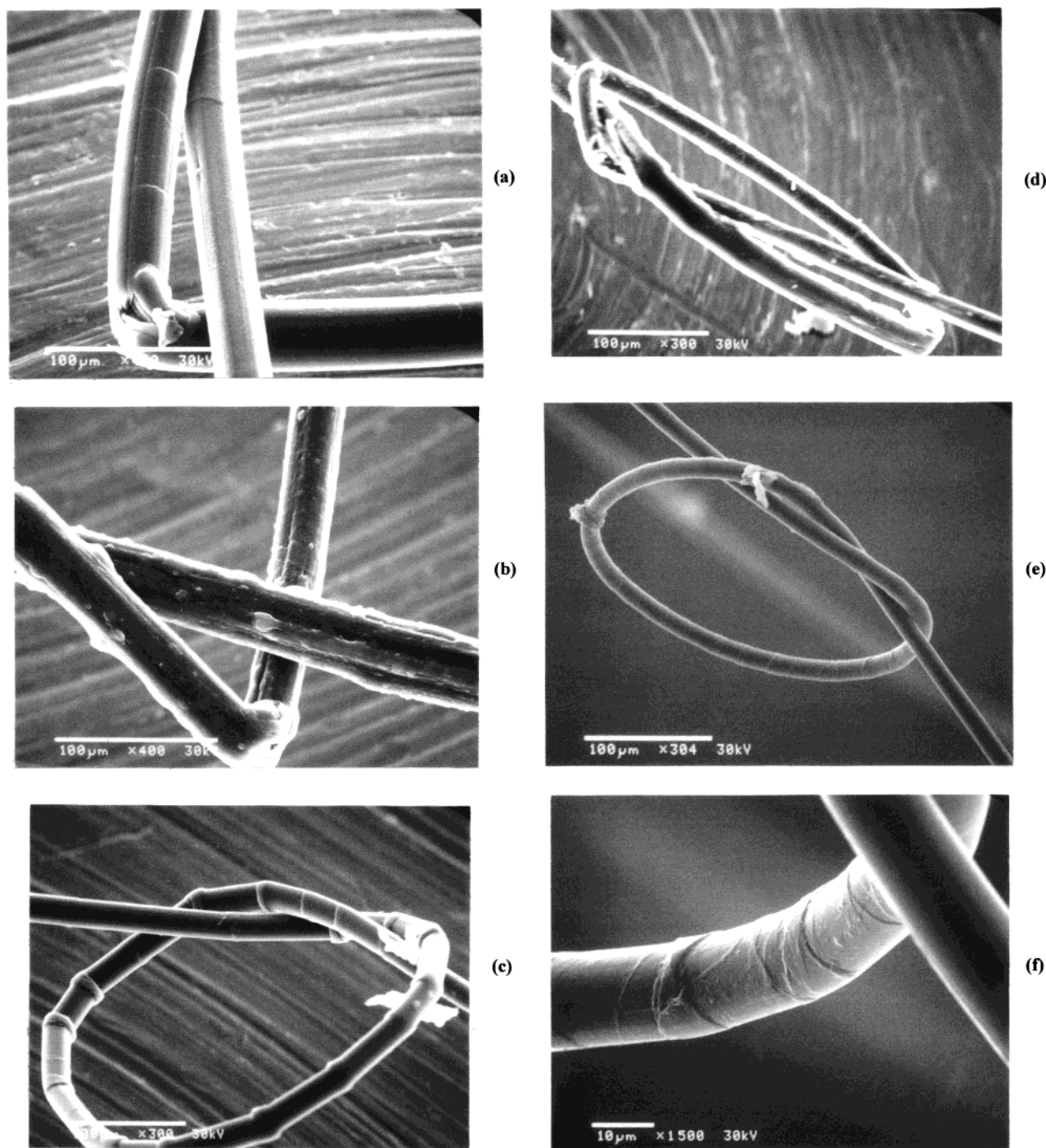
Although LCPs have been widely used as high-performance polymers, two major problems prevent their extensive use. One is poor transverse and compressive properties in contrast to very high axial properties, often 1–2 orders of magnitude lower, both of which are inherent to highly uniaxially oriented polymers.<sup>2</sup> Another problem is poor miscibility and adhesion with other polymers, when LCPs and conventional polymers are mixed to produce polymer blends, which are widely used to enhance polymer properties.<sup>9,10</sup> Both problems basically arise from weak intermolecular interactions either in the LCP itself or in a LCP/polymer blend.<sup>2</sup> These interactions are usually weak secondary bonds (van der Waals bonds and hydrogen bonds), in contrast to strong covalent bonds along chain directions. These problems hinder the development of LCPs into a wide range of applications, including conventional composites.<sup>7</sup>

Various approaches have been used to develop thermotropic LCPs with improved transverse and compressive strengths with only marginal success.<sup>7</sup> One approach to accomplish this is to enhance interchain interactions of LCP molecules via chemical cross-linking.<sup>2,7,11</sup> 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.<sup>11</sup> This is also true for fibers made from random coil polymers.<sup>7</sup> Heat treatment of thermotropic LCPs may increase tensile strength by raising the molecular weight of the polymers, but the transverse properties are essentially the same.<sup>12</sup> Thus, a major challenge is to enhance transverse/compressive properties of LCPs without sacrificing desirable tensile properties.<sup>7</sup>

We are currently developing ionic thermotropic LCPs by introducing ionic groups (and ionic bonds) into LCP chains to obtain better tensile and compressive properties.<sup>13–15</sup> It is known that strong ionic interactions (bonds) between polymer chains can significantly enhance mechanical properties, as demonstrated for flexible ionomers.<sup>16–18</sup> In ionic polymers, polymer chains are ionically cross-linked through nondirectional ionic bonds, which are strong but are thermally labile.<sup>16</sup> Thus, unlike chemically cross-linked polymers, they melt upon heating and re-form upon cooling.

In the previous work,<sup>13,15</sup> we synthesized and characterized ionic NTPs 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 metal 5-sulfoisophthalate (SI). All the ionic NTPs 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. We also observed increased tensile strength for ionic LCP films (Na and Ca salts).<sup>15</sup>

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**Figure 1.** SEM micrographs of fibers from knotted single loop test: (a) nonionic NTP; (b) ionic NTP (Na salt); (c) Vectran; (d) ionic NTP (Ca salt); (e) Kevlar 49; (f) higher magnification of (e).

For example, the ionic NTP with divalent Ca ions shows 76% increase in modulus and 147% in strength compared with the nonionic NTP of comparable molecular weight. We have shown that an increase in tensile properties arises from strong 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 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 again arises from the nondirectional nature of ionic bonds, which makes these bonds thermally labile; thus, aligned chains are reinforced effectively upon melting.<sup>15</sup>

In this article, we report compressive properties of ionic NTP fibers. Especially, we are concerned with observation of kink band formation under compression in these fibers. Polymer fibers deform under compression by the mechanism of kink band formation, as well-known for high-performance fibers.<sup>2</sup> Kink bands are localized regions of the fiber in which the chains are deformed to rotate away from the compression axis. Kinks are the common features of materials with highly anisotropic mechanical nature.<sup>2,19</sup> By studying kink band initiation, kinking process, and the resulting structures of kinks, the information on compressive properties can be obtained for rigid-rod polymer fibers. Because ionic bonds are nondirectional, the overall lateral interactions, i.e., those between chains and those

between any other supermolecular units such as microfibrils, can be enhanced. As a result, reinforcing effect may occur to the usual micromechanisms of kink band formation, e.g., by chain buckling,<sup>20,21</sup> microfibril buckling,<sup>19,22</sup> or fibril buckling,<sup>21</sup> in the polymer fibers.

To see whether improvement in compressive properties is achieved as compared with nonionic NTP, we conducted two testings on both the nonionic and ionic NTP fibers: a qualitative single knotted loop test and a semiquantitative compressive composite test. Tests were also conducted for high-performance thermotropic LCP Vectran and high-performance lyotropic LCP Kevlar fibers for comparison.

## Experimental Section

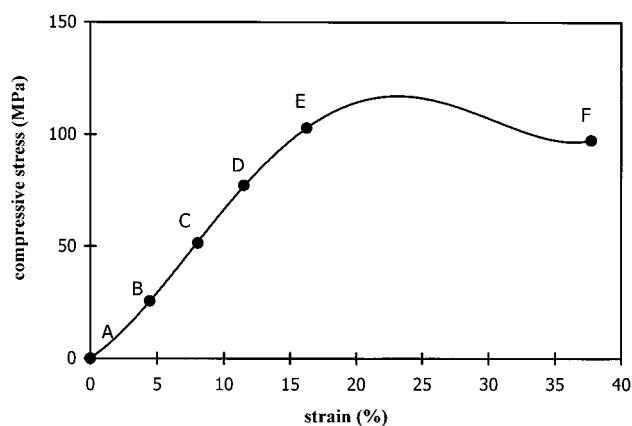
**Materials.** Naphthalene thermotropic polymers (NTPs) based on wholly aromatic copolyesters were synthesized with the following compositions: a nonionic NTP contained 74 mol % of 4-hydroxybenzoic acid (HBA) and 26 mol % of 6-hydroxy-2-naphthoic acid (HNA), and ionic NTPs contained 73 mol % of HBA, 26 mol % of HNA, and 1 mol % of meta-linked dicarboxy monomer, metal (either Na or Ca) 5-sulfoisophthalate. The details of the synthesis of these polymers are described elsewhere.<sup>13,15</sup> A wholly aromatic copolyester thermotropic LCP fiber, Vectran, was obtained from Hoechst Celanese, and a wholly aromatic polyamide lyotropic LCP fiber, Kevlar 49, was obtained from Du Pont.

**Specimen Preparation.** Fibers were prepared by melt spinning using a Micro-melt extruder (Hoechst Celanese) with a single-hole spinneret at a hole diameter ranging from 0.005 to 0.003 in. and a depth of 0.007 in. The polymer melt was maintained at the spinneret temperatures of 290–300 °C. The melt-spun fibers were cooled at ambient temperature and collected by a wind-up roll with a take-up speed of 12–380 m/min. The specimens used were as-spun fibers, which refer to those without being drawn or heat-treated after spinning and normal windup.

**Compression Testing.** Two tests were conducted to evaluate compressive properties. In a single knotted loop test, knotted fibers were stretched gradually to see whether kink bands are formed inside the loop, where the compressive stress is developed. In a compressed composite test, sample preparation and testing were made as follows: first, as-spun fibers were embedded in a monomer, 2-hydroxypropyl methacrylate (HPMA), which was placed in a gelatin capsule with cylindrical shape. Then, the capsule was kept at 70 °C for 30 h for polymerization reaction. A resulting cylindrical resin block, 6.0 mm in length and 4.7 mm in diameter, containing one to three fibers along the cylinder long axis, was then axially compressed in a tensile machine (Instron) at a crosshead speed of 0.25 mm/min. All cylindrical specimens for the compression test had the same cross-sectional area of 17.3 mm<sup>2</sup>. Finally, deformed polymer fibers were taken out of a resin block by dissolving the resin in dimethyl sulfoxide (DMSO). Then, the fibers were washed with methanol and acetone, vacuum-dried at 60 °C, and stored in a desiccator for SEM examination.

**Scanning Electron Microscopy (SEM).** Fibers before and after compression testings were examined by SEM. SEM specimens were mounted on a stub with conducting double-sided carbon tape and coated with gold in a sputter coater (Polaron, SEM coating unit E 5100) for 4 min. They were examined with a scanning electron microscope (Amray 1200C) operating at 30 kV, and images were recorded directly from the cathode ray tube on Polaroid films.

**Tensile Testing.** Monofilament tensile properties were measured on a Minimat Materials Tester (Polymer Laboratories) at room temperature under normal laboratory atmosphere. Both ends of a single fiber were glued using an epoxy adhesive along a vertical line drawn on a rectangle paper substrate. The rectangle paper substrate containing a fiber specimen was then placed and tightened between two grips of the tensile tester. The paper substrate was then cut in the middle, leaving the fiber intact.<sup>23</sup> The gauge length was 30



**Figure 2.** A typical compressive stress–strain curve of fiber-embedded cylindrical composite specimens. A letter indicates each stress: (A) 0 MPa; (B) 25.7 MPa; (C) 51.4 MPa; (D) 77.1 MPa; (E) 103 MPa; (F) fracture.

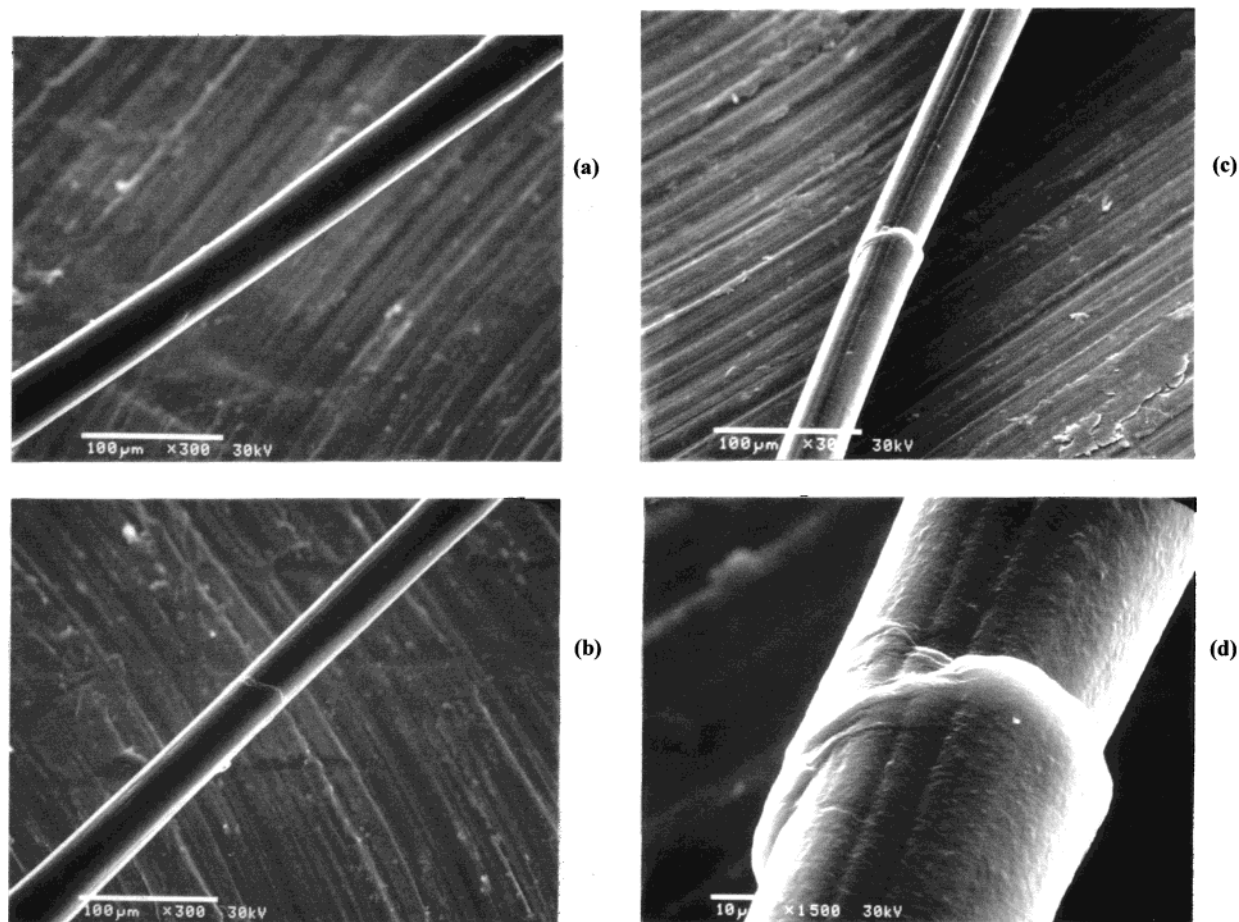
mm, and a crosshead speed of 0.1 mm/min was used. The cross-sectional area of each filament was calculated from the filament diameter, which was evaluated by microscopic measurements with SEM. Average tensile properties of at least five specimens are reported.

## Results and Discussion

**Kink Band Formation of Fibers in a Knotted Single Loop.** Two methods were used to demonstrate enhanced compressive properties upon addition of ionic groups to NTPs. A first method used to evaluate compressive strength is to observe kink band formation for fibers that are knotted in a single loop. Figure 1a–f shows the SEM micrographs of various knotted fibers, i.e., nonionic NTP fiber, ionic NTP fiber, Vectran fiber, and Kevlar 49 fiber. Specimens were made by knotting the fibers in the form of a single loop such that compressive force was developed inside the loop. At least five specimens were examined for each fiber.

The knotted nonionic NTP fibers clearly show kink bands inside the loop (see Figure 1a), but no such bands are observed for the ionic NTP fibers (Na salt) (see Figure 1b) under similar conditions. Smooth skin surface is noted for the nonionic NTP fiber and coarse surface for the ionic NTP fiber, consistent with observations made on manually drawn fibers.<sup>13</sup> Many kink bands are also revealed for the Vectran fibers (Figure 1c), but no such bands are visible in the ionic NTP (Ca salt) fibers under similar conditions (Figure 1d). For comparison, Kevlar 49 fibers were also tested using the same method (Figure 1e,f), since Kevlar 49 fiber has been extensively studied and relevant information can be found.<sup>20,24–27</sup> The easy formation of compressive kink bands in the Kevlar 49 fibers, reflecting poor compressive strength, is a result of weak lateral interactions due to relatively weak van der Waals and hydrogen bonds between chains.<sup>2,20</sup>

**Kink Band Formation of Fibers in a Compressed Composite.** A second method used to evaluate compressive properties is to observe kink band formation of fibers after they are embedded in a matrix polymer and compressed. Figure 2 shows a typical compressive stress–strain curve of the cylindrical specimen in which fibers are embedded. The figure is consistent with the stress–strain curve reported for the composites made of the same matrix polymer and Kevlar 29 fiber.<sup>26</sup> Since a very small number (1–3) of fibers are embedded in the matrix, the stress–strain



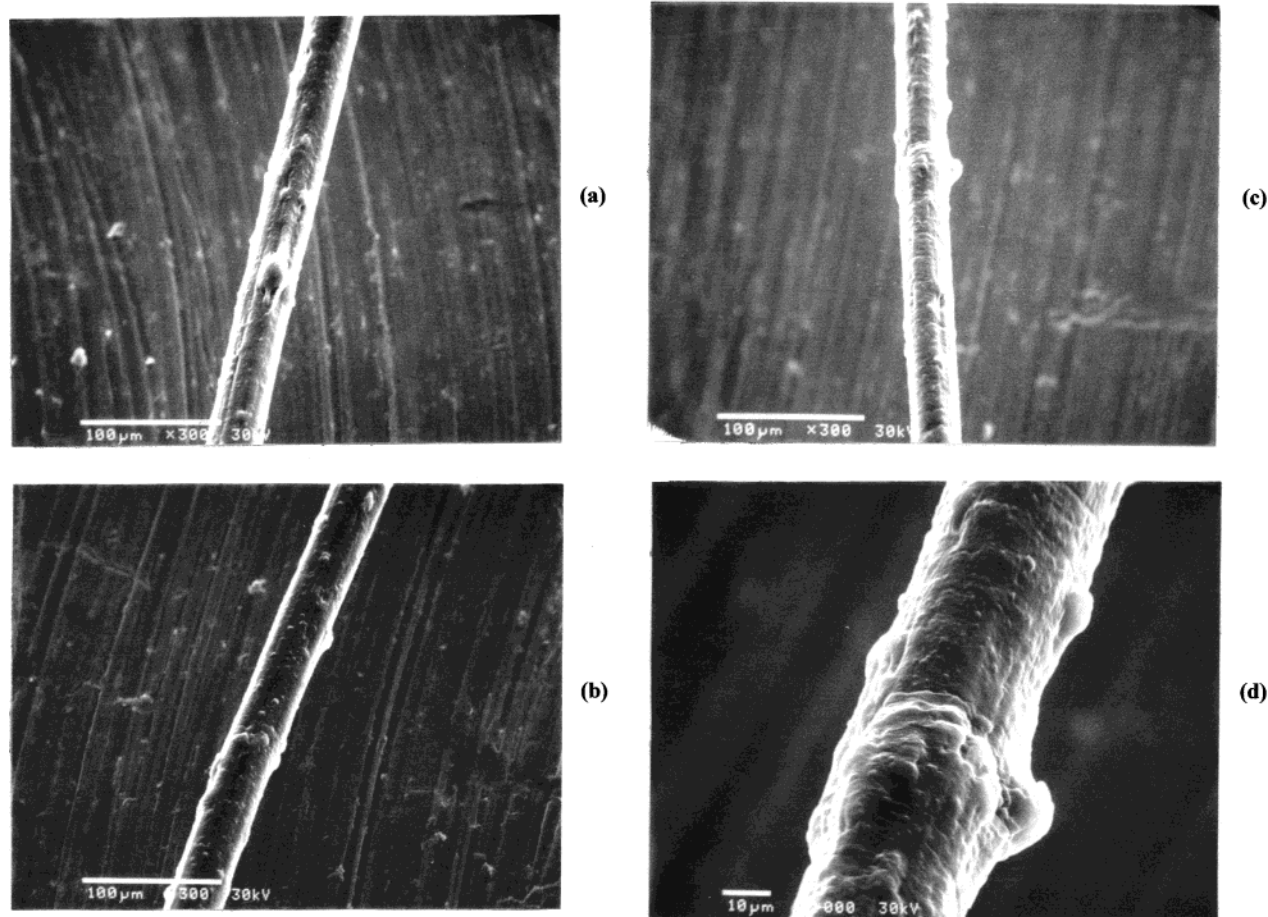
**Figure 3.** SEM micrographs of the nonionic NTP fibers extracted from the composite specimens: (a) no stress; (b) compressive stress of 77.1 MPa; (c) after the composite specimen failed; (d) higher magnification of (c).

curve is practically identical to that of the matrix polymer.<sup>26</sup> Each cylindrical composite specimen with embedded fibers was compressed to one of the five different loading levels: no load (A), compressive loads of 100 lb (corresponding to 25.7 MPa) (B), 200 lb (51.4 MPa) (C), 300 lb (77.1 MPa) (D), and 400 lb (102.8 MPa) (E), and failure point (F), where capital letters correspond to the points on the stress-strain curve of Figure 2.

After fibers were taken out of the composites by dissolving the matrix polymer with DMSO, SEM examinations were made on fiber specimens.<sup>26</sup> Figures 3–5 show SEM micrographs of uncompressed and compressed fibers for both the nonionic and ionic NTPs. Again, like manually drawn fibers from the same polymers,<sup>13</sup> a smooth surface with the skin being aligned along the long fiber axis is seen for the nonionic NTP sample (see Figure 3). In contrast, all the ionic NTP fibers exhibit a coarse skin surface (see Figures 4 and 5). It is also noted that kink band formation is observed at different points for the nonionic and ionic NTP fibers; i.e., at point D in Figure 2 for the nonionic NTP fibers (Figure 3b), whereas at point F both for the ionic NTP (Na salt) fibers (Figure 4c,d) and for the ionic NTP (Ca salt) fibers (Figure 5d). As a reference, results on Vectran fiber are shown in an optical micrograph of Figure 6, where kink bands develop at point D. Table 1 summarizes the compressive stress that is needed for the initiation of kink band for both the ionic and nonionic NTP fibers. It is apparent that the ionic NTP fibers need higher compressive stress than the nonionic NTP fibers to form kink bands. For example, a kink

band appears at 77 MPa for both the nonionic NTP fiber and the Vectran (nonionic) fiber, whereas kink bands are only noted at the failure point (which needs to pass the maximum stress of ca. 120 MPa) for both the ionic NTP (Na salt) fiber and the ionic NTP (Ca salt) fiber. These data indicate better compressive properties for the ionic NTP than for the nonionic NTP. Also, it is noted that kink band formation leads to fracture as a result of large plane slip at the failure point (F) for the nonionic NTP (Figure 3c), whereas lateral slip and resulting fiber fracture do not occur for the ionic NTP (Figures 4d and 5d). This also suggests that the ionic NTP fibers have greater resistance than the nonionic NTP fibers to compressive failure.

Despite the rather qualitative methods that we used, our purpose for comparing the compressive properties of the ionic NTP fibers with those of the nonionic NTP fibers is achieved, and a major conclusion about the usefulness of ionic bonds in enhancing compressive properties can be drawn from our current data. Other methods may be used for more quantitative analysis. For example, several methods have been used to determine compressive properties of high-performance fibers. These methods include elastica loop test,<sup>24,25</sup> matrix shrinkage,<sup>28</sup> and beam bending,<sup>21</sup> all of which involve marking failure by the onset of visible kink band formation. The compressive strength is calculated from the product of the tensile modulus and the critical strain for kinking, by assuming that the fiber behaves in a linear elastic fashion to compressive failure and that the tensile and compressive moduli are identical, but these assumptions cause substantial uncertainty in



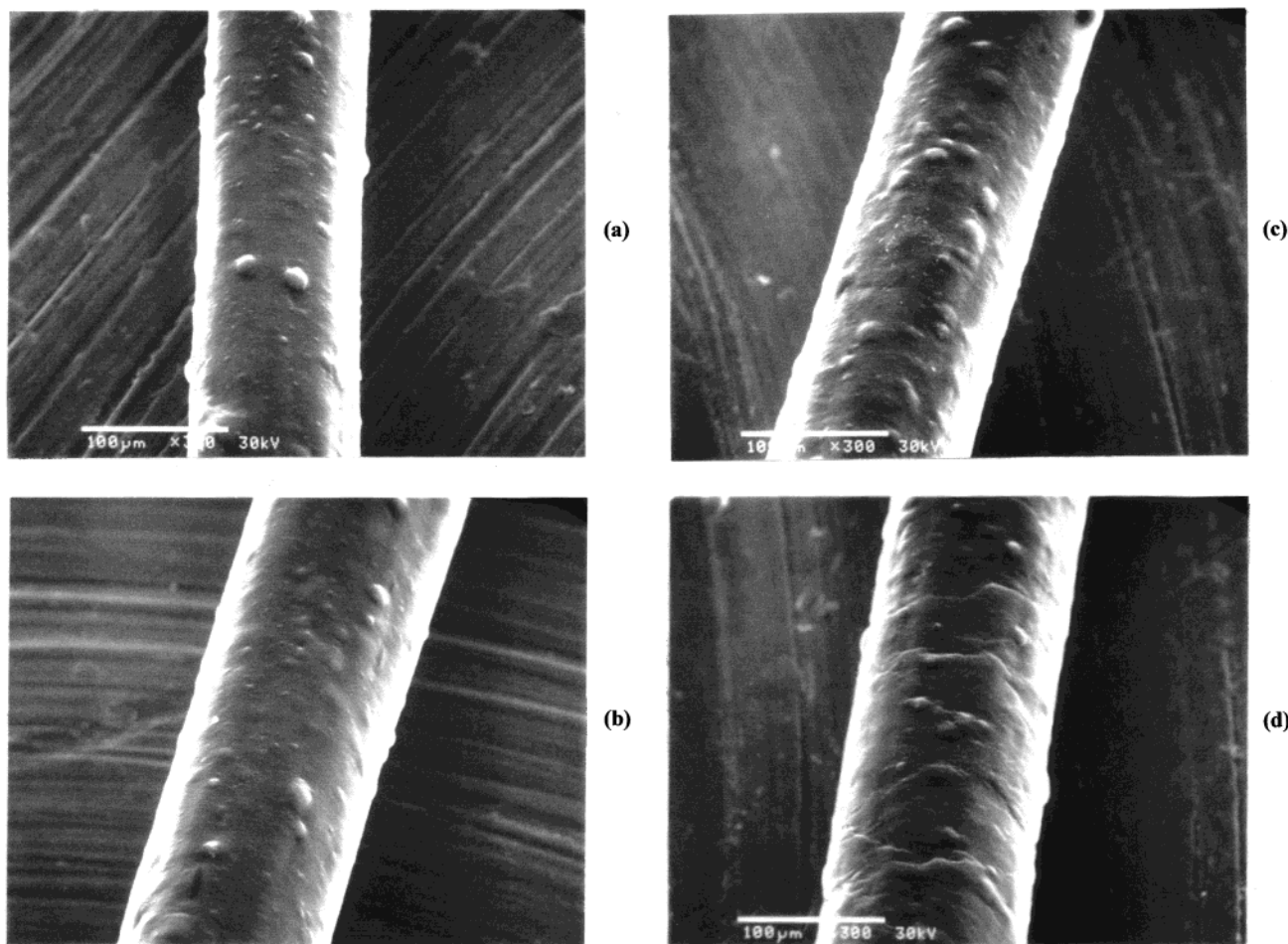
**Figure 4.** SEM micrographs of the ionic NTP (Na salt) fibers extracted from the composite specimens: (a) no stress; (b) compressive stress of 103 MPa; (c) after the composite specimen failed; (d) higher magnification of (c).

compressive strengths.<sup>21,29</sup> A more direct measurement of a single fiber compressive strength may be conducted by the tensile recoil (snap-back) test.<sup>30</sup> Reflected recoil stresses created from tensile failure cause compressive damage in the fiber, from which the compressive strength is determined. Although this is a method that measures the stress directly, reproducibility is rather poor due to the difficulty in symmetrically cutting the tensile specimens at different stress levels.<sup>29</sup> We will conduct more detailed and systematic work on the ionic NTP fibers in the future: the work includes conducting compressive testing by using some of the methods described above.

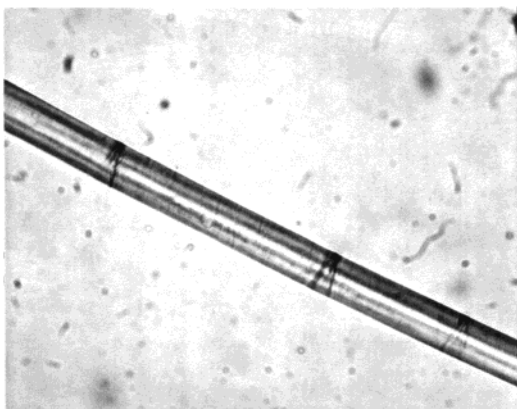
**Mechanism of Enhanced Compressive Properties and Some Tensile Properties.** Kink bands are localized regions of polymer fibers, in which the chains cooperatively rotate away from the compressive axis.<sup>2</sup> The presence of kink bands at lower stress in the nonionic NTP fibers indicates a lower compressive strength, presumably due to the weak lateral cohesion between the highly aligned polymer chains.<sup>2</sup> We have observed that the resistance to compressive failure of the ionic NTP fibers is enhanced upon introduction of ionic bonds. Since chain buckling is needed for kink band formation and since, prior to chain buckling, interchain bonds must be broken, the enhancement in interchain bonds hinders kink band formation. In other words, higher compressive stress is needed to produce kink bands. This is shown schematically in Figure 7: weak lateral cohesion between molecules is enhanced by the strong ionic bonds, leading to enhanced compres-

sive properties for the ionic NTP. The formation of ionic bonds in these ionic NTPs is previously shown by FTIR.<sup>15</sup>

Some, although limited, tensile tests were also made for these fibers to obtain additional information. Table 2 summarizes the tensile properties of the nonionic and ionic NTP fibers. It should be added that our fiber specimens are all as-spun fibers; no special treatment was made. The postspun heat treatment of NTP fibers under tension can significantly raise tensile strength and modulus.<sup>8</sup> Relatively low modulus and strength values are, however, comparable to those reported by Turek and Simon;<sup>31</sup> they studied the relationship between the processing conditions and mechanical properties of Vectra A950. They found that, at a low draw ratio, modulus and strength values are as low as 25 GPa and 400 MPa, respectively, which can be increased up to 60 GPa and over 1 GPa by increasing the draw ratio. These somewhat low values are comparable to those observed in this work. It should also be mentioned that fiber specimens could not be obtained at the same take-up speed under the conditions employed. In general, higher take-up speed leads to higher orientation of polymer chains and thus higher modulus and strength.<sup>32</sup> This is exactly seen for the modulus; the modulus increases in the order nonionic NTP > ionic NTP (Na salt) > ionic NTP (Ca salt). However, the strength values of the ionic NTPs are higher, although slightly, than those of the nonionic NTP. The strength is determined not only by orientation but also by lateral interactions.<sup>20,21</sup> Thus, higher strength value of these



**Figure 5.** SEM micrographs of the ionic NTP (Ca salt) fibers extracted from the composite specimens: (a) no stress; (b) compressive stress of 77.1 MPa; (c) compressive stress of 103 MPa; (d) after the composite specimen failed.

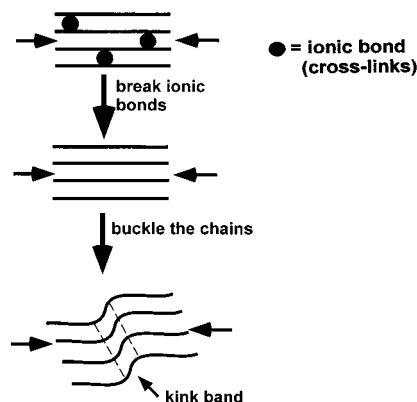


**Figure 6.** An optical micrograph of Vectran fibers extracted from the composite specimens (compressive stress of 77.1 MPa); magnification  $\times 400$ .

**Table 1. Stress Needed for the Initiation of Kink Bands in Embedded Fibers**

fiber	stress (MPa)
nonionic NTP	77.1
Vectran	77.1
ionic NTP (1 mol %; Na salt)	> 103
ionic NTP (1 mol %; Ca salt)	> 103

ionic NTPs is due to the effect of ionic bonds. Our previous study on extruded films made from these nonionic and ionic NTPs, which were made using the same conditions (i.e., film take-up speed of 5 m/min), showed that both the tensile strength and modulus were



**Figure 7.** A schematic figure, showing kink band formation in ionic NTP fibers under compression.

higher for the ionic NTPs than for the nonionic NTPs.<sup>15</sup> For example, the modulus increased from 13.3 GPa for the nonionic NTP to 23.4 GPa for the ionic NTP (Ca salt) and the strength from 142 to 351 MPa. It is shown that the presence of ionic bonds provides an additional molecular mechanism in enhancing tensile properties via strong lateral molecular interactions<sup>12,15</sup> in addition to the molecular mechanism, axial molecular orientation. Therefore, it is reasonable to see that the ionic NTP fibers show slightly higher strength than the nonionic NTP fibers, although the orientation of the ionic NTP fibers is lower.

A question arises as to the contribution of chain orientation to the compressive properties, since the

**Table 2. Tensile Properties of Nonionic and Ionic NTP (1 mol % Ionic Content) Fibers**

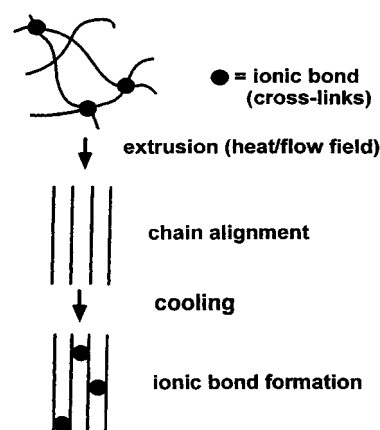
fiber sample	take-up speed (m/min)	strength (MPa)	strain at break (%)	modulus (GPa)	IV <sup>a</sup> (dL/g)
nonionic NTP	380	256	1.28	34.1	5.12
ionic NTP (Na salt)	175	269	1.00	23.1	5.66
ionic NTP (Ca salt)	12	273	1.49	22.9	4.83

<sup>a</sup> Inherent viscosity, which reflects the molecular weight.

degrees of orientation are different in the current systems. It is expected that the degree of orientation of the ionic NTPs will be lower than that of the 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 melt viscosity and thus 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 the ionic NTP by polarizing optical microscopy.<sup>13</sup> DeTeresa et al. pointed out that fibers with better average orientation should have higher compressive strengths: with theoretical analysis and experimental verification of a microbuckling model for the axial compressive failure of high-performance polymer fibers, they concluded that the critical compressive stress for microbuckling is a function of only intermolecular (or interfibrillar) interactions when the chains (or fibrils) are long.<sup>20,21</sup> Therefore, the improvement in compressive properties observed for the ionic NTPs can be explained as arising from increased lateral interactions via ionic bonds, which surpasses the negative effect via some ordering loss.

Finally, it may be added that we did not intend to develop practical ionic NTP fibers with extremely high tensile strength and modulus at this time. Commercial fibers, whose superior mechanical data are well-known, are made under special processing conditions, including heat treatment, poststretching, etc., to achieve optimum properties. In our work, fibers studied are all as-spun fibers; no special treatment was made. We are aware that postspun heat treatment of NTP fibers under tension can significantly raise tensile strength and modulus.<sup>8</sup> The purpose of this work is to demonstrate the beneficial effect of ionic bonding (cross-links) for improving compressive properties by comparing results on nonionic and ionic NTP fibers made and studied by using the same techniques.

As we reported in our previous publication on ionic NTP films,<sup>15</sup> tensile mechanical properties of the ionic NTP films are better than those of common high-performance polymers. For example, the modulus and strength values of the ionic NTP (Ca salt) are 23 GPa and 351 MPa, respectively, which are better than commercial high-performance films, e.g., 3 GPa and 172 MPa for Kapton (polyimide film).<sup>33</sup> We could achieve practical take-up speed for film spinning (e.g., 5–12 m/min) for both the nonionic and ionic NTP. The work clearly indicates enhanced mechanical properties due to enhanced lateral (intermolecular) interactions via formation of ionic bonds, which is proved by FTIR. However, preparation of *fiber specimens* was more difficult than that of films, since higher take-up speed

**Figure 8.** A schematic figure showing chain alignment and ionic bond formation during melt extrusion of ionic NTP.

is needed for fiber spinning. Unfortunately, ideal ionic NTP fibers specimens could not be obtained due to higher melt viscosity; ionic NTP fibers were made at lower take-up speed than nonionic NTP fibers under the conditions and equipment used, as shown in Table 2.

We have shown in this work that ionic bonds are effective in improving mechanical properties of LCPs, whereas covalent bond (cross-links) are reported to show little success.<sup>2,7</sup> 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,<sup>16</sup> while covalent bonds are highly directional and thus more difficult to re-form, in addition to the possibility of degradation. In the case of LCPs, 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<sup>15</sup> (see Figure 8). Thus, ionic bonds are re-formed after the proper chain alignment. It should be stressed that Figure 8 is a schematic figure, simplifying the structural changes during processing. In fact, ionic bonds in the melt are not broken at the same time. They are either weakened or partially broken at high temperatures. Under stress, some ionic groups may move to other locations via an ion-hopping mechanism,<sup>34</sup> interacting with other groups to release stress. 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 the thermal reaction led to undesirable side reactions and that the temperature for the cross-linking reaction was too low for good molecular orientation.<sup>11</sup> Therefore, incorporation of ionic bonds may be a promising approach in enhancing mechanical properties of LCPs.

## Conclusions

Fiber samples of ionic NTPs having 1 mol % ionic groups (Na salt or Ca salt) have been prepared, and their compressive properties have been studied. In knotted fibers, in which compressive stress is developed inside the single loop of a fiber, kink bands appear in the nonionic NTP fibers, but no such kink bands are formed in the ionic NTP fibers. In addition, in axially compressed fibers embedded in a composite, kink bands are initiated at higher compressive stress for the ionic NTP fibers than for the nonionic NTP fibers. This is due to the presence of strong lateral ionic bonds in the ionic

NTP fibers, which can form interlinks between molecular and supermolecular domains.

Our results demonstrate that improved compressive properties are achieved without sacrificing tensile properties for the ionic NTP fibers. Coupled with the thermally labile nature of ionic bonds, the introduction of a small amount of ionic groups can be a useful method for improving mechanical properties of LCPs.

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## References and Notes

- (1) Weiss, R. A.; Ober, C. K., Eds.; *Liquid-Crystalline Polymers*; American Chemical Society: Washington, DC, 1990.
- (2) Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: Cambridge, 1992.
- (3) Isayev, A. I.; Kyu, T.; Cheng, S. Z. D., Eds.; *Liquid-Crystalline Polymer Systems*; ACS Symp. Ser. 632; American Chemical Society: Washington, DC, 1996.
- (4) Adams, W. W.; Eby, R. K. *MRS Bull.* **1987** (Nov), 22.
- (5) Kwolek, S. L. US Pat. 3600350, 1971, assigned to E. I. DuPont de Nemours and Co.
- (6) Calundann, G. W. US Pat. 4184996, 1980; 4256624, 1981; assigned to Celanese Co.
- (7) *Liquid Crystalline Polymer*; National Academy Press: Washington, DC, 1990.
- (8) Yoon, H. N.; Charbonneau, L. F.; Calundann, G. W. *Adv. Mater.* **1992**, 4, 206.
- (9) Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, 1978.
- (10) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979.
- (11) Dang, T. D.; Wang, C. S.; Click, W. E.; Chuah, H. H.; Tsai, T. T.; Husband, D. M.; Arnold, F. E. *Polymer* **1997**, 38, 621.
- (12) Yoon, H. N. *Colloid Polym. Sci.* **1990**, 268, 230.
- (13) Xue, Y.; Hara, M. *Macromolecules* **1997**, 30, 3803.
- (14) Ma, X.; Sauer, J. A.; Parker, G.; Chen, W.; Tsou, L.; Xue, Y.; Hara, M. *Proceedings of 9th International Conference on Deformation, Yield and Fracture of Polymers*, 1997; p 133.
- (15) Xue, Y.; Hara, M.; Yoon, H. *Macromolecules* **1998**, 31, 7806.
- (16) Holliday, L. In *Ionic Polymers*; Holliday, L., Ed.; Applied Science: London, 1975; Chapter 1.
- (17) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic Press: New York, 1977.
- (18) Hara, M.; Sauer, J. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, C34, 325.
- (19) Vezie, D. L.; Thomas, E. L. *Proceedings of 9th International Conference on Deformation, Yield and Fracture of Polymers*; Cambridge, U.K., 1994; p 14/1.
- (20) DeTeresa, S. J.; Porter, R. S.; Farris, R. J. *J. Mater. Sci.* **1985**, 20, 1645.
- (21) DeTeresa, S. J.; Porter, R. S.; Farris, R. J. *J. Mater. Sci.* **1988**, 23, 1886.
- (22) Fidan, S.; Palazotto, A.; Tsai, C. T.; Kumar, S. *Comput. Sci. Technol.* **1993**, 49, 291.
- (23) Garg, A. K. Ph.D. Thesis, Rutgers University, 1988.
- (24) Dobb, M. G.; Johnson, D. J.; Saville, B. P. *Polymer* **1981**, 22, 960.
- (25) Greenwood, J. H.; Rose, P. G. *J. Mater. Sci.* **1974**, 9, 1809.
- (26) Takahashi, M.; Miura, M.; Sakurai, K. *J. Appl. Polym. Sci.* **1983**, 28, 579.
- (27) Soggi, E. P.; Thomas, D. A.; Eby, R. K.; Grubb, D. T.; Adams, W. W. *Polymer* **1996**, 37, 5005.
- (28) DeTeresa, S. J.; Farris, R. J.; Porter, R. S. *Polym. Comput.* **1982**, 3, 57.
- (29) McGarry, F. C.; Moalli, J. E. *Polymer* **1991**, 32, 1811.
- (30) Allen, S. R. *J. Mater. Sci.* **1987**, 22, 853.
- (31) Turek, D. E.; Simon, G. P. *Polymer* **1993**, 34, 2751.
- (32) Allen, S. R.; Farris, R. J. *Mater. Res. Soc. Symp. Proc.* **1989**, 134, 297.
- (33) Spoog, C. E. *Mater. Res. Soc. Symp. Proc.* **1993**, 305, 59.
- (34) Hara, M.; Eisenberg, A.; Storey, R. F.; Kennedy, J. P. *ACS Symp. Ser.* **1986**, 302, 176.

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