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Ionic naphthalene thermotropic copolyesters with *para*-linked ion-containing units

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Abstract

Novel ionic naphthalene thermotropic polymers (NTPs) based on wholly aromatic copolyesters were synthesized, in which ionic monomer was introduced in the form of *para*-linked metal hydroquinone disulfonate (HQDS). These ionic NTPs contained ionic groups of up to 4 mol%, with counterions of either monovalent K or divalent Ca, and exhibited thermotropic liquid crystallinity. The K-salts exhibited the crystalline and liquid crystalline behaviors, typically observed for a non-ionic NTP; and they developed excellent thermal and mechanical properties. Testing was made as a function of ionic content under similar processing and testing conditions. The value of glass transition temperature rose as the average molecular weight increased. Both the melting temperature, T_m, and the crystallization temperature, T_c, remained nearly constant over the composition range studied. All the K-salt ionic NTPs showed enhanced tensile properties over a non-ionic NTP. The strength increased significantly as the ionic content increased despite the decrease in the molecular weight, reflecting the dominant effect of ionic interactions over the effect of molecular weight. Enhanced tensile properties arise from enhanced interchain interactions via ionic bonds (cross-links) between highly aligned NTP chains. The incorporation of HQDS-type ‘straight’ ionic units into a NTP copolyester can provide useful information about the effect of ionic interactions on the thermal/mechanical properties of NTPs.

Keywords: Thermotropic liquid crystalline polymers; Ionic polymers; Mechanical and thermal properties

1. Introduction

Non-ionic NTPs (Vectra® type) are rod-like polymers whose backbone chain packing is frustrated due to the presence of randomly introduced naphthyl moieties along the chain [1–3]. These main-chain thermotropic liquid crystalline polymers (LCPs) have melting temperatures (T_m) near 280 °C, which falls within a convenient temperature range of melt-processing. They possess such desirable properties as high strength/stiffness, high-temperature performance, chemical resistance, dimensional stability, and ease of processing [1–3]. However, like other LCPs, these polymers exhibit rather poor mechanical properties in the transverse direction in contrast to the longitudinal direction, due to weak intermolecular interactions [2,4]. We have been exploring a new approach by which ionic groups (and ionic bonds) are introduced into thermotropic LCP chains to achieve better transverse/compressive properties in addition to better tensile properties [3,5,6].

In our previous work [3,5,6], we synthesized and characterized novel ionic NTPs that are wholly aromatic polyesters having *meta*-linked sulfoisophthalate (SI) units. All these ionic NTPs had fiber-forming molecular weights and exhibited liquid crystallinity with nematic mesophase texture over a wide range of temperature, without showing a transition to an isotropic phase at least up to 380 °C. The ion-containing *meta*-linked SI units introduce ionic bonds as well as ‘kinks’ into the backbone chains. These ‘kinked’ units reduce melting temperature, and thus processing temperature, which is beneficial for processing. However, such units also add problems: they reduce the rigidity of the polymer chains, resulting in decreased T_g, liquid crystallinity, and spontaneous fibrillation [2]. They also add more structural and compositional heterogeneity in the polymer [3]; and, these effects overlap those of ionic interactions. To see directly the effects of ionic interactions on liquid crystalline behavior and thermal/mechanical properties, it

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may be helpful to eliminate the effects of 'kinked' units. This may be achieved by incorporation of ionic 'straight' units instead of 'kinked' units.

In this study, we prepared ionic NTPs having ion-containing *para*-linked hydroquinone disulfonate (HQDS) 'straight' units. All these ionic NTPs (K and Ca salts) possessed molecular weights high enough for fiber forming and exhibited liquid crystallinity. Since ionic NTPs with divalent metal salts, such as Ca, did not exhibit good mechanical properties under the conditions employed, only ionic NTPs with a monovalent ion (K^+) were investigated in detail. They formed anisotropic melts and were melt extruded to form films with high strength and modulus. The effect of ionic content on thermal properties, optical textures, and tensile mechanical properties of ionic NTPs is discussed.

2. Experimental section

2.1. Preparation of ionic NTPs

All the ionic NTP samples were prepared by using the method that was similar to the one described elsewhere [3,5]: three base monomers, 4-hydroxybenzonic acid (HBA), 6-hydroxy-2-naphthoic acid (HNA), and an ion-containing monomer, were used for polymerization (melt acidosis). For the ion-containing monomer, a *meta*-linked ionic monomer, 5-sulfoisophthalate (SI), was used in our previous work. In this work, a *para*-linked ionic monomer, hydroquinone-2,5-disulfonate (HQDS), was used to make novel ionic NTPs. The chemical structures of these two ion-containing monomeric units are shown in Fig. 1. Note that 1 mol% incorporation of unit I leads to an ionic NTP of 1 mol% ionic content, whereas 1 mol% incorporation of unit II leads to an ionic NTP of 2 mol% ionic content.

Ionic NTPs that contain divalent metal ions were prepared by in situ cation exchange during the heating process of reaction mixture: i.e. divalent metal acetate was added to three base monomers, HBA, HNA, and HQDS (K salt), in the beginning of the reaction. The feed monomer compositions of the *para*-linked ionic NTPs are listed in Table 1.

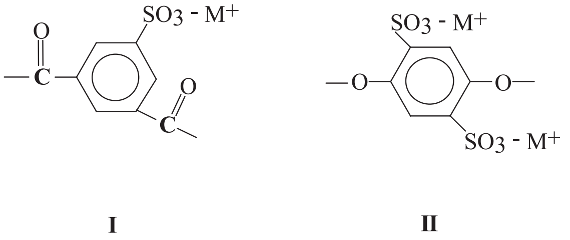

Fig. 1. Chemical structures of ionic monomeric units: (I) 5-sulfoisophthalate (SI); (II) hydroquinone-2,5-disulfonate (HQDS).

Table 1
Composition of feed monomers (mol%) for HQDS-containing ionic NTPs (K and Ca salts)

No	HBA	HNA	HQDS (K)	HQDS (Ca)
1	73	26	1	–
2	72.5	26	1.5	–
3	72	26	2	–
4	73.5	26	–	0.5
5	73	26	–	1

2.2. Viscosity

Viscosity measurements of ionic NTP polymers were conducted with a capillary viscometer at 0.1 wt% concentration in a solvent mixture, pentafluorophenol (PFP) /hexafluoroisopropanol (HFIP) (50/50 v/v), at 25 °C [5]. Inherent viscosity (I.V.) values were determined by the following equation: $\mathrm{I.V.} = \ln(\eta_{\mathrm{rel}})/c$, where c is the polymer concentration and η_{rel} is the relative viscosity, defined as the ratio of the flow time of the polymer solution to that of the solvent mixture.

2.3. 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^{-1}, followed by cooling to ambient temperature under a nitrogen atmosphere. The melting and crystallization temperatures (T_m and T_c) are determined from peak temperatures of the melting endotherm and the crystallization exotherm on DSC thermograms, respectively.

2.4. 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^{-1} under a nitrogen atmosphere.

2.5. Tensile tests

Tensile tests were conducted on thin film specimens, with Minimat Materials Tester (Polymer Laboratories), according to the ASTM standard (D882-91). The cross-head speed used was 0.1 mm min^{-1}. Films were melt extruded with Micro-Melt extruder (Hoechst Celanese) having a film die of 0.013 cm thickness and 0.64 cm width, cooled at ambient temperature, and then collected with a wind-up roll at a take-up speed of 5 m min^{-1}. Film thickness was measured with a micrometer at the various points of the film and an average value, usually in the range of 30–50 μm, was used. At least five specimens were tested for each sample at room temperature and the 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 the strain at break (the maximum strain) were those at the break point.

2.6. Dynamic mechanical thermal analysis (DMTA)

DMTA was also used for thermal analysis, since glass transition temperatures were not detected by DSC for HQDS-containing ionic NTPs, and since DMTA is known to be more sensitive than DSC to smaller structures [7]. Specimens of 6 mm length and 2 mm width were cut from melt-extruded films. Dynamic mechanical thermal analyser (Thermal Sciences) was used for testing at 0.3 Hz. All the measurements were conducted in the tensile mode at a heating rate of 4 °C $\min^{-1}$.

2.7. Polarizing light microscopy (PLM)

Polarizing light microscopy was used to examine the liquid crystalline structure of the ionic NTP samples. 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 made from in situ melting between two glass slides on a hot stage (Mettler F52), and the other made from melt extrusion.

2.8. 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 FTIR measurements. IR spectra were collected with average scan of 25 at a resolution of 2 cm^{-1} in a transmission mode with ATI Mattson spectrometer (Genesis Series FTIR).

3. Results and discussion

3.1. Characterization of HQDS-containing ionic NTPs

Introduction of sulfonate groups (ionic groups) into the NTP chains was confirmed by using FTIR [3,5]. The IR spectra in the range of 500–850 cm^{-1} of HQDS-containing ionic NTPs were used for that purpose (figures not shown): S–O stretching mode (of sulfonate groups) was clearly identified at 642–644 cm^{-1} for the HQDS-containing ionic NTPs, whereas no such as mode was detected for the non-ionic NTP. Similar comparison was made between a non-ionic NTP and ionic NTPs with *meta*-linked ionic groups (1 mol%; Ca and Na salts) [3,5].

Birefringence was observed with an optical microscope under cross polarizers; and a thread-like texture, characteristic of the nematic liquid crystalline structure [2], was observed for all the samples studied. These characteristic features were retained even after being cooled to an ambient temperature. Fig. 2 shows two PLM micrographs of HQDS-containing ionic NTPs. Like non-ionic NTPs, but unlike SI-containing ionic NTPs [3], the HQDS-containing ionic NTP films display clear banded textures perpendicular to the shear direction (manually applied to make thin films suitable for PLM examination). The banded texture has also been reported for other thermotropic LCPs [2,8,9]. From the periodicity of the bands, it is believed that the bands correspond to supermolecular structure with many molecules changing orientation systematically and concertedly [2]. The mechanism of band formation, and its correlation with bulk mechanical properties and molecular morphology, are not well understood despite their importance [2,9]. Nevertheless, the presence of bands indicates that the orientation regularly changes; and such change is subsequent to the stop of flow in shear or elongation, which is desirable for melt processing.

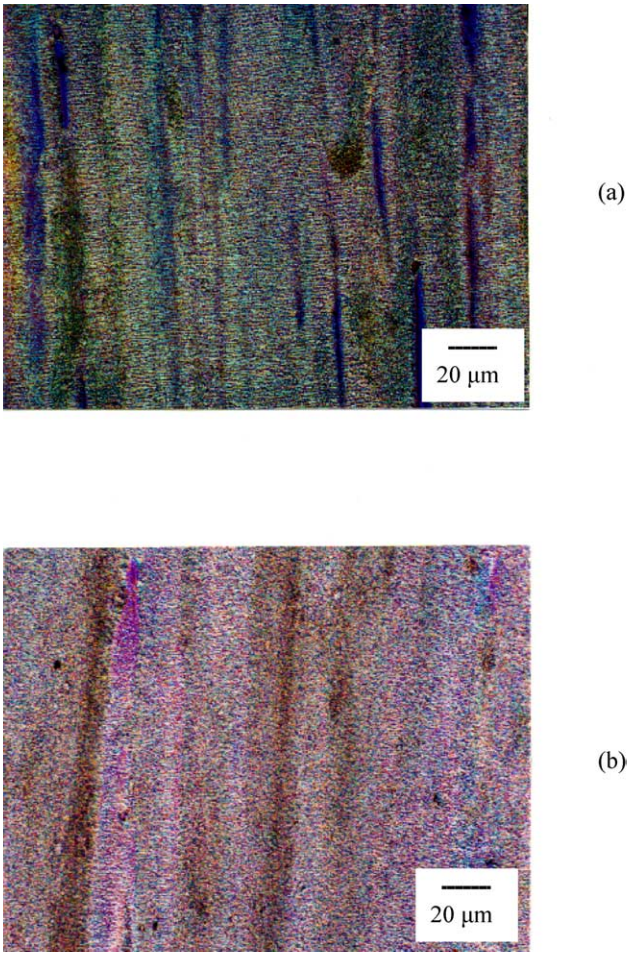

Fig. 2. Polarized light micrographs (magnification×400) of HQDS-containing ionic NTPs (K salt) with two different ionic contents: (a) 2 mol%; (b) 3 mol% (shear direction is vertical).

3.2. Thermal properties of HQDS-containing ionic NTPs

In this work, DSC was used to study the effect of ionic content and counterion on the thermal properties of ionic NTPs. DSC is commonly used to study primary transitions, such as melting (i.e. a transition from a solid crystal to a nematic liquid melt) and crystallization of ionomers [10]. All the DSC measurements were performed on as-made polymers.

Tables 2 and 3 list transition temperatures (T_m and T_c), the heat of fusion (ΔH_m), and the heat of crystallization (ΔH_c), for the K and Ca salts, respectively, which were determined from DSC thermograms. It is of interest to note that T_m and T_c are nearly constant against ionic content for HQDS-containing ionic NTPs, as more clearly seen in Fig. 3. This is in marked contrast to the results on ionic NTPs containing *meta*-linked SI units (Na salt), where both T_m and T_c decrease as the ionic content increases [3]. The nearly constant T_m values should be related to the presence of *para*-linked HQDS 'straight' units in two ways. First, two large substituent groups ($SO_3^-M^+$) attached to a benzene ring of a HQDS unit introduce bulkiness (irregularities) into the chain, reducing the effective chain packing and bonding in the crystal [2], which may reduce the T_m value. On the other hand, its *para*-linked structure adds 'straightness' (stiffness) into the chain, which is beneficial for chain packing and effective bonding in the crystals, and T_m may rise. These two opposing factors are balanced within a composition range studied and keep the T_m value essentially constant. As cited in the literature [2], chain irregularities and chain stiffness ('straightness') are two distinct properties that are separately incorporated into main-chain LCPs. The *para*-linked HQDS units possess these two distinct properties combined together. In contrast, the *meta*-linked SI units introduce 'kinked' structure into ionic NTP chains, which decrease the rigidity of the backbone chains and disturb the chain packing; as a result, the T_m value is reduced. As discussed in our previous report, reduction in the T_m value comes from 'kinked' units and not from ionic interactions [3].

At the comparable ionic content, in contrast to very broad melting endotherm peaks observed for the SI-containing ionic NTPs (Na salt), a well-defined sharp melting endotherm peak is revealed for the HQDS-containing ionic NTPs (K salt), which is similar to their non-ionic NTP precursor (Fig. 4). This is again the result of rigid chain nature of the HODS-containing ionic NTP. The SI-containing ionic NTPs contain structural heterogeneity due to more 'kinked' structure; and, this leads to the diversity in size and in the arrangement of crystallites, broadening the endothermic peaks, whereas the HQDS-containing ionic NTPs have more homogeneous structure. The heat of fusion (ΔH_m) and the heat of crystallization (ΔH_c) for the HQDS-containing ionic NTPs (K and Ca salts) remain essentially constant as noted in Tables 2 and 3, which indicates no significant change in crystallinity.

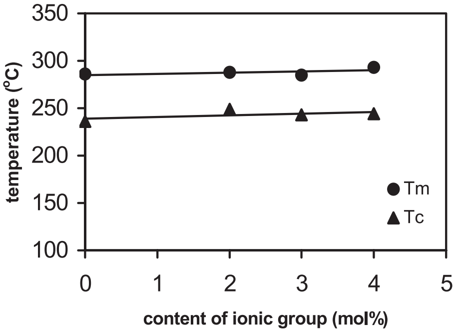

Fig. 3. Melting temperature, T_m, and crystallization temperature, T_C, against ionic content (mol%) of HQDS-containing ionic NTPs (K salt).

The Ca salts of HQDS-containing ionic NTP seem to show slightly lower T_m and T_c values than the K salts do. This may be due to stronger ionic aggregation in the Ca (divalent) salts than in the K (monovalent) salts, which disturbs crystalline structure and disturbs crystal growth from the melt due to stronger ionic interactions within the chains [5]. More study is needed, however, to substantiate this reasoning.

Although no glass transitions were detected by DSC for the HQDS-containing ionic NTPs, they were detected by DMTA, which is known to be more sensitive than DSC to detect glass transition of small structures [7]. This was also noted for non-ionic NTP and SI-containing ionic NTPs (Na salts) of low ionic contents (1 mol%) [3,5]. The T_g values of the HQDS-containing ionic NTPs (K salt), determined as the maximum peak positions in the loss modulus (E'') versus temperature curves in DMTA, are 103 °C at 2 mol% ionic content, 108 °C at 3 mol% ionic content, and 91 °C at 4 mol% ionic content. It is of interest to note that the order of the T_g value is parallel to that of the I.V. value (Table 4). Since the I.V. value increases with molecular weight, the data seem to reflect the difference in the average molecular weight of the polymers.

Finally, thermogravimetric analysis (TGA) showed that all the HQDS-containing ionic NTP samples were thermally stable (i.e. no weight loss) up to ca. 380 °C, a temperature far above their melting temperatures. This was also noted for non-ionic NTP and SI-containing ionic NTPs (Na and divalent metal salts) [3,5].

Table 2
DSC results for HQDS-containing ionic NTPs (K salt)

Sample	Ionic content (mol%)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)
A	2	288	249	3.9	2.3
B	3	285	243	3.1	2.2
C	4	293	244	1.5	4.1

T_m and ΔH_m, from the second heating run; T_c and ΔH_c, from the first cooling run.

Table 3
DSC results for HQDS-containing ionic NTPs (Ca salt)

Sample	Ionic content (mol%)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)
A	1	282	237	4.1	4.9
B	2	272	236	3.7	5.1

T_m and ΔH_m, from the second heating run; T_c and ΔH_c, from the first cooling run.

3.3. Effect of ionic content on mechanical properties

It is well known for conventional ionomers that molecular parameters, such as ionic content and the nature of the counterion, influence mechanical properties with the effectiveness depending on the type of an ionomer [11]. Although we have reported that the incorporation of *meta*-linked SI units in the main chain reduces the rigidity of the polymer chain, resulting in decreased T_g and liquid crystallinity [3,5,6], mechanical properties has not been studied. This is because we could not obtain by melt processing useful samples for mechanical testing for the samples having more than 1 mol% ionic content under the method employed. Thus, it is useful to have ionic NTP systems having various ionic contents, which are melt processable at a convenient temperature range, and suitable for mechanical testing. This is the case for the current system.

Fig. 5 shows typical stress–strain curves for the HQDS-containing ionic NTPs (K salt) with ionic content of 2–4 mol% and for a non-ionic NTP. The initial slope of the stress–strain curve increases with the ionic content, reflecting an increase in the tensile modulus (stiffness). The stress–strain curves also indicate that the NTP polymer becomes stronger and tougher, i.e. more energy is needed to break the sample with an increase in the ionic content. Table 4 summarizes the tensile properties, average values of at least five samples obtained from stress–strain curves. The values of inherent viscosity (I.V.), which reflect the average molecular weight of polymers [12], are also listed. It has been reported that the tensile strength of non-ionic NTP fibers increases as the I.V. value (molecular weight) increases [12,13]. The tensile strength increases significantly as the ionic content is increased (Fig. 6): from 142 MPa for a non-ionic NTP to 364 MPa for an ionic NTP with 4 mol% ionic content, an 156% increase. Tensile modulus also shows appreciable increase as compared with non-ionic NTP (a 92% increase at 4 mol% ionic content level).

Calundann and Jaffe reported that tensile properties of non-ionic NTP extrudates were a strong function of molecular parameters, such as polymer molecular weight

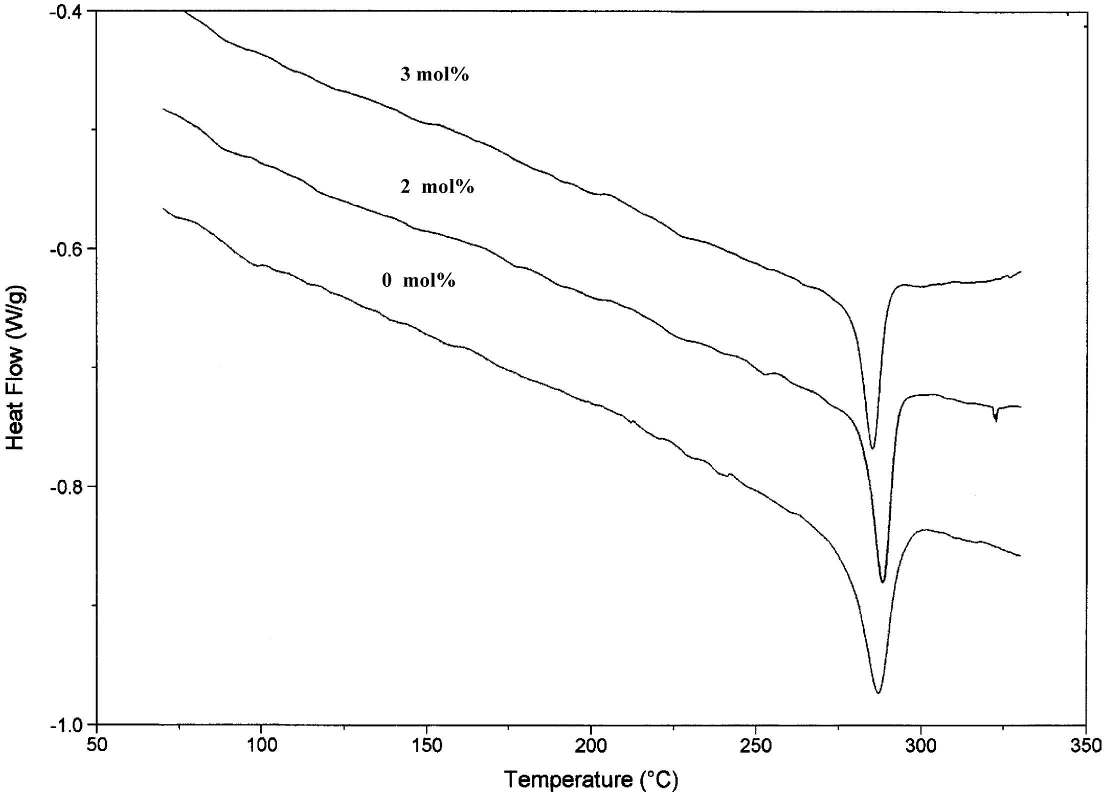

Fig. 4. DSC thermograms of HQDS-containing ionic NTPs (K salt) with an ionic content range of 0–3 mol%.

Table 4
Tensile properties of HQDS-containing ionic NTP (K salt) films

Ionic content (mol%)	0	2	3	4
Tensile modulus (GPa)	13.3	19.2	24.6	25.6
Tensile strength (MPa)	142	232	292	364
Strain at break (%)	1.27	1.53	1.47	1.80
I.V. (dl/g)	5.12	4.42	5.36	2.95

and molecular orientation [13]. The incorporation of ionic bonds into NTP chains can provide an additional molecular parameter to enhance tensile properties. The tensile strength of the HQDS-containing ionic NTPs may be compared with the theoretical prediction based on the highly oriented LCP fibers [12]. The main assumption of 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 successfully describes the strength of non-ionic NTP fibers quantitatively [12]. According to this model, when the local inter-chain load exceeds a critical value, the inter-chain bond 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 [12]. Our results on the HQDS-containing ionic NTPs confirm this prediction: because inter-chain interaction is greatly enhanced with ionic bonds and because it increases with increasing an ionic content within a reasonable ionic content range, the strength increases accordingly (Fig. 6). Also, because ionic bonds can provide additional lateral support to the aligned ionic NTP chains, a positive contribution to the tensile modulus is expected: and, this is indeed observed in our results. It should be added that the enhanced shear strength is also expected to enhance compressive strength of fibers [2], as observed for SI-containing ionic NTPs [5,6].

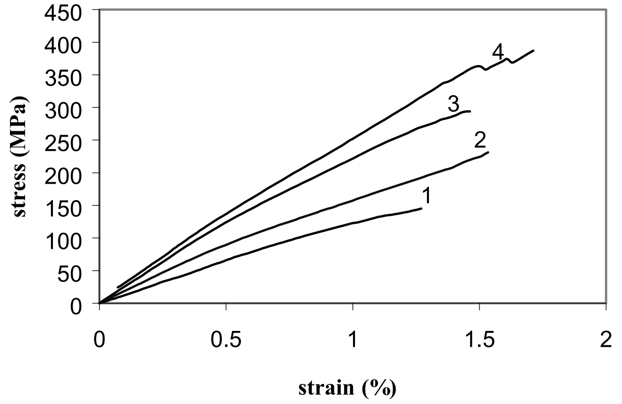

Fig. 5. Typical stress–strain curves for film samples of non-ionic NTP and HQDS-containing ionic NTPs (K salt) with various ionic contents: (1) 0; (2) 2; (3) 3; (4) 4 mol%.

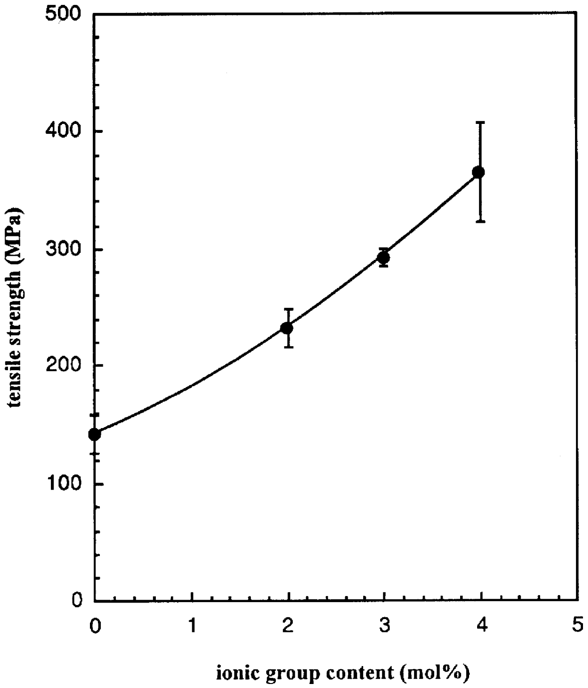

Fig. 6. Tensile strength versus ionic content for HQDS-containing ionic NTPs (K salt).

We cannot overemphasize the important role of ionic bonds in enhancing mechanical properties of NTPs. It is expected that the degree of orientation of ionic NTPs is lower than that of non-ionic NTP, and that the orientation is less at higher ionic contents than at lower ionic contents under similar processing conditions. This is because ionic interactions between ionic NTP chains can increase melt viscosity substantially and thus the internal friction under flow. As a result, polymer chains tend to align less along the applied force (or elongational flow) field. This was shown in our previous studies on ionic NTPs (Na salt) by polarizing optical microscopy [3]. Therefore, the significant improvement in tensile properties observed for the HQDS-containing ionic NTPs having higher ionic contents is attributed to increased lateral interactions via ionic bonds, which can more than compensate the negative effects due to some ordering loss and lower average molecular weights.

3.4. *Effect of thermal treatment*

Table 5 shows the effect of heat treatment on the tensile properties of the HQDS-containing ionic NTPs (K salt). Heat treatment was applied by heating the extruded film samples at 240 °C for 32 h under tension-free and vacuum. Upon heat treatment, the tensile strength and the strain at break are significantly enhanced, whereas the tensile modulus is little changed. The results are consistent with those of non-ionic NTP fibers upon heat treatment [12,13]: the increases in strength and strain at break arise from an

Table 5
Tensile properties of HQDS-containing ionic NTP (K salt) films with/without heat treatments

Ionic content (mol %)	2			3		
	Non-HT	HT	Change (%)	Non-HT	HT	Change (%)
Tensile modulus (GPa)	19.2	19.1	−1	24.6	23.0	−1
Tensile strength (MPa)	232	433	87	292	415	42
Strain at break (%)	1.53	2.39	56	1.47	1.98	35

Film take-up speed, 5 m min^{-1}; Non-HT, as-extruded film; HT, heat treatment at 240 °C under vacuum for 32 h.

increase in the average molecular weight upon heat treatment, as reported for non-ionic NTP polymers [12–14]. A significant increase in inherent viscosity for the heat-treated samples supports this reasoning: e.g. the I.V. value of an HQDS-containing ionic NTP (2 mol% ionic content) increased from 4.42 to 7.33 dl g^{-1} upon heat treatment.

We have shown that ionic bonds are very effective in improving mechanical properties of thermotropic LCPs, whereas covalent bonds have been reported to be less effective [2,4,15]. It is well known that polymers with ionic cross-links are reformed upon heating, but those with covalent cross-links are not. This is because ionic bonds are non-directional and easier to reform upon cooling after melting [16], while covalent bonds are highly directional and thus more difficult to reform. 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 reformed (rearranged) upon cooling. Thus, ionic bonds are reformed after proper chain alignment. Therefore, incorporation of ionic bonds without disturbing the rod-like nature of the chains, e.g. an introduction of *para*-linked HQDS ionic units, is a promising method to enhance mechanical properties of main-chain LCPs.

4. Conclusions

Novel ionic NTPs that contain *para*-linked HQDS ionic groups of up to 4 mol% have been prepared. All the ionic NTPs (K and Ca salts) prepared exhibit thermotropic liquid crystallinity.

Ionic NTPs (K salt) exhibit nearly constant T_m and T_c values up to 4 mol% ionic content without showing any signs of disturbance of both crystalline and liquid crystalline behaviors, typically observed for their non-ionic NTP precursors. The glass transition temperatures, determined by DMTA, rise with an increase in molecular weight, without showing dependence on ionic content within the composition range studied. This provides evidence that ionic interactions between ionic NTP chains exert no significant effect on chain stiffness. The ionic NTPs (K salt) also show a significant increase in the tensile properties over a non-ionic NTP. The strength increases by nearly 160% with an increase in the ionic content to 4 mol%. Also, the modulus nearly doubles for a 4 mol% ionic NTP over a non-ionic NTP. The strong interchain interactions via ionic bonds in the ionic NTP, which surpass the negative effect due to lower molecular weight of higher ionic content samples, should be responsible for enhanced strength and modulus. Heat treatment, which leads to a significant increase in the molecular weight, can further improve the tensile strength and the strain at break of these ionic NTPs. All the ionic NTP (K salt) films fractured by splitting into continuous parallel strips along the extension direction, as previously observed for SI-containing ionic NTP (1 mol%; Ca salt) [5].

The ionic NTPs that contain divalent Ca counterions showed poor solubility, difficulty in melt extrusion, and rather poor mechanical properties. This could result from stronger ionic aggregation of the HQDS monomeric units due to much stronger ionic bonds that involve divalent Ca ions. Despite enhanced properties expected for divalent-salt samples, we have not yet found the proper processing conditions for these ionic polymers.

We have demonstrated that the incorporation of ‘straight’ ionic units into NTP backbone chains does not interfere with its crystalline and liquid crystalline behaviors at relatively low ionic contents.

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