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# Miscible blends of a thermotropic liquid crystalline polymer and sulfonated polystyrene ionomers

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**Abstract**

The miscibility of a wholly aromatic thermotropic liquid crystalline polyester (LCP), Vectra® A, with lightly sulfonated polystyrene ionomers (SPS) was assessed. Blends were prepared by melt mixing in an intensive mixer. The sulfonation level and the choice of the cation used to neutralize the ionomer influenced miscibility. Zinc salts of an SPS with 5.3 mol% sulfonation were miscible at all compositions with the LCP, but lithium salts with the same sulfonation level formed two phases, a pure LCP phase and an ionomer-rich mixed phase. Zinc salts of an ionomer with 10.8 mol% sulfonation were also miscible with the LCP when the blend was richer in the ionomer, but two-phase blends were obtained for LCP-rich compositions. FTIR analyses failed to identify a specific intermolecular interaction between the ionomers and the LCP. That and the fact that increasing sulfonation did not improve miscibility of the zinc salt ionomers with the LCP led to the conclusion that miscibility in this system arose from intramolecular repulsive interactions along the ionomer chain. The addition of 5.3Zn-SPS to the LCP lowered the tensile modulus, the ultimate strength and the ultimate elongation. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Liquid crystalline polymers; Sulfonated polystyrene ionomers; Miscibility

## 1. Introduction

For the past two decades, many authors have tried to exploit the superior mechanical properties of thermotropic liquid crystalline polymers (LCP) by blending them with flexible thermoplastic polymers. A number of reviews summarize the published literature on this subject [1–4]. In general, the blends exhibit poor interfacial adhesion between the LCP and the thermoplastic, which limits the usefulness of these materials. Recently, a number of authors have published papers dealing with reactive compatibilization of LCPs with polymers such as polyesters, polycarbonate, polypropylene and polyethylene [5–11].

Previous work in our laboratory [12,13] suggested that lightly sulfonated polystyrene (SPS) ionomers were miscible with wholly aromatic liquid crystalline polyesters. Our current research seeks to confirm that observation, determine the effects of sulfonation level, cation and blend composition on the limits of miscibility and determine the effect of adding SPS on the processing and mechanical properties of a liquid crystalline polymer (LCP) and *compatibilized* blends containing LCP and SPS.

In this paper, we describe the effects of sulfonation level and cation on the miscibility of SPS ionomers with LCP and the effect of adding small amounts of SPS on the mechanical properties of the LCP.

## 2. Experimental details

### 2.1. Materials

The ionomers were prepared from a commercial atactic polystyrene, Styron® 666, obtained from Dow Chemical Co The number-average ($M_n$) and weight-average ($M_w$) molecular weights as determined by gel permeation chromatography (GPC) were 106 and 280 kg/mol, respectively. SPS ionomers containing 5.3 and 10.8 sulfonate groups per 100 styrene repeat units (hereafter, referred to as mol% sulfonation) were prepared by sulfonating polystyrene with acetyl sulfate in a 1,2-dichloroethane solution following the procedure of Makowski et al. [14]. That procedure substitutes sulfonate groups primarily at the para-position of the styryl ring and randomly along the chain. The zinc and lithium salts were prepared by neutralizing the SPS samples with a 50% excess of either zinc or lithium acetate. The neutralized ionomers were recovered by steam stripping (using de-ionized water),

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filtered, washed several times with distilled water, and dried for several days at 70°C under vacuum. The nomenclature used to denote the ionomers was *x.y*MSPS, where *x.y* signifies the mol% sulfonation and M represents the cation (Zn for $Zn^{2+}$; Li for $Li^{+}$; or H for the free acid derivative).

The liquid crystalline polymer (LCP) used was Vectra® A, a wholly aromatic thermotropic copolyester produced by Ticona Corp. The LCP composition is reported to be 73% hydroxybenzoate and 27% hydroxynaphthoate. The LCP was dried at 100° for 24 h under vacuum before using.

### 2.2. Materials characterization

Blends of the SPS ionomers and the LCP were prepared by melt mixing under a dry nitrogen atmosphere in a Brabender intensive mixer at 300°C using a 30 $cm^3$ mixing head with two counter-rotating rotors and a mixing speed of 30 rpm. Mixing was carried out by first fluxing the LCP for several minutes and then adding the SPS ionomer and mixing for an additional 10 min. Compositions of 100/0, 75/25, 50/50, 25/75 and 0/100 LCP/ionomer (w/w) were prepared. Thermal transitions were measured by differential scanning calorimetry (DSC) using a Perkin–Elmer model DSC-7. A heating rate of 20°C/min was used, except for the neat LCP, which was scanned at 40°C/min in order to enhance the resolution of the transitions. The DSC temperatures were calibrated for a scanning rate of 20°C/min; the error at the higher scanning rate was likely to be within a couple degrees. Glass transition temperatures ($T_g$) were defined at the midpoint of the change in specific heat. Miscibility of a blend was inferred from the observation of a single $T_g$; multiple $T_g$s indicated phase-separation. Thermal transitions were also measured by dynamic mechanical thermal analysis using a Polymer Laboratories model MkII dynamic mechanical thermal analyzer (DMTA). A tensile fixture and a heating rate of 2°C/min were used. The glass transition temperature was defined at the peak maximum in tan $\delta$ at a frequency of 1 Hz.

Infrared spectra were measured with a Mattson Polaris Fourier transform infrared spectrophotometer. Fifty scans were signal averaged and the resolution was 4 $cm^{-1}$. The spectrometer was purged with dry, carbon dioxide-free, air before measurements were taken.

### 2.3. Scale-up and mechanical properties

Three ~150 g batches of SPS were prepared from 12.5% solutions of polystyrene in 1,2-dichlorethane at ~55–60°C. The sulfonation level of the three batches, determined by titrating the sulfonic acid derivative of SPS in a 90/10 toluene/methanol solution with a phenolphthalein indicator, were 3.5, 5.7 and 6.1 mol%. All the SPS samples were neutralized to the zinc-salt, and the three batches were dry-mixed together to achieve ~450 g of a Zn-SPS with an average sulfonation level of 5.1 mol%.

A 50/50 masterbatch of 5.1Zn-SPS and Vectra® A LCP was prepared on a twin-screw extruder. The masterbatch extrudate was chopped into pellets and dried under vacuum at elevated temperature. It was then let-down with virgin LCP in a Wayne Machine & Die Co 'Yellow Jacket' one-inch single-screw extruder equipped with a mixing screw to produce blends with compositions of 5, 10 and 15 wt% ionomer. The extruder was run at 20–50 rpm and the temperatures were set at 260, 300, 300 and 280°C for the feed zone, zone 2, zone 3 and the die, respectively. The blend extrudates were pelletized with a Randcastle Extrusion Systems pelletizer, Model RCP-2.0 DD.

ASTM type V tensile specimens were injection molded with an Arburg Allrounder® 221-75-350 injection molding machine using a temperature profile of 261, 285, 305 and 292°C for the feed zone, zone 2, zone 3 and the die, respectively. Tensile tests were run following ASTM Standard D-638 using an Instron 1011 Universal Testing Machine equipped with a 1000 lb load cell and mechanical grips and using an extension rate of 10 mm/min. Excessive slippage of the specimen in the grips occurred when pneumatic grips were used. Force-elongation data were acquired at a rate of ~100 data points per second using a analog/digital data acquisition system developed in-house, and the tensile properties were calculated by a computer program written by Gordon and Shaw [15] called TENSIL.

## 3. Results and discussion

### 3.1. Miscibility of LCP and ionomers

#### 3.1.1. Zn-SPS with Vectra® A

DSC thermograms for the LCP/5.3ZnSPS blends and the component polymers are shown in Fig. 1, and the $T_g$s are summarized in Table 1. The glass transition temperatures ($T_g$) for the neat ionomer (5.3ZnSPS) and LCP (Vectra® A)

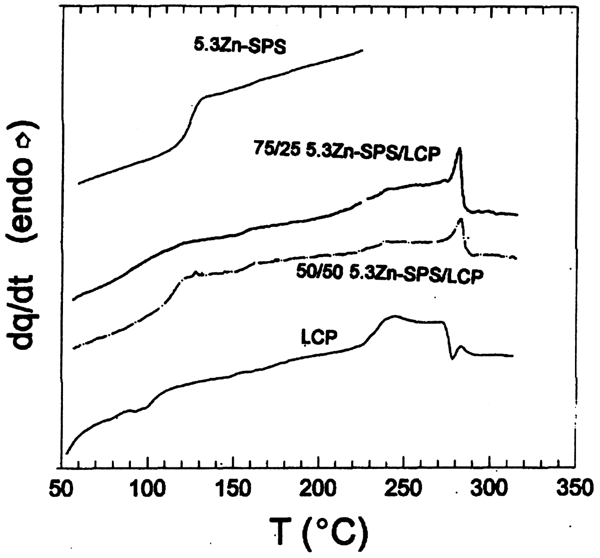

Fig. 1. DSC heating thermograms of 5.3Zn-SPS, Vectra® A LCP and their blends.

Table 1
Glass transition temperatures of Vectra® A/5.3ZnSPS blends

| Composition (wt%) | | $T_g$ (°C) | |
|---|---|---|---|
| LCP | Ionomer | DSC | DMTA |
| 100 | 0 | 103 | 106 |
| 75 | 25 | 105 | 115 |
| 50 | 50 | 110 | 120 |
| 40 | 60 | | 122 |
| 25 | 75 | 112 | |
| 0 | 100 | 120 | 132 |

were 120 and 103°, respectively. Miscibility of the LCP and the ionomer was inferred from the observation of a single $T_g$ for the blends, intermediate between those of the pure components. The DSC thermograms of the blends in Fig. 1 also show a thermal transition near 150°C that looks similar to a second-order transition. However, 150°C is much too high to be the $T_g$ of either an ionomer-rich or LCP-rich phase and a similar thermal transition is seen in thermogram of the neat LCP. The origin of that transition is not known, but it does not appear to arise from phase separation of the blend.

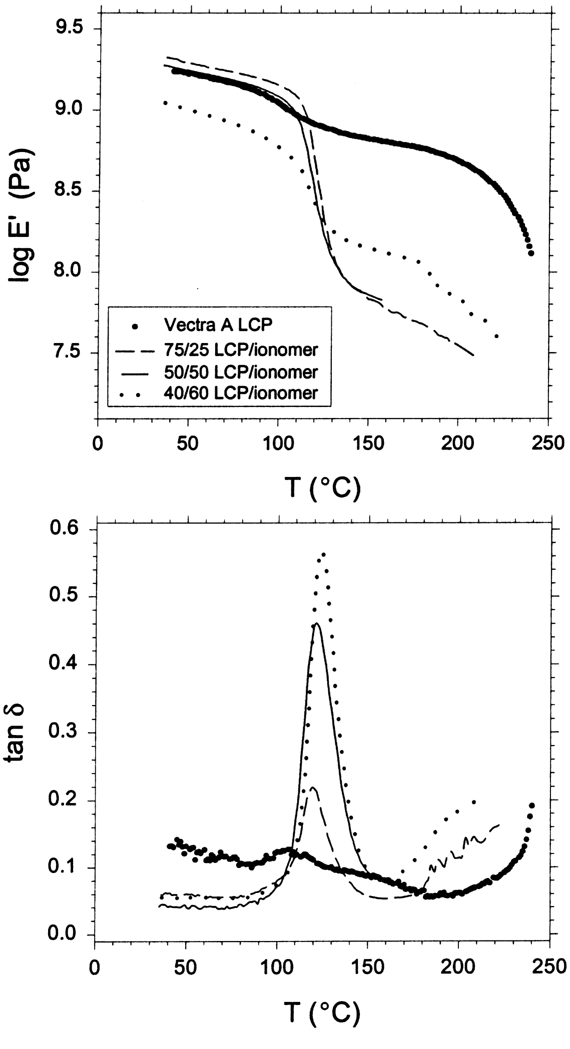

Fig. 2. Dynamic mechanical properties of LCP/5.3Zn-SPS blends.

The glass transition region for the blends was broader than for the two pure component polymers, which is not uncommon for miscible polymer blends. The broadening of the glass transition of miscible blends is believed to arise from the intrinsically distinct segmental mobility for each component [16,17]. The possibility of two phases with close $T_g$s in the LCP/5.3ZnSPS blends, however, cannot be excluded on the basis of the DSC results alone. Because the $T_g$s of the two components were only ca. 20°C apart, the broad transition seen in Fig. 1 for the blends may contain two poorly resolved $T_g$s. That possibility was evaluated using DMTA, which is better able to resolve close $T_g$s.

Fig. 2 shows the DMTA results for the Vectra® A/5.3ZnSPS blends. Only a single tan $\delta$ peak corresponding to $T_g$ was observed for each component polymer and for the blends, which confirms that the two polymers were miscible. The $T_g$, defined as the temperature of the peak in tan $\delta$ is plotted against composition in Fig. 3. The experimental data agree reasonably well with the Fox equation [6] predictions for $T_g$ of a miscible blend, which is the solid line in Fig. 3. The error bars in Fig. 3 correspond to the breadth of the tan $\delta$ peak. Fig. 4 gives the dynamic modulus and mechanical tan $\delta$ data for the Vectra® A/10.8Zn-SPS blends. Each tan $\delta$ curve in Fig. 4(a) is shifted vertically by a factor of 0.1 for clarity (the data for the LCP are not shifted), and in Fig. 4(b) the $E'$ data for each material are shifted relative to the data for the ionomer by the amount shown in parentheses. The tan $\delta$ peak for $T_g$ ($f = 1$ Hz) for the ionomer and the LCP are at ca. 152 and 106°C, respectively. Blends that were richer in LCP exhibited a tan $\delta$ peak at ca. 145°C and a low temperature shoulder at ca. 106°C that may be due to an ionomer-rich phase and a pure LCP phase, respectively. For a $T_g$ of 145°C, the Fox equation provided an estimate of the composition of the ionomer-rich

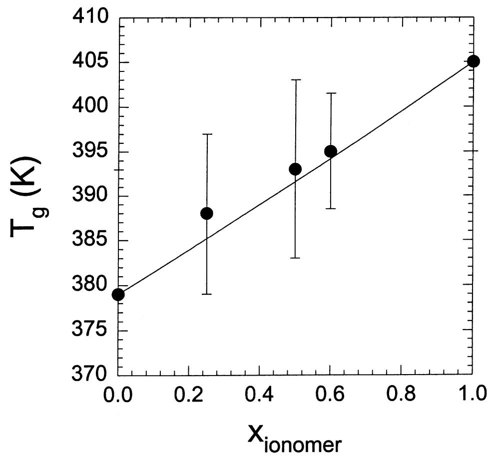

Fig. 3. $T_g$ of 5.3Zn-SPS/Vectra A blends determined by DMTA. The solid line is the Fox equation [6] prediciton.

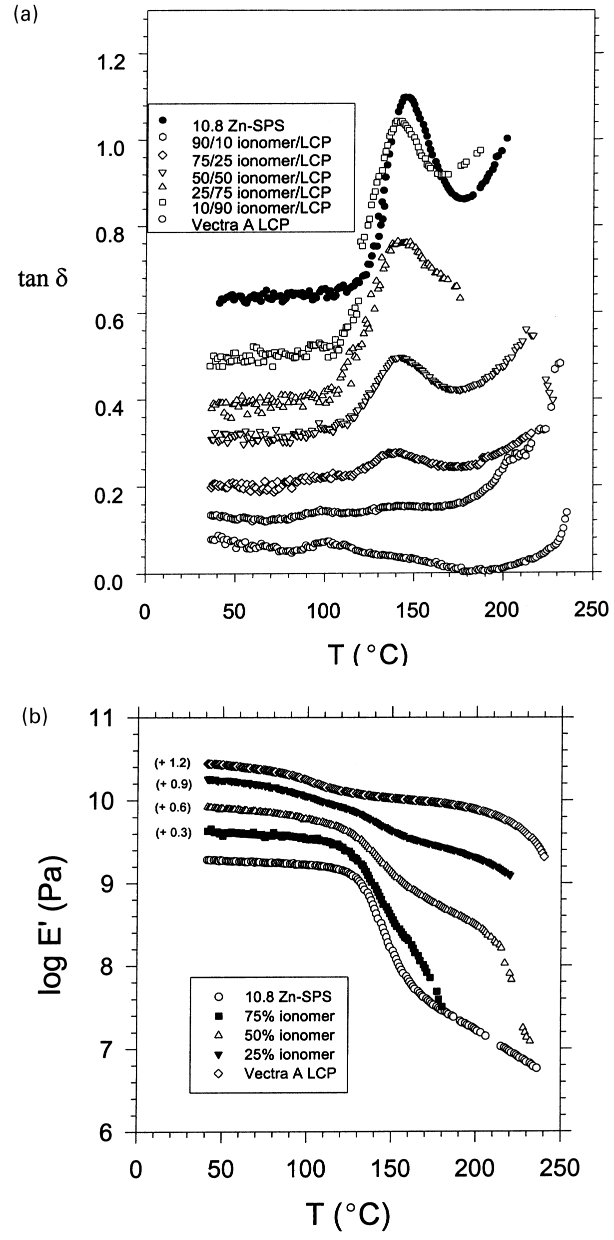

Fig. 4. Temperature dependence ($f = 1$ Hz) of (a) tan $\delta$ and (b) dynamic modulus for LCP/10.8Zn-SPS blends.

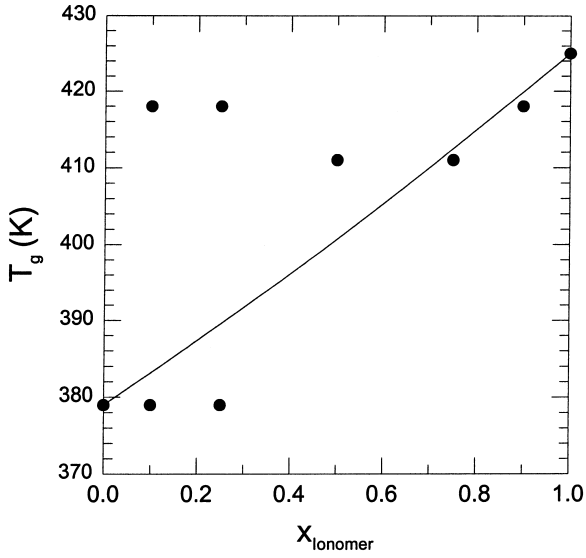

Fig. 5. $T_g$ of 10.8Zn-SPS/Vectra A blends determined by DMTA. The solid line is the Fox equation [6] prediction.

phase of 86 wt% ionomer and 14% LCP. For the 50/50 blend and the blends richer in the ionomer, only a single tan $\delta$ peak at 138°C was resolved, but according to Fox equation [18], that $T_g$ corresponds to a composition of about 72% ionomer and 28% LCP. That result suggests that there must also be a pure LCP phase in order to balance the overall composition of the blend. However, when the blend composition was richer in the ionomer, only a single tan $\delta$ peak was observed in the dynamic mechanical data and the temperature of the peak maximum corresponded to the Fox equation prediction for a miscible blend, see Fig. 5. The $E'$ data in Fig. 4(b) do not clearly resolve two $T_g$s in any of the blends. The $T_g$s for the blends are plotted against composition in Fig. 5. Whereas the LCP and the zinc salt of the ionomer with 5.3 mol% sulfonation were miscible for all compositions, the LCP is only partially miscible with the ionomer with the higher sulfonation.

Fig. 6 shows the FTIR spectral region for the carbonyl group of the LCP in the neat LCP and two blends with 5.3Zn-SPS. The addition of the ionomer had no influence on the position and shape of the C=O stretching vibration at 1735 $\text{cm}^{-1}$, and similarly, there was no change of the characteristic bands for the sulfonate anion in the spectral region from 900–1300 $\text{cm}^{-1}$ (not shown). Those results indicate that no specific intermolecular interaction between the LCP and the ionomer is responsible for the observed miscibility. If there were a specific interaction between these polymers, which presumably would involve the metal sulfonate group and the ester group of the LCP, one would also expect that the miscibility would increase as the concentration of interacting groups increased, i.e. as the sulfonation level of the ionomer increased. In general, research directed at improving miscibility of flexible-chain polymers with LCPs has emphasized the introduction of specific strong intermolecular interactions between the two polymers. That the miscibility in the LCP/ionomer system actually decreased when the sulfonation level was increased from 5 to 11 mol% and the fact that no specific interactions were observed by FTIR indicate that specific intermolecular interactions were not the origin of the miscibility in this system.

Miscibility in these blends is believed to be due to the copolymer effect [19–21]—that is, mixing occurs because the repulsive *intra*molecular interactions between the ionic and non-ionic species on the ionomer chain are stronger (i.e. more unfavorable) than the repulsive *inter*molecular interactions between the components of the ionomer and the components of the LCP. Usually for blends where the copolymer effect is responsible for mixing, miscibility is

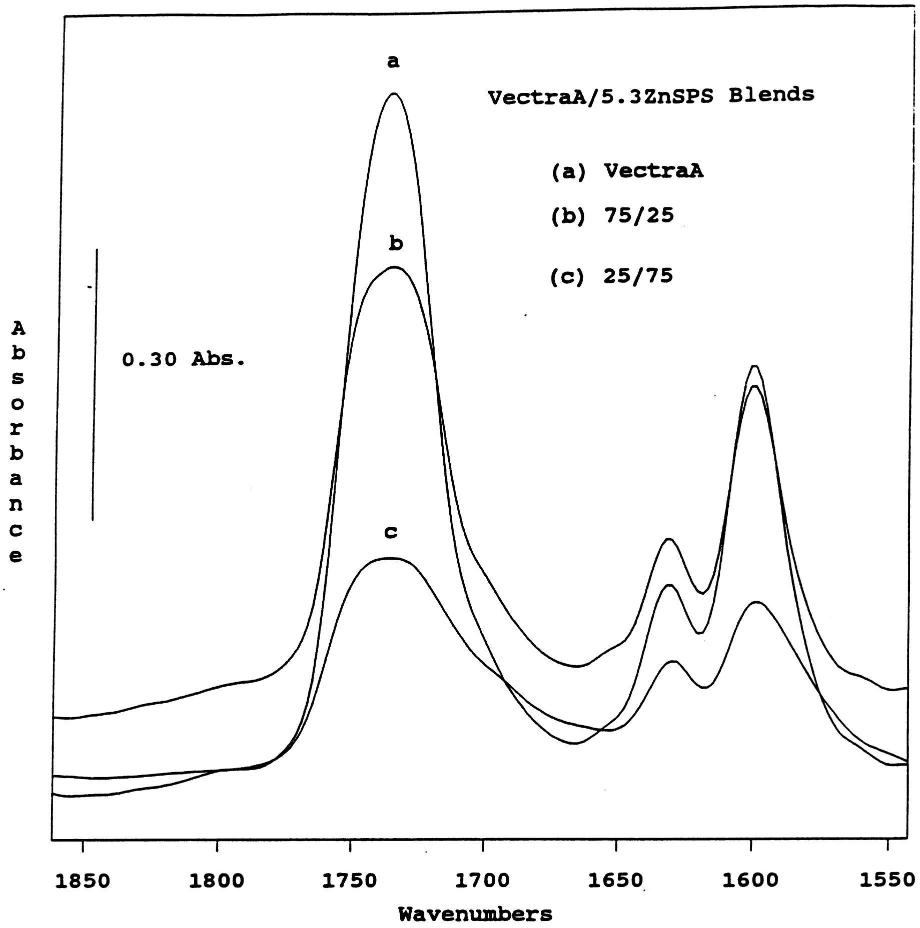

Fig. 6. FTIR spectra of LCP and blends with 5.3Zn-SPS showing the spectral region characteristic of the carbonyl stretching vibrations.

observed only for a small range of copolymer compositions—in this case, sulfonation level. We have previously reported that the copolymer effect is responsible for miscibility between SPS ionomers and polycarbonate [22,23]. It appears that miscibility of the ionomer with the Vectra LCP is due to a similar mechanism, and these results represent, to our knowledge, the first instance where intrapolymer repulsive effects are responsible for mixing between relatively flexible and rigid-chain polymers. Presumably, this mechanism may also provide a unique method for compatibilizing LCP with other thermoplastic polymers, as was demonstrated in Ref. [12].

### *3.1.2. Effect of the ionomer cation: blends of Li-SPS with Vectra® A*

Whereas blends of 5.3ZnSPS and Vectra® A were judged to be miscible on the basis of a single $T_g$ measured by DSC and a single tan $\delta$ peak observed by DMTA, blends of Vectra® A with the lithium salt (5.3LiSPS) of the same SPSwere immiscible. $E'$ and tan $\delta$ of the component polymers and a 60/40 (LCP/ionomer) blend are shown in Fig. 7. In contrast to the blends containing the zinc salt (cf. Figs. 2 and 7), the blend with the lithium salt exhibits two loss dispersions, a distinct peak at 122°C and a shoulder at ca. 105°C. The latter corresponds to the temperature for the tan $\delta$ maximum for the neat LCP and, therefore, it was attributed to a pure LCP phase. The 122°C peak for the blend is at a little lower temperature than that for the neat 5.3LiSPS ionomer, and based on the Fox equation, it corresponds to a phase with a composition of ca. 77 wt% ionomer and 23% LCP. Therefore, it appears that the LCP had some solubility in the ionomer, but the Li-salt of SPS was not soluble in the LCP.

The striking change in the miscibility of the LCP and the 5.3SPS ionomers that resulted from simply replacing the $Zn^{2+}$ cation with $Li^{+}$ demonstrates the strong effect the ionic environment of the sulfonate group has on miscibility. Similar effects have been previously observed in ionomer blends in which miscibility results from either specific intermolecular interactions [24] or from the copolymer effect [22]. For the latter type of blend, one would expect that a miscibility window would exist for the LCP/5.3LiSPS blends over some range of sulfonation level, which is different than that for the Zn-salt blends. Li-SPS blends with other sulfonation levels were not, however, prepared in this research project, so it is not

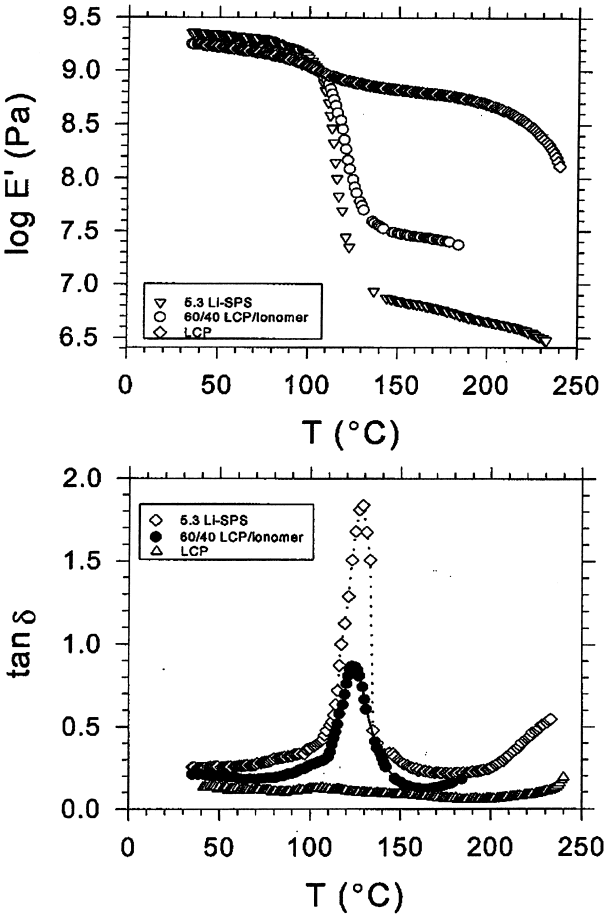

Fig. 7. DMTA behavior of 5.3Li-SPS/Vectra A blends. The tan $\delta$ data for the blend and ionomer are shifted by 0.05 and 0.2 relative to the data for the LCP.

known for what sulfonation levels a miscibility window exists—if one does.

### 3.2. Mechanical properties of 5.3Zn-SPS/Vectra® blends

The tensile properties of the injection molded LCP and blends with 5.3Zn-SPS are given in Table 2. The addition of the ionomer decreased the stiffness of the material, which is expected because the ionomer has a much lower modulus. The ionomer also tended to embrittle the LCP, lowering the tensile strength and the ultimate elongation. The standard deviation of the modulus values was exceptionally high, which may be due to difficulty in gripping samples that were very stiff and relatively brittle. The wide variation in the modulus values suggests that some of the specimens slipped in the grips at the start of the tensile experiment. Generally, the error in the secant modulus measured at 1% elongation was smaller, though the standard deviations of those values were still of the order of 35%. The percent uncertainty of the ultimate properties (strength and elongation) was much lower. That result suggests that the samples were fairly homogeneous, since the ultimate properties are expected to be especially sensitive to any sample imperfections due to molding or concentration heterogeneities.

## 4. Conclusions

Calorimetry and dynamic mechanical thermal analyses indicate that Vectra® A liquid crystalline polymer (a random copolymer of 73% hydroxybenzoate and 27% hydroxynaphthoate) forms miscible blends with the zinc salt of lightly SPS ionomers. No specific intermolecular interactions between the sulfonate and ester groups were detected by infrared analysis. That result and the fact that the miscibility decreased as the sulfonation level of the ionomer was increased from 5.3 to 10.8 mol%, suggests that miscibility in this system is due to the strong intramolecular repulsive interactions that occur between the ionic and non-ionic species in the ionomer.

This apparent mixing of a flexible, coil polymer with a relatively rigid polymer raises questions concerning the effect of the packing on the conformation of the ionomer and packing of the LCP. One might expect that at high ionomer concentrations, the additional combinatorial entropy gained by mixing and the dilution of unfavorable styrene/sulfonated styrene contacts are sufficient to disperse the LCP in the ionomer. At high LCP concentrations, there should be a tendency for the LCP to exclude the ionomer in order to maximize its orientational entropy. However, the strong repulsive interactions between the ionic and non-ionic species along the ionomer chain and the nearest neighbor interactions with the LCP may stiffen the ionomer and give it a more extended conformation. That result might favor its incorporation into an LCP phase, though it would also decrease the conformational entropy of the ionomer. These arguments are merely speculation at this time, but they do suggest that measurements of the effect of the LCP on the chain conformation of the ionomer (e.g. by small angle neutron scattering) may provide some understanding of the thermodynamics of these surprising mixtures.

Table 2
Tensile properties of LCP/ionomer blends

| Composition (wt%) LCP | 5.3Zn-SPS | Modulus (GPa) | 1% Secant modulus (GPa) | Tensile strength (Mpa) | Ultimate elongation (%) |
|---|---|---|---|---|---|
| 100 | 0 | 4023 (2459) | 1321 (488) | 268 (33) | 19.2 (3.2) |
| 95 | 5 | 3562 (1318) | 1364 (298) | 176 (26) | 12.6 (2.2) |
| 90 | 10 | 3150 (1018) | 1254 (265) | 148 (16) | 11.0 (1.3) |

Whereas, the 5.3Zn-SPS was miscible with the LCP at all compositions, the 10.8Zn-SPS was miscible only for ionomer-rich compositions. Limited studies of the lithium salt of the 5.3 mol% SPS indicated that blends of that ionomer with the LCP were only partially miscible. Those blends exhibited two phases: a pure LCP phase and an ionomer-rich phase that contained roughly 25% LCP.

Mechanical measurements of injection molded samples of the 5.3Zn-SPS/LCP blends indicated that the addition of the ionomer decreased the tensile modulus, tensile strength and ultimate elongation of the LCP. The blends were noticeably more brittle than the neat LCP.

## Acknowledgements

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