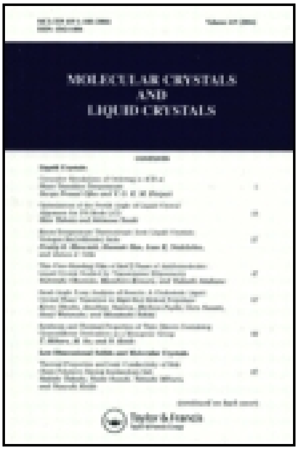

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Randomly Sulfonated Liquid Crystalline Polymers Containing Triad Mesogen of Butylene Terephthalate

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Randomly Sulfonated Liquid Crystalline Polymers Containing Triad Mesogen of Butylene Terephthalate

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A thermotropic liquid crystalline polymer (LCP) containing a terephthaloyl bis(4-oxybenzoyl) (Triad) rigid moiety and a butylene terephthalate flexible unit was solution-polymerized and was subsequently partly sulfonated. It was found that the introduction of sulfonic acid groups to the LCP did not change the position of the DSC peak for the nematic-to-isotropic transition of the LCP ($T_{n\text{-}i}$). However, the sulfonation induced a peak related to the melting of crystalline phase of the Triad domains ($T_{m(T)}$). When the acid groups of the sulfonated LCP were neutralized with NaOH, the $T_{n\text{-}i}$ DSC peak shifted to lower temperatures with a strong decrease in its size, but the $T_{m(T)}$ DSC peak did not change its position strongly. Furthermore, a new peak for the melting of crystalline phase of the butylenes domains ($T_{m(BT)}$) appeared at much lower temperatures. The above results suggested that the sulfonation introduced ionic characters to the TLCP polymer successfully; as expected, it changed the liquid crystalline characters of the TLCP significantly.

Keywords: ionomer; liquid crystalline; mesogen; nematic

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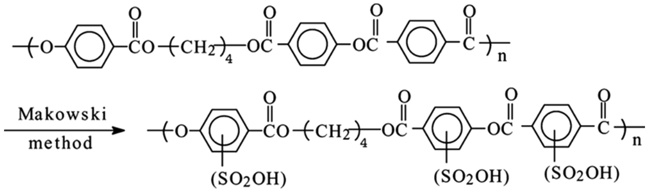
1. INTRODUCTION

Ionomers are polymers that contain a relatively small amount of ionic groups along the relatively non-polar polymer backbone chains [1,2]. In comparison with non-ionic polymers, the ionomers show improved mechanical and physical properties; e.g., high melt viscosity, enhanced dimensional stability, and conductivity. These enhanced properties are caused by the formation of ionic aggregates, i.e., multiplets, in the matrix phase of low dielectric constants. According to the Eisenberg-Hird-Moore (EHM) model for random amorphous ionomers, the multiplets reduce the mobility of chains surrounding them [3]. The size of the single reduced mobility region surrounding the multiplet is assumed to be in the range of ca. 2–3 nm [3]. In addition, the size of the multiplet and restricted mobility region is one of the key factors controlling the physical properties of the ionomers [1,2].

In general, liquid crystalline polymers have either rod-like structures or spherulitic molecular structures and are classified as materials that have the properties of both liquid crystals and polymers, and, thus, exhibit both mesophase characteristic of liquid crystals and many of the useful properties of polymers [4]. The major problem found in common non-ionic liquid crystalline polymers is, however, their very weak interactions between the polymer chains, leading to poor transverse properties of the oriented, extruded polymer samples and weak shear and compressive strengths. This is due to the high stiffness of polymer chains, which results in only few chain entanglements. From these non-ionic liquid crystalline systems, we anticipate only weak disperse forces between the polymer chains. One can find the solution to solve this problem by the introduction of functional groups to the polymer chains to generate specific interactions between the polymer chains. Among the specific interactions, an ionic interaction is the most effective interaction because it is strongest among secondary interactions. Therefore, the synthesis and characterization of liquid crystalline ionomers have been studied extensively [5–16].

The liquid crystalline copolymer containing terephthaloyl bis(4-oxybenzoate) (Triad) mesogen with a butylene terephthalate flexible segment was synthesized by the Group of Lenz [17,18]. This Triad LCP is known as a thermotropic liquid crystalline polymer that shows its liquid crystalline transitions in the temperature range of ca. 250–290°C. In the present work, we prepared new liquid crystalline ionomer system via the synthesis of non-ionic liquid crystalline polymer based on a triad mesogen with a butylene terephthalate flexible segment and the subsequent conversion of this polymer to ionic LCP via sulfonation (see Scheme 1).



SCHEME 1 Synthetic route for the preparation of ionic LCP.

2. EXPERIMENTAL

2.1. Materials

Liquid crystalline polyester (LCP) containing Triad units was prepared using the method reported elsewhere [18]. For homogeneous sulfonation, the method developed by Makowski *et al.* was used to obtain the sulfonated LCP (SLCP) sample [19]. For the readers' convenience, only a short procedure is given below. The LCP was dissolved in a mixture of 1-chloronaphthalene/1,2-dichloroethane, and different amounts of acetyl sulfate were added slowly to the polymer solution to obtain desired degrees of sulfonation. The reaction temperature was kept at 60°C, and the reaction time was 1 h. The samples were recovered by precipitation into hot water, filtered and washed several times with water and subsequently with ethanol. The filtered samples were then dried under a vacuum at 100°C for 1 day. The chemical structure of the acid form of LCP polymer is shown in Scheme 1. To determine the acid contents of the SLCP polymers, the samples were dissolved in a benzene/methanol (9/1/ v/v) mixture to make a 5% (w/v) solution, and titrated with standard methanolic NaOH to the phenolphthalein end point. The acid contents were found to be 0.279, 0.345, and 0.457 mmol/g. For the neutralization of the acid groups of the SLCPs, the predetermined amount of NaOH was added to the polymer in a benzene/methanol mixture. The sodium-neutralized samples (Na-SLCPs) were freeze-dried and dried further under a vacuum at 130°C for 1 day.

2.2. Thermal Property Measurements

For the measurements of the thermal properties of the LCP, SLCPs and Na-SLCP samples, TA differential scanning calorimeter DSC 3000 and Thermogravimetric Analyser TGA 2050 (New Castle, DE) were used. The DSC was calibrated with indium. The sample cell containing ca. 8 mg of a sample was stored under a nitrogen atmosphere.

The samples were scanned from 30°C to 300°C to span the transition temperatures of the samples, and the heating rate was 20°C/min. The DSC data were obtained from the second scan. In the case of the TGA study, the heating rate was 20°C/min, and the samples were heated to 600°C.

2.3. X-Ray Diffraction and Polarized Light Microscopy

The x-ray diffraction (XRD) patterns of the samples were recorded using a PANalytical x-ray diffractometer X'pert PRO MPD (Almelo, the Netherlands). The Cu radiation ($\lambda = 0.1542\,\mathrm{nm}$) was utilized, and the power of the x-ray generator was 40 kV and 30 mA. The scanning speed and the sampling width were 1°/min and 0.05°, respectively. For the morphological study, a Carl Zeiss AG's cross polarized-light microscope (Oberkochen, Germany) equipped with Linkam Scientific Instruments THMS 600 hot stage (Surrey, United Kingdom) was utilized.

3. RESULTS AND DISCUSSION

Figure 1 shows DSC thermograms of the non-ionic LCP, SLCPs and Na-SLCPs. In the case of the LCP, an endothermic peak starts to appear at ca. 275°C, and the peak maximum locates at ca. 290°C that is a so-called isotropic temperature for a phase transition from a nematic liquid crystalline phase to an isotropic liquid, $T_{\text{n-i}}$; the texture type of liquid crystalline phases will be discussed later. This result is in good accotdance with the results reported by the group of Lenz [18]. As expected, the exothermic peak was also detected at ca. 270°C, when

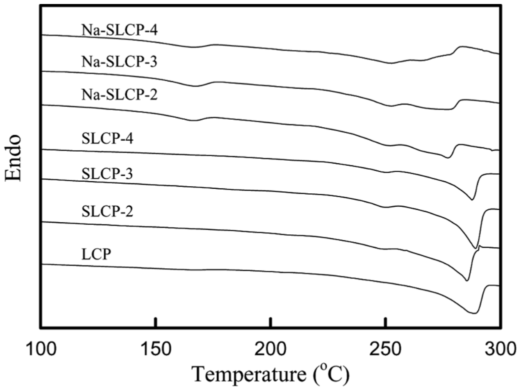


FIGURE 1 DSC thermograms for LCP, SLCP, and Na-SLCP polymers.

the sample in an isotropic liquid form was cooled down to room temperature. The second heating showed the endothermic peak, again, at the same temperature, i.e., ca. 290°C (not shown here).

In the case of the SLCP polymers, the endothermic peak for the nematic-to-isotropic transition is seen at similar temperatures in comparison with to the peak of the LCP. In addition, a weak endothermic peak is shown at ca. 250°C, which is due to the transition of a crystalline phase of the Triad domains to a nematic phase of the polymer ($T_{m(T)}$) [18]. These transition temperatures are listed in Table 1. The positions of the two peaks seem to change only slightly with increasing degree of sulfonation, and the size of the peak at ca. 290°C decreases a little. The presence of the two peaks for the SLCP, instead of only one peak for the LCP, implies that the introduction of the sulfonic acid groups to the LCP results in hydrogen bonding between polymer chains, which, in turn, leads to the formation of the liquid crystalline domains of Triad segments, to some more extent. At the same time, the introduction of the acid groups induces irregularity in a chemical structure of the polymer chain segments, which decreases the degree of the crystallinity of polymers, as a whole. Thus, the size of the $T_{m(T)}$ peak becomes more noticeable, and the $T_{n\text{-}i}$ peak at ca. 290°C, related to the amount of crystalline domains, decreases in its size slightly with increasing degrees of sulfonation.

For the Na-SLCP ionomer system, two peaks related with $T_{n\text{-}i}$ and $T_{m(T)}$ are also observed. In addition to the two peaks, however, a third peak at ca. 165°C is also seen, which is due to the melting of the crystalline domains of butylene terephthalate (BT) moieties [18].

TABLE 1 Contents of the Functional Groups, Melting Temperatures of the Crystalline Regions of BT Units ($T_{m(BT)}$s) and Triad Units ($T_{m(T)}$s), and the Temperatures for Nematic-to-isotropic Transitions ($T_{n\text{-}i}$s), Obtained from DSC Thermograms

Samples	Contents of functional groups (mmol/g)	$T_{m(BT)}$ (°C)	ΔH *(J/g)*	$T_{m(T)}$ (°C)	ΔH *(J/g)*	$T_{n\text{-}i}$ (°C)	ΔH *(J/g)*
LCP	0	–	–	–	–	288.7	18.19
SLCP-2	0.279	–	–	247.0	0.17	285.3	16.70
SLCP-3	0.345	–	–	248.9	1.12	289.1	15.89
SLCP-4	0.457	–	–	249.3	1.62	287.6	11.60
Na-SLCP-2	0.279	166.4	3.59	251.2	2.82	276.7	8.09
Na-SLCP-3	0.345	165.9	3.63	249.2	2.60	274.3	7.21
Na-SLCP-4	0.457	165.6	3.85	251.5	4.10	266.9	4.43

It is seen that the position of the $T_{\text{n-i}}$ peak shifts to low temperatures significantly and that upon neutralization it moves to lower temperatures slowly as the ion content increases; in addition, the size of the peak becomes smaller. However, the position of the $T_{\text{m(T)}}$ peak seems to be unchanged at ca. 250°C. At this point, it should be mentioned that the presence of the three peaks for the Na-SLCP ionomers indicates that the neutralization results in the formation of the crystalline domains of BT moieties, to some extent, in addition to the crystalline domains of Triad moieties,. This can be understood. In the case of SLCPs, only the H-bonding between polymer chains leads to the formation of crystalline domains containing Triad moieties. However, the BT units, rather flexible sequences, do not form crystalline domains easily. Once the acid groups are neutralized with NaOH, the interactions between the ionic groups of polymer chains would make polymer chains close together. Then, the polymer chains have more chance to form crystalline domains containing BT units. At this point, it should be mentioned that ionic interactions between polymer chains reduce the mobility of chains significantly. Thus, it is not easy for the polymer chains to form a nematic phase in the temperature range for the LC behavior. As a result, the position of the $T_{\text{n-i}}$ peak shifts to lower temperatures strongly, and the size of the $T_{\text{n-i}}$ peak decreases with increasing ion contents.

Shown in Figure 2 are the photomicrographs with crossed polarizers of the LCP, SLCPs, and Na-SLCPs, taken at the temperature where the polymers showed typical liquid crystalline textures. In the case of the LCP, showing a typical nematic liquid crystalline texture (see Fig. 2(a)), it shows a birefringence at ca. 250°C, and flow behavior at ca. 275°C, and becomes an isotropic liquid at ca. 320°C. In the cases of SLCP polymers, also giving rise to a nematic liquid crystalline texture (see Figs. 2(b), (c) and (d)), the polymers show a birefringence at ca. 240°C and flow behavior at ca. 265°C, and become an isotropic liquid at ca. 310°C. In comparison with Figures 2(b) and (d), it is seen that the increasing amounts of acid groups in the SLCPs reduce slightly the size of the regions that show liquid crystalline behavior. In the cases of Na-SLPCs, at ca. 160°C the ionomers give rise to a nematic liquid crystalline texture (see Figures 2(e), (f) and (g)) and flow behavior at ca. 225°C, and the ionomers became an isotropic liquid at ca. 280°C. Figures 2(e), (f) and (g) show that the size of the liquid crystalline phases of Na-SLCP ionomers decreases strongly upon neutralization. These slight and strong decreases in the size of the liquid crystalline phases of the SLCP and Na-SLCP polymers, respectively, found in photomicrographs are in good accordance with the relative sizes of the DSC $T_{\text{n-i}}$ peaks of the corresponding polymers.

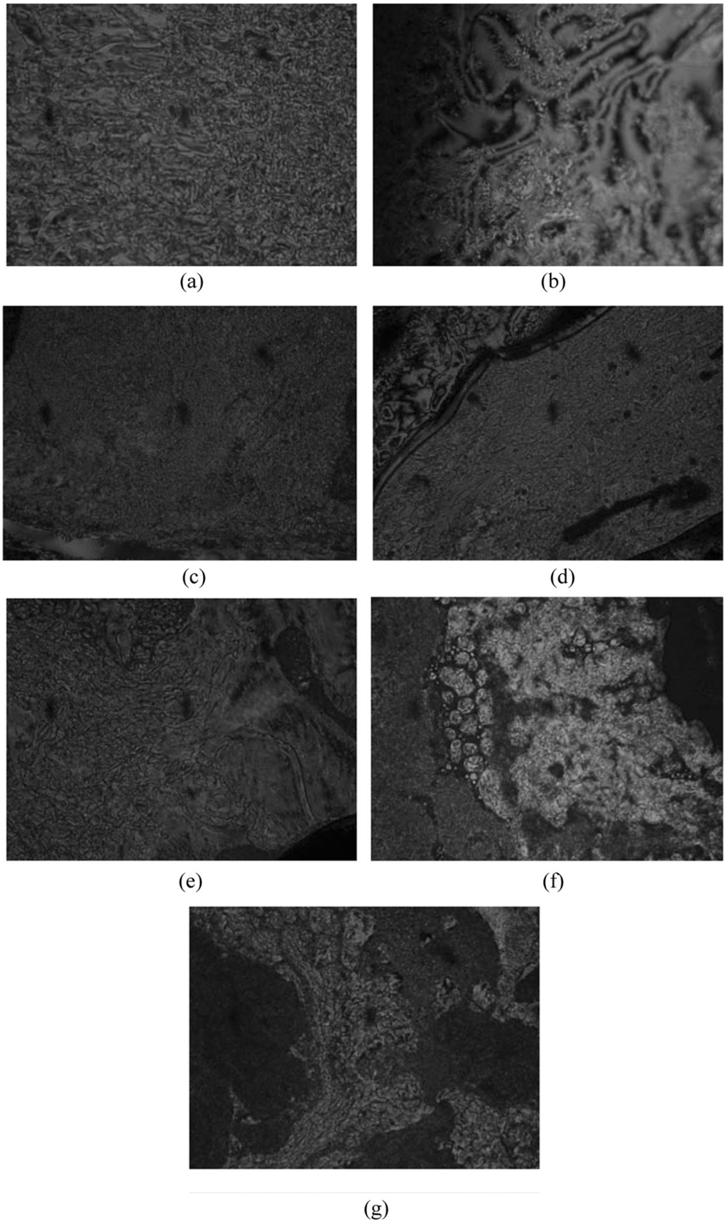


FIGURE 2 Photomicrographs with crossed polarizers of (a) LCP, (b) SLCP-2, (c) SLCP-3, (d) SLCP-4, (e) Na-SLCP-2, (f) Na-SLCP-3, and (g) Na-SLCP-4 polymers.

Shown in Figure 3 are the x-ray diffraction (XRD) patterns of the LCP, SLCP, and Na-SLCP polymers. It is seen that the LCP polymer shows XRD peaks at $2\theta = 18°$, $23°$, and $27°$. Generally, it is known that nematic liquid crystalline materials show XRD peaks mainly in the angle (2θ) range 17°–30°. Thus, the XRD results of the LCP in the present study support that the LCP has, indeed, a nematic liquid crystalline phase. In the case of the SLCPs, the XRD peaks in their positions and sizes are very similar to those of the LCP. In the case of Na-SLCP ionomer, however, even though the positions of the peaks are the same, the sizes of the peaks are relatively smaller than those of the LCP and SLCPs. At this point, it should be mentioned that the same positions of the XRD peaks imply that the structures of the polymer chains in the crystalline domains are identical. The decreasing size of XRD peak, however, indicates that the amount of the liquid crystalline domains decreases. Again, the trend in the XRD peak sizes is in good accordance with those found in both the DSC results and the photomicrographs, as mentioned above. This implies that the introduction of the acid group to the LCP and the neutralization affect the liquid crystalline behavior of the polymer slightly and strongly, respectively.

Figure 4 shows the weight loss of the samples studied here as a function of temperature. The temperatures of 5% weight loss ($T_{\text{d-5\%}}$) are listed in Table 2 that also includes the temperatures at which the maximum loss rate occurred ($T_{\text{d-max}}$), and the weight percentages of the sample residue at 550°C. First of all, the $T_{\text{d-5\%}}$ of the SLCPs decreases with increasing acid contents. This might be due to the fact

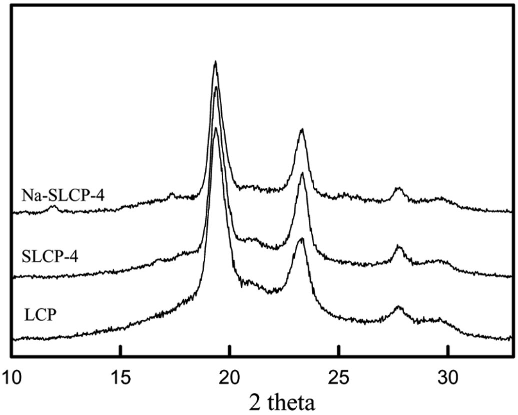


FIGURE 3 XRD patterns of LCP, SLCP-4, and Na-SLCP-4 polymers.

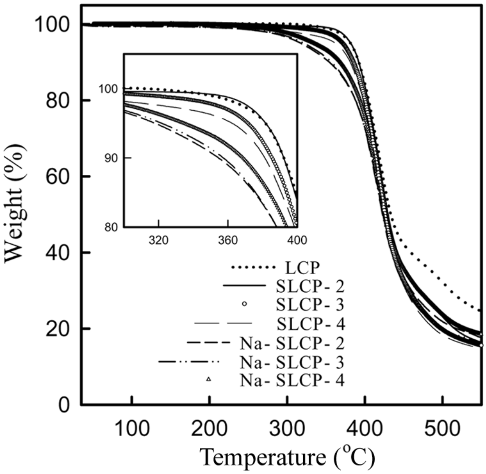


FIGURE 4 TGA results of LCP, SLCP, and Na-SLCP polymers.

that the presence of sulfonic acid groups in polystyrene is known to initiate thermal decomposition above 200°C [20]. Thus, in the present work, the decreasing $T_{d\text{-}5\%}$ of SLCPs with increasing acid contents can be understood. In the case of Na-SLCP ionomers, they start to decompose at lower temperatures than the LCP and SLCPs and the $T_{d\text{-}5\%}$ decreased drastically from ca. 382°C for the LCP to 318°C for Na-SLCP-2 and then increased to ca. 335°C for Na-SLCP-4 with increasing ion contents. At this point, we do not have any clear explanation for this finding. However, it is worth recalling that once the acid groups are neutralized with NaOH, the amounts of liquid crystalline domains decrease significantly. The $T_{d\text{-max}}$s of all the samples remain more or less constant at 419 ± 2.5°C. These thermal degradation results along with the DSC and XRD results suggest that the

TABLE 2 Thermogravimetric Analysis of the LCP Polymer, SLCP Copolymers and Na-LCP Ionomers

Samples	$T_{d\text{-}5\%}$ (°C)	$T_{d\text{-max}}$ (°C)	Residue at 550°C (%)
LCP	381.6	421.8	24.6
SLCP-2	381.8	420.5	14.7
SLCP-3	371.4	420.0	15.1
SLCP-4	362.4	415.1	15.5
Na-SLCP-2	317.8	419.3	15.9
Na-SLCP-3	321.6	419.2	17.5
Na-SLCP-4	334.6	415.1	18.5

$T_{\text{d-5\%}}$ is related with the amount of crystalline domains as a whole, and the $T_{\text{d-max}}$s is dependent mainly on the chemical structure of the LCP polymer backbone chains.

4. CONCLUSIONS

This study showed that the sulfonation of the LCP copolymer gave ionic characters to the LCP polymer successfully. At the same time, the ionization of the LCP changed the liquid crystalline character of the TLCP significantly; i.e., the formation of crystalline regions containing either Triad units or BT units and the disruption of the LC phase as a whole.

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