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Synthesis, structure, and mesomorphic properties of main-chain liquid-crystalline ionomers containing sulfonate groups

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Abstract The mesogenic monomer M and a series of main-chain liquid crystalline ionomers (LCIs) containing sulfonate groups were synthesized. The LCIs were prepared by an interfacial condensation reaction of mesogenic monomer 1,4-phenylene-dicarbonic acid bis (4-carboxyl phenyl) ester, brittle yellow (BY), 1,10-sebacoyl dihydroxy, and 1,12-dodecanedioyl dihydroxy. The sulfonate groups introduced to the main-chain backbone were confirmed by ultraviolet spectroscopy. The mesomorphic properties were investigated by differential scanning calorimetry (DSC), thermo gravimetric (TG), and polarizing optical microscopy (POM). Experimental results demonstrated that the glass-transition temperatures increased slightly, melting temperature decreased, and the mesophase temperature ranges increased first and then decreased with increasing content of sulfonate group. All of the polymers were thermally stable up to 320 °C. The LCI$_n$s exhibited typical nematic schlieren textures.

Introduction

Nowadays, many studies have received great attention for liquid-crystalline polymer (LCP) because of their high modulus, strength, and stiffness [1–3]. However, a major shortcoming is the large anisotropy of the mechanical properties that leads to weak transverse properties in oriented molding [4]. The second shortcoming is their poor interfacial adhesion with other thermoplastic polymers [5]. One approach for improving their transverse properties and their adhesion with other polymer is to introduce specific functional groups into LCP molecules. Recently, many articles [6–8] have been devoted to the functionalization of LCP with ionic groups. The aim of the work was to combine the self-organization properties of LCPs and of ionomers. On the one hand, they show a behavior analogous to that of isotropic ionomers, i.e., the formation of cluster of ionic groups that belongs to different polymer and the formation of a temporary network structure. Ionic functional groups also offer the possibility for strong physical intermolecular interactions through hydrogen bonding, or ion-dipole associations, complexes based of polysalt formation, in the case of polymers or polymer pairs possessing acid and basic groups. On the other hand, the liquid crystalline gives rise to an organization by ordering of mesogenic fragments [9–15].

It is of interest to investigate how the ionic interactions modify liquid crystalline, liquid-crystalline structure, and overall morphology of the LCP. Zhang and Weiss [9, 10] utilized interfacial polymerization methods for the preparation of liquid-crystalline polyester ionomers with flexible spacers. In previous studies, we reported the synthesis of a series of main-chain thermotropic LCIs containing sulfonate group [13, 16, 17]. In this article, we reported the synthesis of a series of main-chain LCIs containing sulfonate ionic monomer, which were prepared by mesogenic monomer 1,4-phenylene-dicarbonic acid bis (4-carboxyl phenyl) ester, brittle yellow (BY), 1,10-sebacoyl dihydroxy, and 1,12-dodecanedioyl dihydroxy. Their characterizations by UV spectroscopy, DSC, TG, and POM were presented. The effect of ionic aggregation on the mesomorphism, thermal stability, and textures were discussed.

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Experimental

Material

4-hydroxy-benzoic acid was purchased from Beijing Chemical Co. (Beijing, china). Terephthalic dichloride, Tetrahydrofuran (THF), pyridine, thionyl chloride, chloroform, and *N*, *N*-dimethylformanide (DMF) were obtained from Shenyang Chemical Co. (Shenyang, china). Brittle yellow was obtained from Beijing Chemical Industry Company (Beijing china). 1,10-sebacoyl dihydroxy and 1,12-dodecanedioyl dihydroxy were purchased from Zibo Guangtong Chemical Limited Company (Shandong, china). Pyridine and chloroform were purified by distillation over KOH before using.

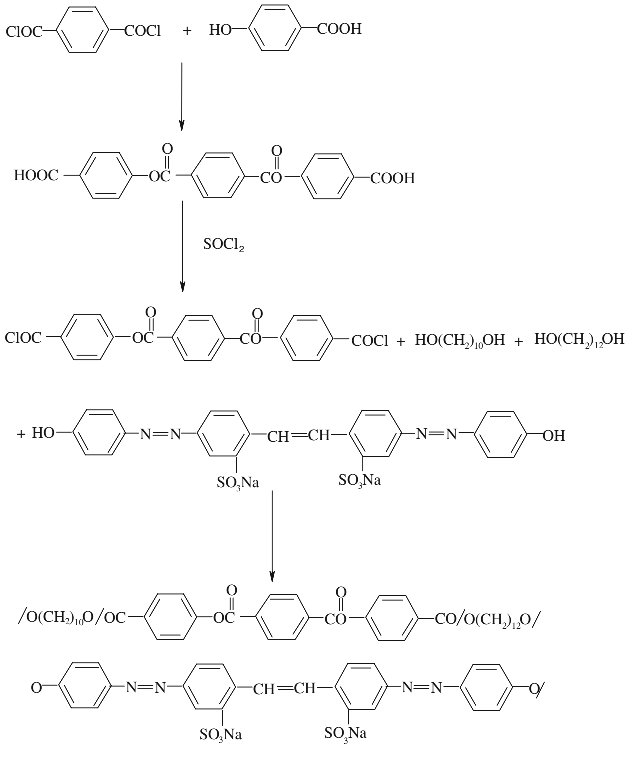
Monomer synthesis

The synthetic routines of monomers (M) are shown in Scheme 1. Terephthalic dichloride (0.1 mol) was dissolved in THF (40 mL), slowly added to a solution containing 4-hydroxy benzoic acid (0.2 mol), pyridine (20 mL), DMF (5 mL), and then was reacted for 1 h at room temperature. The mixture was heated at 60 °C in a water bath for 5 h. The mixture was washed with ether for three times and filtrated to obtain 1,4-phenylene-dicarbonic acid bis (4-carboxyl phenyl) ester. (Monomer M). Yield: 30 g (74%); m.pt: 268 °C.

IR (KBr): 3438 (–OH); 2668, 2547 (–COOH); 1740, 1689(C=O); 1605, 1509 (Ar–), 1266 cm^{-1} (C–O–C).

^{1}H NMR (CDCl3, TMS, δ, ppm): 7.36–8.29 (m, 12H, Ar–*H*); 4.8 (s, 2H, –COO*H*).

^{13}C NMR (CDCl3, TMS, δ, ppm): 172.0 164.7 (4C, C=O); 130.5, 121.3, 130.0 (12C, tert. C); 127.4, 158.3, 135.8 (6C, quat. C).



Scheme 1 Synthesis pathways of monomers and LCI$_n$s

Polymer synthesis

The synthetic routines are shown in Scheme 1. The chloride of the monomer M was prepared by *M* (20 mmol) and thionyl chloride (20 mL) containing 1 drop of *N*, *N*-dimethyl formanide (DMF). The mixture was refluxed in a round flask equipped with an absorption instrument of hydrogen chloride at 65 °C. The excess thionyl chloride was removed under reduced pressure to obtain the chloride of the monomer M. All polymers synthesized are listed in Table 1. For synthesis of polymer LCI$_0$–LCI$_6$, the same method was adopted. The synthesis of LCI$_6$ is given as an example. Monomer A (9.2 mmol), monomer B (9.2 mmol), and BY monomer C (1.6 mmol) were dissolved in 50 mL of pyridine and 10 mL of DMF. The mixture was stirred to obtain solution, and then it was added to the chloride monomer M that was dissolved in chloroform (50 mL) at 70 °C for 5 h. The solution was cooled and washed with ethanol for many times. After filtration, the product was dried at 80 °C for 8 h in vacuum to obtain 30 g of polymer at a yield of 68.4%.

Characterization

IR spectra were measured using a Perkin–Elmer spectrum (Perkin–Elmer Instruments, Wellesley, MA), as KBr pellets. The UV spectra of solutions of the LCI$_n$s in *N*, *N*-dimethylformamide (1 g/L) were measured with a Perkin–Elmer model 950 UV–Vis spectrometer. Thermal-transition temperatures were determined with a differential scanning calorimetry (DSC) 204 (Netzsch instruments) equipped with a liquid nitrogen cooling system at a heating and cooling rate of 20 °C/min in a nitrogen atmosphere. The reported thermal-transition temperatures were collected during the second heating cycle. The textures of the liquid-crystalline phase were observed with a Leica DMRX polarizing optical microscope (POM) equipped with a Linkam THMS-600 hot stage. Dilute solution viscosity measurements were carried out in pyridine/dimethylsulfoxide (volume ratio 1:1) solution at 25 ± 0.1 °C using Ubbelohde capillary viscometer, NO.2-0.59. The flow times were sufficiently long, i.e., >100 s, so that kinetic energy corrections were neglected.

Table 1 Polymerization

Sample	Feed					Polymer	
	M (mmol)	BY (mmol)	Sebacoyl dihydroxy(mmol)	Dodecanedioyl dihydroxy (mmol)	BY (%)	Yield a(%)	η (dL/g)
LCI_0	20	0	10	10	0	88.6	0.91
LCI_1	20	0.02	9.99	9.99	0.1	86.4	0.89
LCI_2	20	0.1	9.95	9.95	0.5	82.1	0.74
LCI_3	20	0.2	9.9	9.9	1	76.5	0.63
LCI_4	20	0.6	9.7	9.7	3	73.4	0.57
LCI_5	20	1	9.5	9.5	5	70.2	0.46
LCI_6	20	1.6	9.2	9.2	8	68.4	0.22

Results and discussions

Polymerization

The results of polymerization experiments were summarized in Table 1. The yield and the intrinsic viscosity of LCI series decreased with the increasing content of BY, which might be the reason that once the BY reacted, the chain ceased to grow, which would leave the BY primarily at the chain ends. That is, addition of the hydrophilic BY pulls the growing chain into the aqueous phase and by doing so, removes the reactive end from the interface. As a result, the reactive end of the chain cannot react further with the acid chloride monomers in the oil phase [9, 10]. This hypothesis is explained by the fact that the yields and the inherent viscosities of polymer decreased with increasing content of BY in the feed.

UV spectroscopy

Figure 1 exhibited the UV absorption spectra of LCI series in the region $\lambda = 300–800$ nm. The LCI_ns containing BY showed two absorption at $\lambda = 340$ nm and $\lambda = 420$ nm. The first absorption peak was due to the conjugative effect of N=N and benzene, the second absorption peak was attributed to the BY of the LCI_ns [17]. The absorbance intensity of the peak increased with increasing BY content in the reaction batch. The UV analysis showed that the amount of BY in the LCI_ns increased with increasing amount of BY in the reaction batch. We are sure that the increase of the absorbance intensity of the peak ($\lambda = 420$ nm) was not due to the BY monomer because BY monomer is soluble in the methanol, and the LCI_ns were washed repeatedly with fresh methanol until the filtrate was clear and colorless, which showed that BY monomer was washed away. Base on the above analysis, we are sure that the increase of the absorbance intensity of the peak ($\lambda = 420$ nm) was due to the increase of BY content in the LCI_ns. The UV result not only showed successful incorporation of BY groups, but also verified that the amount of BY in LCI_ns increased with the increase of BY in the feed.

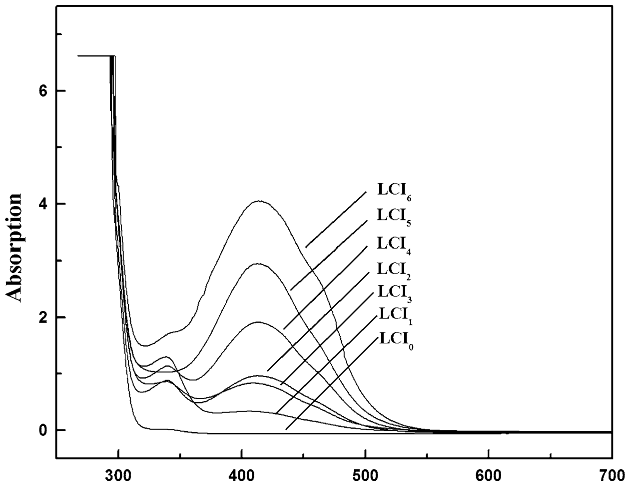


Fig. 1 UV absorption spectra of LCIs as a function of sulfonate content

Thermal analysis

The thermal transition of the LCIs was measured by DSC by heating the samples from 0 to 250 °C, then cooling to 20 °C at 20 °C/min. Their phase-transition temperatures and corresponding enthalpy changes, obtained on the second heating and first cooling scan, are summarized in Table 2. According to the data in Table 2, the glass-transition temperature of LCI_0–LCI_6 increases with an increase in BY contents slightly. The glass-transition temperature (T_g) is an important parameter in connection with structures and properties of polymer. The glass-transition temperature (T_g) is an important parameter in connection with structures and properties of polymer. T_g is affected by many factors such as molecular weight, chain flexibility, and interchain interactions. In general, T_g decreases with the molecular weight. It was proposed that the ionic monomer exhibits two opposing influences on the stability of the liquid-crystalline phase [16]. One aspect is that T_g decreases with an increasing pendant concentration in the

Table 2 Phase-transition temperatures of the LCIs

Sample	T_g (°C)	T_m (°C)	ΔH_c (J/g)	$T_{5\%}$ (°C)	ΔT^a (°C)
LCI_0	58.1	101.9	1.284	350.4	248.5
LCI_1	58.3	95.3	1.042	356.0	260.7
LCI_2	59.7	93.8	0.574	355.1	261.3
LCI_3	59.6	92.7	0.67	341.4	248.7
LCI_4	60.0	91.9	0.649	331.9	240
LCI_5	61.2	91.5	0.719	333.2	241.7
LCI_6	61.5	88.4	0.696	320.8	232.4

[a] The mesomorphic temperature range ($\Delta T = T_{5\%} - T_m$)

LCI_ns, which is due to the large free volume occupied by the polymer chains. The polymer chains containing pendant sulfonate group occupied a large volume and could not pack closely, and the single bond provide easy internal rotation. The other aspect is that T_g increases with an increasing salt group concentration, which attributes to intermolecular ionic interactions. All these factors interact, which consequently result in the minor change of T_g with the increase of BY content in LCI_ns.

Figure 2 shows the effect of BY content on the phase-transition temperatures of the LCI_ns. The results are summarized in Table 2. In general, the peak temperatures and the heats of transition decreased with increasing BY contents, which partly attribute to the decrease in molecular weight. Table 1 illustrates the inherent viscosities of LCI_ns decrease with increasing BY content, i.e., the molecular mass of the LCI_ns decreased with the increasing of BY content. Besides, there may also have been an influence of the sulfonate groups in disrupting the molecular order. In Table 2, the melting temperature (T_m) of LCI series decreases with the increase of BY content, which may be partly due to the decrease of molecular mass, the large free volume of the pendant concentration also has an effect. No clearing temperature (T_i) values were observed before all LCI_ns were carbonized in DSC themogram. Textures seen under POM did not disappear until the LCIs were carbonized; therefore $T_{5\%}$ (the temperature at which 5% mass loss occurred in TGA) was adopted as the final temperature of the mesophase in the present study (because the mesogenic phase is meaningless after the LCIs decompose). The mesogenic region $\Delta T = T_{5\%} - T_m$ increased from 248.5 °C for LCI_0 to 261.3 °C for LCI_2 when the content of BY increased from 0 to 0.5 mol% and then decreased from 261.3 °C for LCI_2 to 232.4 °C for LCI_6.

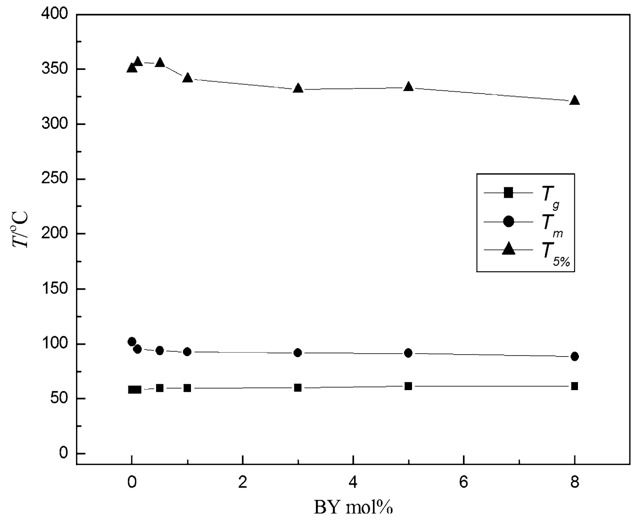


Fig. 2 Effect of BY content on the phase-transition temperatures of the LCI_ns

The thermal stability of LCI_ns is usually detected with TGA. The percent mass loss at various temperatures in tabulated in Table 3. The temperature at which 5% mass loss occurred decreased with increase of the BY content, and the mass loss enhanced with increase of the BY content at 300 °C and 400 °C, respectively, which was consistent with other reported article [16]. The thermal stability of the ionomers decreased with an increasing BY content, which may attribute to the decreased molecular weight for the introduction of the ionic groups.

Texture analysis

The textures of the LCIs observed by POM are shown in Fig. 3. The samples were placed on glass plates, covered with a glass slide, and observed by POM using the hot stage of the microscope in order to obtain their liquid-crystalline behavior and thermo-optical properties. All of the LCIs exhibit thermotropic LC properties during heating and cooling. When the LCI_0 sample is melted at 103 °C, only a small portion (thin section) of sample transmits light and exhibits image with schlieren texture in fine scale, while a large portion (thick section) of the sample is opaque. The cover glass is then pressed down, along with a slight manual shear force, to confirm relatively homogeneous thin films. When LCI_0 was heated to 109 °C, the

Table 3 TG results of the LCIs

Sample	$T_{5\%}$(°)	Weight loss (%)		
		300°	350°	400°
LCI_0	350.4	1.43	5.04	18.16
LCI_1	356.0	1.3	4.25	17.52
LCI_2	355.1	0.88	4.13	18.56
LCI_3	341.4	1.51	6.36	20.27
LCI_4	331.9	1.98	8.22	22.83
LCI_5	333.2	2.03	7.56	23.23
LCI_6	320.8	2.73	10.46	26.94

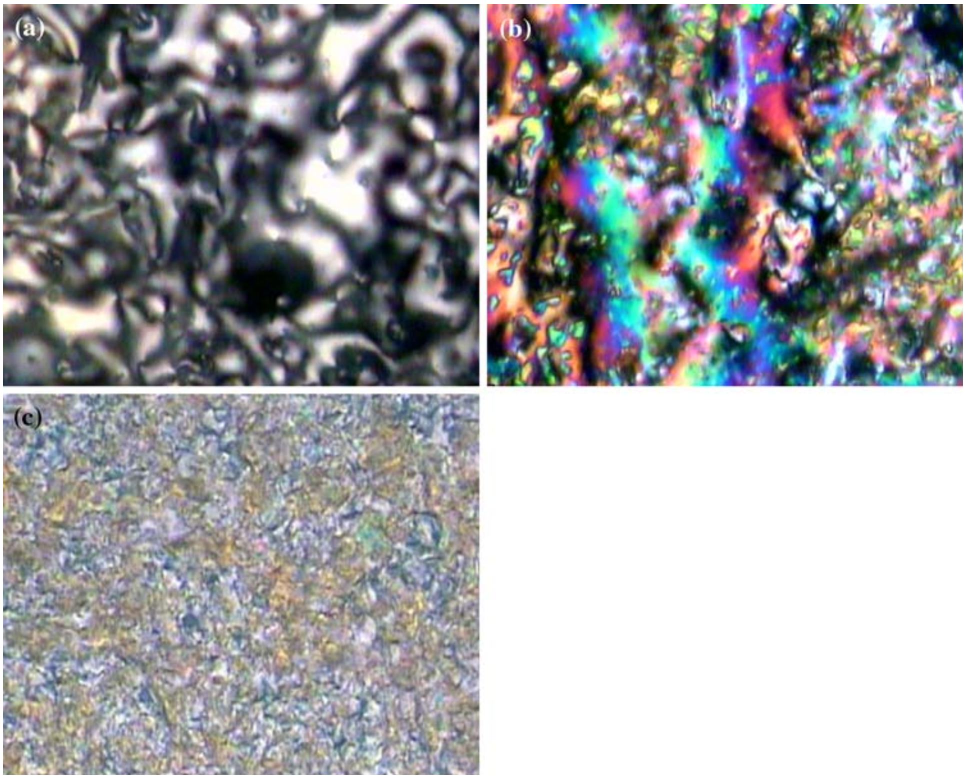


Fig. 3 Optical textures of LCI$_n$s. **a** LCI$_0$ on heating to 248 °C. **b** LCI$_1$ on heating to 209 °C. **c** LCI$_5$ on heating to 192 °C

crystals disappeared completely and turned into a schlieren texture in Fig. 3a. Texture did not disappear until the LCI$_0$ was carbonized. This result is also consistent with the DSC results, which show no nematic to isotropic transition on the thermograms under the thermal-degradation temperature.

In the case of LCI$_{1–5}$ containing sulfonate group, even though all melt-quenched films exhibit nematic schlieren texture, the size and patterns of these texture are different as shown in Fig. 3b and c. Compared to the LCI$_{1–5}$, the LCI$_0$ without sulfonate group shows a more homogeneous structure that contains schlieren texture. This type of clearly defined optical texture with a fine scale is well known for main-chain thermotropic copolyesters. For the LCI$_{1–5}$, the randomness and size scale of textures increase with the increase of the ionic content. The sulfonate groups in the polymer structures influence the LC behavior of the polymers. The ions aggregate in domains due to their electrostatic interactions, thus forcing an increase in chemical structure inhomogeneities associated with an increase of ionic monomer content. The textures were also observed for ionomer LCI$_6$ by POM, but also no clear photos could be taken, i.e., the liquid-crystalline properties of the LCIs were somewhat weakened as the concentration of sulfonate increased to higher than 5 mol%. Therefore, this result shows that the addition of the ionic group to the main chain doesn’t change the texture of the original polymer.

Conclusions

We have synthesized a series of main-chain LCIs containing sulfonate group. The LCI$_n$s were prepared by an interfacial condensation reaction of mesogenic monomer (1,4-phenylene-dicarbonic acid bis (4-carboxyl phenyl) ester, 1,10-sebacoyl dihydroxy, 1,12-dodecanedioyl dihydroxy, and brittle yellow (BY content between 0 and 8%)). UV spectroscopies determined the sulfonate group of BY introduced to the main-chain liquid-crystalline backbone. The liquid-cytstalline properties were characterized by DSC, TGA, and POM. The LCI$_n$s exhibited a broad mesogenic range of 110–320 °C and good thermal stability up to 330 °C. The glass-transition temperature increased slightly with increasing the sulfonate content. However, the melting temperature decreased with increasing the sulfonate content. The liquid-crystalline mesogenic regions of the LCI$_n$s became broad first and then narrow with increasing sulfonate content. They were main-chain LCIs with nematic schlieren textures. Besides, the liquid-crystalline properties of the LCI$_n$s were somewhat weakened as the concentration of sulfonate increased to higher than 5%.

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