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Liquid Crystals

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Synthesis and characterization of a novel liquid crystal-bearing ionic mesogen

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A new ionic liquid crystal bearing a sulphonate group in the mesogenic core, potassium 2-allyloxy-5-cholesteryloxycarbonylbenzenesulphonate, was synthesized. Its chemical structure was determined by various techniques including FTIR and ^{1}H NMR. Its liquid crystalline properties were characterized by DSC, POM and SAXS; it exhibits a smectic C mesophase. In dielectric constant measurements a maximum $\Delta\varepsilon$ value of -43.0 D was obtained at 210°C. The morphology of this ionic liquid crystal indicated a slant array of ionic mesogenic units under a static electric field.

1. Introduction

Liquid crystal (LC) phases combine the long range order of crystals with the mobility of liquids. Their formation from molecules with anisotropic forms, so-called mesogenic groups, has long been known for low molar mass liquid crystals (LMMLCs). These thermodynamically stable LC phases exist in a temperature range between the crystalline phase and the isotropic melt. Because novel LC materials possess a great potential for use in electronics and optics, many LMMLCs have been synthesized [1–4]; they have attracted interest for applications in the fields of non-linear optics, optical storage and electro-optic displays [5–7].

Alignment in response to an external field is a defining property of LMMLCs; it may be caused by mechanical shearing, or induced by a thin film surface, an electric field or a magnetic field [8, 9]. Electric field-induced alignments are based on the dielectric anisotropy of liquid crystal molecules. It is enhanced by long range orientation order along the molecular axis in the LC phase [10]. The efficiency of electric field-induced alignment in LC molecules is dependent upon the magnitude of dielectric anisotropy of the molecules, molecular mobility and the direction and voltage of the applied electric field. In some cases, the electric field can also change arrangements of the chain alignment from originally aligned LC samples.

Recently, much attention has been paid to ionic thermotropic LC compounds. Some stilbazole-type metal –containing LCs and pyridinium type ionic LC compounds have been reported [11–13]. We are currently developing ionic LMMLCs to investigate the effect on LC behaviour of introducing ionic groups into the mesogenic core.

Ions exist in abundance in the mesophase, and these positive and negative charges tend to move under the influence of the electric field. This motion, in turn, changes the field and exerts forces on the melt [14]. In this system, the vector summation of the dipoles of mesogens and ionic groups leads to a permanent dipole moment, which has a fixed relationship with respect to the molecular axis. This results in a combination of mesomorphic orientational ordering and strong orienting forces due to ions in electric fields. This leads to dynamic scattering and, a substantial reduction in the magnitude of external fields due to the strength of the ionic orienting force [15].

One would like to know the fundamental link between the ionic aggregation found in LMMLCs and the behaviour of the liquid crystalline phase in terms of molecular order and stability. It is also of interest to investigate how the ionic interactions modify liquid crystallinity, liquid crystalline structure and overall morphology of the LMMLCs. In the present study, therefore, we have prepared a novel ionic low molar mass liquid crystal, potassium 2-allyloxy-5-cholesteryloxycarbonylbenzenesulphonate.

2. Experimental

2.1. *Characterization*

Fourier transform infrared spectroscopy (FTIR) of the synthesized liquid crystalline monomer and intermediates in the solid state were obtained by the KBr method

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performed on a Nicolet 510P FT IR Spectrometer. ^1H NMR (300 MHz) spectra were obtained with a Varian WH-90 NMR spectrometer with Fourier transform, using dimethyl sulphoxide-d$_6$ (DMSO-d$_6$) or $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard.

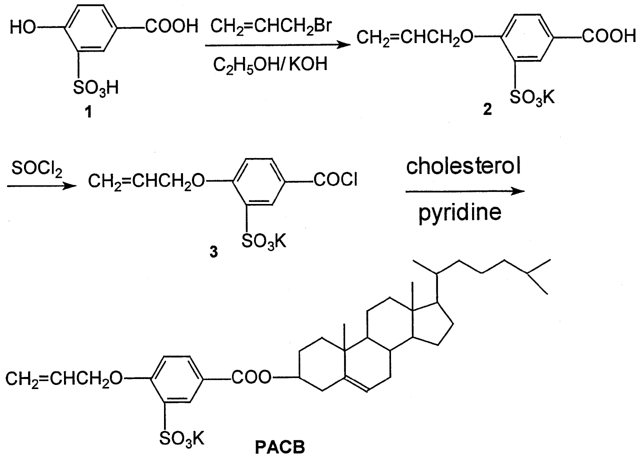
Thermal transition properties were characterized by a TA Instruments V2.3C at a heating rate of 10°C min^{-1} under nitrogen. Visual observation of liquid crystalline transitions under crossed polarizers light was made by a Leits Laborlux S polarizing optical microscope (POM) equipped with a THMS-600 heating stage.

Dielectric constants were measured by a Hewlett Packard 4140B impedance analyser, with a Mettler FP80 hot stage in the presence of a magnetic field of 3.0 kG. Small angle X-ray scattering (SAXS) measurements were performed using CuK$_\alpha$ (λ=1.542 Å) radiation monochromatized with a Ni filter and a totally reflecting glass block (Huber Small-angle Chamber 701). Intensity curves were measured using a linear position-sensitive detector (Mbraun OED-50M).

2.2. *Synthesis*

3-Bromopropene, p-hydroxybenzoic acid, sulphuric acid, potassium iodide, potassium hydroxide and cholesterol were obtained from Beijing Chemical Company and used without further purification. Pyridine, thionyl chloride, ethanol, chloroform, potassium iodide, hydrochloric acid and methanol were purchased from Shenyang Chemical Co. All solvents were purified by standard procedures. The synthesis of the ionic liquid crystalline monomer and intermediates is shown in the scheme.

2.2.1. 4-Hydroxy-3-sulphobenzoic acid, 1. 4-Hydroxy-3-sulfo-benzoic acid was synthesized according to a reported procedure [16].



Scheme. Synthesis of the ionic liquid crystalline monomer.

2.2.2. Potassium 2-allyloxy-5-carboxylbenzenesulfonate, 2. 3-Bromopropene (24.3 g, 0.21 mol) and compound **1** (44.0 g, 0.20 mol) were dissolved in 100 ml ethanol. This was added dropwise to a solution of potassium hydroxide (44.0 g, 0.79 mol) and 0.2 g potassium iodide in 55 ml water, and the reaction mixture stirred at 85°C for 16 h. After cooling to room temperature, the mixture was poured into 100 ml cold water and acidified with hydrochloric acid. The precipitate was isolated by filtration and dried in a vaccum oven. Recrystallization from water gave white crystals of potassium compound **2** yield 62%, m.p. 218–219°C. IR (KBr, cm^{-1}): 3080(=C–H); 2928,2856(CH_3– and –CH_2–); 2680–2510 (–OH in –COOH); 1698 (C=O); 1605, 1504, 1270, 1230, 1209,1121, 1050, 630 (S–O stretching). ^1H NMR (DMSO-d$_6$, δ/ppm): 4.83–5.07 (d, 2H), 5.67–5.78 (m, 1H), 6.08–6.19 (m, 2H), 7.23–7.27 (d, 1H), 8.24–8.32 (d, 1H), 8.57 (s, 1H).

2.2.3. Potassium 2-allyloxy-5-cholesteryloxycarbonylbenzenesulphonate, PACB. Compound **2** (16.0 g, 0.056 mol), 80 ml of thionyl chloride and 1.0 ml of pyridine were mixed and stirred at room temperature for 2 h; the mixture was then heated to 60°C and held for 24 h in a water bath to ensure completion of the reaction. Excess thionyl chloride was distilled off under reduced pressure; 100 ml of cold pyridine was then added to the residue at 20°C to obtain a pyridine solution of potassium 2-allyloxy-5-chlorocarbonylbenzenesulfonate (**3**). This solution was added dropwise to a solution of cholesterol (22.0 g, 0.056 mol) in 60 ml pyridine. The mixture was reacted at 80°C for 28 h, cooled, poured in 200 ml of cold water and acidified with hydrochloric acid. The precipitated crude product was filtered, dried, recrystallized from chloroform and dried overnight under vacuum to five potassium 2-allyloxy-5-cholesteryloxycarbonylbenzenesulphonate (**PACB**) as a brown powder in 61% yield. IR (KBr, cm^{-1}): 2931, 2853, 1702, 1604, 1505, 1268, 1216, 1121, 1026, 755, 619. ^1H NMR (DMSO-d$_6$, δ/ppm): 0.82–0.98 (t, 12H), 1.32–1.58 (m, 24H), 1.85–2.09 (m, 2H), 2.20–2.38 (m, 2H), 2.49–2.54 (m, 2H), 2.81–3.01 (m, 2H), 4.94–5.22 (m, 3H), 5.63–5.89 (m, 1H), 6.09–6.20 (m, 2H), 6.73–6.85 (t, 1H), 7.15–7.24 (m, 2H).

3. Results and discussion

3.1. *FTIR and ^1H NMR spectra*

The structure of PACB was confirmed by FTIR analysis with the following characteristic absorptions (cm^{-1}): 3051 (=C–H stretching), 2931, 2853 (C–H aliphatic), 1702 (C=O stretching in ester modes), 1604, 1505 (aromatic skeleton stretching), 1268, 1216, 1121, 1026, 755 (=C–H out of plane bending), 619 (S–O stretching). For organic sulphonates, the FTIR absorption range of the O=S=O asymmetric and symmetric stretching modes lies in the regions 1120–1230 and 1010–1080 cm^{-1}, respectively; that of the S–O stretching mode lies in the range 600–700 cm^{-1}. Because of the overlap found for both asymmetric and symmetric stretching bands of SO_2 with C–O stretching bands in the monomer under study, the S–O stretching mode is chosen for identification of sulphonate groups in this ionic liquid crystal [17].

The structure of the ionic liquid crystal PACB was also determined by use of ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum shows characteristic chemical shifts at (δ values) 0.82–0.98, 1.32–1.58 and 1.85–3.01 ppm for CH_3, $-CH_2-$, and –CH– groups on cholesteryl units; 4.94–5.22 and 5.63–5.89 ppm for protons on vinyl group; 6.09–6.20 ppm corresponding to $-CH_2O-$; and 6.73–6.85 and 7.15–7.24 ppm signals identifying the aromatic protons.

3.2. *Liquid crystalline behaviour*

The LC phases of the ionic liquid crystal PACB under investigation were characterized by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Under DSC the ionic monomer PACB displayed a smectic C mesophase (figure 1). The samples were placed on glass plates, covered with a glass slide, and observed under hot stage POM for their liquid crystalline behaviour and thermo-optical properties. Transition temperatures thus obtained were corroborated by thermal data gained from DSC.

The heating cycle thermogram of PACB contains two endotherms of phase transition. A large endotherm with enthalpy of 60.6 J g^{-1} at 139°C indicates the crystalline to smectic phase transition. The small endotherm at 238°C denotes the transition of the SmA phase to the isotropic state accompanied by decomposition of the sample. When heated on the hot stage of the polarizing microscope, the monomer PACB appeared crystalline/SmA, see figure 2 (*a*); it developed into a broken focal-conic and fan-shaped texture of the SmA phase, (figure 2 (*b*)). When the sample was heated continuously, the decomposition was preceded by isotropization.

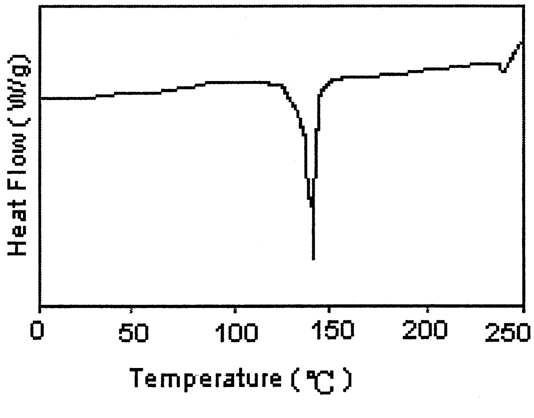
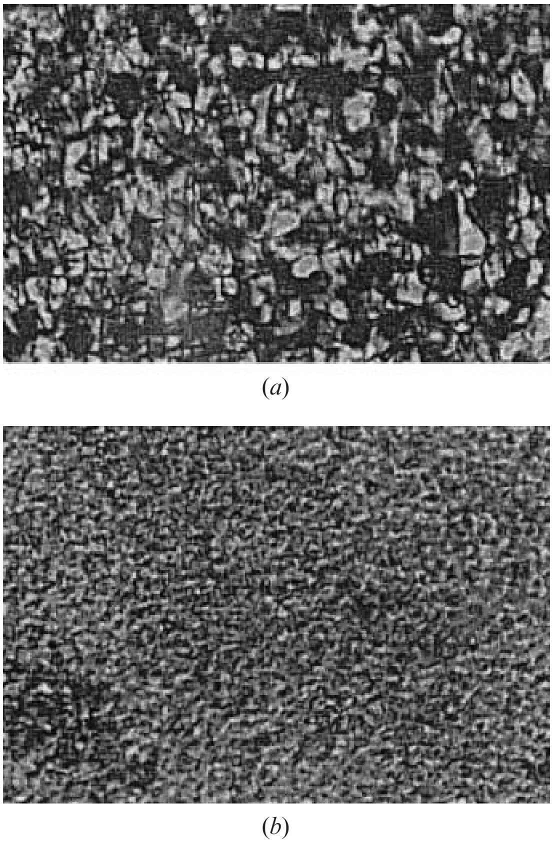


Figure 1. DSC thermogram of PACB on the second heating (10°C min^{-1}).

In PACB, the smectic nature of the LC phase is characterized by the presence of reflections at q=1.50 nm^{-1} in the SAXS profile as shown in figure 3 (*a*), clearly revealing the lamella structure of the sample. The stacking periods d measured are 42 Å.

3.3. *Measurement of dielectric constant*

It is known that LC molecular alignments depend on their molecular dielectric anisotropy. Two principle dielectric constants, $\varepsilon_{\parallel}$ parallel and $\varepsilon_{\perp}$ perpendicular to the molecular axis, can be recognized. The dielectric constant difference, $\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$, represents the dielectric anisotropy of LC molecules. These dielectric constants are determined by the detailed chemical structure of the


(*a*)

(*b*)

Figure 2. Polarizing optical micrographs for PACB at (*a*) 158°C, (*b*) 236°C (200 ×).

molecules in which each polar chemical bond possesses a dipole [18]. When the molecules are uniaxially oriented, the vector summation of all the dipoles attributed to each chemical bond becones a permanent dipole moment, which has a fixed relationship with respect to the molecular axis. If there is a permanent dipole moment parallel or nearly parallel to the long molecular axis, the dipole can be oriented efficiently by an electric field along the chain axis. But an electric field normal to the chain axis has only a weak effect on the dipole. Thus, in this case, $\Delta\varepsilon > 0$ and molecules favour an alignment parallel to the electrostatic field. If a molecule has a permanent dipole moment that is more or less perpendicular to the molecular axis, the molecules then favour an alignment perpendicular to the direction of an electrostatic field since $\Delta\varepsilon < 0$.

In order to determine the dielectric anisotropy of the ionic liquid crystal PACB, $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ were measured with varying temperature, as listed in the table. The maximum values of dielectric constant difference was −43.0 D at 210°C. It exhibits negative dielectric anisotropy. For ionic liquid crystalline systems bearing ionic mesogens, the vector summation of the dipole of mesogens and the sulphonate groups becomes a permanent dipole moment. In this system, the dipole moment would be perpendicular to the molecular axis due to the strong polarity of the ionic groups.

3.4. *Morphology of the ionic liquid crystal under a static electric field*

The study of electric field-induced orientation has previously been performed on LMMLCs [19–21]. While an understanding of the interaction of the liquid crystalline and the ionic aggregates is still at an early stage, their electric field-induced orientability makes them interesting in academic research and applications. Among the many factors that can affect the orientation process, it is of interest to know the correlation between the macroscopic orientation and the intrinsically oriented microstructure which characterizes the mesophases in LMMLCs. Since the random incorporation of ionic groups results in a perturbation of the microstructure, it is necessary to investigate the morphology of ionic LMMLCs in order to reveal the effects of ionic groups on electric field-induced orientation.

Table. Dielectric constants of the ionic liquid crystal PACB.

	Dielectric constant		
Temperature/°C	$\varepsilon_{\|}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
30	2.71	3.01	−0.30
60	2.73	3.12	−0.39
90	2.81	3.25	−0.44
120	2.84	3.54	−0.70
150	2.92	40.33	−37.41
180	2.98	43.10	−40.02
210	3.01	46.08	−43.07
240	3.50	3.51	−0.01

X-ray experiments permit the determination of both the structure of the ionic liquid crystal PACB oriented under a static (d.c.) electric field and that of an unoriented sample. The unoriented PACB was heated to isotropization, cooled at about 0.5°C min^{-1} to its texture forming temperature and quenched, afterwards measuring by SAXS; the oriented PACB sample was cooled from the isotropic state with static electric field intensity of 2 kV cm^{-1} and quenched. The small angle X-ray scattering profiles of the ionic PACB samples are shown in figure 3. A common feature of both profiles is the presence of a peak at small angles, indicating the smectic nature of the LC phase. In addition, the appearance of shoulder peaks suggests a supramolecular organization of the multiplets. However, there are some differences. For unoriented PACB, the smectic nature of the LC phase is characterized by the presence of reflections at $q=1.50\,\mathrm{nm}^{-1}$ in the SAXS profile as shown in figure 3 (*a*), and the stacking period d is measured at 42 Å. For the sample treated under a static electric field, the reflection occurs at $q=1.73\,\mathrm{nm}^{-1}$ corresponding to a d-spacing of 36 Å. Furthermore, the intensity of the reflection is stronger than that of the unoriented PACB, indicative of a higher degree of order.

In the unoriented ionic PACB, the interaction of ions forms ionic clusters. In the meantime, the liquid crystal molecules array alternately to form a smectic layer of 42 Å spacing. The proposed structure is depicted in

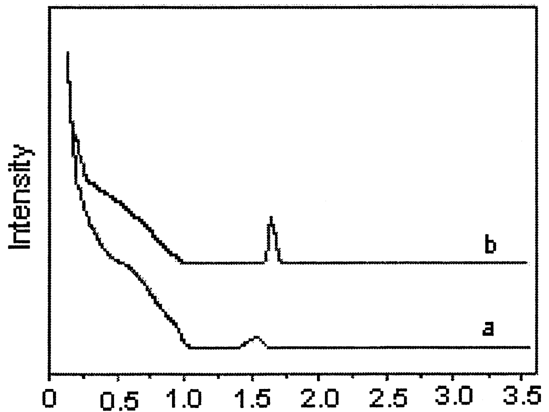
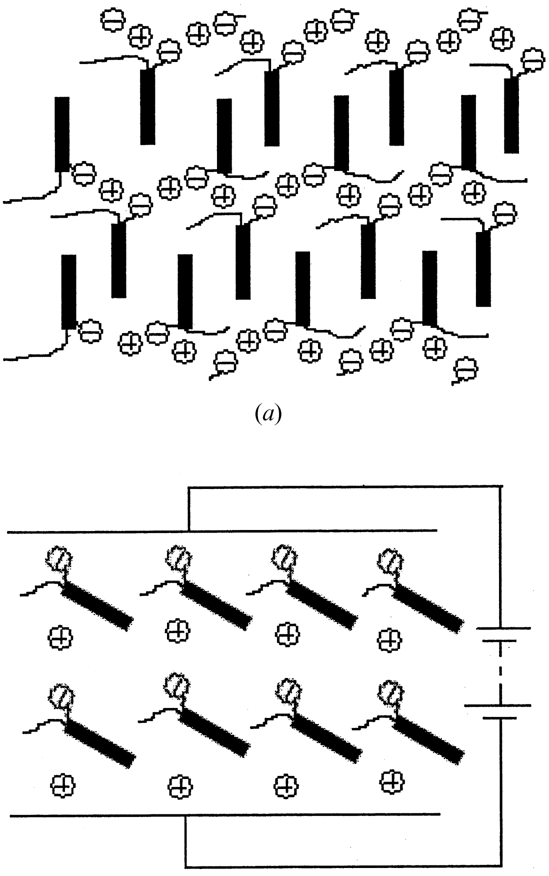


Figure 3. SAXS profiles of the ionic monomer PACB for (*a*) an unoriented sample and (*b*) a sample under a static electric field.


(*a*)

(*b*)

Figure 4. Schematic structures for (*a*) unoriented ionic liquid crystalline PACB and (*b*) the sample oriented under a static electric field.

figure 4 (*a*). In the sample oriented under an electric field, the oriented arrays of liquid crystal molecules would be perpendicular to the electric field due to their negative dielectric anisotropy. On the other hand, the movement of ions located in the ionic mesogens under the electric field results in a slant array of the mesogenic units, resulting in a smectic layer of 36 Å spacing, with a higher degree of order. The proposed schematic structure is shown in figure 4 (*b*).

4. Conclusion

One of the most obvious advantages of liquid crystalline systems bearing ionic mesogens is their polar structure, which would be sensitive towards both electric and magnetic fields, leading to the feasibility of applications in electro-opic displays. In these systems, the mesogens lead to mesomorphic orientational ordering, with strong orienting forces due to ions in electric fields. We have synthesized a novel kind of liquid crystal 2-allyloxy-5-cholesteryloxycarbonylbenzenesulphonate bearing an ionic mesogenic group containing sulphonate groups. Its chemical structure was determined by FTIR and ^{1}H NMR spectrum; its liquid-crystalline properties by DSC, POM and SAXS. Dielectric constant measurements exhibited negative dielectric anisotropy with a maximum $\Delta\varepsilon$ of -43.0 D at 210°C. The ionic liquid crystal was with the help of an oriented sample under a static (d.c.) electric field to determine its morphology under this field. Ions exist in abundance in the mesophase, tending to move under the influence of the electric field. In this system, mesomorphic orientational ordering is formed by mesogens under strong orienting forces due to ions in an electric field.

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