Synthesis and properties of new ionic liquid crystals based on para-nitroazobenzene with substitution vinylimidazolium ion group

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A new series of ionic liquid crystals (ILCs), 1-(4-(4-nitrophenylazo)phenyloxy) vinyl-3-methyl-1H-imidazol-3-ium bromide salts (C n, n = 6, 10) were synthesised. Their chemical structures were determined by 1H NMR, 13C NMR, UV spectroscopy and elemental analysis. The liquid crystalline properties were investigated by differential scanning calorimetry, polarising optical microscopy, and powder X-ray diffraction. These measurements showed that C n (n = 6, 10) exhibit smectic liquid crystalline phases with focal-conic fan-shaped textures. The introduction of vinylimidazolium group onto the azobenzene enhances the thermal stability of the smectic state, which play an important role in forming the smectic layer structure.

Keywords: azobenzene derivatives; ionic liquid crystal; smectic phase; vinylimidazole

1. Introduction

Liquid crystalline materials have attracted increasing attention due to their extensive applications in such as organic electronics (1), optoelectronic devices (2), biological medical fields and non-linear optics (3, 4), etc. Ionic liquid crystals (ILCs) are a class of liquid crystalline compounds containing anions and cations, which possess both properties of ionic liquids (ILs) and liquid crystals (LCs) (5–11). ILs show many useful properties, such as a very low vapour pressure, high thermal stability, non-flammability, high chemical stability, high ionic conductivity and a wide electrochemical window, and may serve as a new generation of solvents in synthesis, catalysis, separation, and electrochemistry (12–14). Vinylimidazolium salts have received increasing attention since they were first reported in 1973 (15). For example, they have served as good electrolytes in dye-sensitised solar cells (16, 17) due to their high charge density and mobility, and also have been used in combination with lithium salts as ion-conductive matrices, which provide a high ionic conductivity (18). Azobenzene units have been widely used as a mesogenic group in LCs. The liquid crystalline materials containing azobenzene chromophores are easily induced through trans–cis–trans isomerisation cycles by irradiating with linearly polarised light (19, 20). Incorporation of vinylimidazolium ion functionalities into paraffin side-chain-terminated azobenzene derivatives could lead to a new series of ILCs materials for research and industrial applications, such as azobenzene derivatives with a broad mesophase range, which are promising for high-density optical data storage and photochemical devices (21, 22). In addition, the presence of a vinyl moiety makes these azobenzene derivatives polymerisable, often yielding polymerisable ILs (23). The behaviour of polymerisable ILs that contain mesogenic groups has previously only been investigated by a few groups (24, 25).

In this paper, vinylimidazolium ion group-functionalised nitrophenylazo with different alkyl chain lengths are reported in detail. We described the synthesis of these compounds and the characterisation of their thermotropic liquid crystalline properties; moreover, the influence of ionic interaction between imidazolium salt on the mesomorphic properties was also explored. These result showed that the attached vinylimidazolium units induce the self-assembly of ILs and, therefore, the occurrence of liquid crystalline phases. The introduction of the vinylimidazolium group enhances the thermal stability of the smectic state, which plays an important role in forming the smectic layer structure.

2. Experimental details

2.1 Synthesis of compounds C n

The synthetic strategy is shown in Scheme 1. The following are typical synthetic procedures. The intermediates A and B n were first prepared as previous

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Scheme 1. Synthetic route of compounds C_n.

reported (26, 27). Their structures were confirmed further by 1H NMR.

2.1.1 Compound A

1H NMR (400 MHz, CDC13): 8.37 (d, J = 59.6 Hz, 2H, Ar-H), 7.96 (t, J = 59.0 Hz, 4H, Ar-H), 7.00 (d, J = 58.6 Hz, 2H, Ar-H), 5.36 (s, 1H, Ar-OH).

2.1.2 Compound B

1H NMR (400 MHz, CDCl3), (ppm, from TMS): 8.36 (d, J = 8.1 Hz, 2H, Ar-H), 7.95–7.99 (m, 4H, Ar-H), 7.02 (J = 8.4 Hz, 2H, Ar-H), 4.05–4.12 (m, 2H, OCH2), 3.44 (m, 2H, CH2Br), 1.83–1.89 (m, 4H, CH2), 1.43–1.56 (m, 4H, CH2).

2.1.3 Compound B

1H NMR (400 MHz, CDCl3): 8.37 (d, J = 59.0 Hz, 2H, Ar-H), 7.95–7.99 (m, 4H, Ar-H), 7.01 (d, J = 58.6 Hz, 2H, Ar-H), 4.04–4.08 (m, 2H, OCH2), 3.39–3.43 (m, 2H, CH2Br), 1.83–1.85 (m, 4H, CH2), 1.48–1.54 (m, 4H, CH2), 1.26–1.32 (m, 8H, CH2).

2.1.4 1-(4-(4-nitrophenylazo)phenyloxy)hexyl-1H-imidazole-3-ium bromide salts C6 and C10 compounds

Vinylimidazole (1.882 g, 0.02 mol) was placed in a double-necked flask equipped with a reflux condenser. A suspension of B6 (8.125 g, 0.02 mol) in 10 ml of chloroform was added dropwise to vinylimidazole, while the suspension became a solution. After heating to reflux 72 h and then cooling to room temperature, 20 ml of chloroform was added. The crude product was precipitated by addition of excess hexane, then recrystallised by ethanol and finally dried under vacuum giving pure C6 as a yellow solid. Yield 90%, m.p.133.5°C. 1H NMR (400 MHz, CDCl3): 11.43 (s, 1H, imidazolium ring), 8.36–8.34 (m, 2H, Ar-H), 7.94–7.99 (m, 4H, Ar-H), 7.50 (1H, s, imidazolium ring), 7.47–7.41 (m, 1H, CH=C), 7.31 (s, 1H, imidazolium ring), 7.02–7.00 (m, 2H, Ar-H), 5.95–5.90 (m, 1H, C=CH2), 5.45–5.43 (m, 1H, C=CH2), 4.48–4.45 (t, 2H, N-CH2), 4.09–4.06 (t, 2H, OCH2), 2.06–2.02 (m, 2H, CH2), 1.87–1.83 (m, 2H, CH2), 1.6–1.2 (m, 4H, CH2).
As shown in Scheme 1, the intermediates A and B were first prepared according to literature methods (26, 27). C were prepared by the addition reaction of vinylimidazole and B. The structures of the intermediates and the final compound were confirmed by spectroscopic analysis.

3. Results and discussion

3.1 Synthesis

3.2 Liquid crystalline properties

The phase behaviour of C compounds was examined by DSC, POM and XRD. Figure 1(A) displays polarised optical micrographs of compound C in the mesophase, which shows focal-conic fan-shaped textures in the cooling runs. The liquid crystalline properties of C were similar to the C. Figure 1(C) and (D) show focal-conic fan-shaped textures in micrographs of compound C in the mesophase, which displays focal-conic fan-shaped textures in both heating runs and cooling runs. Moreover, a pseudo-homeotropic area coexisted with focal-conic fan-shaped texture and, under shearing, only pseudo-homeotropic texture appeared, indicating enantiotropic SmA behaviour. These observations confirmed that the introduction of a thermotropic mesogenic para-nitroazobenzene moiety to vinylimidazole gives a liquid crystalline phase. Figure 1(B) displays polarised optical micrographs of compounds C at 156°C in the second heating scan. We cannot conclude that the molecules are in the smectic A phase from these optical textures. The phase transition temperatures, as well as the phase transition enthalpy changes, of C will be further determined using DSC.

No liquid crystalline phases were detected in B, while C exhibits smectic phases by the covalent incorporation of imidazolium ion groups into B. Thus the ionic interaction between imidazolium salts can induce mesomorphism. Furthermore, the SmA phases by the covalent incorporation of imidazolium ion groups into B. Thus the ionic interaction between imidazolium salts can induce mesomorphism. Furthermore, the SmA phases by the covalent incorporation of imidazolium ion groups into B. Thus the ionic interaction between imidazolium salts can induce mesomorphism. Furthermore, the SmA phases by the covalent incorporation of imidazolium ion groups into B. Thus the ionic interaction between imidazolium salts can induce mesomorphism. Furthermore, the SmA phases by the covalent incorporation of imidazolium ion groups into B. Thus the ionic interaction between imidazolium salts can induce mesomorphism. Furthermore, the SmA phases by the covalent incorporation of imidazolium ion groups into B. 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the second heating run, though there is no exothermic peak on the first heating run, which is due to the recrystallisation of the sample. The ionic liquids based on imidazolium salts are difficult to crystallise from the liquid crystalline state. The crystallisation cannot be easily observed for either C$_6$ and C$_{10}$ on the cooling run, even with a cooling rate of 5°C min$^{-1}$. This feature was also confirmed by the POM observation that the focal-conic fan texture could be preserved to room temperature. A similar phenomenon was also reported for other ionic LCs with imidazolium moieties (30). Generally, ionic liquids based on imidazolium salts are difficult to crystallise from the liquid state or mesophase (31); a supercooled state with partial crystallisation which is characteristic of polymer materials can often be observed in the case of the low molar mass imidazolium salt derivatives (32).

Combined with the results of DSC and POM, we can conclude that the mesomorphic structures are SmA. All the transitional temperatures and associated enthalpies are summarised in Table 1.

### 3.3 Mesophase structure of C$_6$

In order to evaluate the molecular arrangements in their mesophases, XRD was performed on C$_6$ at 130°C during the cooling scan. The theoretical molecular length of C$_6$ estimated from the molecular model created using CS Chem3D Ultra 8.0 software was 24.53 Å (Figure 3(A)). Figure 3(B) shows the XRD patterns of C$_6$ in the mesophase (at 130°C).

The XRD pattern of C$_6$ at 130°C shows one sharp diffraction peak in the small-angle region, implying the formation of a layered structure. On the other hand, a broad diffraction peak is observed in the wide-angle region with d-spacings of 4.0 Å, which indicates a liquid-like arrangement of the molecules within the layers. The d-spacing based upon the sharp peak (~3.0°) in the small-angle region is estimated as ca. 29.41 Å, which is about 5 Å longer than the calculated molecular lengths. Therefore, the smectic layer of C$_6$ would consist of an interdigitated structure formed by the mesogens. The d-spacing values and the observation of a focal-conic fan texture indicated that the molecules of C$_6$ would be a SmA arrangement in their liquid crystalline phases.

Combining the results of the theoretical calculation and experimental observations, the possible molecular packing mode for C$_6$ in the smectic phase could be proposed. As shown in Scheme 2, C$_6$ neighbouring mesogenic groups overlapped each other and the azobenzene groups are facing each other in the lateral direction. The interdigitated structure of the azobenzene derivatives in the SmA phase would be
dependent upon the spacer length and the counter anion of imidazolium salt. The imidazolium salt parts became associated to form a smectic layer (SmA), and all the layers are further linked with the imidazolium ions through electrostatic interactions (33). We believe that the organisation of the imidazolium salt parts contributes to the formation of the smectic layer structure through electrostatic interactions.

Table 1. Phase-transition temperatures and corresponding enthalpies of $C_n$ (kJ mol$^{-1}$, in parentheses) determined by DSC (second heating and cooling cycle, 5°C min$^{-1}$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition $^a$</th>
<th>$T$/°C heating ($\Delta H$ / kJ mol$^{-1}$)</th>
<th>Transition</th>
<th>$T$/°C cooling ($\Delta H$ / kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6$</td>
<td>$C_{r1}$–$C_{r2}$</td>
<td>151.8 (15.3)</td>
<td>Iso–SmA</td>
<td>143.4 (5.5)</td>
</tr>
<tr>
<td></td>
<td>$C_{r2}$–Iso</td>
<td>177.8 (59.6)</td>
<td>SmA–$C_{r1}$</td>
<td>84.1 (17.1)</td>
</tr>
<tr>
<td>$C_{10}$</td>
<td>$C_{r}$–SmA</td>
<td>150.0 (95.6)</td>
<td>Iso–SmA</td>
<td>159.4 (8.1)</td>
</tr>
<tr>
<td></td>
<td>SmA–Iso</td>
<td>161.5 (7.6)</td>
<td>SmA–Cr</td>
<td>40.8 (16.3)</td>
</tr>
</tbody>
</table>

Notes: Abbreviations: Cr: crystal; SmA: SmA liquid crystal; Iso: isotropic phase.
Figure 4. UV-vis spectra of (A) B₆ and (B) C₁₀ compounds in chloroform.

Table 2. XRD data of C₁₀ and C₆ (here, SmA: SmA phase).

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Molecular length (l) (Å)</th>
<th>Temperature (°C)</th>
<th>Layer spacing (d) (Å)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆</td>
<td>24.53</td>
<td>130</td>
<td>29.42</td>
<td>SmA</td>
</tr>
<tr>
<td>C₁₀</td>
<td>30.43</td>
<td>145</td>
<td>31.52</td>
<td>SmA</td>
</tr>
</tbody>
</table>

ₐ Calculated molecular length by Chemdraw.
₇ Measured temperatures.

XRD patterns of compound C₁₀ are similar to those of C₆. One sharp peak is observed in the small-angle region, and a broad peak in the wide-angle region of the XRD pattern. Data for layer spacings (d) and molecular lengths (l) of Cₙ in their mesophases are summarised in Table 2.

### 3.4 UV-vis spectra

The optical properties of Cₙ were also analysed; UV–vis spectra in CHCl₃ solution are shown in Figure 4 (the concentrations were ca. 10⁻⁴ M). The compounds all exhibit their absorption maximum at ca. 378 nm which are related to π–π* transitions of the azobenzene trans-cis configuration (34). The spectra of B₆ and B₁₀ exhibit their maxima at 437, 438 and 439 nm, respectively, and the UV–vis spectra of Cₙ is similar to Bₙ. These UV results suggest that the imidazolium salts have no influence on the arrangement of the azobenzene groups.

### 4. Conclusions

In conclusion, a series of monomers Cₙ have been synthesised and characterised by DSC, POM, XRD, and UV–vis measurements. Results showed that C₆ and C₁₀ exhibited monolayer SmA phase textures. Ionic interaction between imidazolium salts and the flexible chain plays an important role for the stabilisation of the smectic phases. They are both difficult to crystallise from the mesophase during the cooling scan. Their SmA mesophases can be maintained even to room temperature. This finding may contribute to the development of novel anisotropic materials for high-density optical data storage (35, 36). The monomers of Cₙ have been polymerised by a free-radical mechanism, and the thermal behaviour of the resulting cross-linked polymers will be reported in our other paper.

### References


