LIQUID CRYSTAL BEHAVIOR AND PHOTO-INDUCED BIREFRINGENCE IN AZOBENZENE SURFACTOMESOGENS COMPLEXED WITH OPPOSITELY-CHARGED POLYELECTROLYTES

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Introduction

Over the past decade and more, a wide variety of supramolecular side-chain liquid crystal polymers (SCLCP’s) have been synthesized. Many of these involve either hydrogen-bonding of small molecules (“complexants”) to complementary terminal groups of already present polymer side-chains (thus effectively lengthening the side-chains) or ionic complexation of surfactants to oppositely charged polyelectrolytes (thus effectively creating side-chains). Fewer involve the complexation of molecules possessing both a typical mesogenic core and a flexible spacer group capped with a complexing moiety (which we term “surfactomesogens”) to complementary, often readily available, polymers. Of these, the most successful systems, in terms of stability and equimolar complexation, are based on strong ionic interactions, such as those involving sulfonate groups. Weaker interactions tend to be those involving hydrogen bonding, hydrogen bonding to oppositely charged polyelectrolytes (thus effectively creating side-chains). These involve either hydrogen-bonding of small molecules (“complexants”) to complementary terminal groups of already present polymer side-chains (thus effectively creating side-chains). The complexes with amine linkers may not decouple between the ionic backbone and the mesogenic cores for LC order in crystalline. Probably, a spacer length of 6 is too short to permit adequate birefringence could be detected and in other cases (in particular, the mesogens with faster cis-trans isomerization rates) birefringence was induced by the polarized light itself during the POM observations. For complexes involving SM’s with 10-carbon spacers, all except those with ethyl and methyl amine linking groups show intrinsic birefringence in POM and appear to be liquid crystalline. Probably, a spacer length of 6 is too short to permit adequate decoupling between the ionic backbone and the mesogenic cores for LC order to appear in those complexes. The complexes with amine linkers may not show LC order even for the 10-spacer SM’s due to the disruptive role of the ethyl and methyl lateral substituents. In comparison, the pure SM’s are crystalline, with melting points above 120 °C, except for 10-NEt-CN, which appears to be an isotropic liquid at ambient.

Results and Discussion

All of the complexes shown in Table 1 were free of Na and Br counterions according to EDS and could therefore be assumed to be equimolar, which was confirmed by NMR. POM observations indicated that the complexes involving SM’s with 6-carbon spacers are essentially amorphous materials, although in some cases (notably, 6-O-OMe) very weak birefringence could be detected and in other cases (in particular, the mesogens with faster cis-trans isomerization rates) birefringence was induced by the polarized light itself during the POM observations. For complexes involving SM’s with 10-carbon spacers, all except those with ethyl and methyl amine linking groups show intrinsic birefringence in POM and appear to be liquid crystalline. Probably, a spacer length of 6 is too short to permit adequate decoupling between the ionic backbone and the mesogenic cores for LC order to appear in those complexes. The complexes with amine linkers may not show LC order even for the 10-spacer SM’s due to the disruptive role of the ethyl and methyl lateral substituents. In comparison, the pure SM’s are crystalline, with melting points above 120 °C, except for 10-NEt-CN, which appears to be an isotropic liquid at ambient.

Materials and Complexation Procedure

The sodium salt of poly(styrene sulfonate) (PSS, Aldrich, MW=70,000) was dissolved in a small amount of Milli-Q water, to which about twice as much spectrograde DMSO was added, and warmed to about 50°C. A slight molar excess of surfactomesogen was dissolved separately in DMSO, and then added dropwise to the PSS solution, which gave a clear solution. This solution was kept warm under stirring for up to 24 h, and then dialyzed against Milli-Q water (SpectroPor membrane, cutoff 3500; VWR) for at least 4 days with the water changed at least once a day. The resulting precipitate (the complex is soluble in DMSO, but not H2O) was freeze-dried for several days, and further dried in vacuum at about 60-80 °C for two days.

Instrumentation.

Energy dispersive analysis (EDS) was carried out with a FEI Quanta 200 FEG environmental scanning electron microscope attachment; H NMR in DMSO-d with a Bruker Avance 400 MHz spectrometer; differential scanning calorimetry (DSC) with a TA Instruments Q1000 DSC, using heating and cooling rates of 10 °C/min; polarizing optical microscopy (POM) with a Zeiss Axioskop 40Pol microscope; and X-ray diffraction (XRD) with a Bruker D8 Discover system equipped with a 2D Bruker AXS wire-grid detector, using Cu Kα radiation, with samples packed in 1.0-mm diameter capillaries (Charles Supper) and temperature controlled by a HCS410 heating stage and a STC200 temperature controller from Instec. The dipole moments of the mesogenic cores, with the functionalized alkyl spacer replaced by a methyl group, were calculated using the ab initio method in HyperChem 7. Light-induced birefringence was performed using a set-up described elsewhere, with the sample chamber flushed with dry N2.

Table 1. Molecular representations of the complexes studied, their calculated dipole moments, phase structures and clearing points.

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>m</th>
<th>(\mu)</th>
<th>state</th>
<th>(T_c/°C)</th>
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<tr>
<td>NMMe</td>
<td>NO2</td>
<td>6</td>
<td>9.96</td>
<td>am</td>
<td>10</td>
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<td>NO2</td>
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<td>10.0</td>
<td>am</td>
<td>10</td>
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<td>CN</td>
<td>6</td>
<td>8.74</td>
<td>am</td>
<td>10</td>
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<tr>
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<td>NO2</td>
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<td>7.49</td>
<td>am</td>
<td>10</td>
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<tr>
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<td>OMe</td>
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<td>am</td>
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<tr>
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<td>Me</td>
<td>6</td>
<td>2.00</td>
<td>am</td>
<td>10</td>
</tr>
</tbody>
</table>

\(\mu\), dipole moment; \(T_c\), clearing temperature (POM); am, amorphous

\(^a\) 9.94 in ref. 7
\(^b\) sensitive to starting conformation

Experimental
order reflection, since, at 20 Å, it corresponds to about half the side-chain molecular length. As indicated in Figure 1 by the downward pointing arrow, there is a hint of a similar reflection for 6-O-NO₂, whereas 6-O-OMe shows a hint of the first-order reflection; but, overall, these two complexes can be considered amorphous, according to XRD, as can 10-NEt-NO₂.

DSC curves (second scans) of selected complexes are shown in Figure 2. For 6-O-OMe and 10-NEt-NO₂, there is a clearly defined, relatively narrow glass transition. Neither of these complexes are LC. In contrast, the complexes, m-O-NO₂, show broader glass transitions, and possibly even two, as indicated in Figure 3 and as observed previously for m=10.² The glass transition for the LC complex 10-O-OMe is also broader than those of the non-LC complexes shown. In all cases, the glass transition temperature (the lower-temperature one in the cases where there appear to be two) is lower for the complexes with 11-carbon spacers (about 50-60 °C) compared to those with 6-carbon spacers (about 80 °C), as would be expected from an internal plasticization effect. In addition, the LC complexes show a clear (and reversible) LC-isotropic transition. The data in Table 1 for the LC complexes suggest that there is a correlation between the temperature of this transition and the polarity (dipole moment) of the mesogenic core; i.e. the higher the dipole moment, the greater the stability of the LC phase and the higher the clearing point.

Some preliminary photo-induced birefringence (PIB) curves of three dried SM complexes are shown in Figure 3. They indicate that all three show significant fast relaxation after the writing laser is turned off, followed by much slower relaxation. The complex with the 6-carbon spacer appears to relax somewhat more slowly. In contrast, the PIB for a complex of methyl orange (MO) with fully methylated poly(4-vinyl pyridine) (P4VP), where there is no spacer and which possesses a smectic A phase, appears very stable over the time period investigated.²

Acknowledgements. NSERC (Canada) is gratefully acknowledged for their financial support. We acknowledge our membership in the multi-university Centre for Self-Assembled Chemical Structures (CSACS) supported by FQRNT (Quebec). Ximin Chen is thanked for synthesizing two of the SM’s.

References
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