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

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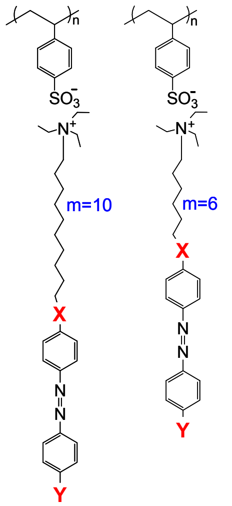
Introduction

Over the past decade and more, a wide variety of supramolecular side-chain liquid crystal polymers (SCLCP's) have been synthesized.[1] 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" [2]) 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 insufficient to compensate for driving forces to small-molecule phase separation and crystallization and/or steric hindrance, etc., and therefore only partial complexation is attainable. With regards to applications, some of the surfactomesogens include azo groups[2,3] in view of obtaining relatively easily synthesized materials for potential optical applications.[4]

With regards to the present communication, we are investigating ionic complexes of a series of azo-containing quaternary ammonium-functionalized surfactomesogens (SM's) to an oppositely charged polyelectrolyte, sulfonated polystyrene (PSS), focussing in particular on the influence of the spacer length and the mesogen polarity on the LC behavior (see Table 1). In addition, we report preliminary photo-induced birefringence measurements on some of these materials. The complexes will be referred to hereafter as m-X-Y (Table 1).

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



X	Y	μ	m	state	T_{cl}/°C
NMe	NO_2	9.96 [a]	6	am	
			10	am	
NEt	NO_2	10.0	6	am	
			10	am	
NEt	CN	8.74	6		
			10	am	
O	NO_2	7.49	6	am	
			10	LC	165
O	CN	5.57	6	am	
			10	LC	120
O	OMe	3.03 [b]	6	am	
			10	LC	140
O	Me	2.00	6	am	
			10	LC	80

μ, dipole moment; T_{cl}, clearing temperature (POM); am, amorphous
[a] 9.94 in ref. 7
[b] sensitive to starting conformation

Experimental

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 H_2O) 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; ^1H 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,[5] with the sample chamber flushed with dry N_2.

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 ionic liquid at ambient.

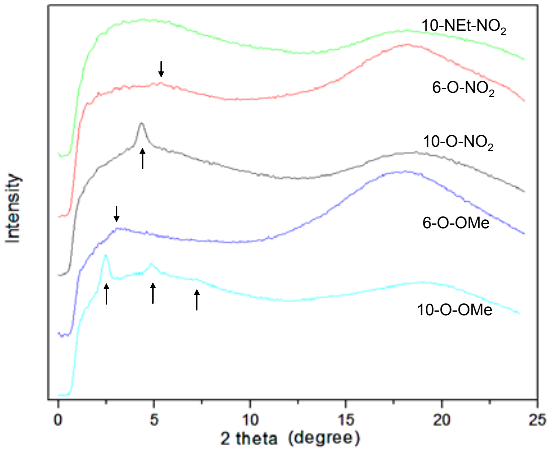


Figure 1. Ambient temperature X-ray diffractograms of the complexes indicated.

The nature of the phases is confirmed by XRD (ambient temperature) for the complexes tested so far, shown in Figure 1. All of those complexes show an amorphous halo at wide angles. The 10-O-OMe complex shows three equidistant smaller-angle reflections, giving a Bragg spacing of 36 Å, which is similar to the length of the complexed side-chain in extended conformation, thus indicating a single-layer smectic A phase. Only one reflection is found for 10-O-NO_2 (in contrast to ref. 2), which might be associated with a second-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-NO_2, 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-NO_2.

DSC curves (second scans) of selected complexes are shown in Figure 2. For 6-O-OMe and 10-NEt-NO_2, there is a clearly defined, relatively narrow glass transition. Neither of these complexes are LC. In contrast, the complexes, m-O-NO_2, 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.

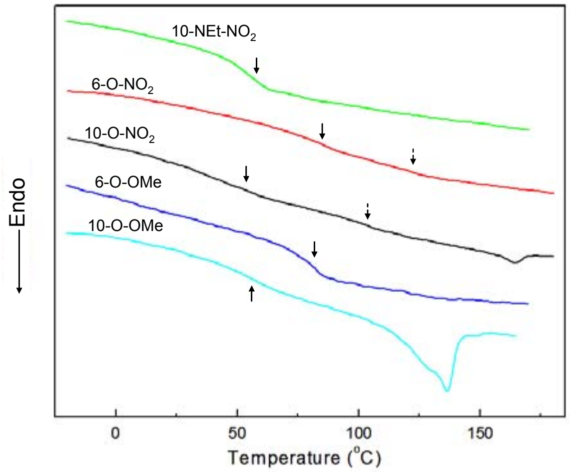


Figure 2. Differential scanning calorimetry thermograms (second heating scans) of the complexes indicated. The arrows point to glass transitions (a possible second one for the broken arrow).

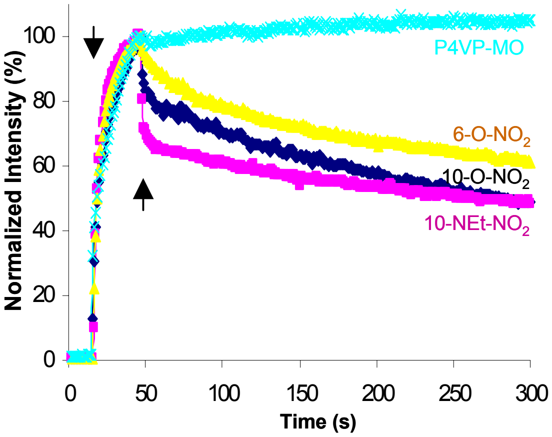


Figure 3. Photo-induced birefringence (ambient temperature) of the complexes indicated. Arrow down: write on. Arrow up: write off.

It was also observed by XRD that the structural order of the complexes can be strongly influenced by humidity. The 6-O-NO_2 complex, which is amorphous when dry (and when under 58.8%RH), forms a hexagonal phase under 100%RH (RH = relative humidity). The amorphous 10-NEt-NO_2 complex also develops order (not yet identified) both under 58.8 and 100%RH. In contrast, the LC order in the dry 10-O-OMe complex is greatly diminished under 100%RH. The 10-O-NO_2 complex, for which only the presumably second-order small-angle reflection is visible in XRD when dry, develops a strong lower-angle reflection, which might be the corresponding first-order reflection, under 100%RH.

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.[6]

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