ABSTRACT SUMMARY

Cross-polarizing light microscopy (CPLM) and small-angle X-ray scattering (SAXS) were employed to structurally characterize liquid crystalline (LC) nanostructures formed at interfaces between oppositely charged surfactant (S) and polymer (P) solutions at 'non-equilibrium'. The effect of temperature and salt on the stability and release of a dye from these LC systems were also investigated.

INTRODUCTION

The phenomenon of LC formation within mixtures of oppositely charged surfactant-polymer solutions at 'equilibrium' has been known since the late 1970s. However, the advent of methods for understanding the structural aspects of these interactions is relatively new and research into the dynamics of nanostructure development at the S-P interface have not yet been explored.

In previous studies, we have found that exposing cationic polymer solutions such as poly(diallyldimethylammonium chloride) (polyDADMAC) with anionic surfactant solutions such as sodium dodecyl sulphate (SDS) can produce hexagonal phase at the S-P interface. In contrast, creating a well-defined interface between oppositely charged biocompatible materials such as negatively charged bile salt (sodium taurodeoxycholate hydrate, STDC) and positively charged chitosan resulted in the appearance of lamellar phase.

LC systems are excellent candidates as drug delivery matrices for their ability to solubilize hydrophilic, hydrophobic and/or amphiphilic drugs. We know that LC nanostructure is an important determinant in controlling drug release, therefore having control over which mesophase forms is advantageous in the development of novel tailored release nanomaterials. These materials provide greater versatility in structure manipulation over similar drug delivery systems such as layer-by-layer (LbL) engineered capsules because the hydrophobic and/or electrostatic interactions that occur between the two species can be readily modulated by introducing variables such as surfactant/polymer concentration, polymer molecular weight, surfactant chain length, pH, temperature, addition of salt etc.

RESULTS AND DISCUSSION

Fong et al. have shown that temperature can be employed as an external stimulus to trigger reversible phase switching in certain lipid-based LC systems. The heat applied to the sample leads to the disruption in lipid packing within the LC matrix, altering the geometry of the molecules relative to each other and thus a change in mesophase nanostructure was observed by SAXS.
For the polyDADMAC/SDS mixture (Figure 1.A) micelles and hexagonal phase were present at room temperature. At >60 °C, the nanostructure became more highly ordered as depicted in a more pronounced Bragg peak at q ~0.17 Å⁻¹. On the other hand, micelles and lamellar phase existed at room temperature in the chitosan/bile salt mixture and the ‘ordered’ structure was lost at >45 °C (Figure 1.B). The temperature at which the lamellar phase was lost carries some significant support in the possibility of this system to act as a novel controlled release drug delivery system. Theoretically, drug can be encapsulated within the lamellar phase, which in practice would have to be dispersed into liposomes for subcutaneous or IV administration and remain stable at physiological temperature. Introducing a heat pack to the site of action would disrupt packing within the LC matrix, leading to the disintegration of structure and trigger the release of the therapeutic. Conversely, this effect could also be applicable to the deposition of active ingredient from a shampoo formulation upon washing of hair in warm water.

Formation of hexagonal phase at the disc boundary was evident when oppositely charged surfactant and polymer solutions were in contact (Figure 1.C). The addition of salt solution revealed a decrease in ‘ordered’ structure at the S-P interface (Figure 1.D), which was comparable to the effect temperature had on the stability of the LC structure.

![Figure 1](image)

**Figure 1.** Effect of temperature and salt solution on the stability of LC nanostructure(s) formed at interfaces between oppositely charged S-P solutions. Top panel: scattering profiles of mixtures containing 10 wt% SDS/10 wt% polyDADMAC/80 wt% H₂O (A) and 15 wt% STDC/2 wt% chitosan/83 wt% H₂O (B) when heated from 25 to 80°C at 5°C steps; Bottom panel: scattering profiles across the S-P interface between 20 wt% polyDADMAC (drop) and 20 wt% SDS (continuous phase) before and after addition of 100 mM NaCl solution.

The LC structure surrounding the polymer-dye filled disc appeared to remain intact for samples kept at room temperature (Figure 2.A) and elevated temperature (Figure 2.C), however, no release of dye was observed from these systems. A plausible explanation could be the association of the negatively charged Allura Red with the positively charged polymer preventing the dye from diffusing across the S-P interface. As demonstrated earlier, addition of salt leads to the breakdown of structure and subsequent release of the dye (Figure 2.B).

**CONCLUSION**

Temperature and salt demonstrate potential parameters that may be exploited to modulate release from LC nanostructures formed between these oppositely charged surfactant and polymer solutions. Therefore, controlling interfacial structural attributes in these complex systems may provide an interesting route to tailored release nanomaterials.

**REFERENCES**


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