

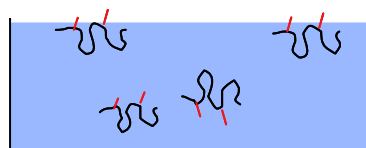
Ellipsometric Study of the Aggregation of Hydrophobically Modified Polysaccharides in Solution at the Air / Water Interface

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 **UVISEL**

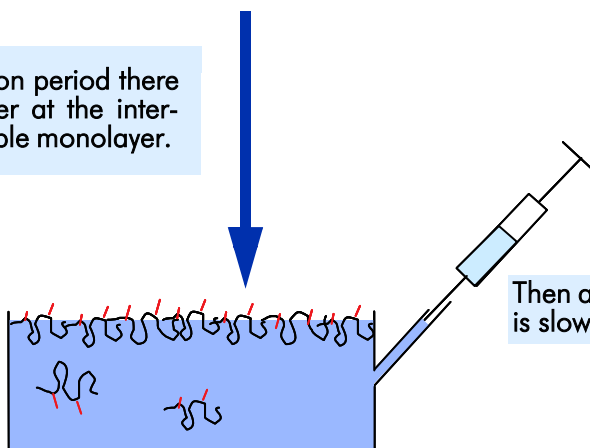
Pullulan is a natural, water-soluble polysaccharide used in the production of foods, pharmaceuticals and cosmetics. From the consumer side it is popular as it is of non-animal origin being manufactured from corn, and from the technical side it is easily formed into films suitable for use in capsules.

In this study, we have compared the physico-chemical properties of two ionic pullulan derivatives (CMP) modified by 10% and 35% C₈ chains in aqueous solutions. These derivatives exhibit an associative behaviour which stems from intra and intermolecular interactions between the hydrophobic C₈ groups grafted onto the molecules.



10% or 35% CMP modified polymer solutions.

During a 24 hour stabilisation period there is adsorption of the polymer at the interface, and formation of a stable monolayer.



Then a buffer solution is slowly injected.

Characterisation of the CMP polymer solutions

The work was performed using a Jobin Yvon UVISEL Visible Spectroscopic Phase Modulated Ellipsometer.

To make meaningful measurements of ellipsometric spectra requires the ultimate sensitivity for the technique as the contrast in refractive index between the solvent and polymer molecules is extremely weak. The measurements described here were made at an incident angle close to 53° (which is the Brewster angle for the system under consideration), across the spectral range 250-800 nm.

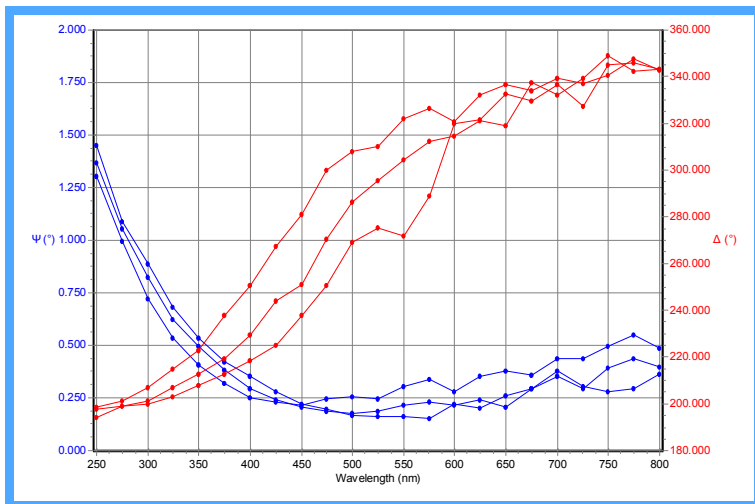
Moreover, such transparent ultrathin layered systems generate a Δ angle near 0 [180°]. When compared to conventional ellipsometers, the phase modulated ellipsometer configuration is unique in that it allows the highest sensitivity and precision of the Δ angle across the full [0°, 360°] range, even when Δ is close to 0°.



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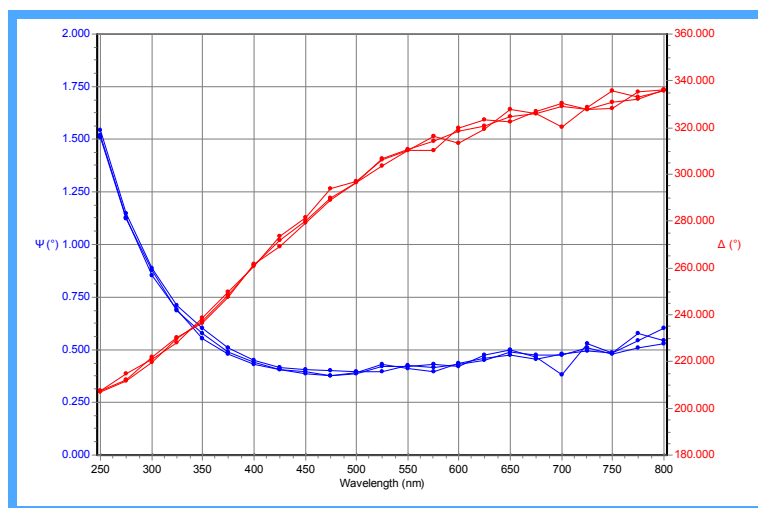
Spectroscopic Ellipsometry

The figure shows three spectra of the ellipsometric angles Ψ and Δ showing how the signals change within 10 minutes after perturbation of the air/liquid interface. The effect can be observed on the molecules modified by 10% C_8 chains only.



Change in surface properties measured 3 times during a 10 minute interval for 10% modified.

Stable surface for 35% modified measured 3 times.



Conclusion

This interpretation has been supported by both surface tension measurement for the liquid phase and fluorescence spectroscopy for bulk behaviour.

From this study there is clear evidence that increasing the substitution rate from 10% to 35% induces a reinforcement of the hydrophobic interactions and thus the formation of more compact and stable aggregates which can complex hydrophobic compounds. The use of CMP 35% C_8 could be envisaged in drug formulations where dispersion of a hydrophobic drug in an aqueous phase is required.

The authors would like to thank Véronique Rosilio from Paris-Sud University for her support in this work.

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