Playing the Blues, the Greens and the Reds with Cellulose-based Structural Colours

Ricardo Chagas,^a Pedro E. S. Silva,^a Susete N. Fernandes^a, Slobodan Žumer^{b, c} and Maria Helena Godinho^{a*}

^a i3N/CENIMAT, Department of Materials Science, NOVA School of Science and Technology, NOVA University Lisbon, Campus de Caparica, 2829-516 Caparica, Portugal.

^bJozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia.

^cFaculty of Mathematics and Physics, University of Ljubljana, 1000 Ljubljana, Slovenia.

Supplementary Material (S1):

Phase Diagram:

The existence of a lyotropic cholesteric phase (polymer/solvent solutions) implies the determination of the critical concentration (C^*). The critical concentration is the value of the solution concentration for which anisotropic domains start to develop, as the polymer concentration increases.

In all studied anisotropic solutions, at room temperature, the increase of temperature results in the formation of a biphasic region that develops between the anisotropic and the isotropic phase. The upper values presented in the phase diagram (Figure S1) correspond to the complete disappearance of the anisotropic phase.



Figure S1. Simplified phase diagram of HPMC/TFA system. Only temperatures to the isotropic phase are given. TFA bp – boiling point of TFA.

Supplementary Material (S2): Dependence of the pitch with temperature:



Figure S2. Variation of the pitch with temperature for C_B sample. a. POM pictures taken in reflection mode, parallel to the optical axis of the cholesteric, between cross polarizers, scale bar 100 µm. b. spectra acquired as a function of temperature. The arrow indicates increasing temperature, heating rate 2 °C.min⁻¹. c. Temperature dependence of the wavelength of maximum reflection for C_B sample. The linear equations evidence the two different slopes of the curves 1.8 to 3.6 nm.K⁻¹.



Figure S3. Variation of the pitch with the degree of substitution for C=21%w/w (HPMC/TFA), initial sample (21DS0) and with a degree of esterification of 0.5 (21DS5). The graph represents the temperature dependence of the wavelength of maximum reflection for samples 21DS0 and 21DS5. Heating rate 2 °C.min⁻¹. The esterification of the HPMC was performed in the presence of the trifluoro acetic acid and the anhydride.

Supplementary Material (S3):

Gif animations : anim20F_t2.gif, anim20A_t2.gif (Fig. 5) and anim23F_t2.gif (Fig. 4 e. and f.) are HSV colour diagrams of C_A and C_B solutions, respectively, recorded at a given time, (from the periphery to the centre of the samples, regions A to B, between cross polars. Colour diagrams show, in polar coordinates, the variation of hue (angle) with value (radius). Each point corresponds to the average colour of each POM image. Summary: .gif animations files: anim20F_t2.gif, anim23F_t2.gif and anim20A_t2.gif and capillary animation.gif correspond to the evolution in time of a capillary prepared from C_B .

Supplementary Material (S4):

HPMC and HPMC-OCOCF₃ FTIR analysis

Chemical characterisation via Fourier Transform Infrared (FTIR) spectroscopy:



Figure S4. FTIR spectra of hydroxypropyl methyl cellulose (HPMC) and HPMC-OCOCF₃. The vertical dashed lines mark different HPMC and HPMC-OCOCF3 (HPMC-TFA) characteristic absorption bands.

In both spectra a wide absorption band, centred at 3425 cm⁻¹, and 2910 cm⁻¹ are associated with stretching of O-H and C-H bonds, respectively, indicative of hydrogen and C-H bonds that are present in both samples. The absorption bands located at 1790 cm⁻¹ and 1210 cm⁻¹ ^{SM1, SM2} are linked with stretching of C=O and O-C bonds, respectively, present in the HPMC-OCOCF₃ carbonyl group. The broad bands between 1100 and 1010 cm⁻¹ indicate the presence of C–O–C bonds, characteristic of the cellulose backbone^{SM3}.

Supplementary Material (S5):



Figure S5. Variation of the hue channel (HSV color space) from the border to the centre of a HPMC/TFA cholesteric solution confined in a closed capillary. (a) One hour after filling the capillary, colour changes from red to blue, while (b) after 2 days, colour shifts from blue to red. (b) The region close to the border displays no colour.

Supplementary Material (S6):

To describe the space and time dependencies of the relevant concentrations (hydroxyl- [OH], carboxylic acid - [COOH], ester - $[OCOCF_3]$ groups and $[H_2O]$) the reaction diffusion equations of the corresponding chemical reaction should be solved (work underway).

When the chemical reactions and diffusion are added, focusing on 1D diffusion (neglecting radial variations due to lateral diffusion) the following equations are obtained^{SM4, SM5}:

$$\frac{\partial [\text{COOH}]}{\partial t} = D_{[\text{COOH}]} \frac{\partial^2 [\text{COOH}]}{\partial x^2} + f([\text{COOH}], [\text{OH}])$$
(1)

$$\frac{\partial [OH]}{\partial t} = D_{[OH]} \frac{\partial^2 [OH]}{\partial x^2} + g([COOH], [OH])$$
(2)

$$\frac{\partial [OCOCF_3]}{\partial t} = D_{[OCOCF_3]} \frac{\partial^2 [OCOCF_3]}{\partial x^2} + h([OCOCF_3], [H_2O])$$
(3)

$$\frac{\partial [H_2 0]}{\partial t} = D_{[H_2 0]} \frac{\partial^2 [H_2 0]}{\partial x^2} + j([0C0CF_3], [H_2 0])$$
(4)

Being f and g and h and j the reaction rate expressions for the reaction of the alcohol with the acid, and for the reverse reaction (of the ester with water), respectively, and $D_{[COOH]}$, $D_{[OH]}$, $D_{[OCOCF_3]}$ and $D_{[H_2O]}$ the diffusion rate constants of the acid (TFA), hydroxyl groups (HPMC), the ester (HPMCOCOCF₃) and water, respectively.

References:

 [[]SM1] K. Nakanishi, Infrared Absorption Spectroscopy-Practical; Holden-Day, Oakland, CA, 1962, p 42.
[SM2] A. M. Ritcey, K. R. Holme, D. G. Gray, *Macromolecules*, 1988, 21, 2914-2917.

[SM3] M. Hudlicky, Organic Fluorine Chemistry; Plenum: New York, 1971; Chapter 5.

- [SM4] (= [34]) H. F. Nijhout, Proc. R. Soc. B, 1990, 239, 81-113.
- [SM5] (= [35]) A.M. Turing, Philos. Trans. R. Soc. Lond. Ser. B Biol. Sci., 1952, 237, 37-72.