

Supporting Information

Latex Synthesis

The synthesis was carried out in a 5-necked 1 L protected from light, glass reactor equipped with a glass, anchor-shaped mechanical stirrer fitted in the middle neck of the reactor. The temperature in the reactor was constantly monitored by a temperature probe directly inserted through one of the four peripheral necks. The reactor was partially immersed in a thermostated oil bath, the temperature of which was also constantly monitored and recorded. The procedure followed for the synthesis of the latex loaded with 4.9 w/w % 2-ethylhexyl-4-methoxycinnamate (EMC) during the last monomer addition step formation is described below.

The polymerization reactor was evacuated and backfilled with nitrogen twice. 115.17 g (2.68 mmol) of Na₂HPO₄ buffer stock solution (0.33 w/w %) were loaded in the reactor under nitrogen flow followed by the addition of a pre-emulsified solution composed of 16.67 g (6.82 mmol) SLSar stock solution (12.0 w/w %), 54.16 g (422.56 mmol) BuA, 23.22 g (234.92 mmol) MMA and 0.82 g (4.14 mmol) BDDA. The mixture was left to equilibrate at 70 °C under continuous stirring. Subsequently, 2.62 g (0.73 mmol) of NaHSO₃ stock solution (2.88 w/w %) were added at a constant addition rate of 3 mL / min using an isocratic pump. The mixture was once again left to equilibrate under continuous stirring and 7.66 g (1.20 mmol) of K₂S₂O₈ stock solution (4.25 w/w %) were added at a controlled addition rate of 3 mL / min using an isocratic pump. Subsequently, the polymerization was left to proceed at 70 °C for one hour. The prepared nanogel latexes were collected and stored in glass bottles.

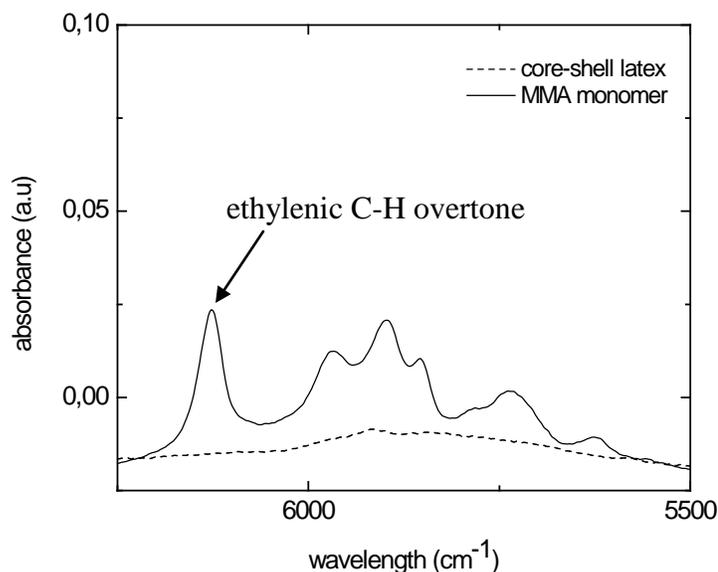
150 g of the previously prepared latex was transferred into the reactor under inert conditions and the reaction temperature was set at 70 °C. A pre-emulsified solution composed of 1.36 g (10.61 mmol) BuA, 3.37 g (33.66 mmol) MMA, 0.30 g (1.53 mmol) diallyl maleate and 0.49 g of NaHSO₃ stock solution (2.88 w/w %) was added in the reactor at a constant addition rate for two minutes. Subsequently 0.35 g of K₂S₂O₈ stock solution (4.25 w/w %) was added using a peristaltic pump for ten minutes. The reaction was left to proceed at 70 °C for one hour and 2.23 g of sodium hydroxymethanesulfinate stock solution (1.74 wt %) was added. Following, a pre-emulsified solution of 3.61 g (18.98 mmol) EMC, 11.72 g (117.1 mmol) MMA and 3.84 g (213.3 mmol) milli-Q water was added simultaneously with 9.98 g (mmol) of APS stock solution (0.5 wt %) at a constant addition rate using a peristaltic pump for fifteen minutes. The reaction was left to proceed for thirty minutes after which a mixture of 0.47 g APS stock solution (15.6 wt %) and 0.34 g NaHSO₃ – Na₂S₂O₅ stock solution (2.71 wt %) was added. The reaction was left to proceed at 70 °C for thirty more minutes followed by the removal of the heating bath. The latex was left to reach room temperature and collected in light-protected glass bottles.

For the synthesis of the core-loaded latexes the appropriate amount of EMC was dissolved in the BuA, MMA, BDDA mixture used for the preparation of the pre-emulsion. The non-loaded core-shell latex was prepared using the same amount of reactants without the addition of EMC.

Latex characterization

All the latexes were investigated by Dynamic Light Scattering (DLS) using an ALV/CGS3 Compact Goniometer System, equipped with an ALV/LSE 5004 multi- τ digital correlator and a vertically polarised He-Ne laser operating at a wavelength of $\lambda = 632.8$ nm. The measurements were performed at seven scattering angles ranging from 60° to 120° with 10° increments, whereas the system was thermostated at 23°C . 20 mL of milli-Q water were filtered twice through $0.22\ \mu\text{m}$ syringe driven filters in glass vials followed by the addition of $5\ \mu\text{L}$ of latex using a micropipette. The samples were loaded in 10 mm borosilicate glass cells. Three 60-seconds runs were performed for each angle and the data were analysed by Cumulant analysis. The results are shown in Table 1 of the manuscript.

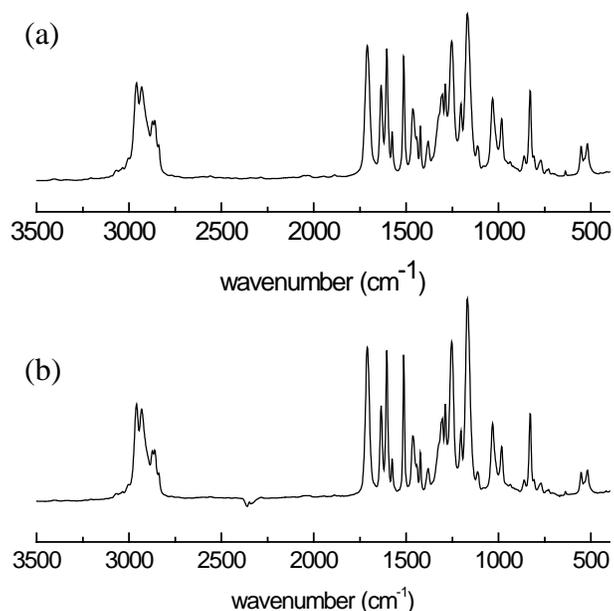
The core-shell latexes were investigated in terms of monomer residuals by near-IR spectroscopy before and after the last addition of the APS and $\text{NaHSO}_3 - \text{Na}_2\text{S}_2\text{O}_5$ redox couple. The trace recorded for the core-shell latex before the addition is shown and compared to that obtained for pure MMA in Supplementary Figure 1 by the dashed and the solid line respectively. Unlike the spectrum corresponding to the MMA, the one obtained for the core-shell latex does not present the peak at $6\ 165\ \text{cm}^{-1}$ attributed to the ethylenic C-H overtone attesting the absence of monomer residuals in the core-shell latexes.



Supplementary Figure 1. Near-IR spectra recorded for the core-shell latex (dashed line) and for the MMA monomer (solid line).

EMC stability

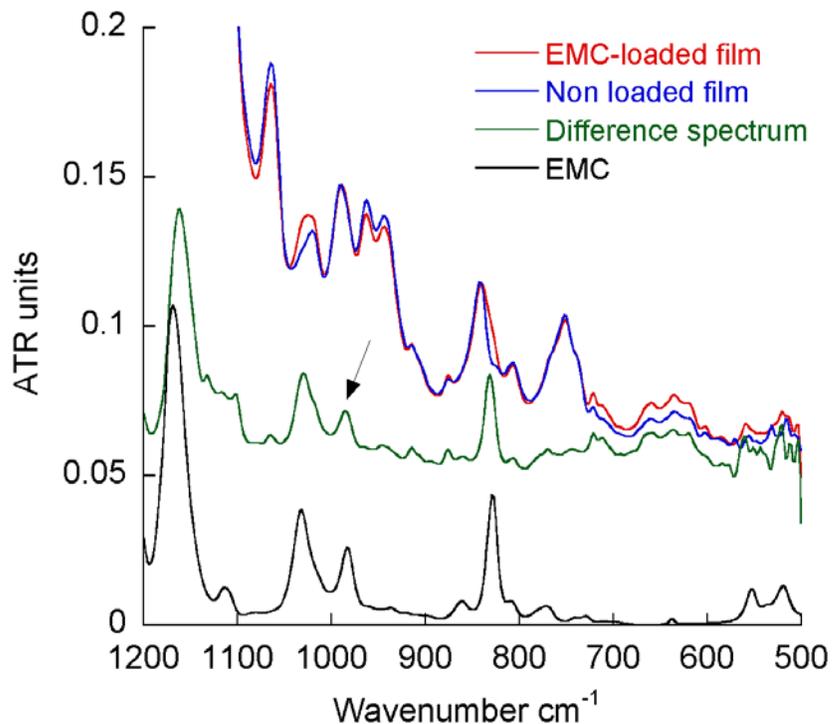
As mentioned in the manuscript, as a part of the EMC stability studies under conditions representative of the emulsion polymerization, the UVB-filter was heated at 72 °C for four hours in contact with APS – CH₂NaHSO₃ aqueous solution. The FTIR spectrum is shown in Supplementary Figure 2(a), whereas the spectrum corresponding to the non-thermally treated EMC is given in Supplementary Figure 2(b). The two spectra appear to be identical suggesting that heating of EMC in the presence of APS – CH₂NaHSO₃ aqueous solution does not affect a change in the conformation of the former from *trans*- to *cis*- form.



Supplementary Figure 2. FTIR spectra recorded for EMC sample (a) heated at 72 °C for four hours in contact with APS – CH₂NaHSO₃ aqueous solution and (b) non-thermally treated.

Confirmation of EMC presence in the films

As described in the manuscript, EMC was detected on the surface and the interior of the films using ATR-IR. Supplementary Figure 3 shows the region between 1100 cm⁻¹ and 500 cm⁻¹ of the spectra recorded for the EMC-loaded film in red and the non-loaded film in blue. In the same Figure, the trace obtained from the subtraction of the spectrum corresponding to the non-loaded film from the one of the loaded-film is shown in green, whereas the trace of neat EMC is shown in black. The difference spectrum shows a peak at 980 cm⁻¹ (highlighted by the arrow) attesting that EMC is in *trans*- configuration.



Supplementary Figure 3. Part of the ATR-IR spectra obtained for the (a) EMC-loaded film (shown in red), (b) EMC-free film (shown in blue), (c) difference spectrum (shown in green). The trace shown in black corresponds to the IR spectrum of the neat EMC.