

Exploring polyethylene glycol/cyclodextrin hydrogels with spin probes and EPR spectroscopy

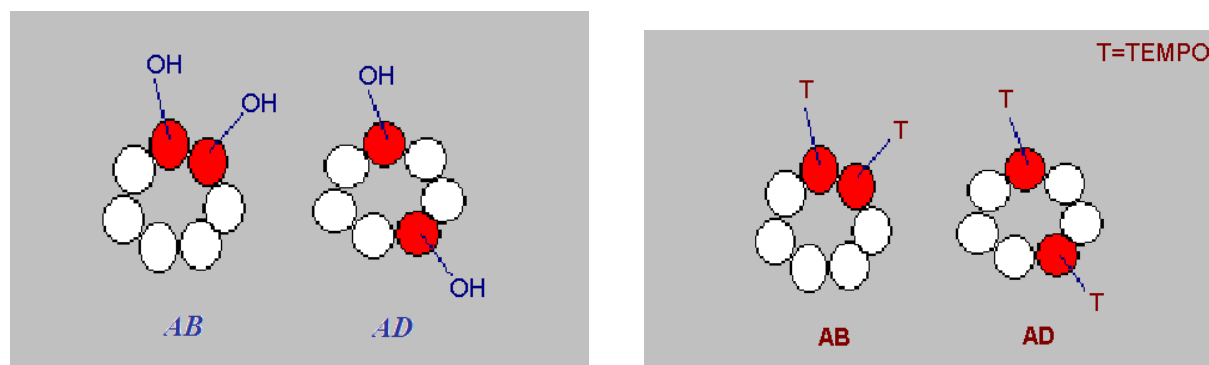
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SUPPLEMENTARY INFORMATION

Synthesis of and separation MCT.¹



Schematic representation of AB and AD isomers of permethylated β -CD

Dihydroxy permethylated β -CDs were synthesised following a literature procedure.² Carboxy-TEMPO (440 mg, 2.2 mmol) was added to a solution of dihydroxy-6A,6B-permethylated β -CD (1.4 g, 1 mmol) in dichloromethane (50 ml), followed by the addition of dicyclohexylcarbodiimide (495 mg, 2.4 mmol) and 4-dimethylaminopyridine (120 mg, 1 mmol). After stirring for 1 d at room temperature, the reaction mixture was washed successively with 0.1 M aq. HCl and 0.1 M aq. NaHCO₃. The organic layer was dried (Na₂SO₄), the solvent removed on a rotary evaporator and the crude reaction mixture purified by column chromatography using 10% ethyl acetate/dichloromethane as an eluent. Monoradical MCT was obtained as a by-product. TLC (10% ethyl acetate/dichloromethane, silica gel): R_f = 0.6 (AB), 0.6 (AD) and 0.4 (MCT). Yields: 20% (AB and AD) and 30% (MCT).

ESI-HR-MS data for MCT: calc. for $[C_{71}H_{124}NO_{37} + NH_4]^+$ 1600.8196, found for $[M + NH_4]^+$ 1600.8189.

Preparation of hydrogels.

The β -CD/PEG 600 hydrogels were prepared following the procedure reported by Cesteros *et al.* [3,4] Briefly, PEG 600 and cyclodextrins were dehydrated for 24 hours at 65 and 100 °C, respectively. In the first step, PEG 600 and hexamethylene diisocyanate were reacted in the 1:2 ratio in dry DMF using dibutyltin dilaurate as a catalyst in order to end-cap the polyethylene chains with an isocyanate group. In the second step, a solution of β -CD in DMF was injected in a three-necked flask containing isocyanate-PEG solution under N₂ atmosphere

at 55 °C, and the agitation was maintained in for 30 min. The ratio between β -CD and PEG 600 was 1:10. The reaction mixture was then transferred to smaller vials and kept under nitrogen for several days to achieve gelation. The spin probes were introduced in order to monitor the gel formation. Once formed, the gels were extracted and washed with DMF and water.

Calculation of rotational correlation times

The reported rotational correlation times were calculated for spectra in the fast motion regime (Redfield limit). For this regime, computer simulation is not necessary, and the rotational correlation time can be calculated using the following equation:⁵

$$\tau = 6.5 \times 10^{-10} \Delta H_0 \left[\sqrt{\frac{h_0}{h_{-1}}} + \sqrt{\frac{h_0}{h_{+1}}} - 2 \right]$$

ΔH_0 represent the peak-to-peak width (in Gauss) of the central line, h_{-1} , h_0 , h_{+1} are the heights of the lines in EPR spectra (at low field, central and high field, respectively; τ is the rotational correlation time (s).

References.

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