Fluorescence enhancement of the water soluble poly{1,4-phenylene-[9,9-bis(4-phenoxy-butylsulfonate)]fluorene-2,7-diyl}copolymer in *n*-dodecyl pentaoxyethylene glycol ether ($C_{12}E_5$) micelles

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Supporting Information

Synthesis of monomer and polymer

2,7-Dibromo-9,9-bis(4-sulfonylbutoxyphenyl)fluorene (dibromomonomer)

The dibromomonomer, 2,7-dibromo-9,9-bis(4-sulfonylbutoxyphenyl)fluorene was synthesized in three steps. The first step involves oxidation of 2,7-dibromofluorene with sodium dichromate/acetic acid to 2,7-dibromofluoren-9-one. In the second step, 2,7- dibromofluoren-9-one was reacted with phenol/methane sulfonic acid to give 2,7-dibromo-9,9-bis(4-hydroxyphenyl)fluorene. The last step was the etherification of 2,7-dibromo-9,9-bis(4-hydroxyphenyl)fluorene with 1,4-butane sultone to 2,7-dibromo-9,9-bis(4-sulfonylbutoxyphenyl)fluorene in dioxane/NaOH. The monomer was obtained in 71% yield (three steps).

Poly[9,9-bis(4-sulfonylbutoxyphenyl)fluorene-co-1,4-phenylene]

The copolymer was prepared by a Suzuki-type coupling.[1] For this, a mixture of 2,7-dibromo-9,9-bis(4-sulfonylbutoxyphenyl)fluorene (0.824 g, 1 mmol), 1,4-phenylenediboronic acid (0.166 g, 1 mmol), $Pd(PPh_3)_4$ (50mg) Na_2CO_3 (1.0 g) in 5 ml of distilled water, 50 mL of toluene and 5 ml of butanol was reacted for 3 days at 135°C (reflux). The aqueous layer was washed with chloroform and concentrated to dryness. The residue was redissolved in water and purified by dialysis using a membrane with a cut off of 3,500 g/mol to yield 0.50 g (54 %) of poly[9,9-bis(4-sulfonylbutoxy phenyl)fluorene-*co*-1,4-phenylene] as a slightly brown powder.

^{1}H NMR-spectrum (300 MHz, D_2O): $\delta(^1H)$ [ppm] : 6.8-7.9 (ar-H), 3.4-4.0 (α, δ -CH_2), 1.2-2.0 (β,γ -CH_2)

GPC (NMP/LiBr) :) : $\overline{M}_n$ = ~ 6,500 gmol^{-1}

Instrumentation and Methods

Absorption and luminescence spectra were recorded on Shimadzu UV-2100 and Jobin-Ivon SPEX Fluorolog 3-22 spectrometers, respectively. Fluorescence spectra were corrected for the wavelength response of the system. Solutions of polymers were prepared by stirring overnight in Millipore MilliQ water. All samples were kept in the absence of light. Fluorescence quantum yields were measured using quinine sulfate in 0.5 M sulfuric acid as standard.[2]

Fluorescence decays were measured using a home-built Time-Correlated Single Photon Counting apparatus with an N_2 filled IBH 5000 coaxial flashlamp as excitation source, Jobin-Ivon monochromator, Philips XP2020Q photomultiplier, and Canberra instruments Time-to-amplitude converter and Multichannel Analyser. Alternate measurements (1000 counts per cycle), controlled by Decay® software (Biodinâmica-Portugal), of the pulse profile at 337 or 356 nm and the sample emission were performed until 1-2 x 10^4 counts at the maximum were reached.[3] The fluorescence decays were analysed using the modulating functions method of Striker with automatic correction for the photomultiplier "wavelength shift".[4]

Solution electrical resistances were measured with a Wayne-Kerr model 4265 Automatic LCR meter at 1 kHz. A Shedlovsky-type conductance cell was used.[5] The cell constant (approximately 0.8465 cm^{-1}) was determined to ± 0.02 % from measurements with KCl (reagent grade, recrystallised and dried using the procedure and data from Barthel *et al*.[6] Measurements were made at 25.00 ± 0.01 ºC in a Grant thermostat bath.

Attempts to measure sodium ion concentrations in solution resulting from incorporation of PBS-PFP into $C_{12}E_5$ micelles were made using both sodium ion selective electrodes and ultrafiltration. In the latter case, a filter which retains species of molecular weight 500 was used under a nitrogen pressure of 3 bars, and the supernatant sodium concentration was determined using atomic emission spectroscopy. Values of sodium ion concentration in the supernatant solution of 0.15 mM (PBS-PFP alone), 0.16 mM (PBS-PFP 1 with 0.05 mM $C_{12}E_5$) and 0.21 mM (PBS-PFP with 0.1 mM $C_{12}E_5$) were observed. Whilst the values are only qualitative, and the differences are quite small, they are consistent with incorporation of the polymer into the micelle increasing the free sodium ion concentration.

^{1}H NMR spectra of PBS-PFP were run on solutions in D_2O on a Varian Unity 500 MHz spectrometer. Spectra of the aromatic region of the polymer alone and in the

presence of $C_{12}E_5$ are shown in Figure A, and clearly show the effect of surfactant on the bandshapes of these protons.

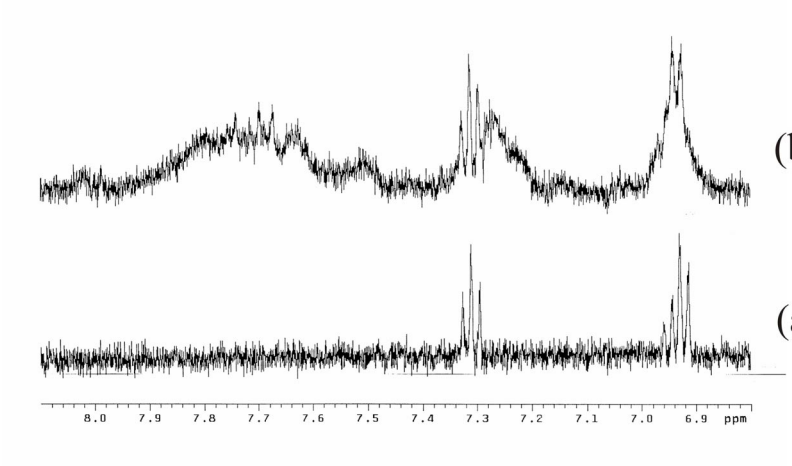

Figure A. NMR spectra of PBS-PFP in D_2O solutions (0.152 g/L): (a) alone; (b) with $C_{12}E_5$ (3.4×10^{-4} M).

References

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