Communications to the Editor

Fluorescence Enhancement of the Water-Soluble Poly{1,4-phenylene-[9,9-bis-(4-phenoxybutylsulfonate)]fluorene-2,7-diyl} Copolymer in *n*-Dodecylpentaoxyethylene Glycol Ether Micelles

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Interest is increasing in water-soluble conjugated polymers in areas such as chemical/biological sensors[1,2] and self-assembly systems.[3] In addition, introduction of ink jet printing for fabricating light-emitting diode (LED) displays[4] will increase demand for these water-based systems. Marked changes in fluorescence occur on adding surfactants.[1b,2c] Both surfactant complexation[1b] and breakup of polymer aggregates[2c] have been proposed as explanations. The high fluorescence yields and blue emission of polymers involving 2,7-linked fluorene units make them among the most attractive classes of conjugated polymers for devices[5] and good candidates for the above applications. We report the effect of the nonionic *n*-dodecylpentaoxyethylene glycol ether ($C_{12}E_5$) on properties of the water-soluble poly{1,4-phenylene-[9,9-bis(4-phenoxybutylsulfonate)]fluorene-2,7-diyl} copolymer (PBS−PFP, Figure 1B). The polymer (M_n= ~6500 g mol^{-1}) was synthesized by condensation of 2,7-dibromo-9,9-bis(4-sulfonylbutoxyphenyl)fluorene (A) and 1,4-phenylenediboronic acid using Pd(PPh₃)₄ as catalyst.

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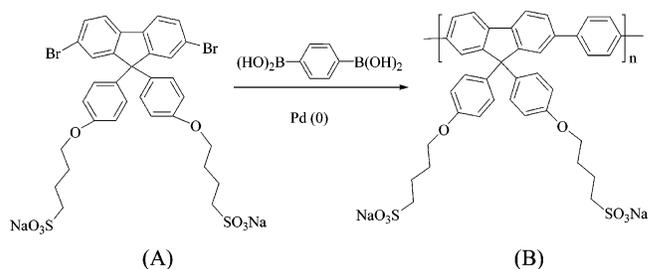
Figure 1. Synthetic scheme and structure of poly{1,4-phenylene-[9,9-bis(4-phenoxybutylsulfonate)]fluorene-2,7-diyl}.

Details of synthesis and characterization are given in the Supporting Information.

Aqueous solutions of PBS−PFP showed a broad absorption around 381 nm and a structured fluorescence (λ_{max} 424, 448, 475 nm (shoulder)). Band shapes are similar to the related copolymer poly[2,7-(9,9-bis(2′-ethylhexylfluorene)-*alt*-1,4-phenylene] (PFP).[6] Upon addition of $C_{12}E_5$ (3.3×10^{-8}−5.34×10^{-4} M) to PBS−PFP (6 mg/L, 9.2×10^{-7} M),[7] blue shifts in absorption (11 nm) and emission (13 nm, Figure 2) maxima, and marked increases in absorbance and fluorescence intensity were observed.

With a poly(ethylene oxide) of similar size to $C_{12}E_5$ headgroup (PEG 200 $\leq 2.3 \times 10^{-4}$ M), only a decrease in fluorescence intensity was observed, with no change in band shape, showing the importance of the surfactant. Fluorescence quantum yields (Φ_f), lifetimes, and shifts in emission maxima are shown as functions of surfactant concentration (Figure 3).[7] Although the decay should strictly be treated as biexponential, with the time resolution of our system and the relatively small difference in the lifetimes, it was not possible to obtain a statistically significant separation into two exponentials, and the decay was taken as monoexponential.

All these properties change at surfactant concentrations greater than the $C_{12}E_5$ critical micelle concentration (cmc, $(5 \pm 2) \times 10^{-5}$ M),[8,9c] suggesting they result from incorporation of polymer into micelles. PBS−PFP
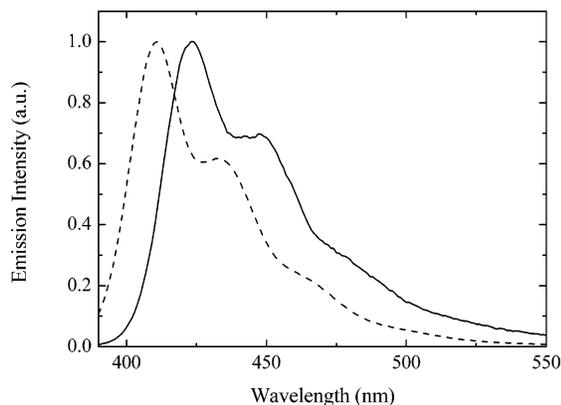
Figure 2. Normalized fluorescence spectra of PBS−PFP (6 mg L⁻¹) in aqueous solution: alone (solid line) and with C₁₂E₅ (5.3 × 10⁻⁴ M, dotted line).
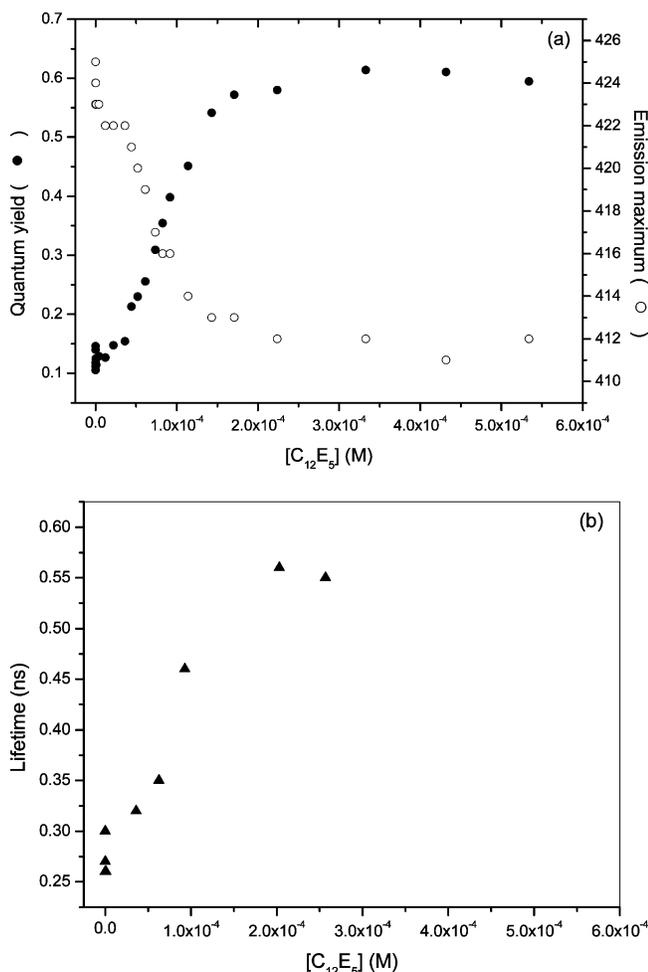
Figure 3. Changes in (a) quantum yield (bold circles) and emission maxima (open circles) and (b) fluorescence lifetime for aqueous solutions of PBS−PFP with C₁₂E₅ concentration. For quantum yields, solutions were adjusted to have absorption ≤0.1 at excitation wavelength.

is a polyelectrolyte, and this behavior contrasts with that of many surfactant−polyelectrolyte systems,[9] including some water-soluble conjugated polymers,[1] where interaction occurs at surfactant concentrations (critical aggregation concentrations, cac) below the cmc.[9]

These effects can be explained either by changes in environment resulting from surfactant complexation[1b] or by surfactant-induced breakup or formation of polymer aggregates.[2c] Fluorescence quantum yields in water
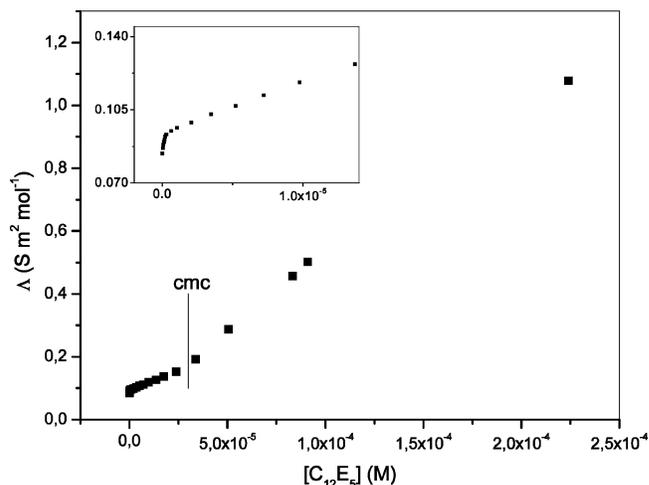
Figure 4. Molar conductivity of PBS−PFP solutions as a function of surfactant concentration. Note the change in slope at the cmc. Inset: changes observed at very low surfactant concentrations.

may be an order of magnitude lower than in nonpolar solvents,[10] and the effect of changing polarity on the polymer nonradiative processes by incorporation into micelles may explain these differences. However, we feel this is not the dominant effect, since the lowest energy absorption band of fluorene is relatively insensitive to solvent polarity,[11] in contrast to the observed pronounced blue shift, and we feel breaking up of aggregates explains both this shift and the increased quantum yield. With aggregates, similar interchain interactions are present to those in polyfluorene films, and breaking these up by incorporation into micelles is equivalent to going from thin films to isolated polymer chains. The differences between emission spectra and fluorescence quantum yields with PBS−PFP in water and C₁₂E₅ micelles are similar to those seen with fluorene copolymers between thin films and cyclohexane solutions,[6] supporting this model. Breakup of an aggregate of a water-soluble poly(p-phenylenevinylene) on adding an oppositely charged surfactant has been confirmed by small-angle neutron scattering.[12]

Since PBS−PFP is a polyelectrolyte, electrical conductivity may be informative. This was studied in water,[7] and the molar conductivity (Λ) was calculated using

$$\Lambda = (\kappa - \kappa_0)/(c \times 1000) \quad (1)$$

where κ and κ_0 are electrolytic conductivities of solution of molar concentration c and solvent, respectively. The experimental electrolytic conductivity is around 3.5 × 10⁻⁵ S m⁻¹. The molar conductivity depends on the square root of concentration, in agreement with the Kohlrausch equation[13]

$$\Lambda = \Lambda^0 - Ac^{1/2} \quad (2)$$

(Λ^0 = 0.362 ± 0.011 S m² mol⁻¹, A = 8.50 ± 0.27 S mol⁻³/² m⁷/²). The molar limiting conductivity Λ^0 is similar to that of other polyelectrolytes in water.[14]

On adding C₁₂E₅, ionic conductivity increases with concentration (Figure 4). Two distinct changes were observed. At very low surfactant concentrations (see inset), there was a change in the slope of the plot, which we believe is associated with initial interactions between PBS−PFP and the surfactant. The second change occurs

around the surfactant cmc, where an increase in the slope is observed. While the mobility of the polymer may be expected to be reduced on micellization, PBS−PFP molecules will be distributed between the different micelles, until at the limit there will be a maximum of one polymer per micelle. Associated with each polymer/surfactant micelles will be the corresponding counterions, and the equilibrium between these and bulk solution is expected to lead to an increase of the free counterion concentration and, hence, molar conductivity. In support, qualitative studies using both ultrafiltration and ion selective electrodes do show increased free sodium ion concentrations above the cmc.[7]

In water, $C_{12}E_5$ forms elongated cylindrical micelles, which grow with concentration, temperature, or solute incorporation.[15] Support for incorporation of polymer into such micelles comes from ^1H NMR spectra. The aromatic protons appear in the region δ 6.8−7.9 ppm, and with PBS−PFP in D_2O solutions (0.152 g/L) these appear as relatively sharp signals. However, on adding $C_{12}E_5$ (3.4×10^{-4} M), they become broadened (see Supporting Information). This broadening is not observed in spherical micelles but is common in large, rodlike micelles and results from slow tumbling.[16]

We have shown that dramatic increases in the fluorescence quantum yield occur in PBS−PFP on incorporation into $C_{12}E_5$ micelles and at low surfactant concentrations provide a stable medium for the polymer in aqueous solutions. Further, the surfactant $C_{12}E_5$ forms a variety of phases in two- and three-component systems, including lamellar, hexagonal, and cubic bicontinuous structures.[17] Incorporation of PBS−PFP into these structures may be important for sensor applications and can produce structures, e.g. columnar mesophases, with interesting properties.

Supporting Information Available: Details of synthesis and characterization and NMR spectra of PBS−PFP in D_2O solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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