Self-assembly of amphiphilic poly(phenylene ethynylene)s in water–potassium dodecanoate–decanol lyotropic liquid crystals†

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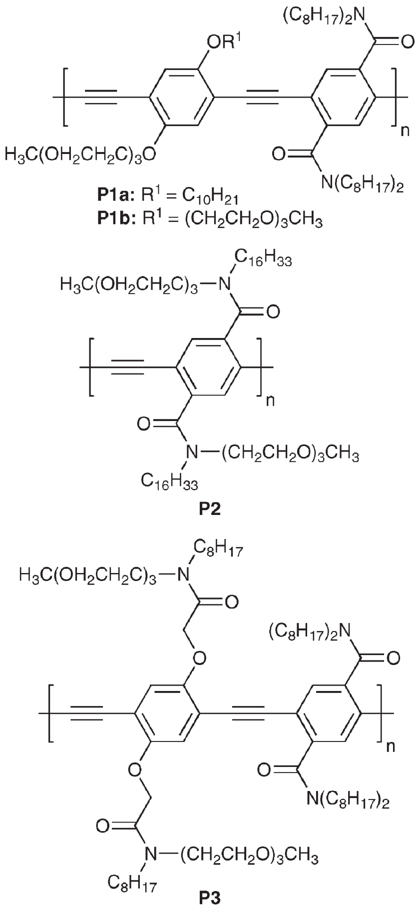
Poly(phenylene ethynylene)s bearing a high density of branched amphiphilic side-chains self-assemble at the air–water interface and in water–potassium dodecanoate–decanol lyotropic liquid crystals.

The achievement of complete control over the conformation of conjugated polymer single chains and their assembly into functional structures remains an elusive goal, despite its relevance to the understanding of energy transfer and conductivity and the importance of these properties in applications ranging from PLEDs to CP-based solar cells to biosensors.[1] In a plurality of cases, structural control in the condensed phase is achieved empirically wherein the annealing of polymer films may or may not lead to the desired improvement in properties.[2]

Elegant strategies previously developed for the control of conjugated polymer chain conformation, alignment and assembly are accomplished in templated matrices such as stretch-aligned polymers,[3] nematic liquid crystals,[4] roll-cast block copolymers,[5] mesoporous silica,[6] designed supramolecular aggregates,[7] and controlled deposition from an air–water interface.[8] Herein, we describe the extension of the last strategy to include polar interfaces of lyotropic liquid crystals (LLCs).

Surfactants typically self-assemble upon dissolution in water to form the well-known soap micelles. When many of such amphiphiles are dissolved in higher concentrations, the micelles can coalesce and/or self-assemble into a large number of liquid crystalline phases (*e.g.* nematic, cubic, hexagonal, bicontinuous and lamellar), which have been extensively studied for a wide array of binary (*e.g.* water–amphiphile), ternary (*e.g.* water–amphiphile–hydrophobe) and higher order mixtures.[9]

Non-ionic conjugated polymer amphiphiles such as **P1a** and **P1b** (Scheme 1),[8c] bearing a comparatively low density of linear side-chains, have previously been shown to self-assemble in 2D nematic phases at the air–water interface.[8d,e] However attempts to introduce **P1a–b** within lyotropic liquid crystalline lattices have been unsuccessful, presumably due to the low density of amphiphilic side-chains, limited solubility and/or propensity of the polymers to self-aggregate in LLC media. Polymers **P2** and **P3** were designed and synthesized (see ESI† for details) to circumvent these limitations by incorporating a larger density of branched[10] amphiphilic side-chains along the poly(phenylene ethynylene) (PPE) backbone.



Scheme 1 Conjugated polymer amphiphiles **P1–P3**.

The amphiphilic properties of polymers **P2** and **P3** were first investigated by the Langmuir–Blodgett technique.[8c,d] Solutions of **P2** or **P3** in $CHCl_3$ spread evenly at the air–water interface to form very stable self-assembled monolayers. Extrapolated surface area per repeating unit of 200 $Å^2$ and 230 $Å^2$ were found for **P2** and **P3**, respectively.[11] These values, together with the characteristic shape of the P–A isotherm and *in situ* spectroscopy (Fig. 1; see ESI† for details) are consistent with a polymer chain conformation wherein the phenylene units lie cofacial with the air–water interface (*i.e.* face-on

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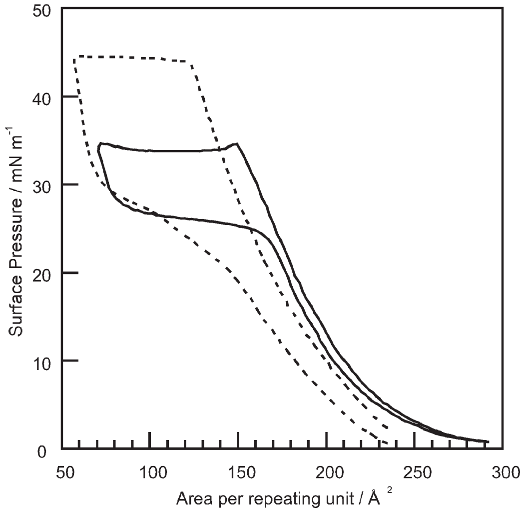

Fig. 1 Pressure–area isotherms of **P2** (dashed) and **P3** (plain) at the air–water interface.

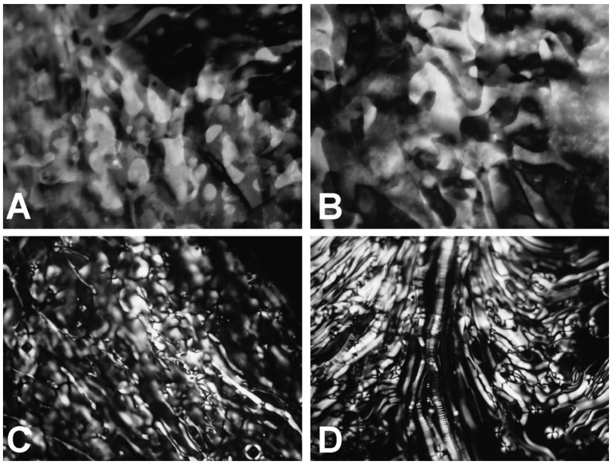

Fig. 2 Micrographs (100× magnification) of lyotropic liquid crystal textures under cross-polarizers: (a) **LLC-1**; (b) **P2** in **LLC-1**; (c) **LLC-2**; (d) **P3** in **LLC-2**.

structure). As the monolayers are compressed, folding into multilayers is observed at 44 mN m^{-1} (122 Å^2) for **P2** and 35 mN m^{-1} (150 Å^2) for **P3**. That folding into multilayers occurs, especially for **P2**, at significantly higher pressures than typically observed for *face-on* amphiphilic PPEs (*e.g.* **P1b**, 30 mN m^{-1})[8b–e] is interpreted as evidence that a higher density of amphiphilic side-chains along the polymer backbone increases the stability of the monolayer through an anchoring effect.

Water (D_2O)–potassium dodecanoate–1-decanol (**LLC-1**; 67.5 : 26.2 : 6.3% w/w) and water (D_2O)–potassium dodecanoate–1-decanol–potassium chloride (**LLC-2**; 60.0 : 30.0 : 6.0 : 4.0% w/w) lyotropic liquid crystalline mixtures[12] incorporating **P2** and **P3** were prepared from 1-decanol solutions (~1 mg mL^{-1}) of the polymers. The PPEs remain fully soluble in the LLC mixtures and no precipitation is observed. Similar optical textures (Fig. 2) are observed for samples containing the polymers and those that do not, indicating that the introduction of the polymers at these concentrations does not significantly disrupt the nematic phases of **LLC-1** and **LLC-2**.

Polymers **P2** and **P3** remain highly fluorescent in the lyotropic liquid crystalline mixtures. The absorption spectra of **P2** and **P3** in LLC media are significantly red-shifted from those in solution ($\Delta\lambda_{\max}$ = 23 nm for **P2** in **LLC-1**, 22 nm for **P3** in **LLC-2**) (Fig. 3, Table 1). Smaller bathochromic shifts are similarly observed in the emission spectra ($\Delta\lambda_{\max}$ = 7 nm for **P2** in **LLC-1**, 14 nm for **P3** in **LLC-2**). These shifts, together with a narrowing of the absorption band that is

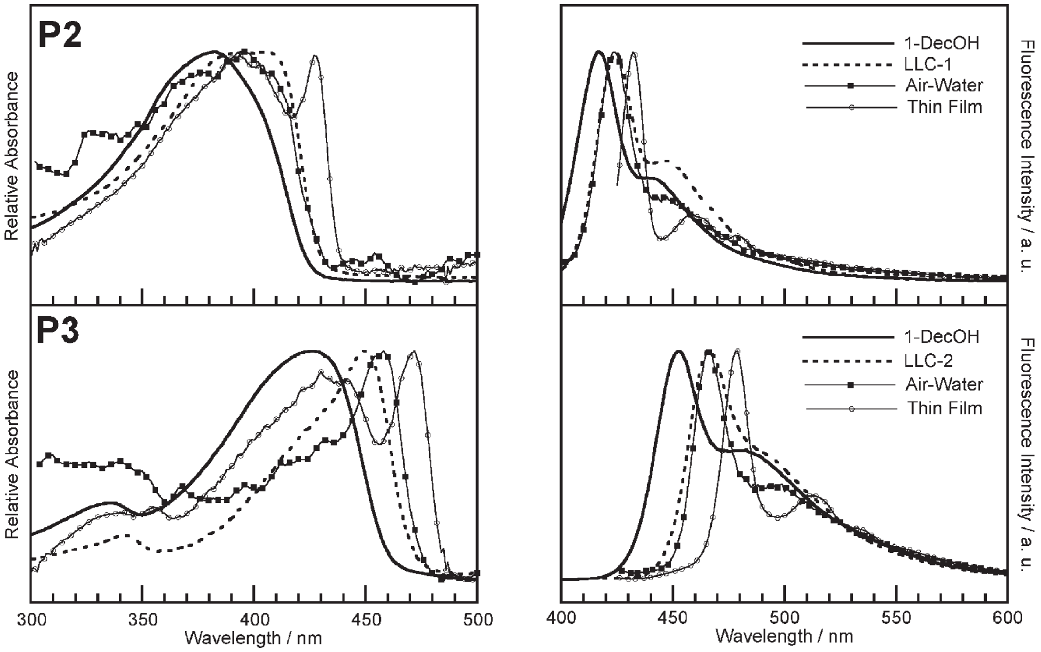

Fig. 3 Normalized absorption (left) and emission (right) spectra of **P2** (top) and **P3** (bottom) in 1-decanol (plain), lyotropic liquid crystals (dashed; **LLC-1** for **P2** and **LLC-2** for **P3**), monolayers at the air–water interface (black squares) and thin solid films (open circles).

Table 1 Summary of photophysical properties of **P2** and **P3**

	P2		**P3**	
	$\lambda_{\text{max, abs}}$/nm	$\lambda_{\text{max, em}}$/nm	$\lambda_{\text{max, abs}}$/nm	$\lambda_{\text{max, em}}$/nm
$CHCl_3$	387	420	417	450
1-DecOH	382	417	427	453
Air–water interface	406	424	460	467
LLC-1	405	424	451	467
LLC-2	387	422	449	467
LLC-3	407	422	451	466
Solid film	393, 427[a]	432	440, 472[a]	479

[a] Aggregation peak.

especially marked for **P3**, are indicative of a planarized polymer chain conformation that extends π-conjugation relative to the distribution of effective conjugation lengths found in solution, as previously observed with PPEs and small-molecule models.[4,8c,d,13] The bathochromic shifts are not consistent with polymer aggregates, for which a characteristic sharp absorption peak is found another 20–23 nm to the red in solid films. The absorption and emission spectra of the polymers in LLC media are most similar to that observed in Langmuir monolayers at the air–water interface, though the extent of the bathochromic shift with respect to the solution value in LLC media is inferior to that of the monolayers. We interpret these as evidence that **P2** and **P3** reside at the polar interfaces present within the LLC and adopt a π-extended face-on conformation analogous to that found at the air–water interface. Curvature of the polar interfaces within the LLCs and/or a looser confinement of the polymer chain to the interface would result in a less extended conjugation and a concomitant bathochromic shift smaller than in Langmuir monolayers.

In summary, the branched amphiphilic PPEs **P2** and **P3** have been shown to form stable monolayers at the air–water interface where the polymer chain adopts a planar face-on structure. These polymers have been introduced in self-assembled lyotropic liquid crystalline media and spectroscopic data provide support for a similar planar face-on structure of the polymer chains at polar interfaces within the LLC. Further studies will include the crosslinking of conjugated polymers self-assembled in LLCs to generate porous networks[14] relevant for vapour sensing and gas storage applications[15] and the confinement of conjugated polymers on other self-assembled polar interfaces such as liposomes and cell membranes.[16]

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