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## Liquid Crystals

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# Monodomain alignment of thermotropic fluorene copolymers

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Conjugated copolymers of 9,9-dioctylfluorene alternating with benzothiadiazole and dithiophene moieties in the main chain were found to be ‘hairy rod’ type thermotropic liquid crystalline polymers as well as yellow to red photoluminescence emitters. Thin films of both copolymers were found to align into monodomains on standard liquid crystal alignment layers as well as on rubbed precursor route poly(*para*-phenylenevinylene) (precPPV), which is transparent to red light. This observation is of importance for the use of precPPV as a hole transporting alignment layer for fluorene copolymers in polarized electroluminescence devices.

## 1. Introduction

Since the original report on polymer electroluminescence (EL) [1], the field has rapidly established itself as a new branch of applied science. The extensive activities in the field have recently been reviewed by several authors [2]. However, gaining a foothold in the flat panel display market is difficult for any emerging technology since it has to compete with the mature and cheap liquid crystal displays (LCDs) that are set to dominate the market in the foreseeable future [3]. It is hence of particular interest for the organic EL community to find an application of their technology that can coexist symbiotically with LCDs. Such an opportunity was first discussed in 1995, when Dyreklev *et al.* [4] demonstrated an organic EL device based on a stretch-aligned conjugated polymer that directly emitted polarized light. They realized that such devices would be particularly useful as backlights for conventional LCDs.

In principle, there is a variety of methods to align organic EL materials for polarized emission: oriented Langmuir–Blodgett films [5], mechanically aligned films, e.g. stretched films [4], combined stretching and conversion procedures [6] or direct rubbing of films [7]. There is also precursor conversion on aligned substrates [8], epitaxial vapour deposition [9], or the use of liquid crystals (LCs), both low molecular mass [10] and polymeric [11–14]. For recent reviews, see [15].

To exploit LC self-organization for polarized EL applications, it is crucial to align the LC into a monodomain. Wendorff and coworkers [11, 12] have reported monodomain alignment of thermotropic, segmented conjugated arylenevinylene, ‘rigid rod–flexible spacer’ main chain liquid crystalline polymers (LCPs) on rubbed polyimide (PI) layers. These showed polarized absorption, photoluminescence (PL) and EL. The LC approach to polarized EL allows devices to be manufactured in a way that is similar and only slightly more complex than the fabrication of unpolarized devices. The EL dichroic ratio reported in [12] ( $D \approx 7$ ) compares favourably with those for alternative methods.

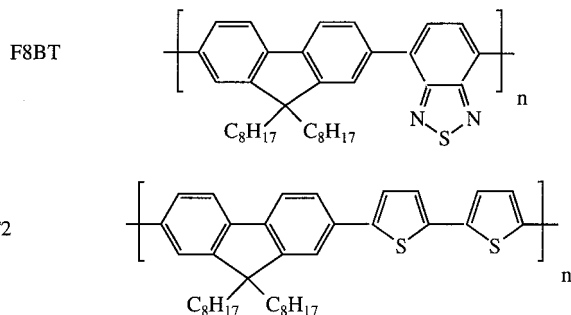
Depending on application, the requirements for the polarization ratio of the emitted light can vary between  $D \approx 12$  and 200 [16]. It is doubtful whether the degree of molecular order required for such high dichroic ratios can be achieved with ‘rigid rod–flexible spacer’ main chain LCPs, or with side group LCPs. Also, the interruption of backbone conjugation by flexible spacers may be detrimental to charge transport along the chain. Typically, LC order parameters are higher for ‘hairy rod’ type LCPs [17], but although liquid crystallinity was found for poly(*para*-phenylenevinylene) homopolymers as well as related copolymers with fully conjugated backbones [18], no monodomain alignment was reported for either of these materials.

Recently, several polyfluorene homo- and co-polymers have been synthesized and investigated [19–24]. Grice *et al.* have found excellent EL properties for a poly-(dioctylfluorene) device with a hole injecting layer [20].

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Grell *et al.* [13] reported on the thermotropic LC properties of the same polymer and have demonstrated monodomain alignment. The LC order parameter was found to be as high as  $S \approx 0.9$  [21]. Recently, Grell *et al.* [14] have reported on blue, polarized EL with a polarization ratio  $P \approx 15$  from a very similar polyfluorene.

In this communication, we report on the monodomain alignment of liquid crystalline fluorene copolymers, namely, poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly(9,9-dioctylfluorene-co-dithiophene) (F8T2). Synthetic methods have been described elsewhere [19, 23].



## 2. Materials characterization

Polystyrene (PS) equivalent molecular weights for F8BT and F8T2 are given in table 1. Since it is known that for very rigid polymers, PS calibration leads to an overestimate of molecular mass [22, 25], no degrees of polymerization can be computed from these results. For thermophysical characterization, samples were investigated by differential scanning calorimetry (DSC). A sample of F8BT that was rapidly cooled ('quenched') from 250°C crystallized on heating at 130°C. This indicates that quenching is at least partially successful in suppressing crystallization and forming a glassy state; F8BT then melted at 220°C. On slow (10°C min<sup>-1</sup>) cooling, a well defined recrystallization was found at 102°C. Samples that were annealed for 1 h at 140 and 175°C showed melting transitions again at 220°C, both with enthalpies between 9 and 10 J g<sup>-1</sup>. A sample of F8T2 that was quenched from 300°C crystallized on heating at 119°C, again indicating at least partial suppression of crystallization by quenching. F8T2 then melts at 265°C.

Table 1. PS equivalent molecular masses (g mol<sup>-1</sup>) for fluorene copolymers.  $M_n$  number average molecular mass;  $M_w$  weight average molecular mass;  $M_p$  peak molecular mass.

Copolymer	Molecular mass		
	$M_n$	$M_p$	$M_w$
F8BT	14500	44200	48400
F8T2	15700	32900	26800

On slow cooling, the sample recrystallized with a well defined peak at 159°C. A sample that was annealed for 30 min at 180°C melted at 262°C with an enthalpy of 5.2 J g<sup>-1</sup>. Above their melting temperatures, films of both polymers showed, when viewed between crossed polarizers in a polarization microscope, a birefringent, fluid phase, i.e. they were liquid crystalline.

To summarize, both copolymers show a phase behaviour similar to that of the corresponding polyfluorene homopolymer (liquid crystallinity, and control over room temperature morphology via cooling rate [13]), but characteristic temperatures are around 100°C higher. This can be understood as a result of having relatively fewer flexible side groups per unit length than the homopolymer.

## 3. Alignment properties

Since thin films of the polyfluorene homopolymer were found to align on a conventional LC alignment layer (rubbed precursor-route polyimide) [13], we have also investigated the alignment properties of F8BT and F8T2. Figure 1(a) and 1(b) show the polarized absorption spectra of F8BT and F8T2 films, respectively, on a rubbed PI coated substrate after annealing in the LC phase. Both show pronounced dichroism with dichroic ratios of  $D \approx 10$  for F8BT and  $D \approx 8$  for F8T2, somewhat higher than for the fluorene homopolymer [13]. For F8T2, the alignment was found to be remarkably fast: annealing for 1 min at 290°C was sufficient for full alignment.

Figures 2(a) and 2(b) show PL spectra for polarized excitation of aligned samples of F8BT and F8T2, respectively. Again, pronounced polarization dependences are found. In both cases, the spectra with 'parallel' excitation are very similar to the PL spectra of freshly spin-coated (isotropic) samples. In the case of F8T2, aligned samples show a small additional contribution from an unstructured, long wavelength emission overlaid on the spectrum of the untreated sample. This points to excimer formation which typically is the result of thermo-oxidative degradation [26]. The PL spectra show that light emitted from both polymers (particularly, F8T2) will be able to escape through a thin layer of precursor route poly(*para*-phenylenevinylene) (precPPV) for which the absorption edge lies at 550 nm.

PrecPPV combines transparency for the emission from F8BT and F8T2 with hole transporting properties and high temperature resistance: precursors are converted at 250°C. It was thus of interest to investigate whether rubbed precPPV can act as an alignment layer for F8BT and F8T2. Figures 3(a) and 3(b) show spectra for the polarized absorption of F8BT and F8T2, respectively, on rubbed precPPV films after the same thermal alignment procedure used on rubbed PI layers. The absorption

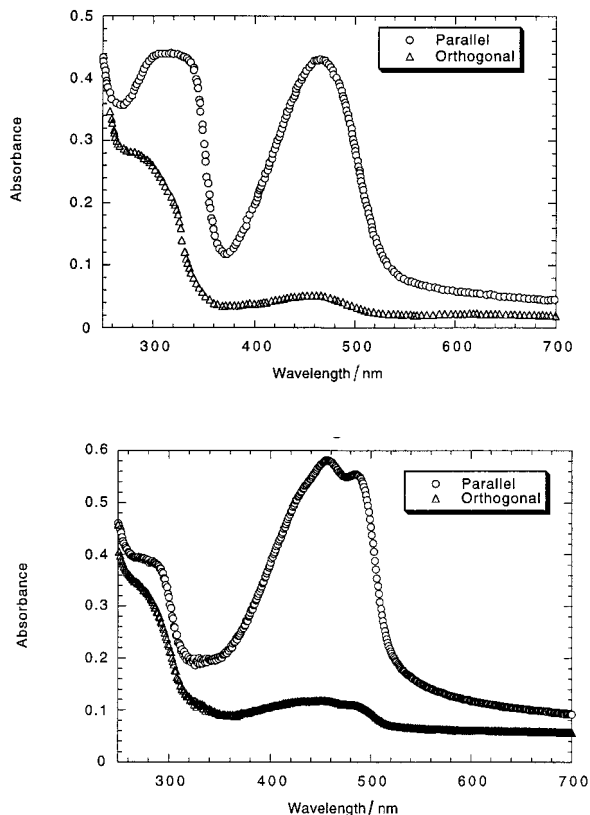


Figure 1. Polarized absorption spectra for F8BT (a) and F8T2 (b) aligned on a rubbed polyimide substrate. Alignment was facilitated by annealing in the LC phase according to the following temperature programmes: (a) 265°C ( $-1^{\circ}\text{C min}^{-1}$ ) to 235°C, quenched to room temperature (F8BT); (b) 1 min at 290°C, quenched to room temperature (F8T2).

of the rubbed precPPV layer was measured before coating the LC polymers and was subtracted to show the absorbance due to F8BT and F8T2 alone. It is not clear at this stage if the apparently better resolved vibronic structure, as compared with figure 1, is a real phenomenon or an artefact of the subtraction procedure. Again, we find pronounced dichroism, indicating that rubbed precPPV can induce monodomain alignment in F8BT and F8T2.

#### 4. Conclusions

F8BT and F8T2 copolymers are 'hairy rod' type thermotropic LCPs that can be aligned into monodomains in analogous fashion to the corresponding fluorene homopolymer. PrecPPV is shown to be a useful alignment layer for F8BT and F8T2. It transmits the light emitted from both copolymers. A device architecture using an indium tin oxide (ITO) anode, precPPV hole transporting alignment layer, thermally aligned F8T2 or F8BT emissive layer, an optional electron

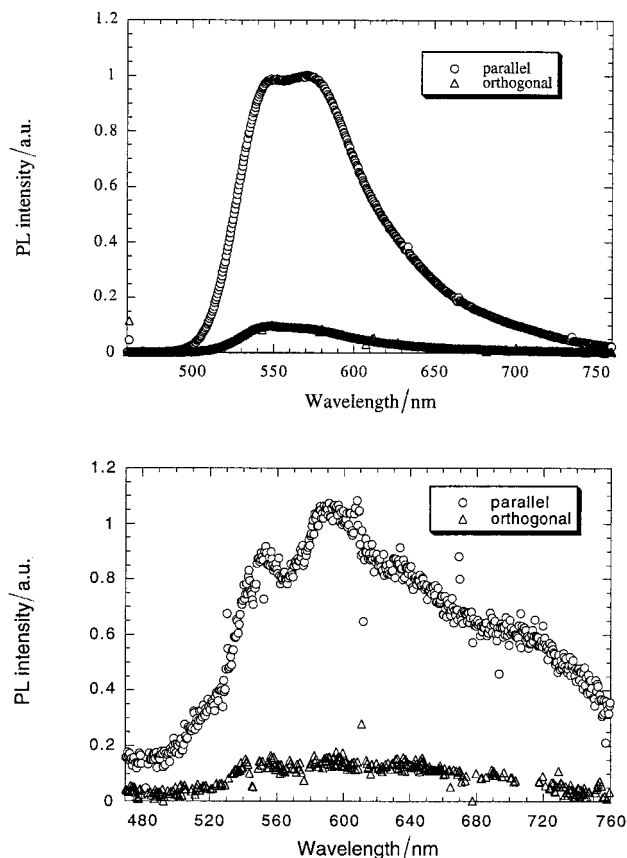


Figure 2. Polarized photoluminescence of aligned F8BT (a) and F8T2 (b). Excitation was with 450 nm light polarized parallel/perpendicular to the sample director.

transport/injection layer and a suitable cathode metal such as Al or Ca holds promise for good quality, polarized EL devices. Fabrication and testing of EL devices is underway.

#### 5. Experimental

GPC was carried out with  $1\text{ g l}^{-1}$  solutions of polymer in chloroform using 0.1% (by volume) toluene as end marker. A HP 1090 liquid chromatograph with a guard and two PLGel  $5\mu\text{m}$  'C' columns was equilibrated at 40°C with a flow rate of  $1\text{ ml min}^{-1}$ . An absorption detector set to 270 nm was used. Data were processed using Polymer Laboratories 'LogiCal' software.

For calorimetry, a Perkin-Elmer DSC 7 was used with a scan rate of  $20^{\circ}\text{C min}^{-1}$  (F8BT) and  $10^{\circ}\text{C min}$  (F8T2).

Polyimide alignment layers were fabricated from the MERCK 'ZLI 2650' precursor route alignment layer kit according to the manufacturers' instructions, and subsequently rubbed with a cloth mounted on a rotating drum. Films of F8BT and F8T2 were prepared by spin coating solutions of  $10\text{ g l}^{-1}$  of polymer in HPLC grade toluene (Aldrich) at 2000 rpm.

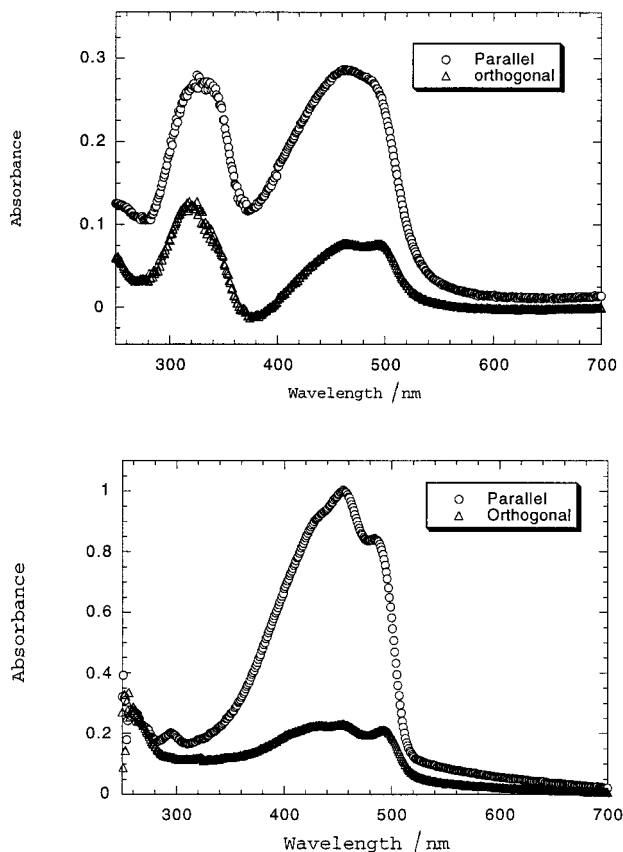


Figure 3. Polarized absorption spectra of F8BT (a) and F8T2 (b) thermally aligned on rubbed precPPV. The polarized absorption of the rubbed precPPV film was measured before coating the respective fluorene copolymer, and was subtracted from the measured absorbance of the aligned bilayer films.

PPV films were prepared from spin-coated films of a precursor. The precursor was converted thermally under dynamic vacuum for 1 h at 100°C and 10 h at 250°C.

Polarized absorption spectroscopy was carried out using a UNICAM 4 UV/Vis spectrophotometer with the help of a Glan-Thomson polarizer. Baseline scans were recorded with the polarizer in both orientations before every measurement to account for the polarization bias of the instrument.

PL was excited with the light from a GaN diode that was filtered through a 450 nm narrow pass interference filter and was polarized with a sheet polarizer. PL spectra were recorded with a cooled Oriel Instaspec IV spectrograph combined with a CCD detector.

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