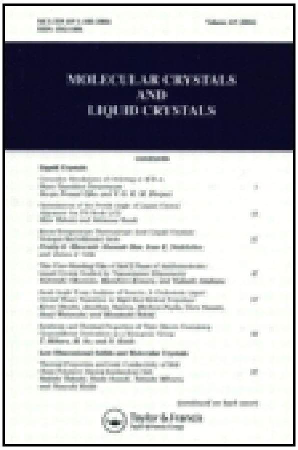

Molecular Crystals and Liquid Crystals

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Emissive Anisotropic Polymeric Materials derived from Liquid Crystalline Fluorenes

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EMISSIVE ANISOTROPIC POLYMERIC MATERIALS DERIVED FROM LIQUID CRYSTALLINE FLUORENES

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The synthesis and characterization of photoluminescent crosslinking agents containing a fluorene core are described. They exhibit an efficient fluorescence and have a promesogenic molecular shape that depending on the substitution results in the development of thermotropic mesophases. A difunctionalized fluorene derivative has been incorporated into a liquid crystal host in order to produce polarized light emitting films. These films have been prepared by the in-situ photopolymerization technique.

Keywords: fluorenes; liquid crystals; photoluminescence; photopolymerization; polarized emission

INTRODUCTION

Over the last decade, the market for flat panel display technology has been dominated by the liquid crystal displays for most applications where their low cost, low power consumption, low operating voltage and light weight constitute advantages not easily surpassed [1]. Nevertheless, the

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*Corresponding author: E-mail: loriol@unizar.es combination of polarizers and color filters form the basis of numerous of these commercial devices and such combination of elements reduces their overall efficiency because part of the incident light is converted into thermal energy. This limitation can be overcome by using emissive displays that emit light without requiring absorbing polarizers, therefore improving their brightness and viewing angle dependence. In the last few years, the development of polarized light emitting films has gained attention because they can provide linearly polarized emission, which is required for liquid crystal display backlight applications.

Linearly polarized luminescence can be produced very efficiently from the use of materials that are optically anisotropic and can be oriented in a specific direction [2]. From the different ways of producing films containing highly aligned chromophores, liquid crystalline self-organization offers an excellent control over microscopic orientation that can be macroscopically extended using appropriate processing techniques. Therefore, a common approach to prepare a polarized light-emitting film is based on the incorporation of a luminophore into a polymeric liquid crystal matrix. The chromophore must be a liquid crystal or at least compatible with the liquid crystalline order and can be incorporated either as a guest or covalently bonded to the matrix. In this context, *in-situ* photopolymerization of oriented reactive liquid crystals provides an excellent, versatile and facile method to produce such anisotropic films [3]. This strategy has already been successfully applied to the production of oriented luminescent films and it has been reported that highly cross-linked networks where the luminophore is bonded to the polymeric matrix show properties that are almost temperature independent and whose luminescence is thermally stable and photostable [4,5].

One major problem encountered on the production of light-emitting polarized films by *in-situ* photopolymerization is the selection of a luminophore that combines in a single molecule all the requisite properties. Amongst the requirements are thermal and photochemical stability, a narrow emission at the required wavelength and none of its functional groups should interfere in the free-radical polymerization process. In addition, the structure has to be compatible with the formation of mesophases. This last condition is probably one of the most difficult to fulfill because the structural criteria for achieving highly efficient luminophores are not always the same than for developing liquid crystallinity. In this context, fluorenes have been reported as blue-emitting luminophores with good thermal stability and high quantum yield. In particular, a high research effort has been carried out on polyfluorenes as materials for light-emitting diodes [6].

For some time, we have been interested on the preparation of cross-linked anisotropic films with luminophores covalently bonded to the

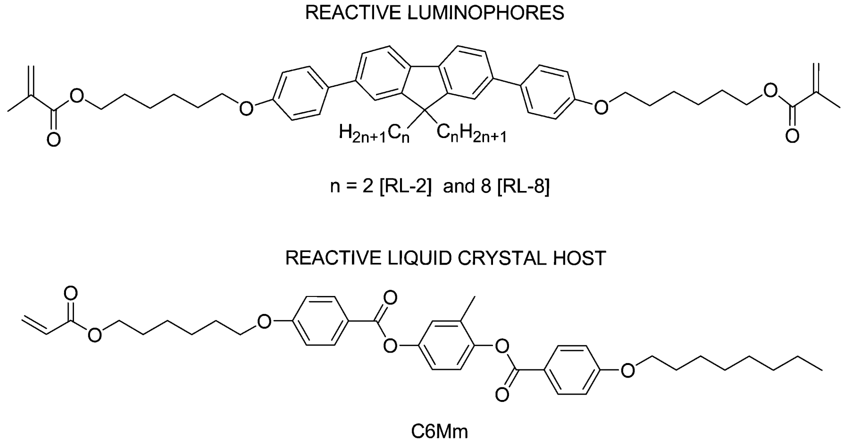

FIGURE 1 Molecular structure and nomenclature of the reactive luminophores and the reactive liquid crystal host.

polymeric matrix. The most common approach to this objective describes the mono-functionalization of a luminophore that is incorporated into a reactive matrix, which might contain a variable percentage of a non-emissive cross-linker [4,5,7,8]. A less common approach consists on the di-functionalization of a luminophore that would also be able to act as a cross-linking agent [9]. In that sense, electroluminescent networks have been successfully prepared by photopolymerization of direactive fluorene-based liquid crystals [10,11]. Therefore, in the present work, we describe the synthesis and characterization of fluorene-containing dimethacrylates (RL-2 and RL-8) that have been used for the production of anisotropic light-emitting films. The structure of these compounds is shown in Figure 1. As the host reactive matrix we have used a monoacrylate liquid crystal (C6Mm) whose synthesis and characterization is also presented. We have investigated their thermal behavior and optical properties in solution. In addition, the photopolymerization of polymerizable mixtures and the photoluminescence of the polymeric films have been studied.

EXPERIMENTAL SECTION

The synthetic routes followed for the preparation of the different monomers are outlined in Figures 2 and 3.

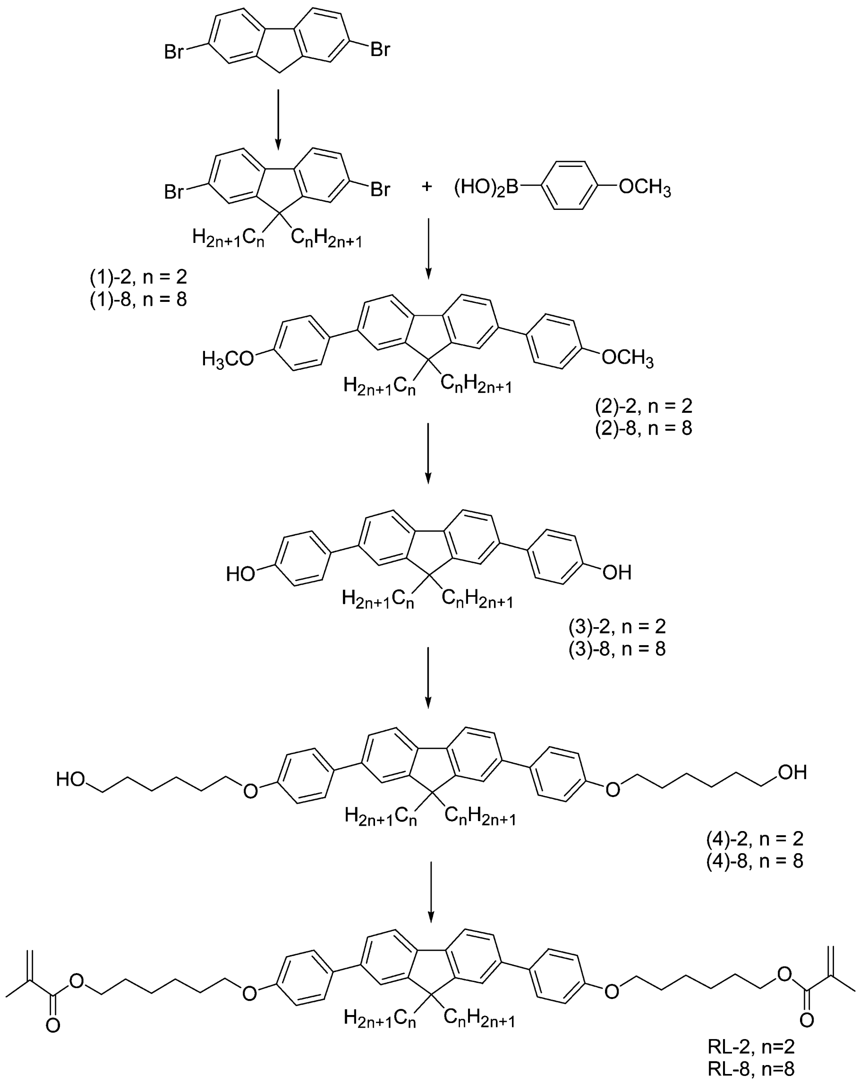

FIGURE 2 Synthetic pathway of the reactive luminophores.

Synthesis of the Fluorene-containing Monomers RL-2 and RL-8

2,7-dibromo-9,9′-dialkylfluorenes (1)-2 and (1)-8

To a mixture of 2,7-dibromofluorene (42.8 mmol) and tetrabutylammonium bromide (2.1 mmol) in toluene (80 mL) a 50% aqueous solution of NaOH (80 mL) was added. Then, the required 1-bromoalkane (97.0 mmol)

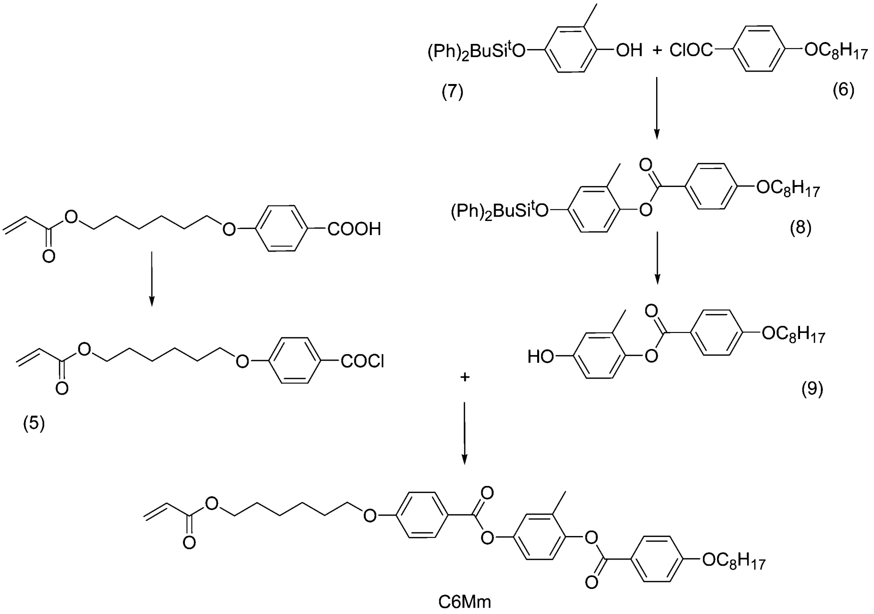

FIGURE 3 Synthetic pathway of the reactive liquid crystal host C6Mm.

in toluene (20 mL) was added dropwise and the reaction was vigorously stirred overnight at 60°C. Once cooled down to room temperature, the organic layer was separated and washed with water, dried over magnesium sulphate and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel using hexane as eluant. The crude product was purified by recrystallization from ethanol to yield the corresponding product (60–65%). *Characterization data for (1)-2.* ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.51 (dd, $J = 7.5$, 1.4 Hz, 2H), 7.47–7.39 (m, 4H), 1.97 (q, $J = 7.2$ Hz, 4H), 0.29 (t, $J = 7.5$ Hz, 6H). *Characterization data for (1)-8.* ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.51 (dd, $J = 7.5$, 1.4 Hz, 2H), 7.47–7.39 (m, 4H), 1.92–1.87 (m, 4H), 1.24–0.97 (m, 20H), 0.81 (t, $J = 7.5$ Hz, 6H), 0.64–0.48 (m, 4H).

2,7-Bis-(4-methoxyphenyl)-9,9′-dialkylfluorenes (2)-2 and (2)-8

A mixture of the desired 2,7-dibromo-9,9′-dialkylfluorene (3.6 mmol), 4-methoxyphenylboronic acid (10.7 mmol), sodium carbonate (22.0 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.29 mmol) was dissolved in water (20 mL) and dimethoxyethane (100 mL). The reaction mixture was heated at reflux temperature for 36 h. Then, the reaction was cooled and additional 4-methoxyphenylboronic acid (6.5 mmol) was added. The reaction was heated at reflux temperature for 24 h. The reaction mixture was cooled to room temperature and 2 N HCl (100 mL) was added. The product was extracted with diethyl ether, washed with water, then washed with brine and dried over $MgSO_4$. The organic solution was concentrated and the precipitated solid isolated by filtration. The product was purified by recrystallization from 96% ethanol to yield the required product as a white solid (61–63%). *Characterization data for (2)-2.* ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.74 (d, $J = 7.8$ Hz, 2H), 7.61 (d, $J = 8.7$ Hz, 4H), 7.55–7.51 (m, 4H), 7.00 (d, $J = 8.1$ Hz, 4H), 3.86 (s, 6H), 2.09 (q, $J = 7.3$ Hz, 4H), 0.41 (t, $J = 7.2$ Hz, 6H). *Characterization data for* (2)-8. ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.72 (d, $J = 7.8$ Hz, 2H), 7.60 (d, $J = 8.7$ Hz, 4H), 7.55–7.51 (m, 4H), 7.00 (d, $J = 8.8$ Hz, 4H), 3.84 (s, 6H), 2.03–1.98 (m, 4H), 1.21–1.05 (m, 20H), 0.78 (t, $J = 6.9$ Hz, 6H), 0.75–0.63 (m, 4H).

2,7-Bis(4-hydroxyphenyl)-9,9′-dialkylfluorenes (3)-2 and (3)-8

The appropriate 2,7-bis-(4-methoxyphenyl)-9,9′-dialkylfluorene (2.7 mmol) was dissolved in dichloromethane (80 mL) and then cooled to 0°C. A solution of boron tribromide (1 M in dichloromethane) (8 mmol) was added dropwise under inert atmosphere and the mixture stirred overnight at room temperature. Then, the solution was poured in water (300 mL) and stirred for 2 h. The reaction was extracted with diethyl ether, washed with sodium carbonate, dried over $MgSO_4$ and the solvent removed under vacuum. The crude was purified by flash column chromatography on silica gel using ethyl acetate/hexane (3:7) as eluant to yield the desired product as a pale yellow solid (80%). *Characterization data for (3)-2.* ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.72 (d, J = 7.5 Hz, 2H), 7.57–7.49 (m, 8H), 6.94 (d, $J = 8.7$ Hz, 4H), 2.09 (q, $J = 7.3$ Hz, 4H), 0.41 (t, $J = 7.2$ Hz, 6H). *Characterization data for (3)-8.* ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]. 7.73 (d, $J = 7.5$ Hz, 2H), 7.58–7.45 (m, 8H), 6.94 (d, $J = 8.6$ Hz, 4H), 2.03–1.98 (m, 4H), 1.20–1.05 (m, 20 H), 0.78 (t, $J = 6.9$ Hz, 6H), 0.76–0.65 (m, 4H).

2,7-Bis[4-(6-hydroxyhexyloxy)phenyl]-9,9′-dialkylfluorenes (4)-2 and (4)-8

A mixture of the corresponding 2,7-bis(4-hydroxyphenyl)-9,9′-dialkylfluorene (1.3 mmol), K_2CO_3 (5.2 mmol) and 6-chlorohexanol (3.6 mmol) in DMF (60 mL) was heated overnight at reflux temperature. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate and the organic phase separated, washed with water and dried over $MgSO_4$. The solution was concentrated and the residue placed onto silica gel and purified by flash column chromatography on silica gel using ethyl acetate/hexane as eluant (4:1) to yield the required product as a white solid (50–54%). *Characterization data for (4)-2.* ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.71 (d, $J = 7.6$ Hz, 2H), 7.53–7.45 (m, 8H), 6.94 (d, $J = 8.5$ Hz, 4H), 4.01 (t, $J = 6.6$ Hz, 4H), 3.57 (t, $J = 6.5$ Hz, 4H), 2.09 (q, $J = 7.3$ Hz, 4H), 1.82 (m, 4H), 1.72 (m, 4H), 1.53 (m, 8H), 0.40 (t, $J = 7.2$ Hz, 6H). ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.73 (d, $J = 7.6$ Hz, 2H), 7.55–7.45 (m, 8H), 6.96 (d, $J = 7.5$ Hz, 4H), 4.01 (t, $J = 6.6$ Hz, 4H), 3.58 (t, $J = 6.5$ Hz, 4H), 2.04–1.82 (m, 8H), 1.72–1.53 (m, 12H), 1.22–1.06 (m, 20H), 0.75 (t, $J = 7.0$ Hz, 6H), 0.69 (m, 4H).

2,7-Bis[4-(6-methacryloyloxyhexyloxy)Phenyl]-9,9′-dialkylfluorenes RL-2 and RL-8

Methacryloyl chloride (1.3 mmol) was added dropwise to a solution of the corresponding 2,7-bis[4-(6-hydroxyhexyloxy)phenyl]-9,9′-dialkylfluorene (0.56 mmol) and triethylamine (1.3 mmol) in THF (50 mL) under argon atmosphere. The reaction mixture was heated at reflux temperature for 3 days. Afterwards, the reaction was cooled and the precipitate filtered off. The organic phase was washed with water, dried over magnesium sulphate, filtered, and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel using hexane/ethyl acetate/hexane (9:1 for RL-2 or 6:1 for RL-8) as eluant and subsequent recrystallization from 96% ethanol to yield the compound as a white solid (49–53%). *Characterization data for RL*-2. IR (nujol, cm^{-1}) ν: 1716, 1737, 1607, 1515, 1404, 1320, 1296. ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.72 (d, $J = 8.5$ Hz, 2H), 7.55 (m, 8H), 6.97 (d, $J = 8.7$ Hz, 4H), 6.09 (s, 2H), 5.54 (s, 2H), 4.16 (t, $J = 6.6$ Hz, 4H), 4.00 (t, $J = 6.2$ Hz, 4H), 2.07 (q, $J = 6.9$ Hz, 4H), 1.94 (s, 6H), 1.82 (m, 4H), 1.73 (m, 4H), 1.51 (m, 8H), 0.39 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR [300 MHz, $CDCl_3$, δ (ppm)]: 167.53, 158.52, 150.72, 139.92, 139.59, 136.49, 134.07, 128.10, 125.22, 125.55, 121.07, 119.77, 114.76, 67.87, 64.64, 56.16, 32.84, 29.17, 28.56, 25.76, 18.32, 8.64. Anal. calcd. for $C_{37}H_{50}O_6$: C, 75.22; H, 8.53. Found: C, 74.98; H, 8.00. *Characterization data for RL-8*. IR (nujol, cm^{-1}) ν: 1712, 1637, 1606, 1518, 1324, 1293. ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.71 (d, $J = 7.8$ Hz, 2H), 7.54 (m, 8H), 6.97 (d, $J = 8.0$ Hz, 4H), 6.09 (s, 2H), 5.54 (s, 2H), 4.16 (t, $J = 6.6$ Hz, 4H), 4.00 (t, $J = 6.6$ Hz, 4H), 2.02 (m, 4H), 1.94 (s, 6H), 1.82 (m, 4H), 1.70 (m, 4H),1.50 (m, 8H), 1.24–1.04 (m, 20H), 0.75 (t, $J = 7.0$ Hz, 6H), 0.70 (m, 4H). ^{13}C NMR [300 MHz, $CDCl_3$, δ (ppm)]: 167.49, 158.54, 151.56, 139.55, 136.53, 134.18, 128.10, 127.99, 125.50, 125.14, 121.04, 119.77, 114.79, 67.89, 64.61, 55.14, 40.41, 31.72, 29.97, 29.12, 28.56, 25.75, 23.76, 22.52, 18.27, 13.98. Anal. calcd. for $C_{49}H_{74}O_6$: C, 77.53; H, 9.83. Found: C, 77.25; H, 9.41.

Synthesis of the Liquid Crystal Host Monomer C6Mm

4-(6-Acryloyloxyhexyloxy)Benzoyl Chloride (5)

To a mixture of 4-(6-acryloyloxyhexyloxy)benzoic acid (6.4 mmol), a catalytic amount of *N,N*-dimethylformamide, and 2,6-di-*tert*-butyl-4-methylphenol (0.15 g) as thermal inhibitor in CH_2Cl_2 (15 mL), and thionyl chloride (3.5 mmol) were added over a period of 20 min. After the addition of thionyl chloride was complete the mixture turned yellowish. The solution was stirred overnight and then CH_2Cl_2 and $SOCl_2$ were removed by distillation under reduced pressure. The product was used without further purification (98%). ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 8.03 (d, $J = 9.0$ Hz, 2H), 6.91 (d, $J = 9.0$ Hz, 2H), 6.38 (dd, $J = 17.0$, 1.0 Hz, 1H), 6.13 (dd, $J = 17.0$, 10.0 Hz, 1H), 5.80 (dd, $J = 10.0$, 1.0 Hz, 1H), 4.16 (t, $J = 7.0$ Hz, 2H), 4.01 (t, $J = 7.0$ Hz, 2H), 1.81 (q, $J = 7$ Hz, 2H), 1.56–1.41 (m, 4H).

4-octyloxy Benzoyl Chloride (6)

The compound was prepared by alkylation of 4-hydroxybenzoic acid and subsequent formation of the corresponding acyl chloride as it was described above.

Tert-butyl-diphenylsilyl 4-hydroxy-3-methylphenyl Ether (7)

Tert-butylchlorodiphenylsilane 3.85 mmol) was dropwise added to a mixture of methylhydroquinone (3.85 mmol), triethylamine (3.85 mmol) 4-*N,N*-dimethylaminopyridine (0.15 mmol) in dichloromethane (30 mL) under inert atmosphere. After vigorously stirring for 14 h, the solvent was removed under vacuum the residue was purified by flash column chromatography on silica gel using hexane/ethyl acetate (25:1) as eluant to yield the product (30%). ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.71–7.68 (m, 6H), 7.43–7.31 (m, 6H), 6.58 (d, $J = 3.0$ Hz, 1H), 6.44 (d, $J = 9.0$ Hz, 1H), 6.41 (dd, $J = 9.0$, 3.0 Hz, 1H), 4.28 (s, 1H), 2.07 (s, 3H), 1.07 (s, 9 H).

4-Hydroxy-2-methylphenyl 4-octyloxybenzoate (9)

4-octyloxybenzoyl chloride (1.65 mol) in dichloromethane (10 mL) was added dropwise to a solution of tert-butyl-diphenylsilyl 4-hydroxy-3-methylphenyl ether (1.66 mol) and (2.47 mol) of triethylamine (2.47 mol) in dichloromethane (200 mL). The mixture was stirred at room temperature for three days and then was poured into a mixture of water (10 mL), ice (10 g) and concentrated HCl (0.5 mL). The organic layer was separated, washed with a saturated solution of NaCl, dried over $MgSO_4$, and the solvent was removed under pressure. The crude product was purified by flash column chromatography on silica gel using dichloromethane/hexane (3:2) as eluant. Subsequent recrystallization in absolute ethanol gave 4-[tert-butyl-diphenylsilyl]-2-methylphenyl 4-octyloxybenzoate (8) as a white solid (40%). A round bottom flask was charged with 4-[tert-butyl-diphenylsilyl]-2-methylphenyl (1.35 mol) in THF (100 mL) and tetrabutylammonium fluoride hydrate (1.35 mol). The solution was vigorously stirred for 5 h and finally water (150 mL) was added. The resulting mixture was extracted with dichloromethane, washed with a brine solution, dried over $MgSO_4$ and finally, the solvent was removed under vacuum. The residue was purified by flash column chromatography on silica gel with using hexane/ethyl acetate (15:1) as eluant to render the required product (75%). ^1H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 8.12 (d, $J = 8.6$ Hz, 2H), 6.95 (d, $J = 9.4$ Hz, 4H), 6.70–6.68 (m, 3H), 4.02 (t, $J = 6.6$ Hz, 2H), 2.14 (s, 3H), 1.53 (s, 3H), 1.46 (m, 2H), 1.30–1.27 (m, 8H), 0.87 (t, $J = 6.6$ Hz, 2H).

1-[4-(6-acryloyloxyhexyloxy)Benzoyloxy]-2-methyl-4-(4-octylbenzoyloxy)Benzene(C6Mm)

The compound was prepared from 4-(6-acryloyloxyhexyloxy)benzoyl chloride and 4-hydroxy-2-methylphenyl 4-octyloxybenzoate as described for 4-(tert-butyl-diphenylsilyl)-2-methylphenyl 4-octyloxybenzoate. The crude reaction mixture was purified by flash column chromatography on silica gel using dichloromethane/hexane (4:1) as eluant. Subsequent recrystallization from 96% ethanol gave the product as a white solid (87%). IR (nujol, cm^{-1}) ν: 1729, 1605, 1580, 1254, 1182, 1163, 1069. ^1H NMR [300 MHz, $CDCl_3$, δ (ppm)]: 8.15 (d, $J = 7.3$ Hz, 2H), 8.12 (d, $J = 8.4$ Hz, 2H), 7.00–7.20 (m, 3H), 6.96 (m, 4H), 6.40 (d, $J = 17.4$ Hz, 1H), 6.11 (dd, $J = 17.2$, 11.3, 1H), 5.81 (d, $J = 11.3$ Hz, 1H), 4.17 (t, $J = 6.8$ Hz, 1H), 4.04 (t, $J = 6.4$ Hz, 4 H), 2.22 (s, 3H), 1.90–1.65 (m, 6H), 1.60–1.40 (m, 8H), 1.40–1.20 (m, 6 H), 0.88 (t, $J = 6.2$ Hz, 3H). Anal. calcd. for $C_{38}H_{46}O_8$: C, 72.36; H, 7.35. Found: C, 72.01; H, 6.98.

Photopolymerization

Preparation of Photopolymerizable Mixtures

Samples for photopolymerization were prepared by dissolving the appropriate amounts of mono- and/or direactive compounds in freshly distilled dichloromethane together with the photoinitiator Irgacure 784-DC (1% weight) and the thermal inhibitor 2,6-di-*tert*-butyl-4-methylphenol (200 ppm). The solvent was evaporated first at room temperature and then at 30°C under vacuum.

Preparation of Films by In-situ Photopolymerization

Light-induced photopolymerization was carried out by irradiation of the molten samples in commercial LC cells for planar alignment (Linkam 5 μm). The monomeric mixture was introduced by capillarity at 100°C and cooled down to the polymerization temperature. Uniaxial orientation was checked by optical microscopy. The irradiation process was performed using an OSRAM Ultravitalux 300 W lamp using a 400 nm long pass filter between the lamp and the sample. Irradiation was maintained for 10 min while the lamp was kept at 20 cm from the cell.

Techniques

IR spectra were measured on a ATI-Matsson Genesis Series FTIR from nujol mulls between NaCl disks. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unit-300 spectrometer.

Mesogenic behaviour and transition temperatures were determined using an Olympus BH-2 polarizing microscope equipped with a Linkam THMS hot-stage central processor and a CS196 cooling system. Differential scanning calorimetry (DSC) was performed using a DSC 2910 from TA Instruments with samples sealed in aluminium pans and a scanning rate of 10°C/min under nitrogen atmosphere. Temperatures were read at the onset of the peak. *In-situ* photopolymerization was studied by DSC using a Perkin-Elmer 7 apparatus modified for light irradiation[12]. The sample (2–4 mg) was placed in an aluminum pan that was irradiated under a nitrogen atmosphere using an OSRAM Ultravitalux lamp. A 400 nm long-pass filter and water to filter the IR radition were placed between the sample and the light source. The lamp was kept at 30 cm from the sample holder.

Optical absorption spectra were recorded with an UV-vis spectrophotometer UV4-200 from ATI-Unicam in THF. Luminescence measurements were performed using a Perkin-Elmer LS50B spectrofluorimeter. Spectra were recorded in THF solution of ca. 0.01 optical density under excitation in the absorption maximum [13]. Fluorescence quantum yields were determined by comparing the integrated photoluminescence with that of a reference with a known quantum yield. 9,10-Diphenylanthracene (99%, Acros Organics) in cyclohexane was used as a reference (quantum yield 0.90). The method was validated by measuring the quantum yield of a previously reported luminophore [8]. Polarized luminescence measurements were recorded using the same equipment with a sample holder designed to measure LC cells [4]. The measurements were taken with the excitation beam polarized in parallel to the rubbing direction of the cell and the detection polarizer either parallel or perpendicular, these two experimental configurations are noted as vvv or vvh respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Monomers

The synthesis of the functionalized fluorenes was accomplished in several steps starting from 2,7-dibromofluorene (Fig. 2). First, two alkyl chains were incorporated at the 9 position of the fluorene system by a phase transfer catalytic process. Alkyl chains with 2 and 8 carbon atoms were incorporated in order to establish their influence on the properties of the fluorene derivatives. Short alkyl chains at the 9-position would not disturb the potential mesomorphism by hindering lateral interactions [11] but long alkyl chains may improve the solubility of the otherwise insoluble fluorenes. The rigid core of the fluorene system was elongated by incorporation of phenyl rings at the 2 and 7 positions by Suzuki coupling. In order to avoid undesired lateral reactions, the flexible and methacrylic segments were incorporated in the last two steps of the synthetic sequence.

In relation to the host liquid crystal monomer C6Mm, the key step was the incorporation of the asymmetrically substituted 2-methylhydroquinone whose less hindered hydroxyl group at the 4-position was selectively protected using a bulky protective group such as the *tert*-butyl-diphenylsilyl one. The remaining steps were adapted from the literature [14].

Thermal characterization data of the synthesized compounds is collected in Table I. As might be expected RL-8 did not show liquid crystalline properties. This fact is explained because the long lateral octyl chains prevent the efficient formation of liquid crystalline aggregates and determines its low melting temperature, 42°C. However, RL-2 melts at higher temperature, 65°C, and shows a monotropic smectic mesophase. The sample showed no crystallization in the DSC scan on cooling. On the subsequent heating the isotropization temperature is detected at 23°C. When the sample is observed under the microscope the mesophase is relatively stable at room temperature and crystallizes very slowly. In fact, when a sample of RL-2 previously heated to the isotropic state, cooled down and maintained

TABLE I Properties of the Synthesized Monomers

Compound	Thermal transitions (°C)[a]	λ_{abs} (nm)	λ_{em} (nm)	Φ_{fl}
RL-2	K 65 (SmC 22) I	335	369, 388	0.65
RL-8	K 42 I	336	372, 388sh	0.66
C6Mm	K 62 N 136 I	265	–	–

[a] Thermal properties of reactive luminophores were read in the first heating scan, and in second heating scan for C6Mn.

at room temperature for 3 days was again studied by DSC, only the mesophase-isotropic state was detected. This very low tendency to crystallize was also observed in RL-8. The reactive liquid crystal C6Mm exhibits a N mesophase between 62 and 136°C (measured in the second heating scan).

In relation to the optical properties both fluorenes are very efficient emitters. The maximum emission wavelengths have been determined at 388 and 372 nm for RL-2 and RL-8, respectively, in THF solutions of 0.01 optical density being the respective fluorescence quantum yields of 0.66 and 0.65.

In-situ Photopolymerization Study of Fluorene-containing Liquid Crystal Mixtures

The first studies on photopolymerization of these materials have been carried out with RL-8 in order to evaluate its orientation in a liquid crystalline matrix despite its non-mesogenic nature. Photopolymerizable samples and their liquid crystalline properties are collected in Table II. The samples contain C6Mm blended with RL-8 in 5 or 10% molar percentage. They also contain 1% (weight) of a photoinitiator of the titanocene type, Irgacure 784-DC® from Ciba-Geigy, which absorbs between 400–500 nm where none of the components of the mixture absorbs. The mixtures develop a N mesophase on between approx. 58 and 105°C and no phase separation was observed. The mesophase is stable on cooling, with no crystallization of the sample at room temperature observed.

Photopolymerization of the mixtures was investigated by photo-DSC at different temperatures both in the N and the isotropic liquid states. In all cases, as deduced from the polymerization exotherm (Fig. 4a), the reaction progresses at high rate on exposing the samples to the light source. The conversions calculated from these exotherms were higher than 90% in all cases. Photopolymerization rate against conversion was also evaluated from the polymerization exotherms (Fig. 4b). From the plot, a high polymerization rate can be inferred at relatively low conversions that slows down

TABLE II Thermal Transitions of the Photopolymerizable Samples

Mixture	Thermal transitions (°C)[a]
5% RL-8 + 95% C6Mm	K 59 N 118 I
10% RL-8 + 90% C6Mm	K 58 N 104 I

[a] First heating scan.

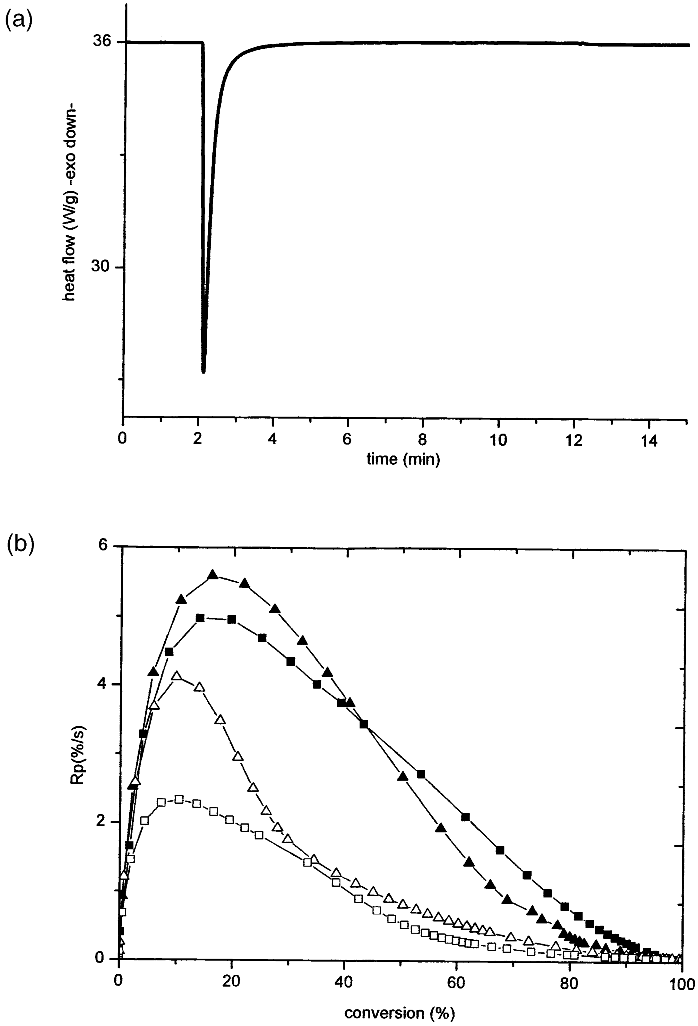

FIGURE 4 (a) Photo-DSC curve corresponding to the photopolymerization at 50°C – nematic phase- of the sample 10% RL-8 + 90 % C6Mm; (b) polymerization rate in percentage of $C=C$ reacted per second as a function of the conversion at different temperatures: (▲) 30°C, nematic phase, (■) 50°C nematic phase, (△)100°C nematic phase and (□) 125°C isotropic state.

as polymerization progresses. The autodeceleration phenomenon is more marked at high temperatures either in the mesophase or the isotropic state, therefore, indicating that the temperature of polymerization has a higher influence in comparison to the phase ordering [15].

Anisotropic Films

Anisotropic films were produced by light-initiated polymerization of the samples in cells for planar alignment. Molecular orientation was qualitatively demonstrated by optical microscopy observing the film between crossed polarizers.

To determine the order parameter, dichroism in the optical absorption spectrum was measured using polarized UV-vis (Fig. 5a). Absorbance in two orthogonal directions, one parallel to the molecular orientation and

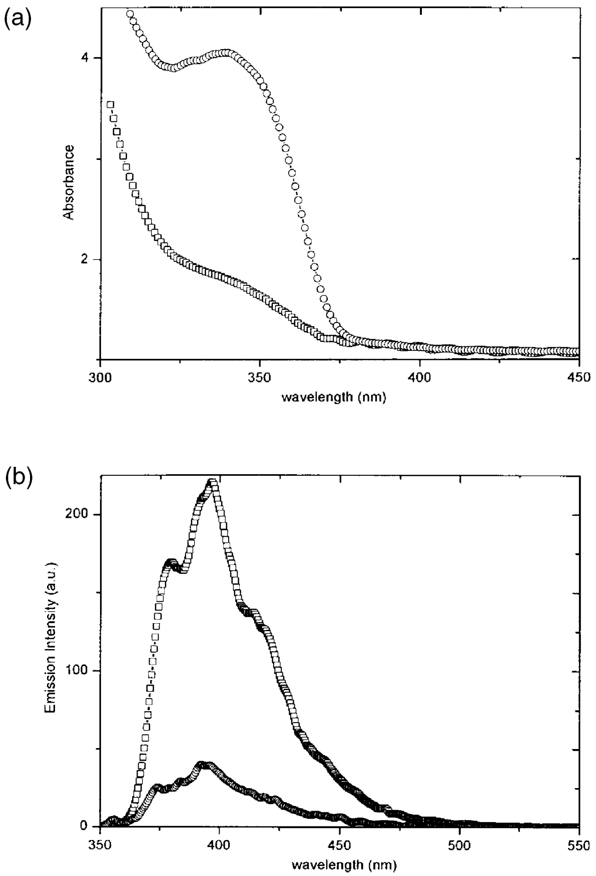

FIGURE 5 (a) Polarized optical absorption spectra of the a the sample 5% RL-8 + 95% C6Mm photopolymerized at 50°C – nematic phase- in a Linkam cell measured with light polarized parallel and perpendicular to the nematic director; (b) Polarized photoluminescence of the same sample measured at room temperature.

the other perpendicular to it was measured which are related to the order parameter by the following equation:

$$S = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$$

The difference between both spectra shows that there is a preferential orientation of the luminophore. The order parameter has been roughly estimated at about 0.6.

Polarized emission spectra of the films were measured at room temperature (Fig. 5b). First of all, it has to be mentioned that the emission wavelength of films was slightly red-shifted when compared to solutions. This fact has been related to a more planar structure of the excited state for the film [16]. Again, the differences on the emission spectra corresponding to vvv and vvh configurations (see experimental) reveal the existence of a preferential orientation for the luminophore. From this spectra, the dichroic ratio on emission, defined from the maximum intensity as

$$R = I_{vvv}/I_{vvh}$$

was calculated to be 6.5 and 5.7 for RL-2 and RL-8, respectively.

In conclusion, we have synthesized and characterized novel luminophores, which can be blended with reactive liquid crystals and polymerized to yield anisotropic films. These films showed a good orientation and polarized photoluminescence. Current work is devoted to the study of the RL-2 mixtures as well as the study of the dependence of the luminescence intensity on the temperature and the excitation wavelength irradiation.

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