Synthesis and characterization of novel liquid-crystalline azo-dyes bearing two amino-nitro substituted azobenzene units and a well-defined, oligo(ethylene glycol) spacer

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ABSTRACT

Four novel liquid-crystalline azo-dyes bearing two amino-nitro substituted azobenzene units linked by a well-defined oligo(ethylene glycol) spacer (DIRED-PEG series): (E)-N,N′-(2,2′-oxybis(ethane-2,1-diyl))bis(N-methyl-4-((E)-(4-nitrophenyl)diazenyl) benzenamine) (DIRED-PEG-2), (E)-N,N′-(2,2′-(ethane-1,2-diylbis(oxy)) bis(ethane-2,1-diyl)) bis(N-methyl-4-((E)-(4-nitrophenyl) diazenyl) ben-zenamine) (DIRED-PEG-3), (E)-N,N′-(2,2′-(2,2′-oxybis (ethane-2,1-diyl) bis(oxy)) bis(ethane-2,1-diyl)) bis(N-methyl-4-((E)-(4-nitrophenyl) diazenyl) benzenamine) (DIRED-PEG-4) and N1,N17-dimethyl-N1,N17-bis (4-((E)-(4-nitrophenyl) diazenyl) phenyl)-3,6,9,12,15-pentaoxaheptadecane-1,17-diamine (DIRED-PEG-6) have been synthesized. These dyes were fully characterized by FTIR, ^{1}H and ^{13}C NMR spectroscopies, and their thermal and optical properties were studied. Besides, the liquid-crystalline behaviour of these compounds was monitored in function of the temperature by light polarized microscopy. Finally, Langmuir films were prepared with these dyes.

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1. Introduction

Azopolymers and some related azo-dyes have been considered as highly versatile materials due to the photoinduced motions, which occur on them, when they are irradiated with laser polarized light [1]. Several reviews covering most of the implications of azobenzene in polymer structures have been published [1–4]. In the last 15 years, various azo-polymers and azo-dyes bearing amino-nitro substituted azobenzene units have been synthesized and characterized [5]. In general, they exhibit maxima absorption wavelength close to those reported for similar push–pull azo-compounds [6,7]. In these materials, both J and H-aggregates have been observed in cast films [5].

In a previous work, we reported the synthesis, characterization and optical properties of a series of amphiphilic amino-nitro substituted azobenzenes bearing end-capped oligo(ethylene glycol) side chains (RED-PEGM series) [8–10]. Azobenzene and poly(ethylene glycol) have been incorporated into various sophisticated systems such as copolymers [11,12], nanomaterials [13,14], cellulose derivatives [15,16] and cyclodextrin polymers [17,18], in some cases forming supramolecular complexes with interesting properties [19]. Poly(ethylene glycol) moieties provide flexibility and water solubility to the systems to whom they are incorporated. On the other hand, we published the synthesis and characterization of a series of azo-dyes bearing terminal hydroxyl groups (RED-PEG series) [20]. These dyes were incorporated into low density polyethylene (LDPE) plates, using acryloyl chloride as grafting agent and gamma radiation, in order to obtain a series of grafted azo-polymer films containing oligo(ethylene glycol) segments (AC-g-PE-RED-PEG series). These materials showed to be very sensitive to moisture, giving rise to solvatochromic effects after exposure to steam, which make them good prospects for the elaboration of humidity sensors [20].

In order to push further our investigations about azobenzene-oligo(ethylene glycol) systems, we carried out the synthesis and characterization of a new series of polymethacrylate based azo-polymers bearing well-defined oligo(ethylene glycol) segments (p*n*PEGMAN series), where p means polymer, *n* indicates the number of ethylene glycol units in the spacer, PEG indicates the presence of a short poly(ethylene glycol) segment, M means methacrylate and AN indicates the presence of an amino-nitro substituted azobenzene unit. Four different p*n*PEGMAN polymers with *n* = 2, 3, 4 and 6 were synthesized and characterized. These polymers exhibited a good thermal stability with T_{10} values between 188 and 227 °C. On the other hand, these polymers exhibited maxima absorption wavelength at 468–477 nm in THF solution and they readily form aggregates in the solid state. Due to their amphiphilic behaviour, the p*n*PEGMAN polymers are

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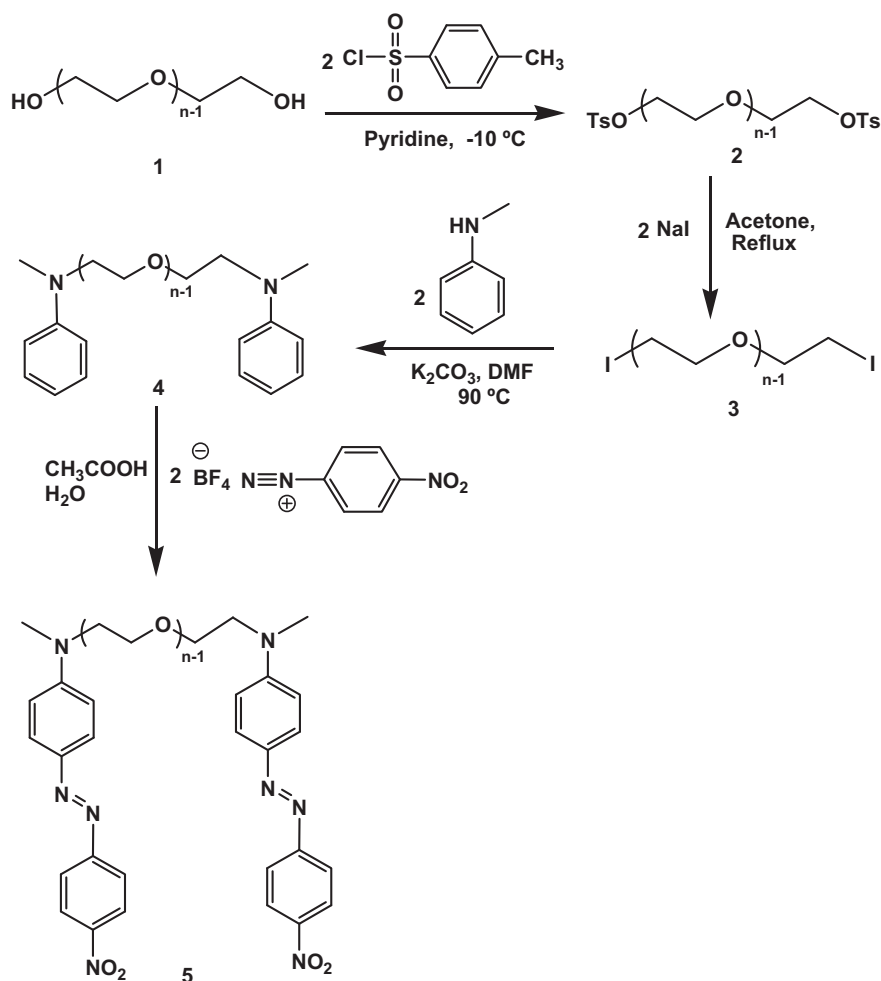*E-mail address:* riverage@iim.unam.mx (E. Rivera).

Fig. 1. Synthesis of the DIRED-PEG dyes: DIRED-PEG-2 ($n = 2$), DIRED-PEG-3 ($n = 3$), DIRED-PEG-4 ($n = 4$), DIRED-PEG-6 ($n = 6$).

suitable for the preparation of Langmuir and Langmuir–Blodgett films [21]. In this work, we report the synthesis and characterization of four novel azo-dyes bearing two amino-nitro substituted azobenzene units linked by a well-defined oligo(ethylene glycol) spacer (DIRED-PEG series): (E)-N,N'-(2,2'-oxybis(ethane-2,1-diyl))bis(N-methyl-4-((E)-(4-nitrophenyl)diazenyl)benzenamine) DIRED-PEG-2, (E)-N,N'-(2,2'-(ethane-1,2-diylbis(oxy)) bis(ethane-2,1-diyl)) bis(N-methyl-4-((E)-(4-nitrophenyl) diazenyl) benzenamine) DIRED-PEG-3, (E)-N,N'-(2,2'-(2,2'-oxybis (ethane-2,1-diyl)bis(oxy)) bis(ethane-2,1-diyl)) bis(N-methyl-4-((E)-(4-nitrophenyl) diazenyl) benzenamine) DIRED-PEG-4 and N1,N17-dimethyl-N1,N17-bis(4-((E)-(4-nitrophenyl)diazenyl)phenyl)-3,6,9,12,15-pentaoxaheptadecane-1,17-diamine DIRED-PEG-6, as well as their incorporation in Langmuir films. The structure of the DIRED-PEG dyes is illustrated in Fig. 1 (compound **5**)

2. Experimental details

2.1. General conditions

All reagents used in the synthesis of the DIRED-PEG dyes were purchased from Aldrich and used as received. These dyes were synthesized according to the method previously reported in the literature for the preparation of the RED-PEG series, using different molar ratios [20] (see Fig. 1).

2.2. Molecular modelling and characterization

Molecular modelling was performed on the obtained compounds employing HyperChem^{TM} 6.03 for Windows, using the semi-empirical methods AM1 and PM3, employing the Polak Ribière algorithm with a maximum of 1100 cycles and RMS gradient of 0.05 kcal Å^{-1} mol^{-1}. FTIR spectra of the DIRED-PEG dyes were carried out on a Spectrum 100 (Perkin Elmer PRECISELY) spectrometer in solid sate. ^{1}H and ^{13}C NMR spectra of these compounds in CDCl$_3$ solution were recorded at room temperature on a Bruker Avance 400 MHz spectrometer, operating at 400 and 100 MHz for ^{1}H and ^{13}C, respectively.

Thermal properties of the obtained azo-dyes were studied by determining T_{10} (10% weight loss temperature) and T_m (melting point). Thermogravimetric analysis (TGA) was conducted on a Hi-Res TGA 2950 Instrument (from 20 to 800 °C) under inert atmosphere and differential scanning calorimetry (DSC) was carried out in a DSC 2910 Instrument (from 20 to 250 °C), in both cases with a heating rate of 10 °C min^{-1}.

All DIRED-PEG dyes were dissolved in spectral quality solvents purchased from Aldrich, and their absorption spectra were recorded on a Varian Cary 1 Bio UV–vis (model 8452A) spectrophotometer at room temperature, using 1 cm quartz cells. Absorption spectra of these dyes were also recorded in cast films, using the same instrument. Cast films were prepared from a saturated solution of the dye in CHCl$_3$, which was deposited over a glass substrate, with further evaporation of the solvent.
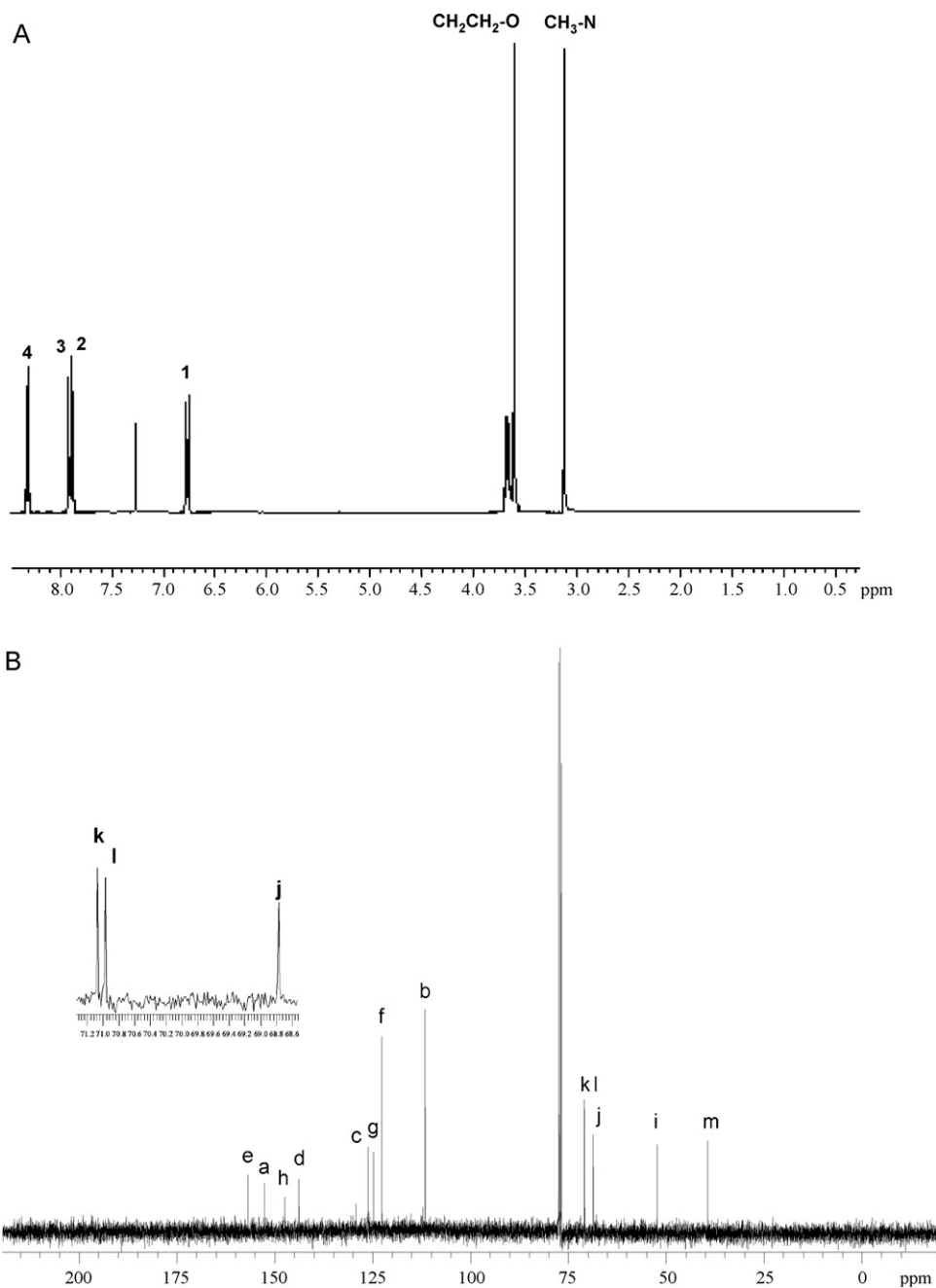
Fig. 2. (a) ^{1}H-NMR spectrum of DIRED-PEG-4, (b) ^{13}C-NMR spectrum of DIRED-PEG-4.

2.3. Synthesis of the DIRED-PEG dyes

DIRED-PEG-2, DIRED-PEG-3, DIRED-PEG-4 and DIRED-PEG-6 have been synthesized according to the method previously reported by us [20], which is illustrated in Fig. 1. The spectroscopical characterization of the DIRED-PEG compounds was carried out by FTIR, ^{1}H and ^{13}C NMR spectroscopies. Although we only describe the synthesis of DIRED-PEG-2 in this section, spectroscopical data are given for all DIRED-PEG dyes.

2.3.1. 2,2′-Oxybis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate) (2)

In a bottom round neck flask under an ice–salt–acetone bath, p-toluenesulphonyl chloride (27.6 g, 145 mmol) was added to a mixture of di(ethylene glycol) (7 g, 66 mmol), in piridine (80 mL) at 0 °C for 5 min. The reaction mixture was vigorously stirred for 30 min at −10 °C and for 2 h at room temperature. Furthermore, it was put in the refrigerator overnight and then the mixture was poured into an aqueous HCl solution (30%). The crude product was extracted with chloroform (3 portions of 100 mL) and the organic phase was washed with water (4 portions of 100 mL) until pH = 7. The solution was dried with anhydrous MgSO$_4$, filtered and concentrated at reduced pressure. The crude product was purified by flash column chromatography in silica gel, using hexanes: CH$_2$Cl$_2$ as eluent, starting with hexanes: CH$_2$Cl$_2$ 20:80, increasing gradually the polarity of the solvent until pure CH$_2$Cl$_2$. The final product was concentrated at reduced pressure to obtain a white solid (18 g, 43.4 mmol). Yield: 66%.
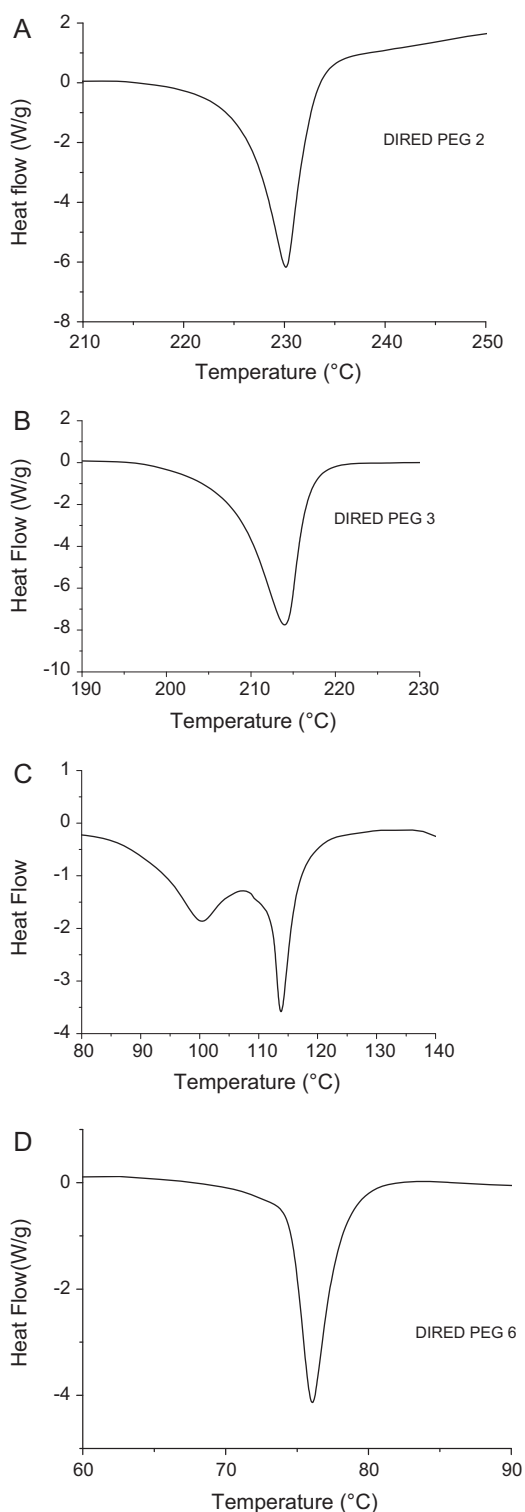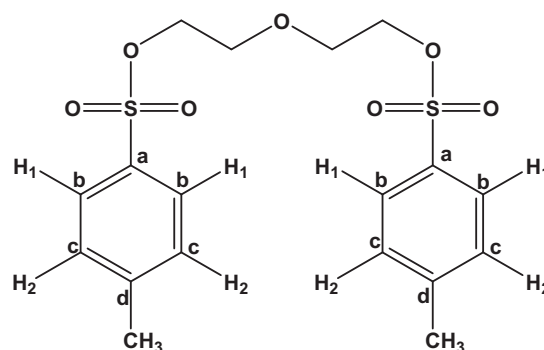
Fig. 3. DSC of (a) DIRED-PEG-2, (b) DIRED-PEG-3, (c) DIRED-PEG-4, (d) DIRED-PEG-6.

IR (solid state) ν = 3064 (C–H aromatic), 2914 (CH$_2$, CH$_3$), 1596 (C=C) and 1450, 1352, 1187 (O=S=O), 1017 (S–O), 1095 (C–O), 922 and 814 (H–C out of plane) cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz) (Scheme 1) δ = 7.77 (d, 4H, J = 8.1 Hz, H^1), 7.34 (d, 4H, J = 8.5 Hz, H^2), 4.08 (t, 4H, J_1 = 4.5 Hz, J_2 = 4.5 Hz, OTs), 3.60 (t, 4H, J_1 = 4.5 Hz, J_2 = 4.5 Hz, OCH$_2$), 2.44 (s, 6H, CH$_3$) ppm.

Scheme 1.

^{13}C NMR (CDCl$_3$, 100 MHz) (Scheme 1) δ = 145.1 (2C, C^a), 132.9 (2C, C^b), 130.1 (2C, C^c), 128.1 (2C, C^d), 69.2 (2C, C^e), 68.9 (2C, C^f), 21.8 (2C, C^g) ppm.

2.3.2. 1-Iodo-2-(2-iodoethoxy)ethane (3)

NaI (15.3 g, 102.6 mmol) was added to a solution of **2** (10 g, 24.1 mmol) in acetone (22.5 mL) and the reaction mixture was heated to reflux for 24 h. Afterwards, the mixture was filtered and the product was extracted with chloroform (2 portions of 100 mL) and washed with water (3 portions of 100 mL) in order to remove the TsONa formed during the reaction. Then, the organic phase was dried with anhydrous MgSO$_4$, filtered and concentrated at reduced pressure. The corresponding alkyl iodide was obtained (6.12 g, 18.77 mmol) as an yellow-orange oil. Due to its instability, this intermediate was identified by TLC and immediately used in the next step without further purification. Crude product yield: 78%.

2.3.3. N,N'-(2,2'-Oxybis(ethane-2,1-diyl))bis(N-methylbenzenamine) (4)

To a solution of N-methylaniline (3.3 g, 30.7 mmol) and K$_2$CO$_3$ (2.7 g, 27.6 mmol) in DMF (40.5 mL), another solution of **3** (5 g, 15.34 mmol) in DMF (20 mL) was added the reaction mixture was heated with vigorous stirring at 90 °C for 30 h. Afterwards, the resulting solution was poured into water and the product was extracted with CHCl$_3$ (2 portions of 100 mL); then it was washed with water (3 portions of 100 mL) in order to remove the remaining DMF. The organic phase was dried with anhydrous MgSO$_4$, filtered and concentrated at reduced pressure. The crude product was obtained as dark red liquid, which was purified by column chromatography, using hexanes as eluent, increasing gradually the polarity of the solvent until hexanes: ethyl acetate 98:2. The pure product **4** was obtained as a beige solid (5.6 g, 19.95 mmol). Yield: 65%.

IR (solid state) ν = 3100 (C–H aromatic), 2958, 2851 (CH$_2$, CH$_3$), 1620 (C=C aromatic), 1494, 1229 (N–CH$_3$), 1118 (CH$_2$–O), 924 and 754 cm^{-1} (H–C out of plane)

^{1}H NMR (CDCl$_3$, 400 MHz) (Scheme 2) δ = 7.28 (m, 4H, H^2), 6.91 (m, 6H, H^3 and H^1), 3.86 (t, J_1 = 5.0 Hz, J_2 = 4.5 Hz, 4H, CH$_2$O), 3.15 (t, J_1 = 5.0 Hz, J_2 = 4.5 Hz, 4H, NCH$_2$), 2.95 (s, 6H, H^6, NCH$_3$) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz) (Scheme 2) δ = 151.5 (2C, C^a), 129.4 (4C, C^c), 120.2 (2C, C^d), 115.9 (4C, C^b), 67.1 (2C, OCH$_2$CH$_2$), 49.5 (2C, NCH$_3$) ppm.

(E)-N,N'-(2,2'-oxybis (ethane-2,1-diyl)) bis (N-methyl-4-((E)-(4-nitrophenyl) diazenyl) aniline) DIRED-PEG-2 (**5**).

A solution of **4** (1 g, 3.51 mmol) in acetic acid (17 mL) was poured into an addition funnel and added dropwise to a suspension of p-nitrobenzenediazonium tetrafluoroborate (1.66 g, 7 mmol) in acetic acid 50% (38 mL) at 0 °C. Once completed the addition, the
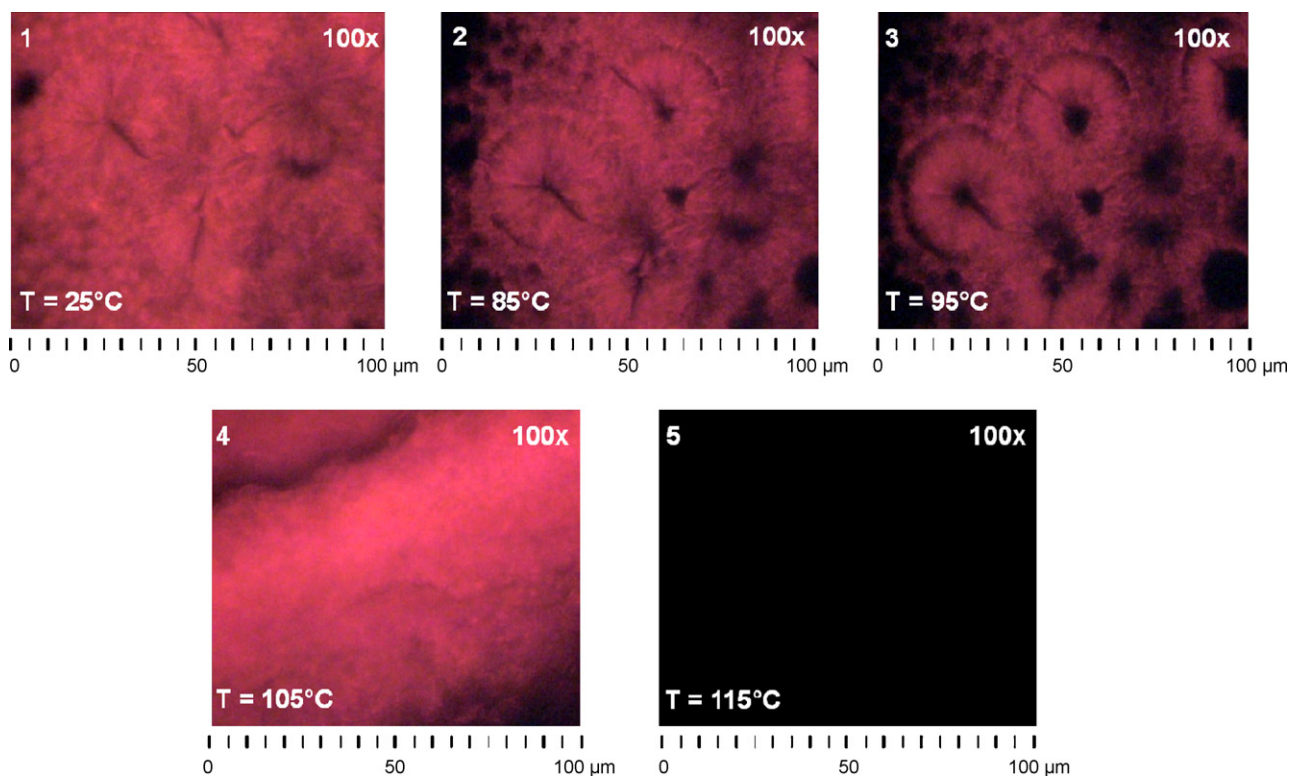
Fig. 4. Light polarized microscopy image of DIRED-PEG.

resulting suspension was stirred at room temperature for 5 h; then it was neutralized with a saturated solution of K_2CO_3 and extracted with $CHCl_3$ (2 portions of 100 mL). The organic phase was washed with water (2 portions of 100 mL) and the solution was dried with anhydrous $MgSO_4$, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel, using hexanes as eluent, employing different mixtures hexanes: CH_2Cl_2, increasing the polarity until CH_2Cl_2 100%. The final product was obtained as a dark red solid (2.01 g, 3.44 mmol). Yield: 98%. Elemental analysis: calcd for $C_{30}H_{30}O_5N_8$:C, 61.85%; H, 5.19%; N, 19.23%. Found: C, 61.83%; H, 5.21%; N, 19.21%.

IR (solid state) $\nu = 3091$ (C–H aromatic), 2869 CH_2 and CH_3, 1603 (C=C aromatic), 1509 (NO_2), 1435 (N=N), 1337 (N–CH_3), 1234 (N–CH_2), 1097 (CH_2–O), 868 and 752 cm^{-1} (H–C out of plane).

^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme 3) $\delta = 8.33$ (d, $J = 8.1$ Hz, 4H, H^4), 7.94 (d, $J = 8.1$ Hz, 4H, H^3), 7.92 (d, $J = 8.5$ Hz, 4H, H^2), 6.96 (d, 4H, H^1), 3.88 (t, $J_1 = 5.0$ and $J_2 = 4.5$ Hz, 4H, OCH_2), 3.37 (t, $J_1 = 5.0$, $J_2 = 4.5$ Hz, 4H, NCH_2), 3.10 (s, 6H, NCH_3).

^{13}C NMR ($CDCl_3$, 100 MHz)) (Scheme 3) $\delta = 156.6$ (2C, C^e), 154.2 (2C, C^a),148.1 (2C, C^h), 145.6 (2C, C^d),125.8 (2C, C^c), 124.8 (2C, C^g),123.1 (2C, C^f), 124.8 (2C, C^b), 77.4 (2C, OCH_2), 66.7 (2C, NCH_2), 47.8 (2C, NCH_3) ppm.
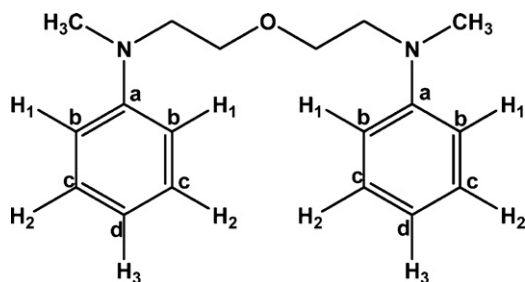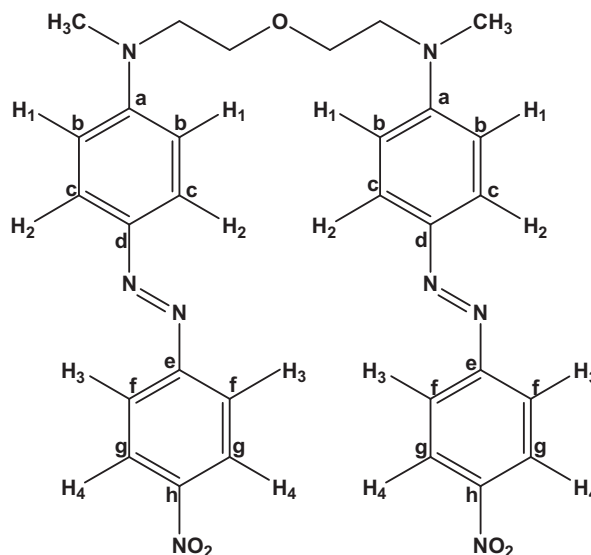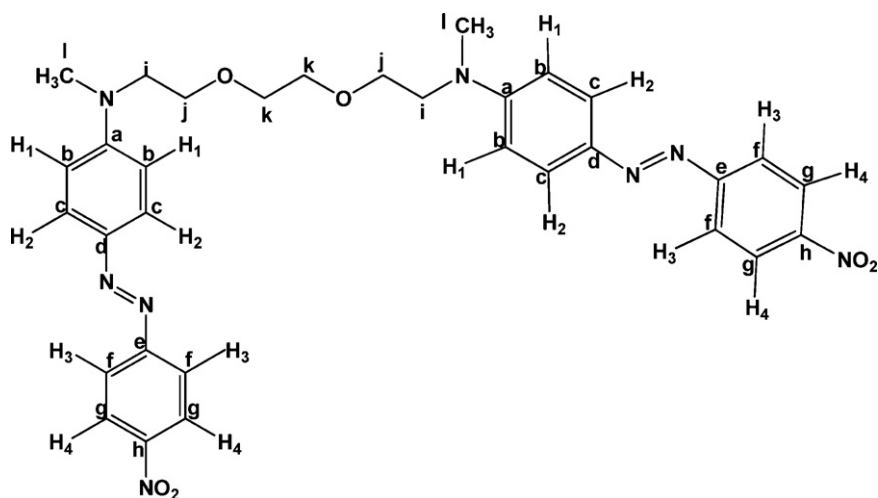
2.3.4. For DIRED-PEG-3

Yield: 98%. Elemental analysis: calcd for $C_{32}H_{34}O_6N_8$:C, 61.33%; H, 5.47%; N, 17.88%. Found: C, 61.31%; H, 5.49%; N, 17.87%.

^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme 4) $\delta = 7.24$ (d, $J = 7.1$ Hz, 4H, H^4), 7.22 (d, $J = 7.1$ Hz, 4H, H^3), 6.73 (d, $J = 8.1$ Hz, 4H, H^2), 6.69 (d, $J = 7.5$ Hz, 4H, H^1), 3.59 (m, CH_2CH_2O), 2.98 (s, 6H, NCH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz)) (Scheme 4) $\delta = 156.6$ (2C, C^e), 154.2 (2C, C^a),148.2 (2C, C^h), 145.5 (2C, C^d),125.9 (2C, C^c), 124.7 (2C, C^g), 123.1 (2C, C^f), 124.8 (2C, C^b), 70.95 (2C, C^k), 68.82 (2C, C^j), 52.55 (2C, C^i), 39.1 (2C, C^l) ppm.

Scheme 2.

Scheme 3.

Scheme 4.

2.3.5. For DIRED-PEG-4

Yield: 93%. Elemental analysis: calcd for $C_{34}H_{38}O_7N_8$:C, 60.88%; H, 5.71%; N, 16.71%. Found: C, 60.87%; H, 5.73%; N, 16.69%.

^{1}H NMR (CDCl$_3$, 400 MHz) (Scheme 5) δ = 8.31 (d, J = 9.1 Hz, 4H, H^4), 7.90 (d, J = 9.1 Hz, 4H, H^3), 7.88 (d, J = 9.1 Hz, 4H, H^2), 6.76 (d, J = 9.6 Hz, 4H, H^1), 3.60 (m, 12H, CH$_2$CH$_2$O), 3.12 (s, 6H, NCH$_3$).

^{13}C NMR (CDCl$_3$, 100 MHz) (Scheme 5) δ = 156.9 (2C, C^e), 152.7 (2C, C^a), 147.6 (2C, C^h), 143.9 (2C, C^d), 126.2 (4C, C^c), 124.8 (4C, C^g), 122.8 (4C, C^f), 111.7 (4C, C^b), 71.1 (2C, C^k), 70.9 (2C, C^l), 68.7 (2C, C^j), 52.4 (2C, C^i), 39.5 (2C, C^m) ppm.

2.3.6. For DIRED-PEG-6

Yield: 92%. Elemental analysis: calcd for $C_{38}H_{46}O_9N_8$:C, 60.15%; H, 6.11%; N, 14.77%. Found: C, 60.15%; H, 6.13%; N, 14.75%.

^{1}H NMR (CDCl$_3$, 400 MHz) (Scheme 6) δ = 8.29 (d, J = 9.1 Hz, 4H, H^1), 7.88 (d, J = 9.1 Hz, 4H, H^2), 7.86 (d, J = 9.6 Hz, 4H, H^3), 6.75 (d, J = 9.1, 4H, H^4), 3.61 (m, 24H, CH$_2$CH$_2$O), 3.12 (s, 6H, NCH$_3$) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz) (Scheme 6). δ = 156.7 (2C, C^e), 152.5 (2C, C^a), 147.3 (2C, C^h), 143.7 (2C, C^d), 126.1 (2C, C^c), 124.6 (2C, C^g), 122.6 (2C, C^f), 111.5 (2C, C^b), 70.8 (2C, C^n), 70.6 (2C, C^m), 70.5 (2C, C^l), 68.5 (2C, C^k), 52.2 (2C, C^j), 39.4 (2C, C^i), 30.9 (2C, C^o) ppm.

2.4. Preparation of Langmuir films

Langmuir films were prepared with DIRED-PEG dyes, using a KSV-5000 system 3 (KSV Instruments Ltd., Finland) equipped with a Wilhelmy plate, bearing a sensor to measure the surface pressure. Different solutions were prepared with these dyes, using CHCl$_3$ (HPLC) with concentrations ranging between 0.8 and 1.5 mg mL^{-1}. The monolayer was formed spreading 100–150 μl of the solution over the water subphase, which was previously purified with a Milli-Q system (Millipore) system. The layers were compressed after a break of 10 mm min^{-1} in order to reach the equilibrium, using a constant compression rate of 5 cm^2 min^{-1}; the corresponding isotherms were recorded at a temperature of 22 ± 1 °C.

3. Results and discussion

3.1. Synthesis and characterization of the DIRED-PEG dyes

The synthesis of the DIRED-PEG dyes [8,20] was carried out according to the synthetic sequence shown in Fig. 1.

DIRED-PEG dyes were prepared from oligo(ethylene glycol) with the appropriate n value (n = 2, 3, 4, 6) (**1**), which was reacted in the presence of 2 eq. of tosyl chloride (TsCl) in pyridine at −10 °C to give the corresponding tosylate (**2**). This intermediate was treated with 2 eq. NaI in acetone, heating to reflux in order to obtain the corresponding alkyl iodide (**3**). Afterwards, 2 eq. of N-methylaniline were reacted in the presence of 1 eq. of **3** to yield the diamino compound **4**. Finally, this intermediate was coupled in the presence of 2 eq. of 4-nitrobenzenediazonium tetrafluoroborate, using an aqueous solution of acetic acid 50% as solvent, to give the desired DIRED-PEG dye (**5**).

Intermediates involved in the synthesis and the obtained azo-dyes were fully characterized by FTIR, ^{1}H and ^{13}C NMR spectroscopies. For instance, DIRED-PEG-2 was selected as model compound, in order to describe concisely and briefly the characterization this azo-dyes series.

The FTIR spectrum of DIRED-PEG-2 (not shown) exhibited two bands at 3091 and 2869 cm^{-1}, due to the aromatic C–H bonds and the methylene groups present in the oligo(ethylene glycol) spacer, respectively. In addition, we can observe other bands at 1603 (C=C aromatic), 1509 (NO$_2$) and 1435 (N=N) cm^{-1}, as well as two more bands at 1337 and 1234 cm^{-1}, corresponding to the tertiary amines (N–CH$_3$, N–CH$_2$). Moreover, an additional band was seen at 1097 cm^{-1}, resulting from the vibrations of the (CH$_2$–O) bonds. Finally, two more bands at 868 and 752 cm^{-1}, which can be attributed to the C–H bonds (out of plane) were also observed.

The ^{1}H NMR spectrum of DIRED-PEG-2 (Fig. 2a) showed four signals in the aromatic region at δ = 8.33, 7.94, 7.92 and 6.96 ppm, due to the four types of aromatic protons present in the azobenzene unit H^4, H^3, H^2 and H^1, respectively. Moreover, we can perceive two triplets in the aliphatic region at δ = 3.88 and 3.37 ppm, related to the methylene groups OCH$_2$ and NCH$_2$, respectively, followed by a singlet at δ = 3.10 ppm, due to the CH$_3$–N group.

On the other hand, the ^{13}C NMR spectrum of DIRED-PEG-2 (Fig. 2b) exhibited 4 down-field signals, due to the eight type of aromatic carbons C^e, C^a, C^h, C^d, C^c, C^g, C^f and C^b present in the azobenzene units, which appear at δ = 156.6, 154.2, 148.1, 145.6, 125.8, 124.8, 123.1 and 114.1 ppm, respectively. Besides, we can distinguish three more intense signals in the aliphatic zone at δ = 77.4, 66.7 and 47.8 ppm, due to the methylenes OCH$_2$, NCH$_2$ and the methyl group NCH$_3$, respectively.

The ^{1}H and ^{13}C NMR spectra of DIRED-PEG-3, DIRED-PEG-4 and DIRED-PEG-6 are very similar to those of DIRED-PEG-2, the main
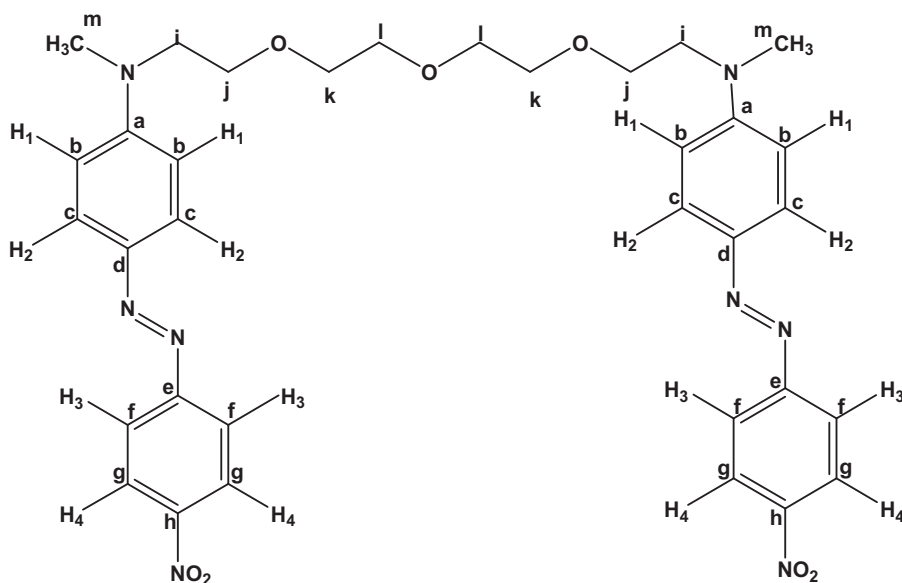
Scheme 5.
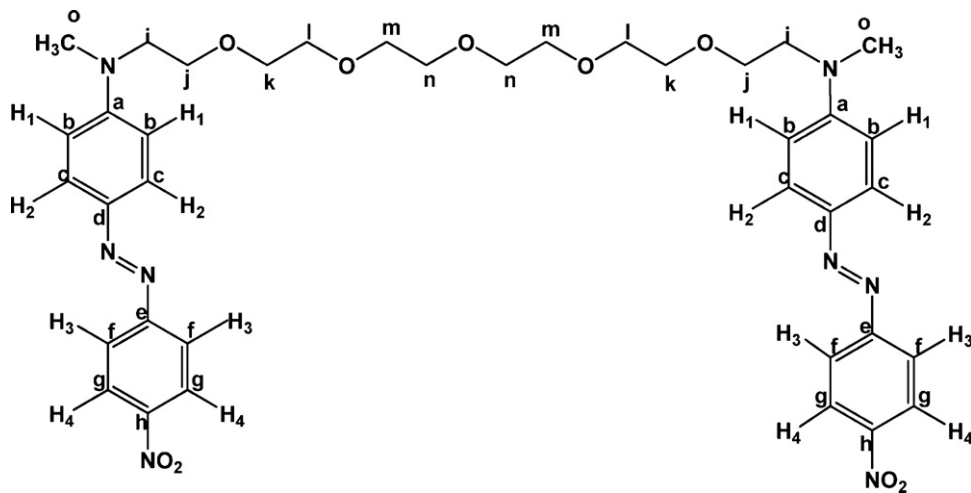
Scheme 6.

difference is the number of signals present in the aliphatic region, due to the methylene groups of the oligo(ethylene glycol) chain.

3.2. Thermal properties of the dyes

Thermal properties of the obtained azo-dyes were determined by thermogravimetric analysis (from 25 to 800 °C) and differential scanning calorimetry (from 20 to 250 °C), in both cases with a heating rate of 10 °C min^{-1}; the results are summarized in Table 1.

DIRED-PEG-2 exhibited a T_{10} = 282.5 °C, showing drastic degradation between 250 and 368 °C. On the other hand, DIRED-PEG-3, DIRED-PEG-4 and DIRED-PEG-6 showed T_{10} values of 327, 334.5 and 332 °C, respectively. As we can see, the thermal stability of the dye slightly increases as the oligo(ethylene glycol) segment length augments. This can be due to the fact that longer spacers make more difficult the fragmentation of the molecule and allow the azobenzene chromophores to aggregate intramolecularly, which augments their thermal stability. In general, all these dyes showed fast degradation in the range between 305 and 453 °C. Differential scanning calorimetry (DSC) of the DIRED-PEG dyes showed an asymmetric endotherm; in most of the cases, we can observe the presence of a mesophase, which reveals the existence of liquid-crystalline domains in these compounds. Unfortunately, no glass transition temperature was detected for these dyes in the studied range of temperatures. DSC curves were recorded for the different DIRED-PEG dyes and are shown in Fig. 3. DSC of DIRED-PEG-2 and DIRED-PEG-3 exhibited broad asymmetric endotherms at 206 and 227 °C, respectively. The broadness of the curves indicates the presence of a discrete mesophase, which appears prior to the melting point. This behaviour was confirmed repeating the DSC experiments after cooling down at a heating rate of 10 °C min^{-1}. A similar broadness was observed in DSC curves of some dendrons con-

Table 1
Thermal properties of the DIRED-PEG dyes.

Dye	T_{10} (°C)	Degradation range (°C)	T_m (°C)
DIRED-PEG-2	282.5	250–358	226
DIRED-PEG-3	327	307–399	207
DIRED-PEG-4	334.5	305–374	113
DIRED-PEG-6	332	309–453	74
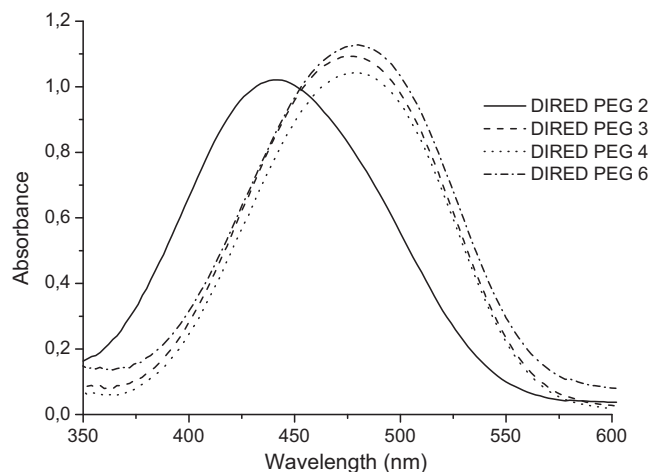
Fig. 5. Absorption spectra of the DIRED-PEG dyes in solution.

lar case, no mesophase was detected because the extremely long oligo(ethylene glycol) spacer of this dye prevents the formation of liquid-crystalline domains.

In order to confirm the liquid-crystalline (LC) behaviour of the DIRED-PEG dyes (n = 2, 3, 4), light polarized optical microscopy studies in function of the temperature were carried out [23,24], using a heating rate of 1 °C min^{-1}. Thus, the samples were gradually heated, which allowed us to remark a LC behaviour in the range of temperatures of the mesophase. DIRED-PEG dyes bearing n = 2, 3, 4 values behaved similarly; however, the most evident LC behaviour was observed for DIRED-PEG-4, whose images along the heating process are illustrated in Fig. 4. Along gradual heating, the formation circular "micelle-like" structural arrangements were seen in the range of temperatures of the mesophase. For DIRED-PEG-4 (Fig. 4 Picture 1, T = 25 °C), we can notice a structure with slightly ordered crystalline domains. At the beginning of the mesophase (Picture 2, T = 85 °C), we can distinguish the formation of a LC arrangement, where the red and black regions clearly show the presence of crystalline and liquid domains, respectively. Then, in the range of temperatures of the mesophase (Picture 3, endotherm at T = 95 °C), we can notice the appearance of a well-structured LC domain with circular arrangement, in spite of the calamitic structure of these compounds. In contrast, in Picture 4 (T = 105 °C), after the melting zone was overcome, a transition from the LC to the isotropic phase (I) takes place with the disappearance the circular arrangements. Finally, in Picture 5 (T = 115 °C), DIRED-PEG-4 pass totally from the LC to the isotropic phase, so that only a
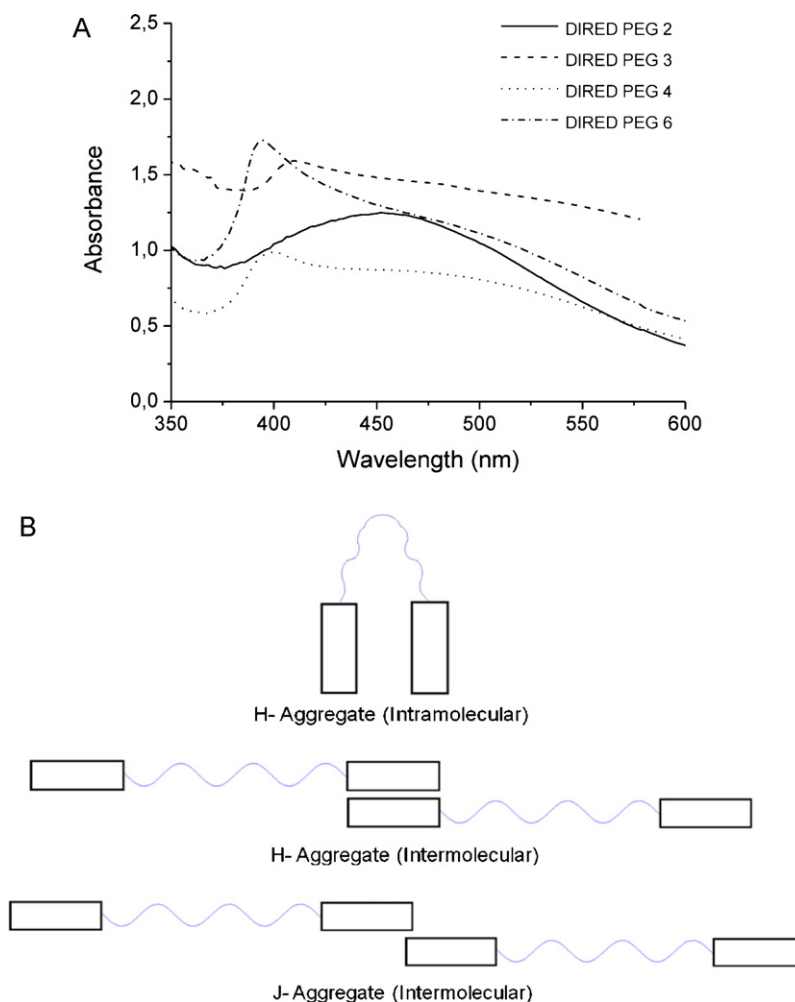
taining azobenzene units, triazole, alkyl chains and poly(ethylene glycol) segments in their structure. [22] In the particular case of DIRED-PEG-4, a well defined endotherm can be observed at 100 °C, revealing the presence of evident mesophase, followed by a second endotherm at 113 °C, due to the melting point of the dye. In contrast, DIRED-PEG-6 only showed a symmetric endotherm at 74 °C, which is related to the melting point of this compound. In this particu-

Fig. 6. (a) Absorption spectra of the DIRED-PEG dyes in cast film, (b) possible structures for H and J-aggregates of the DIRED-PEG dyes.

Table 2
Optical properties of the DIRED-PEG dyes.

Dye	λ max (nm) CHCl₃	Cut off (nm)	ε (M⁻¹ cm⁻¹)	λ aggregate (nm) in film
DIRED-PEG-2	440	574	46,770	454
DIRED-PEG-3	476	604	42,670	410
DIRED-PEG-4	478	608	57,030	398
DIRED-PEG-6	480	610	64,950	394

darkness can be observed. Experiments performed with light polarized microscopy allowed us to detect the C-LC and CL-I transitions for these dyes.

3.3. Optical properties of the DIRED-PEG dyes

Absorption spectra of the DIRED-PEG dyes in chloroform solution are shown in Fig. 5 and their optical properties are summarized in Table 2. All these dyes showed maxima absorption wavelength in the range between λ = 440–480 nm [5,8–10]. Since these compounds contain high dipole moment azobenzene units in their structure, they exhibit the typical photochemical behaviour of azobenzenes belonging the "pseudostilbenes" category. According to H. Rau, these compounds exhibit a total overlap of the π–π* and n–π* bands, which are inverted in the energy scale, so that only one band can be observed in their absorption spectra [6]. In fact, the longer the oligo(ethylene glycol) segment is the more red-shifted the absorption band appear, which is an indication of the high charge transfer character of these molecules. On the other hand, in cast film these dyes behave differently and their UV–vis spectra are shown in Fig. 6a.

As we can see, the absorption spectra of the DIRED-PEG dyes (n= 2, 3, 4 and 6) in cast film showed a hypsochromic shift of the maxima absorption bands. Besides, we can observe the presence of additional blue-shifted bands at λ = 410, λ = 398, λ = 394 nm for DIRED-PEG-3, DIRED-PEG-4 and DIRED-PEG-6, respectively, which reveals the presence of H-aggregates (Fig. 6b, parallel interactions) [25] for these azo-dyes. A similar behaviour was observed with other related dyes previously synthesized by us [8–10,20] and for the pnMAN polymers [23]. Since DIRED-PEG-2 did not show any additional band in its absorption spectrum, we can affirm that no aggregation occur because the flexible oligo(ethylene glycol) spacer is not long enough to allow the azobenzene units to interact intramolecularly. In the other azo-dyes, bearing longer flexible spacers, azobenzene chromophores can easily form intramolecular H-aggregates (parallel interactions) [23,25]. Moreover, in the

absorption spectra of DIRED-PEG dyes in cast film, we can notice the presence of red-shifted absorption tails, which reveal to the existence of traces of intermolecular J-aggregates (Fig. 6b, head to tail interactions) [25].

3.4. Preparation of Langmuir films

Langmuir films were prepared with all azo-dyes (DIRED-PEG-2, DIRED-PEG-3, DIRED-PEG-4 and DIRED-PEG-6) on the air–water interface. These monolayers were characterized by plotting their surface pressure (Π) vs molecular area (Å² molecule⁻¹) isotherms and by the means of hysteresis curves [10]; the obtained monolayers exhibited good reversible behaviour upon successive compression/expansion cycles. The isotherms were recorded at 20 °C and are shown in Fig. 7.

Molecular area values obtained for the DIRED-PEG dyes were compared to those previously estimated by semi-empirical calculations (Hyperchem) and the results are summarized in Table 3. For DIRED-PEG-2 and DIRED-PEG-4, the molecular area diminishes as
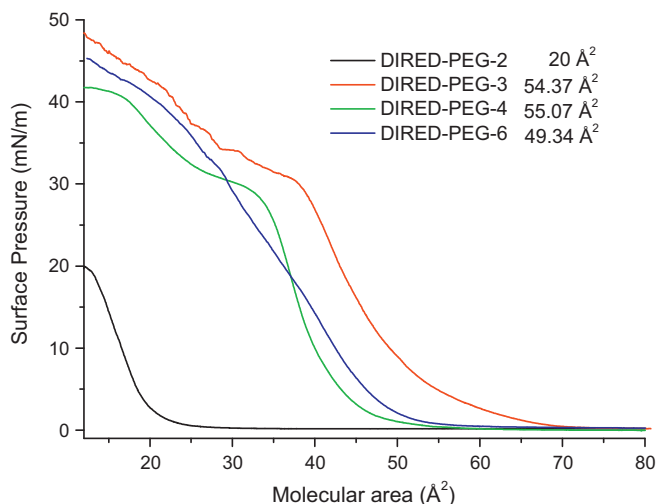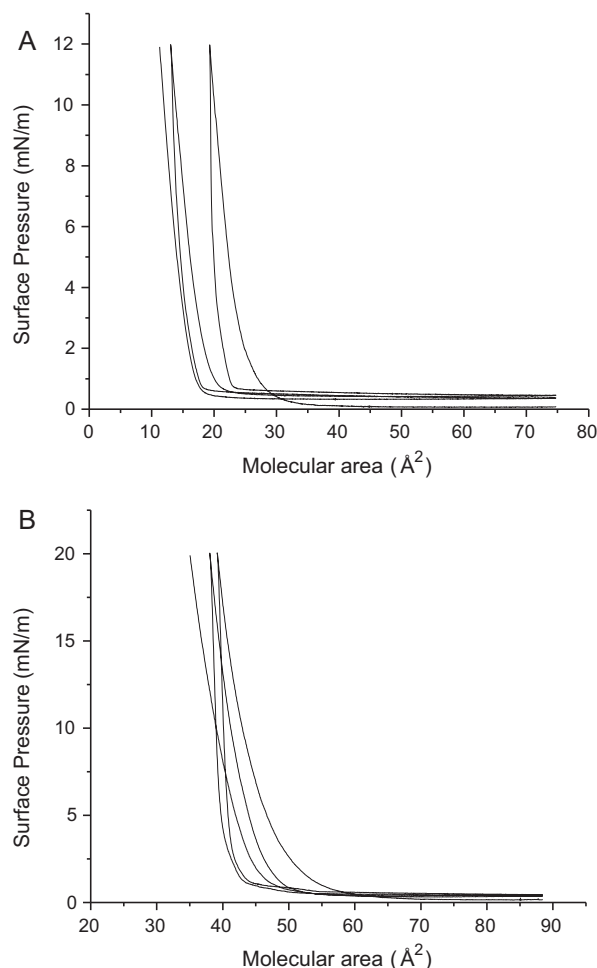
Fig. 7. Isotherms Langmuir monolayers.

Legend in Fig. 7:
- DIRED-PEG-2   20 Å²
- DIRED-PEG-3   54.37 Å²
- DIRED-PEG-4   55.07 Å²
- DIRED-PEG-6   49.34 Å²

Fig. 8. Hysteresis curves for: (a) DIRED-PEG-2, (b) DIRED-PEG-4.

Table 3
Molecular areas of the DIRED-PEG dyes.

Molecular area	DIRED-PEG-n			
	$n = 2$	$n = 3$	$n = 4$	$n = 6$
Experimental (Å^2)	19.9	54.4	43.5	49.4
Theoretical (Å^2)	21.6	57.9	56.4	63.5

the surface pressure increases by compression of the barriers; these dyes exhibit typical amphiphilic behaviour. Nevertheless, according to the hysteresis curves it is difficult for DIRED-PEG-3 to arrange on the surface, since it exhibits a higher standard deviation, which can be due to the even-odd effect in LC. Surprisingly, with DIRED-PEG-6 a higher molecular area value was obtained at lower surface pressure than with the other dyes bearing shorter oligo(ethylene glycol) spacers [10]. This is due to the fact that this compound is partially soluble in water because of its extremely long oligo(ethylene glycol) chain.

As we can observe in Fig. 7, DIRED-PEG-2 shows a significantly lower molecular area with respect to their homologues DIRED-PEG-3, DIRED-PEG-4 and DIRED-PEG-6, which exhibit close molecular area values in the range of 49.34–55.07 Å. This can be due to the fact that the short spacer of DIRED-PEG-2 restrains the mobility of the azobenzene units, thereby preventing the expansion of the molecule. This was confirmed by the hysteresis curves (Fig. 8). On the contrary with the other dyes an increase in the spacer length shifts the isotherms to higher molecular areas reaching a top value.

In the hysteresis curves of DIRED-PEG-2 (Fig. 8a), we can observe that after a first compression cycle this dye is compacted, shows a slight expansion (relaxing) coming back by the same pathway, but after the second compression cycle it shows a reversible behaviour. With the other dyes the hysteresis curves did not exhibit a perfect reversible behaviour, showing light deviations between expansion and compression cycles, as we can see for DIRED-PEG-4 (Fig. 8b).

4. Conclusion

A novel series of DIRED-PEG dyes was synthesized and fully characterized. All compounds exhibited fast degradation between 305 and 453 °C, T_{10} values from 282 to 334 °C and T_m values about $T_m = 74$–225 °C. The melting points of these dyes decrease as the oligo(ethylene glycol) segment length augments. Absorption spectra of these dyes in $CHCl_3$ solution showed maxima absorption bands between $\lambda_{max} = 440$–480 nm. Except for DIRED-PEG-2, in cast film these dyes showed the appearance of additional blue shifted bands at $\lambda = 394$–410 nm, which reveals the formation of H-aggregates. The liquid-crystalline behaviour of these dyes was confirmed by light polarized microscopy in function of the temperature. DIRED-PEG-2, DIRED-PEG-3 and DIRED-PEG-4 can easily form Langmuir films on the air–water interface, which make them suitable prospects for the future elaboration of multilayer Langmuir–Blodgett films.

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