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Liquid-crystalline polymers bearing phenylene(azobenzene) moieties substituted with an electron-donor or electron-acceptor lateral group. Synthesis, mesomorphic behavior and photo-induced isomerization

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ABSTRACT

Methacrylic polymers bearing phenylene(azobenzene) moieties substituted with a OCH₃ (electrondonor) or a CN (electron-acceptor) lateral group were synthesized and their liquid-crystalline (LC) and photo-induced isomerization properties were studied. The thermotropic LC properties were analyzed by DSC, POM, and XRD. All polymers showed a mesomorphic behavior that extends over wide temperature ranges (>100 °C) displaying smectic type mesophases. The effect of the lateral group was reflected in the packing of mesogens in the smectic phases; the polar interactions of the CN groups seem to counterbalance the hindering effects of this lateral group. On the other hand, the photoisomerization of all polymers was induced in dilute solution and films (spin coated and casted). All polymers photoisomerize relatively fast with the CN-substituted polymers reaching high *cis*-isomer contents (>95%) at the photostationary state. Light induced birefringence experiments indicated a tight interplay between the photo-induced orientation and the LC intrinsic order. Homogeneous sinusoidal surface relief gratings were obtained.

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1. Introduction

Over the last 25 years, liquid-crystalline polymers (LCPs) bearing azobenzene moieties have attracted much attention because of synergistic effects produced by coupling the spontaneous molecular order of liquid crystals with the photo-sensitive response of azocompounds [1]. The interplay between these two physical properties has been of great interest for applications in optics [2], photonics [3], photo-mechanics [4,5], among others [6,7]. One of the main characteristics of azobenzenes is their clean photoisomerization produced under a specific UV–Vis irradiation [8]. Depending on the material and irradiation conditions, the *trans* \leftrightarrow *cis* cyclic photoisomerization can induce motions at molecular, nanometric (domain), and micrometric (mass motion) levels [9].

In 1987, Wendorff et al. synthesized LC polymers bearing azobenzene mesogens whose cooperative motion (nanometric level) lead to a significant molecular photo-alignment, which turned out to be stable once the irradiation was stopped [10,11]. Moreover, the attachment of azobenzene moieties to a polymer backbone gives rise to a photo-induced mass migration, which at that time was unknown and became a promising tool for the fabrication of regular micro scale surface relief gratings (SRG) [12-14]. More recently, several groups have synthesized new LCPs aiming to improve the photo-induced properties taking advantage of the intrinsic molecular order of liquid crystals [15–19]. It is noteworthy that the higher birefringence values so far reported for azocompounds belong to LCPs. Ikeda et al reported in 2006 remarkably high birefringence values ($\Delta n = 0.48-0.76$) for LCPs bearing side chain azotolane moieties [20]. Such outstanding birefringence values were associated not only with the long π -conjugation of the azotolanes but also to their LC order [11]. In these moieties, the additional rigid group, which is directly linked to the azobenzene moiety, maintains the linearity of the mesogen and increases the lateral cohesive interaction between molecules in the mesophase. This increased molecular anisotropy may induce a richer polymorphism, and higher thermal and mesophase stabilities. These

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effects were also demonstrated in azobenene derivatives substituted with a biphenylene group, which display a mesomorphic behavior that extends over 200 °C [21]. In spite of such remarkable results, there are few reports on side-chain liquidcrystalline polymers (SCLCPs) bearing highly anisotropic azobenzene mesogens and this is probably due to solubility (or processing) problems. Rigid rodlike molecules are insoluble in most common solvents and this is normally associated to the strong $\pi - \pi$ lateral interactions that maintain the molecules close together. A common practice to reduce such interactions is the introduction of relatively small lateral groups like Cl, Br, OCH₃, among others [22]. The presence of such lateral groups not only improves the solubility of the rigid rodlike azobenzenes but also influences their mesomorphic behavior [23]. Moreover, if such groups are polar in nature they may have important effects on the spectroscopic properties [8] as well as on the photoisomerization process [24]. In the present work, the synthesis, the liquid-crystalline properties and the photoisomerization of new side-chain liquid-crystalline polymers bearing phenylene(azobenzene) moieties substituted with a OCH₃ or a CN group is presented and discussed.

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich and used without further purification unless otherwise noted. Azobisisobutyronitrile (AIBN) was recrystallized from methanol (MeOH). Reactive grade acetone, methanol, chloroform (CHCl₃), and hexanes were purchased from J. T. Baker and were used without further

purification. Tetrahydrofuran (THF) was dried over a sodium/ benzophenone complex and distilled prior to use.

2.2. Synthesis

Two groups of azopolymers were prepared from monomers obtained following the synthetic route outlined in Scheme 1. The first group corresponds to polymers having phenylene(azobenzene) moieties substituted with a lateral OCH₃ group. In these polymers the length of the spacer is 0, 4 and 6 methylene groups, whereas the length of the tail (terminal chain) is kept constant (12 carbon atoms). These polymers were named pOCH₃12,0, pOCH₃12,4 and pOCH₃12,6, respectively. The second group corresponds to polymers bearing phenylene(azobenzene) moieties substituted with a lateral CN group. In these polymers the length of the tail is 6, 10 or 12 carbon atoms, whereas the flexible spacer is kept constant (6 methylene groups). These polymers were named pCN6,6, pCN10,6 and pCN12,6, respectively.

Intermediates **1a**–**d**, **3**, **4a** and **4b** were synthesized according to known procedures [21,24–26]. For the other precursors typical procedures are presented below.

2.2.1. 3-Cyano-4-(decyloxy)phenylboronic acid. (2b)

In a 250 mL three-neck round-bottom flask, equipped with two addition funnels (100 mL) and septa, 3 g (8.87 mmol) of **1b** were dissolved in about 120 mL of freshly distilled THF. The solution was cooled down to -78 °C and then 6.2 mL (9.92 mmol) of BuLi in hexanes 1.6 M was added dropwise keeping the temperature below -70 °C. The reaction mixture was stirred for 90 min and then 4.5 mL (19.57 mmol) of triisopropyl borate (TIPBO) were added



Scheme 1. Synthesis route for the preparation of the phenylene(azobenzene) monomers.

dropwise. The reaction mixture was stirred overnight allowing the temperature to increase up to room temperature. Next, 30.5 mL of HCl 2 N were added and the solution was stirred for 90 min. The solution was then transferred to a separation funnel where diethyl ether was added. The organic layer was separated and washed with water until neutral pH. The organic solvent was evaporated and the product was suspended in cold diethyl ether. The suspension was stirred for 1 h and then filtered and washed with diethyl ether. The solid (**2b**) was obtained as a white powder (Yield: 67%). ¹H NMR (300 MHz, THF– d_8 , δ = ppm): 0.88 (t, CH₃, 3H, J = 6.56 Hz); 1.54–1.29 (m, CH₂, 12H); 1.83 (m, CH₂, 2H); 4.11 (t, CH₂, 2H, J = 6.47 Hz); 7.06 (d, CH, 1H, J = 8.91 Hz); 7.28 (d, OH, 2H, J = 0.86 Hz) and 7.95 (m, CH, 2H).

2.2.2. (E)-4'-((4-(6-bromohexyloxy)phenyl)diazenyl)-4-(decyloxy) biphenyl-3-carbonitrile. (**CN10,6**)

In a 250 mL two-neck round-bottom flask, 1.03 g (3.40 mmol) of **2b**, 1.60 g (3.63 mmol) of **4b** and 50 mL of THF (freshly distilled) were introduced and the mixture was stirred to complete dissolution. Then, 0.1 g (0.09 mmol) of tetrakis(triphenylphosphine) palladium(0) and 21.5 mL of Na₂CO₃ 2 M were added to the solution and the reaction was heated to 65 °C and stirred overnight. Next, the reaction was cooled to room temperature and the organic phase was separated from the aqueous phase; the organic layer was then washed with water until neutral pH. The crude product was passed through a column chromatography on silica gel using CHCl₃ as eluent in order to remove the catalyst and some other residual solids. The mesogen CN10,6 (recrystallized from acetone) was obtained as an orange solid (Yield: 62%). ¹H NMR (300 MHz, CDCl₃, $\delta = ppm$): 0.88 (*t*, CH₃, 3H, I = 6.71 Hz); 1.56–1.28 (*m*, CH₂, 18H); 1.94-1.80 (*m*, CH₂, 6H); 3.44 (*t*, CH₂, 2H, I = 6.75 Hz); 4.06 (*t*, CH₂, 2H, *J* = 6.40 Hz); 4.12 (*t*, CH₂, 2H, *J* = 6.53 Hz); 7.02 (*m*, CH, 3H); 7.64 (*m*, CH, 2H); 7.84–7.77 (*m*, CH, 2H) and 7.97–7.91 (*m*, CH, 4H).

2.2.3. (E)-6-(4-((3'-cyano-4'-(decyloxy)biphenyl-4-yl)diazenyl) phenoxy)hexylmethacrylate. (**MCN10,6**)

In a 250 mL three-neck round-bottom flask, 0.38 g (3.80 mmol) of KHCO₃, 0.37 mL/0.38 g (4.41 mmol) of methacrylic acid and 15 mL of DMF were introduced and stirred to complete dissolution. Then, 1 g (1.62 mmol) of CN10,6 and 0.02 g (0.18 mmol) of hydroquinone were added to the solution. The reaction mixture was heated to 80 °C and stirred overnight. Next, the solution was cooled down to room temperature and then 50 mL of H₂O and 50 mL of CHCl₃ were added. The organic/aqueous phases were separated and the organic layer was subsequently washed with aqueous solutions of HCl 5%, K₂CO₃ 5% and finally with water until neutral pH. The organic layer was dried with Na₂SO₄ and the solvent was evaporated. The monomer MCN10,6 was obtained as an orange solid (Yield: 69%). ¹H NMR (300 MHz, CDCl₃, $\delta = ppm$) 0.88 (t, CH₃, 3H, J = 6.53 Hz); 1.6–1.16 (*m*, 18H); 1.9–1.66 (*m*, 6H), 1.95 (*s*, CH₃, 3H); 4.06 (t, CH₂, 2H, I = 6.74 Hz); 4.12 (t, CH₂, 2H, I = 6.02 Hz); 4.17 (t, CH₂, 2H, *J* = 6.62 Hz); 5.55 (*s*, 1H, =CH); 6.10 (*s*, 1H, =CH); 7.03 (*m*, CH, 3H); 7.64 (m, 2H), 7.84-7.77 (m, 2H); 7.94 (m, CH, 4H). FT-IR (KBr, cm⁻¹) 2923 (s, v_{as} CH₂), 2854 (m, v_s CH₂), 2227 (w, CN stretch), 1718 (m, C=O stretch), 1602, 1490, 1472 (m, C=C ring stretch), 1290 (m, C–(C=O)–O stretch), 1252 (m, C–O–C asym. stretch), 1173 (m, O-C-C asym. stretch), 1011 (m, C-O-C sym. stretch), 852, 817 (m, C–H out of plane bending). ¹³C NMR (75 MHz, $CDCl_3$, $\delta = ppm$): 167.6, 161.9, 160.6, 152, 147, 140.5, 136.6, 133.1, 132.9, 132.2, 127.3, 125.3, 125, 123.4, 116.4, 114.9, 112.8, 102.7, 69.5, 68.3, 64.7, 32, 29.6, 29.6, 29.4, 29.2, 29, 28.7, 26, 25.9, 25.8, 22.8, 18.4. 14.2.

The other intermediates and monomers were obtained by similar methods. They were all characterized by ${}^{1}\text{H}$ NMR as described below.

2.2.4. 5-Bromo-2-(hexyloxy)benzonitrile. (1a)

White solid (Yield: 89%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 0.90 (*t*, CH₃, 3H, *J* = 6.77 Hz); 1.54–1.22 (*m*, CH₂, 6H); 1.83 (*p*, CH₂, 2H, *J* = 6.6 Hz); 4.04 (*t*, CH₂, 2H, *J* = 6.5 Hz); 6.84 (*d*, CH, 1H, *J* = 9.06 Hz); 7.59 (*dd*, CH, 1H, *J* = 2.8, 9.2 Hz) and 7.61 (*d*, CH, 1H, *J* = 9.5 Hz).

2.2.5. 5-bromo-2-(decyloxy)benzonitrile. (1b)

White solid (Yield: 80%). m.p. 41.4 °C ¹H NMR (300 MHz, CDCl₃, $\delta = ppm$): 0.87 (*t*, CH₃, 3H, *J* = 6.7 Hz); 1.47–1.26 (*m*, CH₂, 14H); 1.84 (*p*, CH₂, 2H *J* = 7.1 Hz); 4.04 (*t*, CH₂, 2H, *J* = 6.5 Hz); 6.84 (*d*, CH, 1H, *J* = 8.95 Hz); 7.59 (*dd*, CH, 1H, *J* = 2.5, 8.9 Hz) and 7.64 (*d*, CH, 1H, *J* = 2.5 Hz).

2.2.6. 5-Bromo-2-(dodecyloxy)benzonitrile. (1c)

White solid (Yield: 80%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 0.87 (*t*, CH₃, 3H, *J* = 6.7 Hz); 1.53–1.18 (*m*, CH₂, 18H); 1.84 (*p*, CH₂, 2H, *J* = 6.6 Hz); 4.04 (*t*, CH₂, 2H, *J* = 6.5 Hz); 6.84 (*d*, CH, 1H, *J* = 8.95 Hz); 7.59 (*dd*, CH, 1H, *J* = 2.5, 8.9 Hz) and 7.64 (*d*, CH, 1H, *J* = 2.4 Hz).

2.2.7. 4-bromo-1-(dodecyloxy)-2-methoxybenzene. (1d)

White solid (Yield: 87%). ¹H NMR (300 MHz, CDCl₃, δ = ppm) 0.88 (*t*, CH₃, 3H, *J* = 6.4 Hz); 1.45–1.19 (*m*, CH₂, 18H); 1.82 (*p*, CH₂, 2H, *J* = 6.9 Hz); 3.84 (*s*, CH₃, 3H); 3.96 (*t*, CH₂, 2H, *J* = 6.9 Hz); 6.73 (*d*, CH, 1H, *J* = 8.4 Hz), 6.98 (*dd*, CH, 1H, *J* = 2.21, 4.68 Hz) and 7.01 (*d*, CH, 1H, *J* = 2.29 Hz).

2.2.8. 3-cyano-4-(hexyloxy)phenylboronic acid. (2a)

White powder (Yield: 70%). ¹H NMR (300 MHz, THF– d_8 , $\delta = ppm$) 0.92 (t, CH₃, 3H, J = 7.11 Hz); 1.57–1.30 (m, CH₂, 6H); 1.83 (p, CH₂, 2H, J = 6.74 Hz); 4.11 (t, CH₂, 2H, J = 6.48 Hz); 7.07 (d, CH, 1H, J = 8.93 Hz); 7.29 (s, OH, 2H) and 7.96 (m, CH, 2H).

2.2.9. 3-cyano-4-(dodecyloxy)phenylboronic acid. (2c)

White powder (Yield: 34%). ¹H NMR (300 MHz, MeOH– d_4 , δ = ppm): 0.88 (*t*, CH₃, 3H, *J* = 6.75 Hz); 1.56–1.16 (*m*, CH₂, 18H); 1.81 (*m*, CH₂, 2H); 4.11 (*t*, CH₂, 2H, *J* = 6.36 Hz); 7.08 (*d*, CH, 1H, *J* = 8.41 Hz) and 7.92 (*m*, CH, 2H).

2.2.10. 3-methoxy-4-(dodecyloxy)phenylboronic acid. (2d)

White powder (Yield: 76%). ¹H NMR (300 MHz, THF– d_8 , $\delta = ppm$) 0.89 (t, CH₃, 3H, J = 6.67 Hz); 1.56–1.22 (m, CH₂, 18H); 1.77 (m, CH₂, 2H, J = 6.70 Hz); 3.78 (s, CH₃, 3H), 3.95 (t, CH₂, 2H, J = 6.47 Hz); 6.83 (d, CH, 1H, J = 7.89 Hz); 6.93 (d, OH, 2H); 7.30 (d, CH, 1H, J = 1.49 Hz) and 7.33 (dd, CH, 1H, J = 1.43, 3.92 Hz).

2.2.11. (E)-4-((4-bromophenyl)diazenyl)phenol. (3)

Reddish solid (Yield: 74%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 5.39 (*s*, OH, 1H); 6.95 (*d*, CH, 2H, *J* = 8.82 Hz); 7.62 (*d*, CH, 2H, *J* = 8.71 Hz); 7.75 (*d*, CH, 2H, *J* = 8.69 Hz), and 7.87 (*d*, CH, 2H, *J* = 8.82 Hz).

2.2.12. (E)-1-(4-(4-bromobutoxy)phenyl)-2-(4-bromophenyl) diazene. (**4a**)

Orange solid (Yield: 79%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 2.15–1.94 (*m*, CH₂, 4H); 3.51 (*t*, CH₂, 2H, *J* = 6.45 Hz); 4.09 (*t*, CH₂, 2H, *J* = 5.92 Hz); 6.99 (*d*, CH, 2H, *J* = 9.10 Hz); 7.62 (*d*, CH, 2H, *J* = 8.88 Hz); 7.76 (*d*, CH, 2H, *J* = 8.86 Hz) and 7.90 (*d*, CH, 2H, *J* = 9.08 Hz).

2.2.13. (E)-1-(4-(6-bromohexyloxy)phenyl)-2-(4-bromophenyl) diazene. (**4b**)

Orange solid (Yield: 68%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 1.53 (*m*, CH₂, 4H); 1.91–1.82 (*m*, CH₂, 4H); 3.44 (*t*, CH₂, 2H, J = 6.75 Hz); 4.05 (t, CH₂, 2H, J = 6.38 Hz); 6.99 (d, CH, 2H, J = 9.05 Hz); 7.62 (d, CH, 2H, J = 8.83 Hz); 7.76 (d, CH, 2H, J = 8.81 Hz) and 7.90 (d, CH, 2H, J = 9.05 Hz).

2.2.14. (E)-4'-((4-(6-bromohexyloxy)phenyl)diazenyl)-4-(hexyloxy) biphenyl-3-carbonitrile. (**CN6,6**)

Orange solid (Yield: 83%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 0.92 (*t*, CH₃, 3H, *J* = 7.03 Hz); 1.56–1.30 (*m*, CH₂, 10H); 1.96–1.80 (*m*, CH₂, 6H); 3.44 (*t*, CH₂, 2H, *J* = 6.75 Hz); 4.05 (*t*, CH₂, 2H, *J* = 6.40 Hz); 4.12 (*t*, CH₂, 2H, *J* = 6.54 Hz); 7.02 (*m*, CH, 3H); 7.64 (*m*, CH, 2H); 7.80 (m, CH, 2H) and 7.94 (*m*, CH, 4H).

2.2.15. (E)-4'-((4-(6-bromohexyloxy)phenyl)diazenyl)-4-(dodecyloxy)biphenyl-3-carbonitrile. (**CN12,6**)

Orange solid (Yield: 70%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 0.88 (*t*, CH₃, 3H, *J* = 6.70 Hz); 1.58–1.20 (*m*, CH₂, 22H); 1.96–1.80 (*m*, CH₂, 6H); 3.44 (*t*, CH₂, 2H, *J* = 6.75 Hz); 4.06 (*t*, CH₂, 2H, *J* = 6.38 Hz); 4.12 (*t*, CH₂, 2H, *J* = 6.55 Hz); 7.02 (*m*, CH, 3H); 7.64 (*m*, CH, 2H); 7.80 (*m*, CH, 2H) and 7.94 (*m*, CH, 4H).

2.2.16. (E)-1-(4-(4-bromobutoxy)phenyl)-2-(4'-(dodecyloxy)-3'methoxybiphenyl-4-yl)diazene. (**OCH**₃**12**,**4**)

Orange solid (Yield: 73%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 0.88 (*t*, CH₃, 3H, *J* = 6.70 Hz); 1.56–1.16 (*m*, CH₂, 18H); 2.2–1.80 (*m*, CH₂, 6H); 3.51 (*t*, CH₂, 2H, *J* = 6.49 Hz); 3.96 (*s*, CH₃, 3H); 4.07 (*m*, CH₂, 4H); 6.98 (*m*, CH, 3H); 7.21 (*m*, CH, 2H); 7.69 (*d*, CH, 2H, *J* = 8.43 Hz) and 7.93 (*m*, CH, 4H).

2.2.17. (E)-1-(4-(6-bromohexyloxy)phenyl)-2-(4'-(dodecyloxy)-3'-methoxybiphenyl-4-yl)diazene. (**OCH₃12,6**)

Orange solid (Yield: 86%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 0.88 (*t*, CH₃, 3H, *J* = 6.74 Hz); 1.57–1.20 (*m*, CH₂, 22H); 1.96–1.79 (*m*, CH₂, 6H); 3.44 (*t*, CH₂, 2H, *J* = 6.75 Hz); 3.96 (*s*, CH₃, 3H); 4.05 (*t*, CH₂, 2H, *J* = 6.32 Hz); 4.07 (*t*, CH₂, 2H, *J* = 6.88 Hz); 6.99 (*m*, CH, 3H); 7.20 (*m*, CH, 2H); 7.69 (d, CH, 2H, *J* = 8.6 Hz) and 7.93 (*m*, CH, 4H).

2.2.18. (E)-6-(4-((3'-cyano-4'-(hexyloxy)biphenyl-4-yl)diazenyl) phenoxy)hexyl methacrylate. (**MCN6,6**)

Orange solid (Yield: 84%). ¹H NMR (300 MHz, CDCl₃, $\delta = ppm$): 0.92 (*t*, CH₃, 3H, *J* = 7.04 Hz); 1.60–1.3 (*m*, 10H); 1.93–1.68 (*m*, 6H); 1.94 (*dd*, CH₃, 3H, J = 0.71, 1.75 Hz); 4.05 (*t*, CH₂, 2H, J = 6.43 Hz); 4.12 (*t*, CH₂, 2H, *J* = 6.54 Hz); 4.17 (*t*, CH₂, 2H, *J* = 6.61 Hz); 5.55 (*p*, 1H, =CH, J = 1.61 Hz); 6.10 (m, 1H, =CH); 7.00 (d, CH, 2H, *J* = 8.98 Hz); 7.04 (*d*, CH, 1H, *J* = 8.87 Hz); 7.64 (*d*, 2H, *J* = 8.44 Hz), 7.79 (*dd*, CH, 1H, *J* = 2.38, 8.75 Hz), 7.84 (*d*, CH, 1H, *J* = 2.35 Hz); 7.94 (*dd*, CH, 4H, J = 6.94, 8.67 Hz). FT–IR (KBr, cm⁻¹) 2939 (s, v_{as} CH₂), 2869 (m, v_s CH₂), 2229 (w, CN stretch), 1703 (m, C=O stretch), 1603, 1490, 1475 (m, C=C ring stretch), 1278 (m, C-(C=O)-O stretch), 1260 (m, C–O–C asym. stretch), 1174 (m, O–C–C asym. stretch), 1018 (m, C-O-C sym. stretch), 849, 818, 802 (m, C-H out of plane bending). ¹³C NMR (75 MHz, CDCl₃, $\delta = ppm$): 167.6, 161.9, 160.6, 152.1, 147, 140.5, 136.6, 133.1, 132.9, 132.2, 127.3, 125.34, 125, 123.4, 116.4, 114.8, 112.8, 102.7, 69.5, 68.3, 64.7, 31.6, 29.2, 29, 28.7, 25.9, 25.8, 25.6, 22.6, 18.4, 14.1.

2.2.19. (E)-6-(4-((3'-cyano-4'-(dodecyloxy)biphenyl-4-yl)diazenyl) phenoxy)hexyl methacrylate. (**MCN12,6**)

Orange solid (Yield: 62%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 0.88 (t, CH₃, 3H, *J* = 6.5 Hz); 1.56–1.2 (*m*, 22H); 1.93–1.68 (*m*, 6H); 1.95 (*dd*, CH₃, 3H, *J* = 0.99, 1.58 Hz); 4.05 (*t*, CH₂, 2H, *J* = 6.42 Hz); 4.12 (*t*, CH₂, 2H, *J* = 6.55 Hz); 4.17 (*t*, CH₂, 2H, *J* = 6.6 Hz); 5.55 (*p*, 1H, =CH, *J* = 1.59, 1.60 Hz); 6.10 (*qd*, 1H, =CH, *J* = 0.96, 1.95 Hz); 7.02 (*m*, CH, 3H); 7.64 (*m*, 2H), 7.79 (*dd*, CH, 1H, *J* = 2.40, 8.76 Hz), 7.84 (*d*, CH, 1H, *J* = 2.23 Hz) and 7.94 (dd, CH, 4H, *J* = 6.97, 8.90 Hz). FT–IR (KBr, cm⁻¹) 2924 (s, v_{as} CH₂), 2853 (m, v_s CH₂), 2227 (w, CN stretch), 1719 (m, C=O stretch), 1601, 1491, 1468 (m, C=C ring stretch), 1287 (m, C–(C=O)–O stretch), 1254 (m, C–O–C asym. stretch), 1164 (m, O–C–C asym. stretch), 1012 (m, C–O–C sym. stretch), 851, 816 (m, C–H out of plane bending). ¹³C NMR (75 MHz, CDCl₃, δ = ppm): 167.6, 161.9, 160.6, 152.1, 147, 140.5, 136.6, 133.1, 132.9, 132.2, 127.3, 125.3, 125, 123.4, 116.4, 114.8, 112.8, 102.7, 69.5, 68.3, 64.7, 32, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 29, 28.7, 26, 25.9, 25.8, 22.8, 18.4, 14.2.

2.2.20. (E)-4-((4'-(dodecyloxy)-3'-methoxy-[1,1'-biphenyl]-4-yl) diazenyl)phenol. (**OCH₃12,0**)

This compound was prepared from **3** and **2d** following the same procedure as for compound **CN10,6**. The mesogen **OCH₃12,0**, recrystallized from acetone, was obtained as an orange solid (Yield: 64%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 0.83 (*t*, CH₃, 3H, *J* = 6.70 Hz); 1.5–1.10 (*m*, CH₂, 18H); 1.82 (*m*, CH₂, 2H); 3.91 (*s*, CH₃, 3H); 4.02 (*t*, CH₂, 2H, *J* = 6.90 Hz); 6.98 (*m*, CH, 3H); 7.14 (*m*, CH, 2H); 7.64 (*m*, CH, 2H) and 7.84 (*m*, CH, 4H).

2.2.21. (E)-(4-((4'-dodecyloxy)-3'-methoxybiphenyl-4-yl)diazenyl) phenyl)methacrylate. (**MOCH₃12,0**)

In a 100 mL two-neck round-bottom flask, 0.87 g (1.78 mmol) of OCH₃12,0 and 40 mL of THF (freshly distilled) were introduced and the mixture was cooled to T = 0-5 °C. Then 0.36 g (3.56 mmol) of triethylamine and 0.24 g (2.30 mmol) of methacryloyl chloride were added dropwise. The reaction temperature was allowed to increase gradually up to room temperature and stirred overnight. Then, 30 mL of CH₂Cl₂ and 30 mL of H₂O were added and the organic phase was separated from the aqueous phase; the organic layer was subsequently washed with aqueous solutions of HCl 5%, K₂CO₃ 5% and finally with water until neutral pH. The organic layer was dried with Na₂SO₄ and the solvent was evaporated. The monomer MOCH₃12,0 (recrystallized from acetone) was obtained as an orange solid (Yield: 77%). ¹H NMR (300 MHz, CDCl₃, $\delta = ppm$): $0.88 (t, CH_3, 3H, J = 6.71 Hz); 1.53 - 1.18 (m, 18H); 1.88 (m, 2H); 2.09$ $(dd, CH_3, 3H, J = 0.95, 1.47 Hz); 4.04 (s, CH_3, 3H); 4.07 (t, CH_2, 2H, CH_2, 2H); 4.07 (t, CH_2, 2H);$ *J* = 6.9 Hz); 5.8 (*m*, 1H, =CH); 6.40 (*m*, 1H, =CH); 6.97 (*d*, CH, 1H, *J* = 8.31 Hz); 7.18 (*d*, CH, 1H, *J* = 2.08 Hz); 7.21 (*dd*, CH, 2H, *J* = 2.14, 8.24 Hz); 7.29 (*d*, CH, 2H, *J* = 9.03 Hz); 7.71 (*d*, CH, 2H, *J* = 8.82 Hz) and 7.98 (m, CH, 4H). FT–IR (KBr, cm⁻¹) 2919 (s, v_{as} CH₂), 2852 (m, v_s CH₂), 1742 (m, C=O stretch), 1592, 1493, 1467 (m, C=C ring stretch), 1257 (m, C-O-C asym. stretch), 1202 (m, C-(C=O)-O stretch), 1151 (m, O-C-C asym. stretching), 1122 (m, O-C-C asym. stretch), 1024 (m, C-O-C sym. stretch), 844, 802 (m, C-H out of plane bending). ¹³C NMR (75 MHz, CDCl₃, $\delta = ppm$): 165.6, 153, 151.4, 150.4, 149.8, 149, 143.8, 135.8, 133, 127.8, 127.4, 124.1, 123.5, 122.4, 119.8, 113.2, 110.9, 69.2, 55.3, 32, 29.8, 29.7, 29.7, 29.7, 29.5, 29.5, 29.3, 26.1, 22.8, 18.5, 14.2.

2.2.22. (E)-4-(4-((4'-(dodecyloxy)-3'-methoxybiphenyl-4-yl) diazenyl)phenoxy)butylmethacrylate. (**MOCH₃12,4**)

Orange solid (Yield: 89%). ¹H NMR (300 MHz, CDCl₃, δ = ppm): 0.88 (*t*, CH₃, 3H, *J* = 6.65 Hz); 1.52–1.2 (*m*, 18H); 1.94–1.81 (*m*, 6H), 1.95 (*m*, 3H); 4.07 (*t*, CH₂, 2H, *J* = 6.95 Hz); 4.09 (*t*, CH₂, 2H, *J* = 5.58 Hz); 4.25 (*t*, CH₂, 2H, *J* = 5.91 Hz); 5.56 (*p*, 1H, ==CH, *J* = 1.61 Hz); 6.12 (*m*, 1H, ==CH); 6.96 (*d*, CH, 1H, *J* = 8.36 Hz); 7.01 (*d*, CH, 2H, *J* = 9.06 Hz); 7.19 (*m*, CH, 3H); 7.69 (*d*, 2H, *J* = 8.74 Hz), 7.93 (*dd*, CH, 4H, *J* = 3.68, 8.85 Hz). FT–IR (KBr, cm⁻¹) 2919 (s, v_{as} CH₂), 2852 (*m*, v_s CH₂), 1718 (*m*, C=O stretch), 1594, 1497, 1468 (*m*, C=C ring stretch), 1255 (*m*, C–O–C asym. stretch), 1155 (*m*, O–C–C asym. stretch), 1024 (*m*, C–O–C sym. stretch), 846, 805 (*m*, C–H out of plane bending). ¹³C NMR (75 MHz, CDCl₃, δ = ppm): 167.5, 161.6, 151.5, 149.8, 148.9, 147.1, 143.1, 136.5, 133.1, 127.4, 125.5, 124.9, 123.2, 119.8, 114.8, 113.2, 110.9, 100, 69.2, 67.5, 64.4, 56.3, 32.0, 29.8, 29.7, 29.7, 29.7, 29.5, 29.5, 29.3, 26.1, 26, 25.5, 22.8, 18.4, 14.2.

2.2.23. (E)-6-(4-((4'-dodecyloxy)-3'-methoxybiphenyl-4-yl) diazenyl)phenoxy)hexylmethacrylate. (**MOCH₃12,6**)

Orange solid (Yield: 83%). ¹H NMR (300 MHz, CDCl₃, δ = ppm) 0.88 (*t*, CH₃, 3H *J* = 6.68 Hz); 1.92–1.18 (*m*, 28H); 3.96 (*s*, CH₂, 2H); 4.06 (*m*, CH₂, 4H); 4.17 (*t*, CH₂, 2H, *J* = 6.59 Hz); 5.55 (*s*, 1H, =CH); 6.10 (*s*, 1H, =CH); 6.98 (*m*, CH, 3H); 7.19 (*m*, 2H); 7.69 (*m*, 2H) and 7.93 (*m*, CH, 4H). FT–IR (KBr, cm⁻¹) 2923 (*s*, v_{as} CH₂), 2853 (*m*, v_s CH₂), 1719 (*m*, C=O stretch), 1594, 1497, 1467 (*m*, C=C ring stretch), 1260 (*s*, C–O–C asym. stretch), 1152 (*s*, O–C–C asym. stretch), 1024 (*m*, C–O–C sym. stretch), 846, 804 (*m*, C–H out of plane bending) ¹³C NMR (75 MHz, CDCl₃, δ = ppm): 167.6, 161.7, 151.5, 149.8, 148.8, 147, 143.1, 136.6, 133.2, 127.4, 125.3, 124.9, 123.2, 119.7, 114.8, 113.2, 110.9, 100, 69.2, 68.2, 64.7, 55.3, 32, 29.8, 29.7, 29.7, 29.7, 29.5, 29.5, 29.3, 29.2, 28.7, 26.1, 25.9, 25.8, 22.8, 18.4, 14.2.

All polymers were obtained via free-radical polymerization using AIBN as initiator. A typical procedure is described below.

2.2.24. pCN10,6

In a Schlenk tube 0.49 g (0.79 mmol) of the monomer **MCN10,6**, 0.013 g (0.08 mmol) of AIBN and 4 mL of freshly distilled THF were introduced and the solution was degassed three times by freezepump-thaw cycles. The Schlenk tube was closed and heated to 65 °C for 48 h. The obtained polymer was purified by subsequent precipitation with methanol, re-dissolved in CHCl₃ and reprecipitated in hexanes. The polymer pCN10,6 was obtained as a yellow powder (Yield: 72%).

Some polymers were re-dissolved in CHCl₃ and re-precipitated with hexanes, acetone and/or methanol. All final polymers showed good purity with yields ranging between 68 and 79%.

2.3. Characterization

The average molecular weights $(M_n \text{ and } M_w)$ and polydispersity (M_w/M_n) of polymers were determined by size exclusion chromatography using a Hewlett–Packard instrument (HPLC 1100 series) equipped with a refractive index detector. A series of PLGel columns covering a wide range of molecular weights $(10^3 - 10^7)$ were used. Tetrahydrofuran HPLC-grade (Aldrich) was used as solvent and as eluent. Monodisperse polystyrene standards were used for calibration. The chemical structure of synthesized products was verified by ¹H NMR and ¹³C NMR using a 300 MHz Jeol spectrometer (JNM-ECO300) and CDCl₃, MeOH $-d_4$, or THF $-d_8$ as solvents. The thermal stability of compounds was determined on vacuum dried samples and using a thermal analyzer from Dupont instruments (TGA 951) connected to a nitrogen vector gas and heating at a rate of 10 °C/min from 30 to 800 °C. DSC traces were obtained in a differential scanning calorimeter from TA instruments (MDSC 2920). The scanning rate was 10 °C/min and heating-cooling cycles range from -20-250 °C; reported data correspond to the second heating scans. Optical textures of mesophases were captured upon cooling using a polarized optical microscope from Olympus (BX60) coupled with a temperature controlling hot stage from Mettler (FP82HT) and a digital camera from Hitachi. X-ray diffraction analysis was performed in an SWAXS from Anton Paar (SAXSess mc^2) equipped with a sample holder unit (TCS 300-C), an image plate detector, and a temperature control unit (TCU50). Each sample was sealed in a Lindeman glass capillary with an outer diameter of 1.0 mm and a wall thickness of 0.01 mm. X-rays (Cu k_{α} radiation; $\lambda_{max} = 0.1542$ nm) were generated at 40 kV and 50 mA. X-ray patterns were captured at different temperatures upon cooling from the isotropization temperature. UV-Vis spectra were recorded in a spectrophotometer from Shimadzu (UV-2401PC) using a standard quartz cell. All polymers were dissolved in spectrophotometric grade THF (0.05 mg/mL). The photoisomerization was studied by irradiating the polymer solutions and films at time intervals until the photostationary state was reached. For irradiation experiments, a 366 nm non-polarized handheld UV lamp (UVGL-58) was used.

2.3.1. Films preparation

Thin films (300–450 nm) were prepared by spin-coating as follows: 50 μ L of a polymer solution (40 mg/mL in CHCl₃) was deposited onto a clean glass substrate at a spinning rate of 800–2000 rpm. The film was spun for 60 s and then dried overnight in a vacuum oven at 35 °C. For films obtained by casting (3–15 μ m), 80–120 μ L of a polymer solution (40 mg/mL in CHCl₃) were deposited onto a glass substrate and then dried overnight at 35 °C in a vacuum oven. The film thickness of both spin coated and casted films was measured by using an AFM-3100 (DI-Veeco) and a Surfanalyzer 4000 (Federal), respectively.

2.3.2. Photo-induced birefringence

Spin coated films were irradiated with a linearly polarized semiconductor laser beam ($\lambda = 413$ nm, 20 mW). At the same time a laser beam at 633 nm (25 mW) was used as a probe and the change in the polarization state was measured with a Stokes polarimeter using the equation:

$$\Delta n = \frac{\lambda}{2\pi d} \tan^{-1} \left(\frac{V_o}{U_o} \right) \tag{1}$$

where λ is the wavelength of the laser probe (633 nm), *d* is the film thickness, V_o and U_o are the third and fourth Stokes parameters, which represent the components of linear polarized light at $\pm 45^{\circ}$ and the left/right circular polarized light, respectively.

2.3.3. Surface relief gratings (SRG)

Spin casted films were irradiated with an interference pattern employing a Lloyd arrangement. A 413 nm laser was split into two equal intensity beams but with a different polarization state (right/ left circularly polarized light). The two beams hit the sample in the same spot with an incidence angle of 4°. The irradiation time for all samples was 30 min. The diffraction efficiency was calculated as the ratio between the incident light (633 nm) and the first order diffracted beam. AFM images were captured in an AFM-3100 from DI-Veeco.

3. Results and discussion

3.1. Synthesis

All azopolymers were synthesized by free-radical polymerization using AIBN as initiator. The number (M_n) and weight (M_w) average molecular weights, the M_w/M_n , the temperature of 5 wt% loss ($T_{5\%}$), and the glass transition temperature (T_g) of each azopolymer are summarized in Table 1. The M_n ranged between 12,000 and 24,000 g/mol and the M_w/M_n between 2.11 and 2.61, which are

fable 1	
Molecular weights and thermal behavior for the azopolymers.	

Polymer	$M_{\rm n}({\rm g/mol})$	$M_{\rm w}/M_{\rm n}^{\rm a}$	<i>T</i> _{5%} (°C)	$T_{g}^{b}(^{\circ}C)$
pCN6,6	23,677	2.23	328	60
pCN10,6	23,790	2.40	335	65
pCN12,6	21,726	2.39	329	62
pOCH₃12,6	12,160	2.11	337	57
pOCH ₃ 12,4	15,459	2.61	331	69
pOCH ₃ 12,0	20,562	2.52	325	_

^a Determined by gel permeation chromatography (GPC) in THF on the basis of a polystyrene calibration.

^b Measured in the second heating cycle.

typical values for this kind of polymers synthesized via free-radical polymerization [27]. These relatively low molecular weights are in fact desirable for a good solubility, which is necessary for the preparation of high quality thin films from solution. The thermal stability ($T_{5\%}$) for all azopolymers was above 300 °C, which is much higher than that reported for acrylic SCLCPs bearing azobenzene moieties (around 200 °C) [28]. This increase in the thermal stability is due to the presence of one extra phenylene ring in the azo-compound as reported by Rodríguez-González et al [21]. The high $T_{5\%}$ values allowed us to study the thermotropic behavior of azopolymers at relatively high temperatures.

3.2. Thermotropic behavior

Fig. 1 shows the DSC thermograms for all synthesized azopolymers. In some of the curves a second order thermal transition, indicative of a glass transition temperature (T_g) , is clearly seen. For some other curves (transition barely perceived) the T_g is indicated between dashed lines in Fig. 1; its corresponding value is shown in Table 1. For pOCH₃12,0 it was not possible to detect a T_g even if it is brittle at room temperature. It can also be noted that all polymers (except pOCH₃12,0) show a first order thermal transition above 220 °C corresponding to the liquid-crystalline to the isotropic liquid transition (T_i) , as confirmed by POM. Upon cooling to room temperature no crystallization was observed (DSC traces not shown here) meaning that the mesophase remained fixed below T_{g} . On the other hand, polymers bearing OCH₃ groups showed differences in the mesomorphic behavior depending on the length of the flexible spacer: pOCH₃12,0 (no spacer) showed no thermal transitions, pOCH₃12,4 displayed one first-order thermal transition around 230 °C corresponding to the T_i , and pOCH₃12,6 developed two first order thermal transitions, one at 120 °C and the other around 220 °C (T_i). These results confirm the decoupling effect exerted by the flexible spacer allowing the mesogens to self-organize in a liquid crystalline state [29].

3.3. Nature and structure of mesophases

All polymers were studied by POM to get a first approach of the possible nature of mesophases. Polymers bearing CN groups exhibited focal-conic fan and sanded-like textures, whereas those bearing OCH₃ groups displayed only focal-conic fan textures as



Fig. 1. DSC thermograms (second heating scan) of azopolymers at a scan rate of $10 \degree C/min g = glassy state, T_g = glass transition temperature, LC = liquid-crystalline region, I = isotropic state.$

shown in Figs. 2 and 3, respectively. In viscous polymer liquids it is sometimes difficult to observe identifiable typical textures, particularly for some smectic type mesophases; rather, a fine granulated (or sanded-like) texture of birefringent domains is frequently seen between crossed polars [29]. Focal-conic fan textures were preceded by the presence of bâtonnets that appear at the isotropic to the liquid-crystalline transition (not shown here) and that grow up to coalesce. For pOCH₃12,6, the expected transition around 120 °C (according to DSC) was not observed by POM; only a smooth change in color (Fig. 3) was perceived probably associated to a phase transition, although such change in color could be simply due to a variation in the lamellar spacing as reported by Goodby and Gray for liquid crystals with tilted molecules within the mesophase [30].

The nature of mesophases for all the polymers was confirmed by X-ray diffraction (XRD) analysis. X-ray diffraction patterns, captured upon cooling, showed in the small angle region one or two equidistant sharp Bragg reflections (d_{001} and d_{002}), indicating a lamellar arrangement, which is typical for smectic phases (Fig. 4). Also, all polymers displayed only a single broad diffraction peak (centered around 4.3 Å) in the wide angles region of the X-ray patterns confirming the presence of a non-ordered smectic phase; the X-ray patterns of the polymer pOCH₃12,6 were selected as examples (Fig. 5). It is noteworthy that for all the polymers such broad peak remained unchanged up to room temperature meaning that the smectic order is maintained below T_{g} . Fixed mesophases in glassy polymers is desirable, particularly for liquid crystals bearing azo groups whose intrinsic order can amplify the light induced effects.

To elucidate the packing of mesogens in the mesophase, the experimental interlayer distance (or smectic period) d_{001} was compared to the lamellar spacing L calculated using molecular modeling software from Spartan 2010. L is the distance between an H-atom of the end-methyl group of the mesogen (full extended) and the carbon atom to which such mesogen is linked to the polymer chain. The d/L ratios for all smectic phases are presented in Table 2. For pCN6.6, the d/L ratio is close to unity indicating a single layer packing of mesogens whereas for the rest of polymers such ratio is around 1.5, indicating either a double layer packing with mesogens tilted with respect to the normal of the smectic plane or with mesogens perpendicular to the smectic plane but partially interdigitated the ones to the others. On the other hand, the dependence of the interlayer distance with temperature provides a deep insight into the structure of the smectic phase. This structural parameter may remain constant within the mesophase range or it can change for instance as a result of variations in the tilt angle [30]. The dependence of the interlayer distance with temperature for all the polymers is presented in Fig. 6. This figure shows that the interlayer distance for polymers bearing CN groups remains almost constant whereas for polymers bearing OCH₃ groups such distance decreases upon cooling. Taking into account these differences, and considering some related works, three models for molecular packing are proposed.

For the polymer pCN6,6, a $d/L \approx 1$ suggests a single layer packing with mesogens fully interdigitated and oriented on average perpendicular to the smectic plane (SmA₁). Such an arrangement assures an optimum interaction between different moieties (Fig. 7A and B). In this antiparallel packing not only the alkyl–alkyl and aromatic–aromatic lateral interactions are satisfied but also the molecular dipole moment interaction between rigid cores (polarized by the CN group) is energetically favorable, in such a way that the dipolar energy is minimized. A similar fully interdigitated monolayer structure with antiparallel arrangement of mesogens was proposed by Laus et al for SCLCPs containing alkyl sulfide substituents, for which the smectic interlayer spacing (*d*) was



Fig. 2. Mesomorphic textures for the polymers bearing CN groups (A) pCN6,6 (200 °C) and (B) pCN10,6 (223 °C) observed on cooling from their isotropic state.

constant in the all temperature range, and in close agreement with the length of the respective side chains [31].

For the polymers pOCH₃12,4 and pOCH₃12,6, a $d/L \approx 1.5$ along with an important variation in the interlayer distance (Fig. 6) implies a bilayer smectic packing with tilted molecules (SmC₂) as is schematically represented in Fig. 8. This significant change in *d* or in the tilt angle appears to concur with the color change previously observed by POM (Fig. 3). A similar variation in the interlayer distance was observed in liquid-crystalline methacrylic polymers with ω -hexyloxysalicylaldimine side-groups carrying *p*-alkyl chains, for which an SmC₂ structure was also proposed [32,33].

Finally, for the polymers pCN10,6 and pCN12,6 a $d/L \approx 1.5$ together with an interlayer distance practically invariable in all the temperature range (250–80 °C) suggests a bilayer smectic packing with mesogens partially interdigitated and orthogonal to the smectic plane (SmA_d), as represented in Fig. 9. The existence of an interdigitated mesophase deserves an explanation in more detail. Let us explain the case of the azopolymer pCN10,6. For a partial interdigitation of mesogens one would expect a full interaction between adjacent terminal alkyl chains, however such an arrangement implies an interlayer distance of around 66 Å (Fig. 9A).

The obtained experimental d value for the polymer pCN10,6 is barely 59 Å, suggesting a compactness of the smectic layers (Fig. 9B). For an orthogonal smectic mesophase, a 7 Å difference may be solely explained as a consequence of either a deeper interpenetration of mesogens or a coiling of both the spacer and the terminal chain (tail). The former seems more plausible under the following arguments. It was reported that molecular dipoles play a significant role in crystal packing but they are not decisive if other types of interactions like bond dipole-bond dipole interactions are involved (a bond dipole is a dipole moment associated with a given bond). In this polymer the bond dipole-bond dipole interaction occurring between CN groups is thought to be the driving force for a deeper interdigitation of mesogens even if it implies a partial overlay of alkyl chains and aromatic groups. It is noteworthy that among the bond dipole moments one of the largest is that of the cyano group [34]. Although unusual, molecular arrangements with alkyl chains and aromatic groups facing each other can occur; the only condition is to minimize the repulsions between all different parts of the mesogens [35,36]. The involved forces for a smectic stacking are the mutual effective repulsions between alkyl chains and aromatic cores, and the bond dipole-bond dipole interaction



Fig. 3. Mesomorphic textures for the polymers bearing OCH₃ groups (A) pOCH₃12,6 (180 °C) (B) pOCH₃12,6 (89 °C) (C) pOCH₃12,4 (200 °C) (D) pOCH₃12,4 (120 °C) observed on cooling from their isotropic state.



Fig. 4. XRD patterns for the azopolymers in the small angle region. Polymers were heated near the isotropization temperature and patterns were taken at 200 $^\circ$ C on cooling.

between cyano groups (antiparallel pairs). In this case, the strong interactions between CN groups seem to retain them relatively close to each other, reducing in this way the length of the smectic period. Interdigitated smectic phases have been reported in polymers bearing mesogens substituted with polar groups, where the antiparallel pairs seem to dominate the lamellar stacking [36–39].

To conclude this structural analysis, pOCH₃12,6 is compared to its counterpart pCN12,6. The only difference between these two polymers is the nature of the lateral group, one being electrondonor and the other electron-withdrawing group. This difference in electronic properties seems to be at the origin of the observed dissimilar molecular arrangement. The CN groups induce dipolar interactions between mesogens leading to interdigitated smectic layers, whereas the OCH₃ groups push out each other resulting in a segregation of mesogens from one smectic layer to the other, which in this case has conducted to tilted mesophases.

3.4. UV-Vis optical properties

Azobenzene derivatives are well known by their light-induced properties, which essentially depend on their ability to photoisomerize under the effect of light irradiation. Before irradiating the synthesized azopolymers, it is important to explore their light absorption characteristics.



Fig. 5. XRD patterns for the azopolymer $pOCH_312,6$ at different temperatures on cooling from the isotropic state.

Table	2
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Structural parameters for the azopolymers determined from SWAXS.

Compound.	$L(Å)^{a}$	T (°C).	d_{001} (Å).	$d_{001}/L.$	Tilt angle ^b	Mesophase. ^c
pCN6,6	35.2	200	33.3	0.946	_	g 60 SmA ₁ 244 I
pCN10,6	39.4	200	58.8	1.492	_	g 65 SmA _d 228 I
pCN12,6	42.3	200	65.3	1.544	_	g 62 SmA _d 224 I
pOCH ₃ 12,6	42.1	100	55.2	1.311	49.0	g 57 SmC ₂ 220 I
		200	60.3	1.432	44.3	
pOCH ₃ 12,4	39.3	160	55.1	1.402	45.5	g 77 SmC ₂ 233 I
		200	59.5	1.514	40.8	

^a Measured from molecular modeling using Spartan 2010.

^b Calculated from $\theta = \cos^{-1}(d/2L)$.

 $^{\rm c}~g=glassy~state,~SmA_1=Smectic~A~phase~monolayer,~SmA_d=Smectic~A~phase~interdigitated,~SmC_2=Smectic~C~phase~bilayer,~I=isotropic state.$

3.4.1. UV–Vis absorption

The optical properties obtained from the UV-Vis spectra (no shown here) are summarized in Table 3. The reported unsubstituted phenylenazobenzene displays one strong ($\lambda_{max} = 372 \text{ nm}$) and one weak ($\lambda_{max} = 460 \text{ nm}$) absorption bands due to the $\pi - \pi^*$ and $n-\pi^*$ electronic transitions, respectively [21]. For polymers bearing CN groups the corresponding bands appear at 368 and 460 nm whereas for those with OCH₃ groups both absorption bands overlap to each other and only one λ_{max} at 375 nm is observed. As noted, for polymers bearing CN groups the strong absorption band is blue shifted with respect to the unsubstituted phenyleneazobenzene whereas for polymers bearing OCH₃ groups it is red shifted. This different behaviors come out from the opposite electronic affinity of the CN and OCH₃ groups, the former being an electron-withdrawing and the latter an electron-donor group. The peak shift for both types of polymers was relatively small probably due to the fact that the lateral group is substituted into the second phenyl ring far apart from the azo group. Only the polymer pOCH₃12,0 showed an opposite behavior (blue shift, $\lambda_{max} = 368 \text{ nm}$) compared to the other polymers of the same series and it is certainly related to the electron withdrawal character of the methacrylate group, which is directly linked to the azobenzene. On the other hand, all polymers showed a molar absorptivity coefficient for the *trans* isomer (ε_{trans}) falling in the range of $10^5 \text{--} 10^6 \ \text{L} \ \text{mol}^{-1} \text{cm}^{-1}$ with values for the CN-substituted polymers doubling those of the OCH₃ substituted ones. It should be said that these values are much higher than those reported $(10^4 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1})$ for polymers bearing highly anisotropic azotolane mesogens for which high photo-induced birefringence values



Fig. 6. Interlayer distance – temperature dependence for azopolymers in the smectic phase on cooling from their isotropic state. The solid lines are drawn as a guide.



Fig. 7. Schematic representation for the monolayer stacking (SmA1) of pCN6,6. (A) 3-D view. (B) Lateral view (solid circles represent the polymer chains viewed end-on).



Fig. 8. Schematic representation for the bilayer structure (SmC₂) of pOCH₃12,4 and pOCH₃12,6. (Solid circles represent the polymer chains viewed end-on).

were observed [20]. High ε values are desirable as more photons are absorbed by the chromophores and that may be reflected in the photoisomerization levels.

3.4.2. Photoisomerization of polymers in solution

The photoisomerization kinetics for the azopolymers was first measured in solution using THF as solvent (Fig. 10). Under UV–Vis irradiation all polymers photoisomerize, showing a marked progressive decrease in the intensity of the strong $\pi - \pi^*$ absorption band and a slow increase of the weak $n-\pi^*$ absorption band up to a photostationary state (pss). The presence of isosbestic points confirms that distinct absorbing species are in equilibrium with each other and indicate that no degradation or side reactions take place during the photoisomerization experiments. Polymers bearing CN groups reached the pss in shorter time intervals compared to those bearing OCH₃ groups (Table 3). In this kind of polymers one would intuitively expect a decrease in the photoisomerization rate as the length of the terminal chain increases, however this was not the case as the rate of the photoisomerization for pCN(6,6) and pCN(12,6) was practically the same, both reaching cis isomer contents of around 95%. Conversely, the effect of the flexible spacer was clearly evidenced by the strong differences found not only in the photoisomerization rate, but also in the cis isomer contents (%cis) at the pss. For the polymer with no spacer (pOCH₃12,0) the elapsed time to attain the pss was 2.5 times that corresponding to the polymer with the longest spacer ($pOCH_312,6$), the latter reaching twice the content of the cis isomer. This contrasting result arises from the fact that the azobenzene moiety in the polymer pOCH₃12,0 photoisomerizes under the structural constraints imposed by the backbone.

An azocompound under illumination will eventually achieve a photostationary state, with a steady-state *trans-cis* ratio that



Fig. 9. Schematic representation of the interdigitated bilayer packing (SmA_d) for pCN10,6 and pCN12,6. (A) Expected packing with a full interaction of terminal chains. (B) Proposed model with deep interdigitation and bond dipole-bond dipole interactions of CN groups. Solid circles represent the polymer chains viewed end-on.

Table 3	
UV-Vis absorption and photo-induced properties of the azopolymers in sol	ution
(THF).	

Polymer	λ _{max} (nm)	ϵ_{trans}^{a} (L mol ⁻¹ cm ⁻¹)	pss ^b (s)	%cis ^c	$(\phi_{cis}/\phi_{trans})^{c}$	$\begin{array}{c} k_{ct} \times \ 10^{5d} \\ (s^{-1}) \end{array}$
pCN6,6	368	1.44×10^{6}	66	94.5	0.45	3.94
pCN10,6	368	1.47×10^{6}	77	94.6	0.37	3.84
pCN12,6	368	1.19×10^{6}	65	94.8	0.52	3.02
pOCH₃12,6	375	6.30×10^{5}	80	82.5	0.34	4.98
pOCH ₃ 12,4	375	8.29×10^{5}	96	78.1	0.30	3.60
pOCH ₃ 12,0	368	9.59×10^{5}	204	40.8	_	3.16

^a Calculated from $A = \varepsilon lc$ at different concentrations.

^b Irradiation at 365 nm until no change in absorbance is observed.

^c Calculated from Eq. (2) in the text.

 $^{\rm d}\,$ Calculated from Eq. (3) in the text.

depends on competing effects namely the photoisomerization to the *cis* state, the thermal relaxation back to the *trans* state, and the *cis* reconversion upon irradiation [1]. The *trans-cis* ratio at the steady state is characteristic to each system, as it depends on the quantum yields for the two processes and the thermal relaxation rate constant. Therefore, it is important to determine the quantum yield ratio and the thermal back relaxation for each synthesized polymer.

For the calculation of the quantum yield ratio the Fischer equation was used [40]

$$\left(\frac{A_{trans}}{B_{cis}}\right)_{\lambda} = \left(\frac{\varepsilon_{cis}}{\varepsilon_{trans}}\right)_{\lambda} \left(\frac{\phi_{cis}}{\phi_{trans}}\right)_{\lambda}$$
(2)

where A_{trans} and B_{cis} denote the content of the *trans* and *cis* species at the pss, ε_{trans} and ε_{cis} are the molar absorptivity coefficients, and ϕ_{trans} and ϕ_{cis} are the quantum yields for each isomer as labeled.



Fig. 10. Photoisomerization kinetics for (A) pCN12,6 and (B) $pOCH_312,6$ in solution using THF as solvent and irradiating at 365 nm.

Calculated quantum yields ratios (Table 3) for the polymers ranged from 0.3 to 0.52. Those polymers with the highest quantum yields ratio showed a high content of the *cis* isomer, emphasizing the direct correspondence between these two parameters. On the other hand, the first order rate constant (k_{ct}) of the thermal back relaxation (*cis-trans* isomerization) was determined by fitting the experimental UV–Vis spectroscopy data to the equation

$$ln\left(\frac{A_{\infty}-A_{t}}{A_{\infty}-A_{0}}\right) = -k_{ct}t$$
(3)

where A_{α} , A_t , and A_0 denote the absorbance at infinite time, at time t, and at time zero, respectively [41]. These data are plotted in Fig. 11 for the two polymer series and the calculated k_{ct} values are listed in Table 3. For all polymers Eq. (2) gave a good fit to the thermal *cis*-trans isomerization. Reconversion times from the *cis* into the *trans* state depend on the type of substituted groups. For azobenzenes, aminoazobenzenes, and pseudostilbenes the reconversion times are in general on the order of days, hours and seconds, respectively. k_{ct} values of our polymers range between 2.9 and $5.24 \times 10^{-5} \text{ s}^{-1}$ indicating that relaxation times are in the order of hours, therefore corresponding to the aminoazobenzene type [8].

3.4.3. Photoisomerization of polymers in film

It was demonstrated that the reversible light induced *trans-cis* isomerization of thin films of azocompounds gives rise to specific molecular arrangements that can be manipulated by light to obtain interesting macroscopic properties. Compared to small molecules, the mobility of chromophores in azopolymers is markedly reduced in a way that photoisomerization creates an alignment quasipermanent, useful for instance as a writing-erasing optical memory. Before analyzing the photo-induced properties it is also



Fig. 11. Thermal back relaxation for the azopolymers bearing (A) CN and (B) OCH₃ groups, measured at 25 °C. Irradiated polymers (365 nm) were stored in the dark and the *cis-trans* isomerization was measured at time intervals.

necessary to explore the spectroscopic features of polymers, which might surely change with respect to those observed in solution where chromophores are much less constrained. The UV-Vis spectra of two distinct azopolymer films are shown in Fig. 12. From the spectra it is clear that some other phenomena occur in films that were not seen in solution. In dilute regime there are no interchain interactions, and if the polymer-solvent interaction is good enough, the chromophores will respond to irradiation as independent units. On the contrary, for polymers deposited as thin films, inter and intrachain interactions between chromophores will produce aggregates as deduced from the observed marked peak shifts (Table 4). For almost all polymers the peak shift $\Delta \lambda_{max}$ (λ_{max} in film minus λ_{max} in solution) is of around -18 nm indicating the formation of H-aggregates [42]. It is interesting to note that for the polymer with no flexible spacer ($pOCH_312.0$) the hypsochromic shift is much less significant (-7 nm) than for all others due to motion restrictions the polymer chain imposes to the directly linked chromophores. Taking into account that polymers display liquid crystalline properties it was of our interest to test the effect of the self-induced order in the spectroscopic characteristics. To look for such effect a polymer film (pCN10,6) was heated above the clearing temperature and then it was cooled-down to room temperature in order to freeze a liquid-crystalline phase. This polymer was named pCN10,6T to differentiate it from the nonthermally treated pCN10,6. The consequence of such heating was an important hypsochromic peak shift of -27 nm indicating a stronger interaction between chromophores than that produced in the H-aggregates of the pCN10.6 and that may arise from the higher molecular order fixed upon cooling from the liquidcrystalline phase. It was reported that peak shifts higher than -25 nm might correspond to the aggregation over extended domains of parallel packed π -conjugated chromophores as it may



Fig. 12. Photoisomerization kinetics for the azopolymers (A) pCN12,6 and (B) $pOCH_312,6$ in film, irradiated at 365 nm at time intervals up to photostationary state.

	Table	e 4
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UV-Vis absorption and	photo-induced	properties for the	azopolymers in film.

$\lambda_{\max}(nm)$	pss ^a (s)	%cis ^b	λ_{max}^{c}
349	600	61.9	-19
350	600	50.0	-18
352	1000	56.1	-16
341	2000	38.3	-27
357	2000	71.4	-18
359	-	_	-16
365	5000	55.2	-7
	$\lambda_{max} (nm)$ 349 350 352 341 357 359 365	$\begin{array}{c c} \lambda_{max}(nm) & pss^a(s) \\ \hline 349 & 600 \\ 350 & 600 \\ 352 & 1000 \\ 341 & 2000 \\ 357 & 2000 \\ 357 & 2000 \\ 359 & - \\ 365 & 5000 \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^a Irradiation at 365 nm until no change in absorbance is observed.

^b Amount of *cis*-isomer in the photostationary state.

^c Calculated as the difference between λ_{max} in solution and film.

occur upon cooling from a liquid crystal [42]. It may be reminded that this polymer showed no crystallization upon cooling from the mesophase; the molecular order was then preserved at room temperature as a glassy liquid crystalline state.

Once the spectroscopic features were analyzed, it was important to study the light-induced behavior of polymer films in which chromophores are densely packed. The photoisomerization rate is much slower for polymers in film than for polymers in solution, reaching the pss state after longer irradiation times ranging from 600 to 5000 s, depending basically upon the lateral substituent group (CN or OCH₃) in the chromophore. Polymers bearing CN-substituted chromophores reached the pss state much faster than those bearing OCH₃-substituted chromophores, a difference not observed in solution in such an extent. It should be said that these latter polymers showed no isosbestic points (Fig. 12B) indicating that not only the photoisomerization is taking place, but some other phenomena like photo-bleaching or degradation. On the other hand, the extremely large time to reach the pss state for the pOCH₃12,0 is evidently due to the lack of a flexible spacer.

3.4.4. Birefringence

One of the advantages of highly anisotropic azobenzenes is the fact that large changes in birefringence can be induced in thin films by photoisomerization [20]. Moreover, high stability of the lightinduced properties along with good mechanical properties makes these films excellent candidates for high-density optical storage.



Fig. 13. Photoinduced birefringence for the spin coated polymer films determined by Eq. (1). The polymers were irradiated at 413 nm up to saturation and the change in birefringence was measured at 633 nm.

Table 5	
Birefringence values for spin co	ted thin and casted polymer films

Polymer	Δn ^a (spin coating)	Δn ^a (casting)	Diffraction efficiency ^b (%)
pCN6,6	0.066	0.030	4.74
pCN10,6	0.063	0.028	0.20
pCN12,6	0.078	0.07	1.4
pOCH₃12,6	0.068	0.057	0.82
pOCH ₃ 12,4	0.065	0.030	0.24
pOCH ₃ 12,0	0.051	0.049	0.17

^a Calculated from Eq. (1).

^b Determined as the percentage ratio between the incident beam and the first order diffracted beam.

Photo-induced birefringence (Δn) experiments were performed in films prepared by spin coating (300–450 nm), all of them showing good optical quality. The Δn versus time plots (Fig. 13) showed clear differences in the saturation value and in the time to reach it. The polymer showing the highest Δn saturation value (0.078) was the pCN12,6 while the one showing the lowest value (0.051) was the polymer pOCH₃12,0 (Table 5). In all polymers the saturation value was reached in less than 30 s, except for the polymer pOCH₃12,0 that took 60 s. Once again the proximity of chromophores to the polymer backbone in the polymer pOCH₃12,0 perturbs to some extent the photo-induced response. Some experiments were



Fig. 14. Switch-on – switch-off cycles for untreated pCN12,6 and thermally treated pCN12,6T.

performed in films prepared by casting showing similar trends, although the saturation times were much longer (>10 min) which is normal taking into account the optical path length of thick films.

In order to test the influence of the liquid-crystalline order on the relaxation kinetics of light-induced effects, one of the films pCN12.6 was subjected to pump-off-pump-on cycles (Fig. 14). Initially there is a rapid increase in the birefringence value up to saturation ($\Delta n = 0.08$). At this point the irradiation was switchedoff and contrary to the expected relaxation process, the birefringence continues to increase monotonically. It is also noticeable that, once the irradiation was switched-on again a slight decrease in the birefringence value is produced restoring the initial saturation value. In subsequent switch-off-switch-on cycles the same behavior is reproduced. To explain this atypical behavior one should remember that in liquid crystals there is an intrinsic thermodynamic tendency to self-organize into ordered phases. So, when the azo groups are subjected to a polarized light they move in concert following the direction given by the polarization direction reaching certain directional order, although once the pump is switch-off the liquid-crystalline domains do not relax, but in some way they continue to improve the molecular order in a minor extent [43]. The contrary effect produced in switching-on may be justified by the fact that light produces cis isomers that tend to disturb the liquid-crystalline order [44]. Taking into account that the polymer is in a glassy state, the loss in birefringence is not significant. In a second experiment, a film of pCN12.6 was heated up to the isotropization temperature (T_i) and then it was quenched in order to fix the liquid-crystalline phase at room temperature (glassy state). This thermally treated film (pCN12,6T) was then subjected to several pump-off-pump-on cycles as shown in Fig. 14. In this figure also a rapid increase in the birefringence value was observed but it was much limited compared to that observed for the untreated film. In this case the switch-off produced a slight decrease in the birefringence level whereas a switch-on again restores the birefringence to its highest previous value. Inducing molecular order in a smectic phase, however, involves moving the azobenzene groups from a thermodynamically stable state of domains with various director distributions to a specific unidirectional oriented state. This requires longer times of irradiation and the level of orientation is limited as it was observed in this experiment. Conversely, in amorphous polymers one would see in switch-off-switch-on cycles important relaxation-reorientation processes [45]. Results shown here indicate that there is a tight interplay between the photo-induced order and the LC intrinsic order present in films.



Fig. 15. AFM micrographs of surface relief gratings of azopolymers (A) pCN12,6 and (B) pOCH₃12,6 obtained by irradiation with an interference pattern at 413 nm.

3.4.5. Surface relief gratings

Because of their light-induced mass migration property, the polymers were tested as potential materials to construct surface relief gratings (SRG). The AFM micrograph of CN-substituted polymers showed perfect sinusoidal profiles with an average depth of around 150 nm (Fig. 15A). For polymers substituted with OCH₃ groups a mass migration was also observed but showing irregular profiles (Fig. 15B), although we would expect some improvements by changing both the method of film preparation and irradiation conditions. Only for casted films the diffraction efficiency was measured as the ratio of the first order diffracted beam and the incident beam. From all the obtained SRGs that of the pCN6,6 produced, in preliminary experiments, the highest diffraction efficiency (4.74%).

4. Conclusion

New side-chain liquid-crystalline polymers bearing highly anisotropic phenylene(azobenzene) moieties substituted with a OCH₃ or a CN lateral group were synthesized. These polymers exhibited smectic-type mesophases that extend over broad temperature ranges. Monolayer and bilayer smectic arrangements were observed depending on the length of the spacer and tail, as well as on the nature of the lateral substituent. In polymers bearing CN groups the interdigitated structures may arise from dipolar interactions between cyano groups. Polymers bearing OCH₃ groups displayed preferentially tilted mesophases. The introduction of a phenylene ring in the azobenzene increases the quantum yield ratio which allows a better optical response of the material. The inclusion of a OCH3 or CN lateral group in the phenylene(azobenzene) mesogens shifts the wavelength of maximum absorption and also affects their photoisomerization properties. Birefringence values between 0.05 and 0.08 and regular sinusoidal SRG were obtained. Results shown here indicate that there is a tight interplay between the photo-induced order and the LC intrinsic order present in films. These materials are suitable for a variety of optical applications as the holographic storage information.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2012.03.024.

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