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Synthesis and phase transitions of monomers carrying a biphenyleneazobenzene or an

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ABSTRACT

Four functional methacrylate monomers, two of them carrying a biphenyleneazobenzene group, and the other two an azotolane group, were synthesized. The synthetic route involved several reactions, among which are the Suzuki-Miyaura and Sonogashira cross-coupling reactions that allowed us to prepare long rigid rodlike azobenzene cores. The chemical structure of these new azo-monomers was confirmed by proton nuclear magnetic resonance (¹H NMR) spectroscopy, and the thermotropic liquid-crystalline behavior was determined from differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD) analyses. The four monomers showed a mesomorphic behavior that extends over a broad temperature range. The phase transitions of the monomers carrying a biphenyleneazobenzene core were much broader and weaker than those of monomers carrying an azotolane group. Also, the former showed no crystallization in cooling to room temperature. The four studied monomers displayed liquid crystal phases with lamellar order (SmA and SmC), but only those carrying an azotolane core developed an additional nematic phase. The lamellar stacking of monomers is discussed in terms of lateral interactions between the rigid rodlike cores. Both types of monomers showed a trans to cis photo-conversion of around 90% when irradiated with UV-light. These new monomers are precursors of photo-responsive liquid crystal polymers.

Key words: azobenzene, azotolane, liquid crystal, monomer

1. Introduction

The current increasing demand for digital storage devices of high capacity has motivated the development of new functional materials with specific properties [1,2]. This has been the case for the azobenzene-based liquid crystal (LC) polymers, which combine the unique molecular selforganization characteristic of liquids crystals with the exceptional light-induced response (molecular photo-alignment) of the azobenzene groups [3], and that have found potential application in high density (volume or 3D) optical data storage devices [4,5]. The preparation of such photo-responsive LC polymers requires the design and synthesis of functional monomers with a specific chemical structure. Such monomers can homopolymerize or co-polymerize with other monomers, either functional or non-functional, leading to an almost unlimited possibility of polymeric structures [6-9]. LC polymers bearing long or highly anistotropic "azo-mesogenic" groups have attracted great attention because they have shown to exhibit a mesomorphic behavior over broad temperature ranges and/or high response (photo-alignment) to light stimuli at the UVvis wavelengths [10,11]. Examples of highly anisotropic azo-mesogens are the biphenyleneazobenzene and azotolane groups substituted with terminal alkyl chains. The former develop mesophases of high thermal stability [11], whereas the latter reach high photo-induced birefringence (Δn) values [12-14]. It is worth to mention that the highest photo-induced birefringence values so far reported for azo-compounds belong to LC polymers bearing azotolane groups $(\Delta n > 0.5)$ [15]. In spite of such outstanding properties, there are relatively few reports on the synthesis of photo-responsive monomers carrying a highly anisotropic azo-mesogenic group. Their poor solubility is undoubtedly the main drawback as it restrains their own synthesis as well as that of their corresponding polymers. Common practices to improve the solubility of long aromatic cores are the substitution of their two ends with long alkyl chains and the introduction

of one or more short lateral groups; the former improve the mobility of molecules, whereas the latter impede their close packing (aggregates with tightly held molecules) [16]. Also, the lateral groups depress the melting and clearing temperatures as compared with those of their homologous molecules without such groups [17].

Recently, we reported the synthesis and thermotropic liquid crystal properties of monomers carrying a phenyleneazobenzene group substituted with two terminal alkyl chains and a lateral cyano (CN) group [18]. These monomers displayed nematic, smectic A, and smectic C phases in a broad temperature range. They also showed long induction periods for crystallization in such a way that, upon cooling, the lowest temperature mesophase remained temporarily unchanged up to room temperature. In this paper we report on the synthesis procedures and the thermotropic characterization of new methacrylate monomers carrying a highly anisotropic azobenzene derivative substituted with a lateral cyano group. Such a derivative is either, a biphenylene-azobenzene core having three successive phenyl groups, or an azotolane core possessing two phenyls linked through an ethynylene group; the former is longer (extra phenyl group) than that reported by us in a recent paper [18], whereas the latter shares some chemical characteristics with those reported by Okano et al. and that showed outstanding photo-induced optical properties [15].

2. Experimental section

2.1. Materials

4-Bromoaniline, n-bromodecane, n-bromohexane, 1,6-dibromohexane, 5-bromo-2-hydroxybenzonitrile, 4-bromo-phenylboronic acid, 1.6 M butyllithium in hexanes (BuLi), phenol,

bis(triphenylphosphine)palladium(II) dichloride (PdCl₂(PPh₃)₂), trimethylsilylacetylene (TMSA), tetrakis(triphenylphosphine)palladium(0) (Pd[0]), hydroquinone (HQ), sodium carbonate, sodium hydroxide, sodium nitrite, potassium carbonate, potassium hydrogen carbonate, copper iodide, potassium iodide, methacrylic acid (MA), and triisopropyl borate (TIPBO), were purchased from Sigma-Aldrich and used as received. Chloroform (CHCl₃), deuterated chloroform (CDCl₃), dimethylformamide (DMF), 1,4-dioxane, carbon tetrachloride (CCl₄), methylene chloride (CH₂Cl₂), tetrahydrofuran (THF), deuterated tetrahydrofuran (THF- d_8), triethylamine (TEA) acetone, ethanol, methanol, ethyl ether and hexanes were purchased from J.T. Baker. TEA (over KOH) and THF (over a Na/benzophenone complex) were always freshly distilled before use.

2.2. Synthesis

The route for the synthesis of the new biphenyleneazobenzene and azotolane–functionalized monomers is outlined in Scheme 1. For the sake of brevity, these azo-monomers were named B6, B10, A6, and A10, where B and A refer to the biphenyleneazobenzene and azotolane chromophores, respectively. The numbers 6 and 10 indicate the carbon atoms in the terminal alkyl chain. The spacer (chain of 6 carbon atoms between the methacrylic group and the azobenzene core) was not considered in these encoded names because it is identical for the four studied monomers. Intermediates 1, 2, and 4 to 7 were prepared as described in previous reports for similar compounds [11,16,19]. Procedures for the synthesis of the intermediates 3 and 8 to 13, as well as those for the preparation of the monomers B6, B10, A6, and A10, are detailed below.



Scheme 1. Route for the synthesis of monomers A6, A10, B6 and B10

(E)-1-(4-((6-bromohexyl)oxy)phenyl)-2-(4-bromophenyl)diazene (3)

In a 250 mL two-neck round-bottom flask, under inert atmosphere (Argon) and magnetic stirring, 4 g (9.09 mmol) of 2, 0.15g (0.13 mmol) of tetrakistriphenylphosphine palladium[0], 60 mL of THF, and 29.5 mL of Na₂CO₃ 2M (aqueous solution), were introduced. The reaction mixture was heated to 60 °C, and then, a solution (THF solvent) containing 0.91 g (4.54 mmol) of 4-bromophenyl boronic acid and tetrakistriphenylphosphine palladium(0) (catalytic amount) was added dropwise very slowly during 48 h. The reaction was held at 60 °C for 70 h under argon atmosphere and stirring. After this reaction period, the solution was allowed to cool down to room temperature and 40 mL of CHCl₃ were added. Next, the solution was introduced into a separation funnel and the organic phase was washed with water (until pH 7) and evaporated. Then, the residual solid was introduced into a silica-gel chromatographic column (CHCl₃ as eluent) to remove the catalyst. Finally, the solution was evaporated and the intermediate 3 (orange crystals, yield 65 %) was recrystallized from ethyl acetate. ¹H NMR (CDCl₃, $\delta = ppm$): δ = 1.43-1.61 (m, CH₂, 4H); 1.74-1.94 (m, CH₂, 4H); 3.45 (t, CH₂, 2H, J = 6.9 Hz); 4.07 (t, CH₂, 2H, *J* = 6.3 Hz); 7.02 (d, CH, 2H, *J* = 9.1 Hz); 7.53 (d, CH, 2H, *J* = 8.5 Hz); 7.59 (d, CH, 2H, *J* = 8.5 Hz); 7.70 (d, CH, 2H, J = 8.5 Hz); 7.89-7.98 (m, CH, 4H).

(E)-1-(4 -((6-bromohexyl)oxy)phenyl)-2-(4-((trimethylsilyl)ethynyl)phenyl)diazene (8)

In a 250 mL two-neck round-bottom flask, under inert atmosphere and stirring, 2 g (4.54 mmol) of 2, 0.14g (0.77 mmol) of CuI, 0.15 g (0.23 mmol) of PdCl₂ (PPh₃)₂, 0.29g (1.13 mmol) of PPh₃, 60 mL of TEA and 60 mL of THF, were introduced. The reaction mixture was heated to 60 °C and maintained under vigorous stirring for 30 min. Next, 1.28 mL (0.89 g, 9.08 mmol) of

trimethylsilylacetylene was added, and the reaction was heated to reflux for 24 h under argon atmosphere and stirring. After this reaction period, the solution was allowed to cool down to room temperature before being transferred to a separation funnel where diethyl ether was added for solids extraction. Then, the recuperated solid was introduced into a short chromatographic column (silica-gel and CHCl₃ as eluent) to remove the catalyst. Finally, the compound 8 (orange powder, yield 62 %) was purified by column chromatography using CHCl₃:hexane 8:2 as eluent. ¹H NMR (CDCl₃, δ = ppm): δ = 0.26 (s, CH₃, 9H); 1.52-1.56 (m, CH₂, 4H); 1.83-1.95 (m, CH₂, 4H); 3.45 (t, CH₂, 2H, *J* = 6.7 Hz); 4.06 (t, CH₂, 2H, *J* = 6.3 Hz); 7.01 (d, CH, 2H, *J* = 7.99 Hz); 7.58 (d, CH, 2H, *J* = 8.3 Hz); 7.81 (d, CH, 2H, *J* = 8.5 Hz); 7.91 (d, CH, 2H, *J* = 9.1 Hz).

(E)-1-(4-((6-bromohexyl)oxy)phenyl)-2-(4-ethynylphenyl)diazene (9)

In a 250 mL one-neck round-bottom flask, 0.7 g (1.59 mmol) of compound 8, 0.015 g (0.63 mmol) of K₂CO₃, 8 mL of THF and 35 mL of methanol, were introduced. Next, the reaction mixture was stirred for 3 h at room temperature. The solvent was then evaporated and the solid was introduced into a silica-gel chromatographic column (CH₂Cl₂:hexane 1:1 as eluent) to recuperate the compound 9 as an orange solid (yield 90 %). ¹H NMR (CDCl₃, δ = ppm): δ = 1.37-1.64 (m, CH₂, 4H); 1.84-1.95 (m, CH₂, 4H); 3.22 (s, CH, 1H); 3.45 (t, CH₂, 2H, *J* = 6.7 Hz); 4.06 (t, CH₂, 2H, *J* = 6.3 Hz); 7.01 (d, CH, 2H, *J* = 8.5 Hz); 7.65 (d, CH, 2H, *J* = 8.3 Hz); 7.85 (d, CH, 2H, *J* = 8.3 Hz); 7.93(d, CH, 2H, *J* = 8.3 Hz).

(E)-4"-((4-((6-bromohexyl)oxy)phenyl)diazenyl)-4-(hexyloxy)-[1,1':4',1"-terphenyl]-3carbonitrile (10)

In a 250 mL two-neck round-bottom flask, under inert atmosphere and magnetic stirring, 0.5 g (0.97 mmol) of 3, 0.239 g (0.97 mmol) of 6, 30 mL of THF, 6.3 mL of Na₂CO₃ 2M (aqueous solution), and 0.033g (0.03 mmol) of tetrakistriphenylphosphine palladium(0), were introduced. Next, the reaction mixture was heated to 60 °C and during 8 h catalytic amounts of tetrakistriphenylphosphine palladium[0] were added at intervals of 2 h. The reaction was held at 60 °C for 24 h under argon atmosphere and stirring. After this reaction period, the solution was allowed to cool down to room temperature and 30 mL of CHCl₃ were added. The organic phase was then separated from the aqueous phase, and it was subsequently washed with water until pH 7, dried with sodium sulfate, and evaporated. The recuperated solid was introduced into a silicagel chromatographic column (CHCl₃ as eluent) to remove the catalyst. Finally, the compound 10 (orange solid; yield 74 %) was purified by column chromatography using CHCl₃:hexane 1:1 as eluent. ¹H NMR (CDCl₃, δ = ppm): δ = 0.92 (t, CH₃, 3H, J = 6.5 Hz); 1.26-1.65 (m, CH₂, 12H); 1.87-1.92 (m, CH₂, 4H); 3.45 (t, CH₂, 2H, J = 6.7 Hz); 4.07 (t, CH₂, 2H, J = 6.1 Hz); 4.13 (t, CH_2 , 2H, J = 6.1 Hz); 6.94-7.09 (m, CH, 3H); 7.63 (d, CH, 2H, J = 8.4 Hz); 7.70-7.84 (m, CH, 6H); 7.90-8.01 (m, CH, 4H).

(E)-4"-((4-((6-bromohexyl)oxy)phenyl)diazenyl)-4-(decyloxy)-[1,1':4',1"-terphenyl]-3carbonitrile (11)

Orange powder (yield 57 %).¹H NMR (300 MHz, CDCl₃, $\delta = ppm$): $\delta = 0.89$ (t, CH₃, 3H, J = 6.5 Hz); 1.26-1.55 (m, CH₂, 20H); 1.85-1.93 (m, CH₂, 4H); 3.45 (t, CH₂, 2H, J = 6.7 Hz); 4.07

(t, CH₂, 2H, *J* = 6.3 Hz); 4.13 (t, CH₂, 2H, *J* = 6.5 Hz); 6.96-7.09 (m, CH, 3H); 7.63 (d, CH, 2H, *J* = 8.5 Hz); 7.71-7.86 (m, CH, 6H); 7.90-8.07 (m, CH, 4H).

(E)-5-((4-((6-bromohexyl)oxy)phenyl)diazenyl)phenyl)ethynyl)-2-(hexyloxy)benzonitrile (12)

In a 250 mL two-neck round-bottom flask, under argon atmosphere and stirring, 0.46 g (1.66 mmol) of 4, 0.034 g (0.18 mmol) of Cul, 0.048 g (0.07 mmol) of PdCl₂ (PPh₃)₂, 0.09 g (0.35 mmol) of PPh₃, 30 mL of TEA and 30 mL of THF, were introduced. The reaction mixture was heated to 60 °C and stirred for 30 min. Then, 0.493 g (1.38 mmol) of 9 were added and the reaction was held for 24 h under reflux. After this reaction period, the solution was allowed to cool down to room temperature to be further transferred into a separation funnel for solid extraction with THF. The extracted solid was then introduced into a short silica-gel chromatographic column (CHCl₃ as eluent) to remove the catalyst. Finally, the compound 12 (orange powder, yield 28 %) was recrystallized twice from hexane:ethyl acetate 8:2. ¹H NMR (CDCl₃, δ = ppm): δ = 0.93 (t, CH₃, 3H, *J* = 6.9 Hz); 1.36-1.56 (m, CH₂, 12H), 1.85-1.95 (m, CH₂, 4H); 3.44 (t, CH₂, 2H, *J* = 6.3 Hz); 4.07 (t, CH₂, 2H, *J* = 6.3 Hz); 4.11 (t, CH₂, 2H, *J* = 6.3 Hz); 7.93 (d, CH, 2H, *J* = 9.1 Hz).

(E)-5-((4-((6-bromohexyl)oxy)phenyl)diazenyl)phenyl)ethynyl)-2-(decyloxy)benzonitrile (13)

This compound was synthesized from 9 and 5 following a procedure similar to that described for the synthesis of 12. The compound 13 (orange powder, 27 %) was recrystallized from acetone. ¹H NMR (CDCl₃, $\delta = ppm$): $\delta = 0.93$ (t, CH₃, 3H, J = 6.9 Hz); 1.36-1.56 (m, CH₂,

12H), 1.85-1.95 (m, CH₂, 4H); 3.44 (t, CH₂, 2H, *J* = 6.3 Hz); 4.07 (t, CH₂, 2H, *J* = 6.3 Hz); 4.11 (t, CH₂, 2H, *J* = 6.3 Hz); 6.90-7.05 (m, CH, 3H); 7.59-7.71 (m, CH, 3H); 7.75 (d, CH, 1H, *J* = 1.9 Hz); 7.88 (d, CH, 2H, *J* = 8.5 Hz); 7.93 (d, CH, 2H, *J* = 9.1 Hz).

(E)-6-(4-((3"-cyano-4"-(hexyloxy)-[1,1':4',1"-terphenyl]-4-yl)diazenyl)phenoxy)hexyl methacrylate (B6)

In a 250 mL round-bottom flask, under argon atmosphere and stirring, 0.15 g (1.55 mmol) of KHCO₃ and 0.13 mL (1.55 mmol) of methacrylic acid, were introduced. Next, 0.0062 g (0.06 mmol) of hydroquinone, 0.365 g (0.55 mmol) of 10, and 40 mL of DMF were added to the reaction flask. The reaction mixture was heated to 80 °C and held under stirring and argon atmosphere for 24 h. After this reaction period, the solution was allowed to cool down to room temperature to be further transferred into a separation funnel where 30 mL of CHCl₃ and 30 mL of H₂O were added. The organic phase then subsequently washed with HCL 5% (aqueous solution), K₂CO₃ 5% (aqueous solution), and water until pH 7. Then, it was dried with sodium sulfate, filtered and evaporated. Finally, B6 (orange powder, yield 72 %) was purified by silicagel column chromatography using CHCl₃:hexane 9:1 as eluent. ¹H NMR (CDCl₃, δ = ppm): δ = 0.94 (t, CH₃, 3H, *J* = 6.6 Hz); 1.49-1.58 (m, CH₂, 10H), 1.70-1.94 (m, CH₂, 6H); 1.96 (s, CH₃, 3H); 4.07 (t, CH₂, 2H, *J* = 6.3 Hz); 4.12-4.21 (m, CH₂, 4H); 5.56 (s, =CH, 1H); 6.12 (s, =CH, 1H); 6.97-7.14 (m, CH, 3H); 7.63 (d, CH, 2H, *J* = 8.3 Hz); 7.70-7.86 (m, CH, 6H); 7.89-8.02 (m, CH, 4H).

(E)-6-(4-((3"-cyano-4"-(decyloxy)-[1,1':4',1"-terphenyl]-4-yl)diazenyl)phenoxy)hexyl methacrylate (B10)

Orange powder (yield 75 %). ¹H NMR (CDCl₃, δ = ppm): δ = 0.88 (t, CH₃, 3H, *J* = 6.9 Hz); 1.27-1.57 (m, CH₂, 18H), 1.68-1.89 (m, CH₂, 6H); 1.94 (s, CH₃, 3H); 4.05 (t, CH₂, 2H, *J* = 6.3 Hz); 4.06-4.18 (m, CH₂, 4H); 5.53 (s, =CH, 1H); 6.10 (s, =CH, 1H); 6.92-7.13 (m, CH, 3H); 7.64 (d, CH, 2H, *J* = 8.3 Hz); 7.70-7.86 (m, CH, 6H); 7.89-8.02 (m, CH, 4H).

(*E*)-6-(4-((4-((3-cyano-4-(hexyloxy)phenyl)ethynyl)phenyl)diazenyl)phenoxy)hexyl methacrylate (A6)

Orange powder (yield 76 %). ¹H NMR (CDCl₃, $\delta = \text{ppm}$): $\delta = 0.92$ (t, CH₃, 3H, J = 6.9 Hz); 1.34-1.57 (m, CH₂, 10H), 1.69-1.89 (m, CH₂, 6H); 1.95 (s, CH₃, 3H); 4.04-4.20 (m, CH₂, 6H); 5.56 (s, =CH, 1H); 6.12 (s, =CH, 1H); 6.90-7.05 (m, CH, 3H); 7.58-7.71 (m, CH, 3H); 7.75 (d, CH, 1H, J = 1.9 Hz); 7.87 (d, CH, 2H, J = 8.5 Hz); 7.92 (d, CH, 2H, J = 8.8 Hz).

(E)-6-(4-((4-((3-cyano-4-(decyloxy)phenyl)ethynyl)phenyl)diazenyl)phenoxy)hexyl methacrylate (A10)

Orange powder (yield 90 %). ¹H NMR (CDCl₃, δ = ppm): δ = 0.91 (t, CH₃, 3H, *J* = 6.9 Hz); 1.35-1.57 (m, CH₂, 18H), 1.68-1.89 (m, CH₂, 6H); 1.94 (s, CH₃, 3H); 4.04-4.20 (m, CH₂, 6H); 5.55 (s, =CH, 1H); 6.10 (s, =CH, 1H); 6.90-7.05 (m, CH, 3H); 7.58-7.71 (m, CH, 3H); 7.74 (d, CH, 1H, *J* = 1.9 Hz); 7.87 (d, CH, 2H, *J* = 8.5 Hz); 7.92 (d, CH, 2H, *J* = 8.8 Hz).

2.3. Instruments

The chemical structure of intermediates and monomers was confirmed by proton nuclear magnetic resonance (¹H NMR) spectroscopy using a Jeol 300 MHz spectrometer (model JNM-ECO300) and THF- d_8 or CDCl₃ as solvents. The thermal stability of monomers was determined by thermogravimetry using a TGA 951 thermal analyzer from DuPont Instruments connected to a N₂ vector gas and heating at 10 °C min⁻¹ from 30 to 800 °C. The transition temperatures were measured in a MDSC 2920 differential scanning calorimeter from TA Instruments at heating/cooling rates of 10 °C min⁻¹. The optical textures were obtained from samples confined between two glass cover slides and observed between crossed polarizers in an Olympus BX53 optical microscope coupled to a Linkam LTS420E hot stage and to a T95-LinkSys controller. The presented textures were captured with a Micropublisher 3.3 RTV digital camera. The layer spacing of the smectic phases was determined from the X-ray diffraction patterns registered at different temperatures on cooling from the isotropic liquid using a SAXSess mc² from Anton Paar GmbH, equipped with a sealed cooper tube (Cu K_{α} 0.154 nm), a sample holder unit (TCS 300-C), an image plate detector, and a temperature controller (TCU50). XRD experiments were conducted with samples encapsulated in glass capillaries (Hampton Research) having an outer diameter and a wall thickness of 1.0 and 0.01 mm, respectively. The photo-isomerization experiments were performed in solution (THF as solvent) using a laboratory UV lamp (UVGL-58; $\lambda = 365$ nm). A CARY 5000 spectrophotometer was used to record the spectrum just after each irradiation interval (5 seconds).

3. Results and Discussion

3.1. Synthesis and characterization of monomers

The monomers B6, B10, A6 and A10 were prepared through the intermediates 1 to 13 as shown in Scheme 1. The intermediate 1 was obtained from 4-bromoaniline, phenol and NaNO₂ via the *in situ* formation of a diazonium salt [19]. This intermediate was next reacted with 1,6dibromohexane through a Williamson reaction to get the intermediate 2, which was in turn coupled with the 4-bromophenyl boronic acid to produce 3, using the Suzuki-Miyaura crosscoupling reaction mediated by Pd[0] [20]. In a parallel way, the intermediates 4 and 5 were obtained by reacting 5-bromo-2-hydroxybenzonitrile with bromohexane and bromodecane (Williamson reaction), respectively. These two intermediates were then reacted with butillitium and triisopropyl borate to prepare the corresponding alkyloxy-cyanophenyl boronic acids 6 and 7, which were subsequently coupled with 3 to get the long bromo end-functionalized biphenyleneazobenzene precursors 10 and 11, respectively [21]. The Suzuki-Miyaura cross-coupling reaction is perhaps the most popular method for the aryl-aryl coupling. It proceeds under mild conditions, tolerate a variety of functional groups, and uses boronic acids (laboratory-made or commercially available), which are fairly stable and easy to handle [22]. The relatively low temperature (often less than -40 °C) required for the preparation of boronic acids is the only significant drawback, particularly when their preparation involves long rigid rodlike intermediates (oligoaryls), which become fairly insoluble at such temperatures [23]. For our intermediates the Suzuki-Miyaura reaction resulted in relatively good yields (> 50 %). The general catalytic cycle of this coupling reaction is known and has been described elsewhere [24].

On the other hand, the intermediate 2 was coupled with trimethylsilylacetylene to obtain 8 using a Sonogashira coupling reaction mediated by $PdCl_2(PPh_3)_2/CuI/PPh_3$ [25]. This C–C coupling method has become a practical and useful tool not only for the synthesis of compounds with terminal alkynes, but also of those with internal alkynes like tolanes or longer conjugated molecules like the oligo- and poly-phenyleneethynylenes [26,27]. The further elimination of the trimethylsilyl group from 8 using K₂CO₃ gave the intermediate 9, which was later coupled (Sonogashira-coupling reaction) with 4 and 5 to produce the bromo end-functionalized azotolane precursors 12 and 13, respectively. Finally, the monomers B6, B10, A6 and A10 were prepared by reacting the bromo end-functionalized precursors (10, 11, 12 and 13, respectively) with methacrylic acid [16]. All the synthesized compounds were obtained in good yields (> 60%), except for some of the long final intermediates whose conversion was rather low (yield ~26%).

The ¹H NMR spectra of 1, 2, 3, 10 and B6 are grouped in Figure 1. The chemical modification can be simply followed by comparing the spectra of each one of these compounds. The alkylation of 1 with 1,6–dibromohexane to obtain 2 was confirmed by the presence of two triplets at 4.05 (Ar–O–CH₂) and 3.44 ppm (CH₂–Br), and also by various multiplets between 1.5 and 2.0 ppm (rest of the alkyl chain). The compound 2 was then coupled with the 4-bromophenyl boronic acid, which can also react with itself to produce oligo and poly(*p*-phenylene)s [28]. In order to minimize this polycondensation reaction, the bromophenyl boronic acid was added dropwise very slowly over 48 h. Under this condition, the intermediate 3 was obtained and isolated in a relatively good yield (~65%). The spectrum of the intermediate 3 displayed additional signals at low fields (around 7.6 ppm) as compared with that of the intermediate 2, such signals were attributed to the protons of the extra phenyl group in the intermediate 3, supporting the

accomplishment of the C–C coupling reaction. To further increase the conjugation length of the azobenzene core, the intermediate 3 was next reacted with the 4-hexyloxy-(3-cyano)phenyl boronic acid (6) in the presence of Pd[0], producing 10 at a relatively good yield (74%). The inserted hexyloxyphenyl group can be readily identified in the spectrum of 10 by new signals at low (doublet at 6.9 ppm, CH *o*- to the oxygen atom), medium (triplet at 4.1 ppm, $-CH_2-O$), and high fields (triplet at 0.9 ppm, CH₃) of the spectrum. Finally, the precursor 10 was reacted with methacrylic acid to obtain the azo monomer B6. The spectrum of B6 shows new signals between 5.5 and 6.15 ppm, and around 4.1 ppm (overlapped), corresponding to protons of the vinyl ($-CH_2=C-$) and ester ($-CH_2-O-CO-$) groups, respectively. These new signals and the absence of the triplet at 3.5 ppm (CH₂–Br) indicate that the functionalization of the acrylic monomer has proceeded as expected. The ¹H NMR spectra of 11 and B10 are not shown here because they are similar to those of 10 and B6, respectively. The only change is the relative higher intensity of the mehylene signal at high fields (between 1.0 and 1.6 ppm) resulting from the difference in the terminal alkyl chain length (decyloxy for 11 and B10, and hexyloxy for 10 and B6).



Figure 1. ¹H.NMR spectra of the precursors 1, 2, 3, 10 and monomer B6.

The ¹H NMR spectra of 8, 9, 12 and A6 are depicted in Figure 2. The intermediate 8 was synthesized from 2 and trimethylsilylacetylene (Sonogashira coupling reaction) under rigorous inert conditions [29]. Compared with the spectrum of the intermediate 2, the spectrum of 8 displays one additional singlet at 0.26 ppm, which was assigned to the protons of the trimethylsilyl group. It also shows signals with different multiplicity at low fields, indicating that the electronic environment produced by the trimethylsilylacetylene group (non-polar group) in 8, is some different to that produced by the bromine atom (electron attracting group) in 2. The

purification of the trimethylsilyl-functionalized azocompound (8) by column chromatography was particularly difficult because the elusion rate of both 2 and 8 was similar in most tested solvents (pure and mixed solvents), finding that only CCl₄ allowed a relatively good separation (yield of 47.3 %) in long silica-gel columns. The trimethylsilyl group of the intermediate was then removed from 8 using K_2CO_3 [30]. The spectrum of the resulting product (compound 9) shows a singlet at 3.2 ppm associated to the proton of the remaining terminal acetylene group [31]. This singlet and the absence of the singlet close to 0 ppm provide evidence of the elimination of the trimethylsilyl group from 8. In a further step, the intermediates 4 and 9 were coupled to each other through a Sonogashira reaction to form the compound 12. This later reaction gave low yields (around 25%) due to purification problems associated to the separation of this later compound from byproducts (non-identified). The hexyloxyphenyl group of 12 can be readily identified by new signals at low (doublet at 6.9 ppm, CH o- to the oxygen atom), medium (triplet at 4.1 ppm, CH₂–O), and high fields (triplet at 0.9 ppm, –CH₃) in the spectrum. Finally, the cyano azotolane-functionalized methacrylate monomer (A6) was obtained by reacting 12 with methacrylic acid. The spectrum of A6 clearly shows the proton signals of the vinyl group between 5 and 6 ppm, as well as that of the ester group at 4.1 ppm. These signals and the absence of the triplet at 3.5 ppm (CH₂–Br) confirm the right synthesis of the monomer A6. The ¹H NMR spectra of 13 and A10 (not shown here) are similar to those of 12 and A6, respectively. The only difference is the relative higher intensity of methylene signal at high fields (between 1.0 and 1.6 ppm).



Figure 2. ¹H.NMR spectra of the precursors 8, 9, 12 and monomer A6.

3.2. Thermal behavior

The azo-monomers B6, B10, A6, and A10 start to decompose above 260 °C, as determined by TGA (not shown here). This temperature was fixed as the limiting temperature for their further thermotropic examination by DSC, POM and XRD. By DSC, B6 and B10 displayed only broad and weak transitions in both heating and cooling runs (Figure 3). Despite the lack of sharp DSC transitions, clear optical changes between typical liquid crystal textures were observed by POM for both monomers (Figure 4). Such changes correspond to transitions from the isotropic to the focal conic fan / homeotropic texture (Figure 4A, around 200 °C); from the focal conic fan /

homeotropic texture to the broken focal conic fan / gray schlieren texture (Figure 4B; around 184°C); and from the broken focal conic fan / gray schlieren texture to a paramorphotic texture (Figure 4C; around 80°C). As the optical textures were quite similar for both monomers, only those of B10 are shown here. The focal conic fan / homeotropic texture is characteristic of a smectic A phase, whereas the broken focal conic fan / gray schlieren texture is typical of the smectic C phase [32]. It is to point out that the paramorphotic texture remained unchanged up to room temperature, indicating that B6 and B10 do not crystallize. These monomers were then analyzed by X-ray diffraction at room temperature (Figure 5). In both cases, the X-ray patterns showed two sharp equidistant Bragg diffractions peaks (001 and 002) confirming the smectic order (lamellar stacking).



Figure 3. DSC thermograms of the monomers B6 and B10 obtained on heating and cooling runs at 10 $^{\circ}$ C min⁻¹.



Figure 4. Optical textures of the monomer B10 observed on cooling from the isotropic state.





Figure 5. X-ray diffraction patterns of the monomers B6 and B10 captured at room temperature.

On the other hand, the DSC traces of the azotolane monomers (A6 and A10) showed various thermal transitions at both heating and cooling runs, indicating the presence of enantiotropic liquid crystal phases (Figure 6). Only the transition from the liquid-crystalline to the crystalline state showed a marked hysteresis that can be attributed to the long induction period for the crystallization process. Monomers might crystallize at low rate upon cooling since some exotherms were registered under heating. The expected decrease in the clearing temperature, by increasing the alkyl chain length, can be readily seen by comparing the highest temperature endotherm of A6 (155 °C) with that of A10 (138 °C) [17]. The phase transitions detected by DSC for A6 and A10 were next corroborated by polarizing optical microscopy (POM) at variable temperature. By this technique, typical optical textures of liquid crystal phases were observed. As both A6 and A10 displayed similar optical textures, only those of the monomer A6 are shown here (Figure 7). Upon cooling, this monomer displayed a schlieren texture (Figure 7A) characteristic of a nematic phase, followed by a focal conic fan texture surrounded with a large homeotropic zones (Figure 7B), which is typical for a smectic A phase [33]. An additional transition (non-observed by DSC) was detected on cooling to around 100 °C. At this temperature the focal-conic fan texture gradually turned into a broken focal conic fan / gray schlieren texture, which is typical of the tilted smectic C phase (Figure 7C).



Figure 6. DSC thermograms of the monomers A6 and A10 obtained on heating and cooling runs

(10 °C min⁻¹).



Figure 7. Optical textures of the monomer A10 observed on cooling from the isotropic state. A)

138 °C, B) 130 °C and C) 100 °C.

To determine the exact nature of the liquid crystals phases, A6 and A10 were next studied by XRD at variable temperature. Several XRD patterns were captured upon cooling, but only those obtained from a phase transition are here presented for discussion (Figure 8). At high temperature (just below the clearing temperature according to DSC and POM analyses), the absence of sharp diffraction peaks at both low and wide angles in the XRD patterns corroborates the nematic phase. On cooling from this mesophase, the development of one diffraction peak (001) at low angles (the broad peak at wide angles remains unchanged) confirms the presence of a smectic phase of low order. Around 100°C this sharp peak vanishes whereas other diffraction peak appears at higher angles (the broad peak at wide angles still remaining unchanged), suggesting the occurrence of a phase transition between two smectic phases of low order, the former more expanded than the later. The experimental smectic period (d_{001}) of these two smectic phases was compared with the theoretical length of molecules (L) in their most extended conformation calculated by molecular modelling (Spartan 10). For A6, the calculated d_{001}/L ratios were 0.9 at 110 °C and 0.81 at 90 °C. These values are close to unity, indicating that mesophases are single layered with molecules orthogonal (at 110°C) and tilted (at 90°C) with respect to the normal of the smectic planes. The average tilt angle $(\cos^{-1} 0.81)$ of molecules in the tilted mesophase is 35.9°. These results corroborate the presence of a smectic A and C phases, as it was anticipated by POM. For A10, the calculated d_{001}/L ratios were 0.89 at 110 °C and 0.8 at 190 °C (tilt angle = 36.9°), also indicating the presence of single layer smectic A and C phases, respectively. A summary of the thermal and mesomorphic behavior of both A and B monomers is gathered in Table 1.

Table 1. Thermal transitions (*T*), mesophases, and decomposition temperature (T_{id}) of the monomers A6, A10, B6, and B10.

Monomer	T °C (mesophase)	$T_{\rm id}, {}^{\circ}{\rm C}$
A6	Crystal -3.1 (SmC) 96.8 (SmA) 138 (N)155 Isotropic	293
A10	Crystal 28 (SmC) 106.7 (SmA)133 (N) 138 Isotropic	277
B6 ^a	SmX 120 (SmC) ? SmA (277) Isotropic/Degradation	266
B10 ^a	SmX 128 (SmC) 192 SmA (255) Isotropic	267

a) Determined by POM as no sharp transitions were detected by DSC.



Figure 8. X-ray diffraction patterns of the monomers A6 and A10 captured at different temperatures.

The observed lamellar stacking of monomers may be determined by the strong π -interaction occurring between their long rigid rodlike aromatic cores (biphenylene-azobenzene or azotolane). Such interaction may also induce a segregation of the two different parts of the monomers (aromatic cores and aliphatic chains), which are fairly incompatible to one another and may lead

to the formation two distinct domains (sublayers) within the lamellae [11]. For the biphenyleneazobenzene such interactions might be stronger than those for the azotolane core. This was reflected on the poor solubility and high clearing temperature (overlaps with the initial decomposition temperature) of the monomers B6 and B10.

3.3 Light-induced isomerization

The azobenzene derivatives are able to isomerize from the *trans* to the *cis* isomer when they are irradiated with UV light [3]. This photo-isomerization process is helpful to align the chromophore units into a preferential direction leading to birefringence and dichroic properties [16]. The photo-isomerization is also useful to record surface reliefs gratings of a specific topological pattern. These light-induced properties and patterns are being explored for a number of practical applications [34].

In this work the ability of the monomers A6 and B6 to photo-isomerize was tested in solution using THF as solvent. The obtained UV-Vis absorption spectra for the initial and irradiated solutions are shown in Figure 9. As can be noticed, the initial spectrum (0 s) exhibits a strong band around 374 nm, which is due to the $\pi - \pi *$ electronic transition of the *trans* isomer [35]. On irradiating the solution at time intervals of 5 seconds this strong band decreases whereas a weak band centered around 455 nm (n – $\pi *$ electronic transition of the *cis* isomer) increases. Both monomers attained a *trans-to-cis* photo-conversion of around 90 % in only 20 seconds. These values are slightly smaller than those reported for shorter azo-monomers whose corresponding polymers have shown a good photo response [16, 18].



Figure 9. UV-Vis spectra of A6 and B6 (in THF) before and after irradiation with a UV lamp (λ = 365 nm) at time intervals of 5 seconds.

The four new functionalized methacrylate monomers (A6, A10, B6 and B10) are precursors of liquid crystal homopolymers and copolymers whose highly anisotropic azo-mesogenic pendant groups may be favorable for the development of liquid crystal phases in broad temperature ranges. A liquid crystal behavior is in turn favorable for high photo-induced alignments (large birefringence), particularly for highly anisotropic azobenzene chromophores, like reported for side chain LC polymers bearing long azotolane pendant moieties [15], whose π -electrons are delocalized all along this aromatic core [10].

4. Conclusion

Four new functional methacrylate monomers carrying a biphenyleneazobenzene or an azotolane group, substituted at both ends with alkyl chains (terminal chain and spacer) and a lateral cyano group, were synthesized through several reactions, including the Suzuki-Miyaura and Sonogashira reactions that allowed the coupling of aryl-aryl and aryl-ethynyl groups, respectively. Most intermediates were obtained at relatively good yields (> 60 %), except for some of the long final intermediates (yields of 25-30 %) whose purification was difficult. The ¹H NMR analysis confirmed the right synthesis of each one of the intermediates and final azomonomers. The combined DSC, POM and XRD results indicated that the new azo-monomers develop nematic and/or smectic crystal phases, which are low viscous and low ordered liquid-like mesophases. The smectic phases appeared in wide temperature intervals due to the strong π -interactions between the long azobenzene cores, particularly for monomers carrying a biphenylene-azobenzene chromophore. The monomers here studied are precursors of functional LC azopolymers that may show good photo-induced response.

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Graphical abstract

Highlights

New phenyleneazobenzene and azotolane monomers were synthesized.

Both types of monomers display a liquid crystal behavior of the smectic type.

The molecular stacking in smectic phases may be determined by π -interactions.

Monomers are precursors of photo-active liquid crystal polymers for optical devices.

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