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Synthesis of 3,5-Disubstituted Isoxazolines as a Template for Liquid-Crystalline Polymers

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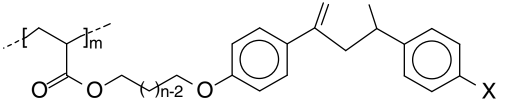
Summary

The synthesis and mesomorphic properties of new polyacrylate liquid crystals 3,5-disubstituted isoxazolines **8a-d** are discussed. 1,3-Dipolar cycloadditions of nitrile oxides generated in situ from oximes **2a-b** in the presence of 4-substituted styrene **3** (X = Br, Cl and CH_3) provided 3,5-disubstituted isoxazolines **5a-d**. The monomers **7a-d** were submitted to AIBN conditions and all the final polymers showed a stable nematic phase. The mesophase stability was dependent on the spacer length and terminal group at mesogenic core. Also, a small molecular weight effect was observed.

Introduction

1,3-Dipolar cycloadditions of nitrile oxides to alkenes offer an interesting one-step route for the synthesis of isoxazolines which are versatile intermediates for the synthesis of bifunctional compounds [1]. Among isoxazolines we can find compounds with pharmacological properties like analgesic [2], anti-inflammatory [3], antibacterial [4] and GPIIb/IIIa inhibiting [5] activity. Also, 3,5-isoxazolines containing aryl groups at C_3 and C_5 positions in the heterocyclic ring can exhibit LC properties and their study is an excellent opportunity to establish the relationship between molecular structure and mesomorphic behavior. The molecular topology of the isoxazoline ring can guide liquid-crystalline parameters as a template for materials with potential technological applications and that only a few examples of high performance materials having a five-membered heterocycle as a central bridge in the mesogenic core have been reported in the literature [6].

Herein we reported our preliminary results about the synthesis and mesomorphic behavior of a polymeric liquid crystals 3,5-disubstituted isoxazolines series **8a-d** (Figure 1).



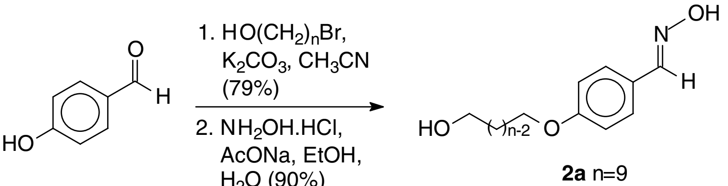
8a n=9 X=Br
b n=11 X=Br
c n=11 X=Cl
d n=11 X=CH_3

Figure 1. Molecular structure of the homopolymers synthesized.

Results and Discussion

Synthesis

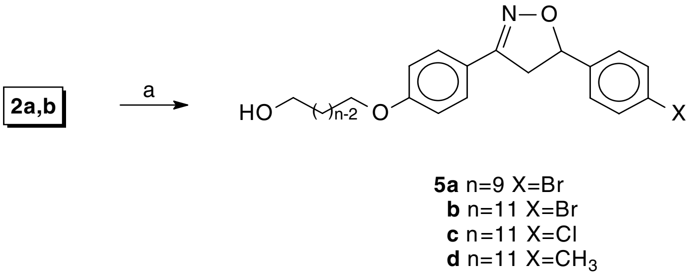
The synthetic strategy of 3,5-disubstituted isoxazolines **7a-d** and their homopolymers **8a-d** began with the preparation of intermediates **2a-b** described in the Scheme I.



Scheme I. Synthetic step for oximes **2a-b** preparation.

The oximes **2a,b** were prepared from aldehyde **1** by a two-step sequence. The spacer group containing nine or eleven methylene units was introduced by alkylation reaction of **1** with ω-bromoalkanol giving the corresponding alkylated products in 79% yield, according to procedure described by Hsiue and Chen [7]. Oximes **2a,b** were obtained through condensation reaction using hydroxylamine salt under basic conditions. The products were isolated from the reaction mixture by recrystallization at room temperature in 90% yield.

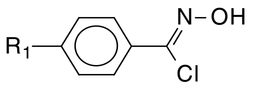
The synthesis of cycloadducts **5a-d** were achieved by exposure of **2a,b** to 4-substituted styrene **3** (X=Br, Cl, CH_3) through a 1,3-dipolar cycloaddition reaction [3+2] according to Scheme II. The one-pot reactions were carried out in the sequence (i) chlorination reaction of **2a-b** with *N*-clorosuccinimide in chloroform solution to yield the arylhydroximinoyl chloride (**4a**), (ii) addition of the dipholarofile, and (iii) dehydrohalogenation reaction by addition of triethylamine as basic agent for *in situ* generation of the nitrile oxide.



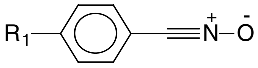
Reactions Conditions. a. NCS, NEt_3, $CHCl_3$, (**3**) *p*-$XC_6H_4CH{=}CH_2$ X=Br, Cl, CH_3 (60-84%).

Scheme II. Synthesis of cycloadducts **5a-d.**

The *in situ* generation of nitrile oxides is based on the fact that the equilibrium between hydroximic acid chloride (**4a**) and nitrile oxides (**4b**) normally lies in favor of **4a**. However, the equilibrium can be shifted to **4b** by heating a solution of **4a** in the presence of a suitable dipolarophile alkene acceptor. The nitrile oxides **4b**, which is present at very low stationary concentration, is immediately consumed.

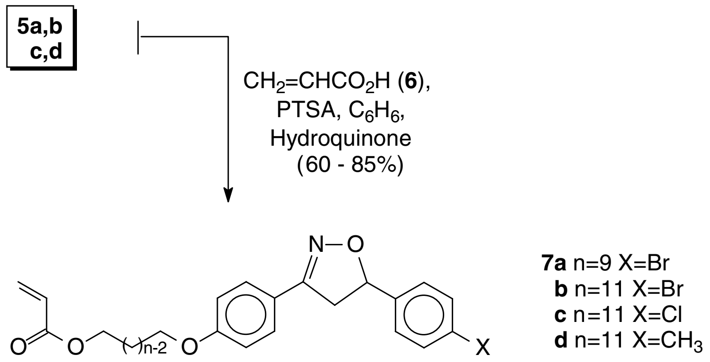


4a



4b

The completion of the synthesis of monomers **7a-d** required the introduction of a polymerizable acrylate group. It was accomplished using a large excess of acrylic acid in presence of *p*-toluene sulfonic acid and hydroquinone [8]. The target monomers 3,5-disubstituted isoxazoline **7a-d** were isolated and purificated by silica gel column chromatography followed by recrystallization from isopropanol or an aqueous ethanol solution in 60-85% yield (Scheme III).



Scheme III. Synthesis of the monomers **7a-d**.

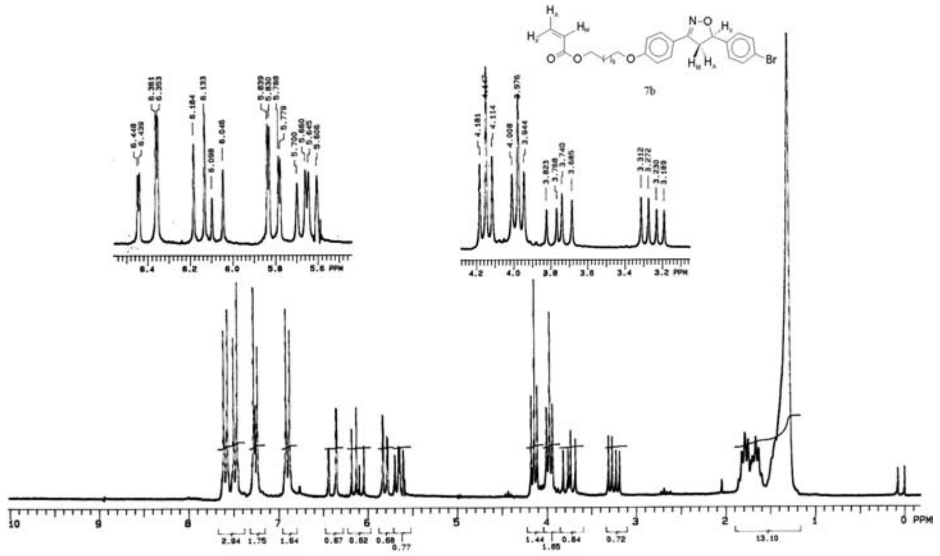


Figure 2. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of the monomer **7b**.

The NMR analysis of the all monomers confirmed the correct regiochemistry of cycloaddition reaction. The ^1H NMR spectrum for monomer **7b** is shown in Figure 2. The expansions in the upper trace are showed to make the splitting patterns clear.

The two sets of three doublet of doublets located between 3.00 ppm and 6.50 ppm belong to the same splitting pattern. The set of resonance lines cited are associated to the 3,5-disubstituted isoxazoline ring and acrylate system, respectively.

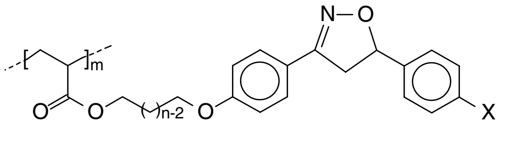
The first set of the three doubled doublets signals which has the resonance lines centered at 3.25 ppm, 3.75 ppm and 5.65 ppm belong to the AMX pattern related to the chemically and magnetically nonequivalent protons H_A, H_M and H_X. The chemical shifts observed for the hydrogens on the heterocyclic ring provide support for the fact that only a 3,5-disubstituted regioisomer is formed. With a 3,4-disubstituted regioisomer, the chemical shifts for diastereotopic methylene hydrogens and methine hydrogen are at 5.10 ppm and 4.50 ppm, respectively.

The first doubled doublet signal at 3.25 ppm in Figure 2 was assigned to the proton H_A of the heterocyclic ring with coupling constants $^2J_{gem}$ (J_{AM}) and $^3J_{cis}$ (J_{AX}) of 16.5 Hz and 8.0 Hz, respectively. The second doubled doublet signal at 3.75 ppm assigned to the proton H_M has identical coupling constant $^2J_{gem}$ of H_A (16.5 Hz) and coupling constant $^3J_{trans}$ (J_{MX}) equal to 11.0 Hz. The third resonance line centered at 5.65 ppm was assigned to the proton H_X. Again, we see that H_X gives rise to four peaks (double doublet) with coupling constants $^3J_{trans}$ and $^3J_{cis}$ of 11.0 Hz and 8.0 Hz, respectively. The chemical shifts and coupling constants of these signals are in accordance with 3,5-diphenylisoxazoline data from the literature [9].

The stereochemical non-equivalence concept can be extracted from these data looking at the diastereotopic methylene hydrogens on the isoxazoline ring. The splitting patterns for the pro-*R* and pro-*S* hydrogens consist of two doubled doublets [10]. The relative chemical shifts of pro-*R* and pro-*S* are quite different. The resonance line at high field (3.25 ppm) is assigned for the pro-*R* and at low field (3.75 ppm) for the pro-*S* hydrogen.

The acrylate group gives a resonance line in the NMR spectrum typical of a compound with three hydrogens substituted on a double bond. Each proton has a non-equivalent chemical shift and characteristic coupling constants. Each hydrogen is split into a doublet of doublets (four peaks). The second AMX pattern consists of three doublet of doublets located at 5.81 ppm for H_A, 6.12 ppm for H_M and 6.40 ppm for H_X. For acrylate systems, the coupling constant $^3J_{trans}$ are larger than $^3J_{cis}$ and $^2J_{gem}$ is very small. For compound **7b**, the values of the coupling constants $^3J_{trans}$, $^3J_{cis}$ and $^2J_{gem}$ calculated were 17.4 Hz, 10.3 Hz and 1.8 Hz, respectively. These resonance lines were used as a reference to control the purity of the homopolymers **8a-d**.

The liquid-crystalline polymers were obtained through radical polymerization. The monomers **7a-d** were submitted to free polymerization with AIBN (5 wt %) as the radical initiator in toluene solution to give the polyacrylates **8a-d**. For polymer **8b₂**, the polymerization was carried out using 2% wt of AIBN. All polymerizations were performed at 65 °C for 72 h under N_2 atmosphere. Then, the polymers were precipitated into cold methanol, filtered, and purified by reprecipitation from THF solutions until no signal of ethylene protons in NMR spectra could be observed. The comparative data of the homopolymers **8a-d** are shown in Table 1.



8a n=9 X=Br
b n=11 X=Br
c n=11 X=Cl
d n=11 X=CH_3

Table 1. Comparative data of the homopolymers **8a-d**.

Sample	M_n	M_w/M_n	DP	Yield %
8a	6857	1.26	13	77
8b$_1$	4059	1.47	08	73
8b$_2$	8804	1.54	16	83
8c	5517	1.24	11	67
8d	4033	1.39	08	64

Mn: g.mol^{-1}; DP: number average degrees of polymerization

Liquid Crystalline Properties

Taking into account the experimental data obtained, the dependence of phase transitions temperatures on structural parameters of the homopolymers will be discussed. The effect of the spacer length, the molecular weight and the terminal mesogenic unit group on thermal behavior of the novel materials having 3,5-isoxazoline ring as a template for liquid crystals properties will be considered. Mesomorphic properties were studied by means of differential scanning calorimetric (DSC) and polarizing optical microscopy (POM). As a previous result, analysis made by POM revealed that the monomeric structural units **7a-d** do not display liquid crystalline properties.

Figure 3 shows representative DSC traces (recorded on heating) of the homopolymers **8a-d**. Table 2 summarizes the DSC data acquired. All polymers synthesized exhibit the same curve profile. They display a barely visible glass transition (T_g) and only one exothermic peak which is ascribed to a liquid-crystalline to isotropic transition during heating (T_i). It is important to mention here that the accurate determination of T_g for some samples was dependent on the rate used for DSC curve acquisition and the thermal manipulation of the sample (quenching procedure). By this reason, the data in Table 2 was collected after a quenching procedure. Under thermal manipulation, all the samples were heated above its isotropic transition temperature for ten minutes and

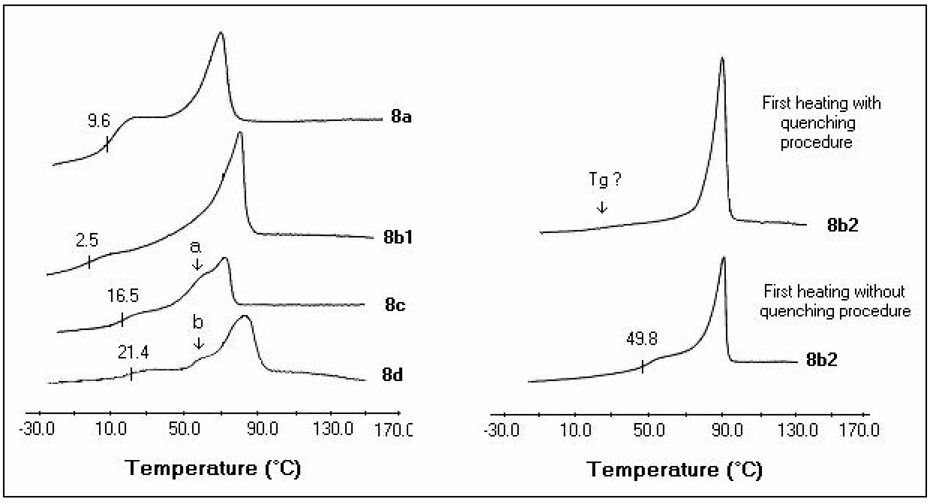


Figure 3. DSC traces recorded on heating of the homopolymers **8a-d**.

quickly dropped into small Dewar flask containing N_2 (liquid). However, for homopolymer **8b₂**, T_g value was determined at the first heating without quenching procedure (see DSC thermogram at right down side of the Figure 3). The shoulders (*a* and *b*) seen in Figure 3 for polymers **8c** and **8d** are related with some crystallinity degree of the polymers.

Qualitatively, an enantiotropic nematic mesophase was visible under polarized light for the homopolymers **8a-d**. Figure 4 shows, as a representative example, the texture of the mesophase produced by the sample **$8b_2$**. In the micrograph, recorded on cooling from the isotropic liquid state, the optical texture was assigned as schlieren. This texture remains essentially unchanged for several weeks.

Considering **8a** and **$8b_1$** which have the same mesogenic core and spacer lengths of 9 and 11 carbons respectively, a higher isotropisation temperature was monitored for the second one. In fact, an increase in T_i increasing the spacer length in LC polymers is suggested by the "spacer decoupling" model [11,12], which means a partial independent motion of the mesogenic group in relation to the motion of the backbone. The mesophase range of sample **8a** and **$8b_1$** were 60.8 °C and 79.9 °C, respectively. It was larger for sample **$8b_1$;** and, the T_g is lower, considering that the sample **$8b_1$** has a longer spacer group then **8a**.

It is well known that isotropisation temperatures are associated to the mesogenic side groups. On the other hand, the values of glass transition temperatures are related to the polymer backbone. Thus, it is believed that the T_g value monitored for samples **8a-d** can be linked to a special arrangement of the mesogenic groups in relation to the polymer backbone. This arrangement may give more flexibility to the polyacrylate having a nematic phase, especially for polymer **$8b_1$**. No conclusion about mesofase range for polymer **$8b_2$** can be inferred. As pointed out by Warner et al., a variety of nematic phases arrangement can exist dependently on the length and chemical configuration of the coupling chain [13]. To get a more precise description of this behavior, a small-angle neutron scattering study of SCLCP should be undertaken. In this way, our result from academic point of view remains still unclear and is being studied.

Table 2. Phase thermal transition parameters for the homopolymers **8a-d**.

Polymer	T_g (ºC)	N	T_i (ºC)	ΔT (°C)	ΔH_i (J/g)
8a	9.6	●	70.4	60.8	8.8
$8b_1$	2.5	●	82.4	79.9	23.3
$8b_2$	a	●	90.7	41.5^a	25.2
8c	16.5	●	72.1	55.6	16.3
8d	21.4	●	83.4	62.0	24.4

All temperature data were recorded from the first heating after quenching procedure. T_g – glass transition temperature; T_i – isotropization temperature. Scan rate of 20 ºCmin^{-1}. ^{a} Tg was obtained without quenching procedure. The mesofase range was taking into account considering the first heating at 20 °Cmin^{-1}. In this case the sample **$8b_2$** has the following transition temperatures: Tg 49.8 °C N 91.3 °C I.

Thermodynamic parameters were also changed due to the different spacer lengths. Sample **$8b_1$** has higher values of isotropization enthalpy (Table 2) and entropy (data not showed), which are also expected and attributed to the addition of -CH_2- to the mesogenic group. Consequently, it increases the conformational contribution to the disordering transition [14].

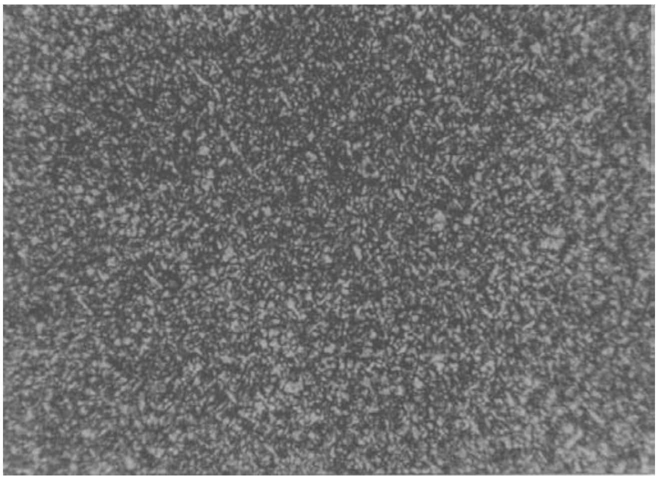


Figure 4. Polarizing optical micrograph displayed by the homopolymer **$8b_2$** (10x magnification).

Sample **$8b_2$** was synthesized in order to study the influence of the molecular weight in the liquid crystalline parameters, in comparison with sample **$8b_1$**. The homopolymer **$8b_2$** has a molecular weight around two times higher than **$8b_1$** (Table 1). A slight difference of 8.3 ºC in the T_i values was detected considering the two samples. Even though we can not get a more precise description of the mesophase range for these two polymers - due to the absence of Tg value for **$8b_2$** at the same thermal condition - a comparison between T_i for two polymers is valid. These results point out that a higher molecular weight produces a more stable nematic phase, probably due to the greater flexibility of polymer **$8b_2$**. Some research groups, studying SCLC polymers based in a polyacrylate backbone, found out that phase transition becomes molecular weight independent when the degree of polymerization (DP) exceeds values between 12 and 40 units [8,15]. Conversely, the DP determined by GPC measurements for homopolymer **$8b_1$** is lower than this value (Table 1). Percec and coworkers studied extensively the effect of molecular weight in the phase transitions of SCLC polymers. They showed, for polymetacrylates [16], a molecular weight dependence in the nematic-isotropic transition up to degrees of polymerization of approximately 10-12. In this case, a molecular average weight around 5.10^3 g mol^{-1} was the limit of the dependence and normally the samples studied also showed a smectic mesophase besides the nematic one. These results and the experimental data in this work, which show only a small dependence in the phase transition temperatures with a high difference in the molecular weight and in the degrees of polymerization make us believe that homopolymers **$8b_1$** and **$8b_2$** are at least close to the molecular weight phase transition independence regime.

The results observed considering the "polymer effect" could be understood considering simply thermodynamic approaches. For homopolymers **$8b_1$** and **$8b_2$**, it was observed only very small differences in the values of ΔH of isotropisation considering different molecular weights achieved. This is in agreement with some results already reported, where isotropisation enthalpy seems to be essentially molecular weight independent up to degrees of polymerization of 40 [8]. In addition, as already mentioned in this contribution, the monomeric structural unit does not display a liquid-crystalline behavior. Otherwise, when the monomer is polymerized, it is possible to observe a schlieren texture by POM which characterizes a liquid-crystalline mesophase formation (see, for example Fig. 4). The polymerization of the monomeric units decrease the entropy of the liquid phase and as consequence, an increase on the free energy parameter takes place. The liquid crystalline texture is observed only when a determined degree of polymerization is achieved [17]. The stability of the mesophase normally increases until the entropy of the liquid-crystalline state remains almost constant increasing the molecular weight of the polymeric material.

Considering the homopolymers **8b$_1$**, **8c** and **8d**, where the terminal group was modified, we noticed only small changes in the isotropization temperatures. On the other hand, huge differences were recorded in glass transition temperatures. The T_g values decrease in the sequence **8d > 8c > 8b$_1$**. The temperatures recorded were 2.5, 16.5 and 21.4 ºC. At the same time, the nematic range increases in the sequence **8b$_1$ > 8d > 8c**, being the values respectively equals to 79.9, 62.0 and 55.6 ºC. Thus, the efficiency of the terminal group in stabilizing the nematic liquid crystal phase in this series are in the order –Br > $-CH_3$ ~ –Cl, which is in agreement with what is typically observed in low molecular mass liquid crystals [18]. The significance of this latest results in terms of molecular structure is being studied to the other isoxazolines systems. However, in our knowledge, it is the first time that 3,5-disubstituted isoxazolines are being used as part of a mesogenic group to produce SCLC polymers. In this way, the results can be generalized in bases of low molecular weight liquid crystals, even we are working with considerable differences comparing with classical liquid crystals, such as polarizability of the isoxazoline template and the deviation of linearity of the mesogenic unit.

Experimental Section

Materials. 4-hydroxybenzaldehyde, 11-bromoundecanol, hydroxylamine chloridrate, acrylic acid, *N*-clorosuccinimide (NCS), triethylamine (NEt_3), *p*-bromostyrene, *p*-chlorostyrene, *p*-methylstyrene, hydroquinone and *p*-toluenesulphonic acid (pTSA) were used as received from Aldrich. Analytical thin layer chromatography (TCL) was conducted on Merck aluminum plates with 0.2 mm of silica gel 60F-254. Anhydrous sodium sulphate was used to dry all organic extracts. Toluene was first heated at reflux over sodium and then distilled under argon. AIBN was freshly recrystallized from methanol. Purification by column chromatography was carried out on 70-230 mesh Merck silica gel 60. All other solvents and reagents were used without previous purification.

Synthesis. 4-(11-Hydroxyalkyloxy)benzadehyde oxime (**2a-b**). The titles compounds were prepared from benzaldehyde (**1**) by a two-step sequence. *(a) Alkylation reaction.* The alkylated products were obtained according to reference 7.

Data for nonyloxy spacer group 2a. Yellow pale solid; Yield 84 %; m.p. 48-53 ºC. **^{1}H NMR** ($CDCl_3$, 200 MHz) δ 1.3 (m, 12H, $(CH_2)_6$); 1.8 (m, 2H, $C\underline{H_2}CH_2O$); 3.6 (t, 2H, CH_2O, *J* = 6.4 Hz); 4.0 (t, 2H, CH_2O, *J* = 6.6 Hz); 7.0 (d, 2H, Ar, *J* = 8.6 Hz); 7.8 (d, 2H, Ar, *J* = 8.6 Hz); 9.8 (s, 1H, CHO). **^{13}C NMR** ($CDCl_3$, 50 MHz) δ 25.8; 26.0; 28.9; 29.1; 29.2; 29.6; 32.7; 62.8; 68.2; 114.6; 129.5; 131.9; 164.2; 190.8. **I.R.** $\nu_{max/}cm^{-1}$ 3460; 2940; 2860; 1690; 1600; 1568; 1460; 1370; 1260; 1220; 1170; 1040; 1020; 829; 720 (nujol).

Data for undecyloxy spacer group 2b. Yellow pale solid; Yield 79 %; m.p. 62 ºC. **^{1}H NMR** ($CDCl_3$, 200 MHz) δ 1.3 (m, 16H, $(CH_2)_8$); 1.8 (m, 2H, $C\underline{H_2}CH_2O$); 3.6 (t, 2H, CH_2O, J = 6.4 Hz); 4.0 (t, 2H, CH_2O, J = 6.6 Hz); 6.9 (d, 2H, Ar, J = 8.6 Hz); 7.8 (d, 2H, Ar, J = 8.6 Hz); 9.8 (s, 1H, CHO). **^{13}C NMR** ($CDCl_3$, 50 MHz) δ 25.5; 25.7; 28.9; 29.3; 29.4; 29.5; 29.6; 32.7; 63.0; 68.0; 114.5; 129.4; 132.0; 164.0; 191.0. **I.R.** ν_{max}/cm^{-1} 3463; 2933; 2855; 1678; 1600; 1572; 1460; 1376; 1258; 1221; 1167; 1042; 1023; 829; 720 (nujol).

(b) Condensation reaction. Representative procedure for **2a**. In a 100 mL round bottom flask equipped with a mechanical stirrer and an efficient reflux condenser fitted with a calcium chloride drying tube was placed the corresponding aldehyde (17 mmol), hydroxylamine chloridrate (51 mmol) and 40 mL of ethanol. The solution was stirred during 10 minutes and then was added sodium acetate (68 mmol) in water (20 mL). The mixture was heated during 40 minutes at 70 °C. Then, the solution was cooled and white crystals were filtered and dried in vacuum.
Data for **2a**. m.p. 105-110 ºC; yield: 64 %; **^{1}H NMR** ($CDCl_3$, 200 MHz) δ 1.3 (m, 12H, $(CH_2)_6$); 1.7 (m, 2H, $C\underline{H}_2CH_2O$); 2.1 (broad, 1H, OH); 3.6 (t, 2H, CH_2O, J = 6.6 Hz); 3.9 (t, 2H, CH_2O, J = 6.6 Hz); 6.8 (d, 2H, Ar, J = 8.8 Hz); 7.5 (d, 2H, Ar, J = 8.8 Hz); 8.1 (s, 1H, CHO). **^{13}C NMR** ($CDCl_3$, 50 MHz) δ 25.6; 26.0; 28,8; 29.0; 29.3; 29.6; 32.5; 62.4; 68.1; 114.3; 125.0; 128.0; 149.0; 160.1. **I.R.** ν_{max}/cm^{-1}: 3370; 2910; 2860; 1696; 1600; 1509; 1460; 1370; 1300; 1250; 1170; 1112; 1050; 875; 830; 720 (nujol).

Data for **2b**. m.p. 82-85 ºC; Yield: 90 %. **^{1}H NMR** ($CDCl_3$, 200 MHz) δ 1.3 (m, 16H, $(CH_2)_8$); 1.8 (m, 2H, $C\underline{H}_2CH_2O$); 2.0 (s, 1H, OH); 3.6 (t, 2H, CH_2O, J = 6.6 Hz); 3.9 (t, 2H, CH_2O, J = 6.6 Hz); 6.7 (d, 2H, Ar, J = 8.8 Hz); 7.5 (d, 2H, Ar, J = 8.8 Hz); 8.1 (s, 1H, CHO). **^{13}C NMR** ($CDCl_3$, 50 MHz) δ 25.6; 25.8; 29.0; 29.1; 29.2; 29.3; 29.4; 32.6; 62.5; 67.9; 114.4; 124.9; 128.1; 148.9; 160.1. **I.R.** ν_{max}/cm^{-1} 3375; 2921; 2851; 1677; 1603; 1511; 1460; 1376; 1304; 1256; 1169; 1112; 1046; 875; 832; 717 (nujol).

11-{4-[5-(4-bromophenyl)-4-5-dihydroisoxazol-3-yl]phenyloxy}-1-undecanol (5b). Representative procedure for compound **5b**. To a solution of the *p*-bromostyrene (9.7 mmol), chloroform (20 mL), *N*-chlorosuccinimide (10 mmol) and pyridine (1.17 mL, 14 mmol) at 0 ºC and under argon atmosphere was added dropwise to the solution of **2b** (3g, 8.7 mmol) in chloroform. The solution was heated at 60°C for 4 hours and finally at room temperature. The mixture was washed with HCl 0.5N (3x50 mL), $NaHCO_3$ 5% (2x50 mL), water (2x50 mL) and brine (2x25 mL) and then dried with Na_2SO_4. After solvent evaporation the product was recrystallized from ethanol.
Data for **5a**. Yield 84 %; m.p. 99-102 ºC. **^{1}H NMR** ($CDCl_3$, 200 MHz) δ 1.4 (m, 12H, $(CH_2)_6$); 1.9 (m, 2H, $C\underline{H}_2CH_2O$); 2.7 (broad, OH); 3.3 (m, 1H, $C\underline{H}HCH$); 3.6 (t, 2H, CH_2O); 3.8 (m, 1H, $CH\underline{H}CH$); 4.0 (t, 2H, CH_2O); 5.7 (m, 1H, $C\underline{H}CHH$); 6.9 (d, 2H, Ar, J = 8.6 Hz); 7.3 (d, 2H, Ar, J = 8.4 Hz); 7.5 (d, 2H, Ar, J = 8.2 Hz); 7.6 (d, 2H, Ar, J = 8.6 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz) δ 25.3; 25.6; 28.6; 29.2; 32.5; 39.7; 43.1; 62.5; 67.7; 81.2; 114.4; 121.1; 127.3; 128.0; 131.5; 139.9; 155.5; 160.5. **I.R.** ν_{max}/cm^{-1} 3350; 2918; 2848; 1605; 1600; 1515; 1462; 1382; 1302; 1240; 1185; 1100; 1059; 1048; 1008; 917; 868; 713 (nujol).

Data for **5b**. Yield 63 %; m.p.120 ºC. **^{1}H NMR** ($CDCl_3$, 200 MHz) δ 1.5 (m, 16H, $(CH_2)_8$); 1.8 (m, 2H, $C\underline{H}_2CH_2O$); 3.3 (dd, 1H, $C\underline{H}HCH$, ^2J = 16.6 Hz; $^3J_{cis}$ = 8.0 Hz); 3.6 (t, 2H, CH_2O, J = 6.4 Hz); 3.8 (dd, 1H, $CH\underline{H}CH$, ^2J = 16.6 Hz; $^3J_{trans}$ = 10.8 Hz); 4.0 (t, 2H, CH_2O, J = 6.6 Hz); 5.6 (dd, 1H, $CHHC\underline{H}$, $^3J_{trans}$ = 10.8 Hz, $^3J_{cis}$ = 8.0 Hz);

6.9 (d, 2H, Ar, J = 9.0 Hz); 7.2 (d, 2H, Ar, J = 8.6 Hz); 7.4 (d, 2H, Ar, J = 8.4 Hz); 7.5 (d, 2H, Ar, J = 8.8 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz) δ 25.5; 25.7; 28.8; 29.1; 29.2; 29.3 32.5; 39.8; 43.2; 62.3; 67.9; 81.2; 114.4; 121.1; 127.3; 128.0; 131.5; 139.9; 155.5; 160.5. **I.R.** ν_{max}/cm^{-1} 3339; 2922; 2852; 1609; 1594; 1515; 1460; 1376; 1307; 1251; 1179; 1111; 1063; 1048; 1011; 912; 875; 720 (nujol).

Data for **5c**. Yield: 60 %. m.p. 110 ºC. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.4 (m, 18H, $(CH_2)_9$); 3.2 (dd, 1H, $C\underline{H}HCH$, ^2J = 16.5 Hz, $^3J_{cis}$ = 8.1 Hz); 3.6 (t, 2H, CH_2O, J = 6.6 Hz); 3.7 (dd, 1H, $CH\underline{H}CH$, ^2J = 16.5 Hz, $^3J_{trans}$ = 10.8 Hz); 3.9 (t, 2H, CH_2O, J = 6.6 Hz); 5.6 (dd, 1H, $CHHC\underline{H}$, $^3J_{trans}$ = 10.8 Hz, $^3J_{cis}$ = 8.1 Hz); 6.9 (d, 2H, Ar, J = 9.0 Hz); 7.3 (s, 4H, Ar); 7.6 (d, 2H, Ar, J = 9.0 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz) δ 25.7; 25.9; 29.1; 29.3; 29.4; 29.5; 29.6; 32.7; 43.5; 63.0; 68.1; 81.4; 114.6; 121.4; 127.2; 128.2; 128.8; 129.1; 129.1; 155.6; 160.7. **I.R.** ν_{max}/cm^{-1} 3353; 2922; 2852; 1650; 1642; 1607; 1536; 1462; 1376; 1250; 1181; 1100; 1064; 1051; 1016; 874; 829; 722 (nujol).

Data for **5d**. Yield: 65 %. m.p. 108-110 ºC. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.45 (m, 18H, $(CH_2)_9$); 2.3 (s, 3H, CH_3); 3.2 (dd, 1H, $C\underline{H}HCH$, ^2J = 16.5 Hz, $^3J_{cis}$ = 8.4 Hz); 3.6 (t, 2H, CH_2O, J = 6.6 Hz); 3.7 (dd, 1H, $CH\underline{H}CH$, ^2J = 16.4 Hz, $^3J_{trans}$ = 10.9 Hz); 3.9 (t, 2H, CH_2O, J = 6.6 Hz); 5.6 (dd, 1H, $CHHC\underline{H}$, $^3J_{trans}$ = 10.8 Hz; $^3J_{cis}$ = 8.4 Hz); 6.9 (d, 2H, Ar, J = 8.7 Hz); 7.2 (d, 2H, Ar, J = 8.1 Hz); 7.3 (d, 2H, Ar, J = 8.1 Hz); 7.6 (d, 2H, Ar, J = 8.7 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz) δ 21.1; 25.7; 25.9; 29.1; 29.3; 29.4; 29.5; 29.6; 32.7; 43.3; 62.9; 68.0; 82.2; 114.5; 121.7; 125.8; 128.1; 129.3; 137.8; 137.9; 155.7; 160.6. **I.R.** ν_{max}/cm^{-1} 3356; 2922; 2852; 1677; 1603; 1547; 1513; 1461; 1376; 1303; 1254; 1168; 874; 830; 811; 720 (nujol).

11-{4-[5-(4-bromophenyl)-4,5-dihydroisoxazol-3-yl]-phenyloxy}undecyl Acrylate (7b). Representative procedure for **7b**. In a flask equipped with a Dean-Stark was placed **5b** (1.50 g, 3 mmol), acrylic acid (1.89 g, 26 mmol), benzene (35 mL), pTSA (0.7 mmol) and hydroquinone (1.1 mmol). The mixture was kept under reflux until no more water was collected in the Dean-Stark trap. Afterward, the heat mixture was filtered and the solvent was evaporated. The resultant solid was dissolved in diethyl ether and washed with water (3x25 mL), $NaHCO_3$ 5% (2x20 mL) again with water (2x20 mL) and then dried with Na_2SO_4. The solvent was then evaporated and the product was recrystallized from isopropanol.

Data for **7a**. Yield 60 %; m.p. 75-80 ºC. **^{1}H NMR** ($CDCl_3$, 200 MHz) δ = 1.4 (m, 10H, $(CH_2)_5$); 1.8 (m, 4H); 3.3 (dd, 1H, ^2J = 16.6 Hz, $^3J_{cis}$ = 8.0 Hz, $C\underline{H}H$); 3.8 (dd, 1H, ^2J = 16.6 Hz, $^3J_{trans}$ = 10.9 Hz, $C\underline{H}H$); 4.0 (t, 2H, CH_2O, J = 6.6 Hz); 4.2 (t, 2H, $C\underline{H_2}O$, J = 6.8 Hz); 5.7 (dd, 1H, $^3J_{trans}$ = 10.6 Hz, $^3J_{cis}$ = 8.0 Hz, $C\underline{H}CHH$); 5.8 (dd, 1H, $^3J_{cis}$ = 10.4 Hz, ^2J = 1.6 Hz, $CH{=}CH_2$); 6.1 (dd, 1H, $CH{=}CH_2$, $^3J_{trans}$ = 17.3 Hz, $^3J_{cis}$ = 10.3 Hz,); 6.4 (dd, 1H, $CH{=}CH_2$, $^3J_{trans}$ = 17.2 Hz, ^2J = 1.8 Hz); 6.9 (d, 2H, J = 9.0 Hz, Ar); 7.3 (d, 2H, Ar, J = 8.4 Hz); 7.5 (d, 2H, Ar, J = 8.4 Hz); 7.6 (d, 2H, Ar, J = 8.8Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz) δ 25.7; 25.8; 28.5; 29.1; 29.2; 29.4; 43.4; 64.6; 68.0; 81.4; 114.7; 121.4; 121.9; 127.5; 128.2; 130.4; 131.7; 140.1; 155.6; 160.6; 166.2. **I.R.** ν_{max}/cm^{-1} 2920; 2849; 1719; 1605; 1518; 1464; 1380; 1294; 1252; 1191; 960; 911; 868; 819; 727 (nujol).

Data for **7b**. Yield: 85 %. m.p. 56 ºC. **^{1}H NMR** ($CDCl_3$, 200 MHz) δ 1.3 (m, 14H, $(CH_2)_7$); 1.6 (m, 2H, $C\underline{H_2}CH_2CH_2O$); 1.8 (m, 2H, $CH_2C\underline{H_2}CH_2O$); 3.2 (dd, 1H, $C\underline{H}HCH$, ^2J =16.5 Hz, $^3J_{cis}$ = 8.0 Hz); 3.7 (dd, 1H, $CH\underline{H}CH$, ^2J = 16.6 Hz, $^3J_{trans}$ = 11.0

Hz); 3.9 (t, 2H, CH$_2$O, J = 6.4 Hz); 4.1 (t, 2H, CH$_2$O, J = 6.8 Hz); 5.6 (dd, 1H, CHHCH, $^3J_{\mathrm{trans}}$ = 11.0 Hz, $^3J_{\mathrm{cis}}$ = 8.0 Hz); 5.8 (dd, 1H, CH=CH$_2$, ^2J = 1.8 Hz, $^3J_{\mathrm{cis}}$ = 10.3 Hz); 6.1 (dd, 1H, CH=CH$_2$, $^3J_{\mathrm{trans}}$ = 17.0 Hz, $^3J_{\mathrm{cis}}$ = 10.3 Hz); 6.4 (dd, 1H, CH=CH$_2$, $^3J_{\mathrm{trans}}$ = 17.4 Hz, ^2J = 1.8 Hz); 6.90 (d, 2H, Ar, J = 8.8 Hz); 7.3 (d, 2H, Ar, J = 8.6 Hz); 7.5 (d, 2H, Ar, J = 8.6 Hz); 7.6 (d, 2H, Ar, J = 8.8 Hz). **^{13}C NMR** (CDCl$_3$, 50 MHz) δ 25.8; 25.9; 28.5; 29.0; 29.1; 29.2; 29.4; 43.4; 64.6; 68.0; 81.4; 114.6; 121.3; 121.9; 127.5; 128.2; 128.5; 130.4; 131.7; 140.1; 155.6; 160.7; 166.2. **I.R.** ν_{max}/cm^{-1} 2922; 2852; 1723; 1607; 1513; 1460; 1376; 1296; 1252; 1195; 961; 910; 874; 820; 722 (nujol).

Data for **7c**. Yield 60 %. m.p. 52-54 ºC. **^{1}H NMR** (CDCl$_3$, 300 MHz) δ 1.3 (m, 14H, (CH$_2$)$_7$); 1.6 (m, 4H, (CH$_2$)$_2$); 3.2 (dd, 1H, CHHCH, ^2J = 16.8 Hz, $^3J_{\mathrm{cis}}$ = 8.1 Hz); 3.7 (dd, 1H, CHHCH, ^2J = 16.5 Hz, $^3J_{\mathrm{trans}}$ = 11.0 Hz); 3.9 (t, 2H, CH$_2$O, J = 6.6 Hz); 4.1 (t, 2H, CH$_2$O, J = 6.6 Hz); 5.6 (dd, 1H, CHHCH, $^3J_{\mathrm{trans}}$ = 10.5 Hz, $^3J_{\mathrm{cis}}$ = 8.1 Hz); 5.8 (dd, 1H, CH=CH$_2$, $^3J_{\mathrm{cis}}$ = 10.5 Hz, ^2J = 1.5 Hz); 6.1 (dd, 1H, CH=CH$_2$, $^3J_{\mathrm{trans}}$ = 17.1 Hz, $^3J_{\mathrm{cis}}$ = 10.2 Hz); 6.4 (dd, 1H, CH=CH$_2$, $^3J_{\mathrm{trans}}$ = 17.1 Hz, ^2J = 1.4 Hz); 6.9 (d, 2H, Ar, J = 9.0 Hz); 7.3 (d, 4H, Ar); 7.6 (d, 2H, Ar, J = 9.0 Hz). **^{13}C NMR** (CDCl$_3$, 50 MHz) δ 25.8; 25.9; 28.5; 29.0; 29.1; 29.3; 29.4; 29.5; 43.4; 64.6; 68.0; 81.4; 114.6; 121.4; 127.2; 128.2; 128.5; 128.8; 130.4; 133.8; 139.6; 155.6; 160.7; 166.3. **I.R.** ν_{max}/cm^{-1} 2952; 2852; 1722; 1607; 1460; 1376; 1300; 1253; 1196; 1042; 1014; 992; 907; 874; 826; 719 (nujol).

Data for **7d**. Yield 65 %. m.p. 60 ºC. **^{1}H NMR** (CDCl$_3$, 200 MHz) δ 1.3 (m, 14H, (CH$_2$)$_7$); 1,70 (m, 4H, (CH$_2$)$_2$); 2,3 (s, 3H, CH$_3$); 3.3 (dd, 1H, CHHCH, ^2J = 16.6 Hz, $^3J_{\mathrm{cis}}$ = 8.6 Hz); 3.7 (dd, 1H, CHHCH, ^2J = 16.6 Hz, $^3J_{trans}$ = 10.8 Hz); 3.9 (t, 2H, CH$_2$O, J = 6.4 Hz); 4.1 (t, 2H, CH$_2$O, J = 6.8 Hz); 5.6 (dd, 1H, CHHCH, $^3J_{\mathrm{trans}}$ = 10.6 Hz, $^3J_{\mathrm{cis}}$ = 8.8 Hz); 5.8 (dd, 1H, CH=CH$_2$, $^3J_{\mathrm{cis}}$ = 10.2 Hz, ^2J = 1.8 Hz); 6.1 (dd, 1H, CH=CH$_2$, $^3J_{\mathrm{trans}}$ = 17.4 Hz, $^3J_{\mathrm{cis}}$ = 10.2 Hz); 6.4 (dd, 1H, CH=CH$_2$, $^3J_{\mathrm{trans}}$ = 17.4 Hz, ^2J = 1.6 Hz); 6.9 (d, 2H, Ar, J = 8,8 Hz); 7.1 (d, 2H, Ar, J = 7.8 Hz); 7.2 (d, 2H, Ar, J = 8.0 Hz); 7.6 (d, 2H, Ar, J = 8.8 Hz). **^{13}C NMR** (CDCl$_3$, 50 MHz) δ 21.1; 25.8; 25.9; 28.5; 29.1; 29.2; 29.3; 29.4; 43.2; 64.6; 68.0; 82.1; 114.5; 121.7; 125.8; 128.1; 128.5; 129.2; 130.3; 137.8; 137.9; 155.6; 160.5; 166.2. **I.R.** ν_{max}/cm^{-1} 2922; 2852; 1723; 1607; 1517; 1460; 1376; 1303; 1252; 1195; 1040; 993; 894; 875; 839; 807; 719 (nujol).

Polymerization. Polymerization reactions were carried out in toluene solution at 65ºC using as initiator 2,2`-azobisisobutyronitrile AIBN (5% wt) except for the **8b$_2$** reaction, carried out with an amount of AIBN of 2% wt. The yields were 60-85 % based on total monomer added to the reaction. All reactions were refluxed for 72 hours and, after cooling, were precipitated from cold methanol. The precipitates were purified by precipitation in methanol from toluene solution and dried in vacuum. The purity of the compounds was checked by ^{1}H NMR.

Methods. IR spectra were recorded in KBr discs, nujol dispersions or film with a 3000 Galaxy Series Spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained in CDCl$_3$ with Varian-200 and 300 MHz spectrometers, using TMS as internal standard. Molecular weights reported in this contribution are relative to polystyrene standards and they have been characterized by using Waters GPC Systems (Waters 150C refractomer). The liquid crystalline properties were investigated by means of polarizing optical microscopy (POM) and differential scanning calorimetric (DSC).

The textures of the samples were observed using an Olympus BX41 polarizing microscope in conjunction with a Leitz Wetzlar 417 heating stage. Phase transitions were monitored using a Perkin Elmer DSC4. Heating and cooling rates of 10 or 20 ºC/min were used.

Conclusions

1,3-Dipolar cycloadditions of nitrile oxides were successfully used to produce isoxazolines as template for polymer liquid crystals. Homopolymers were synthesized through radical polymerization with 60-85% in yield. The liquid-crystalline behavior of the homopolymers was studied by DSC and POM and a nematic mesophase was observed in all of them. The nematic range was dependent on the spacer length as well as the terminal mesogenic unit group, being the bromine group the more efficient in stabilizing the nematic liquid crystals phase, providing a low glass transition for homopolymers based on 3,5 disubstituted isoxazolines. A small molecular weight effect in the liquid crystalline stability was also observed.

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