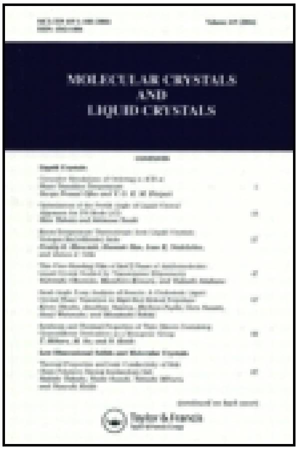

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

New Liquid Crystalline Stilbene Derivatives Containing 1,2-Dienylalkoxy Chains

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To cite this article: Giuseppe Chidichimo, Giovanni De Filpo, Giuseppe Salerno, Lucia Veltri, Bartolo Gabriele & Fiore Pasquale Nicoletta (2007): New Liquid Crystalline Stilbene Derivatives Containing 1,2-Dienylalkoxy Chains, Molecular Crystals and Liquid Crystals, 465:1, 165-174

To link to this article: http://dx.doi.org/10.1080/15421400701205784

Mol. Cryst. Liq. Cryst., Vol. 465, pp. 165–174, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701205784

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New liquid crystalline stilbene derivatives containing 1,2-dienylalkoxy chains **1** *($n = 7, 9, 11$) have been synthesized and their mesomorphic properties have been measured by polarizing optical microscopy, differential scanning calorimetry, and absorption spectroscopy. The effect of terminal alkoxy chain length and polimerisable function on the mesomorphic behaviour is discussed.*

Keywords: electro-optical devices; liquid crystals; stilbenes

INTRODUCTION

Liquid crystals represent an interesting class of materials for their applications in optics and electro-optics [1,2]. The anisotropic properties of liquid crystals allow them to be easily aligned by an electric or magnetic field, a mechanical action (e.g. shear flow), an alignment agent. The most common alignments are homeotropic and homogeneous, i.e. the liquid crystal directors form, respectively, a 0° and 90° angle with the normal to the cell substrates. Generally, a preferential direction is obtained by

MIUR, the Italian Ministry for Research and University is acknowledged for financial supports (grants PRIN 2005 and EX-60%).

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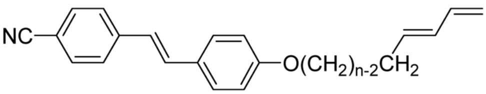
mean of an alignment agent (inorganic layers, Langmuir-Blodgett films, surface gratings, surfactants, lecithins, polyimides, which are coated onto cell substrates) and then it is changed by an electric field with a consequent change of the optical properties of the cell. Recently, it has been investigated the effect of UV or visible light on alignment layers doped with dyes [3] and on the agents bearing chemical groups, which can undergo a *trans*→*cis* isomerization [4], a photo-dimerization [4], or UV photo-polymerization [5]. The importance of such an investigation is that the illuminated regions can change their preferential alignment by a light beam and the original alignment can be gained by a subsequent illumination. This light induced alignment change has been attributed to a different dye orientation or to a change of molecular shape. More recently, a great interest has aroused on polymers bearing both liquid crystalline and photo-responsive units [6]. These molecules can be homogeneously oriented by alignment agents owing to the presence of liquid crystalline units. This preferential alignment can be changed via irradiation of photo-responsive groups with a suitable frequency light beam [7]. Such technique has allowed the development of devices with a response time of some microseconds [7]. The synthesis of such interesting polymers has been carried out starting from a polymerizable mixture, which showed mesomorphic behaviour. The mixture in its nematic state was aligned by agents coated on glass supports and then thermo-polymerized. The application of UV light allowed a phase transition for the azobenzene pendants from a homogeneous state (characteristic of *trans* isomers) to an isotropic state (or disordered state, characteristic of *cis* isomers). However, it is known that *cis* isomers of azobenzenes are unstable, so after irradiation they tend to relax to the *trans* form. Another disadvantage in the use of azobenzenes is related to their thermal and photo-chemical degradation with a consequent formation of free radicals, which can destroy the device [8]. On the contrary, it is known that stilbenes are thermally and photochemically more stable than molecules bearing azobenzene groups. In fact, their relaxation back to the original *trans* form can be achieved only by irradiating the cells with a light beam at a different frequency [9]. In the framework of our continous interest for the development of high quality liquid crystalline



1 (n = 6, 7, 9, 11)

FIGURE 1 Molecular structures of synthesized molecules.

monomers bearing photo-responsive units, we have recently reported the synthesis of new liquid crystalline monomers for cationic polymerization, consisting of stilbene derivatives containing vinyloxyalkoxy chains [10]. We now wish to report the synthesis and the study of mesomorphic properties of a novel class of liquid crystalline stilbene derivatives **1** (see Fig. 1), bearing a dienyl function suitable for radical polymerization. This kind of polymerization may result more indicated than others for the growth of aligned polymer as thin films.

EXPERIMENTAL

Methods

The transition temperatures and phase assignments were determined with a Leitz Laborlux 12 POL polarizing optical microscope in conjunction with a Linkam TH600 hot stage. The observed textures were compared with those reported in the literature [11]. The enthalpies of transitions were measured by differential scanning calorimetry using a Netzsch 2000-T4 calorimeter with a heating–cooling rate of 10°C min^{-1}.

An evaluation of the homogeneous alignment of compounds **1** and **2** (Fig. 2) was performed by filling glass cells (5 μm thick, anti-parallel polyimide coating, Linkam) with compounds **1** and **2** in their nematic state and measuring the transmittance of the polarized probing He-Ne beam as a function of the rotational angle ϕ for the cross configuration of the polarizer and analyzer (see Fig. 3).

Photo-isomerisation of compounds **1** was monitored by UV-VIS absorption spectroscopy with a Yasco 550 V spectrometer as a function of energy supplied at 340 nm and 260 nm by a 200 W high-pressure mercury lamp.

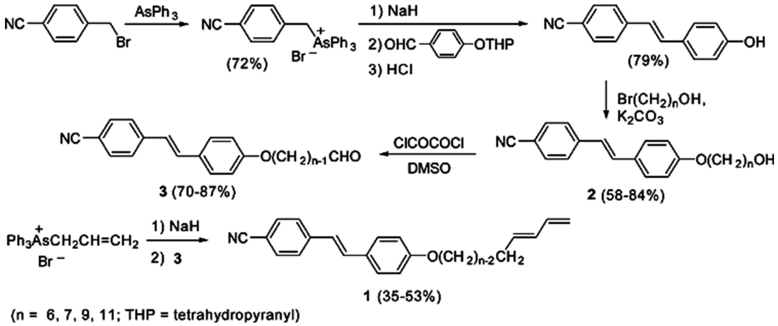


FIGURE 2 Synthesis of compounds **1**.

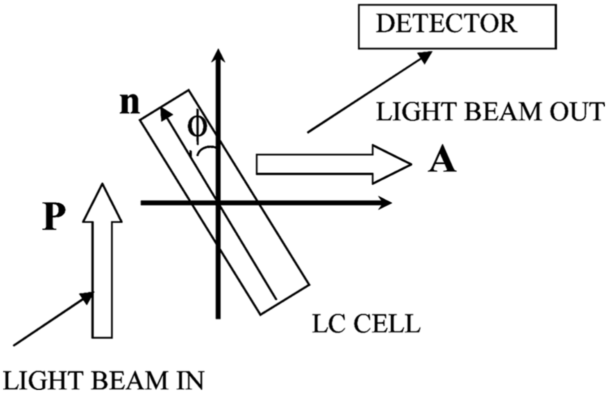


FIGURE 3 Experimental set up. **P**, polarizer; **A**, analyzer, **n**, easy axis for homogeneous alignment; ϕ, tilt angle.

Synthesis

All compounds **1** were synthesized according to the general route shown in Figure 2, involving the following steps: (a) Wittig reaction between (4-cyanobenzyl)triphenylarsonium bromide and *O*-protected 4-hydroxybenzaldehyde, followed by deprotection to give 4-[2-(4-hydroxyphenyl)-vinyl]benzonitrile; (b) Williamson reaction between the latter and the appropriate bromoalcohol to give alcohols **2;** (c) Swern oxidation [12] of **2** to aldehydes **3;** (d) Wittig reaction between the latter and allyltriphenylarsonium bromide. We have already reported the synthesis of compounds **2** with n = 7, 9, and 11, which showed liquid crystalline behaviour [10]. In the present work, we have also synthesized compound **2** with n = 6, which also shows a liquid crystalline phase.

All reactions were analyzed by TLC on silica gel 60 F_{254} or by GLC using a Shimadzu GC-14A gas chromatograph and capillary columns with polymethylsilicone + 5% phenylsilicone as the stationary phase (HP-5). Column chromatography was performed on silica gel 60 (Merck, 70–230 mesh). Starting triphenylarsine, 4-cyanobenzyl bromide, 4-hydroxybenzaldehyde, 3,4-dihydro-2*H*-pyran, hexane-1,6-diol, heptane-1,7-diol, nonane-1,9-diol, 11-bromoundecan-1-ol, oxalyl chloride, allyl bromide were commercially available and were used without further purification. 4-(Tetrahydropyran-2-yloxy)benzaldehyde [13], 6-bromohexan-1-ol [14], 7-bromoheptan-1-ol [14], 9-bromononan-1-ol [14], (4-cyanobenzyl)triphenylarsonium bromide [10], 4-[2-(4-hydroxyphenyl)vinyl]benzonitrile [10],(*E*)-4-{2-[4-(ω-hydroxyalkyloxy) phenyl]vinyl}benzonitrile derivatives **2** (n = 7, 9, 11) [10], and allyltriphenylarsonium bromide [15] were prepared according to literature procedures. (*E*)-4-{2-[4-(6-hydroxyhexyloxy)phenyl]vinyl}-benzonitrile (n = 6, 70%) was prepared according to the general procedure reported in ref. 10, and purified by column chromatography on silica gel using CH_2Cl_2 as eluent.

General Procedure for Swern Oxidation of Derivatives 2 to 4-{2-[4-(ω-Oxoalkyloxy)Phenyl]Vinyl}Benzonitrile Derivatives 3

A solution of DMSO (5.8 mL) in anhydrous CH_2Cl_2 (97 mL) was added drop wise under nitrogen to a cooled (−78°C), mechanically stirred solution of oxalyl chloride (3.5 mL) in anhydrous CH_2Cl_2 (97 mL). After a few minutes, a solution of **2** (20.5 mmol) in anhydrous CH_2Cl_2 (70 mL) was added drop wise and the mixture was allowed to stir for additional 40 min. at −78°C. After the addition of Et_3N (14.3 mL), the mixture was allowed to warm to rt, water was added and phases were separated. The aqueous layer was extracted with CH_2Cl_2, and the collected organic phases were washed several times with water and brine and eventually dried over Na_2SO_4. After elimination of the solvent by rotary evaporation, crude products were purified by column chromatography on silica gel using as eluent 9:1 $CHCl_3$/hexane (n = 6, 82%), 9:1 CH_2Cl_2/hexane (n = 7, 75%); 9:1 $CHCl_3$/hexane (n = 9, 72%); 9:1 $CHCl_3$/hexane (n = 11, 87%).

General Procedure for the Preparation of 4-{2-[4-(Dienylalkoxy)Phenyl]Vinyl}Benzonitrile Derivatives 1

The method of Tewari [16] was employed. To a stirred suspension of NaOH (32 mg, 1.3 mmol) in anhydrous THF (30 mL) was added under nitrogen allyltriphenylarsonium bromide (555 mg, 1.3 mmol). After additional stirring at rt for 0.5 h, **3** (1.3 mmol) was added and the resulting mixture was allowed to stir at rt for 48 h. After acidification with 0.1 N HCl (7 mL), $CHCl_3$ was added and phases were separated. The aqueous layer was extracted with $CHCl_3$, and the collected organic phases were dried over $CaCl_2$. After elimination of the solvent by rotary evaporation, crude products were purified by column chromatography on silica gel using as eluent 9:1 $CHCl_3$/hexane (n = 6, 35%); 8:2 $CHCl_3$/hexane (n = 7, 42%); 7:3 $CHCl_3$/hexane (n = 9, 53%); 6:4 $CHCl_3$/hexane (n = 11, 49%).

Chemical Characterization of Representative Products

All products were fully characterized by spectroscopic techniques and elemental analysis. Here we report data for compounds **1**, and **3** with n = 9.

Melting points were determined on a Reichert Thermovar melting point apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba Elemental Analyzer Mod. 1106. ^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker AC300 spectrometer and run on $CDCl_3$ solutions with Me_4Si as internal standard and recorded at 300 MHz and 75 MHz, respectively. Chemical shifts and coupling constants (J) are given in ppm (δ) and in Hz, respectively. IR spectra were taken on a Perkin-Elmer Paragon 1000 PC FT-IR spectrometer.

4-[2*E*-(Dodeca-9*E*,11-Dienyloxyphenyl)Vinyl]Benzonitrile 1 (n = 9)

Colourless solid. IR (KBr) 2925 (m), 2853 (m), 2224 (m), 1598 (s), 1513 (m), 1251 (s), 1173 (m), 833 (m), 757 (m), 556 (m) cm$^{-1;}$ ^{1}H NMR ($CDCl_3$) δ7.64–7.59 (m, 2 H aromatic), 7.57–7.52 (m, 2 H aromatic), 7.49–7.43 (m, 2 H aromatic), 7.17 (distorted d, J 16.1, 1 H, =CHAr), 6.99–6.87 (m, 3 H, aromatic + =CHAr), 6.31 (dt, J 17.1, 10.3, 1 H dienic), 6.11–5.99 (m, 1 H dienic), 5.77–5.65 (m, 1 H dienic), 5.08 (dd, J 17.1, 1.5, 1 H, =C*H*H), 4.98–4.92 (m, 1 H, =CH*H*), 3.98 (t, J 6.6, 2 H, OCH_2), 2.13–2.03 (m, 2 H, CH_2), 1.85–1.74 (m, 2 H, CH_2), 1.52–1.24 (m, 10 H, 5 CH_2); ^{13}C NMR ($CDCl_3$) δ159.7, 142.3, 137.3, 135.5, 132.5, 132.1, 130.9, 129.2, 128.9, 128.2, 126.5, 124.4, 119.1, 114.9, 114.6, 68.1, 32.5, 29.4, 29.3, 29.22, 29.16, 29.12, 26.0. Anal. Calcd for $C_{27}H_{31}NO$: C, 84.11; H, 8.10; N, 3.63. Found C, 84.02; H, 8.12; N, 3.61.

4-{2*E*-[4-(9-Oxononyloxy)Phenyl]Vinyl}Benzonitrile 3 (n = 9)

Colourless solid, mp 128–129°C. IR (KBr) 2927 (m), 2859 (m), 2225 (m), 1709 (s), 1598 (s), 1513 (s), 1467 (w), 1255 (s), 1215 (s), 1174 (s), 1023 (w), 839 (s), 555 (m) cm$^{-1;}$ ^{1}H NMR ($CDCl_3$) δ9.76 (t, J 2.0, 1 H, CHO), 7.61–7.56 (m, 2 H aromatic), 7.55–7.49 (m, 2 H aromatic), 7.48–7.41 (m, 2 H aromatic), 7.15 (distorted d, J 16.1, 1 H, =CH), 6.93–6.86 (m, 2 H aromatic), 6.92 (distorted d, J 16.1, 1 H, =CH), 3.96 (t, J 6.6, 2 H, OCH_2), 2.42 (td, J 7.3, 2.0, 2 H, CH_2CHO), 1.85–1.72 (m, 2 H, CH_2), 1.69–1.57 (m, 2 H, CH_2), 1.52–1.29 (m, 8 H, 4 CH_2); ^{13}C NMR ($CDCl_3$) δ202.8, 159.7, 142.3, 132.4, 132.0, 128.9, 128.3, 126.5, 124.4, 119.1, 114.8, 110.0, 68.0, 43.9, 29.26, 29.18, 29.14, 29.07, 26.0, 22.0. Anal. Calcd for $C_{24}H_{27}NO_2$: C, 79.74; H, 7.53; N, 3.87. Found C, 79.85; H, 7.51; N, 3.88.

RESULTS AND DISCUSSION

We have synthesized compounds **1** with n = 6, 7, 9, 11. The transition temperatures and enthalpy changes of compounds **1** are reported in

TABLE 1 Transition Temperatures/°C and Enthalpy Changes ()/Jg^{-1} for Compounds **1** with different Alkoxy chain length, n. Cr, Crystal; Sm A, Smectic A phase; N, nematic phase; I, isotropic phase

6	Cr 107.2 (100.6) I
7	Cr 47.7 (17.9) N 50.9 (14.6) I
9	Cr 48.8 (24.2) N 74.8 (10.1) I
11	Cr 81.0 (15.8) SmA 127.8 (42.5) N 134.7 (21.1) I

Table 1. All compounds **1** with an alkoxy chain length larger than 6 exhibit a nematic phase. The absence of mesomorphism for $n = 6$ can be attributed to the fact that a short chain length does not give enough lateral cohesion. Compounds with a long alkoxy chain length ($n = 9$, $n = 11$) show a large mesomorphic range. This is because the lateral intermolecular cohesions increase with increasing alkoxy chain lengths stabilising in such a way the mesophases. A long chain length ($n = 11$) stabilizes a smectic A phase, too. It is important to note that even precursors **2** show liquid crystalline behaviour. The transition temperatures and enthalpy changes of compounds **2** with $n = 5$, 7, 9, and 11 have already been reported [10]. The transition temperatures and enthalpy changes of compounds **2** with $n = 2$, 3 and 6 are shown in Table 2 (results for $n = 5$, 7, 9, and 11 are included for completeness). All compounds **2** show a nematic phase. Compound **2** with $n = 5$ also shows a smectic A phase.

The evaluation of the homogeneous alignment of **1** gave a repeated pattern of valleys and peaks with a typical separation of 90° (see Fig. 4). This confirms that cells are well homogeneously aligned. It is known that stilbenes show appreciable absorption in the solar spectral region. UV spectra and changes induced by the indicated periods of irradiation at 340 nm are shown in Figure 5 for $n = 11$ (0.1 M in $CHCl_3$ at 25°C, quantum yield 0.21).

Before illumination all samples consisted of only the *trans* form of the stilbene derivative, because this isomer is thermodynamically

TABLE 2 Transition Temperatures/°C and Enthalpy Changes ()/Jg^{-1} for compounds **2** with different Alkoxy Chain Length, n. Cr, crystal; Sm A, smectic A phase; N, nematic phase; I, isotropic phase

2	Cr 166.1 (68.7) N 170.5 (50.1) I
3	Cr 86.9 (49.6) N 100.3 (17.3) I
5	Cr 88.8 (40.4) SmA 94.9 (53) N 104.8 (17.7) I
6	Cr 127.9 (20.0) N 131.0 (84.7) I
7	Cr 83.4 (46.4) N 91.3 (28.7) I
9	Cr 91.0 (79.2) N 98.4 (33.0) I
11	Cr 98.2 (36.3) N 101.2 (67.5) I

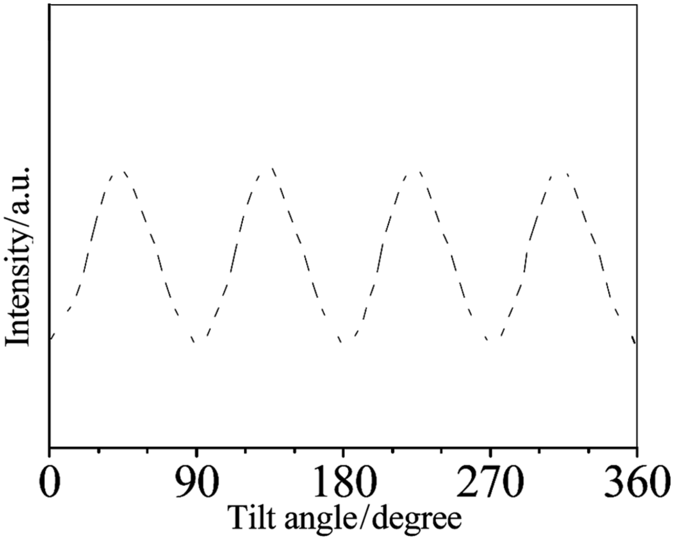


FIGURE 4 Repeated pattern of valleys and peaks in homogeneously aligned compound **1** (n = 11).

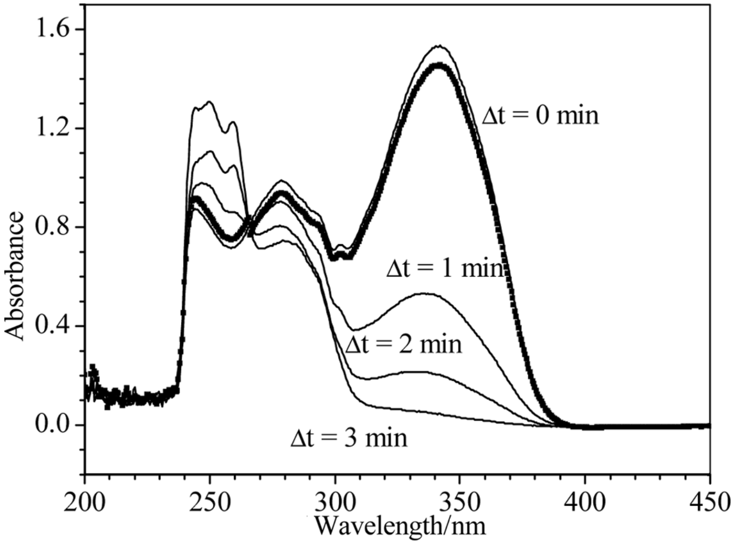


FIGURE 5 Changes in the UV spectra for compound **1** (n = 11) induced by irradiation at 340 nm for different time intervals. Dotted line represents the UV spectra of compound after 5 minutes of irradiation at 260 nm.

more stable than its *cis* form. Upon illumination with UV light (340 nm), all compounds **1** clearly undergo a photo-transformation to the *cis* isomer in an almost complete manner. No by-products were formed in this process, as confirmed by TLC and NMR ($CDCl_3$) analysis. The photo-transformation is manifest by the decreasing intensities of $\pi \rightarrow \pi^*$ absorptions at 340 nm. No thermal back reaction to *trans* isomers was found in agreement with literature [14]. Upon irradiation with UV light at 260 nm for 5 minutes, we observed the relaxation back to the initial state as shown by the dotted curve in Figure 5.

The photo-isomerization was also confirmed by photo-irradiation of aligned thin cells. In fact, if a UV beam (340 nm) impinged on a homogeneously aligned sample in its nematic phase we observed, by using the experimental set up described in Figure 3, a phase transition to the isotropic state, due to the fact that the *cis* isomers are no longer liquid crystalline. As shown in Figure 6, the depolarized light intensity decreases a lot as a function of irradiation time. If such a cell is afterwards irradiated with a 260 nm light beam, one can induce a relaxation back to the *trans* form with a consequent increase of scattered light.

These experiments confirm the potential use of stilbene molecules as information processing and data storage materials.

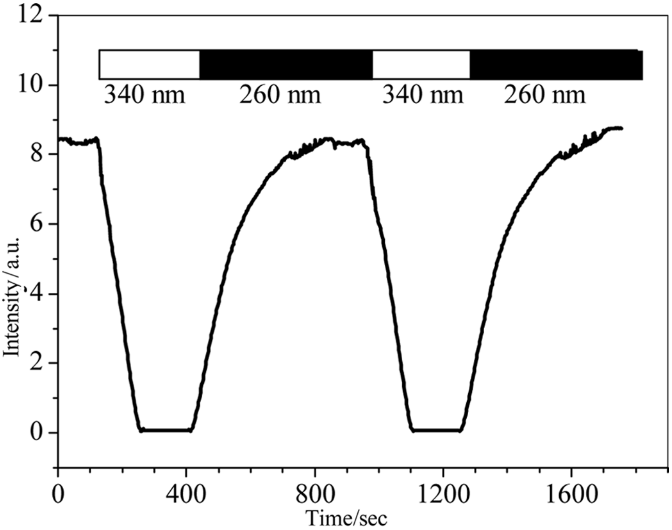


FIGURE 6 Depolarized light scattering behaviour for compound **1** (n = 11) as a function of UV irradiation at 340 nm and 260 nm.

CONCLUSIONS

We have successfully synthesised a novel type of liquid crystalline stilbene molecules having a dienyl function suitable for radical polymerization. All compounds with a rather long alkoxy chain (n > 6) show a nematic phase. The temperature range of mesomorphism is rather large for long alkoxy chain lengths. Further investigation is now in progress to polymerize the obtained homogeneously aligned films and to study their optical response to a light beam.

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