

Photo-induced anisotropic films based on liquid crystalline copolymers containing stilbene units

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Abstract

New poly(methacrylate) copolymers containing 90 mol% of a promesogenic unit based on the 4-butoxybenzamide, 4-cyanobiphenyl or 4-cyanoterphenyl cores and 10 mol% of a photosensitive push–pull substituted 4-(*N*-methylamino)-4'-nitrostilbene group have been prepared. All polymers are liquid crystalline and thermally stable with decomposition temperatures above 320 °C. The irradiation with linearly polarised light (either 325, 365 or 488 nm) results in the induction of a small optical anisotropy in the films due to an angular-selective photoreaction, whereas the absorbance perpendicular to the electric field vector of the incident light becomes larger compared to the absorbance parallel to it. In films of the copolymer containing 4-cyanobiphenyl and 4-(*N*-methylamino)-4'-nitrostilbene units, the anisotropy was significantly enhanced by annealing above T_g up to a dichroism $D = 0.5$. A thin film aligned by this procedure shows an anisotropic red emission with a ratio of 2.8 between emission intensities in the parallel and perpendicular directions due to the presence of oriented fluorescent stilbene units.

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1. Introduction

Polymer films with anisotropic properties are of great interest for different applications such as optical data storage, photoalignment of liquid crystals (LC) or the fabrication of optical components. One way to create such films is based on the interaction of photosensitive polymers with linearly polarised (LP) light. The anisotropy can be caused by an angular-selective bleaching of chromophores or the angular-selective formation of photoproducts (both one-step photoselection processes), or by the photoorientation process in the steady state of a reversible photoreaction via repeated photoselection steps [1–4]. The

photoinduction of anisotropy carries some advantages compared to other orientation techniques such as the opportunity of a pixelwise orientation or the defined control of the orientational direction via a non-contact method at room temperature. The strongest anisotropy has been generated in LC side chain polymers, because in this case the photo-induced order can be significantly amplified by thermotropic self-organisation due to a thermal treatment [5–11]. Widely studied photosensitive systems are azobenzene-containing polymers. In particular, it has been shown that both ordering principles, the light-induced orientation and the self-organisation process, work co-operatively in azobenzene LC side chain and main chain polymers [12–17]. The photoorientation process resulting from a number of angular-selective *E/Z* photoisomerisation cycles and rotational diffusion in the steady state is well known [2,4,18–20] and the existence of the co-operative effect has been proved

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in a number of LC polymers [8–10,15,21,22]. This technique can be used to obtain films with anisotropic properties such as dichroism or birefringence; however, azobenzene polymers have some disadvantages such as absorption in the visible range and fluorescence quenching of added fluorophores [17,23].

The aim of the present work is to develop new side chain LC polymers with a photosensitive group different from azobenzene that might give an angular-selective photoreaction allowing the subsequent alignment of the LC polymer in order to obtain films with anisotropic emission. We have chosen the 4-(*N*-methylamino)-4'-nitrostilbene unit, a push–pull disubstituted stilbene, for different reasons. Stilbenes are highly photosensitive species, which undergo several photoreactions under light exposure; namely, *E/Z* isomerisation, [2 + 2] photocycloaddition and unimolecular ring-closing photoreaction of the *Z* isomer forming dihydrophenanthrene. In the presence of oxygen, the dihydrophenanthrene is irreversibly converted to phenanthrene. However, for donor–acceptor disubstituted stilbenes, this last photoreaction is less efficient compared to the non-substituted or the donor–donor disubstituted derivatives [24,25]. With respect to the required free volume, the *E/Z* photoisomerisation of stilbenes is more restricted in polymeric films as that of azobenzene derivatives; moreover, the *Z* isomer of stilbenes is more stable as that of azobenzenes excluding the thermal back reaction to the *E* isomer [26,27]. In spite of that, induction of anisotropy in stilbene-containing oligomers has been reported [24]. Photocycloaddition has also been reported to occur in photoresponsive LC polymers containing stilbene units in the backbone and substituted azobenzenes in the side chain. In this case, the photo-crosslinking effect of the stilbene and the reversible photoisomerisation process of azobenzene groups take place simultaneously [28]. Finally, substituted stilbenes are luminescent, therefore, both properties, photosensitivity and luminescence are combined in the same functional unit [29].

By this reason, we prepared three polymethacrylates (Fig. 1), which contain the cited stilbene unit (**Stl**), and alternatively a promesogenic unit of 4-butoxybenzylidene (**Am**), 4-cyanobiphenyl (**CNB**) or 4-cyanoterphenyl (**CNT**) type. The major component in the three copolymers is the promesogenic unit up to 90 mol%, which acts as LC matrix. The stilbene monomer, which accounts for the photo-response and luminescence properties of the polymer, has been incorporated in a 10 mol% [12,15]. With these copolymers, we report here the induction of anisotropy in films and the appearance of a polarised luminescence as a consequence of angular-selective photoreactions and subsequent bulk-alignment of polymer films.

2. Experimental

2.1. Synthesis of the monomers

All monomers contain a methacrylate-end as the reactive group. The stilbene monomer (**Stl**) was synthesised according to the method described by Robello [30]. The promesogenic monomers **CNB** and **CNT** were prepared by procedures

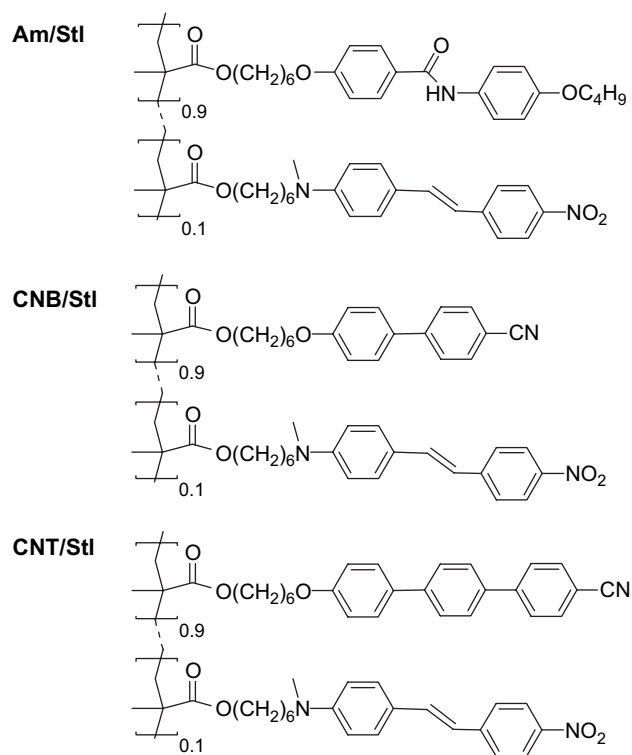


Fig. 1. Structures of the synthesised copolymers.

described in the literature [31,32]. The monomer **Am** was obtained by condensing 4-butoxyaniline with 6-[4'-chloro-carbonylphenoxy]hexyl methacrylate by adapting a method previously reported by Ruhmann [33]. The structures of the monomers were confirmed by ^1H and ^{13}C NMR, FTIR and elemental analysis.

2.2. Synthesis of the polymers

All polymers were synthesised by thermal radical polymerisation in solution, from a mixture of the corresponding monomers in the required proportion (90 mol% of the promesogenic unit and 10 mol% of the **Stl** monomer), using AIBN as thermal initiator (1–2 wt%) in freshly distilled DMF (ca. concentration 10% w/v). After degassing, the solution was heated up to 70 °C under Ar atmosphere and stirred for at least 2 days, monitoring the consumption of the monomers by TLC. After cooling to room temperature, the polymer was precipitated by pouring the reaction mixture into cold ethanol and the solid isolated by filtration, except for the polymer **CNT/Stl** which precipitated in the reaction media and was directly filtered.

Purification of the **Am/Stl** copolymer was carried out by dissolving the polymer in dichloromethane and by precipitation in ethanol. Copolymers **CNB/Stl** and **CNT/Stl** were purified by solid–liquid extraction with ethanol in a Soxhlet apparatus. In all cases, the final product was dried in vacuo at 40 °C for 24 h.

Copolymer Am/Stl: Red solid. 45% yield. ^1H NMR (300 MHz, chloroform- d_3) δ in ppm: 8.20–8.00, 7.86–7.61, 7.59–7.40, 7.01–6.50, 4.23–3.60, 3.44–3.10, 3.00–2.70, 2.10–1.15. IR (KBr pellet) ν in cm^{-1} : 3315 (NH), 1726

(C=O), 1646 (C=O amide, C=C), 1606, 1579, 1511 (aromatic C–C), 1246 (C–O). Anal. found (calcd): %C: 71.16 (71.50), %H: 7.74 (7.66), %N: 3.62 (3.42). GPC (THF) M_w , 10,295; M_n , 6350; M_w/M_n : 1.6.

Copolymer CNB/StI: Red solid. 45% yield. ^1H NMR (300 MHz, chloroform- d_3) δ in ppm: 8.10–7.98, 7.70–7.30, 6.98–6.72, 6.65–6.50, 4.10–3.72, 3.28–3.15, 2.95–2.80, 2.10–1.18, 1.16–0.75. IR (KBr pellet) ν in cm^{-1} : 2221 (C \equiv N, st), 1721 (C=O), 1600, 1575, 1517, 1490 (aromatic C–C), 1245 (C–O). Anal. found (calcd): %C: 74.92 (75.53), %H: 7.24 (6.86), %N: 4.12 (4.17). M_w , 30,045; M_n , 19,000; M_w/M_n : 1.6.

Copolymer CNT/StI: Red solid. 77% yield. IR (KBr pellet) ν in cm^{-1} : 2224 (C \equiv N), 1725 (C=O), 1643 (C=C), 1601, 1577, 1522, 1509, 1488 (aromatic C–C), 1249 (C–O). Anal. found (calcd): %C: 78.21 (78.50), %H: 6.22 (6.62), %N: 3.56 (3.20).

2.3. Characterisation techniques

Elemental analysis was performed with a Perkin–Elmer 240C microanalyser. FTIR spectra were measured on an ATI–Matsson Genesis Series FTIR from KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Unity or a Bruker ARX spectrometers operating at 300 MHz. Gel permeation chromatography (GPC) was carried out on a Waters liquid chromatography system equipped with a 600E multisolvent delivery system and a 996 photodiode array detector, using a combination of two Ultrastaygel[®] columns with pore sizes ranging from 500 to 10^4 Å, THF as the mobile phase at 0.8 mL/min flow rate and calibration using polystyrene standards.

Mesogenic behaviour and transition temperatures were determined using an Olympus BH-2 polarising microscope equipped with a Linkam THMS hot-stage central processor and a CS196 cooling system. Differential scanning calorimetry (DSC) was performed using a DSC 2910 from TA Instruments with samples sealed in aluminium pans and a scanning rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Transition temperatures were read at the maximum of the peaks. Glass transition temperatures were determined at the midpoint of the heat capacity increase. Thermogravimetric analysis (TGA) was performed using a TA Instruments STD 2960 simultaneous TGA–DTA at a rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. TGA data are given as the onset of the decomposition curve. In addition, the first derivative of the decomposition curve (DTGA) was read. X-ray diffraction experiments were carried out in a Pinhole camera (Anton–Paar) placing the sample into a quartz Lindemann capillary (1 mm diameter) and using an irradiation wavelength of 1.54 Å.

Optical absorption spectra in THF solution were recorded with a UV–vis spectrometer UV4-200 from ATI–Unicam. Luminescence measurements in THF solution were performed using a Perkin–Elmer LS50B spectrofluorimeter.

2.4. Preparation and irradiation of the films

Thin films of the polymers were prepared by spin-coating using a Karl Süss CT60 spin-coater (2000 rpm and an

acceleration of 700 rpm for 30 s) from 0.15 M solutions of the polymers in THF or CHCl_3 onto quartz substrates. The films were stored at room temperature for 24 h before starting the irradiation experiments.

The irradiation processes were performed either with 325, 365 or 488 nm linearly polarised (LP) light. The irradiation with 325 nm LP light was carried out using an He/Cd laser with a power density of $18\text{--}24\text{ mW cm}^{-2}$. The light from a 100 W Hg-lamp passing through a Glan–Thompson polarising prism (B. Halle) and an interference filter was used for the irradiation of the films at 365 nm providing a power density of $30\text{--}34\text{ mW cm}^{-2}$. A quartz glass vessel with water was placed between the light source and the other components in order to absorb the IR radiation emitted by the lamp. For the irradiation with LP visible light, the green line at 488 nm of an Ar^+ laser (Innova 4 Coherent) with a power density of 100 mW cm^{-2} was employed.

After the irradiation procedure, the films were annealed in the liquid crystalline state for 15 h up to 3 days. The absorbance before and after irradiation was controlled by UV–vis measurements with non-polarised light using a Lambda 2 spectrometer (Perkin–Elmer). The decrease of the absorbance due to the light exposure was used for calculating the degree of photodegradation. The absorption anisotropy was characterised by angular-dependent UV–vis spectroscopy. The measurements were carried out using a diode array spectrometer Polytec X-dap-04 V2.3 or, alternatively, a Perkin–Elmer Lambda 19 in combination with a Glan–Thomson prism. The absorption dichroism of the films, D , was calculated from the measured absorbance perpendicular (A_{\perp}) and parallel (A_{\parallel}) to the electric field vector of the incident light (Eq. (1)).

$$D = \frac{A_{\perp} - A_{\parallel}}{A_{\perp} + A_{\parallel}} \quad (1)$$

Polarised emission of the polymeric films was measured using a set-up with a linear arrangement consisting of a 100 W XBO lamp, a monochromator, a Glan–Thomson prism, a cut-off filter and a diode fluorimeter Tidas (J&M). The excitation was carried out at 450 nm, corresponding to the absorption band of the stilbene unit, at angles of 0° and 90° to the electric field vector of the actinic light. The emission anisotropy of the oriented films, R_{em} , was calculated dividing the maximum emission intensity (Em_{max}) by the minimum emission intensity (Em_{min}) of the angular-dependent value of the emission.

3. Results and discussion

3.1. Synthesis and characterisation of the polymers

All the polymers were synthesised by free-radical polymerisation, in solution, of the methacrylate monomers at 70°C using DMF as the solvent and AIBN as the initiator [23]. Copolymers **Am/StI** and **CNB/StI** were soluble in the reaction media and they were isolated as red powders by precipitation in ethanol. Their physical characterisation was undertaken by IR, ^1H NMR, UV–vis spectroscopy and GPC, and the data

were consistent with the expected structures. Copolymer **CNT/Stl** precipitated from the reaction media during the course of the polymerisation, after 30 min. The limited solubility of this polymer in the reaction media (DMF) is associated to the poor solubility of the promesogenic unit that contains three aromatic rings. Accordingly, a complete physical characterisation of **CNT/Stl** was restricted by the lack of solubility in common organic solvents.

The composition of the polymers **Am/Stl** and **CNB/Stl** was determined both by integration of the signals in the ^1H NMR spectra and UV–vis spectroscopy. The results are shown in Table 1, together with the spectroscopic data and molecular weight. The calculated composition of the polymers was in good agreement with the monomeric feed ratio.

UV–vis spectra in solution of **Am/Stl** and **CNB/Stl** show two main absorption bands, which are related to the absorption of the two monomers in an additive way. The lowest energy band, at 440 nm, corresponds to the absorption of the 4-(*N*-methylamino)-4'-nitrostilbene chromophore. The highest energy band is mainly associated to the absorption of the LC unit, at 280 nm for **Am** or 296 nm for **CNB**, that overlaps to a weak absorption band of the stilbene unit at 300 nm. In relation to the emission properties in solution, a red emission with the maximum at 601 nm was observed in the spectra of **Am/Stl** and **CNB/Stl** when exciting at 440 nm due to the presence of the stilbene unit.

In some attempts of characterising the optical properties of **CNT/Stl** and preparing films, we tried to dissolve this polymer in harsher conditions by heating in a high boiling point solvent such as tetrachloroethane, finding that the initial red suspension became a colourless solution. In the UV–vis spectrum, the absorption band at 440 nm completely disappeared, therefore a loss of conjugation occurs due to decomposition of the **Stl** chromophore. We believe that it could be related to the nature of the solvent as we have also observed this behaviour with other chlorinated solvents such as hot chloroform or hot dichloromethane. Acidic solvents may decompose the stilbene unit by addition of acid to the double bond; however, we were not able to confirm this hypothesis, as a study by ^1H NMR was not conclusive due to the low concentration of the stilbene monomer in the polymer and the overlapping of signals.

The mesomorphic properties of the polymers were studied by polarising optical microscopy (POM), differential scanning

microscopy (DSC) and X-ray diffraction experiments. The thermal stability was determined by thermogravimetric analysis (TGA). Data are shown in Table 2.

All polymers exhibit a good thermal stability and the thermal decomposition detected by TGA starts at temperatures above 320 °C. There are no significant differences in stability depending on the constitutive units of the polymer.

Copolymer **Am/Stl** is a semi-crystalline solid with T_g , T_m and T_i values of 57, 114 and 132 °C, respectively as determined by DSC. A very viscous fluid phase was observed by POM that did not develop a typical texture which could be associated to a specific mesophase. For this reason, powder X-ray diffraction studies were carried out. The diffraction diagram of the as-obtained solid consists of some well-defined rings, which indicates some crystalline character. After heating the sample above T_i and fast cooling to room temperature, diagrams were registered at room temperature (Fig. 2a), 100 and 115 °C. In all cases, the X-ray diagrams display similar features. An intense ring is observed at small angles and two rings with lower intensity at medium angles, with diameters twice and thrice the diameter of the small angle ring. These are associated to the first, second and third order reflections of a lamellar mesophase, compatible with an SmA or SmC. The distance between layers, calculated from the diameter of the small ring by applying the Bragg's law, is 28 Å. The length of the benzanilide unit, in a totally extended conformation calculated with Dreiding models, is 32 Å. The similarity between both values indicates that the mesophase is of the SmA type. Moreover, a weak halo in the large angle region corresponds to the average distance between the terminal aliphatic chains of the molecules in the molten LC phase, corresponding to a distance of 4.7 Å.

For **CNB/Stl** polymer, transition temperatures are lower than those observed for **Am/Stl**. This could be associated to the existence of intermolecular H-bonding interactions due to the amide groups of the benzanilide unit in the **Am/Stl** copolymer. On the DSC heating scan, the T_g of the **CNB/Stl** polymer was measured at 57 °C. In addition, two overlapped peaks with maxima at 106 and 109 °C were detected (also during the cooling scan). When **CNB/Stl** was studied by POM, cooling from the isotropic liquid led to a highly viscous mesophase that remained fluid until 90 °C. The texture resembles the Schlieren texture of a nematic mesophase. In order to confirm the mesophase, X-ray diffraction experiments under different conditions

Table 1
Composition, spectroscopic data and molecular weight for the synthesised copolymers^a

Polymer	Stl unit content (%)		λ_{abs}	λ_{em}	M_w	M_w/M_n
	^1H NMR	UV–vis				
Am/Stl	13	15	280, 440	601	10,295	1.6
CNB/Stl	8	12	296, 444	601	30,045	1.6
CNT/Stl	—	—	(312) ^b	—	—	—

^a Absorption spectra were recorded in 10^{-4} M THF solutions for **Am/Stl** and **CNB/Stl** and 1,1,2,2-tetrachloroethane solution for **CNT/Stl**. Emission spectra were recorded in 10^{-7} M THF solutions.

^b The solution becomes colourless after heating in 1,1,2,2-tetrachloroethane, the band at ca. 440 nm corresponding to the **Stl** unit is not observed.

Table 2
Thermal and mesomorphic properties of the polymers^a

Polymer	TGA	DTGA	T_g	T_m (ΔH) ^b	T_i (ΔH) ^b	Mesophase
Am/Stl	353	397	57	114 (—)	132 (—)	SmA
CNB/Stl	324	350, 397	57	—	109	N
CNT/Stl	349	368, 400	—	181 (5.1)	298 (1.9)	SmA

^a Temperatures are given in °C. TGA: onset of the weight loss curve; DTGA: first derivative of the weight loss curve; T_g : glass transition temperature; T_m : melting temperature; T_i : clearing temperature. Transition temperatures and associated enthalpies were determined by DSC during the second heating scan except for **CNT/Stl** due to thermal degradation.

^b Enthalpy values are given in kJ per mol of repeating unit using the theoretical values calculated from the feed composition.

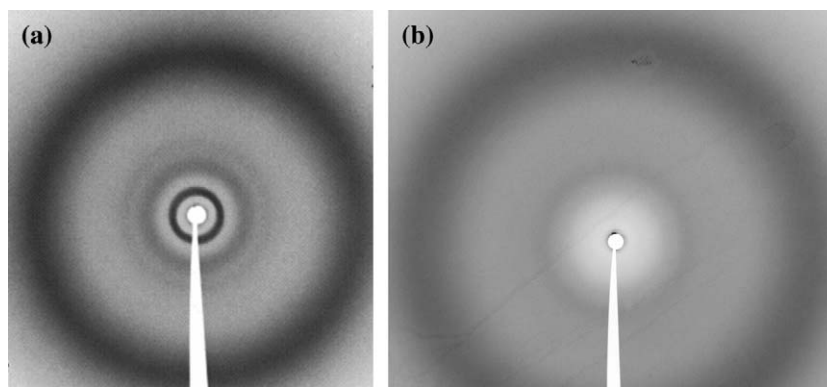


Fig. 2. X-ray diffraction pattern at room temperature for (a) polymer **Am/Stl** (b) polymer **CNB/Stl**.

were performed. The diagram corresponding to the as-obtained polymer indicates a high degree of disorder, since two diffuse halos are observed at medium and large angles. Diagrams were also registered at room temperature (Fig. 2b), 104 and 106 °C after heating up the sample to the isotropic liquid and cooling down to room temperature. In all cases, the X-ray patterns are similar to that observed for the as-obtained powdery polymer. From the observations, we might conclude that the polymer develops a nematic mesophase that vitrifies on cooling, since no typical reflexions corresponding to a more ordered mesophase or a crystalline phase are observed.

The copolymer **CNT/Stl** displays higher transition temperatures and crystalline character than **CNB/Stl**. In the first heating curve of **CNT/Stl** in the DSC, the melting peak is observed at 181 °C as well as a transition to isotropic liquid at 298 °C. Nevertheless, some degradation is probably taking place since these transitions were not observed in subsequent scans. From the POM observations, the nature of the mesophase is SmA according to the fan-shaped texture that becomes homeotropic after mechanical stress.

3.2. Photoinduction of anisotropy

The induction of orientational order by exposure to LP light was investigated for copolymers **Am/Stl** and **CNB/Stl**. The study of **CNT/Stl** was discarded due to its highly crystalline character and the resulting low solubility, preventing the preparation of spin-coated films.

The irradiation of the copolymer films of **Am/Stl** or **CNB/Stl** with LP light at different wavelengths (325, 365 or 488 nm) caused two effects. Firstly, the absorbance of the stilbene group corresponding to the maximum at 460 and 300 nm decreased (Fig. 3). Secondly, a small dichroism D of about 0.03–0.09 for different irradiation conditions was induced in the films of **Am/Stl** and **CNT/Stl** (Table 3). These values are significantly small compared to polymers with azobenzene moieties, but they correspond to values that can be induced in cinnamate-containing polymers [25]. These small photo-induced anisotropies at room temperature were amplified by annealing above T_g , in particular at 93 °C, in the mesophase range of the polymers.

LP irradiation at 325 nm of **Am/Stl** films induced a very small anisotropy with a dichroism D of about 0.01 at 460 nm

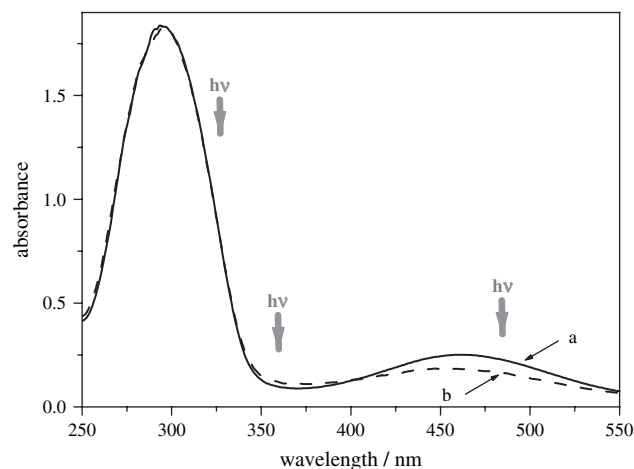


Fig. 3. UV-vis spectra of a **CNB/Stl** film (a) before and (b) after irradiation (LP 325 nm, 25 mW cm⁻², 135 s and a photoconversion of about 27%). The arrows show the excitation at 325, 365 and 488 nm.

that increased to $D = 0.13$, still a quite low value, after annealing at 93 °C. Annealing at higher temperatures up to 118 °C did not improve the anisotropy. The order after the two-step process – irradiation and annealing – was not significantly enhanced either by changing the irradiation doses or by changing the irradiation wavelength and the dichroism achieved remained always below $D = 0.15$.

In all cases, the direction of maximum absorbance was perpendicular to the electric field vector of the incident light. This

Table 3

Light-induced dichroism (D_{ind}) and thermal amplified anisotropy (D_{ann}), measured at 460 nm for films of **CNB/Stl** under different irradiation conditions

325 nm ^a			365 nm ^a			488 nm ^a		
PR ^b	D_{ind}	D_{ann}	PR ^b	D_{ind}	D_{ann}	PR ^b	D_{ind}	D_{ann}
1.7	0	0.06	11.16	0.02	0.22	15.2	0.02	0.18
6.3	0	0.09	12.2	0.03	0.34	17.7	0.02	0.20
16.3	0.02	0.42	21.5	0.02	0.43	57.3	0.06	0.21
20.5	0.03	0.44				73.5	0.09	0.20
26.8	0.02	0.48						
39.3	0.03	0.40						

^a Irradiation wavelength.

^b PR: degree of photoreaction (%) determined from the decrease of the absorbance before and after irradiation, measured at 460 nm.

rules out that the alignment is caused by any photoproduct formed preferentially and angular-selectively parallel to the electric field vector. For this reason, the alignment by photocycloaddition products can be excluded. As reported for cinnamate-containing polymers, a [2 + 2] cycloaddition should produce photodimers oriented parallel to the electric field vector of the incident light, inducing an alignment of the mesogenic units also parallel to it [34]. *A priori*, the orientation perpendicular to the polarisation plane can be a consequence of two possible angular-selective processes. Firstly, any photodecomposition of the rod-like *E*-stilbene forming more globular groups. This could be the photocycloaddition, the formation of phenanthrene or the *E*-to-*Z*-photoisomerisation. Secondly, the observed anisotropy – perpendicular to the electric field vector – could be explained by the photoorientation in the steady state of the *E*-to-*Z*-photoisomerisation as for comparable azobenzene-containing copolymers. However, as we have mentioned before, the push–pull substituted stilbene units seem to be photooriented less

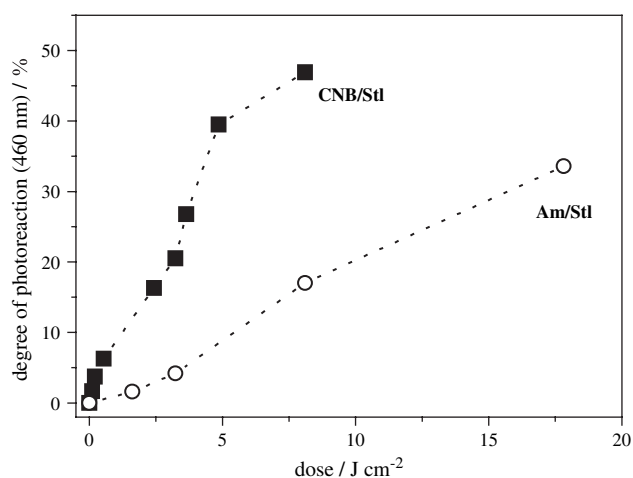


Fig. 4. Degree of photoreaction in films of **Am/Stl** and **CNB/Stl** at different irradiation doses of LP light at 325 nm.

efficiently than azobenzene groups. Therefore, an additional possibility to explain the result could be a one-step angular-selective photoreaction of the stilbene units parallel to the electric field vector, whereas the alignment is caused by the remaining *E*-stilbene units existing perpendicular to it.

To account for the low anisotropy values obtained for **Am/Stl**, we could argue that the formation of hydrogen bonds between the mesogenic benzanilide units might stabilise the polymer matrix by restricting the photoisomerisation process. However, studies on azobenzene-containing polymers with benzanilide side groups have shown that high values of anisotropy can be reached by irradiation and subsequent annealing at LC phase temperatures [15,22]. Therefore, the observed behaviour in **Am/Stl** should be caused by the larger required free volume for the stilbene photoisomerisation compared to azobenzene units. Results reported in the literature on the photoisomerisation kinetics of 4-methoxystilbene (4-MeOStl) into a PMMA matrix [35] induced by irradiation with linearly polarised light in the glassy state indicate that the photoisomerisation of 4-MeOStl requires a certain critical free volume (V_f^*) for the internal rotations of the molecule around the C=C double bond. For the 4-MeOStl molecules located in the environments with the $V_f \approx V_f^*$, it was found that the reaction proceeds slowly, whereas the photoisomerisation takes place much faster in the regions satisfying $V_f \gg V_f^*$.

The irradiation of **CNB/Stl** with LP light at 325 nm, using the same energy dose as for **Am/Stl** generated a faster decrease of absorbance and a slightly larger anisotropy (Fig. 4). Indeed, the study has revealed that the generated dichroism after irradiation and annealing of the **CNB/Stl** films is higher than for the **Am/Stl** ones. In particular, a dichroism of $D = 0.03$ at 460 nm, corresponding to the stilbene group, was reached after irradiating for 135 s with LP light of 325 nm. Annealing in the mesophase, at 92 °C, gives rise to an amplification of the photo-generated order in the same direction up to a value of $D = 0.47$ at 460 nm and $D = 0.51$ at 293 nm (Fig. 5).

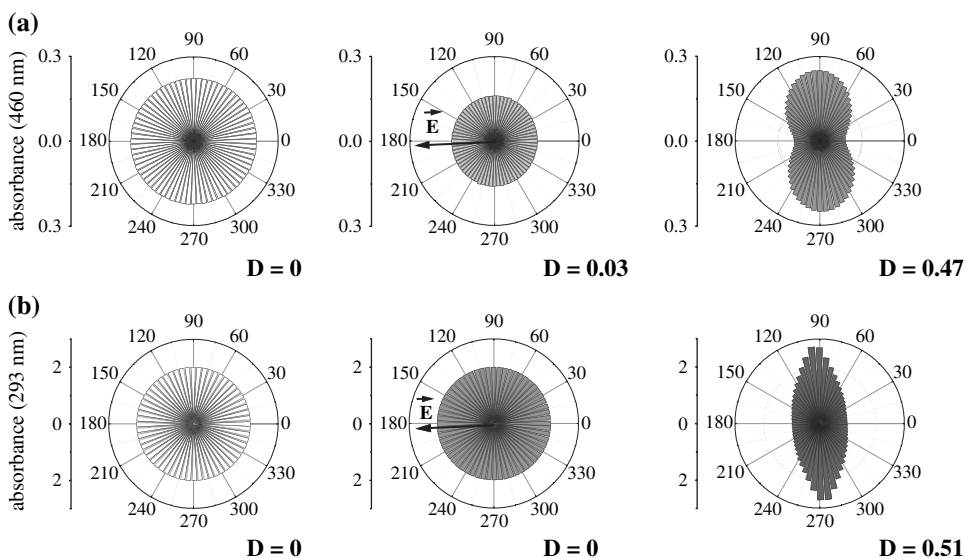


Fig. 5. Angular-dependent absorbance of a film of **CNB/Stl** (a) at 460 nm (stilbene group) and (b) at 293 nm (cyanobiphenyl group). From left to right: initial film after 215 s irradiating with LP light of 325 nm and after annealing at 92 °C.

Irradiation of **CNB/StI** using LP light of 365 nm caused dichroism values up to $D = 0.03$. However, a dichroism up to $D = 0.1$ was generated upon irradiation at 488 nm. Subsequent annealing of the irradiated films resulted in an amplification of the light-induced order perpendicular to the electric field vector up to a value of $D = 0.43$ for UV-irradiated films and only up to 0.20 for vis-irradiated films. It is remarkable that the annealed UV-irradiated films (325 and 365 nm) possess a significantly higher order compared to annealed vis-irradiated films (488 nm), whereas the photo-induced anisotropy is larger in the latter case. Fig. 6 represents the wavelength dependence of the amplified order against the degree of photoconversion. The evolution of the amplified order could be related to the wavelength dependence of the photoreactions, two or more, contributing to the induction of anisotropy. In the case of the photoorientation mechanism, it can be explained by different steady states with respect to different absorbance of *E* and *Z* isomers. UV light (325 or 365 nm) exciting both *E* and *Z* isomers causes *E*-to-*Z* isomerisation and subsequent photocyclisation, whereas at 488 nm the *E* isomer is exclusively transferred to the *Z* isomer, which cannot be excited with this wavelength, therefore only a one-step angular photoselection process takes place.

As it was mentioned, the stilbene moiety does not only undergo photoreactions upon exposure, the push–pull substituted *E* isomer shows a red fluorescence as well. In order to check the existence of an anisotropic emission, a thinner film of **CNB/StI** polymer, prepared from a 0.05 M CHCl_3 solution, was irradiated for 70 s with LP light of 325 nm decreasing the absorbance of 22% at the π – π^* transition of the stilbene (see Fig. 3). Further annealing resulted in a dichroism of $D = 0.3$, which is slightly smaller compared to the dichroism obtained for thicker films. Fig. 7 shows the fluorescence of this film excited at the maximum absorbance of the stilbene group, 460 nm, perpendicular and parallel to the electric field vector of the incident light. An emission anisotropy of $R_{\text{em}} = 2.83$ with a maximum of emission perpendicular to the electric field vector is obtained as a consequence of the existence of some orientation of the *E*-stilbene moieties and demonstrating that

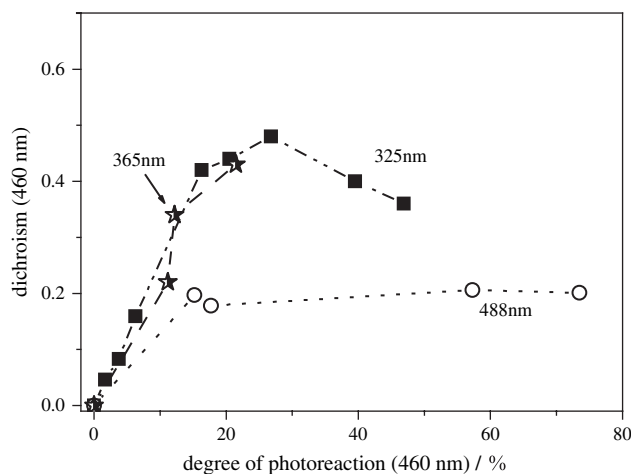


Fig. 6. Dichroism of **CNB/StI** films after irradiation and subsequent annealing using different wavelengths.

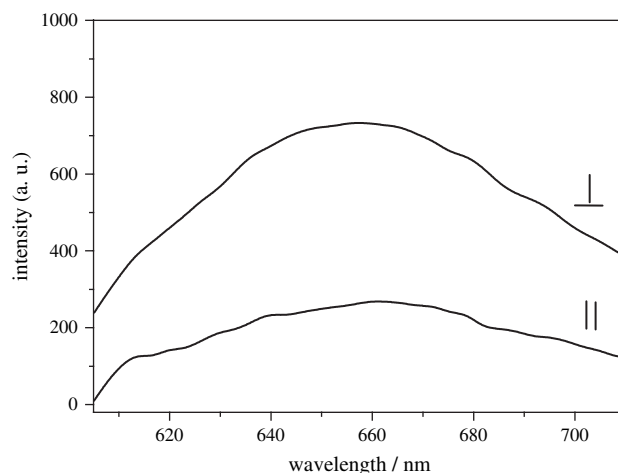


Fig. 7. Fluorescence of a **CNB/StI** film excited perpendicular and parallel to the electric field vector upon excitation with linearly polarised light of 460 nm.

the two-step irradiation/annealing procedure induces an anisotropic fluorescence.

4. Conclusions

A series of side chain LC copolymers containing a fluorescent and photo-sensitive push–pull substituted stilbene unit (**StI**), in combination with three different promesogenic moieties have been prepared by free-radical polymerisation in solution. All polymers show a good thermal stability and display mesophases that have been identified as SmA for the polymers with the benzanilide (**Am**) and the terphenyl (**CNT**) promesogenic units, and as N in the case of the polymer with the cyanobiphenyl (**CNB**) moiety.

The irradiation with LP vis or UV light causes the induction of small anisotropies in films of the stilbene-containing polymers, which can be amplified by annealing above T_g due to the thermotropic self-organisation of the LC polymers. The results show that the presence of the mesogenic **CNB** side groups gives rise to higher degrees of photoreaction, as calculated from the decrease of absorbance, and implies less limitation for the dynamics and the opportunity of alignment than the mesogenic **Am** groups. In this way, dichroism values up to 0.5 were generated for the polymer **CNB/StI** but the photo-induced anisotropy was hardly enhanced in the case of polymer **Am/StI**. This can be probably due to the formation of hydrogen bonds between the benzanilide units in **Am/StI** films, which is not possible in **CNB/StI** films where the mesogenic 4-cyanobiphenyl group cannot form an intermolecular hydrogen bonded network, and weaker dipole–dipole interactions of the 4-cyanobiphenyl side groups are only possible. For **CNB/StI** films, a wavelength dependence of the light-induced and thermally amplified order was observed, which could be interpreted by the wavelength dependence of two or more contributing photoreactions. The *E*-stilbene side groups act also as fluorophores, and after this two-step photoalignment procedure in the bulk, these films show anisotropic fluorescence.

Acknowledgements

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