Spectroscopic and Optical Characterization of a Series of Azobenzene-Containing Side-Chain Liquid Crystalline Polymers

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ABSTRACT: A series of azobenzene-containing side chain liquid crystalline polymers with various spacer lengths (**p*X*MAN**, where *X*, the number of methylene units, varies from 4 to 12) have been synthesized and characterized. Phases and aggregation have been studied by UV−visible spectroscopy as a function of temperature. Polarized spectra were measured before and after irradiation with a resonant pump light at 488 nm. The annealing process on polymers with short spacers (**p4MAN**−**p8MAN**) induces a hypsochromic shift while, for longer spacers (**p9MAN**−**p12MAN**), it induces a large bathochromic shift. These effects may be due to the strong dipolar interaction and interdigitation of the side chain chromophores in an antiparallel orientation. The irradiation of such organized films with either circularly or linearly polarized light induces a bathochromic shift by breaking the antiparallel organization. This is a consequence of the angular reorientation of the azobenzene moieties as a result of trans−cis photoisomerization. To estimate the orientation of the side chain azobenzene photoactive group, of the aliphatic spacer and of the main chain, linear dichroism in the infrared spectral range was measured using the polarization-modulation technique with in situ irradiation. From these experiments, a high and stable value of photoinduced linear dichroism reveals a strong interaction and self-organization of azobenzene side chain molecules during the relaxation process. The anisotropic reorientation of the polymer main chain and of the spacer is small when compared to the reorientation of the azobenzene side chains, which become perpendicular to the linearly polarized pump beam. Additional birefringence measurements were carried out with in situ irradiation followed by a relaxation cycle for the whole series of polymers in various phases. The stability and the rate of the induced birefringence depend on the initial degree of organization within the thin film and on its thermal history. It is noteworthy that annealing can lead to a significant improvement of the birefringence level (+44%). The results obtained on photoinduced orientation and phase organization are correlated with the polymer properties.

Introduction

Azobenzene-containing side chain liquid crystal polymers (SCLCPs) have drawn considerable attention in the past decade.[1,2] Their most attractive feature is the large and reversible photoinduced birefringence or linear dichroism, rendering them suitable for numerous applications in the field of photonics and, more particularly, for holographic storage applications.[3−6] More recently, it has been found that circular dichroism and circular birefringence can be optically generated under resonant irradiation.[7−11] Polymer dispersed liquid crystals (PDLCs) with azobenzene molecules have attracted a large interest for optical or electrooptical switching.[12−14] Also, a binary composite containing liquid crystalline small molecules and a cross-linked polymer bearing azobenzene was shown to exhibit thermally stable birefringence.[15−17]

As in the case of amorphous azo polymers, the optical properties of SCLCPs result from the reversible trans−cis photoisomerization of the N=N double bond followed by an angular reorientation of the azo chromophore to a preferred orientation perpendicular to the direction of polarization of the incident actinic light. Amorphous polymers containing these photosensitive dyes are interesting because the orientation process occurs below the polymer glass transition temperature (T_g) and because chromophore orientation is stable over long periods of time. The main feature that makes these materials, amorphous and liquid crystalline polymers, suitable for reversible optical storage is that the photoinduced anisotropy can be completely erased and that thousands of cycles can be recorded before significant fatigue of the material is observed.[18,19] However, in the case of liquid crystalline polymers, these properties are influenced by the change of aggregation under polarized light, supramolecular order, and, more generally, the liquid crystallinity, which depend on several parameters, including the polymer main chain properties, the spacer length, and the chromophore mobility.[20,21]

Recently, Kulinna et al. have systematically investigated the reorientation of aliphatic groups on a selectively deuterated cyanoazobenzene SCLCP's by FTIR spectroscopy in order to separate the photoinduced orientation of the main chain and of the spacer.[22] In this thorough study, they have characterized the main chain and the side chain spacer reorientation as a function of the spacer length.

The effect of the backbone and the flexible side chain has also been extensively investigated on Langmuir−Blodgett films of polyglutamates containing azobenzene moieties using polarized UV−visible spectroscopy and X-ray reflectivity.[23] The results obtained have led to a deeper insight into the various possible types of aggregation at different steps of the photoisomerization

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Chart 1

CH₃
|
−CH₂−C−
|
C=O
|
O
|
(CH₂)x
|
N−CH₃
|
[benzene ring]
|
N
‖
N
|
[benzene ring]
|
NO₂
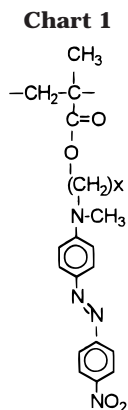
and annealing. Similar studies on Langmuir−Blodgett multilayers of amphotropic polymers have focused on the dependence of the photoinduced reorientation process on the structure, supramolecular order and aggregation of the azobenzene moieties in the ordered layers.[24−26]

In the present study, we examine the optical properties of a series of side chain liquid crystalline polymers shown in Chart 1 and whose generic name is **p*X*MAN**, where *X*, the number of methylene groups of the spacer, varies from 4 to 12; the generic chemical name of *X*MAN is 4-[(*x*-methacryloxy*alkyl*)methylamino]-4-nitroazobenzene) where the alkyl group varies from butyl to dodecyl.

The goal of this work is to study the role of the photoisomerization and reorientation processes in relation to the observed mesophases and physical polymer properties.

We first performed a UV−visible study of the different phases and organizations in conjunction with polarized microscopy. A large color shift is observed in thin films after annealing and also after irradiation with circularly or linearly polarized light. Strong cooperative motions of the side chain groups produce self-organization that depends on the side chain spacer and on the T_g of the polymer. The dynamics of the photoinduced linear dichroism (LD) was investigated using polarization modulation infrared spectroscopy (PM−IRLD). The degree of ordering is higher in the organized phase than in the amorphous phase and the spacer and the main chain do not exhibit significant anisotropy. Additional birefringence measurements as a function of temperature reveal that the ordering can be strongly enhanced by annealing the sample above its glass transition temperature.

Experimental Section

Details about the synthesis, polymer thermotropic properties and X-ray diffraction analysis are described elsewhere.[27]

Thin films (about 200−400 nm thickness) were obtained by dissolving the polymer in dry THF followed by spin casting the solution onto clean glass substrate for UV−visible experiments, and NaCl windows for infrared measurements. The solvent was allowed to evaporate for 5 h at room temperature. In situ irradiation was performed with the 488.0 nm line of an Ar⁺ laser for the visible measurements. The polarized spectra in the UV−visible region were recorded with a single beam Shimadzu 1201 spectrometer, using a Polaroid sheet to polarize the probe beam linearly. Time-resolved PM−IRLD spectra were obtained using a Bomem Michelson MB-100 spectrophotometer coupled with a ZnSe photoelastic modulator (model Hinds II/ZS 50) and using an Ar⁺ laser ($\lambda = 514.5$ nm, $I = 20$ mW/cm²) to induce orientation of the azobenzene moieties. Details concerning the optical setup and signal

processing have been previously described.[28] The total acquisition time for the orientation and relaxation kinetics was set to 1 h. By using a proper calibration procedure, the differential signal is directly proportional to the photoinduced linear dichroism, $\Delta A = A_\parallel - A_\perp$, where $A_\parallel$ and $A_\perp$ are the parallel and perpendicular absorbances with respect to the electric field vector of the reference pump beam.[29]

Birefringence was measured using a photoelastic modulator with a fused silica crystal (model Hinds II/FS50) operating at a wavelength of 674 nm and with a retardation set at 2.407 rad. The wavelength of the pump beam was set to 488 nm with an irradiance of 70 mW/cm². More details about this differential method can be found elsewhere.[30]

Results and Discussion

It is generally observed that in most substituted azobenzene-containing polymers, the UV−visible spectrum exhibits a symmetrical intense absorption band in the visible range. In the case of a reference system like a Disperse Red 1-doped poly(methyl methacrylate), the maximum absorption is observed at 492 nm and the extinction coefficient of the trans isomers is estimated to be about 3.20×10^4 L·mol⁻¹·cm⁻¹. In the case of functionalized polymers, like pDR1A,[31] this absorption band is still symmetric but shows a slight blue shift ($\lambda_{max} = 455$ nm) due to the dipole association in antiparallel conformation at a high chromophore concentration.[32]

The origin of this intense absorption band is a vibronic coupling between the n−π* and π−π* electronic transitions due to the high charge transfer between the donor group (amino group) and an electron-withdrawing group (nitro group) along the azobenzene axis with a typical dipole moment of about 8.7 D.[33]

Depending on the donor−acceptor groups, azobenzene thin films can exhibit photochromic properties under irradiation with linearly polarized light which are due to the coexistence of the trans azobenzene and the metastable cis isomers. In some cases the absorption bands of cis and trans isomers are well separated,[34,25] and from the extinction coefficients of both species, the percentage of photogenerated cis species can be estimated. In our polymer series, and more generally for azobenzene-containing high charge-transfer substituents, the cis and trans absorption bands overlap and the cis concentration can be determined by photophysics methods with the knowledge of the cis extinction coefficient.[35]

Thermal Effects. The UV−visible spectra of the whole series of polymers were recorded as a function of temperature (Figure 1a−i), and the wavelength shifts ($\Delta\lambda_{max}$) are given in Table 1. Two types of behavior are observed and discussed as a function of the spacer length and subsequently the polymer transition temperature. Let us first consider the series from **p4MAN** to **p8MAN**, and focus our interest in **p4MAN** spectra (Figure 1a) which is representative of the series.

In Figure 1a, the spectrum of **p4MAN** in THF solution displays a symmetrical intense band at 476 nm due to the isolated chromophores (weak chromophore intermolecular interaction). After spin casting and solvent evaporation, the thin films present a maximum absorption at 431 nm with a shoulder around 500 nm (spectrum 1). Infrared spectroscopy confirms that no solvent is present. When the film is annealed at 90 °C for 20 min, a blue shift of −11 nm occurs and the sample color changes drastically from red to orange (spectrum 2). The absorbance increases (hyperchromic effect), and the absorbance at 500 nm appears as a shoulder. The
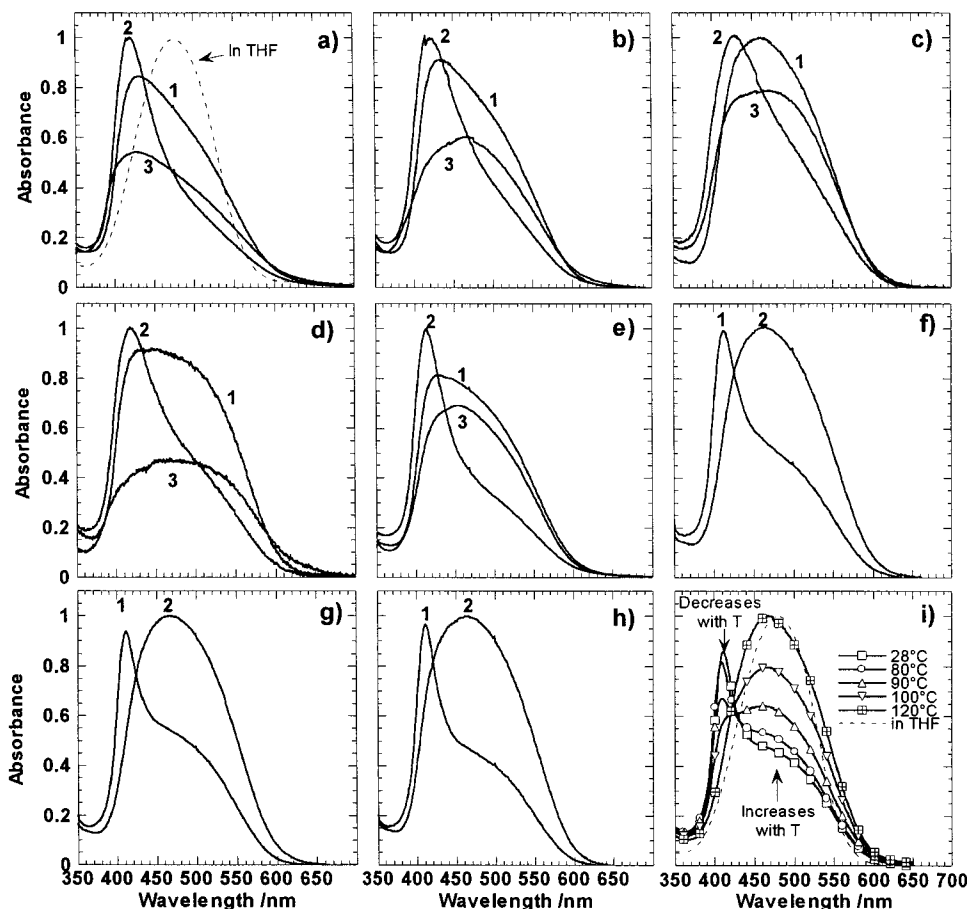
Figure 1. UV−visible spectra of thin films of the **p*X*MAN** series as a function of temperature. *X* is the number of methylene units and varies from 4 (a) to 12 (i). Spectra 1 were recorded at room temperature while spectra 2 and 3 were recorded in situ at $T_g + 20$ °C and $T_g + 60$ °C, respectively.

Table 1. UV−visible Spectral Parameters of Thin Films of PXMAN as a Function of Temperature[a]

polymer	T_g/°C	after spin coating (amorphous), λ_{max} /nm	after annealing, λ_{max}/nm ($\Delta\lambda_{max}$/nm)	cloudy state (smectic), λ_{max} (nm) ($\Delta\lambda_{max}$/nm)
p4MAN	74	431	420 (−11)	428 (−3)
p5MAN	60	428	418 (−10)	456 (+28)
p6MAN	60	455	422 (−33)	476 (+21)
p7MAN	57	431	416 (−15)	471 (+40)
p8MAN	39	428	414 (−14)	453 (+25)
p9MAN	40	412	464 (+52)	not seen
p10MAN	37	410	466 (+56)	not seen
p11MAN	40	411	462 (+51)	not seen
p12MAN	35	410	468 (+58)	not seen

[a] Wavelength shifts at the maximum absorption ($\Delta\lambda_{max}$) are given in reference with the initial amorphous film. A positive value indicates a red shift.

film is still clear and does not present any mesophase under the polarized optical microscope. When the sample is annealed at 140 °C for 20 min (spectrum 3), the film becomes cloudy and a smectic texture is clearly seen between crossed polarizers and confirmed by X-ray diffraction. The λ_{max} shift varies from −3 (**p4MAN**) to +40 nm (**p7MAN**), and the absorbance decreases. All these states (or phases) are stable, and no changes are observed when the sample is cooled to room temperature.

The **p9MAN**−**p12MAN** series has different behaviors, and we consider **p12MAN** as a representative example of the series, as shown in Figure 1i. After spin coating, the films are orange and their electronic spectra

are strongly asymmetric with a maximum absorption centered at 410 nm and a shoulder around 490 nm. When the film is annealed up to 120 °C, the absorption band becomes symmetric with a maximum absorption band at 468 nm. In this case, the initial absorption band is recovered by cooling the sample and many thermal cycles can be achieved without degradation of the sample. No texture is observed under polarized microscope for all the thin film series from **p9MAN** to **p12MAN**. However, on thicker films and after long heating periods, X-ray diffraction analysis has revealed organization for all polymers except for **p10MAN**.[27]

To investigate a possible homeotropic smectic phase, which has been recently reported in an azobenzene-containing LCP,[36] polarized spectra have been recorded on isotropic films along the directions parallel and perpendicular to the reference axis (the pump light polarization vector), at normal incidence and with an angle of incidence of 45°. However, as shown in Figure 2, no dichroism is observed for the untreated films and the polarized spectra obtained at oblique incidence for **p12MAN** do not indicate an orientation of the chromophores perpendicular to the film plane. The difference in absorption between polarized spectra at normal incidence and oblique incidence comes from the thickness difference and is in agreement with the law of Huygens−Fresnel:

$$A_{45} = A_0[1 - n^{-2}\sin^2 45]^{-0.5} \qquad (1)$$

where *n* is the refractive index of the polymer, A_0 and
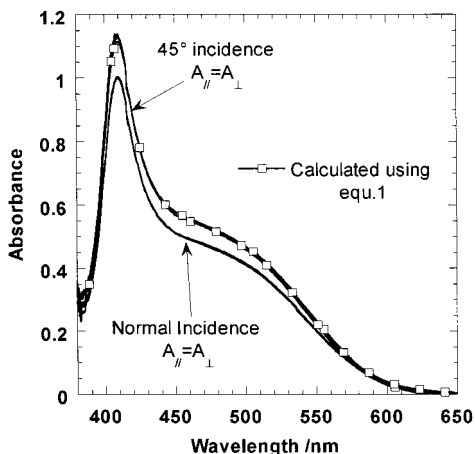
Figure 2. Polarized UV−visible spectra of a nonirradiated **p12MAN** film at normal and 45° incidence. The symbols ∥ and ⊥ refer to the reference direction of the linear polarization of the pump beam.
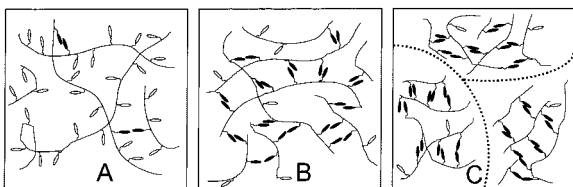

| Spacers 4-8 | New film | Annealed | Cloudy |
| Spacers 9-12 | Annealed | New film | - |

Figure 3. Schematic illustration of molecular organizations for the two series (long and short spacers) of **pXMAN**: (A) amorphous sample with weak chromophore interactions; (B) amorphous sample with strong antiparallel dipolar interactions; (C) smectic texture with formation of domains with high dipolar interactions.

A_{45} are the absorbances at normal incidence and 45° incidence, respectively. Considering a polymer refractive index of 1.6, eq 1 fits the recorded spectra perfectly at tilted incidence as shown in Figure 2. Therefore, no homeotropic phase is observed.

To explain the above observations, we suggest that different organizations occur during the processing of the film. Two cases will be discussed, and a schematic illustration is presented in Figure 3.

For the series with the short spacers (**p4MAN**−**p8MAN**), the films obtained are amorphous and a weak asymmetry of the band results from interactions between chromophores of the same chain (intrachain interactions) or between chains (interchain interactions). The comparison of the absorption spectra in thin films and in solution clearly shows that strong interactions within the polymer are present in the solid state. When the films are annealed slightly above their glass transition temperatures, they are still amorphous and they present no mesophase under the polarized microscope, but the electronic transition is now strongly structured (Figure 1, spectrum 2). This probably occurs because of a self-organization of the chromophores which tend to associate in an antiparallel fashion. Moreover, the fact that the electronic transition undergoes a blue shift and becomes narrower suggests that the chromophore moieties may be interdigitated with their dipolar moments opposite to the adjacent chromophores. Globally, this organization produces a weaker charge transfer between the donor amino group and the
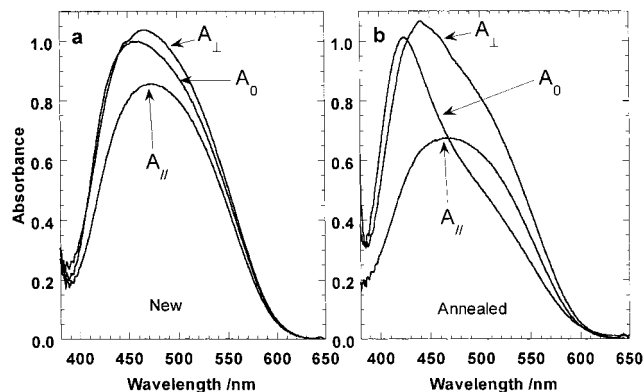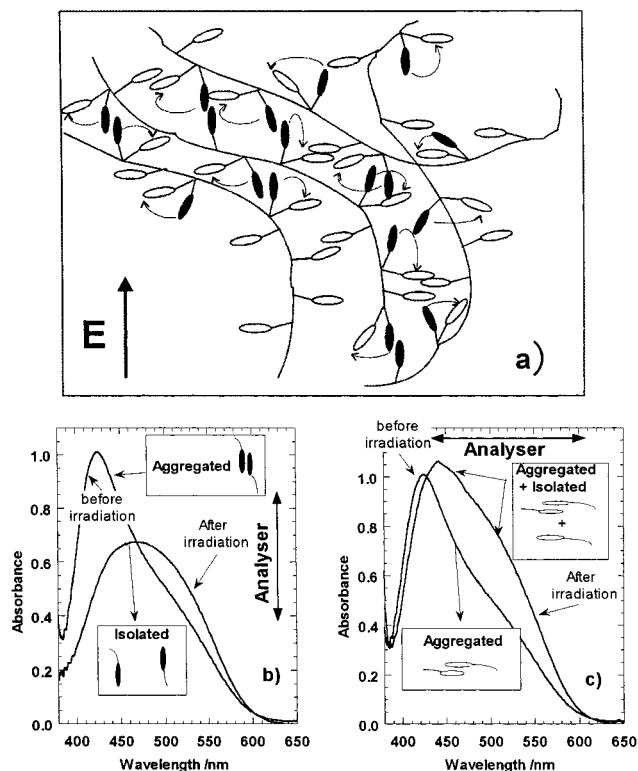

Figure 4. Polarized UV−visible spectra of a **p6MAN** film irradiated for 10 min at 100 mW/cm². Irradiation has been performed on the thin films at room temperature (a) and after annealing for 20 min at 90 °C (b).

withdrawing nitro group. Subsequently, if the charge transfer decreases, the electronic transition has a π → π* character rather than a n → π* and a blue shift is observed. When the temperature is increased—and the smectic texture is observed under microscope—the absorbance of the thin film is weaker. So far, there is no obvious explanation for this, but it may come from the organization of the smectic layers perpendicular to the plane of the film. Surprisingly, a red shift occurs, revealing that the interdigitation is probably changing from the previous organization (Figure 1, spectrum 3). The X-ray measurements indicate a strong interdigitation since the layer spacing is close to the estimated side chain length.[27]

For the series with longer spacers (**p9MAN**−**p12MAN**), only two states, and no liquid crystalline phase, are observed. These polymers have lower T_gs (Table 1) and, consequently, higher side chain flexibility. After spin coating, the absorption spectra resembles that assigned to an antiparallel association of the chromophores with interdigitation. The shoulder located between 450 and 500 nm may come from isolated chromophores in the polymer matrix. After the film is annealed above T_g, a large red shift occurs and the sample goes through the orange to red color change. The maximum shift is seen for **p12MAN** at about 58 nm. Moreover, the similarities between the absorption spectra in solution and in films baked at 120 °C suggest that at temperatures above T_g the chromophores can be considered to be isolated. This process is reversible, and when the film is cooled to room temperature, the initial spectrum is recovered. Many heating−cooling cycles can be performed on such samples before significant fatigue of the film. However the dynamics of the color change is very different. For instance, **p12MAN** recovers its initial orange color right after cooling to room temperature while **p9MAN** requires at least 48 h.

Photoinduced Linear Dichroism. Irradiation has been performed on three different **p6MAN** thin films: after spin coating (new film), after annealing at 90 °C and in the stable mesophase (smectic). The polarized UV−visible spectra were recorded by analyzing the transmitted light both in parallel and perpendicular directions with respect to the polarization vector of the reference pump beam. The isotropy of the films was checked before each experiment, and the irradiance of the pump laser was set at 100 mW/cm² for 10 min.

In the first experiment (Figure 4a), a new (nonbaked) **p6MAN** film was irradiated. There is a significant

Figure 5. Schematic diagram of the proposed structure in an annealed sample (**p4MAN**) before and after irradiation (a). The corresponding polarized UV−visible spectra in the parallel (b) and perpendicular (c) directions with respect to the linearly polarized pump are characteristic of the single or aggregated chromophores.

Figure 6. Polarized UV−visible spectra of a **p6MAN** film annealed for 20 min at 90 °C, then irradiated at 100 mW/cm^2, then annealed again at 110 °C.

decrease of the absorbance in the parallel direction ($A_∥$) while the absorbance in the perpendicular direction increases slightly. If we compare these two spectra with the isotropic one (A_0), the increase of the perpendicular absorbance ($A_⊥$) is approximately equal to half the decrease of the parallel absorbance ($A_∥$), revealing a uniaxial orientation of the azobenzene chromophores perpendicular to the polarization direction of the pump. Also, a bathochromic shift ($Δλ_{irr} = +10$ nm) is observed after laser irradiation for both the parallel and perpendicular directions. Such a spectral inhomogeneity has been reported by Dumont et al.,[37] and in addition to the trans−cis photoisomerization process, it is probably a consequence of the various polar environments in the polymer in the locations where photoinduced orientation processes are occurring. No separate absorption band of the cis isomers is observed, so that the global absorption in the visible is due to both trans and cis isomers.

In the second experiment, polarized spectra were recorded on annealed films. The spectrum displays the same shape previously discussed for **p4MAN** (Figure 1a). After irradiation, an average bathochromic shift of about $Δλ_{irr} = +40$ nm is observed. The irradiated area clearly changes from orange to red. In addition, the two polarized spectra display different shapes (Figure 4b). $A_∥$ has a symmetrical shape quite similar to the untreated (new) sample while $A_⊥$ has an asymmetrical shape close to the annealed material.

First, let us consider a strong antiparallel association of the chromophores with interdigitation in the starting (annealed) film (Figure 5a). The irradiation of the sample, either with linear or circular light will induce
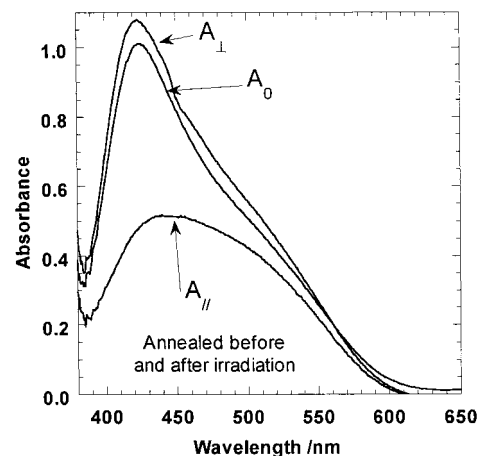
photoisomerization cycles and subsequent angular orientation of the chromophores. These cycles will destroy the initially organized aggregated phase and the chromophores will become isolated. In the case of a linearly polarized pump, the polarized spectra $A_∥$ (symmetrical shape) confirm that the chromophores parallel to the incident electric field have been pumped and that the remaining chromophores in this direction can be considered as isolated (Figure 5b). The singular shape of $A_⊥$ (Figure 5c) suggests that the chromophores in this direction are antiparallel (aggregated) and that isolated chromophores are also present as a consequence of the orientation process.

After irradiation, the film was annealed again at 110 °C and the polarized spectra are reported in Figure 6. The irradiated spot which was red after irradiation has disappeared and the film is uniform. The polarized spectra of $A_∥$ and $A_⊥$ suggest that the thermal treatment above the T_g provided enough motion to the polymer side chains to reorganize, leading to a homogeneous antiparallel organization of the azo chromophores but keeping the photoinduced orientation. With the increase of the temperature, the mobility of the mesogens for angular motion and stabilization increases, leading to a high and stable value of the linear dichroism as shown in Figure 6.

Similar observations were made for **p12MAN** but because of its low T_g, the sample recovers its initial color without any thermal treatment after a few minutes.

Study of Induced Linear Dichroism by Time-Dependent Infrared Spectroscopy. As an illustrative example, the infrared spectrum in the 1000−1800 and 2750−3050 cm^{-1} regions of **p12MAN** film is presented in Figure 7, parts a and b. The most intense band located at 1339 cm^{-1} is assigned to the symmetric stretching vibration $ν_s(NO_2)$ while the antisymmetric stretching vibration ($ν_a(NO_2)$) appears at 1509 cm^{-1}. In the case of **p12MAN** this band clearly presents another contribution at 1517 cm^{-1}, which may come from the $ν_{19a}(C=C)$ stretching mode of the substituted phenyl groups.

As reported previously by Buffeteau et al.,[31] the band at 1385 cm^{-1} is assigned to a vibrational coupling between the $ν(N=N)$ and the $\phi-N$ stretching vibration because of the high charge transfer along the uniaxial trans isomer. The band at 1727 cm^{-1} is assigned to the ester carbonyl group. The bands located at 1601 and
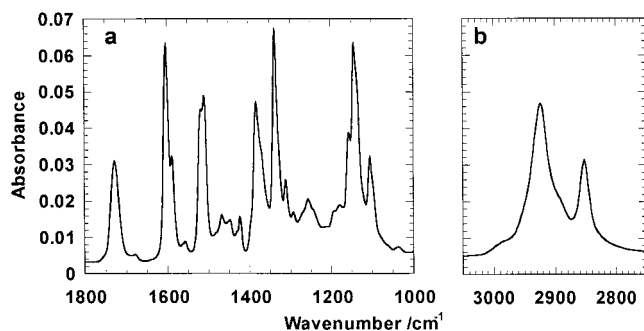
Figure 7. Absorbance spectra of an isotropic sample in the infrared region (a) between 1000 and 1800 cm^{-1} and (b) between 2750 and 3050 cm^{-1} of a **p12MAN** thin film.
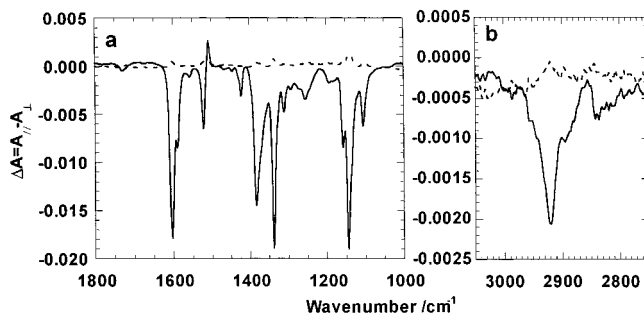
Figure 8. PM−IRLD spectra in the infrared region (a) between 1000 and 1800 cm^{-1} and (b) between 2750 and 3050 cm^{-1} of a **p12MAN** thin film after 1 h irradiation (λ_{pump} = 514.5 nm and I_{pump} = 20 mW/cm^2). The dashed line is the signal recorded before turning on the pump beam.

1588 cm^{-1} are assigned to the stretching vibration of para-substituted phenyl rings ν_{8a}- and ν_{8b}(C=C), respectively. The bands located at 1105 and 1143 cm^{-1} are associated with the ring deformation modes. The asymmetric stretching mode of the ester group appears at 1157 cm^{-1}. The bands observed at 2852 and 2923 cm^{-1} are assigned to the spacer methylene symmetric and antisymmetric stretching modes, respectively.

Before measuring the induced linear dichroism, infrared spectra were recorded at various temperatures on freshly prepared films, but no significant changes in frequency and absorbance were observed. Moreover, Figure 8 shows that the films were isotropic. The experiments on the **p4MAN**−**p8MAN** polymer films were performed after annealing the samples so that the absorption bands in the visible range could be compared to spectra 2 in Figure 1, parts a−e. The polymers with the longer spacer were not subjected to a specific thermal treatment and the pump irradiance was set to 20 mW/cm^2 for these measurements.

The photoinduced linear dichroism of a **p12MAN** thin film after 1 h of irradiation at 514.5 nm is shown in Figure 8, parts a and b.

First, it is noteworthy that the dichroic signal is negative for most of the bands associated with the chromophore vibrational modes, indicating a perpendicular orientation of the chromophore. However, a significant positive signal at 1509 cm^{-1} suggests a dipole reorientation in a direction parallel to the pump polarization direction. This band can be assigned to the orientation of the antisymmetric stretching mode of the nitro group since its dipole transition moment is perpendicular to the long molecular axis of the side chain. However, as suggested earlier,[31,38] it may be partly due to the contribution of the ν(N=N) stretching mode of

the cis isomer which overlaps the ν_a(NO$_2$) mode. It is not clear why this effect is much more emphasized for **p12MAN** than for the other polymers.

The aliphatic spacer band located at 2923 cm^{-1} (Figure 8b) presents a weak linear dichroism when compared to the chromophore bands. Since the same experiments were performed for the whole series with similar results whatever the spacer length, the low orientation of the spacer is probably due to the high rotational flexibility of the chromophore around the methylene groups they are linked to. As the chromophores reorient, they may drag with them the first methylene groups they are linked to, thus inducing a small orientation of the transition moment of the antisymmetric stretching mode (ν_a(CH$_2$)), perpendicular to the pump beam polarization.

A strong shift of the frequency of both the ν_a(CH$_2$) and ν_s(CH$_2$) bands is observed with the increase of the spacer length. For the antisymmetric mode, the wavenumber varies from 2951 (**p4MAN**) to 2923 cm^{-1} (**p12MAN**). The same observation is reported for the symmetric mode where its wavenumber varies from 2861 (**p6MAN**) to 2852 cm^{-1} (**p12MAN**). This indicates that, for longer spacers, the aliphatic chain is more ordered, with more C−C bonds in the trans conformation. This result is in agreement with Figure 3b where the LCPs from **p9MAN** to **p12MAN** are associated in an antiparallel fashion, unlike in Figure 3a.
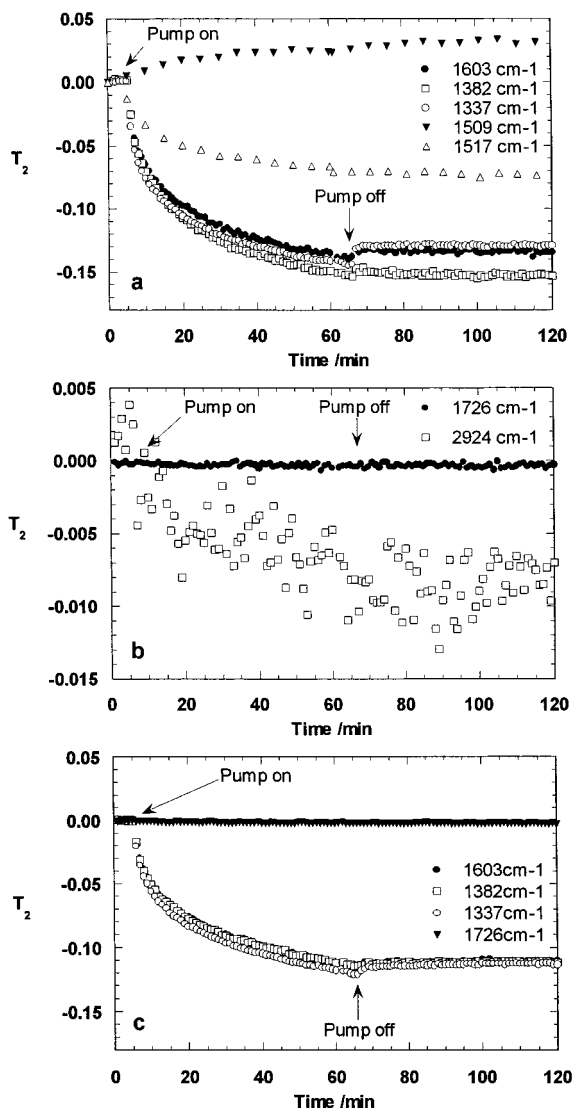
The orientation of the main chain is also very small, as the carbonyl band located at 1726 cm^{-1} does not present a significant dichroism indicating that the polymer main chain remains isotropic.

To get more insight into the reorientation mechanism of the different chemical groups, the dynamics of the photoinduced orientation in the liquid crystalline polymer series was studied using the PM−IRLD technique during the writing (pump on) and the relaxation (pump off) cycles. In a first step, $A_{\parallel}$ and $A_{\perp}$ were measured separately, to demonstrate that the orientation was uniaxial and that the average absorbance of the sample A_0 after irradiation could be related to the polarized absorbances by the relation: $A_0 = A_{\parallel} + 2A_{\perp}$. Considering this uniaxial orientation, the parameter T_2 (eq 2a) rather than $\langle P_2 \rangle$ (eq 2b) will be used, since the PM−IRLD technique does not permit the analysis of separate polarized spectra. Subsequently, ΔA is normalized using the average isotropic absorbance, A_0, of each considered vibrational mode, which allows a quantitative comparison of the time-dependent behavior of the different bands.

$$T_2 = \frac{A_{\parallel} - A_{\perp}}{3A_0} \quad (2a)$$

$$\langle P_2 \rangle = \frac{A_{\parallel} - A_{\perp}}{2A_{\perp} + A_{\parallel}} \quad (2b)$$

The results are presented for **p12MAN** and **p4MAN** in Figure 9, parts a and b and Figure 9, part c, respectively. The rate of orientation is slow, and after 1 h of irradiation, the steady state is not reached. The level of maximum-induced orientation is higher for **p12MAN** (T_2 = −0.15) than for **p4MAN** (T_2 = −0.12), and it generally appears that higher T_2 values are observed for systems containing longer spacer systems. The T_2 values for the modes located at 1603, 1382, and 1337 cm^{-1} have similar behaviors, meaning that their transi-

Figure 10. Optically induced birefringence for **p4MAN** films in three different states: freshly prepared (1), annealed for 20 min at 90 °C (2) and annealed at 140 °C for 20 min. The linear laser pump is turned on at $t = 0$ for 900 s. The laser is turned off at $t = 900$ s for a 400 s relaxation period. The erasing circularly polarized beam is turned on at $t = 1300$ s for 300 s. ($\lambda_{pump} = 488.0$ nm and $I_{pump} = 70$ mW/cm²).

Table 2. Birefringence Values for the PXMAN Series in Their Three States, Amorphous (1), Annealed (2), and Smectic (3)[a]

	maximum birefringence $(-\Delta n)$			remnant birefringence (%) after 500 s relaxation period		
polymer	1	2	3	1	2	3
p4MAN	0.121	0.104	0.092	91	91	92
p5MAN	0.115	0.153	0.126	82	89	90
p6MAN	0.087	0.118	0.087	85	85	90
p7MAN	0.079	0.101	0.101	73	85	85
p8MAN	0.080	0.102	0.086	62	68	72
p9MAN	0.076	0.088		41	57	
p10MAN	0.063			27		
p11MAN	0.062			36		
p12MAN	0.067			65		

[a] For P9MAN to P12MAN, no smectic phases were observed. For P10MAN to P12MAN, as the organized state (2) was not stable at room temperature, the birefringence has not been measured.
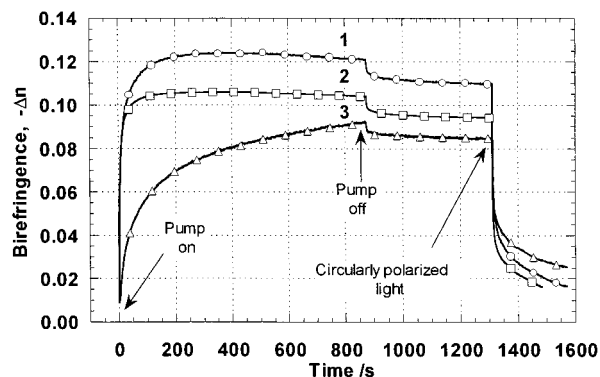

Figure 9. Time dependence of the normalized linear dichroism T_2 for several infrared bands of **p12MAN** (a, b) and of **p4MAN** (c) films during the writing and the relaxation periods ($\lambda_{pump} = 514.5$ nm and $I_{pump} = 20$ mW/cm²).

tion dipole moment has the same orientation close to the main axis of the chromophore. This indicates that the side-chain chromophore is moving as a whole unit.[31] The level of stable orientation, after turning off the pump, is very high for all polymers and ranges between 90 and 100% depending on the considered vibrational modes. In the case of the two bands at 1517 and 1509 cm⁻¹ (Figure 9a), the degree of ordering actually tends to increase after turning the pump off. However, since the assignment of these bands is not clear, such an effect could be explained by the strong self-ordering of the polymer where dipolar interactions are strong and lead to an association of the chromophores after turning the pump off. Indeed, as the T_g is about 35 °C for **p12MAN**, the side chains are very flexible and continue to move slightly until an antiparallel stable arrangement is reached.

In Figure 9, parts b and c, it is clear that the orientation of the main chain, and the spacer are not playing a major effect during the reorientation process (the scale of Figure 9b is 10 times smaller).

Dynamic Birefringence Measurements. Birefringence measurements were performed on each polymer in the series in their amorphous, aligned and smectic organizations during orientation (linearly polarized pump on), relaxation (pump off), and erasing (circularly polarized pump beam on) cycles. The measurements for **p4MAN** films (thickness = 200 nm) in its three different organizations, freshly prepared (film 1), annealed 20° above its T_g (film 2), and in its smectic state (film 3) are shown in Figure 10. For the amorphous phases (1 and 2), the birefringence increases rapidly and a plateau value is rapidly reached. In the smectic phase (3), the high stability of the mesophase plays an important role, reducing the rate of photoinduced birefringence and no plateau is reached even after 900 s of irradiation at 70 mW/cm².

When the pump is turned off, the remnant birefringence, in the case of **p4MAN**, is estimated to about 90% of its initial value for films 1, 2, or 3. This very stable birefringence confirms the infrared dynamic measurement results. However, as presented in Table 2, the maximum-induced Δn for longer spacer LCP's is around 0.06 and the remnant birefringence is no more than 65% (**p12MAN**). This result does not agree with the infrared measurements shown in Figure 9a, where the remnant linear dichroism was estimated at about 90%. This discrepancy can be explained considering the difference between the irradiance of the pump beam used for PM−IRLD ($I_{pump} = 20$ mW/cm²) and birefringence measurements ($I_{pump} = 70$ mW/cm²). Indeed, for long chain polymers (**p10MAN**−**p12MAN**) with low T_g's (Table 1),
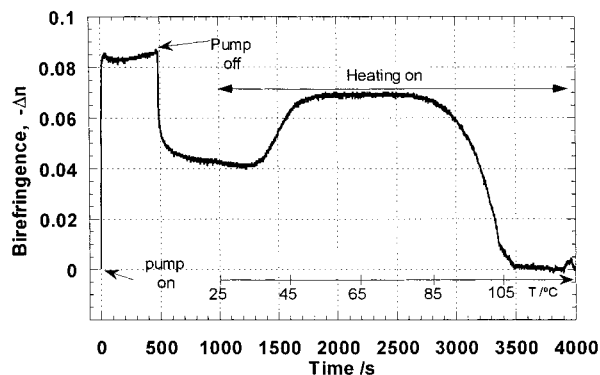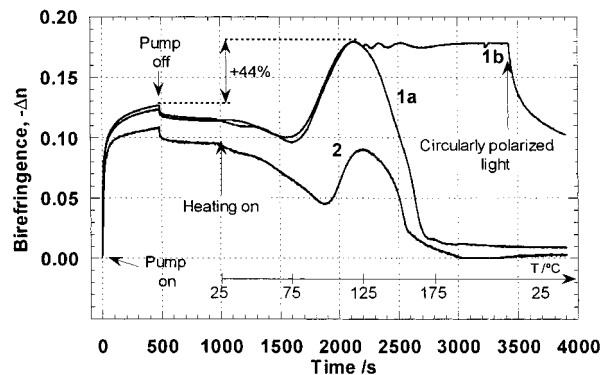
Figure 11. Photoinduced birefringence on a **p12MAN** film during orientation (laser on—500 s) and relaxation periods (laser off—500 s). At $t = 1000$ s, the sample is heated to 120 °C at a rate of 2 °C/min.

Figure 12. Birefringence cycles on **p4MAN** films freshly prepared (1a and 1b) or annealed (2). For films 1a and 2, the linearly polarized light is turned on at $t = 0$ for 500 s and after a 500 s relaxation period, the sample is in situ heated at a rate of 5 °C/min to 175 °C and then cooled to room temperature. For film 1b, the sample is cooled rapidly when the maximum birefringence is reached at approximately $t = 2200$ s as the temperature reached 120 °C.

the irradiance is a critical parameter since it can destroy the induced orientation at room temperature, close to the glass transition temperature. In the case of **p12MAN** for instance, the relatively high irradiance may heat the sample above its T_g, reducing the photoinduced birefringence since the cis—trans thermal back photoisomerization rate is faster than the angular reorientation process. Also, as seen in Figure 11, the relaxation after turning the pump off is a very fast process after 500 s of irradiation. As the polymer temperature is probably higher than its T_g, when the pump is turned off, a large portion of chromophores will tend to reorganize in a more stable position but with a random orientation leading to a small value of remnant birefringence (Table 2).

The erasing process with a circularly polarized light is easier to achieve for the two amorphous phases 1 and 2 (Figure 10). A longer time is needed to erase the induced birefringence when the polymers are in their smectic phases. This is probably due to the high interaction and stability of the orientation within the smectic domains which require more energy to break and randomize the orientation of the single azobenzene groups. Once again, the higher the self-association, the more difficult it is to induce photoisomerization and consequently angular reorientation of the azobenzene molecules.

To evaluate the effect of the phase organization on the induced birefringence, **p4MAN** and **p12MAN** samples were annealed in situ while birefringence was measured. In Figure 12, after an orientation—relaxation cycle of a freshly prepared **p4MAN** film, the sample was heated at a rate of 5 °/min to 175 °C. It is remarkable (Figure 12, curve 1a) that the heating process induces a significant increase in the level of the birefringence ($\Delta(\Delta n)/\Delta n_{max} = +44\%$). Above 120 °C (i.e., when the film starts to show a neat texture under crossed polarizers), the birefringence is thermally erased due to the randomization of chromophores orientation. In a second experiment, a similar film was irradiated in the same conditions, but at 120 °C the sample was quickly cooled to room temperature. The thermally enhanced birefringence was quite stable, and the UV—visible absorbance of the film is similar to spectra 2 in Figure 1a, corresponding to a preannealed film. Such a thermal gain is very stable and could be interesting from a technological point of view, to improve the optical properties of such LCP for optical storage devices.[4] However, if this experiment is performed on an annealed sample (Figure 12, curve 2), the thermal gain is not significant, leading to

the conclusion that such a thermal enhancement of the birefringence properties needs a phase transition from amorphous (spectrum 1, Figure 1a) to organized (spectrum 2, Figure 1a). For a film pre-ordered with linearly polarized light, the aggregation of the chromophores in an antiparallel organization improves the ordering and birefringence level. This is in agreement with the UV—visible polarized measurement, since we observe in Figures 4b and 6 that a thermal treatment increases the induced linear dichroism. To confirm this assumption, a similar measurement has been performed on a **p12MAN** film displaying an organized structure at room temperature as discussed previously (Figure 11). Once again, it is clear that baking the sample does not increase the initial maximum birefringence as observed in **p4MAN**. A slight effect leading to an increase of the remnant birefringence is however reported which proves that the organization of the film can be still enhanced.

Conclusions

Thin films of a series of side-chain liquid crystalline polymers present different organizations depending on their thermal history. The amorphous, antiparallel organization and smectic phases can be clearly distinguished by UV—visible measurements for short side chain polymers (**p4MAN**—**p8MAN**) while only organized phases are reported for polymers with longer spacer at room temperature (**p10MAN**—**p12MAN**). Irradiation of such organized films induces a large color shift, adding new photochromic properties to the induced birefringence and linear dichroism properties. A color change arising from a change in arrangement from organized aggregated molecules to isolated chromophores in the polymer network underlines the effect of strong dipolar interaction of the azo moieties. For longer spacers (polymers with $T_g \leq 40$ °C), the pump irradiance is a critical parameter since it can heat the sample above T_g.

In terms of molecular orientation, PM—IRLD experiments have shown that the azo moieties are moving as whole units, and neither the polymer main chain nor the spacer is strongly involved in the orientation process.

Birefringence measurements have revealed the importance of the initial state on the birefringence dynamics. For the polymers with short spacers the remnant

birefringence reaches about 90% whatever the starting phase, but the rate of inducing and erasing birefringence is strongly dependent on the initial organization.

The influence of the thermal treatment has also been demonstrated and a net increase of the birefringent properties for a short spacer polymer can be achieved. For polymers with longer spacers such an enhancement cannot be performed, since the starting phase is already organized. Further experiments as a function of temperature and irradiance are being performed by infrared and birefringence measurements.

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