

Dynamics of Photoinduced Orientation of Nonpolar Azobenzene Groups in Polymer Films. Characterization of the Cis Isomers by Visible and FTIR Spectroscopies

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ABSTRACT: To better characterize the cis state and the reorientation processes in polymers containing azobenzene groups, the in situ dynamics of photoinduced orientation of a polymer with azobenzene groups bearing no donor and acceptor substituents such as poly[4-[2-(methacryloyloxy)ethyl]azobenzene] polymer (pMEA) was carried out using real-time UV–vis and infrared spectroscopies. Thin films of pMEA were irradiated at 488 nm with either linearly or circularly polarized light ($I_{\text{pump}} = 10 \text{ mW/cm}^2$). The different mechanisms occurring during the photoisomerization cycles were revealed by following the time dependence of the normalized average absorbance (T_0) and the normalized linear dichroism (T_2) during the orientation (laser on) and relaxation (laser off) periods. Therefore, the normalized average absorbance has allowed an estimation of the cis isomer fraction (f_{cis}) at the photostationary state. The photoisomerization is more efficient when the film is irradiated using a circularly polarized light ($f_{\text{cis}} = 0.15$) than using linearly polarized light ($f_{\text{cis}} = 0.11$). The cis state has been characterized for the first time in azopolymers by infrared spectroscopy using a band at 1515 cm^{-1} characteristic of the cis isomers. The time dependence of the intensity of this band during the relaxation period has shown that the cis state is very stable and has a lifetime of about 12 h. Finally, a significant dichroism of the trans and cis isomers has been observed when the films were irradiated with a linearly polarized light.

Introduction

In the past few years, azo-dye-containing polymer systems have been the subject of intensive research because of their potential uses in photonics, optoelectronics, and optical signal processing.^{1,2} One of the main interests of these polymer systems is their birefringence properties when they are irradiated with a linearly polarized light.³ This birefringence comes from the reorientation of the azobenzene groups through trans–cis–trans isomerization cycles, which lead to an excess of photochromic entities oriented perpendicularly to the laser polarization direction. When the laser is turned off, a large part of the photoinduced orientation is preserved (between 60% and 80%) in polymers containing azobenzene side chains.^{4,5} Most of the previously published studies were performed on polymer films containing azobenzene groups with electron-donor and electron-acceptor substituents which strongly absorb in the visible region of the electronic spectrum. For example, polymers containing 4-amino-4'-nitro-substituted azobenzene groups (such as Disperse Red 1 (DR1)) display a maximum absorbance near 490 nm. Therefore, it is possible to investigate the reorientation mechanisms of the azobenzene chromophores by irradiating the polymer film with a polarized argon laser (at 514.5 or 488 nm) and by recording its birefringence or its linear dichroism (using visible or infrared spectroscopy) during the orientation (laser on) and the relaxation (laser off) periods.^{4–8} The time dependence of the photoinduced orientation in azobenzene polymers has

been explained by Dumont et al. using a theoretical model that takes into account the population in both the trans and cis metastable states.^{9–11} This model takes into account that the polarized light induces a selective optical pumping ("angular hole-burning (AHB)") followed by angular reorientations (AR) during the direct trans–cis and reverse cis–trans photoisomerizations and the cis–trans thermal back-relaxation. However, for polymers containing polar azobenzene groups, it is difficult to obtain direct information into the reorientation process within each isomerization step. Indeed, the time dependence properties of the trans and cis isomers cannot be followed individually since both isomers absorb in the same region of the visible spectrum.^{12,13} Consequently, the time-dependent curves obtained during the irradiation period are governed by the angular reorientation of the azobenzene groups during both the trans–cis and cis–trans isomerization processes. Moreover, the cis lifetime is relatively short (less than 10 s),¹⁴ making the characterization of the cis state (identification of the infrared absorptions, anisotropy of the cis state) very difficult. Generally, the theoretical models for the photoinduced orientation assume an isotropic distribution of orientation of the cis isomer, on account of its globular shape.

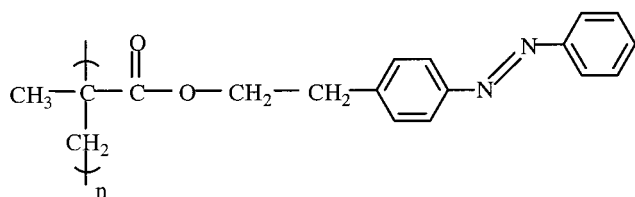
In contrast, if the azobenzene groups have no donor/acceptor substituents (azobenzene-type in Rau's classification), the trans isomer absorbs in the UV region near 320 nm while the cis isomer absorbs in the visible region near 450 nm, and the cis–trans thermal back-relaxation is relatively slow.¹² These systems allow a better characterization of the cis state and then a better understanding of the reorientation processes in polymers containing azobenzene groups. Indeed, in a recent study, Sekkat et al.¹⁵ have investigated the photo-

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Scheme 1



induced orientation in an azobenzene-containing polyglutamate film. An anisotropy in the *cis* isomer orientation has been found when the film was irradiated with a linearly polarized UV light (360 nm), and the time dependence of this anisotropy has been described by a theoretical model. Furthermore, Natansohn et al.^{16,17} have studied the time dependence of the birefringence of poly[4-[2-(methacryloyloxy)ethyl] azobenzene] film (called pMEA) using polarized UV (360 nm) or visible (514.5 nm) light. A similar birefringence has been measured for the two wavelengths, but its value was lower than that observed in various polymers containing polar azobenzene groups. Pump irradiance and temperature dependences of the photoinduced anisotropy in a pMEA polymer film have also been studied and compared to simple theoretical predictions.¹⁸

In this context, we have investigated in the present study the time dependence of the photoinduced orientation in pMEA films using UV-vis and infrared spectroscopies. The pMEA films have been irradiated at 488 nm using either a linearly or a circularly polarized laser, and their polarized absorbances have been measured at 350 and 450 nm during the orientation and relaxation periods. To obtain more quantitative information, the normalized average absorbance (T_0) and the normalized linear dichroism (T_2) were calculated. Thus, the anisotropies of the *trans* and *cis* isomers as well as the *cis* isomer population in the photostationary state have been estimated. The infrared results have shown for the first time in these "azopolymers" a band at 1515 cm^{-1} due to N=N stretching vibration of the *cis* isomers. The time dependence of this band during the relaxation period has allowed to measure the lifetime of the *cis* isomer. Finally, the anisotropy of the *cis* isomers has been confirmed from infrared linear dichroism experiments.

Experimental Section

Materials. The synthesis and properties of poly[4-[2-(methacryloyloxy)ethyl]azobenzene] polymer have been described in a previous publication,¹⁶ and its structure is shown in Scheme 1. To prepare thin films, the polymer was dissolved in chloroform, and the solution was deposited by spin-coating onto fused silica (UV-vis measurements) or sodium chloride (infrared measurements) optical windows. Films were then heated for 30 min at 80 °C to remove any remaining solvent. The film thicknesses were about 0.35 and 3 μm for UV-vis and infrared measurements, respectively.

Experimental Setup. UV-vis absorption measurements were recorded with a double-beam spectrometer (SAFAS 190 DES). Photoisomerization of the azobenzene groups was induced by irradiating the sample with a vertically polarized Ar^+ laser light (ILT 5490, $\lambda = 488 \text{ nm}$). The laser beam was expanded with a visible beam expander and passed through an aperture (6 mm diameter) to obtain an homogeneous irradiance on the sample of 10 mW/cm^2 . Polarized spectra were obtained by analyzing the probe transmitted light using a Polaroid film in order to measure the absorbance of the sample in the parallel (A_{\parallel}) and perpendicular (A_{\perp}) directions with respect to the pump laser polarization. Kinetic measurements were performed, during the orientation (laser on) and relax-

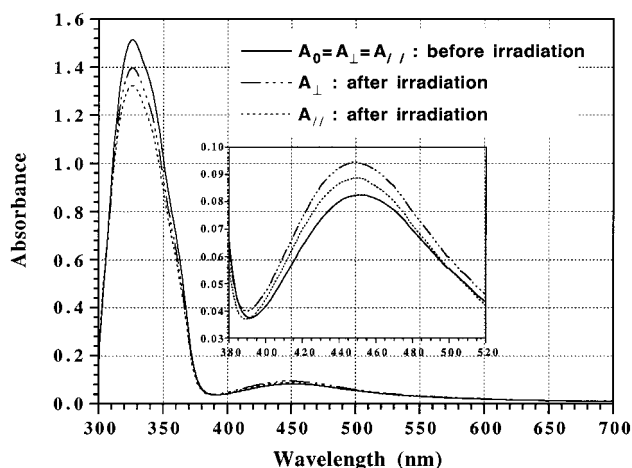


Figure 1. UV-vis absorbance spectra of a pMEA film before irradiation and after a 1200 s exposure to linearly polarized light ($\lambda = 488 \text{ nm}$, $I_{\text{pump}} = 10 \text{ mW}/\text{cm}^2$) and a 1200 s relaxation period. The probe light was unpolarized for the nonirradiated sample (A_0) and linearly polarized parallel (A_{\parallel}) and perpendicular (A_{\perp}) with respect to the laser polarization direction for the irradiated sample. The inset is an expanded view of the 450 nm absorption band.

ation (laser off) periods, by analyzing the polarized transmitted light using a probe beam fixed at 350 and 450 nm. An holographic notch filter (Kaiser, $\lambda = 488 \text{ nm}$, $\Delta\lambda = 20 \text{ nm}$) has been placed in front of the detector in order to eliminate the scattered light due to the diffuse reflections of the Ar^+ laser inside the sample compartment. The total acquisition time for the orientation and relaxation kinetics was about 1 h with a time resolution of 2 s. Kinetic measurements were also performed by irradiating the sample with a circularly polarized Ar^+ laser light, using the same experimental conditions. Circular polarization was produced by inserting a Soleil-Babinet compensator on the laser light.

Infrared absorption measurements were performed using a Nicolet 740 FTIR spectrometer. The optical anisotropy in the polymer films was induced in situ, in the sample compartment of the spectrometer, using a vertically or a circularly polarized Ar^+ laser light ($\lambda = 488 \text{ nm}$, $I_{\text{pump}} = 10 \text{ mW}/\text{cm}^2$). Unpolarized absorbance spectra were recorded during the orientation (1 h) and the relaxation (20 h) periods with a time resolution of about 15 min per spectrum (302 scans, 4 cm^{-1} resolution). Infrared linear dichroism (IRLD) spectra obtained by polarization modulation (PM) were recorded with a Bomem MB-100 FTIR spectrometer using the optical setup and the two channel electronic processing previously described.⁶ A vertically polarized frequency-doubled Nd:YAG laser ($\lambda = 532 \text{ nm}$) was used to irradiate the sample. By using a proper calibration procedure,¹⁹ any PM-IRLD spectrum can be related quantitatively to the dichroic difference spectrum $\Delta A = A_{\parallel} - A_{\perp}$. Dichroic difference spectra were collected during the orientation (1 h) and relaxation (1 h) periods with a time resolution of 30 s.

Results

UV-Vis Spectroscopy. Figure 1 shows the absorption spectrum in the 300–700 nm region of a pMEA film before irradiation (A_0). This UV-vis spectrum displays a high-intensity $\pi \rightarrow \pi^*$ band in the UV (at 324 nm) and a low-intensity $n \rightarrow \pi^*$ band in the visible region (at 450 nm). These bands are characteristic of "azobenzene type molecules" in Rau's classification.¹² Considering the absorption spectra of *trans*- and *cis*-azobenzene,²⁰ the band at 324 nm corresponds essentially to the absorption of the *trans* isomers while the band at 450 nm is mainly due to the absorption of the *cis* isomers. Indeed, in the former case the ratio of the molar

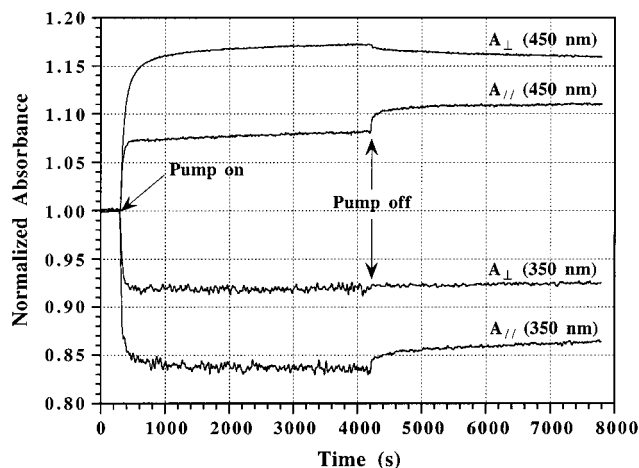


Figure 2. Time dependence of the normalized perpendicular and parallel absorbances at 350 and 450 nm of a pMEA film during the orientation (laser on) and relaxation (laser off) periods ($I_{\text{pump}} = 10 \text{ mW/cm}^2$).

absorption coefficient of the cis and trans isomers, ϵ_c/ϵ_t , is equal to 0.05 whereas in the latter case this ratio is equal to 2.8. However, the weak absorption observed at 450 nm in the A_0 spectrum of pMEA is essentially due to the intrinsic absorption of the trans isomers and also to a small amount (about 2%) of cis isomers which is estimated to be present in the polymer film in the photostationary state at room temperature.¹⁶ Before irradiation, the isotropy of each film was verified by measuring their polarized absorbances. After irradiation with linearly polarized light ($\lambda = 488 \text{ nm}$, $I_{\text{pump}} = 10 \text{ mW/cm}^2$) and relaxation period in the dark for 1200 s, significant absorbance variations in the parallel (A_{\parallel}) and perpendicular (A_{\perp}) directions for both the 324 and 450 nm bands were observed (Figure 1). The parallel and perpendicular absorbances corresponding to the trans isomers (324 nm) decrease while those of the cis isomers (450 nm) increase, indicating that the pump laser has induced trans–cis isomerization.

Typical perpendicular and parallel absorbance variations at 350 and 450 nm of a pMEA film during the irradiation and the relaxation periods are shown in Figure 2. The kinetic measurements for the trans isomer band have been performed at 350 nm because of the very low intensity of the probe light at 324 nm. To compare the time dependence of the polarized spectra, we have used the normalized absorbances obtained by dividing A_{\parallel} and A_{\perp} by the absorbance of the film before irradiation, A_0 . When the laser is turned on, the polarized absorbances at 350 nm decrease rapidly and remain constant after about 100 s. The fast decrease of the two polarized absorbances is essentially due to the selective optical pumping and transformation from the trans to cis isomers, which produce an angular hole burning (AHB) in the angular distribution of the trans isomers. Then, the constant values of the A_{\parallel} and A_{\perp} components indicate that a photostationary state is reached due to the competing processes of the direct trans–cis and the reverse cis–trans photoisomerizations. In contrast, the polarized absorbances of the 450 nm band increase strongly during the first 100 s of irradiation and very slightly afterward. This behavior confirms that the optical pumping produces cis isomers. When the laser is turned off, the parallel absorbances at 350 and 450 nm increase, mainly in the first few seconds and very slightly after 40 s. This behavior is essentially due to

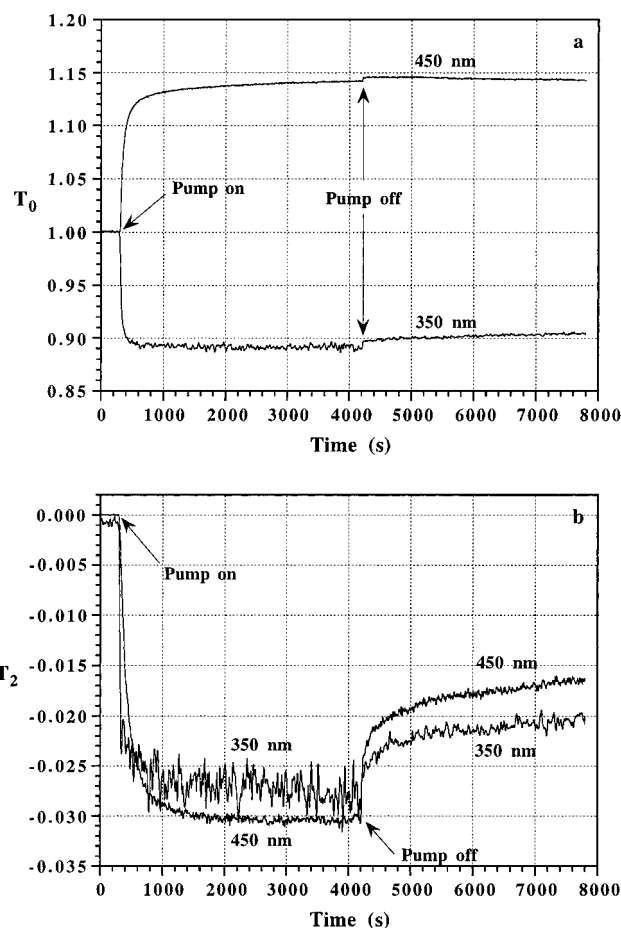


Figure 3. Time dependence of (a) the normalized average absorbance (T_0) and (b) the normalized linear dichroism (T_2) for the electronic transitions at 350 and 450 nm of a pMEA film during the orientation (laser on) and relaxation (laser off) periods ($I_{\text{pump}} = 10 \text{ mW/cm}^2$).

the angular redistribution (AR) of trans and cis isomers according to their abilities to rotate by thermal random interactions. Indeed, this process becomes efficient as soon as the direct and reverse optical pumping are stopped. Concurrently, another consequence of the AR process is the slight decrease of the perpendicular absorbances at 350 and 450 nm.

As previously mentioned,^{7–11} more quantitative information can be obtained by calculating the normalized average absorbance ($T_0 = (2A_{\perp} + A_{\parallel})/3A_0$) and the normalized linear dichroism ($T_2 = (A_{\parallel} - A_{\perp})/3A_0$). The time dependence of the T_0 parameter at 350 and 450 nm is shown in Figure 3a. When the writing laser is turned on, T_0 decreases at 350 nm during the first 10 s and reaches a plateau value (≈ 0.89) which is characteristic of a photostationary state. In contrast, T_0 at 450 nm increases and reaches a value of about 1.14. The value of the normalized average absorbance at the photostationary state is essentially related to the cis isomer population which can be estimated using the Fischer approach,²¹ as later discussed. When the laser is turned off, T_0 relaxes (increasing at 350 nm and decreasing at 450 nm) slightly and very slowly. These T_0 kinetics during the relaxation period are mainly governed by the thermal cis–trans back-relaxation and consequently by the cis lifetime. The very slow variation of T_0 indicates that the cis lifetime is quite large for this azopolymer (more than several hours).

The time dependence of the T_2 parameter at 350 and 450 nm is shown in Figure 3b. The T_2 parameter at 350 nm is essentially representative of the trans isomers since the cis isomers absorb very little at this wavelength. When the laser is turned on, T_2 decreases strongly for the first few minutes and reaches a value of -0.028 after 1 h of irradiation. When the laser is turned off, the system relaxes as shown by the increase of T_2 value, but the initial isotropy is never reached under our experimental conditions. (The value of T_2 is equal to -0.020 after 1 h of relaxation.) During the writing period, the AR contribution is superimposed to the AHB process, while the relaxation period is mainly governed by the AR of the trans isomers. The negative value of T_2 indicates that the transition moment of the electronic absorption is rather perpendicular to the laser polarization direction. Since the direction of the transition moment of the trans isomers is nearly along the long molecular axis of the MEA groups, the linearly polarized laser light induces an orientation of the chromophores in the perpendicular direction. On the other hand, the understanding of the time dependence of the normalized linear dichroism at 450 nm is not straightforward, since T_2 is representative of both the trans and cis isomers at this wavelength. The photoinduced orientation is apparently larger (-0.030) than that obtained for the only trans isomers, but the relaxation is more important since the value of T_2 is equal to -0.016 after 1 h of relaxation. Since the 450 nm band is essentially due to the cis species, the values obtained for T_2 during the irradiation indicate that the orientation distribution of the cis isomers must be considered as anisotropic.

When the pMEA film is irradiated with a circularly polarized light, the behavior of T_0 at 350 and 450 nm (during the orientation and relaxation periods) is similar to that reported on Figure 3a. However, the value of T_0 at the photostationary state is different and equal to 0.85 at 350 nm and to 1.24 at 450 nm. Moreover, we have checked that no normalized linear dichroism is induced under these experimental conditions. This is obviously an expected result since the laser displays no preferential polarization in the plane of the films.

Infrared Spectroscopy. The infrared spectrum in the $1350\text{--}1650\text{ cm}^{-1}$ region of a pMEA film recorded before irradiation (A_0) is reported in Figure 4a. The band due to the $\nu(\text{N}=\text{N})$ stretching vibration of the trans isomers appears at 1446 cm^{-1} whereas bands associated with the $\nu(\text{C}=\text{C})$ stretching vibrations of the phenyl rings are located at 1485, 1501, 1582, and 1604 cm^{-1} .^{22–25} The infrared spectrum of the same sample irradiated during 1 h, $A(t)$, with a linearly polarized light ($\lambda = 488\text{ nm}$, $I_{\text{pump}} = 10\text{ mW/cm}^2$) is also shown in Figure 4a (dashed line). The intensity of all the absorption bands decreases very slightly, except in the $1500\text{--}1530\text{ cm}^{-1}$ region where the absorbance of the irradiated film increases. To reveal the modifications induced by the irradiation, the difference infrared spectrum $A(t) - A_0$ was calculated, as shown in Figure 4b. Most of the absorption bands in the difference spectrum exhibits a dispersion shape, except for the strong positive band at 1515 cm^{-1} , which can be assigned to the $\text{N}=\text{N}$ stretching vibration of the cis species.^{22–25} The negative components of the dispersion bands are located at the same wavenumbers of the band maxima observed in Figure 3a; they can thus be explained by the loss of trans isomers in the plane of the film during irradiation. On

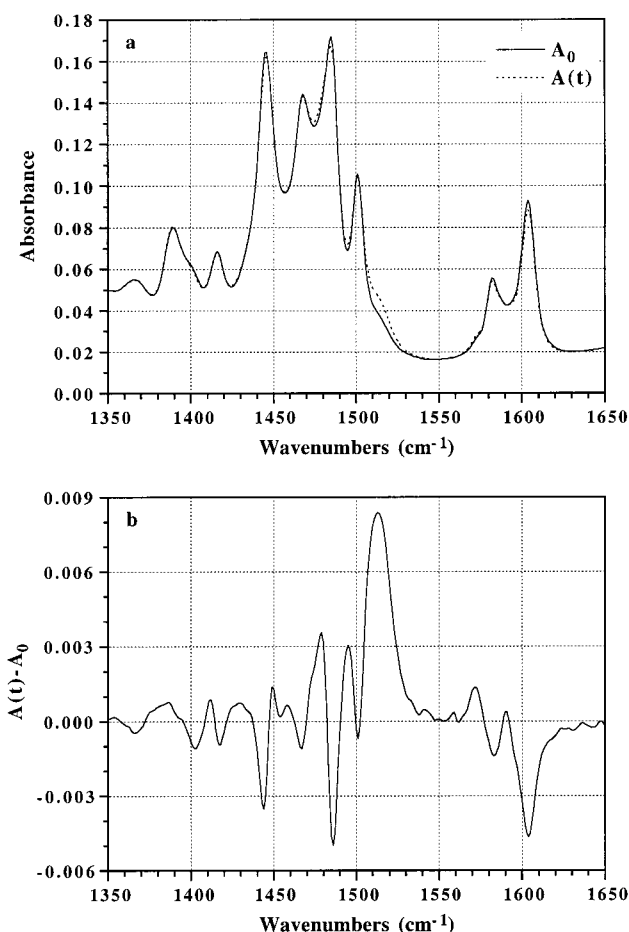


Figure 4. (a) Absorbance spectra in the infrared region between 1350 and 1650 cm^{-1} of a pMEA film before irradiation (solid line) and after 1 h of irradiation with a linearly polarized light (dashed line). (b) Difference absorbance spectrum of a pMEA film.

the other hand, the weak positive components of the dispersion bands are likely due to absorption of the cis isomers at lower wavenumbers. It is noteworthy that a similar difference spectrum is obtained when the polymer film is irradiated with circularly polarized light. Thus, the kinetics of photoinduced production and disappearance of the cis isomers can be followed by measuring the time dependence of the 1515 cm^{-1} band in the difference spectrum during the orientation and relaxation periods, as shown in Figure 5. These measurements were performed over a very long period, for 20 h with the pump off, to study in detail the thermal cis–trans back-relaxation process. Indeed, the relaxation curve of the absorbance of the 1515 cm^{-1} band can be very well fitted by a monoexponential function. Such a simple approach allows us to estimate the lifetime of the cis isomers, τ_c , corresponding to a decay of $1/e$ of the initial value, equal to about 12 h. This indicates that the thermal cis–trans back-relaxation process is very slow in the pMEA polymer and is not very sensitive to the distribution of the free volume cavities.

The PM-IRLD spectrum in the 1350 and 1650 cm^{-1} region recorded on a pMEA film irradiated for approximately 1 h with a linearly polarized light is shown in Figure 6. It is remarkable that the signal-to-noise ratio of this difference spectrum is very good, even though the largest ΔA value is only -0.008 . The bands appear upward or downward the baseline depending on

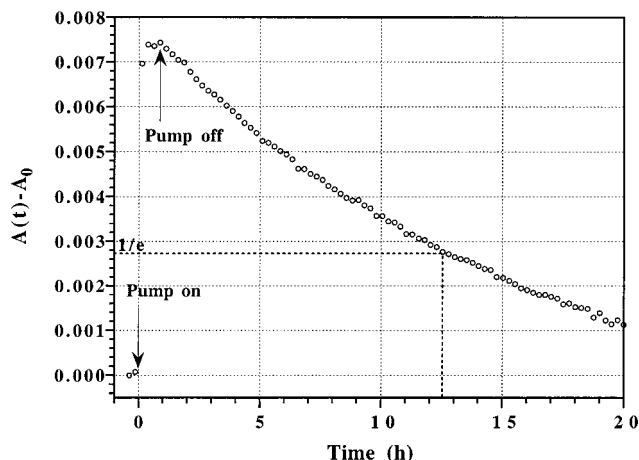


Figure 5. Time dependence of the absorbance of the band due to the N=N stretching vibration of the cis isomers at 1515 cm^{-1} during 1 h of irradiation with linearly polarized light ($\lambda = 488 \text{ nm}$, $I_{\text{pump}} = 10 \text{ mW/cm}^2$) and 20 h of relaxation (laser off).

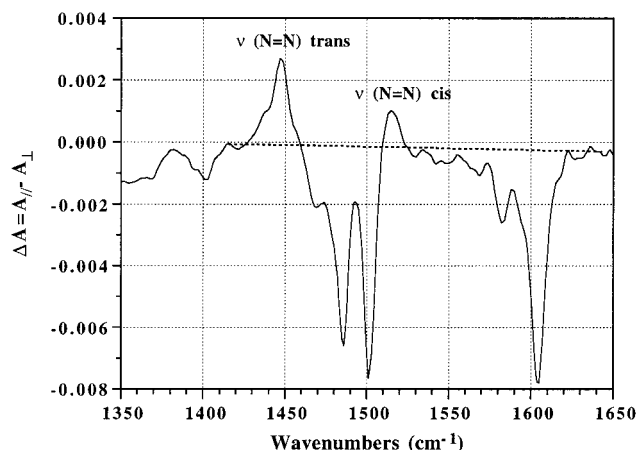


Figure 6. PM-IRLD spectrum between 1350 and 1650 cm^{-1} of a pMEA film after 1 h of irradiation with a linearly polarized light ($\lambda = 532 \text{ nm}$, $I_{\text{pump}} = 10 \text{ mW/cm}^2$). The dashed line represents the baseline used to calculate the intensity of the 1446, 1515, and 1604 cm^{-1} bands.

the orientation of the transition dipole moment of the considered vibration with respect to the laser polarization direction. Thus, the positive values of the 1446 and 1515 cm^{-1} bands indicate that the transition dipole moments of the $\nu(\text{N}=\text{N})$ stretching vibrations of the trans and cis isomers orient rather parallel to the laser polarization direction. Likewise, the negative values of the 1485, 1501, 1582, and 1604 cm^{-1} bands indicate that the transition dipole moments of the $\nu(\text{C}=\text{C})$ stretching vibrations of the phenyl rings are preferentially oriented perpendicular to the laser polarization direction. Since the direction of the transition dipole moments of the latter bands is nearly along the long molecular axis of the MEA groups, the linearly polarized laser light induces a perpendicular orientation of the chromophores, as already concluded from visible spectroscopic measurements.

To allow a quantitative comparison of the time dependence of the different bands, the normalized linear dichroism T_2 has been calculated for the most important bands. Figure 7a shows the time dependence of T_2 for the 1446 and 1604 cm^{-1} bands during the orientation and relaxation periods. The T_2 variation of the 1604 cm^{-1} band looks like that obtained from UV-vis mea-

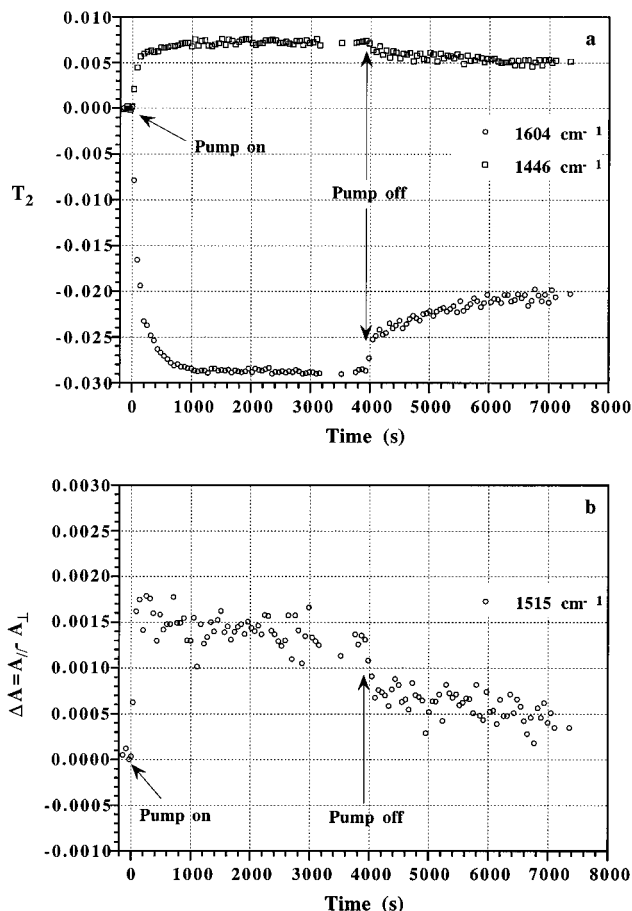


Figure 7. Time dependence of (a) the normalized linear dichroism (T_2) and (b) the dichroic difference ΔA for several infrared bands of a pMEA film during the orientation (laser on) and relaxation (laser off) periods ($\lambda = 532 \text{ nm}$, $I_{\text{pump}} = 10 \text{ mW/cm}^2$).

surements at 350 nm (see Figure 3b). The maximum value obtained after 1 h of irradiation is about -0.029 . After 1 h of relaxation, the normalized linear dichroism increases up to -0.020 . Similar values (unshown results) have been obtained for the 1501 cm^{-1} band while the 1485 and 1582 cm^{-1} bands exhibited a lower dichroism. Finally, the time dependence of the band associated with the $\nu(\text{N}=\text{N})$ stretching vibration of the cis isomers (at 1515 cm^{-1}) is reported in Figure 7b. Since it was not possible to measure the absorbance of the cis isomers before the sample irradiation, only the dichroic difference has been plotted during the orientation and relaxation periods. When the laser is turned on, the dichroic difference rapidly increases and slightly decreases after few minutes. This result confirms that the orientation distribution of the cis isomers is anisotropic. The positive value of dichroic difference indicates that the transition dipole moment of the $\nu(\text{N}=\text{N})$ stretching vibration of the cis isomers is preferentially oriented parallel to the laser polarization direction. When the laser is turned off, the dichroic difference decreases significantly, indicating a fast angular reorientation process of the cis isomers.

Discussion

Lifetime of the Cis Isomers. A band characteristic of the cis species has been observed at 1515 cm^{-1} in the infrared spectra of irradiated pMEA films. This is the first time that an infrared band characteristic of the cis isomer is observed for azopolymers. The time depen-

Table 1. Normalized Average Absorbance (T_0) and Normalized Linear Dichroism (T_2) Calculated at 350 and 450 nm after 1 h of Relaxation^a

	linear polarization		circular polarization	
	350 nm	450 nm	350 nm	450 nm
T_0^b	0.907 ± 0.016	1.140 ± 0.030	0.870 ± 0.010	1.203 ± 0.033
% cis	9.4 ± 1.6	7.8 ± 1.7	13.1 ± 1.0	11.3 ± 1.8
T_2^b	-0.0202 ± 0.0011	-0.0163 ± 0.0024	-0.0010 ± 0.0017	-0.0015 ± 0.0035

^a The films were first irradiated 1 h with a linearly or a circularly polarized light using an irradiance of 10 mW/cm² ($\lambda = 488$ nm).

^b Averages from five experiments.

dence during the relaxation period of the intensity of the 1515 cm⁻¹ band has allowed a direct determination of the lifetime of the cis isomers (τ_c). Values of 12.6 and 12.3 h have been measured for thin films irradiated with a linearly and a circularly polarized light, respectively. Thus, the rate constant γ ($\gamma = 1/\tau_c$) of the cis-trans thermal back relaxation is very slow at room temperature (about 2.2×10^{-5} s⁻¹) and can be neglected in any photoisomerization model of nonpolar azobenzene compounds. In other words, the cis state is stable within the relaxation period considered in this study (i.e., 1 h). This result explains the very weak variation of the normalized average absorbance at 350 and 450 nm observed during the relaxation period.

Cis Isomer Fraction. The cis isomer fraction, f_{cis} , can be easily determined, at any wavelength λ , from the normalized average absorbance, T_0 , by the relation²¹

$$f_{\text{cis}} = \frac{1 - T_0}{1 - \epsilon_c/\epsilon_T} \quad (1)$$

where ϵ_c and ϵ_T are the molar absorption coefficients of cis and trans isomers, respectively, at a wavelength λ . Values of the molar absorption coefficients between 220 and 600 nm for *cis*- and *trans*-azobenzene dissolved in isooctane have been reported in the literature.²⁰ The ratio ϵ_c/ϵ_T is equal to 0.01 at 350 nm, to 2.8 at 450 nm, and to 2.1 at 488 nm. Assuming that these ratios can be applied to pMEA, the cis isomer fraction has been calculated using the normalized average absorbances measured at 350 and 450 nm after 1 h of relaxation. (The films were first irradiated with a linearly or a circularly polarized light.) As shown in Table 1, whatever the polarization state of the laser pump, the calculated f_{cis} fraction is slightly smaller at 450 nm. This result is certainly due to an underestimation of T_0 on account of the measurement of the absorbances at 450 nm (no baseline has been used) and of the residual amount of cis isomers already contained in the polymer film before irradiation. Moreover, the photoisomerization seems more efficient when using a circularly polarized light (13% of cis isomers after relaxation) than a linearly polarized light (9.5% of cis isomers after relaxation). Finally, it is noteworthy that during irradiation the cis isomer fractions are estimated to be equal to 0.15 and 0.11 for polymer films irradiated with a circularly and a linearly polarized light, respectively. This discrepancy could be partly due to the expected difference in the population of the cis isomers for the two states of polarization (see Appendix A) or, more likely, to the out-of-plane orientation of the chromophores produced by an irradiation with a circular polarized light. Indeed, the excess of chromophores oriented perpendicular to the surface of the film decreases the value of the normalized average absorbance T_0 and consequently increases the value of the cis isomer fraction, f_{cis} . However, the values measured on

pMEA film under irradiation can be compared with the f_{cis} value calculated for azobenzene.²⁰ Indeed, if the rate constant γ of the cis-trans thermal back-relaxation is assumed to be zero and if the polymer film is irradiated with a circularly polarized light (or unpolarized light), a simple hole-burning model taking into account the reverse cis-trans isomerization predicts that the cis isomer fraction is given, at the photostationary state, by (see the Appendix)

$$f_{\text{cis}} = 1 - \frac{\bar{\sigma}_c \phi_{\text{CT}}}{\bar{\sigma}_c \phi_{\text{CT}} + \bar{\sigma}_T \phi_{\text{TC}}} \quad (2)$$

where $\bar{\sigma}_T$ ($\bar{\sigma}_c$) is the average absorption cross section of trans (cis) isomers at the wavelength of the pump laser (488 nm), and ϕ_{CT} (ϕ_{TC}) is the quantum yield of the direct trans-cis (reverse cis-trans) photoisomerization. Considering the values of the molar absorption coefficients of cis and trans azobenzene ($\bar{\sigma}_c/\bar{\sigma}_T = \epsilon_c/\epsilon_T = 2.1$ at 488 nm) and the quantum yields of photoisomerization ($\phi_{\text{CT}}/\phi_{\text{TC}} \approx 2$ at 488 nm),²⁰ a maximum f_{cis} value of 0.19 is obtained for azobenzene solutions irradiated at 488 nm. The somewhat weaker values obtained for pMEA films are certainly due to a matrix effect (i.e., free volume cage). Indeed, only a fraction of the chromophores participate to the photoisomerization processes in a polymer matrix. This behavior has been already discussed in the literature.²⁶

Anisotropy of the Trans Isomers. UV-vis and infrared experiments show a photoinduced orientation of pMEA when the polymer film is irradiated with a linearly polarized light. Nevertheless, the maximum value of the normalized linear dichroism, T_2 , is relatively weak and equal to -0.028 after 1 h of irradiation. This indicates that the orientation effects in pMEA are definitely weaker than those obtained using similar experimental conditions of irradiation on azopolymers containing 4-amino-4'-nitro-substituted azobenzene groups.⁶⁻⁸ Indeed, in pDR1M polymer films, a larger value of T_2 (equal to -0.09) was obtained after 1 h of irradiation under similar conditions. These results are in agreement with birefringent measurements performed on the same systems¹⁸ and can be explained by a theoretical model of photoisomerization.^{7,9-11} In such a model, whatever are the reverse pumping rate and the rate constant of the cis-trans thermal back-relaxation, the photostationary order parameter $\langle P_2(\cos \theta) \rangle = T_2/T_0$ is given by the relation

$$\langle P_2(\cos \theta) \rangle = \frac{-2I/15}{\Gamma_2 + 11I/21} \quad (3)$$

where $I = I_{\text{pump}}\Phi_{\text{TC}}\bar{\sigma}_T$ represents the direct pumping rate and Γ_2 represents the rotational diffusion constant of the trans species. Equation 3 shows that the absolute value of the order parameter increases when the direct pumping rate increases. Since the trans absorption cross

section σ_T of pMEA is smaller than that of pDR1M, this model predicts weaker photoinduced orientation effects in pMEA.

Another interesting point concerns the time dependence of the band associated with the $\nu(\text{N}=\text{N})$ stretching vibration of the trans isomers. This band, located at 1446 cm^{-1} for pMEA, displays positive values of T_2 during the orientation and relaxation periods. In contrast, for azopolymers containing 4-amino-4'-nitro-substituted azobenzene groups such as pDR1M, this band was located at 1385 cm^{-1} , and its T_2 negative value was slightly weaker than those obtained for the bands associated with the $\nu(\text{C}=\text{C})$ stretching vibrations. Assuming an uniaxial orientation of the chromophore groups, the angle α between the transition moments of the $\nu(\text{N}=\text{N})$ and $\nu(\text{C}=\text{C})$ stretching vibrations can be calculated using the Legendre polynomials addition theorem: $P_2(\nu(\text{N}=\text{N})) = P_2(\cos \alpha) P_2(\nu(\text{C}=\text{C}))$. This angle was estimated to $\approx 20^\circ$ for pDR1M, indicating that the $\nu(\text{N}=\text{N})$ stretching vibration was strongly coupled with the ϕ -N stretching vibration, because of the strong electron delocalization along such 4,4'-substituted azobenzene molecules in their trans configuration. In contrast, this angle is calculated close to 65° for pMEA films: this demonstrates that the higher frequency 1446 cm^{-1} band is now due to a pure or uncoupled $\text{N}=\text{N}$ stretching vibration.

Anisotropy of the Cis Isomers. UV-vis and infrared experiments clearly indicate that the orientation distribution of the cis isomers is not isotropic in the pMEA films under laser irradiation by a linearly polarized light. The normalized linear dichroism of the 350 and 450 nm absorptions shows that the transition moments of both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands are preferentially oriented perpendicular to the laser polarization direction (see Figure 3). Since the transition moment of the $\pi \rightarrow \pi^*$ band is rather along the long molecular axis of the trans isomers, we can conclude that the chromophores are preferentially oriented perpendicular to the laser polarization direction. This result is corroborated by the normalized linear dichroism measured in infrared experiments on the $\nu(\text{C}=\text{C})$ stretching vibrations of the phenyl rings. However, it is not straightforward to draw quantitative information about the orientation mechanism of the cis isomers because (i) it is difficult to define a director axis in this isomer and (ii) the $n \rightarrow \pi^*$ band corresponds to an absorption in both cis and trans isomers. In fact, only the infrared linear dichroism of the $\nu(\text{N}=\text{N})$ stretching vibration provides clear information on the orientation of the cis isomers. During the irradiation, the $\text{N}=\text{N}$ bonds of cis isomers are preferentially oriented parallel to the laser polarization direction. After 1 h of relaxation, the fraction of remaining linear dichroism is 30% for cis isomers while it is 70% for trans isomers. This result can be understood from geometrical arguments: the cis isomers relax more easily in surrounding cavities of the polymer matrix because they suffer weaker constraints than trans isomers to reorient.

Conclusion

The photoinduced orientation of pMEA has been studied by real-time UV-vis and infrared spectroscopies. Using these spectroscopic techniques, it was possible to follow the time dependence of the normalized average absorbance (T_0) and the normalized linear dichroism

(T_2) during both the orientation and relaxation periods. The photoinduced orientation of the trans isomers has been investigated from the time dependence of the 350 nm band. When the polymer films are irradiated with a linearly polarized light, the chromophores are oriented preferentially perpendicular to the laser polarization direction. The normalized linear dichroism is relatively weak (≈ -0.03) and has been confirmed by the infrared linear dichroism of the phenyl ring vibrations. The cis isomer fraction has been estimated from the normalized average absorbance of the bands at 350 and 450 nm. Values of 0.15 and 0.11 have been calculated for thin films of pMEA irradiated with a circularly and a linearly polarized light at 488 nm, respectively. Moreover, the cis state has been characterized by infrared spectroscopy. Indeed, we have observed, for the first time in these azopolymers, a band at 1515 cm^{-1} characteristic of the cis isomers. The time dependence of its intensity during the relaxation period allows the determination of the lifetime of the cis isomers ($\approx 12\text{ h}$). Finally, the infrared linear dichroism measurements have provided evidences for the anisotropy of the cis isomers.

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Appendix A. Hole-Burning Model

If molecules do not rotate during the direct trans-cis and reverse cis-trans isomerizations and if we assume that the lifetime of excited levels is negligible, the dynamical equations for the population of the trans and cis isomers are

$$\frac{\partial n_T(\theta)}{\partial t} = -\phi_{TC} \text{Pr}_T(\theta) n_T(\theta) + \phi_{CT} \text{Pr}_C(\theta) n_C(\theta) + \gamma n_C(\theta) \quad (\text{A1})$$

and

$$n_T(\theta) + n_C(\theta) = \frac{N}{2} \quad \text{since} \quad \int_{-1}^{+1} \frac{N}{2} d(\cos \theta) = N \quad (\text{A2})$$

where ϕ_{TC} (ϕ_{CT}) is the quantum yield of the direct trans-cis (reverse cis-trans) isomerization, $\gamma = 1/\tau_c$ is the rate constant of the cis-trans thermal back-relaxation, N is the total molecular density of chromophores, and $\text{Pr}_T(\theta)$ ($\text{Pr}_C(\theta)$) is the probability of absorption of a photon by a molecule in the trans (cis) state.

For a linearly polarized light, the probability of absorption is given by

$$\text{Pr}_J(\theta) = I_{\text{pump}} \bar{\sigma}_J [1 + 2e_J P_2(\cos \theta)] \quad (\text{A3})$$

and, for a circularly polarized light, by

$$\text{Pr}_J(\theta) = I_{\text{pump}} \bar{\sigma}_J \quad (\text{A4})$$

where $\bar{\sigma}_J$ and e_J are the average cross section and the molecular anisotropy, respectively, of trans ($J = T$) and cis ($J = C$) isomers.

If the rate constant γ is assumed to be zero and the molecular anisotropy of cis state (e_C) is assumed to be much smaller than 1.0, the population of the trans

isomers is given at the photostationary state ($\partial n_T(\theta)/\partial t = 0$) by the following relations:

$$n_T(\theta, \infty) = \frac{N \left(\frac{\phi_{CT} \bar{\sigma}_C}{\phi_{CT} \bar{\sigma}_C + \phi_{TC} \bar{\sigma}_T [1 + 2e_T P_2(\cos \theta)]} \right)}{2} \quad (\text{A5})$$

for a linearly polarized light and

$$n_T(\theta, \infty) = \frac{N \left(\frac{\phi_{CT} \bar{\sigma}_C}{\phi_{CT} \bar{\sigma}_C + \phi_{TC} \bar{\sigma}_T} \right)}{2} \quad (\text{A6})$$

when using a circularly polarized light.

Following eq A2, one obtains straightforwardly $n_C(\theta, \infty)$ and, therefore, the cis isomer fraction, $f_{cis} = n_C(\theta, \infty)/(N/2)$.

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