Room-Temperature Photoinduced Poling and Thermal Poling of a Rigid Main-Chain Polymer with Polar Azo Dyes in the Side Chain

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We report on room-temperature photoinduced poling (PIP) and thermal poling (TP) of a new polyester with rigid main chain and disperse red 1 (DR1) molecules in the side chain (DR1–polyester). The experimental findings are discussed within the framework of our phenomenological theory of the PIP process. The molecular order created by TP is more efficient and more stable than that created by PIP and shows that PIP cannot induce a conformational change in the rigid main chains of this DR1–polyester. This may originate from the importance of the free volume in the DR1–polyester or from the inability of the main chains to move with the photoinduced movement of the azo chromophores they are covalently linked to. The evolution of the polar orientation during PIP is probed by the electrooptic Pockels effect using an attenuated total reflection setup.

Introduction

The development of information processing systems that use photons instead of electrons as the carrier signal stimulated the current extensive investigations of the linear and nonlinear-optical properties of organic molecules and molecular crystals. Amorphous polymers that incorporate nonlinear-optical molecules with high nonlinear-optical response (hyperpolarizabilities) are particularly interesting for their attractive properties which facilitates their use in practical devices.[1–4] Films of poled polymeric materials take advantage of the high optical quality of polymer glasses and allow the use of organic molecules presenting high molecular hyperpolarizabilities. For creation of second-order susceptibility required for second-harmonic generation or electrooptic modulation, it is necessary to induce a polar orientation of molecules with high second-order hyperpolarizabilities. This is usually performed by poling at elevated temperatures in a process by which the polymer is heated up above its glass transition temperature (T_g) to allow a free rotation of the polar molecules which then can be aligned in the presence of an external dc electric field. When the polymer film is cooled with the electric field applied to room temperature, the polar orientation of the molecules is preserved after the removal of the poling dc field. Poling at room temperature using CO_2 as a swelling agent was reported by Barry and Soane.[5]

Another method of poling polymeric films containing polar azo dyes at room temperature was reported recently.[6–12] This new method of poling makes use of the photoisomerization of azobenzene derivatives. By application of a dc electric field at room temperature during the photoisomerization process, the centrosymmetry is broken and an important and a stable $\chi^{(2)}$ signal (electrooptic Pockels and second harmonic) was obtained using a polymer film of poly(methyl methacrylate) (PMMA) functionnalized by disperse red 1(DR1) chromophores.[8] This implies that the polymer chains are flexible and do not hinder the motion of the DR1 chromophores they are covalently linked to. This conformational change of the polymer main chains is induced by the photoisomerization reaction and provides the azo dye molecules with a certain mobility, which makes a polar orientation in the direction of the dc field possible. This can be considered as a change of the local viscosity through a change in the free volume available to the molecules during the photoisomerization reaction, since the poling field alone does not induce any orientation at room temperature: the mobility of the nonlinear-optical chromophores is very much reduced and there is nearly no spontaneous angular relaxation. In contrast to TP, PIP presents two major advantages for practical applications: first, it eliminates the heating which is necessary in TP, and second it allows the drawing of patterns of oriented molecules. This could

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be useful for producing electrooptical integrated devices without complex electrode structures.

The isomerization reaction of azobenzene derivatives is a light- or heat-induced interconversion of their cis and trans geometric isomers. The thermal isomerization proceeds generally in the "cis → trans" direction because the trans form is generally more stable than the cis form (50 kJ mol^{-1} in the case of azobenzenes),[13] light induces both "trans → cis" and "cis → trans" isomerizations. When the isomeric forms absorb a photon, they are raised to electronically exited states from which a nonradiative decay brings them back to the ground state either in the trans form or in the cis form. Once the molecule is in the cis form, it recovers the trans form by either the back thermal reaction or the inverse photoisomerization cycle.

The photoisomerization of the push—pull azobenzene derivative DR1 occurs efficiently in PMMA thin films at room temperature,[14] the quantum yields of the direct and reverse photoisomerizations have been measured, and the absorption spectra for the thermally unstable cis form has been deduced.[15] Many publications deal with photoisomerization of azobenzene molecules in a polymeric environment.[16,17] As classified by Rau,[13] the DR1 molecule is a pseudo-stilbene type molecule which means that the high-energy $\pi-\pi^*$ transition is overlapping the low-energy $n-\pi^*$ transition and leads to a large structureless band in the trans isomer with an absorption maximum strongly dependent on the polarity of the host material which may be either a polymer or a solvent. Frequently the geometrical change of the azo molecules during the isomerization process leads to a loss of their initial orientation; anisotropy can then be induced in a system containing anisometrically shaped photosensitive molecules which are known to align perpendicular to the polarization of the irradiating light. The resulting anisotropy depends on the viscosity of the surrounding medium and can be negligible in low-viscosity solutions where the reorientation time of the molecules is very short and allows the thermal agitation to restore instantaneously the isotropy destroyed by the light. In azo dye doped polymeric films where the mobility of the guest molecules is appreciable, photo-isomerization leads to reversible polarization hologra-phy.[18] In azo dye functionalized polymeric films where the mobility of the azo chromophores is very much reduced, the photoisomerization creates a permanent alignment which may lead to writing erasing optical memories[19,20] or to permanent second-order nonlinear-optical effects at room temperature in the presence of a poling dc electric field.[7,8,21]

In contrast to flexible main-chain polymers, PIP of rigid main-chain polymers would be of a particular

interest since it may provide valuable information about the capability of the polymer main chains to hinder the movement of the azo dye chromophores induced by the photoisomerization reaction. Recently, the preparation of NLO-active rigid-rod main-chain polymers having NLO chromophores and long alkoxy side chains was reported.[22,23] Although the second-order nonlinear opti-cal susceptibility for those polymers were not so high, they showed a great deal of promise for the development of main-chain NLO polymers in that the materials retained alignment and activity for long periods of time. In our efforts to synthesize rigid main-chain NLO polymers having two-dimensional layered structure,[24] we prepared a rigid main-chain polyester having DR1 NLO chromophores and long alkoxy groups as side chains. It is well-known that the azo linkage is stable under polymerization conditions and the relatively large ground-state dipole moment of the chromophore assists orientation in the polymer by the applied electric field. Moreover the bathochromic shift induced by substitution with donor and acceptor groups facilitates resonance enhancement effects.[25,26] In this paper we report on PIP and TP of a new rigid main-chain polyester. The evolution of the induced polar order during PIP is probed with the electrooptic Pockels effect obtained by using an ATR setup. The polar order obtained by TP is studied and compared to that observed in the case of PIP. This provides valuable information about the coupling of the polymer main chains to the movement of the azo units induced by the photoisomerization reaction.

Experimental Section

Materials. The polymer used in this study was prepared by solution polymerization as shown in Figure 1a. The polymer structure is shown in Figure 1b. This polyester is a rigid main-chain aromatic copolyester containing only rigid aromatic segments and connecting ester bonds without any of flexible segments such as polymethylene or oxyethylene etc. in the main chain. The intrinsic viscosity of the polymer obtained from 1,1,2,2-tetrachloroethane (TCE) solution at 25 °C is 0.47 dL/g. Details of the polymer synthesis and char-acterization will be described elsewhere.[27] The glass transition temperature (T_g) obtained from differential scanning calorim-etry (DSC) at the heating rate of 10 °C/min was 42 °C. This polymer is a random copolymer, which means that the tere-phthaloyl and the 2,5-dihexadecylterephthaloyl comonomers are randomly distributed in the main chain. This random distribution of the comonomers can produce large amount of free volume in the polymer matrix.[28–30] Moreover the inclusion of the kink resorcinol unit in the main chain may hinder the packing of the polymer chains in solid state.[31] Both of these reasons may cause the low T_g of the present polymer.

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(a)

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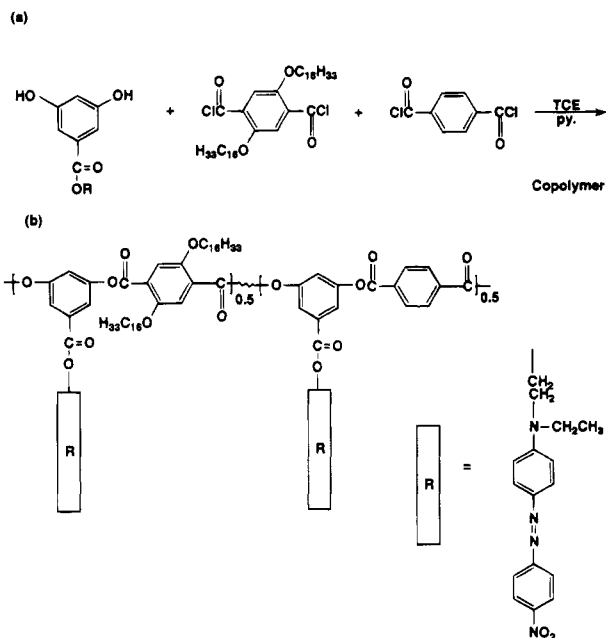
Figure 1. (a) Synthetic scheme and (b) structure of the polymer.

Figure 2. UV-visible spectra of (a) DR1 compound and (b) polymer in TCE solution.

Since this polymer is soluble in common organic solvents, optical-quality films can easily be prepared. All the polymer films for optical measurement were prepared by spin-casting techniques from TCE solution. Samples for ATR measurement were prepared in the following way. A 2–3 nm thick layer of chromium was evaporated on the cleaned glass substrate followed by 30–50 nm thick layer of gold as a lower electrode. Polymer films (1–2.5 μm) were spin-cast on the gold layer. These films were dried at 65 °C for 30–50 h using a vacuum oven to remove the last traces of solvent from the films. Finally, an upper gold layer of 100 nm thickness was evaporated on the polymeric film. The electrodes were contacted with silver paste and the film was poled appling dc voltage at certain temperature.

Electrooptic Measurements by the ATR Method.[9,33] For the electrooptic measurements by the ATR method,[33] the polymer films were deposited onto glass slides as described previously, and the gold layers, which acts as electrodes, were evaporated prior to and after the spin casting of the polymer films. The glass slide was put in optical contact with a prism through which a HeNe (632.8 nm) laser was reflected onto the sample. The power of the HeNe laser was reduced to a few microwatts in order to avoid any absorption from the sample, and our ATR and electrooptic modulation spectra showed perfect shapes (at 632.8 nm the absorption of the DR1 molecules is almost negligible as shown by the UV–vis aborption spectra in Figure 2, but the wave-guiding resonance condition enhances the energy inside the polymer film and may cause some absorption from the sample if the incident intensity is not enough reduced).[14] The prism and the detector were placed on a Θ-2Θ goniometer, and the reflectivity of the HeNe probe beam with transverse electric (TE) and transverse magnetic (TM) polarizations was studied for incidence angles ranging from 20° to 82° (see Figure 3a). Some of these fulfill the wave-guiding resonance condition, and dips occur in the reflectivity corresponding to TM- and TE-guided modes in the polymer film (Figure 3b). The experimental reflectivity curves are fitted by a computer programm which calculates theoretical reflectivities of layered media and gives, with a very good accuracy, the thickness (h) and the indexes of refraction n_x, n_y, and n_z in the three principal directions of the polymer film. x and y correspond to the principal directions in the plane of the film, and z is the normal to the sample.

When an external perturbation is applied to the polymer film, the ATR guided modes shift their angular positions, and
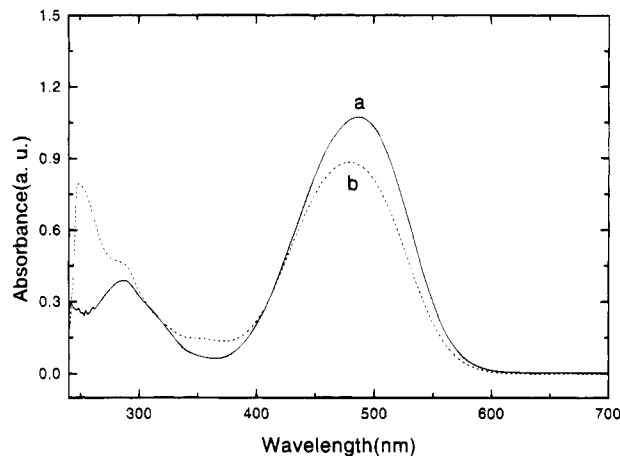
the reflectivity is modulated (Figure 3c). These angular shifts are very small in the case of electrooptic experiments: they correspond to refractive index variations on the order of 10^{-5}. One has then to modulate the measuring electric field at a low frequency Ω ($E = E_1 \cos \Omega t$) and to detect the modulated signal with lock-in amplifiers. The lock-in signals detected at the modulation frequency and its second harmonic give respectively the linear (or Pockels) and the quadratic (or Kerr) electrooptic effects. The amplitude of the modulation of the thickness and the refractive indexes is evaluated by a computer fit and allows the determination of Pockels (r) and Kerr (s) coefficients. These are related to the electrooptic susceptibilities by the following formula (eq 1 and 2). $\Delta n_i(\Omega)$ and

$$2\chi_{iiz}^{(2)} = -r_{iz}n_i^4 = 2n_i\Delta n_i(\Omega)(h/V_1) \qquad (1)$$

$$3\chi_{iizz}^{(3)} = -s_{iz}n_i^4 = 4n_i\Delta n_i(2\Omega)(h/V_1)^2 \qquad (2)$$

$\Delta n_i(2\Omega)$ are the index variations measured from the Ω and 2Ω lock-in modulated signals, respectively and i refers to x, y, and z. The piezoelectric effect and the electrostriction are estimated from the thickness modulation, and their contribution to the index variations is almost negligible in our material.

For PIP experiments the sample is irradiated by the green light of a frequency-doubled laser diode (532 nm; at this wavelength the absorption cross section allows a good penetration in the sample) through the prism and the gold layer as shown in Figure 3. The power of the pump beam incident on the sample is estimated to be 70 mW/cm², taking into account the reflection on the gold sample. The variations of $\chi^{(2)}$ during PIP are followed by setting the goniometer at a fixed angle of incidence corresponding to the TM mode at high incidence angles, which provides a high sensitivity to the n_z refractive index variations, and recording the signal modulated at Ω from the lock-in amplifier. When the sample is irradiated, the mode shifts its angular position and must be followed manually. This is not a very precise procedure, but it allows valuable information about the dynamics of the PIP process to be obtained. The recording of the whole set of TM and TE modes at a stationary state of the pumping or of the relaxation process gives a precise measurement of the electrooptic susceptibilities and the higher the number of the modes the better the precision.

Results and Discussion

Figures 4 and 5 show the evolution of the electrooptic Pockels coefficient r_{33} of our polymeric film (thickness $\sim$ 1.8 μm) during typical PIP cycles at room temperature. These curves were obtained as explained before by recording continuously the lock-in signal modulated at Ω near the largest incidence TM mode which gives the direct measurment of Δn_z. When the measuring ac

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(E_1) and poling dc (E_0) electric fields are applied simultaneously to the polymer film, the Δn_z (z is equivalent to 3) variation is given by (eq 3).

$$2n_z\Delta n_z(\Omega) = 2\chi_{333}^{(2)}(E_0 + E_1 \cos \Omega t) + 3\chi_{3333}^{(3)}(E_0 + E_1 \cos \Omega t)^2 = (2\chi_{333}^{(2)} + 6\chi_{3333}^{(3)}E_0)E_1 \cos \Omega t + {}^3/_2\chi_{3333}^{(3)}E_1^2 \cos 2\Omega t + \text{unmodulated terms} \quad (3)$$

In this case, the apparent r_{33} electrooptic coefficient given by the signal modulated at Ω contains a contribution from the electrooptic Kerr effect given by $\chi^{(3)}$. This can be measured easily using the signal modulated at 2Ω. At the time $t = 0$ where the sample is centrosymmetric ($\chi^{(2)} = 0$), the dc poling field E_0 is applied; then the Pockels effect appears rapidly and grows slowly in the long time range. The contribution of the Kerr effect $2E_0S_{33}$ ($3\chi_{3333}^{(3)} = 110 \times 10^{-21}$ m^2 V^{-2}) to the apparent Pockels coefficient is indicated by $2E_0S_{33}$ in Figures 4 and 5 and shows the existence of a large and appreciable pure $\chi^{(2)}$ signal above this level resulting from a polar orientation of the nonlinear-optical azo chromophores in the direction of the poling dc field. This is the electric field induced Pockels effect (EFIPE) which is the analogue of the electric field induced second harmonic (EFISH).[8] This indicates that the mobility of the majority of the chromophores is significant even at room temperature ("free molecules"), since they can rotate under the action of the dc poling field alone without heating. The onset and the decay of the EFIPE is fast in the short time range and indicates that the mobility of the "free molecules" is significant at room temperature. The slow effect observed at long times originates from molecules situated in a more viscous environment ("non-free" molecules). When the sample is illuminated with a pump beam linearly polarized in the y direction in the presence of the dc poling field, the electrooptic Pockels signal increased strongly. The polarization of the pumping light is very important for photoinduced anisotropy experiments where the molecules align perpendicular to the pump polarization, but it is not an important parameter for PIP because the molecules orient in the direction of the dc field. When the pump beam is switched off in the presence of the dc field, the $\chi^{(2)}$ signal decreases slightly and keeps an r_{33} value higher than that obtained with the dc field alone. When this is removed, the electrooptic Pockels signal drops rapidly but keeps an appreciable r_{33} value corresponding to 1.65 pm V^{-1}.

The macroscopic second-order susceptibility $\chi^{(2)}$, which describes the electrooptic Pockels effect and second harmonic generation, is related to the molecular second order hyperpolarizability β and the orientation of the nonlinear-optical molecules (eq 4). It is a good approximation to consider that the second order hyperpolarizability β has only one component, β_{aaa}, along the principal axis (a) of the molecule. This includes the local field factor. N is the density of the molecules. At the steady state of the EFIPE, the orientational distribution function is a Maxwell−Boltzmann function and all the order parameters (A_n, $n = 1, 2, 3, ...$) are given exactly

$$\chi_{333}^{(2)} = N\beta_{aaa}(3A_1 + 2A_3)/5$$

$$\chi_{113}^{(2)} = N\beta_{aaa}(A_1 - A_3)/5 \quad (4)$$
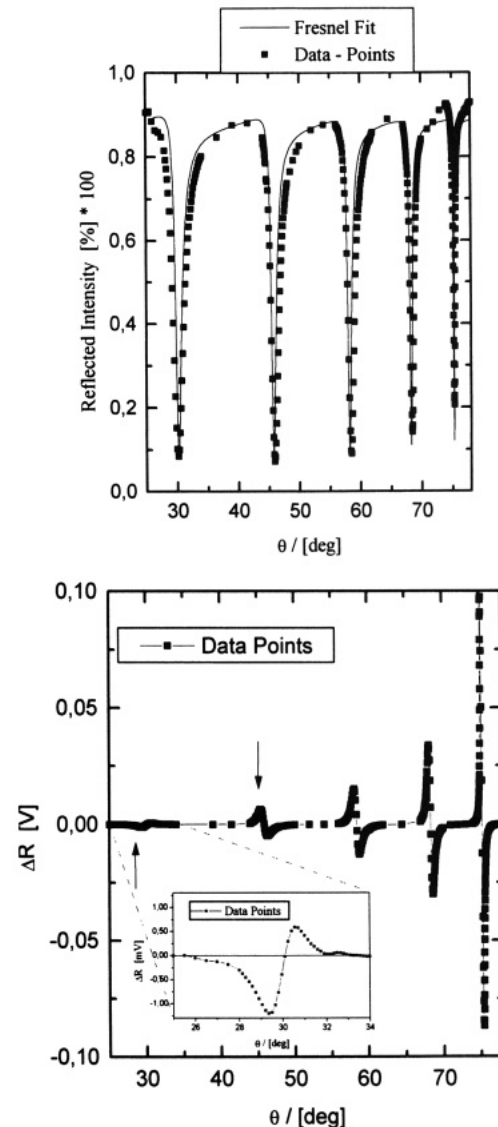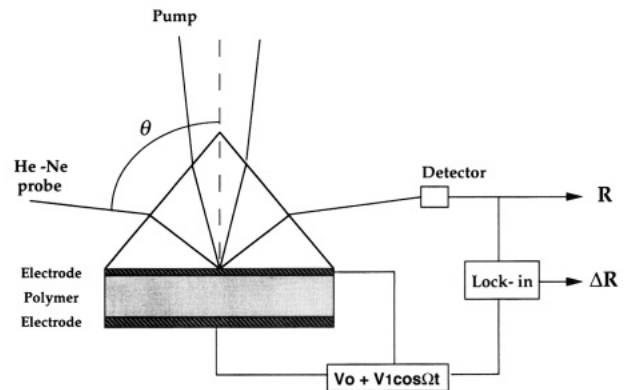
Figure 3. (a, top) ATR experimental setup and an example of the record of (b, middle) the reflectivity and (c, bottom) electrooptic modulation.

by the spherical modified Bessel functions and can be related to Langevin functions.[34,35] Using the following expression for the theoretical value of the first odd order parameter A_1 (eq 5) at the steady state of the EFIPE (this expression is an excellent approximation of the first order Langevin function for values of u up to 2 which

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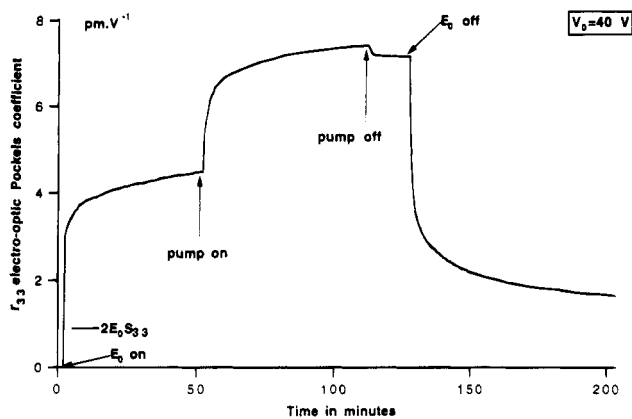
Figure 4. PIP of a DR1–polyester 1.8 μm thick film, with a 40 V poling voltage. The moments of turning this latter and the pumping light (70 mW/cm²) on and off are indicated by arrows. $2E_0S_{33}$ shows the estimated value of the Kerr effect contribution ($2E_0S_{33}$) to the apparent Pockels effect. The signal above this level characterizes a pure polar orientation of the azo chromophores.
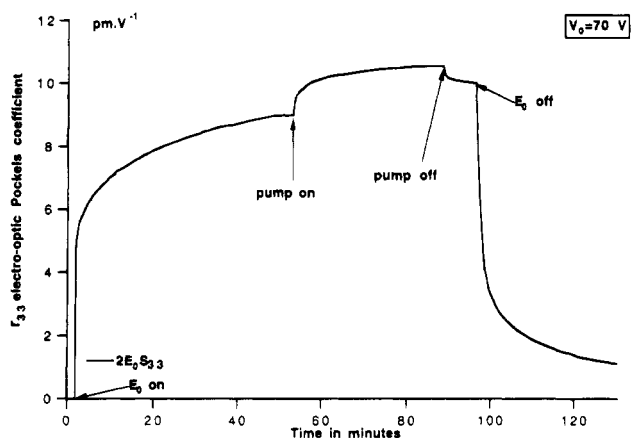
Figure 5. As in Figure 4, but with a 70 V poling voltage.

correspond to very high strength of the poling field[35]), we can compare our experimetal results with Maxwell–Boltzmann statistics.

$$A_1(u) = 5u/(15 + u^2) \quad \text{with} \quad u = \mu E/kT \quad (5)$$

With 298 K and 14.2 D as a values for the absolute temperature and the local field effect corrected ground-state dipole moment of the DR1 molecule,[36] we obtain for 40 and 70 V as a poling voltage, 0.236 and 0.413 for the parameter $\mu E/kT$ characterizing the balance between the thermal agitation and the alignment of the dipoles with the poling field. By inserting these values into eq 5, we find $r_{33}(70\text{ V})/r_{33}(40\text{ V})$ approximately equal to 1.75, which is not in very good agreement with the ratio (2.17) given by the experimental steady-state values obtained (at 50 min) with 70 and 40 V poling voltage. This difference (0.42) is probably due to the free volume distribution which leads to different magnitude of mobility for molecules situated at different polymer sites. The neglect of A_3 in the theoretical calculation of $r_{33}(70\text{ V})/r_{33}(40\text{ V})$ could not be a reason because it is almost zero for the above values of u.[35] With these assumptions we can see that the polar order is small as shown in eq 5 ($A_1 \sim 0.136$ for 70 V).

The PIP cycle performed on our copolymer shows a behavior quite similar to that obtained with DR1-doped PMMA thin films[7] and shows that the photoisomerization process allows a certain mobility to the "non-free" molecules since they can experience a polar orientation with the simultaneous application of the dc poling field. This can be seen as an enhancement of the mobility of the azo chromophores during the isomerization reaction and can be described theoretically as we will discuss later. Another important point in these experiments is that the photoinduced polar order (step induced by the pumping light at the steady state of the EFIPE: difference between the order obtained with the dc field alone and that obtained by combining the dc field and the pumping light) obtained with 70 V as a poling voltage is at least 2 times smaller than that obtained with 40 V as a poling voltage. This indicates that a certain fraction of the azo chromophores which cannot rotate under 40 V can rotate under the action of the 70 V poling voltage and demonstrates that the isomerization process lowers the threshold for the viscous polar orientation in the direction of the poling field. This change of the apparent viscosity during the photo-isomerization reaction can be introduced formally in a phenomenological theory[37,38] and can be described by a phase transition theory. In a forthcoming paper,[38] we present a detailed analysis of this phenomenon with detailed calculations and useful analytical solutions which describe both the steady state and the dynamics of the photoisomerization-induced polar order and its related anisotropy. The azo chromophores could experience a polar orientation in a hypothetical excited state where the mobility is less reduced than in the trans state. This state could be assigned with the cis lifetime because the lifetimes of all the other excited states are very short compared to the cis lifetime. Once the mobility of the molecules is enhanced in this state, polar orientation occurs naturally by a rotational diffusion in the presence of an external torque exerted by the dc field. The most important condition for building a polar orientation in the trans state is retaining memory (even partial) of the polar orientation during the "cis → trans" back isomerization cycles (thermal and photoinduced). One could also imagine a polar orientation during these back reactions, but the relative magnitude of the reorientation time which mostly depends on the viscosity and the time of the optical transition seems to allow only a weak polar orientation. In other words, the azo chromophores do not have enough time in the optical transitions to experience an efficient polar orientation. With these assumptions we can reproduce very well all the steps of the PIP cycle with a real physical insight of the phenomena concerning PIP.[37,38] The final magnitude of the photoinduced polar order in the trans state relaxes according to the thermal diffusion theory.[37,38] It is stable when the mobility in the trans state is very much reduced as in the case of PMMA–DR1 copolymer.[8] The most important factor for practical devices is the final magnitude of the $\chi^{(2)}$ produced by PIP. We show as a first approximation, that this is proportional to the strength of the poling field.

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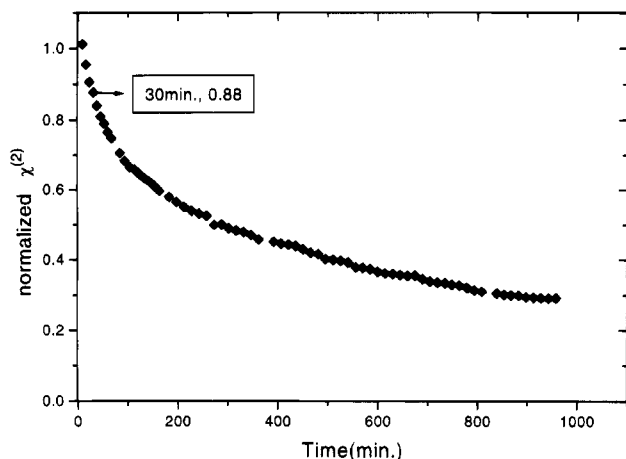
Figure 6. Relaxation of the polar order after thermal poling monitored by Pockels effect from the ATR electrooptic modulation.

The difference $(T-T_g)$ between the operating temperature T and the T_g of the polymer is a very important factor in the relaxation processes which occur in polymers.[1] Indeed, for the same operating temperature T, NLO chromophores will present more mobility in a low-T_g polymer than they would present in a high-T_g polymer. This would lead to a more rapid relaxation in a low-T_g polymer as we can remark from the behavior of the present DR1—polyester. This shows an appreciable relaxation (Figures 4—6) contrarily to the DR1—PMMA where the induced order was stable over several months.[8] Furthermore the appreciable mobility of the NLO chromophores in a low-T_g polymer leads to a more efficient alignment with an external dc field. This is also exhibited by the present DR1—polyester where the induced order is characterized by a r_{33} value approximately equal to 11 pm V^{-1}, while the r_{33} value obtained in a DR1—PMMA copolymer in similar conditions and similar azo dye density was[8] about 5 pm V^{-1}.

Next we discuss the thermal poling results and compare them with the PIP experiments. Both TP and PIP experiments were performed on the DR1—polyester. We poled a 2.4 μm thick film of the copolymer following the TP procedure at 60 °C with 79 V/μm poling voltage. The r_{33} electrooptic Pockel coefficient obtained just after the TP was 15.5 pm V^{-1} and is much higher than the r_{33} coefficient obtained just after PIP when the dc field is removed (1.65 pm V^{-1}). The relaxation process after

TP shows the behavior reported in Figure 6 where we can see that 30 min after removing the poling dc field, only 10% of the initial signal obtained just after removing the dc field (15.5 pm/V) disappears. In the case of PIP, the majority of the signal drops rapidly when the dc field is removed. Keeping in mind that the copolymer used in this study has rigid main chains, the data suggest that the thermal poling process performed above T_g of the polymer affects the conformation of the main chains and thus can change their orientation, but the PIP affected only the orientation of the azo chromophores through the free volume of the polymer matrix without an appreciable effect on the main-chain motion. This may originate from the rigidity of the polymer main chains which hinder the photoinduced motion of the azo dye chromophores. This is in contrast to the results we obtained with a PMMA—DR1 copolymer because the PMMA main chains are flexible and do not hinder the photoinduced motion of the covalently linked azo chromophores. This may originate from a very much reduced free volume in the DR1—PMMA copolymer in which the DR1 chromophores can produce only a change in the conformation of the polymer main chains during the photoisomerization reaction in order to experience an alignment. The free-volume distribution seems to be very important for producing a stable polar order either by TP or by PIP, as we can remark from the above behavior of the present DR1—polyester. These results seem to indicate that PIP is more efficient when the azo dye chromophores are covalently linked to polymers with flexible main chains and reduced free volume such as PMMA.

Conclusion

The data presented in this paper suggest that further PIP and TP investigations in a high-T_g rigid main-chain polymer should be considered. This could provide valuable information about the ability of the photoisomerization reaction to change the conformation of the stiff main chains through the photoinduced movement of the azo chromophores.