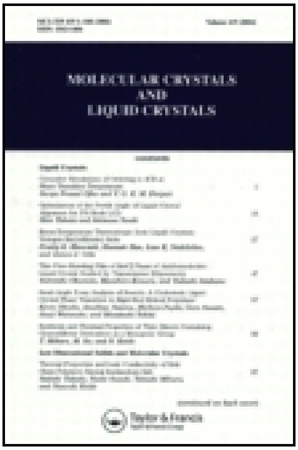


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromism and Photoassisted Poling in Polyimides

Jerome Chauvin [a], Jacques A. Delaire [a] & Keitaro Nakatani [a]

[a] PPSM, UMR 8531 of CNRS, Ecole Normale Supérieure de Cachan, 61 avenue du President Wilson, 94235, CACHAN, Cedex, FRANCE

To cite this article: Jerome Chauvin, Jacques A. Delaire & Keitaro Nakatani (2000): Photochromism and Photoassisted Poling in Polyimides, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 353:1, 471-483

To link to this article: http://dx.doi.org/10.1080/10587250008025682

Mol. Cryst. and Liq. Cryst., 2000, Vol. 353, pp. 471-483
Reprints available directly from the publisher
Photocopying permitted by license only

Photochromism and Photoassisted Poling in Polyimides

JEROME CHAUVIN, JACQUES A. DELAIRE and
KEITARO NAKATANI

PPSM, UMR 8531 of CNRS, Ecole Normale Supérieure de Cachan, 61 avenue du President Wilson, 94235 CACHAN Cedex, FRANCE

Soluble side-chain polyimides bearing Disperse Red One groups (PI-DR1) have been synthesized and characterised for second order nonlinear optics (second order NLO). Thermally oriented samples show a very good orientational stability. In order to overcome the degradation of DR1 inherent to the orientation process which is performed at 210°C, photoassisted poling was carried out and the second harmonic generation signal measured during the poling. The degradation ratio decreases to less than 2 % with this method, but there is also a decrease in the orientational stability compared with thermally assisted poling. However, by carrying out photoassisted poling at different temperatures varying from 20 to 150°C, it has been shown that the second order susceptibility d_{33} increases, the degradation ratio keeps a low value, and the orientational stability increases and becomes comparable with the one observed for thermally poled samples provided the poling temperature is higher than 120°C. This last temperature has been identified in a previous work as a secondary glass transition temperature for this polyimide.

Keywords: polyimides; second order NLO; photoassisted poling; orientational stability; secondary glass transition temperature

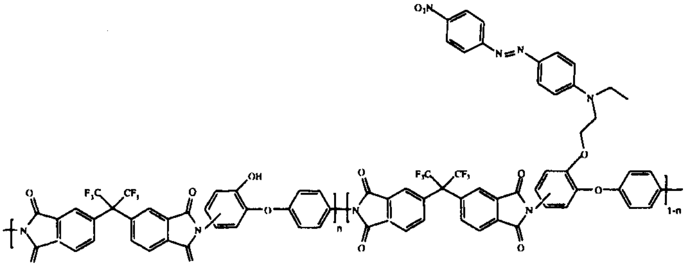
INTRODUCTION

Second order NLO polymers and copolymers seem very promising for applications in second harmonic generation (SHG) and electro-optical modulation[1]. One of the major problems to solve is the orientational stability of the NLO active chromophores which always tend to disorient in initially oriented films. Different solutions to this problem have been proposed and thoroughly explored; one approach is the use of polymers which can be cross-linked during or after poling[2]-[7]. Another approach consists in using polymers or copolymers with a high (primary) glass transition temperature (T_g^{α}). In this respect, polyimides[8] and copolyimides[9]-[14] have been widely studied. We have already described the synthesis and physical characterization of soluble copolymers of NLO chromophores and polyimides[15]. Such copolyimides, which have a high glass transition temperature ($T_g^{\alpha} \approx 250°C$), give long orientational relaxation times. We have shown that thermally assisted poling (TAP) at 210°C of films prepared from this material showed appreciable degradation[16]. On the contrary, films poled by photoassisted poling (PAP) at room temperature showed much less degradation[16]. PAP is based on the E → Z → E photoisomerization reaction that occurs in DR1 moiety. In this paper, we want to explore in more details PAP performed at different temperatures and to compare this method with TAP at 210°C with a particular attention to the second order susceptibility, the degradation fraction and the orientational stability of the poled samples.

EXPERIMENTAL

The synthesis of the soluble copolyimide PI-DR1 has been described elsewhere[15]. Its structure in Figure 1. The copolymer sample which will be studied here has a chromophore content of 13.9 % (w/w), a number averaged molecular weight of 33 600, a (primary) glass transition temperature T_g^{α} of 250°C determined by thermomechanic analysis, and a decomposition temperature of 270°C determined by thermogravimetric analysis. A homopolyimide (PI in the text below) was also synthesized with DR1 groups replaced by OH in the structure of Fig.1. The T_g^{α} of this polymer was slightly higher (270°C) than for the copolymer. Furthermore, by dielectric loss measurements at different frequencies, we put into evidence a subglass transition temperature T_g^{β} around 120°C for this polymer[17].

For the film preparation, the copolymer is dissolved in a mixture of tetrahydrofuran (THF) / N-methyl 2-pyrrolidone (NMP) in a 4:1 v/v ratio, with a polymer concentration of 6 % w/w. Films of polymers with thicknesses ranging from 0.6 to 0.75 μm were spin cast on glass slides covered by ITO from these solutions after filtration through a Millipore filter (pore size 0.5 μm). They were first dried at 100°C for 30 minutes. After this step, physico-chemical characterization of the films shows that they are swollen with residual NMP which plays the role of a plasticizer during poling.



PI-DR1

FIGURE 1 : Structure of the copolyimide PI-DR1.

The experimental set-up used to study the E → Z photoisomerization reaction[17] of DR1 consists of a pump beam at 547 nm (500 W middle pressure xenon-mercury lamp) and a probe beam (75 W xenon arc) both with nearly normal incidence to the sample. The probe beam was analyzed with a photodiode array which allows to get one full spectrum every ten milliseconds.

For preparing films for SHG, non centrosymmetry is required. Two poling methods have been used : TAP and PAP. For TAP, the above prepared samples were heated at 210°C under nitrogen atmosphere. Then, an electric field was applied by a corona discharge (electrode at a voltage of 6 kV and a distance of 1 cm from the surface of the film) which was kept during 10 mn at 210°C and then during all the cooling process towards room temperature (rate of cooling : 0.5°C/mn). For photoisomerization measurements and PAP, the sample was previously heated under vacuum at 120°C during 5 h in order to eliminate any trace of solvent, then placed under the same corona discharge as discussed above and simultaneously irradiated with the circularly polarized light of an Ar^+ ion laser (514 nm, 500 $\mu W.cm^{-2}$) at normal incidence[19]. The sample was placed in a thermoregulated housing allowing on the same time poling at variable temperatures between 20 and 150°C and in situ measurements of SHG. The same housing was used (without the corona discharge and the Ar^+ ion laser beam) for temperature studies of the relaxation processes.

The experimental method developed for determining independently the degradation ratio δ of the DR1 chromophores during the poling process and the order parameter Φ has been described previously[16] : it is based on absorption measurements at variable incidence and with polarized light. These absorption measurements were made in a conventional spectrophotometer (Varian Cary V).

The experimental set-up for SHG measurements has already been described[18]. A nanosecond Nd:YAG laser (1064 nm, 1 mJ, 10 ns FWHM) was used as the fundamental beam with p polarization. Assuming that the second order susceptibility component d_{33} equals 3 times d_{31}, we determined d_{33}. The thermoregulated housing described above allowed in situ SHG measurements during PAP at different temperatures or different temperature cycles after TAP or PAP (see below). In all cases, the SHG signal was recorded and averaged over 10 laser shots for every set of parameters on a fast numerical oscilloscope (Tektronix TDS 620B) connected with a PC computer.

RESULTS AND DISCUSSION

Photoisomerization of DR1 in a polyimide matrix

A PI-DR1 film prepared on a glass slide as described before was irradiated at 547 nm with a flux of 8.5 $mW.cm^{-2}$. The change in transmission is registered at 500 nm during and after irradiation. The irradiation time is 5 mn, which allows to reach the steady-state. The decrease of the optical density at this wavelength is attributed to E → Z conversion[18]. After the end of irradiation, there is a fast increase of absorbance due to the reverse thermal reaction which concerns 90 % of the change in optical density, then a much slower increase towards the initial value. The analysis of the fast component according to a monoexponential law gives the main rate constant for this reaction. The E → Z quantum yield is calculated from the initial slope of the change in optical density at 500 nm with the following simplification :

- the Z isomer has a negligible concentration at the beginning of irradiation, which allows to write :

$$\frac{d[Z]}{dt} = \Phi_{EZ} I^{E}_{abs} \qquad (1)$$

where Φ_{EZ} is the quantum yield for the $E \rightarrow Z$ reaction and I^{E}_{abs} is the energy absorbed by E species;

- the optical density (OD) of the sample does not vary at the beginning of the irradiation, and is equal to the initial optical density OD_0. Then, we can write :

$$I^{E}_{abs} = I_0\left(1 - 10^{-OD_0}\right) \tag{2}$$

where I_0 is the incident energy. Coupling equations (1) and (2) gives the following expression for Φ_{EZ} :

$$\Phi_{EZ} = \frac{\Delta OD/\Delta t}{I_0\left(1 - 10^{-OD_0}\right)\left(\varepsilon_Z - \varepsilon_E\right)l} \tag{3}$$

where $\Delta OD/\Delta t$ is the initial slope of the change in optical density, l is the cell optical path and ε_Z-ε_E the difference of extinction coefficients between the Z and E isomers (these extinction coefficients are supposed to be the same as in PMMA where they have been determined). Finally the quantum yield for the Z → E reaction could be determined by applying the following steady state relationship :

$$\Phi_{EZ}\frac{\varepsilon_E l[E]}{OD_{ss}} I_0\left(1 - 10^{-OD_{ss}}\right) - \Phi_{ZE}\frac{\varepsilon_Z l[Z]}{OD_{ss}} I_0\left(1 - 10^{-OD_{ss}}\right) - k_{back}\,[Z] = 0 \tag{4}$$

where OD_{ss} is the steady state optical density and k_{back} the reverse thermal reaction rate constant. From the determined values of Φ_{EZ} and k_{back}, the value of Φ_{ZE} can be determined.

The values of Φ_{EZ}, Φ_{ZE} and k_{back} are gathered in Table 1 and compared with those determined in a PI film doped with DR1 10 % w/w (PI/DR1) and a PMMA film doped with DR1 10 % w/w (PMMA/DR1)[18].

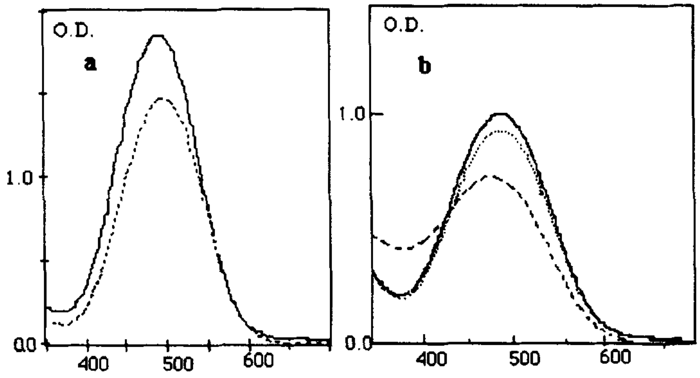
TABLE I : Quantum yields and back thermal rate constant for photoisomerization of DR1 in polymers.

	PI-DR1	PI/DR1	PMMA/DR1
E-Z conversion ratio (%)	14.2	10.6	16.1
Φ_{EZ}	0.020	0.016	0.11[18]
Φ_{ZE}	0.09	0.051	0.7[18]
k_{back} (s^{-1})	$1.3\ 10^{-1}$	$1.2.10^{-1}$	$1.5\ 10^{-1}$

The above results show that the isomerization reaction of DR1 in a rigid matrix as polyimide is feasible. The quantum yield Φ_{EZ} is smaller for PI doped with DR1 than for PMMA doped with DR1, but similar with the value obtained for PI/DR1. However, the back thermal reaction rate constants are similar for the three films. This similarity can be a consequence of the photoisomerization reaction which creates a cavity around the chromophore, thus facilitating the back isomerization, whatever the polymer is.

In-situ photoassisted poling, orientation and degradation of chromophores

Figure 2 shows the absorption spectra before and after poling of a PI-DR1 film prepared as described in the experimental part and poled thermally at 210°C. These spectra are compared with those of a PMMA film doped with DR1 and poled at 110°C. This figure shows that the spectrum of DR1 in PMMA taken after poling presents the normal decrease in absorbance due to the alignment of molecules (visible dichroism)[20] and a red shift attributed to the Stark effect[21]. PI-DR1 film also exhibits a larger decrease in absorbance but a blue shift of the absorption maximum and an increase of the absorbance below 350 nm. We interpreted both this shift and this increase of absorbance in the UV as being due to a partial degradation of the DR1 chromophore at 210°C. Indeed, previous thermogravimetric analysis has shown that DR1 starts to decompose at 200°C[22].



Wavelength (nm)

FIGURE 2 : Absorption spectra of a PMMA film doped with DR1 (curve a) and of a PI-DR1 film (curve b). Full line : before poling; dashed line : after TAP (110°C in curve a, 210°C in curve b); dotted line : after PAP at room temperature.

By measuring the absorbance of the films under polarized light and at variable incidence angle, we have been able to measure independantly the degradation ratio δ (fraction of molecules degraded during thermal poling) and the order parameter Φ, equal to the mean value of the second Legendre polynomial $<P_2>$ ($<P_2> = 1/2 <3\cos^2\theta - 1>$, θ being the angle between the direction of the poling field and the dipole moment of the chromophore)[16]. For the previously described PI-DR1 film, the fraction δ was estimated to be 11 % and the order parameter $\Phi = 3$ %. So the degradation ratio can be substantial after poling. For that reason, we investigated another method of poling, namely photoassisted poling (PAP). This method is based on the E → Z photoisomerization reaction of DR1 : under excitation by a circularly polarized light at normal incidence, the chromophores tend to orient in a direction perpendicular to the plane of the film; if an electrostatic field is simultaneously applied, the dipoles align preferentially in the direction of the field, which creates non centrosymmetry[23]-[28].

Figure 3 presents the SHG intensity during PAP of a PI-DR1 film at room temperature. This signal shows four distinct steps : during step 1, under the static electric field generated by a corona discharge, there is a fast increase of the SHG signal, followed by a slight decay, which is in fact due to an EFISH contribution (polarization term $\chi^{(3)}E_0E_\omega^2$ which generates second harmonic generation without orientation of dipoles); during step 2, when both static electric field and visible laser light are on, there is an increase of the SHG intensity due to the photoinduced orientation of dipoles stimulated by the E → Z reaction; during step 3, when the visible irradiation is switched off, there is a fast increase of the SHG intensity, mainly due to the back thermal Z → E reaction of DR1, and finally, during step 4, the SHG signal stabilizes to a high value after a relatively fast decay (2 to 3 mn) due to the annihilation of the electric field associated with the flow of surface charges towards ground.

We determined absolute values of second order susceptibilities and also order parameters and degradation ratios by the same method as above. The values are gathered on Table 2 and compared with the corresponding ones obtained for the same films prepared by TAP. The d_{33} value measured after PAP at room temperature (11 pm/V) is lower than the one observed after TAP at 210°C (37 pm/V), but the degradation ratio is much lower (2 % for PAP, compared to 11 % for TAP).

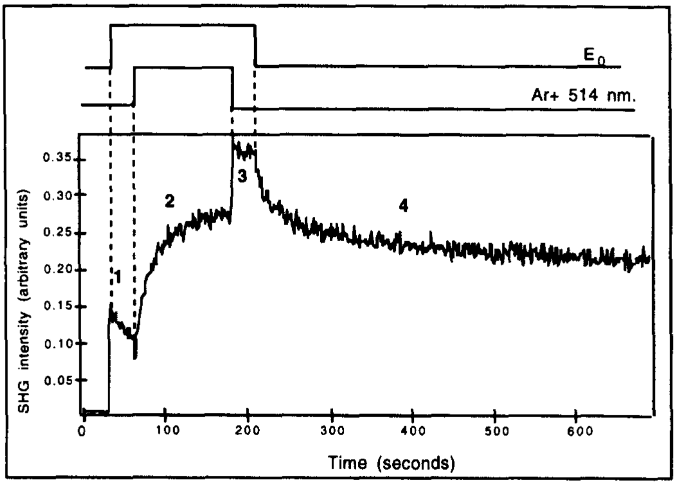


FIGURE 3 : SHG signal of a PI-DR1 film measured in-situ during and after PAP at room temperature (fundamental wavelength : 1064 nm).

In order to increase the poor efficiency of PAP when performed at room temperature in this very rigid matrix, we increased the temperature at which PAP was done. For this purpose, the temperature of the film was rapidly increased to some fixed value (150°C or below), which is still far below T_g, and then both electric field and visible light were applied on the film. After switching off the visible light, the temperature was decreased towards room temperature and the electric field was maintained as long as the temperature was higher than 30°C. The electric field was then switched off. Figure 4 gives an example of SHG signals obtained during PAP and TAP of a PI-DR1 film at 150°C. This figure shows that PAP at 150°C leads to a SHG signal larger than TAP at the same temperature. However it is worthwhile to note that, in spite of the high T_g^{α} of this copolymer, it is possible to pole it at temperatures larger than 120°C, which corresponds to the above mentionned T_g^{β}, which is still far below T_g^{α}. In addition, on both curves of PAP and TAP, we observe a significant decay of the SHG signal during cooling of the sample from 150°C towards room temperature under an applied electric field. This decay could be due to different origins. The first hypothesis was that the dipoles disorient upon cooling, which is unrealistic; the second hypothesis was that the refractive indices of the copolymer at fundamental and second harmonic wavelengths (n_{ω} and $n_{2\omega}$) change with temperature, which leads to a change in SHG intensity : a blank experiment made on the SHG intensity of a film initially poled by TAP at 210°C shows that its intensity increases when the temperature decreases from 150 to 30°C; so this hypothesis does not hold. Finally, we retained a third hypothesis which was that the EFISHG term (polarisation $\chi^{(3)}E_0E_\omega^2$) decreased with temperature. As the tensor terms of $\chi^{(3)}$ are mainly independant of temperature, as well as the E_ω^2 term, we are forced to admit that the applied film E_0 due to the corona field is decreasing with temperature. The physical reason is not clear, but it has been already observed in other doped polyimides[29],[30], and in hybrid sol-gel materials[31].

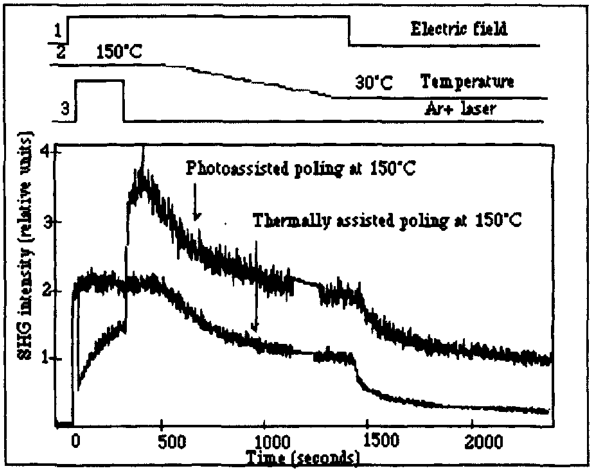


FIGURE 4 : SHG signal of a PI-DR1 film measured in-situ during and after PAP at 150°C (upper curve) and TAP at 150°C (lower curve) (fundamental wavelength : 1064 nm). PAP : 1, 2 and 3 applied; TAP : 1 and 2 applied.

Finally, Table 2 compares d_{33} values (measured at 1064 nm) for a series of PI-DR1 films prepared in the same conditions and poled in different conditions. These results show that SHG efficiency is increased when PAP is made at high temperature. For example, it is possible to get a higher d_{33} value by PAP at 150°C than by TAP at 210°C, which shows the efficiency of PAP. Figure 5 shows that the increase in d_{33} with the poling temperature presents a transition temperature which coincides with T_g^β. Furthermore, the degradation ratio of the chromophores in samples poled by PAP has the same value (≈ 2 %) whatever the poling temperature is.

TABLE II : Comparison between d_{33} values (at 1064 nm), order parameters and degradation ratios of a series of PI-DR1 films.

Method of Poling	PAP	PAP	PAP	PAP	PAP	TAP
Poling Temp. (°C)	25	50	90	120	150	210
Film thickness (nm)	580	650	510	540	560	850
Order parameter	6 %	7 %	4 %	8.2 %	5 %	3 %
Degradation ratio	2 %	1.5 %	2.2 %	2.5 %	2.4 %	11 %
d_{33} at 1064 nm (pm/V)	11	17	26	30	47	37

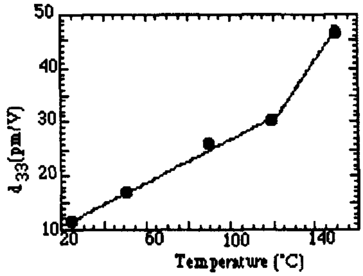


FIGURE 5 : SHG efficiency of PAP as a function of the poling temperature.

Orientational relaxation of chromophores

PAP has been demonstrated to be as efficient as TAP in preparing oriented films of PI-DR1. However, the question arises whether the orientational stability has been preserved with this new way of poling. In order to check this stability, we measured SHG intensity of films poled in different ways and heated gradually at a constant rate of 5°C/mn. In-situ SHG decay measurements of films oriented by PAP at different temperatures and by TAP at 210°C are reported on Figure 6. The film prepared by TAP disorients at 120°C, which is near the secondary glass transition temperature T_g^{β}. The film prepared by PAP at room temperature relaxes at a much lower temperature (55°C). This observation has already been made by Blanchard and Mitchell in a PMMA matrix doped with DR1[28]. The interesting feature of Figure 6 is the increase in orientational stability of the PI-

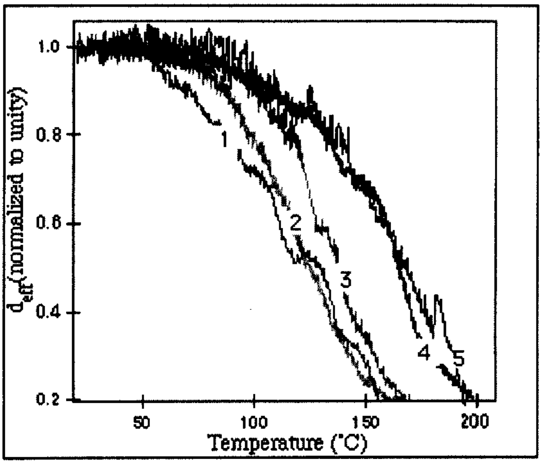


FIGURE 6 : Decay of SHG intensity following orientational relaxation of PI-DR1 films poled in different conditions. 1 : PAP at room temperature; 2 : PAP at 90°C; 3 : PAP at 120°C; 4 : PAP at 150°C; 5 : TAP at 210°C.

It comes out that a film poled by PAP at 150°C is as stable as a film poled by TAP at 210°C. Once again, it appears a threshold poling temperature around 120°C, above which the stability of the film is strongly increased. This observation can be explained if we consider that, at room temperature, photoisomerization reaction induces additional free volume which is freezed at this temperature and which will lead to a limited stability. At temperatures above T_g^β, local movements of the polymer chains become possible, which make chromophore orientation easier. Moreover, local rearrangements of the polymer chain around the oriented chromophore will occur inside the microcavity created by the isomerization reaction; they are possible above T_g^β, which explains the better stability. The increased stability of PAP when increasing the poling temperature has also been described by Bauer-Gogonea et al.[32][33]. The role of β transitions on orientational relaxation of NLO chromophores has been put into evidence in acrylic and epoxy polymers[34]-[36]; it has been shown that this relaxation can be strongly induced by these transitions due to local movements of the side chain groups. In some aromatic polyimides, such a secondary transition has also been observed and attributed to the oscillations or rotations of phenyl groups[37]. In our case, on the basis of the activation energy measured for this transition, we attributed this subglass transition to the breaking of hydrogen bonds between two different chains through residual OH groups[17].

CONCLUSION

We have shown that soluble copolyimides containing azo chromophores for second order NLO can be easily oriented by photoassisted poling at different temperatures lower than the main glass transition temperature. This method uses the reversible E → Z photoisomerization reaction of the azo dye, which occurs readily in polyimide, although with quantum yields five times lower than in PMMA matrix. The thermal degradation of the DR1 chromophores which follows photoassisted poling is much lower than for thermally assisted poling, and does not vary with the poling temperature (for $T \leq 150°C$). However, the second order susceptibilities measured after photoassisted poling at 150°C are higher than those measured after thermally assisted poling at 210°C, for equivalent orientational stability of the poled films. Photoassisted poling may be useful to prepare optically active circuits like electro-optical modulators. Deriving benefit from the easiness of the photochemical reaction and from the stability of the matrix, all-optical poling[38] can also be achieved in these copolymers[39].

ACKNOWLEDGEMENTS

The authors wish to thank Régis Mercier, Cathy Marestin and Bernard Sillion (LMOPS, Vernaison, France) for the synthesis of the copolymer, and Jean-François Delouis, Vincent Bova and Caroline Chardel (PPSM, ENS de Cachan) for their help during these experiments.

References

[1] D.M. Burland, R.D. Miller and C.A. Walsh, *Chem. Rev.* **94,** 31 (1994).

[2] M. Eich, B. Reck, D.Y. Yoon, C.G. Willson and G.C. Bjorklund, *J. Appl. Phys.* **66,** 3241 (1989).

[3] D. Jungbauer, B. Reck, R. Twieg, D.Y. Yoon, C.G. Willson and J.D. Swalen, *Appl. Phys. Lett.* **56,** 2610 (1990).

[4] S. Marturunkakul, J.I. Chen, L. Li, R.J. Jeng, J. Kumar and S.K. Tripathy, *Chem. Mater.* **5,** 592 (1993).

[5] C. Wu, B. Wu, L.R. Dalton, Y. Shi, P.M. Ranon and W.H. Steier, *Macromolecules* **25,** 6714 (1992).

[6] M.A. Hubbard, T.J. Marks, W. Lin and G.K. Wong, *Chem. Mater.* **4,** 965 (1992).

[7] K.M. White, E.M. Cross, C.V. Francis and R.S. Moshrefzadeh, *Polymers for Second-Order Nonlinear Optics,* G.A. Lindsay and K.D. Singer Eds., ACS Symposium Series 601, 1995, p.401.

[8] J.W. Wu, E.S. Binkley, J.T. Kenney, R. Lytel and A.F. Garito, *J. Appl. Phys.* **69,** 7366 (1991).

[9] G.H. Hsiue, J.K. Kuo, R.J. Jeng, J.I. Chen, X.L. Jiang, S. Marturunkakul, J. Kumar and S.K. Tripathy, *Chem. Mater.* **6,** 884 (1994).

[10] R.D. Miller, D.M. Burland, M. Jurich, V.Y. Lee, C.R. Moylan, J.I. Thackara, R.J. Twieg, T. Verbiest and W. Volksen, *Macromolecules* **28,** 4970 (1995).

[11] D. Yu, A. Gharavi and L. Yu, *Macromolecules* **29,** 639 (1996).

[12] T.-A. Chen, A.K.-Y. Jen and Y. Cai, *J. Am. Chem. Soc.* **117,** 7295 (1995).

[13] R. Inaba, M. Sagawa, M. Isogai and A. Kakuta, *Macromolecules* **29,** 2954 (1996).

[14] M. Ahlheim and F. Lehr, *Makromol. Chem.* **195,** 361 (1994).

[15] C. Marestin, R. Mercier, B.Sillion, J. Chauvin, K. Nakatani and J.A. Delaire, *Synthetic Metals* **81,** 143 (1996).

[16] J. Chauvin, K. Nakatani, J.A. Delaire, C. Marestin, R. Mercier and B.Sillion, *SPIE Proceedings,* **2998,** 205 (1997).

[17] J. Chauvin, K. Nakatani, J.A. Delaire, S. Faure, R. Mercier and B. Sillion, *Synthetic Metals,* to be published.

[18] R. Loucif-Saïbi, K. Nakatani, J.A. Delaire, M. Dumont and Z. Sekkat, *Chem. Mater.* **5,** 229 (1993).

[19] Y. Atassi, J. Chauvin, J.A. Delaire, J.-F. Delouis, I. Fanton-Maltey and K. Nakatani, *Mol. Cryst. Liq. Cryst.* **315,** 11 (1998).

[20] M.A. Mortazavi, A. Knoesen, S.T. Kowel, B.G. Higgins and A. Dienes, *J. Opt. Soc. Am. B* **6,** 733 (1989).

[21] R.H. Page, M.C. Jurich, B. Reck, A. Shen, R.J. Twieg, J.D. Swalen, G.C. Bjorklund and C.G. Willson, *J. Opt. Soc. Am. B* **7,** 1239 (1990).

[22] R.B. Prime, G.Y. Chiou and R.J. Twieg, *Journal of Thermal Analysis,* **46,** 1133 (1996).

[23] Z. Sekkat and M. Dumont, *Appl. Phys. B* **54,** 486 (1992).

[24] R. Loucif-Saibi, C. Dhénaut, K. Nakatani, J.A. Delaire, Z. Sekkat and M. Dumont, *Mol. Cryst. Liq. Cryst.* **235,** 251 (1993).

[25] Z. Sekkat, C.-S. Kang, E.F. Aust, G. Wegner and W. Knoll, *Chem. Mater.* **7,** 142 (1995).

[26] Z. Sekkat, J. Wood, E.F. Aust, W. Knoll, W. Volksen and R.D. Miller, *J. Opt. Soc. Am. B* **13,** 1713 (1993).

[27] A. El Osman and M. Dumont, *SPIE Proceedings* **34,** 36 (1998).

[28] P.M. Blanchard and G.R. Mitchell, *Appl. Phys. Lett.* **63,** 2038 (1997).

[29] M. Stahelin, C.A.Walsh, D.M. Burland, R.D. Miller, R.J. Twieg and W. Volksen, *J. Appl. Phys.* **73,** 8471 (1993).

[30] R. Inaba, M. Sagawa, M. Isogai and A. Kakuta, *Macromolecules* **29,** 2954 (1998).

[31] D. Riehl, Ph-D. Thesis, University of Paris Sud-Orsay (1996).

[32] S. Bauer-Gogonea, S. Bauer, W. Wirges and R. Gerhard-Multhaupt, *J. Appl. Phys.* **76,** 2627 (1994).

[33] S. Bauer, S. Bauer-Gogonea, S. Yilmaz, W. Wirges and R. Gerhard-Multhaupt, *Polymers for Second-Order Nonlinear Optics,* G.A. Lindsay and K.D. Singer Eds., ACS Symposium Series 601, 1995, p.304.

[34] S.C. Brower and L.M. Hayden, *J. Polym. Sci. Part B : Polym. Phys.* **36,** 1013 (1998).

[35] I. Teraoka, D. Jungbauer, B. Reck, D.Y. Yoon, R. Twieg and C.G. Willson, *J. Appl. Phys.* **69,** 2568 (1991).

[36] R. Hagen, O. Zobel, O. Sah, M. Biber, M. Eckl, P. Strohriegl, C.-D. Eisenbach and D. Haarer, *J. Appl. Phys.* **80,** 3162 (1996).

[37] Y.T. Chern, *Macromolecules* **31**, 1898 (1998).

[38] J.M. Nunzi, F. Charra, C. Fiorini and J. Zyss, *Chem. Phys. Lett.* **219,** 349 (1994).

[39] J.Si, T. Mitsuyu, P. Ye, Y. Shen and K. Hirao, *Appl. Phys. Lett.* **72,** 762 (1998).