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Optical anisotropy and non-linear optical properties of azobenzene methacrylic polymers

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Abstract

Photoinduced optical anisotropy has been studied in several methacrylic copolymers, either amorphous or liquid crystalline, with cyano azobenzene chromophores in the side chain. Illumination with linearly polarised 488 nm light gives rise to high and stable values of birefringence and dichroism, mainly in liquid crystalline films. Both dichroism and birefringence decrease with the azo content in the copolymer series while some increase can be achieved by the incorporation of biphenyl molecules to the copolymers. Photoinduced anisotropy disappears above the glass transition temperature in amorphous polymers, whereas it increases in liquid crystalline polymers (LCP) due to a thermotropic self-organisation.

The non-linear optical (NLO) properties of the films have been studied by second harmonic generation (SHG) measurements. The intensity of the harmonic signal from in situ corona poled polymeric films has been measured. The effect of 488 nm light irradiation on the azo chromophores orientation and consequently on the NLO response of the films was investigated at different temperatures. The intensity and thermal stability of the second harmonic signals obtained after the two different (thermal and photoassisted) corona poling processes have been compared.

Keywords: Azobenzene; Photoinduced optical anisotropy; Non-linear optics

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1. Introduction

Photoinduced optical anisotropy in azobenzene films has been extensively studied [1–16]. In most of the reported works, anisotropy has been induced by illumination with linearly polarised 488 nm light from an Ar^+ laser. Under this illumination, the orientation of the azo units changes through *trans–cis–trans* isomerization processes. A preferential orientation of the *trans* molecules, with its axis perpendicular to the polarisation direction of the exciting light, can be achieved.

High and stable values of the optical anisotropy, which can be checked by dichroism and birefringence measurements, have been obtained mainly in films of liquid crystalline polymers (LCP) with the azo units in the side chain. The strong molecular interactions among the azo molecules in LCP seems to enhance the photoinduced anisotropy and to improve its stability. However, due to the presence of liquid crystalline domains with different orientations these films usually show a high light scattering that is detrimental for many applications [17]. Trying to keep strong molecular interactions while decreasing light scattering, we have prepared a series of copolymers with different contents of a non-mesogenic methacrylic unit and a promesogenic azobenzene one. This allows us to range from liquid crystalline to amorphous materials. We report in this paper the results of dichroism and birefringence measurements performed on these copolymers after illumination with 488 nm light.

On the other hand, azopolymer films with donor and acceptor substitutions in the azobenzene moieties can be used for second order non-linear optical (NLO) applications [18,19]. To have a second order response in a film, a polar orientation of the molecules has to be induced. This can be achieved by several procedures. In particular, a corona

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discharge on the film at temperatures at which the molecules are mobile can give rise to such a polar orientation. An advantage of using azo-compounds is that the photoinduced mobility of azobenzene units can be used to reduce the poling temperature. The fundamental mechanisms of the photoassisted electric poling process have been described in the literature [20–23]. Besides, by changing the content of azobenzene molecules their interactions also change and so does the polar orientation of the films. An investigation of these behaviours in our polymers using different experimental conditions has also been performed in the present work.

2. Experimental section

The chemical structure of the polymers used in this study is shown in Fig. 1(a), whereas the *trans* and *cis* configurations of the azo chromophore are given in Fig. 1(b). The compounds were synthesised at 70 °C by radical polymerisation using DMF as solvent and AIBN as thermal initiator, according to a method to be published elsewhere. Depending on their composition the copolymers were either liquid crystalline or amorphous. Their thermal properties were determined from differential scanning calorimetry (Perkin–Elmer DSC-7) measurements (scan rate: 10 °C/min). The composition, transition temperatures and molecular weights are given in Table 1. Their molecular weights were measured by Gel Permeation Chromatography (GPC). GPC was carried out on a Waters liquid chromatography system equipped with a 600E multisolvent delivery system and a 996 photodiode array detector, using a combination of two Styragel (HR2 and HR4) high resolution columns. THF was used as the mobile phase and the calibration was performed with polystyrene standards. The presence of conductive impurities on the resulting polymers could inhibit the polar orientation induced by the electric field in the corona poling process. In order to avoid this undesired effect the polymers were purified by flash chromatography using silica gel and dichloromethane as eluant. Several purification cycles were performed until the second harmonic (SH) signal (see below) reached a saturation value. The molecular weight and thermal data correspond to the purified samples used for optical measurements.

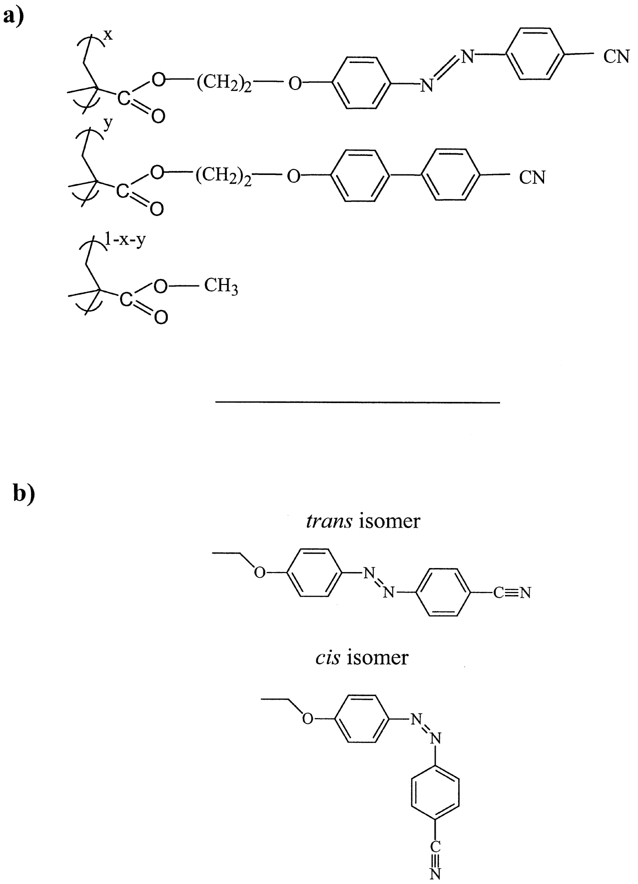

Fig. 1. (a) Chemical structure of the studied methacrylate polymers. (b) Scheme of the *trans* and *cis* configurations of the azo chromophore.

Table 1
Composition, thermal data and molecular weights of the studied polymers

Name	Composition		Transition temperatures (°C)	M_w[a]	M_w/M_n[a]
	X	Y			
PC2	1	0	g 105 N 158 I	32,000	3.13
PC2-90	0.9	0	g 110 N 138 I	22,475	1.40
PC2-70	0.7	0	g 98 I	15,450	1.88
PC2-10	0.1	0	g 96 I	24,200	1.65
Ter-10	0.1	0.7	g 99 I	52,550	1.49

[a] GPC data determined from THF solutions using PS standards as reference.

Films were produced either by casting or by spin coating a solution of the polymers in chloroform onto clean glass substrates. Then, films were dried in a vacuum oven at 40 °C overnight to eliminate the residual solvent. To extend the optical absorption measurement range in Ter-10 films down to 200 nm (see below) some films of this polymer were prepared on fused silica substrates. Films used in second harmonic generation (SHG) measurements were prepared on ITO coated glass plates. Film thickness was measured using a DEKTAK profilometer. The thickness values ranged from 0.2 to 0.5 μm for birefringence and dichroism measurements and from 1.5 to 2 μm for SHG measurements. Before performing any experiment each film was heated 20 °C above its glass transition temperature, T_g (amorphous polymers), or above its isotropization temperature, T_i (LC polymers), for 5 min in order to erase any influence of the morphology induced during the preparation process, as well as any previously photoinduced effect. Films were then fast quenched to room temperature (RT) by putting them on a metallic plate.

Polarised optical absorption measurements were performed in a Cary 500 Scan UV–Vis-NIR spectrophotometer. Linear (vertical/horizontal) polarisation of the

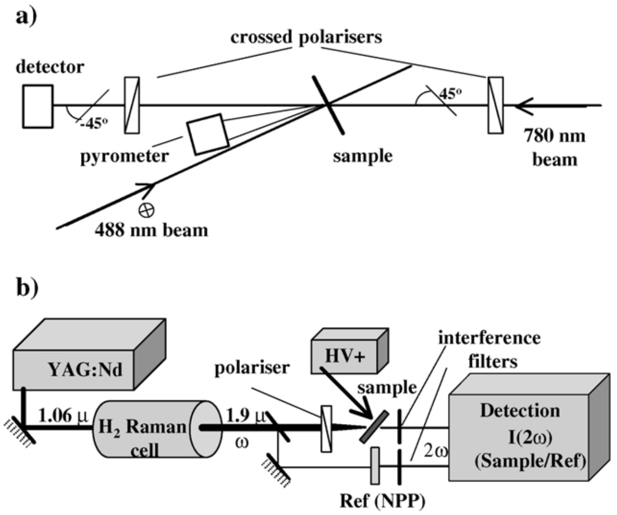

Fig. 2. Experimental set-up for (a) birefringence measurements and (b) second harmonic generation measurements.

measuring beams was achieved using a Glan–Thomson prism. Photoinduced birefringence measurements were performed using the set-up shown in Fig. 2(a). The sample was mounted on a hot stage with an optical access. A 488 nm vertically polarised light beam (4 mm in diameter, 150 mW/cm^2) from an Ar$^+$ laser was used as the pumping light source. The sample was placed between crossed polarisers with their polarisation directions at ± 45° with the vertical axis. To probe the photoinduced anisotropy, the light from a 780 nm diode laser transmitted through the polariser-sample-polariser system was measured with a Si detector. This light, with a power of about 3 W/cm^2, does not produce any changes in the optical anisotropy of the film within the experimental accuracy of our setup ($\Delta n \approx 10^{-3}$) after 1 h irradiation. The transmitted intensity I, is given by the equation:

$$I = I_0 \sin^2(\pi|\Delta n|d/\lambda) \qquad (1)$$

where I_0 is the intensity transmitted with parallel polarisers, when the film is in the initial isotropic state, d the film thickness, Δn the birefringence of the sample and λ the wavelength of the measuring light (780 nm). An optical pyrometer was used to measure the temperature of the film. The field of view of the pyrometer sensor head was adjusted to fall within the area of the film illuminated by the Ar$^+$ laser.

SHG measurements were performed using the set-up shown in Fig. 2(b). The 1.9 μm fundamental radiation was obtained from a H_2 Raman cell excited by a Q-switched Nd:YAG laser (1064 nm). The repetition rate was 10 Hz and the pulse width 8 ns. A computer controlled NLO spectrometer (from SOPRA) completes the SHG experimental set-up. The 1.9 μm polarised light is split in two beams. The less intense one is directed to a *N*-(4-nitrophenyl)-(L)-prolinol (NPP) powder sample whose SH signal is used as a reference to correct the laser fluctuations. The other beam is used to generate the SH signal in the film under study. The SH light from both the film and the reference are measured with two photomultipliers (Hamamatsu R406). Interference filters are used to remove the residual excitation light beyond the film and the NPP reference.

The films were held on a thermoregulated fixed stage for in situ SHG measurements during the poling processes. The angle of incidence of the 1.9 μm fundamental beam on the film was about 45°. A positive electric discharge was applied across the film using a standard corona poling set-up. A DC voltage of +5 kV was applied to a needle, perpendicular to the film. The distance between the needle and the film surface was about 1 cm. In photoassisted corona poling processes we used 488 nm light from an Ar$^+$ laser. This light was depolarised by passing it through an optical fibre. The light power used in this process was 150 mW/cm^2.

In order to obtain the d_{33} non-linear coefficients, the poled films were held on a stage that rotates around a vertical axis, perpendicular to the incidence plane of the light. The fundamental light was p-polarised and the p-polarised SH signal was detected as a function of the angle. The experimental data obtained rotating the sample (Maker fringes) were analysed following the Jerphagnon and Kurtz method [24] using a X-cut quartz crystal ($d_{11} = 0.4$ pm/V) as reference.

3. Results and discussion

3.1. Dichroism and birefringence

The polarised optical absorption spectrum of the films was measured with linearly polarised light (vertical/horizontal). Those measurements were performed at RT, before and after irradiation with vertically polarised 488 nm light. Since the results obtained in all the PC2-X films were similar we only show in Fig. 3 those corresponding to one of these films (PC2-90) together with those of Ter-10. No dichroism has been observed before blue light irradiation. The spectra show an absorption band at about 360 nm and a small shoulder in the 450 nm region. These bands are due to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the azo units, respectively. The band at 290 nm in the Ter-10 film is due to the biphenyl molecules. The optical density of the films at 488 nm was lower than 0.05 for all of them. Because of this, we have not taken into account the attenuation of the 488 nm exciting light when the results of the different films have been compared.

All the films have been irradiated at 30 °C for 1000 s with vertically polarised 488 nm light. The induced dichroism has been measured at different times after switching the 488 nm irradiation off. It has been found that the photoinduced dichroism slightly decreases with time (while keeping the sample in darkness) and reaches a stable value in about 24 h. Dichroism is due to a preferential alignment

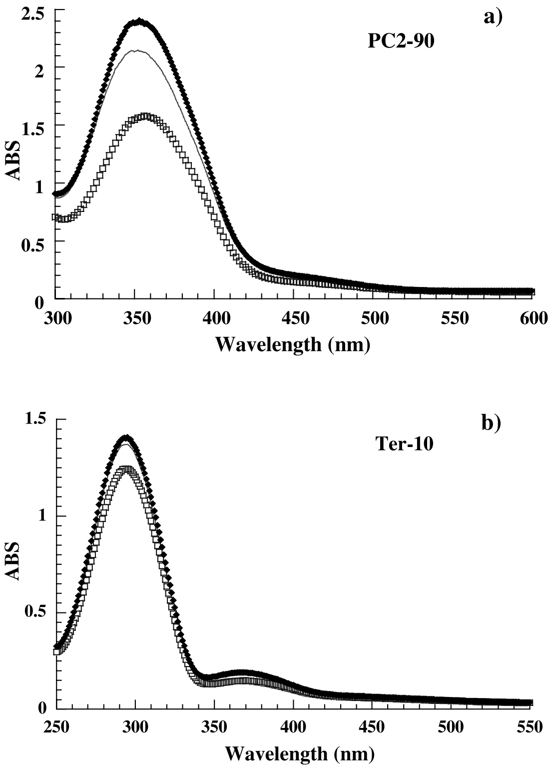

Fig. 3. Polarised UV–Vis absorption spectra of the (a) PC2-90 and (b) Ter-10 films before (−) and after irradiation (□ vertical detection, ◆ horizontal detection) with vertically polarized 488 nm light.

of *trans* azobenzene molecules in a plane perpendicular to the polarisation direction of the 488 nm light. The evolution with time after irradiation is mainly due to the back thermal relaxation of the light induced *cis* isomers.

From dichroism measurements we have evaluated the in plane spectroscopic order parameter S of azobenzene molecules. This parameter is given by [9]:

$$S = (A_{||} - A_{\perp})/(A_{||} + 2A_{\perp}) \qquad (2)$$

where $A_{||}$ and $A_{\perp}$ are the optical absorption densities at 360 nm measured with light horizontally and vertically polarised, respectively. The order parameters corresponding to the different films, measured 24 h after irradiation, are given in Table 2. Photoinduced reorientation of azo polymers depends on polymer structure and azo concentration [5,10,16,25]. In our case, it can be seen that S is higher in the LC polymers and decreases in the copolymers when the concentration of azobenzene molecules decreases. The orientation of azo-molecules seems to be favoured by co-operative interactions among them. When the azo concentration decreases so does this interaction and, consequently, the order parameter decreases. However the S value in the terpolymer is higher than that in the PC2-10 film, although the azo concentration (number of azo moieties in a given mass of polymer) is higher in this last compound than in the former one. In this case, the interaction among azo and biphenyl moieties can assist the molecular order. In fact, dichroism is also observed in the 290 nm band of the terpolymer films that is due to the biphenyl molecules. However, the order parameter for the biphenyl molecules ($S = 0.05$) measured in the 290 nm band is lower than that for the azo ones ($S = 0.14$) measured in the 360 nm band. Similar results have been previously reported [2,6–10].

Table 2
Spectroscopic order parameter S evaluated from dichroism measurements (at 360 nm) after irradiation at *RT* during 1000 s.

Polymer	S
PC2	0.20
PC2-90	0.18
PC2-70	0.13
PC2-10	0.12
Ter-10	0.14

The thermal stability of the photoinduced dichroism has been checked in the different films. In all the amorphous polymers dichroism disappears by heating up the films to temperatures above the glass transition temperature T_g. However, in the LCP (PC2-90 and PC2) dichroism increases after annealing the films above T_g. Besides, the absorption spectra (mainly the one measured with light horizontally polarised, perpendicular to the 488 nm light) change. As shown in Fig. 4, the band broadens likely due to new bands that appear both in the high and low energy side of the 360 nm band. These new bands have been associated to H and J aggregates of azo units, respectively [15,16,26].

The birefringence (Δn) induced in the different polymers under irradiation with linearly polarised 488 nm light at 30 °C for 1000 s has also been measured. The evolution of Δn with irradiation time is given in Fig. 5. It can be seen that in all the PC2-X polymers birefringence increases with irradiation time and reaches a saturation value. In Ter-10 films birefringence increases more slowly than in the PC2-X and continues increasing for several hours (not shown in the figure) reaching a saturation value higher than that of PC2-10. When the 488 nm light is switched off a slight decrease

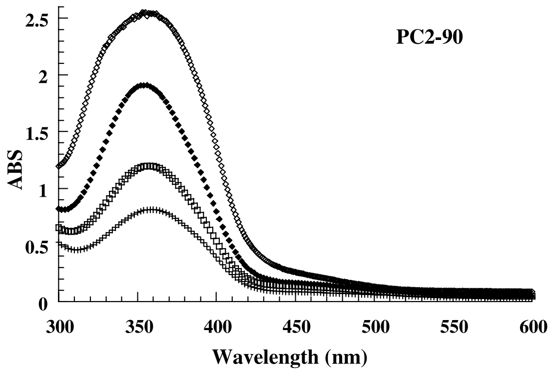

Fig. 4. Polarised UV–Vis absorption spectra of the PC2-90 films irradiation with vertically polarized 488 nm light: before (□ vertical detection, ◆ horizontal detection) and after (+ vertical detection, ◇ horizontal detection) thermal annealing at a temperature between T_g and T_i.

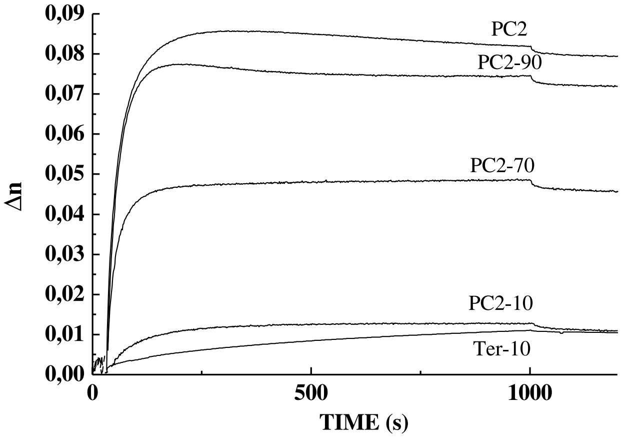

Fig. 5. Birefringence (Δn) versus irradiation time measured at 30 °C. The irradiation with linearly polarized 488 nm light starts at $t = 30$ s and finish after 1000 s.

of Δn is observed in all the samples. Afterwards, Δn remains constant remains constant within our experimental accuracy for at least 4 h if the films are kept in darkness (only under illumination with the 780 nm reading light).

The saturation value of Δn decreases with the concentration of azo units in the PC2-X copolymers. The terpolymer shows the lowest induction rate but as we said above, the saturation value of Δn is higher than that of PC2-10, although the last one has a higher azo concentration. In the copolymers, birefringence is mainly due to the photoinduced orientation of *trans* azo molecules and thus increases with the azo content. However, in the terpolymer Δn is associated not only to the orientation of azo units but also to that of biphenyl moieties [8–10,27]. This explains why Δn is higher in Ter-10 than in PC2-10. The small decrease of Δn when the 488 nm light is switched off can be associated with the back thermal relaxation of *cis* molecules to the *trans* state. The results of birefringence are in agreement with those of dichroism measurements.

The Δn induced at 30 °C in the amorphous polymers goes back to zero by heating them up above T_g. On the other hand, if the heating process is performed in the LCP a strong increase of Δn is observed. The results corresponding to PC2-90 are shown in Fig. 6. Δn shows a fast increase when T goes above T_g. Then, if T is stabilised at $T < T_i$, Δn slowly increases and saturates after a few hours (depending on temperature). The saturation value of Δn can increase up to seven times the initial one induced at 30 °C. That increase in birefringence, that remains stable when the film is cooled down to RT, agrees with the dichroism results given in Fig. 4 and has been associated with a thermotropic self-organisation of the LCP [25,28–30]. In our case it seems to be related with the formation of the oriented molecular aggregates that have been observed in dichroism measurements. Besides the thermotropic self-organization, another behaviour, not found in the amorphous polymers, has been observed in the liquid crystalline ones. When the birefringent liquid crystalline films are heated above T_i and depending on heating temperature and heating time a memory effect is observed. For heating temperatures only few degrees above T_i and short heating times (of a few seconds) birefringence is partly recovered when the film is cooled down again below T_i (memory effect). However, for higher heating temperatures and/or longer heating times no recovery is observed. This effect has been associated with a partial orientation of the main chain of the polymer that persists for some time at $T > T_i$ [30].

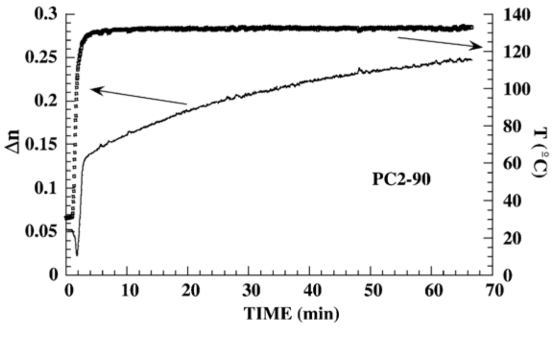

Fig. 6. Thermal enhancement of birefringence of a PC2-90 film.

3.2. Non-linear optical properties

The second order NLO properties of the films have been evaluated by SHG measurements. It should be mentioned that Altomare et al. [31] did not found any SH signal in a series of poled polymeric samples of several polymethacrylates with cyano-azobenzene molecules. These authors attributed in part this behaviour to the interchromophore interactions, larger than dipolar forces induced by the external electric field. However, we have obtained a noticeable NLO response in all our polymers. Since, we have found that the SH signal increased as the purification of our polymers went on, it is possible that the presence of impurities could increase the electrical conductivity of the film and inhibit the polar order in Altomare's samples.

The SHG signal intensity from in situ corona poled films was recorded as a function of temperature. The samples were held on a fixed stage at 25 °C and the poling electric field was switched on whereas the SH signal was detected. After 2 min, the heating process at a rate of 5 °C/min was started. In all the films the SH signal increases, due to the enhanced mobility of the chromophore segments that can be oriented under the electric field. The SH signal shows a maximum value and then decreases. This decrease takes place at temperatures clearly higher than T_g and can be associated with an increase of the polymer conductivity and thermal disorder. If the temperature continues going up, a degradation of the film surface appears. The results for PC2, PC2-10 and Ter-10 films are shown in Fig. 7(a), but similar pictures were obtained for the rest of the samples. From these poling profiles it can be observed that all the polymers give a maximum SH intensity at a temperature between 145 °C and 160 °C. However, a cyclic repetition of poling processes up to temperatures about 150 °C, followed by the

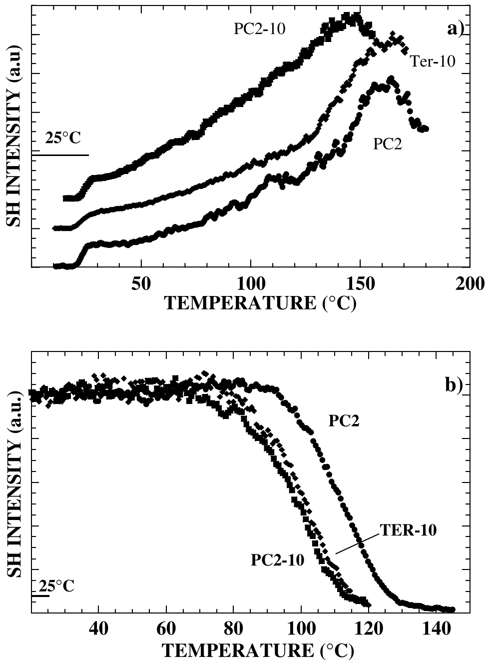

Fig. 7. (a) Second harmonic signal versus temperature for different polymeric samples. The heating rate 5 °C/min. (b) Thermal stability of the remaining second harmonic signal as measured one weak after the thermal poling performed at T_{op}: PC2 (●), PC2-10 (■) and Ter-10 (◆) polymeric films.

thermal quenching described in the experimental section, results too in progressive film degradation. That is the reason why we performed the poling processes of the polymers up to a temperature 25 °C above their respective T_g (in the text, $T_g + 25\ °C = T_{op}$).

The usual thermal corona poling process was performed as described below. The films were heated up to T_{op} with the electric field on and maintained at this temperature until signal saturation was observed (typically 15 min). Then, the films were cooled down to RT in the presence of the poling field and finally, this field was switched off. A decay of the SH signal is observed after switching off the poling field. This behaviour has been associated with the neutralisation of charges trapped at the film surface during corona poling and with different relaxation processes. After a few days all the samples showed a remaining SH signal stable at RT. Then the films were held on a rotating stage and the SH intensity was detected as a function of the angle. The analysis of the measured curves allowed us to obtain the non-linear coefficient d_{33} (assuming $d_{33} \approx 3d_{31}$) of the polymers. The estimated error in d_{33} values is ± 15%. The obtained values were 3.0 pm/V for PC2, 3.4 pm/V for PC2-90, 2.9 pm/V for PC2-70, 1 pm/V for PC2-10, and 1.7 pm/V for Ter-10. The lower d_{33} value found for PC2 as compared to the one for PC2-90 could be due to the interactions between neighbouring chromophores [19,32]. The d_{33} values decrease with the azo content in the rest of the PC2-X copolymer series. It should be noted that the d_{33} value of Ter-10 is higher than the one obtained for PC2-10, although the azo concentration is higher in PC2-10 than in Ter-10 samples. This result can be explained by the contribution of the cyano-byphenil pending groups to the NLO response. Similar d_{33} values have been reported for other methacrylic copolymers with cyano-azobenzene in the side chain [32,33]. A larger value (26 pm/V) was reported for a polymethacrylate functionalised with 4-dialkylamino-4′cyanoazobenzene [34]. The higher hyperpolarizability (β) value of this chromophore, with a stronger electron donor, as well as the shorter fundamental wavelength (1064 nm) used in the experiments described in Ref. [34] can justify the difference.

The thermal stability of the poling was analysed from the evolution of the remaining SH signal versus temperature. These measurements were performed a week after finishing the poling processes. The samples were heated up from RT at a rate of 3 °C/min. The results for the PC2, PC2-10 and Ter-10 films are shown in Fig. 7(b). We do not show the evolution of the PC2-90 and PC2-70 signals due to its similarity with the others. A decrease of the SH signal at temperatures near T_g has been observed for all the samples.

The effect of light irradiation on the SH signal intensity has also been studied. We show in Fig. 8 the SH signal from a PC2-90 copolymer film during photoassisted corona poling (PAP) processes performed at different temperatures. The beginning of the different steps is marked in the figure. The sample was first heated up to the chosen temperature and then the electric field was switched on (step 1). The SH signal grew and after three minutes reached a stationary state. Then, with the electric field still on, the irradiation with 488 nm depolarised light at normal incidence on the film was switched on (step 2). SH signal grew again and reached a new stationary state in about 4 min. Then the light was switched off and a new increase of the SH signal was observed (step 3). Subsequently the sample was cooled down to RT, without any significant change in the SH intensity. Finally the electric field was switched off and the SH signal decreased to a final value that depended on the poling temperature (step 4). The increase of the SH signal

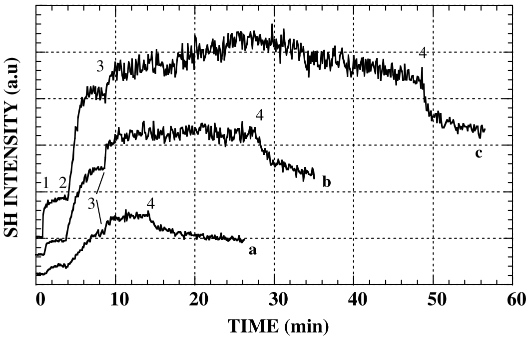

Fig. 8. Second harmonic signal from a PC2-90 film during photo-assisted electric poling processes performed at different temperatures: (a) 25 °C, (b) 50 °C and (c) 100 °C. Labelling indicates: 1, electric field on; 2, 488 nm laser light on; 3, 488 nm laser light off; 4, electric field off. Between 3 and 4 the temperature is brought to RT in (b) and (c).

when the irradiating light is switched on can be related with the increased mobility of azobenzene moieties stimulated by the photoinduced presence of azobenzenes in the *cis* state. Under the combined effect of this increased mobility (together with the poling effect of the electric field) and the orientational rearrangements introduced by irradiation through *trans–cis–trans* isomerizations, saturation of the signal is reached at the end of step 2. Now, when the light is switched off, the irradiation induced molecular rearrangements disappear. This gives place to a new increase of the SH signal. Finally the signal achieves a maximum stable value in presence of the electric field that increases with the poling temperature. The enhancement of this maximum value with temperature has been reported in different polymethacrylates [22] and polyimides [35,36]. We have found that PAP process provides a way to increase the second order NLO response of the films. In fact, we have observed that, at any temperature ($\leq T_{op}$), the SH signal obtained using photoassisted corona poling is bigger than the one achieved with thermal corona poling. Even at T_{op}, a short illumination (30 s) of the polymers increases the SH signal by a factor of 1.5. When the irradiating beam is switched off, the signal remains at a higher level than in the thermal poling process performed at T_{op} without light.

The above described PAP processes, performed at any temperature, lead to a remaining SH signal stable at RT. The thermal stability of this signal, measured a week after finishing the PAP process, increases with the poling temperature. In all the polymers, the SH signal obtained after a RT photoassisted poling process disappears at temperatures clearly lower than T_g, in contrast with the SH signal obtained in corona poled films at T_{op}. However, PAP processes performed at higher temperatures (about 90 °C) give rise to similar stability results than thermal poling at T_{op}. The poorer thermal stability of the remaining SH signal after a PAP process at RT as well as the increase of the stability when the PAP is performed at higher temperatures has been associated with the fact that, at low temperatures, light can enhance the molecular mobility and the dipoles can be oriented by an electric field without inducing a rearrangement of the polymeric main chain [22, 23,35–37]. However, when the temperature is increased, local rearrangements of the chain around the oriented dipoles can occur, leading to a better stability of the polar order and consequently of the SH signal.

4. Conclusion

The orientational order induced in a series of azobenzene methacrylate copolymers is bigger in the LC polymers than in the amorphous ones and decreases with the azobenzene content. The introduction of biphenyl moieties gives place to an increase of the order parameter. A similar behaviour is observed in birefringence measurements.

The photoinduced anisotropy disappears in the amorphous polymers when they are heated above T_g. However, the LCP show a thermotropic increase of birefringence that, in our samples, can be associated with the aggregation of azobenzene moieties.

The non-linear d_{33} coefficient increases going from PC2 to the copolymer PC2-90 and then decreases with the azo content. The polar order disappears when polymers are heated near T_g. Photoassisted poling enhances both the induction rate and saturation values of the NLO response with respect to thermally poled films.

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