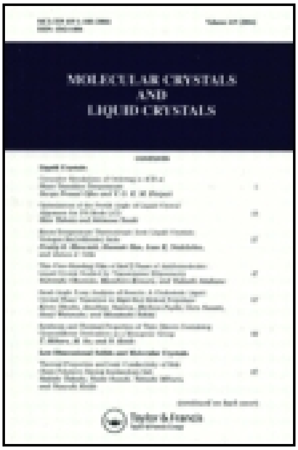

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NON-LINEAR OPTICAL PROPERTIES OF LIQUID CRYSTALLINE AZOBENZENE POLYMERIC FILMS

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Non-linear optical (NLO) properties of thin films of two methacrylic homopolymers and a copolymer with cyano azobenzene chromophores in the side chain 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 at different temperatures. The effect of 488 nm light irradiation on the azo chromophores orientation and consequently on the non-linear response of the films was investigated at several temperatures. The intensity and thermal stability of the remaining second harmonic signals obtained after the two different (thermal and photoassisted) Corona poling processes have been compared. The second order non linear coefficients have been obtained by the Maker fringes method.

Keywords: azobenzene; photoassisted poling; polymethacrylates, second order NLO

INTRODUCTION

In the past years the importance of organic non-linear optical materials for applications in optoelectronics or photonics has been widely recognised and a great deal of research has been developed in this field [1]. Among all the materials explored, photochromic systems have attracted much interest. In particular, azo-dyes containing polymers still play an important role [2]. It is well known that the geometrical molecular changes during trans-cis-trans photoisomerization of azo chromophores can lead to a molecular orientation perpendicular to the polarisation of the irradiating light [3]. This photoinduced orientation (PIO) process results in optical anisotropy whose magnitude and stability depends on the molecular

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environment. Photoinduced birefringence and dichroism as well as grating formation have been widely studied in several kinds of azo containing polymers, looking for the best properties for their potential applications as reversible optical storage [4] or holography [5].

In the domain of non-linear optics, conjugated azo molecules ended with appropriate donor and acceptor groups could achieve large hyperpolarizabilities. However, in order to obtain a second order NLO response from bulk polymeric materials a non centrosymmetrical orientation of the polar molecules is required. The most commonly used poling method is to apply a static electric field perpendicular to the film heated over its glass transition temperature (T_g). Then the sample is usually cooled slowly with the electric field still on. In the nineties a new method of poling making use of azo derivatives photoisomerization was reported [6]. This method is based on the enhancement of the molecular mobility in the film during irradiation, which is very low at temperatures far from the polymer T_g. Under excitation by circularly polarised or depolarised light at normal incidence, the azo molecules tend to orient in a direction perpendicular to the film; if during this process an electric field is applied, an appreciable polar orientation of the molecular dipoles can be achieved, giving rise to a photoassisted electric poling (PAP). The application of an electric field is still necessary, but poling can be achieved at temperatures much lower than T_g, avoiding thermal degradation of the films. Another advantage of PAP process is that it allows the drawing of patterns of poled and unpoled molecules [6b,7] which is interesting in the search of quasi phase matched configurations or in the fabrication of optically active circuits like electro-optical modulators.

The materials studied in this work are 4-cyano-azobenzene derived polymethacrylates, with polymethylene spacers of different length as shown in Figure 1. A lot of papers on photochromic and NLO properties of polymethacrylates with different azo chromophores in the side chain have been published [8]. In particular, SHG measurements of several cyano-azobenzene functionalised polymers have been reported [9]. The absence of harmonic signal from a series of poled polymeric samples of several polymethacrylates containing cyano-azobenzene group spaced from the methacryloyl moiety by a polymethylene spacer of different length (including PC6 polymer) has been recently pointed out [10]. The authors attributed in part this behaviour to the interdigitated structure of the mesophases of the polymeric samples. However, previous linear optical measurements of PC6 thin films performed in our group showed a large and stable photo induced birefringence [11] so we planned to investigate their second order non linear properties in photoassisted as well as in thermal electrically poled PC6 samples and to extend these studies to PC2 homo and copolymer films.

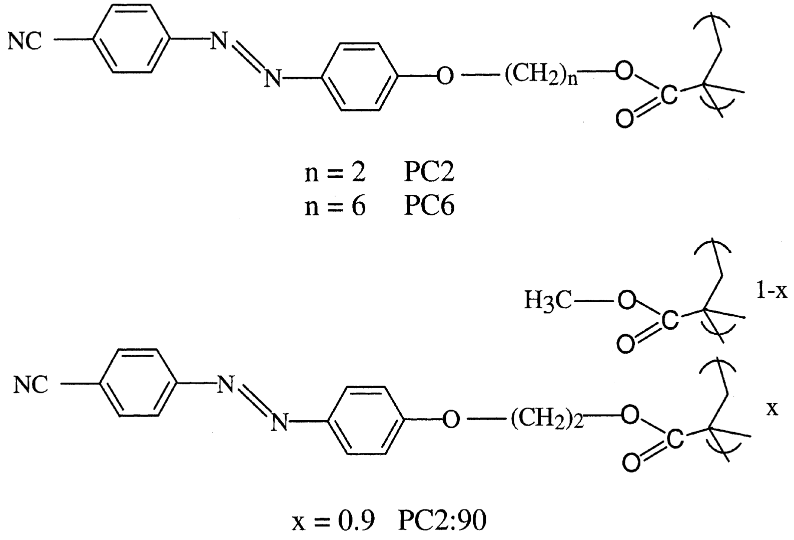

FIGURE 1 Chemical structure of the methacrylate homopolymers PC2 and PC6 and the copolymer PC2:90.

EXPERIMENTAL

The compounds studied in this work (Fig. 1) were synthesised by radical polymerisation using DMF as solvent and AIBN as thermal initiator. The polymers were passed through a silica gel column using dichloromethane as solvent. This purification was required in order to prevent the presence of conductive impurities, which could inhibit the effect of the electric field used in the Corona poling process. All the polymers are liquid crystalline and their thermal properties were determined from DSC measurements (scan rate: 10°C/min) and optical microscopy. The smectic-isotropic phase transition of PC6 polymer had been reported previously [12]. With respect to PC2, a SmA phase had been reported by Kidowaki *et al.*, [13] although these authors observed a narrow nematic phase near the isotropization temperature. Recently, Liang *et al.* reported a nematic phase between 110 and 166° [14]. Optical microscopy and X ray measurements performed in our group support the latter assignation. The phase transition temperatures as well as molecular weights of the studied polymers are shown in Table I.

Films about 2 microns thick were obtained from THF solution casting or spin coating onto glass plates with the opposite side coated with ITO (Indium Tin Oxide). The samples were dried in a vacuum oven at 40°C overnight. The films were subjected to thermal annealing at a temperature

TABLE 1 Phase Transitions Temperatures of the Three Polymers Studied

Polymer	Transitions temp. (°C)	M_w	M_w/M_n
PC2	g 105 N 158 I	32 000	3.14
PC2:90	g 110 N 138 I	22 500	1.41
PC6	g 56 SmA 163 I	17 000	2.1

Molecular weights and polydispersity index are shown.

5 or 10°C above their respective T_i (during 60 seconds) prior to any optical measurement. The thickness was measured by using a contact profilometer (DEKTAK).

A positive electric discharge was applied across the film using the standard Corona poling set-up. A DC voltage of 5 kV was applied to a needle, acting as positive electrode, perpendicular to the film. The distance between the needle and the film surface was about 1 cm.

In photoassisted Corona poling process we used 488 nm depolarised light from an Ar^+ laser. The intensity used was about 100 mW/cm^2 for the PAP processes.

Second harmonic generation measurements were performed in a usual configuration. A H_2 Raman cell excited by a Q-switched Nd:YAG laser and emitting at 1.9 µm was used as fundamental source. The repetition rate was 10 Hz and the pulse width 8 ns. A computer controlled NLO spectrometer completes the second harmonic generation experimental set-up. The 1.9 µm polarised light is separated in two beams. The less intense of them is directed to a NPP powder sample whose second harmonic signal is used as reference to monitor the laser fluctuations. Interference filters are used to remove the residual excitation light beyond the sample and the NPP reference. Finally the light coming out from them is directed to the photomultiplier tubes.

The films were held on a thermoregulated fixed stage for in situ measurements during the poling processes. The angle of incidence of the fundamental beam was 45°. In order to obtain the d_{33} non-linear coefficients we used a rotating stage for Maker fringes measurements using an X cut quartz crystal ($d_{11} = 0.4$ pm/V) as a reference. The experimental data were analysed following the Jerphagnon and Kurtz method [15].

It should be noted that preliminary SHG measurements of these polymers showed a noticeable difference depending on what side of the ITO coated glass substrate was coated with the polymer. In some cases we obtained a null NLO response when the polymer was directly deposited over the ITO, which we attributed to the presence of conductive impurities that could inhibit the electric field poling effect. The purification process described above was performed until the SHG results were roughly similar in the two cases (polymer over the ITO or over the opposite side).

EXPERIMENTAL RESULTS AND DISCUSSION

Thermal Corona Poling

We have measured the second harmonic generation (SHG) signal intensity profiles of Corona poled thin films versus temperature. The temperature controller was programmed at a heating rate of 5°C/min. The initially low signal at RT increases noticeably when the temperature increases as can be seen in Figure 2a for PC6 and PC2 samples. From these measurements 85°C and 150°C, both higher than their respective T_g, appear to be the optimal poling temperatures (T_{op}) for PC6 and PC2 respectively. The poling profile for PC2:90 is similar to that obtained for PC2 which seems reasonable considering that the T_g values are similar. However, a cyclic repetition of poling processes at 150°C followed by thermal annealing, results in progressive PC2 and copolymer film degradation. That is the reason why finally the chosen T_{op} was 130°C, 20 or 25°C above their T_g.

The SHG signal from the samples was recorded during the thermal poling process. The films were heated up to T_{op} under electric field and maintained at this temperature until signal saturation was observed (typically for 15 minutes). Then the samples were cooled down in presence of the field and finally the field was switched off. The SHG signal experiences an initial sharp decrease due to the disappearance of the EFISH (χ^3) contribution. After that, the SHG signal experiences a slower decay usually associated with the elimination of charges trapped during poling process and with some molecular reorientation. After a few days all the samples showed a remaining SHG signal which was stable at RT.

We have measured the SHG intensity signal at RT during sample rotation. From the obtained Maker fringes and using an X-cut crystal quartz as reference we deduced the polymer non linear coefficients d_{33}, assuming $d_{33} \approx 3d_{31}$. The values obtained were about 3 pm/V for PC6 and 3 and 3.5 pm/V for PC2 and PC2-90 respectively, similar to that reported in some methacrylic copolymers with cyano-azo-benzene in the side chain [9b,c]. A larger value (26 pm/V) was reported for a polymethacrylate functionalised with 4-dialkylamino-4′cyanoazobenzene [9a]. The higher hyperpolarizability value β of the chromophores, with a stronger electron donor, as well as the shorter wavelength used in Maker fringe experiments can justify the difference.

The thermal stability of the poling was analysed from the evolution of the remaining SHG signal versus the temperature. The samples were heated up from RT at a rate of 3°C/min. As we show in the Figure 2b,

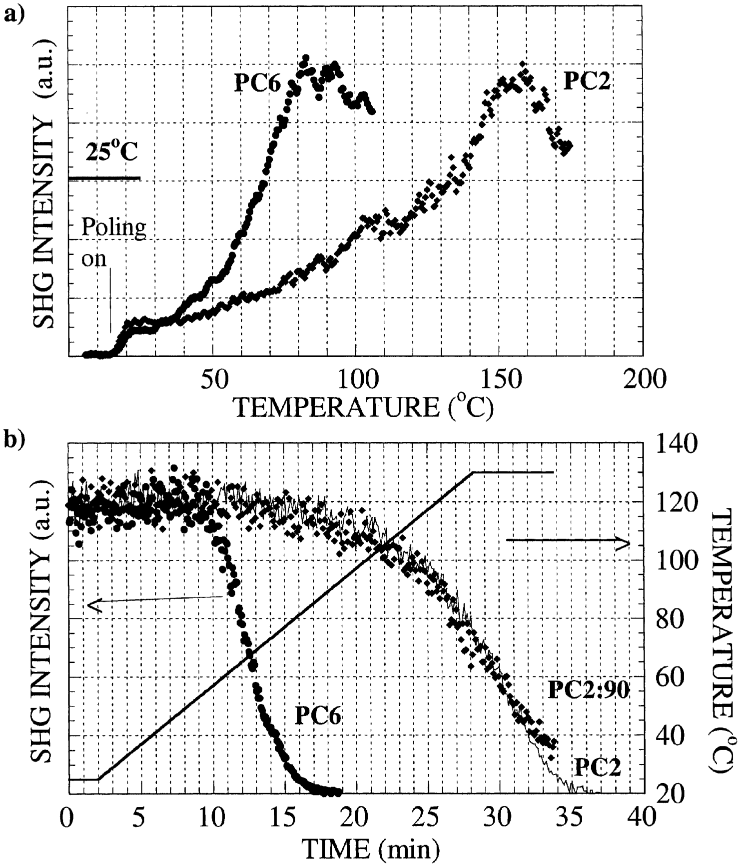

FIGURE 2 a) Second harmonic signal versus temperature for PC2 and PC6 samples. The heating rate was 5°C/min. b) Thermal stability of the remaining second harmonic signal as measured one weak after the thermal poling of PC6 (•), PC2 (continuous line) and PC2:90 (◆).

the signal is stable up to 55°C in PC6 and up to 90°C in PC2 and PC2:90 films, which again is in reasonable agreement with their respective T_g values.

We wish to point out that, as we mentioned in the introduction, Altomare *et al.* did not found any NLO response from poled PC6 polymeric samples [10]. This result was partly attributed by the authors to he interdigitated structure of the mesophases. However, we have achieved a nonlinear response of the same polymer. Since this response increased as the purification of our polymers went on, it is possible that the presence of conductive impurities could inhibit the polar order in Altomare's PC6 samples.

Photo-assisted Thermal Corona Poling

The effect of light irradiation at normal incidence on the SHG signal intensity from the films has been studied. We have used depolarised 488 nm light with an intensity of 100 mW/cm^2. In Figure 3 we show the SHG signal from a PC2:90 copolymer film during the photoassisted Corona poling process at various temperatures. One can notice the increase of the SHG when the irradiating light is switched on, due to the photoinduced orientation of dipoles stimulated by the trans-cis isomerisation. When the light is off, the signal experiences an enhancement mainly due to the back thermal cis-trans reaction, under the orientating electric field. Finally the signal achieves a maximum stable value in presence of the electric field. The enhancement of this maximum value with the temperature has been reported in different polymethacrylates [6b] and polyimides [16]. When the temperature at which we perform the PAP process is about 50°C in PC6 and about 100°C in PC2 and PC2:90, the maximum of the SHG signal in the presence of the field closely approaches the one obtained with Corona poling at T_{op}. The intensity of the remaining SHG signal (when the electric field is switched off and the initial decay has finished) is also similar. At T_{op}, the irradiation induces a positive effect on the orientation. In fact we have observed a

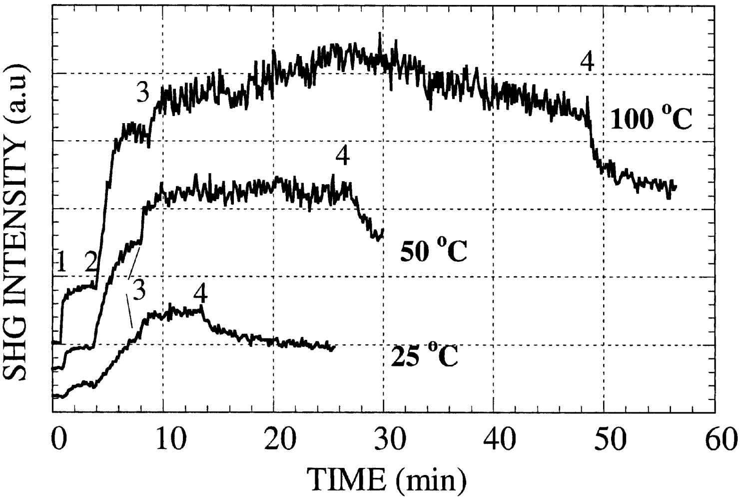

FIGURE 3 Second harmonic signal from a PC2:90 film during photoassisted electric poling processes at different temperatures. Labelling indicates: 1, electric field switched on; 2, 488 nm laser light on; 3, 488 nm laser light off; 4, electric field switched off. Between 3 and 4 the temperature is brought to RT.

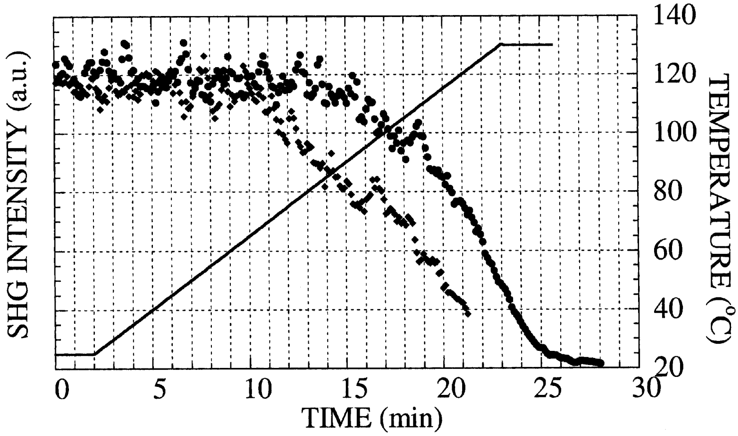

FIGURE 4 Thermal stability of the remaining second harmonic signal from a PC2 film subsequent to an optimal thermal poling (•) and a photoassisted poling at RT(◆).

sharp increase of the film SHG intensity signal if the sample is illuminated during half a minute at T_{op}. When the light is switched off the signal remains at a higher level than in the optimal thermal poling process.

The thermal stability of the remaining signal after a PAP process at room temperature is less than that from the thermal poling as can be seen in Figure 4. However PAP processes at higher temperatures (about 50°C and 100°C in PC6 and PC2 samples respectively) give similar stability results as was found after thermal poling. The increased stability of PAP samples when increasing the poling temperature has already been observed in other azo doped polymers [16,17].

CONCLUSION

We have shown that polymethacrylates functionalised with cyano-azochromophores can be oriented by thermal and photoassisted electric poling. The importance of purification in order to avoid conductive impurities has been evidenced. Photoassisted poling has been performed at temperatures lower than T_g giving rise to non linearity values comparable in magnitude and stability with those obtained from optimal thermal poling, performed at higher temperatures. For this reason, the sample degradation is much lower in photoassisted poled films compared to films subjected to optimal thermal poling.

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