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Aleksandra Apostoluk, Vincent Boucher, Raynald Seveno, C. Fiorini, B. Sahraoui, et al.. Structural and dynamic studies of the polar orientation induced by corona poling and all-optical poling in crosslinkable polymer thin films. NATO Science Series, 2003, 10.1007/978-94-010-0103-8_30 . hal-01511978

HAL Id: hal-01511978

https://hal.science/hal-01511978v1

Submitted on 27 Apr 2022

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STRUCTURAL AND DYNAMIC STUDIES OF THE POLAR ORIENTATION INDUCED BY CORONA POLING AND ALL-OPTICAL POLING IN CROSSLINKABLE POLYMER THIN FILMS

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1. Introduction

The fast development of photonics and progress in laser technologies has created the necessity for materials possessing high nonlinear photoactivity. Polymers containing various dye molecules in grafted as well as doped systems have recently been in the limelight of many research groups because of their various potential applications in electro-optic devices and integrated optics, as they possess large second order nonlinear properties, low dielectric constants, the possibility of inducing large nonlinearities, low attenuation and ease of processing [1-3]. Yet, some important issues concerning temporal stability of induced order and optical loss are still a challenge to researchers [4-7]. A polymer matrix containing non-centrosymmetric molecules is a macroscopically centrosymmetric solution in which second order nonlinear processes are forbidden due to symmetry reasons. Yet, the system properties may be altered by a non-centrosymmetric external field. In order to create second order nonlinear properties in polymer materials, they have to be prepared with required noncentrosymmetry, which is usually accomplished by poling techniques. Some years ago it was demonstrated that the all optical poling technique permits purely optical orientation of molecules and thus induction of the large second order susceptibilities $\chi^{(2)}$ [1, 8]. The important advantage of the all-optical technique is that it leads to a periodic ordering of the molecules with the spatial period fulfilling automatically the phase matching condition for second harmonic generation (SHG) [8]. The experiment consists of two phases: the writing (so called "seeding") period and the readout one. In seeding phase two beams, the fundamental one (ω) and its second harmonic (SH, 2ω) illuminate the sample and encode in the material the second order $\chi^{(2)}$-susceptibility grating. In the readout period only the fundamental beam irradiates the sample and the second harmonic generation is observed at the sample output. The coherent superposition of two beams at ω and 2ω frequencies results in the presence of a polar field E(t) inside the material, which is able

F. Charra et al. (eds.), Organic Nanophotonics, 355–366.
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to break the centrosymmetry of the medium. More accurately the temporal average cube $<E^3>_t$ of this field $E(t) = E_\omega(t) + E_{2\omega}(t)$, is non-zero, which can lead to an orientation-selective excitation of the molecules. The physical origin of the effect is attributed to an orientational hole burning in the initially isotropic distribution of molecules. Efficient all optical poling requires optimization of the seeding beam intensities and their relative phase difference. We report here on all-optical poling of a new material with improved stability of the induced order (when compared to Disperse Red 1) in a novel configuration of the experimental set-up where there is no need for taking into account the phase difference between seeding beams.

2. Sample preparation

The chemical structure of the electro-optic monomer (PIII) is given in the fig.1. Nitro- and tertiary amines were chosen as efficient acceptor and donor groups, respectively, and placed at the end of the p-extended molecule in order to obtain a large electro-optic coefficient. Moreover, the carboxylic group (cross-linking group) is placed on one of the aromatic groups in order to perform anchoring after the poling process. Because of its location and its electronic configuration, the anchoring function retains a high level of hyperpolarizability. This monomer can undergo free-radical copolymerisation with the methacrylic monomer bearing the second cross-linking function. This function is an epoxy one. The sample was 350 nm thick, coherence length $l_c = 2\pi/\Delta k = \lambda_{2\omega}/(n_\omega - n_{2\omega}) = \lambda_{2\omega}/\delta n$, where n_ω and $n_{2\omega}$ are the refractive indices for the fundamental and the second harmonic wave, respectively, is equal to 11,6 μm, optical density at 532 nm was equal to 1,57.
We also prepared the reticulated sample, of the similar - as close as it was possible - optical density at 532 nm as the non-reticulated sample, in which the reticulation reaction was performed via heating the sample to 150°C in an oven in ambient conditions (without applying the electric field). The sample thickness was 600 nm, optical density at 532 nm was equal to 1,35, the coherence length is 3,99 μm.

3. Poling and cross-linking procedure

We describe hereafter the poling and cross-linking processes to yield electro-optic copolymers with stable NLO properties. Preparation of thin films consists in dissolving the polymer powder in 1,2-dichlorethane. The solution is filtered through a Millipore Teflon filter (0,45 μm). The final polymer solution is then spin-coated onto glass substrates to form thin films. Corona poling involves heating of the NLO polymer to just above its glass transition temperature (T_g), applying a large electric field to orient the chromophore molecules, and cooling the NLO polymer while the field is still applied. As T_g of the non reticulated polymer is 65°C, the poling of the chromophores can be achieved at 70°C under an electric field (5,8 kV) applied by the Corona method for 30 minutes. Heating is performed in ambient conditions and the temperature is controlled with the thermocouple. The distance between the sample surface and the needle electrode is 20 mm and the poling current of about 1,5 μA (positive on the

needle). The next step is the anchoring process, which has to be done at a temperature, T_c = 150°C, higher than the poling one. The two functions must not react at the poling temperature to ensure an optimum chromophore orientation in the electric field. On the other hand, the anchoring kinetic has been studied [9] to determine the most efficient temperature to achieve the cross-linking between the NLO poled molecules and the epoxy function of the copolymer. This study has shown that the reaction involving epoxy and carboxylic functions is thoroughly achieved after 30 minutes at 150°C. The reticulation process involves changing of the colour of the sample, from deep pink to red. The absorption spectra made before and after the reticulation procedure revealed the blue shift of 11 to 39 nm in the spectrum of the reticulated sample when compared to the spectrum of the non-reticulated one, the value of the blue shift depending on the sample (see fig.1).

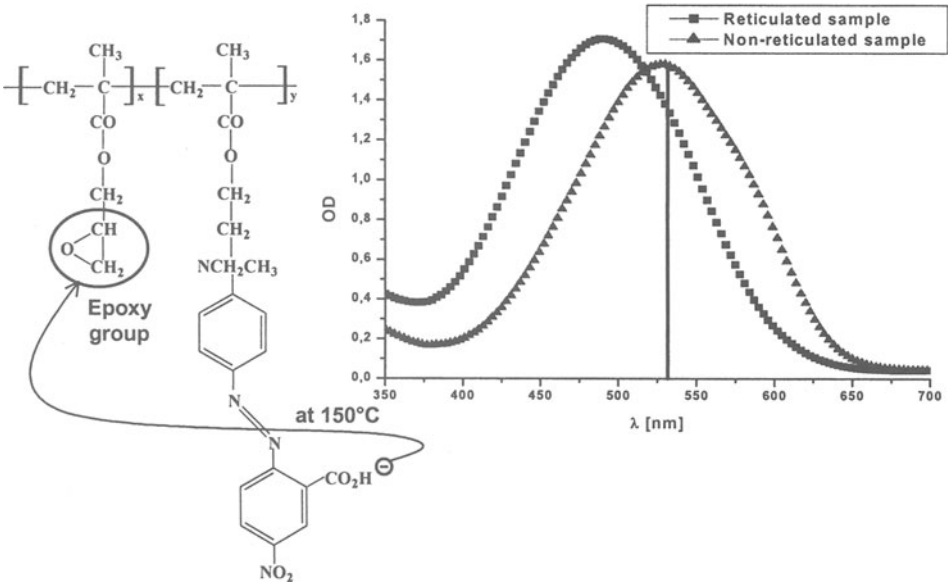

Fig.1. Structure of the cross-linkable PIII polymer synthesized for this study and absorption spectra of the non-reticulated sample (350 nm thick) and the reticulated one (600 nm of thickness). Optical densities (OD) at 532 nm were, respectively, 1,57 and 1,35. The straight line indicates the 532 nm wavelength. Blue shift between the two absorption spectra is equal to 37 nm.

4. Raman spectroscopy studies of the Corona poled samples

Raman spectroscopy permitted us to obtain information about the orientation of chromophores in a polymer film. The spectra were recorded in the backscattering geometry configuration with the use of a Jobin-Yvon T64000 spectrometer in conjunction with the microscope objective (×50). The preliminarily Corona poled film was illuminated by the linearly polarised in the plane of the sample beam from the continuous argon laser (514,5 nm). The radiation was collected by the microscope objective and its intensity measured and analysed by the spectrograph and the CCD camera. Different peaks observed in the spectrum characterise the vibrations of the dye molecules. It was demonstrated that the "breathing" mode intensity of para-substituted benzene rings (observed at 992 cm^{-1}) splits into several modes [10, 11]. Particularly, the intense peak observed at 1600 cm^{-1} is associated to the C-C stretching. This vibrational mode rings can be observed only if the incident field is polarized in the plane of the benzene rings. Therefore it is expected that it will disappear after the orientation profess is performed. Indeed, this peaks is no longer observed in the spectrum after orientation, when the chromophores are oriented perpendicularly to the sample surface. This leads to the first qualitative conclusion – in the scanned area (20 to 30 μm, the incident beam being defocalized so that the film would not degrade) that the benzene rings are oriented in the cone of about 10° around the 0*z* axis (axis perpendicular to the film plane). In fig.2 are presented the Raman spectra registered before and after orientation process, for the incident light power of 10 mW (above this value the sample is burnt) and time of exposition of 10 s.

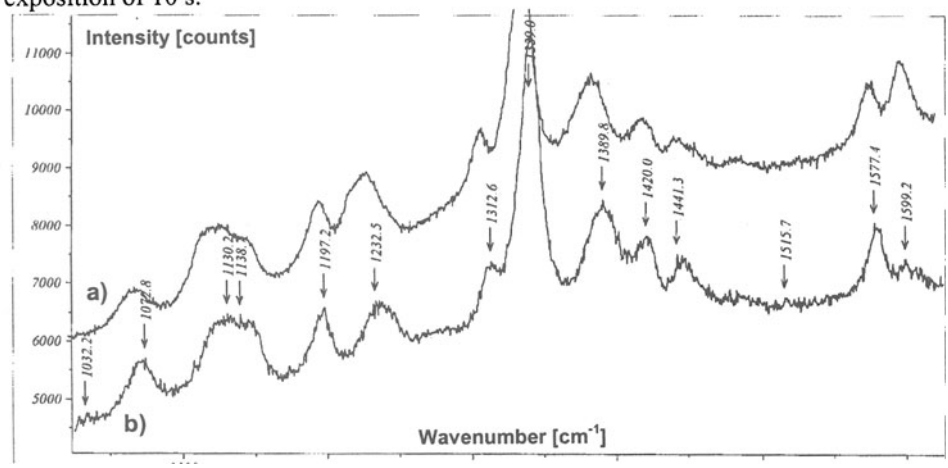

Fig.2. Raman spectra of the a) non-reticulated (upper curve) and b) reticulated and oriented via Corona poling method sample (lower curve).

5. Experimental set-up for all-optical poling

The scheme of the experimental set-up is presented in fig.3. The beam source was the actively Q-switched Nd:YAG laser (YG 580, Quantel) delivering 7 ns pulses at 1064 nm with a 10 Hz repetition rate. An external cavity potassium dihydrogen phosphate (KDP, KH_2PO_4) crystal (type II) permitted frequency doubling of the fundamental beam. At the crystal output the coherent superposition of copropagating generated SH beam and the residual fundamental one. The half-wave plate is used to turn the polarization of the fundamental beam. A polarizer assures linear and parallel polarization of the two beams. The pulse energies were 20 mJ and 17 μJ, respectively, for the fundamental and SH beam. The beams diameter was about 3 mm at the sample location. The experiment consists in two alternating phases: writing (seeding) and probing one. The sample was placed onto a 21,6° acute angle prism. In the writing periods, the two seeding beams ω and 2ω are incident onto the sample. The fundamental beam passing through the sample was blocked with the KG3 filter (heat absorber) inserted behind the prism and the sample and leaving only the SH beam pass. In the probing period the second order susceptibility was measured through the SH generation in the sample. The SH signal was detected by a photomultiplier tube (PMT), with the 2ω seeding beam blocked by a RG 630 filter (green cutting filter, 3 mm thick, infrared transmitting) and the ω beam left incident onto the sample. A set of calibrated filters was used to ensure correct scaling of the SH signal. The signal delivered by the PMT was measured and averaged by an oscilloscope. Moreover, an electronically controlled shutter was placed in front of the PMT in order to avoid the possible saturation due to the strong green seeding beam during seeding step. The fundamental beam served as a seeding and the probing beam, while the SH beam was used as a seeding beam only. The configuration with the prism and the beam arrangement at the sample output during the readout phase is shown in fig.4.a), wavevectors configuration – in fig.4.b). For the polymer system studied the intensity of the strong 2ω signal was registered.

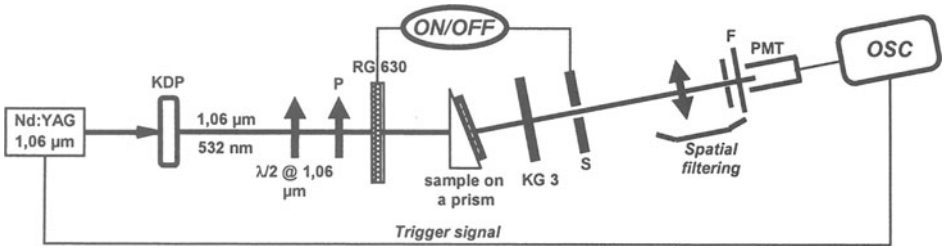

Fig.3. Experimental set-up for all-optical poling. P – polarizer, λ/2 for 1,06 μm – half wave plate at 1,06 μm, RG 630 – Schott green blocking filter, 3 mm thick, KG3 – Schott heat blocking filter; shutter (S) is synchronized with the insertion of the red filter (Schott RG 630) which cuts the 2ω beam during $\chi^{(2)}$ readout process; F - spatial filter for 532 nm. The signal is detected by the photomultiplier tube (PMT) and registered on the oscilloscope (OSC).

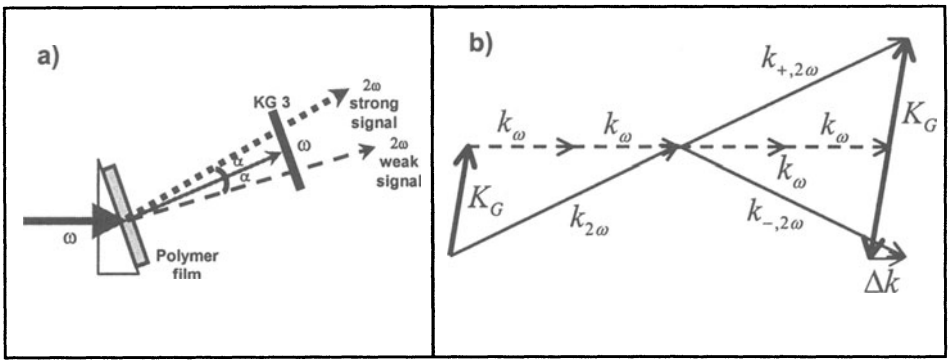

Fig.4. Part (a) shows schematically the beam configuration at the output of the prism; (b) scheme of the interacting fields' wavectors – k_ω , $k_{2\omega}$– wavevectors of the fundamental and second harmonic frequency fields, respectively, $k_{+,2\omega}$ – wavevector of the strong SH signal, $k_{-,2\omega}$ – wavevector of the weak SH signal, K_G – grating wavevector, Δk - wavevector mismatch.

6. Results and discussion

In order to test the real harmonic conversion potentialities in optimized conditions, it is necessary to determine the optimal phase difference between the seeding beams. Any other phase difference will lead to an "overpainting" of the polar interference pattern, and finally result in a limited (less effective) polarization of the sample. The configuration with the prism permits us to become independent of the influence of the relative phase difference ($\Delta\Phi$) between the seeding beams on the induced polar order [12]. In the case of a freestanding sample the intensity of the generated SH signal reveals a sinusoidal variation with $\Delta\Phi$ with a period of 180° [8]. In our experiments the value of the generated second harmonic signal remains constant, irrespective of the relative phase difference. The SH signal observed at the sample output is a response averaged over all the points on the beam diameter, allowing to ignore local cancellation of the encoded $\chi^{(2)}$, which results in the constant SH signal as the $\Delta\Phi$ is varied. This is of crucial importance especially when new materials are studied, as for every new polymer system it would be necessary to adjust the relative phase difference between the seeding beams due to the difference in absorption and refractive indices between new systems and the material of reference (usually DR1-MMA). The presented method allowed us to avoid the long adjustment procedure. In addition, the presence of the weak signal at the prism output permitted us to perform the real-time monitoring of the all-optical poling process [12].

The growth and dynamics of the seeding-type preparation of both samples is illustrated in fig.5. The preliminarily reticulated sample gave higher signal than the non-reticulated one, which was surprising. Both samples reveal a good stability of the photoinduced second order susceptibility $\chi^{(2)}$ under constant illumination with strong fundamental beam (the same one as in the seeding phase) over 5 hours. The decay dynamics of the normalized photoinduced $\chi^{(2)}$ is presented in fig.6 and fig.7.

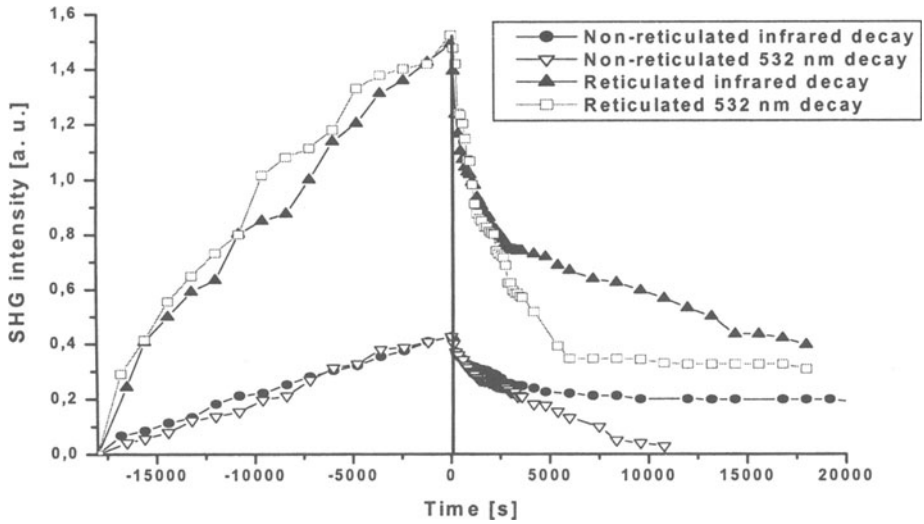

Fig.5. Time evolution of the SH generated signal (in arbitrary units) in the non-reticulated sample (circles – decay under infrared beam, down triangles – decay under 532 nm beam, sample 350 nm thick) and in the reticulated one (up triangles – decay under 1,06 μm beam, squares – decay under green beam, sample 600 nm of thick). Negative times correspond to the seeding preparation phase. At time zero the seeding process is stopped (straight vertical line). Positive times correspond to the temporal decay of the photoinduced $\chi^{(2)}$ susceptibility. The samples were placed on a prism.

When the material is irradiated by either of the two writing fields after the seeding process is stopped, it was observed that the dynamics of the relaxation of the induced susceptibility $\chi^{(2)}$ is much faster than for the dark decay [8]. However, for a mono-frequency 2ω irradiation, the induced birefringence persists [8]. It clearly indicates that the irradiation of a formerly seeded area with a beam at frequency ω or 2ω destroys only the photoinduced polar order [13, 14]. Under monochromatic irradiation, the molecules are re-excited and reoriented. This excitation is axial, so solely the photoinduced polar order is erased. The fact that the birefringence is preserved during the irradiation with the single frequency beam clearly shows that the axial terms of the excitation probability are at the origin of the birefringence related to the seeding process.

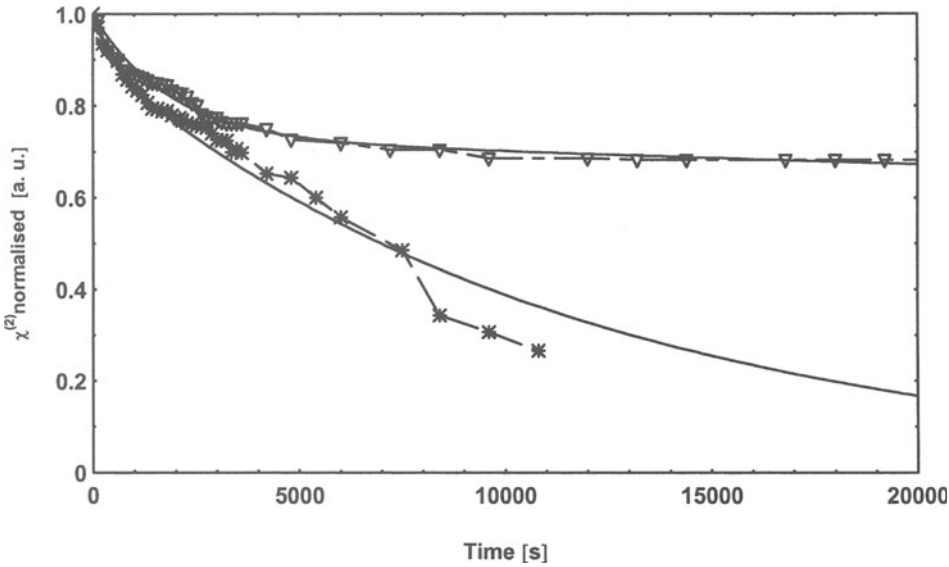

Fig.6. Decay of the normalized $\chi^{(2)}$ of the non-reticulated sample under constant illumination with fundamental beam (triangles) and green beam (stars). Solid lines are fittings to the eq. (1).

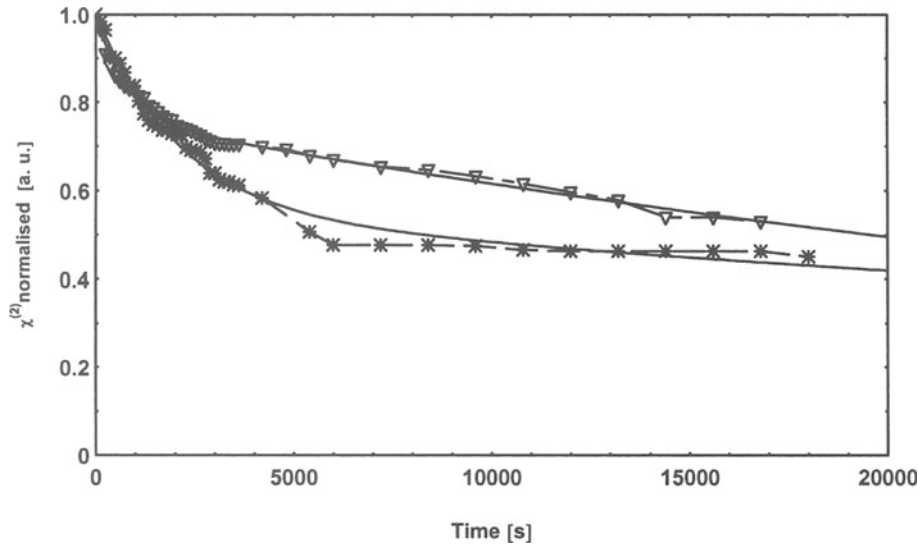

Fig.7. Decay of the normalized $\chi^{(2)}$ of the reticulated sample under constant irradiation with 1,06 μm beam (triangles) and with 532 nm beam (stars). Solid lines are fittings to the eq.(1).

As it can be seen from fig.6, after the seeding process is stopped, two time domains of the decay of the second order nonlinear susceptibility $\chi^{(2)}$ can be observed: an initial very fast decay occurring within a few seconds after interruption of the preparation

process, and a second, much slower, multiexponential one. As the hyperpolarizability β of DR1 is different in the *cis* and *trans* isomers [15], the first very rapid decay contains a contribution, which corresponds to lifetime of the *cis* form (produced through the photoinduced *trans-cis* isomerization in the seeding phase), which comes back to the *trans* form without any net orientation [13, 15]. The second component originates from an orientational scattering of the polarly oriented molecules of the *trans* form inside the matrix. The first fast decay of the thermodynamically unstable *cis* form is a thermally induced reaction. The second one (*trans* isomer orientational scattering) depends on the matrix scattering constant (rigidity of the polymer matrix), laser repetition rate, the way the dye molecule exists in the polymer host, etc.
It was found that the decay experimental curves could be fitted with the biexponentional function, given by the following equation [16]:

$$y(t) = A \cdot \exp(-t / \tau_A) + B \cdot \exp(-t / \tau_B) \qquad (1)$$

where $y(t)$ is the normalized value of the $\chi^{(2)}$ at point t after the seeding is stopped: $y(t) = \frac{|\chi^{(2)}(t)|}{|\chi^{(2)}_{\max}|}$. The first term depicts the faster decay process with the time constant τ_A, the second term - describes the slower one, with the τ_B time constant. A and B are contributions to the saturated value of $\chi^{(2)}$ (y at time zero) and $A + B = 1$. The parameters (τ_A , τ_B , A, B) obtained through the fitting procedure are summed up in Table 1.

	Infrared decay				*Green decay*			
Sample	τ_A [s]	A	τ_B [s]	B	τ_A [s]	A	τ_B [s]	B
Non-reticulated	1750	0,26	203218	0,74	580	0,1	11876	0,9
Reticulated	753	0,23	46233	0,77	2124	0,45	73617	0,55

Table 1. Parameters derived from the fitting of the decay of the photoinduced $\chi^{(2)}$ curves to the eq.(1).

The value of the τ_A could be attributed to the thermal *cis-trans* back reaction, which in different polymer systems may vary from seconds to minutes [16, 17]. The τ_B correspond to the *trans* isomer orientational scattering inside the matrix. The value of the A parameter indicates that the loss of the polar order originates mostly from the reorientation of the *trans* isomer inside the matrix, however the observed stabilization of the signal on a certain level indicates that a large fraction of the chromophore molecules stay fixed in the oriented position. The thermal cross-linking reaction may be induced by the seeding beams themselves – the sample heats as it absorbs light. This could be tested by increasing the laser repetition rate, but we could not perform this experiment with our experimental set-up (we already use the maximal repetition rate of the laser). The reticulation procedure strongly influences the rigidity of the polymer matrix, as it occurs that for the polymer system studied, the reticulation leads to the increase of the matrix rigidity. The reaction of crosslinking performed before poling hinders the mobility of the dye molecules, which leads to the decrease of the photoinduced nonlinearity. In the reticulated sample some of the bounds which attach the molecules to

the epoxy group are weakened, molecules are excited and then re-attached – that is probably why we observe photoinduced SHG. Surely, not all dye molecules are re-attached and that is why we observe fast decay of the induced orientation. However, the process of reticulation appears much more accented in the non-reticulated sample and concerns bigger population of photochromic molecules. The non-reticulated polymer studied has a very low T_g, lower than the crosslinked one, and as the sample is seeded, the reticulation reaction progresses, but the randomization process goes on simultaneously, and the final result is the competition between these two. The photoinduced polar order is preserved via the reticulation, as the polarly oriented molecules are fixed in their positions, but it is also destroyed by molecular orientational scattering of non-fixed molecules. The fact that the saturation of the second order susceptibility $\chi^{(2)}$ is not attained after 5 hours of the seeding process indicates that the dynamical equilibrium is not established. The reticulation reaction through light absorption has a significant contribution to the temporal stability of the photoinduced order, as there stays a part of nonlinear optical moieties cemented in the matrix and difficult to reorient. Similar experiment was performed on the high T_g (180°C) polyurethane polymer grafted system by Si et al. [18]. They observed that photoinduced crosslinking resulted in better stability of the induced orientation, when compared to the case when the sample was seeded with green seeding beam 10 times weaker and at lower laser repetition rate, however lower than the stability of the orientation induced when the sample was oriented in conditions of low power and low repetition rate, but with simultaneous heating of the sample to 85°C.

We also tested the dark decay process in both samples and it turned out to be much longer than the photostimulated one, which indicates that the orientational scattering is slow in both samples. It should be also noticed that the photoinduced polar orientation is erased in the probing process by the strong laser fundamental ω beam. However the observed decay of the SH signal reveals very good temporal stability even under the influence of this optical erasure, in comparison to the DR1-MMA grafted system, in which the loss of one order of magnitude in the value of the SH signal is observed after two hours of constant illumination with fundamental beam [8].

The photostimulated relaxation erasure is the major obstruction of the use of such systems. The stability of the induced polar order would increase if the dye molecules were fixed after or during orientation process, with the reduction of their free volumes. The thermal cross-linking reaction is induced by the seeding beams themselves – the sample heats as it absorbs light. We also tested the stability of the polar orientation induced by Corona poling method. The sample was placed at 45° incidence angle, in the *s*-incidence beam polarization configuration, as in the Corona poling method dye molecules are oriented perpendicularly to the surface of the film. The SH signal generated by the sample remained stable over two hours of constant irradiation with strong fundamental beam. The same test was performed under the irradiation with the second harmonic beam and the SH signal generated by the corona poled sample was also constant.

7. Conclusions

Structural and dynamic studies of the induced noncentrosymmetry were performed in a reticulable polymer system with azobenzene chromophores. Growth and decay kinetics of the photoinduced second order susceptibility $\chi^{(2)}$ was tested through photoinduced SHG in the samples. From fitting of the experimental results to the theoretical equation, parameters representing the *cis-trans* thermal backreaction and orientation scattering of *trans* molecules with net orientation were obtained. In particular good photostability of the induced polar orientation was demonstrated, presumably due to the fraction of molecules, which remained fixed in their positions via photoinduced reticulation reaction.

Erasure mechanisms following an intense monochromatic irradiation appear to be the major limitation to the use of such systems, as the decay process determines their potential application to optical storage for instance. Yet, experiments performed recently by some research groups with crosslinkable polymers [18] turned out to be an attractive way of improving the photo-stability of the photoinduced polar order. Another method could be the self-seeding of the optically induced orientation [19].

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