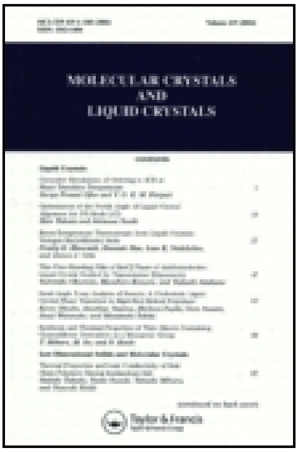

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Optical Preparation of Polymers for Phase-Matched Frequency Doubling

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OPTICAL PREPARATION OF POLYMERS FOR PHASE-MATCHED FREQUENCY DOUBLING

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Abstract: The nonlinear optical process which permits the optical preparation of centrosymmetric materials for frequency doubling is described in terms of an orientational hole-burning effect induced through non-zero $\mathbf{E}^3$ resonant six-wave mixing. A permanent all-optical poling is achieved by seeding preparation under backward and forward geometries in an azoaromatic acrylic copolymer. The frequency doubling second order susceptibility reaches 90 pm/V, as large as using the more classical corona poling technique. This offers a new molecular engeneering route to the control and optimization of phase-matched oriented microstructures for frequency conversion and also for electro-optic organic devices.

1. INTRODUCTION

The multi-functionality of organic materials which is given by organic synthesis diversity as well as physico-chemical tailoring opens new directions in the control and optimization of material properties from the molecule to the device. A major technical problem which is a recognized question of molecular engineering is the practical realization of devices for frequency conversion, with an aim at building a compact blue laser source.

In a general description, nonlinear optical properties of materials including frequency conversion are discribed in terms of susceptibility tensors $\chi^{(n)}$. They are the successive terms in the expansion of materials polarization **P** with respect to powers of fields:

$$\mathbf{P}_i = \chi^{(1)}_{ij}\mathbf{E}_j + \chi^{(2)}_{ijk}\mathbf{E}_j\mathbf{E}_k + \chi^{(3)}_{ijkl}\mathbf{E}_j\mathbf{E}_k\mathbf{E}_l \ldots \tag{1}$$

The first term describes the linear index of refraction. The second term describes second harmonic generation, electro-optic effect, parametric mixing and optical rectification. The third term describes third harmonic generation, optical Kerr effect and all the so-called third order effects. First and third order terms $\chi^{(1)}$ and $\chi^{(3)}$ are non-zero in all materials. However, the second order term is zero in all materials exhibiting inversion symmetry. Obviously, with inversion symmetry, polarization must change sign simultaneously with the electric field. This implies that $\chi^{(2)}_{ijk} = 0$. In order to build devices for frequency doubling, with $\chi^{(2)}_{ijk} \neq 0$, molecules have thus to be organized into noncentrosymmetric structures. The polar orientation of molecules is essential in order to achieve noncentrosymmetric assemblies of molecules.

2. POLAR ORIENTATION

Polar ordering is not a universal tendancy of molecules. It is naturally achieved by means of the short range interactions between molecules which take place in some specific supramolecular assemblies such as crystals, Langmuir-Blodgett films, liquid crystals and ferroelectrics. Those effects have already been reviewed with the aim at optimizing the related nonlinear optical properties [1].

Polar orientation is not spontaneous in dispersed media such as liquid and polymer solutions. It is usually achieved using the so called electric field poling method. It can be performed with molecules having a strong permanent dipole moment μ. Molecules align their dipole moment parallel to the applied electric field E_0 (figure 1a), in order to minimize rotational energy $-\mu E_0 \cos\theta$. Starting from an isotropic solution, this leads to a net molecular orientation which, under thermal equilibrium gives an average angle $\langle\cos\theta\rangle \propto \mu E_0/kT$ with respect to the field direction.

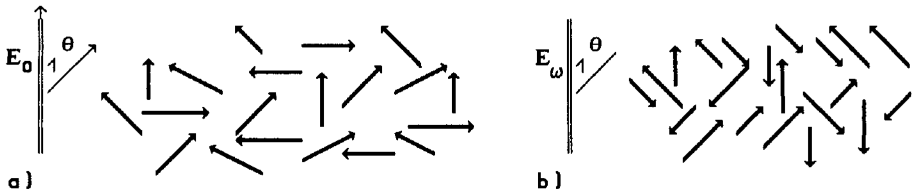

Figure 1: *(a) Electric field poling of molecules. (b) Optically induced anisotropy in molecular solutions.*

No polar orientation is achieved by monochromatic optical fields E_ω. They change sign periodically at rates as high as 10^{15}Hz. They thus only induce optical anisotropy in molecules which have an anisotropic polarizability α $(\alpha_{\parallel}-\alpha_{\perp} \neq 0)$. Molecules align their induced dipole moment αE_ω in the same direction as the polarization of the electric field E_ω (figure 1b), in order to minimize the rotational energy $-\frac{1}{2}\alpha E^2 \cos^2\theta$. Starting from an isotropic solution, this leads to a net molecular alignment which, under thermal equilibrium gives an average angle $\langle\cos^2\theta\rangle \propto \alpha E^2/kT$ with respect to the field polarization. No polar orientation is achieved because the net effect is quadratic in field. Indeed, the field itself has no polarity.

3. OPTICAL NON-CENTROSYMMETRY

The discovery that combinations of optical fields could exhibit polarity opens up new possibilities for the optical handling of molecules [2]. Let us figure a standard situation in which an optical field exhibits polarity. This is the coherent superposition of a field E_ω at a fundamental frequency ω with its harmonic $E_{2\omega}$ at frequency 2ω as pictured in figure 2. Polarity of this combination appears in its non-zero average cube $\langle E^3\rangle_t$ where the subscript t represents the average over time. As each component is oscillating, $\langle E\rangle_t=0$.

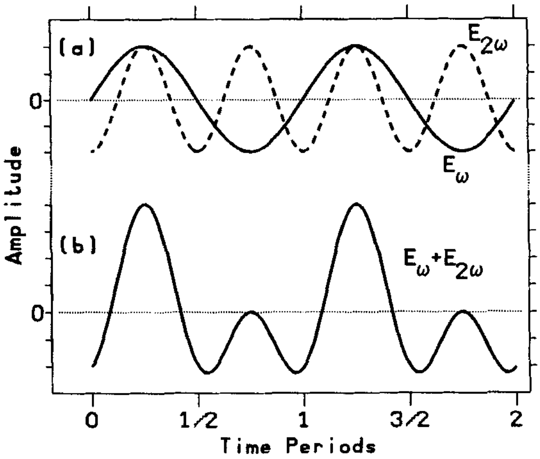

Figure 2: *(a) Time evolution of fields* E_ω *at fundamental (continuous line) and* $E_{2\omega}$ *at harmonic frequency (broken line). (b) Coherent superposition of the fields* $E_\omega+E_{2\omega}$ *exhibiting polarity.*

Sign of the polarity $\langle E^3\rangle_t$ is determined by the relative phase between ω and 2ω beams. It is pictured in figure 3 in which the cube of $E_\omega + E_{2\omega}$ is represented along the propagation coordinate in a dispersive medium with $n_{2\omega}-n_\omega= 0.05$. Since in condensed materials propagation speed is different for fundamental and harmonic frequencies, optical polarity alternates between positive and negative extrema. In dispersive materials with index $n(\omega)$, the periodicity is $\lambda/2(n_{2\omega}-n_\omega)$ were λ is the fundamental wavelength. It is the periodicity necessary to achieve quasi phase-matching for frequency doubling [3].

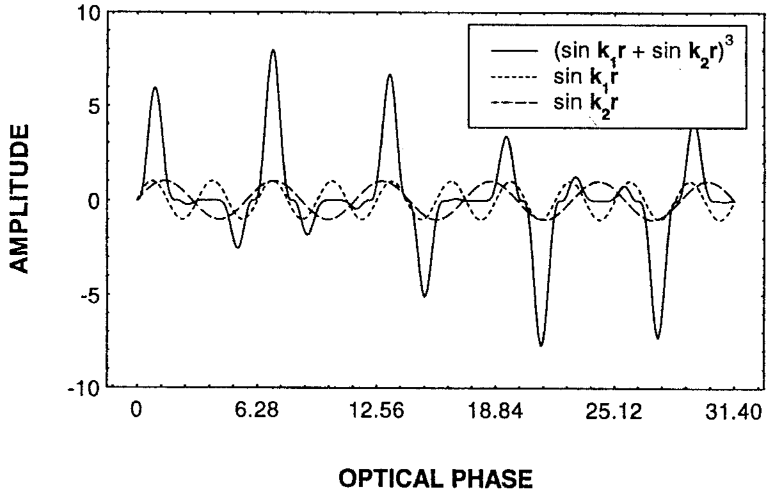

Figure 3: *Cubic interference* E^3 *between* E_ω *(dotted line) and* $E_{2\omega}$ *(dashed line) propagating at different speeds with 0.05 index difference inside a dispersive material. Optical phase is given for the harmonic wave in multiple of* π.

4. NONLINEAR OPTICAL INTERACTION

The observation of second-harmonic generation in optical fibers prepared by an intense light at 1064nm [4] or with a simultaneous seeding light at double frequency (532nm) [5] revealed the possibility of inducing a $\chi^{(2)}$ by light in a centrosymmetric material. It is the first application of a mechanism involving the non-zero average of the third power of the optical field $\langle E^3\rangle_t \neq 0$. In order to build the molecular engineering rules which permit control of the effect, it is necessary to identify processes by which materials record $\langle E^3\rangle_t$.

$\langle E^3\rangle$ effects can be viewed as six-wave mixing proceses [6]. Many processes such as the nonlinear electric field induced second harmonic generation permit the recording of $\langle E^3\rangle$ [2]. In the case of a solution of molecules excited under resonant conditions, they find another simple description. The origin of the nonlinearity can then be pictured in terms of a hole burning into the distribution of molecular orientations [7] (figure 4). Indeed, a molecule which is irradiated at resonance with fields E_ω and $E_{2\omega}$, respectively at fundamental and harmonic frequencies, experiences a polar combination of one and two photon absorptions. The time-averaged rate of absorption $\dot{W}$ contains a polar term which is third order in the field $E_\omega + E_{2\omega}$. It is

$\dot{W} = -2i\omega(\beta-\beta^*)E^*_{2\omega}E_\omega E_\omega$ + *cc*. where β is the second-order polarizability. Under stationnary conditions, the resonant excitation at energy $2\hbar\omega$ statistically results in an induced second-order polarizability $\beta_{ind.} = \Delta\beta\,\tau\dot{W}/2\hbar\omega$ where $\Delta\beta$ is the second-order molecular polarizability difference between excited and ground states and τ is the excited-state lifetime. The average induced second-order polarizability tensor is thus:

$$\beta_{ind.} = 2\hbar^{-1}\tau\,\Delta\beta\,\beta''(E_{2\omega}E^*_\omega E^*_\omega + E^*_{2\omega}E_\omega E_\omega) \qquad (2)$$

where β'' is the imaginary (absorption) part of β. The average $\langle\beta_{ind.}\rangle_{or.}$ over random orientations is non-zero even in isotropic solutions because it behaves as an even order tensor of rank 6. The overall frequency doubling process is fifth order in field; it can be described by a $\chi^{(5)}$. For a density N of molecules, the optically induced second-order susceptibility is, neglecting the local field factors, $\chi^{(2)}_{ind.} = N\langle\beta_{ind.}\rangle_{or.}/\varepsilon_0$. It is modulated following the spatial dependence of the field product given in figure 3. It is a situation of optically-induced quasi phase-matching [3]. Unlike usual quasi phase-matching techniques, there is no simultaneous induction of an index grating [8]. This is an advantage over periodic poling techniques because index gratings can have deleterious scattering effects on the signal.

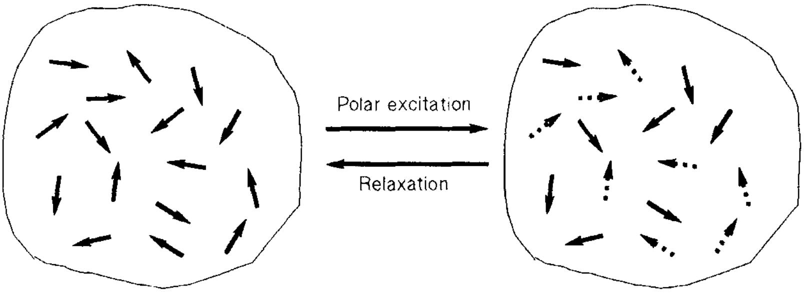

Figure 4: *Hole burning into the distribution of molecular orientations (arrows). The polar dual-frequency absorption selectively excites the molecules oriented to the top of the figure (dotted arrows). This yields a net second order susceptibility, in negative print, as a result of the non-centrosymmetric unexcited molecules. Relaxation back to a centrosymmetric state processes via de-excitation or molecular rotational diffusion into the matrix.*

5. OPTICAL PREPARATION OF PLASTIC MATERIALS

The first experimental observation of an optical selection of molecular orientations is the transient picosecond induction of non-centrosymmetry recorded using phase-matched frequency doubling in a solution of the polar molecule 4-diethylamino, 4'-nitrostilbene in tetrahydrofuran [9]. The same procedure was also applied to the orientation of non-polar molecules such as the triphenyl-methane dye ethyl-violet which exhibits octupolar symmetry [10]. It also permits the orientation of ionic molecules which, owing to their conductivity in solution, cannot be oriented using static electric field poling [11]. A complete understanding of the optical orientation processes has been recently developped for solutions of the highly nonlinear azo-dye disperse red 1 [13]. Unlike the electric field poling in which molecules undergo electric field assisted rotation as pictured in figure 1, the optical selection of orientations corresponds to a bleaching of molecules (figure 4). A cause of relaxation of the induced non-centrosymmetry is thus recovery of this bleaching. However, in liquid solutions, loss of orientation has been identified as the fastest relaxation process [7]. It is related to viscosity and it completes within a nanosecond, leading to isotropy. Orientational diffusion can be damped by the incorporation of molecules into solid matrices such as glassy polymers [1]. For this purpose, we used a random acrylic copolymer with nonlinear 4-nitro, 4'-amino, diazobenzene chromophores grafted as pendant side groups (figure 5) [12].

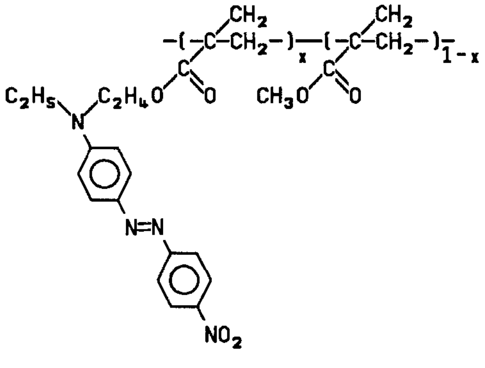

Figure 5: *Acrylic copolymer with disperse-red-1 type nonlinear pendant groups* (x=0.35).

In this polymer, the induced non-centrosymmetry lifetime whose evolution is diplayed in figure 6 is increased by more than 11 orders of magnitude with respect to liquid solutions. Indeed, the bleached azobenzene chromophores undergo a *trans to cis* isomerisation which reduces their free volume. It enables a net reorientation of the excited molecules during their *cis* lifetime

[13]. Hence, the anisotropic excitation leads to a long lived change in the distribution of orientations which is frozen after back *cis* to *trans* relaxation [14].

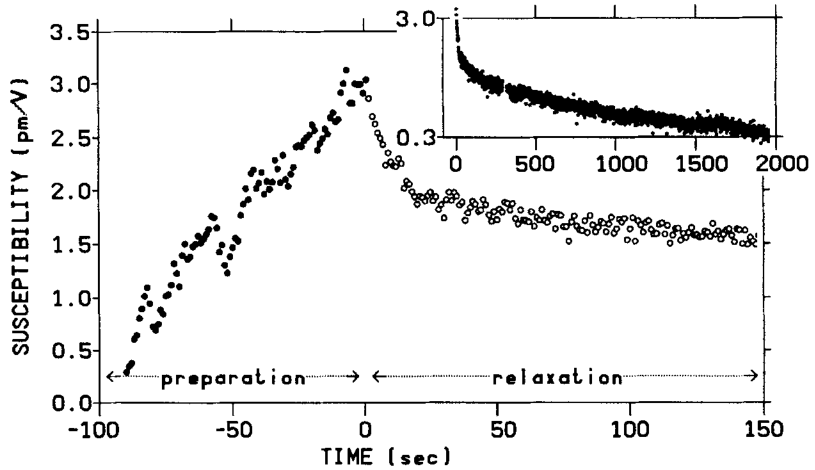

Figure 6: *Time evolution of the* $\chi^{(2)}$ *susceptibility grating in a 0.7μm copolymer film spin-coated on a fused silica substrate. It is induced by a mode-locked YAG laser delivering 33psec pulses at 1064nm at 10Hz repetition rate. Orienting beam fluence is 1GW/cm*^{2} *for the fundamental and 50MW/cm*^{2} *for the harmonic beam. It is probed in a non-colinear phase-matched geometry by the second harmonic of a 1GW/cm*^{2} *beam at 1064nm, during (close circles) and after (open circles) 100sec preparation by orienting beams. The inset shows the evolution on a longer time-scale .*

Chromophores in this example where oriented in a non-colinear geometry, with separated fundamental and harmonic preparation beams as well as fundamental test beam. It is the phase-conjugation geometry [15] pictured in figure 7a which permits analysis of the temporal, polarization and intensity dependances with a large signal-to-noise ratio.

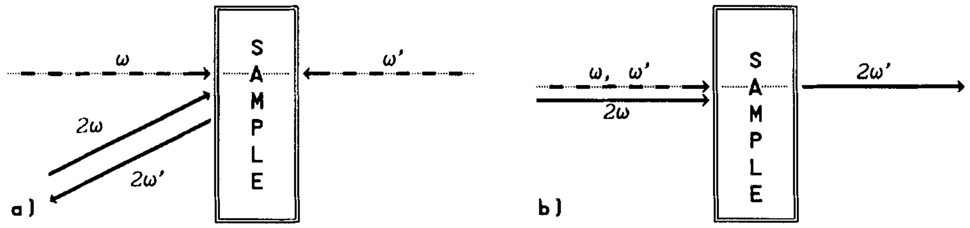

Figure 7: *(a) Beam arrangement for the backward non-colinear phase-matched geometry of phase conjugation, (b) and for the forward colinear seeding geometry. Unprimed and primed frequencies correspond respectively to preparation and test beams. Polarizations were set parallel in these experiments.*

Larger nonlinearities have been achieved in the same polymer using an electric-field poling procedure [16]. Since it appears in figure 6 that saturation is not attained after a few minutes of preparation, and as non-colinear configurations are unstable with respect to microscopic fluctuations in the optical path length [17], larger nonlinearities are expected from the more mechanically-stable forward colinear seeding configuration pictured in figure 7b. Another optimisation of the seedind process is obtained by carefull control of the relative intensities and phases of the preparation beams [18]. This is what appears in figure 8 where the optically induced SHG nonlinearity adds during 2 hours, up to an order of magnitude nonlinearity gain with respect to the non-colinear experiment in figure 6. The 90 pm/V nonlinearity achieved by all-optical poling is the same as that achieved using the more classical corona poling technique. This implies an orientation ratio $\langle\cos^3\theta\rangle$ close to 0.2 and an electro-optic coefficient r_{33} close to 10pm/V at 1.3μm, but in a direction parallel to the substrate [16].

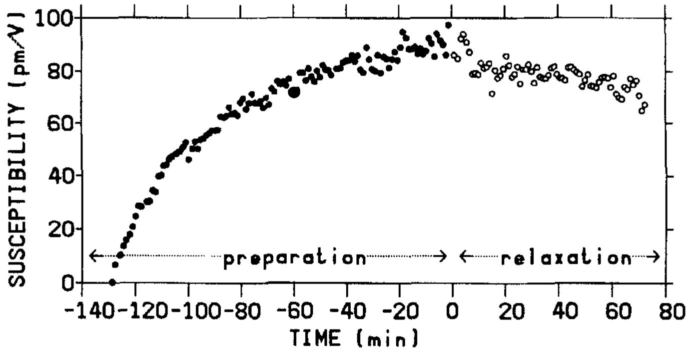

Figure 8: *Construction of the $\chi^{(2)}$ susceptibility in a spin-coated copolymer film under forward colinear propagation conditions. It is induced at 10Hz repetition rate and probed each minute without harmonic preparation beam, during (close circles) and after (open circles) 2 hour preparation by orienting beams.*

6. CONCLUSION

The possibility of inducing a long-lived optical orientation in organic materials opens a door to the microscopic control of organized structures suitable for frequency conversion. The ratio of oriented molecules in seeded plastics is now close to 0.2. It is the same magnitude as that achieved using corona or electrode poling DC field techniques. The magnitude of the induced $\chi^{(2)}$ close to 90 pm/V is the largest achieved by seeding preparation of optical materials [19]. A breakthrough with this technique is the possibility of inducing a large r_{33} electro-optic coefficient in a direction parallel to the substrate, unlike with corona poling which is perpendicular. The major practical breakthrough is the possibility of inducing a phase matched orientation over large distances, up to tenth of centimeters, in a straightforward manner. Experiments are now in progress in order to improve in this direction, with an aim at orienting molecules in a plastic fiber. With the use of organic materials, we have the possibilities offered by molecular engineering to tailor their optical properties in order to achieve the optimization of phase-matched materials for frequency conversion devices.

7. REFERENCES

1. D.S. CHEMLA and J. ZYSS, Nonlinear Optical Properties of Molecules and Crystals, Academic Press (Orlando, 1987).
2. N.B. BARANOVA and B.YA. ZEL'DOVICH, JETP Lett. **45**, 716 (1987).
3. J.A. ARMSTRONG, N. BLOEMBERGEN, J. DUCUING and P.S. PERSHAN, Phys. Rev. **127**, 1918 (1970).
4. U. OSTERBERG and W. MARGULIS, Opt. Lett. **11**, 516 (1986).
5. R.H. STOLEN and H.W.K. TOM, Opt. Lett. **12**, 585 (1987).
6. F. CHARRA and J.M. NUNZI, J. Opt. Soc Am. **B 8**, 570 (1991).
7. C. FIORINI, F. CHARRA and J.M. NUNZI, *Six wave mixing probe of light induced second harmonic generation: example of dye solutions*, submitted (1994).
8. G. KHANARIAN, R.A NORWOOD, D.HASS, B. FEUER and D. KARIM, Appl. Phys. Lett **57**, 977 (1990).
9. F. CHARRA, F. DEVAUX, J.M. NUNZI and P. RAIMOND, Phys. Rev. Lett. **68**, 2440 (1992).
10. J.M. NUNZI, F. CHARRA, C. FIORINI and J. ZYSS, Chem. Phys. Lett. in press (1994).
11. D. MARKOVITSI, H. SIGAL, C. ECOFFET, P. MILLIE, C. FIORINI, F. CHARRA, J.M. NUNZI and H. STRZELECKA, Chem. Phys. in press (1994).
12. F. CHARRA, F. KAJZAR, J. M. NUNZI, P. RAIMOND and E. IDIART, Opt. Lett. **18**, 941 (1993).
13. Z. SEKKAT and M. DUMONT, Appl. Phys. **B 54**, 486 (1992).
14. C. JONES and S. DAY, Nature **351**, 15 (1991).
15. F. CHARRA, J.M. NUNZI and J. MESSIER, in Photoinduced Self-organization Effects in Optical Fibers, F. OUELLETTE, Ed., *SPIE Procs.* **1516**, 211 (1991).
16. P.A. CHOLLET, G. GADRET, F. KAJZAR and P. RAIMOND, in Nonlinear Optical properties of Organic Materials V, SPIE Procs. **1775**, 121 (1992).
17. D.M. KROL, M.M. BROER, K.T. NELSON, R.H. STOLEN, H.W.K. TOM and W. PLEIBEL, Opt. Lett. **16**, 211 (1991).
18. C. FIORINI, F. CHARRA, J.M. NUNZI and P. RAIMOND, *Photoinduced non centrosymmetry in azo-dye polymers*, submitted (1994).
19. F. OUELLETTE, Photoinduced Self-organization Effects in Optical Fibers, SPIE Procs. **1516** (1991).