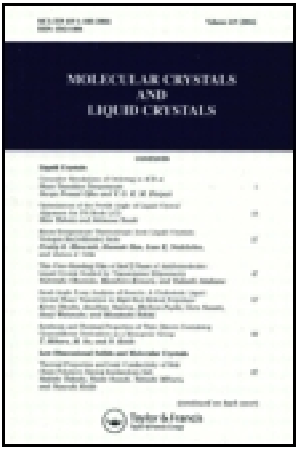

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On the Mechanisms of Relaxation in Electro-Optic Polymers

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On the Mechanisms of Relaxation in Electro-Optic Polymers

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Electro-optic polymers have emerged as an interesting class of nonlinear optical materials suitable for application in broad band optical signal transmission. They take advantage of excellent propagation properties of amorphous polymer matrix with large nonlinear optical response of embedded chromophores. Different, important from practical point of view, aspects of material elaboration and chromophore orientation as well as its temporal stability are reviewed and discussed. A special attention is paid to the recently discovered problems of relaxation of nonlinear optical susceptibility due to the chromophores diffusion and aggregation, particularly important in the guest host systems.

Keywords: depoling; electro-optic modulation; electro-optic polymers; poling; relaxation; second order NLO effects

INTRODUCTION

It is commonly admitted that organic quasi 1-D charge transfer (CT) molecules exhibit the largest first hyperpolarizability β tensor values, with enhanced β_{zzz} component in the charge transfer direction z (cf. Fig. 1). This type of molecules act as one dimensional optical diodes with enhanced polarizability when excited with electric field oriented in the charge transfer direction. However these molecules exhibit a large ground state dipole moment and because of strong dipole-dipole interaction in order to minimize the ground state energy they

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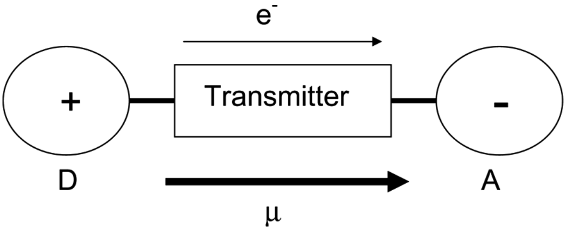


FIGURE 1 Schematic representation of a charge transfer molecule with electron donating (D), electron accepting (A) and conjugated π electron interaction transmitter parts. Arrow shows the molecule ground state dipole moment.

crystallize usually with antiparallel alignment of dipolar moments. Such structures are macroscopically centrosymmetric, characterized by a zero value of second order nonlinear optical (NLO) $\chi^{(2)}$ susceptibility, thus useless for practical applications. Even if these molecules crystallize in noncentrosymmetric system, they exhibit usually large light propagation properties because of scattering by crystallites. This is an important drawback as most of practical applications are targeted in waveguiding configuration, with light propagation length of ten or more millimetres. One of important application targeted here is the electro-optic modulation for optical signal transmission.

In 1979 Havinga and Van Patel [1] have shown that it is possible to obtain good optical quality noncentrosymmetric media using σ – conjugated, amorphous polymers in which are dissolved the active chromophores, oriented by applying external DC field (DC poling). Later it was shown that the NLO chromophores can be oriented by optical field too (all optical poling) [2].

Electro-optic polymers have been the object of intense studies for the last two decades owing to their particular interest for device applications (for a review, see e.g. Kajzar *et al.* [3] and Dalton *et al.* [4]). These polymers combine the good light propagation properties of the amorphous polymer matrix and the enhanced molecular NLO response of quasi 1D CT chromophores. They present also an important advantage, when using soluble polymers, which is the thin film processability by solution cast (spinning).

There are four ways to introduce chromophores into the polymer matrix:

(i) solid solution (guest host systems)
(ii) side chain polymers
(iii) main chain polymers

(iv) thermally – or photo crosslinked polymers with active chromophores are binding elements.

In the first (cf. Fig. 2(a)) chromophores are simply dissolved in polymer matrix. They may diffuse through the matrix, the diffusion cross section depending on temperature, increasing with its increase. In the second case Figure (2(b)) chromophores are chemically bonded to the polymer chain and their diffusion ability is limited, although still possible. This is connected not only with individual movement of chromophores but also with collective motion of polymer chains. Again this mobility depends on temperature. In the third case (Fig. 2(c)) the

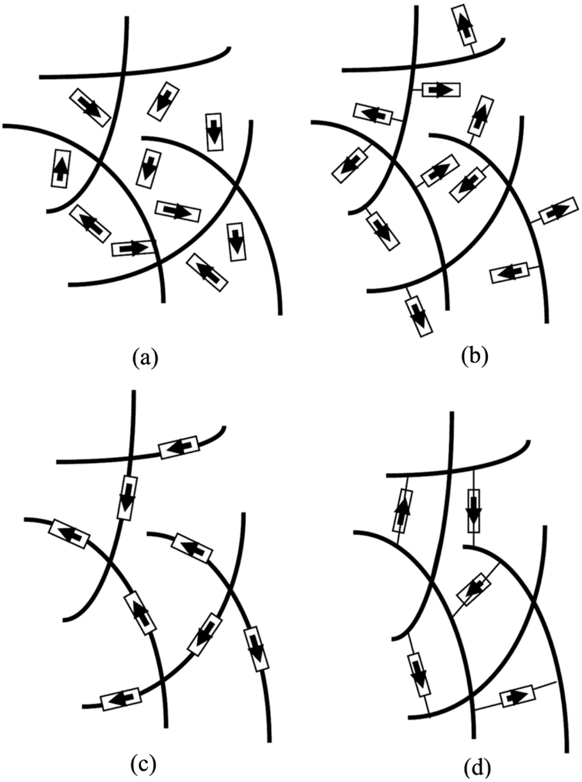


FIGURE 2 Schematic presentation of commonly used functionalized polymers: solid solution (guest host systems) (a), side chain polymers (b) main chain polymers (c), thermally – or photo crosslinked polymers with active chromophores (d). Arrows represent active chromophores and solid lines the polymer chains.

chromophores are incorporated into the polymer chain and the individual motion of chromophores is suppressed, although the aggregation may occur through the collective motion of polymer chains. In the last case the chromophores make a chemical bond with one or two chains by the thermal or photocrosslinking processess. In the last case limited chromophore diffusion is present (Fig. 2(d)) when the chromophores are bond to two polymer chains. In the case when chromophores are bond to one chain only, the situation is equivalent to the side chain polymers (ii).

CHROMOPHORE ORIENTATION

Usually the chromophore orientation in thin film is done by applying an external electric DC field, either through electrodes or by corona poling (cf. Fig. 3). It is done either by chemical bonding of chromophores (grafting or cross linking) or by simply dissolving them (guest host systems) in the polymer matrix (solid solutions). In the case of corona poling high voltage is applied to the electrodes. The created by electric discharge charges deposed on thin film surface create inside a large poling field.

A schematic presentation of corona poling setup is given in Figure 3. A high voltage (usually 6–8 kV) is applied to the needle electrode. Its importance depends on the used material (damage threshold) and on the distance of the needle electrode from the thin film surface. The applied high voltage creates the corona discharge and, as consequence,

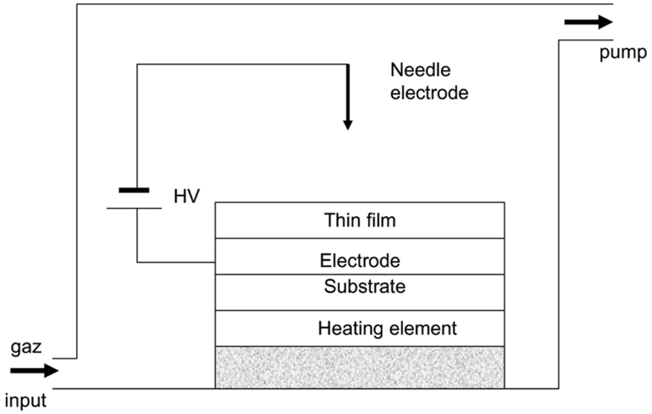


FIGURE 3 Schematic representation of a corona poling set-up with controlled atmosphere.

ionization of the gas, kept inside the atmosphere controlled poling system. In some cases it is better, in order to avoid chemical degradation of poled material, to use another gas than air (e.g. nitrogen). If the polarization of the electrode is positive, as it is usually the case (opposite is possible too) the positive charges will depose on the surface of the poled thin film and create large electric film inside. The importance of the field will depend on the voltage applied to the needle electrode, poling time and sort of gas inside the chamber. Therefore in order to avoid damage to the poled material it is important to control both the poling time and the applied voltage.

The point symmetry of poled films is ∞ mm. From this symmetry and Kleinman conditions it follows that there are two nonzero tensor components:

$$\chi^{(2)}_{ZZZ}(-\omega_3;\omega_1,\omega_2) = NF\beta_{zzz}(-\omega_3;\omega_1,\omega_2)\langle\cos^3\Theta\rangle \tag{1}$$

and

$$\chi^{(2)}_{XXZ}(-\omega_3;\omega_1,\omega_2) = \frac{1}{2}NF\beta_{zzz}(-\omega_3;\omega_1,\omega_2)\langle\sin^2\Theta\cos\Theta\rangle \tag{2}$$

where $\omega_1, \omega_2, \omega_3$, with $\omega_3 = \omega_1 + \omega_2$ are frequencies of interacting photons, N is the chromophore density and Θ is the angle between the applied electric field and the molecule dipole moment. Brackets denote average values on molecule orientation.

F in Eqs. (1)–(2) is the total field factor, taking account of the electric field screening by the molecular field:

$$F = \frac{(n^2_{\omega_1}+2)}{3}\frac{(n^2_{\omega_{12}}+2)}{3}\frac{(n^2_{\omega_{13}}+2)}{3} \tag{3}$$

in which n_ω and $n_{2\omega}$ are the refractive indices at ω and 2ω frequencies.

The orientation averages in Eqs. (1)–(2) are given by:

$$\langle\cos^3\Theta\rangle = \frac{1}{N_A}\int_0^\pi G(\theta)\cos^3\Theta\sin\theta\, d\theta \tag{4}$$

and

$$\langle\sin^2\Theta\cos\Theta\rangle = \frac{1}{N_A}\int_0^\pi G(\theta)\sin^2\Theta\cos\Theta\sin\theta\, d\theta \tag{5}$$

where G(Θ) is the orientation distribution function. It gives the probability of finding the dipole moment (molecular axis) in the Θ direction. Here the obvious in poled materials azymuthal symmetry is assumed. N_A is the normalization constant.

At higher temperatures (above or slightly below, close to the glass transition temperature for polymers), when molecules may rotate (free gas model) one uses for G(Θ) the Gibbs-Boltzmann distribution function given by:

$$G(\Theta) = e^{-\frac{U(E_p)}{kT}} \tag{6}$$

where

$$U(E_p) = \mu E_p + \frac{1}{2}(\alpha_{II} - \alpha_{\perp})E_p^2 \cos^2 \Theta \tag{7}$$

is the orienting energy (interaction energy between ground state dipolar moment μ and the induced moment), E_p is the poling field, and kT is the thermal randomizing energy. $\alpha_{II} - \alpha_{\perp}$ is the anisotropy of linear molecular polarizability. Neglecting the induced dipole moment interaction energy with the poling field (isotropic model) the orientation distribution function G(Θ) can be developed into the Legendre polynomials giving:

$$G(\Theta) = \sum_{n=0}^{\infty} \frac{2n+1}{2} \langle P_n(\cos\Theta)\rangle P_n(\cos\Theta) \tag{8}$$

The expansion coefficients in Eq. (8) are the order parameters. Obviously they depend on temperature T through Eq. (6). They can be expressed in terms of the modified spherical Bessel functions I_n (x) [5]:

$$\langle P_n(\cos\Theta)\rangle = \frac{I_n(x)}{I_0(x)} \tag{9}$$

where

$$x = \frac{\mu E_p}{kT} \tag{10}$$

The odd order parameters $\langle P_{2n+1}\rangle$ (n = 0, 1, 2,...) describe the polar order (the dipole moments aligned in majority in one direction, noncentrosymmetry surely present), whereas the even order describe the axial order (noncentrosymmetry not necessarily present). For quasi 1D molecules, considered here, the two nonzero susceptibility tensor components (cf. Eqs. (1)–(2)) are given by:

$$\chi^{(2)}_{ZZZ}(-\omega_3;\omega_1,\omega_2) = NF\beta_{zzz}(-\omega_3;\omega_1,\omega_2)\left[\frac{3}{5}\langle P_1(\cos\theta)\rangle + \frac{2}{5}\langle P_3(\cos\theta)\rangle\right] \tag{11}$$

and

$$\chi^{(2)}_{XXZ}(-\omega_3;\omega_1,\omega_2)=NF\beta_{zzz}(-\omega_3;\omega_1,\omega_2)\left[\frac{1}{5}\langle P_1(\cos\theta)\rangle-\frac{1}{5}\langle P_3(\cos\theta)\rangle\right] \tag{12}$$

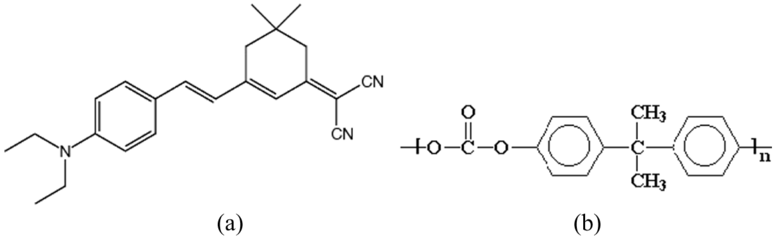
The kinetics of the orientation of chromophores by the applied electric field, expressed by the dependence of the size of the two susceptibility tensor components (cf. Eq. (12)), in function of poling time t, can be described by a monoexponential function [5]–[6], as measured by *in situ* second harmonic generation (SHG) experiments. The square of the SHG intensity, proportional to the corresponding susceptibility tensor component, depending on the configuration of the polarization of interacting fields, is given by:

$$[I_{SHG}]^{1/2}=\left[I^{sat}_{SHG}(T)\right]^{1/2}\left(1-e^{-\frac{t}{\alpha(T)}}\right) \tag{11}$$

where the depending on temperature coefficient α(T) describes the kinetics of orientation (time constant) at a given temperature [5]–[6]. The orientation efficiency, given by the square of the SHG intensity saturation value $[I^{sat}_{SHG}]^{1/2}$ depends on the temperature too. It is proportional to the effective $\chi^{(2)}$ susceptibility tensor, which, on the other hand, depends on the polarizations of interacting beams.

Concentration Dependence

According to Eqs. (1)–(3) the NLO susceptibility of the doped polymer medium should increase linearly with number of chromophores present in the matrix. However the theoretical observations show that this is true up to some limiting concentration as it was observed in guest-host Lemke chromophore- poly(bisphenol A carbonate) system [9], whose chemical structures are shown in Figure 4. At higher



(a) (b)

FIGURE 4 Chemical structures of Lemke chromophore (a) and poly(bisphenol A carbonate) (b).

chromophore concentration one observes a saturation of the corresponding $\chi^{(2)}$ susceptibility component ($\chi^{(2)}_{XXZ}$ or $\chi^{(2)}_{ZZZ}$), where Z is direction of the poling field (cf. Ref. [9]). Therefore there is a limiting chromophore concentration value up to which the $\chi^{(2)}$ susceptibility grows linearly with it [9], as it is shown in Figure 5, displaying the chromophore concentration variation of the off diagonal tensor component $\chi^{(2)}_{XXZ}$, measured by the SHG technique for a thin film of already mentioned Lemke chromophore – poly(bisphenol A carbonate) guest-host system, poled by corona poling for 10 mins. We have chosen this tensor component as it is obtained directly from the THG measurements. After the loss of linear dependency concentration value the increase is slower, reaches a maximum and then decreases.

Similar behaviour was observed in other systems too (cf. [2]–[3]). It is attributed to the aggregation of chromophores with increasing concentration. Up to this limiting concentration value chromophores are well dissolved in the polymer matrix and behave as monomers. For higher concentration the chromophores start to aggregate. Such aggregation is associated with increasing light scattering, thus the worsening of optical propagation properties.

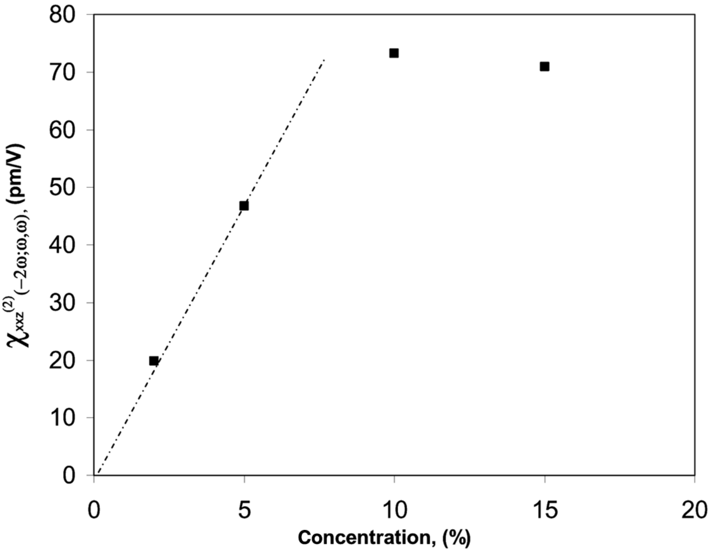


FIGURE 5 Chromophore concentration dependence of off-diagonal component $\chi^{(2)}_{XXZ}$ on chromophore concentration in poled Lemke chromophore – poly(bisphenol A carbonate) guest-host system (after Rau *et al*. [9]) for a thin film poled 10 mins. Squares show experimental values whereas the dashed line depicts linear behaviour.

RELAXATION

An important problem connected with the development of electro-optic polymers is the temporal stability of the induced polar order. It is well known that the polar order decreases with time. This decrease is usually described by the Kohlrausch-Williams-Watt (KWW) stretched exponential function [7–8]:

$$\chi^{(2)}(t) = \chi^{(2)}(t=0)e^{-(\frac{t}{\tau})^{\beta}} \tag{12}$$

where β $(0 < \beta < 1)$ is a parameter which depends on temperature and describes the kinetics of relaxation and τ is the relaxation time constant, also depending on temperature.

However this description predicts a complete disappearance of polar order after a time, what is in disagreement with observation and has no physical meaning. It is well known that different mechanisms contribute to the relaxation of polar order in poled polymers. Therefore closer to the reality is the proposed biexponential description ([5–6], [10]).

$$[I^{p}_{2\omega}(t)]^{\frac{1}{2}} = R_1 e^{-t/\tau_1} + R_2 e^{-t/\tau_2} + C \tag{13}$$

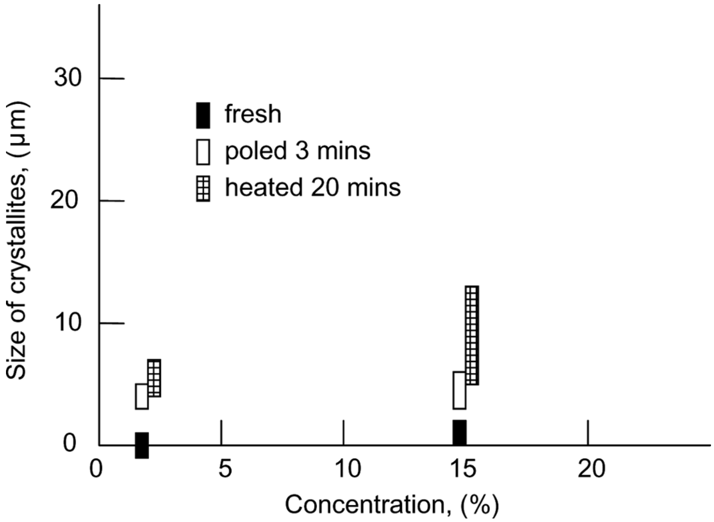


FIGURE 6 Diagram showing the size of aggregates in guest-host Lemke chromophore – poly(bisphenol A carbonate) system at two chromophore concentrations: 2 and 15 w% for freshly prepared films and for films which have undergone a 3 mins of corona poling or were heated at glass transition temperature for 20 mins (after Rau *et al.* [11]).

Where τ_1 and τ_2 are time constants of two different, distinct processes, contributing to the decay of NLO susceptibility (polar order) with R_1 and R_2 being corresponding relaxation rates and C is the time independent, constant value, important for practical applications.

Rau *et al.* [11] reported very recently another mechanism of relaxation, not mentioned in the bibliography before. It consists of the aggregation of chromophores due to their diffusion in the polymer matrix. It takes place already at room temperature and accelerates with its increase. In the case of already mentioned Lemke chromophore – poly(bisphenol A carbonate) guest-host system (cf. Fig. 2) one observes grows of aggregates, whose size depends on thermal treatment of the sample, as observed by optical microscopy [11]. Figure 6 shows a diagrammatic presentation of the growth of aggregates for two guest-host concentrations of 2 and 15 w%. If in freshly deposed films with 2 w% of Lemke chromophore no aggregates are observed, they are present at higher concentration of 15 w%. The aggregates appear at the lower concentration after 3 mins of corona poling increase after 20 mins of heating at elevated temperature, becoming up to *ca.* 15 μm large and oblong.

CONCLUSIONS

In this article we have presented and discussed different problems connected with creation and relaxation of the polar order in electro-optic polymers. As we have shown here, despite a lot of research and application efforts done with electro-optic polymers, there are still some problems which need to be addressed. Particularly the new mechanism of relaxation of polar order through the chromophore aggregation has to be taken into account. Although it has been observed in guest-host systems only (cf. Fig. 2(a)) [11] most likely it is present in other systems too, because of thermal motion of both chromophores and polymer chains. However, we can expect that this mechanism will be weaker in other systems presented in Figure 2 ((b)–(d)), because of limited degree of freedom of chromophores by their chemical binding to polymer chains.

There are other aspects, not discussed here, which will limit application of systems discussed here in optical signal processing, such as

(i) photodegradation [12–13] and
(ii) light induced depoling [14–15]

In the first case the photodegradation can be limited by encapsulating the active elements and protecting them from the action of oxygen.

Also working far of the absorption band will limit this effect. However, the transitions, like photoizomerization, favorizing the light induced depoling can be excited by two photon absorption too (cf. [16]), although with lower cross section. Therefore it is important to avoid the operation wavelength corresponding to the double of the absorption band range too.

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