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FUNCTIONALIZED POLYMERS FOR SECOND ORDER NONLINEAR OPTICS

FRANCOIS KAJZAR^{1,2} and ILEANA RAU¹

¹ University “Politehnica” of Bucharest, Faculty of Applied Chemistry and Materials Science,
1 Polizu Str., Bucharest, Romania

E-mail: ileana_brandusa@yahoo.com; tel/fax: +40213154193

² Université d'Angers, UFR Sciences, Laboratoire POMA CNRS UMR 6136, 2, Bd Lavoisier, 49045
Angers, France

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Abstract. In this paper we review and discuss the recent developments in the field of electro-optic polymers. These polymers, combining the excellent light propagation properties of the matrix with enhanced nonlinear optical (NLO) response of noncentrosymmetric, doping charge transfer molecules have emerged as a very promising class of materials for practical applications, not only on devices based on second-order NLO effects, but also in third-order ones. Basing on a two level quantum model we derive also the relationship between the linear electro-optics (Pockels) coefficient and the second order NLO susceptibility. In particular we show that their relationship is not as simple as it is often assumed because of different dispersions due to the different excited states resonant contributions. Practical applications of these polymers are also discussed.

Key words: electro-optic polymers, linear electro-optic effect, second harmonic generation, electro-optic modulation, Pockels effect, optical parametric amplification

1. INTRODUCTION

One of the important class of materials for photonics applications are those exhibiting large second-order nonlinear optical (NLO) susceptibilities, important for practical applications, such as, in particular, frequency doubling by second harmonic generation (SHG), frequency tuning through optical parametric oscillation (OPO), light amplification through optical parametric amplification (OPA), electro-optic modulation (EOM) for optical signal transmission and ultrashort electric pulses generation through the linear rectification effect. As most of applications are targeted in waveguiding configuration for integration of different elements in practical devices, highly responsive noncentrosymmetric thin films are required.

Different, less or more successful approaches in making noncentrosymmetric thin films were employed, such as Langmuir-Blodgett (LB) layers [1], epitaxy [2]

or quasi epitaxy [3, 4], intermolecular charge transfer layers (ICTL) [5] and functionalized [6], called also electro-optic as primarily developed for EOM application, soluble polymers. In first case the difficulty is connected with the thermodynamically vaporized centrosymmetric arrangement of dipolar molecules with no second-order NLO response. Usually the noncentrosymmetry is observed only for few layers [7]. Moreover the aliphatic chain side groups used in this approach (for more details see Petty [8]) crystallize easily leading to large light scattering losses. To our knowledge there is only one work reporting obtaining of noncentrosymmetric, herring bone like, arrangement of noncentrosymmetric NLO chromophores [9, 10] in LB layers. Obviously the LB films approach requires synthesis of molecules with aliphatic chains as side groups, making possible the formation of well defined monolayers on water subphase. In epitaxy and quasi epitaxy approaches similar problems with light scattering by crystallites are encountered. The ICTL structures, consisting on very thin (*ca* 2 nm) alternate electron donating/electron accepting/neutral layers show some problems with temporal stability.

In the search for noncentrosymmetric materials for application in second-order NLO in waveguiding configuration (for a review see *e.g.* Dalton [11, 12], Kajzar *et al.* [13], Cabanetos *et al.* [14]) the most successful was the last approach, *i.e.* electro-optic polymers. The materials take advantage of very good optical properties of amorphous polymers, used primarily as matrix for electro-optic chromophores [15]. This approach was introduced some 40 years ago by Havenga and Pelt for making thin, electroluminescent films. A few years after Singer and coworkers [16], have shown that the concept of solid solutions can be successfully extended to fabrication of second order-NLO materials. In that case the isotropic, amorphous polymers are used as a host material and the highly electric field responding second-order NLO active chromophores, with enhanced first hyperpolarizability β , are used as guest molecules. The matrix provides good optical propagation properties while the chromophores the NLO response. The commonly used dopants are the intramolecular charge transfer molecules with a large ground state dipole moment as well as large first molecular hyperpolarizability. The polar order, necessary to obtain the nonzero second-order susceptibility of initially isotropic, *i.e.* centrosymmetric thin films is obtained by the DC poling. Both doping molecules and the bulk materials have to lack center of symmetry. Optimization of molecules is called molecular engineering approach, while that of material the material engineering, respectively.

2. MATERIALS

As already mentioned the NLO active chromophores used in fabrication of EO polymers are intramolecular charge transfer molecules (ICT), shown schematically in Fig. 1. As electron donating usually the following side groups are

used: $N(CH_3)_2$, NH_2 , OCH_3 , OH , while as electron accepting groups the following ones: NO , NO_2 , CHO , CN , respectively. The π electron conjugated segment serves to transmit the charge. Such molecule behaves as a molecular diode: excitation is possible with one direction of electric field (or its component).



Fig. 1 – Schematic presentation of an intramolecular charge transfer molecule.

There are four different ways of functionalization of amorphous polymers, which are illustrated in Fig. 2, such as: guest-host system which is just a solid solution (Fig. 2a), side chain polymer (Fig. 2b), when the NLO active chromophores are covalently attached to the polymer chain. In the case of main chain polymers (Fig. 2c) the chromophores are introduced to the polymer chain. The last case are the thermally- or photo crosslinking polymers (Fig. 2d). In that case the NLO active chromophores are used to link the polymer chains either by heating or by curing with UV light. Some examples of chemical structures of functionalized polymers are given in Fig. 3.

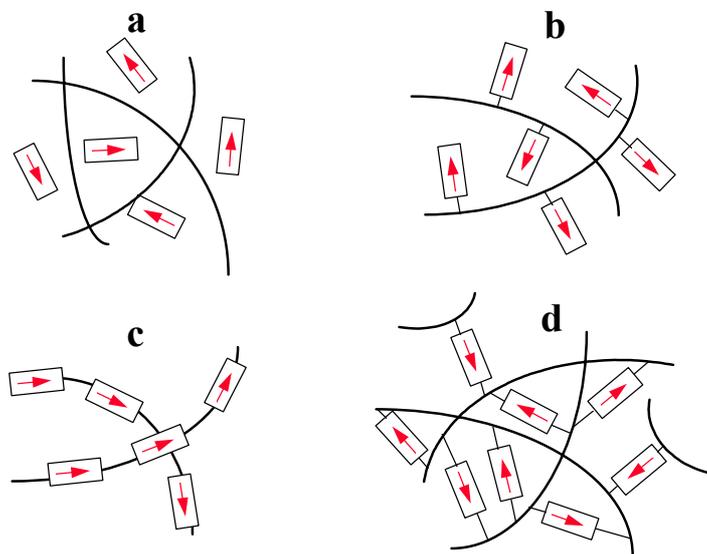


Fig. 2 – Schematic presentation of different ways of functionalization of amorphous polymers: guest-host system (a), side chain polymer (b), main chain polymer (c), thermally and photocrosslinking polymers (d).

The simplest cases are the solid solutions, however here the concentration of active chromophores is strongly limited by their aggregation. Aggregation is also present in side chain polymers, but takes place at a higher chromophore load [17]. The main chain polymers are difficult to pole, although some scattered results were reported [18, 19]. The thermal and photo crosslinking polymers are very attractive as, they offer a better stability of induced polar order. However their practical utilization is presently limited due to the shrinking problems occurring during the cross-linking. Also the poling process is delicate as the glass transition temperature T_g varies during the curing process [20, 21]. Therefore the most of synthesis and device applications were done with guest-host systems and with side-chain polymers. Different polymer amorphous polymers were used, such as polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), polyurethane (PUR), polyimides, etc.

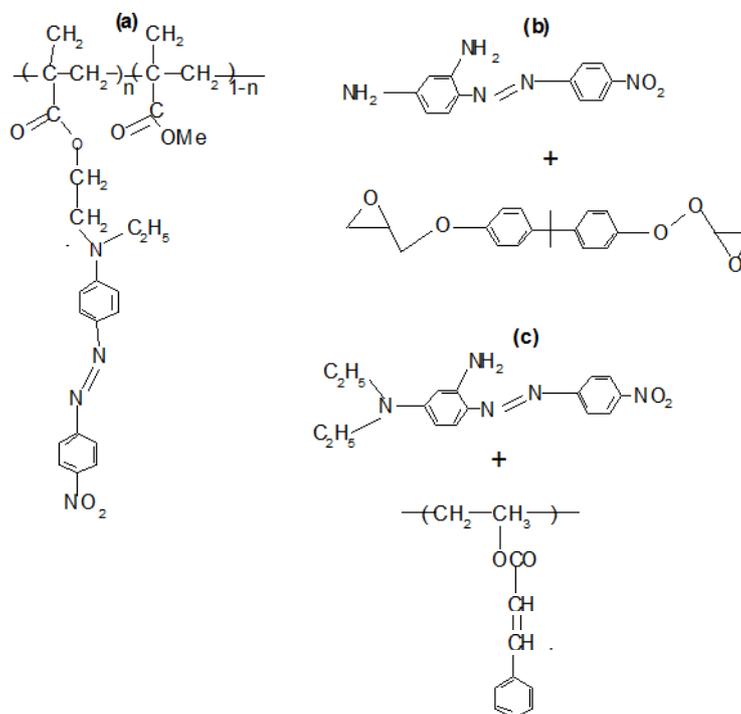


Fig. 3 – Examples of chemical structures of functionalized polymers: side chain (a), matrix and active chromophore cross linking thermally (b) or matrix and active chromophore cross linking under UV irradiation (c).

As already mentioned the amorphous, σ conjugated polymers, are used as matrix for the highly responsive NLO chromophores, which are the intramolecular charge transfer molecules, as shown schematically in Fig. 1. These molecules

exhibit a large first hyperpolarizability β , with the enhanced component β_{zzz} in the charge transfer direction z , so the others from 27 possible can be neglected with respect to this one. The molecule is composed of electron donating (+) and electron accepting (-) side groups, as shown in Fig. 1. As already mentioned they behave as a molecular diode: being excitable if the optical electric field is directed in the CT direction. It is also characterized by a large ground state dipole moment, what is very interesting for orientation efficiency of these dipolar molecules by the applied DC field.

3. MATERIALS CHARACTERIZATION

3.1. PROPAGATION LOSSES

The optical propagation losses in a waveguide are defined by the attenuation of signals passing between two points of a transmission path, distant by l and are expressed as

$$P_L = \frac{10}{l} \log \frac{I(l)}{I(0)}, \quad (1)$$

where $I(0)$ is the light intensity at the entrance, $I(l)$ intensity at the output of the waveguide with length l , respectively. The propagation losses are usually given in dB/cm. They arise principally from:

- (i) material absorption,
- (ii) light scattering.

Although the presently available polymers, such as *e.g.* polymethyl methacrylate exhibit a high degree of purity they still absorb light in near infrared (NIR) range, and more particularly at the telecommunication wavelengths. This is due to the harmonics of high frequency C-H and OH vibrations. Although these absorptions are weak and difficult to measure by usual spectrophotometric techniques, for propagation on few cm length the losses they produce can be significant. For thin films these absorptions are measured by sophisticated techniques like the photothermal deflection (mirror method) [22] (see also Wong *et al.* [23]).

The usually used measurement technique is the cutback method. Its drawback is that it is destructive. In fact it consists on coupling and decoupling light into a waveguide, whose length is gradually shortened by cutting it and measuring the input and output intensities. It is done either by complex interferometric measurements [24, 25] or by sliding the decoupling prism along the waveguide and measuring the outcoupled light intensity. The main drawback of the technique is that the measured light intensity contains also losses coming from the propagating beam coupling and decoupling.

Another approach is by measuring the scattered light along the waveguide using either a moving optical fiber to collect it [26], or a CCD camera [27] as shown schematically in Fig. 4. The advantage of this technique is that it is non-destructive. It allows also measuring easily the light propagation losses dependence on its polarization by rotating the prism located in the input part of beam (Fig. 4). It doesn't require to know the input intensity. The method assumes, *a priori*, that the scattered light intensity at a given point is proportional to the actual propagating light one. In other word that only a linear scattering is present in the waveguide.

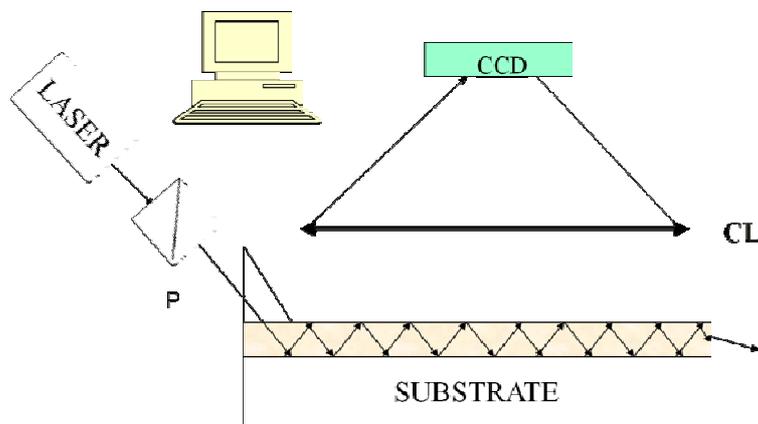


Fig. 4 – Schematic presentation of an experimental set up for propagation losses measurements. CL – is a cylindrical lens, CCD is a camera and P is a polarizer.

Figure 5 shows, as example, the observed CCD camera image of the scattered light from a 1 cm optical waveguide made of functionalized polystyrene with Disperse Red 19 molecule [28].

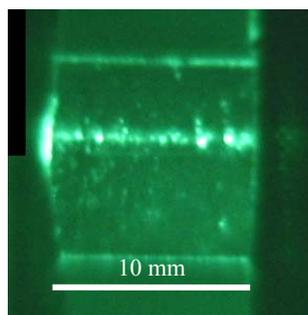


Fig. 5 – CCD image of light scattered from a waveguide obtained using the experimental set up shown in Fig. 3.

3.2. CHROMOPHORE ORIENTATION

One of the most important advantages of functionalized polymers is the facility in thin films fabrication with good optical propagation properties. However such films are obviously isotropic with no second-order NLO properties. These are created by applying a large electric field which orients the molecule dipole moments. It can be done either by electrode poling or by corona poling. In the first case the poled film is kept between two electrodes and a high electric field is applied. To increase the rotational mobility of chromophores the film is heated close to the glass transition temperature, but not above. Above the glass transition temperature the ionic conductivity increases and application of high electric fields may result in a permanent damage to the poled film. In practice the whole waveguide structure, including the active layer and the buffer layers are subjected to the electric field. Therefore it is very important using not only the propagation loss free buffer layers, but also with lower conductivity to get a favourable, more efficient for active thin film poling the electric field distribution across the structure (Fig. 6).

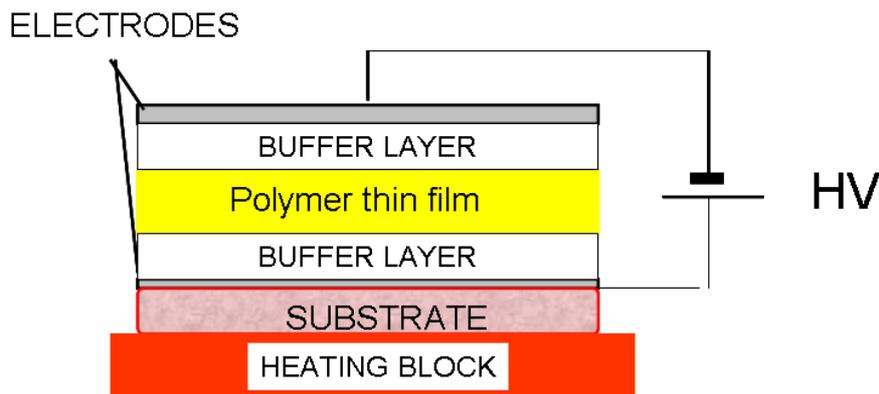


Fig. 6 – Electrode poling setup for a structure with two buffer layers.

In corona poling technique (Fig. 7) the high poling field is obtained by deposited charges on the film surface, which are created by the gas ionization in surrounding discharge needle atmosphere. The film is also heated close to the glass transition temperature using a heating block. A resistance R in poling circuit (Fig. 7) protects thin films against the dielectric breakdown. While in electrode poling technique the poling occurs at any applied voltage (although its efficiency depends on it), the corona poling is a threshold phenomenon and requires usually application of relatively high voltages (around 6–8 kV) with needle electrode distant by 1.5–2.5 cm from the thin film surface. More about poling can be found in Kajzar and Nunzi [29]. We note also a purely optical technique for polar

chromophores orientation as shown by Charra *et al.* [30]. The all optical poling can be done at any temperatures. Thus there is no necessity for heating the polymer. The poled in this wave films can find application in an efficient frequency conversion.

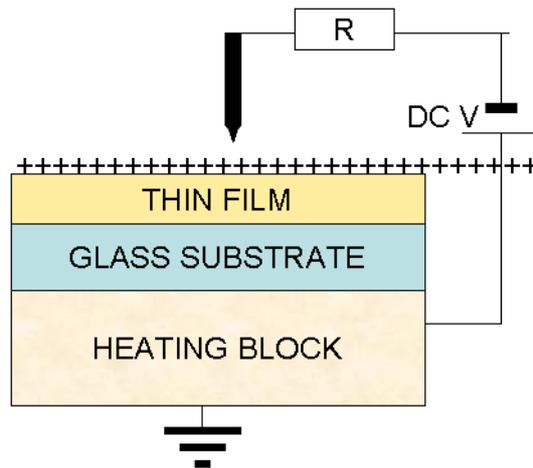


Fig. 7 – Corona poling setup.

The degree of orientation can be easily obtained from the variation of the thin film optical absorption spectrum before and after poling, as it is show in Fig. 8 [31].

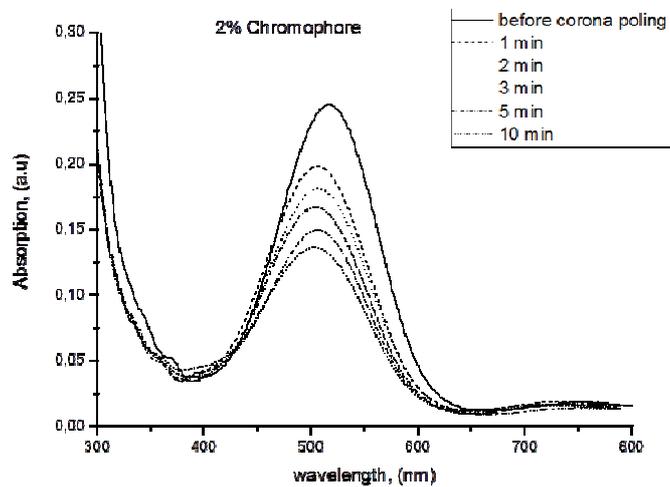


Fig. 8 – Optical absorption spectrum before poling and during the corona poling for Lemke chromophore embedded in poly bis(phenol A carbonate) matrix. A simultaneous decrease of absorption and its blue shift is observed (after Rau *et al.* [17]).

The axial order parameter is given by (cf. *e.g.* Rau and Kajzar [32])

$$\langle P_2 \rangle = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} = 1 - \frac{A_{\perp}}{A_0}, \quad (2)$$

where A_{\parallel} and A_{\perp} are absorbances (optical densities) measured with the incident light polarization parallel and perpendicular to the poling field direction, respectively. In Eq. (2) we used the relationship $A_{\parallel} + 2A_{\perp} = 3A_0$ valid for an isotropic azimuthal distribution of molecular axes as it is the case. Although $\langle P_2 \rangle$ is describing the axial order, from the experiment arrangement we know that in fact the order created is polar. The information on polar order can be obtained by using NLO techniques. The observed frequency blue shift of absorption spectrum in Fig. 8 is due to the DC Stark effect. It is given by [33]

$$\Delta\nu = \frac{\Delta\mu}{\hbar c} E_p,$$

where $\Delta\mu = \mu_e - \mu_g$ is the difference of dipole moments between excited (e) and ground (g) levels and E_p is the poling field. Depending on the sign of $\Delta\mu$ we can have blue or red shift of the absorption spectrum.

The decrease of the thin film optical density with poling time is due to the chromophore orientation. As the testing electric field is within the thin film plane and the molecules align with their dipole moments towards the applied electric field, which is perpendicular to the thin film surface, the in plane projection of dipole transition moments is decreasing with orientation efficiency.

The build up of the order parameter with poling time t may be well described by a monoexponential function (cf. Refs. [34])

$$\langle P_2(t) \rangle = \langle P_2(t = \infty) \rangle e^{-\frac{t}{\tau}}. \quad (3)$$

The point symmetry of poled films (electric field perpendicular to the thin film surface) is ∞mm with ∞ axis perpendicular to it. Thus there are two nonzero tensor components $\chi^{(2)}$: the diagonal given by

$$\chi_{ZZZ}^{(2)} = NF\beta_{zzz} \langle \cos^3 \Theta \rangle \quad (4)$$

and the off diagonal one

$$\chi_{XXZ}^{(2)} = \frac{1}{2} NF\beta_{zzz} \langle \cos \Theta \sin^2 \Theta \rangle, \quad (5)$$

where capital letters refer to the laboratory, while the lower case ones to the molecular reference frame, respectively. Z is the direction of the applied external

field, N is the number density of NLO chromophores, F is the local field factor taking account of the screening of the external field by the molecular one, β_{zzz} is the enhanced first hyperpolarizability tensor component in the charge transfer direction (z); the others are neglected with respect to this one and Θ is the angle between the applied electric field and the CT direction.

3.3. EXPERIMENTAL METHODS AND RELATION BETWEEN SHG SUSCEPTIBILITY AND LINEAR ELECTRO-OPTIC COEFFICIENT

One of the important problems encountered in the characterization of NLO properties of thin films fabricated in view of their application in electro-optic modulators for optical signal transmission is the relation between the SHG susceptibility $\chi_{zzz}^{(2)}(-2\omega; \omega, \omega)$ and the linear electro-optic r_{zzz} coefficient, where Z is the direction of the electric poling field (perpendicular to the thin film surface in corona poling). Indeed, usually the characterization is done by SHG, which has advantage to yield the fast, electronic origin, NLO susceptibility, while for device application important is the knowledge of the linear electro-optic coefficient r_{ijk} and can be measured from the refractive index variation under the applied field.

Both the SHG process and the EO effect are described by different second-order NLO susceptibilities, which are related to the electric field E power expansion. A direct comparison between the NLO coefficients derived using them is not a straight one and may mislead as it will be shown below.

The action of an external forcing electric field E changes the medium polarization. Within the dipolar approximation it can be developed in its power series as follows

$$P_{NL} = P_0 + K_1 \chi^{(1)} : E + K_2 \chi^{(2)} : EE + K_3 \chi^{(3)} : EEE + \dots \quad (6)$$

where the development coefficients $\chi^{(n)}$ are three dimensional $(n+1)$ rank tensors describing linear ($\chi^{(1)}$) and nonlinear optical (NLO) response ($\chi^{(2)}$, $\chi^{(3)}$, ...) in the laboratory reference frame. P_0 in Eq. (6) is a static polarization, present in noncentrosymmetric materials, the factors K_i depend on conventions and system of units used, as well as on the taking into account or not the degeneracy factors. They depend on the NLO process under consideration. Here we use the following convention for the Fourier transform of the electric and polarization fields:

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{2} \left[\mathbf{E}(\mathbf{r}) e^{i(kr - \omega t)} + \text{c.c.} \right] \quad (7)$$

and

$$\mathbf{P}(\mathbf{r}, t) = \frac{1}{2} \left[\mathbf{P}(\mathbf{r}) e^{i(kr - \omega t)} + \text{c.c.} \right]. \quad (8)$$

Within this convention and taking explicit account of the degeneracy factors we have for the NLO polarizations for these two processes the following expressions

$$P_{EO} = 2\chi_{EO}^{(2)}(-\omega; \omega, 0) : EE \quad (9)$$

and

$$P_{SHG} = \frac{1}{2}\chi_{SHG}^{(2)}(-2\omega; \omega, \omega) : EE \quad (10)$$

for linear electro-optic (EO) effect and for SHG, respectively.

Historically the EO effect is defined as the variation of the inverse of dielectric constant of a material under the applied electric field E

$$\Delta\left(\frac{1}{\varepsilon}\right)_{ij} = r_{ijk} E_k, \quad (11)$$

where r_{ijk} is the already mentioned linear electro-optic coefficient. In Eq. (2) and throughout the text the Einstein's summation convention is used. In the refractive index ellipsoid reference frame we get the following formula for the variation of its diagonal components

$$\Delta n_{ii} = \frac{n^3}{2} r_{ij} E_j^\Omega, \quad (12)$$

where the superscript Ω refers to the frequency of forcing field which is usually in GHz range.

Extracting from Eqs. (6) and (9) the variation of refractive index and comparing it with Eq. (12) one gets the following relationship between the electro-optic coefficient and the $\chi_{EO}^{(2)}(-\omega; \omega, 0)$ susceptibility

$$r_{ijk}(-\omega; \omega, 0) = \frac{\chi_{ijk}^{(2)}(-\omega; \omega, 0)}{n^4} \quad (13)$$

It shows that the definition of electro-optic coefficient given by Eq. (12) implies a wavelength dependent proportionality between r and $\chi_{EO}^{(2)}$ susceptibility through the refractive index dispersion. For some materials it can be quite important.

To compare SHG with EO measurements data usually in Eq. (13) the $\chi_{EO}^{(2)}$ susceptibility is simply replaced $\chi_{SHG}^{(2)}$ susceptibility. If this simplification can be justified for static limits, it is no more true when the operation frequencies are not far from the molecule absorption band. Such a simplification may be source of an important error. Figure 9 shows the energetic diagrams for SHG (a) and EO (b) processes. Solid lines show ground and the excited (n , m) levels of the unperturbed

system while the dashed lines show the virtual states. The NLO processes go through the virtual states. If one of the virtual states matches with an excited state of unperturbed system than a resonant enhancement in corresponding NLO susceptibility will occur, associated with its wavelength dispersion. From Fig. 9 one can see that for EO effect only a one photon resonance takes place when the exciting photon energy is equal to the transition energy between n and g states: $\hbar\omega \approx \hbar\omega_{ng}$. In contrary, for SHG process one and two photon resonances are possible: $\hbar\omega \approx \hbar\omega_{ng}$ and $2\hbar\omega \approx \hbar\omega_{ng}$. This should result in quite different dispersions for both susceptibilities. To prove it we consider a simple two level model, taking into account only g and n states.

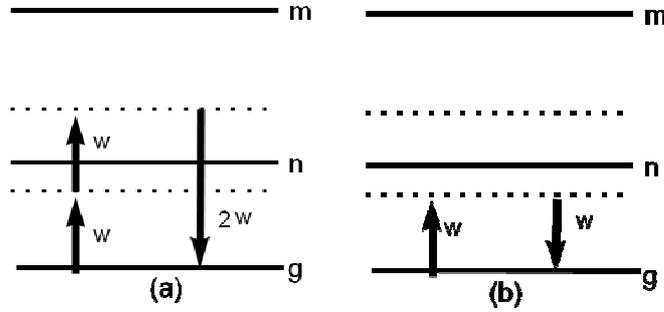


Fig. 9 – Energetic diagram for SHG (a) and EO processes. Solid lines show ground (g) and the excited (n, m) levels of unperturbed system while the dashed lines show the virtual states.

The EO and SHG susceptibilities within this model are given by the following equations [35]

$$\chi_{SHG}^{(2)}(-2\omega; \omega, \omega) = \frac{NF}{6\hbar^2} |\mu_{gn}|^2 |\Delta\mu| R_{SHG}(\omega, \omega_0, \Gamma) \quad (14)$$

for SHG, and

$$\chi_{EO}^{(2)}(-\omega; \omega, 0) = \frac{NF}{12\hbar^2} |\mu_{gn}|^2 |\Delta\mu| R_{EO}(\omega, \omega_0, \Gamma) \quad (15)$$

respectively. In Eqs (14)-(15) $\Delta\mu = \mu_n - \mu_g$ is the difference of dipole moment between excited and fundamental state, μ_{gn} is the transition dipole moment between the ground state (g) and the first excited (n) level. The functions R_{EO} and R_{SHG} describe dispersion of the corresponding susceptibilities and are given by [36]

$$R_{SHG}(\omega, \omega_0, \Gamma) = \frac{1}{(\Omega - 2\omega)(\Omega - \omega)} + \frac{1}{(\Omega^* + 2\omega)(\Omega^* + \omega)} + \frac{1}{(\Omega - \omega)(\Omega^* + \omega)}, \quad (16)$$

$$R_{EO}(\omega, \omega_0, \Gamma) = \frac{1}{(\Omega - \omega)^2} + \frac{1}{\Omega^*(\Omega - \omega)} + \frac{1}{\Omega^*(\Omega^* + \omega)} + \frac{1}{\Omega(\Omega - \omega)} + \frac{1}{\Omega(\Omega^* + \omega)} + \frac{1}{(\Omega^* + \omega)^2} \quad (17)$$

where $\Omega = \omega_{ng} - i\Gamma$, $\Omega^* = \omega_{ng} + i\Gamma$. Γ is the damping term. Figure 10 shows the calculated dispersions of $\chi_{SHG}^{(2)}$ (dashed line) and $\chi_{EO}^{(2)}$ (solid line) susceptibilities for a very common and frequently studied side chain polymer: polymethyl methacrylate (PMMA) – Disperse Red 1 chromophore. The computation is done taking the maximum absorption wavelength for this chromophore at 480 nm and the damping term of 2000 cm^{-1} . Indeed, as expected, only a one photon resonance is present in EO susceptibility and two: one photon and two photon resonances in SHG. The two photon resonance in SHG susceptibility is significantly larger than the one photon. This can be well understood by the inverse on the square of frequency dependence in Eqs. (16) – (17). For the wavelength above ca 0.7 μm the SHG susceptibility is significantly larger than EO, particularly close to the two photon resonance. Below this wavelength larger is EO susceptibility, although at lower wavelength the higher lying states, neglected here, can contribute significantly to the SHG susceptibility by two photon resonances.

At the present the thin film electro-optic coefficient is measured mainly by the modulated ellipsometry method [37–39]. The technique is simple and doesn't require expensive apparatus. However it may be source of large errors if the multiple reflections are not taken correctly into account [40, 41].

3.4. RELAXATION

One of the important problems encountered with the electro-optic polymers is the temporal stability of the induced polar order by application of the external or corona DC field. This is usually described by the Kohlrausch-Williams-Watts (KWW) [42, 43] stretched exponential equation:

$$\chi^{(2)}(t) = \chi^{(2)}(0) e^{-\left(\frac{t}{\tau}\right)^\beta}, \quad (18)$$

where τ is the, depending on temperature, relaxation time constant, and β ($0 < \beta < 1$) describes the width of relaxation (departure from a monoexponential behaviour). Sometimes the relaxation can be fitted by the sum of two exponential functions [44]

$$\chi^{(2)}(t) = \chi_1^{(2)}(t) e^{-t/\tau_1} + \chi_2^{(2)}(t) e^{-t/\tau_2} + \chi_\infty^{(2)}, \quad (19)$$

where τ_1 and τ_2 are the time constants for the given initial contributions $\chi_1^{(2)}$ and $\chi_2^{(2)}$. $\chi_\infty^{(2)}$ is the final susceptibility, whose value is important for practical applications. Although it introduces more fitting parameters, thus an ease in fitting,

sometimes it allows to separate contributions originating from different degrees of rotational freedom of a given molecule. Thus the relaxation process can be easier to interpret. It's worthy to note that the KWW equation gives zeroth value for $\chi_{\infty}^{(2)}$. It is generally admitted that higher is the polymer glass transition temperature, better is the temporal stability of induced orientation. Therefore a lot of synthetic effort was devoted to obtaining such polymers (see *e.g.* Shi *et al.* [45], Chen *et al.* [46], Ermer *et al.* [47], Van den Broeck *et al.* [48], Caruso *et al.* [49], Lee *et al.* [50]).

4. APPLICATIONS

As already mentioned the discussed here polymers were developed mainly for electro-optic modulation for optical signal transmission in waveguiding configuration. Indeed, a lot of demonstrations were done [51]. Realization of large band (110 GHz) and low V_{π} modulators (below 1 V) was reported [52–59]. Several start up companies were created in USA offering packaged electro-optic polymer based modulators. To the first belong Pacific Wave and Tacan on California coast. More recently the GigOptix's company on East coast, was created; offering EO Mach-Zehnder intensity modulators [60], operating at 40 GHz and at 100 GHz with a low driving voltage.

Another applications, although with a much weaker effort, concerned the waveguide second harmonic generation through the modal phase matching [51, 61–63], demonstrating the feasibility of such devices.

Using the poled electro-optic polymer thin films Khalil *et al.* [64] have demonstrated optical parametric amplification (OPA). It was done using an ion exchange waveguide, coated with a thin layer (ca 1 μm) of para-nitro aniline (PNA) chromophore, grafted polymethyl methacrylate (PMMA). Thin film was deposited by spin coating of polymer solution on a passive waveguide obtained by the Tl ion exchange in a KF3 Schott glass plate. Such waveguides are characterized by good optical quality with low propagation losses (~ 0.1 dB/cm). The propagation losses in active layer were of 1–2 dB/cm. With the pump at 532 nm, originating from the frequency doubled fundamental beam of Nd:YAG laser a modal phase matching for parametric generation process ($\omega_p \rightarrow \omega_s + \omega_i$) was achieved for the following TM modes (indices) and wavelengths (in brackets):

$$TM_1^p(532 \text{ nm}) \rightarrow TM_0^s(814 \text{ nm}) + TM_1^i(1535.6 \text{ nm}),$$

where p refers to pump, s to signal and i to idler, respectively. The light amplification was realized on a beam originating from an OPO with 814 nm wavelength. A 1dB gain was obtained in a 0.5 cm long waveguide.

Because of their very good light propagation properties the electro-optic polymers were also used for third-order NLO. In particular a waveguide all optical

light modulator [65, 66], exploiting large refractive index variation due to the photochromism of active chromophore was demonstrated.

5. CONCLUSIONS

Electro-optic polymers continue to attract the interest of chemists, physicists and optical device engineers. Indeed, these are materials which presently offer the best optical waveguides with the lowest propagation losses and the highest second-order NLO susceptibilities. There is still a continuing effort on fabrication of high rate electro-optic modulators for future wide band telecommunication and internet transmission systems. Very recently Zheng *et al.* [67] reported realization of a Mach Zehnder EOM operating at 1.55 μm wavelength. As active NLO material a poled guest-host electro-optic polymer DR1/SU-8, was used.

The important problem to address, although not dramatic because of usually short waveguides used as active element, are the propagation losses. They come essentially from the CT chromophores aggregation. This phenomenon, which depending on the chromophore and the matrix used, may start at low concentrations already [17]. As result the value of $\chi^{(2)}$ susceptibility decreases and the propagation losses increase [68]. Another problem is the relaxation of the induced polar order. Here a big progress is observed in synthesis of high Tg as well as cross – linking polymers. An important problem which may be encountered with EO polymers is influence of light on polar order. Large *et al.* [69] have observed that shining the poled PMMA-DR1 side polymer thin films in the absorption band kills in a reversible way, the polar order. This was tentatively interpreted by the chromophore reorientation through the trans-cis-trans light induced process. This effect was confirmed in EO polymers functionalized with a zwitterionic chromophore [70], which doesn't undergo trans-cis-trans type izomerization process.

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