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# Polymer Architectures for Optical and Photonic Applications

*Ana-Maria Albu and Vlad Marian Târpă*

## Abstract

The last decade of the last century is marked by a revolution in the synthesis of materials for optical and photonic applications, against the background of the growing need for new high-performance materials to increase the efficiency, reliability and speed of response linked to environmental aspects. The diversity of requirements and the optimization of the responses has led to a major dispute over the structure and composition of these materials: Inorganic or Organic, Natural or Synthetic, Hybrid or Pure, which has stimulated interest in the development of various architectures. Special attention shall be paid to establishing a fundamental relationship to correlate the non-linear optical response and chemical structure, especially for the category of organic materials- particularly polymers- distinguished by structural/compositional versatility and suitable for processing by simple technique which allows serial production. In fact, optical nonlinearity (NLO) is not an exotic phenomenon. Indeed, all materials are optically nonlinear if light is sufficiently intense. The synthesis of functional photonic organic materials is a major challenge of contemporary community of material scientists to imagine new functional materials based of “collective” phenomena by virtue of the “engineered” molecule- molecule interactions and spatial relationships. In this context, this paper aims to highlight the most important features concerning the structural - compositional relationship of polymeric materials used in optoelectronic and photonic applications.

**Keywords:** polymer, azo-polymer, optical material, azo-chromophor, non linear optics, solvatochromic, photochromic, self assembly

## 1. Introduction

Presently, one can remark a continuous increase of the need for new technologies adjusted to the market request. This involves obtaining new high-performance materials and new microelectronic, optical devices, whence appearing these requests. Because we begin will be habitually with these advantages, our expectations demand a higher efficiency, faster and more reliable materials answers, safe environmentally technologies.

Optical nonlinearity (NLO) is not an exotic phenomenon. Indeed, all materials are optically nonlinear if light is sufficiently intense.

The last decade of past century was marked by a revolution in the field of materials synthesis for optical and photonic applications. It is noteworthy major dispute regarding the origin of these materials: inorganic or organic, natural or synthetic, hybrid or pure?

Thus, the fundamental problem in the development of this class of materials still remains the formulation of a theoretical model, which generalizes the particularities of interaction of the stimulating electromagnetic field with the specific micromolecular constituents for each class of compounds.

In this regard, perhaps the greatest challenge is (outside the design synthesis, characterization and understanding of novel molecular and macromolecular assemblies with applicability in non-linear optical fields) the interfacing nature of research, which brings together specialists in chemistry, physics and materials science. Initially, a test stone for chemists, photonics materials require the rational construction of supramolecular assemblies characterized by preordained collective phenomena consequence of intermolecular interactions and their spatial relationships.

It is classic that the high values of the electronic polarization are characteristic for  $\pi$ -conjugated molecules. This justifies the many generalizing predictions that material systems with extended  $\pi$ - conjugation will be characterized by high values of hyperpolarizabilities.

## 2. Principles of the non-linear optical media

The basic nonlinear optical polarization can be studied at the molecular level. That involves an effort devoted to understanding the relation between the molecular structure and materials properties. Another perspective regards the discussion of the effective arrangement of the nonlinear molecules into macroscopic responses (single crystal, quasi-crystalline thin film, and a polymer matrix, etc.). To describe the nature of nonlinear optical response in materials is necessary to consider the aspects of frequency dependence and symmetry.

A molecular medium, such as an organic crystalline or polymeric solid, is generally non-conducting and non-magnetic and the electrons are regarded as being tightly bound to the nuclei. For such media, the interaction with light can generally be regarded within the framework of a dielectric subjected to an electric field [1–3].

At molecular level, the interaction of molecule with electric field can be described by the polarizability ( $p$ ):

$$p = \alpha E + \beta E^2 + \gamma E^3 + \dots \quad (1)$$

where:  $\alpha$ ,  $\beta$ ,  $\gamma$  are the molecular polarizabilities (1st, 2nd, 3rd order).

The fundamental relationship describing the induced charge in molecular dipole moment (polarization) upon interaction with an oscillating external field (light) can be expressed in a power series:

$$p_i = \sum_j \alpha_{ij} E_j + \sum_{j \leq k} \beta_{ijk} E_j E_k + \sum_{j \leq k \leq l} \gamma_{ijkl} E_j E_k E_l + \dots ; \quad (2)$$

here  $p_i$  is the electronic polarization induced along the  $i^{\text{th}}$  molecular axis,  $E_j$  is the  $j^{\text{th}}$  component of the applied electric field,  $\alpha$  is the linear polarizability,  $\beta$  is the quadratic hyperpolarizability and  $\gamma$  is the cubic hyperpolarizability. Starting with the second term of equation are described the nonlinear response to the radiation field and account for terminology “nonlinear optics”. Importantly, the even order tensor,  $\beta$  is responsible for doubling frequency of incident light (second harmonic generation, SHG) and  $\gamma$  describe the third order response of material at molecular level (third harmonic generation, THG).

At macroscopic level, nonlinear optics is concerned with the electric polarization  $P$  (dipole moment per unit volume) induced in a material by an electric field  $E$ .

Typically, P is proportional to E and oscillates at the same frequency. So, the response is linear! As the magnitude of the field increases, P deviates from proportionality and nonlinear phenomena appear:

$$P_i/\epsilon_0 = \sum_j \chi_{ij}^{(1)} E_j + \sum_{j \leq k} \chi_{ijk}^{(2)} \beta_{ijk} E_j E_k + \sum_{j \leq k \leq l} \chi_{ijkl}^{(3)} E_j E_k E_l + \dots \quad (3)$$

$\chi^{(n)}$  = electric susceptibilities of order n; linear for n = 1, quadratic: n = 2, cubic: n = 3. Considering the dual character of light, electric and magnetic:

$$E = E(\omega) + E(\Omega) = E_0 \cos(\omega t) + E(\Omega), \quad (4)$$

where  $E(\omega)$  is the optical component of field and  $E(\Omega)$  is characteristic for external applied field, can be written the mathematical expression of polarization as function of frequency:

$$P(\omega) = \left( \chi^{(1)} + 2\chi^{(2)}E(\Omega) + 3\chi^{(3)}E(\Omega)^2 - \frac{3}{4}\chi^{(3)}E_0^2 \right) E_0 \cos(\omega t), \quad (5)$$

where: the second term describe the Pockels or linear electrooptic effect (1th order) the third is for the Kerr of quadratic electrooptic effect (2th order), and the last is specifically for optical Kerr effect.

$$P(2\omega) = \left( \frac{1}{2}\chi^{(2)} + \frac{3}{2}\chi^{(3)}E(\Omega) \right) E_0^2 \cos(2\omega t), \quad (6)$$

where the first terms specifically for second harmonic generation (SHG) and the second describe the electric-field induced SHG (EFISH),

$$P(3\omega) = \left( \frac{3}{2}\chi^{(3)}E(\Omega) \right) \frac{1}{4}\chi^{(3)}E_0^3 \cos(3\omega t) E = E_0 \cos(\omega t) + E(\Omega), \quad (7)$$

which is specifically equation for third harmonic generation (THG).

Starting from this fundamental description of interaction light-material, without forgetting about the multicomponent structure of materials (different polar species), can be formulate two fundamental aspects for the researchers interested by the synthesis of such materials:

- The design of this materials suppose an biunivocal interdependence of macroscopic and microscopic optimization;
- If a microscopic level is very important to enlarge  $\beta$  and  $\gamma$  values, at macroscopic level very important is the effective arrangement of the nonlinear molecules into macroscopical response. So macroscopic susceptibility describe the nature of nonlinear optical response in materials; considering aspects of frequency dependence and symmetry. Generally:

$$\chi^{(2)} = Nf\beta, \text{ respectively } \chi^{(3)} = Nf\gamma, \quad (8)$$

where N is the number of molecular dipoles (polar or polarizable molecules), f is the local field factor.

Synthetic materials of interest in ONL applications are not isotropic. For example:

- Organic crystals consist of molecules with specific orientations of structuring the constituent motif. Thus, the molecules themselves often have electronic structures with a high degree of anisotropy and consequently, the response of

the material to the applied electromagnetic field will not always respect the direction of incidence, as is usual in classical optics.

- Similarly, in terms of orientation, polymeric chains comply with the principle of minimum energy. If these materials are generally characterized by the random orientation of chains - isotropic structure - depending on the composition, the chains constituting them may be oriented preferentially, so that their energy distribution will require their response to external stimuli.

For this reason, susceptibilities are tensor quantities related to the polarization response in one of the three directions of the field. The material characteristic that reflects the degree of anisotropy is the dielectric constant  $\epsilon_{ij}$ , defined by the electric field and the dielectric displacement, being a second-degree tensor. The birefringence phenomenon is one of the consequences of this dielectric anisotropy. Visualizing a uniaxial crystal with  $n_x = n_y \neq n_z$ , the refractive index of the materials,  $n$ , is given as

$$n \approx \sqrt{\epsilon} \quad (9)$$

and with a light wave propagating from left to right along the  $x$ -axis with its electric field polarized in the  $z$ -direction, the propagation constant  $k_z$  will be determined by  $n_z$  from:

$$k_z = \frac{\omega}{c} n_z \quad (10)$$

Thus, while all material structures from the point of view of the optical properties, are characterized by the presence of the both hyperpolarizabilities ( $\beta$ ,  $\gamma$ ), do not display simultaneous second and third order nonlinear response. That is due to the peculiar structural requirement for the two NLO properties. The high concentration of chromophores with large product of the dipole moment,  $\mu$ , and the first hyperpolarizability,  $\beta$ , stimulate aggregation tendency, diminishing their contribution to the electrooptic effect of materials. The last decade of the 1990s has established that high electro-optical coefficients for guest-host material systems, with polymeric matrix, are essentially due to electrostatic chromophore-chromophore interactions. Thus, when doping the polymer matrices with chromophore species characterized by high electrostatic interactions, there is a decrease of the electro-optical coefficients in the value with an increase of the chromophore concentration. As well, the poling efficiency is limited because a disruption in alignment of chromophores appears when the polarization field is stopped, owing to the electrostatic interactions and thermal randomization. This behavior is the result of a major relaxation phenomena of chromophores' in the first moments after stopping the polarization field [4, 5].

The improvement in the value of electro-optical coefficients requires intervention in the composition and structure of the chromophore, without perturbation of the  $\pi$ -electron structure to avoid changing the molecular hyperpolarizability  $\beta$ . In such cases, the syntheses that favor the perpendicular orientation of constituent segments with distinct polarity (i.e. acceptor, donor) to the chromophore conjugation system, are preferred. Such sterical hindrance limits the distance at which chromophoric molecules can approach each other, thus reducing undesirable dipole-dipole interactions; finally becoming competitive with lithium niobate [6].

## 2.1 Origin and maximization of molecular hyperpolarizabilities $\chi^{(2)}$ , $\chi^{(3)}$

Early on, the correlation of the  $\beta$  size value with the permanent dipole moment difference, between the ground and excited electronic state, underlines the

dependence of the SHG signal magnitude on the material structure. Although considerable efforts have been made to create new “push-pull” conjugate sequences, that generate a large charge in the excited state, the predicted response values have not always been obtained.

The correlation of the material response with the extension of double/single bonds alternation in the polyene structures served as a model in development of an elegant model for understanding the relationship of the chemical structure-nonlinear optical response. The model is still a useful guide to design the materials with predicted SHG properties, highlighting, as a key element in generating the NLO response, the size of the electronic conjugation at the level of the donor-acceptor substituted chains [7–15].

Centrosymmetric media are materials with a high density of polarizable electrons, which stimulates the apparition of strong third order NLO phenomena.

Increasing the magnitude of NLO phenomena in polarizable polymers involves either maximizing the intensity of the applied polarization field or designing molecules with intrinsic steric hindrance and an adequate maximization of electronic conjugation at level of the substituted donor-acceptor sequence [16–18].

As extended conjugation is a key element for third-order NLO materials, several constructive restrictions need to be observed [19]:

- high molecular symmetry of the material sequences that generate the excited and de-excited states, respectively;
- involving the high energy excited state in the material response;
- a large molecular dipole moment variation for transition ground state to excited state.

Theoretical and experimental paper of the field highlights that the best candidates for these applications must be characterized by a high level of extended conjugation to the chain level as well as by strong monophotonic absorptions. Thus, structures similar to polyene compounds are ideal, such as: poly (di)acetylenes, polyarylenes or poly (vinylarylenes) as good as the aromatic structures of chinoids (push-pull). [10, 11, 20–23].

The length of the conjugate sequences as well as the molecular geometry and the electrical charge of the ground state are the key factors for the type of application of the material.

### **3. Structural features of NLO polymer materials**

In the previously outlined context, the researchers’ attention was focused on studies to generalize the NLO response-chemical structure correlation, while spending efforts on applied research aimed at creating new photonics and photoelectric devices. The variety of physicochemical properties as well as the compositional versatility of conjugate organic materials placed them at the center of these studies. The  $\pi$  conjugate organic materials with large electronic polarizabilities and, since the nonlinear response is a weighted summation of higher molecular polarizabilities, it becomes reasonable for conjugate molecules to possess substantial hyperpolarizabilities.

#### **3.1 NLO chromophors**

The researches activities in the materials fields as well as application development mainly based on multiphoton absorption (MPA) process continue with

consistency to demonstrate the successful proof-of-concept in diverse areas, such as microfabrication, bioimaging, photodynamic therapy, frequency upconverted lasing, etc. The mid-1990 is marked by tempestuously development in the design and synthesis of the new dyes, which are more efficient than those commercially available. Consequently, in the coming decades it became evident that these together with their processability, photostability, and durability, that depends on the application, are the basic elements for the specificity of physical motif. The great continuous challenge for technological exploration remain how to establish and fine-tune structure-properties relationships for these large numbers of organic, organic-inorganic materials assemblies, taking into account to the varied molecular structural factors preserving the reproducible NLO properties. It was known that molecular hyperpolarizability increases with the  $\pi$ -electron conjugation length of the chromophore. Although it would be expected that the increase in chemical reactivity and optical absorption would be directly proportional to the length of the conjugation at the chromophore level, it has experimentally proved that it is not the best approach to optimize nonlinearity. Theoretical models developed for molecules prone to charge transfer show that the strength and energy balance of donor-acceptor sequences, correlated with the length of the electronic bridge, directly affect the value of molecular hyperpolarization [24–26]. Thus, by adjusting the strength of the donor and acceptor sequences, the moment of the fundamental state, respectively excited, is directly determined. These peculiarities claim that the increase of the value  $\beta$  is the consequence of the mesomeric interactions of the strong donor-acceptor groups. In conclusion, in the case of organic compounds, the structure-properties relationship is closely related to the strength of the D-A bond, as well as to the widening of the conjugation in the structural unit:

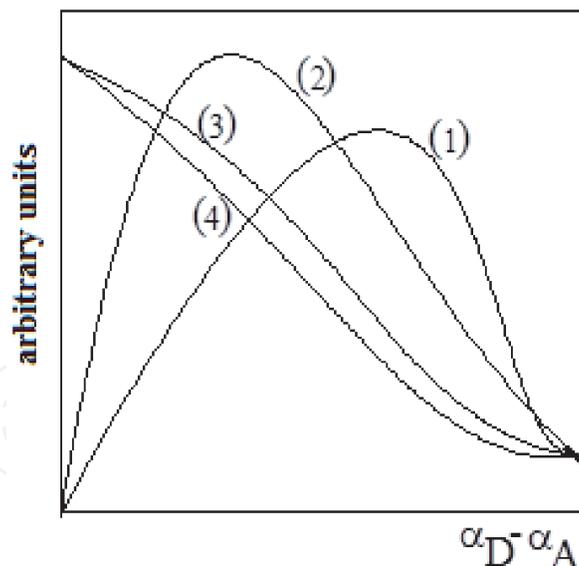
$$\beta \approx (\mu_{ee} - \mu_{gg}) \mu_{ge}^2 / E_{ge}^2,$$

where: g = ground state index; e = excited state index;  $\mu_{gg}$  = ground state molecular dipole;  $\mu_{ee}$  = excited state molecular dipole;  $\mu_{ge}$  = transition state molecular dipole;  $E_{ge}$  = transition energy.

Pursuant to this equation, hyperpolarizability is directly determined by the change of the dipole moment and the oscillator power (expressed by the square of the matrix of the dipolar elements) and is inversely proportional to the square of the transition energy. Each of these parameters has a maximum value closely related to the chemical structure of the molecule. The specific function (electronic exchange) which determine the NLO character, as well as the strength D-A, shall be decided by the variation of all mentioned factors. This dependence can be found in the dominant  $\beta$  value, approximate by Hückel series for molecular orbitals calculation.

Thus the coulombic energetical difference between donor ( $\alpha_D$ ) and acceptor ( $\alpha_A$ ) can be explained as energetical HOMO-LUMO dissimilarity. The parameters  $\mu_{ge}^2$  and  $E_{ge}^{-2}$  show maxima value for the null molecular asymmetry, so:  $\mu_{ee} - \mu_{gg} \approx \alpha_D - \alpha_A$  (**Figure 1**) [8]. Consequently, at increasing of molecular asymmetry  $\alpha_D - \alpha_A > 0$ ,  $\mu_{ee} - \mu_{gg}$  increase with the difference  $\alpha_D - \alpha_A$ . Increasing the  $\alpha_D - \alpha_A$ , the mixing of bridge orbital's D-A decrease in the same time with transition HOMO-LUMO. At the same time, there is a decrease in the charge transfer character, specific to stilbenic molecules substituted with D -A groups.

The D-A molecular structures are limited on the one hand by the coulombic factor (which may have negative, positive or zero values depending on the level of charge separation in the molecule) and on the other hand by the resonance energy, the consequence of the aromatic electrons involved in the conjugate DA.



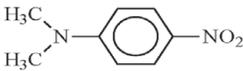
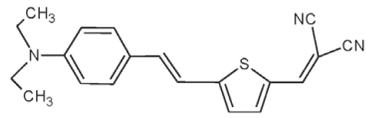
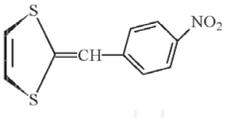
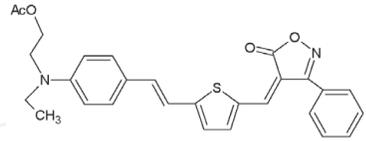
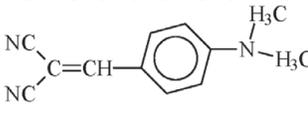
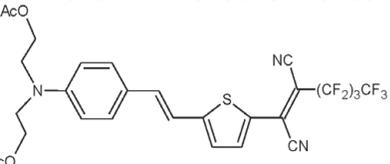
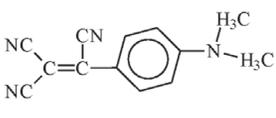
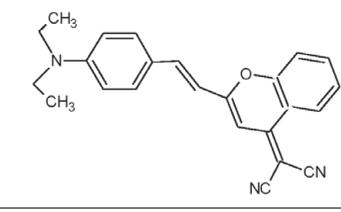
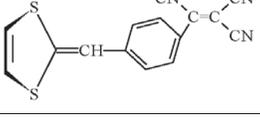
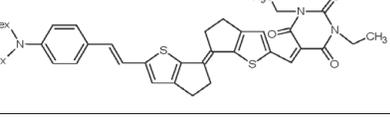
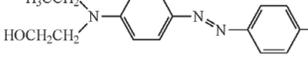
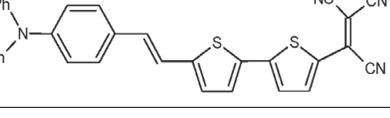
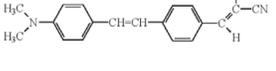
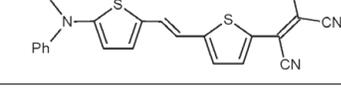
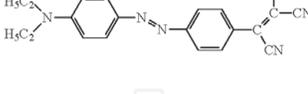
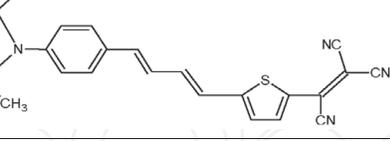
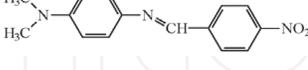
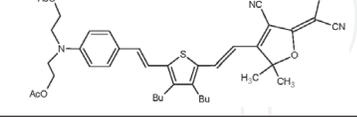
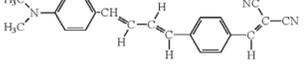
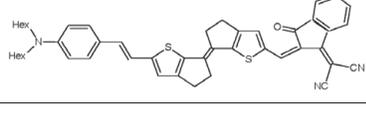
**Figure 1.**  
The dependence of  $\mu_{ee}-\mu_{gg}$  (1),  $\beta$  (2),  $\mu_{ge}^2$  (3), and  $1/E_{ge}^2$  (4) as function to  $\alpha_D - \alpha_A$ .

In addition, the dipolar transition moment show a sinusoidal variation for  $\beta$  with D-A strength while maintaining a consistent bridge of the conjugate bridge (**Figure 1**). Chromophores that were initially used in the NLO study were of limited success as they failed to reach the required absorption maxima in the near IR wavelength range (**Table 1**). There is a strong correlation between intramolecular charge transfer processes and NLO response, if discussed in terms of electronic structures and physical processes. Therefore, the design of an ideal chromophore structure with high NLO activity is based on some fundamental aspects at the molecular level. In this idea the intermolecular charge transfer, as a driving force, is necessary but not enough, so it is clear that there must be a high electronic density in the material. On the other hand, another fundamental problem in the operation of NLO materials is the length of the conjugate (i.e., the path length), which determine the high and permanent charge separation at molecular level [18, 29–35].

At the outset of revealing the particularities of molecular structures with NLO properties, two general types of organic molecules predisposed for these phenomena are defined (**Figure 2**) [36]:

- a. The Type I Chromophores have a symmetrical structure and, in general, are made up of an aromatic bridge, rich in electrons, flanked on both sides either by deficit heterocyclic groups or by electronic surplus;
- b. Type II chromophores are asymmetric molecules formed by an aromatic/olefinic bridge, rich in electrons, flanked by an electro-donating group, respectively, electron acceptors.

Improved solubility required the attachment of pendant alkyl chains to the aromatic sequence. At the same time, the attachment of electron-donor/acceptor groups models the intrinsic electronic density of high molecular weight polymers. The criteria for achieving symmetrical structures (type I (a) and I (b)) are based on the correlation between the large loads of the quadrupole moment during photoexcitation and the cross section. Consequently, molecules characterized by the alternation of vinyl and 1,4-arylene groups as well as the connectors between two identical end groups (i.e., electron- acceptor or donor) are preferred to realise of many NLO chromophores. Such structures are described generically as “push-push”

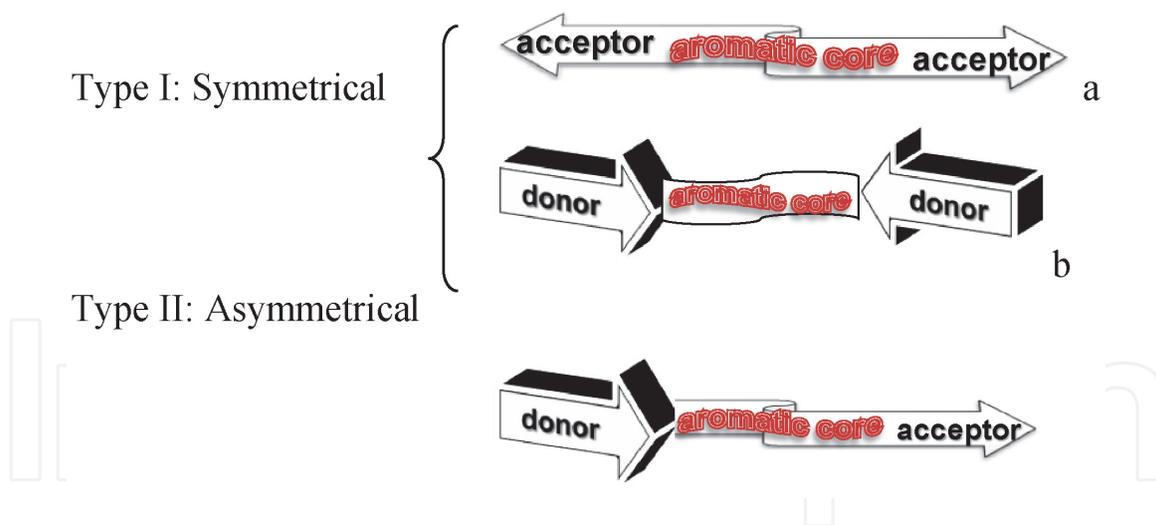
NLO chromophore	$10^{-30}\beta\mu$ ( $\text{cm}^5/\text{esu}$ )	NLO chromophore	$10^{-48}\beta\mu^*$ ( $\text{cm}^5/\text{esu}$ )
	138		1 300
	358		2 000
	271		3 300
	846		1 720
	1 200		10 400
	1 090		10 600
	2 650		10 200
	4 110		9 800
	500		18 000
	1 320		19 400

At 1907 nm.

**Table 1.**

Most investigated NLO chromophores and their  $\beta\mu$ -values [27, 28].

(I (a)) or “pull-pull” (Type I (b)), depending on the direction of intramolecular load transfer: from the end to the centre of the molecule, or vice versa. This model has subsequently gained growing popularity, proving very useful in the design of one-dimensional molecules [29]. The molecular coplanarity is another key parameter in enhancing the intramolecular charge transfer efficiency [37]. At the same



**Figure 2.**  
*Classical molecular structures for NLO chromophores: An aromatic block.*

time, for organic molecules, the strength of dipole in the ground- state of nonsymmetric molecules as well as the multipolar transition-dipole strength in the centrosimetric molecules are also energy factors that determine the NLO response magnitude [29, 38, 39]. Both experimental and theoretical, it has been demonstrated that the multiplication of the number of conjugation path or the connection of more than one linear path to generate two- or three-dimensional configurations, leads, in the material, to a major increase of the NLO responses value [31, 32, 38, 40].

Remarkable is the fact that when assessing the properties of NLOs, the energy changes caused by the interaction with the environment should not be neglected [41]. Thus, the polarity of the solvent, expressed by its dielectric constant, is an important structuring parameter determining on the one hand solvation by hydrogen bonds or by promoting colloidal-microaggregate dissolution. Thus, the efficiency of the cross section is more sensitive to the polarity of the local environment than to the intrinsic NLO aspects (properties) of the material [42].

### 3.2 Functionalized polymer materials systems

The NLO polymeric films are usually composed of long chains with chromophore sequences. Thus, chromophores, which are seen as net dipoles, are the origin of optical non-linearity in polymers. The interaction between the 'non-polar' molecules from bulk material and the chromophore, the molecular orientation (either random or of a certain symmetry) can introduce an overall orientation of the molecular assembly. This orientation will tend to cancel the individual molecular contributions. It is therefore important to ensure that all molecules are aligned correctly. The first information on this issue can be obtained by analyzing the chromophore sequence.

The starting point in developing technical strategies for the real NLO polymers synthesis is both the design of the assembly at the molecular level and the design and characterization of chromophore molecules with high molecular hyperpolarizabilities ( $\beta$ ,  $\gamma$ ), able to be, easily and efficiently, incorporated in a polymeric matrix.

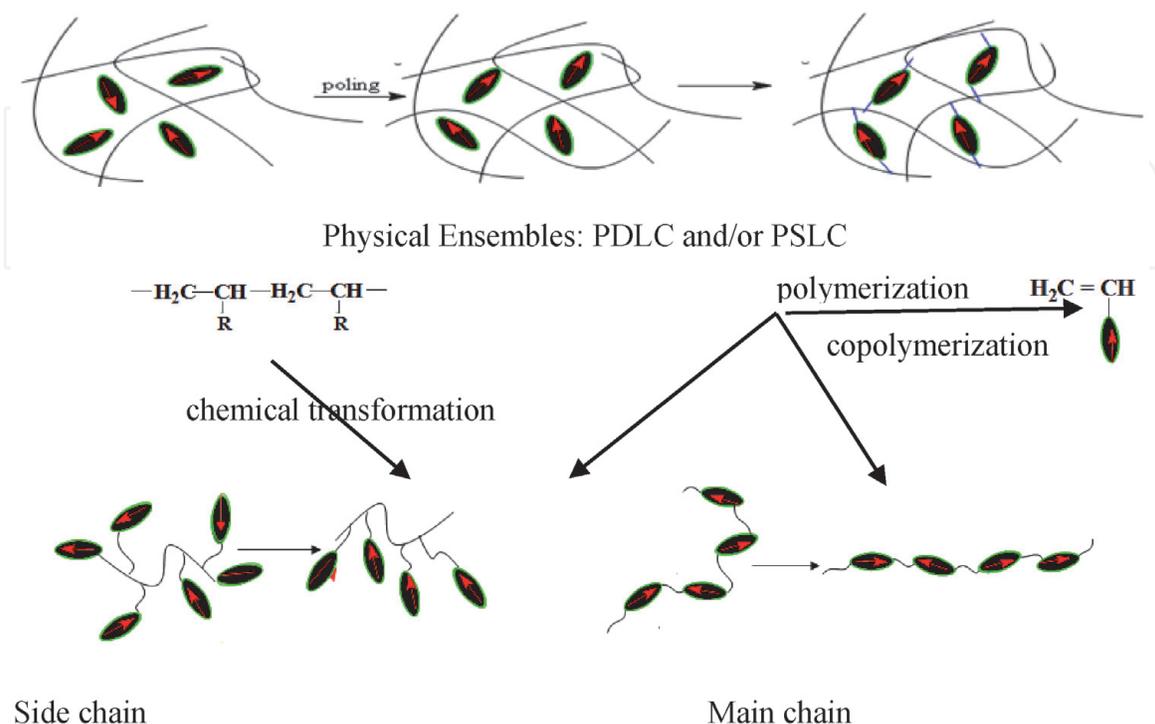
The generous literature information, both experimental and theoretical, on the use of organic materials (especially polymers) in NLO applications is based on the composition-properties relationship. A particularly important aspect relates, in addition to practical assembly techniques, to their composition, synthesis and characterization. Therefore, for polymerist researchers, it becomes defining the aspects of the synthesis and reactivity of the monomers bearing NLO sequences as well as

the establishment of techniques for incorporating these NLO sequences into the global polymeric architecture.

A particular aspect in the synthesis of NLO polymers, beyond optimization of the individual response of the constituent chromophore, is how the chromophore density can be maximized while preserving micro- and supra-structuring properties, respectively. The experimental studies, developed in this context, outlined two alternative strategies (**Figure 3**):

1. A first alternative is offered by the chemical modification of preformed macromolecular chains with chromophore sequences suitable for the desired application. This path offers the advantage of using chains with dimensions useful to the target application. The method is limited to relatively low degrees of transformation, does not provide a rigorous control of the distribution of the attached chromophore and last but not least, involves a series of purifications subsequent to the synthesis, in order to remove the unreacted chromophore.
2. However, a macromolecular structure with a predefined architecture can be easily obtained by (co) polymerization of monomers carrying an electrooptically active sequence. The major advantage of this method is the rigorous control of the chromophore fraction in the macromolecular structure both as a weight and as a sequential distribution. The only restriction imposed concerns the intrinsic structure and purity of the monomers which should not impede the (co) polymerization process.

Based on theoretical prediction and quantum the most promising macromolecular materials were, initially, the electron -conductive polymers such polyacetylenes, polythiophene or poly(p-vinyl phenylene)'s. Few research groups underlined that the lengths of conjugate sequences is not a necessary preconditions for increasing the intern polarity value (implicit  $\chi^{(2)}$ ,  $\chi^{(3)}$ ). Therefore the oligomers segments can be understood as inactive spacer with broaden the NLO activity,



**Figure 3.**  
Design Motifs of NLO polymers materials.

simultaneous facilitate the processability of materials [43–45]. Moreover, the susceptibility tensor calculus, with theory the disturbing torque- Hertree-Fock, for polyene series  $C_{22}H_{24}$ , underline the dependence  $\gamma_{xxxx} \approx L^4$ ; (L chain length) [45]. Afterwards were demonstrate that  $\gamma_{xxxx} \approx L^{4,6 \pm 0,22}$  [46].

For poly (p-vinyl phenylene), the predictions of the value rapport  $\gamma/N$ , pointing out a decreasing with increasing N(dipols number). In this context, it is outlined the idea that the best polymeric structures are those consisting of conjugated oligomeric segments, connected with spacers with or without NLO activity (**Figure 4**) [22, 47].

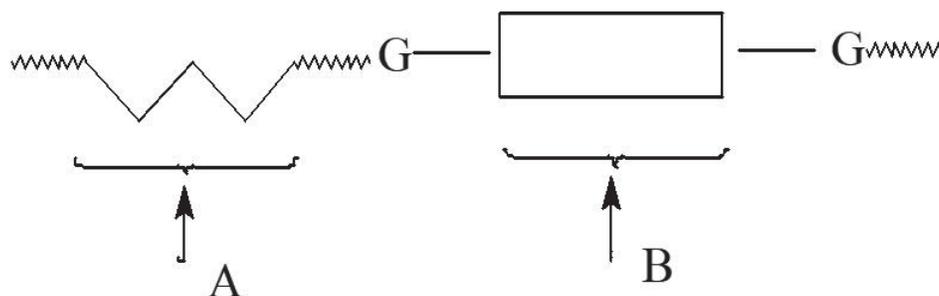
Through processing limitations (low solubility in the usual solvents) the researcher works were directed towards finding a new modality for including these sequences in polymer structure. So, the ladder hyperconjugate moieties thiophene oligomers and/or polyamide/imide were attached to the polyenic skeletons. Such materials were characterized by high values of hyperpolarizability,  $10^{-11} \div 10^{-12}$  esu/cm.

The copolyamides structures with polyvinylthiophene, obtained by interfacial polymerization ( $M_n = 10^5$ ), were characterized by thermal resistance until 400°C. The electro-optical analysis of these films denotes the existence of conjugate phase which generated  $\chi^{(3)}/\alpha \sim 10^{-3}$  esu/cm. This technique offers the possibility to tune the NLO activity by the number of the electrooptic segments of different species [48, 49].

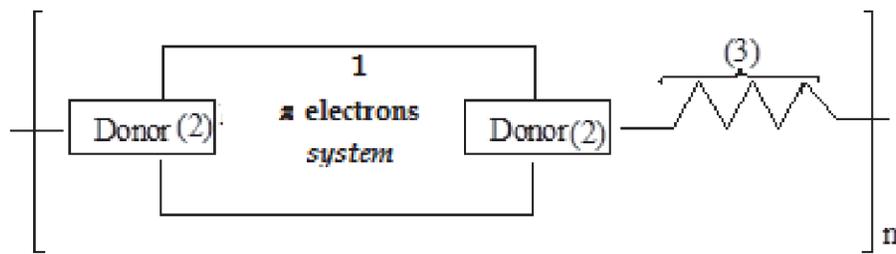
The similarity of poly(urea)s properties with NLO “piezoelectrical polymers” (poly(vinyl fluorine), poly(vinyl triflourine), copolymers of the triflourine ethylene and tetra- fluorine ethylene, nylon, vinyl cyanide entitle their NLO activity. The strong interchains bond (hydrogen bonds) rule the dipoles alignment in the electric field, [50].

The  $d_{33}$  coefficients evolution highlight a very slow relaxation, emphasize the lead of hydrogen bond for maintaining the NLO properties of the material. Starting with these conclusions great efforts were dedicated to investigation of the polymer structures showed in the **Figure 5** [51]. The NLO properties are due to the junction of the donating electrons (2) with the  $\pi$  electrons system. The flexible chain ( $\sigma$  bonds (3) (**Figure 5**) play an important role regarding the solubility, transparence and fusibility of the polymers.

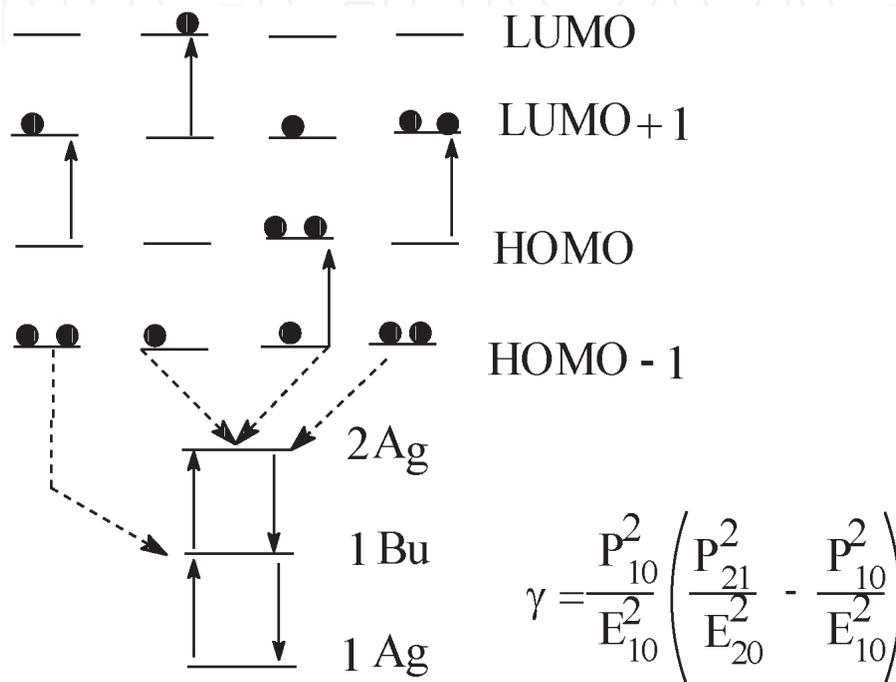
The constitutive- compositional similitude with polyureeas and the peculiar features: (i) the easy chromophores alignment for each synthesis step, the relative low viscosity; (ii) the high rate of polymerization (few seconds to several minutes) –reaction izocianate/alcohol; stabilization of NLO response by the hydrogen bonds, characteristics for polyurethanes; justifying the investigations of NLO polyurethane comporment [52–54]. The study of stability discloses in this case the importance of simultaneous development of polymerization and poling. So, by this procedure were diminished the phenomena of loss of property to reorientation (keeping 40–60% of the initial value) [54].



**Figure 4.**  
 The structural scheme proposed for NLO copolymers: A = segments with low NLO activity; B = oligomers segments with high NLO activity; G = functional groups [22].



**Figure 5.**  
Macromolecular materials structure used for waveguide fabrication.

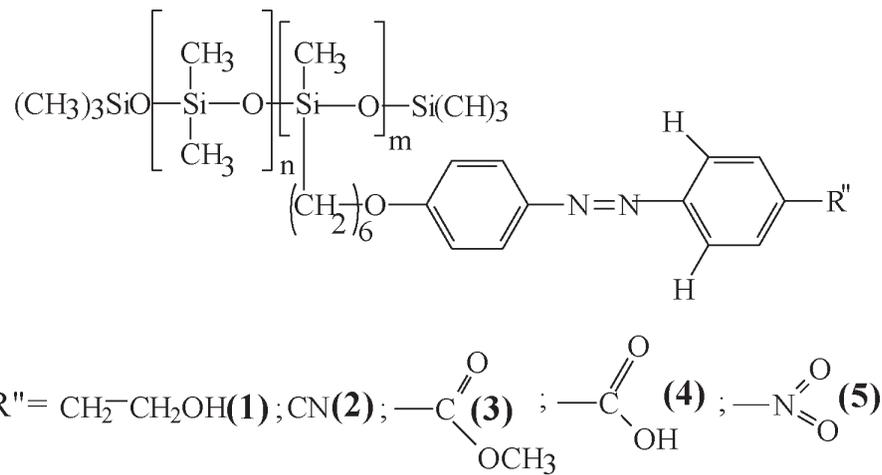


**Figure 6.**  
Representation of the two excited states which contribute to the  $\gamma$  value:  $E$ : energy of band gaps;  $P$ : transition dipole moment; for conversion the three electronic states are denoted as:  $0 = G(1Ag)$ ;  $1 = 1Bu$ ;  $2 = 2Ag$  [51].

The contribution of  $\pi$ -electron sequence, their length, is not crucial for increasing the hyperpolarizability value (specially  $\chi^{(3)}$ ). In this case significant is the sequence planarity. On the other hand, the symmetrical substitution, broadening results the enlargement of the transition bands from HOMO-1 to HOMO and similarly from LUMO to LUMO-1. These transitions promote the third order susceptibility, theoretical prevue by relation showed in the **Figure 6**.

A special attention was granted to the epoxy macromolecular structures. These investigations are supported by the potential stabilization of the chromophore, by its covalent binding to the carrier matrix [55–57]. Another very important aspect, especially if the polymer precursor has a high reactivity, was giving rise to the crosslinked structures. The major advantage, in these cases, is using an amine chromophore monomer. So, the dipoles chromophores alignment is accomplished by crosslinking control simultaneous with polymerization process. A wide range are getting the epoxydic compounds, which is a gain for the electrooptics coefficients (10–50 pm/V) [58–63].

Also of interest for the NLO has proved to be polysiloxane structures (**Figure 7**). This orientation is justified by their versatility, ability to form the films, very useful for monolayers deposition (Lagmuir-Blodgett) and the possibility of obtaining the self- stabilized dipolar structures [64–66]. The assessment of the SHG value, for all



**Figure 7.** General structure of polyorganosiloxanes for NLO applications:  $\text{R}''$ ,  $m = 6 \pm 2$ ;  $n = 8 \pm 2$  ( $\text{R}$  and  $\text{R}'$  are hydrogen's atoms) [65].

monolayers, highlights a significant increase while increasing the substituent polarity. This suggests that the package of each polymer chain in the monolayer is orderly, and the interchain bonds are essential in achieving the non-centrosymmetric structure.

Perhaps the most investigated NLO material class is azobenzene derivatives, known and studied for a very long time, their initial use being dye for a variety of substrates. Azobenzenes Photoisomerization is a well-known phenomenon, dedicated to reference materials [67, 68].

The key to exploiting the unique behavior of the azobenzene sequence is defined by how it can be included in the functional materials. For the generation of new properties, the most effective method of incorporation of azobenzene is the covalent attachment to polymers. The materials thus obtained will show both properties specific to polymers: inherent stability, rigidity and processability as well as conformational change under the action of electromagnetic radiation, specific to azo segments - photoisomerization processes. The covalent incorporation of the azo sequence in the polymer, through its photoisomerization process can generate a wide range of phenomena, even unexpected ones [69].

About 25 years ago, at dispersing of azobenzene groups in the polymer matrix, the unique phenomenon recorded was associated with their photoisomerization [70].

Under the action of polarized laser radiation, in polymer films with azobenzene sequence, their orientation is perpendicular to the polarization direction. Dichroic phenomena are thus generated.

This type of phenomenon is reported in the years '80 in liquid crystal polymers with photoactive azobenzene mesogenic sequences [71, 72]. Simultaneously, in Japan, the "command surfaces" concept [73] is opened, in which the azobenzene group acts as 'commander' and the Langmuir — Blodgett liquid films play as 'soldiers', which are aligned in trans/cis conformations by azoderivatives — the switching initiated by illumination [69]. After 1991, the applicative exploitation of these phenomena expanded worldwide, highlighting interesting and unexpected phenomena, which diversify use in reversible optical memory applications as well as photonic applications. Over the last 40 years, an exponential development of the domain has been observed and there is still no analysis covering all these new implications of azobenzene photoisomerization in polymeric structures. Remarkable and still of real interest remain the reviews which treat, generally or in a specific way, phenomena generated by the presence of azoderived sequences

[74–78]. However, the best available analysis covering both photoinduced birefringence and surface relief grating dates back to 2000 [79].

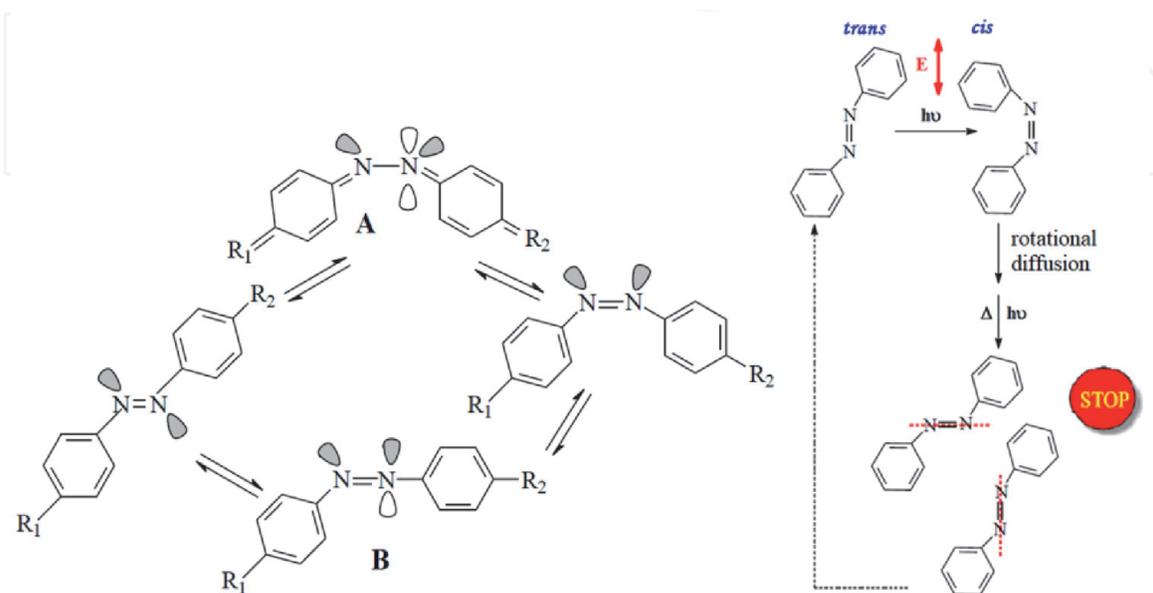
The special interest in azobenzene polymers is the result of their particular properties, which are useful in the processing and storage of optical information [69, 80–82]. The *sin-anti* conformational conversion process at the bond  $N = N$ , presumes some distinct transformations, highlighted in **Figure 8a**): (i) decoupling of the  $\pi$  electrons from the double bond, (ii) rotation around the single bond  $N-N$  followed by (iii) restoring the double bond,  $N=N$ , in a new configuration. Assisted by the adequate wavelength radiation, this phenomenon is governed by electronic transitions  $\pi-\pi^*$ , respectively  $n-\pi$  [23].

The molecular photoorientation of chromophore sequences is governed by anisotropic absorption, so that under the action of incident radiation, the dipole moment of chromophore sequence aligns along the molecular axis (**Figure 8b**). The linear polarized light is capable to induce a centro-symmetrical orientation in which the azoic sequence is directed perpendicular to the light plane. These oriental oscillations of the dipole moment's are transferred to the macro-scopical level, stimulating the emergence of optical dichroism and birefringence.

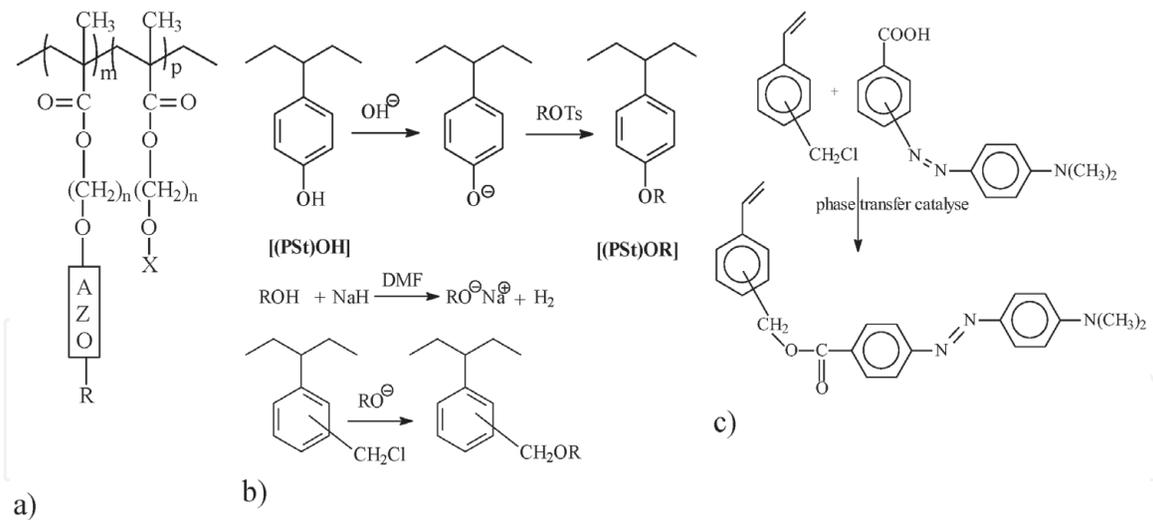
Therefore, the energy metastability of the *sin*-isomer plays a decisive role in both the theoretical interpretation and the practical application of the photoinduced phenomena in azoic polymers. For example, applications that rely on the modulation of the molecular alignment of CL will use materials with high stability of the *sin*-isomer (holography, optical data storage) while operational devices based on optical birefringence and dichroism phenomena will only use structures with rapid reversion of the *sin*-isomer.

The Red Dispers-based materials are the most representative in the class of polymers with the azobenzene side-chain NLO sequence [83–87]. Although noted by good temporal stability of the orientation (preserving about 80–90% of the maximum property value at 1000 hours after orientation) and, in addition, they admit a wide range of refractive index values from UV exposure, a still ongoing problem remains the stabilization of their orientation through photo crosslinking [88].

As the free radical mechanism is easily accessible, an informational richness covers the synthesis, characterization and use of (meta)acrylic and styrenic (co) polymers, with side-chain azo sequence (**Figure 9**) [74, 88–98].



**Figure 8.** Conformational changes in azobenzene: (a) A: Rotation of substituents around  $N = N$  bond; B: Inversion of substituents; (b) the azobenzene - light interaction.



**Figure 9.** Structures for methacrylate and styrene materials for NLO applications: a)  $R = \text{CN}; \text{NO}_2; \text{N}(\text{CH}_3)_2; \text{OCH}_3, \text{CH}_3; X = \text{alkyl}$ ; Chemical modifications of polystyrene and/or chloromethylstyrene; c) synthesis of NLO styrene monomer structure.

The versatility and easily processing of methacrylic polymers recommend these for NLO applications. The new monomers structures are investigated for chemical reactivity in the (co)polymerization [99–101] as well their electrooptic characterization [102–105]. These research points the inclusion of these chromogene sequences in copolymer structures without major difficulties. A peculiarity of these monomers is their predisposition to an high chain transfer, which involves the design of syntheses in compositional-operational conditions so as not to drastically reduce the degree of polymerization. In addition, the presence of coloured monomers leads an increase in the rate of polymerization, the phenomenon of self-acceleration becoming obvious. The sequential distribution confirms the predictions obtained from the capitalization of the reactivity ratios and at the same time, the characterization of the material proves the preservation of the optical characteristics of the chromophore.

The styrene materials are preferred relative to methacrylic materials. They are so much easier obtained by chemical modifications (**Figure 9b**): usually is used one of the vinyl benzyle chloride isomers. The drawback of these polymers is the relative rigidity of the chromogen sequence due to the aromatic spacer. The major advantage for these SC structures is the decoupling of the chromogene, which facilitates the molecular dipole orientation; but the poling-induced order in organic/polymeric materials is thermodynamic unstable. Thus, an important objective for the NLO polymer synthesis is the structural induction of slow relaxation in the acquired polarization orientation.

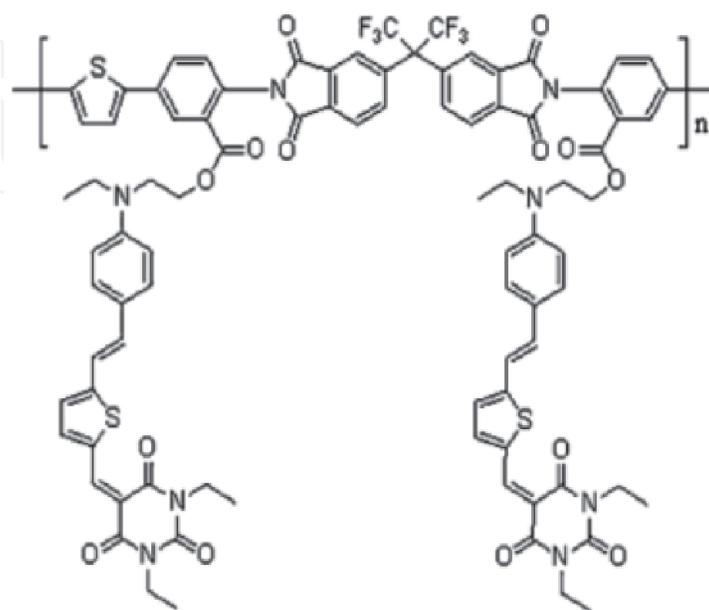
A promising alternative is azobenzene SC liquid crystalline polyester architecture [106, 107]. These, by their own nature, extend flexibility at the base-catene level by interactions with both acid and glycolic sequences that can serve as the link sequence of the mesogene. Thus, by modular construction, can be adjusted the length of the flexible methylene spacer in the lateral chain, the substitute on the azobenzoic fragment, the length of the methylene sequence in the main chain (all aliphatic) and the molecular weight of the polyester. Moreover, each parameter obtained by the versatility of the esthetically bond significantly influences the optical storage behaviour of the materials [108]. All materials (with a wide range of substitutes: cyano, nitro, methoxy, hydrogen, methyl, n-butyl, phenyl, fluorine, trifluoromethyl, chlorine, brom) have a diffraction efficiency of over 50%, giving these materials great diffraction properties. The stored information on azo copolymer media (75–100% azo- dye content) can be partially erased up to 80°C [109].

The copolymers of maleamic monomers with styrene and vinyl benzyl chloride and their preliminary characterizations of these materials proves that these monomers can be used for build NLO materials [110–112].

A critical issue of materials used in applications based on NLO properties is their thermal stability. This shortcoming can be addressed by promoting (after polarization) cross-linked structures, in particular by photochemical processes. Preferred for this direction are aromatic polyimides (PI), attached to the polymer frame. The chromophore can be 'grafted' onto PI sequence through transformation reactions. The method is advantageous because it allows the attachment of a different range of chromophores to polymer supports with a wide compositional variety, promoting the production of materials with high  $T_g$  (around 220°C), excellent solubility and processability. In addition, the topological stiffness, induced by the aromatic sequence, results in the preservation of high values of electro-optical coefficients during long periods of use [113]. In this way, by coupling reaction, was synthesized the poly(phenylene-imide thiophene) materials (PPIT) (**Figure 10**) [114]. They showed high  $T_g$  and consequently high temporal stability of the SHG, as demonstrated by dynamic signal decay behaviour studies that attest their stability at temperatures up to 150°C, preserved more than 82% of the SHG signal after 1500 h of operation.

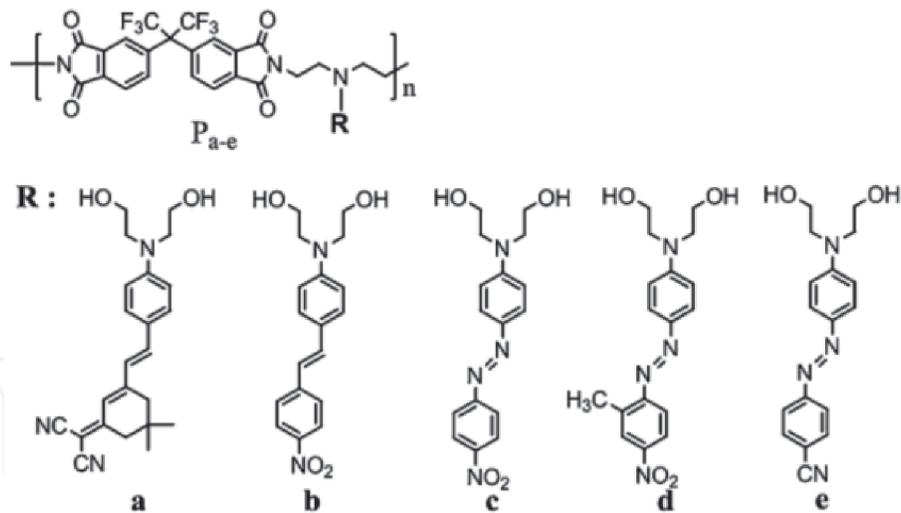
An elegant and efficient method of synthesis of PImss functionalized with second-order NLO, is the one-step synthesis (**Figure 11**) [115], which allows the use of the most popular electron-acceptor moieties. This give the materials with  $T_g$  values in the range 205–224°C [113, 116–119], whose thin films, corona-poled and SHG analyzed, are characterized by enhanced  $d_{33}$  value (30 pm / V at  $\lambda = 1064$  nm). The study of the preservation of SHG properties under thermal stress – as a function of annealing time at 125°C - reveals that the NLO response, after 9–20% initial decrease, does not change significantly over a period of 210 h for polymers: (PIc-e). (PIc), (PI d) and (PIe), with better stability than PIb at 125° C, retaining about 70% of the NLO properties (**Figure 11**).

Step-by-step polyaddition reactions is another tool for synthesis of thermally stable, second-order NLO chromophore PIm and poly (urea), starting from



**Figure 10.**

Structure of new poly(phenyleneimide) (50.85% chromophores,  $T_g = 170^\circ\text{C}$ ;  $T_d = 245^\circ\text{C}$ ,  $\Phi = 23$ ;  $r_{33} = 35$  pm/V).



**Figure 11.** Poly(imide)s containing NLO chromophores based on 2-(5, 5-dimethyl-cyclohex-2-enylidene)-malonitrile and conventional chromophores.

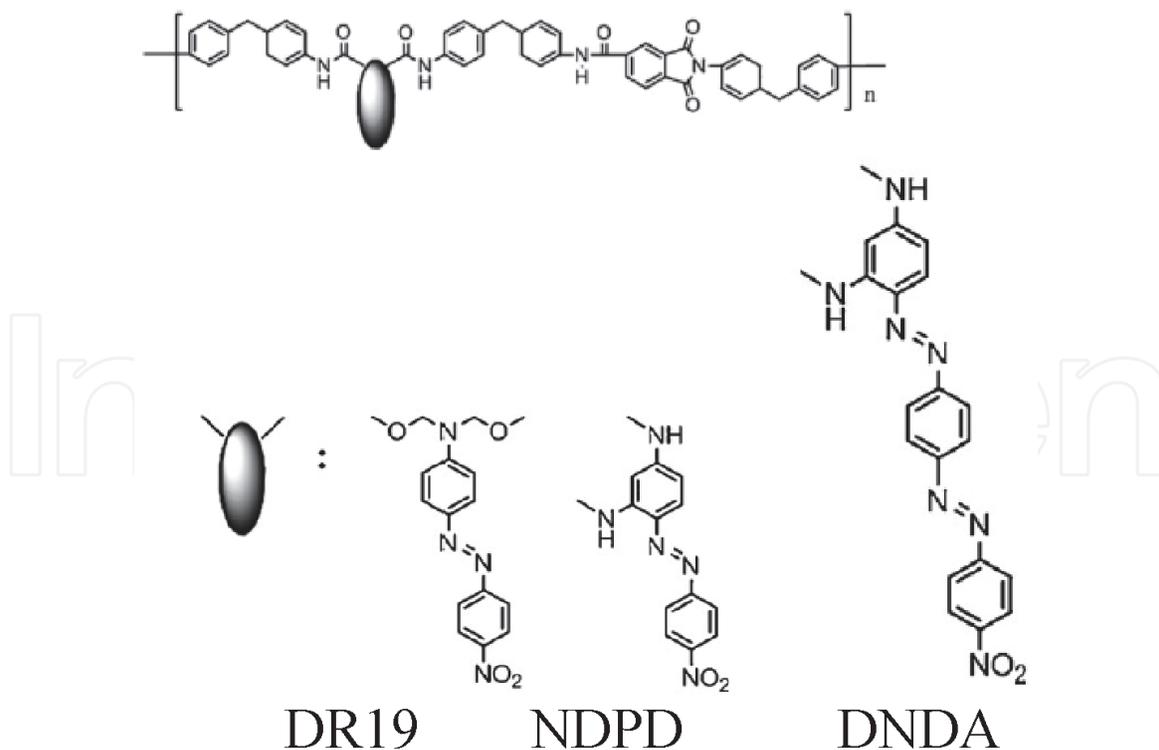
2,3-bis (4-aminophenyl) -5,6-dicyanopyrazine (BAPDCP), who's the first order molecular hyperpolarizability,  $\beta$ , was evaluated as  $123.5 \times 10^{-30}$  esu [120].

Using a new polymerization methodology, were produced the high  $T_g$  polymers [121] introducing into polymer backbone an imide-siloxane linkage containing NLO-active chromophores. As expected, introduction of dimethylsiloxane linkages in the backbone led to enhanced solubility and thermal stability of the functionalized PImS while retaining their useful physical characteristics, such as  $T_g$ : These polymers show SHG efficiencies comparable to those for functionalized PImS or polyurethanes and exhibit high temporal stability of resultant SHG signals.

Poly (maleimide) polymers functionalized with aminoalkyl sequences have a transition temperature in the range of 178–228° C, as well as a stable NLO response at high temperatures: such systems lose 24% of their property after 1000 hours at 125° C. The value  $d_{33}$  of SHG coefficient, 64.0 pm/V measured at 1064 nm, suggests that these polymers could be useful for NLO-applications [122].

The synthesis of polymers with electro-optical characteristics by sequential self-repetitive reaction (SSRR) [123] offers the possibility of making poly (amide-imide) structures. The promotion, in this case, of the reaction between dysfunctional azo chromophores (DR19, NDPD, DNDA), with an excess of 4,4-methylene-diphenylisocyanate (MDI), ends with the formation of a carbamic structure, useful for obtaining poly (carbamate diphenylisocyanate) (poly CDI- **Figure 12**). Subsequent addition of trimellitic anhydride (TMA) to the poly-CDI solution leads to the poly (N-acylurea) intermediate, characterized by good solubility. The in-situ poling and curing process, of this reactive mixture, favors the formation of the amide-imide structure of the N-acylurea sequence. The correlation of the thermal behaviour with the electro-optical characteristics, for these polymers, highlights values of  $r_{33}$ , in the range of 5.2–25.2 pm / V at 830 nm. There is also a proportionality of these values with the chromophore concentration. Such structures are characterized by good thermal stability- (80°C and optical waveguide losses (3.8–6.6 dB/cm at 830 nm) [124], which argues that when using the SSRR technique, the values of the EO coefficients are the consequence of the orientation of the chromophores on the polarization direction before lattice hardening.

Carbazole and its derivatives remain in the attention of chemists, mainly due to the fact that the carbazole skeleton has proven to be a versatile platform for the development of materials with applications in specialized fields such as optics, thermoelectronics as well as medical and pharmaceutical applications.



**Figure 12.**  
Poly(amide-imide)s NLO polymers structures obtained by SSRR.

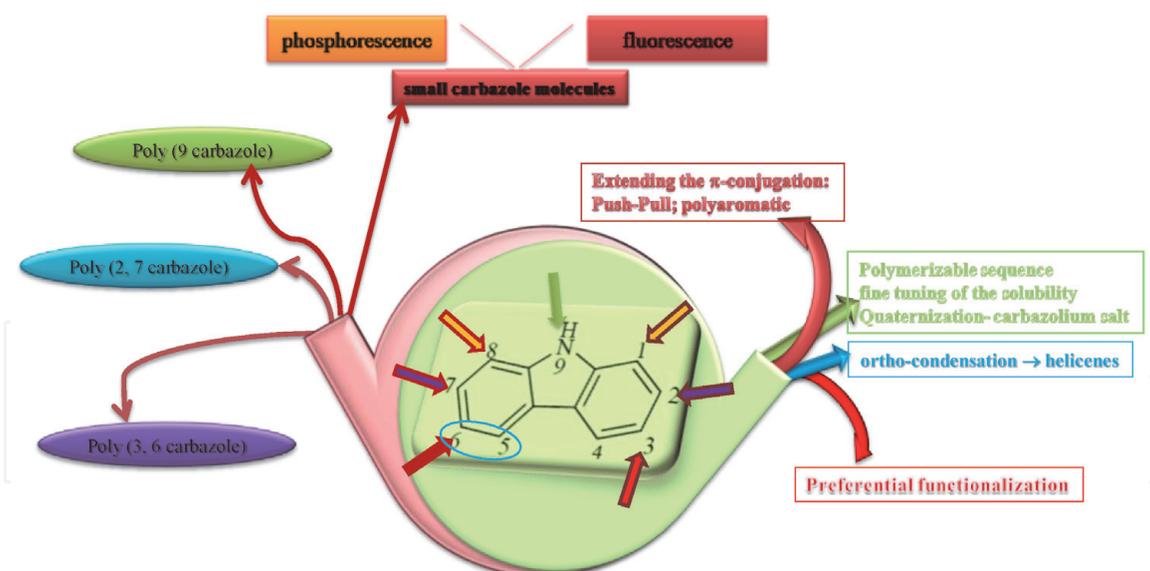
Belonging to a very interesting and relatively new class of material-conjugated polymers, carbazole and its derivatives are mainly characterized by the existence of  $\pi$ -mobile electrons, which can be used as chromophores, respectively electrophores [125]. The size of the energy difference between the conduction band and valence band, customizes the wavelength of absorption and / or radiative emissions, configuring the conduction capacity. What differentiates conductive polymers, expressly carbazoles, in the vast class of polymeric materials (known as true insulators) is their ability to carry electrical charges. This behaviour brings them closer to the electrical conductors - metallic or semiconductor.

Such materials are used both in the field of powerful light transmitters for sensors or as active components in electronic (opto) devices and batteries [126–129].

The main advantages of carbazole compounds are related to the economical, processability and their properties, particularly regarding few aspects:

- a cheap raw material readily available from coal–tar distillation, furthermore a large category is retrieved in the plants
- Different substituents can be easily introduced into the carbazole ring the presence of the nitrogen atom in the centre of symmetry, facilitates functionalization with various substituents. Consequently, the properties of the material can be modulated without potentiating the steric interactions with the basic carbazole backbone (**Figure 13**).
- The aromatic configuration gives them high thermal and photochemical stability as well as relatively high mobility of charge carriers;
- Carbazolyl groups easily forms relatively stable radical cations (holes).

Due to the mentioned advantages, a wide range of materials for transporting holes [130, 131], molecular glasses [132–135] or light-emitting materials [136–140]



**Figure 13.** Carbazole structures: reactive positions correlated with material structure and its particular properties.

have been designed with carbazole. Favourable to the synthesis of different dyes architectures (push-pull dyes; push-push or pull-pull), through substitution reactions to aromatic nuclei, carbazole was and remains an excellent candidate for the design of light harvesting materials for solar cells and numerous dyes with large and wide molar extinction coefficients the absorption spectra were obtained with this plan electron donor [141, 142].

Carbazole derivatives are intensely studied because of their well-known potential as precursors of materials for optical/ optoelectronic applications. The characteristics that recommend them for use are their special photorefractive, electrical, and chemical properties. Carbazoles are well known as a conjugated, good hole-transporting, electron-donor, planar compound and ease to introduce solubilizing groups to rigid ring structure. Carbazole can polymerize and couple in positions 3, 6, 9 and 1, 8 respectively. However, due to the very rigid structure of the carbazole, the last pair of positions is sterically hindered [143, 144]. The very high reactivity of positions 3, 6, favors the rapid synthesis of carbazole derivatives starting from 9H-carbazole, by direct bromination of the carbazole group with N-Bromo succinimide (NBS) [145].

In the context of the progress of new techniques for the manufacture of intelligent devices, the constructive versatility of the carbazole sequence, stimulated the development of design new dyes classes with photoinitiation activity in UV, near-UV or visible light, very useful in the development of 3D printing [146].

Substitution reactions at the carbazole unit can generate poly (3,6-carbazole) and poly (2,7-carbazole), respectively. These structures, due to the effective difference in the length of the conjugate sequence ((2, 7) is the longest, being similar to polyp phenylenes) have different properties and potential applications. In addition, using specialized modification strategies, the properties of both polycarbazole classes can be improved / fine-tuned, thus diversifying high-performance applications in the electronic and electro-optical field, such as polymeric light emitting diodes (PLEDs), organic field-effect transistors (OFETs), and photovoltaic cells (PCs). For both categories of polycarbazoles, an elegant and very complete presentation of the structure-properties-application correlation is summarized in several reviews, among which we recommend [147–149].

From this multitude of papers, the authors summarize studies dealing with novel aspects in poly (3,6-carbazole) synthesis, particular aspects of the photoactive

properties of polyvinyl carbazole copolymers, as well as other derivatives with polymerizable group in position 9 of carbazole, adjacent to the poly (2,7 carbazole) derivatives, strongly predisposed for optoelectronic applications such: organic LED, photovoltaic cells and biosensors.

Thus, the first decades of the 21st century are distinguished by the extension of studies dedicated to the synthesis and characterization of new optically active photochromic polymeric structures, with two distinct functional sequences: azo and a chiral group [150–153]. The simultaneous presence of these functions, sensitive to electromagnetic stimuli, creates the premises to display both the typical properties of asymmetric systems (optical activity, exciton division of dichroic absorption) and the typical characteristics of photochromic materials (photo refractivity, photo reactivity, N properties). In this context, it seemed interesting to investigate the properties of new multifunctional copolymer materials containing both photo responsive azobenzene and the photoconductive carbazole chromophore directly bound to the polymeric side chain through the chiral fragment: the presence of the electron-rich carbazole sequence as partner of the electron-poor azobenzene chromophores can induce charge transfer interactions fundamental in the operation of photoconductive materials [154].

The literature highlights the appearance of charge transfer interactions in achiral copolymers of N-vinyl carbazole (NVK) with methacrylic azoderivatives, the intensity of which is stimulated by the alternation of monomer sequences [155–159].

Due to their complexity of structural behaviour, they are able to generate sophisticated synthetic architectures, with high sensitivity and selectivity, which expands the application range. By consequence, they may be adopted special applicative functions, such: with molecules and ions they can be utilized in different separation and purification techniques; by interactions with the electromagnetic stimulus in solar cells fabrication, organic light emitters and optical elements, by specific interaction with the biological sequences they developed applications in anti-biofouling or specific binding proteins, by specific interactions in adhesive assemblies, they can generate bonding-disbonding phenomena's, by peculiarity of their response to the stimulus action they can behave as self-healing agent for other different materials, by interactions between different polymer's sequences can be achieved a multi-layered polymer materials with different functionalities in applications: screen printing, stamping ink-jet-as commercial used technology or optical waveguide, elastomeric light-emitting devices and displays or molecularly stretchable electronics- as specialized technologies.

#### **4. Conclusions**

Exhausting analyzing of the bibliographic information of the NLO materials shows great promise of polymer for device applications in the communications and photonics industries. Usually, these were used as host for chromophore structures as well as statistical (co)polymers, which include the NLO sequence in the macromolecular assembly.

At present there are a large number of NLO applications that use inorganic crystals. A few of these processes include optical switches, EO modulators, optical data storage, and optical fiber-based devices. The study of organic NLO chromophore-doped polymers would allow them to replace their inorganic counterparts. It should be clear to the reader that chromophore design has progressed significantly due to new classes of heterocyclic moieties used to optimize chromophore properties. However, with such novel designs, considerable research is required to achieve highly improved EO activities.

NLO chromophore functionalized polymers (obtained by polymerization or chemical transformation method) were found to be more effective because chromophore mobility is hindered by its attachment to the polymer. Functionalized SC NLO polymer systems with high and stable NLO effects, i.e.  $\chi^{(2)}$  and  $\chi^{(3)}$  were synthesized. The rigid aromatic backbone approach was found to be promising for making highly stable NLO polymeric systems. Polymers with rigid polymer backbone exhibiting high  $T_g$  values were found to suppress reorientation significantly. Theirs exhibiting high thermal stability in dipole orientation, relatively high optical nonlinearity and low optical loss are very promising for practical applications as has been reported.

Few work directions were showed for synthesis of the new stable NLO organic materials:

- Copolymerization provides a general approach to the enhancement of the thermal stability and the NLO stability of the materials within a tolerable trade-off range in optical nonlinearity. Introduction of an imide– siloxane linkage into polymer backbone containing NLO-active chromophores led to enhanced solubility and thermal stability, high glass transition temperatures and exhibit high temporal stabilities of the resultant SHG signals.
- Another strategy for stable polymeric systems is crosslinking technique. Extensive research on this topic for the past few years has shown that the NLO stability is profoundly enhanced by crosslinking the MC.
- More recently, functional dendrimers have been proposed to prepare multi-chromophore material systems that possess unique molecular architecture and characteristics. It is noticeable that a polymer host is not required for certain dendrite materials because they have unique film forming properties due partly to the reasonably high molecular weight and partly to the polymeric character inherent in these molecules. These dendrimer properties allow an appropriate solution viscosity when mixed with traditional spin-casting solvents to create amorphous glassy films. Those demonstrate dramatic enhancements in poling efficiency due to larger free volume and reduced dipolar interactions allowing diminished mobility constraints in comparison to the tethered polymer systems.
- Finally, it should be pointed out that our aim was to underline the main aspects regarding the relation structure- material properties and for that is practically impossible to mention here all investigations. What is not understood for real materials is how medium and chromophore-chromophore interactions modify/ can be used to tune, the response of the individual chromophore molecules.

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