

Non-linear optical polymers (NLOPs) for photonic devices

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ABSTRACT

Non-linear optics (NLO) has taken a key position in the technology of integrated optical circuits, and the area is undergoing intensive development for optical processing / storage of information and optical computing. Polymers have some very desirable features and are repeatedly being recognized as the materials of the future for non-linear optics. The present state of knowledge in the field of non-linear optical polymers (NLOPs) is highlighted in the following.

INTRODUCTION

Since the work of Meredith et al.¹ showing that poled polymer films exhibit large second order non-linear effects, and the work of Singer et al.² on a poled chromophoric poly(methyl methacrylate) system, polymers are seen as an important NLO material. Such materials are used to convert red light into a shorter wavelength by frequency doubling or tripling. Second harmonic generation (SHG) and third harmonic generation provide for the conversion of near-infrared (near-IR) light into green or blue light. The advantage offered by the shorter wavelengths is their higher capacity for processing and storage of information and optical computing.

Polymers have some very desirable features compared to traditional inorganic NLO materials: they are highly processable, unlike fragile inorganic materials they are robust, and synthetic organic chemistry can be used to a great extent to increase the NLO response.

Consequently, these materials are of interest for constructing photonic devices like switches, modulators and waveguides. The optical damage threshold for polymer materials (easily $>10 \text{ GW/cm}^2$) is high in comparison with other classes of materials (Prasad and Williams³). Good transparency and low light scattering, which are important factors for optical applications, are advantageous too.

However, careful consideration needs to be given to the time dependence (stability) of NLOPs. In particular, the instability of non-linear optical properties induced by the thermal history of the chromophoric film (physical ageing) needs to be understood for the benefit of stable non-linear optical devices.

The interest in developing the field of optically non-linear materials and second (and higher) harmonic generation is not solely industrial. These techniques offer new possibilities for fundamental research. A particularly interesting opportunity is to study molecular motion of sidechains, mainchains and dipoles in NLOP materials, by monitoring the orientation of chromophores attached to macromolecules (side- or mainchains) or as a guest-host system.

In the present description some terms need to be explained. Such explanations are briefly given in the following. However, for more detailed understanding further references need to be consulted.

FUNDAMENTAL EQUATION AND COEFFICIENTS FOR NON-LINEAR OPTICAL MEDIA.

When a material is subjected to an intense electric field from a laser pulse, the polarization behaviour is described by a non-linear relation (Lindsay⁴):

$$P = P_0 + \chi^{(1)} E + \chi^{(2)} EE + \chi^{(3)} EEE + \dots \quad (1)$$

where P is the polarization, E is the field strength and $\chi^{(j)}$ ($j=1,2,\dots$) are susceptibilities. The $\chi^{(1)}$ term describes ordinary linear behaviour (refraction and absorption). The $\chi^{(2)}$ term describes the optical effects resulting from an interaction of two electric fields, usually laser and radio frequency fields. $\chi^{(2)}$ is a 3rd rank tensor characterizing non-linear properties and therefore is of great importance. The $\chi^{(3)}$ term and further are related to higher than second order generation and are not discussed here. A similar to equation (1) relationship governs an isolated chromophore's dipole moment: $\mu = \mu_0 + \alpha E + \beta EE + \gamma EEE + \dots$, where β is the chromophore's second order susceptibility tensor, also called the hyperpolarizability. $\chi^{(2)}$ and β are related. β of the chromophore can be measured using the electric-field induced second harmonic generation (EFISH) measurement (Levine and Bethea⁵). A single scalar β value is calculated from the sum of the β tensor elements and, in general, a good chromophore has a high β value. β is a basic NLO coefficient. Further optical coefficients can also be measured, e.g. d_{33} .

CHROMOPHORIC POLYMERS FOR NON-LINEAR OPTICS

A fruitful approach to the development of NLO materials is the use of poled chromophoric polymers. Broadly speaking, chromophores are conjugated organic molecules with an asymmetric charge distribution produced, for example, by a donor substituent on one end of the

molecule and an acceptor on the other end. Several commercially available or individually developed chromophores are used. Most frequently the following chromophores are used: e.g. Disperse Red 1 (DR1) (azo dye), Disperse Orange 3 (DO3), DANS: [4-(dimethylamino)-4'-nitrostilbene], etc. Chromophores can be simply mixed (guest-host system) with the polymer (e.g. methacrylate systems) or attached to the side- or mainchain. Other polymer based systems are also used (Lindsay⁵).

Chromophoric films are spin or blade cast from solutions. Different solvent / polymer proportions are reported in literature, e.g. 1 to 5 wt. %. Typically the film thickness is of the order of microns. After casting, the solvent is extracted under vacuum.

Bulk or macroscopic optical properties of NLOPs are induced by aligning the chromophores in a process of poling by subjecting the polymer film to an electric field at a temperature near the glass transition (T_g to T_g+10 °C), where the mobility of the polymer structure is high. This is often carried out by *in-situ* corona poling or electrode poling. Next, the alignment is locked in by quenching the film to a temperature well below T_g , with the electric field on.

SECOND HARMONIC GENERATION (SHG)

In optical circuits the signal is processed at a frequency in the range of several tens of GHz. Frequency doubling of a pulsed laser near-IR beam of 1064 nm wavelength is used to obtain a wavelength of 532 nm (green light). This process is called second harmonic generation (SHG).

A typical SHG experiment is shown in Fig. 1. The source of light is a Nd:YAG pulsed laser. The polarized beam is guided through a system of mirrors to a poled chromophoric film. Next, the second

harmonic signal of wavelength 532 nm generated by the polymer film passes through an analyzer, and is detected.

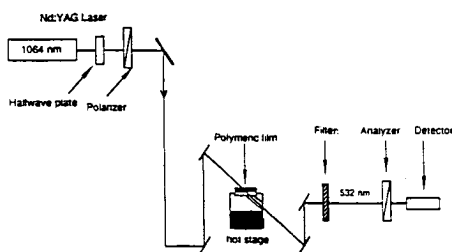


Fig. 1 A typical SHG configuration.

INSTABILITY OF THE NON-LINEAR OPTICAL PROPERTIES

The stability of aligned chromophores of NLOPs is of utmost importance for their long-term optical properties. Physical stability and chemical stability are relevant here. In this overview the physical instability is discussed. Generally, polymers with high T_g show good orientational stability of chromophores. Covalent bonding of the dopant is advantageous, here chromophores can be attached as sidechains to the polymer backbone, or polymers can incorporate the chromophores with their dipole moments head-to-tail in the mainchain. Also, cross-linking has been used to improve stability. However, the actual mechanisms responsible for the relaxation of order in NLOPs (de-alignment of chromophores) are subject to much debate.

Hampsch et al.^{6, 7, 8} carried out studies of SHG instability for PMMA and PS with different chromophores. The authors indicate two distinct regions of the time dependent SHG signal. Also, the authors show that the decay is more rapid in PMMA, implying that the higher structure mobility, or more sub- T_g motion, or β relaxation which is higher in PMMA, plays an important role. Further, it was shown that the relaxation depends on the size of

the dopant molecule, and faster relaxation was observed with smaller sizes of the chromophore molecules. These observations suggest an influence of the excess free volume and thermal motion on the alignment of chromophores. In particular, the increased restriction of dopant rotation with time, due to the decreasing number of larger regions of local free volume, or decreasing mobility, is discussed by the authors.

Studies have been carried out on guest-host systems among others by Hampsch et al.^{8, 9}. Guest-host systems are less stable than systems in which the chromophores are covalently attached to the polymer, e.g. a mainchain system. Here substantial improvement in the stability of non-linear optical susceptibilities was achieved in a random copolymer of methyl methacrylate and a 4-dicyanovinyl-4'-(dialkylamino)azobenzene-substituted methacrylate (DCV-MMA) compared to a guest-host analogous dicyanovinylazo dye dissolved in poly(methyl methacrylate) (DCV/PMMA) system (Singer et al.¹⁰). Also, studies have been carried out to show that the degree of freedom for rotational diffusion of the chromophore influences the stability. Then it comes as no surprise that 2-D randomization is slower than 3-D randomization.

VIEWS ON PHYSICAL AGEING

There are different views presented in non-linear optical polymers literature about the mechanism of optical relaxations. To start with, the poling which is carried out at a temperature just above T_g is followed by rapid cooling to a temperature below T_g , in order to freeze in the alignment of the dipoles. It is well known that such quenching triggers off physical ageing, and therefore physical ageing must be considered an integral part of dipole relaxation (Lindsay¹¹). Moreover, it can be expected that physical ageing will hinder dipole relaxation due to decreasing

mobility on ageing. In other words, immediately after cooling the system is in non-equilibrium and next evolves towards (apparent) equilibrium. It has been shown that the cooling rate influences the behaviour significantly. Here, the faster the film is cooled, and the larger the amount of trapped free volume, the more unstable are the optical properties, this in agreement with physical ageing principles. Also, if NLOP films are aged in the applied electric field below the T_g for some time before cooling them further to the use temperature, then physical ageing is greatly retarded because of the reduced free volume. Some further evidence supporting a direct relation between physical ageing and the instability mechanisms of non-linear optical behaviour comes from comparing timescales to equilibration. It is well known that enthalpy relaxation is used to characterize the evolution of physical ageing, enthalpy being considered sensitive to all conformational relaxations. Dhinojwala et al.¹² report that in poly(isobutyl methacrylate) (PIBMA) and poly(ethyl methacrylate) (PEMA) doped with 2 wt. % DRI there is reasonable agreement between the timescale to equilibration for enthalpy and that of $\chi^{(2)}$. Also, by monitoring the decay of $\chi^{(2)}$ at higher temperatures, Jacobson et al.¹³ found that the relaxation of a poled methacrylate copolymer containing stilbene chromophore below T_g is closely related to the free volume content.

Recently, a comparative study of SHG instability and physical ageing has been undertaken by the authors.

CONCLUSIONS

Non-linear optical (NLO) properties and second harmonic generation (SHG) are areas of intense applied research. Non-linear optical polymers offer attractive possibilities for constructing photonic

devices. The mechanisms of NLOPs time instability require better understanding.

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REFERENCES

1. Meredith GR, VanDusen JG, and Williams DJ, (1982) *Macromolecules*, 15, 1385
2. Singer KD, Sohn JE, and Lalama SJ, (1986) *Appl. Phys. Lett.*, 49 (5), 248
3. Prasad PN and Williams DJ, (1991) *Introduction to Nonlinear Optical effects in Molecules Polymers*, John Wiley & Sons
4. Lindsay GA, (1995) In: *Polymers for Second-Order Nonlinear Optics* (eds: Lindsay GA and Singer KD), ACS Symposium Series 601
5. Levine BF and Bethea CG, (1975) *J. Chem. Phys.*, 63, 2666
6. Hampsch HL, Yang J, Wong GK, and Torkelson JM, (1988) *Macromolecules*, 21, 528
7. Hampsch HL, Yang J, Wong GK, Torkelson JM, (1989) *Polym. Communic.*, 30, 40
8. Hampsch HL, Yang J, Wong GK, and Torkelson JM, (1990) *Macromolecules*, 23, 3648
9. Hampsch HL, Torkelson JM, Bethke SJ, Grubb SG, (1990) *J. Appl. Phys.*, 67, 1037
10. Singer KD, Kuzyk MG, Holland WR, Sohn JE, and Lalama SJ, (1988) *Appl. Phys. Lett.* 53(19), 1800
11. Lindsay GA, (1993) *Trends in Polym. Sci.*, Vol.1, No. 5, 138
12. Dhinojwala A, Wong GK, and Torkelson JM, (1993) *Macromolecules*, 26, 5943
13. Jacobson S, Landi P, Findakly T, Stamatoff J, and Yoon H, (1994) *J. Appl. Polym. Sci.*, 53, 649