Study of Nonlinear Polymers Operating Parameters for Laser Pulse Chirping

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Abstract. In this study, the optimization of the operating parameters of nonlinear polymers for self-phase modulation is reported. The effect of delocalization length and adding function groups (donor-acceptor groups) on the nonlinear refractive index are investigated. Based on nonlinear Schrödinger equation, the pulse chirping factor, for a set of nonlinear polymers, at different operating conditions, is studied. The comparison between laser pulse chirping factor resulting from saturated and conjugated polymers is presented. It is noticed that the chirping factor that evolved from conjugated polymers is greater than its equivalent in saturated polymers. Moreover, laser pulse chirping factor is increased with increasing of delocalization length. Therefore, this study may initiate the synthesis of new nonlinear polymers in order to produce appropriate nonlinear optical properties for high broadening materials in laser compression systems.

1. Introduction

Synthesized third-order nonlinear optical materials (NLO) are widely used in various fields such as optical communications, optical switching, optical data processing, optical limiting and photodynamic therapy [1–3]. The organic materials are featured by their synthetic flexibility of altering the optical properties at molecular level; as well as, the fast response time and high optical nonlinearity. It is generally known that the process of electron transfer is usually considered as the significant factor for enhanced NLO response [4]. This enhancement is usually accompanied by a larger cross section, which increases with increasing the donor/acceptor strength and conjugation length [5,6].

One of the aspects of the third order nonlinearity effects is the Self-Phase Modulation (SPM), which leads to spectral broadening of optical pulses [7]. Self-phase modulation is the common nonlinear process of the spectral broadening induced by the interaction between the material and laser beam. This interaction results in phase modulation of the beam along the material. This phase modulation in time leads; in turn, to the spectral broadening of the laser pulse due to the induced intensity-dependent refractive index change of the material. The change in refractive index can be expressed as:

\[ n_2 = n_0 + \gamma I \] (1)
where \( n_{ro} \) is the linear refractive index, \( \gamma \) is nonlinear index intensity coefficient and \( I \) is the peak pulse intensity. The propagated laser pulses in nonlinear polymer experiencing SPM exhibit broadening. This broadened pulse can be compressed by introducing a dispersive delay line such as grating pair or chirped mirror [8]. Therefore, the aim of the present study is to study some of the polymer parameters yielding to a higher chirping factor for an optimum compression factor.

2. Polymers Structure

Nonlinear response of bound electrons to an applied optical field results into non-resonant electronic nonlinearities, which are extremely fast, since they involve only virtual processes [9]. The set of energy Eigenstates of the individual atoms is the natural basis for describing the optical properties of a collection of free atoms. However, in the case of a crystal, the outer electrons are localized within the bonds that confine the atoms to their lattice sites. Therefore, linear and higher-order polarizabilities can be ascribed to each bond in a molecule or crystalline solid [9]. In this case, the polarizability of one bond is reasonably unaffected by the nature of nearby bonds. Thus, the susceptibility of a complex system can be predicted by summation of the responses of various bonds present in the material.

A polymer has large number of bonds and it is said to be saturated if it contains only single (\( \sigma \)) bond. Some of the saturated polymers contain other bonds with different atoms such as chlorine in Polyvinyle chloride (PVC) and oxygen in Polymethyl Methacrylate (PMMA). Moreover, the structure of the polymer itself affects the third order susceptibility. PVC has a lower nonlinear refractive index than that of PMMA [8, 10] as the latter one has double bonds with oxygen atoms. This is attributed to the presence of \( \pi \) - bond in PMMA. As shown in figure 1, where PMMA monomer has a larger number of chemical bonds than PVC and it has a double bond conducting to a higher nonlinear response of the former than that of the latter, since it carries delocalized electrons.

![Chemical structure of PMMA and PVC](image)

A polymer is said to be conjugated if it contains a sequence of double (\( \pi \)) bond and single (\( \sigma \)) bond as shown in figure 2.a [8]. \( \sigma \) electrons (that is, electrons contained in a \( \sigma \) bond) tend to be localized in space as shown in figure 2.b. In contrast, \( \pi \) electrons tend to be delocalized as shown in figure 2.c. Therefore, \( \pi \) electrons tend to exchange their positions as shown in figure 2.d. In this case, the actual form of the polymer chain is thus a superposition of the two configurations as shown in part (d) of the figure. This perspective is reinforced by noting that p orbitals extend both to the left and to the right of each carbon atom. As a result of this configuration, \( \pi \) electrons tend to be reactively free having a high response to an external applied field and can be modeled as moving in one dimensional square well potential with length equals the polymer chain length. This configuration leads to increase of the nonlinear response with increasing of delocalization length.
Figure 2: (a) Two common representations of a conjugated chainlike polymer. (b) Standard representation of a single bond (left) and a schematic representation of the electron charge distribution of the single bond (right). (c) Standard representation of a double bond (left) and a schematic representation of the electron charge distribution of the double bond (right). (d) Two representations of the same polymer chain with the locations of the single and double bonds interchanged, suggesting the arbitrariness of which bond is called the single bond and which is called the double bond in an actual polymer chain. (e) Representation of the charge distribution of a conjugated chainlike polymer. [9]

The strong delocalization of electrons or the presence of any hetero atoms in the organic backbone determines a very high molecular polarizability and thus a remarkable third order optical nonlinearity. In general, the large hyper polarizabilities are the result of an optimum combination of various factors, such as delocalization length and donor-acceptor groups [6, 11]. The effects of both of these two parameters on the laser pulse chirping are studied in Pyrene-Aldehyde derivatives with chemical structure as shown in figure 3 [11]. The higher nonlinear response due to the presence of donor group (Pyrene core) and acceptor group (aldehyde groups) can be explained by the existence of charge transfer between these groups.

Figure 3: Molecular structures of asymmetry pyrene-aldehyde derivatives PA-1 and PA-2. [11]
3. Numerical Simulation of Laser Pulse Chirping

The Nonlinear Schrödinger Equation (NLSE), that describes the propagation of a laser pulse in nonlinear materials, is written in the form of [7]

\[
i \frac{\partial U}{\partial z} = \frac{\beta_2}{2L_D} \frac{\partial^2 U}{\partial t^2} - \frac{\exp(-\alpha z)}{L_{NL}} |U|^2 U
\]

where \( U \) is the normalized amplitude of the laser pulse, \( L_D \) is the dispersion length \( (L_D = t_0^2/|\beta_2|) \), \( \beta_2 \) is the value of group velocity dispersion parameter, \( \alpha \) accounts for material losses, \( L_{NL} \) is the nonlinear length defined as \( L_{NL} = \frac{c}{\omega_0 \gamma I} \) where \( c \) is the speed of light and \( \omega_0 \) is the angular frequency. The first term represents the effect of the Group Velocity Dispersion (GVD), while the second term acts for the Self-Phase Modulation (SPM).

According to the polymer thickness with respect to the dispersion and nonlinear lengths, four propagation regimes can be classified as follows indicating the dominance of one or more of the nonlinear effects [7,9]. When polymer thin film thickness \( L \) is much smaller than both of the dispersion length and nonlinear length, the polymer acts as a transparent material without any dispersive or nonlinear effects. On the other hand, when the polymer thickness \( L \) is comparable to both of the dispersion length and nonlinear length, the combined effect of group velocity dispersion and self-phase modulation takes place. While in case of polymer thickness \( L \ll L_{NL} \) and \( L \) is comparable or longer than \( L_D \), the nonlinear term in Eq.(2) is negligible compared to the dispersion term. Finally, in case of polymer thickness \( L \ll L_D \) and \( L \) is comparable or longer than \( L_{NL} \), the dispersion term in Eq.(2) is negligible compared to the nonlinear term [7].

Hence, by operating under the appropriate pulse duration and peak power, whereas, the group velocity dispersion can be neglected and the self-phase modulation is the counterpart of the broadening of the laser pulse, the NLSE can be simplified into the following form

\[
\frac{\partial U}{\partial z} = i \frac{e^{-\alpha z}}{L_{NL}} |U|^2 U
\]

Equation (3) can be solved by using \( U = V \exp(i\varphi_{NL}) \) where the phase variation can be expressed as

\[
\frac{\partial \varphi_{NL}}{\partial z} = \frac{e^{-\alpha z}}{L_{NL}} V^2
\]

The phase equation can be integrated analytically to obtain the general solution

\[
U(L, T) = U(0, T) \exp[i\varphi_{NL}(L, T)]
\]

where, \( T \) is the time normalized to the pulse duration and \( U(0, T) \) is the normalized field amplitude at \( z = 0 \), and

\[
\varphi_{NL}(L, T) = |U(0, T)|^2 \left( \frac{L_{eff}}{L_{NL}} \right)
\]

where, \( L_{eff} \) is the effective length including the material losses \( (L_{eff} = (1 - \exp(-\alpha L))/\alpha) \). Equation (5) shows that SPM gives rise to an intensity-dependent phase shift, while the pulse shape remains unaffected as shown in figure 4.
The intensity of a Gaussian pulse with and without chirping in the temporal domain (curves are overlapped).

The nonlinear phase shift $\varphi_{NL}$ in Eq. (6) increases with material length and for negligible losses $L_{eff} \sim L$. The maximum phase shift $\varphi_{max}$ occurs at the pulse center located at $T = 0$. Let $U$ is normalized such that $|U(0,0)| = 1$ and the maximum nonlinear phase shift is given by

$$\varphi_{max} = \frac{L_{eff}}{L_{NL}} \quad (7)$$

For a given laser pulse, the spectral broadening can be calculated by

$$\Delta \omega = \omega_0 \left(1 + \frac{4}{3\sqrt{3}} \varphi_{max}^2\right)^{1/2} \quad (8)$$

Therefore, the time-bandwidth product of the chirped pulse will increase by the factor $\sqrt{1 + \alpha^2}$, where $\alpha$ is the chirping factor, as [12].

$$\Delta t \Delta \omega = \frac{3\omega_0^2}{\pi} \sqrt{1 + \alpha^2} \quad (9)$$

4. Results and Discussion

The chirping factor is calculated for the four polymer structures of 1 cm thickness at an operating wavelength at 1064 nm. The pulse duration is considered 100 fs, while the input peak intensity varies from 0.1GW/cm$^2$ to 50 GW/cm$^2$ (according to each polymer performance).

Given that the nonlinear refractive indices of PMMA and PVC are $2.7 \times 10^{-14}$ cm$^2$/W [10] and $3.6 \times 10^{-16}$ cm$^2$/W [8], for an input pulse intensity of 50 GW/cm$^2$, the laser pulse chirping obtained from propagation through PMMA is higher than that of PVC as illustrated in figure 5. The corresponding nonlinear lengths are 125 $\mu$m and 9.14 mm, respectively. The chirped electric field amplitudes of the laser pulse in PMMA and PVC are illustrated in comparison to the originally unchirped pulse shown in figure 6.
Figure (5): Laser pulse chirping of a laser pulse 100fs and 50 GW/cm² through propagation in 1 cm of PVC and PMMA

Figure 6: Electric field amplitude of a) unchirped pulse. b) chirped pulse using PVC. c) chirped pulse using PMMA.

The effect of both longer delocalization length and the presence of donor-acceptor groups leads to high third order nonlinear response of Pyrene – Aldehyde derivation as the nonlinear refractive indices of PA1 and PA2 are $2.38 \times 10^{-14}$ cm²/W and $2.15 \times 10^{-14}$ cm²/W, respectively [11]. The laser pulse chirping is larger than that of saturated polymer, such as PMMA as illustrated in figure 7. In this figure, the chirping of pulse at an intensity of 0.1 GW/cm² has larger values for PTS than that of PMMA since the nonlinear length is 0.5μm and 6 cm, respectively. However, it is comparable to the value of laser pulse chirping of PMMA obtained at 50 GW/cm² shown in figure (5). The amplitude of the electric field of the chirped pulse is illustrated in figure 8 as well and it indicated larger chirping factor values after propagation through PTS than that of PMMA at 0.1GW/cm² and that of PMMA at 50GW/cm² (figure 6.c).
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Figure (7): Laser pulse chirping for pulse duration of 100 fs and input intensity of 0.1 GW/cm² through propagation in 1 cm of PTS and PMMA

![Laser pulse chirping](image1.png)

Figure 8: Electric field amplitude of a) chirped pulse using PMMA. b) chirped pulse using PTS.

The effect of both longer delocalization length and the presence of donor-acceptor groups leads to high third order nonlinear response of Pyrene – Aldehyde derivation as the nonlinear refractive indices of PA1 and PA2 are $2.38 \times 10^{-14}$ cm$^2$/W and $2.15 \times 10^{-14}$ cm$^2$/W, respectively [11]. The chirping factor is calculated for an input intensity of 1GW/cm$^2$ as for lower intensity, there was no clear chirping effect. The higher nonlinearity of PA1 results into a higher laser pulse chirping than that of PA2. Figure 9(a) shows the chirping factor of Pyrene derivation as compared to PVC, which is a saturated polymer. The corresponding nonlinear lengths of PA1, PA2 and PVC at 1GW/cm$^2$ are 0.7 mm, 0.8 mm and 46 cm, respectively. When using a high input intensity of 50 GW/cm$^2$, PA1 and PA2 show a comparable performance to PMMA, while it is still much higher than PVC. The corresponding nonlinear lengths of PA1 and PA2 at 50GW/cm$^2$ are 0.14 μm and 0.16 μm, respectively. PTS is not included in this figure as it performs an extremely high chirping factor at high input intensity ($L_{NL}=0.1 \mu m$ at 50GW/cm$^2$). The electric field amplitude at input intensity 50GW/cm$^2$ of the chirped pulse is illustrated in figure 10 and it indicated that there are comparable chirping factor values after propagation through PA1 and PA2 with respect to PMMA.

![Chirping factor vs propagation length](image2.png)

Figure 9: Variation of laser pulse chirping with propagation length through a) PA1 and PA2 and PVC at 1GW/cm² b) PVC, PMMA, PA1 and PA2 at 50 GW/cm².
By comparing all the above results, it can be observed that the chirping factor of different polymers varies with the polymer structure; saturated (PVC), saturated with side double bond (PMMA), conjugated with single and double bonds sequence (PTS) and conjugated with donor-acceptor groups (PA1 and PA2). The PVC showed its higher chirping factor (=2) only at high input pulse intensity (fig. 5), while the PMMA showed much higher chirping factor (=20). This can be referred to that PMMA contains larger number of bonds and it has a carbonyl group in its monomer, which leads to a high nonlinear response. However, the PMMA can as well exhibit chirping (=2) for much lower input pulse intensity (fig. 7). On the other hand, at this low input pulse intensity, PTS prohibited a higher chirping factor up to 25 as compared to PMMA saturated polymers. This can be explained as the π electrons tend to be delocalized. Because π electrons are easily delocalized, they tend to be less tightly bound and can respond more freely to an applied optical field. Thus, they tend to produce larger linear and nonlinear optical responses.

Increasing of the delocalization length in the presence of the donor-acceptor groups in Pyrene polymer increases the attained chirping factor input intensity of 1 GW/cm² in comparison with that of saturated polymers, such as PVC. The minute difference between PA1 and PA2 polymers is attributed to the presence of Carbonyl group, which was a strong electron withdrawing group. The performance of Pyrene with the other polymers was compared to other polymers at high pulse intensity and it showed a comparable chirping factor with respect to PMMA.

Finally, it can be conducted that conjugated polymers with single and double bond sequence can perform a high chirping factor at low input pulse intensity due to self-phase modulation.

5. Conclusion

According to the present study, it can be concluded that high laser pulse chirping factor can be achieved by using saturated polymers with side double bonds. On the other hand, conjugated polymers introduce a higher laser chirping factor than that of saturated polymer even with lower pulse intensities due to the presence of sequence of double and single bonds. Therefore, laser chirping pulse increases with the increasing of delocalization length in conjugated polymers. The presence of donor acceptor groups in the polymer enhances the obtained laser pulse chirping values. Finally, considering these parameters, nonlinear polymers that exhibit a higher laser pulse broadening can be obtained for laser pulse compression systems.
6. References

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