Polymeric materials for non-linear optics and photonics

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The third-order non-linear optical effect providing mechanisms for light control by light is expected to play a major role in the future technology of photonics. Conjugated polymers have emerged as an important class of third-order non-linear optical materials. This paper reviews basic concepts of non-linear optical effects in polymeric materials. Then results from experimental measurements of third-order non-linear optical processes in some representative polymeric structures are presented. These results have been obtained using the state-of-the-art femtosecond time-resolved degenerate four-wave mixing, optical Kerr gate and transient absorption techniques. Experimental studies of optical non-linearities in polymeric waveguides are also described. The paper concludes with a discussion of relevant issues and opportunities in this field for polymer scientists.

(Keywords: non-linear optics; photonics)

INTRODUCTION

One emerging technology that has captured the imaginations of scientists and engineers worldwide is non-linear optics and photonics. Photonics has been labelled by many as the technology for the 21st century. It is the technology in which photons, instead of electrons, are used to acquire, store, process and transmit information. Photonics technology provides high-density optical data storage, optical processing of information, image analysis and sensor protection against laser threats, i.e. the protection when the incident optical power exceeds the danger level. Some of the necessary operational functions for photonics technology are frequency conversion, light modulation and optical switching. To perform these functions one needs non-linear optics. The two important non-linear optical effects are second-order and third-order effects. The second-order effect is characterized by the non-linear susceptibility $\chi^{(2)}$, which provides frequency doubling. The second-order non-linear optical interaction also generates an electro-optic effect, which describes the change of refractive index of the medium by electric field. The third-order non-linear optical interactions characterized by the non-linear susceptibility $\chi^{(3)}$ generate third-harmonic 3ω with an input optical frequency of ω. Furthermore, it also makes the refractive index of the medium dependent on the intensity. This intensity dependence of refractive index provides a convenient mechanism for light control by light. That is, a strong beam of light can be used to affect the propagation of an optical signal by changing the refractive index of the medium.

One can design photonic circuits such as integrated optical chips, which are equivalent to integrated electronic circuits. They will utilize guided-wave optics. Photons of different wavelengths can be conducted through different optical channels, which are the photonics analogue of wires in electronics. These optical channels can be fibres or channel waveguides embedded in a film strip. Light can be switched from one channel to another at certain junction points. For optical switching at junctions, one needs to use non-linear optical effects.

Polymers, along with other molecular materials, are being recognized as an important class of non-linear optical materials[1,2]. Because of their unique structural features, polymers exhibit extremely fast non-linear optical response, even in the region of their optical transparency. They are also the media in which all, and not just some, non-linear optical processes can be observed. Polymeric structures offer tremendous flexibility at both the molecular and bulk levels. With certain modifications of the side-chain structure, we have also been able to prepare ultra-thin monolayer and multilayer Langmuir–Blodgett films in which the conformation and optical properties of the polymer can be varied by the control of fabrication conditions[3,4].

Actually, polymers are strong candidates for multifunctional materials, which will be materials for future use, as they would possess many functionalities needed for one or more than one application. The same polymeric system can be optically non-linear, electrically conductive and photoconductive, as well as having other functionalities incorporated by side-chain modification or composite and blend formation.

In our Photonics Research Laboratory, we have developed a very comprehensive research programme in the area of non-linear optical effects in molecular and polymeric materials. This programme covers microscopic theory of optical non-linearity, design and synthesis of novel structures, materials processing for guided waves, measurements of optical non-linearities and study of device processes. In this paper we focus only on third-order non-linear optical processes in polymeric materials.

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THEORETICAL BACKGROUND

Optical response of a material is generally described in the approximation of electric-dipole interaction with the radiation[5]. In this model, the oscillating electric field of radiation induces a polarization in the medium. When a material is subjected to a strong optical pulse from a laser, the electric field is intense and the induced polarization shows a non-linear behaviour, which can be expessed by the following power series expansion[2,5]:

$$P=\chi^{(1)}\cdot E\times\chi^{(2)}:EE+\chi^{(3)}\vdots EEE+\ldots=\chi_{\mathrm{eff}}\cdot E \qquad (1)$$

In equation (1), $\chi^{(1)}$ is the linear susceptibility, which is generally adequate to describe the optical response in the case of a weak optical field. The terms $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order non-linear optical susceptibilities, which describe the non-linear response of the medium. At optical frequencies[5]:

$$n^2(\omega)=\varepsilon(\omega)=1+4\pi\chi(\omega) \qquad (2)$$

where $n(\omega)$ is the refractive index and $\varepsilon(\omega)$ is the dielectric constant at frequency ω. For a plane wave, we have the wavevector $k=n\omega/c$ and the phase velocity $v=c/n$. In a non-linear medium, $\chi(\omega)=\chi_{\mathrm{eff}}(\omega)$ of equation (1) is dependent on E; therefore, n, k and v are all dependent on E.

The two important consequences of the third-order optical non-linearities represented by $\chi^{(3)}$ are third-harmonic generation and intensity dependence of the refractive index. Third-harmonic generation (THG) describes the process in which an incident photon field of frequency ω generates, through non-linear polarization in the medium, a coherent optical field at 3ω. Through $\chi^{(3)}$ interaction, the refractive index of the non-linear medium is given as $n=n_0+n_2I$, where n_0 is the linear refractive index, n_2 describes the intensity dependence of refractive index and I is the instantaneous intensity of the laser pulse.

At the microscopic level, the non-linearity of a molecular structure is described by the electric-dipole interaction of the radiation field with the molecules. The resulting induced dipole moment and the Stark energy are given as[1,2]:

$$\mu_{\mathrm{ind}}=\alpha\cdot E+\beta:EE+\gamma\vdots EEE+\ldots \qquad (3)$$

$$\varepsilon_{\mathrm{Stark}}=-E\cdot\mu_0-\frac{1}{2}E\cdot\alpha\cdot E-\frac{1}{3}E\cdot\beta:EE-\frac{1}{4}E\cdot\gamma\vdots EEE-\ldots \qquad (4)$$

In the above equation α is the linear polarizability. The terms β and γ, called first and second hyperpolarizabilities, describe the molecular non-linear optical interactions and are microscopic analogues of $\chi^{(2)}$ and $\chi^{(3)}$.

In the weak-coupling limit, as is the case for most molecular systems, each molecule can be treated as an independent source of non-linear optical effect. Then the macroscopic susceptibilities $\chi^{(n)}$ are derived from the microscopic non-linearities β and γ by simple orientationally averaged site sums using appropriate local field correction factors, which relate the applied field to the local field at the molecular site. Therefore[1,2]:

$$\chi^{(3)}(-\omega_4;\omega_1,\omega_2,\omega_3)=\mathrm{F}(\omega_1)\mathrm{F}(\omega_2)\mathrm{F}(\omega_3)\mathrm{F}(\omega_4)\sum_n\langle\gamma^n(\theta,\phi)\rangle \qquad (5)$$

The symbols used for $\chi^{(3)}$ indicate that three input waves ω_1, ω_2 and ω_3 generate an output wave ω_4. For THG, $\omega_1=\omega_2=\omega_3=\omega_4$ and $\omega_4=3\omega$. The terms $F(\omega_i)$ are the local field corrections for a wave of frequency ω_i. Generally, one utilizes the Lorentz approximation for the local field, in which case[2,5]:

$$F(\omega_i)=[n_0^2(\omega_i)+2]/3 \qquad (6)$$

In equation (6), $n_0(\omega_i)$ is the intensity-independent refractive index at frequency ω_i. The sum in equation (5) is over all the sites (n); the angle bracket $\langle\ \rangle$ represents an orientational averaging over angles θ and ϕ. Unlike for the second-order effect, this orientational average for the third-order coefficient is non-zero even for an isotropic medium because it is a fourth-rank tensor. Therefore, the first step to enhance third-order optical non-linearities in organic bulk systems is to use molecular structures with large γ. For this reason, a sound theoretical understanding of microscopic non-linearities is of paramount importance.

STRUCTURAL REQUIREMENTS FOR THIRD-ORDER OPTICAL NON-LINEARITY

Although the understanding of structure–property relationships for third-order non-linear effects is highly limited, all microscopic theoretical models predict a large non-resonant third-order optical non-linearity associated with delocalized π-electron systems[1,2]. Conjugated polymers with alternate single and multiple bonds in their backbone structures provide a molecular frame for extensive conjugation and have emerged as the most widely studied group of $\chi^{(3)}$ organic materials. Examples of conjugated polymers are polydiacetylenes, poly(p-phenylene vinylene) and polythiophene.

The optical non-linearity is strongly dependent on the extent of π-electron delocalization from one repeat unit to another in the polymer (or oligomer) structure. This effective delocalization is not always equally manifested but depends on the details of repeat-unit electronic structure and order. For example, in a sequentially built structure, the π-electron delocalization effect on γ is found to be more effective for the thiophene oligomers than it is for the benzene oligomers[6,7].

The largest component of the γ tensor is in the conjugation direction. Therefore, even though no particular bulk symmetry is required for a non-zero $\chi^{(3)}$, a medium in which all conjugated polymeric chains align in the same direction will have a larger $\chi^{(3)}$ value along the chain direction relative to that in an amorphous or disordered form of the same polymer. Studies of $\chi^{(3)}$ in ordered or stretch-oriented polymers as discussed below confirm this prediction. Finally, the polymeric chains should pack as closely as possible in order to maximize the hyperpolarizability density and hence $\chi^{(3)}$.

Extensive π-conjugation is also often associated with enhanced conductivity in organic systems[8]. Polyacetylene and polythiophene, which in the doped state exhibit very high electrical conductivity, also exhibit relatively large third-order non-linear optical effects in the undoped (non-conducting) state. However, it should be remembered that conductivity is a bulk property that is heavily influenced by intrachain as well as interchain carrier transports. In contrast, the origin of third-order non-linearity in conjugated polymers is primarily microscopic, determined by the structure of the polymer chain. Therefore, a conjugated polymer may be a very good $\chi^{(3)}$ material but not necessarily a good conductor.

Polydiacetylene is a good example; it exhibits a large non-resonant $\chi^{(3)}$ value but is a wide-gap semiconductor.

EXPERIMENTAL MEASUREMENTS

For experimental investigation of third-order optical non-linearities we use degenerate four-wave mixing, optical Kerr gate and transient absorption. The transient absorption studies are useful for determining if one-photon or two-photon absorption in a material contributes to its non-linear time response. Degenerate four-wave mixing (DFWM) provides a convenient method for measuring $\chi^{(3)}$ both in solution and in solid (film) forms and obtaining information on the time response of the optical non-linearity.

In this method two beams of the same frequency interfere in the non-linear medium, setting up an intensity modulation pattern. Since the refractive index of a medium with third-order non-linearity is intensity-dependent, the intensity modulation results in a spatial variation of the refractive index, which forms a grating. A third beam, the probe beam, also of the same frequency, is Bragg diffracted from this grating to produce the signal (the diffracted beam). The intensity of the signal, when the probe pulse beam is coincident in time with the grating-forming pulses, is proportional to the square of $\chi^{(3)}$. The time decay of the signal as a function of the time delay of the probe pulse with respect to the grating-forming pulses provides direct information on the response time of the non-linearity (the decay of the intensity-dependent refractive index modulation). In our laboratory, we use two laser systems for DFWM. One laser system provides 400 fs pulses of $\sim$0.5 mJ energy per pulse at a repetition rate of 30 Hz. Another laser system involving the state-of-the-art amplified colliding pulse mode-locked system provides 60 fs pulses of energy 20 μJ per pulse at a repetition rate of 8 kHz.

The Kerr gate and the transient absorption studies involve two-beam pump–probe experiments. In a transient absorption experiment, a strong pump beam is incident on a sample; the non-linear optical response of the medium is monitored by the change in the transmission characteristics of a weak probe beam. The optical Kerr gate experiment differs from the above experiment in that the polarization state of the probe beam is analysed[5,9]. In a homodyne version of the Kerr gate experiment, a probe beam of a given polarization interacts with the sample pumped by a strong beam[9]. As a result, a perpendicular polarization component in the probe beam is created through optically induced birefringence due to the pump beam. This component is then detected after passing the probe beam through a crossed analyser. The optical Kerr gate and transient absorption studies require an extremely low pulse-to-pulse fluctuation. For this reason, the amplified colliding pulse mode-locked system producing 60 fs pulses is found to be more suitable for these studies.

For applications in photonics, the polymeric systems will most likely be used in the form of optical waveguides, which confine the propagation of the light beam in certain directions. For this reason, we have also investigated the non-linear optical responses of polymeric materials in the form of optical waveguides. The laser system generally used for this work involves a mode-locked and Q-switched Nd:YAG laser. At 1·06 μm, single pulses are selected from the mode-locked train to produce pulses of width $\sim$100 ps at a repetition rate of 500 Hz. To get into the visible range, the entire mode-locked and Q-switched pulse train is frequency doubled and used to pump a dye laser, which is cavity dumped. The resulting dye pulses are $\sim$60 ps.

We have investigated the non-linear response of many conjugated polymers unoriented as well as stretch-oriented. The third-order non-linear optical susceptibility was investigated for a 6:1 stretch-oriented uniaxial film of poly(2,5-dimethoxy-*p*-phenylene vinylene) using femtosecond degenerate four-wave mixing at 602 nm[10]. A relatively large $\chi^{(3)}$ value with a subpicosecond response was observed. A large anisotropy in the $\chi^{(3)}$ value was found, the largest component of $\chi^{(3)}$ ($(4\pm1)\times10^{-9}$ esu) being along the draw direction. This is in agreement with theory, which predicts the largest component of $\chi^{(3)}$ along the polymer chain which will preferentially align along the draw direction. A simple model that involves transformation of the fourth-rank tensor $\chi^{(3)}$ from a film-based coordinate to the laboratory-based coordinate can explain the polar plot of $\chi^{(3)}$ obtained by rotating the film with respect to the polarization vectors of the beams[11,12]. For the measurements reported here using DFWM, all the electric field vectors were vertically polarized, giving rise to measurements of the $\chi^{(3)}_{1111}$ tensor components in the laboratory frame.

Electronically resonant third-order optical non-linearities in several photoresponsive polymers were studied by picosecond and femtosecond degenerate four-wave mixing as well as by femtosecond Kerr gate and transient absorption. Specific systems investigated by the femtosecond DFWM, Kerr gate and transient absorption techniques are poly(*p*-phenylene vinylene), polythiophene, poly(4-BCMU) and poly(3-BCMU). In the former, we have observed the importance of two-photon absorption at high intensities. For polythiophene, the relative role of phase-space filling of the initially photogenerated excitons and that of subsequently formed polarons by conformational deformation have been investigated[13,14]. Our result shows that for poly(*p*-phenylene vinylene) in the polymeric: sol–gel processed composite (discussed below) two-photon absorption plays an enhanced role at high intensities. In addition to the instantaneous electronic response, the DFWM signal at high intensities (*Figure 1*) shows a long-lived component due to population gratings formed by two-photon excited species. The transient absorption spectrum shows an enhanced absorption (reduced transmission), which is proportional to intensity, confirming the presence of two-photon absorption. The Kerr gate result shows that the intensity-dependent change in the real part of the refractive index of poly(*p*-phenylene vinylene) is purely electronic.

For polythiophene, the transient absorption reveals an increase of transmission at higher intensities due to the saturation of the one-photon absorption at 620 nm. The time response of the DFWM signal is in agreement with that of transient absorption, indicating that the initial non-linear optical response is derived from the saturation of the initially photogenerated excitons due to phase-space filling and not due to the subsequent conformational deformation producing polarons.

For waveguide non-linearities we have investigated non-linear optical processes in planar waveguides and

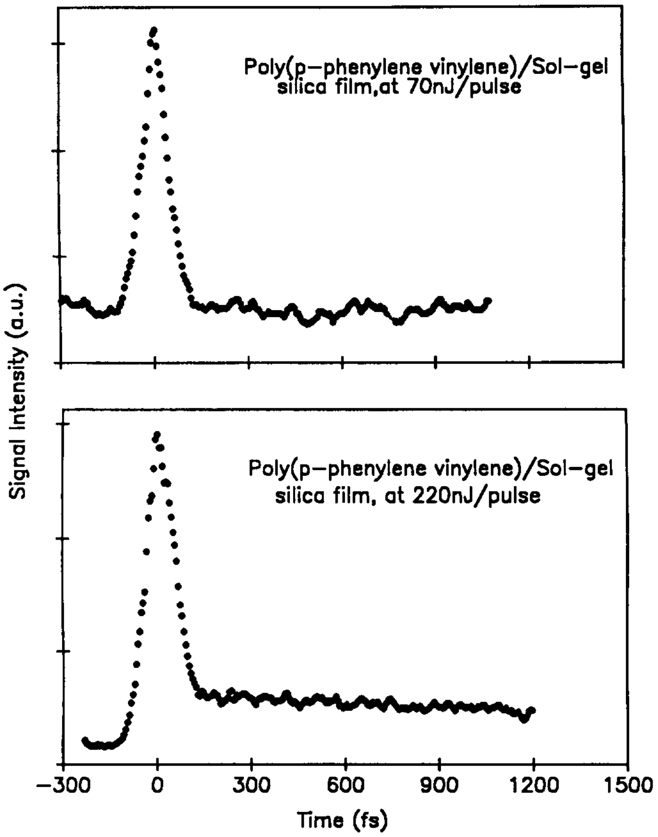


Figure 1 The time-resolved degenerate four-wave mixing signal in poly(*p*-phenylene vinylene): sol–gel processed silica composite at low (upper) and high (lower) optical intensities

fibres. Light can be coupled into a planar (slab) waveguide using a prism coupler or a grating coupler arrangement. Efficient coupling into the waveguide occurs at a specific incidence angle determined by, among other things, the refractive index of the guiding film. Since the refractive index of a third-order non-linear medium is dependent on the optical intensity, the coupling angle for a waveguide made of this non-linear material will be intensity-dependent. Alternatively, if the low-intensity coupling angle is retained, then because of inefficient coupling at higher intensity the optical output of the waveguide (power coupled into the wave guide) will level off as the input optical intensity is increased. This is a power limiter behaviour. In our studies of optical waveguides made of optically non-linear polymeric films we have used both prism and grating coupling arrangements. We reported the first clear demonstration[15] of intensity-dependent coupling angle due to electronic non-linearity in a non-linear polymer waveguide in which propagation distances over 5 cm were achieved with total attenuation of $\sim 1.2\ \mathrm{cm}^{-1}$. Intensity-dependent coupling angle and limiter action behaviour (useful for power limiter sensor protection devices) were observed in the poly(amic acid), poly(4-BCMU) and sol–gel:poly(*p*-phenylene vinylene) waveguides using the grating excitation technique. A non-linear grating coupler analysis identifies the subpicosecond and picosecond processes with electronic non-linearity, but the dominant effect in the nanosecond experiment is due to thermally induced refractive index change derived from weak absorptions. The sign of n_2 of electronic non-linearity was determined from this study to be positive.

RELEVANT ISSUES AND OPPORTUNITIES FOR POLYMER SCIENTISTS

Compared to materials for second-order non-linear devices, the third-order materials are even further away from being ready for device applications. The relevant issues for third-order materials are as follows.

Improvement in the currently achievable non-resonant $\chi^{(3)}$ values

Inorganic multiple-quantum-well semiconductors exhibit large resonant non-linearities[16]. It is doubtful that molecular and polymeric materials will offer any challenge to the inorganic semiconductors for resonant non-linearities. The attractive feature of molecular materials such as conjugated polymers is the high non-resonant $\chi^{(3)}$ they exhibit, which naturally has the fastest response time in femtoseconds. However, even the currently achievable highest non-resonant value ($<10^{-9}$ esu) is not large enough for any practical devices that would require only a small switching energy. Therefore, there is a need for enhancing optical non-linearity. For achieving this goal, a better understanding of the relation between molecular structure and microscopic non-linearity, γ, is required in order to identify structural units that enhance optical non-linearity. It will require improved theoretical modelling of optical non-linearity coupled with synthesis of sequentially built and systematically derivatized structures and measurements of their optical non-linearities. Clearly, theoretical modelling as well as synthetic approaches can play an important role on this issue.

Our theoretical understanding of third-order optical non-linearity at the microscopic level is really in its infancy. Currently no theoretical method exists that can be reliably used to predict, with reasonable computational time, molecular and polymeric structures with enhanced optical non-linearities. The two important theoretical approaches used are: the derivative method[1,17] and the sum-over-states method[18]. The derivative method is based on the power expansion of the dipole moment or energy given by equations (3) and (4). The third-order non-linear coefficient γ is, therefore, simply given by the fourth derivative of the energy or the third derivative of the induced dipole moment with respect to the applied field. The derivatives can be evaluated either by the finite field method (numerically) or analytically. In the simplest form, one uses only a time-independent Hamiltonian involving a static field. Consequently, one computes only static non-linearity at zero frequency, which is not the same as that measured at an optical frequency. At optical frequencies, the electronic transitions of a molecular structure may provide pre-resonance enhancements and large dispersion effects (frequency dependence) in the γ value. However, the advantage of the time-independent derivative method is that only the ground-state properties need to be computed. One can, therefore, use an *ab initio* approach for a reasonable size molecule to compute optical non-linearities. The calculations require a careful choice of the basis functions, such as inclusion of diffuse and polarization functions, which strongly influence the computed non-linearity[17]. The *ab initio* computations have a sound theoretical foundation but they cannot realistically be conducted for large molecules or heavy atoms. One has to rely on semiempirical methods, which can be used for large molecules and polymers. However, the parameters used in the various semiempirical methods are optimized for other properties and cannot be relied upon for calculations of optical non-linearity.

The sum-over-states method is based on the perturbation expansion of the Stark energy term in which non-linearities are introduced as a result of mixing with excited states. For example, the expression for $\gamma(-3\omega;\omega,\omega,\omega)$, which will be responsible for third-harmonic generation, is given as[18]:

$$\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)=\left(\frac{e^4}{4\hbar^3}\right)\sum_{m_1m_2m_3}\frac{\langle g|r_i|m_3\rangle\langle m_3|r_j|m_2\rangle\langle m_2|r_k|m_1\rangle\langle m_1|r_l|g\rangle}{(\omega_{m_1g}-\omega)(\omega_{m_2g}-2\omega)(\omega_{m_3g}-3\omega)} \qquad (7)$$

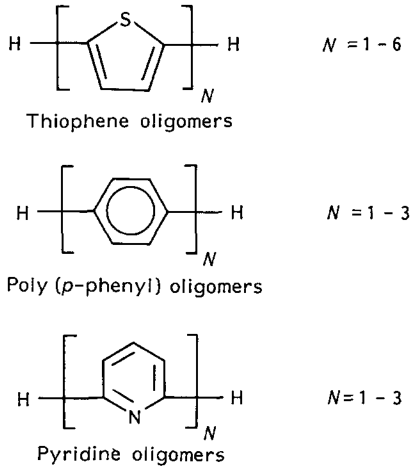
In this calculation one computes the energies and various expectation values of the dipole operator for various excited states. These terms are then summed to compute γ. If one does an exact calculation, in principle, both the derivative and the sum-over-states methods should yield the same result. However, such exact calculations are not possible. The sum-over-states method requires that not only the ground states but all excited-state properties be computed as well. For this reason one resorts to semiempirical calculations and often truncates the sum over all states to include only a few excited states.

Electron-correlation effects are expected to play an important role in determining optical non-linearities. Both the configuration-interaction and Moeller–Plesset perturbation correction approaches have been used to incorporate electron-correlation effects[19,20].

Although both the *ab initio* derivative method and the semiempirical sum-over-states approach have been used with some success to predict qualitative trends, they are not sufficiently developed to have predictive capabilities for a structure–property relationship. Clearly, there is a need to develop semiempirical theoretical methods that can reliably be used to predict, with cost-effectiveness and with reasonable computational time, molecular and polymeric structures with enhanced optical non-linearity.

A chemical approach to improve our microscopic understanding of optical non-linearities involves study of non-linear optical behaviour of sequentially built and systematically derivatized structures. Most past work for third-order non-linearities has focused on conjugated polymers. This *ad hoc* approach is not helpful in identifying functionalities necessary to enhance optical non-linearities. A systematic study and correlation of γ values of systematically varied structure is an important approach for material development.

Zhao *et al.* have investigated the non-linearities of the following series of oligomers[6,7,21] (*Scheme 1*). As a function of N, the γ value increases much more rapidly for the thiophene oligomers than for the benzene and pyridine oligomers, indicating that the π-electron delocalization from one ring to another is much more effective for thiophene units. In addition, the d orbital of sulphur may be contributing to optical non-linearity. The γ value for the thiophene oligomers follows a power law $\sim N^4$ (N = number of repeat units), which is close to what is predicted by an *ab initio* calculation on polyenes. Zhao *et al.* have also investigated systematically derivatized thiophenes, and found that placing NO_2 groups at the end 2,2′-positions of thiophene enhances the non-linearity[6].



Scheme 1

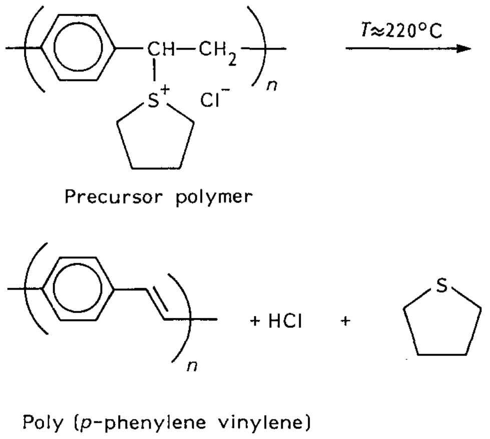
Recently, a joint effort of the Material Laboratory at Wright Research and Development Center and the Photonics Research Laboratory at SUNY at Buffalo has resulted in a comprehensive study of structure–non-linear optical properties relation for a large number of systematically varied aromatic heterocyclic compounds involving fused-ring benzimidazole and benzthiazole structures[22,23]. This study has provided many useful insights, some of which are as follows: (a) A sulphur ring in a conjugated structure is much more effective than a phenyl ring or other heteroaromatic ring such as furan or pyridine in increasing optical non-linearity. (b) An olefinic double bond provides a highly effective π-delocalization and consequent increase of the third-order non-linearity. (c) Grafting of pendant aromatic groups through attachment to a nitrogen atom in a fused benzimidazole ring provides a means for producing two-dimensional π-conjugation leading to an enhancement of γ and also improved solubility.

The search of third-order materials should not just be limited to conjugated structures. However, only with an improved microscopic understanding of optical non-linearities can the scope, in any useful way, be broadened to include other classes of molecular materials. Incorporation of polarizable heavy atoms may be a viable route to increase γ. A suitable example is iodoform (CHI_3), which has no π-electron but has a $\chi^{(3)}$ value comparable to that of bithiophene[24]. Organometallic structures represent another vast class of molecular materials, which are largely unexplored.

Improvement in materials processing through chemistry

Another important issue concerning the conjugated polymeric structure as third-order non-linear materials is their processibility. The conjugated linear polymeric structures tend to be insoluble, and therefore cannot readily be processed into device structures. The lack of processibility may render a material totally useless for practical application even if it may have a large $\chi^{(3)}$ value.

Synthetic chemists can play a vital role by designing chemical approaches for processing of important non-linear materials. Two specific examples presented here are: (a) soluble precursor route and (b) chemical derivatization for improving solubility. In the soluble precursor route, a suitable precursor is synthesized that can be cast into a device structure (i.e. film) by using solution processing. Then it can be converted into the final non-linear structure upon subsequent treatment (such as heat treatment). This approach has been used for poly(*p*-phenylene vinylene) as shown below[25]:



In the chemical derivatization approach one introduces a pendant long alkyl or alkoxy group to increase solubility. Polythiophene itself is insoluble but poly(3-dodecylthiophene) is soluble in common organic solvents. We have also successfully used poly(3-dodecylthiophene) to form mono- and multilayer Langmuir–Blodgett films[26].

Improved optical quality

Optical quality of the materials is of prime concern for integrated optics applications, which will involve waveguide configurations. Most conjugated polymeric structures are optically lossy. There is a need for chemical approaches that will provide a better control of structural homogeneities so that optical losses can be minimized. Another approach is through the use of composite structures where both the optical quality and $\chi^{(3)}$ can be optimized by a judicious choice of the two components. The best optical-quality medium is provided by inorganic glasses such as silica. However, they by themselves have very low $\chi^{(3)}$. A composite structure such as that of silica and a conjugated polymer may be a suitable choice. Chemical processing of an oxide glass using the sol–gel chemistry provides a suitable approach to make such composite structures. Using the sol–gel method, a composite of silica glass and poly(*p*-phenylene vinylene) has been prepared[27] in which the composition can be varied up to 50%. The procedure involves molecular mixing of the silica sol–gel precursor and the polymer precursor in a solvent in which both are soluble. During the gelation, a film is cast. Subsequent heat treatment converts the precursor polymer to the conjugated poly(*p*-phenylene vinylene) polymeric structure. The optical quality of the film was found to be significantly improved and high enough to use them as optical waveguides at 1.06 μm.

CONCLUSIONS

To conclude this paper, it is hoped that the discussion of relevant issues and opportunities for polymer scientists presented here will sufficiently stimulate the interest of the polymer science community. Their active participation is vital for building our understanding of optical non-linearities in polymeric systems as well as for the development of useful non-linear optical polymers.

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