

Structure/Property Relations in Conjugated Polythiophenes for Photonics Applications

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Pseudo-one-dimensional conjugated polymers are an interesting class of materials which have been developed for a number of photonics applications. A wide range of variation in the electronic and optical properties can be achieved through changes in the polymer structures. The underlying photophysics results from delocalized electrons along the main polymer chain and the nature of localization is controlled in principle by electronic structural changes in conjunction with conformational changes by, e.g., chemical substitution, doping and interchain interactions. We review these basic ideas and present results of a comprehensive effort developing polythiophenes, a well-studied member of the class of one class of pseudo-one-dimensional conjugated polymers. The value of polythiophenes in photonic applications is based on what is perhaps the most important structure-property relationship in conjugated polymers, which is the chemical stability and processibility as a function of the molecular structure.

Keywords: Polythiophene, Conjugated polymer, Delocalized electrons, Third order nonlinear optics, Structure/property relations

INTRODUCTION

Conjugated polymers have long been proposed as ideal materials for various photonics applications. Their potential is due to a number of factors:

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possessing key electronic/optical properties such as good conductivity, large oscillator strengths (interaction with optical fields) and fast response times, as well as the many processing and cost advantages of polymers compared to inorganic materials such as semiconductors. However, until about a decade ago, this potential was never fulfilled due to the inability to attain necessary values for critical parameters, e.g., third order nonlinearities for all-optical switching, or because of other materials properties that prevented applications, e.g., poor stability of polyacetylene as a conducting polymer. Limited applications did see success, for example conducting polymers such as poly(3,4-ethylenedioxythiophene) [1, 2] (PEDOT) and polyaniline have been implemented in microelectronics applications such as electrostatic discharge protection and electromagnetic shielding [3]. With the discovery of efficient electroluminescence in poly(phenylene)vinylene in 1990 [4, 5], the potential of conjugated polymers began to be realized commercially as organic light emitting diodes. The progress in this area has been rapid, and commercial devices are presently available, and expected to take over a sizable share of the flat panel display market.

Polythiophene (PT) is a well-studied member of the class of pseudo-one-dimensional conjugated polymers [6, 7]. It can be polymerized both chemically [8] and electrochemically [9]. It and its derivatives have found use in a number of applications including as conducting polymers, [7] chemical and gas sensors [10, 11], photovoltaic devices [12], electrochromic displays [13], image sensors [14], smart pixels [15] microcavity lasers [16] and in electroluminescent devices [17, 18]. The sulfur heteroatom stabilizes the main conjugated chain chemically, so that unlike polyacetylene, it is relatively stable in air. With substitution at the 3(4) position of the thiophene rings, e.g. by alkyl groups, it can be made soluble in common organic solvents and spin-coated films with good optical quality can be prepared. It has been extensively investigated for third order nonlinear optics because of its good stability, large optical nonlinearity [19] and fast response time [20, 21, 22]. Sensors such as ionochromic probes have been demonstrated using PTs [23].

There have been attempts to develop a general understanding of conjugated polymers at various levels. Basic theoretical descriptions have been proposed modeling the electronic structure either as one-dimensional semiconductors [24, 25] or using a molecular approach [26, 27]. While the properties of the various types of conjugated polymers differ in many specifics, the common underlying structure and the close link between electronic and optical properties enables a basic description to be developed and applied regardless of the particular polymer or application [28, 29, 30].

The variety of types of repeat unit, side chain substituents and other structural changes implemented to affect material properties lead to variations in the basic model. Energy levels, oscillator strengths, the nature of the charge carriers, the decay mechanisms and rates, can all be understood from the basic model, and yet may also be tuned by appropriate changes in structure. This is also a key advantage of organic chemistry: the ability to create an infinite number of structures, limited only by the imagination and skill of the synthetic chemist.

This chapter is organized as follows. We begin in section II, with a general description of the basic electronic and optical properties of quasi-one-dimensional chains and the effects of substituents on the conformational change and in altering electronic structure. This leads to a discussion of fundamental structure property relations in conjugated polymers in section III. In both of these sections, we focus on properties in oligo- and PTs. While mentioning some results from theory and computer modeling, we concentrate on experimental studies of the structure property relations. Excellent reviews on theory and modeling can be found in references 31 and 32. Finally, section IV goes into detail on a specific application, namely, the development of PT derivatives for third order nonlinear optics.

PHOTOPHYSICS IN CONJUGATED POLYMERS

Conjugation, in the context of chemical structure, is the alternation of single atomic bonds with double or triple bonds along a polymer chain. In C based conjugated systems, the mixing of s and p atomic orbitals generally leads to sp^2 hybridization of the carbon atoms. Two of these form σ bonds with the adjacent carbon atoms, and the third bonds to hydrogen or some other substituent. The remaining p orbitals overlap along the polymer chain to form π -orbitals, in which the electrons are delocalized over the length of the chain. The single π -electron per bond formally leads to a conducting (metallic) structure, but the Peierls distortion, similar to that in one-dimensional metals, opens a gap at the band edge, resulting in the polymer being a semiconductor. At the molecular level, this is equivalent to the bonds dimerizing into single and double bonds, which lowers the total electronic energy. The prototypical conjugated polymer is polyacetylene (PA) (Figure 1), a linear chain of carbon atoms with alternating single and double bonds. Other conjugated polymers have backbones based on the PA

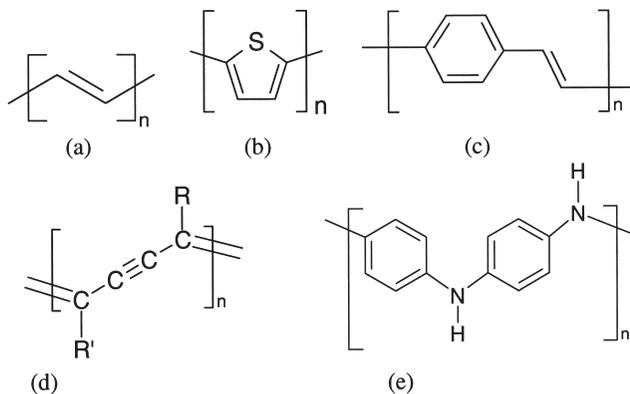


FIGURE 1
Conjugated polymer structures (a) polyacetylene, (b) polythiophene, (c) polyphenylenevinylene, (d) polydiacetylene, (e) polyaniline.

structure (see figure 1(a)). Polythiophene, figure(1.b), like PA, has a main chain of alternating single and double bonds, with the heteroatom sulfur stabilizing the carbon chain with respect to oxidation, allowing for easier processing. This can be viewed as a substitution in the backbone, where the S is not involved in the conducting path of the 1-D conductor. Polyphenylenevinylene (PPV) (figure 1(c)) has the same base, along with an additional conjugation path through the phenyl ring. Polydiacetylene (PDA) has additional electron density in the main chain in the sp hybridization leading to the triple bond. When doped, the hydrogen in polyaniline is removed and the conjugation path is through the nitrogen. Finally, while we restrict our discussion to pseudo-one-dimensional polymers with a single main chain, conjugation may occur through cross-linking or in three-dimensional structures such as ladder polymers [33].

The π -orbitals are the highest occupied molecular orbitals (HOMO) in most conjugated polymers and therefore, along with the lowest unoccupied molecular orbitals (LUMO), dictate the electronic and optical properties of the materials with respect to molecular configuration. The electrons in the π -orbitals may be excited into the antibonding π^* orbital, typically with visible or UV light, and often with large oscillator strengths. This accounts for the preponderance of dyes containing unsaturated bonds, first noted by Gräbe and Liebermann in 1868 [34].

The visible absorption spectra of a given conjugated polymer will depend primarily on the π - π^* transition energy. The basis for the large oscillator strengths and relatively low energies of the π - π^* transition is due to the delocalized nature of the electrons. König investigated the dependence of optical transition energy on chain length experimentally in 1926 [35], and an early quantum mechanical analysis by Kuhn using a free electron model gave insight into the dependence of the optical absorption spectra of polymethine dyes on conjugation length [36]. The term conjugation length used here is loosely defined as the average number of successive undistorted single/double bonds along the polymer main chain. Conjugation length is essentially the degree of delocalization (on average) along a conjugated polymer molecule backbone, controlled by local defects in the chain. These early determinations of length dependence have counterparts in more recent research clarifying the effects of conjugation length on band gaps [37] and various optical properties [38, 39, 40].

Modeling at the molecular level, nanometer scale structure should yield properties consistent with ideal molecular structure. This level of modeling derives from the fundamental variational treatment for minimization of total energy for a molecule alone in space. Electronic structure of such a molecule is idealized, however it also results from a tractable calculational problem and allows for reasonably simple understanding of the underlying effect of a molecular configuration. Calculations based on single molecules – an individual repeat unit from the perspective of a polymer molecule – yield first order estimation of transition energies. This energy difference is generally an overestimate due to the standard approach of neglecting differential overlap in the atomic orbitals as a molecule is formed from the linear combination of those atomic orbitals. The assumption of zero overlap in the atomic states can be addressed by considering non-zero overlap, however this is often absorbed by adjusting the covalent energy to allow for the real non-zero overlap in the molecular orbitals. As more repeat units are added to the modeling approach, oligomer properties can be calculated. This in turn will affect the estimation of the π - π^* energy separation, and is again taken into account most easily through parameterization and correction compared to experimental measurement. Salzner, et al., have shown a simple progression of molecular calculations for oligothiophenes from $n=1$ -4, and compared to a band structure calculation [41]. Hybridization of molecular orbitals from $n=1$ to $n=2$ broadens the density of states around the π and π^* states resulting in a lowering of the π - π^* energy difference. This reduction continues as n is increased to 4, and when compared to the band

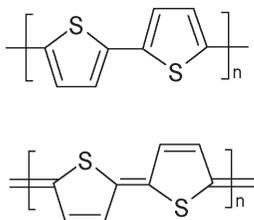


FIGURE 2
Aromatic (upper) and quinoid (lower) form of polythiophene.

structure calculation for PT (infinite chain) the progression of band gap reduction is clear.

The band gap for PT is approximately 2 eV. The magnitude of this gap is understood as a property dependant to a large degree on the bond length alternation along the backbone. PT has a somewhat large band gap due to the nature of the alternating bonds in the ground state. This can be understood by considering again PA. If PA consisted of totally delocalized π bonds, it would be a conductor with zero band gap. The dimerization of the bonds into single and double bonds, quantified as the bond length alternation (BLA), leads to the nonzero value of the band gap. Consequently, the degree of BLA in conjugated polymers is closely linked to the band gap as well as other properties such as fluorescence [42] the third order nonlinear optical susceptibility [43]. One focus of “band gap engineering” (control of the band gap through designed structural modification at the molecular level) is the control of the BLA [44, 45]. In conjugated polymers such as PT, the BLA is closely linked to the two structural forms, aromatic and quinoidal, that have significant difference in total energy. These two forms are depicted in Figure 2. In the corresponding oligomers, the amount of alternation is also sensitive to finite chain lengths as well as end group substitution, since the quinoidal form requires unpaired electrons and/or charged species on the ends.

The modeling of the system in the next step up with regard to complexity is the greatest leap of faith. At this point, the need to accurately account for the intermolecular interactions [46] or electronic correlations [47] makes modeling increasingly difficult. The best one can hope for is minimal effects of steric hindrance, chain alignment, or overall bulk effects changing drastically the estimated properties resulting from the idealized structure.

Conjugated polymers, particularly with respect to optical properties, are most easily viewed as the equivalent of inorganic semiconductors when considering electronic energy levels. The differences arise from the method by which doping, substitution, and conformational changes are used in the organic materials to achieve the desired electronic structure and thus the desired properties. In inorganic semiconductors, doping is easily understood as a substitution of an electron rich or electron poor atom (with respect to the host lattice atom) where the dopant atom resides in a lattice site normally occupied by the host atom. In most conjugated polymers, doping is quite different. There is no crystal lattice as such, the extent of conjugation length defines the 1-D "lattice" based on delocalized electron density. Thus the lattice is significantly larger in spatial extent compared to inorganic crystalline materials. Substitution of an electron density center is not possible in the same manner as inorganic semiconductors. A simple example of doping in a conjugated polymer is to add an iodine atom to the mix. The iodine does not substitute in a crystal lattice, it resides near the conjugated polymer electron density and essentially pulls a charge off the chain, yielding the equivalent of a hole as a charge carrier in the 1-D conduction path. This kind of doping may be viewed as interstitial activity, but has a very different effect compared to inorganic semiconductors. In many cases doping of polymers affects the molecular conformation as well as intermolecular interactions. Typically, doping, substitution, and conformational changes are all important, separately and combined, for affecting electronic structure and therefore optical properties of conjugated polymers. Therein lies the difficulty in directly designing structure at the molecular level and correlating changes in molecular properties to the macroscopic properties that are measured.

Optical and electronic properties of conjugated polymers are tied in to the nature of the charge carriers and types of fundamental excitations, which vary depending on the material, preparation conditions and environment. In addition, the theoretical treatment and understanding of these phenomena is a matter of continued debate. As in inorganic materials, electron-hole pairs may couple through the Coulomb interaction, forming localized excitons. The energy of these is lower than that of the free electron hole pairs, and they play a large role in optical properties since they often have large oscillator strengths and nonlinear optical susceptibilities [48]. Determination of their energies can yield critical insight into the underlying photophysics of conjugated polymers [49, 50]. In particular, exciton binding energies are critical to optoelectronic devices applications, since in order to

generate mobile charge carriers, this energy needs to be supplied in addition to the energy needed to excite to the lowest excited state.

Coupling to the lattice and the confinement of the π -electrons to one-dimension may result in novel types of excitations. In polyacetylene (PA), the lattice coupling results in the existence of solitons, discontinuities in the bond length alternation. These are mid-gap excitations arising from the degenerate ground state and play an important role in the electronic and optical properties of PA. They consist of a C atom with an unpaired electron surrounded by carbon-carbon single bonds. On either side the bond length alternation resumes, but with opposite symmetry. Additional soliton states exist in doped PA – here the carbon atom has either zero (S_+) or two (S_-) unpaired electrons.

In conjugated polymers with less symmetry than PA, the two bond arrangements are not equivalent and have different energies. In materials like PT, the existence of two possible forms of the bonds in the polymer chain, aromatic and quinoidal (see figure 2) is important for the optical and electronic properties [45, 51]. On one hand, while the aromatic form is generally the lower energy configuration, the quinoidal form has a lower band gap. One strategy that we have employed for reducing the band gap of PT derivatives is substitution at the (3,4) positions to reduce the energy of the quinoidal form and thereby mix more of it into the ground state of the polymer.

A second reason for the importance of the two forms is that they give rise to polarons, bipolarons and self-trapped excitons as important low-energy excitations [25, 52, 53, 54]. This is particularly true in doped polymers, in which the excess charge carriers are coupled to the lattice to make charged polarons and bipolarons. In these excitations, electrons and/or holes, from photoexcitation or doping, may be stabilized by a change in the nearby bond lengths. Self-trapped excitons, electron-hole pairs coupled by electrostatic interaction but separated by a change in the BLA, are known to be primary excitations in neutral PT. In charged PT, polarons and bipolarons are the main charge carriers. These have two intergap states, split off from the conduction and valence bands. In the positive polaron ground state, the lower state is half filled (single occupancy). In the negative polaron the lower state is doubly filled, the upper is half filled. In both cases, optical excitation is possible from the lower to upper mid-gap states and between the states and the conduction or valence bands, generally leading to characteristic infrared absorption bands. In the positive (negative) bipolaron, the states are completely empty (filled). The lower state is less localized than the upper state. In this case, a negative polaron is created,

with additional electron density in the single bond regions near the defect.

Contrary to semiconductor doping, which creates a band state near (below) the conduction band edge or near (above) the valence band edge in a semiconductor via lattice substitution, doping of a conjugated polymer inserts charge carriers (electrons or holes) into molecular states via ionically bound molecules that are not part of a crystal lattice, even in 1-D.

At another level, macroscopic effects will also play a role in governing the electronic and optical properties [55]. The primary bulk phenomena affecting optical properties are the formation of charge transfer complexes within the film of material due to intermolecular interactions. Often termed color centers due to the nature of the visible optical properties, these are electron trap states that affect all sorts of optical properties in the material including optical losses. These interactions affect conductivity, with trap state lifetimes associated with electron hopping mechanisms responsible for the bulk material conductivity. Bulk conductivity of conjugated polymer materials are dominated by intermolecular interactions, in order to have a conducting path through a material film, electrons must transfer from molecule to molecule.

Finally, the semiconductor band model assumes infinite chains [24]. This model assumes a strong electron-phonon interaction, which in turn gives a large shift in energy between absorption and emission spectra, a fact experimentally observed. However, other experimental data, in particular, from site selective fluorescence (SSF) measurements [26, 56], cannot be fully explained by this model. The ideal of a perfect chain cannot be supported by what is known about disorder and defects in typical polymer films, however it is clear that the semiconductor band model is based on a molecular scale structure and the perfect chain modified by defects or disorder is not tractable from the point of view of modeling. A more realistic picture of the physics of conjugated polymers has been developed by Bäbller's group, which uses a molecular approach to describe the polymer properties [57]. In this model, disorder and defects lead to a distribution of localized subunits within the main chain. These in turn lead to localization of the electronic wave functions and broadening of the density of states. As a result, the properties are closer to those of a distribution of oligomers, with the primary low energy excited states being bound electron hole pairs [58, 59]. The SSF spectra reveal only a small Stokes shift, suggesting a weak lattice interaction. The larger Stokes shift observed in standard fluorescence spectra is due to spectral relaxation [60]. This model has implications for the generation of charge carriers, which now must come from secondary

processes [61]. Interesting results from combined experiments measuring third order nonlinearities and photoconductivity in a PT derivative have also been explained using this model [62]. In general, the best models will still only provide a reasonable estimate of actual properties, and understanding the variation of those properties relative to the model is an open field for speculation. Design from such modeling is not simple from a test and verification standpoint.

Nonlinear optical properties

In the end, most characterization techniques measure bulk polymer properties, averaged over many molecules, each with different conjugation lengths, conformations, etc. This is particularly true for third order nonlinear optical properties, which we discuss in detail in section IV. The third order nonlinear optical response of materials is described generally utilizing both molecular level and bulk polarizability, which dictates the result of interaction between an electromagnetic field and a medium. At the molecular level, polarization is field dependent and in frequency space is given by:

$$\mu(E) = \mu_0 + \alpha E + \beta EE + \gamma EEE + \dots \quad (1)$$

where μ is the molecular dipole moment, μ_0 is the intrinsic dipole moment of the molecule, α is the polarizability, β is the hyperpolarizability, and γ is the second hyperpolarizability. The bulk polarization of a material can be described as:

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

Where $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$ are the first, second, and third order susceptibilities, P is the bulk polarization of the medium and P_0 is the permanent polarization of the material.

Nonlinear responses in bulk material are described by the susceptibilities both second, third, and higher order terms. Hyperpolarizabilities and susceptibilities are tensor quantities, and from equations (1) and (2) we note that all materials can exhibit third order nonlinearities and second hyperpolarizability, however second order effects require non-centrosymmetric molecules. The imaginary part of the first order susceptibility is related to the linear absorption coefficient.

Third order nonlinear optical properties can be measured in a number of

ways. Later we discuss results obtained using several of these: Third Harmonic Generation (THG), Z-scan and Degenerate Four Wave Mixing (DFWM). Interpretation of the results is often difficult, since third order effects may arise from a number of underlying phenomena, including nonresonant electronic effects, resonant excitation, thermal nonlinearities, etc., each with a different characteristic time scale. The basic quantity measured is the third order nonlinear optical susceptibility, $\chi^{(3)}(-\omega; \omega_1, \omega_2, \omega_3)$, which describes the polarization response at frequency ω to the third power of the incident field with frequency components at ω_1 , ω_2 and ω_3 . Alternately, the third order nonlinear optical properties are quantified as the nonlinear refractive index and nonlinear absorption coefficient. These are proportional to the real and imaginary parts respectively of the third order susceptibility $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$.

For applications in high speed all-optical switching, ultrafast response times from nonresonant effects or from resonant excitations with short decay times are desired. This is contrary to resonant excitations for second order susceptibility, which are essentially useless for E-O applications because decay times cannot be short enough to allow for effective switching. Third harmonic generation has the advantage of providing only the electronic nonlinearity. In this method, an incident infrared beam is tripled in frequency through a parametric third order nonlinear process. The irradiance of the tripled beam is proportional to the square of $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ [63]. Values for this third order susceptibility are generally one or two orders of magnitude lower than those measured using Z-scan or DFWM.

In the Z-scan method, the nonlinear refractive index and nonlinear absorption coefficients are measured directly by scanning the sample through the focus of a Gaussian profile beam [64]. To first order, the nonlinear refractive index and absorption coefficients are proportional to the real and imaginary parts of $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$, respectively, although saturation effects resulting from higher order terms may also be determined directly from the data [65].

In degenerate four wave mixing (DFWM), three spatially distinct beams intersect in the sample [66]. Two of these create a grating through the third order nonlinearity. The deflection of the third beam from this grating is measured, giving the value for the magnitude of the third order susceptibility, $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$. While the information on the relative contributions of the real and imaginary parts is not available from DFWM, the ability to delay the timing of the third pulse allows one to measure the decay times of the nonlinearities.

Other materials properties may also display disparity between microscopic and macroscopic properties. Electrical conductivity is normally measured in bulk samples, but often the charge transport varies depending on the length scale. For example, in many conjugated polymers, the charge transport along chain (or conjugated chain sections) is coherent, but between chain segments transport is diffusive hopping.

STRUCTURE/PROPERTY RELATIONS

Bulk effects will arise due to modifications in structure on the molecular scale. At the most basic level, the modifications cause changes in the potentials experienced by the electrons, and perhaps changes in the number of electron states as well. These lead to changes in changes in electron densities, degree of localization, energy levels, decay times and oscillator strengths, etc. In turn, the macroscopic optical properties are affected by how the electrons in their new environments interact with applied optical fields.

Variations in microscopic structure may arise from a number of different external influences [67]. The most direct is chemical substitution, either in the main chain or as side groups. Doping (adding or removing charges to the polymer) is also a key means of directly changing electron density in conjugated polymers. Preparation conditions may have a significant effect on the microscopic structure, especially the main chain conformation [68]. They may also affect the properties through the meso- or macroscopic morphology, for example in the importance of surface effects in films or nanoparticles.

Many studies have been performed in which a systematic variation of structure was used to isolate causes of particular behavior [44]. The materials themselves often limit these types of studies, in that synthesis of a series with incremental changes is not always possible, or that variations in the preparation conditions needed to effect these changes cause other differences as well. Furthermore, underlying causes are not always clear; as side-chain substituents may alter conformation or cause aggregation in addition to affecting the electronic properties in the main chain, or interchain interactions may be affected when forming a film or bulk material. Finally, polymers are generally not homogeneous on a microscopic scale, possessing a distribution of molecular weights and varying amounts of disorder and defects. These can be very sensitive to preparation conditions and make comparisons among materials difficult and again will lead to mesoscopic structural effects.

At a basic level, chemical substitution has a direct effect on the underlying physical characteristics such as energy levels, density of states and excited state lifetimes. These are photophysical properties that are fundamental to conjugated polymers, and so enable structure property relations in one type of material to be applied to others. The specific outcome of these changes, and their relation to other properties of the polymers, lead to material specific differences among the various conjugated polymers. For example, the weak fluorescence of polyacetylene compared to the strong fluorescence in PPV has been attributed to the fact that a strong two photon allowed state lies just below the one photon allowed state in PA, and above it in PPV [69-74]. Thus, radiative transitions to the ground state are likely in PPV, while in PA the excitations decay to the two-photon state from which radiative transitions are forbidden. This illustrates the structural difference leading to a change in basic characteristics (energy levels) finally resulting in very different macroscopic optical properties.

In many cases, a study of the corresponding oligomers may be used to determine the relation between delocalization length and macroscopic properties. Oligothiophenes have been extensively studied in this way, because of the numerous straightforward synthesis methods available for preparing well-defined samples with varying length. The third order nonlinear optical properties as a function of the number of repeat units in oligothiophenes have been looked at by a number of groups. Both linear absorption coefficients [75] and hyperpolarizabilities of oligothiophenes from monomer to octamer showed a strong dependence on the number of repeats units [76, 77, 78], while some work reported saturation of the nonlinearities for larger oligomers [79]. These results are similar to those found in other conjugated oligomers [80, 81]. Other work has focused on time dependent spectra [82], absorption and fluorescence emission spectroscopy [83, 84], Raman Spectroscopy [85], photoinduced dichroism [86], X-ray [87], and NMR [88] as functions of the oligomer length. Theoretical modeling has also been used to study the dependence of optical and electronic properties on oligothiophene length [84, 89, 90].

Study of well-defined oligomeric analogs of polymers can also remove effects such as chain length distributions and allow effects due to chemical substitution or doping to be isolated. This may also be achieved with oligomer segments that are part of a main polymer chain, i.e., oligomers polymerized with spacers [91]. Molecular design of regular structural variations in oligothiophenes has been used to study structure property

relations in oligothiophene and related heterocyclic oligomers [92, 93, 94, 95]. In oligomers, the effect of the end groups can be important in governing whether the aromatic or quinoidal forms have lower energy, and in setting the charge density in the oligomer chain [96, 97]. A number of studies have looked at conjugated oligomers with both electron donating and accepting groups, so-called "push-pull" molecules [98]. These are generally attached as end groups of a conjugated oligomer, although they can also be incorporated as alternating units in a polymer main chain.

Structure property relations have a particular importance in studies of third order optical nonlinearities because of the lack of a unifying strategy for understanding how to improve these properties [99, 100, 101, 102]. Marder et al. found a strong correlation between the bond length alternation and the second hyperpolarizability in studies of linear polymethine dyes [43, 103]. This basic idea has led to a consistent picture of structure/property relations for third order nonlinear optical (NLO) properties in these materials [104]. From theoretical and experimental data, Nalwa et al. determined that the π -bonding sequence played a role in determining the NLO properties of conjugated polymers [105]. Other workers have looked at main chain variations in PT [106, 107, 108] and PPV derivatives [109]. The effects of side chain substitution, most often done by altering the chemistry of the monomers, has been the goal of work on PDA [110, 111], PT [112] and recently in much work on PPV [113, 114].

Because of the availability of synthetic strategies for chemical substitutions and the stability of the modified polymers, a considerable amount of research has been done on the development of PT derivatives. Typical chemical substitution of PTs involves attachment of pendant groups such as alkyl chains at the 3(4) positions to improve solubility. The alkyl chain substituent has significant effects on the linear optical and electrical properties of the polymers [115, 116, 117, 118]. The effects are generally indirect ones, caused by changes in polymer chain conformation [68]. In PT and its derivatives, this is most often seen in terms of the regioregularity of poly(alkylthiophenes) [119, 120, 121]. Substitution of alkyl chains at the 3(4) position of the thiophene ring is a common means of obtaining a polymer soluble in common organic solvents. However, the random order of the chain being at the 3 or 4 position in the polymer can have significant effects on the final properties. McCullough et al. synthesized PTs with nearly all "head to tail" arrangement of the 3-alkylthiophene rings, and found that they self assemble and possess longer conjugations lengths and had larger conductivities than random arrangements of the side chains

[122]. The steric interaction between the side groups, and the ability of the polymer to rotate about the C-C bond between rings, leads to twisting of the chain and a decrease in the overlap of the π electrons and corresponding decrease in the conjugation length. Other work has looked at “head to head” and “tail to tail” PTs, with the observation of increased torsional angle between units and corresponding decrease in conjugation length and blue shift of the absorption band [123]. The degree of regioregularity has also a strong influence on the nature of the primary photoexcitations [124], charge carrier mobility [125] and photoluminescence [126].

More direct effects result for substitution of electron donating or accepting groups at the 3(4) position, i.e., directly onto the conjugated chain. Electron donating alkoxy chains instead of alkyl have been attached and have resulted in large changes in optical properties, for example quantum efficiency of luminescence, oscillator strength and band gap [127, 128, 129], even when the alkoxy chain is not directly attached to the thiophene ring, but through fused rings such as pyrazine [130]. Other side chain substituents include azo dyes for second order NLO applications [131] and hydrogen bond forming urethane groups yielding polymers with strong temperature dependent luminescence [132]. Substituents can also be used to force planarity of the thiophene rings by having fused pendant groups [133, 134, 135].

Demanze et al. specifically tried to influence the charge confinement by creating “push-pull” PTs [136] with alternating substitution of electron donating and withdrawing side groups. One clear effect of these substitutions is the alteration of the relative energies of the aromatic and quinoidal forms of the heterocycles, and thereby the stabilization of polaron and bipolaron states [137, 138]. Daminelli et al. used modeling to investigate a number of PTs with electron donating or accepting groups attached to the main chain [139]. Substituents linked to the heteroatom have also been investigated for thiophene and pyrrole [140]. Oligothiophenes containing thienyl-S,S-dioxide have been shown to have good electroluminescence properties [141, 142, 143]. The influence of the heteroatom has also been studied theoretically [144, 145], with predictions of increases in nonlinear optical susceptibility vs. atomic number of the heteroatom. These increases have been observed in neat thiophene, furan and selenophene [146], but not in polythiophene/selenophene derivatives [147].

The copolymerization of two or more moieties has also been widely used to obtain novel properties in conjugated polymers. As an example, NLO active segments were interspaced with flexible segments in order to obtain

polymers with good solubility and film forming properties combined with large third order nonlinear optical susceptibilities [148]. Various types of polyarylene(vinylene) such as polythienylene(vinylene) [149] and related systems [150, 151, 152] have also been synthesized and the linear and nonlinear optical properties investigated [153, 154].

Other substitution can be more substantial, especially in the synthesis of the low band gap and conducting PT derivatives poly(3,4-ethylenedioxythiophene) [1, 2] and polyisothianaphthene [155] and its derivatives [156]. These types of PT derivatives, with extended rings attached at the 3(4) position of the thiophene, have shown a remarkable variety of electronic and optical properties, and will be discussed in more detail in the next section.

CONJUGATED POLYMERS FOR PHOTONIC SWITCHING

Conducting and semiconducting polymers have been used in applications relating to photonics both directly, as active materials, and indirectly, as components of drive and interface electronics and packaging [157]. The common origin of both electronic and optical properties makes many of these materials interesting for applications utilizing both of these properties. Materials displaying strong second order non-linear optical (NLO) properties have long been considered for application in optoelectronic devices as switches and frequency converters [158]. The ability to take advantage of these properties have been strongly influenced by processing technology that enables preparation of bulk material or thin films maintain the molecular level structure from which the property arises, e.g., the noncentrosymmetry needed for electrooptic materials.

Materials with large third order NLO properties have long been proposed for all-optical switching applications. "All-optical" in this context means actual switching of light using light. Advantages include the possibility of creating all-optical computers and the inherent fast response times of many effects resulting in third order phenomena. The delocalization of the π -electrons along the main chain in conjugated polymers is the origin of large third order nonlinearities, with additional enhancements possible from excitonic resonances and confinement of the excitations to one dimension [159]. Theoretical predictions based on one-dimensional semiconductor band models predict a dependence of the third order susceptibility on the inverse sixth power of the band gap. This relationship has motivated efforts

to develop low band gap materials for third order nonlinear optics applications, in addition to their use as conducting polymers.

Many of the conjugated polymers listed earlier (figure 1) have been investigated for third order effects [160], in particular PDA [110, 161], polyacetylene [162] and PT [6]. Despite the intensive activity in this area, in particular in the 1990's, structure property relations are well understood only for specific classes of materials [163, 164].

For optical switching applications, large values of the third order susceptibility are needed to be able to switch signals using commercial laser diodes and without significant heating effects or signal loss due to optical absorption. In most device structures, it is the real part (dispersive) of $\chi^{(3)}$ (or nonlinear refractive index) that must be large in order to obtain switching at low input power and with minimal loss. Typical values of $\chi^{(3)}$ needed for switching devices have been reported to be around 10^{-7} esu, although the required values also depend on the specific device architecture. In addition, the linear absorption coefficient, α , and the response time, τ , are also critical parameters for good device operation. The ratio between the third order susceptibility and the linear absorption coefficient, $\chi^{(3)}/\alpha$, or a parameter proportional to it, is often used as a figure of merit [165, 166], with values on the order of 10^{-9} esu-cm needed for commercially viable devices. Other materials parameters may also be important, for example strong two-photon absorption is detrimental to device operation [167].

Low band gap polythiophene derivatives

A great deal of work has been done to develop synthetic strategies for derivatization of PT [168]. Many of these synthesis efforts have aimed to determine the effects of regular structural changes on particular properties such as chromism [127], nonlinear optical properties [169] and conductivity [170, 171], and the connection between conjugation length and conductivity [172]. Variation of the chemical substitution at the 3(4) position of the thiophene rings is a common strategy for affecting both the electronic structure of the main chain directly as well as the conformation. For example, alkylsulphonate, alkoxy, amide, polyether and acyl groups were introduced in 3-position of thiophene and these compounds were polymerized electrochemically [173].

These studies have been based on general methods of PT synthesis, including chemical [6, 174] or electrochemical [173] polymerization of a single precursor monomer to form isopolymers linked at the 2,5 positions of the thiophene ring, and catalytic coupling of Grignard (or other

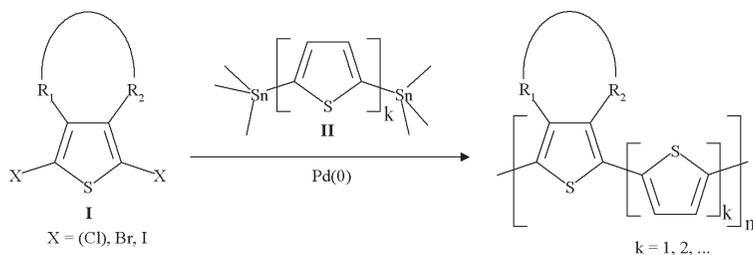


FIGURE 3
Stille coupling reaction for the synthesis of oligo- and polythiophene derivatives.

organometallic) reagents [174, 175]. Chemical and electrochemical polymerization of single precursors tends to produce polymers with various degrees of doping or overoxidation [176] and structural defects such as binding through positions 3(4). These defects can have serious consequences for the resulting properties of the polymer, since they interrupt the conjugation path. In polymers synthesized using Grignard reagents, structural defects are lower, but the processing conditions with this method limit the types of functional groups that can be used, i.e., only a few types of pendant moieties may be attached to the polymer backbone.

Polythiophene derivatives synthesized with Stille coupling

A number of synthetic strategies have been developed to minimize the problems of derivatizing PT and enable their properties to be “tuned” by changing the electronic density distribution. One of the authors (EVK) was part of a group at BASF AG that developed a number of new PT derivatives as part of a MITI-sponsored long-term research project to develop nonlinear photonic materials [177, 178, 179]. These polymers were synthesized by a novel application of the Stille coupling reaction [180] to thiophene. The reaction, schematically depicted in Figure 3, can be used to create polymers with alternating substituted and unsubstituted thiophene or selenophene rings [147]. The resulting materials have minimum structural defects, doping or overoxidation and may have a wide range of functional groups incorporated as side groups. This method has the additional advantage of enabling the synthesis of polymers with alternation of rings with different substitution patterns, substituted and unsubstituted at positions 3 and 4, or even copolymers with two different thiophene units. This last possibility is particularly critical, since the presence of unsubstituted “spacers” can

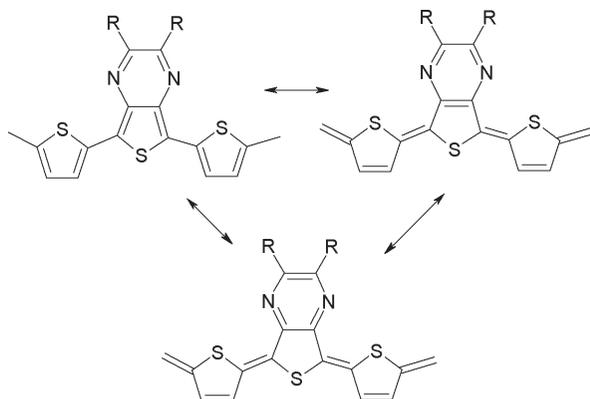


FIGURE 5
Resonance structures for the thienopyrazine unit

competing with each other. On one hand, the substituents directly effect the π -electrons in the main chain by both inductive and resonance effects. On the other hand, the type and position of the side groups will alter the conformation of the chain through steric interactions. In particular, we find that the ratio of the number of unsubstituted “spacer” thiophene rings to the substituted rings in the main chain will shift the band gaps and oscillator strengths. By varying the number of these “spacer” thiophenes, the solubility of the polymer could be improved and thereby the final film quality. The unsubstituted thiophene rings also acted as electron donors to the main chain, while the thieno[3,4-b]pyrazine rings were electron acceptors. This strategy of alternating electron donors and acceptors in conjugated polymers has been demonstrated to result in very low-band gap materials, i.e., absorption out to longer wavelengths. This could be especially seen in some of our PTs with additional cyclic rings substituted at the 3(4) position of the pyrazine ring. Despite being separated from the main polymer backbone, the electron donating effect from these rings greatly shifts the absorption bands into the near infrared, with the onset of optical absorption in some cases above 1500 nm. These band gaps (photon energies ~ 0.8 eV) are some of the lowest ever reported for conjugated polymers.

The thieno[3,4-b]pyrazine group generally shifted the absorption maxima up to several hundred nanometers to the red as compared to unsubstituted PT. Dialkyl substituents on the pyrazine ring shift the

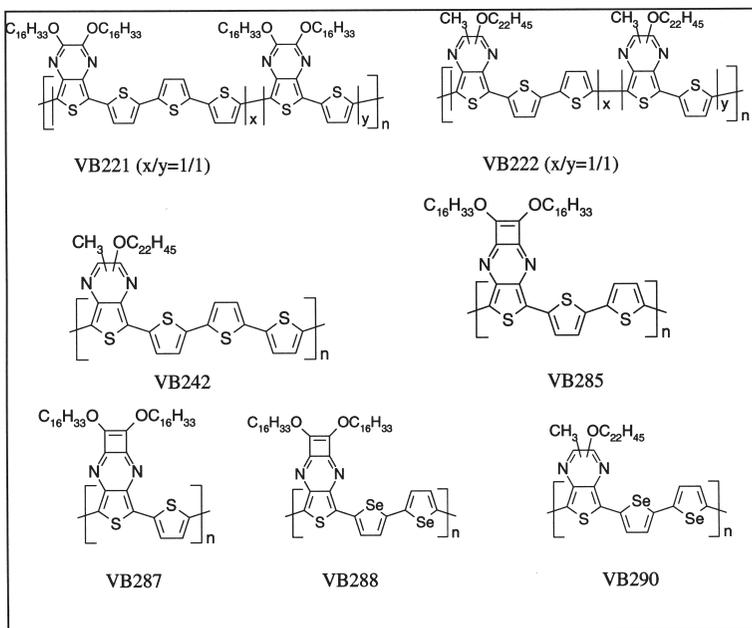


FIGURE 6
Polymers synthesized using Stille coupling.

absorption maximum to the red, while dialkoxy substituents give a blue shift and large increase in oscillator strength. The presence of the dialkoxythienopyrazine further shifted the absorption into the infrared wavelength region. Substitution with asymmetric substituents (sample VB242) reduced steric interactions and crystallization of the final films. The sample 366-189, shown in Figure 7, represents the optimum of the red shift and increased oscillator strength: at this ratio the competing influences of the substituted and unsubstituted units seems to be optimized in terms of both steric interactions and effect on the main chain electronic structure.

This polymer, with a ratio of about 0.56 substituted/unsubstituted units, had the lowest band gap for dialkoxythienopyrazine based polymers, with an absorption maximum at 680 nm with peak value $6.27 \times 10^4 \text{ cm}^{-1}$. More important, this material had the largest value of the third order nonlinear optical susceptibility, $\chi^{(3)}$, measured in these derivatives, over 10^{-8} esu as measured by DFWM with 100 fs pulses, and nearly 10^{-7} esu as meas-

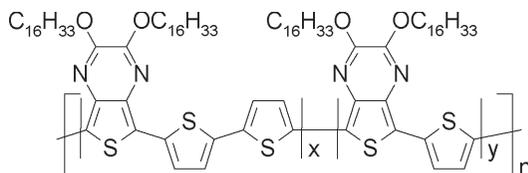


FIGURE 7
Polythiophene derivative 366-189 ($x/y=4/1$).

ured using Z-scan with 12 ps pulses. The discrepancy can be easily explained by the accumulation real excited states over the longer pulse width in the Z-scan experiment [187].

Wavelength dispersive DFWM measurements were carried out in the forward-wave geometry using the apparatus described in references 178 and 188. Figure 8 shows the wavelength dispersive of $|\chi^{(3)}|$ in the visible and NIR for 366-189. Strong resonant enhancement was seen in the region of the absorption band, while the nonresonant value of $|\chi^{(3)}|$ was on the order of 10^{-10} esu.

The spectral dependence of the resonant enhancement in $|\chi^{(3)}|$ is interesting in that the peak occurs on the low energy side of the absorption band, while decreasing dramatically on the higher energy side. This is likely due to the onset of photoconduction, as observed in a similar PT derivative [62]. The broad absorption bands in these materials, then, can be attributed to a band of (macroscopically) localized states at lower energies overlapping with a conduction band at higher energies.

Some additional spectral measurements on the sample 366-189 shed light on the physics of the fundamental excitations. The linear absorption and photoluminescence (PL) spectra are shown in Figure 9. The absorption peaks at around 1.8 eV (680 nm). The PL quantum yield is very low, on the order of $<10^{-5}$. It has been proposed that the weakness of PL in conjugated polymers may be due to the lowest energy state of the polymer being the two photon-allowed $2A_g$ rather than the $1B_u$ [42]. From the figure, one can observe some vibronic progression, as well as very little Stokes shift (independent of the excitation wavelength), indicating that the lowest dipole allowed excitation is reached via a 0-0 transition. This contrasts with the case of alkyl-substituted PTs [126], as well as a number of other conjugated polymers, and suggests that the conformational changes in the excited state

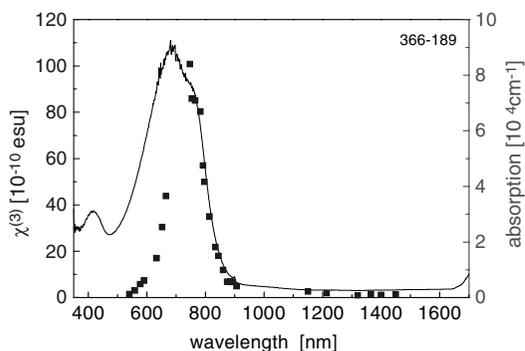


FIGURE 8
Absorption coefficient and $|\chi^{(3)}|$ from fs-DFWM.

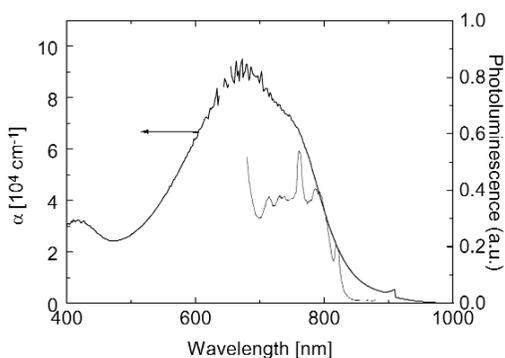


FIGURE 9
Absorption and PL spectra of 366-189.

are minimal. Stokes shifts in various PTs have been attributed to relaxation of torsional strain in the excited state [126]. The predicted planar ground state of similar polymers [189] leads us to believe that a planar conformation of our polymers leads to little torsional strain in the ground state.

Recent efforts to increase the nonlinearities in the infrared for possible telecommunications applications have produced materials incorporating a dialkoxycyclobuta[e]thieno[3,4-b]pyrazine unit (1c in figure 4), which shifts the absorption band into the infrared wavelength

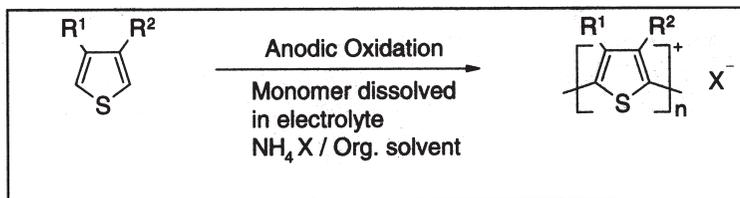


Figure 10
Reaction scheme for electrochemical polymerization.

region with the corresponding increase in third order nonlinearity due to resonant enhancement. In addition, the figures of merit in these materials are larger than those in 366-189 by a factor of almost 2. The nonlinearities of the low band gap polymers VB287, VB288 and VB290 were measured at a wavelength of 1100 nm using the Z-scan technique. The results are given in table 1. This wavelength is just below the resonance for both VB287 ($\lambda_{\text{max}} \sim 960$ nm) and VB288 ($\lambda_{\text{max}} \sim 1070$ nm) and just at the band edge for VB290 ($\lambda_{\text{max}} \sim 732$ nm). Comparing 287 and 288 it would seem that the replacement by Se had the opposite effect than intended, namely decreasing the figure of merit. However, VB290, also with selenophene rings had a good figure of merit. The figures of merit for VB287 and VB290 were slightly lower than that measured from 366-189 using Z-scan (1.7×10^{-12} esu-cm), but the nonlinearity in the telecom bands at 1.3 and 1.55 μm are expected to be much larger due to resonant enhancement.

TABLE 1
NIR Z-scan measurements of low band gap PT derivatives.

Sample	real $\chi^{(3)}$ (esu)	imaginary $\chi^{(3)}$ (esu)	α (cm^{-1})
VB287	-5.5×10^{-8}	-1.6×10^{-8}	37400
VB288	-2.3×10^{-8}	-1.6×10^{-9}	67300
VB290	-9.0×10^{-9}	5.8×10^{-9}	5906

In addition to the studies of polymers, series' of oligomeric analogues were synthesized with varying lengths and substituents [184, 190]. In these, the effects of conjugation length could be explicitly determined. Similar to other studies [76, 77, 78, 84], our results showed a strong dependence of the nonlinearities on the chain length. Although the effects of substituents was less clear, several conclusions could be drawn about the effects of side chain substituents on the conformation, and the lack of enhancement in the figure of merit with decreasing band gap. In addition, only a slight increase in the nonlinearity was observed with replacement of the sulfur heteroatom with Se.

Electrochemically polymerized derivatives

Polythiophenes synthesized by standard methods described above have the disadvantage of being always charged. An exact control of doping level is not possible due to the fact that the chemical reaction cannot be interrupted without adding additional chemicals like reduction reagents. Polymers synthesized by Stille reaction give totally neutral (uncharged) polymer systems, but they cannot be modulated by electrochemical doping because of their poor electronic conductivity.

However, heterocyclic polymers like PT or polypyrrole can also be synthesized by electrochemical methods, allowing a precise control of the charge state of the polymer. The basic electrochemical polymerization reaction is depicted in Figure 10. The thiophene-based monomer is dissolved in an electrolyte and polymerizes on the anode of the electrochemical cell. Polymerization occurs through a potential applied across the electrodes and by a computer controlled potentiostat. The process can be monitored by the current flow across the electrodes and the potential measured by a reference electrode near the anode. More details may be found in reference 6.

Electrochemical polymerization was used to produce PT derivatives substituted similar to those synthesized with Stille coupling [191]. As starting materials, a number of tailor-made thiophene monomers were synthesized (Figure 11).

The third order optical nonlinearities of the resulting films were characterized using third harmonic generation and Z-scan. Figure 12 shows the results of THG measurements of $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ from two electrochemically synthesized PT derivatives films polymerized from the monomer VB245 shown in figure 11. There is only a slight amount of resonant enhancement in these films, but the values of $\chi^{(3)}$ are nevertheless good, especially in the off-resonant wavelength regions (≥ 700 nm). These

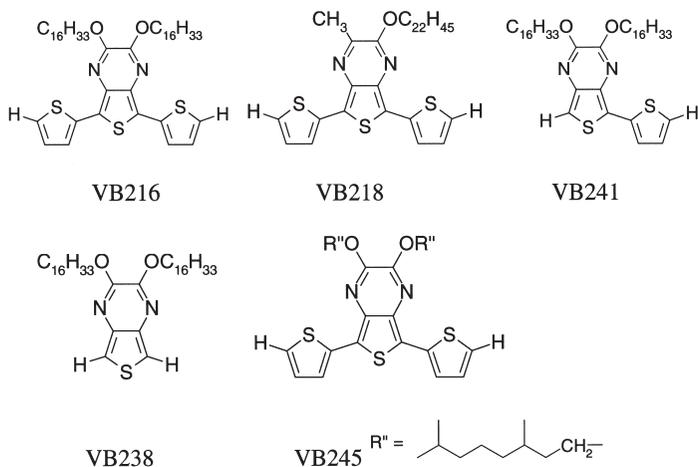


Figure 11
Starting monomers for electrochemical synthesis.

values do have considerable uncertainty, though, due to the difficulty in determining the thicknesses of these very thin films.

Z-scan measurements on the electrochemically synthesized PT derivatives were also performed. The results were qualitatively similar to those from the PTs chemically synthesized using the Stille coupling reaction, i.e., resonantly enhanced $\chi^{(3)}$ values on the order of 10^{-8} to 10^{-7} esu, strong saturable absorption and negative real $\chi^{(3)}$ inside the absorption band. One significant difference is that they do not have the steep drop in $\chi^{(3)}$ on the high-energy side of the absorption band [177]. If the model proposed earlier based on the photoconductivity measurements is valid, this could either mean less interchain interaction (all absorption is excitonic) or very weak excitonic binding energy, i.e. the whole band is conduction. This second reason would seem to suggest a low $\chi^{(3)}$ value, therefore the first is more likely.

SUMMARY

In conclusion, we have presented an overview of the effects of structure, specifically chemical substitution and conformation, on the properties of

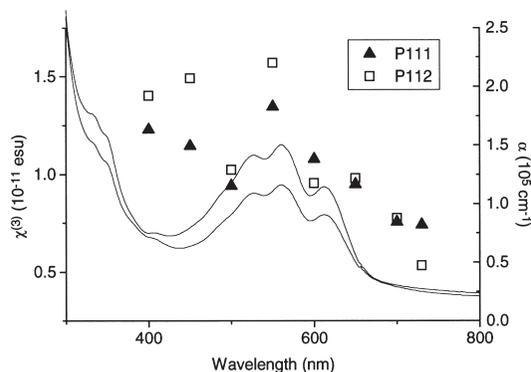


Figure 12
THG measurements of $\chi^{(3)}$ in electrochemically synthesized PT derivatives.

pseudo-one-dimensional conjugated polymers. We've discussed in detail the third order nonlinear optical properties of a number of PT derivatives developed for photonic switching applications. Additionally, we have presented a generalized discussion of the way in which the underlying physics of both the materials and devices makes these considerations exportable to a range of other conjugated polymeric materials and their applications, while pointing out the relationship between molecular design (structure) and macroscopic material properties.

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