New Additions to Nonconjugated Conductive Polymers; Nonlinear Optical Effects

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Recently, new additions to nonconjugated conductive polymers have been made that include: poly(β-pinene), poly(ethylenepyrrolediyl) derivative and polynorbornene. These polymers have different double-bond number fractions per repeat compared to previously reported nonconjugated conductive polymers. Upon doping with electron acceptor (e.g. iodine) the conductivities increase more than ten orders of magnitude to levels consistent with their double-bond number fractions. Radical cations that are formed upon doping have dimensions less than a nanometer leading to unexpectedly large nonlinear optical effects. The measured Kerr coefficient of doped polyisoprene is $\sim 1.6 \times 10^{-10}$ m/V^2 at 633 nm. For doped poly(β-pinene) the Kerr coefficient is $\sim 1.2 \times 10^{-10}$ m/V^2 and for poly(ethylenepyrrolediyl) derivative it is $\sim 1.2 \times 10^{-9}$ m/V^2. Exceptionally large two-photon absorption coefficient (~ 2.6 cm/MW at 810 nm) has been measured for doped poly(β-pinene). The mechanism of the nonlinear optical effect has been explained using a model of subnanometer size metallic quantum dots. These novel materials with wide transparency are expected to have significant applications in photonics.

Keywords: Nonconjugated conductive polymers, nonlinear optical effects, Kerr coefficient, two-photon absorption coefficient, metallic quantum dots

1 Introduction

Polymers having electro-active and nonlinear optical properties have attracted a great deal of research attention due to their unusual characteristics and a wide range of applications (1–4). These materials have also been of interest for fundamental studies on various aspects of chemistry and physics of the condensed matter. While conjugated conductive polymers have been more widely studied, nonconjugated conductive polymers form the foundation of conductive polymers in general (5–13). Recently, exceptionally large nonlinear optical properties have been reported for doped nonconjugated conductive polymers (4, 14–16).

The 2000 Nobel Prize in Chemistry appears to have been awarded for a fundamentally incorrect scientific concept. As stated in the document preserved at the Nobel Foundation website, a polymer must be *conjugated* to become electrically conductive upon doping. However, *nonconjugated* conductive polymers having isolated double bonds have been reported and studied in detail beginning with the first report in 1988 in *Macromolecules* (5a). The band-structural theory developed for conjugated conductive polymers predicts that nonconjugated polymers can not be conductive

while experiments have shown to the contrary. The correct theory for nonconjugated conductive polymers and the fundamental basis of conductive polymers in general have been discussed in the literature.

A conjugated conductive polymer is defined as having alternating double and single bonds between carbon atoms in the backbone. Therefore, the number fraction of double bonds per repeat (number of double bonds divided by the total number of bonds per repeat) in a conjugated polymer is equal to $1/2$. A nonconjugated conductive polymer has a double-bond number fraction of less than $1/2$ per repeat. Earlier examples of nonconjugated conductive polymers include: cis-1,4-polyisoprene, trans-1,4-polyisoprene, poly(dimethyl butadiene), other polybutadiene-based polymers and polyalloocimene (5–7, 10). For example, 1,4-polyisoprene has a double bond number fraction of $1/4$, polyalloocimene has a double bond number fraction of $1/3$ (average), while polyacetylene has a double bond number fraction of $1/2$. Recently, new members of nonconjugated conductive polymers have been added to the list. These include: poly(β-pinene), poly(ethylene-pyrrolediyl) derivative and polynobornene (8, 9, 12, 13).

Electrical conductivity, optical absorption and FTIR spectroscopic characteristics of these new conductive polymers as a function of iodine-doping have been reported. The electrical conductivity in nonconjugated conductive polymers has been found to increase more than ten orders

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Table 1. Electrical conductivities of nonconjugated conductive polymers with different double-bond number fractions

Polymer	Double bond number fraction	Electrical Conductivity (S/cm)
Poly(β-pinene)	1/6	0.008
Polynorbornene	1/5	0.01
Cis-poly(isoprene)	1/4	0.1
Poly(alloocimene)	1/3	1.0
Polyacetylene (Conjugated polymer)	1/2	$\sim$100

of magnitude upon doping with electron acceptors such as iodine. The maximum conductivity in any nonconjugated polymer depends on the double bond number fraction. It increases as a power law with double bond number fraction and becomes highest for the double-bond number fraction of $1/2$ corresponding to a conjugated conductive polymer. The values of conductivities corresponding to different double-bond number fractions are given in Table 1. This table provides the general description of conductive polymers including nonconjugated and conjugated.

Spectroscopic studies including: optical absorption, FTIR, Raman, ^{13}C-NMR, EPR and photoluminescence, along with electrical measurements have clearly shown that radical cations (polarons) are formed upon doping and charge-transfer from an isolated double bond in a nonconjugated polymer to a dopant (electron acceptor such as iodine) (5–13). Unlike in conjugated polymers, the radical cations (polarons) in nonconjugated conductive polymers are highly localized within a dimension less than 1 nm. Such localized species have been attributed as being responsible for the exceptionally large third order optical nonlinearities in these systems. The optical absorption spectra typically show two peaks: one at about 300 nm corresponding to radical cation and the other at about 400 nm which is due to charge-transfer from the double bond to the dopant (Fig. 2). FTIR spectra have shown that C=C stretching and =C-H bending vibration bands decrease upon doping as the double bond transforms into radical cation. Upon treatment with ammonia the vibration bands reappear. ^{13}C-NMR studies also confirmed the decrease of double bonds upon doping. EPR studies have shown generation of radicals upon doping. The radical concentration increases with dopant concentration. Photoluminescence studies have shown strong luminescence (at $\sim$360 nm for excitation at $\sim$280 nm) in new nonconjugated conductive polymers such as poly(β-pinene) in the undoped state. Doping with iodine quenches such photoluminescence.

2 Experimental

2.1 Nonlinear Optical Effects in Doped Nonconjugated Conductive Polymers

Nonlinear optical effects including quadratic electro-optic effect and two-photon absorption have been recently reported for specific doped nonconjugated conductive polymers (4,14–16). Quadratic electro-optic effect or Kerr effect involves a change in refractive index as an electric field is applied on a material: $\mathbf{\Delta n = K\lambda E^2}$, where $\mathbf{K}$ is Kerr coefficient, $\mathbf{\Delta n}$ is the change in refractive index, $\boldsymbol{\lambda}$ is wavelength and $\mathbf{E}$ stands for the applied electric field. In two-photon absorption, two photons are absorbed simultaneously and the absorption coefficient of a material increases with the intensity of light: $\mathbf{\Delta\alpha = \alpha_2 I}$, where $\boldsymbol{\alpha_2}$ is the two-photon absorption coefficient, $\mathbf{\Delta\alpha}$ is the increase in absorption coefficient and $\mathbf{I}$ is the intensity of light. Both (Kerr and two-photon) are third order optical effects. The quadratic electro-optic or Kerr coefficient is related to the nonlinear refractive index or the real part of the third order susceptibility (Re $\boldsymbol{\chi^{(3)}}$). The two photon absorption coefficient is proportional to the imaginary part of the third order susceptibility (Im $\boldsymbol{\chi^{(3)}}$).

Quadratic electro-optic effect in iodine-doped cis-1,4-polyisoprene was first reported in *Macromolecules* in 2004 (4). A Kerr coefficient as large as 66 times that of the standard Kerr material, nitrobenzene was measured at 633 nm. The corresponding value of the nonlinear refractive index is significantly larger than that of conjugated polymers. It is important to note that the nonlinear optical susceptibility ($\chi^{(3)}$) of a conjugated polymer (e.g., polythiophene) deceases upon doping (19) since the material transforms into a metallic state which does not support significant polarization. For nonconjugated conductive polymers, the nonlinearity is too small to measure in the undoped state, while the nonlinearity becomes exceptionally large after doping with iodine. This exceptional magnitude has been attributed to the subnanometer confinement of the charge system in a radical cation in a doped nonconjugated conductive polymer. In the present report, our recent findings on nonlinear optical effects in two new nonconjugated conductive polymers will be discussed.

2.2 Quadratic Electro-optic Effect in the New Nonconjugated Conductive Polymer, Iodine-Doped Poly(β-pinene)

Exceptionally large quadratic electro-optic effect has been observed in the nonconjugated conductive polymer, poly(β-pinene) upon doping with iodine. A thin film (thickness $\sim$500 nm) of poly(β-pinene) was cast on a glass slide from a toluene solution. The film was then doped with iodine to form the nano-optical film via localized charge-transfer (Fig. 1). The electro-optic measurement was performed on a doped film for different molar concentrations of iodine. Upon higher doping the film turns dark in color. The absorption spectra of the thin film for different doping levels are shown in Figure 2. The electrical conductivity increased about twelve orders of magnitude upon doping and saturated at about 0.008 S/cm at a dopant molar concentration of about 0.8. Metal electrodes with a gap ($\sim$100
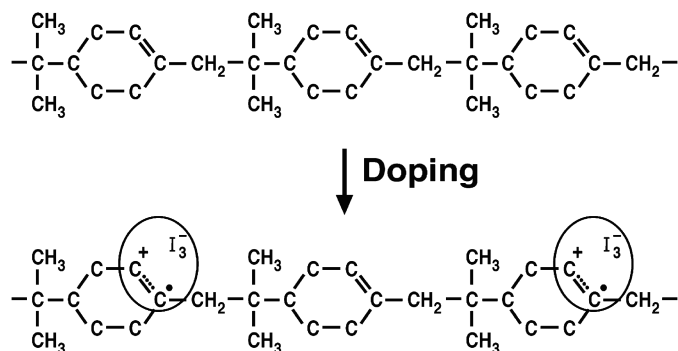
Fig. 1. Molecular structure of poly(β-pinene); doping and charge-transfer to form localized radical cations.

Fig. 3. The quadratic electro-optic modulation signal of doped poly(β-pinene) film. The waveform above is modulation signal; the waveform below corresponds to applied voltage.

microns) were placed on the film for making the electro-optic measurements.

A He–Ne laser (wavelength 633 nm) was used in this measurement. The experiment was performed using field induced birefringence method. The laser beam was polarized at an angle of 45 degrees (using the polarizer) with respect to the electric field and passed through the doped film. The transmitted beam was passed through an analyzer which was cross-polarized with respect to the polarizer and the final beam was collected on a photo-detector. A lock-in amplifier (with 2f synchronization) and an oscilloscope were used to record the modulation signal. The modulation signal was recorded for various applied ac electric fields and was found to depend quadratically on the applied voltage.

An example of the quadratic electro-optic modulation signal is shown in Figure 3 for an applied ac field of 1.25 V/μm. The top waveform is the modulation signal and the bottom waveform corresponds to the applied voltage. The thickness of the doped film is about 1 μm. The Kerr coefficient as determined from the observed modulation depth is 1.2×10^{-10} m/V^2 which was 50 times that

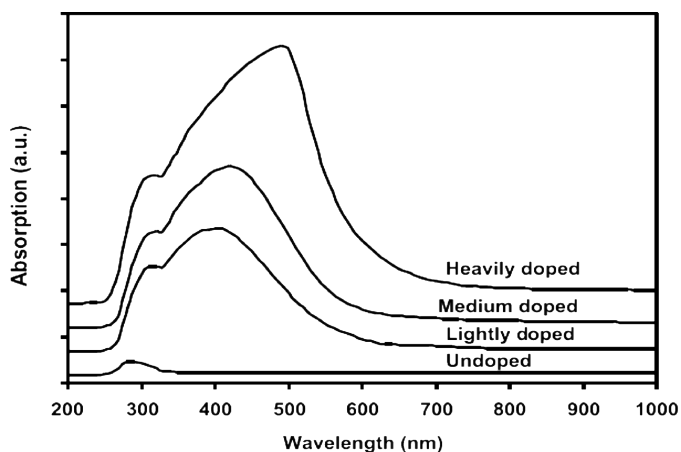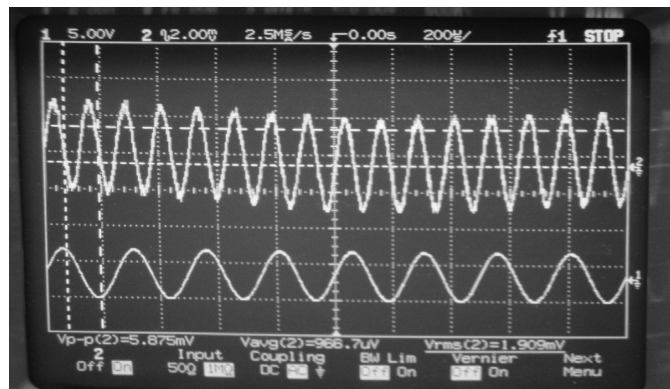of nitrobenzene. Recently, higher Kerr coefficient has been obtained via improvement of film quality of these materials.

2.3 Quadratic Electro-Optic Effect in the New Nonconjugated Conductive Polymer, Iodine-Doped Poly(ethylene-pyrrolediyl) Derivative

Other novel nonconjugated conductive polymer investigated for quadratic electro-optics includes a poly(ethylene-pyrrolediyl) derivative. The molecular structure of the poly(ethylenepyrrolediyl) derivative with butyl side-group is shown in Figure 4.

Electrical and optical measurements for poly (ethylenepyrrolediyl) derivative with a butyl side group have been carried out. The poly(ethylenepyrrolediyl) derivative of the type (R = n-butyl) was dissolved in chloroform to prepare a solution of 5×10^{-3} M concentration. A thin film of this solution was cast on a glass slide. The film was about 0.3 microns in thickness. Upon doping with iodine, the film became dark in color. Using the four-probe method the maximum electrical conductivity of the doped film was found to be $\sim 1.5 \times 10^{-2}$ S/cm. The conductivity is lower than that of doped polyisoprene because of a smaller double-bond number fraction. The large side-group (butyl, Fig. 4) reduces the double-bond number fraction in the polymer repeat.

The optical absorption spectra of poly(ethylenepyrrolediyl) derivative film for different doping levels of iodine
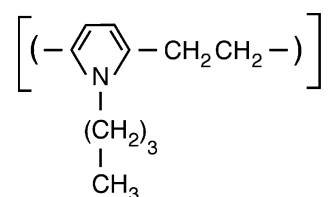

Fig. 2. Optical absorption spectra of poly(β-pinene) for different doping levels.

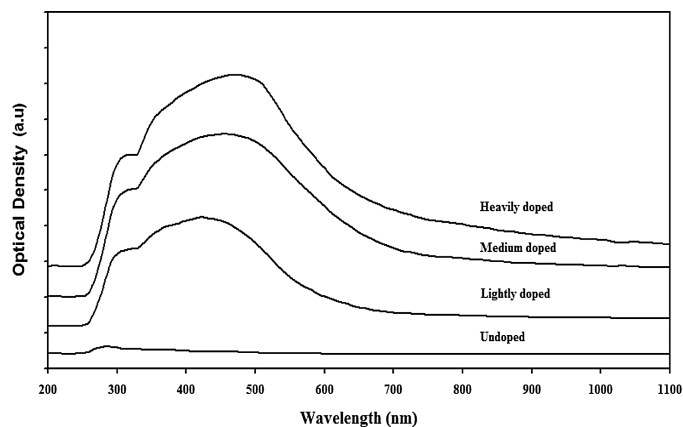**Fig. 4.** The molecular structure of poly(ethylene-pyrrolediyl) derivative.

Fig. 5. Optical absorption spectra of poly(ethylene-pyrrolediyl) derivative for different doping levels of iodine.
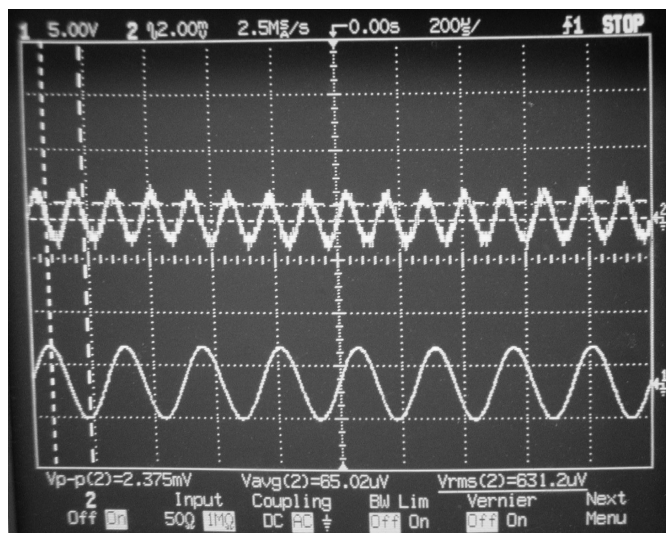

Fig. 6. The quadratic electro-optic modulation signal of doped poly(ethylene-pyrrolediyl) derivative film. The waveform above is modulation signal; the waveform below corresponds to applied voltage.

are shown in Figure 5. In the undoped state, the absorption is negligible in the visible domain, except for a very small peak at 280 nm. For a lightly doped film, two peaks: at 310 nm (4.0eV) and 420nm (2.95 eV) were observed. The first peak at 4.0eV has been attributed to the radical cation and the second peak at 2.95eV has been attributed to charge-transfer between the double-bond and the acceptor. As the level of doping increases the overall absorption increases and the peak at 2.95 eV experiences a red shift, thus covering the entire visible spectrum. The absorption peaks in the present polymer appeared at slightly lower energies compared to doped 1,4-cis-polyisoprene.

For quadratic electro-optic measurements, a thin film of the polymer was cast on a glass slide. The film was about 0.3 microns in thickness and was doped with iodine to medium level. Metal electrodes with a gap were applied on this glass slide containing the thin film of doped poly(ethylenepyrrolediyl) derivative to apply electric field. The method of measurement included field-induced birefringence in the cross-polarized geometry. In short, the laser beam with polarization at 45° with respect to the applied electric field was passed through the sample. After passing through an analyzer the beam was detected with a photodiode and recorded on an oscilloscope for various ac fields. A He-Ne laser operating at a wavelength of 633 nm was used for the experiment. The signal as obtained for a field of 1 V/μm is shown in Figure 6. The lower waveform represents the applied ac field at 4 kHz. The modulation shown in the waveform above is due to the quadratic electro-optic effect in the doped poly(ethylenepyrrolediyl) derivative film. The modulation signal was also recorded using a lock-in amplifier (with 2f synchronization). The signal increased quadratically with the applied voltage. A modulation of 0.1% was observed for a field of 0.66 V/μm and the film thickness was 0.3 μm. The magnitude of the Kerr coefficient was found to be exceptionally large, about 1.2×10^{-9} m/V^2. A larger value of the Kerr coefficient as compared to doped 1,4-cis-polyisoprene is because

the wavelength of measurement, 633 nm is closer to resonance in this polymer compared to that of doped 1,4-cis-polyisoprene. The quadratic electro-optic effects as measured in these materials are significantly larger than that of conjugated polymers such as polyacetylene. Electroabsorption measurement was performed by excluding the analyzer from the above experimental setup. Maximum electroabsorption was obtained when the input beam polarization was parallel to the applied ac electric field. The maximum electroabsorption modulation obtained was 0.05% for an ac electric field of 0.66 V/μm in this film.

2.4 Two-Photon Absorption in Iodine-Doped Poly(β-pinene)

The polymer discussed in this report is poly(β-pinene). The molecular structure, electrical conductivity and optical absorption spectra of poly(β-pinene) have been discussed in an earlier section. Also, as discussed earlier, quadratic electro-optic effect in doped poly(β-pinene) has been measured at 633 nm and exceptionally large Kerr coefficient has been observed. In this section, the two-photon absorption coefficient (α_2) which is proportional to the imaginary part of $\chi^{(3)}$, measured at a specific range of wavelengths, is discussed. As it will be shown, the results are similar in many respects to that of metallic quantum dots.

Poly(β-pinene) pellets purchased from Aldrich Chemicals Corporation were dissolved in toluene. Using this solution, thin films (thickness ~1.5 μm) of poly(β-pinene) were cast on quartz substrates. The samples initially colorless, when exposed to iodine become darker as the doping level is increased.

The optical absorption spectra of poly(β-pinene) as a function of iodine doping are shown in Figure 2. The undoped film of poly(β-pinene) shows a weak peak at 280 nm. And as the doping level increases, two peaks begin to be evident; one appearing at 310 nm (4 eV) and the other at 400 nm (3.1 eV). The peak at 4 eV has been attributed to the radical cation that is formed upon doping. The peak at 3.1 eV has been attributed to the charge transfer that occurs between the double bond and the dopant. The FTIR spectroscopic studies for an undoped sample show peaks at 728 cm^{-1} and 1610 cm^{-1} corresponding to =C-H bending and C=C stretching modes respectively. The intensities of these peaks are reduced as the polymer is doped with iodine indicating formation of the radical cations upon charge transfer from the double bond to iodine. The production of radicals upon doping has been confirmed by electron paramagnetic resonance (EPR) experiments (9).

In order to measure the two-photon absorption coefficient of doped poly(β-pinene), the z-scan technique without an aperture was used. The measurement was made using 150 fs pulses from a Ti:Sapphire laser over the wavelength range of 730–860 nm. The laser beam was passed through an attenuator to control the input power of the beam. The beam was then focused using an objective lens (5×). The sample mounted on a motorized X-Y stage, with a precision of 0.1 micron, was moved through the focus along the beam propagation direction (z-axis). The output power was measured as a function of the sample position (z). Data were recorded for continuous wave (cw) and in modelocked (pulsing) conditions to separate any effect of scattering.

Using a modelocked laser beam with 150fs pulses clear z-scan data were observed and recorded for various wavelengths. In the continuous wave (cw) condition only noise signal was observed indicating no two-photon absorption. As stated earlier, two-photon absorption is given by, $\Delta\alpha = \alpha_2 I$, where $\Delta\alpha$ is the increase in the linear absorption coefficient, α_2 is the two-photon absorption coefficient and I is the peak intensity. From the z-scan data, the magnitude of the two-photon absorption coefficient was determined over the wavelength range of 730–860 nm (Fig. 7). The maximum two-photon absorption coefficient (α_2) was obtained at about 1.53 eV (810 nm) with a magnitude of about 2.6 cm/MW. The maximum is near half of the optical gap (3.1 eV) corresponding to charge-transfer in doped poly(β-pinene). An additional peak was observed at about 1.46 eV (850 nm). The peak at 1.46 eV may be due to electron-phonon interaction involving a phonon band of the charge-transfer complex. The magnitude of α_2 as obtained is comparable to or higher than that of semiconductor and metallic quantum dots [1–6]. The magnitude of α_2 depends on the dopant concentration since the linear absorption spectrum changes with dopant concentration. In this report, results for medium-doped poly(β-pinene) are discussed. The large α_2 in this polymer has been attributed to the special structure of this electronic system confined within a sub-nanometer dimension. As is well known, the size of the quantum dots is the major factor that determines the magnitude and response time of the nonlinearities. The ultrashort laser pulses (150 fs) used in the measurements reported here probe only the electronic or the fast effect.

3 Results and Discussion

3.1 Mechanisms of the Nonlinear Optical Effects in These Novel Systems

As discussed earlier, the magnitudes of the nonlinear optical effect (Kerr coefficient and two-photon absorption coefficient) in these novel polymeric nonlinear optical materials are exceptionally large, in some respects, the largest known. The magnitudes of the third order susceptibilities ($\chi^{(3)}$) as estimated from the Kerr coefficients are similar to that of metal quantum dots (e.g. copper quantum dots in silica and gold quantum dots in alumina) (17, 18). The electrical conductivities of doped nonconjugated polymers are similar to that of indium nanoparticles. The optical absorption band of doped nonconjugated polymers are at a shorter wavelength compared to those of the smaller ($\sim$5 nm) quantum dots of metals (19). This indicates the size of the quantum dots in doped nonconjugated conductive polymers is less than the smallest known metallic quantum dots. In fact based on the known bond length of C=C the dot size in the present system is less than 1 nm (Fig. 8). The absorption band in metallic quantum dots is because of surface plasmon resonance.

Considering all these, the nonlinear optics in quantum dots of nonconjugated conductive polymers can be explained using the known theory of metallic quantum dots. As has been reported, the local field in a metallic quantum dot system is substantially enhanced due to surface
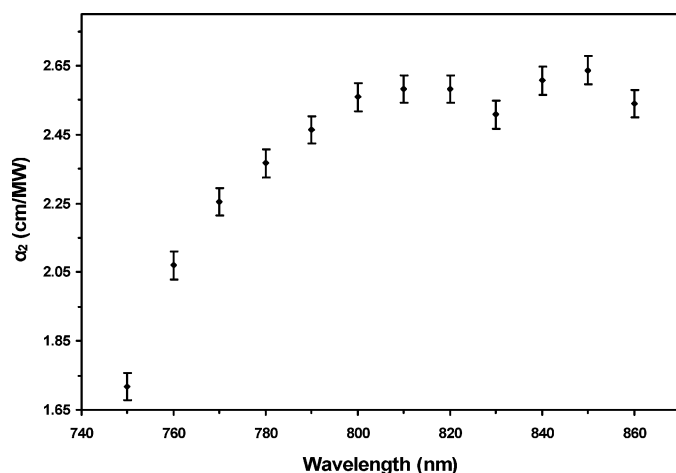

Fig. 7. Two-photon absorption coefficient (α_2) in doped poly(β-pinene) as a function of wavelength.
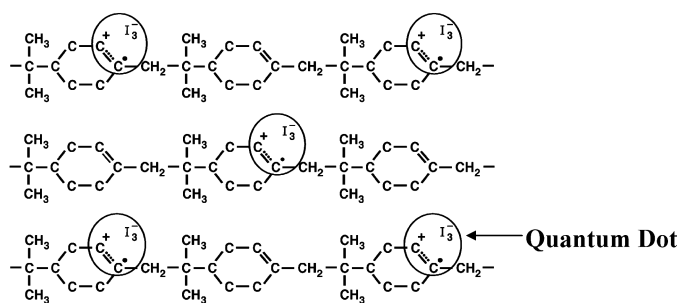
Organic Quantum Dots (Nanometallic)

Fig. 8. Quantum dots (encircled regions) of sub-nanometer dimension formed upon doping and charge-transfer involving isolated double bonds in poly(β-pinene).

plasmon resonance. In the case of a third order optical process, the $\chi^{(3)}$ of a metallic quantum dot increases by this enhancement factor or local field factor to the power four, $(f_L)^4$. The local field factor is given by, $f_L(\omega) = \frac{3\varepsilon_d}{\varepsilon(\omega)+2\varepsilon_d}$ where ε_d is the dielectric constant of the surrounding dielectric medium, $\varepsilon(\omega)$ is the dielectric constant of the metal quantum dot. Thus, the surface plasmon resonance condition involves the denominator of the local field factor becoming equal to zero. This fourth-power enhancement in the local field is the major reason for the enhancement of $\chi^{(3)}$ of metal quantum dots. In addition, considering the intraband transitions in a metal quantum dot, the magnitude of $\chi^{(3)}$ is proportional to d^{-3} where d is the diameter of the quantum dot. Therefore, the exceptionally large $\chi^{(3)}$ in the quantum dots of doped nonconjugated conductive polymers can be explained using these mechanisms that benefit from the unusually small dot size (<1 nm) and large local fields.

4 Conclusions

Exceptionally large third order optical nonlinearities have been measured in doped nonconjugated conductive polymers. These systems are modeled as sub-nanometer size metallic quantum dots to explain such large nonlinearities. As previously reported, the third order susceptibility of conjugated polymer decreases upon doping due to transition to a metallic state (20). In contrast, for a nonconjugated conductive polymer, the third order susceptibility increases many orders of magnitude upon doping due to the transition to this nanometallic/quantum dot structure.

More detailed studies of these novel and unique nonlinear optical material systems are necessary for more quantitative understanding of the mechanisms involved. These materials open up tremendous opportunities for research and significant technological applications in photonics.

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