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Quadratic Electrooptic Effect in a Nonconjugated Conductive Polymer

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Nonlinear optical properties of organic crystals and polymers have received significant research attention in view of a wide range of applications in photonics. Conjugated polymers such as polydiacetylenes are known to possess exceptionally large off-resonant third-order optical susceptibilities along with an ultrafast response.[1−4] These large susceptibilities are primarily due to delocalization of π-electrons along the conjugated chain (quantum wire). Organic molecular crystals and single-crystal films of organic salts have the largest known second-order susceptibilities.

In contrast to conjugated polymers, nonconjugated polymers with isolated double bonds do not have delocalized electrons and are usually not expected to display significant nonlinear optical effects. In this Communication, we will present results to show that specific nonconjugated polymers upon doping show exceptionally large quadratic electrooptic effect or third-order optical susceptibility.

Nonconjugated conductive polymers were previously discussed in detail.[5−10] The electrical conductivity of *cis*-1,4-polyisoprene (natural rubber) increases 100 billion times upon doping with iodine. This increase is due to transfer of an electron from the isolated double bond to iodine, thus forming a hole or a positive charge on the double-bond site. This hole then leads to electrical conduction via intersite hopping. A nonconjugated conductive polymer does not have extended delocalization; the hole is loosely bound to the dopant counterion (acceptor). An applied electric field may influence the movement of the hole without dissociating it from the counterion, thus leading to a large quadratic electrooptic effect.

The nonconjugated conductive polymer that was investigated in this work includes *cis*-1,4-polyisoprene or natural rubber. The results discussed here can be extended to all other nonconjugated conductive polymers as well since nonconjugated conductive polymers are all soluble and readily processable and have isolated double bonds.

cis-1,4-Polyisoprene or natural rubber samples were obtained in the form of latex from Firestone Inc. Evaporation of water from a latex sample led to solid natural rubber. The rubber was dissolved in hexane to prepare a solution. Gold electrodes with a gap of approximately 100 μm were deposited on a glass slide. Then a thin film of natural rubber was cast on the electrodes on the glass slide from the hexane solution. The film was about 2 μm in thickness. Upon doping with iodine, the film became dark in color. The absorption spectra of the polymer film for different doping levels are given in Figure 1 (from ref 6).

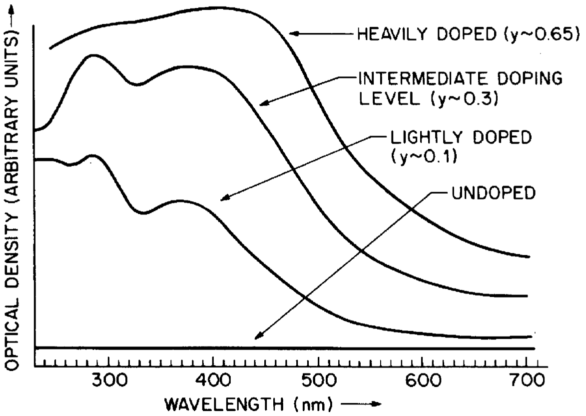

Figure 1. Optical absorption spectra of *cis*-1,4-polyisoprene (natural rubber) for different molar concentrations (y) of iodine (from ref 6).

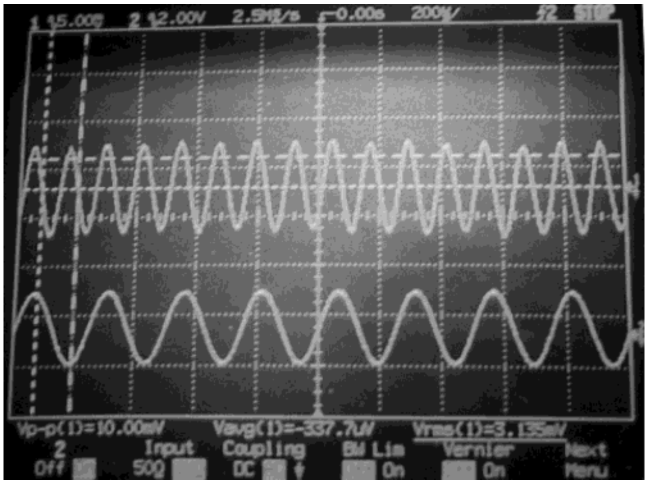

Figure 2. Oscilloscope trace of the modulation signal in quadratic electrooptic measurement of doped *cis*-1,4-polyisoprene. The waveform at the bottom represents the applied voltage at 4 kHz. The waveform above corresponds to the quadratic electrooptic modulation signal.

The doped film was studied for nonlinear optical properties with electric field applied across the gold electrodes. A helium−neon laser with wavelength at 633 nm was used for the experiment. The method of measurement included field-induced birefringence in the cross-polarized geometry. This method has been discussed in other reports. 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. The modulation signal was recorded on the oscilloscope for various applied ac fields. The signal as obtained for a field of 1 V/μm is shown in Figure 2. The lower waveform represents the applied ac field at 4 kHz. The modulation shown in the waveform above (Figure 2) is due to the quadratic electrooptic effect in the doped polyisoprene 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 0.8% was observed for a field of 2.0 V/μm, and the film thickness was 2 μm. The magnitude of the quadratic electrooptic effect is exceptionally large. The change in refractive index, Δn, is 4.0×10^{-4} at a field of 2.0 V/μm. The Kerr constant as determined is about 1.6×10^{-10} m/V^2. For comparison, the Kerr constant of nitrobenzene at 589 nm is 2.4×10^{-12} m/V^2. The Kerr

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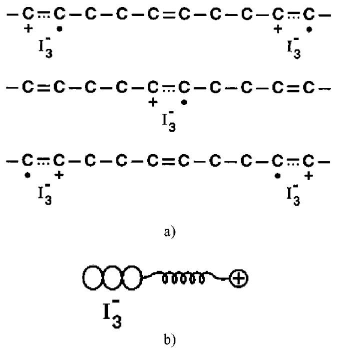

Figure 3. (a) Schematic of the structure of doped *cis*-1,4-polyisoprene. A hole (positive charge) is created at the isolated double bond upon transfer of an electron from the double bond to the dopant (iodine). (b) Schematic of the spring−mass system involving a hole loosely bound to the dopant ion (I_3^-).

constant was determined using the equation $K = (\Delta n)/(\lambda E^2)$, where Δn is the change in refractive index caused by the applied field, λ is the wavelength, and E is the electric field. The quadratic electrooptic effect as measured in this material is significantly larger than that of polyacetylene at a wavelength with a similar detuning with respect to the absorption maximum.[1,4]

As reported earlier, doped polyisoprene absorbs strongly over the wavelength range of 250−625 nm (Figure 1). At an intermediate doping level (iodine molar concentration ∼0.3), the lower energy peak appears at 400 nm. At high doping (iodine molar concentration ∼0.7), the film becomes dark and absorbs throughout the visible. The experiments performed here involved films with doping levels in the intermediate to high range (molar concentration of 0.3−0.8). The wavelength used (633 nm) was away from the absorption maximum (400−450 nm).

The measured large quadratic electrooptic effect has been attributed to the hole (positive charge) loosely bound to the acceptor molecule (I_3^-) (Figure 3) in the doped film. The formation of I_3^- upon doping has been shown earlier.[11] The loosely bound positive charge can be modeled as a spring−mass system with a quartic term in the potential energy (Figure 3b). As is well-known, the quadratic and cubic terms in the harmonic oscillator potential energy lead to the first-order and second-order optical susceptibilities, respectively. The quartic term leads to the third-order optical susceptibility or the quadratic electrooptic effect. The contribution of the quartic term for a loose spring can be significant, leading to exceptionally large third-order optical effects in this system. The material being isotropic, the cubic term is not present, and therefore it does not display a second-order optical or linear electrooptic effect. The third-order optical or the quadratic electrooptic effect is large because of the higher magnitude of the quartic term and also due to the confinement of the charge within a small volume (nanometer scale). Such effects may not be observed in doped conjugated polymers since in that case the materials are significantly more conductive after doping, and the high conductivity leads to rapid movement of the holes away from the counterions upon application of an electric field. Our attempt to make a measurement on a doped polypyrrole film (Sigma-Aldrich Chemical) was not successful since an electric field could not be supported within the gap (was shorted due to higher conductivity). As was previously shown, the third-order optical susceptibility of conjugated polymers (e.g., polythiophene) decreases upon doping. For nonconjugated systems, we observe the opposite effect.

In summary, the quadratic electrooptic effect has been measured in the nonconjugated conductive polymer, *cis*-1,4-polyisoprene, after doping with iodine. The measurement was made with ac field at 4 kHz and using the field-induced birefringence method. An exceptionally large quadratic electrooptic effect (about 66 times that of nitrobenzene) was observed at 633 nm. This effect has been attributed to the loosely bound hole (positive charge) created at the isolated double bond of polyisoprene upon doping with iodine.

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