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The Third-Order Nonlinear Optical-Property of Free-Standing Polythiophene Film

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Conductive ploythiophene (PT) film syntheses are performed in a one-compartment cell, stainless steel sheets are employed as working electrode and counter electrode, then the free standing ploythiophene is obtained. The third-order nonlinear optical property of this free-standing PT film is determined using the degenerate four wave mixing (DFWM) method.

Keywords: ploythiophene; free-standing film; third-order nonlinear optical susceptibility

INTRODUCTION

During the last 10 years electrically conducting polymers have received a great deal of attention due to their conjugated π-electron backbone structure, which is a prerequisite both for charge-transport and non-linear-optical properties. Among the numerous conducting polymers, ploythiophene (PT) has attracted much interest for its both oxygen and moisture stability.[1-2] The quality of the conductive polymer film prepared by electrochemical methods depends strongly on various experimental parameters, such as the properties of the substrate, the solvent, the applied potential and the concentration of the monomer. Conventionally conductive PT films are prepared by the electrochemical polymerization of thiophene in an organic solvent such as acetonitrile, nitromethane, nitrobenzene, or propylene carbonate above 1.6V vs. SCE [3], which irreversibly damages the conjugate system due to overoxida-tion and the gained polymers are brittle and have low mechanical strengths. Furthermore, these materials are insoluble and intract-able or decomposed before melting. Therefore conventional polymer-processing techniques can not be used in shaping these materials into a desired structure. Here we use stainless steel sheets as working electrode and counter electrode, BF_3-ethyl ether (BFEE, solvated strong

Lewis acid) as supporting electrolyte, the electrooxidation of thiophene is carried out at low potentials, then free standing PT film is obtained. These films have good mechanic qualities and high average effective mean conjugation length. [4-6]

In the π-conjugated polymers, π-electrons are delocalized along the backbone, providing high electronic nonlinearly. The nonlinear proper-ties are associated mainly with the length of the conjugate backbone. PT is among the π-conjugated poly-mers with highest nonlinear optical coefficients. We determine the χ^3 of the free-standing PT film using the degenerate four wave mixing (DFWM) at 532 nm, which was larger than the thiophene oligomers .[7]

EXPERIMENTAL

Electrochemical Polymerization:

PT is formed following the method as in references 4-6. Polymerization is performed in a one-compartment three electrode cell using an EG&G model 273 potentiostat and comput-er control (Princeton Applied Re-search) with a 30mM thiophene in BFEE. Stainless steel sheets (1×2.7 cm^2) are used as working electrode and counter electrode, which are polished with abrasive paper (1200 mesh) and diamond paste (1.5 μ m), and are cleaned in an ultrasonic acetonic bath before use. The galvanostatic method is used for electrochemical polymeri-zation at a current density of 1mA.cm^{-2}, and the thickness of the deposited film is controlled by the amount of charge consumed during film growth. All solutions are deaerated by a dry argon stream and maintained at a slight over-pressure during the experiment. An undoped free standing film can be easily peeled off the electrode by hand.

Third-Order Nonlinear Optical Property:

The sample is investigated by the DFWM method. Details of the experimental setup are shown in Figure 1. The pump source used in the present experiment is the second harmonic of Nd:YAG laser delivering pulse of 35ps at 532nm at a 10Hz repetition rate. The pulse energy is 1.3mJ. Having rectified by two small holes, the laser beam is divided into three beams (k_1, k_2 and k_3) by two semitransparent semi-reflectors B_1 and B_2. The intensities of k_1, k_2 and k_3 are 10 percent of the source laser. After adjusted and focused by a lens with 12.5cm focusing, the incident pulse k_1, k_2 and k_3 reaches the sample at the same time, then conjugate optical signal is recorded. This signal is received by an optical diode, sent to Boxcar and

handled by computer then we get the value of χ^3. [8-9]

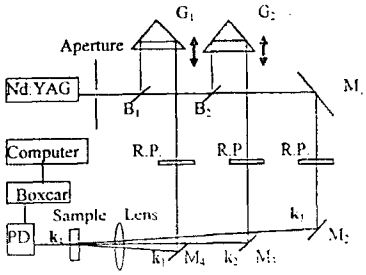

FIGURE 1 Experimental setup for degenerate four -wave mixing R.P.-rotational polariscope

RESULTS AND DISCUSSION

Compared with the films polymer-ized conventionally, the degree of the free standing films got in this method is about 80 in contrast with about 40 in common media and the average effective mean conjugation length is rather high. PT can be de-posited onto the electrode more regularly and compactly. The result-ing film is in high anisotropy and compactly morphology. This free standing PT film has a conductivity of 48.7 siemeses per centimeter, its tensile strength (1200 to 1300 kilo-grams per square centimeter) is greater than that of aluminum (1000 to 1100 kilograms per square centi-meter). It behaves like a metal sheet and can be easily cut into various structures with knife or a pair of scissors.

In our research, in order to determine the third-order nonlinear coefficient, we compare the signals of CS_2 and the free standing PT film and use the following equation:

$$\chi^3 = \left(\frac{I_+}{I_r}\right)^{1/2}\left(\frac{L_+}{L}\right)\left(\frac{n}{n_r}\right)^2\left[\frac{\alpha L \exp(\alpha l/2)}{1-\exp(-\alpha L)}\right]\chi_r^3$$

Where α is the adsorption coefficient of the investigated sample; n is the index of refraction of the sample; L is the thickness of the sample; the subscript r repre-sents CS_2. DFWM signals change with delay time of k_1 as shown in Figure 2.

χ^3 of the free standing PT film at 532nm is larger than 4.5×10^{-10} esu., the response time is less than 35ps limited by the pulse duration of the laser. χ^3 of the free standing PT film is little smaller than that of PT film prepared

conveniently (~10^{-9} esu.) but more larger than the thio-phene oligomers (10^{-13}esu.) because of the high average effective mean conjugation length. This fit the index law, $\chi^3 \sim N^b$, N is the number of double bond, b is a constant. When N=2~16, b can be 6~3.5; when N is very large then b tends to 1.[10-13]

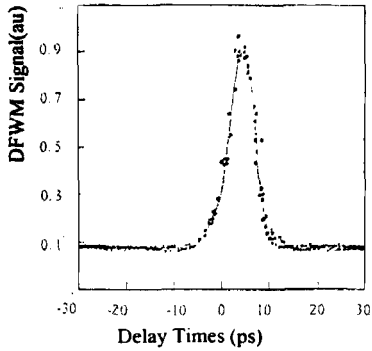

FIGURE 2 The time resolved forward DFWM signal
Dot: DFWM signal for PT; Line: Gaussian fitted results for PT

In summary, PT films deposited onto stainless steel in BFEE solution at low poten-tials display excellent mechanical properties, high χ^3 and fast time response. Those are very important for applications.

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