



Third-order optical susceptibility in polythiophene thin films prepared by spin-coating from high-boiling-point solvents

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ABSTRACT

We examined the enhancements in the third-order optical susceptibility ($\chi^{(3)}$) of spin-coated thin films of poly(3-hexylthiophene) using an anhydrous solvent with a high boiling point. The $\chi^{(3)}$ value was found to be enhanced as the boiling point of the solvent increased. In this study, the largest value of $\chi^{(3)}$ was obtained for thin films that were spin-coated in an inert atmosphere using anhydrous dichlorobenzene and then was subsequently exposed to its vapor for 1 h. The maximum value of the imaginary part of $\chi^{(3)}$ was determined to be 1.8×10^{-9} esu, which is more than three times greater than that of thin films spin-coated in an ambient atmosphere using a solvent with a low boiling point, such as chloroform.

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1. Introduction

π -conjugated polymers have been extensively studied as materials for nonlinear optical devices because of their large third-order optical susceptibility ($\chi^{(3)}$), ultrafast response, [1] and solution processability [2]. Many theoretical and experimental studies [3–7] have revealed that the following relationship exists between the achievable largest $\chi^{(3)}$ value of a π -conjugated polymer and its optical gap energy (E_g): $\chi^{(3)} \propto E_g^{-6}$. This -6 power law suggests that π -conjugated polymers with lower E_g 's, such as polythiophene and its derivatives (PTs), have the potential to exhibit larger $\chi^{(3)}$ values. However, in literature, [8] the reported $\chi^{(3)}$ values of PTs were significantly lower than the $\chi^{(3)}$ values expected on the basis of their E_g 's. These lower-than-expected $\chi^{(3)}$ values are caused primarily by torsions and bends of the main chains, [9,10] which occur in disordered regions of thin films and reduce the coherence length of excitons (i.e., the effective conjugation length). The $\chi^{(3)}$ values may also be degraded by oxygen and water in a solvent or in an ambient atmosphere in the case of π -conjugated polymers with low air stability, such as PTs [8].

Recently, we demonstrated that a $\chi^{(3)}$ value expected from the E_g of PTs could be achieved with poly(3-hexylthiophene) (P3HT) when its thin films were fabricated in an inert atmosphere using an

anhydrous solvent onto quartz substrates; adsorbed water was preliminarily removed from the substrates by baking them at 100 °C in a vacuum chamber [8]. In the experiments, we used the drop-casting technique to prepare thin films instead of the widely used spin-coating technique. In the drop-casting technique, a solution is naturally dried on substrates. Consequently, the P3HT chains have more time to self-organize into a well-ordered π – π stacking structure, where P3HT chains adopt more planar conformations; [11–13] thus, the effective conjugation length is elongated. Therefore, a larger $\chi^{(3)}$ value is obtained more easily with the drop-casting technique than with the spin-coating technique. However, the baking process reduces the surface energy of the quartz substrates, and the resultant poor wettability makes the fabrication of flat, homogeneous thin films with the drop-casting technique difficult (see Fig. 1). For the use of P3HT thin films for nonlinear optical devices, the homogeneity of film is also essential and must be achieved.

On the basis of our experience, homogeneous thin films are difficult to deposit onto baked quartz substrates using the drop-casting technique. Thus, in this study, we employed the spin-coating technique and examined how to enhance the $\chi^{(3)}$ values of spin-coated thin films. In the research field of organic field-effect transistors, a solvent with a high boiling point is often used to obtain ordered spin-coated thin films [14]. Because high-boiling-point solvents evaporate slowly even in the spin-coating technique, an effect similar to that observed with the drop-casting technique can be expected. Vapor treatment is also known to improve the crystallinity of small molecules [15] and to change the polymer conformations into more planar ones [16,17]. The advantage of the latter technique is that it is applicable to fabricated thin films. Thus, the vapor treatment can be performed on thin films that have been spin-coated using a

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Fig. 1. (Color online) Photographs of P3HT (left) spin-coated and (right) drop-cast thin films fabricated in a dry N_2 atmosphere onto quartz substrates that were preliminarily baked to remove adsorbed water.

high-boiling-point solvent. Here we report that a combination of these techniques indeed allowed us to prepare homogeneous thin films with a $\chi^{(3)}$ value close to the largest value expected based on its E_g .

2. Experimental details

As a solvent, we examined chloroform, toluene, and dichlorobenzene, whose boiling points are 61, 110, and 180 °C, respectively. For clarity, we mainly present here the results obtained using chloroform and dichlorobenzene; thin films spin-coated using toluene exhibited properties intermediate between those of the films prepared using the other two solvents. Solvents and P3HT (Rieke Metals, Sepiolid P200, >98% regioregularity) were used as received. Thin films were fabricated by being spin-coated or drop-cast using solutions; the concentrations of the solutions were adjusted so that the thickness of the films was approximately 100 nm. Some spin-coated thin films were exposed to anhydrous solvent vapor for 1 h (vapor treatment). All thin films were subsequently annealed at 100 °C in a vacuum chamber to remove residual solvent. All procedures were performed in a glove box filled with N_2 gas, and the thin films were encapsulated with epoxy before they were removed from the glove box unless otherwise noted. In this study, we determined $\chi^{(3)}$ values using electroabsorption (EA) measurements. For the EA measurements, we prepared quartz substrates, on which interdigitated Al electrodes with 20- μm gaps were photolithographically fabricated. As previously mentioned, these substrates were baked at 100 °C in a vacuum chamber in the glove box before they were used for the spin-coating or drop-casting techniques. The EA measurements were performed at 10 K using a homemade setup [18–20]. The imaginary (Im) and real parts of the $\chi^{(3)}$ spectra were calculated using the Kramers-Kronig transformation (see Ref. [21] for details of the required equations).

3. Results and discussion

Fig. 2(a) shows the absorption spectra of drop-cast and spin-coated thin films fabricated using chloroform. Although chloroform evaporates quickly because of its high vapor pressure, its evaporation rate is accelerated in the spin-coating technique. Thus, the obtained thin films contained a large amount of disordered regions. Twists and bends of the main chains that occur in disordered regions limit the effective conjugation lengths to lengths much shorter than the actual chain length and then disperse the oscillator strength over a broad photon-energy range [9,10]. However, in highly ordered thin films fabricated by the drop-casting technique, torsions and bends are suppressed, and the oscillator strength is concentrated in a lower and narrower photon-energy range. This effect explains why the absorption spectra of drop-cast thin films are redshifted and well resolved with respect to those of spin-coated thin films. Fig. 2(b) shows the absorption spectrum of a spin-coated thin film fabricated using

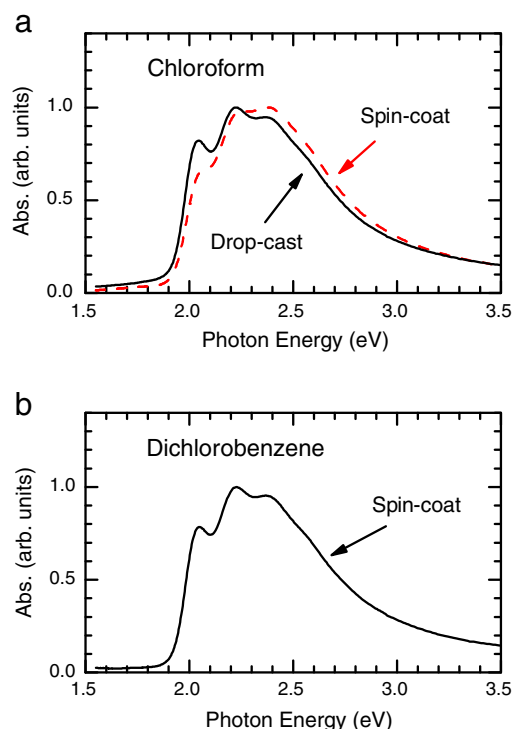


Fig. 2. (Color online) Absorption spectra of P3HT thin films fabricated using (a) chloroform and (b) dichlorobenzene.

dichlorobenzene. The shape of the absorption spectrum is similar to that of thin films drop-cast using chloroform, which indicates that the order of the packing structure of the P3HT chains is significantly improved through the use of dichlorobenzene instead of chloroform. Notably, if the order of the packing structure is improved beyond a certain extent, the narrowing and redshifting of the absorption spectrum become saturated and can no longer be discerned. In contrast, as the order of the packing structure is further improved, the $\chi^{(3)}$ value is enhanced accordingly [9,10]. Thus, the $\chi^{(3)}$ values of the thin films of π -conjugated polymers cannot be estimated from their absorption spectra and have to be directly determined by nonlinear optical spectroscopy.

To determine the $\chi^{(3)}$ values, we measured the EA spectra, some of which are presented in Fig. 3. Their spectral shapes are almost the same, and only their amplitudes vary depending on the fabrication conditions. We first compared the spectra of the thin films prepared using normal (nonanhydrous) dichlorobenzene in an ambient atmosphere with the spectra of those prepared using anhydrous chloroform in an inert atmosphere (the blue curve vs. the red curve in Fig. 3). The former thin films were affected by moisture and oxygen; nevertheless, their EA signals were approximately 40% more intense than those of the latter thin films. This enhancement of the EA signals is caused by the use of a solvent with a high boiling point and can be attributed to an improvement in the ordering of the packing structure. The EA signals were further enhanced by 60% when the thin films were spin-coated using anhydrous dichlorobenzene in an inert atmosphere (the green curve in Fig. 3). However, the amplitudes of these signals were smaller than the largest amplitude obtained for the films prepared using the drop-casting technique [8]. This result suggests that the ordering of the packing structure in the thin films spin-coated using dichlorobenzene is not as extensive as that in the thin films drop-cast using chloroform. To further enhance the EA signal amplitudes of films prepared using the spin-coating technique, we exposed the fabricated thin films to the vapor of a solvent, and thus attained 10% enhancement. The EA spectrum with the greatest intensity was obtained for thin films spin-coated using anhydrous

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