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Nonlinear optical properties of poly(fluorophenyl-diacetylene) evaporated films

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Abstract

A new insoluble polydiacetylene with fluoro-aromatic units directly bound to the π-conjugated main backbone has been obtained via solid-state polymerization induced by UV light, daylight and γ-rays. Third-order harmonic generation has been measured on poly(fluorophenyl-diacetylene) films prepared by the vacuum deposition method. The third-order nonlinear optical susceptibility of this poly(fluorophenyl-diacetylene) film was evaluated as $\chi^{(3)} = 7.3 \times 10^{-11}$ esu.

Keywords: Nonlinear optics; Poly(fluorophenyl-diacetylene); Solid-state polymerization; Optical coefficient susceptibility; Spin-coated films

1. Introduction

The nonlinear optical (NLO) properties of conjugated polymers such as polyacetylenes, polydiacetylenes and poly(*p*-phenylenevinylene) are currently attracting interest due to their large third-order nonlinear optical response $\chi^{(3)}$ and their potential application for nonlinear optics, microlithography, optical memory recording and so forth [1–3]. To date, third-order NLO properties have been extensively studied in various thin films forms of polydiacetylenes, such as shear melt-grown thin crystals [4], Langmuir–Blodgett films [5], solvent-cast films [6,7] and vacuum-deposited films [8–10]. For π-conjugated polymers, $\chi^{(3)}$ is proportional to the fifth power of the number of double bonds [11,12]. In order to obtain large $\chi^{(3)}$ values, several kinds of fluoro-diacetylene monomers for polydiacetylenes with aromatic fluoro rings directly attached to the main chain backbone have been synthesized for nonlinear optical materials [13–15]. From them, the soluble poly(fluorophenyl-diacetylene)s could be obtained by solid-state polymerization [16,17]. Thin films of the soluble poly(fluorophenyl-diacetylene) were prepared by the spin-coating method. The value of the third-order nonlinear optical response is about 6×10^{-11} esu [18]. It is well known that the solid fluoro compounds may be sublimed under vacuum. This property provides a possible method for the formation of thin films by vacuum deposition. In this paper, we would like to report the third-order nonlinear optical properties of vacuum-deposited thin films of poly-{1,4-bis[4-((2,4-dichlorophenyloxy)-2,3,5,6-tetrafluorophenyl]-butadiyne}, PPTFD.

2. Experimental details

The fluoro-diacetylene monomer, 1,4-bis[2,4-dichlorophenyloxy)-2,3,5,6-tetrafluoro-phenyl]butadiyne was synthesized according to a procedure reported previously (as shown in Scheme 1) [14]. Monomer crystals obtained under different recrystallization conditions showed different activities in solid-state polymerization. Monomer crystals obtained from solutions in acetone and water mixtures were the most readily polymerized in the solid state. The crystals changed colour from white to blue under irradiation by daylight.

The first step in the fabrication of the thin film was vacuum deposition of the thin monomer layer (about 0.2 μm thickness obtained using a Dektak IIA surface profiler) on glass or fused silica substrates. It was found that thin films on different substrates showed dramatically different activities in solid-state polymerization. Monomer films on all kinds of substrates, glass or fused silica plates, could be polymerized by γ-ray irradiation to give deep blue polymeric thin films. However, monomer thin films on fused silica plates only exhibited low solid-state polymerization activities towards

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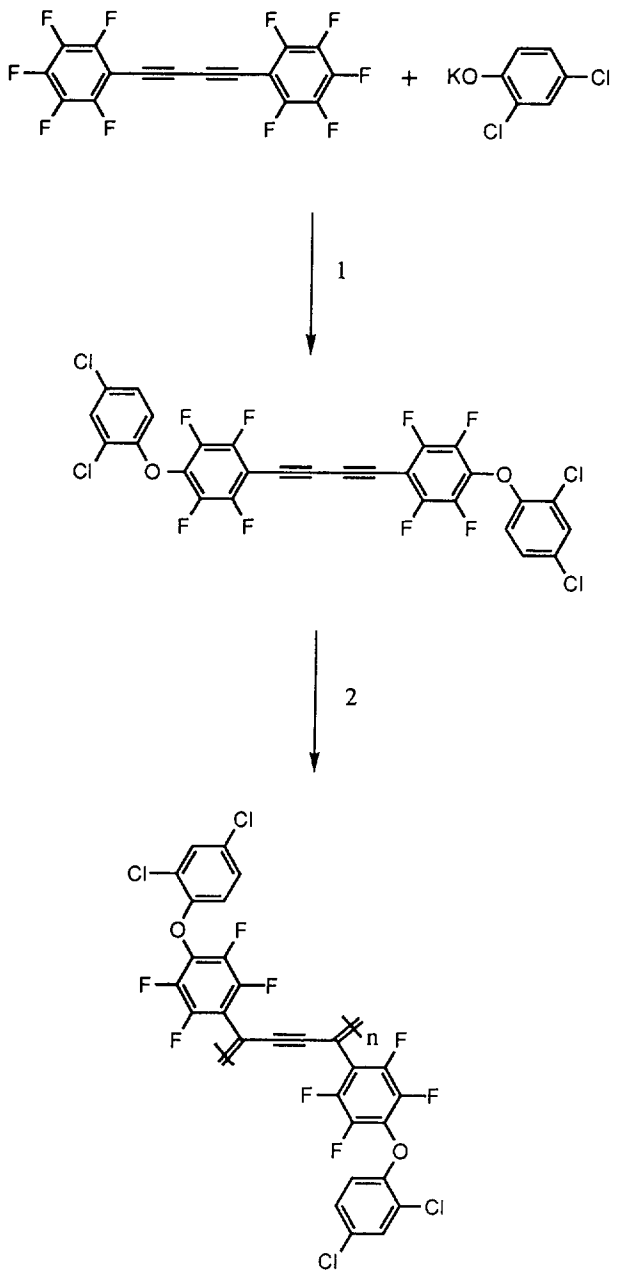

Scheme 1. Reagents and conditions: 1, THF, room temperature; 2, UV, daylight or γ-ray irradiation, room temperature.

UV light and daylight. Only partly polymerized films were obtained in these cases. The monomeric thin films of diacetylene monomer on common glass substrates showed very high polymerization activities in the solid state. Deep blue polymeric thin films could be obtained by UV and daylight irradiation. For daylight irradiation polymerization, the uncovered sample was kept at room temperature for about two months. These results suggest that the packing of monomer crystals can be controlled by the substrates and the vacuum deposition conditions. Detailed research work on the optimization of the vacuum deposition conditions and selection of the substrates is now under way.

3. Results and discussion

Fig. 1 shows the UV–vis absorption spectrum of the thin film of PPTFD obtained by γ-irradiation as measured on a Shimadzu 3100 spectrometer. The other PPTFD thin films obtained by UV and daylight irradiation exhibited similar absorption behavior. This absorption band was due to the extensive π-conjugated backbone in the polymer. The corresponding fluorophenyl-diacetylene monomer did not show any absorption bonds over the 400–800 nm range.

The third-order optical nonlinearities of PPTFD were evaluated by third-harmonic generation (THG) using the standard Maker fringe technique [19]. THG measurements of the PPTFD film were performed at a wavelength of 1.907 μm which was obtained from Q-switched Nd:YAG laser (Spectra-Physics DCR-2A) operating at 1.064 μm wavelength by Stokes shifting though a 1-m Raman cell containing hydrogen gas at 30 atm pressure. The sample of thickness ca. 0.208 μm was mounted on a goniometer and rotated in the vacuum chamber about an axis perpendicular to the laser beam to eliminate the effect of air on THG. The signal intensity of the generated third-harmonic beam (635 nm) was measured as a function of goniometer rotation using a monochromator (Ritsu Oyo Kougaku MC-10N), photomultiplier tube (Hamamatsu R636) and triggered boxcar integrator (Stanford Research System SR245, SR250, SR280). The third-order nonlinear optical coefficient $\chi^{(3)}$ was calculated by comparing the THG signal intensity of sample ($I_{3\omega}$) with that of a standard fused silica plate ($I_{3\omega,s}$) according to Eq. (1) which is applicable when the sample thickness (l) is much smaller than the coherence length (l_c) [19,20]. The interference effect between the PPTFD film and fused silica substrate was calibrated by taking $I_{3\omega}$ form the Maker fringe according to Eq. (2) [19].

$$\chi^{(3)} = \frac{2}{\pi}\chi_s^{(3)}\frac{\sqrt{I_{3\omega}}l_{c,s}}{\sqrt{I_{3\omega,s}}l} \quad (1)$$

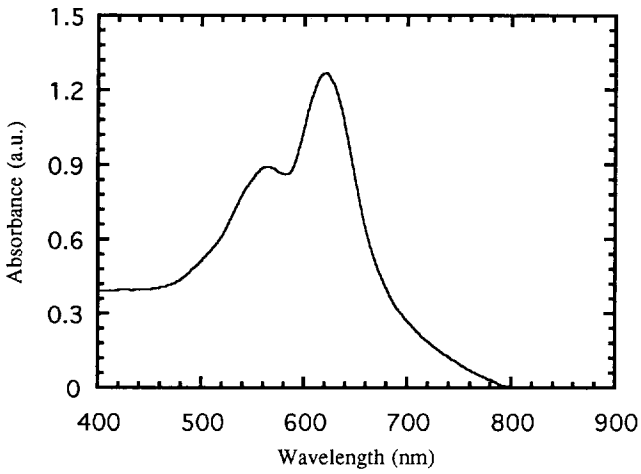

Fig. 1. Absorption spectrum of PPTFD thin film.

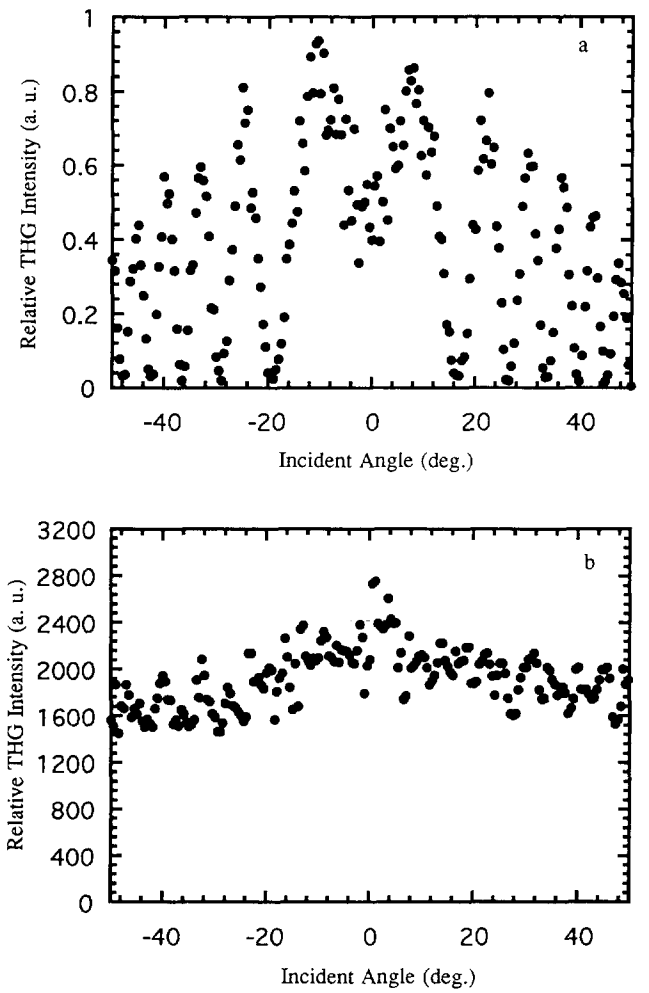

Fig. 2. Maker fringes obtained from the THG experiment at 1.907 μm (a) for the silica reference and (b) for the blue PPTFD film of 0.203 μm thickness.

$$I_{3\omega} = \frac{(I_{3\omega,\max} + I_{3\omega,\min})}{2} - \frac{I_{3\omega,s}}{2} \quad (2)$$

For such calculation, we used a $\chi_s^{(3)}$ value of 2.8×10^{-14} esu for fused silica, as reported by Meredith et al. [21]. The coherence length ($l_{c,s}$) of the 1-mm thick standard fused silica plate was 18.1 μm. Fig. 2 shows the THG Maker fringes of (a) the standard fused silica and (b) the PPTFD film. From these Maker fringe data, $I_{3\omega}$, $I_{3\omega,s}$ could be obtained to enable calculation of the third-order nonlinearity of a 0.203-μm thick film of PPTFD. The third-order nonlinear optical coefficient $\chi^{(3)}$ of PPTFD was evaluated to be about 7.3×10^{-11} esu. The estimated $\chi^{(3)}$ value was a little smaller than the reported value for PTS single crystals (10^{-9}–10^{-10} esu) [22]. This might be caused by a less oriented form of the polymeric thin films. In order to obtain larger values of $\chi^{(3)}$ from PPTFD, further work on highly oriented films of poly(fluorophenyl-diacetylene) obtained by the vacuum deposition is now in progress.

References

[1] G.M. Carter, M.K. Thakur, Y.J. Chen and J.V. Hryniewicz, *Appl. Phys. Lett., 47* (1985) 457.
[2] B.I. Green, J.F. Mueller, J. Orenstein, D.H. Rapkine, S. Schmitt-Rink and M. Thakur, *Phys. Rev. Lett., 61* (1988) 325.
[3] L.R. Dalton, J. Thomson and H.S. Nalwa, *Polymer, 28* (1987) 543.
[4] M. Thakur and S. Meyler, *Macromolecules, 18* (1985) 2341.
[5] F. Kajzar and J. Meissier, *Thin Solid Films, 132* (1986) 11.
[6] S.A. Casalnuovo, K.-C. Lim and A.J. Heeger, *Makromol. Chem., Rapid Commun., 5* (1984) 77.
[7] H. Ohnuma, K. Hasegawa, K. Se and T. Kotaka, *Macromolecules, 18* (1985) 2339.
[8] T. Kanetake, K. Ishikawa, T. Koda, Y. Tokura and K. Takeda, *Appl. Phys. Lett., 51* (1987) 1957.
[9] S. Tomaru, K. Kubodera, T. Kurihara and S. Zembutsu, *Jpn. J. Appl. Phys. Lett., 26* (1987) 1657.
[10] J.L. Moigne, F. Kajzar and A. Thierry, *Macromolecules, 24* (1991) 2622.
[11] J.P. Hermann and J. Ducuing, *J. Appl. Phys., 45* (1974) 5100.
[12] K.C. Rustagi and J. Ducuing, *Opt. Commun., 10* (1974) 258.
[13] Y.D. Zhang and J.X. Wen, *J. Fluorine Chem., 58* (1992) 115.
[14] Y.D. Zhang and J.X. Wen, *J. Fluorine Chem., 51* (1991) 75.
[15] Y.D. Zhang and J.X. Wen, *Synthesis,* (1990) 727.
[16] Y.D. Zhang, Y.Q. Hu and J.X. Wen, *J. Fluorine Chem., 58* (1992) 111.
[17] Y.D. Zhang, T. Wada, H. Sasabe and J.X. Wen, *J. Fluorine Chem., 77* (1996) 27.
[18] Y.D. Zhang, T. Wada, H. Sasabe and J.X. Wen, *J. Fluorine Chem., 77* (1996) 83.
[19] K. Kubodera and T. Kaino, *Springer Proc. Phys., 36* (1989) 163.
[20] S. Tomaru, K. Kubodera, S. Zembutsu, K. Takeda and M. Hasegawa, *Electron. Lett., 23* (1987) 595.
[21] G.R. Meredith, B. Buchalter and C. Hanzlik, *J. Chem. Phys., 78* (1983) 1533.
[22] C. Sauteret, J.P. Hermann, R. Frey, F. Pradere, J. Ducuing, R.H. Baughmann and R.R. Chance, *Phys. Rev. Lett., 36* (1976) 956.