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Third-order nonlinear optical properties of new soluble poly{1,4-bis[2,4,6-tri(4-n-heptylphenyloxy)-3,5-difluorophenyl]butadiyne}

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Abstract

A new soluble polydiacetylene with fluoro-aromatic rings directly attached to the π-conjugated main-chain backbone was synthesized by γ-radiation solid-state polymerization. The blue thin films of poly(fluorophenyl-diacetylene) could be only obtained from its red chloroform solution by a spin-coating technique. The third-order nonlinear optical susceptibilities of spin-coated amorphous thin films of poly(fluorophenyl-diacetylene) were measured by third-order harmonic generation. The third-order nonlinear optical coefficient susceptibility $\chi^{(3)}$, calculated by comparing the 3ω signal intensity of sample with that of a standard fused silica plate, was about 6.4×10^{-11} esu.

Keywords: Nonlinear optics; Polydiacetylene; γ-Radiation solid-state polymerization; Optical coefficient susceptibility; Spin-coated films

1. Introduction

In π-conjugated polymers such as polyacetylenes, polydiacetylenes and poly(*p*-phenylenevinylenes), electron delocalization and π-orbital overlap give materials that exhibit high third-order nonlinear optical response [1–4]. Polydiacetylene is one of the π-conjugated backbone polymers which are considered interesting materials for third-order nonlinear optics. Large third-order nonlinear optical effects have been observed in insoluble polydiacetylenes with single crystals giving the largest $\chi^{(3)}$ values [5]. However, this form of polydiacetylene is intractable, rendering it unsuitable for practical device application. In order to obtain suitable polydiacetylenes for practical application, soluble polydiacetylenes are the focus of recent work in the field of organic nonlinear optics [6].

To date, a number of soluble polydiacetylenes with flexible side-chains, such as n-BCMU, have been prepared and studied extensively for their nonlinear optical properties [7–11] and device fabrication [12,13]. For π-conjugated polymers, $\chi^{(3)}$ is proportional to the fifth power of the number of double bonds [14,15]. The general experimental and theoretical conclusions have suggested that polydiacetylenes with aromatic groups directly attached to the conjugated main backbone (increasing the number of π-electrons in the repeating unit through π-conjugation between the main backbone and side aromatic groups) might be good candidates for enhancing functional properties, such as conductivities, photoconductivities and nonlinear optical properties [16–20].

In this paper, we report a new soluble poly(fluorophenyl-diacetylene), namely poly{1,4-bis[2,4,6-tri(4-n-heptylphenyloxy)-3,5-difluorophenyl]butadiyne} (PBTDB) with pendant fluoro-aromatic rings directly attached to the polymer main backbone (as shown in Scheme 2).

2. Experimental details

2.1. General techniques

The absorption spectra were measured on Shimadzu 3100 spectrometer. Film thickness measurements were obtained using a Dektak IIA surface profiler. A Q-switched Nd:YAG laser (Spectra-Physics DCR-2A) was used in the third harmonic generation (THG) experiments. A 1 m Raman cell with hydrogen gas at 30 atm was used for converting the fundamental wavelength from 1064 nm to 1907 nm. Vertically polarized laser pulses were focused onto the sample with 35 cm focal length lens. A monochromator (Ritsu Oyo Kougaku MC-10N) was used to separate the third harmonic light. A photomultiplier tube (PMT: Hamamatsu R636) was employed to detect the THG signal. The THG signal from the PMT was integrated in a box car (Stanford Research

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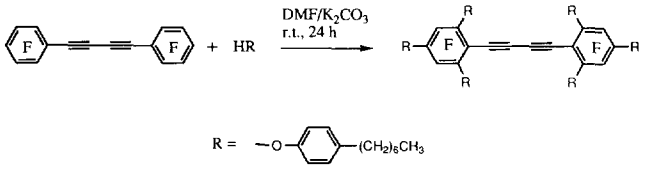
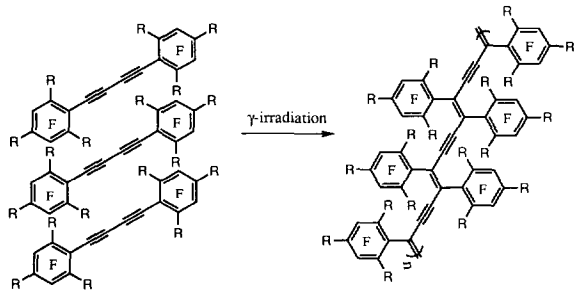
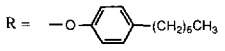


Scheme 1.





Scheme 2.

System SR245, SR250, SR280) triggered by the laser. The THG Maker fringe data were recorded under the control of a computer (NEC PC-9801).

2.2. Materials

The synthesis of the PBTDB monomer starting from pentafluoroiodobenzene has been described in our previous papers (as shown in Scheme 1) [21,22]. The monomer was stored in a dark container in a freezer. To make amorphous PBTDB thin films, the crystalline monomer was irradiated with a ^{60}Co source for a total dosage of 150 Mrad to form blue PBTDB microcrystalline powders as shown in Scheme 2. The polymer was reprecipitated twice from a chloroform/methanol mixture and purified by Soxhlet extraction with ethanol for 24 h. The polymer, obtained in 38% yield, was dried under high vacuum for 12 h. Amorphous thin films of PBTDB of thickness about 200 Å were made by spin-coating from its chloroform solution. All the polymeric films were prepared on fused silica substrates.

3. Results and discussion

The absorption spectra of a chlorofom solution (a) and a thin film (b) of PBTDB are shown in Fig. 1. The deep blue PBTDB crystals obtained by the γ-irradiation solid-state polymerization of white diacetylene monomer crystals were dissolved in chloroform to give red solutions with an absorption maximum at 562 nm. This absorption band in the visible region is due to the delocalized π-conjugated polymeric backbone. The solvatochromic behaviour of PBTDB in a good solvent (chloroform) and nonsolvent (methanol) system has been studied [23]. The conjugated main chains of PBTDB exist in two forms in solution, the disordered form having a

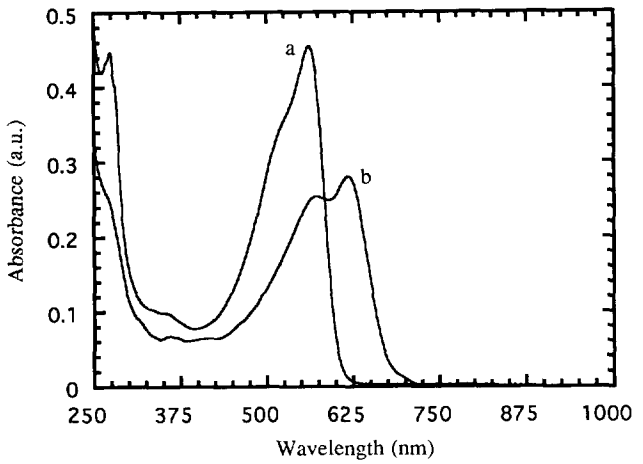


Fig. 1. Absorption spectrum of (a) the red chloroform solution and (b) the blue thin film of PBTDB.

red colour and the ordered form a blue colour. However, the thin films obtained from red chloroform solution were also blue. Red thin films could not be obtained by spin-coating from the solution of the disordered red form of PBTDB. The absorption maximum of the blue PBTDB thin films occurred at 625 nm. This results suggests that the more ordered polymeric main backbone in the solid state could be obtained directly from the more disordered polymeric main backbone in solution. The colour change from red in solution to blue in the solid state was due to the change in the conjugation length of the polymeric main chain. The colour change process occurs in passing from solution to solid. This process corresponds to a band edge shift to the low energy exciton band as a consequence of intra-chain ordering in the polymer which causes enhancement of the third-order nonlinear optical response. In the highly disordered red forms of polydiacetylenes, the degree of intra- and inter-chain order will be low and consequently the π-conjugation length will be short. In the blue form, both intra- and inter-chain order will be high and lead to a larger π-conjugation length. This is consistent with the observed $\chi^{(3)}$ and absorption measurements where the blue polydiacetylene forms always have higher $\chi^{(3)}$ and long wavelength absorption than their red forms [8,9].

The third-order optical nonlinearities $\chi^{(3)}$ of PBTDB thin films were measured by third harmonic generation (THG) using the standard Maker fringe technique [24,25]. For the THG measurement, the fundamental beam (ω), i.e. that at 1907 nm, was obtained from a Q-switched Nd:YAG laser operating at 1064 nm wavelength by Stokes shifting through a 1-m high-pressure H_2-filled Raman cell shifter. THG measurements were performed in the vacuum chamber at several torr pressure in order to eliminate the effect of air. The THG signal (3ω, 635 nm) intensity was measured as a function of goniometer rotation using the monochromator, photomultiplier tube and boxcar integrator. The polarizations for both the fundamental and the third harmonic beams were along the axis of goniometer rotation. The third-order nonlinear optical coefficient $\chi^{(3)}$ was calculated by comparing the 3ω

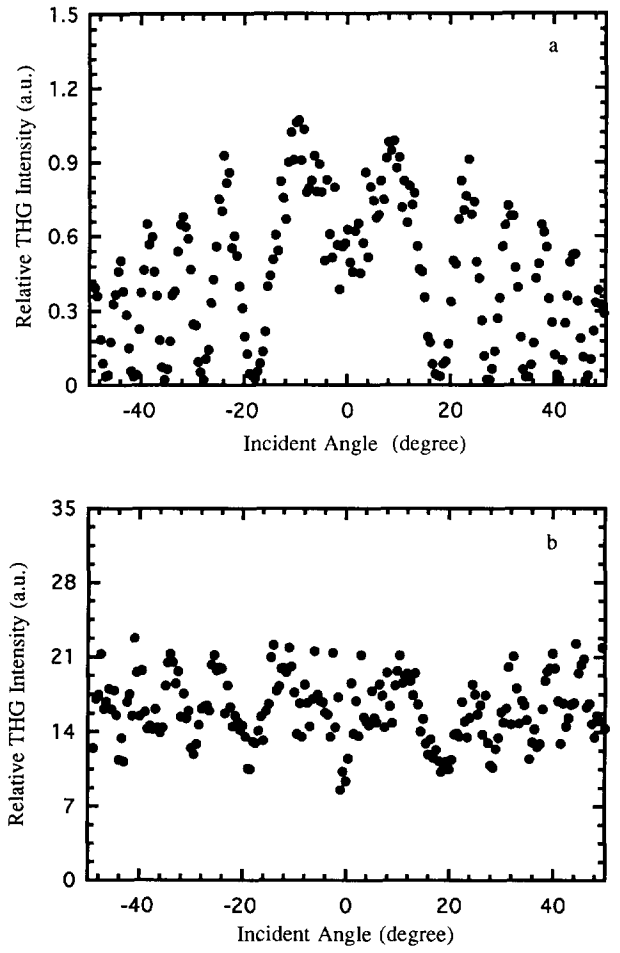


Fig. 2. Maker fringes obtained from the THG experiment at 1.907 nm (a) for the silica reference and (b) for the blue PBTDB film of ca. 208 Å thickness.

signal intensity of the sample ($I_{3\omega}$) with that of a standard fused silica plate ($I_{3\omega,\,s}$) using the simple equation (1) which is applicable when the sample thickness (l) is much smaller than the coherence length (l_c) [25]. The interference effect between the polymer thin film and substrate was calibrated by taking $I_{3\omega}$ from the Maker fringe according to Eq. (2). For this calculation, a third-order nonlinear optical coefficient $\chi_s^{(3)}$ of 2.8×10^{-14} esu and a coherence length $l_{c,\,s}$ of 18.1 μm were used for the 1-mm thick standard fused silica plate. Fig. 2 shows the Maker fringes obtained from the THG experiment at 1907 nm (a) for the fused silica reference and (b) for the blue PDTDB thin film of 208 Å thickness. The value of $\chi^{(3)}$ obtained for the blue films of PBTDB was 6.4×10^{-11} esu. No damage was observed on the surface of the films during the THG measurement. Sauteret et al. [5] have shown that the single-crystal exhibits a large anisotropy in the value of $\chi^{(3)}$. Along the direction parallel to the chain, the value of $\chi^{(3)}$ is more than an order of magnitude larger than that perpendicular to the chain. The solution cast film is amorphous with the interchain alignment being disordered. This is the main reason why the $\chi^{(3)}$ values of amorphous films are smaller than the $\chi^{(3)}$ values obtained from single-crystals along the chain direction. However, soluble polydiacetylenes with easy processing are still considered interesting materials for third-order nonlinear optics.

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

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

In conclusion, poly(fluorophenyl-diacetylene) (PBTDB), a soluble polymer, was found to be good candidate for third-order nonlinear optical materials with a high $\chi^{(3)}$ value (6.4×10^{-11}). It is readily processed, exhibits environmental stability and chemical synthetic flexibility. The blue polymeric thin films with intrachain order could be directly obtained from the red polymeric solution where the polymeric main chain is in intrachain disorder.

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