Femtosecond Third-Order Optical Nonlinearity of Conjugated Polymers Consisting of Fluorene and Tetraphenyldiaminobiphenyl Units: Structure−Property Relationships

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Femtosecond time-resolved optical Kerr effect technique has been used to investigate the third-order nonlinear optical (NLO) properties of a series of conjugated polymers consisting of fluorene and/or tetraphenyldiaminobiphenyl (TPD) units designed to elucidate structure−property relationships for the microscopic second-order hyperpolarizability γ in polymeric materials. The γ per repeated unit of the series of polymers has off-resonant values at 830 nm in the range of 2.0×10^{-33}−2.4×10^{-31} esu, demonstrating a large modulation of nonlinear optical response by simple structural variations. The γ values of alternative copolymers containing fluorene and TPD moieties are 2 orders of magnitude higher than the γ value of the homopolymer polyfluorene, revealing the vital role of the strong electron donor TPD in the NLO enhancement. The fluorene segment was found to result in 4-fold enhancement of γ in TPD-containing copolymers compared to *p*-phenylenevinylene segment, indicating that the planar rigid ring of fluorene is an efficient third-order NLO chromophore. No relationship between the magnitude of γ and the optical band gap was found. The large variation of γ value with molecular structure of these polymers can be explained by molecular exciton theory other than the band theory.

Introduction

Since the advent of nonlinear optics, there has been a long and sustained interest in organic and polymeric materials with significant nonlinear optical (NLO) properties. The interest is driven by the need for devices for the shifting (doubling and tripling) of frequencies into domains where inexpensive and efficient light sources are unavailable[1] and also by the need for devices for optical signal processing, all-optical switching, optical computing, bistable elements, logic devices, and sensor protection.[2−4] The criteria for practical applications and device fabrication include high nonlinear susceptibility, fast response times, adequate optical transparency, excellent environmental stability, and good processability for multilayer integration into large-area devices. Although conjugated quasi one-dimensional polymers with delocalized π-electron backbone have the largest nonresonant third-order NLO susceptibility $\chi^{(3)}$ with ultrafast response times (<1 ps) among all classes of materials, the measured off-resonant $\chi^{(3)}$ values in the range of 10^{-12}−10^{-9} esu are still orders of magnitude less than the projected requirements for practical photonic applications.[5−8] An understanding of the structure−function relationships that underlie the third-order NLO properties of conjugated polymers is currently lacking but is required to guide the rational design of polymers with enhanced optical nonlinearity.[9]

During our search for highly efficient third-order NLO materials,[10−18] we were attracted by the structural feature of the well conjugated, planar, and rigid ring of fluorene with ease to substitute with solubilizing groups.[19] It is well-known that increasing planarity and rigidity helps to enhance third-order

susceptibilities as it optimizes the overlap of π orbitals thus enhancing electron delocalization.[20] On the other hand, we were also interested in the strong electron donating ability of tetraphenyldiaminobiphenyl (TPD) with high charge carrier mobility[21] since the third-order optical nonlinearity can be enhanced by increasing π delocalized electron density and the carrier transport.[22] Thus, we synthesized a series of systematically designed polymers containing fluorene and/or TPD units,[11,23,24] and found that an alternative copolymer consisting of ethynylfluorene and TPD exhibited a large nonresonant second-order molecule hyperpolarizability γ up to 4.5×10^{-30} esu.[11]

In this paper, we investigated the third-order nonlinear optical properties of a series of conjugated polymers containing fluorene and/or TPD moieties using a femtosecond time-resolved optical Kerr effect (OKE) technique. We probed structure−property relationships for the microscopic second-order hyperpolarizability γ in these polymers, and found the important role of the strong electron donor TPD and the planar rigid ring of fluorene in the NLO enhancement.

Experimental Section

Materials. The detailed synthesis and characterization of the polymers investigated here (TPD-PFE, TPD-PF, TPD-PPV, and PF) have been reported elsewhere.[11,23,24] Characterization of the molecular and electronic structures of the polymers was done by ^{1}H NMR and FTIR spectroscopies, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV−vis absorption spectroscopy, photoluminescence spectroscopy, and cyclic voltammetry.[11,23,24] The chemical structures of these polymers are illustrated in Figure 1.

Absorption and Fluorescence Spectra. UV−vis absorption spectra of the polymers in chloroform solution were recorded

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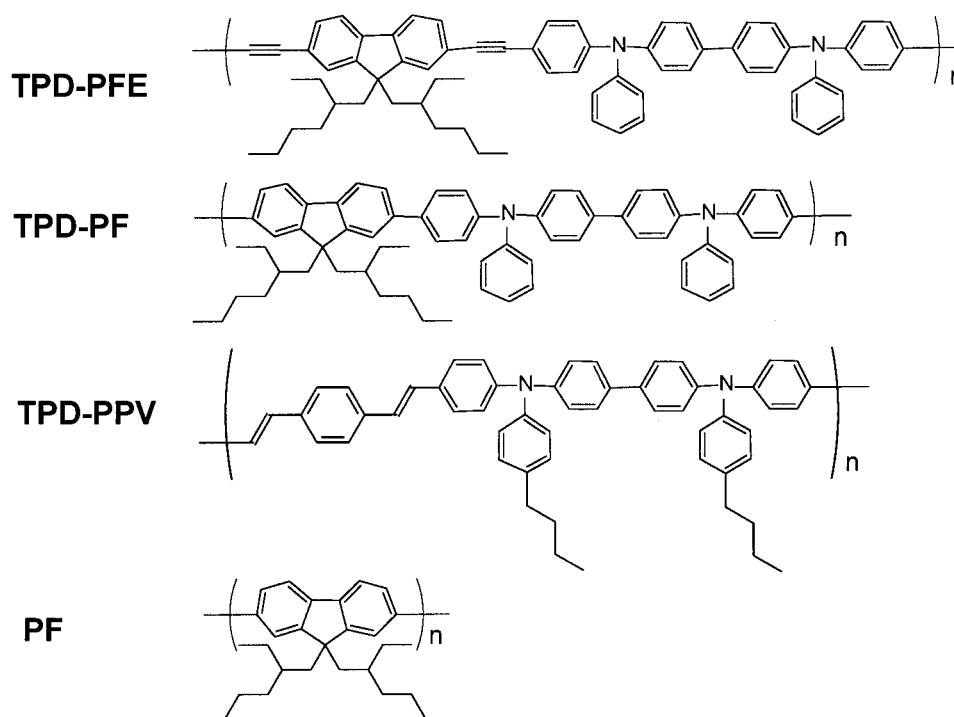‡ Mesoscopic Physics Laboratory & Department of Physics.

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Figure 1. The chemical structures of the polymers.

on a Hitachi U-3010 UV−Vis spectrophotometer. Steady-state photoluminescence (PL) spectra of the polymers in chloroform solution were measured on a Hitachi F-4500 spectrophotometer.

NLO Measurements. To obtain the NLO signal of a sample solution, we performed the ultrafast optical Kerr gate method. The light source was a femtosecond Ti:Sapphire laser (Mira 900F, Coherent Co. Ltd., VA) with a pulse repetition frequency of 76 MHz. The laser output with wavelength centered at 830 nm was split into strong pump and weak probe beams with an intensity ratio of 11:1. The polarization plane of the probe beam was rotated by 45° with respect to the linear polarization of the pump beam. An optical delay line driven by a computer-controlled step motor was inserted into the optical path of the pump beam to obtain a time-resolved signal. Two beams were focused and overlapped spatially in the sample solution filled in a 1 mm thickness cell. An analyzer (polarizer) with a transmission axis perpendicular to the polarization of the probe beam was inserted just before a photodiode so only the generated orthogonal signal, the optical Kerr signal, could be detected. To decrease the undesirable noise, the pump and probe beams were chopped at different frequencies, and the signal was amplified at the sum frequency by a lock-in amplifier connected to the photodiode, then the A/D transferred to a computer was also used to monitor and control the measurement. By replacing the sample cell with a 0.3 mm thick BBO crystal, we determined the zero delay point and obtained the autocorrelation signal of the laser beam. The pulse duration was then deduced to be 120 fs. A more detailed apparatus configuration has been described in our previous publication.[25]

The $\chi^{(3)}$ value was calculated from the intensity of OKE signal (I), the refractive index (n), and the sample thickness (l) and was corrected for absorption using the following equation

$$\chi^{(3)} = \left(\frac{I_S}{I_R}\right)^{1/2} \left(\frac{n_S}{n_R}\right)^2 \chi_R^{(3)} \left[\frac{\alpha\, l}{e^{-\alpha l/2}(1-e^{-\alpha l})}\right] \qquad (1)$$

where the subscripts S and R represent, respectively, the parameters for the sample and reference and α is the linear
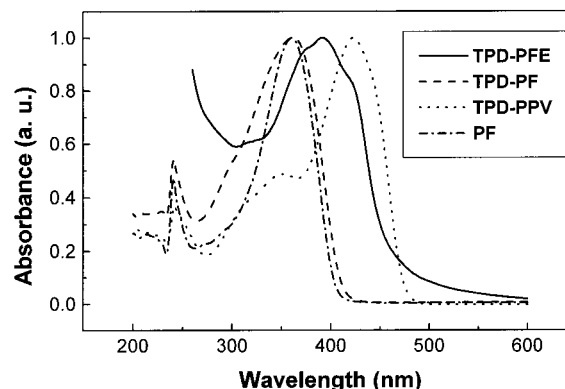

Figure 2. Absorption spectra of the polymers in CHCl₃.

absorption coefficient. The last fraction comes from the sample absorption and equals to 1 while the sample has no absorption around the employed laser wavelength. The excellent and stable third-order optical response solvent, CS₂, was selected as reference. $\chi^{(3)}$ of CS₂ has been measured to be 1×10^{-13} esu on the femtosecond time-scale by Minoshima et al.[26] and the refractive index of CS₂ is 1.62. Further, the second-order hyperpolarizability γ for the sample can be deduced using the following equation

$$\gamma = \chi^{(3)}/NL^4 \qquad (2)$$

Here, N is the number density of repeated units of the polymers, and L is the Lorentz local field factor given by

$$L = (n^2 + 2)/3 \qquad (3)$$

Results and Discussion

The UV−vis absorption spectra obtained for diluted solution of the polymers in CHCl₃ are shown in Figure 2. The absorption peak of PF was observed at 360 nm with an onset absorption edge of 404 nm. The optical band gap (E_g) of PF was determined to be 3.07 eV from the absorption edge. The absorption spectra

TABLE 1: Absorption and NLO Data of the Polymers in Chloroform

| polymer	concentration[a](M)	λ_{max}[b] (nm)	E_g[c] (eV)	$\chi^{(3)}$ (esu)	γ (esu)
TPD-PFE	1.16×10^{-4}	393	2.71	5.7×10^{-14}	2.4×10^{-31}
TPD-PF	1.14×10^{-4}	361	3.00	5.2×10^{-14}	2.3×10^{-31}
TPD-PPV	4.40×10^{-4}	423	2.61	5.6×10^{-14}	6.1×10^{-32}
PF	1.29×10^{-3}	360	3.07	$<5.4 \times 10^{-15}$	$< 2.0 \times 10^{-33}$

[a] Molar concentration of repeated unit. [b] Absorption maximum. [c] The optical band gap derived from the absorption spectrum.

of TPD-PFE, TPD-PF, and TPD-PPV are shown in Figure 2 with that of PF to reveal the effects of changing the polymer backbone structure on band gap and $\pi-\pi*$ transition maximum (λ_{max}). Compared to the absorption spectrum of the homopolymer PF, the introduction of electron donor TPD in the copolymer TPD-PF consisting of TPD and fluorene units brings about somewhat change to the absorption peak in the long wavelength region; the λ_{max} of TPD-PF is 361 nm and the E_g is 3.00 eV. A further red shift of the spectrum is induced when the ethynyl segments are incorporated into TPD-PF. A 32 nm red-shift of λ_{max} and a 0.29 eV reduction of E_g are observed in TPD-PFE constituted of TPD and ethynylfluorene units. Clearly the intrachain charge transfer between the electron-deficient moiety ethynylfluorene and electron-rich moiety TPD exerts bathochromic effect on the electronic transitions of TPD-PFE. Replacing diethynylfluorene in TPD-PFE with divinylbenzene results in a bathochromic shift in λ_{max} from 393 to 423 nm and a reduction in E_g from 2.71 to 2.61 eV due to the electron-donating effect of the divinylbenzene moiety. In other words, the electronic structures of the polymers containing fluorene and/or TPD units can be readily tuned by molecular engineering of counits in the main chain.

The $\pi-\pi*$ transition maximums (λ_{max}) and the optical band gaps (E_g) as determined from the absorption edge are listed in Table 1. The λ_{max} of the lowest energy $\pi-\pi*$ transition is in the range of 360−423 nm; the optical band gaps fall in the range of 2.61−3.07 eV. These absorption data reflect the extent of electron delocalization and the ground-state electron structure of the polymers. The wide range of ground-state electronic structure variations and the associated broad band-gap range offer an opportunity to investigate the effects of structure on the third-order nonlinear optical properties of the polymers.

The origin of the third-order optical nonlinearity is essential to probing the structure-γ relationships of the polymers. The onset absorption edge of these polymers is in the range of 404−476 nm. Their solutions show no absorption at wavelengths longer than 600 nm. One-photon resonance mechanisms are impossible because these polymers show no absorption at the laser wavelength (830 nm).

The frequency dispersion of γ over a sufficiently wide spectral range enables the off-resonant and the multiphoton-resonance-enhanced γ values to be distinguished unambiguously. Figure 3 shows γ of TPD-PFE in chloroform solution as a function of laser wavelength. The laser wavelength can be varied only in the range of 790−850 nm due to the limit of the apparatus. A resonant peak occurs at 790 nm, half of the lowest $\pi-\pi*$ transition energy (393 nm) observed in the absorption spectrum of this polymer. Therefore, this resonance is assigned to the two-photon resonance. The two-photon resonance results in 4.6-fold enhancement of γ value. Albota et al. reported that some triphenylamine-containing organic molecules are two-photon-absorbing materials.[27] Thus, our observation in the triphenylamine-containing polymers is consistent with Albota's early finding. Although the two-photon resonance occurs in the polymers, the two-photon-resonance brings about negligible
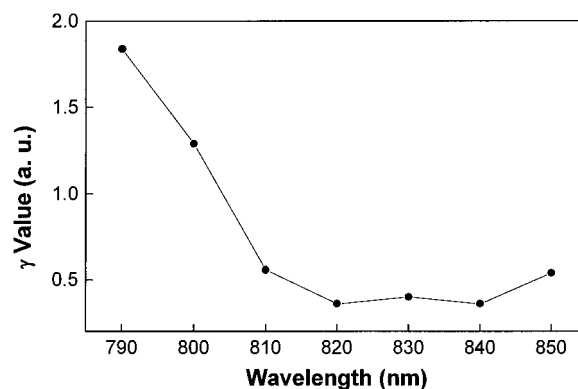
Figure 3. γ dispersion data for TPD-PFE as a function of laser wavelength.
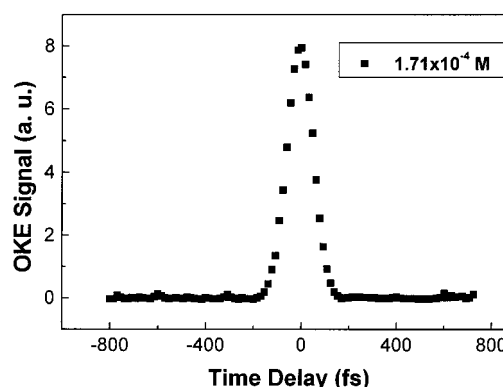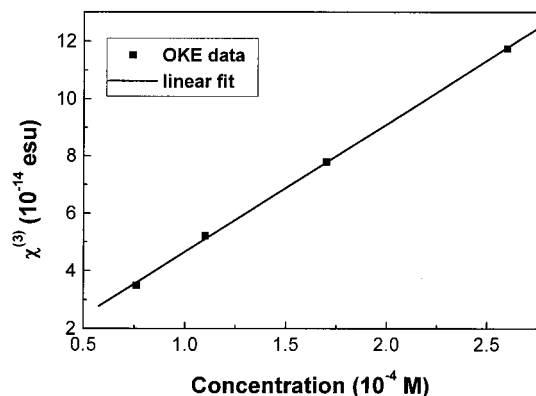

Figure 4. The time-resolved optical Kerr effect response of TPD-PF in CHCl$_3$ solution.

enhancement of the γ value measured at 830 nm. Thus, the γ values at 830 nm of the polymers are two-photon off-resonant.

Time-resolved OKE signals of TPD-PF in CHCl$_3$ are illustrated in Figure 4. The relatively weak background noise and contribution of the solvent has been subtracted. Time response study of $\chi^{(3)}$ has shown a correlation function of the input laser pulse. Thus the nonlinear responses are faster than 120 fs, lending support to the absence of long-lived thermal contributions.[28] On the basis of the ultrafast response, we can argue that the susceptibility of TPD-PF is dominated by an instantaneous electronic polarizability that is one- and two-photon nonresonant.

The nonresonant $\chi^{(3)}$ of the polymers in CHCl$_3$ solution at different concentrations was deduced by comparison with the measurements on a reference CS$_2$ under identical condition. Figure 5 is an example of a linear dependence of the measured $\chi^{(3)}$ on the concentration. It is concluded that our experimental measurement is reliable. We can employ eq 2 to estimate the second-order hyperpolarizability γ from $\chi^{(3)}$ of the sample solution at a certain concentration after accounting for local field factors and average these values as the most acceptable γ of the polymers.

The off-resonant second hyperpolarizability γ data of these polymers are summarized in Table 1. The γ of the homopolymer

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Figure 5. Linear fitting of the concentration dependence of $\chi^{(3)}$ for TPD-PF.

Figure 6. Fluorescence spectra of TPD-PFE in chloroform solution excited at various wavelengths.

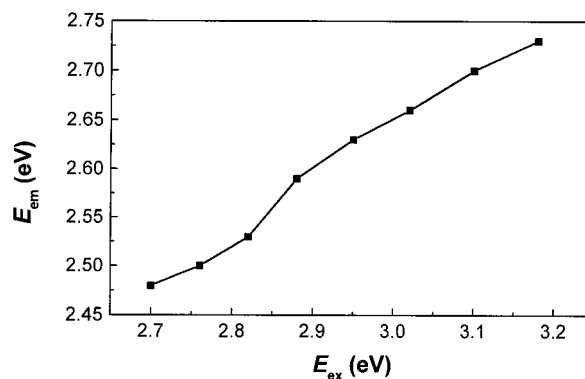**Figure 7.** Fluorescence energy (at emission λ_{max}) of TPD-PFE as a function of excitation light energy.

PF is smaller than 2.0×10^{-33} esu. The γ is 2.4×10^{-31}, 2.3×10^{-31}, and 6.1×10^{-32} esu for TPD-PFE, TPD-PF, and TPD-PPV, respectively. The γ values of the alternative copolymers containing fluorene and TPD moieties, i.e., TPD-PFE and TPD-PF, are 2 orders of magnitude higher than that of the homopolymer polyfluorene, i.e., PF, revealing the vital role of the strong electron donor TPD in the NLO enhancement. The fluorene segment was found to result in 4-fold enhancement of γ in TPD-containing copolymers compared to *p*-phenylenevinylene segment, indicating that the planar rigid ring of fluorene is an efficient third-order NLO chromophore.

Although TPD-PF and PF have almost identical optical absorption (λ_{max}) and band gap (Figure 2 and Table 1), they have significantly different third-order optical nonlinearity. The TPD unit results in 2 orders of magnitude enhancement of γ. In comparison with TPD-PF, the ethynyl segments of TPD-PFE give rise to no considerable increase in the second-order hyperpolarizability, while exerting a dramatic effect on the lowest energy $\pi-\pi^*$ transition (λ_{max}) and the optical band gap (E_g). Although the optical band gap of TPD-PPV is smaller than those of TPD-PFE and TPD-PF, the relative magnitude of the γ values of these polymers indicates that a smaller band gap does not necessarily lead to a larger γ. In fact, a similar finding has been reported by Marder et al. from the study on the γ of conjugated molecules.[29,30] They showed that the optimal γ value occurs at a nonzero bond-length alternation in a series of systematically designed molecules, which means that the largest γ was not found in the molecule with the smallest optical band gap. It is well-known that the γ scales as E_g^{-k} as long predicted ($k = 6$) from band theory[31] and commonly observed in some conjugated oligomers.[32] However, no relationship between the magnitude of γ and the energy of the lowest $\pi-\pi^*$ optical gap (E_g), which is in the range of $2.61-3.07$ eV, was found on the basis of the above experimental results. Jenekhe and co-workers have investigated the structure-$\chi^{(3)}$ relationships in conjugated aromatic polyimines, and found that there is no relationship between the magnitude of $\chi^{(3)}$ and E_g.[8] Our observation in the polymers containing fluorene and/or TPD is similar to Jenekhe's early finding. Clearly, the dramatic enhancement of γ in going from PF to TPD-PF, the almost no changing of γ in going from TPD-PF to TPD-PFE, and the significant reduction of γ in going from TPD-PFE to TPD-PPV cannot be explained by considerations of the optical band gap and electron delocalization variations.

At present, two opinions are influential in the theoretical and experimental studies of third-order NLO properties in conjugated polymers. One is that conjugated polymers are one-dimensional semiconductors which exhibit band-to-band optical transition.[31-33]
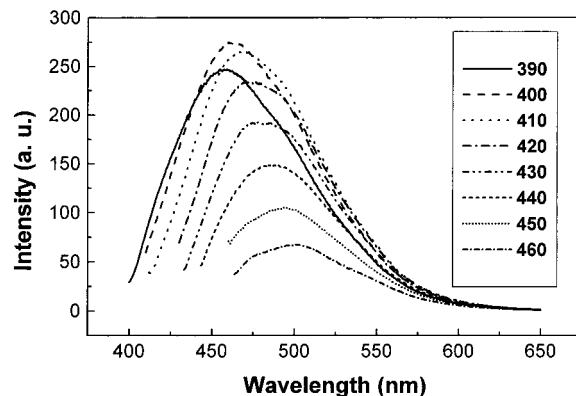
Another is that the excited states of conjugated polymers are molecular excitons in nature.[34-36] Here we employ site-selective fluorescence spectroscopy to probe the excited states of these polymers in Figure 1. The conjugated polymers containing fluorene and/or TPD units are highly fluorescent and have been employed as electroluminescent materials in light-emitting diodes.[23,24] Excitation wavelength variation in fluorescence studies of these polymers provides qualitative insights into their excited-state electronic structures. The excitation wavelength was tuned between the absorption maximum and the onset absorption edge of each polymer. The results are exemplified by those for TPD-PFE solution in chloroform in Figure 6 where the fluorescence spectra corresponding to excitation wavelengths in the range $390-460$ nm are displayed. A progressive red shift of the emission peak with excitation wavelength occurs. The variation of the emission energy with excitation energy of the TPD-PFE solution shown in Figure 7 implies that the emission is not from a band-to-band transition but from a number of discrete states because emission from a band-to-band transition would be completely independent of the excitation wavelength.[36] The site-selective fluorescence spectroscopy demonstrates that the excited states of these polymers are molecular excitons in nature. The large variation of γ value with molecular structure of these polymers may be due to the dramatic changes in the excited-state electronic structure of the molecules.

Conclusions

Femtosecond time-resolved optical Kerr effect technique has been used to investigate the third-order nonlinear optical properties of a series of conjugated polymers composed of fluorene and/or TPD units. The results clearly show that this class of conjugated polymers has a large nonlinear optical

response that is tunable by simple structural variations. The ultrafast nonlinearity originates from the electronic polarization. The off-resonant γ values of alternative copolymers containing fluorene and TPD moieties are larger than those of their counterparts without TPD or fluorene units, revealing the vital role of the strong electron donor TPD and the planar rigid ring of fluorene in the NLO enhancement. No relationship between the magnitude of γ and the optical band gap was found. The large variation of γ value with molecular structure of these polymers can be explained by molecular exciton theory other than the band theory.

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