

Studies of resonant and preresonant femtosecond degenerate four-wave mixing in unoriented conducting polymers

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(Received 28 January 1991; accepted for publication 6 May 1991)

Degenerate four-wave mixing with femtosecond time resolution is used to measure the magnitude and transient response of the third-order nonlinear optical susceptibility $\chi^{(3)}(\omega; \omega, -\omega, \omega)$ at 620 nm in nonoriented conducting polymers including polydiacetylene, polyacetylene, polyaniline, polydiethynylsilane, polythiophene, and polythiophene derivatives. Resonant and nonresonant excitations influence the magnitude and transient response of $\chi^{(3)}$. The electronic response is instantaneous for preresonant excitation, but for resonant excitation it has ultrafast and slow components which illustrate photoexcitation dynamics. The magnitude of $\chi^{(3)}$ for all of the polymers is in the range from 10^{-10} to 5×10^{-8} esu depending on the energy difference between the laser excitation and the polymer absorption maximum.

During the past decade, π -conjugated polymers (or conducting polymers) have been studied extensively because of the high conductivities achieved upon doping and their intrinsic excitations such as solitons, polarons, and bipolarons.¹ Recently, research interest has shifted to the nonlinear optical properties of these materials² which exhibit ultrafast responses and large nonlinearities attributed to one dimensionality and delocalization of the π electrons along the polymer chains. The ultrafast responses and the large third-order nonlinearities of conducting polymers make them attractive candidates for future nonlinear optical devices such as logic gates, optical switches, and modulators, which are likely to operate at bandwidth of hundreds of GHz with only a few mW average laser power. Ease of fabrication and the possibility of engineering structures at a molecular level are additional advantages of conducting polymers for use in optical nonlinear devices. Indeed, practical devices based on conjugated polymers have already been demonstrated.^{3,4}

Optical nonlinearities are usually characterized by values of the third-order susceptibility $\chi^{(3)}(\omega)$. Third-harmonic generation⁵⁻⁷ and four-wave mixing⁸⁻¹⁰ in the nanosecond and picosecond time domains have been used to measure $\chi^{(3)}(3\omega)$ and $\chi^{(3)}(\omega)$, respectively. For device applications, $\chi^{(3)}(\omega)$ is more important than $\chi^{(3)}(3\omega)$. To evaluate the full potential of conducting polymers for optical device applications, additional measurements of the magnitude and transient response of $\chi^{(3)}(\omega)$ for a wide selection of materials are imperative.

We report measurement of $\chi^{(3)}(\omega)$ in a number of π -conjugated polymers, using degenerate four-wave mixing (DFWM) with femtosecond time resolution, which show a clear distinction between resonant and preresonant excitation. With preresonant excitation, $\chi^{(3)}$ is in the range of 10^{-10} esu and has an instantaneous response limited by the experimental time resolution (100 fs). With resonant excitation, however, $\chi^{(3)}(\omega)$ can reach values as high as 5×10^{-8} esu, but its transient response follows the electronic relaxation of the photoexcitations, which can be relatively slow.

Transient DFWM in a folded box coherent anti-Stokes Raman spectroscopy (CARS) configuration¹¹ was used to

measure $\chi^{(3)}(\omega)$. Optical pulses from a colliding pulse mode-locked (CPM) dye laser were amplified by 10^5 using a dye/copper vapor-laser-optical amplifier with a repetition rate of 8 kHz. After passing through two pairs of prisms to compensate for dispersion in the dye amplifier, pulses were obtained with a duration of 90 fs, a wavelength of 620 nm (2 eV), and an energy of 5 μ J. The output beam was then split to obtain two parallel-polarized writing beams (I_1 and I_2), which were spatially and temporally overlapped onto a 50- μ m-diam spot on the sample to form a transient grating, and a reading beam (I_3), which was modulated at 1 kHz using a chopper and time-delayed using a translation stage with 0.5-fs resolution. Power levels at the sample were limited to less than 10 GW/cm² to avoid sample damage. The resulting diffracted-beam intensity (I_4) was measured as a function of the time delay τ for I_3 by a Si detector and lock-in amplifier. The magnitude of $\chi^{(3)}$ was calculated⁸ by comparing the polymer I_4 values to a reference signal $I_{4,r}$ from CS₂ liquid measured under identical experimental conditions using the equation^{8,12}

$$|\chi^3| = \chi_r^{(3)} \gamma (I_4/I_{4,r})^{1/2}, \quad (1)$$

where $\chi_r^{(3)}$ ($= 8.8 \times 10^{-13}$ esu) refers to CS₂, $\gamma = \alpha n^2 L_r / n_r^2 \sqrt{T} (1 - T)$, $T = \exp(-\alpha L)$ is the sample transmission, αL is the sample optical density, L_r is the CS₂ cell thickness, and n and n_r are the refraction indices of the sample and CS₂, respectively. If $(\chi^{(3)})'$ and $(\chi^{(3)})''$ are the real and imaginary parts of $\chi^{(3)}$, Eq. (1) indicates that for nonresonant excitation $I_4^{1/2} \propto (\chi^{(3)})'$, but for resonant excitation $I_4^{1/2} \propto |\chi^{(3)}|$, where $|\chi^{(3)}| = [((\chi^{(3)})')^2 + ((\chi^{(3)})'')^2]^{1/2}$.

All samples were nonoriented thin films with an optical density of about 1, which were either solution cast, electrochemically deposited, or chemically polymerized onto glass or sapphire substrates. The materials studied were polydiacetylene (PDA)—4 BCMU, Shirakawa-polymerized polycetylene—(CH)_x, polydiethynylsilane—PDES,¹³ Emeraldine-based polyaniline,¹⁴ and polythiophene and its derivatives.

Typical results for $I_4(\tau)$ with resonant excitation are shown in Fig. 1 for an electrochemically-polymerized polythiophene sample. with the polarization of I_3 parallel to

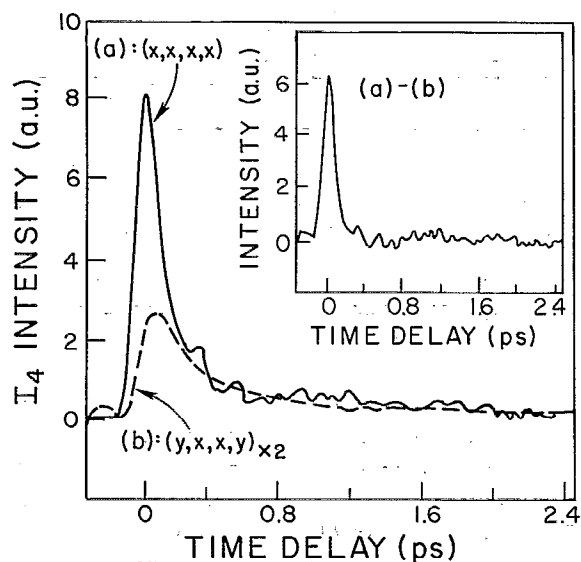


FIG. 1. Transient DFWM signal $I_4(\tau)$ of polythiophene at 620 nm for parallel ($xxxx$) and perpendicular ($yxyx$) polarizations. The latter has been multiplied by 2 for ease of comparison. The shape of the coherent artifact in DFWM, calculated by subtracting the normalized responses ($xxxx$) - ($yxyx$), is illustrated in the inset.

that of the grating-forming beams I_1 and I_2 [Fig. 1(a)], $(I_4)^{1/2} \sim |\chi_{xxxx}^{(3)}|$. With the polarization of I_3 perpendicular to that of I_1 and I_2 [Fig. 1(b)], $I_4^{1/2} \sim |\chi_{yxyx}^{(3)}|$. As shown in Fig. 1, the transient response in the parallel configuration is much shorter than I_4 is larger by about a factor 2 than in the perpendicular case; this is common to all of the polymers studied. The measured $\chi^{(3)}$ anisotropy in polythiophene, $|\chi_{xxxx}^{(3)}|/|\chi_{yxyx}^{(3)}| = \sqrt{2}$ is in good agreement with anisotropy values measured by other techniques.¹⁵ All of the anisotropy values measured for the polymers show a significant deviation from the ideal case of 3 except for polydiacetylene, for which we measured an anisotropy of 3. The shorter response in the parallel case is due to a significant contribution from the coherent artifact,¹⁶ which in DFWM is due¹⁷ to diffraction of one of the writing beams I_1 from the grating formed by I_3 and I_2 . If the parallel and perpendicular responses are normalized at $\tau > 3\tau_c$, where τ_c is the pulse coherence time (~ 70 fs in our case), a measure of the coherent artifact can be obtained (Fig. 1 inset) from the difference between the two normalized responses. As shown in the inset, the artifact has a symmetric shape about $\tau = 0$ which, for nontransform-limited pulses, is shorter than the autocorrelation function. The coherent artifact contribution is reduced in the perpendicular configuration¹⁶ and, therefore, the response appears to be longer.

Figure 2 shows the transient DFWM signal $I_4(\tau)$ measured at 2 eV in the perpendicular configuration ($yxyx$) for several conducting polymer samples. The transients are quite different from one material to another. The response of PDA-4 BCMU is instantaneous. Other polymers show an ultrafast decay with subpicosecond time constant and a slower decay which extends over tens of picoseconds. The different transients can be explained with the aid of Fig. 3

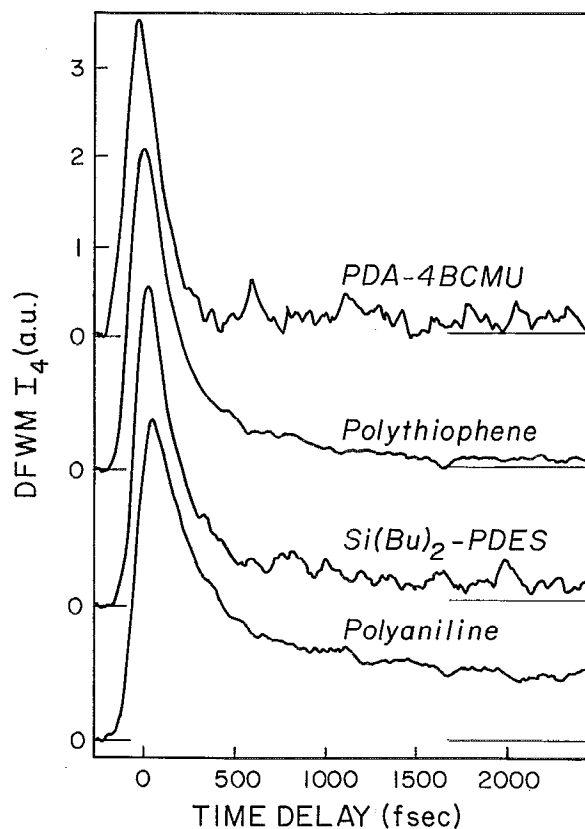


FIG. 2. Transient responses of the diffracted beam I_4 in DFWM at 620 nm in the perpendicular configuration ($yxyx$) for some conducting polymers.

which shows a typical absorption spectrum of a π -conjugated polymer and the position of the laser excitation line (2 eV) with respect to the interband absorption spectrum. Since the excitation line for PDA-4 BCMU is in preresonance below the absorption edge, the instantaneous response is the result of virtual transitions associated with delocalized π electrons.¹⁸ All of the other polymers studied have significant absorption at 2 eV so that the excitation laser line is in or near resonance. Because real carriers⁵ are photogenerated with resonant excitation (as opposed to nonresonant virtual states), we believe that the slow component is caused by electronic relaxation processes associated with the photoexcitations. This relaxation is clearly evident from a comparison of Figs. 2 and 3 which show that the contribution of the slow component to the DFWM signal increases with increasing absorption at 2 eV.¹⁹ Polyaniline has the largest relative slow component in agreement with its strongest absorption at 2 eV, which corresponds to the exciton absorption peak for this material.¹⁴

There are several explanations for the origin of the ultrafast component in the resonant excitation case. One explanation is that it is created by the same process as in the preresonant case; i.e., perturbation of the π electronic distribution. This explanation is particularly appropriate for polythiophene¹⁸ and polydiethynylsilane since the excitation laser line is near the band edge so that $\chi^{(3)}(\omega)$ is likely to be a combination of resonant (r) and nonresonant (nr) terms (i.e., $\chi^{(3)}(\omega) = [\chi^{(3)}(\omega)_r] + [\chi^{(3)}(\omega)_{nr}]$).

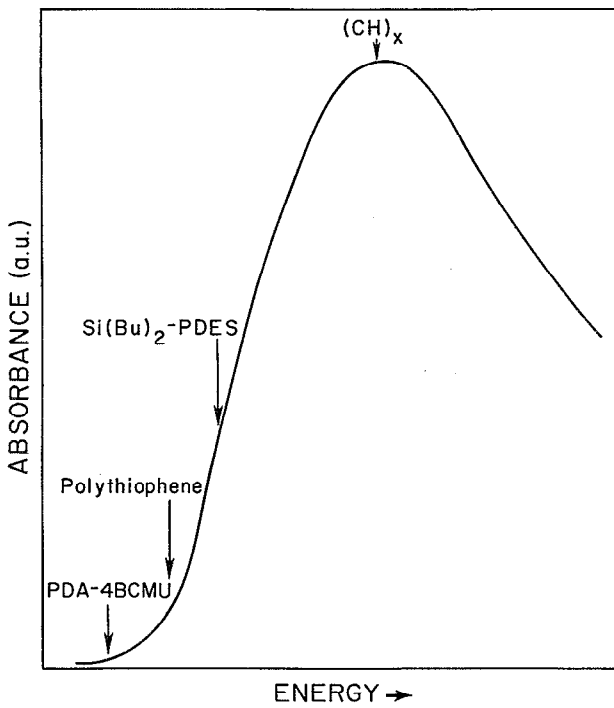


FIG. 3. Typical absorption spectrum of a π -conjugated polymer. The arrows indicate the excitation laser photon energy relative to the absorption maxima for each of the polymers studied by the DFWM technique at 2 eV.

However, the decay time constants of the fast components for these polymers are usually longer than the system temporal resolution (< 100 fs). For example, the fast decay component of the polythiophenes has a time constant of ~ 350 fs [Fig. 1(b)].¹⁸ Another explanation is that the fast decay is due to the rapid relaxation of the initially delocalized photoexcited carriers which can be observed in the transient $\chi^{(3)}(\omega)$ response because the polarizability of the unrelaxed delocalized carriers is expected to be much larger than that of the relaxed localized carriers at later times. In this case the fast decay component is due to $(\chi^{(3)})'$ whereas the slow component is mainly due to $(\chi^{(3)})''$. An ultrafast response of about 100 fs duration has been recently measured in polydiacetylenes using the pump and probe technique,^{20,21} this response does not change at high hydrostatic pressures up to 80 KBar (Ref. 22) and it was conjectured, therefore, that it is intrinsic.

In Table I values of the third order susceptibility $\chi^{(3)}$ for the conducting polymers measured by DFWM together with the figure of merit $\chi^{(3)}/\alpha$, where α is the absorption coefficient at 2 eV are tabulated. As shown in Ref. 23, $\chi^{(3)}$ increases with α and therefore $\chi^{(3)}/\alpha$ is a useful ratio for comparing the nonlinear responses of the polymers. Although $\chi^{(3)}$ varies by more than two orders of magnitude, the variance of $\chi^{(3)}/\alpha$ is much smaller and clearly illustrates the importance of resonance effects in $\chi^{(3)}$. We conclude from Table I that the best spectral range for applications in nonlinear optics requiring rapid response times is probably in preresonance, just below the band edge (as in PDA-4 BCMU) where the absorption is relatively small and yet $\chi^{(3)}$ is still partially enhanced.

TABLE I. The values of $\chi^{(3)}(\omega; \omega, -\omega, \omega)$ as measured by the DFWM technique at 620 nm, and the figure of merit $\chi^{(3)}/\alpha$.

Polymer	$\chi^{(3)}$ (esu)	$\chi^{(3)}/\alpha$ (esu cm)
polyacetylene	5×10^{-8}	5×10^{-13}
polyaniline	8×10^{-10}	2×10^{-14}
polydiacetylene-4 BCMU	2×10^{-10}	2×10^{-13}
polydiethynylsilane	3×10^{-9}	7×10^{-13}
polythiophene	6×10^{-10}	6×10^{-14}
poly-hexyl-thiophene	7×10^{-10}	5×10^{-14}

In summary, we have measured $\chi^{(3)}(\omega)$ for various π -conjugated polymers using the DFWM technique. The effects of resonant excitation are clearly manifested in the temporal response and magnitude of the signal. Comparisons based on the figure of merit $\chi^{(3)}/\alpha$ suggest that the best spectral range for use in high speed nonlinear optical applications is just below the band-edge absorption of the polymer.

The work was partially supported by DOE Grant No. DE-FG02-89.ER.45409 and by the University of Utah Laser Institute. S. G. H. thanks also BP America for research support.

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