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Two photon absorption and photo-induced polymerization in partially polymerized crystals of polydiacetylene poly[4,6-dodecadiyn-1, 10-diol-bis(*n*-butoxycarbonylmethylurethane)]

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Two photon absorption and photo-induced polymerization in partially polymerized crystals of polydiacetylene poly[4,6-dodecadiyn-1,10-diol-bis(*n*-butoxycarbonylmethylurethane)]

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We investigated the validity of noninteracting molecular chain theories for fully polymerized polydiacetylene crystals by measuring the two photon absorption spectrum of poly[4,6-dodecadiyn-1,10-diol-bis(*n*-butoxycarbonylmethylurethane)] chains isolated in their monomer matrix and comparing the results to those obtained previously from polydiacetylene single crystals. Data were taken over 800–940 nm using Z-scan and the measurements were found to be consistent with previously measured results in polydiacetylene single crystal poly[bis(*p*-toluene sulfonate) of 2,4-hexadiyne-1,6-diol], indicating the validity of the isolated molecule theoretical approach. We also report a low photo-induced polymerization threshold. © 2003 American Institute of Physics. [DOI: 10.1063/1.1556751]

Polydiacetylenes (PDAs) are known to have strong electric dipole coupling of the ground state to the one photon allowed state and from this excited state to higher lying two photon states due to one dimensional delocalization of π electrons along the polymerization backbone.^{1,2} This results in large nonresonant third order nonlinearities for $\lambda > 1 \mu\text{m}$.¹ There is a long history of theoretical work explaining these large nonlinearities in terms of the electronic states of single, isolated polymer molecules dating back to the 1970s.^{1,3–12} Many experimental studies of nonlinear properties have been performed on single crystal PDAs, or on oriented or amorphous films,^{13–20} indeed, for nonlinear applications the density of active species, i.e., the polymer chains, should be maximized.^{21–23} Such measurements, however, may be compared to theory only if interchain interactions in the solid are only a small perturbation of the single chain properties. Recent theoretical calculations^{24–27} deal with the effect of interchain interactions on the properties of conjugated polymer crystals, and predict relatively large effects on energy spacings, and the optical observation of new states. Since the modeling for the third order susceptibility, $\chi^{(3)}$, has yet to advance to the same level of sophistication that has occurred for the second order susceptibility, $\chi^{(2)}$, an experimental study of the effect of chain interactions on $\chi^{(3)}$ in the crystalline phase would, therefore, be useful. Experimental results relevant to this question are presented here. Some PDAs are soluble, but the conformation and electronic structure of the isolated PDA chain in solution are very different from those in the crystal and such studies cannot be used to test the influence of interchain interactions. Here we study monomer DA crystals containing small polymer con-

centrations. A concentration of 5 to 8% in weight is small enough for most chains to have no nearest neighbor chain interactions, but still large enough to make measurements possible.

Materials in the PDA family differ primarily from one another in the organic side groups which link the PDA backbone chains, and the electronic states, the vibrational modes, etc. which play a large role in the optical properties are found to be only weakly dependent on these side groups. Hence all PDAs are expected to have comparable linear and nonlinear properties. Two photon absorption in particular has been studied extensively in polydiacetylenes.^{17–20,28–31} However, some of these measurements were made in solution or amorphous thin films where it is known that different conformational forms of many conjugated polymers can exist making the situation complex.^{17,29,30} To date, the most detailed two photon absorption measurements have been performed on the single crystal conjugated polymer poly[bis(*p*-toluene sulfonate) of 2,4-hexadiyne-1,6-diol] (PTS).^{19,20,28,31} Specifically, the strongest two photon state is excited with photons of wavelength 920 nm and the two photon absorption spectrum has vibrational side-bands down to about 700 nm.^{19,20}

Recently polymerized chains of PDAs dilutely dispersed in a 3BCMU monomer single crystal matrix were produced by controlled gamma-ray polymerization and characterized as discussed in Ref. 32. This particular PDA has the advantage that there is minimal stress induced when it is partially polymerized from the monomer crystal, since the room-temperature lattice parameter of the poly[4,6-dodecadiyn-1,10-diol-bis(*n*-butoxycarbonylmethylurethane)] (3BCMU) monomer in the chain growth direction is almost exactly equal to the equilibrium repeat distance of the PDA chain.³³ In such a diluted polymer PDA the interchain interactions are weak.³⁴ A number of features of such dilute polydiacetylenes

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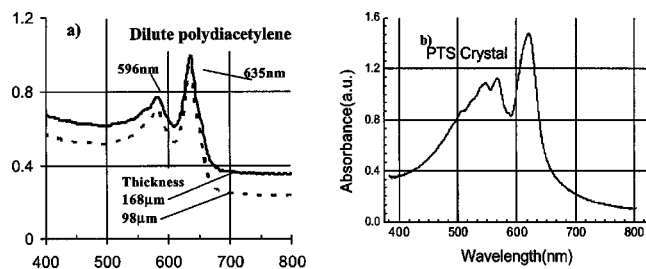


FIG. 1. Absorption spectra of the dilute polydiacetylene in the monomer matrix (a) and of the single crystal poly-PTS (b) (arbitrary units) for input polarization perpendicular to the chain axes.

including the linear absorption, pump-probe triplet and singlet exciton generation and relaxation have already been measured.^{2,35} Since the monomer has optical transitions that occur at higher photon energies than those in the polymer, i.e., in the UV spectral region, it is possible to study the two photon spectrum of aligned individual chains in a transparent dielectric medium. Such an investigation allows a direct comparison of the two photon response of single crystal (or amorphous) PDA with that of an “isolated” but oriented (by the crystal lattice) polymer chain, which in turn is a test of whether the single chain theories should provide a good approximation for solid state polymers. Here we report both on these studies, and the difficulties encountered due to light induced polymerization of the sample.

We performed standard open aperture Z-scan experiments³⁶ at room temperature using 140 fs long, mode-locked pulses from a Ti:sapphire laser operating at 76 MHz, tunable over the wavelength range 800 to 940 nm. Based on the previous PTS results, this range covers the expected two photon resonance peak.^{19,20} The light was collected by Si detectors. Special care was taken to collect all the light at the output to insure the detected power drop is due to intensity dependent absorption.

The samples were fabricated at GPS at Jussieu in Paris, using techniques developed there.³² The pure monomer crystals were clear and colorless and acquired a pink and then red tinge on progressive polymerization. Two samples, 98 μm thick with a polymer concentration of $8.5 \pm 1\%$, and 168 μm with a $6.8 \pm 1\%$ polymer concentration, were used in the experiments. Polymer concentrations were determined by measuring the one-photon absorption spectra for light polarization perpendicular to the chain direction, using the previously determined calibration.³⁵ Polymer chain length is expected to be over 2000 monomer units, based on the molar weight studies of 3BCMU³⁷ and 4BCMU³² (stands for diacetylene poly[5,7-dodecadiene-1,12-diol-bis (*n*-butoxycarbonylmethylurethane)]). Both samples had sufficient surface quality to obtain useful open aperture Z-scans.

The linear absorption spectrum of both samples for light polarization perpendicular to the b-crystalline axis was measured and is shown in Fig. 1. Both spectra exhibit the same features, a strong exciton peak at about 630 nm and vibrational side-bands to shorter wavelengths. Also shown for comparison is the absorption spectrum of a poly-PTS single crystal.³⁸ The gross features of the crystal spectrum associ-

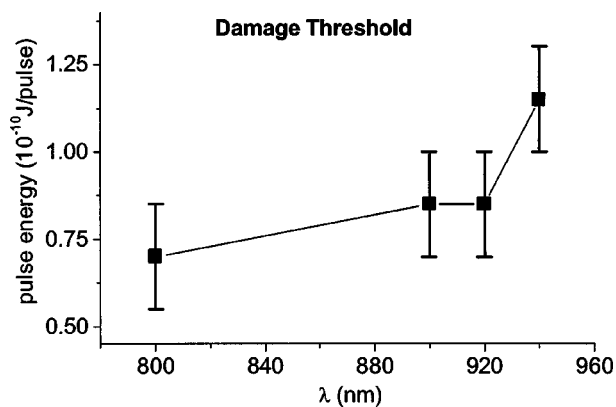


FIG. 2. Pulse energy at which optical damage occurred vs wavelength.

ated with the exciton feature are similar to the dilute samples, although there are some differences in details.

Initial Z-scan experiments near the expected two photon absorption peak around 900 nm indicated that above relatively small pulse energies, an irreversible change occurred in the optical properties of the samples. This became the principal limitation for this experiment. After damage, the Z-scan spectrum showed a large decrease in throughput when the maximum intensity was incident on the sample. This indicates a localized damage of the crystal. We found that the damage depends only on the input energy per pulse and not on the average power. Also, it was shown that the polarization of the incident light had to coincide with the direction of polymerization. These features indicate that the origin of the photo-damage was due to photo-induced polymerization of the monomer which increased the concentration of the polydiacetylene in the monomer crystal. This in turn led to a deeper minimum in the open aperture Z-scan. In retrospect these results are not surprising since photo-induced polymerization is well-known to frequently occur in PDAs.^{1,39} The wavelength dependence of the pulse energy at the 76 MHz repetition rate at which damage first occurs, as evidenced by changes in the Z-scan, is shown in Fig. 2.

Such a low pulse energy damage threshold, 0.1 nJ, which is well below the maximum available laser pulse energy, made the Z-scan experiments very difficult. Working at lower pulse energies meant that the open aperture nonlinear transmission dips were shallow, making it difficult to obtain an accurate measurement of the two photon absorption coefficient α_2 where $\Delta\alpha = \alpha_2 I$ (and I is the intensity). The maximum “dip” observed under condition that no optical damage occurs was approximately 15%.

Some typical results obtained for the coefficient α_2 near the expected two photon absorption peak and taken at pulse energies low enough to avoid damage are shown in Fig. 3. Notice the large uncertainties at low pulse energies due to the small multiphoton absorption minimum in the Z-scan, and the associated uncertainty in its measurement. The measured values are consistent between the two samples whose conjugated polymer concentrations were equal to within 10%. The difference between the coefficients measured for the two different concentrations is well within the uncertainties associated with the measurements. Note that experiments were also

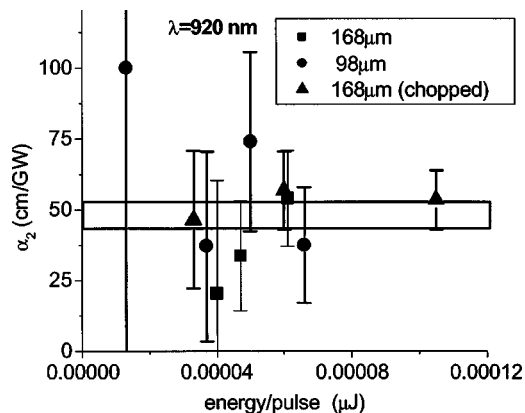


FIG. 3. The measured values of the two photon absorption coefficient α_2 near its expected peak vs pulse energy used.

done with a chopper present which reduced the average power by a factor of 8. This clearly made no difference showing that thermal effects were not important in this case.

The measured wavelength variation in the two photon absorption coefficient is shown in Fig. 4. The dilute samples show evidence for an expected peak between 900 and 940 nm (Ref. 19), although its exact location is uncertain due to large experimental error. The average concentration of the two dilute samples is 7.5% so that a simple linear rescaling of two-photon absorption data for 100% polymerized PTS¹⁹ gives a good overlap for on-peak and off-peak values. The accuracy of PTS measurement is much higher as 2PA values are more than ten times higher and the error bars for PTS measurements are not shown to simplify the representation. In particular, the value obtained previously for PTS is ~ 700 cm/GW at 920 nm, when scaled down to 3BCMU concentration exhibits reasonable agreement.^{19,20} Similarly the value 441 cm/GW for PTS at 800 nm gives 33.1 cm/GW at 800 nm gives, also in reasonable agreement with diluted 3BCMU with two-photon absorption of 30 cm/GW.^{19,20} Therefore, the values of the magnitude and spectral distribution of the two photon spectra are in reasonable agreement

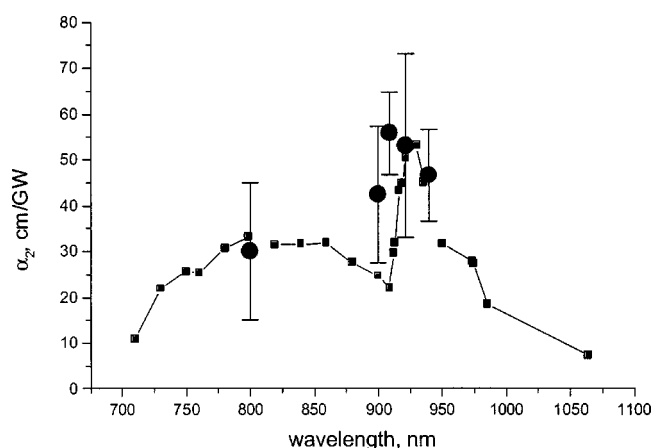


FIG. 4. The measured two photon absorption coefficient vs wavelength in 7.5% 3BCMU, large circles, as compared to 100% polymerized PTS, renormalized to 7.5% polymerization for comparison, black dots. PTS data is taken from the paper of Lawrence *et al.* (Ref. 19).

between the PTS crystal and the dilute isolated polymer chains in the 3BCMU monomer matrix. Note that comparison of the dilute 3BCMU samples with a fully polymerized poly-3BCMU crystal is not possible, since 3BCMU cannot be fully polymerized.⁴⁰

These results indicate that single chain theories of nonlinearities in PDAs should give reasonable predictions for nonlinear optical properties in single crystal PDAs and that any discrepancy between observations on a bulk sample and single chain theories should not be explained by chain interactions in the solid state.

In conclusion, we have investigated the two photon absorption near its predicted peak at about 920 nm in dilute mixtures of diacetylene polymer chains imbedded in a single crystal 3BCMU monomer. Photopolymerization induced by the probe beam used for the Z-scan measurements limited the maximum pulse energy that could be used for 140 fs pulses. Thus the measurements were performed with pulse energies of 0.1 nJ and less. This introduced a large uncertainty into the coefficient measurement. Despite the large uncertainties, good agreement was found with PTS polymer crystal values, when the dilute samples were scaled to a 100% concentration of polymer content. These measurements verify the hypothesis that single crystal values of the imaginary part of the susceptibility $\chi^{(3)}$ reflect the single chain polymer values and, therefore, interpolymer chain interactions are negligibly small.

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