

Optical Nonlinearities in One-Dimensional-Conjugated Polymer Crystals

C. Sauteret, J.-P. Hermann, R. Frey, F. Pradère, and J. Ducuing
Laboratoire d'Optique Quantique, Ecole Polytechnique, 91120 Palaiseau, France*

and

R. H. Baughman and R. R. Chance
Materials Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960
 (Received 23 February 1976)

The one-dimensional electronic delocalization that results from the solid-state polymerization of diacetylenes produces a dramatic enhancement of the optical nonlinearities of these compounds. The third-order susceptibilities of the polymerized crystals reach very high values comparable to those of inorganic semiconductors.

The influence of one-dimensional conjugation and electronic delocalization on the nonlinear optical properties of molecules has already been demonstrated^{1,2} and discussed theoretically.³ A systematic study of the cubic hyperpolarizability of polyenes² showed a strong enhancement for long chains, resulting in an increase of three orders of magnitude for dodecapreno- β -carotene (19 double bonds) as compared to saturated molecules of the alkane family. However, difficulties in growing good optical-quality samples have prevented until now the extension of these studies to crystals. Recent work of Wegner and co-workers⁴⁻⁶ has shown that the solid-state polymerization of diacetylenes $R-C\equiv C-C\equiv C-R$ can yield large, nearly defect-free, single crystals or fully conjugated polymers.⁷ These polymers have planar backbones which can be alternatively represented by two mesomeric structures (Fig. 1). Extensive π -electron delocalization takes place along this polymeric backbone. However, the bond alternation implies a periodic modulation of the electron charge density which produces an energy gap between a filled valence band and an empty conduction band. Optical studies conducted by Bloor *et al.*⁸ on such polymers show a sharp absorption edge and a strong reflection peak, as

expected from one-dimensional systems. We report here the observation of a large increase in the order of magnitude of the optical nonlinearity $\chi^{(3)}$ with the polymerization of diacetylenes. This increase, due to one-dimensional delocalization, results in values of $\chi^{(3)}$ as large as those measured in inorganic semiconductors.

In a first experiment we measured the cubic nonlinearity of the new diacetylene, *bis*-(phenylurethane) of 5,7-dodecadiyne-1,2-diol (TCDU) for which $R = (CH_2)_4OCONHC_6H_5$, by studying third-harmonic generation. The monomer was prepared by the reaction of phenyl isocyanate with 5,7-dodecadiyne-1,2-diol. Platelike single crystals, up to 2 cm² in area and 2 mm thick, were crystallized by allowing slow solvent evaporation at room temperature from an 8-g/l solution in equal volumes of acetone and ethyl acetate. Irradiation at room temperature with 15 Mrad of Co⁶⁰ γ rays produces polymer crystals with nearly the same shape as the precursor monomer crystals. X-ray diffraction measurements indicate that the monomer and polymer phases are isomorphous with space group $P2_1/c$.⁹ The (010) plane, which is the plate plane, is the predominant cleavage plane in both monomer and polymer phases. The polymer chain axis direction is contained in this plane and is parallel to the 100 (*a*) axis. For light propagating normal to the plate along the 010 (*b*) axis there are, for both monomer and polymer, two well-defined directions of polarization along the principal axes. In the polymer one of them is parallel to the chain axis. Refractive index data for light polarized along these directions were obtained in the red and infrared from channeled spectra of thin crystal plates and in the absorption range from reflectivity measurements. Some relevant values are given in Table I. Absorption coeffi-

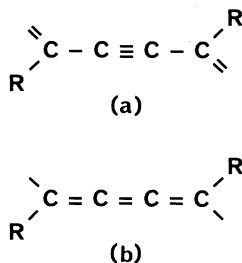


FIG. 1. Mesomeric forms of polyacetylenes.

TABLE I. Optical constants of polydiacetylenes and inorganic semiconductors.

Substance	Direction of light polarization	E_g (cm^{-1})	Refractive index (far from gap)	$ \chi^{(3)}(\omega, \omega, \omega) $ (10^{-13} esu)		$ \chi^{(3)}(\omega_1, \omega_1, \omega_1) /n^2$ (10^{-13} esu)
				at ω_1 (2.62 μm)	at ω_2 (1.89 μm)	
TCDU monomer	$\parallel \eta$	34 250	1.58	...	1.2 ± 0.6	0.48
	$\parallel \xi$	34 700	1.53	...	1.1 ± 0.6	0.47
TCDU polymer	$\parallel z$ (chains)	17 900	1.80	370 ± 140	700 ± 500	110
	$\perp z$	...	1.65	< 4	< 7	...
PTS polymer	$\parallel z$ (chains)	15 800	1.88	1600 ± 1000	8500 ± 5000	450
	$\perp z$	...	1.58	< 20	< 100	...
Germanium ^a	(100)	5400	4.0	4000 ± 2000 (at 10.6 μm)		250
GaAs ^a	(100)	10 900	3.2	480 ± 290 (at 10.6 μm)		50

^aJ. J. Wynne, Phys. Rev. **178**, 1295 (1969).

cients were deduced from transmission measurements on very thin cleaved plates; the results are shown in Fig. 2.

The harmonic measurements were performed first with a source at 1.89 μm giving a linearly polarized, 6-MW, 3×10^{-8} -sec pulse. The source and the experimental arrangement are described in Ref. 1. In all of the following the nonlinear susceptibility components were measured relative to quartz. Absolute values were deduced from the value $\chi_{xxxx}^{(3)}(\text{quartz}) = 3 \times 10^{-14}$ esu obtained by Hermann.¹⁰ The harmonic intensity generated in the monomer plate showed no strong variation when the polarization of the source was rotated. This indicates that all components of $\chi^{(3)}$ have similar magnitudes. For the components along the principal axes η and ξ we obtain

from the study of Maker fringes

$$|\chi_{\eta\eta\eta\eta}^{(3)}| = (1.0 \pm 0.6) \times 10^{-13} \text{ esu},$$

$$|\chi_{\xi\xi\xi\xi}^{(3)}| = (1.2 \pm 0.6) \times 10^{-13} \text{ esu}.$$

The polymer showed an entirely different behavior. The harmonic field was polarized along the chain axis and the harmonic intensity varied strongly with the direction of polarization: Within experimental error $I(3\omega) \propto \cos^6 \theta$ where θ is the angle of the source electric field with the chain axis. The component along the polymeric chain dominates the others by two orders of magnitude and its measured value is

$$|\chi_{zzzz}^{(3)}(\lambda = 1.89 \mu\text{m})| = (7 \pm 5) \times 10^{-11} \text{ esu},$$

a 600-fold increase with respect to the monomer components. The third-harmonic frequency at 15750 cm^{-1} is not far removed from the absorption peak at 19000 cm^{-1} and one can ask how much of the increase is due to a resonance effect. To answer this question we repeated the experiment with a laser source at $\lambda = 2.62 \mu\text{m}$. This source is obtained from double Raman scattering in H_2 gas from a ruby-pumped tunable dye laser¹¹ and yields a 10-MW, 2×10^{-9} -sec pulse. In that case the third-harmonic frequency lies about 8000 cm^{-1} below the absorption peak and no resonant enhancement should occur. We find

$$|\chi_{zzzz}^{(3)}(\lambda = 2.62 \mu\text{m})| = (3.7 \pm 1.4) \times 10^{-11} \text{ esu}.$$

This moderate variation of $\chi_{zzzz}^{(3)}$ is similar to that of the linear susceptibility $\chi_{zz}^{(1)}(3\omega)$ at the harmonic frequency. These results are shown in Table I together with those obtained for another compound of the same family, the *bis*-(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol (PTS) in the polymeric phase. Instability at room

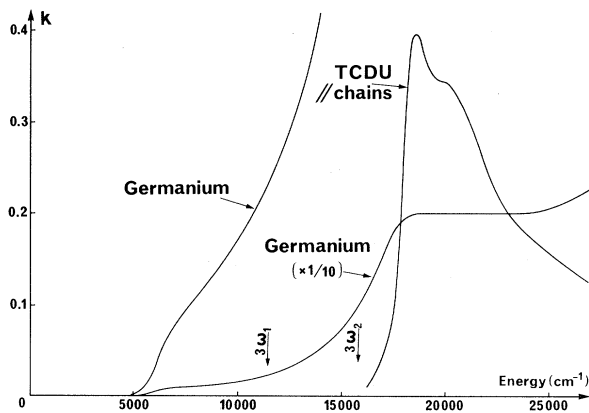


FIG. 2. Imaginary part of the refractive index in TCDU polymer; curve for germanium is given for comparison. $3\omega_1$ and $3\omega_2$ are frequencies of the third harmonics observed in both experiments (respectively, 0.89 μm and 0.63 μm).

temperature with respect to polymerization prevented optical studies of the monomer. The polymer platelike single crystals have symmetry $P2_1/c$.¹² The plane of the plate contains the unique twofold axis which is parallel to the direction of the chain axis. The results are shown in Table I. Again the component along the axis completely dominates. The resonant behavior is more pronounced: For $\lambda = 1.89 \mu\text{m}$ the harmonic frequency lies within 300 cm^{-1} of the absorption peak. We observe that the variation of $\chi_{zzzz}^{(3)}$ seems to parallel that of $\chi_{zz}^{(1)}(3\omega)$ as in the preceding case.

The strong anisotropy of the nonlinear susceptibility in the polymeric phase indicates that the dramatic enhancement of $\chi^{(3)}$ during the polymerization is due to the rearrangement of the π electrons which become delocalized over linear chains. They produce a comparatively smaller anisotropy of the refractive index (see Table I), but dominate completely the nonlinear properties. A simple model in which the π electrons move in a one-dimensional sinusoidal pseudopotential was used in Ref. 3 to predict the hyperpolarizabilities of polyenes. This model can be naturally extended¹³ to describe infinite polymeric chains. It reproduces well the main features of the linear optical properties: steep absorption edge and strong birefringence and dichroism. It predicts a value of the third-order susceptibility

$$\chi_{zzzz}^{(3)} = \frac{2^5}{45} \pi^2 \frac{e^{10}}{\sigma} \left(\frac{a_0}{d} \right)^3 \frac{1}{E_g^6}, \quad (1)$$

where a_0 is the Bohr radius, d an average C-C distance, σ the cross-sectional area per chain, and E_g the gap energy. This expression is valid in the low-frequency range, away from resonances. Using the values $d = 1.35 \text{ \AA}$, $\sigma = 118 \text{ \AA}^2$, $E_g = 17900 \text{ cm}^{-1}$ for poly-TCDU, and $d = 1.35 \text{ \AA}$, $\sigma = 95 \text{ \AA}^2$, $E_g = 15800 \text{ cm}^{-1}$ for poly-PTS, one obtains

$$\chi_{zzzz}^{(3)}(\text{TCDU}) = 1.2 \times 10^{-11} \text{ esu},$$

$$\chi_{zzzz}^{(3)}(\text{PTS}) = 3.0 \times 10^{-11} \text{ esu}.$$

In view of the extreme simplicity of the model which does not account for the different C-C distances in double and triple bonds and does not include local field corrections, the agreement can be considered as satisfactory and confirms the role of the π electrons. A more sophisticated tight-binding calculation¹⁴ leads to similar, slightly higher, values.

It will be noted that the cross-sectional area

per chain is much larger, for instance, than for polyethylene ($18.4 \text{ \AA}^2$) or for diamond in the (110) direction ($4.48 \text{ \AA}^2$). Decreasing the size of the substituent groups would increase the chain density and, if chain interaction can be neglected, the third-order susceptibility. This seems an attractive possibility. However, on decreasing the size of the substituent groups the fractional volume change on polymerization increases, resulting in large elastic strains which can produce phase separation, chain disorder, and/or limited conversion.

The values of $\chi^{(3)}$ measured in the polydiacetylenes are among the largest observed for bound electrons. They are comparable to those of inorganic semiconductors (see Table I). It should be noted, however, that the polydiacetylenes exhibit very different linear optical properties. They show much larger gaps and a much steeper absorption edge (see Fig. 2). This feature, directly related to the one-dimensional character of the π -electron delocalization, results in a transparency range appreciably more extended in the visible. However the rich infrared spectrum of the side groups introduces appreciable absorption at $\lambda > 3 \mu\text{m}$. The refractive indexes are smaller: In poly-PTS the index for light polarized along the chain is 1.88, compared to a value of 4 for germanium. This results directly from the fact that the influence of delocalization increases with the order of the susceptibility¹³ and thus is less strongly felt on $\chi^{(1)}$ than on $\chi^{(3)}$. In consequence, the parameter $\chi^{(3)}/n^2$, shown in Table I, which determines the strength of wave interactions, is large for the polydiacetylenes. An illustration is given by the values of the coefficient n_2 which relates the refractive index variation Δn to the light intensity I ($\Delta n = n_2 I$). From the measured values of $\chi^{(3)}$ and with neglect of dispersion, we deduce $n_2 = 1.8 \times 10^{-6} \text{ MW}^{-1} \text{ cm}^2$ for poly-PTS and for light polarized parallel to the chain axis, which can be compared to the value¹⁵ $n_2 = 3 \times 10^{-8} \text{ MW}^{-1} \text{ cm}^2$ for CS_2 . In the picosecond regime, where a high damage threshold $\approx 50 \text{ GW/cm}^2$ has been observed, this large value of n_2 associated with a fast ($\approx 10^{-14} \text{ sec}$) response time might lead to interesting applications. Four-wave interactions can also become unusually strong. With a $1.06\text{-}\mu\text{m}$, 1-GW/cm^2 pump, the gain for four-wave parametric amplification in the near infrared in poly-PTS is about ten times larger than the gain for three-wave parametric amplification in LiNbO_3 .

These results open attractive prospects for the

use of one-dimensional solid-state systems in nonlinear optics. The strong dependence of $\chi^{(3)}$ on energy gap suggests that the study of small-gap compounds might uncover large nonlinearities in the infrared. In order to study separately the influence of electronic delocalization the present experiments have been conducted on centrosymmetric diacetylenes. In compounds $R-C \equiv C-C \equiv C-R'$, the two different substituent groups will produce an asymmetry of the pseudopotential and allow the existence of a second-order susceptibility $\chi^{(2)}$. This asymmetry might however reduce the delocalization. Experiments are planned to study the possible opposing influences of these two factors on $\chi^{(2)}$.

The authors are indebted to Dr. C. Flytzanis for several valuable discussions, to Mr. M. Lequime for assistance in the reflection measurements, and to Mr. A. Preziosi for monomer and polymer synthesis. One of the authors (J.D.) acknowledges a fruitful discussion with Dr. Bloor on the optical properties of poly-PTS.

*Laboratoire propre du Centre National de la Re-

cherche Scientifique.

¹J.-P. Hermann, D. Ricard, and J. Ducuing, *Appl. Phys. Lett.* **23**, 178 (1973).

²J.-P. Hermann and J. Ducuing, *J. Appl. Phys.* **45**, 5100 (1974).

³K. C. Rustagi and J. Ducuing, *Opt. Commun.* **10**, 258 (1974).

⁴G. Wegner, *Z. Naturforsch.* **24b**, 824 (1969).

⁵G. Wegner, *Makromol. Chem.* **145**, 85 (1971).

⁶E. Hädicker, E. C. Mez, C. H. Krauch, G. Wegner, and J. Kaiser, *Angew. Chem.* **83**, 253 (1971).

⁷R. H. Baughman, *J. Polym. Sci., Polym. Phys. Ed.* **12**, 1511 (1974).

⁸D. Bloor, D. J. Ando, F. H. Preston, and G. C. Stevens, *Chem. Phys. Lett.* **24**, 407 (1973).

⁹V. Enkelmann, J. B. Lando, and R. H. Baughman, unpublished.

¹⁰J.-P. Hermann, *Opt. Commun.* **9**, 74 (1973).

¹¹R. Frey and F. Pradère, *Opt. Commun.* **12**, 98 (1974); see also *Infrared Phys.* **15**, No. 4 (1975).

¹²D. Kobelt and E. F. Paulus, *Acta Crystallogr. Sect. B* **30**, 232 (1974).

¹³J. Ducuing, in *Nonlinear Spectroscopy, Proceedings of the International School of Physics "Enrico Fermi," Course LXIV*, edited by N. Bloembergen (Academic, New York, 1975).

¹⁴G. Agrawal and C. Flytzanis, unpublished.

¹⁵M. J. Moran, C. Y. She, and R. L. Carman, *IEEE J. Quantum Electron.* **11**, 259 (1975).

Optical Coherent Transients by Laser Frequency Switching*

Richard G. Brewer and Azriel Z. Genack

IBM Research Laboratory, San Jose, California 95193

(Received 8 March 1976)

Coherence phenomena such as photon echoes, free induction, and nutation effects are easily detected in molecular iodine using a *frequency-switched* tunable cw dye laser. This technique is generally applicable to atoms, molecules, and solids and offers unique ways for probing dynamic interactions in a selective manner. Elastic and inelastic collision mechanisms for I_2 are examined independently and compared with theory.

We present a simple and versatile laser technique which should prove useful in observing coherent optical transient phenomena in atoms, molecules, and solids. In concept, the method is analogous to pulsed nuclear-magnetic-resonance techniques,¹⁻³ but in practice, it more closely resembles the recently introduced Stark-switching method.⁴⁻⁷

To illustrate its use, we demonstrate photon echoes,⁸ free induction decay (FID),⁵ and nutation effects^{4,9} in numerous lines of the visible electronic transition of I_2 (Fig. 1). Similar observations have been made also on the sodium *D* lines. Our work contrasts with classical optical line-

broadening measurements where the various broadening mechanisms invariably remain hidden within the optical line shape. Coherent transient methods, on the other hand, allow one to distinguish individual dephasing processes. As an initial example, we inspect the collisional properties of I_2 .

In the earlier Stark-switching experiments, a prescribed sequence of low-voltage Stark pulses switched a molecular sample into or out of resonance with an infrared beam from a fixed-frequency cw CO_2 laser.⁴⁻⁶ Coherent emission or absorption transients were detected in the transmitted beam. A variant of this idea was later