Scaling law for second-order hyperpolarizability in poly(triacetylene) molecular wires

U. Gubler, Ch. Bosshard, and P. Günter

Nonlinear Optics Laboratory, Institute of Quantum Electronics, Swiss Federal Institute of Technology ETH,
ETH Hönggerberg, CH-8093 Zürich, Switzerland

M. Y. Balakina, J. Cornil, and J. L. Brédas

Laboratory for Chemistry of Novel Materials, Center for Research on Molecular Electronics and Photonics,
University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium

R. E. Martin and F. Diederich

Institute of Organic Chemistry, Swiss Federal Institute of Technology ETH, ETH Zürich, CH-8092 Zürich, Switzerland

Poly(triacetylenes) are rodlike molecules with electrons delocalized over a one-dimensional path. We show that they exhibit a power-law dependence of the second-order hyperpolarizability γ on the monomer unit n for short molecules and a smooth saturation toward a linear increase in longer molecules. The power law of $\gamma \propto n^a$ with $a \approx 2.5$ from dengenerate four-wave mixing and third-harmonic generation measurements is in good agreement with quantum-chemical calculations. The critical conjugation length for saturation in the three cases is shown to be approximately 60 carbon−carbon bonds, which indicates the upper boundary for the electron delocalization in such a one-dimensional molecular wire. © 1999 Optical Society of America

OCIS codes: 190.4710, 190.4380, 190.4160, 160.4330, 160.4890.

The investigation of the relationships between the structure of a conjugated molecule and its nonlinear optical properties has attracted a great deal of interest. This knowledge is necessary for tailoring chromophores with sufficiently large nonlinearities for applications in photonics technology.[1] Whereas principles for the optimization of first-order hyperpolarizabilities β are well established, rules for the second-order hyperpolarizability γ are less well documented.

One issue under investigation is the evolution of the second-order hyperpolarizability on elongation of the π-electron path in a molecular backbone. Measurements and quantum-chemical calculations provide an empirical power law of the second-order hyperpolarizability γ relative to the conjugation length (or the number of momomer units n) in short oligomers[2]:

$$\gamma = \gamma_m n^a. \tag{1}$$

For longer chain lengths, this power law saturates and reaches a linear increase versus elongation.

Despite much progress in organic synthesis, the preparation of long, well-defined monodisperse oligomers remains quite tedious. Hence it is not surprising that in most studies the nonlinearities of rather short oligomers, which often lay outside the interesting region where the ratio of γ/n to n levels off, were investigated. We have now considerably extended the oligomeric series by including monodisperse octameric, dodecameric, and hexadecameric poly(triacetylene) rods. The experiments performed on oligomers with 1, 2, 4, 6, 8, 12, and 16 monomer units and on two polydisperse samples of 22 and 31 units (Fig. 1) span the entire power-law regime, including the region of saturation and the subsequent linear increase of γ versus n. The different natures of the electronically neutral end groups in the polydisperse samples do not affect the measured nonlinearities, because the saturation regime has already been reached.

We use two different experimental techniques to investigate the hyperpolarizabilities γ: degenerate four-wave mixing (DFWM) in counterpropagating geometry and third-harmonic generation (THG). Using the expansion of polarization $\tilde{p}_i$ as in Eq. (2) below, assuming that $\tilde{A}_j = \{A_j \exp[i(\omega t - \mathbf{k} \cdot \mathbf{r})] + A_j{}^* \exp[-i(\omega t - \mathbf{k} \cdot \mathbf{r})]\}/2$ for electric field $\tilde{E}_i$ and polarization $\tilde{p}_i$, and summing over all possible terms, we define the relevant nonlinearities through

$$\tilde{p}_i = \mu_i + \epsilon_0(\alpha_{ij}\tilde{E}_j + \beta_{ijk}\tilde{E}_j\tilde{E}_k$$
$$+ \gamma_{ijkl}\tilde{E}_j\tilde{E}_k\tilde{E}_l + \ldots), \tag{2}$$

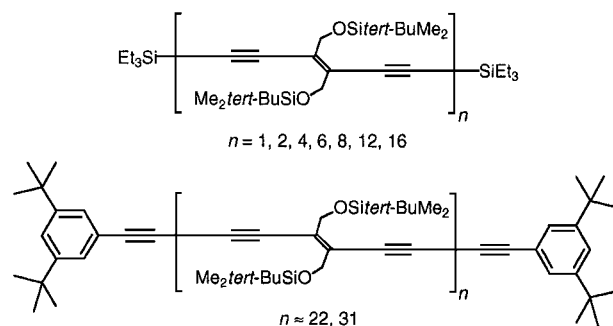$$p_{\text{DFWM}}(\omega) = \frac{3\epsilon_0}{2} \gamma(-\omega, \omega, -\omega, \omega)E_1E_2E_3, \tag{3}$$

Fig. 1. Structure of the poly(triacetylene) investigated here. The lateral, solubility-providing Me$_2$tert−BuSiOCH$_2$ groups are not in conjugation with the backbone. The Et$_3$Si end groups are electronically neutral and do not act as electron-withdrawing or -releasing moieties.

$$p_{\text{THG}}(3\omega) = \frac{\epsilon_0}{4}\, \gamma(-3\omega,\omega,\omega,\omega)E^3, \qquad (4)$$

where E_1, E_2, and E_3 are the electric fields of the three incident beams in DFWM. Because different optical frequencies are involved in the nonlinear processes considered, the experimental results cannot be directly compared without an extrapolation to the static limit of zero frequency. Owing to the presence of degenerate frequencies in DFWM, molecular vibrations may also contribute to nonlinearity γ, unlike for THG.

For DFWM, a 10-ps Nd:YLF laser with a wavelength of 1047 nm and a repetition rate of 10 Hz is used. The counterpropagating weak probe beam can be delayed in time to record the temporal shape of the nonlinearity also. The nonlinearities are calibrated against CS_2 ($n_2 = 3.2 \times 10^{-5}$ GW/cm^2, $\chi^{(3)} = 3.0 \times 10^{-20}$ m^2/V$^2 = 2.1 \times 10^{-12}$ esu).[3]

The sample molecules are diluted in chloroform and measured twice for four different concentrations. From the slope of the nonlinearity of the solution versus concentration, the molecular hyperpolarizabilities are elucidated according to the oriented gas model.[4]

With the short pulse length of 10 ps, we avoid contributions to the nonlinearity from thermal or orientational effects of the solute molecule. The wavelength of 1047 nm is far from any single-photon resonance (Fig. 2). Because of the measured instantaneous response in all poly(triacetylene) (PTA) samples, we can also exclude two-photon resonances.
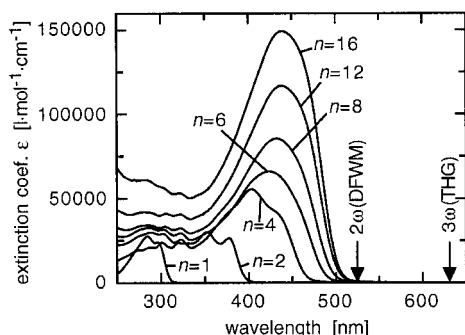

Fig. 2. The absorption of the PTA rods shifts bathochromically to longer wavelengths with increased number of monomer units n. The shift stops near 10 monomer units. The doubled DFWM frequency (523.5 nm) and the third harmonic of the THG experiment (635.7 nm) are clearly in the transparency range.

The THG data are measured with a Raman-shifted (1907-nm) nanosecond Nd:YAG laser, as described elsewhere.[4,5] The setup is calibrated against fused silica [$\chi^{(3)} = 1.62 \times 10^{-22}$ m^2/V$^2 = 1.16 \times 10^{-14}$ esu].[6] The third-harmonic wavelength (635.7 nm) is well below the absorption edge of the linear spectra, and the involved frequencies are thus also in the transparency range.

With respect to the theoretical methodology, we first optimize the geometry of the unsubstituted PTA oligomers with the help of the semiempirical Hartree–Fock Austin Model 1 (AM1) Hamiltonian,[7] assuming all-*trans* planar conformations. We then calculate the average static γ values of the PTA chains by means of the valence effective Hamiltonian[8] (VEH) approach coupled with a sum-over-states (SOS) formalism.[9] The VEH–SOS approach was shown to provide reliable descriptions of the nonlinearities in long organic conjugated chains.[10] The states involved in the SOS development correspond to single Slater determinants obtained following single and double excitations between all the valence levels in short oligomers up to $n = 3$ and between the 40 highest occupied and 40 lowest unoccupied molecular orbitals in longer chains (see Table 1 and Fig. 3).

The nonlinearities measured by DFWM exhibit a smooth saturation of second-order hyperpolarizability γ near 10 monomer units. Below the saturation, the experiment shows a power-law dependence of $\gamma \propto n^a$ with $a = 2.64 \pm 0.20$.

The THG shows a power law with an exponent $a = 2.46 \pm 0.10$, which compares well with the result $a = 2.52 \pm 0.10$ measured for a PTA series[5] with slightly different end groups (trimethylsilyl instead of triethylsilyl).

Comparison of the exponents for DFWM and THG reveals a difference that is small and within the experimental error, which indicates that vibrational contributions to the nonlinearity in the case of DFWM may not be important. The chain-size evolution of the VEH–SOS-calculated average static γ values fits a power law with $a = 2.34$ for PTA oligomers that contain five to eight monomer units, which are expected to be suitably described by our theoretical approach. The calculated values of γ deviate from the power law beyond $n = 9$–10, thus indicating the onset of a saturation regime.

Table 1. Second-Order Hyperpolarizabilities γ versus Number of Monomer Units n of Poly(triacetylenes) Measured by DFWM and THG (Experimental Error, 10%) and Calculated Quantum Mechanically[a]

n	$\lambda_{\max}$(nm)	γ_{DFWM} $\times 10^{-36}$ esu	γ_{DFWM} $\times 10^{-48}$ m^5/V^2	γ_{THG} $\times 10^{-36}$ esu	γ_{THG} $\times 10^{-48}$ m^5/V^2	$\gamma_{\text{VEH–SOS}}$ ($\times 10^{-36}$ esu)
1	296	9	0.13	12	0.16	0.5
2	377	77	1.1	54	0.75	33
4	403	583	8.2	360	5.0	584
6	423	1130	16	890	12	1878
8	432	2180	31	1810	25	3497
12	437	3530	49	2570	36	6892
16	439	4290	60	4230	59	10 315
22	448	7530	105	6510	91	

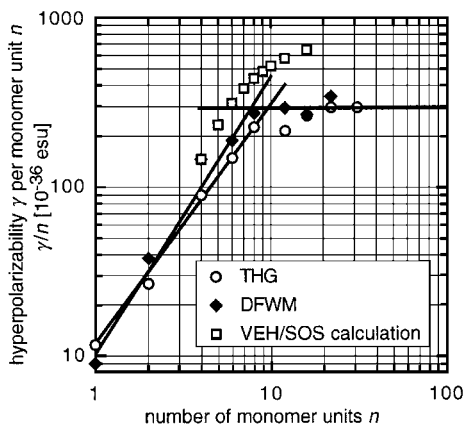[a]The wavelength of the maximum absorption $\lambda_{\max}$ is also given.

Fig. 3. The third-order polarizabilities of the poly-triacetylene molecules show a power-law increase for short oligomeric lengths with smooth saturation near 10 monomer units for DFWM ($\gamma \propto n^{2.46\pm0.10}$), THG ($\gamma \propto n^{2.64\pm0.20}$), and quantum-chemical calculations for n ranging from 5 to 16. In the saturation regime the nonlinearity increases linearly on backbone elongation.

We can compare our results with those of previous experiments, for which information on the saturation regime is, however, missing. Experiments with polyenes give exponents of $a = 2.5$ from THG (Ref. 11) and $a = 3.0$ from electric-field-induced second-harmonic-generation measurements.[12]

The nonlinearities in oligothiophenes measured by THG showed an exponent $a = 2.8$.[13] DFWM and electric-field-induced second-harmonic-generation data revealed exponents[5] $a = 4.05$ (Ref. 14) and $a = 4.6$ (Ref. 15), respectively, for these oligomers. The size of these larger exponents, however, can be explained by a two-photon resonance enhancement in those experiments.

The hyperpolarizabilities of a series of oligo-thienyleneethynylenes were measured by THG at two wavelengths. At the fundamental wavelength, $\lambda = 1.064\ \mu$m, an exponent $a = 3.66$ (Ref. 16) was found, with the harmonic wavelength in resonance. At $\lambda = 1.907\ \mu$m, a smaller exponent $a = 2.4$ (Ref. 17) was measured. The saturation regime was reached for linearly conjugated 60 C—C bonds.

We can conclude that exponent a thus tends to be approximately 2.5 for various polymers in the transparency range. In the presence of two- or three-photon resonances, the measured exponent a increases. Moreover, the values presented here are of similar magnitude for other organic material systems.

To summarize, we have shown by DFWM, THG measurements, and quantum-chemical calculations that the chain-length dependence of the second-order hyper-polarizability γ of poly(triacetylene) molecular wires follows a power law for short oligomers. This power law saturates smoothly near 60 carbon–carbon bonds, which corresponds to an effective conjugation length of 7.5 nm.

For all-optical signal processing applications, large values of γ are required. Because often an increase in γ is related to an increase in the molecular length, a suitable parameter with which to evaluate the potential of the material is γ/n. To maximize the values of γ/n, the extension of the molecular backbone beyond this saturation region is thus not necessary; the maximum can already be reached with oligomers of intermediate length. This behavior seems to be a common feature of many conjugated polymers, because the values for the power-law exponent and the critical conjugation length do not differ significantly among different molecular systems.

References

1. R. R. Tykwinski, U. Gubler, R. E. Martin, F. Diederich, C. Bosshard, and P. Günter, J. Phys. Chem. B **102,** 4451 (1998).
2. J. L. Brédas, C. Adant, P. Tackx, A. Persoons, and B. M. Pierce, Chem. Rev. **94,** 243 (1994).
3. M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **26,** 760 (1990).
4. U. Gubler, R. Spreiter, C. Bosshard, P. Günter, R. R. Tykwinski, and F. Diederich, Appl. Phys. Lett. **73,** 2396 (1998).
5. R. E. Martin, U. Gubler, C. Boudon, V. Gramlich, C. Bosshard, J.-P. Gisselbrecht, P. Günter, M. Gross, and F. Diederich, Chem. Eur. J. **3,** 1505 (1997).
6. Ch. Bosshard, in *Nonlinear Optical Effects and Materials*, P. Günter, ed., Springer Series in Optical Sciences (Springer-Verlag, Berlin, 1999).
7. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, J. Am. Chem. Soc. **107,** 3902 (1985).
8. J. L. Brédas, R. R. Chance, R. Silbey, G. Nicolas, and Ph. Durand, J. Chem. Phys. **75,** 255 (1981).
9. B. J. Orr and J. F. Ward, Mol. Phys. **20,** 513 (1971).
10. Z. Shuai and J. L. Brédas, Phys. Rev. B **46,** 4395 (1992).
11. I. D. W. Samuel, I. Ledoux, C. Dhenaut, J. Zyss, H. H. Fox, R. R. Schrock, and R. J. Silbey, Science **265,** 1070 (1994).
12. G. S. W. Craig, R. E. Cohen, R. R. Schrock, R. J. Silbey, G. Puccetti, I. Ledoux, and J. Zyss, J. Am. Chem. Soc. **115,** 860 (1993).
13. L.-T. Cheng, J. M. Tour, R. Wu, and P. V. Bedworth, Nonlin. Opt. **6,** 87 (1993).
14. M.-T. Zhao, B. P. Singh, and P. N. Prasad, J. Chem. Phys. **89,** 5535 (1988).
15. H. Thienpont, G. L. J. A. Rikken, E. W. Meijer, W. ten Hoeve, and H. Wynberg, Phys. Rev. Lett. **65,** 2141 (1990).
16. T. Geisler, J. C. Petersen, T. Bjornholm, E. Fischer, J. Larsen, C. Dehu, J.-L. Brédas, G. V. Tormos, P. N. Nugara, M. P. Cava, and R. M. Metzger, J. Phys. Chem. **98,** 10102 (1994).
17. I. D. W. Samuel, I. Ledoux, C. Delporte, D. L. Pearson, and J. M. Tour, Chem. Mater. **8,** 819 (1996).