

## Saturation of the second hyperpolarizability for polyacetylenes

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### Abstract

Polyacetylene (PA) polymers  $-(\text{CH}=\text{CH})_N-$  lead to large second hyperpolarizabilities ( $\gamma$ ) that increase with  $N$ . For small  $N$  the increase is quite rapid, eventually saturating (becoming linear in  $N$ ) for  $N \geq N_{\text{sat}}^{\gamma}$ . Both experimental and theoretical attempts have been made to estimate  $N_{\text{sat}}^{\gamma}$ . In 1994 this led to two Science papers, one obtaining  $N_{\text{sat}}^{\gamma} = 20$  (semiempirical theory) and the other obtaining  $N_{\text{sat}}^{\gamma} = 125$  (experiment, but on a substituted disordered form of PA!). We report here ab initio calculations up through  $N = 49$  ( $\text{C}_{98}\text{H}_{100}$ ) and show that  $N_{\text{sat}}^{\gamma} = 45 \pm 5$ . The much larger experimental value,  $N_{\text{sat}}^{\gamma} = 125$ , is explained in terms of the structural defects and disorder introduced by the synthetic method.

There is a great deal of interest in developing organic non-linear optical (NLO) materials for use in optical processing, in storage of data and images, and in optically based telecommunications and computers [1]. Important for these applications are the hyperpolarizabilities, which describe how the dipole moment ( $\mu$ ) depends on an applied electric field ( $E$ ),

$$\mu_i(E) = \mu_i + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots \quad (1)$$

Here  $\alpha$ ,  $\beta$ , and  $\gamma$  are the polarizability, first hyperpolarizability, and second hyperpolarizability, respectively.

The properties of most interest [1] are  $\beta$  and  $\gamma$  which control:

- frequency doubling (better focus, more data),
- changes in refractive index (electro-optical switches for telecommunications), and
- frequency mixing.

Currently  $\text{LiNbO}_3$  is the material of choice for these applications [2]. However, polymers would provide great advantages in ease of processing and for tailoring the properties to match precise requirements [3]. The best such materials are charge-transfer type molecules [3] involving a polyene bridge linking between a donor and an acceptor. The nature of donor, acceptor, and bridge are chosen to optimize  $\beta$  or  $\gamma$ .

It is well known [4–7] that for polyenes,  $-(\text{CH}=\text{CH})_N-$ ,  $\alpha$  and  $\gamma$  increase rapidly with  $N$  for smaller  $N$  but saturate to increase only linearly with

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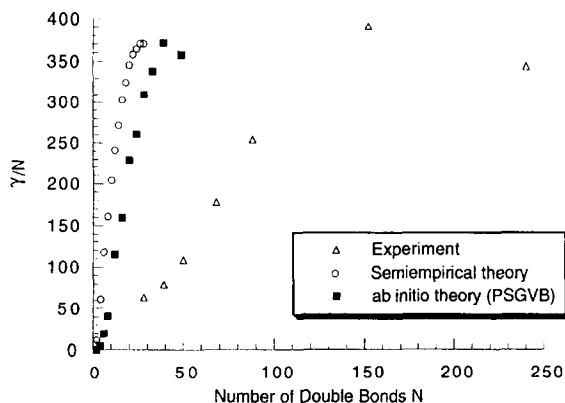


Fig. 1. Recent results on the saturation of  $\gamma/N$  for polyacetylenes (PA). The open squares are from the experiment [6] on a substituted, imperfect PA. The open circles are from semiempirical theory [7]. The filled squares are from the current calculation.

$N$  above some value,  $N_{\text{sat}}$  ( $\beta = 0$  since the molecule is centrosymmetric). For polythiophenes (which have a polyene backbone), it was established [4–7] that  $\alpha$  saturates at  $N = 10$  double bonds (a  $C_{20}$  polyene) whereas  $\gamma$  saturates at  $N = 18$  double bonds ( $C_{36}$ ). For the parent compound, polyacetylene (PA), experiment [17] shows that  $N_{\text{sat}}^{\gamma} > 16$  and theory [15] shows that  $N_{\text{sat}}^{\gamma} > 22$ . However, it has not been possible to study sufficiently large  $N$  to establish  $N_{\text{sat}}^{\gamma}$  experimentally (because of difficulties with synthesis) or theoretically (because of expense). Of two recent reports on long chain polyenes in Science, experiment [8] on a substituted, imperfect PA leads to  $N_{\text{sat}}^{\gamma} \approx 125$  ( $C_{250}$ ), whereas (semiempirical) theory [9] leads to  $N_{\text{sat}}^{\gamma} = 20$  ( $C_{40}$ ), see Fig. 1.

The largest previous ab initio theoretical calculations [15] were on  $N = 22$  ( $C_{44}$ ), far too small to test for saturation. We have developed a new ab initio quantum mechanical program (PS-GVB/NLO) [11–13] which allows predictions of hyperpolarizabilities for large molecules 10–20 times faster than previously possible. We report here ab initio Hartree–Fock (HF) calculations (6-31G basis set)<sup>1</sup> on  $\alpha$  and  $\gamma$

<sup>1</sup>The 6-31G basis set gives accurate predictions for such systems. For example, in Ref. [10] we calculated the hyperpolarizabilities of julolidinyl-*n*-isoxazolone using the 6-31G basis set for  $N = 1$ –6. Adding polarization functions increases  $\gamma$  uniformly by about 10%. Thus the dependence of  $\gamma$  on  $N$  was not affected and led to excellent agreement with experiment. At the HF level the magnitude of  $\beta$  was systematically about half the experimental value.

with  $N$  up to 49 ( $C_{98}$ ). The geometry was obtained from the optimized structure [14] of  $C_{22}H_{24}$  (HF with a 6-31G basis), using the central unit to determine the geometry of all PA polymers. (This led to  $C=C = 1.450 \text{ \AA}$ ,  $C-C = 1.338 \text{ \AA}$  and a bond angle of  $124.3^\circ$ .) We tested the geometry by calculating the energy of  $C_{48}H_{50}$  with bond lengths changed by  $\pm 0.003 \text{ \AA}$  and found that the above structure has the lowest energy.

$\alpha$  and  $\gamma$  were obtained by calculating  $\mu(E)$  with three finite fields (sufficient because of the inversion symmetry). We used electric fields along the chain direction to obtain  $\alpha_{zz}$  and  $\gamma_{zzzz}$ .

There are two contributions to the errors:

– Higher order terms in Eq. (1). By using a fourth electric field for  $C_{78}H_{80}$ , we found that neglect of higher order terms leads to less than 0.01% error for  $\alpha$  and to about 0.4% error for  $\gamma$ .

– Errors in the calculation of the dipole moment (due to lack of convergence or other errors in the wavefunction). By examining the changes of  $\alpha$  and  $\gamma$  with convergence, we estimate that the error from this source is less than 0.01% for  $\alpha$  and less than 3% for  $\gamma$ .

Fig. 2a shows the results for  $\alpha$  (filled squares), where we see that

$$N_{\text{sat}}^{\alpha} = 25 \pm 2 (C_{50}). \quad (2)$$

Fig. 2b shows results for  $\langle \gamma \rangle = \gamma_{zzzz}/5$  where we see that

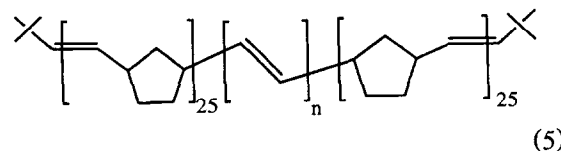
$$N_{\text{sat}}^{\gamma} = 45 \pm 5 (C_{90}). \quad (3)$$

These values are obtained by fitting  $\alpha/N$  and  $\gamma/N$  to smooth curves and setting  $N_{\text{sat}}$  to 95% of the limiting value. For large  $N$  we expect

$$\bar{\gamma}_N = \frac{\gamma}{N} = \bar{\gamma}_{\infty} \left( \frac{1 - \exp(-AN)}{1 + B \exp(-CN)} \right). \quad (4)$$

The solid lines in Fig. 2 represent the fits to such a function.

Direct experimental measurements on  $\gamma$  for polyenes has been made by Craig et al. [17] who synthesized



(5)

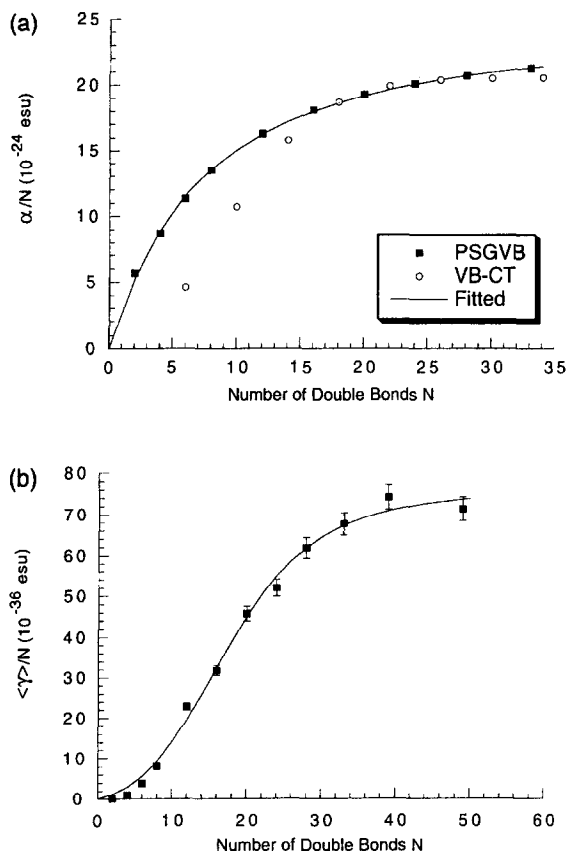


Fig. 2. (a) Polarizability of polyacetylene chains from ab initio calculations (PS-GVB/NLO). The filled squares are from the current ab initio HF calculations. The open circles are for VB-CT using  $t = 0.83$  eV and  $V = 1.0$  eV. The solid line is a fit to an equation like Eq. (4). The parameters are  $\alpha_\infty = 22.6 \times 10^{-24}$  esu,  $A_\alpha = 0.249$ ,  $B_\alpha = 0.84$ , and  $C_\alpha = 0.08$ . (b) Second hyperpolarizability of polyacetylene chains from ab initio calculations (PS-GVB/NLO). The line is a fit to Eq. (4). The parameters are  $\bar{\gamma}_\infty = 380 \times 10^{-36}$  esu,  $A_\gamma = 0.073$ ,  $B_\gamma = 11.4$ , and  $C_\gamma = 0.182$ .

with  $N$  ranging from 4 to 13. The resulting values of  $\gamma$  (in THF) are included in Fig. 3 (filled triangles). The  $N$  dependence from theory and experiment agree well<sup>2</sup>.

Previous ab initio calculations [15] (HF with 6-31G basis) considered only  $N$  up to 22. These results

<sup>2</sup> Because of the correlation effect, the presence of solvent and end groups, and the non-zero frequency, it is difficult to compare the absolute values between the theory and experiment. Consequently, in Fig. 3 we divided the reported experimental value of  $\gamma$  by a factor of 6.

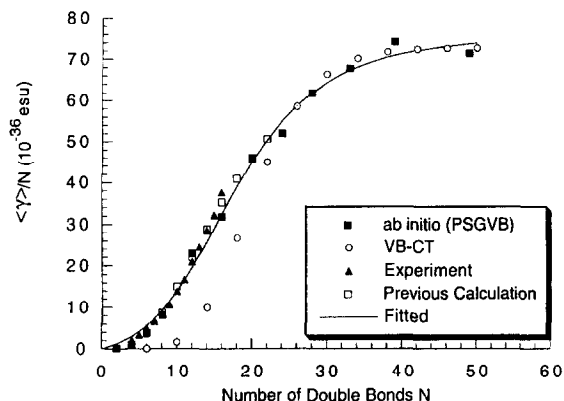


Fig. 3. Second hyperpolarizability of polyacetylene chains. The filled squares are from the current ab initio HF calculations while previous ab initio results (see Footnote 1) are shown with open squares. The open circles are for VB-CT using  $t = 0.83$  eV and  $V = 1.0$  eV. Direct experimental results [15] are shown with filled triangles.

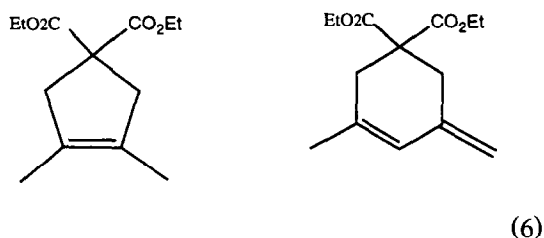
(open squares in Fig. 3) are in excellent agreement with the current results (circle in Fig. 3).

Mukamel and coworkers [9,16] predicted the  $N$  dependence of  $\gamma$  using an electron-hole model (based on semiempirical PPP  $\pi$ -electron calculations) to describe polarization. Their results (crosses in Fig. 2) lead to saturation at  $N_{\text{sat}}^\gamma = 20$  ( $C_{40}$ ). This is substantially smaller than the ab initio results ( $N_{\text{sat}}^\gamma = 45$ ). The difference is probably due to approximation in the semiempirical and electron-hole descriptions.

Previously [5–7] we developed a simple theoretical model, valence bond charge transfer (VB-CT), for predicting polymer length dependence of  $\alpha$  and  $\gamma$ . This method involves two parameters ( $t$  and  $V$ ) which can be fitted to either experiment or theory. (The band gap and valence bandwidth and their dependence can be used on  $N$ ). Using  $t = 0.83$  eV and  $V = 1.0$  eV for VB-CT leads to good agreement with the ab initio results on  $\alpha$  (as shown in Fig. 1, open circles). The VB-CT results for  $\gamma$  in Fig. 3 (open circles, scaled by a factor of 0.457) leads to  $N_{\text{sat}}^\gamma = 45$ , in excellent agreement with the ab initio calculations.

Summarizing, the ab initio theoretical studies lead to  $N_{\text{sat}}^\alpha = 25 \pm 2$  and  $N_{\text{sat}}^\gamma = 45 \pm 5$ . These theoretical results are in strong disagreement with recent experimental results [8], which led to  $N_{\text{sat}}^\gamma = 125$ . However,

these experiments did *not* involve pure all-trans polyenes. The synthetic method [18] led to about a 50:50% mixture of the species in Eq. (6):



We find (*vide infra*) that such disorder can increase  $N_{\text{sat}}^{\gamma}$ . In addition, there appears to be other structural defects [8,18] in the chains that might modify the saturation length. Also the measurement of chain length was indirect [18], leading to additional uncertainties.

Given the limitations in the experiments, we believe that the current estimate of  $N_{\text{sat}}^{\gamma} = 45 \pm 5$  is the most reliable estimate.

In order to examine the role that disorder plays in  $\alpha$  and  $\gamma$ , we used VB-CT theory with the  $t$  and  $V$  parameters discussed above but randomly changed  $V$  (the site energy) by  $\pm 0.4$  eV. The result is shown in Fig. 4 along with that for pure all-trans polyethylene. We find two effects:

- $N_{\text{sat}}^{\gamma}$  increases by a factor of about 1.4.

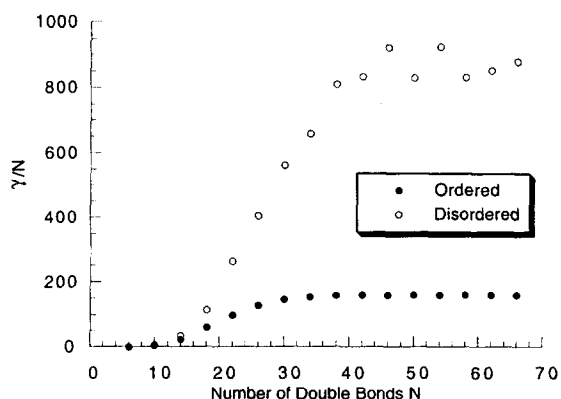


Fig. 4. Effect of disorder in second hyperpolarizability based on VB-CT with  $t = 0.83$  eV and  $V = 1.0$  eV. Filled circles indicate the ordered polyene while open circles are with a random disorder of  $V_i = V \pm 0.4$  eV.

- the magnitude of  $\gamma$  for a given  $N$  also increases by a factor of about 5.

This suggests that deliberate inclusion of disorder may be advantageous. One might do this by including monomers with  $\text{CH}_3$ , Cl, or F substituents. Such monomers might lead to increased solubility in various solvents, allowing synthesis of longer chains. In addition one might achieve the alignment needed for high non-linear performance by using substituents that can be photolytically or thermally cross linked in the applied electric field.

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