well-studied CV, they are present in >80% of the chondrules. FOIs are rare or absent in the EH, H, and L chondrites. No correlation was observed between shock grade and the presence or absence of FOIs. S. E. Haggerty and M. McMahon [*Proc. Lunar Planet. Sci. Conf.* **10**, 851 (1979)] show FOI-like textures from Allende in their figure 1, a, h, and k.

14. Powdered mixtures containing ~60 weight % San Carlos olivine, ~39 weight % Bamble enstatite, and ~1 weight % troilite, pentlandite, magnetite, and Ni-Fe metal were pressed into pellets, heated to 1560°C (just above the enstatite solidus), and then cooled at 0.1° to 0.01°C s^{-1}. Samples were cut into 0.5-mm-thick sections and polished.
15. The largest uncertainties in extrapolating experimentally determined fluxes to nebular conditions result from differences in the heat-transfer properties of 0.5-mm-thick plates and millimeter-sized spheres and from the possibility that chondrules may have been heated by more than one mechanism. If a secondary heat source, such as energetic particles, facilitated chondrule heating, less radiant energy may be required to form FOIs.
16. Data and procedures were followed as described by R. C. Gilman [*Astrophys. J. Suppl.* **28**, 397 (1974)], except for the condition $(2\pi a/\lambda)(n^2 + k^2)^{1/2} > 0.1$. For this case, $Q(a,T)$ was calculated according to the large-particle approximation for $K(\omega)$ given by H. C. van de Hulst [*Light Scattering by Small Particles* (Dover, New York, 1981), p. 175], which yields more realistic Planck mean absorption cross sections for grains >1 μm than the extrapolation method used by Gilman.
17. For a similar evaluation addressing the survival of dust within the radiation field associated with supernovae, see S. W. Falk and J. M. Scalo, *Astrophys. J.* **202**, 690 (1975).
18. R. H. Hewins and P. M. Radomsky, *Meteoritics* **25**, 309 (1990).
19. R. A. Robie, B. S. Hemingway, J. R. Fisher, *U. S. Geol. Surv. Bull.* **1452**, 363 (1979).
20. In estimating peak chondrule temperatures, the greatest uncertainties lie in the spherical approximation used for prechondrule aggregates and in the spectral distribution of the radiation assumed for heating. Nonblackbody spectral distributions produce comparable results if >90% of the total energy is located within the region ~0.4 to 10 μm. Additionally, above ~2300 K, molten chondrules may undergo significant evaporation, reducing their sizes and limiting their peak temperatures [A. Hashimoto, *Geochem. J.* **17**, 111 (1983)].
21. Unique examples exist where mean chondrule diameters are ~0.02 mm and minumums approach 0.001 mm, for example, chondrite ALH85085 and a microchondrule-bearing clast from Piancaldoli. See review in (*3*).
22. D. W. Hughes, *Earth Planet. Sci. Lett.* **39**, 371 (1978).
23. P. M. Martin and D. W. Hughes, *ibid.* **49**, 175 (1980).
24. R. T. Dodd, *ibid.* **30**, 281 (1976).
25. A. E. Rubin, *Geochim. Cosmochim. Acta* **48**, 1779 (1984).
26. A. H. Paxton, R. L. Gardner, L. Baker, *Phys. Fluids* **29**, 2736 (1986).
27. S. J. Weidenschilling, *Icarus* **60**, 553 (1984).
28. H. Mizuno, W. J. Markiewicz, H. J. Fölk, *Astron. Astrophys.* **195**, 183 (1988).
29. S. J. Weidenschilling and J. N. Cuzzi, in (*10*), pp. 1031–1061.

30. We thank J. W. Larimer, J. A. Tyburczy, and S. J. Weidenschilling for helpful discussions, J. Menendez and G. Wolf for use of their laser facilities, A. G. W. Cameron and an anonymous reviewer for thorough and helpful reviews, and J. C. Clark for assistance with the scanning electron microscopy and electron microprobe analysis; the electron microprobe was purchased with the aid of NSF grant EAR-840816. C. F. Lewis, C. B. Moore, and the Center for Meteorite Studies at Arizona State University are gratefully acknowledged for supplying samples. This study was supported by grant NAGW-3386 from the National Aeronautics and Space Administration.

14 March 1994; accepted 8 June 1994

Saturation of Cubic Optical Nonlinearity in Long-Chain Polyene Oligomers

Ifor D. W. Samuel, Isabelle Ledoux, Christophe Dhenaut,
Joseph Zyss,* Harold H. Fox, Richard R. Schrock,
Robert J. Silbey

The scaling of the cubic nonlinearity γ with chain length in polyenic molecules has received considerable theoretical attention. Earlier experimental investigations have been restricted to oligomers with fewer than 20 double bonds because of problems associated with the synthesis and solubility of conjugated molecules. These synthetic difficulties have been overcome in the present study by the use of modern living polymerization techniques. Solution measurements of γ as a function of chain length in long-chain (up to 240 double bonds) model polyene oligomers are reported. A saturation of the increase of γ with chain length is observed, and the onset of this saturation occurs for chain lengths considerably longer than predicted from theory.

The study of polyenes and their oligomers is important for nonlinear optics because these materials have large third-order nonlinearities and because they are used as model conjugated systems and as building blocks for nonlinear optical molecules (*1*, *2*). The magnitude of the cubic nonlinearity γ and its scaling with the number of double bonds N have received considerable theoretical attention (*3*–*18*). These theories range from simple tight-binding (or Hückel) models to fully correlated π-electron models such as that of Pariser, Parr, and Pople (PPP). For small N, a power-law dependence $\gamma = kN^\alpha$ is found to approximate the theoretical results in all models, with α between 3 and 6, depending on the model used and the calculation. For large N (thermodynamic limit), γ becomes linear in N and γ/N therefore becomes constant.

This saturation is predicted to occur at different values of N in different models: Models such as Hückel that do not include electron correlation tend to predict saturation at rather large N (>50), whereas theoretical models that include electron correlation predict saturation at smaller N (~20). Although the latter calculations are subject to large errors in the large N limit as a result of the limitations of computer storage, it is generally believed that they are semiquantitative. However, the implicit assumption of these models is that the parameters in the semiempirical Hamiltonian (that is, PPP) that are valid for small molecules are also valid for large molecules. If this is not so, the calculations may be seriously in error. Experimental investigation has proved difficult as a result of difficulties with synthesis and the poor solubility of polyenic oligomers. This has restricted earlier studies to molecules with fewer than 20 double bonds, and no saturation of γ/N has been observed thus far (*19*–*26*).

The controlled synthesis of long-chain conjugated oligomers has recently become possible as a result of progress in living polymerization techniques (*27*). We report here measurements of γ as a function of N in soluble long-chain model polyene oligomers with up to 240 double bonds (see Fig. 1). We have observed a saturation of γ/N in these very much longer polyenic systems. We synthesized the molecules by cyclopolymerization in a living manner, using a molybdenum alkylidene catalyst to give a polyenic backbone substituted with five- and six-membered rings. This procedure gives good control over the length of the resulting oligomers. Molecular weights were measured by gel permeation chromatography against polystyrene, and the polydispersity was typically 1.2, indicating a fairly narrow distribution of chain lengths. Full details of the preparation and characterization of these molecules are given elsewhere (*27*).

The third-order nonlinearity γ was measured in tetrahydrofuran (THF) solution by the Maker fringe method, and data analysis was performed as previously described (*28*). Excitation at 1.91 μm was provided by a longitudinal monomode Q-switched Nd:yttrium-aluminum-garnet

---

I. D. W. Samuel, I. Ledoux, C. Dhenaut, J. Zyss, France Telecom-CNET-Centre Paris B-Laboratoire de Bagneux, 196 avenue Henri Ravera, 92220 Bagneux, France.
H. H. Fox, R. R. Schrock, R. J. Silbey, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

*To whom correspondence should be addressed.

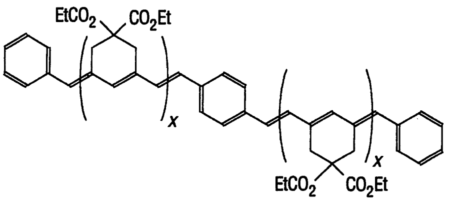

Fig. 1. Chemical structure of the model polyene oligomers studied; Et, ethyl.

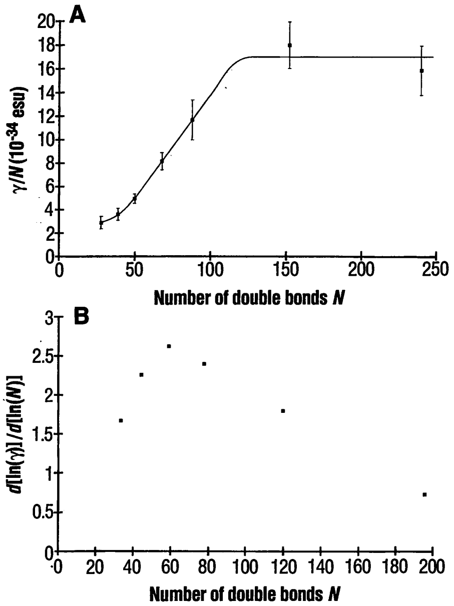

Fig. 2. (**A**) Values of $\gamma(-3\omega;\omega,\omega,\omega)/N$ as a function of the number of double bonds N for the model polyene oligomers of Fig. 1 as measured by third-harmonic generation at 1.9 μm. The solid line is a guide for the eye. (**B**) Plot of $d[\ln(\gamma)]/d[\ln(N)]$ as a function of chain length for the data in (A).

laser, Raman shifted by a hydrogen cell at 40 bar. Excitation intensities were of the order of 100 MW/cm^2, and the concentration of solutions was in the range 10^{-6} to 10^{-3} M. The third harmonic at 636 nm is just below the onset of the main absorption band for the molecules.

The results of these measurements are shown in Table 1 and Fig. 2. The value of γ increases with N, reaching a very large value of $(3794 \pm 500) \times 10^{-34}$ electrostatic units (esu) for $N = 240$ double bonds. Indeed, this value is 1000 times what would be expected in nonconjugated molecules of similar size, and larger by a factor of 40 than the γ previously reported for $N = 16$ (*24*). The plot of γ/N as a function of N (Fig. 2A) clearly shows that γ/N saturates. The saturation is even more evident in Fig. 2B, which shows a plot of N against $p = d[\ln(\gamma)]/d[\ln(N)]$: This quantity would have a constant value of α for a simple power-law dependence of the form $\gamma = KN^{\alpha}$. However, the observed behavior is far more complex: There is a maximum of p for $N \approx 60$ double bonds, and p decreases toward 1 (which corresponds to $\gamma \propto N$) for the longest molecules. We have estimated γ at frequency $\omega = 0$ (see Table 1) from the above data, using a model with a one-photon transition at energy $hc/\lambda_{\max}$ above the ground state, and with two-photon allowed states far from resonance (*22*, *29*):

$$\gamma(0;0,0,0) = [1 - (\lambda_{\max}/\lambda)^2][1 - (3\lambda_{\max}/\lambda)^2]\gamma(-3\omega;\omega,\omega,\omega)$$

where $\lambda = 1.9$ μm is the wavelength of the measurement. The saturation behaviors of $\gamma(0;0,0,0)$ and $\gamma(-3\omega;\omega,\omega,\omega)$ are very similar.

We contrast the saturation of the increase of γ observed here with the approximately power-law scaling previously observed in much shorter molecules (*22*–*24*). We can estimate the corresponding macroscopic cubic susceptibility $\chi^{(3)}$ for the longer molecules from our measured value of γ/N by assuming the same packing density ($= 3 \times 10^{14}$ cm^{-2}) and local field factor ($= 10$) as for polyacetylene. This gives $\chi^{(3)} \approx 2 \times 10^{-10}$ esu (0.5×10^{-10} esu after correction to zero frequency), which is similar to the experimental value in oriented polyacetylene of $(4 \pm 2) \times 10^{-10}$ esu at 1064 nm reported by Sinclair *et al.* (*30*) after taking account of the effects of resonance (which could enhance the latter value by a factor of 2 to 3) and the fact that Sinclair's measurements were made on oriented samples (which gives an enhancement of up to a factor of 5). Higher values of $\chi^{(3)}$ in polyacetylene have been reported at resonance (*31*). The uncertainty in our estimate of $\chi^{(3)}$ is considerable, and, in view of this, we consider that it is in satisfactory agreement with theoretical calculations of $\chi^{(3)} = 2 \times 10^{-10}$ esu at zero frequency (*8*, *10*).

The shape of the curve in Fig. 2A qualitatively resembles the predictions of several theories, but the number of double bonds at which the onset of saturation is observed ($N \approx 120$) is much larger than these theories suggest. The form of the curve in Fig. 2B, with a maximum of p followed by a decrease toward 1 for large N, is qualitatively similar to the calculations of Mukamel and Wang (*11*, *12*) in their electron-hole anharmonic oscillator model and of Spano and Soos (*13*) in Hückel theory (this behavior may also arise in other models, but to date only these investigators have published curves corresponding to that in Fig. 2B). However, although we observe a maximum of p slightly above 2.5 for $N \approx 60$, and p approaches 1 for $N \approx 200$, Mukamel and Wang (using a Hubbard potential $U = 11.26$ eV in a PPP model) calculate a maximum of p for $N \approx 5$, and they note that p falls to 1 for $N = 21$ (*11*). A further difference is that the maximum value of p in our measurements is 2.6, compared with ~6 calculated by Mukamel and Wang. In the work of Spano and Soos (with bond alternation $\delta = 0.07$) saturation is also predicted to occur in relatively short chains; the maximum of p is calculated to be at $N \approx 15$.

We find that the rate of increase of γ with N is also slower than that measured in previous experiments on shorter molecules. For example, in one study $\alpha = 3.5$ was measured in polyenic oligomers with N in the range 4 to 8 (*22*), and a similar value $\alpha = 3.6$ was observed for slightly longer oligomers, with N in the range 10 to 16 (*24*).

Current theoretical models do not agree with our results. These theories refer to idealized planar, all-trans, isolated gas-phase polyene oligomers. Our molecules contain some cis linkages (*32*). In addition, our measurements were made in solution, and so there will be some conformational disorder of the molecules, which would reduce the extent of electron delocalization. The connection between chain length and conjugation length in chains with disorder is at present a challenge to theory (*33*). The saturation occurs for chain lengths considerably longer than expected in existing theories, which suggests that the description of the electronic properties of long-chain conjugated molecules with conformational disorder requires further theoretical investiga-

Table 1. Summary of data for model polyene oligomers. N represents the average number of double bonds in the sample. Each phenyl ring was counted as 1.3 double bonds; MW represents the average molecular weight; M_w/M_n is the polydispersity; $\lambda_{\max}$ is the wavelength of the maximum of the absorption in THF solution; $\gamma_{THG} = \gamma(-3\omega;\omega,\omega,\omega)$ was measured by third-harmonic generation at 1.9 μm; $\gamma_0 = \gamma(0;0,0,0)$ is estimated from γ_{THG} as described in the text.

N	MW	M_w/M_n	$\lambda_{\max}$ (nm)	γ_{THG} (10^{-34} esu)	γ_0 (10^{-34} esu)
28	2,800	1.19	466	81 ± 15	35 ± 7
39	4,100	1.16	486	141 ± 20	54 ± 8
50	5,400	1.14	516	247 ± 20	78 ± 10
68	7,500	1.14	530	553 ± 50	155 ± 16
88	10,000	1.14	538	1025 ± 150	267 ± 40
152	17,600	1.19	550	2731 ± 300	629 ± 70
240	27,900	1.27	552	3794 ± 500	854 ± 110

tion. In addition, the phenyl ring in the center of the molecule might also reduce the extent of electron delocalization. Although the implications of such effects for the saturation behavior are uncertain, we consider that a reduction in the extent of electron delocalization would tend to reduce the chain length at which saturation occurs and therefore does not provide a satisfactory explanation of why we observe saturation at considerably greater chain lengths than theory predicts. In these long-chain polyene oligomers (with terminal and central phenyl groups), it is conceivable that bond alternation is reduced, thereby increasing the chain length at which saturation occurs. However, we do not see any evidence for reduced bond alternation in the absorption spectra. In addition, the effect of the end groups on γ is both expected and observed to be small in such long molecules (*34*).

REFERENCES AND NOTES

1. See, for example, J. L. Brédas and R. Silbey, Eds., *Conjugated Polymers* (Kluwer, Boston, 1991).
2. J. Zyss and D. S. Chemla, Eds., *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic Press, Orlando, FL, 1987), vols. 1 and 2; J. Zyss, Ed., *Molecular Nonlinear Optics: Materials, Physics, and Devices* (Academic Press, Boston, 1993).
3. K. C. Rustagi and J. Ducuing, *Opt. Commun.* **10**, 258 (1974).
4. G. P. Agrawal, C. Cojan, C. Flytzanis, *Phys. Rev. B* **17**, 776 (1978).
5. C. P. de Melo and R. Silbey, *Chem. Phys. Lett.* **140**, 537 (1987).
6. J. R. Heflin *et al.*, *Phys. Rev. B* **38**, 1573 (1988).
7. B. M. Pierce, *J. Chem. Phys.* **91**, 791 (1989).
8. Z. Shuai and J. L. Brédas, *Phys. Rev. B* **44**, 5962 (1991).
9. T. C. Kavanaugh and R. J. Silbey, *J. Chem. Phys.* **95**, 6924 (1991).
10. J. Yu and W. P. Su, *Phys. Rev. B* **44**, 13315 (1991); J. Yu *et al.*, *ibid.* **39**, 12814 (1989).
11. S. Mukamel and H. X. Wang, *Phys. Rev. Lett.* **69**, 65 (1992).
12. H. X. Wang and S. Mukamel, *Nonlin. Opt.* **5**, 281 (1993).
13. F. C. Spano and Z. G. Soos, *J. Chem. Phys.* **99**, 9265 (1993).
14. D. N. Beratan, J. N. Onuchic, J. W. Perry, *J. Phys. Chem.* **91**, 2696 (1987).
15. G. J. B. Hurst, M. Dupuis, E. Clementi, *J. Chem. Phys.* **89**, 385 (1988).
16. Z. G. Soos and S. Ramasesha, *ibid.* **90**, 1067 (1989).
17. L. T. Cheng *et al.*, *J. Phys. Chem.* **95**, 10643 (1991).
18. D. Yaron and R. Silbey, *Phys. Rev. B* **45**, 11655 (1992).
19. J. P. Hermann and J. Ducuing, *J. Appl. Phys.* **45**, 5100 (1974).
20. J. F. Ward and D. S. Elliott, *J. Chem. Phys.* **69**, 5438 (1978).
21. M. T. Zhao *et al.*, *ibid.* **89**, 5535 (1988).
22. J. Messier *et al.*, *Mol. Cryst. Liq. Cryst.* (sec. B: Nonlinear Opt.) **2**, 53 (1992).
23. G. Puccetti, M. Blanchard-Desce, I. Ledoux, J.-M. Lehn, J. Zyss, *J. Phys. Chem.* **97**, 9385 (1993).
24. G. S. W. Craig *et al.*, *J. Am. Chem. Soc.* **115**, 860 (1993).
25. G. S. W. Craig *et al.*, *Macromolecules* **27**, 1875 (1994).
26. M. Blanchard-Desce, J. M. Lehn, M. Barzoukas, I. Ledoux, J. Zyss, *Chem. Phys.* **181**, 281 (1994).
27. H. H. Fox *et al.*, *J. Am. Chem. Soc.* **116**, 2827 (1994).
28. F. Kajzar and J. Messier, *Rev. Sci. Instrum.* **58**, 2081 (1987).
29. M. Barzoukas, P. Fremaux, D. Josse, F. Kajzar, J. Zyss, *Mater. Res. Soc. Symp. Proc.* **109**, 171 (1988).
30. M. Sinclair, D. Moses, K. Akagi, A. J. Heeger, *Phys. Rev. B* **38**, 10724 (1988); M. Sinclair *et al.*, *Synth. Metals* **28**, D655 (1989).
31. W. S. Fann *et al.*, *Phys. Rev. Lett.* **62**, 1492 (1989); C. Halvorson, T. W. Hagler, D. Moses, Y. Cao, A. J. Heeger, *Chem. Phys. Lett.* **200**, 364 (1992).
32. The presence of cis linkages would be expected as a result of steric effects and is consistent with the energy of the maximum of the absorption spectrum extrapolated to infinite chains of 2.19 eV, which is close to the value for *cis*-polyacetylene of 2.09 eV.
33. G. Rossi, R. R. Chance, R. Silbey, *J. Chem. Phys.* **90**, 7594 (1989).
34. I. Ledoux *et al.*, paper presented at the International Conference on Organic Nonlinear Optics, Val Thorens, France, 8 to 12 January 1994; I. D. W. Samuel *et al.*, paper presented at the Second International Topical Conference on Conjugated Polymers and Fullerenes, Salt Lake City, UT, 15 to 19 February 1994.

35. R.R.S. thanks the Director, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy (DE-FG02-86ER13564), for support.

28 March 1994; accepted 24 June 1994

The Use of Graft Copolymers to Bind Immiscible Blends

Dilip Gersappe, Darrell Irvine, Anna C. Balazs,* Yun Liu, Jon Sokolov, Miriam Rafailovich, Steven Schwarz, Dennis G. Peiffer

Computer simulations and experimental studies were combined to design copolymers that enhance the strength of polymer composites. These copolymers contain side chains that associate across the boundary between phase-separated regions to form a "molecular velcro" that effectively binds the regions together. This behavior significantly improves the structural integrity and mechanical properties of the material. Because the side chains can be fabricated from a large class of compounds, the technique greatly increases the variety of copolymers that can be used in forming high-strength polymer blends.

Polymer alloys or blends provide the advantage that the properties of the material can be controlled by varying the type and quantity of polymers that go into the mixture. In this way, the composite can be tailored to exhibit the desired optical, electrical, mechanical, or rheological properties for a variety of specific applications. The actual fabrication of polymer blends, however, poses significant challenges. Most polymer blends are immiscible, and thus, the components phase separate into distinct, macroscopic domains. To enhance the structural integrity and mechanical properties of the resulting material, copolymer "compatibilizers" are added to the mixture. These chains effectively act as high molecular weight surfactants: They localize at the interface between the immiscible polymers, lower the interfacial tension, and disperse the incompatible polymers into smaller domains. Consequently, the degree of adhesion between the phase-separated regions and the mechanical properties of the material are significantly enhanced.

Studies have demonstrated that graft copolymers act as highly effective compatibilizers (*1*). Graft copolymers contain a backbone and side chains ("teeth") that emanate from the backbone. We have coupled computer simulations with experimental studies to design graft copolymers that act as "molecular velcro" (*2*): The teeth intertwine across the polymer-polymer interface and effectively bind the two phase-separated regions (Fig. 1). As our findings show, this behavior dramatically improves the mechanical properties of the composite material. Because the teeth are chemically distinct from the phase-separated homopolymers, and may in fact be incompatible with the homopolymers, this technique significantly increases the variety of materials that can be used as compatibilizers for multiphase and multicomponent materials.

We first describe the results of the Monte Carlo computer simulations and then discuss the findings on the comparable experimental system. Simulations constitute powerful tools in such studies because the model allows the chains to self-assemble into the preferred microstructure. Consequently, the simulations can provide significant information about the morphology of the system. In addition, the computer graphics allow us to visualize the

---

D. Gersappe, D. Irvine, A. C. Balazs, Materials Science and Engineering Department, University of Pittsburgh, Pittsburgh, PA 15261, USA.
Y. Liu, J. Sokolov, M. Rafailovich, Department of Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, NY 11794–2275, USA.
S. Schwartz, Bellcore, Red Bank, NJ 07701–7040, USA.
D. G. Peiffer, Exxon Research and Engineering Company, Corporate Research Science Laboratory, Annandale, NJ 08801, USA.

*To whom correspondence should be addressed.