New York, 1982), pp. 17–51.

23. S. K. Sinha, E. B. Sirota, S. Garoff, H. B. Stanley, *Phys. Rev. B* **38**, 2297 (1988).
24. M. Goulian, N. Lei, J. Miller, S. K. Sinha, *Phys. Rev. A* **46**, R6170 (1992).
25. The chains of the simulated tethered membrane were connected in a hexagonal array, except for 12 fivefold defects needed to close the sphere. The simulations were carried out using molecular dynamics with only excluded-volume interactions between the monomers. Details of the simulation can be found in (*13*) (also, I. B. Petsche and G. S. Grest, in preparation).
26. C. W. M. Haest, *Biochim. Biophys. Acta* **694**, 331 (1982).
27. S. C. Liu, L. H. Derick, J. Palek, *J. Cell Biol.* **104**, 527 (1987).
28. B. T. Stokke, A. Mikkelsen, A. Elgsaeter, *Biochim. Biophys. Acta* **816**, 102 (1985).
29. C. R. Safinya, in *Phase Transitions in Soft Condensed Matter*, T. Riste and D. Sherrington, Eds. (NATO ASI series B, Plenum, New York, 1989), vol. 211, pp. 249–270.
30. We thank S. M. Block, D. Branton, P. A. Janmey, D. P. Kiehart, R. B. Meyer, M. Orkisz, and T. Tanaka for use of their equipment; T. C. Lubensky, D. R. Nelson, and S. K. Sinha for helpful discussions; H. C. Berg and S. M. Block for comments on the manuscript; C. Sun for the artwork in Fig. 1; J. Scarpetti for photographic work; and the Deutsche Forschungsgemeinschaft, the National Institutes of Health, the Department of Energy (DOE), and The Rowland Institute for Science for support. The SAXS experiments were carried out on the wiggler beam line X-25 at the National Synchrotron Light Source at the Brookhaven Laboratories, which is supported by DOE.

21 August 1992; accepted 25 November 1992

Photoinduced Polymerization of Solid C_{60} Films

A. M. Rao, Ping Zhou, Kai-An Wang, G. T. Hager, J. M. Holden,
Ying Wang, W.-T. Lee, Xiang-Xin Bi, P. C. Eklund,*
D. S. Cornett, M. A. Duncan, I. J. Amster

The irradiation of oxygen-free, face-centered-cubic C_{60} films with visible or ultraviolet light phototransformed C_{60} into a different solid phase. Results from laser desorption mass spectroscopy, scanning electron microscopy, Raman and infrared spectroscopy, optical absorption, and luminescence indicate that a photopolymerization of the fullerene molecules within the film occurred.

The discovery of stable fullerenes, or carbon-cage molecules C_n (n = 60, 70, . . .), by Smalley, Kroto, and co-workers (*1–3*) has led to a new class of carbon-based solids with unusual properties (*4, 5*). At room temperature, the molecules in solid C_{60} are centered on lattice positions of a face-centered-cubic (fcc) structure (*6, 7*) and are observed in nuclear magnetic resonance (NMR) experiments to be rapidly rotating about these lattice positions (*8, 9*). This unusual behavior is consistent with the weak intermolecular van der Waals bonding and the nearly spherical character of the C_{60} molecule. In this report, we present results that indicate that the application of visible or ultraviolet (UV) light to solid C_{60} polymerizes the structure, in that the molecules link together in a covalently bonded fcc structure. After phototransformation, the film is no longer soluble in toluene but can be dissolved in boiling isodurene. Recently, Loy and Assink (*10*) reported a polymerized C_{60} network. However, in their study, the C_{60} molecules were linked by a hydrocarbon bridge formed during the reaction of C_{60} in solution (toluene) with the diradical xylylene. In photoconductivity studies of mixtures of C_{60} and polystyrene, Wang (*11*) concluded that C_{60} attaches to the polystyrene polymer.

On the basis of Raman scattering studies, we have reported (*12*) that Ar-ion laser radiation at 514.5 and 488.0 nm that exceeded ~50 mW/mm^2 appeared to initiate an irreversible transformation of fcc C_{60} to a different solid phase with a richer Raman spectrum. In particular, the high-frequency A_g-symmetry "pentagonal-pinch" (PP) mode shifted at room temperature from 1469 to ~1460 cm^{-1} (*12*), while the polarization ratio for this mode deteriorated from 100% in pristine C_{60} to ~80% in the phototransformed phase (*13*). There has been some disagreement about the value of the PP-mode frequency (*13*). In our opinion, the value of 1469 cm^{-1} has been incorrectly associated with only oxygen-contaminated C_{60} (*14, 15*), and this view has recently been supported by others. Fourier transform Raman studies by Chase *et al.* (*16*) that used a yttrium-aluminum-garnet (YAG) laser with photon energy 1.06 eV, which is less than the absorption threshold in C_{60} (*17, 18*), confirm the 1469-cm^{-1} PP-mode frequency for oxygen-free, pristine fcc C_{60} obtained with a low-power Ar-ion laser beam (*12, 13, 19*).

The data presented here were taken on thin solid films of C_{60} vacuum-deposited on either KBr, fused quartz, Si(100), or stainless steel substrates from 99% pure C_{60} (Bluegrass Fullerenes, Inc., Lexington, Kentucky) first degassed in a vacuum of 10^{-5} torr for 3 to 6 hours at temperture (T) = 300°C. For the laser desorption mass spectroscopy (LDMS) studies, the C_{60} film samples were deposited directly onto the end of stainless steel rods that could be transferred under a N_2 atmosphere into the mass spectrometer. The film-deposition apparatus resided in an He-atmosphere glove box (Vacuum Atmospheres, Inc., O_2 and H_2O <1 ppm), and the exposure of the films to oxygen was therefore minimized. Inside the glove box, the film-substrate samples were transferred to a gas-tight cell with a quartz window that allowed the samples to be removed from the glove box and phototransformed by light from a 300-W Hg arc lamp or an Ar-ion laser. All of the phototransformed C_{60} films studied received enough photon irradiation to shift the PP-mode frequency to 1460 cm^{-1}, and no trace of the initial 1469 cm^{-1} peak remained. The film thickness (d) was typically in the range 1000 Å < d < 5000 Å.

A scanning electron microscope (SEM) image was taken of a phototransformed film that had been boiled in isodurene for several minutes (boiling point 198°C) (Fig. 1). The film had broken loose from the substrate, tearing along the line AB and folding over itself along line BC—that is, point A folded to point D. The area enclosed by ABC is associated with a residual film of phototransformed C_{60} that was still attached to the substrate. Striations in the C_{60} film that are evident in the image were not transferred from the glass substrate. The cracks in the film were also not transferred from the substrate and were not evident in the pristine film. They may be the result of heating during irradiation or a small contraction in the lattice parameter. Films such as the one shown in Fig. 1 survived boiling toluene (boiling point 111°C) for several hours but eventually dissolved in boiling isodurene.

We recorded LDMS spectra of phototransformed films (12-hour exposure to a 300-W Hg arc lamp) and pristine C_{60} films (Fig. 2) that spanned the mass range of 720 atomic mass units (amu) (C_{60}) to 15,120 amu (21 × C_{60}). We took the spectra in Fig. 2, A and B, under similar desorption conditions: vacuum at ~10^{-7}-torr, pulsed N_2 laser at wavelength of 337 nm focused to a spot 0.3 mm in diameter, pulse width of 5

A. M. Rao, P. Zhou, K.-A. Wang, Y. Wang, P. C. Eklund, Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506 and Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511.
G. T. Hager, W.-T. Lee, X.-X. Bi, Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511.
J. M. Holden, Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506.
D. S. Cornett, M. A. Duncan, I. J. Amster, Department of Chemistry, University of Georgia, Athens, GA 30602.

---

*To whom correspondence should be addressed.

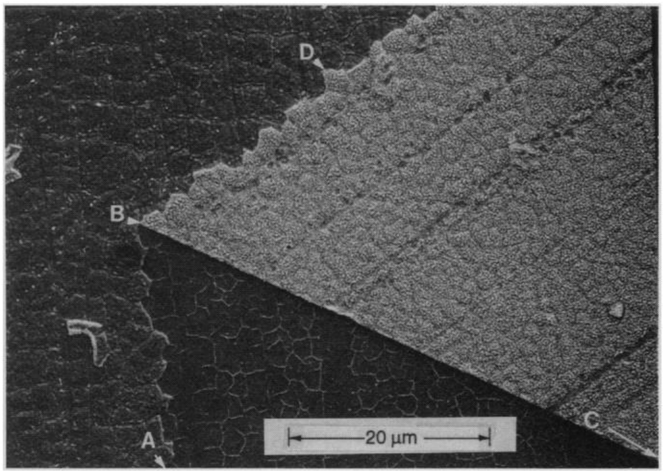


Fig. 1. Scanning electron microscope (SEM) image of phototransformed C_{60} that has been boiled in isodurene for ~1 min. The film has lifted off of the substrate, torn along the line AB, and folded over the line BC, so that point A translated to point D. A residue of phototransformed C_{60} remains on the substrate. Phototransformed films such as this one survived boiling toluene for several hours, in contrast to pristine films, which dissolved completely in seconds in toluene at room temperature.

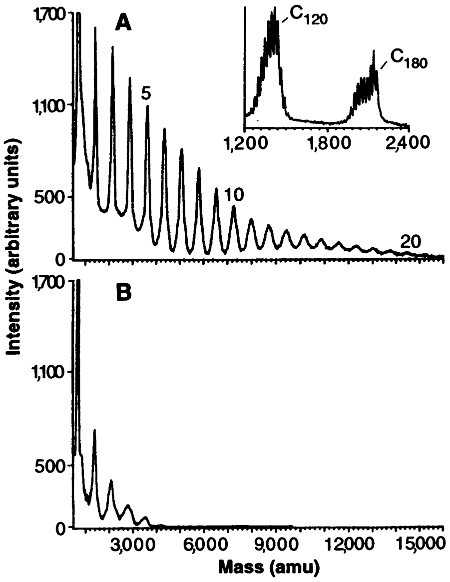


Fig. 2. (**A**) Laser desorption mass spectrum of a C_{60} film (d ~ 2000 Å) phototransformed with UV-visible radiation from a 300-W Hg arc lamp for 12 hours. The material was desorbed from the film with a pulsed N_2 laser (337 nm, ~8 ns, 10 mJ per pulse). A series of 20 peaks are identified with N cross-linked fullerenes of mass ~720N atomic mass units (amu). Inset: LDMS spectrum shown on an expanded scale in the region of the dimer (C_{120}) and trimer (C_{180}) showing C_2 loss or gain in the desorption process. (**B**) Laser desorption mass spectrum of a C_{60} film not previously exposed to light. The data were taken under conditions similar to those in (A). The peaks in the figure are identified with cross-linked fullerenes produced by the desorption laser itself.

to 10 ns, pulse energy of 10 mJ/cm^2, and pulse repetition rate of 10 Hz. The C_2 structure is clearly evident in an expanded-scale view of the data in the vicinity of C_{120} (dimer) and C_{180} (trimer) (Fig. 2A, inset). As a result of the laser ablation, a succession of 20 clear peaks is evident in the mass spectrum of the phototransformed sample (Fig. 2A). We identify these peaks with clusters of cross-linked fullerene molecules $(C_{60})_N$. The LDMS spectrum of a pristine film exhibits peaks out to $N = 5$ (Fig. 2B), which suggests that at high laser power, the N_2 desorption laser itself is capable of producing polymerized C_{60}. At a reduced laser power, an LDMS spectrum of the phototransformed film that was similar to Fig. 2A was obtained, but it terminated at $N = 8$ to 10 (*20*). For comparison, the spectrum of the pristine film under these desorption conditions exhibited only the $N = 1$ peak (*20*).

Our LDMS conditions are much different from those of Yeretzian *et al.* (*21*), who reported the formation of large fullerene cages from plasma generated by the laser desorption of a C_{60} film into an inert-gas (He) atmosphere. They used shorter wavelength UV radiation from a Nd-YAG laser (266 nm, 6 ns, 2 mJ/cm^2) and a pulsed-He nozzle source. They observed four broad patterns in the mass spectrum with maxima at C_{118}, C_{178}, C_{234}, and C_{298} and identified them with large-cage fullerenes (rather than clusters of fullerenes) formed from combinations of C_{60} and C_{70} molecules. The patterns in their mass spectrum are much broader than the $(C_{60})_N$ cluster peaks in Fig. 2A.

We also investigated the effect of the phototransformation (or polymerization) on the vibrational modes of solid C_{60} with room-temperature infrared (IR) transmission and Raman spectra (Fig. 3). The IR and Raman data for pristine C_{60} films are in good agreement with the results of Meijer and Bethune (*22*) and were confirmed more recently by other researchers (*12, 13, 16, 18, 19*). The pristine spectra exhibit primarily intramolecular modes—that is, ten Raman-active ($2\ A_g + 8\ H_g$) and four IR-active (F_{1u}) modes, which is consistent with a weak intermolecular interaction and the icosahedral symmetry of an isolated molecule (*23*). In contrast to the spectra of the pristine phase, the Raman and IR spectra of the phototransformed phase exhibit many more lines, which indicates that the icosahedral symmetry of the C_{60} molecule has been lowered, consistent with the proposed photopolymerization process.

These observations can be compared with Raman scattering results from M_6C_{60}, where M = K, Rb, and Cs, and those from C_{60} modified by the attachment of metal complexes such as $\{[(C_6H_5)_3P]_2M'\}_nC_{60}$, where M′ = Ni, Pt, and Pd (*24, 25*). The molecule M_6C_{60} is an ionically bonded insulator whose Raman spectrum is quite similar to that of solid C_{60} (*13, 26*). Only a few new modes are activated by the ionic M–C_{60} bonds, and most of the Raman-active modes in M_6C_{60} can be identified as frequency-shifted modes of pristine C_{60} (*13, 26*). In the metal-C_{60} complexes, covalent bonds form between the n metal complexes and the C_{60} ball, a structure that appears to effectively activate additional Raman lines associated with the fullerene cage (*25*). The vibrational spectra (Fig. 3) for the phototransformed phase therefore suggest that the fullerenes have been linked together by carbon bonds.

Optical absorption spectra have been collected on pristine and phototransformed C_{60} films in the range of 0.5 to 5.5 eV (*27*). Phototransformation broadened the electronic absorption bands of C_{60} without altering their positions, which indicates that the molecular structure of the monomers was closely related to that of C_{60}. Furthermore, luminescence spectra (T = 300 K) of pris-

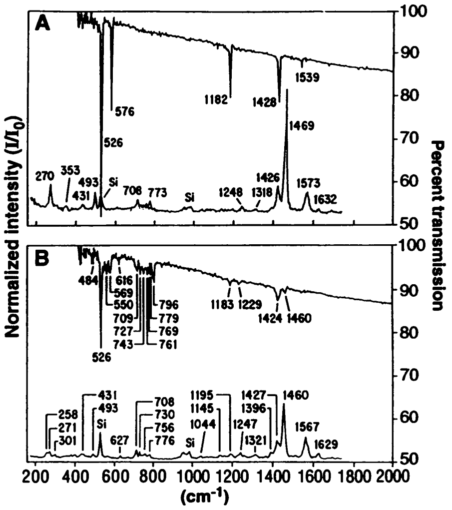
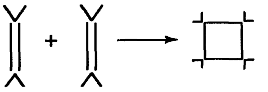


Fig. 3. Raman scattering (lower plot on each graph, left axis) and Fourier transform infrared (FTIR) transmission (top plots; right axis) spectra of pristine C_{60} (**A**) and phototransformed C_{60} (**B**). The Raman spectra were taken at low laser power density (<50 mW/mm^2) with the 488-nm Ar-ion line on samples deposited on Si(100) substrates. FTIR samples for spectra were deposited on KBr substrates.

tine and phototransformed C_{60} films, which were obtained with 488-nm excitation, suggest a similar conclusion (*27*). The strongest peak in pristine C_{60}, which was at ~725 nm, redshifted ~20 nm on phototransformation. The small changes in these electronic spectra are consistent with the polymerization of fullerene molecules.

Finally, the phototransformation of solid C_{60} altered x-ray diffraction of the films. Using Cu K_α x-rays, we observed three clear peaks in ~5000 Å–thick pristine films that could be indexed according to the fcc lattice: (111), (220), and (311). Phototransformation broadened these peaks by ~20%, which indicates an increase in disorder in the film, and the peaks shifted slightly to higher scattering angles, which is expected for an average contraction of ~0.1 Å in the lattice constant. This contraction is much less than one might expect for a simple polymerization of C_{60} units in which the van der Waals bond between C_{60} molecules (~3.0 Å) is replaced by a covalent C–C bond (~1.5 Å). This could occur, for example, if a 2 + 2 cyclo addition photochemical reaction (*28*) were to take place. In the case of adjacent C_{60} molecules, parallel double bonds (C=C), one from each molecule, are broken and reform as single bonds between the molecules, that is



which results in a 1.5 Å contraction in the bond between the molecules, which would appear to be inconsistent with our preliminary x-ray results. However, the phototransformation may involve the conversion of $(C_{60})(C_{60}) \rightarrow C_{60}{=}C{=}C{=}C_{58}$— that is, the formation of a (=C=C=) bridge, which preserves the ~10 Å center-to-center distance between adjacent fullerenes. Further work will be necessary to determine the nature of the photoinduced intermolecular coupling.

Note added in proof: Our recent Raman scattering studies of C_{60} in the range 30 to 200 cm^{-1} clearly indicate that phototransformation introduces a new mode at $\omega \sim$ 116 cm^{-1}, which we identify with an intermolecular vibrational mode. Furthermore, intercalated O_2 has been found in other Raman scattering studies (*12*) to harden the C_{60} films against phototransformation. Because O_2 also quenches the luminescence of the first excited triplet state of C_{60} (*27*), it appears that the nearly 100% efficient transition from the singlet manifold to this triplet state and the reactivity of the molecule in this triplet state are both important to efficiently produce the polymerized form of C_{60}.

REFERENCES AND NOTES

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **318**, 162 (1985).
2. H. Kroto, *Science* **242**, 1139 (1988).
3. R. F. Curl and R. E. Smalley, *ibid.*, p. 1017.
4. For recent reviews of fullerene-based solids, see the special issue of *Acc. Chem. Res.* **25**, 98 (1992).
5. M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, in preparation.
6. P. A. Heiney *et al.*, *Phys. Rev. Lett.* **66**, 2911 (1991).
7. P. A. Heiney *et al.*, *ibid.* **67**, 1468 (1991).
8. C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, J. R. Salem, *J. Phys. Chem.* **95**, 9 (1991).
9. R. Tycko *et al.*, *Phys. Rev. Lett.* **68**, 1912 (1992).
10. D. Loy and R. Assink, *J. Am. Chem. Soc.* **114**, 3977 (1992).
11. Y. Wang, *Nature* **356**, 585 (1992).
12. P. Zhou *et al.*, *Appl. Phys. Lett.* **60**, 2871 (1992).
13. P. C. Eklund, P. Zhou, K.-A. Wang, G. Dresselhaus, M. S. Dresselhaus, *J. Phys. Chem. Solids* **53**, 1391 (1992).
14. S. J. Duclos, R. C. Haddon, S. H. Glarum, K. B. Lyons, *Solid State Commun.* **80**, 481 (1991).
15. K. Sinha, S. Guha, J. Menendez, D. A. Wright, T. Karcher, *Phys. Rev. B*, in press.
16. B. Chase, N. Herron, E. Holler, *J. Phys. Chem.* **96**, 4262 (1992).
17. Y. Wang *et al.*, *Phys. Rev. B* **45**, 14396 (1992).
18. A. M. Rao *et al.*, in preparation.
19. P. H. M. van Loosdrecht, P. J. M. van Bentum, G. Meijer, *Europhys. Lett.*, in press.
20. D. S. Cornett, I. J. Amster, M. A. Duncan, A. M. Rao, P. C. Eklund, in preparation.
21. C. Yeretzian, K. Hansen, F. Diederich, R. L. Whetten, *Nature* **359**, 44 (1992).
22. G. Meijer and D. S. Bethune, *Chem. Phys. Lett.* **175**, 1 (1990).
23. G. Dresselhaus, M. S. Dresselhaus, P. C. Eklund, *Phys. Rev. B*, in press.
24. P. J. Fagan, J. C. Calabrese, B. Malone, *Acc. Chem. Res.* **25**, 134 (1992).
25. B. Chase and P. J. Fagan, *J. Am. Chem. Soc.* **114**, 2252 (1992).
26. K.-A. Wang *et al.*, *Phys. Rev. B* **45**, 1955 (1992).
27. Y. Wang *et al.*, in preparation.
28. J. D. Coyle, *Introduction to Organic Photochemistry* (Wiley, New York, 1986), p. 61.
29. This work was funded, in part, by the University of Kentucky Center for Applied Energy Research and, at the University of Georgia, by NSF grants CHEM-9008246 (M.A.D.) and CHE-9024992 (I.J.A.). We thank A. W. Overhauser (Purdue University) for discussions on the possibility of photoinduced polymerization. Discussions with K. R. Subbaswamy (University of Kentucky), F. Zerbetto (Bologna University), and M. S. Dresselhaus and G. Dresselhaus (Massachusetts Institute of Technology) are also gratefully acknowledged.

24 September 1992; accepted 30 November 1992

Electrochemical Processing of Conducting Polymer Fibers

Shulong Li, Christopher W. Macosko, Henry S. White*

An electrochemical method for growing macroscopic fibers of electrically conductive poly(3-methylthiophene) is described. Single fibers of uniform diameter (~0.1 to 0.7 millimeter) and length greater than 10 centimeters are grown in a capillary flow cell by electrochemical oxidation of the monomer, 3-methylthiophene. The shapes and diameters of the resulting fibers are determined by the fluid flow pattern in the cell. Straight fibers, sawtooth-shaped fibers, and fibers with tapered necks can be grown by varying the capillary shape.

The high electrical conductivity of heteroaromatic polymers, such as polythiophene, polypyrrole, and polyaniline, has spurred interest in the use of these materials in novel electronic and chemical applications (*1*, *2*). Prototype designs of flexible light-emitting diodes (*3*), molecular transistors (*4*), lightweight battery electrodes (*5*), electrochromic displays (*6*), and anticorrosion films (*7*) in which a conductive polymer is the active element have been realized during the past decade. However, most electrically conductive polymers are insoluble or intractable or decompose before melting, which prevents the use of conventional polymer-processing techniques in shaping these materials into desired structures.

Several methods for processing conductive polymer fibers require multistep chemical or mechanical procedures (*8*–*12*). In this report, we describe a one-step electrochemical process for synthesizing macroscopic electrically conductive fibers of poly(3-methylthiophene) [poly(3-MT)]. Conductive poly(3-MT) fibers were grown in a two-electrode flow cell, shown in Fig. 1. The main body of the cell consists of a glass capillary 3 mm in inner diameter, oriented vertically. The electrolyte solution containing the monomer, 3-methylthiophene (3-MT) (*13*), is pumped through the cell with a centrifugal pump. Polymer fibers are grown from a Pt wire 127 μm in diameter, which is encapsulated in glass with ~1 cm of the wire extending past the end of the glass insulation. This electrode is positioned in the center of the capillary ~5 cm from the entrance port to reduce the effects of entrance flow. A second Pt wire 1 mm in diameter and ~2 cm long, is positioned at the bottom of the tube near the exit port. The

---

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455.

*To whom correspondence should be addressed.