PHYSICAL REVIEW B VOLUME 58, NUMBER 24 15 DECEMBER 1998-II

Energetics of polymerized fullerites

Y. Iwasa, K. Tanoue, and T. Mitani
Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923-1292, Japan

T. Yagi
Institute for Solid State Physics, University of Tokyo, Minato-ku, Tokyo 106-8666, Japan

(Received 24 July 1998)

A comparative calorimetry study has been made on three types of single phase C_{60} polymers, i.e., dimers, one-, and two-dimensional polymers. These polymers revert to monomers with an endothermic reaction upon heating to 300 °C, indicating that the monomer form is the least stable phase. By estimating the endothermic heat, it was found that the polymeric forms become energetically unstable as the number of intermolecular bonds increases, in contradiction to the currently available calculation. The present results suggest that molecular deformation plays a crucial role in the energetics of C_{60} polymers. [S0163-1829(98)01948-1]

The families of polymeric fullerenes both neutral and doped have been expanding since their discovery in 1993.[1] Recently discovered single-bonded doped polymers with one-(1D) (Ref. 2) and two-dimensional (2D) networks[3] revealed that a number of alkali metals or a valence of the C_{60} molecule is a crucial parameter for the nature of intermolecular bonds and networks.[4]

In the case of undoped polymers, on the other hand, the intermolecular bonds are always $[2+2]$ cycloaddition, while various polymer networks can be obtained by changing their synthesis conditions. After the discovery of the 2D rhombohedral polymer,[5] three types of polymers have been identified.[6] Subsequently, the synthesis conditions on the pressure-temperature plane have been clarified,[7] followed by an improvement of crystallinity in the 1D polymer.[8,9] Meanwhile, a mechanochemical reaction succeeded in producing C_{60} dumbbell dimers.[10] A variety of neutral polymers means that pure solid carbon has several metastable phases near fullerenes. This phenomenon is another unique aspect of solid-state fullerenes, reflecting the flexible character of sp^2/sp^3 carbon. Moreover, the conversions occurring at moderate temperatures suggest that these polymeric phases compete in a small energy scale. However, the energy differences between the monomeric fcc phase and the polymeric phases have not been determined. Even the relative energy between the monomer and dimer has not converged yet both experimentally and theoretically, as summarized by Núñez-Regueiro.[11]

Here we report an experimental study on the energetics of three types of polymerized fullerites: dimer, 1D, and 2D rhombohedral polymers. Since the polymeric phases are stabilized by the formation of intermolecular bonds, the energetical stability should depend on the structure of polymeric forms. All the polymers were found to be depolymerized by heating, so that the thermal analysis provides useful information on the relative stability of the polymers and the monomer. To investigate the thermal properties of fullerene polymers, high-pressure synthesis is the most useful method since this technique yields single phase materials in large quantities by controlling the synthesis conditions. A comparative calorimetry study on three kinds of polymeric C_{60}'s revealed that all the polymers were energetically stable compared to the monomer form and that the stabilization energy is more than one order of magnitude smaller than the energy difference between C_{60} and graphite. Moreover, the stabilization energy decreases with the increase in the number of intermolecular bonds per molecule. This result is against a simple expectation that the polymeric forms are stabilized by the formation of intermolecular bonds.

High-pressure synthesis of 1D and 2D polymers was carried out using a cubic anvil high-pressure apparatus as described in a previous paper.[5] 2D rhombohedral polymers were synthesized at 5 GPa and 700 °C following the established conditions.[5,6] A new synthesis condition for 1D polymers was recently discovered independently by Agafonov *et al.*[8] and Moret *et al.*[9] They found that pressurization at 1 GPa and 300 °C with a liquid pressure transmitting medium produces a better quality 1D polymer than that by Núñez-Regueiro *et al.*[6] with different lattice parameters. We pressurized C_{60} at 2 GPa and 300 °C using the same apparatus as in the case of a 2D polymer. The powder x-ray-diffraction pattern for our samples was similar to that produced by Agafonov *et al.*[8] but the peaks were broader. This is possibly due to lower hydrostaticity in our setup, since we used solid pressure medium pyrophillyte while they used a liquid medium.

As for the dimers, a new route for selective synthesis of dimers using the high-pressure technique has been discovered by our group using an organic compound ET_2C_{60} as a starting material, where ET denotes bis(ethylenedithio)tetrathiafulvalene.[12] Details of this synthesis procedure are described elsewhere.[13] Spectroscopic and chromatographic studies revealed that this dimer is a $[2+2]$ cycloadduct of C_{60}, which is identical to the mechanochemically synthesized dimer.[10]

Figure 1 shows the infrared absorption spectra for dimer, 1D, and 2D polymers, dispersed in KBr pellets. Earlier works proved that infrared spectroscopy is a useful means to detect and identify C_{60} polymer phases.[14,15] The spectral difference of these materials clearly shows differences in the local structure of C_{60}. The spectra for dimers and 2D polymers are similar to those reported in the literature,[5,13–15]

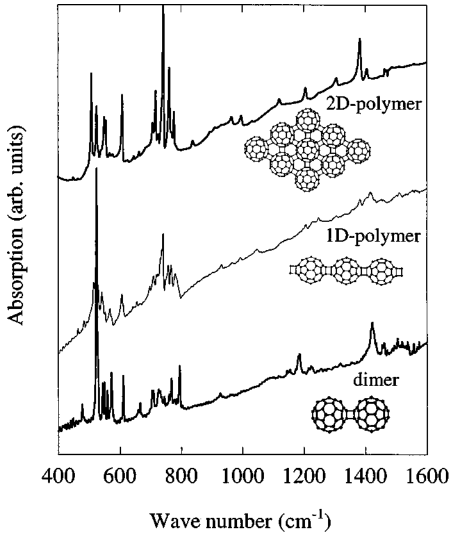

FIG. 1. Infrared absorption spectra for C_{60} dimer, 1D orthorhombic, and 2D rhombohedral polymers, synthesized by high-pressure technique.

while 1D polymers exhibit considerably different spectra from earlier observations,[14] presumably due to the improvement of the crystallinity.

The mass production of dimeric and polymeric materials by the high-pressure technique enables a comparative study of the thermal properties of these systems. A differential scanning calorimetry (DSC) measurement was made on 10–15 mg powder samples each using a Mettler-Toledo TA8000 calorimeter. Figure 2 shows DSC data for a C_{60} dimer, 1D polymer, and 2D rhombohedral polymers in the heating process at a heating rate of 10 °C/min. We found a large endothermic peak in the heating process, but no signal was observed in the cooling scan, indicating that an irreversible transition occurred in the heating process. The substances obtained after the DSC measurements were all monomer C_{60} as confirmed by infrared and x-ray-diffraction measurements. These data clearly showed that all polymeric forms of C_{60} revert to monomers upon heating to 300 °C. This conversion takes place as an endothermic reaction, indicating that all the polymeric forms are energetically stable compared to the monomer.

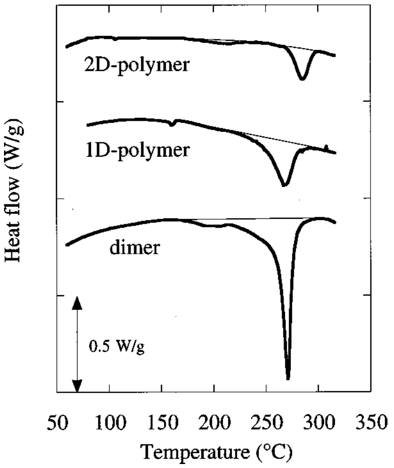

FIG. 2. Differential scanning calorimetry data for the dimer, 1D polymer, and 2D rhombohedral polymer in the heating process of which the heating rate was 10 °C/min. The thick solid lines are experimental data and thin lines display the background assumed when calculating the enthalpy change ΔH. All these materials revert to monomer C_{60} after the DSC measurement.

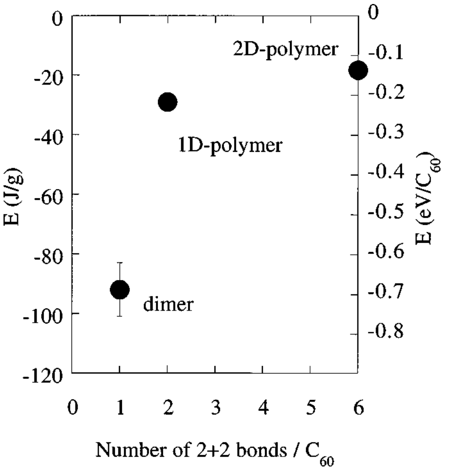

FIG. 3. The relative energy of the C_{60} dimer, 1D orthorhombic, and 2D rhombohedral polymers measured from the energy of monomeric fcc C_{60}, plotted as a function of the number of [2+2] intermolecular bonds per C_{60} molecule.

The transition temperature T_D, defined as the peak temperature of the DSC curve, changes between 250 K and 290 K, depending on the polymeric phases and heating rate. Wang *et al.* reported T_D for mechanochemically synthesized dimers at 162 °C for 1 °C/min scan.[10] The difference in T_D's between their results and the present results indicates that the depolymerization process is controlled by kinetics. In the following we concentrate on the enthalpy change ΔH. The ΔH values are calculated by integrating the peaks in Fig. 2, assuming the background line shown as a thin solid line. The DSC measurement was made on three samples for each phase and the sample dependence of ΔH turned out to be within 20%. As for the heating rate, we tested 10 °C/min and 5 °C/min scans. Although the T_D was about 10 °C lower for the slower scan, the difference in ΔH was within sample dependence. The ΔH value derived here is interpreted as the energy difference between the energy minima of the relevant stable phases rather than the barrier height for the depolymerization process discussed by several authors.[16,17]

Since the volume change associated with the bond breaking is extremely small, the enthalpy change ΔH directly corresponds to the change of internal energy: $\Delta H = -E$, where E is the energy of the polymeric C_{60} measured from that of the monomeric fcc phase at the transformation temperature. Figure 3 summarizes the relation between E and the number of [2+2] bonds per C_{60}. Here the dimer, one-, and two-dimensional polymers contain one, two, and six intermolecular 2+2 bonds per molecule. The negative E values mean that the polymeric phases are more stable than the monomeric phase.

The vertical axis in Fig. 3 is shown in units of J/g and eV/C_{60}, for the left and right side, respectively. It is noted that the energy differences between monomers and dimers are about 0.69 eV/C_{60} or 0.011 eV/C atom. It is interesting to

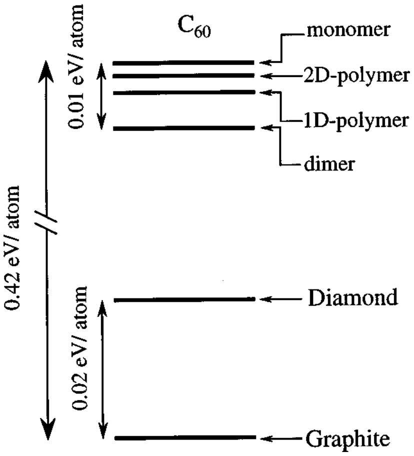

FIG. 4. Schematic energy diagram of various solid carbon phases.

compare this scale with the energy differences between graphite, diamond, and fcc C_{60}. Figure 4 displays a schematic energy diagram of several crystalline phases of pure carbon. The energies of diamond and C_{60} measured from the most stable graphite are known to be 0.020 eV (Ref. 18) and 0.42 eV/C atom,[19] respectively. The observed relative energy between polymeric and monomeric C_{60} is almost two orders of magnitude smaller than the latter value, and slightly smaller than the former. The formation of various solid phases in a considerably small energy range is one of the most peculiar aspects of such polymerized fullerites as carbon allotrope.

Another indication shown in Fig. 3 is that the energy of the polymeric phases becomes higher when the number of $[2+2]$ bonds increases. Since the polymeric phases are stabilized by the formation of intermolecular bonds, the polymers are expected to be more stable in energy as the number of the bonds increases. The unexpected trend in Fig. 3 is explained as follows: In the polymeric forms, one should consider both the energy gain due to the bond formation and energy loss due to the molecular deformation. Since the former contribution dominates, the polymeric forms become lower in energy than the monomer phase. However, the intermolecular bond causes a significant deformation of the C_{60} cage. The deformation energy is able to be absorbed by the intramolecular relaxation in the dimer case. As the number of intermolecular bonds increases, the molecular deformation increases significantly and the stabilization by bond formation is less effective than that of the dimer case. This deformation energy cancels the energy gain by bond formation, so that the energy of polymers increases with the number of $[2+2]$ bonds. This scenario may explain the trend shown in Fig. 3.

Since the polymeric fullerenes are nothing but pure carbon solids, the calculation of the relative energies of polymeric C_{60}'s is a challenging issue for large-scale first-principles calculations. We first focus on the energy of dimers. Although a number of theoretical calculations of E have been made for dimers,[11,20] even the energy difference between the monomer and the dimer phases has not converged yet. The E value for dimers obtained in this study was -80 J/g, which is converted to $-0.57\,\mathrm{eV/C_{60}}$, and could be a good test for these calculations.

Regarding the infinite polymers, Xu and Scuseria made the first calculation on the 1D and 2D tetragonal and 2D rhombohedral phase,[21] and showed that the polymeric phase is stabilized with increasing the number of the intermolecular bonds, in contradiction to the present experimental result. This result suggests that the above calculation does not properly take the molecular deformation into account. Another possible reason for the disagreement is that Xu and Scuseria neglected the interchain or interlayer interaction. More recently, Okada and Saito made calculations on the 2D rhombohedral phase, taking such interactions into account, and obtained a total energy comparable to the monomer fcc phase.[22]

The energies estimated by the theoretical calculations corresponds to the internal energy at $T=0$ K, while experimental values are obtained at finite temperatures. Hence, in order to make a quantitative comparison with the present results and theoretical calculations, we have to take the temperature dependence of the internal energy into account. According to Sundqvist *et al.*, the temperature dependences of the specific-heat capacity for monomeric and polymeric phases are very similar to each other except for near the molecular rotation transition at 260 K.[23] The temperature-dependent part of the internal energy difference between the monomer and the polymer solids is dominated by the enthalpy change at the rotation transition, which is 9.1 J/g.[24] Since the energy of the monomeric phase at $T=0$ K is overestimated, the absolute value of E at $T=0$ K should be subtracted by 9.1 J/g.

It is noted that when we squeeze pure C_{60} solids, we usually obtain the polymers rather than the dimer, which is a more stable substance. This result suggests that the pressure-induced polymerization is not controlled by energetics. A recent calculation showed that the intermolecular deformation plays a crucial role in the mechanism of pressure-induced polymerization.[25] Dynamical aspect of polymerization is an interesting issue.

In summary, a calorimetry study was made on the dimer, 1D, and 2D polymer forms of C_{60}. All these polymeric forms of C_{60} revert to the monomer phase upon heating by an endothermic reaction. From the latent heat, we found that the three polymerized C_{60}'s are more stable than the fcc monomer phase and that the stabilization energy becomes smaller as the number of intermolecular bonds increases. This result suggests that the molecular deformation is so large that the energy gain by the formation of the intermolecular bonds is canceled by the deformation energy. The variety of polymeric phases of C_{60} that exist within a very narrow energy range (0.01 eV/atom) is another unique aspect of carbon solids, in which the sp^3 and sp^2 states are exceptionally close to each other in energy.

The authors wish to thank S. Saito, S. Okada, and T. Ozaki for their valuable discussions. A. Izuoka and T. Sugawara are greatly appreciated for their contribution in the high-pressure synthesis of the C_{60} dimer. T. Uchida is appreciated for his help in high-pressure synthesis. This work has been supported by a grant from the Japan Society for the Promotion of Science (RFTF96P00104, MPCR-363/96-03262), the Ministry of Education, Science, Sports, and Culture.

[1] A. M. Rao, P. Zhou, K.-A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan, and I. J. Amster, Science **259**, 955 (1993).

[2] (a) K. Prassides, K. Vavekis, K. Kordatos, K. Tanigaki, G. M. Bendele, and M P. W. Stephens, J. Am. Chem. Soc. **119**, 834 (1997); (b) G. M. Bendele, P. W. Stephens, K. Prassides, K. Vavekis, K. Kordatos, and K. Tanigaki, Phys. Rev. Lett. **80**, 736 (1998).

[3] G. Oszlányi, G. Baumgartner, G. Faigel, and L. Forró, Phys. Rev. Lett. **23**, 4438 (1997).

[4] S. Pekker, G. Oszlányi, and G. Faigel, Chem. Phys. Lett. **282**, 435 (1998).

[5] Y. Iwasa, T. Arima, R. M. Fleming, T. Siegrist, O. Zhou, R. C. Haddon, L. J. Rothberg, K. B. Lyons, H. L. Carter, Jr., A. F. Hebard, R. Tycko, G. Dabbagh, J. J. Krajewski, G. A. Thomas, and T. Yagi, Science **254**, 1570 (1994).

[6] M. Núñez-Regueiro, L. Marques, J.-L. Hodeau, O. Béthoux, and M. Perroux, Phys. Rev. Lett. **74**, 278 (1995).

[7] L. Marques, J.-L. Hodeau, M. Núñez-Regueiro, and M. Perroux, Phys. Rev. B **54**, R12 633 (1996).

[8] V. Agafonov, V. A. Davydov, L. S. Kashevarova, A. V. Rakmanina, A. Kahn-Harari, P. Dubois, R. Céolin, and H. Szwarc, Chem. Phys. Lett. **267**, 193 (1997).

[9] R. Moret, P. Launois, P.-A. Persson, and B. Sundqvist, Europhys. Lett. **40**, 55 (1997).

[10] G.-W. Wang, K. Komatsu, Y. Murata, and M. Shiro, Nature (London) **387**, 583 (1997).

[11] M. Núñez-Regueiro, in *Fullerene Polymers and Fullerene-Polymer Composites*, edited by P. C. Eklund and A. M. Rao (Springer, New York, 1997).

[12] A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito, and H. Shinohara, J. Chem. Soc. Chem. Commun. **1992**, 1472 (1992).

[13] Y. Iwasa, K. Tanoue, T. Mitani, A. Izuoka, T. Sugawara, and T. Yagi, Chem. Commun. (Cambridge) **1998**, 1411 (1998).

[14] A. M. Rao, P. C. Eklund, J.-L. Hodeau, L. Marques, and M. Núñez-Regueiro, Phys. Rev. B **55**, 4766 (1997).

[15] K. Kamaras, Y. Iwasa, and L. Forro, Phys. Rev. B **55**, 10 999 (1997).

[16] Y. Wang, J. M. Holden, X.-X. Bi, and P. C. Eklund, Chem. Phys. Lett. **217**, 413 (1994).

[17] P. Nagel, C. Meingast, P.-A. Persson, and B. Sundqvist, in *Molecular Nanostructures*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (World Scientific, Singapore, 1997).

[18] G. M. Barrow, *Physical Chemistry* (McGraw-Hill, New York, 1988).

[19] W. V. Steele, R. D. Chirico, N. K. Smith, W. E. Billups, P. R. Elmore, and A. E. Wheeler, J. Phys. Chem. **96**, 4731 (1992).

[20] S. Patchkovskii and W. Thiel, J. Am. Chem. Soc. **120**, 556 (1998), and references therein.

[21] C. H. Xu and G. E. Scuseria, Phys. Rev. Lett. **74**, 274 (1995).

[22] S. Okada and S. Saito, Phys. Rev. B **55**, 4039 (1997).

[23] B. Sundqvist, O. Andersson, U. Edlund, A. Fransson, A. Naba, P. Jacobsson, D. Johnels, P. Launois, C. Meingast, R. Moret, T. Moritz, P.-A. Persson, A. Soldatov, and T. Wagberg, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, edited by K. M. Kadish and R. S. Ruoff (The Electrochemical Society, Pennington, 1996), Vol. 3, p. 1014.

[24] For example, P. A. Heiney, J. Phys. Chem. Solids **53**, 1333 (1996).

[25] T. Ozaki, Y. Iwasa, and T. Mitani, Chem. Phys. Lett. **285**, 289 (1998).