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C_{60} one- and two-dimensional polymers, dimers, and hard fullerite: Thermal expansion, anharmonicity, and kinetics of depolymerization

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We report on high-resolution thermal expansion measurements of high-temperature-pressure treated C_{60} [one-dimensional (1D) and (2D) polymers and ''hard fullerite''], as well as of C_{60} dimers and single crystal monomer C_{60} between 10 and 500 K. Polymerization drastically reduces the thermal expansivity from the values of monomeric C_{60} due to the stronger and less anharmonic covalent bonds between molecules. The expansivity of the ''hard'' material approaches that of diamond. The large and irreversible volume change upon depolymerization between 400 and 500 K makes it possible to study the kinetics of depolymerization, which is described excellently by a simple activated process, with activation energies of 1.9 ± 0.1 eV (1D and 2D polymers) and 1.75 ± 0.05 eV (dimer). Although the activation energies are very similar for the different polymers, the depolymerization rates differ by up to four orders of magnitude at a given temperature, being fastest for the dimers. Preliminary kinetic data of C_{70} polymers are presented as well.
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I. INTRODUCTION

Subjecting pure C_{60} crystals to high-temperature-pressure conditions results in several different polymeric C_{60} phases, which have recently attracted considerable attention.[1–5] In these phases, the weak van der Waals type bonding present between molecules in monomer C_{60} is replaced by covalent bonds via a $2+2$ cycloaddition reaction.[6] Depending on the exact temperature-pressure conditions, one-dimensional (1D) and two-dimensional (2D) polymerized structures have been found.[3,5] It is also possible to photo-polymerize C_{60},[6] and polymerization occurs spontaneously during cooling in the doped $A\,C_{60}$ ($A=\mathrm{Rb,K}$) compounds.[7] Recently, C_{60} dimers have been synthesized using a mechano-chemical technique[8] and by applying pressure to C_{60} in a host lattice.[9] It is possible to study these polymeric forms of C_{60} at ambient conditions since they are metastable. However, heating the polymers to around 500 K breaks the polymeric bonds, and the material reverts back to monomeric C_{60}. At very high temperature ($T>1000$ K) and pressure (3–10 GPa) the C_{60} cage collapses and a ''hard fullerite'' is obtained,[4,5,10,11] which most probably has a cross-linked layered-type structure.

In this paper, we report on high-resolution thermal expansion measurements between 10 and 500 K of high-pressure-temperature synthesized 1D (orthorhombic) and 2D (tetragonal) C_{60} polymers and ''hard'' fullerite, as well as of C_{60} dimers and single-crystal monomer C_{60}. Thermal expansion data are interesting from two points of view. First, polymerization is expected to result in a large reduction of the thermal expansivity from the values of ''normal'' monomeric C_{60} due to the stronger and less anharmonic covalent bonds formed between the C_{60} molecules in the polymeric phase. We will analyze our expansivity data using the Grüneisen formalism and recent specific heat data on similar samples[12] to obtain some information about the anharmonicity of the intermolecular bonds. Second, the large and irreversible volume change upon depolymerization between 400 and 500 K makes it possible to study the kinetics of depolymerization and, of course, the volume increase when the bonds are broken. We will show that depolymerization occurs via a simple activated process, with activation energies of 1.9 ± 0.2 eV (1D and 2D polymers) and 1.75 ± 0.1 eV (dimer). Although the activation energies are very similar for the different polymers, the depolymerization rates differ by up to four orders of magnitude at a given temperature, being fastest for the dimers. Preliminary kinetic data of C_{70} polymers are presented as well.

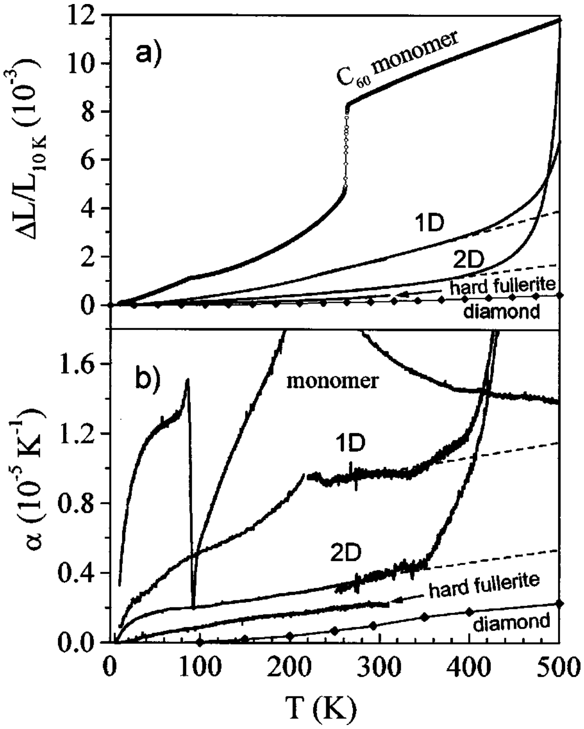

FIG. 1. (a) Linear thermal expansion and (b) expansivity of polymer (1D and 2D), ''hard fullerite'' and monomer C_{60} upon heating. The thermal expansion of the 2D sample is quite anisotropic and the data represent a volume average (see Fig. 2). The deviation of the 1D and 2D data from the dashed lines in (a) and (b) result from the thermally activated depolymerization process. The thermal expansion (expansivity) of diamond is shown for comparison. (See text for details.)

II. EXPERIMENT

The 1D and 2D polymerized samples were prepared by annealing high-purity sublimed polycrystalline C_{60} at 565 K for 2 h at a pressure of 1.1 GPa (Ref. 13) and at 830 K for 5 h at a pressure of 2.0 GPa, respectively. The samples were then cooled before releasing the pressure. The ''hard fullerite'' sample was obtained by treating C_{60} at 8 GPa and 1600 K using a very short synthesis time of only 1 min.[11] The C_{60} dimers were synthesized by a solid-state mechanochemical reaction of C_{60} with potassium cyanide.[8] For comparison, a high-purity C_{60} monomer single-crystal was also examined. Two high-resolution capacitance dilatometers with temperature ranges of 4-300 K (Ref. 14) and 150-500 K,[15] respectively, were used to measure the thermal expansion. Data were taken at constant heating (cooling) rates between 0.2 and 20 mK/s and He exchange gas (10 mbar) was used to thermally couple the samples to the dilatometers. The thermal expansion of the dimer phase, which was available only in the form of fine powder, was measured by placing a small amount (0.5 mg) of powder in the bottom of a hollow capped cylinder. A small steel rod was then inserted into the cylinder, and the thermal expansion of the cylinder, rod, and dimer powder were measured simultaneously. To characterize the dimer phase, Raman spectra were taken with a Fourier transform (FT) spectrometer using a Nd:YAG laser with a wavelength of 1064 nm.

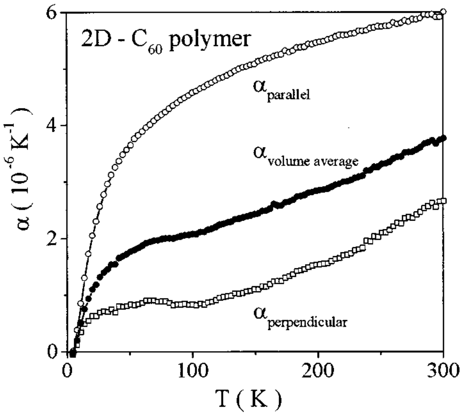

FIG. 2. Linear thermal expansivity of the 2D polymer along two orthogonal directions of a flake-shaped sample showing a large anisotropy. The volume averaged thermal expansivity is estimated by assuming no anisotropy within the plane of the flake-shaped sample.

III. THERMAL EXPANSION RESULTS

The linear thermal expansion, $\Delta L/L$, and linear expansivity, $\alpha = 1/L \cdot dL/dT$, between 10 and 500 K of monomer and polymer phases of C_{60} are compared in Figs. 1(a) and 1(b), respectively.

The thermal expansion (expansivity) of the polymers is much smaller than that of the monomer and decreases as one progresses from the 1D to the 2D polymers and then to the ''hard'' material [The thermal expansion of the 2D material was found to be highly anisotropic (see Fig. 2), and the data in Fig. 1 represent a volume average.] This is what is expected if the weak, anharmonic van der Waals bonds between the C_{60} molecules are replaced by more and more shorter, stronger, and less anharmonic covalent bonds. Interestingly, the expansivity of the ''hard'' fullerite approaches that of diamond. A more detailed discussion of the anharmonicity of the C_{60}-C_{60} bonds will be presented in the next section in connection with recent specific heat measurements on very similar samples.[12] The orientational ''glass'' and ordering transitions, which are prominently seen at 90 and at 260 K, respectively, in the thermal expansion of the monomer phase[16] (see Fig. 1) are, as expected, absent in all high-pressure treated phases. However, noticeable in both Figs. 1(a) and 1(b) is an anomalous upturn in the thermal expansion (expansivity) of the 1D and 2D phases, which sets in at around 350 K. This anomalous thermal expansion is irreversible and is due to the volume increase upon depolymerization. It will be shown further on that the depolymerization is a purely kinetic process, and we will extract various kinetic parameters from our data.

The anisotropic nature of the thermal expansion of the 2D polymer sample is demonstrated in Fig. 2, where data are shown for two perpendicular directions of a flake-shaped sample. The expansivity is much lower perpendicular ($\alpha_{\text{perpendicular}}$) than parallel ($\alpha_{\text{parallel}}$) to the normal of the flake surface. Presumably, the sample was partially textured by the application of a uniaxial pressure component during synthesis. However, the true anisotropy of the 2D material is expected to be greater than the observed one. Also shown in Fig. 2 is the volume averaged linear expansivity, where we

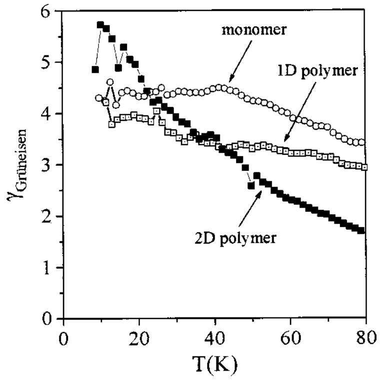

FIG. 3. Grüneisen parameter $\gamma_{\text{Grüneisen}}$ for monomer and 1D and 2D polymer C_{60}.

have assumed that $\alpha_{\text{average}}=(\alpha_{\text{parallel}}+2\alpha_{\text{perpendicular}})/3$. It is α_{average}, which is shown in Fig. 1.

The expansivity of monomer C_{60} has previously been studied in detail only up to 300 K (Refs. 16 and 17). Here we present, in addition to the polymer results, also high-resolution data of single-crystalline monomer C_{60} up to 500 K. An interesting feature of these data [Fig. 1(b)] is that $\alpha(T)$ decreases by about 25% between 260 and 500 K. This represents an unusual T dependence, because $\alpha(T)$ of a normal solid is expected to rise slightly or remain constant at high temperature. Either precursors to the fcc-sc phase transition or a T dependence of the local structural order[18] could cause this behavior, the latter of which is more likely, since no precursors to the transition have been observed.[18]

Below about 50 K, both the expansivity and the specific heat of monomer C_{60} result, to a good approximation, entirely from the excitation of intermolecular modes. The intramolecular contributions can be ignored in this temperature range because they are much higher in energy.[12] This has allowed a simple determination of the intermolecular Grüneisen parameter of monomer C_{60}.[19] Following this spirit, we calculate the total Grüneisen parameter

$$\gamma_{\text{Grüneisen}}=\frac{3\alpha V_{\text{molar}}B_T}{C_V}, \tag{1}$$

from our expansivity and the specific heat[12] data of the polymer phases in order to get some idea of anharmonicity of the intermolecular modes of the polymer phases. We used the presently determined room-temperature molar volumes (V_{molar}) and 14 GPa,[5] 33 GPa,[2] and 45 GPa (Ref. 20) for the isothermal bulk moduli (B_T) of the monomer, 1D and 2D phases, respectively. The value 14 GPa is characteristic of the low-T glassy phase of C_{60}, while for the polymers only room temperature data are available; however, the bulk modulus is not expected to show a strong-temperature dependence for these materials. The resulting Grüneisen parameters as a function of temperature are shown in Fig. 3. Below about 50 K, $\gamma_{\text{Grüneisen}}$ of monomer C_{60} shows little temperature dependence and has a value of about 4.5. This is significantly larger than the previous calculation[19] due to the larger bulk modulus used in the present calculation. Above 50 K, $\gamma_{\text{Grüneisen}}$ of monomer C_{60} decreases with increasing temperature due to the increasing intramolecular contributions to C_v, which are much less anharmonic. Perhaps somewhat surprisingly, $\gamma_{\text{Grüneisen}}$ of both polymer phases have a very similar value as $\gamma_{\text{Grüneisen}}$ of monomer C_{60} at low temperatures (between 10–20 K). This should, however, really be expected since at these low temperatures, only the remaining weak van der Waals type of bonds, i.e. the same kinds of bonds as in monomer C_{60}, contribute to $\gamma_{\text{Grüneisen}}$. At higher temperatures, in contrast, the covalent intermolecular polymeric bonds start to contribute more and more, and this is the reason for the strongly decreasing (especially for the 2D polymer) $\gamma_{\text{Grüneisen}}$ values with increasing temperature for the polymer materials. This clearly demonstrates that the covalent intermolecular polymeric bonds are much less anharmonic than the strongly anharmonic monomeric bonds. Since these polymer materials are very anisotropic, a proper analysis of the Grüneisen parameters will have to be carried out using good expansivity and elastic data on single crystals.

IV. DEPOLYMERIZATION

In this section, we present and discuss the depolymerization experiments of the 1D and 2D C_{60} polymers and of the C_{60} dimers using thermal expansion as a probe. From these experiments, we obtain the volume increase upon depolymerization, and we can also study the kinetics of depolymerization. To study the kinetics of the depolymerization process, we used several different approaches. It has been shown by several groups that the depolymerization results in an endothermic peak in the specific heat around 450–550 K (Refs. 2, 8, and 21) and a similar peak is expected in the thermal expansivity. For the dimers, the shift in temperature of this anomaly in the thermal expansion as a function of heating rate was determined. The disadvantage of this method is that a new polymer sample is needed for each run. For this reason and the fact that our dilatometer is limited to 500 K, we choose a different method for the 1D and 2D polymer samples, in which we cycled the temperature several times between 150 and 500 K at constant heating (cooling) rates. As we show below, this method allows us to determine the relaxation rates as a function of temperature and thus the kinetic parameters using a single sample. Finally, as a consistency check, the time constants were also measured directly by recording the length changes as a function of time at a fixed temperature.

Figures 4(a) and 4(b) shows the thermal expansion and expansivity, respectively, of the 1D polymer for repeated heating (cooling) cycles between 200 and 500 K at a rate of 20 mK/s (−20 mK/s). Clearly seen in Fig. 4(a) are the irreversible increase in length of the sample between 450 and 500 K with each cycle as well as the progressive development of the well-known fcc-sc phase transition near 260 K of the monomer phase. This reappearance of the fcc-sc phase transition clearly demonstrates that the polymer continuously reverts back to monomer C_{60}. The volume change upon depolymerization is 2.2%, if one assumes that the sample is isotropic. This value agrees well with other mechanical studies on similar materials[13] but is considerably smaller than the 8.5% reported by Bashkin *et al.*[2] This difference could arise either because our sample was not fully polymerized or because of a strong disorder in the orientations of molecular chains in the polycrystalline material, which does not allow

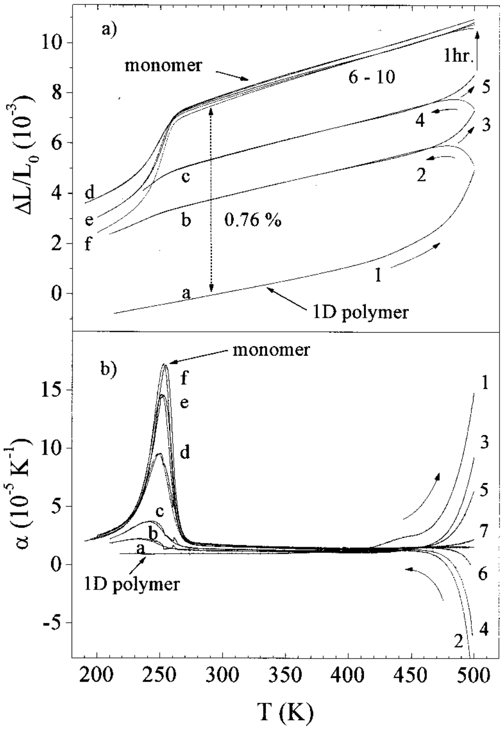

FIG. 4. (a) Linear thermal expansion and (b) expansivity of 1D C_{60} polymer for several heating and cooling cycles between 200 and 500 K. Noticeable are the irreversible length increase between 450–500 K and the restoration of the well-known fcc-sc phase transition of monomeric C_{60} during depolymerization at 260 K.

the crystal volume to decrease by the same fraction on the macroscopic scale as on the intermolecular (microscopic) scale. In the experiment of Bashkin *et al.*, the chains are expected to be at least partially aligned due to the uniaxial pressure component, and a larger volume effect may be expected.

The irreversible thermal expansion between 450 and 500 K [Fig. 4(a)] appears as a large positive (negative) anomaly upon heating (cooling) in the expansivity superimposed upon the usual reversible thermal expansivity, which is quite small in comparison to the anomalous part [see Fig. 4(b)]. The total thermal expansivity $\alpha_{\rm tot}$ is, thus, the sum of the reversible thermal expansivity, $\alpha_{\rm rev}$, and the irreversible part $\alpha_{\rm irr}$

$$\alpha_{\rm tot}=\alpha_{\rm rev}+\alpha_{\rm irr}. \tag{2}$$

$\alpha_{\rm irr}$ arises because the sample length L becomes a function not only of temperature, but also of time, and this time dependence of L is easily extracted by multiplying $\alpha_{\rm irr}$ by the heating (cooling) rate, $\partial T/\partial t$,

$$\alpha_{\rm irr}\cdot\frac{\partial T}{\partial t}=\frac{1}{L}\cdot\frac{\partial L_{\rm irr}}{\partial T}\cdot\frac{\partial T}{\partial t}=\frac{1}{L}\cdot\frac{\partial L_{\rm irr}}{\partial t}\propto\frac{1}{\tau(T)}. \tag{3}$$

If we assume that the fraction of polymer phase in the sample scales linearly with the irreversible length change shown in Fig. 4, we can quantitatively calculate the polymer-monomer transformation rate, $\tau(T)$, via Eq. (3) (for details see Ref. 15). $\tau(T)$ obtained using this procedure for cycles 1–5 are shown in an Arrhenius plot in Fig. 5. Except for the initial part of cycle 1, where the transformation starts at lower temperatures, τ exhibits a simple activated behavior, i.e., $\tau(T)=1/\nu_0\cdot e^{E_a/k_BT}$, over more than a decade in time. We will show later that the anomalous behavior of the first cycle is most likely due to some remaining dimers in the sample, which break up at considerably lower temperatures. The activation energy determined from a fit of the data in Fig. 5 from 470 to 500 K was $E_a=1.9\pm0.2$ eV and the prefactor $\nu_0=6.9\times10^{15}$ Hz for cycles 2–5. For temperatures below 470 K the heating and cooling curves no longer match. This probably has to do with the uncertainty in the background determination, which strongly influences the results for the lower temperatures. To check the validity of the above approach, we also directly measured the time dependence of L between cycles 5 and 6 for 1 h at a constant temperature of 500 K, and the result is shown in Fig. 5(b). The data are described excellently by an exponential relaxation curve with $\tau(500\,\mathrm{K})=2340$ s. This value of τ agrees very well with those obtained from the dynamic heating (cooling) runs using Eq. (1) [see Fig. 5(a)], which clearly justifies our approach.

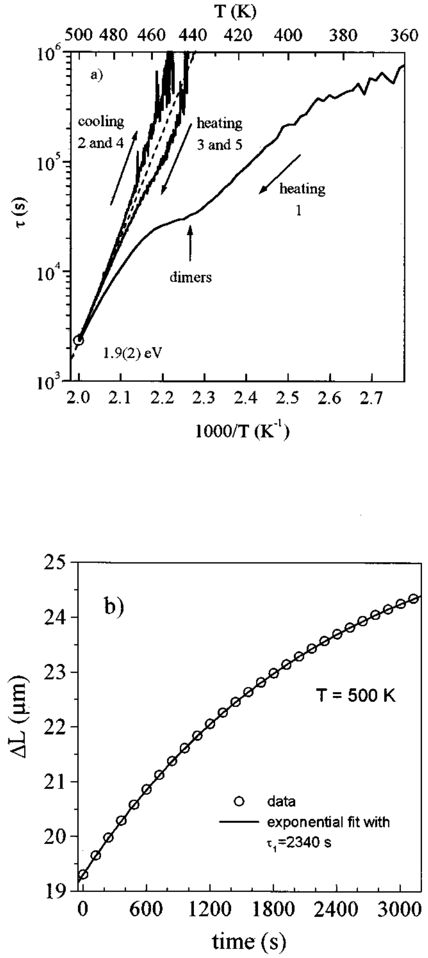

FIG. 5. (a) Arrhenius plot of the depolymerization rate τ for the 1D C_{60}-polymer determined from the expansion data of Fig. 4 (solid lines). Except for the initial part of the first heating cycle, the data exhibit a simple activated behavior with an activation energy of $E_a=1.9\pm0.2$ eV. The open circle data point at 500 K was determined directly (see *b* and text for details). (b) Relaxation of the 1D C_{60} polymer sample length versus time at 500 K. The data were taken for a period of 1 hour between cycles 5 and 6 (see Fig. 4). A simple exponential relaxation curve with τ(500 K)=2340 s (line) excellently describes the data.

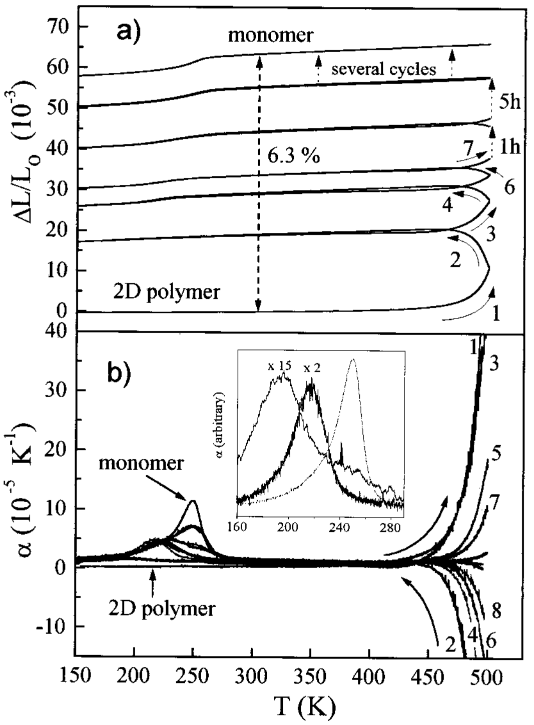

FIG. 6. (a) Linear thermal expansion and (b) expansivity of the 2D C_{60} polymer for several heating and cooling cycles between 150 and 500 K. The irreversible length increase near 500 K is about a factor of 10 larger than for the 1D polymer. The inset in (b) shows that the fcc-sc transition first develops at 190 K and then shifts to the usual value of 250–260 K upon full depolymerization. (See text for details.)

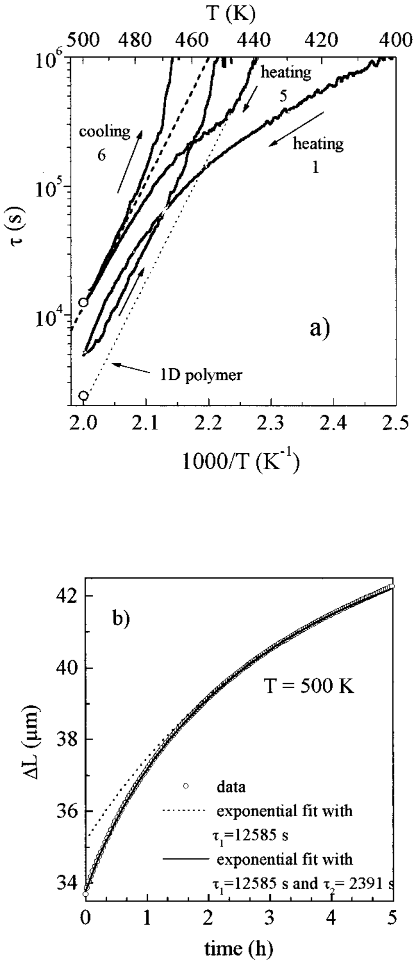

FIG. 7. (a) Arrhenius plot of the depolymerization rate τ for the 2D C_{60} polymer determined from the expansion data of Fig. 6 (solid lines). Except for the initial part of the first heating cycle, the data exhibit an activated type behavior with an activation energy of $E_a = 1.9 \pm 0.2$ eV (dashed line). The open circle data points at 500 K were determined directly (see *b* and text for details). (b) Relaxation of the 2D C_{60}-polymer sample length versus time at 500 K. The data were taken for a period of 5 h between cycles 9 and 10 (see Fig. 6). In contrast to the data of the 1D material [see Fig. 6(b)], the data are not described by a single exponential relaxation, but rather provide evidence for two different rates with $\tau_t(500\,\mathrm{K}) = 2391$ s and $\tau_2(500\,\mathrm{K}) = 12\,585$ s.

The thermal expansion upon depolymerization of the 2D polymer is shown in Fig. 6, again for repeated heating (cooling) cycles between 150 and 500 K at a rate of 20 mK/s (−20 mK/s). In order to get a better idea of the volume increase upon depolymerization, we used a sample which had an initial expansivity close to the volume averaged one of the anisotropic sample. The results upon depolymerization are very similar to those of the 1D material (Fig. 4), but with three important differences. First, the length increase of the 2D polymer is almost a factor of 10 larger than for the 1D polymer (6.3% vs 0.7%). Again assuming that the sample is isotropic, we obtain a very large volume increase of roughly 18%, in fair agreement with the literature.[1,3] Second, the orientational ordering transition is initially observed at 190 K, i.e., much lower than the bulk value of 260 K [see inset of Fig. 6(b)], and then shifts to the bulk value upon further depolymerization. The symmetric shape and the lower T_c of the 190 K transition are reminiscent of two-dimensional behavior, suggesting that depolymerization initially occurs in thin layers. Third, the depolymerization is somewhat slower in the 2D than in the 1D material; an increased number of cycles are needed to convert all of the 2D polymer back to the monomer phase. We performed the same type of analysis of the different heating (cooling) cycles as for the 1D polymer and extracted the bond-breaking rate τ, which is plotted in Fig. 7(a) for several cycles at the beginning and at the end of depolymerization. As in the 1D material, the first cycle shows some feature with a faster rate. The subsequent cycles all exhibit activated behavior with the same activation energy, $E_a = 1.9 \pm 0.2$ eV, for the different heating and cooling cycles between 470 and 500 K. However, the attempt frequency ν_0 decreases during the course of the measurement from an initial value close to the value of the 1D-polymer ($\nu_0 = 7 \times 10^{15}$ Hz) and ends up with $\nu_0 = 7.3 \times 10^{14}$ Hz [see Fig. 7(a)]. This may indicate that the sample is a mixture of 1D-and 2D-polymer phases, which are breaking up at different rates. A direct measurement of the time-dependent length-increase at 500 K between cycles 9 and 10 provides evidence for two different relaxation rates [see Fig. 7(b)], which supports this view. In contrast to the 1D data [Fig. 5(b)], the time dependence of the length of the 2D material cannot be fit with a single exponential curve [see Fig. 7(b)]. A fit with two different relaxation times, on the other hand, provides an excellent description of the data. The faster τ matches the values of the 1D polymer and the slower τ

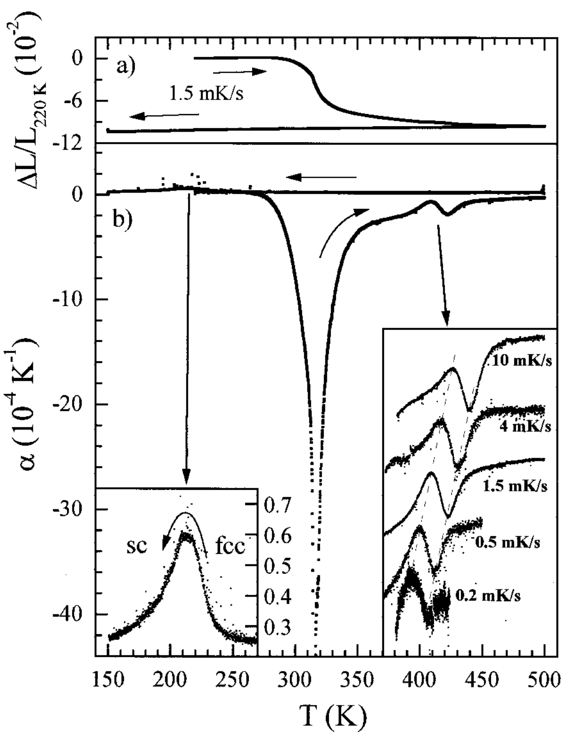

FIG. 8. (a) Linear thermal expansion and (b) expansivity of the C_{60}-dimer sample upon heating and cooling at a rate of 1.5 mK/s. The breaking of the dimers occurs at the small *S*-shaped anomaly near 415 K in (b). The left inset in b) shows that the sc-fcc transition is recovered after heating to 500 K. The right inset demonstrates that the *S*-shaped anomaly shifts approximately linear with the logarithm of the heating rate. (See text for details.)

agrees with the limiting value of the dynamic 2D data [see Fig. 7(a)], which provides further evidence for a two-phase nature of the sample.

We now proceed to discuss the depolymerization of the C_{60} dimers. As mentioned previously, the thermal expansion measurements of the dimers were performed on very small amounts of powdered material, which allowed a study of the kinetics of depolymerization and a qualitative, but not quantitative, determination of the expansivity. In Fig. 8, we thus present the ''apparent'' linear thermal expansion and the expansivity of the C_{60} dimer powder for the first heating cycle from 220 to 500 K and the subsequent cooling cycle from 500 to 150 K. Upon heating a large shortening of the sample occurs near 315 K in Fig. 8(a), which results in a large negative peak in the expansivity [Fig. 8(b)]. A second, much smaller *S*-shaped anomaly, which is only seen in the expansivity, occurs near 415 K. Both anomalies are absent in the cooling curve, indicating irreversible processes. However upon cooling and subsequent heating cycles, a new phase transition arises near 220 K. We identify this transition, which has been shifted down to 220 K presumably due to remaining disorder, with the fcc-sc phase transition, and this, thus, indicates that the dimers have been broken apart by heating to 500 K. In order to determine which of the anomalies upon heating is due to bond breaking, Raman spectra[22] of fresh samples were taken before heating, after annealing at 385 K for three hours and after heating slowly to 500 K. These spectra clearly demonstrate that the 315 K peak is due to evaporating solvent (c-dichlorobenzene) still present in the powdered samples and that bond breaking occurs around 415 K. In contrast to the 1D and 2D C_{60} polymers, there appears to be very little volume change occurring upon depolymerization of the dimers as implied by the *s*-shaped anomaly, and it is not even clear from our data if the volume increases or decreases. The shape of the anomaly was however very reproducible, nearly identical *S*-shaped anomalies were observed for five different samples measured at different rates. The right inset of Fig. 8(b) shows that, as expected, the anomaly shifts to lower temperatures with decreasing heating rates. Defining the bond-breaking temperatures $T_{bb} = T_{\text{bond-breaking}}$ as either the maxima or minima of the anomalies allows one to plot the logarithm of the heating rate r versus $1/T_{bb}$, from which activation energies $E_a = 1.70 \pm 0.05\,\text{eV}$ (maxima) and $E_a = 1.79 \pm 0.05\,\text{eV}$ (minima) are obtained. To convert the heating rate to a bond breaking rate τ_{bb}, the bond breaking was simulated with a simple model in which the fraction of dimers y obeys the differential equation

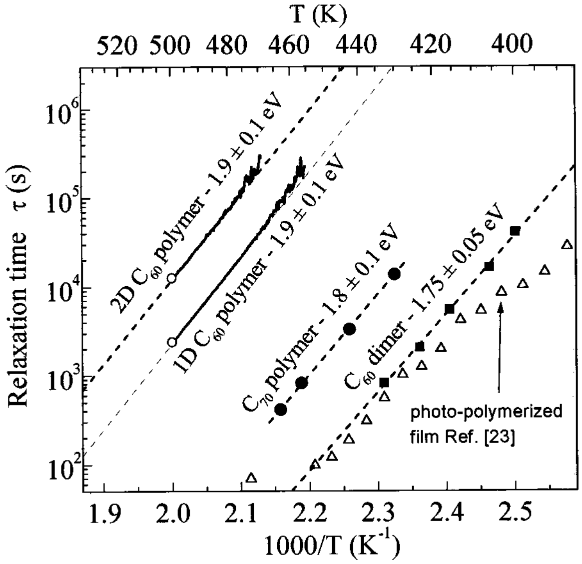

FIG. 9. Comparison of the depolymerization rate τ for the 1D and 2D C_{60} polymers, C_{60} dimers, C_{70} polymers (Ref. 24), and photopolymerized C_{60} films (Ref. 23).

$$\frac{dy}{dT} = \frac{y}{\tau(T) \cdot r}, \tag{4}$$

with an activated rate $\tau(T) = 1/\nu_0 \times \exp(E_a/k_B T)$. The only free parameter in this model is the attempt frequency, which could be determined to $\nu_0 = 2.6 \times 10^{17}\,\text{Hz}$. The resulting relaxation times are plotted in Fig. 9. Our result for the dimers agrees very well with differential scanning calorimetry (DSC) measurements taken at 17 mK/s on the same material,[8] which produce a peak centered at 435 K. Another DSC study, on the other hand, found that the dimers break at a much higher temperature of about 540 K.[21] This difference is much larger than expected from the larger heating rate (166 vs 17 mK/s) of this study, which according to our results should only shift the transition about 20 K [see right inset of Fig. 8(b)]. The origin of this discrepancy is unclear, there must be some major difference between the dimer materials produced using the different methods. We note that the small peak in the first heating cycle of the 1D material [see Fig. 4(b)] at around 440 K excellently matches the depolymerization temperature of the dimers [see Fig. 8(b)], suggesting that there is a small amount of dimers in the 1D sample.

A summary of the kinetic depolymerization data for the 1D and 2D polymers and for the dimers is shown in an Arrhenius representation in Fig. 9. Cooling and heating curves have been averaged for the 1D and 2D materials, which reduces the uncertainties in the activation energies. We have also included data from photo-polymerized C_{60} films from Wang *et al.*[23] and preliminary results of C_{70} polymers.[24] The activation energy for all polymer material is very similar, falling between 1.75 and 1.9 eV. However, the relaxation times at a given temperature differ by up to four orders of magnitude, or, for a fixed relaxation rate, the depolymerization ''temperatures'' differ by up to 100 K. This difference cannot be explained by just the small differences in E_a, but is also the result of higher values of ν_0 for the dimers ($\nu_0 = 2.6\times10^{17}$ Hz) than for the 1D ($\nu_0 = 7.3\times10^{15}$ Hz) and 2D ($\nu_0 = 7.3\times10^{14}$ Hz) polymers. Our τ values for the dimers closely match those of the photo-polymerized C_{60} films,[23] which strongly suggests that the photopolymerized films of Wang *et al.* consist primarily of dimers. We, however, point out that our activation energy for the dimers (1.75 eV) is significantly larger than the one derived by Wang *et al.* (1.25 eV).[23] The depolymerization activation energy of the 1D material is in fair agreement with the value (2.3 ± 0.3 eV) found by Moravsky *et al.*[25]

Since our kinetic data are obtained at finite temperature, they should be analyzed in terms of the ''free activation energy'', as discussed by Petersson *et al.*,[26] in order to compare them to theoretical predictions, which are usually carried out for $T=0$. The relaxation time in this formalism is given by

$$\tau(T) = f_0^{-1}\cdot\exp\left(\frac{\Delta G}{k_B T}\right), \tag{5}$$

where ΔG denotes the free activation enthalpy of the depolymerization process and f_0 is a characteristic phonon frequency. ΔG is related to the activation enthalpy ΔH and the activation entropy through the usual thermodynamic relation $\Delta G = \Delta H - T\Delta S$. Also $\Delta H = \Delta U + p\Delta V$, where ΔU is the potential barrier height and ΔV is the activation volume, i.e., the difference in volume between the minimal and maximal energy positions. Equation (5) can be rewritten as

$$\tau(T) = f_0^{-1}\exp(-\Delta S/k_B)\cdot\exp\left(\frac{\Delta H}{k_B T}\right). \tag{6}$$

We can identify the experimentally determined quantities ν_0 and E_a with $f_0\cdot\exp(\Delta S/k_B)$ and ΔH, respectively. Theoretical studies of the barrier height for the 2D rhombohedral polymer give values of $\Delta U = 1.6$ eV (Ref. 27) and $\Delta U = 1.7$ eV.[28] These values are slightly smaller than our experimentally determined ΔH value of 1.9(2) eV for the 1D and 2D phases. Assuming that this difference is significant, suggests that the $p\Delta V$ term plays a non-negligible role. Our ΔH value of the dimer (1.75 eV), on the other hand, appears to agree much better with the theoretical values. Possibly, this is due to the fact that there is very little volume change during the transition, i.e., the activation volume may be quite small. The prefactor ν_0 of the polymers (especially for the dimers) is significantly larger than a typical phonon frequency, which suggests that the activation entropy ΔS also play a key role in the kinetics of depolymerization. A direct study of the activation volume via kinetic studies under pressure[26] should shed more light upon this issue.

V. CONCLUSION

Subjecting C_{60} to high-pressure and temperature conditions results in large changes of the thermal expansion behavior of the resulting polymer and ''hard fullerite'' phases. The thermal expansivity is greatly reduced by replacing the weak van der Waals type intermolecular bonds of monomer C_{60} by an increasing number of covalent polymer bonds. The smallest thermal expansivity is found for the ''hard fullerite'' material, in which the C_{60} cage has been broken apart. The volume change upon depolymerization is around 2% and 18% for the 1D and 2D material, respectively. Little volume change is seen for the dimer sample. The kinetics of depolymerization follow a simple thermally activated behavior with activation enthalpies between 1.75 eV (dimers) and 1.9 eV (1D and 2D). The kinetics of depolymerization of C_{70} polymer falls between those of the 1D and 2D materials and those of the dimers. The experimentally determined depolymerization barrier of all polymers studied has about the same value and agrees quite well with theory.[27,28] Small differences between theory and experiment may be the result of non-negligible activation volumes. The similarity of the barrier heights also suggests that the energetic stability of the different polymeric bonds are very similar. Despite the very similar barrier heights, the relaxation rate is about a factor of 10^4 faster for the dimers than the 2D polymer. High-pressure studies of the depolymerization kinetics would be very useful in order to gain further insights into the physics of these effects.

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