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High-resolution ^{13}C NMR studies of high-pressure-polymerized C_{60}: Evidence for the [2+2] cycloaddition structure in the rhombohedral two-dimensional C_{60} polymer

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We report on ^{13}C NMR measurements of a rhombohedral two-dimensional polymer of C_{60} obtained under high pressure. By spinning the sample up to 12 kHz, we were able to identify six resonances at 149.1, 147.9, 145.2, 139.6, 134.8, and 73.5 ppm. The static distortion of the C_{60} molecules induced by the transformation under pressure must be at the origin of the observed inequivalent carbons in the polymer. The ^{13}C NMR line shape simulation of the obtained spectrum is compatible with the suggested polymeric structures where the C_{60} molecules are connected by [2+2] cycloadditions. [S0163-1829(96)51630-9]

I. INTRODUCTION

Photoinduced polymerization of solid C_{60} films was reported by Rao *et al.*[1] The cycloaddition [2+2] mechanism between two adjacent C_{60} molecules was proposed to be at the origin of the observed lattice contraction and increase of disorder on phototransformed C_{60} films. The reaction was shown also to be reversible, as the pristine fcc C_{60} structure is recovered by heating the polymer above 500 K. Bulk polymerized C_{60} phases obtained at high pressure and high temperature have also been reported.[2,3] At least three phases were synthesized, characterized, and theoretically investigated.[4–7] The pressure, temperature, and duration synthesis conditions are essential to obtain one of the rhombohedral, orthorhombic, or tetragonal phase. As with other nonsaturated organic molecules similar reactions as in photopolymerization[1] were expected to appear in solid C_{60} under pressure and temperature. By this technique bulk ordered polymerized C_{60} samples can be easily obtained giving access to a larger range of characterization experiments. In this paper we report on ^{13}C NMR MAS measurements on the rhombohedral two-dimensional (rh-2D) polymerized phase. The observed inequivalent carbons in the studied polymer are discussed in terms of the bonding nature between adjacent C_{60} molecules and distortion from the spherical shape of the molecules. Also, we discuss the molecular dynamic in this system.

II. EXPERIMENT

We performed ^{13}C NMR measurements at ambient temperature on rh-2D polymerized fullerene C_{60} and amorphous graphite obtained by extreme compression of C_{60}. About 30 mg of each sample have been used. All the pristine C_{60} starting materials were 10% ^{13}C enriched in order to increase the NMR signal and the samples were kept in air.

NMR measurements were performed using a 200 MHz and 400 MHz Bruker NMR spectrometers with ^{13}C NMR Larmor frequencies of 50.2 and 100.4 MHz, respectively. We used probes with 4 mm rotor diameter that allows to spin the samples up to 15 kHz. The spectra were obtained by a one pulse sequence $\pi/2$ acquisition with repetition time of 900 and 200 s. The samples were obtained by compressing the enriched C_{60} (encapsulated in a Pt container) in a belt apparatus for periods not exceeding two hours. The rh-2D sample was made at 5 GPa and 700 °C and the graphite phase was recovered from a C_{60} sample treated at 4 GPa and 800 °C. The x-ray-diffraction pattern of the polymerized rh-2D sample is nearly the same as the one published earlier.[4]

III. RESULTS AND DISCUSSION

Figure 1 shows the ^{13}C NMR MAS spectra of the rh-2D sample with different spinning rates and repetition times (a) at 900 s, (b) and (c) at 200 s. In both spectra [see Figs. 1(a) and 1(b)] we observed two isotropic lines at the positions 146 and 73.5 ppm and two sidebands corresponding to the line at 146 ppm, which appear at 266 and 26 ppm. The line at the position 146 ppm exhibits a structure. A deconvolution of this group of lines (see Fig. 2) gives us 6 isotropic lines at the following positions 134.8, 139.6, 142.8, 145.2, 147.9, and 149.1 ppm. We suspect the line at 142.8±1 ppm coming from unreacted pristine C_{60} and evaluate its contribution to be about 5% of the total intensity (that could be probably undetected by the x-ray characterization). The relative inten-

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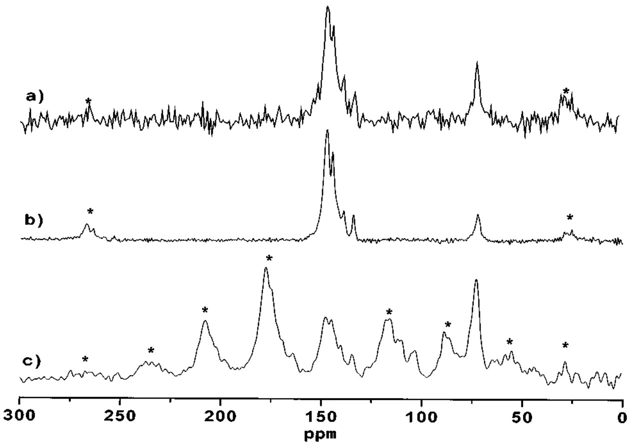

FIG. 1. ^{13}C MAS NMR spectra of rhombohedral (2D) two-dimensional phase with (a) ^{13}C NMR Larmor frequency of 50.2 MHz, spinning rate of 6 kHz, repetition time of 900 s and 1250 scans; (b) ^{13}C NMR frequency 100.4 MHz, spinning rate of 12 kHz and repetition time of 200 s, 3000 scans; (c) ^{13}C NMR frequency 50.2 MHz, spinning rate of 1.5 kHz and repetition time of 200 s, 3000 scans. The stars indicate the sidebands of the line at 146 ppm.

sities of the others five isotropic lines including the side bands are reported in the Table I. The ^{13}C NMR spectrum [see Fig. 1(c)] using a low spinning rate of 1.5 kHz shows the two isotropic lines at 146 and 73.5 ppm and sidebands separated by the spinning frequency. The observed sidebands correspond to the line at 146 ppm and they mimic the envelope of the static spectrum which shows a large extent of anisotropy of about 300 ppm. No sideband was detected for the line at 73.5 ppm indicating a very weak chemical shift anisotropy of the corresponding carbons. In order to avoid confusion in the interpretation of the obtained NMR spectrum of rh-2D polymer sample, we performed ^{13}C NMR measurements on amorphous graphite obtained at high pressure. The latter NMR spectrum, obtained using the same conditions as for the polymerized samples presents a very broad line (not shown here) and no isotropic lines similar to the rh-2D polymerized C_{60} were observed.

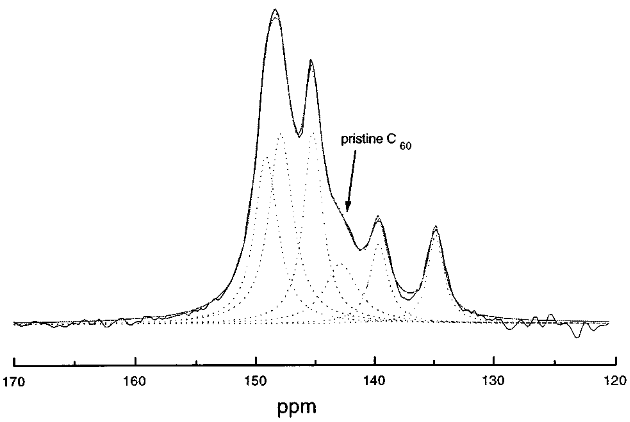

FIG. 2. The line around 146 ppm of the ^{13}C NMR spectrum (b) of rhombohedral (2D) phase. The structure can be deconvoluted using 6 Lorentzian line shapes. Note the presence of about 5% of unreacted pristine C_{60} at 143 ppm.

As expected in such frozen systems of polymerized C_{60}, we found long spin-lattice relaxation time T_1 and very broad static powder spectra. As it has been shown for the A_6C_{60} phase with A=K, Rb, and Cs (Ref. 8) the large extent of anisotropy of about 300 ppm indicates the freezing in of the C_{60} molecules. The latter can be blocked by electrostatic forces in A_6C_{60} or by bonding between the C_{60} molecule and its neighbor C_{60} molecules in polymer configurations. The ^{13}C MAS NMR spectrum reveals inequivalent carbons sites which can be interpreted as sp^2 carbons around the 146 ppm line position and sp^3 bonding carbons between C_{60} molecules at 73.5 ppm. Such covalent bonding have been suggested also in A_1C_{60} polymerized phase where ^{13}C NMR resonances have been observed in the range 60–80 ppm.[9–12] The disagreement in the relative intensities of the sp^2 and sp^3 carbons calculated from structural studies and obtained from experiment with repetition time of 200 s comes from the very long T_1 of the sp^3 carbons, see Table I. The intensity of sp^2 carbon is always overestimated in comparison with the sp^3 carbon intensity due to the chemical shift anisotropy relaxation mechanism which is usually more efficient for sp^2 carbons. Such behavior is visible in the ^{13}C MAS NMR spectrum of rh-2D polymer phase obtained with a repetition time of 900 s which shows the increase of the sp^3 carbon resonance intensity compared with the one obtained with 200 s repetition time (see Fig. 1). But here again all the intensity of sp^3 carbons is not totally covered because of the long T_1, nevertheless the obtained lines intensities are very close to what is expected from the cycloaddition model. Unfortunately such experiments requiring large repetition time were too long to be correctly performed in order to get a good resolution in the structure of the five isotropic lines around 146 ppm.

We turn now to the splitting of the line at 146 ppm, see the ^{13}C MAS NMR detailed spectrum in Fig. 2 and Table I for the relative intensities. It has been shown[4] that the fullerene molecule are no longer spheres, but are deformed by the new bonding and are flattened perpendicular to the plane of polymerization. It is tempting to interpret the five isotropic lines as coming from this distortion from sphericity of the C_{60} molecule. We can expect on the same C_{60} molecule inequivalent carbons due to different neighboring. The carbons involved here are all sp^2 hybridized and they have three neighbors which can be at slightly different positions due to the nonsphericity. The small changes in the angles and the distances are at the origin of the five inequivalent carbons observed. From x-ray studies we know the space group

TABLE I. Relative intensities of the isotropic lines including the sidebands in rh-2D phase.

ppm	experimental (900 s) spectrum 1(a)	experimental (200 s) spectrum 1(b)		calculated from Fig. 3	
149.1	49	13.9	53.9	12	48
147.9		16.1		12	
145.2		13.3		12	
139.6		5.4		6	
134.8		5.2		6	
73.5	11	6.1		12	

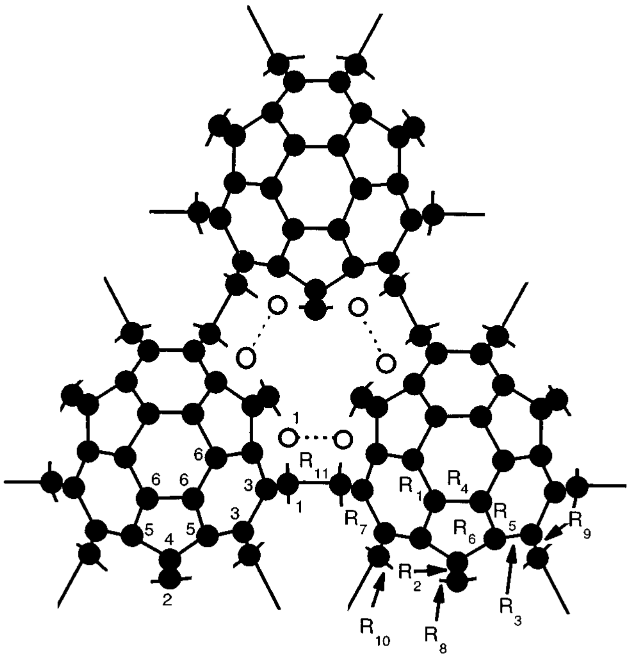

FIG. 3. Schematic representation of rhombohedral (2D) phase for $z>0$, empty circles and dashed lines represent some carbons with $z<0$ participating to the cycloaddition connections.

$R\overline{3}m$ and the six inequivalent coordinates are needed to generate all the other carbons positions. See Fig. 3 for the different positions of the inequivalent carbons labeled from 1 to 6. The same notations as Ref. 4 are used. Our NMR results therefore provide evidence that the carbons 2 and 4 are less numerous and are the closest one to the plane where the bondings are formed. This scenario leads us to think that the carbons close to this plane are more shielded, in agreement with the ratio and the shift of the ^{13}C NMR line positions. The other three carbons labelled 3, 5, and 6 are the numerous ones and are shifted to the low field. We found here an evidence for the distortion of the molecule from the sphericity. The number of inequivalent sp^2 carbons predicted by the structural studies are in good agreement with our NMR results.

IV. CONCLUSION

We have shown here that the [2+2] cycloaddition reactions predicted in polymerized C_{60} is clearly verified by our ^{13}C MAS NMR measurements on the rhombohedral (2D) polymer. The static spectrum indicates the freezing in of the C_{60} molecules. MAS NMR measurements reveal very long spin-lattice relaxation time of carbons and the observed resonance positions and relative intensities are in good agreement with the expected behavior of sp^2 and sp^3 carbons in the polymer. Finally, the splitting of the line at 146 ppm in five components around the position of pristine C_{60} indicates the deformation of the C_{60} molecule spherical shape leading to the observed inequivalent carbons sites. Further magnetic shielding calculations taking into account the nonsphericity of the C_{60} molecule in order to get a better understanding of the observed five components are under progress.

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