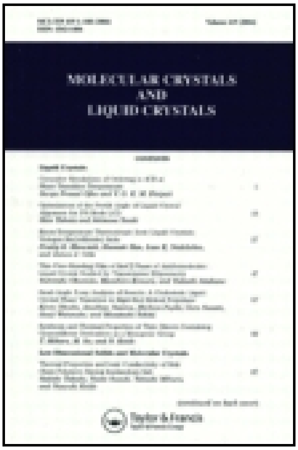

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^{13}C NMR Investigations of Fullerene Black

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^{13}C NMR INVESTIGATIONS OF FULLERENE BLACK

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Abstract Solid-state ^{13}C NMR measurements on differently treated fullerene black samples are reported. The results show that no significant amounts of C_{60} molecules are entrapped in fullerene black in a way that they are not accessible for conventionally used toluene extraction. The broad distribution of chemical shifts in the ^{13}C MAS NMR spectra confirms the large abundance of bent carbon structures in this amorphous carbon material.

INTRODUCTION

The synthesis of fullerenes according to the Krätschmer method[1] provides about 10% yield under conditions of optimized C_{60} output. These fullerenes are embedded in a matrix of an insoluble amorphous carbon material called fullerene black.[2,3] Several structural, electronic, and chemical investigations[2-7] show that fullerene black is really a new kind of amorphous carbon material consisting of globular and irregularly shaped carbon structures as well as stacks of bent and planar carbon sheets in a large variation of size and bending radius.

There is only restricted information[7,8] available about the incorporation of the C_{60} molecules in the fullerene black matrix and the amount of entrapped fullerenes which is not removable by solvent extraction. Since the knowledge of this detail is important in developing production and extraction schemes with higher C_{60} yield we performed solid-state ^{13}C NMR investigations on differently treated fullerene black samples.

EXPERIMENTAL

Fullerene black raw material was produced after the Krätschmer method[1] in a home-made dc electric arc apparatus under conditions of optimized C_{60} output of about 10% using 110 mbar helium pressure.[2,3] To save measuring time we prepared ca. 5% ^{13}C enriched fullerene black raw material taking graphite rods packed with highly ^{13}C enriched amorphous carbon as described in reference 10. The reaction product was mechanically removed from the reactor in a glove box under argon atmosphere and treated as explained below.

All ^{13}C NMR measurements were carried out at room temperature in a 7.05 T field (75.47 MHz resonance frequency) on BRUKER CXP 300 spectrometer equipped with a magic angle spinning (MAS) probe. MAS spectra are recorded at 5 kHz spinning frequency. Chemical shifts are given with respect to TMS.

RESULTS AND DISCUSSION

In Figure 1 we present the spectra of fullerene black raw material without any further treatment. These spectra were recorded with 60 scans and a repetition time of 600 s.

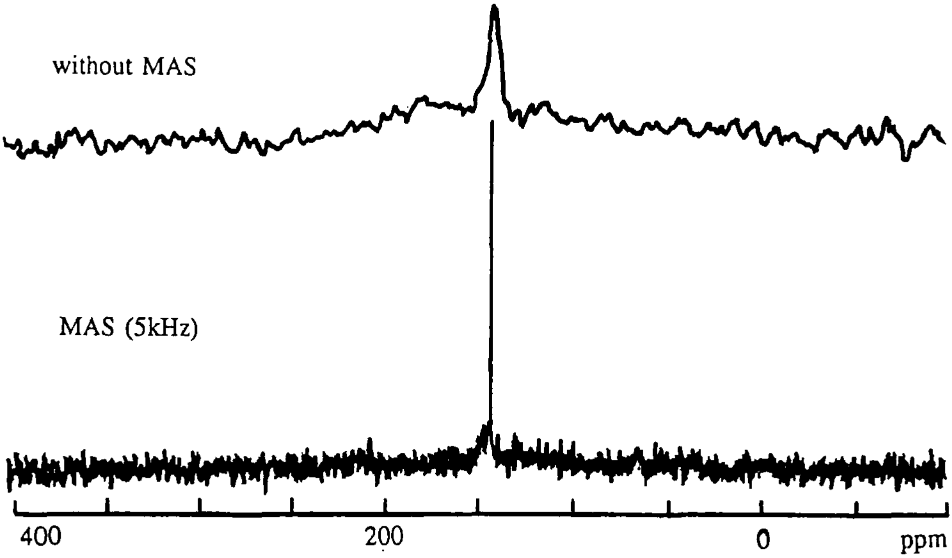

FIGURE 1 ^{13}C NMR spectra of fullerene black raw material.

The spectrum measured without sample spinning shows a rather narrow line at 143ppm and a broad signal with relativly low intensity. Measurements on C_{60} crystallites[11-13] proof that the narrow line has to be assigned to highly mobile C_{60} molecules, which are relaxed by the anisotropy of the chemical shift. The broad signal therefore has to be attributed to immobile ^{13}C atoms of this material. The immobility of these ^{13}C atoms prevents an effective longitudinal relaxation. So is the relaxation time of this part of the black raw material much longer than our repetition time explaining the weakness of the signal. The attempt to measure a uniform longitudinal relaxation time of the incorporated C_{60} molecules failed. This is not surprising because of the amorphous structure of this black one expects a great variation of environments of the C_{60} fullerenes and subsequently a distribution of relaxation times.

To make fullerene black visible by means of ^{13}C NMR one has to introduce an effective relaxation mechanism by adding paramagnetic centers. Results of oxygen adsorption experiments[2,3] on fullerene black and of intercalation of oxygen in the C_{60} solid[14] suggest to expose our samples to oxygen or, more trivial, to air since oxygen molecules are paramagnetic. Figure 2 shows the corresponding spectra, measured with 4800 scans and 10 s repetition time.

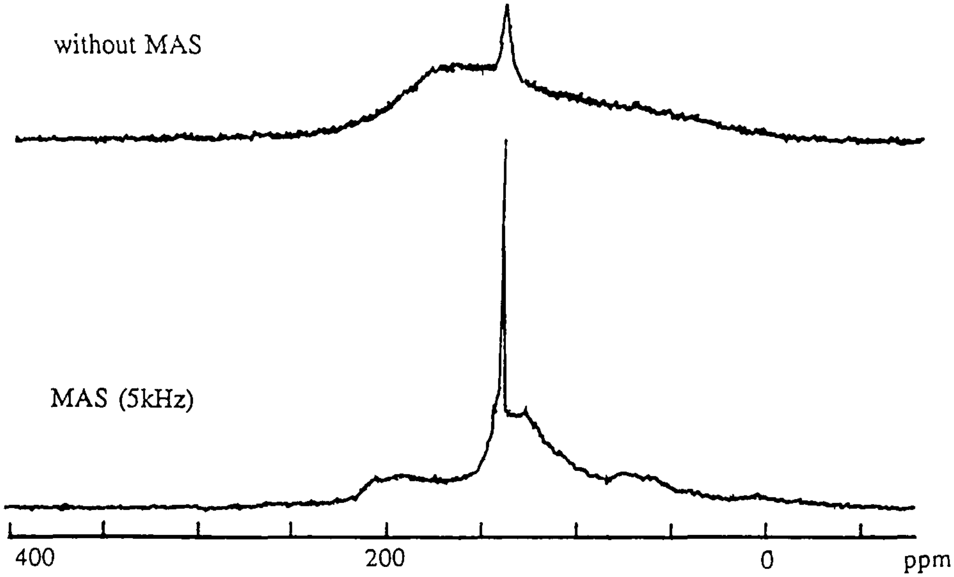

FIGURE 2 ^{13}C NMR spectra of fullerene black raw material exposed to air.

The spectra exhibit a strong signal from the fullerene black. Quantifications of our measurements on different samples give that between 50% and 90% of the ^{13}C spins in this material had been polarized. This large range reflects the limited reproducebility to synthesize structural identical samples which is due to significant sample inhomogeneities[2] and deviations from batch to batch. We did not estimate the possible difference in ^{13}C enrichment for the C_{60} molecules and the fullerene black matrix. Nevertheless the fact that the C_{60} signal was not enhanced and the absence of spinning sidebands for C_{60} in the MAS spectrum in Figure 2 demonstrate that nearly all the C_{60} molecules are highly mobile. This behaviour agrees with ^{13}C NMR results obtained at C_{60} adsorbed on a zeolite.[14]

In a next step we were interested in the amount of entrapped fullerenes as proposed and detected by several authors.[7-9] Therefore we separated the fullerenes from the raw material by conventional toluene extraction. The toluene was then carefully removed from the fullerene black by heating under high vacuum. We checked with ^{1}H NMR that the solvent removal was complete. The disappearence of the C_{60} line in the spectrum of Figure 3 is somewhat surprising. If there are entrapped fullerenes they should by definition be not accessible for solvent molecules, so they keep their high mobility as mentioned above. Hence we conclude that no significant amounts of entrapped fullerenes exist in the fullerene black material produced by the Krätschmer method.

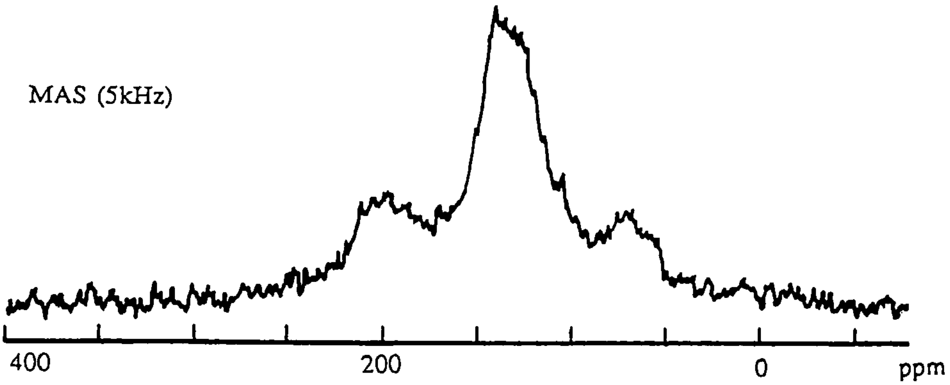

FIGURE 3 ^{13}C NMR spectrum of fullerene black after toluene extraction.

In the ^{13}C MAS NMR spectrum of the fullerene black in Figure 3 we observe in the region between 110 ppm and 160 ppm a line so broad that the spinning sidebands overlap with the central line. This line arises from a distribution of isotropic chemical shifts. If one has the large range of possible isotropic chemical shifts measured for bent fullerene molecules[16] in mind, our work confirms the large abundance of bent carbon structures in this amorphous carbon material.

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