Molecular dynamics of fullerene-nanowhiskers studied by solid state NMR

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Abstract. The properties of molecular motion of as-grown C60 nanowhiskers and C70 nanowhiskers were investigated by 13C-CP/MAS NMR, wideline 13C-NMR and 1H-NMR techniques. It was confirmed that m-xylene molecules are contained in both C60 and C70 nanowhiskers. It was found that C60 nanowhiskers exhibit an orientational order phase transition at 250 K. The activation energy of C60 molecules below 250 K was evaluated to be 14.7 kJ/mol, which is smaller than that of pristine C60 solid. For C70 nanowhiskers, no clear phase transition was found from 270 K to 170 K. The activation energy of C70 molecules was evaluated to be 13.7 kJ/mol between 270 K and 170 K, which is smaller than that of pristine C70 solid.

1. Introduction

Recently, new types of needle-like fullerene crystals called fullerene nanowhiskers were reported to be easily grown by the liquid-liquid interfacial precipitation method [1-9]. The typical C60 nanowhiskers are less than 0.5 µm in diameter and more than 100 µm in length. The preliminary results of C60 nanowhiskers by using a transmission electron microscope showed that the intermolecular distance along the growth axis is shorten by about 4%, compared with that of intrinsic bulk C60 crystals. For the crystal structure of C60 nanowhiskers, polymerized via the “2+2” cycloaddition model was proposed[2]. However, it is well known that C60 molecules in solids are chemically polymerized under irradiation with laser light or electron beam, or at high temperatures and pressures[10-14]. Tachibana et al reported that C60 molecules in the pristine nanowhiskers are bonded by van der Waals forces from Raman scattering measurements[4]. Minato et al reported the solvated structure of C60 nanowhiskers with hexagonal system[9]. For the crystal structure of C70 nanowhiskers, tetragonal structure was proposed[3,6]. However, the detailed structure and properties of molecular motion of both C60 nanowhiskers and C70 nanowhiskers are not fully understood yet. In this study, we report the properties of molecular motions of both C60 nanowhiskers and C70 nanowhiskers by means of solid-state 13C-CP/MAS NMR, wideline 13C- and 1H-NMR measurements.

2. Experimental
C$_{60}$ and C$_{70}$ nanowhiskers used in this study were grown by a liquid-liquid interfacial precipitation method as previously reported [2-4]. The saturated solution of C$_{60}$ or C$_{70}$ and m-xylene was prepared and poured into a glass bottle. Then isopropyl alcohol was added into the bottle to form a liquid-liquid interface. The bottle was capped and kept in the refrigerator for 10 days under the illumination of the fluorescent light. The grown samples sank to the bottom of the bottle. The solvent of the as grown sample was dried by using a paper filter, and the sample was put in a glass tube or rotor for NMR measurements and sealed immediately.

Solid-state $^{13}$C-CP/MAS NMR spectrum was measured in a 7.05 T magnetic field using a AVANCE300WB spectrometer (Bruker) with zirconia rotors (4 mm in diameter) spun in dried air at 9 kHz. Wide-line $^{13}$C- and $^1$H-NMR spectra and their spin-lattice relaxation times ($T_1$) by the saturation recovery technique were measured in a 9.4 T magnetic field using a DSX400WB spectrometer (Bruker).

3. Results and Discussion

3.1. C$_{60}$ nanowhiskers

Figure 1 shows the solid-state $^{13}$C-CP/MAS NMR spectrum of as grown C$_{60}$ nanowhiskers at 297 K. The peak at 143.8 ppm can be assigned to be the carbon on C$_{60}$. Peaks at 135.9, 131.2, 129.8, 126.6 and 23.4 ppm can be assigned to be the carbon on m-xylene. This fact clearly shows that m-xylene are contained in the C$_{60}$ nanowhiskers. No peaks around 30 ppm, which are characteristic to the sp$^3$-like carbon [14-16], are observed. This fact suggests that there is no polymerized C$_{60}$-C$_{60}$ intermolecular bonds in the C$_{60}$ nanowhiskers as previously reported[2].

![Figure 1. Solid-state $^{13}$C-CP/MAS NMR spectrum of C$_{60}$ nanowhiskers.](image)

![Figure 2. Wideline $^{13}$C-NMR spectra of C$_{60}$ nanowhiskers as a function of temperature.](image)

Figure 2 shows wide-line $^{13}$C-NMR spectra of C$_{60}$ nanowhiskers as a function of temperature. A sharp line observed near room temperature broadens slightly and exhibits asymmetry below 250 K. It is thought that this phenomenon is associated with the orientational order transition confirmed in the pristine C$_{60}$ solid[17,18]. That is, the nature of the rotation of the C$_{60}$ molecules in C$_{60}$ nanowhiskers change from rapid isotropic reorientation to uniaxial jump reorientation at 250K. Below 120 K, the line gradually broadens and develops the structure characteristic of a chemical shift anisotropy powder pattern. The $^{13}$C-NMR magnetization recovery data of C$_{60}$ nanowhiskers could be fitted to a single exponential function above 250 K, on the other hand, to a biexponential function below 250 K as follows,

$$1 - M(t)/M(\infty) = F^5 \exp(-t/T_1^5) + F^4 \exp(-t/T_1^4)$$

(1)
with $F^S$, $T_{1S}$, $F^L$, and $T_{1L}$ being the fitting parameters. Here, $M(t)$ is the magnetization at time $t$ after saturation, $F^S (F^L)$ is the fraction of the shorter(longer) component of $T_{1S} (T_{1L})$. In the case of C$_{60}$ nanowhiskers, the dominant spin-lattice relaxation mechanism is considered to be provided by the chemical shift anisotropy (CSA), i.e., the fact that magnitude and direction of the magnetic field at a $^{13}$C nucleus depend slightly on the orientation of the molecule as a result of anisotropic magnetic shielding by the electrons of that molecule [19]. Another possible spin-lattice relaxation mechanism is considered to be dipole interaction with $^1$H nuclei of m-xylene molecules. We attribute the biexponential behavior below 250 K to the inhomogeneity of the dipole interaction with $^1$H nuclei. Although the detailed information about the crystal structure is necessary to identify the relaxation mechanism, it is plausible that uniaxial jump reorientation below 250 K causes the inhomogeneity of the dipole interaction with $^1$H nuclei at carbon sites on C$_{60}$ molecule. Assuming this model, $T_{1L}$ is associated with the CSA. The temperature dependence of $T_1$ (above 250 K), $T_{1S}$ and $T_{1L}$ (below 250 K) are shown in Figure 3.

From the temperature dependence of $T_{1L}$, activation energy of C$_{60}$ molecules below 250 K was evaluated to be 14.7 kJ/mol based on the CSA relaxation mechanism, which is smaller than that of pristine C$_{60}$ solid reported to be 24.1 kJ/mol at simple cubic phase below 260 K [18]. This fact suggests that interaction between C$_{60}$ molecules in C$_{60}$ nanowhisker is smaller than that in pristine C$_{60}$ solid due to m-xylene molecules in C$_{60}$ nanowhisker crystal.

Figure 4(a) shows wideline $^1$H-NMR spectra of C$_{60}$ nanowhiskers as a function of temperature. Two peaks observed at 6.5 and 1.5 ppm at 293 K are attributed to the aromatic and methyl group proton in m-xylene molecule, respectively. As the temperature decreases, the line gradually broadens and slightly develops the triplet structure characteristic of a three spin system such as methyl proton.

**Figure 3.** Temperature dependence of the $^{13}$C - $T_1$ in C$_{60}$ nanowhiskers ($\bigcirc$: $T_{1L}$, $\blacksquare$: $T_{1S}$).

**Figure 4.** Temperature dependences of (a) $^1$H-NMR spectrum and (b) the $^1$H-$T_1$ in C$_{60}$ nanowhiskers.
The temperature dependence of $^1$H-$T_1$ is shown in Figure 4(b). $T_1$ exhibits a minimum at 155 K of 0.9 sec. Assuming that the spin-lattice relaxation mechanism responsible for this minimum is caused by the modulation of dipole interaction caused by the methyl group reorientation around $C_3$ axis, then the activation energy for such motion was evaluated to be 7.0 kJ/mol from the expression of Bloembergen, Purcell, and Pound[20] as corrected by Kubo and Tomita[21]. This is an appropriate value as the thermal activated reorientation of methyl group around $C_3$ axis[22].

3.2. C$_{70}$ nanowhiskers

![Figure 5. Solid-state $^{13}$C-CP/MAS NMR spectrum of C$_{70}$ nanowhiskers.](image)

Figure 5 shows the solid-state $^{13}$C-CP/MAS NMR spectrum of C$_{70}$ nanowhiskers at 298 K. Peaks at 151.0, 148.6, 148.0, 146.1 and 131.6ppm can be assigned to the carbon on C$_{70}$. Peaks at 136.3, 129.2, 128.1 and 23.4ppm are attributed to the carbon of the m-xylene. This fact clearly shows that m-xylene are contained in C$_{70}$ nanowhiskers. No peaks around 30 ppm, which are characteristic to the sp$^3$-like carbon are also observed. This fact suggests that there is no polymerized C$_{70}$-C$_{70}$ intermolecular bond in the C$_{70}$ nanowhiskers.

Figure 6(a) shows the temperature dependence of wideline $^{13}$C-NMR spectra of C$_{70}$ nanowhiskers from 270K to 170K. No remarkable changes are observed in the lineshape. This behavior is quite different for the case of pristine C$_{70}$ solid[23]. It is suggested that C$_{70}$ nanowhiskers reveal no clear phase transition from 270 K to 170 K.

![Figure 6. Temperature dependence of (a) $^{13}$C-NMR spectrum and (b) $^{13}$C-$T_1$ in C$_{70}$ nanowhiskers.](image)
The temperature dependence of $^{13}$C-$T_1$ is shown in Figure 6(b). The activation energy of C$_{70}$ molecular rotation between 270 K and 170 K was evaluated to be 13.7 kJ/mol based on the CSA relaxation mechanism, which is smaller than that of pristine C$_{70}$ solid reported to be 22.0 kJ/mol below 280 K [23]. This fact suggests that intermolecular interaction between C$_{70}$ molecules in C$_{70}$ nanowhisker is smaller than that of pristine C$_{70}$ solid.

![Figure 6(b)](image)

**Figure 6.** Temperature dependence of $^{13}$C-$T_1$.

**Figure 7.** Temperature dependences of (a) $^1$H-NMR spectrum and (b) the $^1$H-$T_1$ in C$_{70}$ nanowhiskers.

Figure 7(a) shows wide-line $^1$H-NMR spectra of C$_{70}$ nanowhiskers as a function of temperature. At 293 K, two peaks observed at 6.4 and 1.6 ppm at 283 K are attributed to the aromatic and methyl group proton in m-xylene molecule, respectively. As the temperature decreases, the line gradually broadens and slightly develops the triplet structure characteristic of a three spin system such as methyl proton. The temperature dependence of $^1$H-$T_1$ is shown in Figure 7(b). Assuming that the spin-lattice relaxation mechanism is caused by the modulation of dipole interaction caused by the methyl group reorientation around C$_3$ axis, then the activation energy for such motion was evaluated to be 6.7 kJ/mol from the expression of Bloembergen, Purcell, and Pound as corrected by Kubo and Tomita.

### 4. Conclusion

The properties of molecular motions of both C$_{60}$ nanowhiskers and C$_{70}$ nanowhiskers were investigated by means of solid-state NMR techniques. For C$_{60}$ nanowhiskers, orientational order transition at 250 K was confirmed. The activation energy of C$_{60}$ molecules below 250 K was evaluated to be 14.7 kJ/mol, which is smaller than that of pristine C$_{60}$ solid. For C$_{70}$ nanowhiskers, no clear phase transition was found from 270 K to 170 K. The activation energy of C$_{70}$ molecules was evaluated to be 13.7 kJ/mol between 270 K and 170 K, which is smaller than that of pristine C$_{70}$ solid. Inter-molecular interaction between fullerene molecules in nanowhisker is considered to be smaller than that of pristine fullerene solid due to the solvated m-xylene molecules.

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