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Interactions between fullerene(C_{60}) and poly(ethylene oxide) in their complexes as revealed by high-resolution solid-state ^{13}C NMR spectroscopy

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Abstract

A series of poly(ethylene oxide) (PEO)/fullerene(C_{60}) complexes are prepared by lyophilization. The intermolecular interaction and molecular motion in the complex are investigated by solid-state ^{13}C NMR spectroscopy. An intense C_{60} signal due to the intermolecular cross-polarization is observed in the ^{13}C CP/MAS spectra of the complex samples, indicating a high degree of dispersion of C_{60}s in the complexes. By measuring the ^{13}C spin-lattice relaxation times and ^{1}H transverse relaxation times of the complex sample and by comparing the static ^{13}C spectrum of the pure C_{60} sample with that of the complex sample, it is demonstrated that there exist n–π interactions between the n-orbitals of the PEO ether oxygen and the π-system of C_{60}. The C_{60} molecules act as physical cross-links in the amorphous region of PEO, which greatly inhibit the mobility of the surrounding PEO chains, while the rapid isotropic rotation of C_{60} molecules is also reduced to some extent due to the interactions with the polymer chains.

Keywords: C_{60}/Poly(ethylene oxide) composite; Intermolecular interaction; Solid-state ^{13}C NMR

1. Introduction

The interactions between polymers and nanoscopic particles can lead to highly organized hybrid materials. The morphology of such composites depends not only on the characteristics of the polymers, but also on the features of the nanoparticle [1]. Recently, there are a number of reports dealing with the fullerene (C_{60})-containing polymer [2]. These C_{60}-based polymer materials are designed to combine the interesting electronic and optical properties of C_{60} with the attractive mechanical properties and processing advantages of the polymer.

C_{60} is sphere-shaped molecule with a diameter of 7 Å and is known to be an excellent electron-acceptor ($E_A = 2.6–2.8$ eV) capable of accepting as many as six electrons [3,4]. It can form donor–acceptor complexes with a variety of electron donors. Wang [5] first reported the enhanced photoconductivity exhibited in fullerene-doped poly(*N*-vinylcarbazole) (PVK) film, a blend of C_{60} and electron–donor polymer. They indicated that the weakly bonded charge-transfer complexes formed between the C_{60} molecules and the carbazole groups of PVK. The binding constant of the charge-transfer complex was determined by the absorption spectrum [6]. After that, a series of polymer/C_{60} complexes were produced [7–9], in which the interaction between the two components is known to form acceptor-like centers on the C_{60} molecules. Recently, NMR and light-scattering measurements revealed that the donor–acceptor bonds between the carbonyl groups of poly(*N*-vinyl-2-pyrrolidone) (PVP) and C_{60} molecules lead to the formation of the complex of PVP with C_{60} fullerene in solution state [10].

Poly(ethylene oxide) (PEO) is a relatively nonpolar linear polymer containing ether oxygens which are good electron-donors in forming hydrogen bonds and coordinatings with other electron acceptors. In recent years, there have been many reports on the molecular complexes of PEO with *p*-dihalogenbenzenes, which are stabilized by weak van der Waals interactions between host and guest

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molecules [11,12]. Edman et al. suggested in their work that C_{60} acts as inert filler in the PEO/$LiCF_3SO_3$ composites by using the Raman spectroscopy. At the same time, they also mentioned the alternative possibility that some coordination interactions may exist between the PEO matrix and C_{60} molecules, which is obviously worth of further study [13].

High-resolution solid-state NMR spectroscopy has been applied extensively to investigate chain dynamics and interactions in polymer blends and composites [14]. The efficiency of cross-polarization (CP), in ^{13}C CP/MAS NMR experiments, depends on the strength of the dipolar interaction between proton spins and ^{13}C spins, which is in turn determined by the distances between these spins and modulated by the molecular motion. Therefore, measuring the efficiency of CP happened between the abundant nuclear spins in the host molecules and the dilute ones in the guest molecules can provide directly the information concerning the intermolecular distance and molecular motion. The relaxation parameters are also widely used to characterize the molecular dynamics of composite molecules in the polymer/inorganic compound complexes.

In the present work, a series of PEO/C_{60} complex samples with different compositions are investigated by ^{13}C CP/MAS NMR spectroscopy. Intermolecular CP, ^{13}C T_1 and ^1H T_2 measurements are carried out to study whether there exists intermolecular coordination interaction between the ether oxygen of PEO and the π-system of C_{60}.

2. Experimental

2.1. Sample preparation

PEO with a molecular weight of 5×10^6 was kindly provided by Shanghai Jiaotong University, China. C_{60} (99.9% pure) was purchased from Wuhan University, China. To enhance the degree of dispersion of C_{60} in the polymer matrix, three C_{60}/PEO complex samples were prepared by lyophilization according to the following procedures. C_{60} and PEO were dissolved separately in benzene under nitrogen atmosphere. Then the solutions were mixed together according to the O/C molar ratio of PEO to C_{60} as 1:1, 5:1 and 25:1, respectively. The mixed solutions were frozen rapidly under liquid nitrogen, freeze-dried at 223 K and then placed in vacuum chamber at room temperature to remove residual solvent for 48 h until no apparent weight loss. The obtained samples were named as [1:1], [5:1] and [25:1], according to their O/C molar ratio of PEO to C_{60}, respectively. A physical mixture of PEO and C_{60} was prepared for the control experiment by simply mixing the two kinds of powder together. The O/C molar ratio of PEO to C_{60} of the sample is 1:1.

2.2. NMR Measurements

The ^{13}C NMR experiments were carried out at room temperature on a Bruker DSX 300 spectrometer operating at a frequency of 75.47 MHz for ^{13}C. The ^{13}C chemical shifts were determined from the lower field signal (176.03 ppm) of glycine relative to tetramethylsilane (TMS). The solid-state high-resolution ^{13}C NMR spectra were obtained by the combined use of CP, high-power proton decoupling (DD) and magic angle spinning (MAS). The MAS rate was 5 KHz for all measurements. The contact time of CP was, unless noted, 1 ms in all CP experiments. The recycle delay was 5 s. The accumulation number was 2000–5000, depending on the signal to noise ratio. For each spectrum acquired, 48 times of dummy scan was employed to eliminate the inherent ^{13}C signal of C_{60}, which we found, cannot be completely removed by the phase cycling of the pulses.[1]

The ^{13}C T_1 relaxation time of the pure C_{60} sample was measured by the inverse-recovery method combined with MAS technique. Fig. 1(a) shows the Torchia [15] pulse sequence for measuring ^{13}C T_1 relaxation times of PEO/C_{60} complexes. ^1H T_2 relaxation times were indirectly measured through ^{13}C resonance by the pulse sequence shown in Fig. 1(b).

3. Results and discussion

The ^{13}C CP/MAS spectra of freeze-dried PEO/C_{60} complexes [25:1], [5:1] and [1:1] at room temperature are shown in Fig. 2(a)–(c), respectively. The signal at about 70.6 ppm is due to the CH_2 group of PEO [16], while the sharp signal at 143 ppm can be unambiguously attributed to C_{60} [17,18]. Since the C_{60} molecules have no directly bonded protons, the C_{60} signal in the spectra must arise from the intermolecular CP happened between the ^{13}Cs of C_{60} and the protons of neighboring PEOs. For $^1H-^{13}C$ CP experiments, the efficiency of polarization transfer depends on the strength of static dipolar interaction between ^1H and ^{13}C spins, which is determined by the $^1H-^{13}C$ internuclear distance. Effective intermolecular CP transfer can occur only when the $^1H-^{13}C$ distances is less than 5 Å [19]. Actually, the intermolecular CP technique has been used successfully to characterize the miscibility of polymer blends [19–21]. It is, therefore, evident that the appearance of C_{60} signal with marked intensity in these ^{13}C CP/MAS spectra of PEO/C_{60} complexes demonstrates that a large part of the C_{60} molecules can find PEO chains in a few

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[1] We found that if one employs a single pulse to excite the ^{13}C signal of pure C_{60} sample under MAS condition, marked signal of C_{60} can still be observed in the spectrum, even when the pulse width is as long as 5 ms. Therefore it is reasonable to say that in ^{13}C CP/MAS experiment, the CP pulse on ^{13}C channel can excite certain amount of ^{13}C inherent magnetization, which cannot be removed completely by phase cycling of the pulse sequence, due to the fact that a recycle delay of 5 s is not sufficient to fully relax the ^{13}C magnetization of C_{60} with a T_1 of several tens of seconds. This part of signal, which is not transferred from ^1H magnetization reservoir and has certain contribution to signal of C_{60} in the obtained CP/MAS spectrum, can be removed by 48 times of dummy scan.

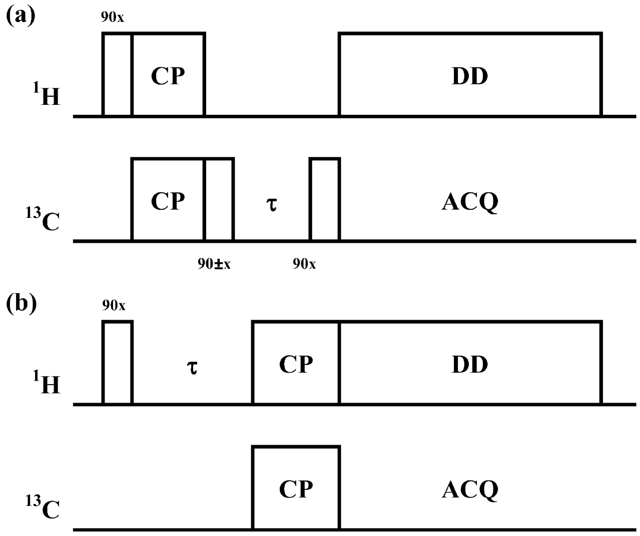

Fig. 1. Pulse sequences employed in this work: (a) Torchia's pulse sequence; (b) pulse sequence for ^{1}H T_2 measurement with CP.

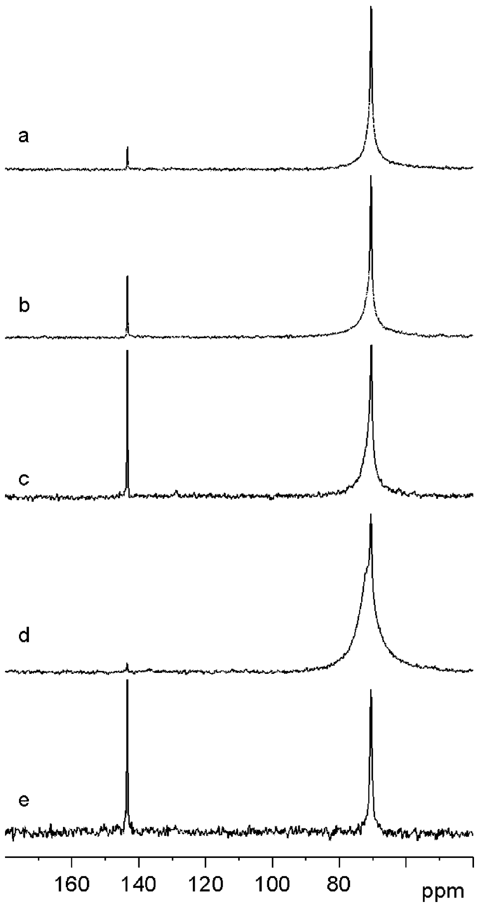

Fig. 2. The ^{13}C CP/MAS spectra of freeze-dried samples [25:1] (a), [5:1] (b), [1:1] (c), [1:1] (e) and the physical mixture sample [1:1] (d). For spectra a–d, the contact time of CP was set to be 1 ms, while for spectrum e, the contact time was set to be 5 ms.

angstroms. In other words, C_{60} molecules are well dispersed in the matrix of PEO. The driving force for such a good dispersion of C_{60} molecules in the matrix, we believe, should be the weak n–π donor–acceptor interactions between the n-orbital of the PEO ether oxygen and the π-system of C_{60} [22,23]. As is shown in Fig. 2(a)–(c), the relative signal intensity of C_{60} increases with increasing the molar content of C_{60} in the complexes. This result indicates that there should be no heavy aggregation of C_{60}s even in the sample of [1:1]. On the other hand, as is shown in Fig. 2(d), only a very weak C_{60} signal can be observed in the ^{13}C CP/MAS spectrum of the physical mixture of PEO/C_{60} [1:1]. This fact demonstrates further that the marked C_{60} signal appeared in the ^{13}C CP/MAS spectra of the freeze-dried PEO/C_{60} [1:1] sample is associated with the high degree of dispersion of C_{60}s in PEO matrix.

As is shown in Fig. 2(a)–(c), the ^{13}C signal of PEO consists of two components, a broad component and a narrow one, corresponding to the crystalline phase and the amorphous phase of PEO, respectively [16]. The amorphous phase of PEO is known to have much longer ^{1}H $T_{1\rho}$ than the crystalline phase. Fig. 2(e) shows the ^{13}C CP/MAS spectrum of sample [1:1] with the contact time of 5 ms. Comparing Fig. 2(c) with (e), we can find that after a contact time of 5 ms, the broad component disappeared nearly completely from the spectrum, due to the $T_{1\rho}$ relaxation of the ^{1}H magnetization of the crystalline region. Only the narrow component corresponding to the amorphous region of PEO signal is left in the spectrum. What is worth to note is the signal intensity of C_{60} has rarely influenced by the long contact time. This means the strong ^{13}C signal of C_{60} is transferred from the ^{1}H magnetization of the amorphous phase of PEO. In other words, this result indicates that the C_{60} molecules in these samples are dispersed in the amorphous domain of PEO.

Fullerene C_{60} is known to undergo isotropic rotation at rates $>10^9$ s^{-1} in the solid state at ambient temperature [17]. The strong C_{60} signal in Fig. 2, which arises from the intermolecular CP, indicates that there exists appreciable dipolar interaction between the ^{1}H nucleus of PEO chains and the ^{13}C nucleus of C_{60}. Such a phenomenon is comparable to the CP behavior of adamantane [24]. Adamantane, which is usually used as a standard sample for Hartman-Hahn condition adjustment in CP experiment, is known to undergo rapid molecular rotation at ambient temperatures. The rapid molecular rotation averages out the intramolecular dipolar interactions. The effective CP for adamantane is believed, therefore, to proceed entirely through the average intermolecular dipolar interactions.

It is of interests to check whether the rapid isotropic rotation of C_{60} is inhibited in the complexes. Fig. 3(a) and (b) shows the single pulse static ^{13}C spectra of pure C_{60} sample and PEO/C_{60} complex [1:1] sample ranged from 120 to 170 ppm. The spectrum of the complex sample is acquired with high-power dipolar decoupling to remove the intermolecular dipolar interaction. The C_{60} signals in

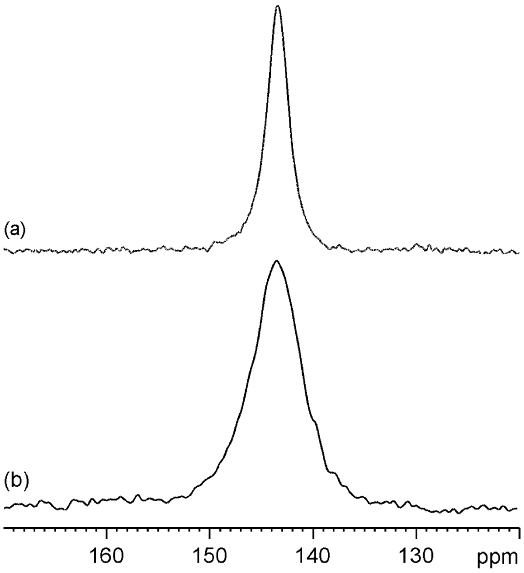

Fig. 3. The ^{13}C static spectra of (a): pure C_{60} sample without ^{1}H dipolar decoupling; and (b): PEO/C_{60} [1:1] complex sample with ^{1}H dipolar decoupling.

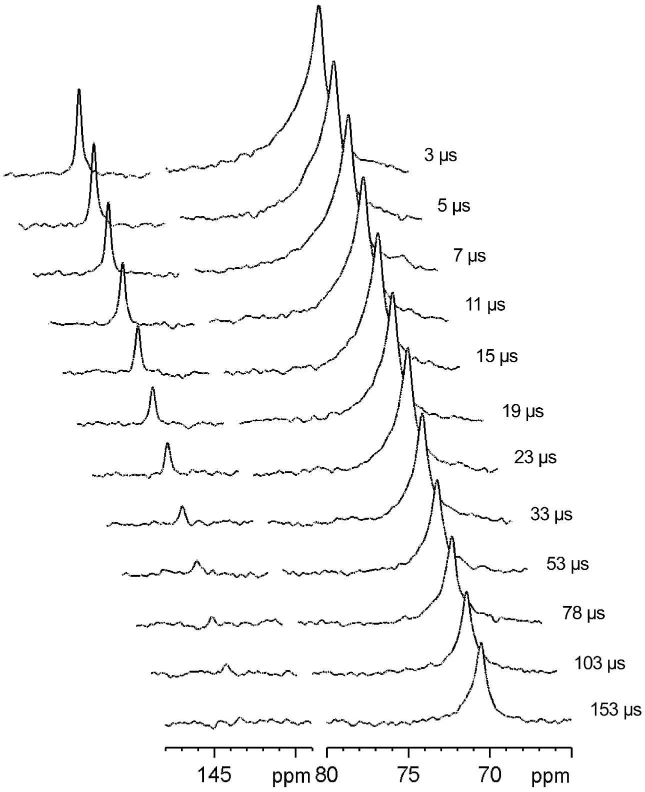

Fig. 4. The stack spectra of PEO/C_{60} [1:1] complex sample acquired with pulse sequence shown in Fig. 1(b).

both static spectra are sharp and nearly symmetric, indicating that the chemical shift anisotropy of the C_{60} molecules has been averaged away, which in turn, suggesting that there exists rapid isotropic rotation of the C_{60} molecule in both samples. It is interesting to find that the half-width of the C_{60} signal of the complex sample is about 430 Hz, which is about twice as large as that of the pure C_{60} sample, say 220 Hz. Such a result demonstrates that the rapid isotropic rotation of C_{60} has been inhibited to some extent. This is apparently a positive evidence for the existence of n–p donor–acceptor interactions between PEO and C_{60}.

To study the molecular motion of C_{60} and PEO in the complexes, we measured the ^{13}C T_1 of pure C_{60} solid by using the inverse-recovery method combined with MAS technique and the ^{13}C T_1s of PEO/C_{60} complexes by Torchia's [15] pulse sequence shown in Fig. 1(a). The values of ^{13}C T_1 of C_{60} are summarized in Table 1. The pure C_{60} solid at room temperature exhibits a single ^{13}C T_1 value of 36.6 s, while the ^{13}C T_1 of C_{60} decreases to 21.8 s in the PEO/C_{60} complex. Because at room-temperature, C_{60} is at the fast motion side of the T_1 minimum, we believe that the marked decrease of ^{13}C T_1 of C_{60} in the complexes compared with that of pure C_{60} sample is a direct support to the conclusion that the isotropic rotation of C_{60} is inhibited in the complex, due to the interaction between C_{60}s and PEO chains. It is noteworthy here that because the Torchia's pulse sequence is based on CP, the ^{13}C T_1 measured with Torchia's is corresponding to C_{60}s that are well dispersed in PEO. The C_{60}s embedded inside the clusters of C_{60}, if there exist, should have no contribution to the value of ^{13}C T_1 we measured.

By using the pulse sequence shown in Fig. 1(b), we measured the ^{1}H transverse relaxation times T_2 of PEO/C_{60} Complex [1:1] at room temperature by monitoring the delay time (τ) dependent ^{13}C signals. Fig. 4 shows the stack spectra obtained from the measurement. The integrals of the C_{60} and PEO signals are plotted as a function of the delay time τ in Figs. 5 and 6, respectively. By carrying out curve fitting on both curves, the ^{1}H T_2s corresponding to individual components can be obtained. The solid lines in the figures represent the results of curve fitting. The decay behavior of C_{60} signal is found to be exponential, while that of the PEO signal is biexponential. The obtained T_2 values of different components are also shown in Table 1. For PEO, as is also revealed by Fig. 4, the fast decay component with

Table 1
Summary of ^{13}C T_1 and ^{1}H T_2 measured in the present work

	Pure C_{60} solid	C_{60} in sample [1:1]	PEO in sample [1:1] (broad component)	PEO in sample [1:1] (narrow component)
^{13}C T_1 (s)	36.6	21.8	–	–
^{1}H T_2 (μs)	–	15	18	617

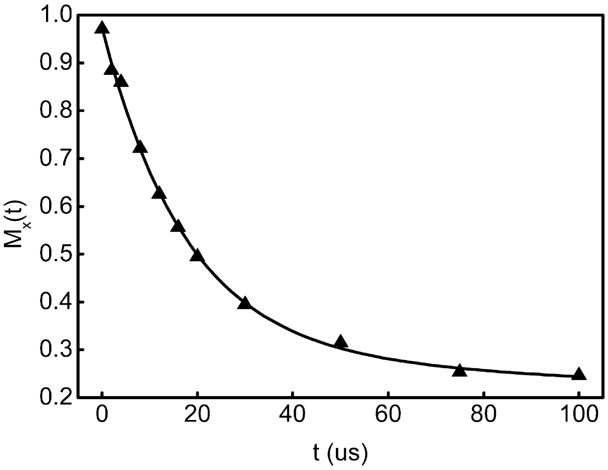

Fig. 5. The variation of the integral of the PEO signal as a function of the delay time τ for PEO/C_{60} [1:1] complex sample.

shorter T_2 is corresponding mostly to the broad part of the signal, i.e. the crystalline signal. On the other hand, the slow decay component with longer ^1H T_2, is due to the narrow part of the signal, i.e. the amorphous signal. The mobility difference between the crystalline and amorphous regions of PEO is extremely large as indicated by their difference in ^1H T_2 values. As discussed above, the ^{13}C magnetization of C_{60} generates from the ^1H magnetization of surrounding PEO by CP. The decay curve of the ^{13}C signal of C_{60} actually reflects the ^1H transverse decay behavior of the PEO chains surrounding C_{60}. In other words, by monitoring the ^{13}C signal of C_{60}, it is possible to selectively study the mobility of PEO chains that surrounds C_{60}s. As is shown in Table 1, the ^1H T_2 associated with the C_{60} signal is as short as 15 μs, indicating that the PEO chains surrounding C_{60} is as rigid as the PEO chains within the crystalline region. With this result, it is easy to visualize that due to the interactions between π-system of C_{60} and the ether oxygen of PEO, some of the PEO chains are fastened around the C_{60} spherical molecules. In this case, the behavior of C_{60} is close to the physical cross-links within the amorphous PEO matrix. It is also worth to note that the fast decay component of the ^1H T_2 decay curve should contain not only the contribution from the crystalline region, but also the contribution from the rigid amorphous PEO chains fastened by C_{60}s.

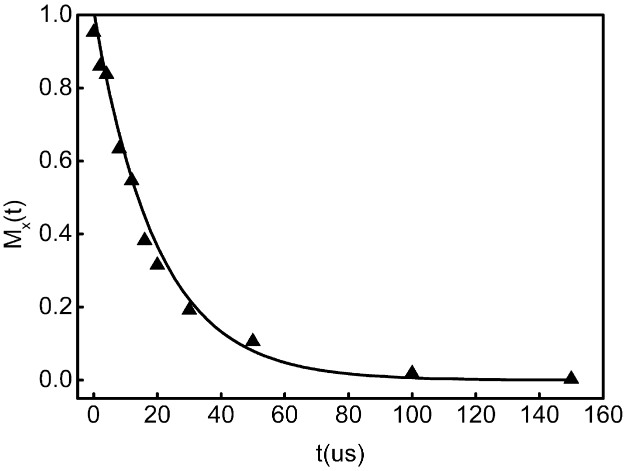

Fig. 6. The variation of the integral of the C_{60} signal as a function of the delay time τ for PEO/C_{60} [1:1] complex sample.

4. Conclusions

A series of PEO/C_{60} complexes are prepared by lyophilization at 223 K. The presented results from solid-state NMR experiments indicate that there exist interactions between the ether oxygen of PEO and the π-system of C_{60} in the PEO/C_{60} molecular complex, which leads to a good dispersion of C_{60}s in PEO. The C_{60} molecules act as cross-links in the PEO amorphous matrix and inhibit the mobility of polymer chains. On the other hand, the interactions between the polymers and C_{60}s also reduce the rapid isotropic rotation of C_{60} molecules to some extent. Finally, We prefer to note that the solid-state NMR methods employed in this work are especially suitable for investigating the interactions between C_{60}s and polymers in C_{60} based composites, because both the mobility of the C_{60}s and the polymers that are involved in interactions can be selectively studied.

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