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Synthesis of $Li_xC_{60}(x = 1–28)$ fullerides under high-pressure and high-temperature conditions and their electrical properties

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Abstract

Li_xC_{60} with compositions of $x = 1–28$ were treated under 5 GPa at 573 K for 1 h in order to explore a new Li-doped C_{60} polymer. Three types of Li-doped phases, i.e., trigonal (3R) two-dimensional (2D-) polymer, tetragonal (T) 2D-polymer, and fcc monomer were obtained as single phases for $x = 1, 4, 16$, respectively by the high-pressure (HP) treatment. The C_{60} molecules in the 3R and T 2D-polymers are linked via $[2 + 2]$ cycloaddition at a distance of 9.3 Å. Li_4C_{60} prepared without the HP treatment was a new T 2D-polymer linked by the $[2 + 2]$ cycloaddition. The IR spectra of the Li_4C_{60} and the $Li_{16}C_{60}$ before and after the HP treatment suggested the existence of some degrees of covalency between the Li and C atoms. The electrical conductivity measurements showed that the $(LiC_{60})_{HP}$ 3R 2D-polymer, the $(Li_4C_{60})_{HP}$ T 2D-polymer, and the $(Li_{16}C_{60})_{HP}$ fcc monomer phases were semiconductors with the conductivities of 1.8×10^{-4}, 1.2×10^{-1}, 6.4×10^{-1} Ω^{-1} cm^{-1} at room temperature, respectively. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Solid C_{60} is transformed into polymers via several methods such as by an irradiation of visible light [1], a high-pressure (HP) and high-temperature treatment [2,3], and reactions with alkali metals [4]. Several types of C_{60} polymers having 1D–3D networks of the C_{60} molecules are formed by the HP and high-temperature treatments depending on the treatment conditions [2,3,5–8]. Iwasa et al. [2] reported that the rhombohedral

(3R) 2D-polymer was synthesized by a treatment of C_{60} under a pressure of 5 GPa at 1073 K. Núñez-Regueiro et al. [3] found three types of C_{60} polymers, orthorhombic (Orth) 1D-polymer, tetragonal (T) 2D-polymer, and 3R 2D-polymer, which were synthesized under different pressure and temperature conditions. The last two polymers were synthesized as a mixture in the HP treated sample. Davydov et al. [5] synthesized the single phase of the T 2D-polymer by optimizing the HP treatment condition. These three types of polymers are formed by the polymerization of C_{60} molecules via $[2 + 2]$ cycloaddition in a direction or planes of [1 1 0], (0 0 1), and (1 1 1) of C_{60} fcc lattice, respectively. Each polymer has several different crystal structures depending on the orientations of the polymer chains or polymer layers in the lattice [9,10]. Besides these three types of

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polymers, Marques and Blank et al. [6–8] reported the formation of an fcc 3D-polymer by a treatment of C_{60} under a pressure of 13 GPa at 820 K, which were polymerized via [2 + 4] and [6 + 6] cycloadditions as well as the [2 + 2] one.

Since the C_{60} polymers prepared by the HP and high-temperature treatments are electrical insulators, it is a promising target to modify the electrical properties by doping with alkali metals into the interstices of the C_{60} polymers. However, the C_{60} polymers are easily decomposed into monomers by heating to 573 K [11]. Therefore, the reaction with alkali metals at elevated temperatures cannot be used as an intercalation method for the most C_{60} polymers. Several alkali-metal-doped C_{60} polymers can be synthesized by a direct reaction of C_{60} with alkali metals at elevated temperatures. AC_{60} (A = K, Rb, Cs) Orth 1D-polymers [4,12,13] and Na_4C_{60} monoclinic 2D-polymer [14] were synthesized by such a way. The C_{60} molecules in the former are linked by the [2 + 2] cycloaddition whereas those in the latter are linked by the C–C single bonds. A (A = K, Rb, Cs) and Na atoms are located at the octahedral and the tetrahedral interstices in the corresponding C_{60} lattice, respectively. Both polymers have a reversible phase transition between the low-temperature polymer phase and the high-temperature monomer phase around 400 [15] and 500 K [16], respectively. These polymers are good electrical conductors [12–14] and the AC_{60} (A = Rb, Cs) 1D-polymers have a metal-insulator transition near 50 K [12,13]. Another type of C_{60} polymer was recently reported: the slow cooling of Na_2RbC_{60} to low temperatures [17] and the compression of Li_3CsC_{60} under HP at ambient temperature [18] lead to the transformations to the monoclinic 1D-polymers linked by the C–C single bonds. The corresponding monomers were superconductors with T_c = 3.5 [19] and 10.5 K [20], respectively, although the Na_2RbC_{60} 1D-polymer was not a superconductor.

HP synthesis is a useful way to obtain not only the C_{60} polymers but also the alkali-metal-doped C_{60} polymers. We reported the HP treatments of A_xC_{60} fullerides (A = Li, Na, K, Rb; x = 1, 2, 3) under a pressure of 5 GPa at 573 K [21,22]. It was found that the LiC_{60} and NaC_{60} were transformed into trigonal (3R) 2D-polymers with Li and Na

atoms intercalated between the C_{60} polymer layers, respectively [21], whereas the KC_{60} and RbC_{60} were transformed into Orth 1D-polymer with K and Rb atoms doped between the polymer chains [22]. For the samples with $x \geqslant 2$, however, non-polymerized phases were observed for A_xC_{60} with larger alkali metals in size, such as A = Na, K, Rb [22]. Even after the HP treatments, K_3C_{60} and Rb_3C_{60} were not transformed to polymers. Those remained as alkali-doped monomers with T_c = 19.5 and 30.0 K, respectively [22], these T_c values being in good agreement with those of K_3C_{60} and Rb_3C_{60} reported by Fleming et al. [23]. In contrast, the Li_xC_{60} samples with x = 2, 3 were transformed into polymerized phases, which were the mixtures of the 3R and T 2D-polymers of Li_xC_{60} [21]. It is likely that the interstices formed between polymer layers or chains are filled with different numbers of alkali atoms with different sizes, resulting in different types of alkali-metal-doped polymers. In this study, the HP treatment of Li_xC_{60} with $x \geqslant 4$ was performed to synthesize new Li-doped C_{60} polymers.

2. Experimental

C_{60} powder (Term USA, >99%) was mixed with lithium azide LiN_3 in several different molar ratios (LiN_3/C_{60} = 4, 6, 8, 10, 12, 16, 20, 24, 28) in an Ar-filled grove box. The mixtures were heated at 533 K for less than 1 h in evacuated Pyrex glass tubes until the complete decomposition of the azide into lithium metal. The resulting mixture was mounted into a gold capsule in the grove box, then set into a cubic pyrophyllite cell with a carbon heater and a pressed NaCl powder as a pressure medium [21,22]. The sample was compressed with a cubic anvil press under a pressure of 5 GPa at 573 K for 1 h, and then quenched to room temperature followed by a release of the pressure. The HP treated samples are hereafter referred to $(Li_xC_{60})_{HP}$, where x denotes the nominal composition of Li/C_{60}.

The deintercalation of lithium from Li_4C_{60} and $(Li_{16}C_{60})_{HP}$ were performed by dispersing the powder samples in an I_2 solution in CH_3CN at room temperature for 5 h. The samples were separated by filtration in an Ar-filled grove box.

X-ray powder diffraction (XRD) patterns were measured by using graphite monochromatized CuKα radiation, the samples being held in an Ar-filled polyethylene container. Infrared (IR) spectra were measured on the powder samples dispersed in KBr pellets by a Fourier transform infrared spectrometer (Perkin Elmer model 1650). Electrical conductivity was measured on the compressed sample by a d.c. four-probe method in a temperature range of 200–300 K in vacuum.

3. Results and discussion

It has been well established that the reaction of alkali azide with C_{60} gives us stoichiometric and uniform sample of alkali-metal-doped C_{60} fullerides in a short time. Bensebaa et al. [24] reported the reaction of RbN_3 with C_{60} at 773 K in vacuum and obtained Rb_3C_{60} with $T_c = 34$ K and the superconducting fraction of about 95%, indicating that the sample almost kept the stoichiometry. In this work, we performed the reaction of LiN_3 with C_{60} by heating the mixture at 533 K in a glass tube until the complete decomposition of LiN_3 to Li metal, and subsequently treated under a pressure of 5 GPa at 573 K in a gold capsule. During these treatments, color changes of the glass tube and the gold capsule were not observed. Evidently, the deviation of Li contents from the nominal values should be very small. The XRD patterns of Li_xC_{60} $(1 \leqslant x \leqslant 28)$ before and after the HP treatment are shown in Fig. 1a and b, respectively. The phases found after the HP treatment are summarized in Fig. 2.

3.1. HP treatment of Li_xC_{60} $(1 \leqslant x \leqslant 4)$

The phases obtained by the HP treatment of Li_xC_{60} with $1 \leqslant x \leqslant 3$ were reported in our previous paper [21]. The fcc LiC_{60} was transformed into trigonal (3R) 2D-polymer by the HP treatment. The samples with $x = 2, 3$ were composed of the mixed phases of fcc monomer and T 2D-polymer before the HP treatment, while they were transformed into the mixtures of the 3R and T 2D-polymers after the HP treatment. The relative

amount of the T 2D-polymer increased with increasing Li content from $x = 2$ to 3. In this study, T 2D-polymer was obtained as a single phase for Li_4C_{60} without the HP treatment. The XRD pattern was similar to that of T 2D-polymer of C_{60}, which was synthesized via a HP and high-temperature treatment by Davydov et al. [5], and was indexed with a body centered T (bct) lattice satisfying a systematic reflection condition of $h + k + l = 2n$ with lattice parameters of $a = 9.33(2)$ Å and $c = 14.94(5)$ Å. The XRD pattern was unchanged even after the HP treatment. The IR spectrum of $(Li_4C_{60})_{HP}$ is compared with that of Li_4C_{60} before the HP treatment in Fig. 3a. The two spectra are quite similar with each other in accordance with the XRD results. They show a loss of I_h symmetry of C_{60} molecules and have some peaks probably arising from the distorted C_{60} molecules with D_{2h} symmetry in the polymer. These spectra have a characteristic broad absorption in a region of 400–800 cm^{-1}. The Li_4C_{60} before the HP treatment and the HP-treated samples $(Li_xC_{60})_{HP}$ with $1 \leqslant x \leqslant 4$ are insoluble in toluene, suggesting that the samples are polymer forms.

The 3R and T 2D-polymers are formed by the $[2 + 2]$ cycloaddition between the C_{60} molecules in the $(1\,1\,1)$ and $(0\,0\,1)$ planes of the fcc lattice, respectively. The dimension of a axis of the unit cells of 3R and T 2D-polymers corresponds to the distances between the centers of adjacent C_{60} molecules, which are about 9.3 Å as shown in Table 1. The lattice parameters and thermal stability of the $(LiC_{60})_{HP}$ 3R 2D-polymer were already reported in the previous papers [21,22]. The lattice parameter c is larger than that of a non-doped $(C_{60})_{HP}$ 3R 2D-polymer prepared by a similar HP treatment. This suggests that the Li atoms are intercalated between the $(C_{60})_n$ polymer layers. This polymer is decomposed into monomers by heating at ambient pressure, as evidenced by an endothermic peak at 502 K in the DSC curve [21]. On the other hand, T 2D-polymer is easily obtained by the reaction of C_{60} with Li at elevated temperature. The reaction seems to lead to the packing of interstices with 4 Li atoms per C_{60} molecule and the $[2 + 2]$ cycloaddition between the C_{60} molecules.

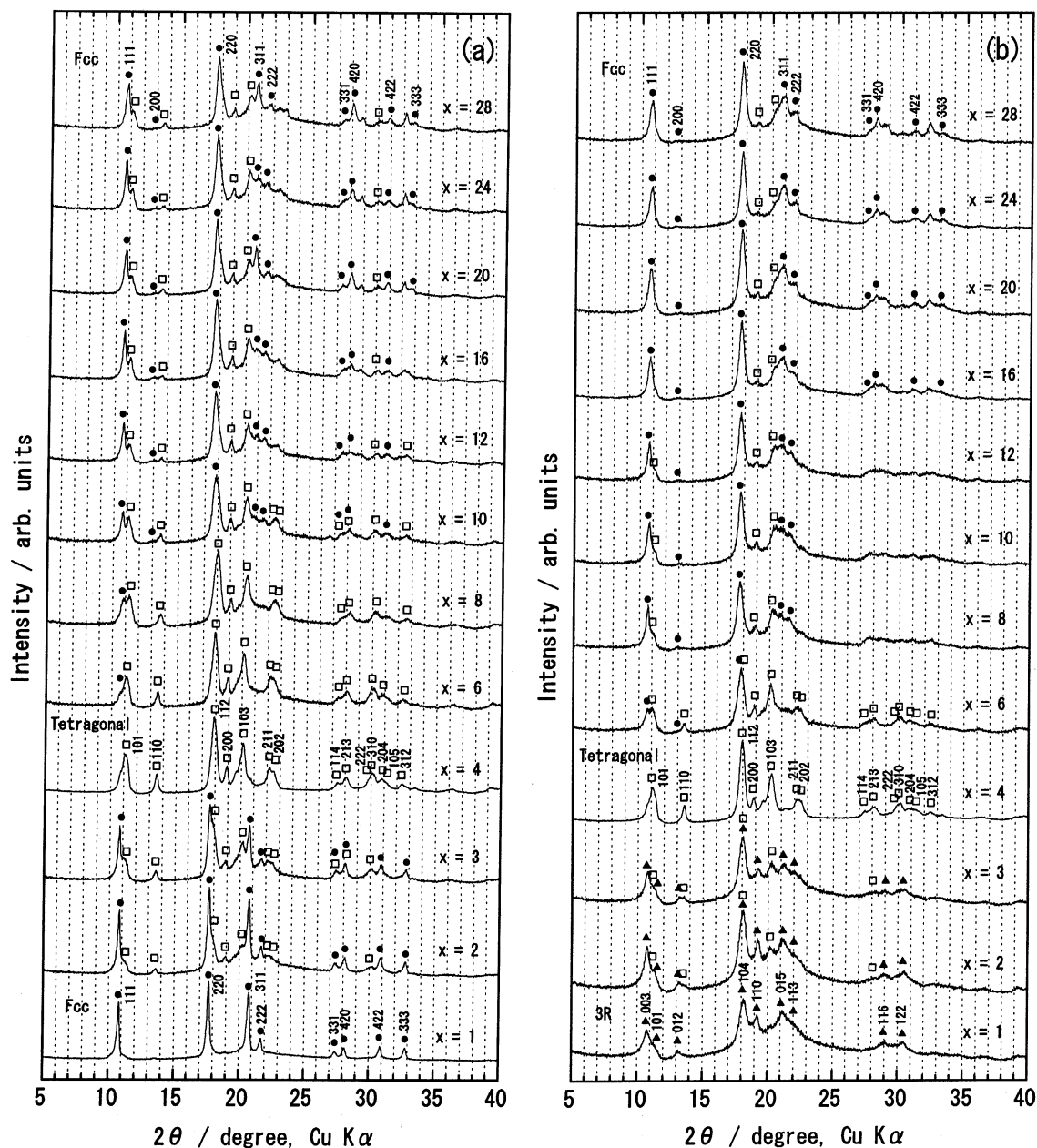Fig. 1. (a) XRD patterns of Li_xC_{60} ($x = 1-28$) before the HP treatment; (b) XRD patterns of $(Li_xC_{60})_{HP}$ ($x = 1-28$) after the HP treatment under 5 GPa at 573 K for 1 h. The diffraction peaks were indexed on the basis of fcc, T, and trigonal (3R) unit cells, respectively.

3.2. HP treatment of Li_xC_{60} ($6 \leqslant x \leqslant 28$)

The decomposition of LiN_3 with C_{60} at 533 K in molar ratios of $LiN_3/C_{60} = 6-28$ resulted in mix-

tures of fcc and T 2D-polymer phases, the fraction of the fcc phase increasing with increasing Li content, as shown in Fig. 1a. The fraction of the fcc phase greatly increased by the HP treatment of
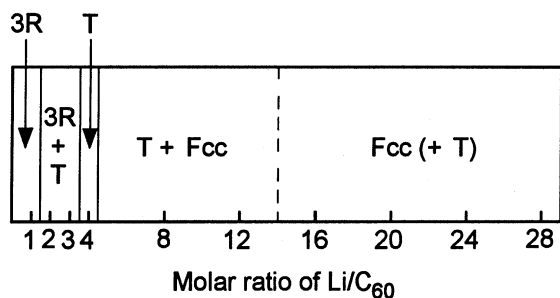
Fig. 2. Li_xC_{60} phases formed by the HP treatment of Li_xC_{60} ($x = 1$–28). The 3R, T, and fcc represent trigonal (rhombohedral) 2D-polymer, T 2D-polymer, and fcc monomer phase, respectively.

these mixtures, as shown in Fig. 1b. The $(Li_xC_{60})_{HP}$ samples with $16 \leqslant x \leqslant 28$ were composed mostly of the fcc phase. The lattice parameters a were slightly smaller than those of the corresponding fcc phases observed before the HP treatment, as shown in Table 1. IR spectra of $Li_{16}C_{60}$ before and after the HP treatment are shown in Fig. 3b. Although some peaks originating from the T 2D-polymer are seen in a 730–800 cm^{-1} region of the spectrum measured before the HP treatment, they disappear after the HP treatment. This finding agrees with the XRD result that the fcc phase largely increased after the HP treatment. In spite of the large fraction of the fcc
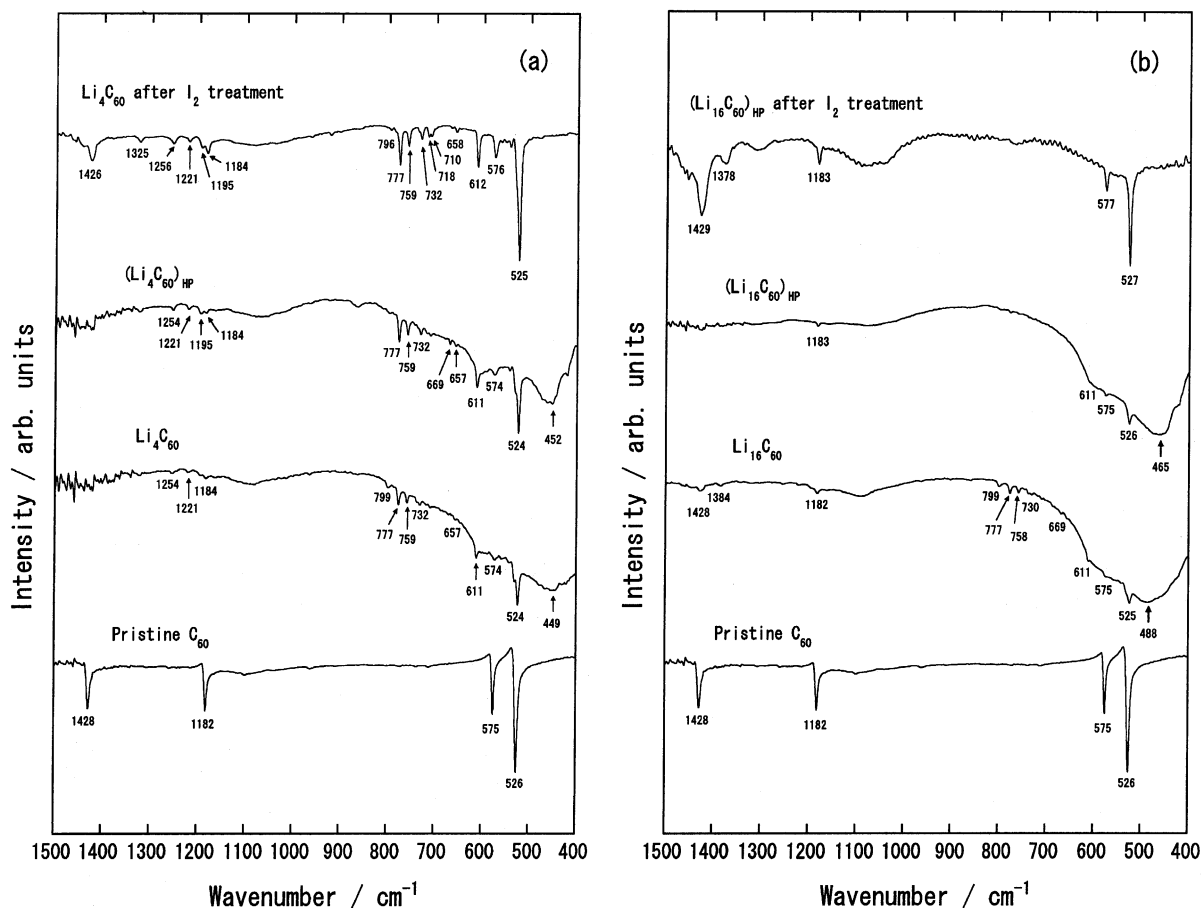

Fig. 3. (a) IR spectra of Li_4C_{60} before the HP treatment, $(Li_4C_{60})_{HP}$ after the HP treatment, and Li_4C_{60} after the I_2 treatment; (b) IR spectra of $Li_{16}C_{60}$ before the HP treatment, $(Li_{16}C_{60})_{HP}$ after the HP treatment, and $(Li_{16}C_{60})_{HP}$ after the I_2 treatment. IR spectrum of pristine C_{60} is also shown for comparison.

Table 1
Lattice parameters of Li_xC_{60} samples before and after the HP treatment

Nominal composition	Symmetry of main phase	Before HP			After HP		
		a (Å)	c (Å)	V (Å³)	a (Å)	c (Å)	V (Å³)
$x = 0$	fcc/trigonal (3R)	14.7	–	711	9.31 (3)	24.22 (7)	606
$x = 1$	fcc/trigonal (3R)	14.175 (2)	–	712	9.26 (2)	24.68 (5)	611
$x = 4$	Tetragonal	9.33 (2)	14.94 (5)	650	9.32 (2)	14.87 (5)	646
$x = 6$	Tetragonal	9.29 (3)	14.97 (6)	646	9.30 (3)	14.97 (6)	647
$x = 16$	fcc	14.16 (3)	–	710	14.13 (2)	–	705
$x = 20$	fcc	14.20 (1)	–	716	14.14 (2)	–	707
$x = 24$	fcc	14.18 (2)	–	713	14.12 (2)	–	704
$x = 28$	fcc	14.171 (9)	–	711	14.12 (3)	–	704

phase, the peaks arising from the I_h symmetry of the C_{60} molecules are hardly observed in both spectra measured before and after the HP treatments. This suggests that the C_{60} molecules in the fcc phases containing large amounts of lithium are distorted from the I_h symmetry. In addition, a broad absorption is observed in a 400–800 cm^{-1} region in the spectra of $Li_{16}C_{60}$ and $(Li_{16}C_{60})_{HP}$ of Fig. 3b, which is more prominent than in the spectra of Li_4C_{60} and $(Li_4C_{60})_{HP}$.

Cristofolini et al. [25] reported the structure of a Li-doped fulleride, $Li_{12}C_{60}$, prepared by a reaction between C_{60} and LiN_3 at elevated temperatures in vacuum and a subsequent moderate annealing. They reported that the $Li_{12}C_{60}$ had an fcc structure at 553 K and distorted to a T structure upon cooling with lattice parameters of $a = 9.894$ Å and $c = 14.209$ Å at room temperature. In the fcc structure at high temperature, the Li atoms are supposedly placed in three unequivalent sites in the octahedral void, (4b, 24e, 32f), where 4b and 32f sites are almost fully occupied but 24e sites are half-occupied, the full occupation of these three sites gives a compound of $Li_{15}C_{60}$. They also pointed out on the basis of the X-ray Rietveld refinement and the ^7Li NMR study that there existed some degrees of covalency between the Li atoms at the 24e sites and the C atoms on the C_{60} unit pointing to each Li atom.

In this study, we had a mixture of fcc and T 2D-polymer phases even at room temperature for Li_xC_{60} with $6 \leqslant x \leqslant 28$. The T 2D-polymer phase was obtained as a single phase at Li_4C_{60}, and the fcc phase increased in the fraction with increasing

Li content. The HP treatment of the Li_xC_{60} with $6 \leqslant x \leqslant 28$ gave rise to a large increase in the fraction of the fcc phase, and the resulting $(Li_xC_{60})_{HP}$ with $16 \leqslant x \leqslant 28$ were mainly composed of the fcc phase. It is likely that the HP treatment urged the reaction between the non-reacted Li metals and the T 2D-polymers existed in the sample before the HP treatment, leading to the formation of the fcc phase. The fcc phase obtained in this study may correspond to the fcc $Li_{12}C_{60}$ as a high-temperature form reported by Cristofolini et al. [25].

3.3. Deintercalation of lithium

The powder samples of Li_4C_{60} and $(Li_{16}C_{60})_{HP}$ were dispersed into an I_2 solution in CH_3CN at room temperature for 5 h, and separated by filtration in an Ar-filled grove box. The IR spectra of the separated samples are shown in Figs. 3a and b for Li_4C_{60} and $(Li_{16}C_{60})_{HP}$, respectively. It is clearly shown that the broad absorption in a 400–800 cm^{-1} region observed before the I_2 treatment disappeared and that the I_h symmetry of the C_{60} molecules recovered for the both samples. The solubility of Li_4C_{60} and $(Li_{16}C_{60})_{HP}$ in toluene were found to increase by the treatment with I_2. The XRD patterns of these samples showed the formation of the fcc C_{60} monomer phase by the I_2 treatment. These results indicate that the Li_4C_{60} T 2D-polymer and the fcc $(Li_xC_{60})_{HP}$ phases reverted to the fcc C_{60} monomer phase by deintercalation of lithium by the treatment with I_2 in CH_3CN. It is also suggested that the broad absorption in a

400–800 cm^{-1} region found in the spectra of Li_4C_{60} and $Li_{16}C_{60}$ before and after the HP treatment may originate from the vibrations of the covalent bonds between Li and C atoms.

Li_4C_{60} was a T 2D-polymer linked by the [2 + 2] cycloaddition between the C_{60} molecules. It was proposed in recent papers [17,26] that the charge state of the C_{60} molecules is an important factor in determining the polymeric bonding geometry; the lower charge states of C_{60}^{n-} anions lead to a polymeric bonding geometry linked by the [2 + 2] cycloaddition like C_{60} polymers [3] and AC_{60} (A = K, Rb, Cs) polymers [4,13], while the higher charge states lead to that linked by the C–C single bonds like Na_2RbC_{60} 1D-polymer [17] and Na_4C_{60} 2D-polymer [14]. Pekker et al. [26] predicted by the theoretical calculation that the boundary lies at $n \sim 3$. It is likely that the C_{60}^{n-} anions of the Li_4C_{60} T 2D-polymer are in a charge state of $n < 3$ due to the covalency between the Li and C atoms, leading to the connection by the [2 + 2] cycloaddition.

3.4. Electrical properties of $(Li_xC_{60})_{HP}$ ($x = 1, 4, 16$)

Three kinds of the HP treated samples, $(Li_xC_{60})_{HP}$ were 3R 2D-polymer, T 2D-polymer, and fcc monomer phases for $x = 1, 4, 16$, respectively. The temperature dependence of the electrical conductivity was measured on each compressed sample by a four-probe method. The results are shown in Fig. 4. All the samples were found to be semiconductors with the conductivities of 1.8×10^{-4}, 1.2×10^{-1}, and 6.2×10^{-1} Ω^{-1} cm^{-1} at room temperature, respectively. The deviation from the linear relationship of log σ vs. T^{-1} at 265 K for $(LiC_{60})_{HP}$ was attributed to a phase transition in a previous paper [21]. The activation energies of the conductivity were determined to be 0.26, 0.28, and 0.14 eV for the samples with $x = 1, 4, 16$, respectively, using the linear relation.

Okada et al. [27,28] reported from the band structure calculations that the 3R and T 2D-polymers of C_{60} should be semiconductors with indirect band gaps of 0.35 and 0.72 eV, respectively. They also predicted that the two kinds of polymers would become metals when they were
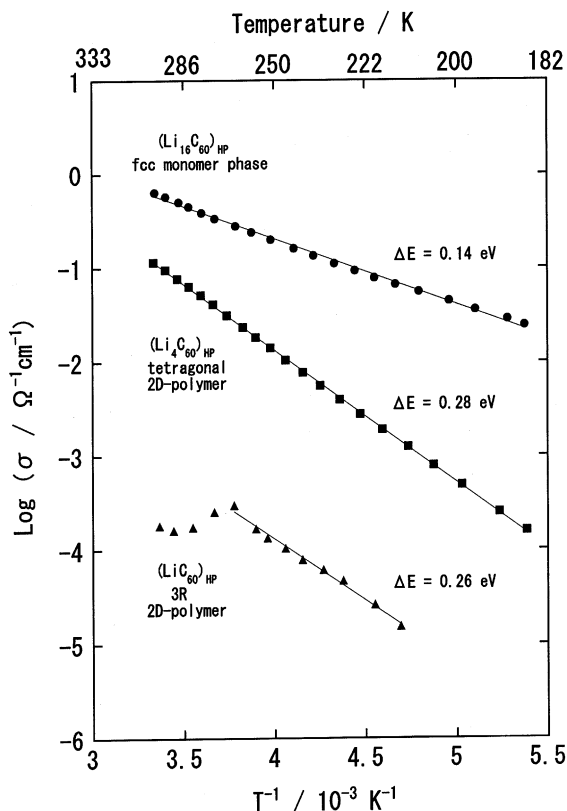

Fig. 4. Temperature dependence of electrical conductivity for $(LiC_{60})_{HP}$ 3R 2D-polymer, $(Li_4C_{60})_{HP}$ T 2D-polymer, and $(Li_{16}C_{60})_{HP}$ fcc monomer phase, respectively. Each activation energy of the conductivity was estimated from the linear relation of ln σ vs. T^{-1}.

electron-doped by the intercalation of alkali metals or alkaline earth metals. However, the $(LiC_{60})_{HP}$ 3R and the $(Li_4C_{60})_{HP}$ T 2D-polymers obtained in this study were semiconductors.

As for AC_{60} (A = K, Rb, Cs) 1D-polymers, it was reported that the KC_{60} polymer was a metal down to 4 K, whereas the RbC_{60} and CsC_{60} polymers were semiconductors below ~350 K and showed SDW transitions near 50 K [13]. This difference in the conduction behavior was attributed to the decrease in the interchain distance in the order of Cs, Rb, K leading to the increase in the electronic dimensionality: the RbC_{60} and CsC_{60} polymers are quasi-1D metal whereas the KC_{60} is a 3D metal [13]. It was also reported that the conduction behavior of the RbC_{60} polymer was

changed from semiconducting to metallic properties by the compression under HP [29]. These results suggest that the conduction behavior is significantly affected by the interchain interactions.

Okada et al. [27,28] pointed out that 2D-polymer layers were electronically coupled by the π–π interactions between the layers, so that the electronic structures around the Fermi level (E_F) were modified depending on the degree of the interaction or the interlayer distance. The $(C_{60})_{HP}$ 3R 2D-polymer prepared under a similar condition was found to be an insulator, agreeing with the calculation result by Okada et al. [27,28]. The insulating property is attributed to an absence of the electron carriers. For the $(LiC_{60})_{HP}$ 3R 2D-polymer, the electron density of the intercalated Li atom is partially transferred to the C_{60} molecule as carriers, but the increase in the basal spacing between the polymeric 2D-layers upon intercalation as evidenced by the increase in the lattice parameter c (Table 1) will give rise to a weaker π–π interaction between the layers. This may lead to the thermally activated hopping conduction of the electron carriers for the $(LiC_{60})_{HP}$ 3R 2D-polymer.

The IR spectra of the Li_4C_{60} and $Li_{16}C_{60}$ before and after the HP treatment showed some degrees of covalency between the Li and C atoms. For the $(Li_4C_{60})_{HP}$ T 2D-polymer, a large part of electron density of the intercalated Li atoms is localized around the Li–C bonds and some degrees of electron density will be transferred to the C_{60} molecules as carriers. Although the carrier density of the $(Li_4C_{60})_{HP}$ T 2D-polymer is higher than that of the $(LiC_{60})_{HP}$ 3R 2D-polymer, the weakening of the π–π interactions between the layers may occur in this polymer as well as the $(LiC_{60})_{HP}$ 3R 2D-polymer.

For the $(Li_{16}C_{60})_{HP}$ fcc monomer, the lattice parameter a (14.13 Å) is slightly smaller than that of the pristine C_{60} (14.17 Å) in spite of the intercalation of Li atoms in a molar ratio of Li/C_{60} = 16. The C_{60} molecules are distorted due to the Li–C covalent bonds as evidenced by the disappearance of the I_h symmetry. As well as the $(Li_4C_{60})_{HP}$ T 2D-polymer, since a large part of electron density of the intercalated Li atoms is localized around the Li–C bonds, some degrees of electron density will be transferred to the C_{60} molecules as carriers. The carrier density of the $(Li_{16}C_{60})_{HP}$ fcc monomer is higher than that of the $(Li_4C_{60})_{HP}$ T 2D-polymer, but the weakening of the π–π interactions between the C_{60} molecules may occur due to the intercalation of a number of Li atoms and the symmetry lowering of the C_{60} molecules, giving rise to the hopping conduction of the electrons.

4. Conclusions

Li_xC_{60} with compositions of $x = 1$–28 were treated under a pressure of 5 GPa at 573 K for 1 h. Three types of Li_xC_{60} fullerides, 3R 2D-polymer, T 2D-polymer, and fcc monomer were formed by the HP treatment depending on the Li content intercalated. The single phases were obtained for $(LiC_{60})_{HP}$, $(Li_4C_{60})_{HP}$, and $(Li_{16}C_{60})_{HP}$, respectively. The C_{60} molecules in the 3R and T 2D-polymers are linked by the $[2 + 2]$ cycloaddition at a distance of 9.3 Å. Li_4C_{60} prepared before the HP treatment was already a T 2D-polymer. The IR spectra of the Li_4C_{60} and $Li_{16}C_{60}$ before and after the HP treatment suggest the existence of some degrees of covalency between the Li and C atoms. The obtained $(Li_xC_{60})_{HP}$ ($x = 1, 4, 16$) were all semiconductors in a temperature range of 200–300 K with the increase in the conductivity in the order of $(LiC_{60})_{HP} < (Li_4C_{60})_{HP} < (Li_{16}C_{60})_{HP}$, and the properties were described in terms of the weakened π–π interactions between the adjacent C_{60} polymers or monomers caused by the intercalation of lithium.

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