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Research for controlling the structures and properties of fullerenes by using the alkyl chain

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The structures and properties of C_{60} derivatives with the non- or the SH- substituted alkyl chain, such as the molecule **1**, were investigated. Among them, the ortho-derivative with the SH-substituted alkyl chain shows unique absorption spectrum. The crystal growth of the derivative deposited on alkali halides is influenced by the ability of the self-assembly of the alkyl chain or SH substitutent. The effect of temperature of the substrate surface was also investigated.

1. INTRODUCTION

Due to their interesting properties such as superconductivity, ferromagnetism or non-linear optics, fullerenes have attracted the interest of many scientists [1]. However most of the crystal structures of fullerenes have the three-dimensional character because of their spherical molecular shapes. If the structures can be controlled to be one- or two-dimensional, some new fascinating properties would be expected. In order to control the structures of fullerenes, there are considered two different strategies. One is to modify their molecular shapes directly by using the chemical techniques, and another is to vary the structural dimensionality with the help of their ability of self-recombination. This ability is peculiar to fullerenes and have been confirmed through the investigations of radioactive fullerene families [2, 3]. In some cases, the lower-dimensional structures of fullerenes have been come true by means of the latter strategy [4]. However, the research for controlling the structures by the use of the former one is also important due to the possibility of the appearance of the different structures. In this proceeding, we report the preliminary results of the structures and properties of C_{60} derivatives with the SH-substituted alkyl chain, such as the molecule **1**. These derivatives are useful for the investigation of the former strategy, because the change of the length or the relative direction to C_{60} of alkyl chain is possible.

2. EXPERIMENTAL

The C_{60} derivatives with the SH-substituted alkyl chain were prepared by the similar method as previously reported [5]. The C_{60} derivative with non-substituted alkyl chain was also synthesized to compare with SH-substituted derivatives. The purification was carried out by the HPLC with the buckyprep column (Nacalai Tesque Co.) and toluene as an eluent. The yield of ortho-derivatives was fairly high, but those of meta- and para-derivatives were low. The

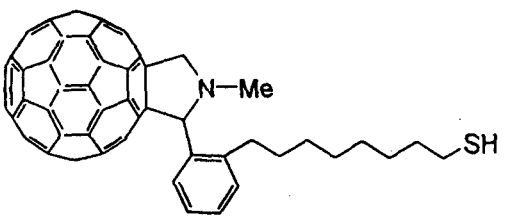

Figure 1. C_{60} ortho-derivative with the SH-substituted alkyl chain, **1**.

derivatives have been confirmed by FAB mass spectrometry and ^{1}H NMR spectroscopy. Their UV-vis spectra were measured in toluene solution. The ortho-derivative with the SH-substituted alkyl chain, -$(CH_2)_8$SH, was deposited on the three kind of substrates, NaCl, KCl and KBr. The substrates were kept from 25℃ to 150℃ in 1 x 10^{-4} Pa during the deposition. In order to investigate the effect of the surface temperature of the substrate, the surfaces of the deposited sample were characterized by

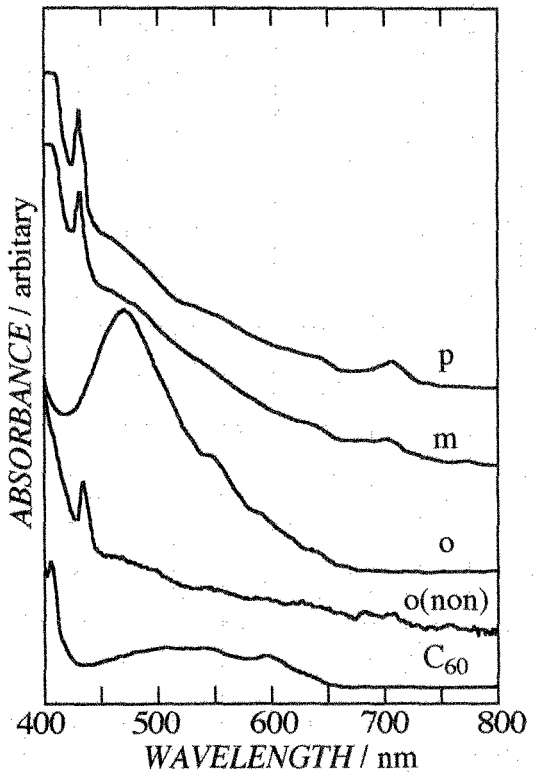

Figure 2. UV-vis spectra of the C_{60} derivatives in toluene solution; o, p, m indicating the ortho-, the meta-. the para-derivatives with the SH-substituted alkyl chain, respectively, and. o(non) indicating the derivative with non-substituted alkyl chain.

TEM. The temperature dependence of UV-vis spectrum of derivatives deposited onto the quartz was also investigated.

3. RESULTS AND DISCUSSION

Figure 2 shows the UV-vis spectra of C_{60} derivatives in toluene solution as compared to that of C_{60}. In the spectrum of the ortho-derivative with the SH-substituted alkyl chain, the strong absorption peak is observed at 480 nm, although there is not such a strong peak around this region in the spectrum of any other derivatives including ortho-derivative with non-substituted alkyl chain. The peak was also reported around the same region in that of the ortho-derivative with the substitutent, - $(CH_2)_4$SH, although the strength of the peak was uncertain [5]. Probably ortho-derivatives with the SH-substituted alkyl chain may have the unique structure with some intermolecular interaction.

Figure 3 shows the TEM images of the ortho derivative with the SH-substituted

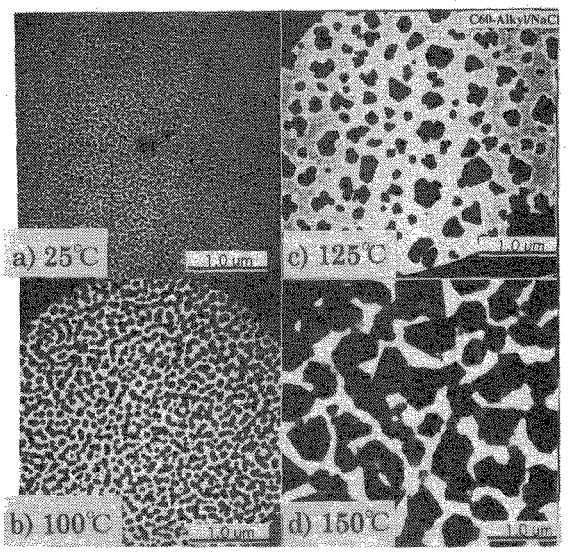

Figure 3. TEM images of the ortho-derivative with the SH-substituted alkyl chain deposited onto NaCl at the different surface temperatures.

alkyl chain at different temperatures. Although the derivative are non-crystal at the substrate temperatures of 25 and 100℃, but the crystal growth are observed at 125 and 150℃. The directions of the crystals are random as shown in Fig. 3d, suggesting that the crystal growth of the derivative with SH substituted alkyl chain is non-epitaxial in contrast to that of C60 [6]. The non-epitaxial crystal growth may be responsible for the ability of the self-assembly of SH substitutent or alkyl chain. Therefore it is important to investigate the crystal growth of the ortho-derivative with non-substituted alkyl chain. The electron diffraction pattern of the crystal at 150℃ indicated that the crystal are belong to the hexagonal system,

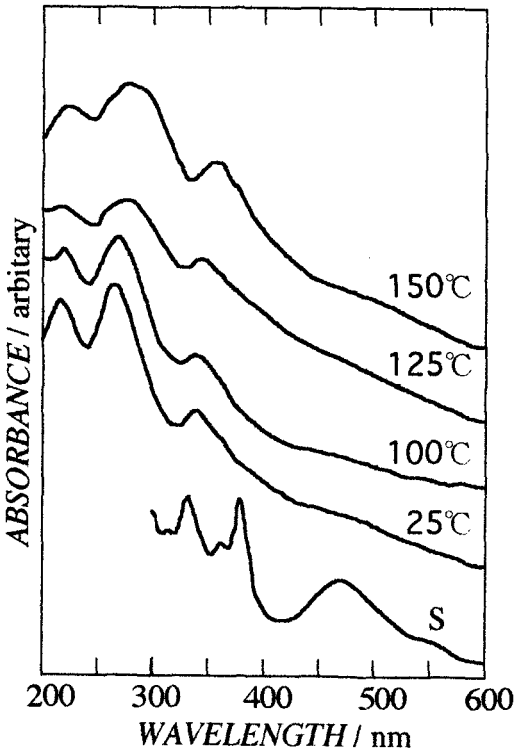

Figure 4. UV-vis spectra of the ortho-derivative with the SH-substituted alkyl chain deposited onto quartz at the different surface temperatures; S indicating the spectra in toluene solution.

although the halo pattern observed at 25 and 100℃. This fact also indicates that the solid deposited at lower temperature than 125℃ is non-crystal.

Figure 3 shows the UV-vis spectra of the ortho-derivative with SH-substituted alkyl chain deposited on the quartz at different substrate temperatures. There is found to be the change of the spectrum between 100 and 125℃. At higher temperature, all three strong absorption peaks shifts by 20～30 nm toward the higher energy. This shift may be related to the crystalzation. The peaks at 340 and 380 nm observed in the solution may correspond to those at 260 and 340 nm observed in the crystal respectively. However in the spectra of the deposited solid, there is not such a strong peak as observed in the solution.

We investigated the structures and properties of C_{60} derivatives with the SH-substituted alkyl chain. Especially, the ortho-derivative with the SH-substituted alkyl chain shows unique absorption spectrum, suggesting the unique structure in solution. The alkyl chain or SH substitutent is found to affect the crystal growth of the derivative deposited onto alkali halides.

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