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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

In Situ FT-IR Study of an Electron-Beam Induced Reaction of C_{60} Film

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Version of record first published: 24 Sep 2006

To cite this article: Toshiki Hara, Jun Onoe, Hideki Tanaka & Kazuo Takeuchi (2000): In Situ FT-IR Study of an Electron-Beam Induced Reaction of C_{60} Film, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 695-700

To link to this article: http://dx.doi.org/10.1080/10587250008025549

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Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 695-700
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In Situ FT-IR Study of an Electron-Beam Induced Reaction of C_{60} Film

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(Received May 30, 1999; In final form June 29, 1999)

The structural modification induced by electron-beam (EB) in a C_{60} film and its kinetics have been studied using *in situ* high-resolution FT-IR spectroscopy. Similar to studies on photoirradiated K_xC_{60} film, it was found that a coalescence reaction between adjacent C_{60} molecules takes place. In order to investigate the interaction between an incident electron and C_{60} molecules, the time-dependence of the amounts of C_{60} on the EB irradiation was examined. It was found that the reaction rate exhibits a linear dependence on the reactant concentration and nonlinear dependence on the incident current.

Keywords: C_{60}; electron-beam; coalescence reaction; kinetics; bucky peanuts

INTRODUCTION

Structural modification of solid C_{60} is of great interest from the point of view of micro-device fabrication[1] and new carbon materials based on C_{60} molecules. It has been revealed that electron-beam (EB) irradiation induces various changes in the structure of solid C_{60} depending on the incident electron energy from the medium region (~1 keV)[2,3] to higher region (10~10^2 keV)[1,4,5]. In the higher energy region, C_{60} molecules in a film are destroyed and amorphous carbon is produced (200 keV)[4] or the C_{60} molecules coalesce to form larger irregular cages (80 keV)[5]. On the other hand, C_{60} in a film provides cross-linking

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between adjacent molecules via a [2+2] four-membered ring by application of the medium energy-EB of 1.5 keV[2]. From these reports, it seems that the EB with a medium energy of a few keV is appropriate to induce the reaction between C_{60} molecules so as to maintain their cage structure. In this paper, we applied an EB of 3 keV to a pristine C_{60} film deposited on a CsI substrate and examined the kinetics of the EB induced reaction in the C_{60} film using *in situ* high-resolution FT-IR spectroscopy.

EXPERIMENTAL

Figure 1 shows a schematic representation of an apparatus for the study of an EB irradiated C_{60} film. A C_{60} film (70 nm) was deposited on a CsI substrate in the ultrahigh vacuum (UHV) chamber (base pressure: 2×10^{-9} Torr) by a sublimation technique[6]. After the formation of the C_{60} film, EB with an energy of 3 keV was applied to the film using an electron gun connected to the UHV chamber. For uniform irradiation of the film, an EB with a spot diameter of about 2 mm was swept over the sample surface (1.8 cm^2) with a frequency of 10 kHz along the x-direction and 1 kHz along the y-direction. To confirm whether or not the C_{60} molecules were desorbed by the EB irradiation, we measured the single-ion mass signals corresponding to C_{60} and its fragments

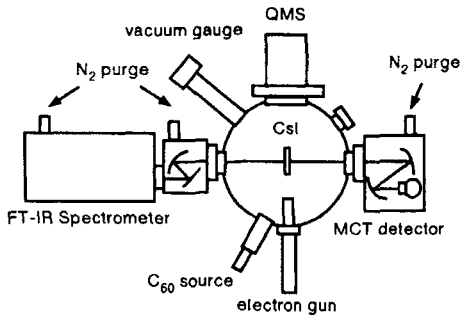

FIGURE 1
Schematic representation of an apparatus for the study of an EB irradiated C_{60} film.

formed by the C_2-loss process during the EB irradiation using a quadrupole mass spectrometer (QMS) and observed no peak due to C_{60} and its fragments desorbed from the film.

The structural change in the C_{60} film after the EB irradiation was examined by *in situ* high-resolution FT-IR spectroscopy. In the FT-IR measurement, an S/N ratio exceeding 180 was obtained for 500 scans at a 0.25 cm^{-1} resolution.

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RESULTS AND DISCUSSION

Products

Figure 2 (a) and (b) show the FT-IR spectra of a C_{60} film before and after 13 h of the EB irradiation, respectively. During the EB irradiation, the emission current from the electron gun was modulated from 0.5 mA to 6.5 mA (corresponding to an incident sample current of 600 μA) with an increment of 0.5 mA per hour. This irradiation condition gave rise to the increase in the substrate temperature up to 393 K. The FT-IR spectrum after the EB irradiation in Fig. 2 was measured after cooling the substrate to 298 K. It was found that many new IR peaks appeared besides the four fundamental IR-active modes (526, 576, 1183, and 1429 cm^{-1}) in the FT-IR spectrum after the EB irradiation. Conversely, the intensity of the four fundamental IR-active modes decreased after the EB irradiation. This indicates that the EB irradiation modified the structure of the C_{60} molecules in the film.

Figure 2 (c) shows the FT-IR spectrum of a photoirradiated C_{60} film obtained from our previous work[7]. We have assigned the new peaks of this spectrum to the vibrational absorption of dumbbell type C_{120} dimers by comparison of the result with theoretical IR spectra of several C_{120} candidates using the tight-binding IR calculations[8]. Since this spectrum is nothing like that of the EB irradiated C_{60} film, the product of the EB irradiated C_{60} film is not

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the dumbbell dimer. Figure 2 (d) shows the FT-IR spectrum of a photoirradiated potassium-doped C_{60} film[9]. It is interesting to note that the FT-IR spectra of the EB irradiated non-doped C_{60} film and photoirradiated potassium-doped C_{60} film coincide well with each other. We have recently demonstrated that peanut-shaped C_{120} (bucky peanuts) were formed in the photoirradiated K_xC_{60} film using FT-MS[10] and FT-IR[9] in combination with IR calculations based on a tight-binding method[9]. These facts suggest that the coalescence reaction between C_{60} molecules was brought about in the present C_{60} film by the EB irradiation, and the new peaks in the FT-IR spectrum originated from the vibrations of the products.

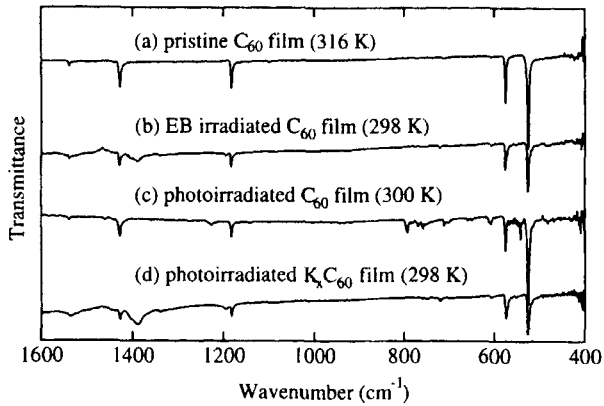

FIGURE 2 FT-IR spectra of pristine C_{60} film (a), EB irradiated C_{60} film (b), photoirradiated C_{60} film (c) and photoirradiated K_xC_{60} film (d).

Kinetics

We next investigated the kinetics of the EB induced reaction in the C_{60} film in order to understand the interaction between EB and the C_{60} molecules. The concentration of the product in the film cannot be estimated, because the IR absorption cross section of the product is still unknown. We then examined the decreased rate of the C_{60} concentration (M) in the film. The rate can be expressed as

$$-dM/dt = k(J)M^n, \quad (1)$$

where $k(J)$ is the rate constant depending on the incident current J. Since C_{60} in the film was uniformly arranged on the CsI substrate and no C_{60} was confirmed to be removed during the EB irradiation by *in situ* QMS, the thickness of the film during the EB irradiation remained unchanged. Thus we estimated M from integrated absorbance of the fundamental IR active mode of C_{60} on the basis of Beer's law.

To obtain n and $k(J)$ in Eq. (1), we measured the irradiation-time evolution of the FT-IR spectra of the C_{60} film at a given value of J for 10 h. To avoid heating the sample by the EB irradiation, the sample holder was maintained at 298 K by a helium flow cryostat.

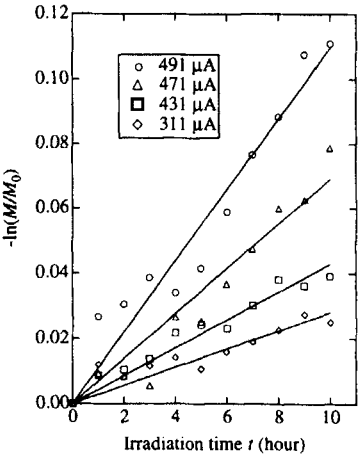

FIGURE 3 The plot of $-\ln(M/M_0)$ as a function of EB irradiation time t.

Assuming that the reaction rate exhibits $n = 1$ at each value of J, we can integrate Eq. (1) and obtain the formulation, $-\ln(M/M_0) = k(J)t$. Figure 3 shows a plot of $-\ln(M/M_0)$ as a function of the EB irradiation time t for the different J values. It was found that $-\ln(M/M_0)$ is proportional to the irradiation time t for different J values. Consequently, the assumption of $n = 1$ is justified.

We next considered the dependence of the rate constant k on the incident current J. From the slope of the fitted lines in Fig. 3, we obtained the rate constant k to be 7.79×10^{-7}, 1.19×10^{-6}, 1.92×10^{-6}, and 3.04×10^{-6} s^{-1} for the incident currents of 311, 431, 471, and 491 μA, respectively. From a plot of k

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as a function of J, it was found that k exhibits a nonlinear dependence on J. We performed the curve fitting of k by assuming the simple power function $k = CJ^m$ where C is a constant. As a result, we obtained C and m to be 2.53×10^5 $s^{-1}A^{-m}$ and 3.32, respectively.

The physical meaning of the nonlinear J dependence of the reaction rate is not well understood at this stage. In general, when fast electrons inelastically collide with target molecules, secondary electrons are formed and lead to the formation of cations, anions, and excited molecules by Coulombic interaction with neighboring molecules. In the coalescence reaction found in the present work, these activated species of C_{60} molecules seem to take part in the reaction as precursors. It is important to know what species contribute to the reaction in order to understand the J dependency. For this purpose, examining the *in situ* FT-IR spectra of a C_{60} film upon EB irradiation is currently in progress.

Acknowledgments

This work was supported by special coordination funds from the Science and Technology Agency of the Japanese Government. One of the authors (T.H.) thanks the Special Postdoctoral Researchers Program of RIKEN.

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