
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

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Version of record first published: 04 Oct 2006

*Mol. Cryst. Liq. Cryst.*, 1998, Vol. 316, pp. 157–160
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# Structural Study on Cast Films of $C_{60}$ Derivatives with Long Alkyl Chains

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Cast films of $C_{60}$ derivatives with a long alkyl chain were prepared and characterized. The high ordered reflection peaks were observed in cast films. As a alkyl chain was longer, the two-dimensional layer structure was more stabilized.

Keyword: $C_{60}$ derivatives; cast films; long alkyl chains; two-dimensional layer structure

## INTRODUCTION

$C_{60}$ is of great interest due to its fascinating physical and chemical properties, such as non-linear optics, ferromagnetism and superconductivity. $C_{60}$ molecules take the tree-dimensional arrangement in almost of crystals, but the two-dimensional arrangement may present some new interesting properties. Recently, there are some reports on the properties of two-dimensional arrangement of $C_{60}$ and $C_{60}$ derivatives in thin films[1].

Long alkyl chains are well-known to have the self-assemble ability as

well as $C_{60}$, so $C_{60}$ derivatives with a long alkyl chain are expected to have two-dimensional structures, where $C_{60}$ layers and long alkyl chain layers stack alternately. In these structures, by changing the length of alkyl chain the distance between $C_{60}$ layers can be varied, which may lead to the control of functionality. In this paper, we report the structures and properties of cast films of $C_{60}$ derivatives with a long alkyl chain.

## EXPERIMENTAL

$C_{60}$ derivatives with a long alkyl chain **1** (n=8,12,16) were synthesized by the similar method as previously reported[2] . Their structures are shown in Figure 1. The samples were purified by the HPLC with a buckyprep column (Nacalai Tesque Co.) and toluene as an eluent, and characterized by FAB-MS and $^1H$ NMR spectroscopy.

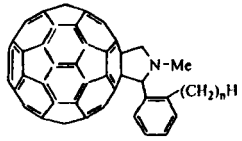


FIGURE 1 Chemical structures of **1** ( n= 8, 12, 16 )

Cast films and spin coat films were prepared from the $CS_2$ solution of **1** (n=8,12,16). The quartz coated by an amorphous carbon film, which was made by a plasma polymerization equipment (NL-OP80NS, Nippon Laser & Electronics Lab.), was used as the substrate. The films were characterized by the X-ray diffraction method and the UV-vis absorption spectroscopy.

## RESULTS AND DISCUSSION

Figure 2 shows the X-ray diffraction patterns for a spin coat film and a cast film of **1** (n=16). In the spin coat film, no apparent peak was observed. This shows that the spin coat film is amorphous. On the contrary, in the cast film,

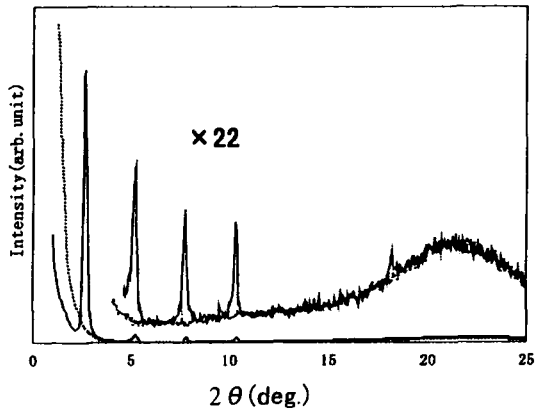


FIGURE 2 X-ray diffraction patterns for a spin coat (dashed line) and a cast film (solid line) of **1** (n =16)

the d-spacing is calculated to be 34.0 Å from Bragg's equation. In a powder, which was scraped from a cast film, a large diffraction peak is observed at 2 $\theta = 8.9°$ , due to the packing of $C_{60}$ ( The d-spacing is about 10 Å.) The d-spacing of 34.0 Å suggests two possible structures as shown in Figure 3.

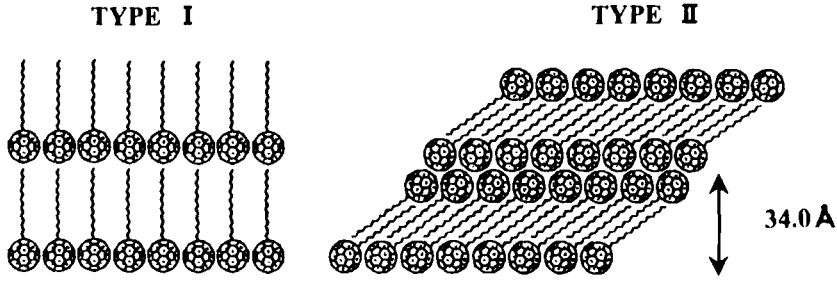


FIGURE3 Two possible structures of **1** (n =16)

In the Type I structure, the $C_{60}$ part is packed densely, but the alkyl part is packed loosely because of the large van der Waals radii of $C_{60}$. On the other hand, in the Type II structure, long alkyl chains have interdigitated structure and tilt by about 60° , so the both of the $C_{60}$ and alkyl parts are packed

densely. As a result, the Type II structure would be more stable. The X-ray diffraction data for cast films of **1** (n=8,12,16) are summarized in Table 1.

TABLE 1 X-ray diffraction data for cast films

| | d-spacing (Å) | I (001) (cps) |
|---|---|---|
| **1**( n=8 ) | 27.2 | $3 \times 10^2$ |
| **1**( n=12 ) | 31.6 | $7 \times 10^3$ |
| **1**( n=16 ) | 34.0 | $1 \times 10^4$ |

As the alkyl chain is longer, intensity of (001) is more enhanced, which means that the two-dimensional layer structure is more stabilized. This result indicates that the interaction between alkyl chains plays an important role for making the two-dimensional layer structure. So Type II structure may also be supported.

In the UV-vis absorption spectrum for the cast film of **1** (n=16) the broad absorption peak was observed at 500nm, although there was not such a broad peak around this region in the spectrum for the spin coat film. This absorption peak may be explained by the increasing of the intermolecular interaction for two-dimensional arrangement of $C_{60}$ part, because the band around 500nm was observed on $C_{60}$ film[3], in which the interaction between $C_{60}$ may be more increased compared with $C_{60}$ solution.

In summary, the cast films and the spin coat films of $C_{60}$ derivatives with a long alkyl chain have been prepared. In the cast films the high ordered reflection peaks were observed. As the alkyl chain is longer, the two-dimensional layer structure is more stabilized.

References

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