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Observation and Electrical Properties of Functionalized Dendrimer Monolayers by Using SPMs

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Abstract

We synthesized dendrimers containing light switchable units, azobenzene group. We also report the example of a dendrimer containing 48 azobenzene that is electrically conducting using STM. The dendrimer with azobenzene group compared trans form and cis form at electrical properties. By irradiation of 365 [nm] light, the trans state current of G4-48 Azo dendrimer was increased, which was originated by the photoisomerization process of the azobenzene group on the periphery from trans to cis form. All of the conductivities were ohmic, there is no evidence of polarization on switching the current direction, and the conductivity values remained constant for several hours. This demonstrates that the conductivity is electronic, not ionic. This suggests that optical behavior and conductivity change are affected by the functional group and symmetric chain.

Keywords: dendrimer, azobenzene, scanning probe microscopy, photoisomerization, organic monolayer

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1. Introduction

Many approaches to control the size of molecules and their physical properties have been attempted for the application to the molecular electronic devices. Dendrimers are a new class of macromolecules constructed with highly regular branching, having a tree-like structure that emanates from a central core. The unique structure of these three-dimensional polymers is a result of the control of their size, shape, molecular weight, topology, and surface chemistry to an extent unprecedented in polymer science[1].

Currently, device miniaturization and highly integrated circuit design are of major interest for the development of electronic devices. Various studies have been conducted to develop new materials and processing techniques [2]. It is obvious that for any molecular device to have uniform and welldefined properties it must consist of molecules that are arranged in a well-ordered configuration. A reliable and long established method for producing ordered molecular thin films is the Langmuir-Blodgett (LB) method [3]. Also, scanning tunneling microscopy (STM) has been demonstrated to be powerful in the observation of the atomic-scale image and in the elucidation of electronic structure [4]

Recently, Vögtle et al reported on the synthesis and characterization of dendrimers containing azobenzene units in the periphery toward photo-switchable dendritic hosts [5]. Molecular switching by an external stimulus is one of the fundamental functions of the superamolecular complex. For all these reasons, we thought that dendrimers bearing azobenzene group in the periphery could play the role of photoswitchable hosts.

In this study, we attempted to fabricate dendrimer LB films functionalized with azobenzene groups in their periphery. It is well known that azobenzene-type compounds undergo an efficient and fully reversible photoisomerization reaction. We investigated monolayer behavior and its characteristics at the air-water interface by LB method. The electrical properties of G4-48 Azo dendrimer were compared with between trans form and cis form using metal/dendrimer LB film/metal (MIM) structure. Also, the electrical properties of the single dendrimer molecule have been investigated by STM. The investigation of the electrical properties of G4-48 Azo dendrimer is important for the potential in molecular electronic nanodevices.

2. Experimental

The fourth generation dendrimer contained in photoisomerizable 48 azobenzene units (G4-48Azo) in the

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periphery was synthesized in an attempt to construct a photoswitchable molecular device system (See Fig. 1). The G4-48 Azo dendrimer was synthesised using siloxanetetramer (2, 4, 6, 8-tetramethyl-2, 4, 6, 8-tetravinylcyclotrtrasiloxane, ((CH$_2$=CH) MeSiO)$_4$) as the core molecule, hydrosilation with HSiMenCl3-n and alcoholysis with allylalcohol. By the two alternative processes, hydrosilation and alcoholysis, the dendrimer carried out up to the fourth generation with 48-Cl on the periphery. Then, G4P-48-Cl dendrimer was terminated with 4-phenyazophenol. Dendrimers have high degree of branch and high density of the terminal functional group.

The surface pressure-area (π-A) isotherms were investigated using an LB trough (Nippon Laser and Electronics Lab., model #NL-LB200-MWC, Moving wall type; trough size: 80×585[mm^2]). The same irradiation wavelength has been used to minimize experimental error. To convert the trans form to the cis form, 365[nm] wavelength light has been irradiated onto the surface and 254[nm] wavelength for back process. The LB films were transferred onto slide glasses for the measurement of the electrical properties. For the determination of the electrical properties, an upper aluminium (Al) electrode with a diameter of 5[mm] was deposited on the film surface using the vacuum evaporation method to form an Al/dendrimer LB film/Al sandwich structure [6]. A DC power supply and an HP 3458A multimeter were used to measure current-voltage (I-V) characteristics. STM (Digital Instruments, Nanoscope IV) were used for investigation of morphology and electrical properties dropped dendrimer film on Au substrate in atmosphere.

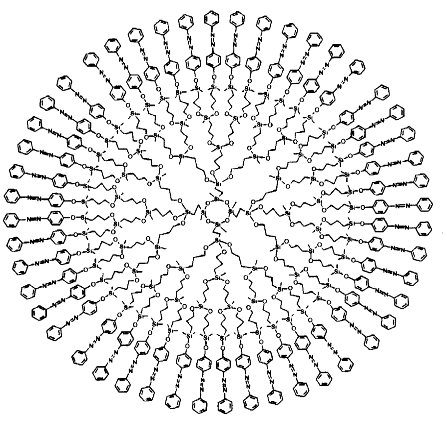

Fig. 1. The chemical structure of the fourth generation dendrimer bearing 48 azobenzene units in the Periphery.

^{1}H ^{13}C-NMR spectrum data of G4-48 Azo dendrimer ; ^{1}H -NMR(ppm, CdCl3) : δ=0.25(s, 288H SiMe(G$_4$), 0.90(s, 72H, SiMe(G$_3$), 0.15(s, 48H, SiMe(G$_0$-G$_2$)), 0.25~0.87, 1.44~1.79(m, 352H, CH$_2$(G$_0$~G$_3$)), 3.57~3.80 (m, 168H, OCH$_2$(G$_1$~G$_3$)), 6.87~7.02, 7.35~7.59, 7.80~7.99(Azo).

^{13}C -NMR(ppm, CdCl3) : δ=-4.98(SiMe(G$_0$~G$_3$)), -1.38 (SiMe(G$_4$)), 9.00(CH2(G$_0$)), 12.49, 26.08 (CH$_2$(G$_3$)), 9.52, 25.97(CH$_2$(G$_1$~G$_2$)), 65.91 (OCH$_2$(G$_1$~G$_3$)), 120.32, 122.56, 124.66, 128.82, 130.39, 147.46, 152.68, 158.04 (Azo)

^{1}H, ^{13}C-NMR spectra was significant for the dendrimer structure, the synthesized dendrimer was identified with the MAILD-TOF-Mass, GPC, and elemental analysis.

3. Results and discussion

The π-A isotherm of the G4-48 Azo dendrimer are shown in Fig. 2 indicating that a monolayer is formed at air/water interface. The stability of the monolayers was further supported by the fact that no change in the total surface area at constant pressure for at least 1 h was observed. But we cannot observe the collapse point on this trough because of the limitation of the area. A linear increase of surface pression is observed during Compression. It is suggested that unclear phase separation of G4-48 Azo dendrimer is a consequence of the weak interaction among dendrimer molecules, no arrangement, and no orientation at air/water interface. The interfacial behavior of G4-48 Azo dendrimer could be characterized by increasing rate, θ and surface pressure at top, which should be limited by trough area. These variables were affected by the barrier speed and showed different value by cyclic π-A isotherm. We could evaluate the monolayer state by θ and maximum pressure.

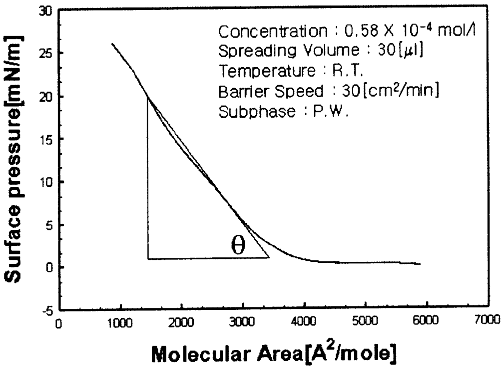

Fig. 2. The π-A isotherm of G4-48 Azo dendrimer at the air/water interface.

Fig. 3 shows the surface pressure-area (π-A) isotherms for the monolayers of G4-48 Azo dendrimer and reveals a linear increase in surface pressure upon compression. The stable condensed films were formed at the air-water interface, which means that the G4-48 Azo dendrimer can be applied to the LB method. The difference in molecular behavior between pure G4-48 Azo dendrimer and its irradiation of 365[nm] light during the process originated from the photo-isomerization process of the azobenzene group in the periphery from trans to cis form. The molecular behavior was fully restored by irradiating 254[nm] wavelength light.