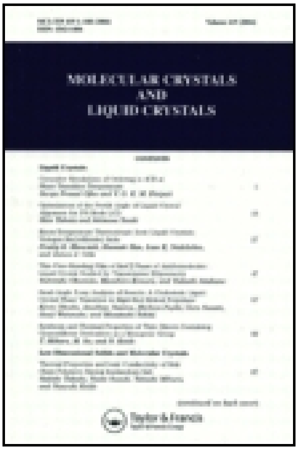

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Electrical properties of dendritic macromolecule containing azo-groups

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ELECTRICAL PROPERTIES OF DENDRITIC MACROMOLECULE CONTAINING AZO-GROUPS

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We synthesized the G4-48Azo dendrimer functionlized with azobenzene groups, fully reversible photo-isomerization reaction, in their periphery. We investigated monolayer behavior and its characteristics at air-water interface by LB method. And we observed the difference of molecular behavior and measured the surface pressure shift by 365[nm] light irradiation because of the photo-isomerization of the azobenzene group in their periphery. The electrical properties of the G4-48Azo dendrimer were compared with between trans form and cis form using metal/dendrimer LB film/metal (MIM) structure and STM system. And we obtained the difference of values in I-V characteristics using STM originating from the photo-isomerization of the azobenzene.

Keywords: azobenzene; dendrimer; electrical properties; STM; thin films

1. INTRODUCTION

One of the major themes in electronics is the construction, measurement, and understanding of the current-voltage response of an electronic circuit in which molecular system act as conducting elements. Traditional metal-molecule-metal junctions comprise thin molecular films between

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macroscopic metal electrodes. These nanoscale molecular interconnects act as novel chemical environments and may help minimize computer circuit dimensions and enhance performance. They can act as switches, gates, or transport elements, providing new molecular functions that need to be characterized and understood [1]. It is obvious that any molecular device to have uniform and well-defined properties must consist of molecules that are arranged in a well-ordered configuration. A reliable and established method for producing ordered molecular thin films is the Langmuir-Blodgett (LB) method [2]. And the scanning tunneling microscopy (STM) has been demonstrated to be powerful in observation of the atomic-scale image and in elucidation of electronic structure [3].

Polymer science has traditionally focused on linear and weakly or strongly crosslinked polymer structures, resulting in the immense variety of synthetic polymer materials currently in use. Only recently, polymers with tree-like structure, often designated "cascade macromolecules" have been attracting rapidly increasing interest. Currently, intense research efforts are being devoted to the development of novel synthetic routes to cascade polymers as well as the investigation of the physical properties of these polymers [4,5]. Also dendrimers have recently been recognized as a promising candidate for a building unit of the organized nanostructures [6]. Furthermore, surface groups of dendrimers can be chemically functionalized through the synthetic manipulation, and their application of the resulting dendrimers in the related areas has been expanding.

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

2. EXPERIMENTAL

The thermodynamically stable trans form of azobenzene groups contained in the periphery of poly(propyleneimine) dendrimers are reversibly switched to the cis form by 365[nm] light and can then be converted back to the trans form by irradiation with 254[nm] light or by heating. The isomerization of azobenzene group can be represented by

$$trans \underset{hv'}{\overset{hv}{\rightleftharpoons}} cis \tag{1}$$

Isomerization of azobenzene group involves a large structural rearrangement. Also, the isomerization is always accompanied by significant changes of physical properties such as dipole moment, melting and boiling points, and refractive index. In going from the trans to the cis form, the distance between the para carbon atoms of azobenzene decreases from 9 to 5.5[Å], and the dipole moment increases from 0 to 3.0[D] [7]. This means that the physical properties of materials with azobenzene group can be controlled by light irradiation.

The forth generation dendrimer contained in photoisomerizable 48 azobenzene units (G4-48 Azo) in the periphery was synthesized in an attempt to construct a photoswitchable molecular device system. 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 $HSiMe_nCl_{3\text{-}n}$ and alcoholysis with allylalcohol. By the two alternative processes, hydrosilation and alcoholysis, the dendrimer carried out up to the fourth generation with 48-C_1 on the periphery. Then, G4P-48-C_1 dendrimer was terminated with 4-phenyazophenol. Dendrimers have high degree of branch and high density of

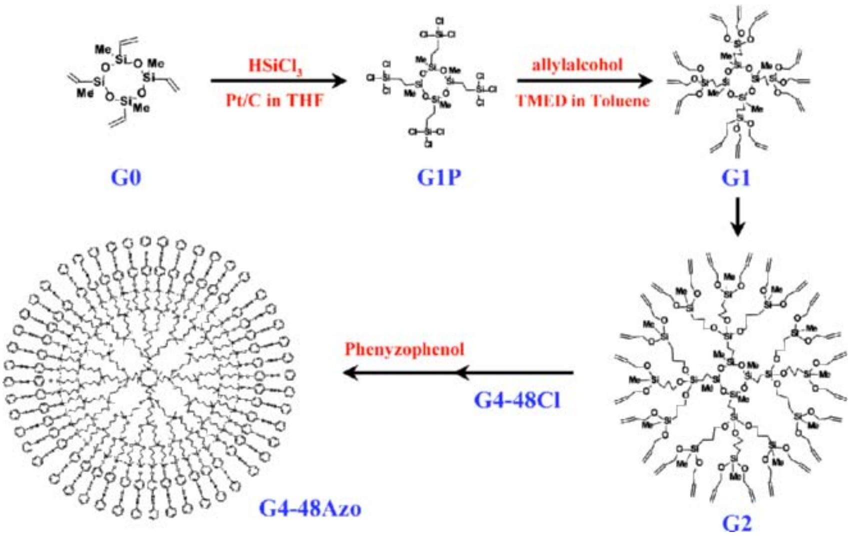

FIGURE 1 Chemical process of G4-48Azo dendrimer.

terminal functional group. Figure 1 represents the chemical process of G4-48 Azo dendrimer.

The surface pressure-area (π-A) isotherms were investigated by using an LB trough (Nippon Laser and Electronics Lab., model #NL-LB200-MWC, Moving wall type; trough size: 80 × 585[mm]). 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 [8]. A DC power supply and an HP 3458 A multimeter were used to measure current-voltage (I-V) characteristics. And STM (Digital Instruments, Nanoscope IV) were used for investigation of morphology and electrical properties dropped dendrimer film on Au substrate in atmosphere.

3. RESULTS AND DISCUSSION

Figure 2 shows the surface pressure-area (π-A) isotherms for the monolayers of G4-48Azo dendrimer and displays a linear increase in surface pressure upon compression. The stable condensed films were formed at the air-water interface, which means that the G4-48Azo dendrimer can be applied to the LB method. The difference in the molecular behavior between pure G4-48Azo dendrimer and it by irradiation of 365[nm] light

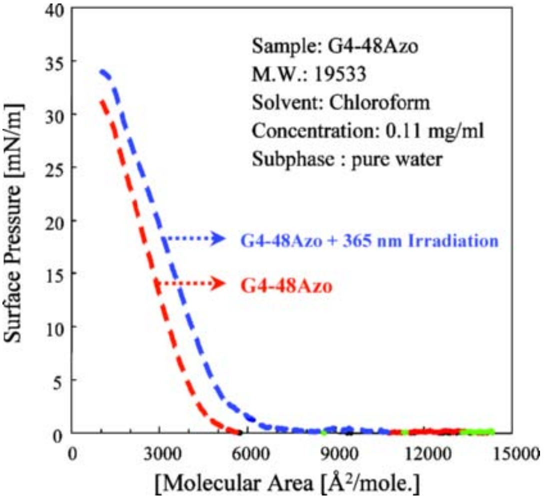

FIGURE 2 π-A isotherm of G4-48Azo dendrimer at the air-water interface.

during process originated from the photo-isomerization process of the azobenzene group in the periphery from trans to cis form. And the molecular behavior was fully restored by irradiating 254[nm] wavelength light.

Figure 3 represents the photo-switching process of G4-48 Azo dendrimer monolayer at the air-water interface. By irradiation of 365[nm] light, the surface pressure was increased, which was originated from the photo-isomerization process of azobenzene group in the periphery from trans to cis form. The increase of the diopole moment (μ), which may increase the interaction among G4-48 Azo dendrimer molecules, played an important role in surface pressure shift. The surface pressure was fully recovered by irradiation of 254[nm] wavelength light and the photo switching was reproducible. The time constant was also calculated to be 30[sec] during photo-isomerization from trans to cis form and faster than back process.

The electrical properties of the dendrimer LB films were investigated by measuring the leakage current I versus applied voltage V, which is shown in Figure 4(a). Figure 4(a) shows the I-V characteristics compared with those of the monolayers of G4-48Azo dendrimer LB films between trans form and cis form. However, they are alike in characteristics. We though that trans form exchanged to cis form because heat was transferred to dendrimer LB films during evaporation process at the upper electrode. And the I-V characteristics appear asymmetric and nonlinear; i.e., large currents are observed for forward voltage. The devices clearly exhibit rectifying behavior. We consider that the asymmetric structures are formed by the LB

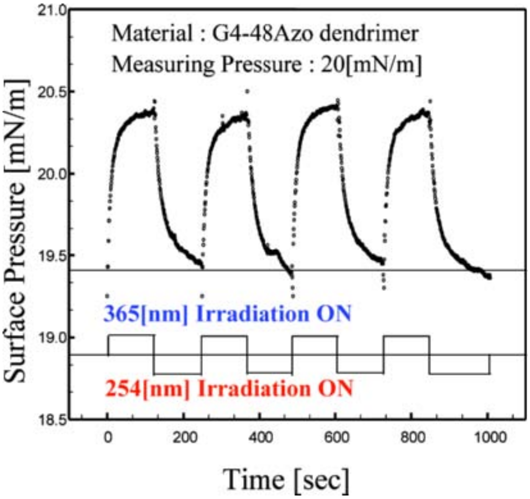

FIGURE 3 Optical response of G4-48 Azo dendrimer at air-water interface. (measuring interval : 2[min], measuring pressure : 20 [mN/m]).

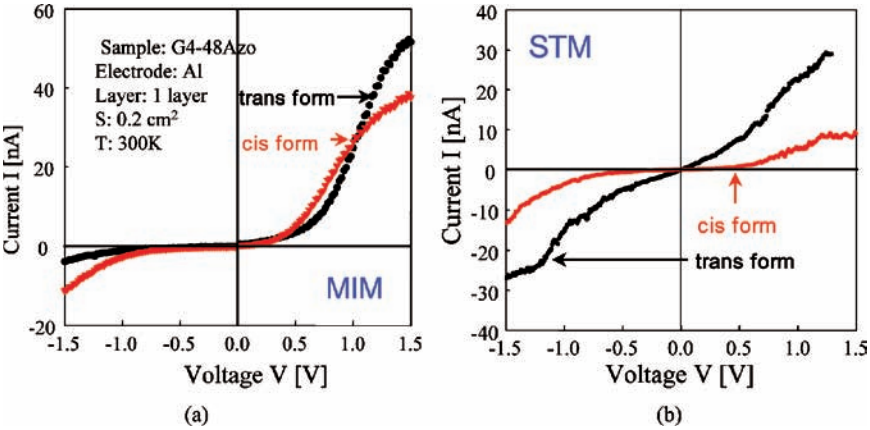

FIGURE 4 I-V characteristics of G4-48Azo dendrimer. (a) MIM structure, (b) using STM.

method [8]. The outmost functional groups are toward the subphase due to its flexibility at the air-water interface, because the azobenzene groups have a hydrophilic property. Thus the G4-48Azo dendrimer LB films deposited might be asymmetric in structure. Figure 4(b) shows the I-V characteristics using STM compared with trans form and cis form at room temperature. We measured the I-V characteristics firstly of its trans form and secondly of its cis form after irradiation of 365[nm] light at the same position. The calculated resistivity values of trans form and cis form of G4-48Azo dendrimer are 6.604×10^7 and $8.655 \times 10^8[\Omega]$, respectively. The difference was originated from the photo-isomerization of azobenzene unit in the periphery of the dendrimer. Therefore, we confirmed a difference of trans form and cis form of the azobenzene groups only in the periphery of the dendrimer.

4. CONCLUSIONS

In this study, we synthesized dendrimers containing light switchable units, azobenzene group. We investigated the monolayer behavior at the air-water interface. And we observed the difference of molecular behavior and measured the surface pressure shift. As a result, the monolayer of the G4-48Azo dendrimer with azobenzene group showed the reversible photo-switching behavior originated from the photo-isomerization of azobenzene unit in the periphery of the dendrimer. There are alike in the I-V characteristics of trans form and cis form of the G4-48Azo dendrimer LB films using MIM structure. We thought that trans form exchanged to cis form because heat was transferred to dendrimer LB films during the evaporation process at the upper electrode. However, we measured the difference in values of the I-V characteristics using STM. This result includes the dendrimer with the azobenzene group showed the difference characteristics by the photo-isomerization of the azobenzene group in their periphery.

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