

Spectral Change and Surface Images of the Azobenzene Functionalized Dendrimer in LB Monolayers

Hoon-Kyu Shin and Young-Soo Kwon

Abstract - The functionalized dendrimer containing 48 azobenzene was synthesized. Many isolated featureless domains were explicitly observed even at the air/water interface. Also, these monolayers were representatively observed, showing the change of surface pressure with irradiation time and wavelength. In AFM images, larger domains irregularly shaped structures on the top, while smaller ones were free from such defects. In the optical absorption spectra of the monolayer films by UV irradiation and heat treatment, only the photoisomerization of the G4-48 Azo monolayers was observed, revealing a decrease of absorbance peaks without any change of the spectral shape. This suggests that the functional group and the symmetric chain affect optical behavior and morphological change.

Keywords - G4-48 Azo dendrimer, functional group, azobenzene, monolayer, photoisomerization

1. Introduction

Dendrimers are a new class of macromolecules constructed with highly regular branching, having a tree-like structure that emanates from a central core. Many approaches to control of particle size and their physical properties have been attempted for the application to the molecular electronic devices[1].

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[2]. Also dendrimers have been recently recognized as a promising candidate for a building unit of the organized nanostructures[3,4]. Furthermore, surface groups of dendrimers can be chemically functionalized through the synthetic manipulation, and the resulting dendrimers expanding their application in the related areas. Engineering nano structures from a materials perspective involves the utilization of organic, inorganic, and composite materials such as carbon nanotubes, inorganic nanowires, metal and semiconductor nanocrystals, nanoparticles, and polymeric material[5]. The highly compact and globular shape, as well as the monodispersity of dendrimers, suggests that they may be ideal candidates to serve as individual pixels in a hypothetical single molecule data storage or nano lithography system.

Recently, Vogtle et al reported on the synthesis and

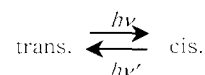
characterization of dendrimers containing azobenzene units in the periphery toward photo-switchable dendritic hosts[6]. Molecular switching by an external stimulus is one of the fundamental functions of supermolecular complex.

In this study, we synthesized the dendrimer functionalized with azobenzene group in their periphery and investigated its characteristics as the optical properties and monolayer behavior of dendrimer molecules. The present paper also summarizes the results of a systematic AFM study on LB monolayers of azobenzene functionalized dendrimer.

2. Experimental

2.1 Synthesis and Chemical Structure

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[7]. The isomerization of azobenzene group can be represented by



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,

This work was supported by the National Program for Tera-level Nanodevices of the Ministry of Science and Technology as one of the 21 century Frontier Programs.

Manuscript received: May 11, 2001 Accepted: Oct. 22, 2001.

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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[6]. This means that the physical properties of materials with azobenzene group can be controlled by light irradiation

The fourth generation dendrimer contained in photoisomerizable 48 azobenzene units (G4-48 Azo) on the periphery was synthesized in an attempt to construct a photoswitchable molecular device system. Fig. 1 represents the chemical structure of G4-48 Azo dendrimer.



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

2.2 Interfacial Characteristics

We investigated the behavior of the G4-48 Azo dendrimer at the air/water interface by Langmuir technique. The two barrier type trough (NIMA, UK) was used to investigate the interfacial behavior. The experimental condition was carefully selected to avoid the possible error. The concentration of solution for spreading is a very important factor because of the aggregate of dendrimer molecules. In this experimental, the concentration of 0.58×10^{-4} [mol/ml] has been used without any comment. The spreading volume was fixed to 30 [μ l]. 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 the back process. The incident light was quantitatively controlled by slit.

3. Results and Discussion

3.1 Monolayer behavior

The π -A isotherm of the G4-48 Azo dendrimer is shown in Fig. 2 and display a linear increase in surface pressure upon compression, indicating the formation of monolayers at the 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 limitation of the trough area. Also they have linear increase of surface pressure during compression. It is suggested that unclear phase separation of G4-48 Azo dendrimer be originated from the weak interaction among dendrimer molecules, no arrangement, and no orientation at the air/water interface.

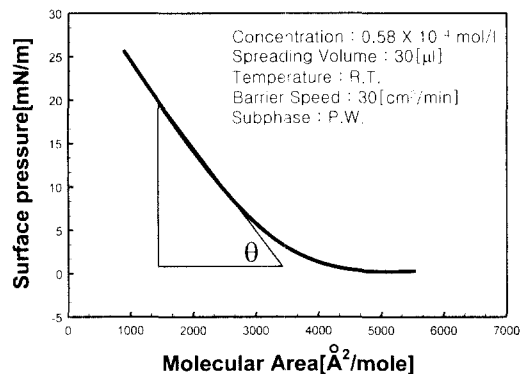


Fig. 2 The π -A isotherm of G4-48 Azo dendrimer at the air/water interface.

The surface pressure began to rise at about 4,000 [$\text{\AA}^2/\text{mole}$]. 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 the trough area. These variables were affected by the barrier speed and showed different values by cyclic π -A isotherm. We could evaluate the monolayer state by θ and maximum pressure.

Fig. 3, 4 show the maximum pressure and θ shift, which were investigated by repeating compression and decompression of barrier. The maximum surface pressure was gradually increased and saturated by cyclic compression and decompression. θ was linearly increased. This suggests that the monolayer of G4-48 Azo dendrimer has a liquid like transient state at spreading and then

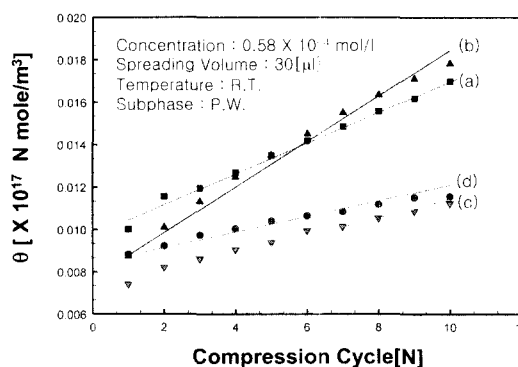


Fig. 3 Slope of π -A isotherm of the G4-48 Azo dendrimer (barrier speed : (a)30[cm²/min], (b) 50[cm²/min], (c) 70[cm²/min], (d) 100[cm²/min], respectively sampling interval from 10mN/m to 20mN/m)

reaches a steady state and a well packed monolayer after the cyclic compression and decompression process.

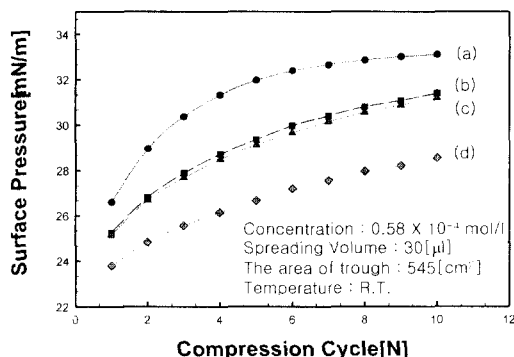


Fig. 4 Maximum pressure of π -A isotherm of the G4-48 Azo dendrimer (barrier speed : (a)30[cm²/min], (b) 50[cm²/min], (c) 70[cm²/min], (d) 100 [cm²/min], respectively sampling interval from 10mN/m to 20mN/m).

3.2 Photoisomerization process at Langmuir trough

Fig. 5 represents the photo-switching process of the G4-48 Azo dendrimer monolayer at the air-water interface. By irradiation of 365 [nm] light, the surface pressure was increased, which was originated by the photo-isomerization process of the azobenzene group on the periphery from trans to cis form. The increase of the dipole moment (μ), which may increase the interaction among G4-48 Azo dendrimer molecules, made an important role on surface pressure shift.

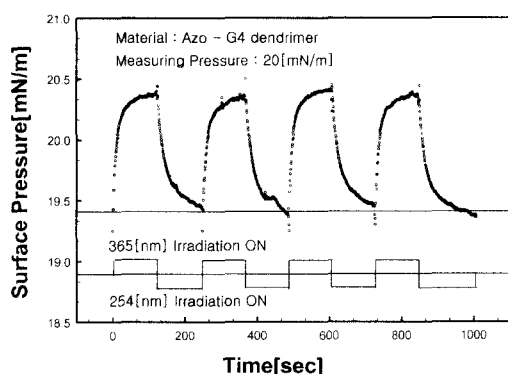


Fig. 5 The optical response of the G4-48 Azo dendrimer at the air/water interface. (measuring interval:2 [min], measuring pressure: 20 [mN/m])

3.3 Changes of absorbance spectrum

Fig. 6 presents the UV-vis spectra of the G4-48 Azo dendrimer LB monolayer by 365 [nm] irradiation. From Fig. 6, we can see that the absorbance in the UV region decreases with the increases of the UV irradiation time, but the peak at 350 [nm] in the LB monolayers is not

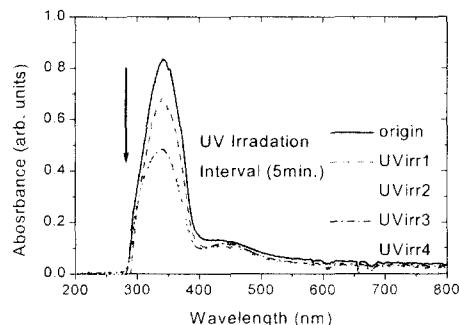


Fig. 6 Spectral changes for the G4-48 Azo dendrimer monolayer caused by UV irradiation for far-field optical modification, but not peak shifts. The irradiation interval is 3 min.

shift until four irradiation cycles. The results indicate that the Azo dendrimer could be photoisomerization reactions.

On the other hand, in the case of the optical absorption spectra of the G4-48 Azo dendrimer LB films by the heat treatment at 70 [°C] in the air, both of the unshifted absorption bands decrease and a monomer absorption peak over 400 [nm] increases instead. Also, the decreases of absorbance peaks and photoisomerization behavior was no longer observed in the heat treated G4-48 Azo dendrimer LB films after seven cycles.

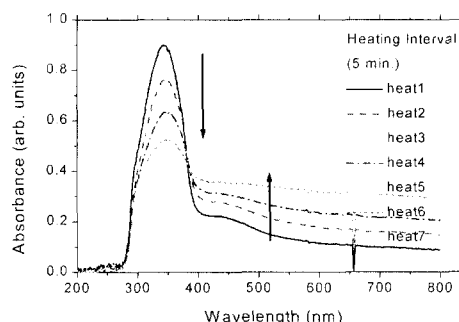


Fig. 7 Spectral changes for the G4-48 Azo dendrimer monolayer after heat treatment at 70 [°C].

3.4 Surface morphology

Fig. 8 shows an AFM image of G4-48 Azo dendrimer on Si surface. G4-48 Azo dendrimer monolayers produced aggregate formation of various sizes and shapes randomly placed on the surface. On the other hand, The solid aggregates of G4-48 Azo dendrimer form dispersed arrays of a network of patches 1-2 μm high. These results indicate that the azobenzene functionalized G4-48 Azo dendrimer is unstrongly adsorbed on the Si surface. The addition of the azobenzene group coagulates G4-48 Azo dendrimer and forms a network of dendrimers.

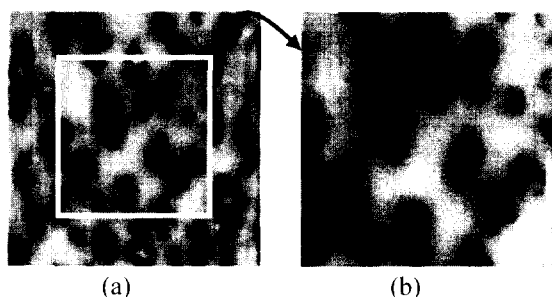


Fig. 8 Surface topography of the G4-48 Azo dendrimer LB film. (a) 100×100 [μm^2], (b) 60×60 [μm^2]

4. Conclusion

We investigated the monolayer behavior using the Langmuir trough. We measured the surface pressure shift originating from the photo-isomerization of azobenzene units on the periphery of dendrimers. As a result, the monolayer of dendrimers with the azobenzene group showed the reversible photo-switching behavior by the isomerization of the azobenzene group on their periphery. The results indicate that the Azo dendrimer could be photoisomerization reactions. In AFM surface morphology, the addition of azobenzene group coagulates G4-48 Azo dendrimer and forms a network of dendrimers.

Acknowledgment

This work was supported by the National Program for Tera-level Nanodevices of the Ministry of Science and Technology as one of the 21 century Frontier Programs.

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