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Optical Behavior and Surface Morphology of the Azobenzene Functionalized Dendrimer in Organic Thin Monolayers

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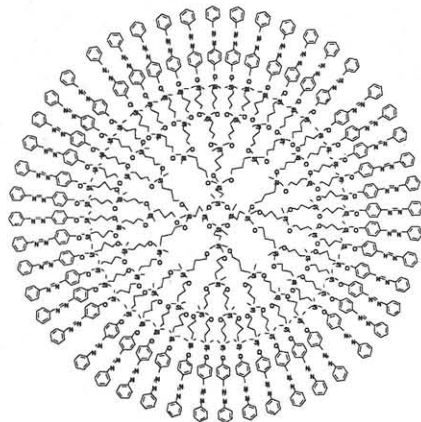
1. Introduction

Spectral change of azo molecules has been investigated extensively in the LB monolayers. Drastic morphological changes to the thin films were also noted. However the thermochromic behaviour of azobenzene functionalized dendrimer(G4-48Az) Langmuir-Blodgett(LB) monolayers has not yet been adequately explained [3]. G4-48Az dendrimer containing photoisomerizable 48 azobenzene groups on the periphery was synthesized in an attempt to construct photoresponsive molecular device system. We investigate the monolayer forming properties of four generation of azobenzene containing dendrimer by LB method.

In this study, we present spectroscopic results of the G4-48Az in a solution and films, that supported the view that the dendrimer became a optical high-gain media, following the light irradiation and spectrum narrowing.

2. Experimental

Photoresponsive switching property of azobenzene containing dendrimer caused by photochemical trans-cis(E/Z) isomerization of the azo moiety. The dendrimer containing 48 azobenzene was synthesised by the use of siloxanetetramer (2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, ((CH₂=CH)MeSiO)₄) as the core molecule, hydrosilation



Scheme 1 G4-48Az, azobenzene functionalized dendrimer

with HSiMe_nCl_{3-n} and alcoholysis with allyl alcohol [4]. By the two alternative processes, hydrosilation and alcoholysis, the dendrimer carried out up to the fourth generation with 48-Cl on the periphery. And then, G4P-48-Cl dendrimer was terminated with 4-phenylazophenol. The chemical structure was confirmed by IR, NMR, UV-vis spectroscopy and elemental analysis. (Scheme 1).

Samples were prepared using the molecular assembly technique developed by Kuhn *et al* [5]. The subphase was distilled water of pH 6 and the subphase temperature was 20 °C during deposition. The substrate, a quarter of an ordinary glass microscope slide, was coated with 5 monolayers of archidic to give a hydrophobic surface or O₃ cleaning to give a hydrophilic surface.

3. Results and discussion

Figure 1 shows representatively the increase or decrease of surface pressure of G4-48Az monolayer with irradiation time and wavelength. When the G4-48Az monolayer were spread on at the air-water interface, strongly light reaction was found by a increase of surface

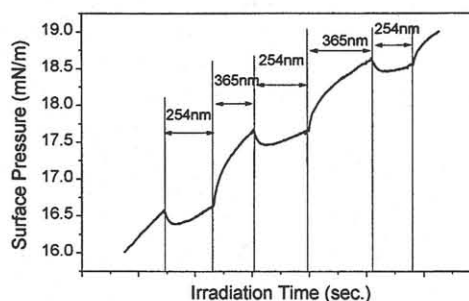


Fig. 1. Behavior of G4-48Az monolayer by UV irradiation

pressure.

The morphology of LB monolayers of G4-48Az was investigated using AFM. Two types of circular domains are seen in Fig. 2: the larger ones with a diameter of

20-30 μm and the smaller ones with a diameter of 5-10 μm . The larger domains have irregularly shaped structures on the top while the smaller ones are free from such defects. When the concentration of the spreading solution is five times higher, only the larger domains are formed (Fig. 2). Some domains have lower regions in the center. This suggests that the number of nuclei for the domain formation on the water surface is larger for spreading solutions with higher concentration. These may be formed by the slow evaporation of the solvent at room temperatures. These results also should be related to the difference in the surface pressure of deposition and the spreading concentration of the materials.

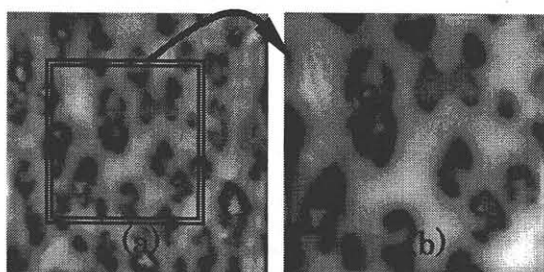


Fig. 2. AFM image of monolayer, scan size is 100 \times 100 μm (a), 60 \times 60 μm (b),

The G4-48Az LB monolayers prepared under the same condition as in Fig. 1 were irradiated with UV light and the subsequent photoreactions were monitored using UV-vis absorption spectroscopy. Fig. 3(a) shows the change in the absorption spectra. Before irradiation, the absorption bands of G4-48Az LB monolayers are seen at ca. 350nm. In the initial regime of the UV irradiation, the main photoreaction is the photoisomerization of trans to cis. The G4-48Az LB monolayers were stable at room temperature even after one month.

Figure 3(b) shows examples of the spectral changes induced by heat treatment. The data were taken on a single-monolayer films by employing heat cycles of 5 min. at 70 $^{\circ}\text{C}$. It is evident that the absorbance band is dissociated by the heat treatment; the absorption maximum, initially located at 350nm. But, in the optical absorption spectra of same LB monolayers by UV irradiation, only photoisomerization of G4-48Az LB monolayers, that is decrease of absorbance peak without change spectral shape.

4. Conclusion

This study demonstrates that the intensity of the absorption peak can be controlled by the UV irradiation and heat treatment conditions of LB monolayers. A large morphological change was noted and flower-like three-dimensional structures appeared from the large

domains but not from the smaller domains. This suggests that the optical behavior and the morphological change are affected by the functional group and symmetric chain.

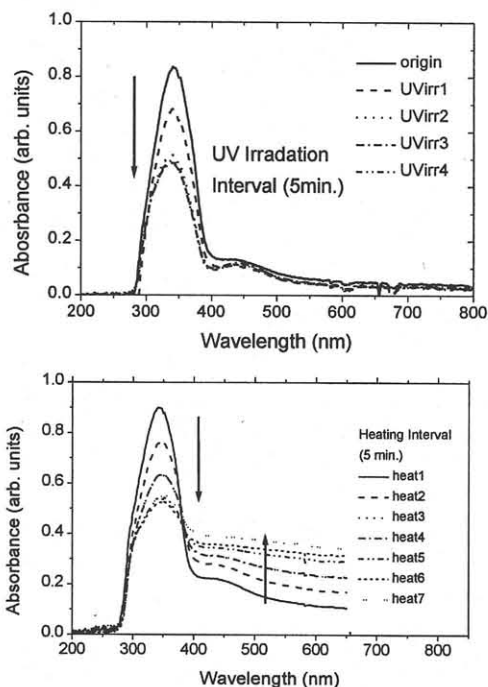


Fig. 3. Spectral changes of UV irradiation (a) and induced by heating at 70 $^{\circ}\text{C}$ (b) in azo-dendrimer monolayer by UV-vis spectroscopy

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References

- [1] G.R. Newkome, Moorefield, C.; Vögtle, F., *Dendritic Macromolecules: Concepts, Syntheses, Perspectives*; VCH: Weinheim, 1996.
- [2] K. Tsuda, G.C. Dol, T. Gensch, J. Hofkens, L. Latterini, J.W. Weener, E.W. Meijer and F.C. De Shryver, *Am. Chem. Soc.* **2000**, *122*, 3445.
- [3] D.M. Junge and D.V. McGrath, *J. Am. Soc.* **1999**, *121*, 4912.
- [4] (a) C. Kim, A. Kwon, *Synthesis* (1998) 105-108, (b) C. Kim, M. Kim, *J. Organomet. Chem.* **563** (1998) 43-51, (c) C. Kim, I. Jung, *Inorg. Chem. Commun.* **1** (1998) 427-430.
- [5] H. Kuhn *et al*, *Techniques of Chemistry*, Wiley, New York, Vol.1, Part III3, 577.