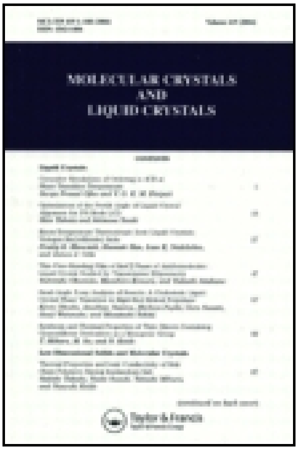

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Functional Dendritic Macromolecules: Preparation and Optical Properties

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FUNCTIONAL DENDRITIC MACROMOLECULES: PREPARATION AND OPTICAL PROPERTIES

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Abstract Repetitive coupling reactions of branched azobenzene derivatives resulted in dendritic macromolecules, or “wedges” and “dendrimers”. These molecules were designed to incorporate aliphatic and polar units in order to prepare Langmuir-Blodgett (LB) films. Atomic force microscopy (AFM), absorption spectroscopy, and second harmonic generation (SHG) measurements revealed structural properties of the LB films in terms of size, aggregation, and orientation. AFM measurements revealed that growth of the branches increased as a function of the generation. In absorption spectroscopy and SHG measurements, results showed that wedges had an unsymmetric orientation in the LB films, while dendrimers had a symmetrically functionalized structure.

INTRODUCTION

Artificial preparation of three-dimensional organizations with desired structures and physical properties has aroused much interest recently. Dendritic macromolecules, also called “dendrimers”, are a novel type of such organization, and have been proposed as an important new concept in macromolecular design.[1] Dendrimers display a treelike architecture having highly branched chains and many exterior end groups. In the last decade there has been explosive growth in the studies of new types of dendrimers because of their unique structural properties and potential utilities. Through judicious choice of building blocks and functional groups, one can precisely modify the physical and chemical properties, such as sharp, dimension, polarity, solubility, and glass transition temperature.[1]

Figure 1 shows our synthetic concept to give functional dendrimers. The compounds consist of a branched mixture of azobenzene repeating units (**2**) and alkyl chain exterior end groups (**1**). Repetitive reactions, referred to as a convergent synthetic method,[2] cause the growth of successive layers or “generation”. Compounds (**1-6**) are parts, called “wedge”, and compounds (**8-10**) are dendrimers with first to third generation. In this study, we prepared thin films of wedges and dendrimers using the LB technique and discussed their size, aggregation, and orientation by means of AFM, polarized absorption spectroscopy, and SHG measurement.

EXPERIMENT

Figure 1 shows the strategy of synthesis which involves the repetitive coupling and deprotection reactions.[3] Structures and purity of the products were confirmed by ^1H and ^{13}C NMR, SEC, and TOFMS techniques. LB films were prepared from a chloroform solution on a Langmuir trough (NL-LB240N-MW). The films were then transferred onto substrates, such as glass and silicon wafers at a surface pressure of 15 mN/m. UV-vis absorption spectra were measured using a Hitachi UV spectrometer. Surface images of the LB films were measured by an atomic force microscope (Nano Scope III) in a tapping mode. Surface symmetrical properties of the LB films were discussed by SHG measurements. Detailed SHG experiments are described in reference 4.

RESULTS AND DISCUSSION

The stable monolayers of wedges and dendrimers on water surface were confirmed by the surface pressure and area curves, and were transferred on the solid surface. The transfer ratios were unity. The surface structure of the one-layer LB films prepared on silicon wafers was determined by AFM. AFM images showed uniform surface morphology in the range of a few micrometers for all the LB films. However, cracks in the films could scarcely be observed. The topological profiles in these areas gave the height differences between the film surface and the bare substrate, which corresponded to the thickness of the LB films (Table I). As expected, growth of wedges in terms of size increased as a

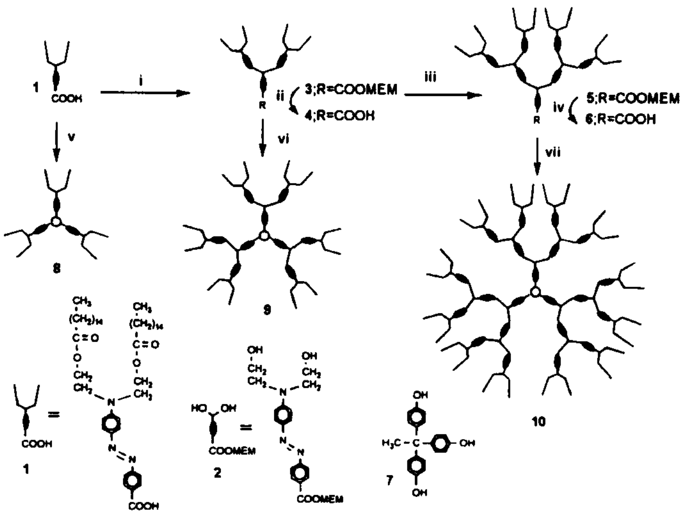

FIGURE 1 Preparation of wedges and dendrimers. *Reactions:* (i) and (iii) **2** and DCC in CH_2Cl_2; (ii) and (iv), HCl in THF; (v), (vi), and (vii) **7** and DCC in CH_2Cl_2.

function of the generation from first to third. On the other hand, the LB films of dendrimers showed a monomeric thickness of about 2 nm for all the cases.

Orientation of azobenzene units in the LB films was determined by polarized absorption spectrum measurement. In Figure 2a, transmitted absorption intensities at the band due to π–π* transition of azobenzene units were measured as a function of the polarization. In the LB film (**1**), the maximum absorption band was observed at 375 nm (Table I), and the orientation was evident in the plane parallel to the LB film dipping direction. Since the azobenzene derivatives used in this study have maximum absorption at 430 nm in solution, a shift of the absorption band is due to the aggregation of the azobenzene units in the LB film. The LB film (**2**) was optically isotropic in the surface plane. The maximum absorption band was observed at 410 nm, which was slightly shorter than that observed in solution. In the LB film (**3**), the absorption band was observed at 430 nm. The orientation was perpendicular to the LB film dipping direction. On the other hand, there is no evidence of the orientation in the LB films of dendrimers (**8-10**) as shown in Figure 2b.

Surface symmetry of wedges and dendrimers were determined by SHG measurement. Transmitted SH light intensities in a p-polarization from the LB films were measured by both p- and s-polarized fundamental light. This technique is sensitive to a π-electron organic adsorbate, having a noncentrosymmetric dipole orientation parallel to a surface normal.[4] In Table I, SH light intensities are compared with the reference of a quartz plate. SHG was observed in the LB films of wedges (**1**, **3**, and **5**). Since the π-π*

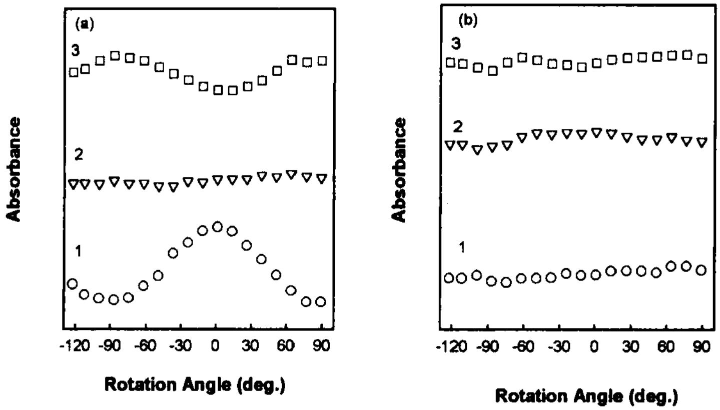

FIGURE 2 Orientation of azobenzene units in the LB films determined by polarized absorption spectroscopy. Rotation angle of 0 deg. is parallel to the LB film dipping direction. (a) wedges **1** (plot 1), **3** (plot 2), and **5** (plot 3), and (b) dendrimers **8** (plot 1), **9** (plot 2), and **10** (plot 3).

transition of the azobenzene unit is only contributed to SHG, the most probable structure of the LB films is one in which the polar head group of the focal point is attached to the substrate, while end groups of alkyl chains align in the exterior surface. On the other hand, SH light intensities from the LB films of dendrimers (**8-10**) were negligibly small, suggesting a centrosymmetric molecular system. SHG results suggest that the qualitative direction of the dipole moment in wedges is unsymmetric along the branching progression, while dendrimers have symmetrically functionalized branched chains, where the branching progression radiated from interior core.

TABLE I One-layer thickness and optical properties of the LB films.

compounds	thickness (nm)	λmax (nm)	SHG[a]	
			p-p[b]	s-p[b]
1	1.17	375	0.8e-4	0.5e-5
3	1.82	410	1.7e-4	1.1e-5
5	2.12	430	0.9e-4	0.6e-5
8	2.17	430	2.3e-7	1.0e-9
9	1.77	430	2.4e-7	2.5e-7
10	2.12	430	2.5e-7	0.2e-9

a: SHG was normalized by a quartz plate ($\chi_{iii}=1.9\times10^{-9}$ esu) at a coherent length.
b: p-p and s-p indicate SHG of p-polarization by p- and s-polarized fundamental light.

In conclusion, these results have demonstrated the ability to prepare the LB films of dendritic macromolecules, having unique structural properties in terms of size, aggregation, orientation, and symmetry. Application of this study may be further extended to other functional dendritic macromolecules giving novel physical and chemical properties.

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