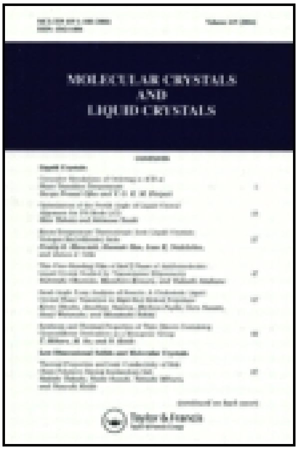

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Photochromic Langmuir-Blodgett Film for a Liquid Crystalline Copolymer with Azobenzene and Cholesterol Side Groups

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PHOTOCHROMIC LANGMUIR-BLODGETT FILM FOR A LIQUID CRYSTALLINE COPOLYMER WITH AZOBENZENE AND CHOLESTEROL SIDE GROUPS

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Abstract Langmuir-Blodgett film for a newly synthesized photochromic liquid crystalline copolymer (P-CO3) containing azobenzene side groups was prepared. The multilayer structure was characterized and was similar to the smectic phase in bulk material. The UV-visible absorption spectra measurements show reversible photoinduced structural changes in the deposited film.

INTRODUCTION

Azobenzene derivatives' monolayers and LB films have been extensively studied for their application potentials in optics, optic-electronics and sensor field.[1-3] However, studies on reaction behaviour of *cis/trans* photoisomerization (*i.e.* photochromism) of azo-benzene moieties in LB films are limited because, in most systems, it is unreactive or shows only a one-way reaction due to aggregation and/or restricted environment. To improve such irreversibility, co-polymerization is an effective path. In this paper we investigate LB film structure of a newly synthesized liquid crystalline (LC) co-polymer composed of mesogenic cholesterol side chains and azo-benzene side groups.

EXPERIMENTAL

The chemical structure of P-CO3 is shown in Figure 1. Its synthesis and characterization are discussed elsewhere.[4] Observations of the spreading behavior of P-CO3 and LB film preparation were carried out in the same way as previously described.[5]

Sufficient care was taken, by working in dimmed red light, to keep the material in the *trans* form during the spreading and film deposition. Low-angle X-ray diffraction patterns were obtained using a D/MAX-γB X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm). A HP 8451A spectrometer was used to take UV-visible absorption spectra. Photoirradiation for LB film was performed with a 200-W high-pressure Hg lamp(ORIEL). UV (360 nm) and visible (470 nm) light were selected by band pass and cut-off filters respectively.

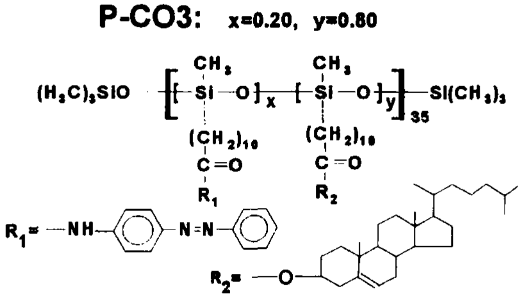

FIGURE 1 Chemical structure of the P-CO3.

RESULTS AND DISCUSSION

Surface Pressure-Area Isotherm

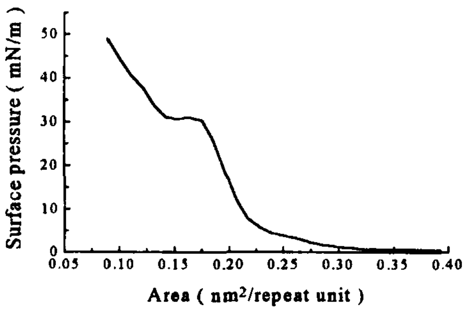

FIGURE 2 Surface pressure-area isotherm for the P-CO3 monolayer on water surface.

The investigated material could form stable monolayer on the pure water surface. Figure 2 shows the surface pressure-area isotherm of the P-CO3 monolayer. The limiting molecular area for each repeating unit is around 0.23 nm^2 that is somewhat smaller than that calculated according to the cross-sectional area of each side chain and their proportions. This might mean that the azo-benzene chains were arranged in the space constructed by the plane of the cholesterol groups (Chol). Under the surface pressure of 20 mN/m, the P-CO3 monolayer can be successfully transferred onto glass plates with deposition ratios close to unity. Y-type LB films were formed.

Structure Characterization for the P-CO3 LB Film

The low-angle X-ray diffraction profile of the P-CO3 LB film exhibited a clear Bragg peak that indicates the film bears a well-defined layer structure. The layer spacing is about 3.34 nm similar to that of the smectic layers in the bulk phase and corresponds to the length of the cholesterol side chain. Considering the low LC transition temperature of P-CO3, we consider that it is most probably due to the rearrangement of the side chains after the film deposition and forming smectic-like layer structure.

The orientation of the side chains characterized by the polarized IR spectra provides further evidence to support such inference. The angles calculated according to Vandevyver's formula[6] show that the side chains are tilted in the film. The schematic picture for the possible structure of the P-CO3 LB film is depicted in Figure 3.

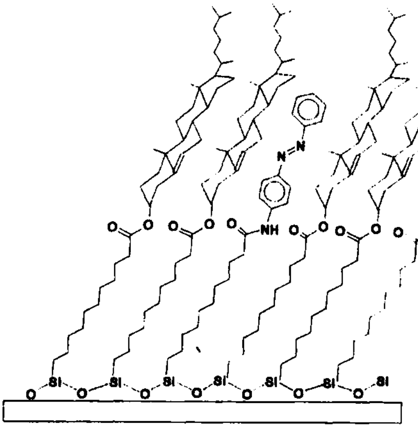

FIGURE 3 The possible structure for the P-CO3 LB film.

Photochromism Measurement of P-CO3 LB Film

Figure 4 is the UV-visible absorption spectra for P-CO3 LB film pre-irradiated with light of different wavelength. The peak at about 360 nm corresponds to the $\pi \rightarrow \pi^*$ transition of the *trans* azo-benzene chromophore. Upon different light irradiation the chromophore shows *cis*/*trans* reversible and repeatable photoisomerization. Such reversible photochromism should be closely related to the reduction of aggregation of the azo-chromophores and relative stable film structure supplied by mesogenic Chol. This is because the large ring plane of the Chol could supply the free space for photoisomerization to ensure ordered film structure as shown in Figure 3.

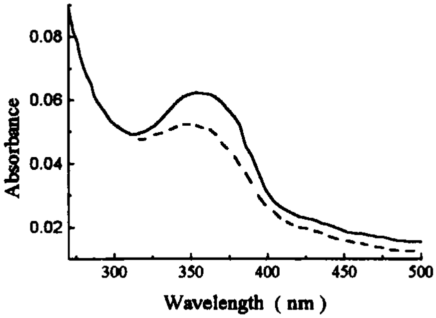

FIGURE 4 UV-visible absorption spectra of the P-CO3 LB film. Solid and dashed curves indicate data for the visible light (470 nm) pre-irradiated and UV light (360 nm) pre-irradiated LB films, respectively.

CONCLUSIONS

Reversible photoisomerization of azo-benzene LB film was realized by forming copolymer with mesogenic Chol. The Chol could stabilize the monolayer and prevent azo-benzene moieties from aggregating to a large extent probably due to the steric hindrance effects. It also constructs stable space for photoisomerization to proceed. This photochromic LB film would be useful for optical information storage.

Acknowledgments

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REFERENCES

1. B. Tieke, Adv. Mater., 2, 222 (1990).
2. Z. F. Liu, K. Hashimoto, and A. Fujishima, Nature, 347, 658 (1990).
3. M. Sawodny, A. Schmidt, M. Stamm, W. Knoll, C. Urban and H. Ringsdorf, Polym. Adv. Technol., 2, 127 (1991).
4. Q. Z. Zhang and Y. Wang, Proceedings of International Conference on Liquid Crystalline Polymers (Beijing, 1994), p.112.
5. X. Chen, Q. B. Xue, K. Z. Yang and Q. Z. Zhang, Langmuir, 11, 4082 (1995).
6. M. Vandevyver, A. Barraud, R. Teixier, P. Maillard and C. Gianotti, J. Colloid Interface Sci., 85, 571 (1982).