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***In situ* Photopolymerization of Polymerizable Liquid Crystal at the Air-Water Interface**

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The π -A isotherms and transfer characteristics of synthesized, polymerizable liquid crystals spread at the air-water interface were investigated. The liquid crystals mixed with a poly(amic acid) salt were spread, and the mixed monolayers were polymerized by UV-irradiation. The *in situ* polymerization was monitored by a multi-channel photo detector.

Keywords: Langmuir-Blodgett; monolayer; liquid crystal; polymerization

INTRODUCTION

The Langmuir-Blodgett(LB) method has been of interest as a powerful technique for fabricating ultrathin organic films^[1]. Those liquid crystalline molecules which have a rod-shaped amphiphilic moiety of aromatic cyano derivatives have been found to form monolayers^[2].

In this paper, the monolayers of liquid crystalline molecules which have cyano biphenyl mesogen and polymerizable vinyl group of various chain lengths and the *in situ* polymerization of the molecules in the presence of the poly(amic acid) alkylamine salt were investigated for possible applications as alignment layers in the liquid crystal display.

EXPERIMENTAL

Polymerizable liquid crystal samples, *n*-[(4-cyano-4'-biphenyl) oxy] undecanyl vinyl ether] (CN-*n*-M, *n*=3,8,10,11), as in Figure 1, were synthesized as reported previously^[3-4]. Poly(amic acid) (SE150, Nissan Co.) was used in the formation of mixed films, which can be spread on the water surface with an alkylamine (*N,N*-dimethyloctadecylamine)^[5]. LB experiments were performed with KSV 3000 and KSV 5000. The films on the water subphase were polymerized by UV ray (50W, $\lambda_{\text{max}}=254\text{nm}$), and were monitored by a multi-channel photo detector with optical fibers (MCPD-1000, Otsuka Electronics).

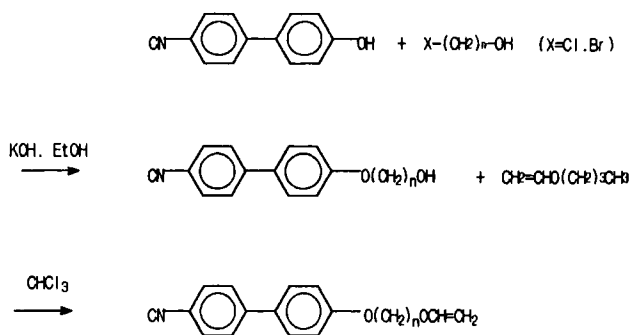


FIGURE 1 Synthesis of CN-*n*-M series (*n* = 3,8,10,11).

RESULTS AND DISCUSSION

Figure 2(a) shows the surface pressure and area (π -A) isotherms of CN-*n*-M. In this Figure, CN-8-M and CN-10-M underwent phase transition, and the limiting areas of CN-8,10,11-M were approximately 10, 13, 17 Å² molecule⁻¹, respectively. All of the limiting areas are much smaller than those of common amphiphiles. It is likely to have a stable layered structure induced from the

balance between their mesogenic interactions and hydrophobic hydrocarbon interaction between the molecular chains^[6].

The films mixed with PAAS were spread to compensate the transferability and to be applied to LCD alignment. Although CN-n-M alone could be polymerized by UV irradiation, the mixed film of CN-n-M and PAAS was more easily polymerized by UV-irradiation at 25 mN/m. Because PAAS causes the alkyl chain of CN-n-M to stand vertically, the vinyl groups easily come in contact with each other. During polymerization, the absorption spectra of the mixed monolayers were measured by a multi-channel photo detector right above the surface. Figure 2(b) shows the UV spectra of the equimolarly mixed films of CN-3-M/PAAS changing with the UV irradiation time. The maximum peak around 265nm disappeared after UV irradiation, which indicates that the photochemical polymerization reaction had occurred in the film. The reaction showed an order of 1.5, as in Figure 3(a), which was found to be reasonable for classical photopolymerization.

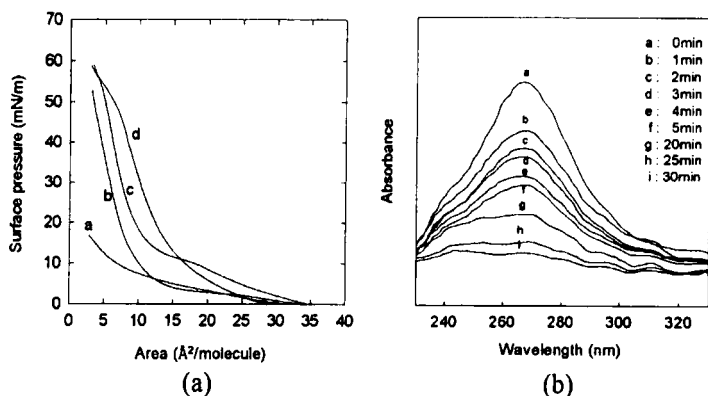


FIGURE 2 (a) The π -A isotherm of CN-n-M series (25°C) (a; CN-11-M, b; CN-10-M, c; CN-8-M, d; CN-3-M), (b) UV spectra of the mixed monolayers of CN-3-M/PAAS changing with the UV irradiation time.

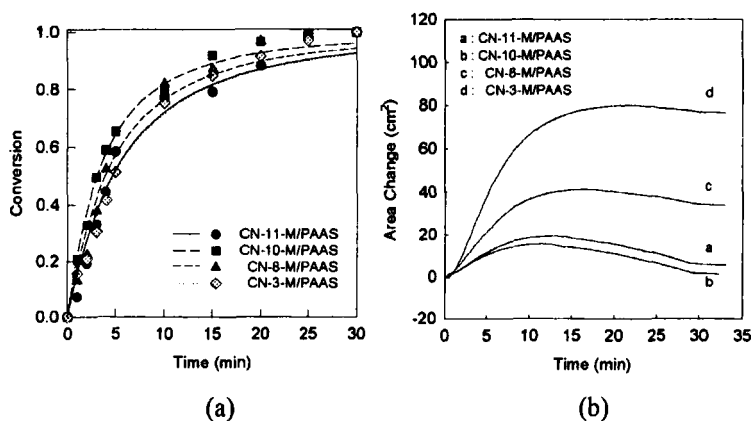


FIGURE 3 (a) Extent of reaction with UV irradiation time, (b) Area change of the mixed films with UV irradiation time.

Figure 3(b) illustrates the area changes of the mixed films at a constant surface pressure of 25mN/m during UV irradiation. The increase of the area in the early stage indicates that phase separation has occurred, and the decrease of the area in the next stage is resulted from the cleavage of the PAAS chain during UV irradiation. As shown in Figure 3(b), the molecules with high viscosity can pin phase separation in the early stage of polymerization. The polymerized films were well transferred as a Y-type LB film, and the films were confirmed by FTIR spectroscopy and ellipsometry.

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