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MONOLAYERS OF POLYMERIZABLE LIQUID CRYSTAL AND *IN SITU* INTERFACIAL POLYMERIZATION AT THE AIR-WATER INTERFACE

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Abstract The π-A isotherm and transfer characteristics of polymerizable liquid crystals spread at the air-water interface were investigated. The limiting areas of n-[(4-cyano-4'-biphenyl)oxy] alkyl vinyl ether (CN-n-M) homologues series of n = 8, 10, and 11 were about 10, 13, and 17 Å^2/molecule respectively, and smaller than the area of hydrophilic cyanobiphenyl group. All the CN-n-M formed apparently stable monolayers and the transferred type of pure CN-11-M monolayer on the hydrophilic surface was Z-type for the first several layers. The monolayer of a mixture with poly(amic acid) salts at 25 mN/m was polymerized by UV-irradiation.

INTRODUCTION

The Langmuir-Blodgett(LB) method has been of interest as a powerful technique for fabricating ultrathin organic films for many applications to electronic devices[1]. Among others, the alignment layers of liquid crystals can be fabricated by transferring the proper monolayers. Even though many different materials are reported, not much attention has been paid for the monolayer and self-organization of liquid crystal[2-4]. The rod-shaped amphiphilic liquid crystals also have been found to form monolayers[4].

In this paper, we report the monolayer behaviors of polymerizable liquid crystals which have cyano biphenyl mesogene. Then we will fabricate liquid crystal cell using these films or mixed film with polyimide, and investigate the effects of conditions of monolayer on the formation of monodomain. The ability of LB film formation on various substrates and UV polymerizations of polymerizable liquid crystals at air-water interface are also reported.

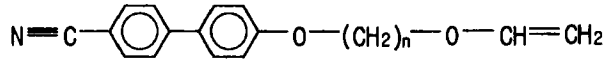
EXPERIMENTAL

Polymerizable liquid crystal samples n-[(4-cyano-4'-biphenyl) oxy] undecanyl vinyl ether] (CN-n-M) were synthesized as reported elsewhere[5-7]. Figure 1 shows the structure of CN-n-M, where n corresponds to 3,8,10, and 11. All of CN-n-M compounds were spread onto the pure water surface as 1 mM chloroform solutions. All experiments were carried out at room temperature with KSV 3000 and constant perimeter type trough. Contact angles on the films were measured with the drop method. UV polymerization of the mixed monolayer of CN-11-M and poly (amic acid) alkylamine salt (PAAS) at air-water interface was performed, keeping the surface pressure at 25 mN/m for 2 hours.

RESULTS AND DISCUSSION

Figure 2(a) shows the surface pressure and area (π-A) isotherms of CN-n-M. In this figure, all the CN-n-M form reproducible monolayer, and CN-8-M and CN-10-M show a phase transition. The limiting areas of CN-8,10,11-M were about 10, 13, 17 $Å^2$ molecule^{-1}, respectively. All of the limiting areas are much smaller than that of cyano biphenyl, 25 $Å^2$. Further, it is also interesting that CN-n-M with a long alkyl chain has a large limiting area. Therefore, the cyano biphenyl slightly tilted and stacked packed in edge-on configuration, and the mesogenic interactions may be balanced by a hydrophobic hydrocarbon interaction between chains[8].

The Subphase pH affected the stability and the limiting area of monolayers. In Figure 2(b), the isotherm at pH 9 is very stiff and gives a small limiting area, while at pH 3.5 and 5.5 the isotherms are almost identical. The orientation and packing of cyanobiphenyl group determines the limiting area. As cyano group is hydrolyzed at high pH, molecules tend to stand vertically.



n = 3, 8, 10, 11

FIGURE 1. Synthesis of n-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether]

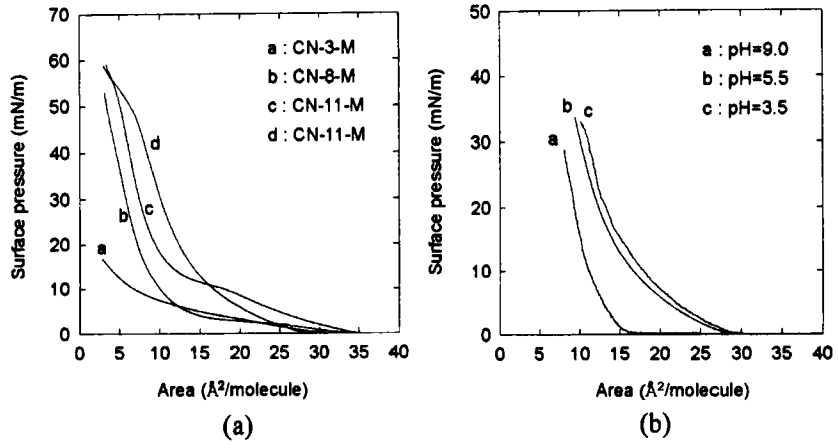


FIGURE 2. (a) The π-A isotherm of CN-n-M series (at 24 °C, pH=5.5)
(b) pH effect on CN-11-M monolayer (at 24°C)

The CN-11-M was not well deposited on both hydrophilic and hydrophobic substrates such as ITO-polyimide coated, Si wafer, glass, and silanized glass at a dipping speed 5 mm/min, and at 15mN/m. For the first several layers, deposition ratios were about 0.8 on a hydrophilic substrate at a dipping speed 5 mm/min. Z-type deposition, based on dipole-dipole interactions between adjacent layers[8], was achieved on the hydrophilic substrate for several layers, but not on the hydrophobic substrate. After depositing the first layer, the contact angles of each sample did not change with the number of layers. Initially, the contact angle on the ITO-polyimide coated glass was about 65°, but that on glass was about 17°. The difference between two contact angles of LB films would explain the surface states of films coherently formed at the time of deposition.

The mixed film of CN-11-M and PAAS with same mole ratio was easily polymerized by UV-irradiation at 25 mN/m. Because PAAS causes the alkyl chain of CN-11-M to stand vertically, therefore vinyl groups are easily contacted each other. After polymerization, ten layers are deposited onto the quartz plate. The absorption spectra were measured by UV-spectrometry. Figure 3(a) shows the change of absorption peak at 250 nm as UV polymerization time. The peak indicates the existence of carbon-carbon double bonds. After 2 hours, the peak of double bonds disappeared because of

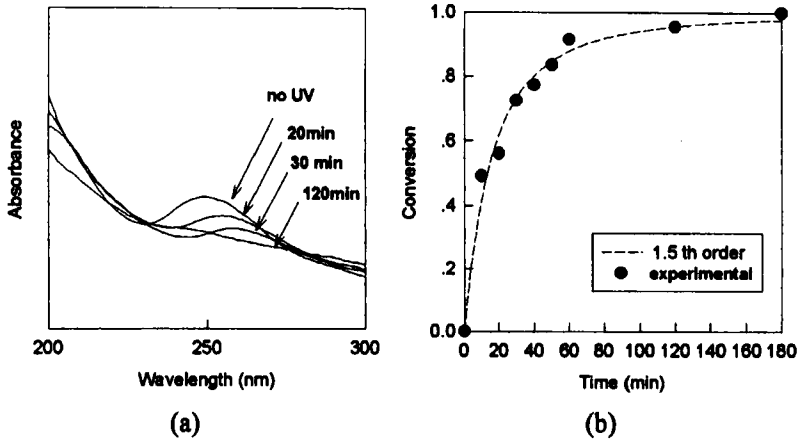


FIGURE 3. (a) UV spectra of the mixed LB films of PAAS and CN-11-M with UV irradiation time (b) Extent of reaction with UV irradiation time

the UV polymerization at the air-water interface. The reaction showed an order of 1.5 which is found to be reasonable for classical photopolymerization in Figure 3(b)

CONCLUSION

The monolayers of liquid crystals with alkyl group and their transfer characteristics were investigated. The limiting areas of CN-8,10,11-M homologues were about 10, 13, 17 $Å^2$ $molecule^{-1}$, respectively. Monolyaer assemblies of CN-11-M on the hydrophilic surface were Z-type for the first several layers. The monolayer of a mixture with PAAS was polymerized by UV-irradiation.

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