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Self-Assembly and Liquid Crystalline Properties of Ionic Polymers and Their Nonionic Family

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Summary: Langmuir-Blodgett (LB) monolayers with an extremely dense azobenzene moiety in a unit area, were prepared using a series of ionic liquid crystalline polymers (ILCPs) and their nonionic family (NLCPs). The isober curves and the compression-expansion isotherms of the ILCPs and NLCPs on water showed that the polymer Langmuir monolayers have good quality. The molecular organization of these polymers on the water surface depended on the length of spacer alkyl chains and the existence of ammonium salts. Low-molecular-weight liquid crystals between the LCP monolayer dipped glass substrates showed a homeotropic alignment.

Keywords: azo polymers; LB films; liquid crystalline polymers; self-assembly

Introduction

Liquid crystalline polymers (LCPs) with embedded mesogenic azobenzene side chains and their thin films have been the focus of considerable attention from the viewpoint of both fundamental aspects and applications. In particular, the photoisomerization reaction of azobenzene induces significant motion of the matrix,[1–3] which shows promise for a wide range of interesting potential applications. For these thin films, the free volume in the matrix is closely related to the functional azobenzene concentration and packing state is of importance.

It is well established that many of azo-LC molecules possess a hydrophobic part and a hydrophilic polar group and are insoluble in water; thus, they are able to form mono- or multilayers at air-water and air-solid substrate interfaces. These methods are practical for preparing condensed and ordered azobenzene containing thin films because the compressed monolayers can provide denced azo-moiety and the resulting layer structure is similar to that of the smectic liquid crystals.[4] In general, amphiphilic copolymers[5] or polyion complexes,[6] which have azobenzene units, were used for the perparation of LB films under the coexistence in surfactants.[7] However, the LB film preparation of amphiphilic homopolymers with azobenzne units are hardly reported.

We are currently developing a thermotropic ionic LCPs (ILCPs) in order to examine the effect of introducing ionic groups into the LC molecules on the LC behavior.[8–11] The ionic group, which is a hydropilic unit, leads to the formation of the micro phase separation; therefore, ILCPs tend to form a smectic layer structure with enhanced thermal stability. Our aim is the reconstruction of this multilayer structure onto a solid surface as an ultra thin film. In this study, we report Langmuir (L) monolayers and Langmuir-Bloddget (LB) films that are formed by azobenzene-containing ionic LC homopolymers and their nonionic family (NLCPs), which are amphiphilic materials. The monolayer structure is retained in order to establish this LB film surface; in addition, we also demonstrated that the ILCP LB monolayer can induce the homeotropic alignment of the 4-cyano-4′-pentylbiphenyl (5CB) LC cell.

Results and Discussion

The bulk LC phase of the ILCPs and NLCPs under investigation was character-

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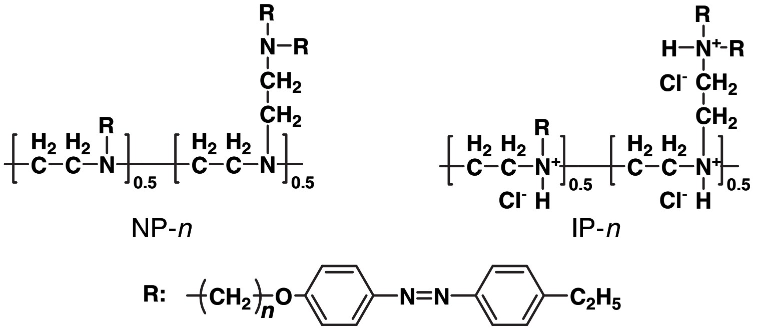

Figure 1.
Structures of nonionic (NP-*n*) and ionic (IP-*n*) liquid crystalline polymers with ethylazobenzene side-groups: $n = 4, 5$: The polymer backbone has equal amounts of primary, secondary, and tertiary amine groups in NP-*n*. The details of the synthesis of all the LCPs used in this study are described in literature.[12]

ized by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The phase transition temperatures of the ILCPs and NLCPs are listed in Table 1. ILCPs with a polyion backbone showed a smectic A phase with a focal conic fan texture and a perpendicular structure. On the other hand, NLCPs, which are amphiphilic, formed only a nematic phase with a schlieren texture. Typical textures and conoscopic figures observed for NP-5 and IP-5 are shown in Figure 2. In ILCPs, the smectic nature of the LC phase is characterized by the presence of reflections in the XRD profile, clearly revealing the lamella structure of the sample. The measured stacking period *d* was longer than twice the extended length of the mesogenic side-group. This finding suggests the existence of an ionic sublayer.[9]

Table 1.
Phase transitions of NP-*n* and IP-*n* liquid crystalline polymers

Sample	Phase transition temp./°C
NP-4	k 4.6 N 75.7 I
NP-5	k 14.0 N 70.1 I
IP-4	g 52.5 M 109.5 SmA 210 (Dec)
IP-5	g 40.3 M 98.0 SmA 202.2 I

I:isotropic, N:nematic, SmA:smectic A, M:mesomorphic, k:solid, g:glassy, Dec:thermal decomposition.

Surface pressure-area (π-A) isotherms of ILCPs and NLCPs were obtained by using a USI (Japan) FSD-300 film balance. The temperature was set by means of a water circulating system equipped with a thermostat. A chloroform solution of a polymer (0.5 mg/ml) was spread on water purified through a Milli-Q filter. After the solvent was evaporated for 30 min, the film was compressed at a speed of 18 cm^2/min to record the surface pressure-area isotherm (25 °C). The isotherms on water for four polymers containing the azobenzene side chain (IP-4, IP-5 and NP-4, NP-5) are shown in Figure 3. It can be observed that on each isotherm, there is an extremely steep region where the surface pressure increases rapidly with compression. The collapse point is considered to be the turning point after this rapid increase. As indicated in Figure 3, the collapse points on the isotherms of IP-4, IP-5, NP-4, and NP-5 are P1 (33.5 mN/m), P2 (32.9 mN/m), P3 (32.4 mN/m), and P4 (25.1 mN/m), respectively. This order indicates that the nature of the spacer length *n* and the ionic group may have a significant influence on not only the bulk LC phase but also the monolayer formation at the air-water interface.

It is a well known fact that the isotherms did not expand represent the tightest packing of azobenzene derivatives and produce the smallest cross sectional area of $0.21 \sim 0.25$ nm^2; [13] this indicates that the

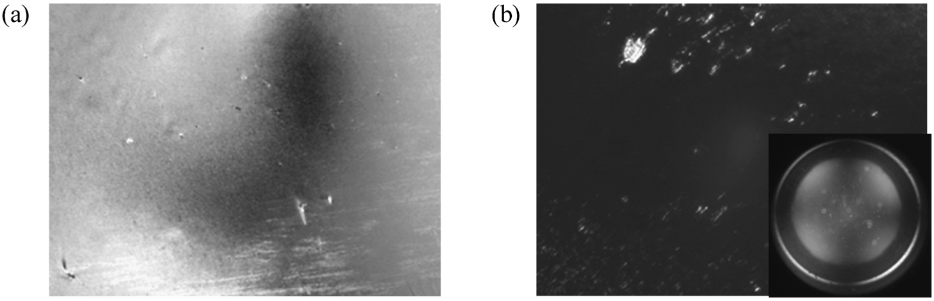

Figure 2.
Typical POM images for LCPs: (a) nematic schlieren texture of NP-5 at 45 °C (b) partially visible small smectic A focal conic fan texture in dark homeotropic alignment and conoscopic figure (inset) of IP-5 at 125 °C.

azobenzene side chain exhibits a closely filled monolayer structure. It can be surmised that the azobenzenes of all the polymers are tightly packed at the collapse pressure with the side chains standing upward on water. The azobenzene side chains are packed very tightly, allowing negligible free space to exist in the monolayer. We hoped that a truly amphiphilic material such as ILCP would be a likely candidate to wet the hydrophilic surface; however, the NLCPs also formed a condensed monolayer. The amphiphilic structures of these LCPs lead to the formation of a highly-dense azobenzene LB thin film.

LC systems modified with Langmuir-Blodgett films of azobenzene derivatives have been reported.[14,15] According to these researchers, such LB films are obtained when the surface of the deposited LB film is sufficiently polar to become wet with water during the upstroke and downstroke of the dipping cycle. In this work, all of the LCPs were transferred onto hydrophilic glass substrates at 21 mN/m at a dipping speed of 0.5 mm/s. The transfer mode was generally found to be Y-type with a transfer ratio close to 1. Figure 4 shows a regular film deposition profile of IP-5. At the first downstroke, the monolayer was not transferred to the hydrophilic glass substrate because of the poor interaction between the hydrophilic glass surface and hydrophobic azobenzene side chains. Next, the upstroke allowed the deposition of the film, which direct the

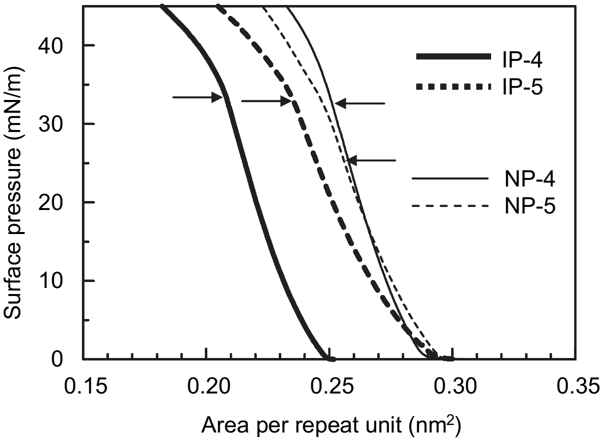

Figure 3.
Surface pressure versus area per repeat unit isotherms for ILCPs and NLCPs.

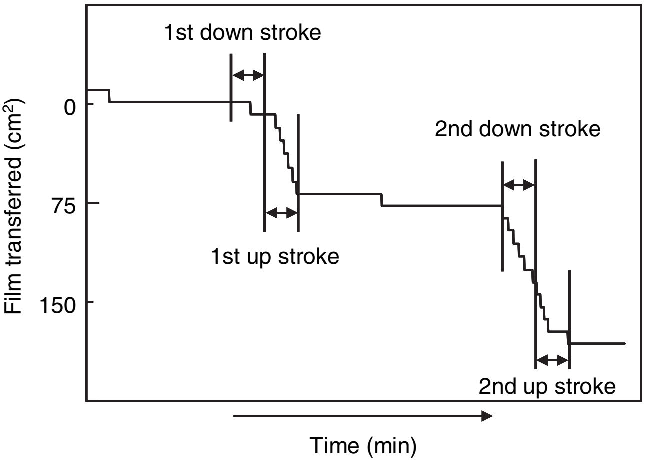

Figure 4.
Deposition trace of the first two deposition cycles for the buildup of the IP-5 LB film on a hydrophilic glass slide.

hydrophilic polymer backbone on the substrate. Consequently, the first step provides a tightly packed azobenzene surface for the glass substrate.

This glass substrate has an ethylazobenzene-covered surface that affected the alignment of the 5CB LC cell, which is reflected in the LCP monolayer packing state. The amphiphilic LC polymers such as IP-5 generally form the perpendicular structure in the liquid crystalline and LB film states.[1,8,9] As shown in Figure 5, only putted 5CB between the IP-5 monolayers formed a very good homeotropic alignment. Moreover, this ILCP-covered glass was reuseable after being washed by chloroform. The other nematic low-molecular-weight LCs also exhibited the

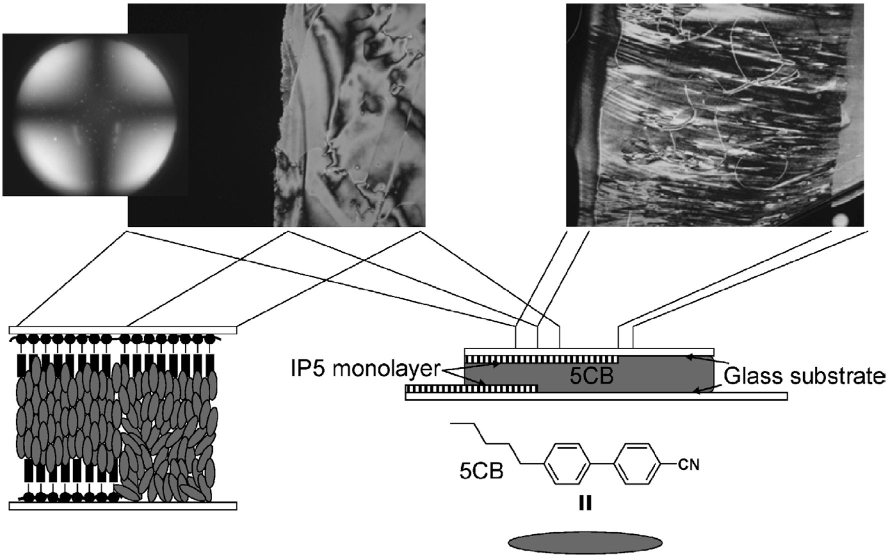

Figure 5.
POM images and schematic illustrations of 5CB homeotropic alignment generated by the IP-5 monolayers.

same phenomenon. The formation of the homeotropic alignment is due to the interactions between the low-molecular-weight LC molecules and the azobenzene side chains of IP-5, which have the perpendicular alignment. This indicates that the LB film of IP-5 possesses the property as a liquid crystal alignemt film.

Conclusion

The surface-pressure isotherms at the air-water interface and the LB deposition onto the glass substrates of ionic liquid crystalline polymers (ILCPs) and their nonionic family (NLCPs) were studied. The result showed that IP-*n* is a truly polyionic material; in addition, NP-*n* formed a condensed monolayer and Y-type LB films. The occupied area of a polymer repeat unit, which gave good agreement for general limited area of an azobenzene moiety, indicated that the water surface was full up with the vertically aligned ethylazobenzene side chains. Since IP-*n* and NP-*n* have the ethylazobenzene side chains in all the polymer repeat units, the density of the azobenzene groups in the system of the L membrane and LB film is extremely high. The LC systems modified with photosensitive azobenzene groups have potential applications in the fields of photomemory, optical storage, and light drive display. The azobenzene concentration and packing state are crucial factors for these functional materials. These amphiphilic LCPs are excellent candidates for producing azo-dense LC thin films by the LB technique. Further studies will be carried out.

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