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Surface-pressure-induced conformation changes of a polymer liquid crystal at the air-water interface

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Surface-pressure–area isotherms are employed to investigate the successive conformation changes of a new polymer liquid crystal at the air-water interface. We have found a first-order phase transition accompanied by a change of molecular conformation.

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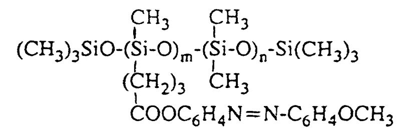
Many types of molecules are spreadable on an aqueous solution under suitable conditions, and can form Langmuir monolayers [1–3]. These insoluble monomolecular layers at the air-water interface provide an ideal two-dimensional model system with an isotropic substrate and an easily controllable density of molecules to elucidate the phase behaviors of the monolayers. Studies of surfactants and polymers at the air-water interface have considerably broadened our understanding of various monolayer phases and other properties that exist in nature [1–12].

Experimentally, it has been found that the more flexible surfactant undergoes a phase transition (tilt phase transition, reorientational phase transition, etc.) when the lateral pressure increases [5]. The monolayer of other materials such as liquid crystals may grow to the third dimension, forming a multilayer structure at the air-water interface [8,9,12]. These transitions are in part due to the freedom of the monolayer. For the polymer monolayer, on the other hand, few experimental data are available [4,7,12]. The polymer monolayer may change from a dilute state to a semidilute state when the occupied area is compressed continuously [4]. As for the isotherm, in this situation it changes from a gas isotherm to a scaling one. During this transition, the area occupied by one monomer is assumed to be constant [4,7].

In this paper we report our studies on a new polymer liquid-crystal (PLC) monolayer at the air-water interface. The molecular structure of the PLC is shown in Fig. 1. Its average molecular weight is $M=3680$, and $m/n=3.380$. At 66 °C, the PLC changes from the crystal phase to the nematic phase, while at 102 °C it changes from the nematic phase to the isotropic phase. Using the surface balance technique [13], we have measured the surface-pressure–area isotherms. We have found that the PLC monolayer at the air-water interface undergoes a first-order phase transition to a stable phase, accompanied by a conformation change. The change in the molecular conformation is due to a delicate balance between molecular interactions in the system.



$$(CH_3)_3SiO\text{-}(\underset{\underset{COOC_6H_4N=N\text{-}C_6H_4OCH_3}{|}}{\underset{(CH_2)_3}{\underset{|}{\overset{\overset{CH_3}{|}}{Si}}}}\text{-}O)_m\text{-}(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}O)_n\text{-}Si(CH_3)_3$$

FIG. 1. Molecular structure of the polymer liquid crystal.

The PLC was spread from a chloroform solution (0.5 mg/ml) onto a doubly distilled water subphase in a Langmuir trough [14] using a microsyringe. The chloroform quickly evaporated, and the PLC's were left uniformly at the air-water interface. The molecular area was then subsequently modified by compressing the monolayer laterally with a constant speed of 0.4 $\mathrm{\AA}^2$/(molecule min). The temperature of the subphase was controlled to within 0.5 °C, and the surface pressure was measured with a precision of 0.1 mN/m.

Figure 2 shows our typical results for surface pressure (π) as a function of molecular area (A) at 25 °C. There are two sharp kinks in the isotherm. The monolayer undergoes phase transitions around the kinks. Before the kink at lower surface pressure, the monolayer is in phase *a*. The monolayer is in phase *b* between the two kinks, and goes to phase *c* after the kink at high surface pressure. The positions of the kinks are temperature dependent. When the temperature is low, e.g., less than 20 °C,

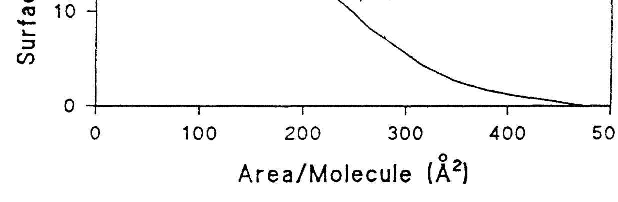


FIG. 2. Typical surface pressure–molecular area isotherm for the polymer liquid crystal at the air-water interface at temperature 25 °C. The conformations of the polymer liquid-crystal molecules are also sketched in corresponding phases.

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the second kink around 25 mN/m is invisible. Figure 3 gives the relationship of the temperatures and surface pressures at which kinks appear. When the temperature increases, the surface pressures where the kinks appear decrease. From this plot we know that the transitions are first order [8].

Recently the scaling concept [15] has been applied successfully to describe the isotherms of polymer films [4,7,12]. In terms of scaling theory, for instance, the radius of gyration for an isolated chain (R_f) can be written as $R_f \sim aN^{v}$, where N is the polymerization index, a the monomer size, and v a critical exponent. For good solvents, $v = 3/(d+2)$, which is known as Flory's formula, where d is the spatial dimensionality. For poor solvents, v stays close to 0.5, independent of d. For the case of a polymer in an interface, furthermore, the osmotic compressibility (surface pressure) can also be expressed in terms of scaling theory as a function of polymer concentration $c: \pi \sim c^{y}$, where y is directly related to v through [4] $y = 2v/(2v-1)$, or equivalently, $\pi \sim A^{-y}$, where A is the area occupied by one molecule at the interface.

To understand the isotherm of the PLC monolayer in terms of scaling theory, Fig. 2 was replotted in a log-log fashion of surface pressure versus molecular area, as shown in Fig. 4. The slope of the isotherm gives the scaling exponent y, which is 6.7, thus $v = 0.60$. The scaling isotherm fits reasonably to the experimental data up to the area per molecule of 300 Å^2. This indicates that the isotherm is dominated mainly by the backbone of the polymer, particularly in the low-surface-pressure region. The siloxane backbone in the polymer studied here is in contact with the water surface.

We note that the scaling isotherm is valid only at relatively low surface pressures. This can be attributed to the effect of polydispersity. If the distribution of the polymerization index is considerably narrow, then we expect that the scaling isotherm will fit to a lower molecular area. The deviation between the scaling isotherm and the real one in a high-surface-pressure region also signals that, in this region, the role of the mesogens cannot be neglected.

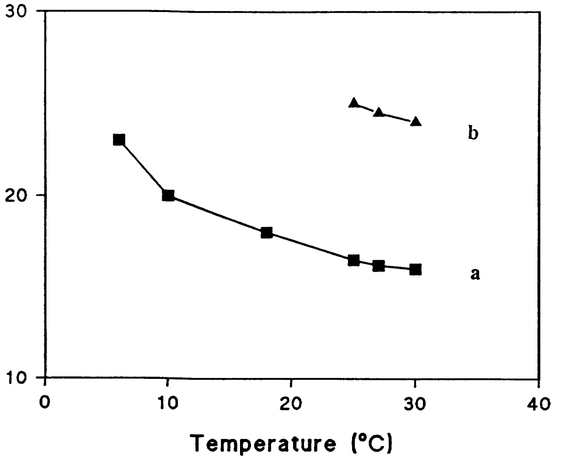

FIG. 3. The relationship between equilibrium surface pressure and the temperature of the polymer liquid crystal monolayer at the air-water interface. Curve *a* is for phases *a* and *b*, and curve *b* is for phases *b* and *c*.

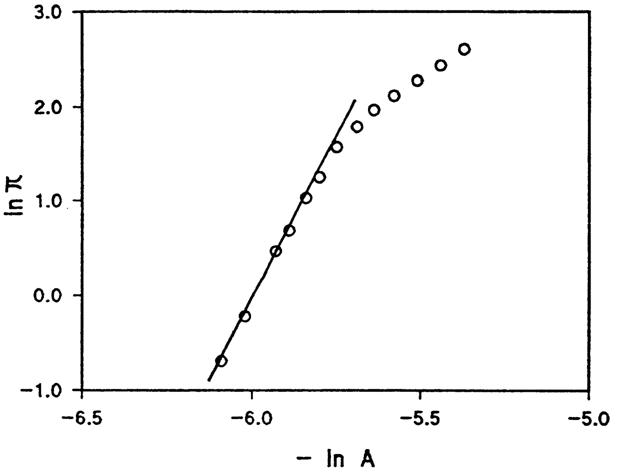

FIG. 4. The log-log plot of surface pressure (π) vs molecular area (A) of the polymer liquid-crystal monolayer. The slope of the solid line fitting the scaling isotherm at low surface pressure gives a value of 6.7. π is in units of mN per meter, and A is in units of square Å per molecule.

It is worthwhile to note that the limit area per molecule in different phases has a ratio of (phase *a*: phase *b*: phase *c*) 1.47:1.14:1.00. We think the difference in molecular area cannot be due to the orientation of side chains, because we have used PLC monolayers deposited onto glass plates under different surface pressures to align nematic liquid crystals, and in all cases a homeotropic alignment has been induced, indicating that the side chains are vertical to the plate surfaces (data not shown here; see [16]). The measured area ratio does not support the supposition that the monolayer may grow to the third dimension, because otherwise it should be close to 3:1.5:1. Then, taking into account the molecular conformations, the phase transitions may be conformation changes (Fig. 2). The above scaling analysis showed that the polymer backbone is anchored on the water surface. In phase *a*, the main chain of the PLC molecule is anchored at the air-water interface. When it is compressed, the monolayer changes to phase *b*, in which the right end of the main chain (see Fig. 1) without side chains is lifted away from the interface. When it is further compressed, the monolayer changes to phase *c*. In phase *c*, the left end of the main chain without azobenzene moieties is also gradually lifted from its anchored position at the air-water interface. The second transition takes less time because the left end is somewhat shorter than the right end. This implies that the phase diagram is plausible. According to the molecular weight and the m/n ratio, the rough estimates of m and n are $m = 10$ and $n = 3$. We can suppose the projection area of each segment —(Si-O)— on the water surface is almost equal. (Although the scaling analysis of the isotherm indicates that at high surface pressure the role of azobenzene group cannot be neglected, as a rough estimation such an assumption is reasonable to some extent). Then, if the above phase diagram is correct, the ratio of molecular areas in phases *a*, *b*, and *c* should be 1.50:1.10:1.00. This ratio is very close to the measured one, also signaling the validity of the above phase diagram.

Our experimental results do not support the assumption of the scaling theory for polymer Langmuir monolayers in which the area per monomer is constant, because as the surface pressure increases some of the monomers are detached from the water surface; it is thus with zero surface area. This may be because the polymer monolayer behavior is strongly molecular structure dependent. As the surface pressure further increases, we did not observe the monolayer develop a multilayer structure.

So far there has been no detailed theoretical work to explain the observed phenomena. It appears that the delicate balance between intermolecular and intramolecular interactions is responsible to this phase transition.

In conclusion, we have observed monolayer phase transitions of a side-chain polymer liquid crystal at the air-water interface between different molecular conformations. The transitions are first order and temperature dependent. We argue that these phenomena are due to a delicate balance between the intermolecular and intramolecular interactions.

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