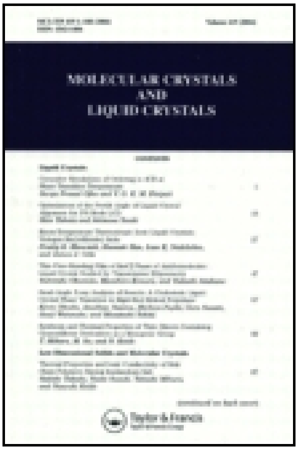

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Effect of Alkyl Chain Length on the Monolayer Formation of Copolysiloxanes Having an 4-Alkoxyphenyl Benzoate Core in the Side Chain

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Effect of Alkyl Chain Length on the Monolayer Formation of Copolysiloxanes Having an 4-Alkoxyphenyl Benzoate Core in the Side Chain

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The effect of the alkyl chain length on the monolayer properties for some members of copolysiloxanes possessing an 4-alkoxyphenyl benzoate core in the side chain at the air/water interface was examined by surface pressure-area measurements. The negative temperature dependency of plateau pressures can be explained as an increase in mobility of main chains and side groups at the higher temperature favoring both removal of the $(CH_3)_2$ SiO segment from the water surface and the closest packing of the side groups.

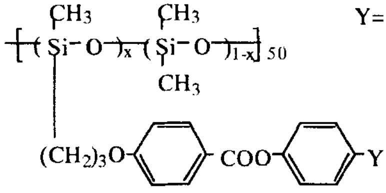
Keywords: LC copolysiloxanes; monolayers; terminal group effect

INTRODUCTION

Possible structures of homopolysiloxanes at the air/water interface have been proposed[1]. At low film pressure all the oxygen atoms in the main chain are in the water surface owing to the presence of hydrogen bonding whereas other groups extend into the air. Due to the various tactic configuration and steric hindrance of the bulky side groups, full extend of the main chain under low pressure is inhibited[2]. A self-ordering mosogenic core incorporated into the side chain enhances the monolayer-forming ability of polysiloxanes[3]. In this paper we will discuss the effect of side groups on the monolayer structure of copolysiloxanes.

EXPERIMENTAL

The chemical structures and thermal bulk phase behavior of liquid crystalline copolysiloxanes are shown in Figure 1. Monolayer experiments were performed on a computer-controlled film balance, FSD-110BP(USI system Ltd., Japan). All materials were spread on water surface (pH=5.7) from 0.3-0.9 mg/mL solutions in spectra grade chloroform. The subphase temperature was controlled within ±0.1 K. After the chloroform was allowed to evaporate for 10 min, the monolayers were compressed at a rate of 0.48 cm^2/s.



Y= OCH_3(**P1**, g262)
OC_2H_5(**P2**,g275N315I)
OC_3H_7(**P3**, g287N307I)
OC_4H_9(**P4**, g287N320I)
OC_5H_{11}(**P5**, g269N312I)
OC_6H_{13}(**P6**, g280N328I)

FIGURE 1. Chemical structures and transition temperatures(K) of polymers. g is glassy transformation; N and I indicate nematic and isotropic phases, respectively.

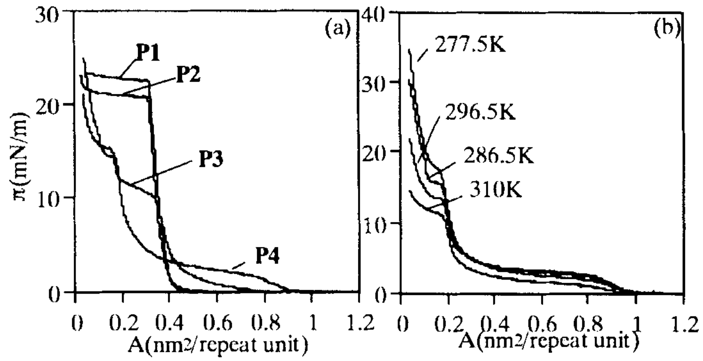


FIGURE 2. (a)π-A isotherms f **P1**-**P4** at 296.5K; (b)Temperature dependancy of π-A isotherms of **P5**.

RESULTS AND DISCUSSION

All of the copolysiloxanes form stable monomolecular films. π-A isotherms of four copolymers at 296.5 K are indicated in Figure 2. **P5** and **P6** show a similar curve to **P4**. **P1** is a non-liquid crystalline copolymer in bulk phase. Figure 2a shows that **P1** is able to form condensed monolayer with the smallest onset area of 0.481 nm^2/repeat unit. The extrapolation of the isotherm in the condensed region to zero pressure leads to a limiting area of 0.388 nm^2/repeat unit, which is in good agreement with twice of the value, 0.193 ±0.013 nm^2/monomer for poly(dimethylsiloxane)[4]. From this result, we assume that the whole main chains are not separated from the water surface even in the close packed state. The collapse pressure remains constant, indicating that the collapse can be ascribed to the formation of subsequent multilayers. **P2** shows a similar curve to that of **P1**, implying that a similar change of the monolayer sructure happens.

The onset area of the **P3** isotherm is located at 0.833 nm^2/repeat unit much larger than those of **P1** and **P2**. The distinct increase in the onset area represents that the steric hindrance and interaction between the side chains become stronger from propoxy so that the mesomorphic side chains cohere with each other at larger area per repeat unit[2]. On compression the monomolecular film first gets into a condensed state ca. 0.4 nm^2/repeat unit. Then the film exhibits a phase transition from the condensed state at ca. 0.4 nm^2/repeat unit through an intermediate to another condensed state at ca. 0.2 nm^2/repeat unit. The area of 0.2 nm^2/repeat unit approximately corresponds to the cross-sectional area of a side chain oriented perpendicular to the water surface. Based on the occupied area per repeat unit the side chains are inferred to be tightly packed and to be oriented perpendicular to the air/water interface. In other words, only the siloxane unit connecting with the mesomorphic side chain is anchored at the water surface while the $(CH_3)_2SiO$ segment is squeezed out of the water surface. Therefore this transition can be ascribed to removal of $(CH_3)_2SiO$ segment from the water surface.

The isotherm of **P2** with nematic phase at room temperature is different from that of **P3**, but similar to that of the non-liquid crystalline **P1**. A possible explanation is that in the case of ethoxy terminal group spread of the main chains on the water surface weakens the interaction between the mesogenic cores. **P2** as like as **P1** can immediately form condensed state on compression without any coherence at large area per repeat unit.

P4 shows a phase transition plateau with an inflection of about 0.774 nm^2/repeat unit and 1.9 mN/m. After passing the transition region the isotherm directly gets to the highly condensed region at ca. 0.2 nm^2/repeat unit. The transition plateau means the occurrence of a definite expanded state before the inflection point. The enhanced interaction and steric hindrance between the mesomorphic side chains due to incorporation of the butoxy group should be responsible for formation of the expanded state. The fact that the condensed region of **P4** is located at ca. 0.2 nm^2/repeat unit suggests that the plateau corresponds to both removal of $(CH_3)_2SiO$ segment in the main chain from the water surface and the closest packing of the mesomorphic side chains. According to the similarity of π-A isotherms for **P4**, **P5** and **P6**, it can be postulated that their monolayers possess similar structure.

The pressure of the plateau region of **P5** decreases with increasing temperature (Figure 2b). The increase of the subphase temperature would increase the mobility of the mesomorphic side chains and allow the polymer chain more freedom to assume the conformations other than one which places all segments in the interface[5]. Therefore, the closest packing of the mesomorphic side chains becomes favorable.

In conclusion, the monolayer behavior of investigated copolysiloxanes is in close relationship with the strong interactions between the mesomorphic side chains and the fluidity of the nematic mesophase in the bulk. This article is first report on monolayer properties of polysiloxanes with nematic phase at room temperature. Further studies are in progress.

Acknowledgments

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