

# Characteristic phase-separated monolayer structure observed for blends of rodlike and flexible polymers

S. Yamamoto, Y. Tsujii\*, T. Fukuda

*Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

Received 12 May 2000; received in revised form 30 June 2000; accepted 7 July 2000

## Abstract

Monolayers of polymer blends composed of a rodlike polymer (tetra(methoxy)-tetra(octyloxy)-phthalocyaninato-polysiloxane (PcPS) or poly( $\gamma$ -benzyl-L-glutamate)(PBLG)) and a flexible polymer (poly(isobutylvinyl ether)(PIBVE)) were studied by atomic force microscopy (AFM), transmission electron microscopy (TEM) and the surface pressure–area isotherm measurements. These blends were completely phase-separated into two pure monolayer phases at the air–water interface, a quasi-2D system. The AFM observation showed that anisotropic string-shaped domains of PcPS formed a networklike structure in the PIBVE matrix monolayer. In the PcPS domains, polymer chains were observed to be aligned parallel to each other along the domain contour, forming a 2D nematic phase. The domain-shape anisotropy decreased with decreasing chain length of PcPS. In addition, PBLG, another rodlike polymer also formed similar anisotropic domains in the PIBVE matrix, indicating the universality of the observed morphologies. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Rodlike polymer; Phase separation; Monolayer

## 1. Introduction

A monolayer of polymer blends spread at the air–water interface and its Langmuir–Blodgett (LB) film transferred on a solid substrate have attracted much attention, for potential applications as high-function ultrathin films. In addition to this practical interest, surface monolayers are of fundamental interest as a model of a 2D polymer system. Since the conformations and interactions of polymers will be dimension dependent, the phase behavior and phase-separated structure of polymer blends in a 2D system should be different from those in a 3D system. In this regard, a number of studies have been made on the miscibility of polymer blends in a monolayer state. In most of these studies, the surface pressure ( $\pi$ )-area ( $A$ ) isotherm and ellipsometric measurements were carried out, and the polymer–polymer miscibility was discussed in comparison with the miscibility in the bulk state [1–12].

On the other hand, the process and structure of phase separation of polymer blends in a monolayer have been less sufficiently characterized. For this purpose, direct microscopic observations of the monolayer structures would be the best way, but the usually poor microscopic

contrast between phases in the monolayer and the difficulty of phase separation due to the poor fluidity of polymer chains at the air–water interface have brought about limited success. Nevertheless, several important results have been reported: Kawaguchi et al. [13] observed LB films of poly(vinyl acetate) (PVAc)/poly(methyl acrylate) (PMA) blends by atomic force microscopy (AFM), noting that PMA components were squeezed out on top of the PVAc film (the “vertical” phase separation). Wu et al. [14,15] made transmission electron microscopic (TEM) observations of the monolayer of a tetra(methoxy)-tetra(octyloxy)-phthalocyaninato-polysiloxane (PcPS) and isopentyl cellulose (IPC) blend at the air–water interface, and found that each component was laterally phase-separated into two nematic phases. Both of these components are rigid polymers with flexible side chains, so-called “hairy-rod” polymers [16]. This type of polymer, including polypeptides, polysiloxanes, cellulose derivatives and polysilanes, has been extensively studied as advanced LB materials with high thermal and mechanical stabilities. These polymers, locally oriented in a monolayer on the water surface, were reported to be macroscopically aligned by the dipping process [17], giving a highly oriented LB film. The orientation behavior of hairy-rod polymers is considered to originate from the excluded volume effect of the rodlike polymer [18,19].

\* Corresponding author. Tel.: +81-774-38-3162; fax: +81-774-38-3170.  
E-mail address: tsujii@scl.kyoto-u.ac.jp (Y. Tsujii).

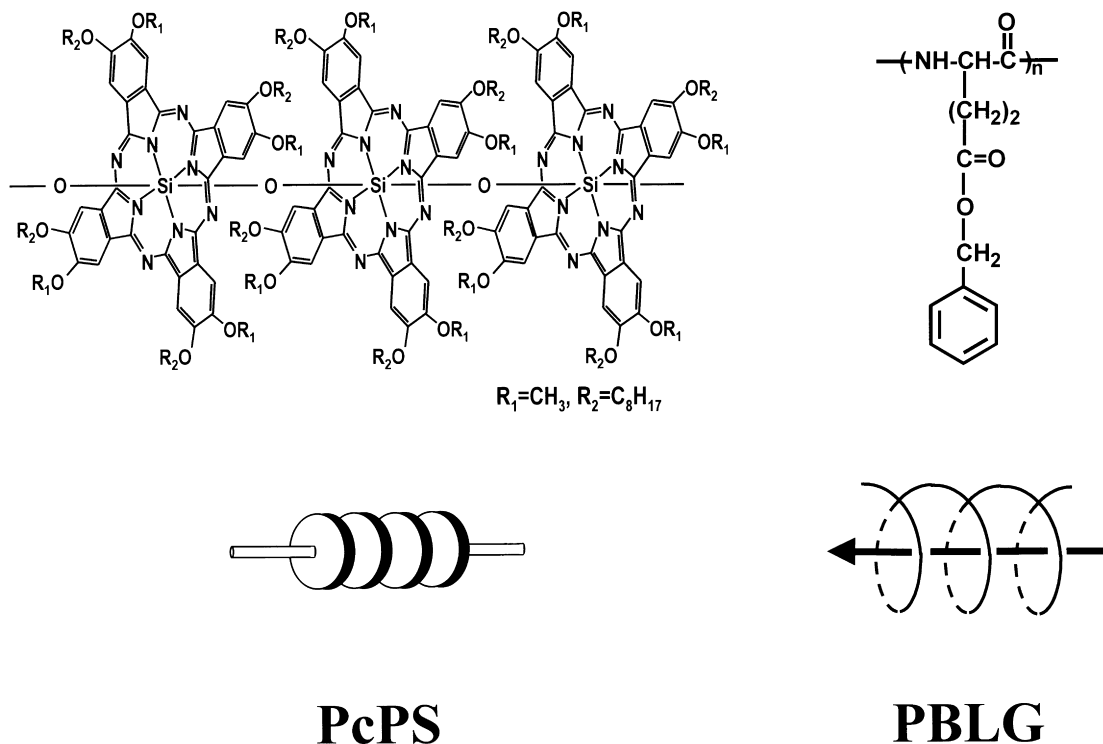


Fig. 1. Chemical structures and schematic illustrations of molecular shape of PcPS and PBLG.

This work focuses on the phase behavior and phase structure of the blend of a rodlike polymer and a flexible polymer on the water surface. In this work, we will study two different types of rodlike polymers, PcPS [20–22] and poly( $\gamma$ -benzyl-L-glutamate) (PBLG) [23,24], blended with poly(isobutylvinyl ether) (PIBVE). PIBVE is a flexible polymer, which is known to have a high fluidity on the water surface, and forms a stable monolayer [25]. As schematically shown in Fig. 1, the rodlike characters of PcPS and PBLG come from the dense stacking of the bulky phthalocyanine moieties and the helical conformation, respectively. The former is decorated with “hairs” of flexible side chains, while the latter has benzyl groups. The phase-separated structures of these blends will be thoroughly characterized by direct observations by AFM and TEM, and discussed in terms of the molecular shape anisotropy of the rodlike polymers.

## 2. Experimental

**Materials.** The PcPS samples were generously donated by Professor Gerhard Wegner of Max Planck Institute for Polymer Research in Germany: two samples, PcPS<sub>H</sub> and PcPS<sub>L</sub>, with an average degree of polymerization of approximately 80 and less than 30, respectively, were investigated. The PIBVE sample was synthesized by living cationic polymerization using a HI/ZnI<sub>2</sub> initiating system [26–29]. Its number-average molecular weight ( $M_n$ ) and polydispersity

index ( $M_w/M_n$ ), estimated by a polystyrene-calibrated gel permeation chromatographic analysis, were 27800 and 1.37, respectively. The PBLG sample, which has a nominal weight-average molecular weight ( $M_w$ ) of 26,000, was purchased from Sigma and used without further purification.

**Preparation of Surface Monolayer.** The sample polymer was spread from a solution of chloroform on the clean water surface in a Teflon-coated rectangular Langmuir trough ( $200 \times 500 \times 3 \text{ mm}^3$ ). Chloroform (Spectrograde, Dojindo Laboratories) was used without further purification. Blend monolayers were prepared by spreading a mixture solution of PcPS (or PBLG) and PIBVE. The total polymer concentration in the solutions was adjusted to about 0.01 wt%, unless otherwise noted. The subphase water was purified by means of a Mitamura Riken model PLS-DFR automatic still, which consisted of a reverse-osmosis module, an ion-exchange column, and a double distiller. By circulating thermostated water, the temperature of the subphase for the PcPS/PIBVE blend monolayers was kept at 20°C unless otherwise noted. For the PBLG/PIBVE blend monolayers, the temperature of the subphase was kept at 5°C to obtain stable and transferable monolayers since PBLG/PIBVE blend monolayers were not transferred on mica surface with a good transfer ratio at 20°C. In each experiment, 0.5 ml of sample solutions was spread on the water surface. After spreading the solution, 30 min was allowed for the solvent to evaporate. The  $\pi$ -A isotherms were recorded at a constant compression speed of 14 cm<sup>2</sup>/min;  $\pi$  was measured by means of a Wilhelmy-type film balance.

Download English Version:

<https://daneshyari.com/en/article/5195299>

Download Persian Version:

<https://daneshyari.com/article/5195299>

[Daneshyari.com](https://daneshyari.com)