

## Surface pressure–area isotherms and surface dilational moduli of poly (N-isopropyl acrylamide) monolayers spread at air–water interface



Yuki Okumura, Masami Kawaguchi\*

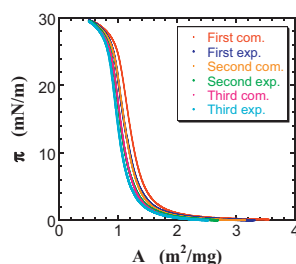
Division of Chemistry for Materials, Graduate School of Engineering, Mie University, 1577 Kurimamachiya, Tsu, Mie 514-8507, Japan

### HIGHLIGHTS

- Poly (N-isopropyl acrylamide) (PNIPAM) monolayers showed negative hysteresis by the compression–expansion cycles.
- Isotherm of a given expansion process almost coincided with that of the following compression process.
- PNIPAM showed much larger surface dilational moduli than PEO and PVAc.

### GRAPHICAL ABSTRACT

Plots of surface pressure ( $\pi$ ) determined using the repeated compression and expansion cycles as a function of surface area ( $A$ ) for PNIPAM monolayers at a fixed rate of 5 mm/min.



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### ABSTRACT

The surface pressure–area isotherms and surface dilational moduli of poly (N-isopropyl acrylamide) (PNIPAM) monolayers spread at the air–water interface were measured during the compression–expansion cycles as a function of surface pressure and frequency at a fixed strain of 10%. The isotherms of the monolayers clearly showed a negative hysteresis, i.e., the decrease in the surface pressure increased with increasing number of cycles. However, the isotherm of an expansion process was in good agreement with that of the following compression process. Therefore, the Lissajous orbits of the monolayers exhibited a negative hysteresis loop with the repeating cycles, and then, the corresponding surface dilational moduli were determined from the first loop of Lissajous orbits. The resulting surface moduli were much larger than those of poly (ethylene oxide) and poly (vinyl acetate) monolayers, while their magnitudes were the same as those of poly (methyl methacrylate) monolayer. Such larger surface moduli may be attributed to the chain entanglements of loops and trains of spread PNIPAM chains in the monolayers.

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### 1. Introduction

A simple oscillating barrier compression–expansion method permits the imposition of an oscillatory dilational strain on a spread monolayer and the measurement of the surface dilational modulus using a surface pressure measurement apparatus [1–3]. Recently, such a method has been used to obtain the surface dilational moduli of monolayers of proteins [4–6], polymers [7–9],

blend polymers [10–13], and particles [14] spread at the air–water interface.

The physical properties of poly (N-isopropyl acrylamide) (PNIPAM) have been widely investigated in various forms, including single chains, gels, thin films, membranes, and fibers [15]. Since an aqueous solution of PNIPAM has a lower critical solution temperature (LCST) at which a hydrophilic/hydrophobic transition occurs, the hydrophobic portion, i.e., the isopropyl group may play a significant role in the adsorption process at the interface between air and aqueous solution [15]. Moreover, it is well-known that PNIPAM forms a stable monolayer spread at the air–water interface. We reported the effects of spreading solvent and temperature on the

\* Corresponding author. Tel.: +81 59 231 9432; fax: +81 59 231 9433.

E-mail address: [kawaguti@chem.mie-u.ac.jp](mailto:kawaguti@chem.mie-u.ac.jp) (M. Kawaguchi).

surface pressure–area isotherms, adsorbed amounts, and adsorbed layer thickness of PNIPAM monolayers spread at the air–water interface [16–18].

Some interesting studies on the surface dynamics of PNIPAM layers adsorbed from their aqueous solutions were reported by using the following techniques: surface light scattering [19], oscillating barrier [20], capillary wave [20], and interfacial stress rheometer [21]. However, no comprehensive study has been performed on the measurements of surface dilational moduli of PNIPAM monolayers spread at the air–water interface. It can be expected that the relatively larger layer thickness of PNIPAM monolayer spread at the air–water interface [17,18] provides a stronger viscoelastic response than poly (ethylene oxide) (PEO) monolayer spread at the air–water interface [13]. Herein, we studied the effects of compression–expansion cycles on the changes in the surface pressure–area isotherms and the characteristics of the surface dilational moduli of PNIPAM monolayers spread at the air–water interface as a function of strain, surface pressure, and frequency, by using the shape of Lissajous orbits, which are obtained by plotting the surface pressure versus the changes in the surface area at a given strain. Moreover, the resulting dilational surface moduli are compared to the surface rheological properties of PNIPAM monolayers adsorbed from their aqueous solutions [20] as well as those of other polymer monolayers [9,11–13] to better understand the interfacial characteristics of PNIPAM monolayers spread at the air–water interface.

## 2. Experimental

### 2.1. Materials

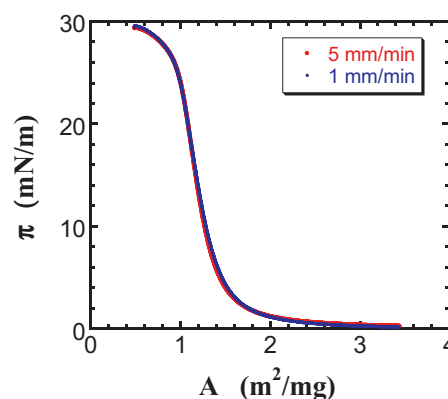
A fractionated PNIPAM sample was used for this study and its molecular weight was determined to be  $46.7 \times 10^3$  from the intrinsic viscosity measurement in water. Its molecular weight distribution was estimated to be 1.22 using gel permeation chromatography (GPC) with HLC-8220 GPC of Tosho, for which 10 mM LiBr solution in DMF was used as a fluent and standard Polystyrenes with known molecular weights were used for calibration.

PNIPAM monolayers at the air–water interface were prepared with spectrograde chloroform, which was used as received without further purification. A time interval of 30 min was allowed before the surface pressure and surface dilational modulus were measured.

Deionized water was prepared using a Milli-Q Academic A10 ultrapure water system. The purity of the deionized water was checked by measuring its resistivity and total organic carbon (TOC) content. The resistivity was higher than  $16 \text{ M}\Omega \text{ cm}$ , and the TOC was less than 20 ppb.

### 2.2. Surface pressure and surface dilational modulus measurements

The surface pressure and surface dilational modulus were measured using a KSV 2000 system (KSV Instrument Ltd., Finland). A Pt plate was used as a Wilhelmy plate attached to a displacement transducer, which was calibrated by using the weighing method. A Teflon-coated trough with an area of  $75 \times 15 \text{ cm}^2$  was filled with the deionized water. Any changes in the surface pressure were not observed by spreading only chloroform at the air–water interface. The PNIPAM solution was then spread on the water surface in the trough with an area of  $700 \text{ cm}^2$  using a Hamilton microsyringe. In order to confirm the reversibility of the surface pressure responses, the spread PNIPAM monolayers were continuously compressed or expanded at two rates of 1 and 5 mm/min from a fixed surface area of  $700\text{--}100 \text{ cm}^2$  or vice versa. In order to prevent the



**Fig. 1.** Plots of surface pressure ( $\pi$ ) determined using the continuous compression method as a function of surface area ( $A$ ) for PNIPAM monolayers at different compression rates of 1 (blue) and 5 mm/min (red).

evaporation of water in the trough, the KSV 2000 system was placed in a homemade box.

The detailed procedures for the surface dilational modulus measurements were previously described by Morioka et al. [9,11]. All the surface dilational modulus measurements of PNIPAM monolayers were performed at various fixed surface areas, and the data were analyzed as a function of surface pressure for changes in both strain and frequency. The experimental error in the surface pressure measurements was  $<0.1 \text{ mN/m}$  and the error bars of the data points for the surface pressures and surface dilational moduli lie within the range for each data point.

## 3. Results and discussion

### 3.1. Surface pressure–area isotherms

Fig. 1 shows the surface pressure ( $\pi$  expressed in mN/m) that was determined using continuous compression as a function of the surface area ( $A$ ,  $\text{m}^2/\text{mg}$ ) of the PNIPAM monolayers at different compression rates (1 and 5 mm/min), and the resulting  $\pi$ – $A$  isotherms were found to be almost independent of the compression rate. Thus, PNIPAM formed thermodynamically stable monolayers at the air–water interface without being affected by any physical disturbance from the compression speed.

The concentration regimes (e.g., dilute, semi-dilute, and concentrated) were estimated from the double logarithmic plots of  $\pi$  as a function of the surface concentration ( $\Gamma = 1/A$ ), according to a power-law analysis for polymer monolayers [22]. The double logarithmic plot of  $\pi$  as a function of  $\Gamma$  consists of three portions, as shown in Fig. 2: (i) the data points below  $\pi = 1.5 \text{ mN/m}$  ( $\Gamma = 0.53 \text{ mg/m}^2$ ) can be fitted with the slope of 3; (ii) the data points of  $5 < \pi < 20 \text{ mN/m}$  ( $\Gamma = 0.92 \text{ mg/m}^2$ ) can be fitted with the slope of 5.22; and (iii) for the data points beyond  $\pi = 20 \text{ mN/m}$ , the  $\pi$  values gradually approach the plateau regime. Although the respective slopes are not consistent with the prediction of the power law analysis under either good solvent or theta solvent conditions, it is assumed that the PNIPAM monolayers below  $\pi = 1.5 \text{ mN/m}$  and above  $\pi = 20 \text{ mN/m}$  are in the dilute and in the concentrated regimes, respectively, and the other surface pressures ranging from 1.5 to  $20 \text{ mN/m}$  are in the semidilute regime. The resulting power-law exponent of 5.22 in the semidilute regime is larger than the mean field theoretical expected value of 3.00 in good solvent condition, suggesting that the water in the present study is somewhat less than a good solvent condition. Thus, such solvent condition could provide that PNIPAM monolayers spread at the air–water interface behave as surface gelation materials described in the surface dilational moduli measurements. Further, the limited surface

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