

# **Work of Adhesion as a Dominant Factor in Formation of Composition-Gradient Thermosensitive Gel**

Hideaki Tokuyama<sup>1</sup>, Masahiro Sasaki<sup>2</sup> and Shuji Sakohara<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

<sup>1</sup>Corresponding information

TEL: +81-52-789-3391, FAX: +81-52-789-3269

E-mail: htoku@nuce.nagoya-u.ac.jp

<sup>2</sup>Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, 739-8527, Japan

## **Abstract**

By copolymerizing a thermosensitive primary component, *N*-isopropylacrylamide (NIPA), and an ionic secondary component, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) between two substrates of hydrophilic glass and hydrophobic polytetrafluoroethylene (Teflon), a novel composition-gradient copolymer gel, in which the AMPS content decreases gradually towards Teflon, is prepared. The formation of the composition-gradient in NIPA-*co*-AMPS gels is discussed in terms of the work of adhesion between a solution and a substrate, i.e. the liquid-solid interfacial free energy. The work of adhesion is determined from the Young-Dupré equation on the basis of the contact angle, and the surface tension measured in the system consisting of an aqueous solution containing NIPA or AMPS monomers or polymers and glass or Teflon as the substrate. The values of the work of adhesion of AMPS monomer and polymer on Teflon were lower than those on glass. Thus, AMPS remains relatively stable at the glass interface and unstable at the Teflon interface. This repulsion of AMPS due to the hydrophobicity of the Teflon wall generates the composition-gradient.

## 1 Introduction

Thermosensitive hydrogels or so-called intelligent gels have attracted a great deal of attentions for applications as actuators, drug delivery systems and sensors. In a previous study [1], the current authors prepared a novel composition-gradient copolymer gel with a thermosensitive component for use as intelligent gels, in which the composition gradually changes with the distance. Attention was focused on the difference in the hydrophilicity/hydrophobicity of the polymers or substrates. The slab-shaped copolymer gels of a thermosensitive primary component, *N*-isopropylacrylamide (NIPA), and an ionic secondary component, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) were prepared between two substrates of hydrophilic glass and hydrophobic polytetrafluoroethylene (Teflon). Poly(NIPA) dissolved in water, has a lower critical solution temperature in the vicinity of 305 K [2,3] and NIPA gels isotropically swell and shrink in three directions, in response to changes in temperature. In the resulting NIPA-*co*-AMPS gel, the AMPS content decreased gradually towards the Teflon wall. The thermosensitive composition-gradient NIPA-*co*-AMPS gel underwent an anisotropic change in shape, i.e. it reversibly bended and stretched in response to the change in temperature, as a function of the hydrophilic/hydrophobic transition of poly(NIPA) in water.

The purpose of this study is to elucidate the factors involved in the formation of the composition-gradient copolymer gel. The results obtained in a previous study [1] imply that the interaction of a solution under gelation and a substrate has a remarkable influence on the formation of composition-gradient gels. Therefore, the aim of the present work is to investigate the work of adhesion between a solution and a substrate, i.e. the liquid-solid interfacial free energy. The work of adhesion,  $W_a$ , was determined from the Young-Dupré equation [4],  $W_a = \gamma (1 + \cos\theta)$ , on the basis of the measured

contact angle,  $\theta$ , and surface tension,  $\gamma$ , in an aqueous solution system containing NIPA or AMPS monomers or polymers and glass or Teflon substrates. The distribution of the composition in the NIPA-*co*-AMPS gels prepared between glass and Teflon substrates at various distances, is discussed in terms of the work of adhesion.

## 2 Experimental

### 2.1 Preparation of Gel and Measurement of Composition

NIPA was kindly supplied by Kohjin Co. and was purified by recrystallization from a benzene/hexane solution prior to use. The AMPS was used without further purification. The NIPA-*co*-AMPS gels were prepared by free radical copolymerization. The materials and the corresponding concentrations used were as follows: NIPA (1455 mol/m<sup>3</sup>), AMPS (45 mol/m<sup>3</sup>), *N,N'*-methylenebisacrylamide of cross-linker (60 mol/m<sup>3</sup>), *N,N,N',N'*-tetramethylethylenediamine of an accelerator (10 mol/m<sup>3</sup>) and ammonium peroxydisulfate of an initiator (1 mol/m<sup>3</sup>). The polymerization was performed in water at 293 or 313 K, under a nitrogen atmosphere for 24 hours. The slab-shaped copolymer gels were prepared by putting the pre-gel solution between two substrates of glass and Teflon, respectively. The cross-sectional area of the reactor was 60 · 60 mm<sup>2</sup> and the distance between two substrates was 3, 5 or 10 mm.

The AMPS content in NIPA-*co*-AMPS gels was determined using the previously described method [1], i.e. neutralization with NaOH aqueous solution. The slab-shaped gels were cut at 1.0 mm intervals in a direction perpendicular to the substrates, thoroughly washed with deionized water and then dried. The dried gels were put in NaOH aqueous solution. After the equilibrium is attained, the outer solution was removed and titrated with HCl aqueous solution. The AMPS content in the sliced gels was calculated by the mass balance of Na ions.

## 2.2 Preparation of Polymer

Each NIPA and AMPS polymer without *N,N'*-methylenebisacrylamide was prepared by basically following the same procedure as for the gel. The free radical polymerization of NIPA or AMPS aqueous solution was carried out at 298 K. The resulting polymers were thoroughly washed with deionized water to remove the unreacted monomers and polymers of low molecular weight, where a cellulose tubular membrane with a molecular weight cut off, MWCO, of 13000 was used.

## 2.3 Surface Tension Measurement

The liquid-gas surface tension was measured by the drop weight method [5]. The liquid samples used were aqueous solutions containing monomer or polymer of NIPA or AMPS, in which the solute concentration was within the range of 1-200 mol-monomer unit/m<sup>3</sup>. The experimental apparatus and procedure are as follows: The apparatus was composed of a syringe pump, a Teflon tube channel, a glass capillary nozzle and a glass test tube. The liquid sample was loaded into the syringe pump. The liquid moved with a flow rate,  $Q$ , of  $1.67 \cdot 10^{-9}$  m<sup>3</sup>/s through the Teflon tube channel from the pump to the capillary nozzle, which was mounted vertically at the end of the channel. The liquid dropped from the tip of the capillary nozzle, which had inner and outer diameters of 1.02 and 1.40 mm, respectively, and a length of 30 mm. The droplets were collected in the glass test tube covering the nozzle. The liquid sample was initially placed in a glass test tube and the liquid dropped in its saturated vapor. The experiments were carried out at 293 or 313 K, i.e., at a temperature lower or higher than the lower critical solution temperature of poly(NIPA). The time required for the number of the fallen droplets to reach fifty,  $t_{50}$ , was measured.

The surface tension was recorded as follows: The weight of a drop having fallen from the capillary is proportional to the surface tension of the liquid and the diameter of

the capillary [5]. The surface tension of a dilute aqueous solution such as the liquid sample in this study was easily determined by comparing it to a reference liquid such as water. In this study, the surface tension,  $\gamma$  [N/m], was determined from the equation,  $\gamma = mg / (\pi D)$ . In the equation,  $m$  [kg],  $g$  [m/s<sup>2</sup>] and  $D$  [m] are the weight of a droplet, acceleration due to gravity, and the effective diameter of the capillary nozzle, respectively. The value of  $D$  was estimated to be 1.11 mm in the experiment using distilled water, where the surface tensions of water are given as 0.0728 and 0.0696 N/m, at 293 and 313 K [6], respectively. The weight of a droplet,  $m$ , was calculated from  $m = Q\rho t_{50}/n$ , in which  $\rho$  is the density of solution, and  $n$  is the number of fallen droplets, that is, fifty in this study. The density of the liquid sample was measured with a pycnometer.

#### **2.4 Contact Angle Measurement**

The contact angle,  $\theta$ , of the liquid sample on the glass or Teflon plate was measured by the sessile drop method. The liquid samples used were the same as those utilized in the surface tension measurement. A droplet of 5  $\mu$ L was deposited using a micropipette on the plate in a thermostatically controlled chamber at 293 or 313 K. Immediately after settling the drop, a photo of it was taken with a digital camera. The contact angle,  $\theta$ , was graphically read from the photo.

### **3 Results and Discussion**

#### **3.1 Composition-Gradient Copolymer Gels**

Fig. 1 shows the contents of AMPS in slab-shaped NIPA-*co*-AMPS gels plotted against the distance between the glass and Teflon. In Fig. 1, the results for three kinds of gels are shown. Both gels (a) and (b), which were prepared at 293 and 313 K, in a reactor having a glass-Teflon distance of 5 mm, shown a similar composition-gradient

decrease of the AMPS content towards the Teflon wall, over a distance of several mm. Thus, it is obvious that hydrophilic AMPS is repelled by the hydrophobicity of the Teflon wall. It is clear from the photos of gel (a) in water at 280 K and 323 K, shown in Fig. 1, that the gel undergoes an anisotropic change in shape, i.e. bending at 323 K and stretching at 280 K. Due to the hydrophilic/hydrophobic transition of poly(NIPA) in water, the macroscopic structures of both the resulting gels (a) and (b) were quite different; the gel prepared at 313 K was porous, which was confirmed by eye-observation that the gels are white (see photos in Fig. 1), and the gel prepared at 293 K was homogeneous, i.e. non-porous, which was confirmed by the fact that the gel was transparent. It is unexpected and interesting that both gels (a) and (b) show similar composition-gradient despite having different macroscopic structures.

The effect of the distance between the glass and Teflon on the content and distribution of AMPS was examined, by the preparation of the gels at 313 K, in a reactor having glass-Teflon distance of 3, 5 and 10 mm. As shown in Fig. 1, the gel (c) formed at a distance of 3 mm and had an AMPS composition-gradient decrease similar to that seen for the gel formed at a distance of 5 mm. However the actual AMPS content in the gel formed at 3 mm is considerably lower than that in the gel formed at 5 mm. Since the ideal value of the AMPS content was calculated as 0.246 mmol/g-dry gel, from the concentrations of NIPA and AMPS in the pre-gel solution, 1455 and 45 mol/m<sup>3</sup>, the decrease in the glass-Teflon distance disturbs the copolymerization and gelation. In the case of the reactor having a glass-Teflon distance of 10 mm, the gel was successfully prepared on a glass-side, but was floppy and incomplete in the region of ca. 2 mm from Teflon wall. The Teflon wall seems to have a negative effect on the gelation process, while glass works in the opposite manner.

From the preparation of the composition-gradient gels, the following questions

arise; (i) Why does the composition-gradient in the decrease of the AMPS content toward Teflon arise? (ii) Why does the composition-gradient behavior appear in the preparations at both 293 and 313 K. (iii) Why is the composition-gradient formed over a distance of several mm? (iv) How the glass-Teflon distance influences the content and composition of the AMPS? These issues will be discussed in terms of the work of adhesion in section 3.5.

### 3.2 Liquid-Gas Surface Tension

Fig. 2 shows the liquid-gas surface tensions,  $\gamma$ , of the aqueous solutions containing NIPA or AMPS monomer or polymer, at 293 or 313 K, as a function of the concentration of the solute. The estimated value of the surface tension of water [6] is also shown as the horizontal line in each figure. In the case where the concentration of NIPA polymer was over 5 mol-monomer unit/m<sup>3</sup>, the determination of  $\gamma$  was unsuccessful at 313 K, since an aggregate of hydrophobic poly(NIPA) was formed. In Fig. 2a), corresponding to the results at 293 K, the values of  $\gamma$  decrease with increasing solute concentration, except for the AMPS polymer. NIPA polymer shows a remarkable decrease in  $\gamma$ . This implies that NIPA polymer has a strong effect on the surface activation. For results at 293 and 313 K,  $\gamma$  for both monomers, and AMPS polymer, shows similar values and behavior. For a NIPA polymer of 5 mol-monomer unit/m<sup>3</sup>, the value of  $\gamma$  at 313 K was higher than that at 293 K, although a smaller value of  $\gamma$  was predicted at 313 K, on the basis of the hydrophobicity of poly(NIPA).

### 3.3 Contact Angle

Fig. 3 shows the contact angles,  $\theta$ , of aqueous solutions containing NIPA or AMPS monomer or polymer on plates of glass or Teflon at 293 or 313 K, as a function



of the solute concentration. The contact angle observed for water is also given as the horizontal line in each figure. As mentioned above, the concentration of NIPA polymer measured at 313 K was limited up to 5 mol-monomer unit/m<sup>3</sup>. In Figs. 3a) and 3c), the contact angles of each solution on the glass plate were generally smaller than those on the Teflon plate, and were not affected by the changes in the concentration and temperature. The smaller contact angles on the glass plate are attributed to the strongly hydrophilic property of water used as solvent. In Figs. 3b) and 3d), the contact angles of each monomer solution on the Teflon plate decrease with the increase in solute concentration. This is due to the decrease in surface tension. The contact angles of AMPS polymer solution on Teflon at 293 K are smaller than those at 313 K. The reason for this is unclear. In contrast, the contact angles for NIPA polymer on Teflon at 313 K are smaller than those at 293 K. That can be attributed to the hydrophobicity of poly(NIPA) at 313 K.

### 3.4 Work of Adhesion

The work of adhesion between a solution and a substrate is the liquid-solid interfacial free energy. A higher value of the work of adhesion corresponds to a stronger interaction between a solution and a substrate. Fig. 4 shows the work of adhesion,  $W_a$ , of the aqueous solution containing monomer or polymer of NIPA or AMPS on a plate of glass or Teflon at 293 or 313 K. The value of  $W_a$  was calculated by the Young-Dupré equation [4],  $W_a = \gamma (1 + \cos \theta)$ , substituting the measured values of the contact angle,  $\theta$ , and surface tension,  $\gamma$ , as shown in Figs. 2 and 3. In addition, the values of  $W_a$  for water are shown as the horizontal line in Fig. 4.

A dependence of the solute concentration on  $W_a$  was found in the results for the NIPA monomer solution to glass, at 293 or 313 K, and the NIPA polymer solution on

glass or Teflon at 293 K. In those cases, the values of  $W_a$  decrease with increasing solute concentration. It is obvious that NIPA monomer or polymer lowers the interaction between water and glass.

An effect of the substrate on  $W_a$  is observed from the results showing that the value of  $W_a$  for each solution to glass is higher than that to Teflon, and for the contact between water to these surfaces. That indicates a lower interaction between aqueous solutions and hydrophobic Teflon.

A remarkable effect of temperature on the  $W_a$  was found for NIPA polymer. The values of  $W_a$  for the NIPA polymer solution to glass and Teflon at 313 K, were higher than those at 293 K. That is attributed to the hydrophilic/hydrophobic transition of the NIPA polymer. On the other hand, the values of  $W_a$  for each monomer solution are constant and independent of the temperature.

### **3.5 Factors Controlling the Formation of Composition-Gradient Gel**

In the previous section, the formation of the composition-gradient gels was discussed in terms of the static work of adhesion measured. This process could be removed from the kinetics and the effect of the experimental composition on the gelation of NIPA-*co*-AMPS gels. The reasons (i) why the decrease in the composition-gradient of the AMPS content towards Teflon occurred, and (ii) why a similar composition-gradient behavior appeared in both preparations at 293 and 313 K, can be explained as follows. The values of  $W_a$  for the AMPS monomer and polymer on Teflon were lower than those on glass at 293 and 313 K. Thus, AMPS is relatively stable at the interface to glass but unstable at the interface to Teflon. This repulsion of AMPS is due to the hydrophobicity of the Teflon wall, and consequently generates the composition-gradient. NIPA also has different values of  $W_a$  to glass and to Teflon,

although the difference for NIPA polymer is smaller than that of AMPS polymer. NIPA-*co*-AMPS gels might also demonstrate the composition-gradient of NIPA, due to the instability towards Teflon. The repulsion of NIPA to the Teflon wall could cause incomplete gelation, when the reactor having a glass-Teflon distance of 10 mm is used. The values of  $Wa$  for the NIPA polymer were different, at 293 and 313 K. However, the differences in  $Wa$  for the NIPA polymer on Teflon and glass at 293 K, are similar to those at 313 K. This may explain the similar composition-gradient behavior at 293 and 313 K.

The other two questions (iii) Why is the composition-gradient formed over a distance of several mm? and (iv) How does the glass-Teflon distance influence the content and composition of AMPS?, are not successfully explained. The attractive or repulsive forces between a solute and a substrate act in the region of the nanometer or sub-nanometer order. Thus, the composition-gradient formed over a distance of several mm is not all attributed to the intermolecular forces. Osada et al. [7,8] reported that in the preparation of AMPS gel using a hydrophobic wall, the polymer density was lower towards the hydrophobic wall over a distance of several mm, which was interpreted in terms of the interfacial energy of the polymer to the wall and the osmotic pressure of the solution. In this study concerning the preparation of the NIPA-*co*-AMPS gels, the repulsion of AMPS to Teflon may trigger the formation of the composition-gradient gel, at a distance of several mm.

#### **4 Conclusions**

The slab-shaped NIPA-*co*-AMPS gels prepared between two substrates of glass and Teflon, at 293 and 313 K, showed a decreasing composition-gradient of AMPS content towards a Teflon wall over a distance of several mm. The composition

distribution in NIPA-*co*-AMPS gels was discussed in terms of the work of adhesion,  $W_a = \gamma (1 + \cos \theta)$ , on the basis of the contact angle and the surface tension measured for a system of aqueous solution containing NIPA or AMPS monomer or polymer, and glass or Teflon substrate. The values of  $W_a$  for AMPS monomer and polymer on Teflon were lower than those on glass, at 293 and 313 K. Thus, AMPS remains relatively stable at the interface to glass and unstable at the interface to Teflon, and is repelled by the hydrophobicity of the Teflon wall. The difference in  $W_a$  for AMPS at the interfaces to glass and Teflon is one of the factors controlling the formation of the composition-gradient gels. The reason why the composition-gradient was formed over a distance of several mm still remains unclear. However, the repulsion of AMPS to Teflon can be seen as a trigger for the formation of the composition-gradient gel at this distance.

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## Figure captions

**Figure 1.** Distribution of AMPS content in slab-shaped NIPA-*co*-AMPS gels prepared between glass and Teflon walls having the distance of (c) 3 and (a) / (b) 5 mm at (b) 293 K or (a) / (c) 313 K.

**Figure 2.** Surface tension,  $\gamma$ , of an aqueous solution containing monomer or polymer of NIPA or AMPS at (a) 293 K, and (b) 313 K.

**Figure 3.** Contact angle,  $\theta$ , of the aqueous solution containing monomer or polymer of NIPA or AMPS on a plate of glass or Teflon, at 293 or 313 K.

**Figure 4.** Work of adhesion,  $W_a$ , of an aqueous solution containing monomer or polymer of NIPA or AMPS on a plate of glass or Teflon, at 293 or 313 K.

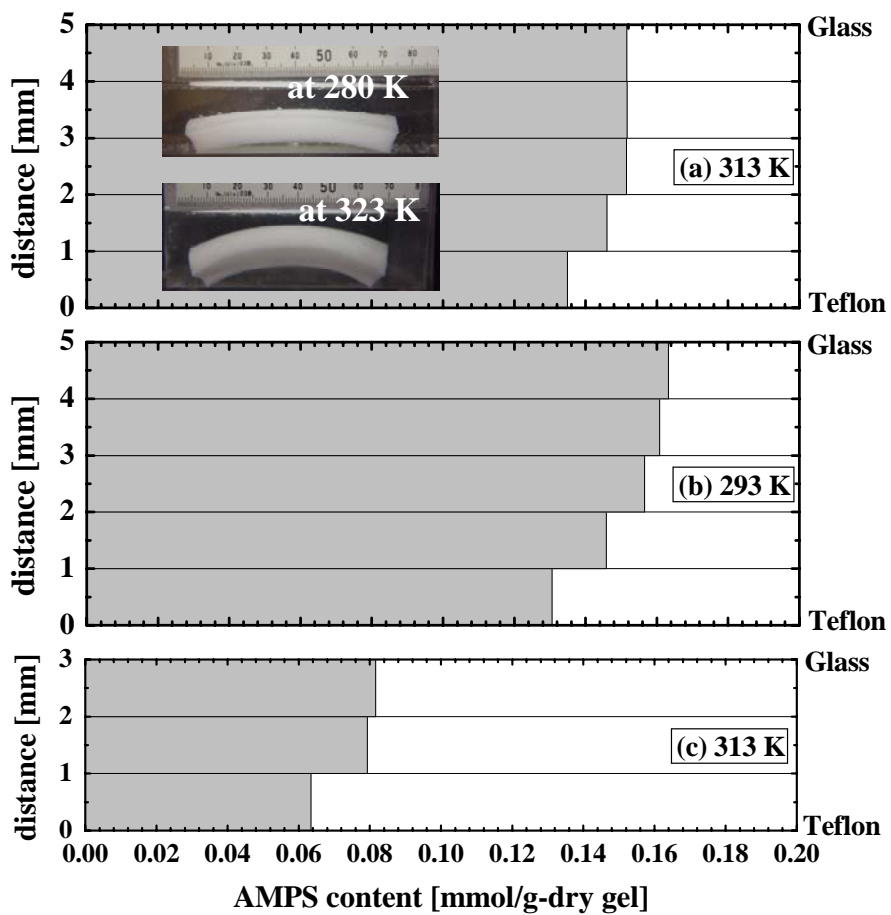


Figure 1, Hideaki Tokuyama

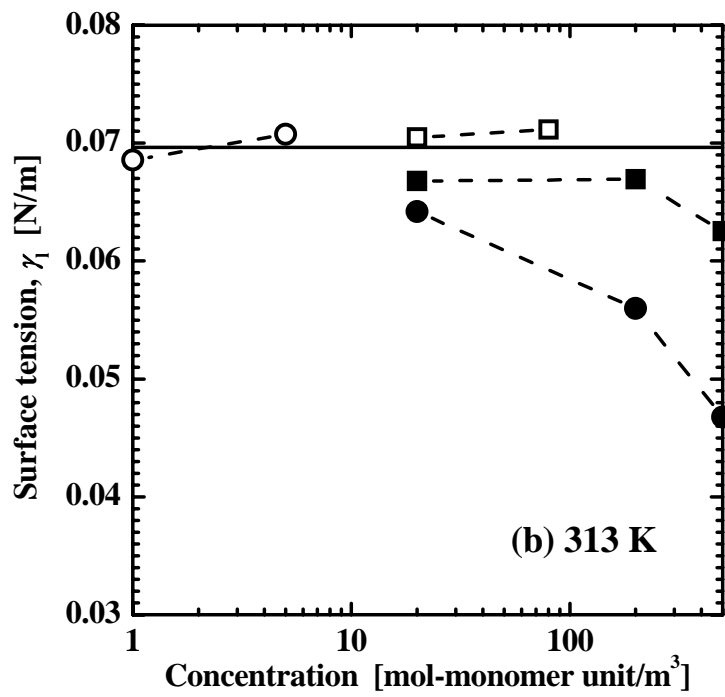
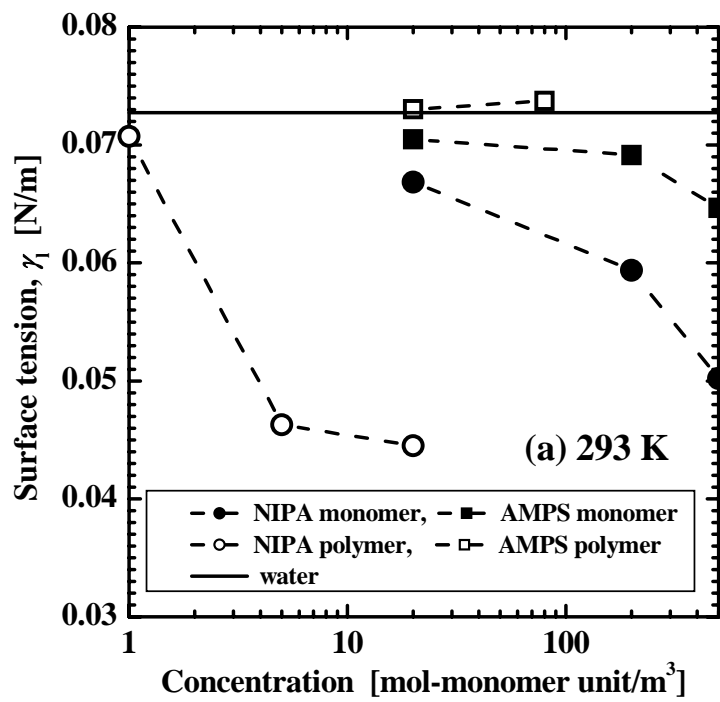


Figure 2, Hideaki Tokuyama



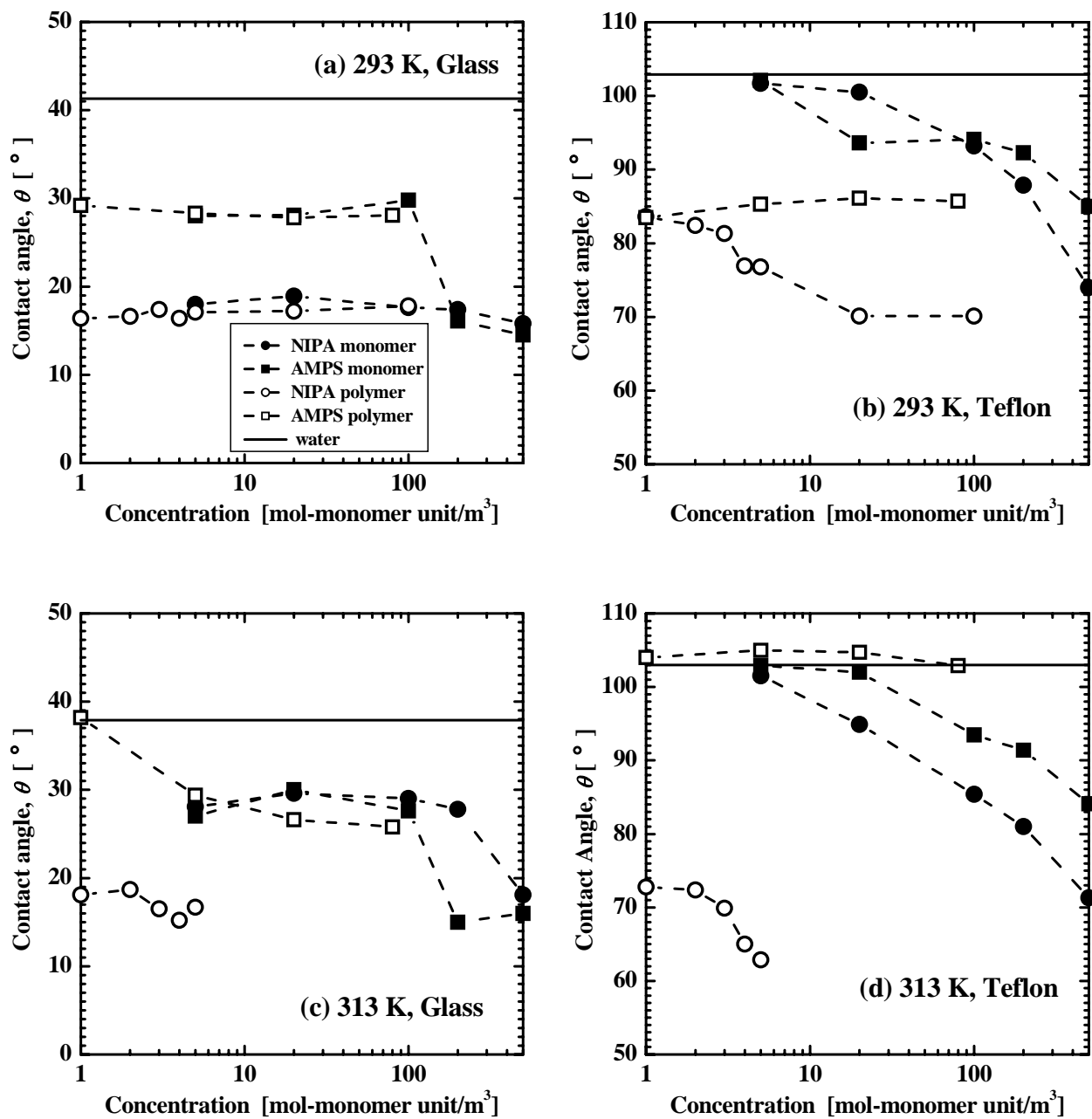


Figure 3, Hideaki Tokuyama

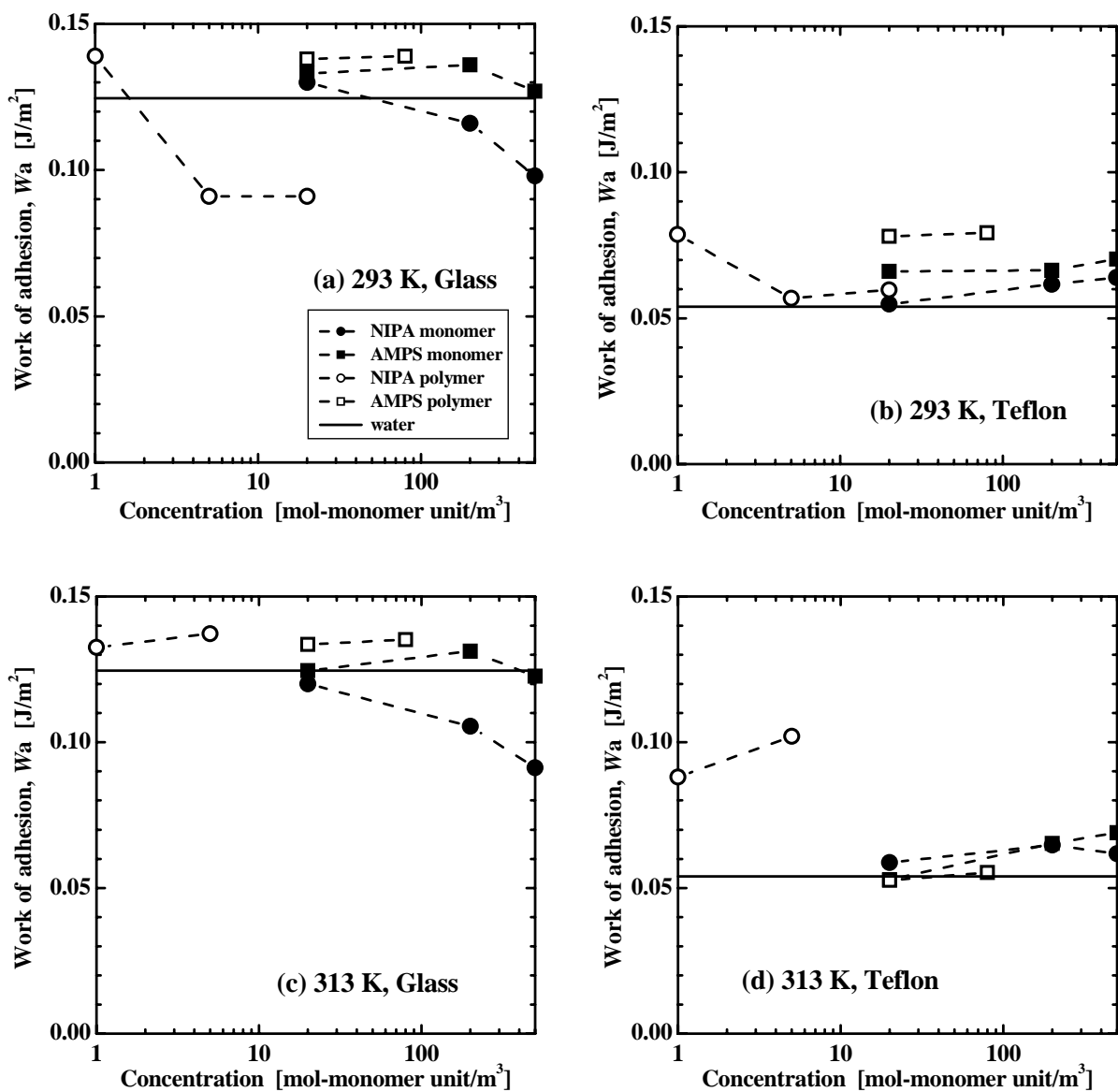


Figure 4, Hideaki Tokuyama