

## Surface free energies of styrene-acrylic acid copolymer plates prepared in various frames

M. Tsuchida and Z. Osawa

Department of Chemistry, Faculty of Engineering, Gunma University

**Abstract:** Styrene (St)-acrylic acid (AA) copolymer plates were synthesized in the frames made of glass, aluminum (Al) and poly(difluoroethylene) (PDFE). Surface properties of the prepared copolymer plates were characterized with regard to critical surface tension ( $\gamma_c$ ), chemical component by IR analysis and surface energies (total energy,  $\gamma_s$ ; dispersion force components,  $\gamma_s^d$ ; polar component,  $\gamma_s^p$ ; hydrogen bonding component,  $\gamma_s^h$ ) and the following results were obtained.

The  $\gamma_c$  values of the copolymer plates increased with AA content and also depended on the sort of the used frame. The increasing order of the  $\gamma_c$  values of the copolymer plates corresponded to those of the used frames, namely, PDFE frame < Al frame < Glass frame.

The prepared copolymer plates with low AA contents (ca. 10 mol%) were enriched in the AA moiety in the surface layer regardless of the kind of the used frame.

The total and the individual components of the surface free energies of the copolymer plates were largely affected by the property of the used frame. The glass frame gave the plate with higher  $\gamma_s^h$  values suggesting preferential orientation of the polar site of AA component.

**Key words:** Styrene-acrylic acid copolymer plate – surface enrichment – critical surface tension – surface free energy – orientation

### 1. Introduction

It has been known that the surface composition of a multicomponent polymer such as a blend polymer and a graft polymer is usually different from the bulk [1–5]. For example, Tezuka and co-workers reported that remarkable surface enrichment of poly(dimethylsiloxane) (PDMS) component was observed in poly(vinyl alcohol) (PVA)-PDMS graft copolymer films prepared by casting. This phenomenon was revealed by contact angle and x-ray photoelectron spectroscopy (XPS) [6, 7] and was explained by the high flexibility of the PDMS segment and the remarkable difference in the critical surface tension ( $\gamma_c$ ) between PDMS and PVA. Kajiyama and co-workers found that highly hydrophobic polystyrene was enriched on the air side of the cast films

of hydroxy-end-capped poly(ethylene glycol methacrylate) (PEGM)/styrene (St) diblock copolymer by means of XPS analysis. They reported a similar effect of the hydrophobic component on methoxy-end-capped PEGM/St diblock copolymer cast films [8, 9].

In addition, the surface properties of a polymeric material varied depending on the processing conditions even for homopolymers. Scholz and co-workers prepared polymer films such as PVA on several substrates by a solvent cast method. They found that the contact angles of the polymer films on the air side differed from those on the substrate side owing to the orientation of the polar groups [10]. Hirasawa and co-workers reported that the polar moiety in a polymer containing polar groups such as carboxyl groups was oriented to the surface and the orientation of the

polar moiety influenced the surface properties related with adhesion and coating [11]. These phenomena mentioned above have been found for molded and/or processed polymers. It is, therefore, expected that the surface property of a polymer synthesized in contact with a reactor wall should vary depending on the material of the reactor. In this study, styrene-acrylic acid copolymer plates were prepared in several frames (made of glass, aluminum (Al) and poly(difluoroethylene) (PDFE)), and their surface properties were characterized. Namely, critical surface tension ( $\gamma_c$ ), surface chemical components, surface free energy ( $\gamma_s$ ) and its individual components (dispersion force component,  $\gamma_s^d$ ; polar component,  $\gamma_s^p$ ; hydrogen bonding component,  $\gamma_s^h$ ) were estimated. The obtained results were discussed in connection with the surface properties of the used frames.

## 2. Experimental

### 2.1. Preparation of copolymer plates

Styrene (St), acrylic acid (AA) (Wako Pure Chemical Ind., Co., Ltd.), divinylbenzene (DVB) and 2,2'-azobisisobutyronitrile (AIBN) (Tokyo Chemical Ind., Co., Ltd.) were purified by the conventional methods [12].

The copolymer plates were prepared in the following manner: St and AA as monomers, DVB (9 mol%) as a crosslinking agent and AIBN (0.1 mol%) as an initiator were added in the frames (made of glass, aluminum and PDFE, 120 mm  $\times$  120 mm, Fig. 1) and was heated at 60°C for 6 h and then at 100°C for 24 h. The yields were 80–90%. The component elements of the frames such as Si, Al, and F were not observed on the plate surface by XPS analysis.

### 2.2. Determination of acrylic acid content

The acrylic acid content of the prepared copolymer plate was determined using a Fourier transform infrared spectrophotometer (FT/IR-8000, Nippon Bunko, Co., Ltd.) by the KBr method. The AA contents of the copolymer plates in the bulk ( $[AA]_B$ , ca. 1000  $\mu$ m thick) were calculated by Eq. (1) and were listed in Table 1 with that in the monomer mixture ( $[AA]_M$ ).

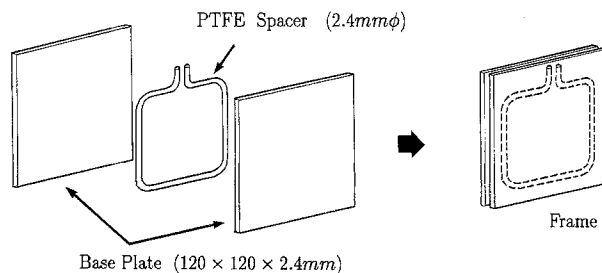


Fig. 1. Schematic illustration of the frame

Table 1. AA fraction of the copolymer plates prepared in the various frames

No.	Frame	$[AA]_M^1)$ (mol%)	$[AA]_B^1)$ (mol%)
1	PDFE	9.1	10.7
2	PDFE	20.2	21.0
3	PDFE	30.2	29.5
4	Al	10.0	9.6
5	Al	18.5	18.7
6	Al	29.2	28.0
7	Glass	8.9	9.9
8	Glass	18.0	19.4
9	Glass	29.6	28.3

<sup>1)</sup>  $[AA]_M$ : AA fraction of the monomer mixture

<sup>2)</sup>  $[AA]_B$ : AA fraction in the bulk polymer

In order to clarify the changes in the AA content from the surface to the inner region, FT-IR measurements were carried out for the surface of the as-prepared polymer plate and the plate which was ground to be required thickness. At first, the measurement was made for the as-prepared plate surface. Then the surface layer was removed by a sharp knife until a prescribed thickness of the plate was attained. The thickness of the plate of which surface layer was removed was checked by a micrometer. The grinding and measurements were repeated until the middle layer of the plate was exposed.

$$[AA] = 100 \varepsilon_{St}^{699} A_{AA}^{1705} / (\varepsilon_{St}^{699} A_{AA}^{1705} + \varepsilon_{AA}^{1705} A_{St}^{699}), \quad (1)$$

where

$[AA]$ : mole percent of AA component (%)  
 $A_{St}^{699}$ : absorbance of C–H bending vibration of St and DVB components at 699  $\text{cm}^{-1}$

$A_{AA}^{1705}$ : absorbance of C=O stretching vibration of AA component at  $1705\text{ cm}^{-1}$

$\varepsilon_{Si}^{699}$ : molar absorption coefficient at  $699\text{ cm}^{-1}$  ( $94.1\text{ l/mol cm}$ )

$\varepsilon_{AA}^{1705}$ : molar absorption coefficient at  $1705\text{ cm}^{-1}$  ( $187.5\text{ l/mol cm}$ )

### 2.3. Contact angle measurement

Contact angles were measured with distilled water, glycerol, formamide, thiodiglycol and ethyleneglycol. The liquids except water were commercially available (Wako Pure Chemical Ind., Co., Ltd.) and were used without further purification. The copolymer plates were washed with methanol in a supersonic washer for 20 s and dried under reduced pressure at room temperature before contact angle measurements. Contact angles (sessile drop method) were measured by use of a contact angle meter (CA-D, Kyowa Interface Science Co., Ltd.) at  $20^\circ\text{C}$  in an air-conditioned room (humidity, ca. 60%).

### 2.4. Estimation of critical surface tension and surface free energy

The critical surface tension of wetting ( $\gamma_C$ ) is defined by the value to which the surface tension of the wetting liquid ( $\gamma_L$ ) extrapolates as the contact angle,  $\cos \theta$ , tends to unity on a Zisman plot, the plot of  $\cos \theta$  vs.  $\gamma_L$  [13–15]. The surface free energy and its components of a polymer plate were calculated using Eqs. (2) and (3) [16]:

$$\gamma_L(1 + \cos \theta) = 2(\gamma_S^d \gamma_L^d)^{1/2} + 2(\gamma_S^p \gamma_L^p)^{1/2} + 2(\gamma_S^h \gamma_L^h)^{1/2} \quad (2)$$

$$\gamma = \gamma^d + \gamma^p + \gamma^h, \quad (3)$$

where

$\theta$ : contact angle (deg.)

$\gamma_S$ : surface free energy of solid ( $\text{mJ/m}^2$ )

$\gamma_L$ : surface free energy of liquid ( $\text{mJ/m}^2$ ) and the superscript are

$d$ : dispersion force component of surface free energy

$p$ : polar component of surface free energy

$h$ : hydrogen bonding component of surface free energy

Contact angles were measured with five kinds of liquids of which components of the surface free energies are known [16]. Optimal solution of  $\gamma_S^d$ ,  $\gamma_S^p$  and  $\gamma_S^h$  were evaluated by applying a nonlinear least square method (Marquardt method) to Eq. (2).

## 3. Results and discussion

### 3.1. Critical surface tension of copolymer plate

The relationship between the  $\gamma_C$  values and the AA contents in the bulk is shown in Fig. 2. It is recognized that the  $\gamma_C$  value depends strongly on the sort of the used frames whose  $\gamma_C$  values are different from each other (see closed symbols in Fig. 2). Judging from the  $\gamma_C$  values of the copolymer plates at similar AA contents, the increasing order of the  $\gamma_C$  value of the copolymer plates corresponds to that of the used frame, namely; PDFE frame < Al frame < Glass frame. It is obvious that the larger the  $\gamma_C$  value of the frame used is, the larger the  $\gamma_C$  value of the prepared copolymer plate becomes. In addition, the  $\gamma_C$  values of the copolymer plates increase with increasing AA contents, while the  $\gamma_C$  values of the PS plates are smaller than those of the used frames.

The fact mentioned above suggests that the surface properties of the obtained polymers are influenced by the contacting material used during

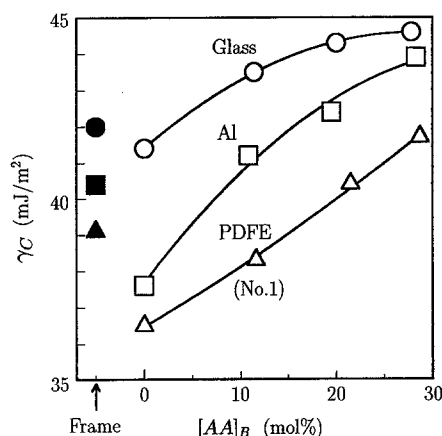


Fig. 2. Relationship between  $\gamma_C$  and  $[AA]_B$  for the styrene-acrylic acid copolymer plates prepared in the various frames.  $\Delta$ : prepared in the PDFE frame,  $\blacktriangle$ : the PDFE frame,  $\square$ : prepared in the Al frame,  $\blacksquare$ : the Al frame,  $\circ$ : prepared in the glass frame,  $\bullet$ : the glass frame

polymerization. However, all the  $\gamma_c$  values of the copolymer plates exceed the  $\gamma_c$  values of the respective frames used except No. 1 copolymer plate (see: PDFE frame,  $[AA]_B = 10.7$  mol%). The  $\gamma_c$  values of the PS plates vary and are affected by the used frames. Therefore, the discussion of surface properties of the plates using only the  $\gamma_c$  value seems to be insufficient.

In this context, Zisman already pointed out that  $\gamma_c$  does not directly represent the surface free energy ( $\gamma_s$ ) of the material. The solution of this problem could be given by the concept on the surface free energy proposed by Fowkes. He first proposed that the surface free energy of a pure phase could be represented by the sum of the contributions arising from different types of surface force components [17–18] and identified seven components.

Since the AA moiety of the copolymer plate has a carboxyl group which could form the hydrogen bonding, it is useful for this system to use Hata's method [16]. Hata suggested that the surface free energy could be expressed by three terms, namely, a dispersion force ( $\gamma_s^d$ ), a polar ( $\gamma_s^p$ ) and a hydrogen bonding component ( $\gamma_s^h$ ). Therefore, detailed discussion will be made in the following section using the extended Fowkes's equation by Hata.

### 3.2. Surface free energy and surface composition of copolymer plate

The total surface free energies ( $\gamma_s$ ) of the styrene-acrylic acid copolymer plates prepared in the three kinds of frames are plotted against the AA contents (mol%) in the bulk of the plates in Fig. 3. The total surface free energies of the frames used and the calculated values of the copolymer plates are also shown with closed symbols in the figure. The calculated values were obtained as the arithmetic mean of the  $\gamma_s$  values for polystyrene ( $32 \text{ mJ/m}^2$ ) and poly(acrylic acid) ( $68 \text{ mJ/m}^2$ ) [19]. The calculated values of the copolymer plates were not influenced by the material of the frames, i.e., they referred to the random orientation of the functional groups on the plate because the literature values of homopolymers are calculated from cohesive energies of structural groups in the polymers.

It is obvious that all of the observed total surface free energies of the copolymer plates is larger than the calculated values. The discrepancy of the

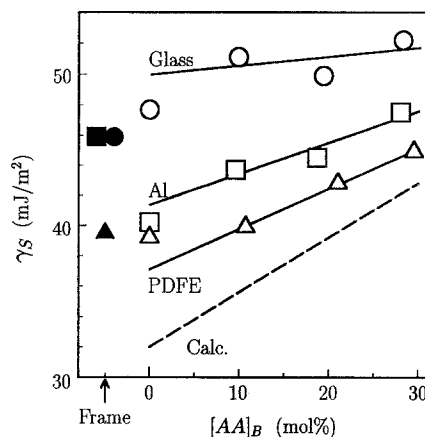


Fig. 3. Relationship between total  $\gamma_s$  and  $[AA]_B$  for the styrene-acrylic acid copolymer plates prepared in the various frames.  $\Delta$ : prepared in the PDFE frame,  $\blacktriangle$ : the PDFE frame,  $\square$ : prepared in the Al frame,  $\blacksquare$ : the Al frame,  $\circ$ : prepared in the glass frame,  $\bullet$ : the glass frame ---: calculated  $\gamma_s$  of the copolymer plate

$\gamma_s$  value between the observed and calculated one seems to be pronounced for the copolymer plates with low AA contents. It seems that the total  $\gamma_s$  values of the plates are rather close to those of the respective frames.

It is presumed that the behavior of the  $\gamma_s$  values in Fig. 3 is correlated to the surface enrichment of the AA component for the copolymer plates and/or the orientation of functional groups on the polymer surface.

It is suggested that the large difference in total value between the observed and calculated plates results in observation of surface enrichment of the AA components. The definitive surface enrichment of the AA component for the copolymer plates with relatively low AA contents (Nos. 1, 4 and 7) is observed. The respective depth profiles of the AA contents of the copolymer plates (Nos. 1, 4 and 7) are shown in Fig. 4, which are plotted with the grinding depth and the ratios of the AA contents in the grinding surface layer against that in the bulk. It is obvious that the AA contents in the plates increase remarkably toward the outermost surface in every frame.

Such an enrichment of the AA components in the surface area should be ascribed to the minimization of the free energy on the interface of the copolymer plate and the frame, and this minimization of the free energy on the interface of a multi-component polymer system is well known [1–9].

If the surface free energy is determined by only chemical composition on the polymer surface, the plots with  $\gamma_s$  and each component of the copolymer plates should be fitted to a universal line. However, none of the plots with  $\gamma_s$  vs.  $\gamma_s^d$ ,  $\gamma_s^d$  vs.  $\gamma_s^p$  and so on gave the universal line. It is, therefore, suggested that the surface free energy is not determined merely by chemical composition on the polymer surface. Furthermore, the different values of polystyrene for the sort of the frames used cannot be explained by only the surface enrichment of component substances.

The facts mentioned above suggest that the particular orientation of the chemical groups such as  $\pi$  orbital of benzene rings and carboxyl groups should occur to minimize the interfacial free energy. Baszkin et al. already reported the similar orientation of the polar groups formed on the

oxidized polyethylene films through the study on the surface free energy and its components [20–22]. They reported that the components of the surface free energy reflect the orientation of functional groups on the polymer surface.

### 3.3. Components of surface free energy for copolymer plate

The total and the individual component surface free energies of the copolymer plates prepared in the three kinds of frames are plotted against the AA content (mol%) in the bulk of the plates in Figs. 5–7.

In the case of the PDFE frame series, the  $\gamma_s^d$  and the  $\gamma_s^p$  values of the plates shown in Fig. 5 increase with the AA contents and the  $\gamma_s^h$  values keep constant. All its components of the copolymer plates are very close to those for the PDFE frame. The small discrepancies of the values between the plates and the frame are recognized in the  $\gamma_s^p$  values. The  $\gamma_s^p$  values of the copolymer plates are larger than that of the PDFE frame. The summation of the slight increases in the  $\gamma_s^p$  and the  $\gamma_s^d$  values contribute to the increases in the total  $\gamma_s$  values.

It should be noted here that the agreements of the  $\gamma_s^h$  values between the copolymer plates and the frame used are almost compatible. The oxygen

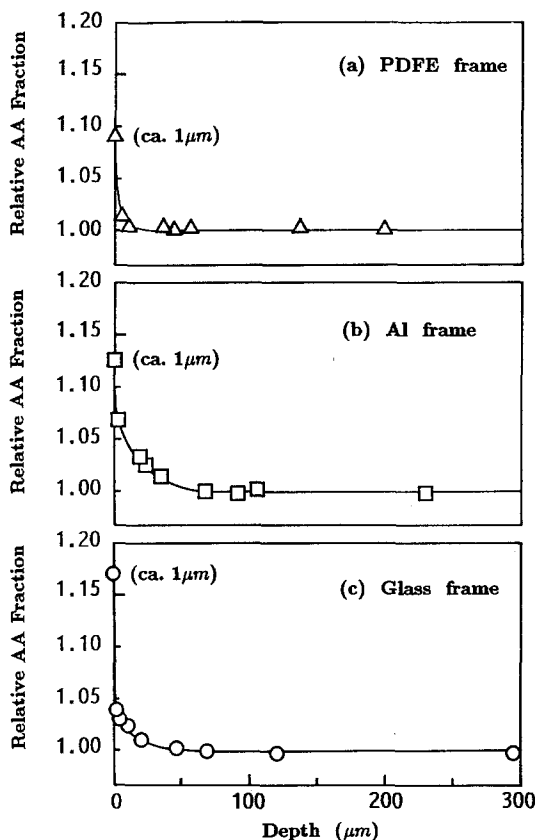


Fig. 4. Depth profiles of the AA contents of the styrene-acrylic acid copolymer plates prepared in the various frames. a) prepared in the PDFE frame ( $[AA]_B$ : 10.7 mol%, No. 1), b) prepared in the Al frame ( $[AA]_B$ : 9.6 mol%, No. 4), c) prepared in the glass frame ( $[AA]_B$ : 9.9 mol%, No. 7)

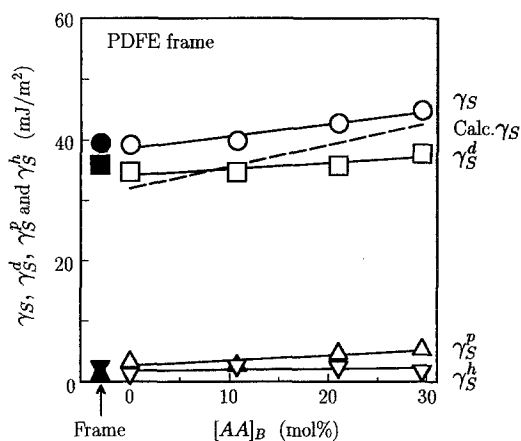


Fig. 5. Changes in the  $\gamma_s$  value and its components against  $[AA]_B$  for the styrene-acrylic acid copolymer plates prepared in the PDFE frame.  $\circ$ : total  $\gamma_s$  of the plate,  $\bullet$ : total  $\gamma_s$  of the frame,  $\square$ :  $\gamma_s^d$  of the plate,  $\blacksquare$ :  $\gamma_s^d$  of the frame,  $\triangle$ :  $\gamma_s^p$  of the plate,  $\blacktriangle$ :  $\gamma_s^p$  of the frame,  $\nabla$ :  $\gamma_s^h$  of the plate,  $\blacktriangledown$ :  $\gamma_s^h$  of the frame, ---: calculated  $\gamma_s$  of the copolymer plate

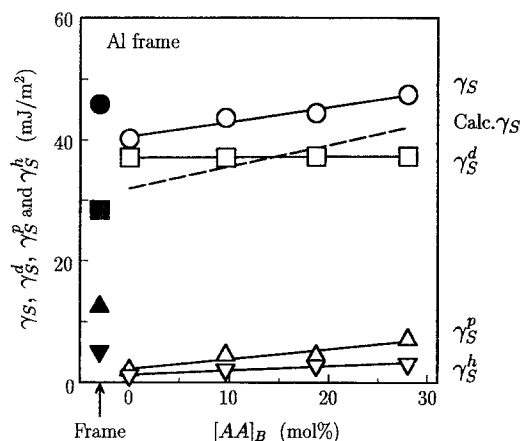


Fig. 6. Changes in the  $\gamma_S$  value and its components against  $[AA]_B$  for the styrene-acrylic acid copolymer plates prepared in the Al frame.  $\circ$ : total  $\gamma_S$  of the plate,  $\bullet$ : total  $\gamma_S$  of the frame,  $\square$ :  $\gamma_S^d$  of the plate,  $\blacksquare$ :  $\gamma_S^d$  of the frame,  $\triangle$ :  $\gamma_S^p$  of the plate,  $\blacktriangle$ :  $\gamma_S^p$  of the frame,  $\nabla$ :  $\gamma_S^h$  of the plate,  $\blacktriangledown$ :  $\gamma_S^h$  of the frame, ---: calculated  $\gamma_S$  of the copolymer plate

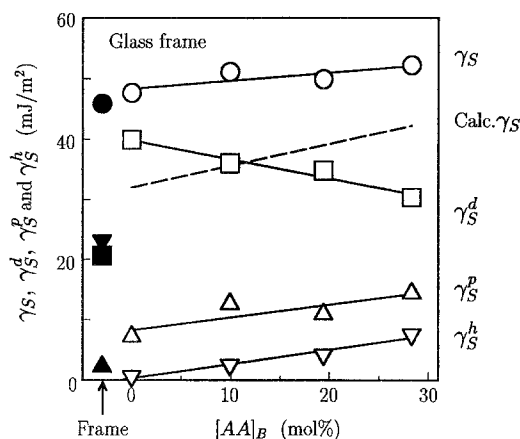


Fig. 7. Changes in the  $\gamma_S$  value and its components against  $[AA]_B$  for the styrene-acrylic acid copolymer plates prepared in the glass frame.  $\circ$ : total  $\gamma_S$  of the plate,  $\bullet$ : total  $\gamma_S$  of the frame,  $\square$ :  $\gamma_S^d$  of the plate,  $\blacksquare$ :  $\gamma_S^d$  of the frame,  $\triangle$ :  $\gamma_S^p$  of the plate,  $\blacktriangle$ :  $\gamma_S^p$  of the frame,  $\nabla$ :  $\gamma_S^h$  of the plate,  $\blacktriangledown$ :  $\gamma_S^h$  of the frame, ---: calculated  $\gamma_S$  of the copolymer plate

parts of the AA moiety which could form the hydrogen bonding might be so poor on the copolymer surfaces as to optimize the  $\gamma_S^h$  values, while the polar parts of the moiety which could not form the hydrogen bonding and the nonpolar parts could orient to the copolymer surface.

In the case of the Al frame series, the surface free energies estimated for the copolymer plates shown in Fig. 6 are all similar to those for the

respective plates prepared in the PDFE frame. The deficiencies of the  $\gamma_S^h$  and the  $\gamma_S^p$  values of the copolymer plates compared with those values of the Al frame are compensated by the excess in the  $\gamma_S^d$  values. Remarkable differences in the  $\gamma_S^d$  and the  $\gamma_S^h$  values are observed between the PDFE and the Al series. The  $\gamma_S^d$  values of the copolymer plates keep constant ( $37.2 \text{ mJ/m}^2$ ) in spite of increases in the AA contents. The  $\gamma_S^h$  values of the copolymer plates slightly increase with the AA contents toward that of the Al frame, which is reflected in the constant  $\gamma_S^d$  values. The orientations of the functional groups in the copolymer plates prepared in the Al frame are supposed to be similar to those in the copolymer plates prepared in the PDFE frame. However, the oxygen parts of the AA moiety which could form the hydrogen bonding exit on the copolymer surface prepared in the Al frame more than that in the PDFE frame.

In the case of the copolymer plates prepared in the glass frame shown in Fig. 7 peculiar features are observed in contrast to previous cases. That is, remarkable increases in both the  $\gamma_S^p$  and the  $\gamma_S^h$  values and decrease in the  $\gamma_S^d$  values with increasing of the AA contents are observed. These are apparently due to the extraordinarily large  $\gamma_S^h$  value of the glass frame ( $23.1 \text{ mJ/m}^2$ ) compared to Al ( $5.1 \text{ mJ/m}^2$ ) and PDFE ( $2.5 \text{ mJ/m}^2$ ). It is, therefore, conceivable that the carboxyl groups of the AA components orient to the plate surface as much as possible and the nonpolar parts on the polymer chain are hidden from the surface when the plate is prepared in the glass frame.

There seems to exist a preferential order for the surface free energies of the polymer plates to be close to those of the frame. The dominant motive should be to minimize the difference of the total surface free energies ( $\gamma_S$ ) between the plate and the frame. The second priority seems to be afforded, at least in the poly(styrene-co-acrylic acid) systems studied in this paper, to the hydrogen bonding component of the surface free energy ( $\gamma_S^h$ ). The other two components of the surface free energy ( $\gamma_S^d$  and  $\gamma_S^p$ ) would be controlled so as to make the accounts balance.

The complex and peculiar features of the components of the surface free energy might relate with the total free energy of the surface phase of the plate including the conformational factors of the polymer. Even if the total surface free energy of the plate was optimized, there could exist some

distortion in the polymer conformation, as is easily expected for the styrene homopolymer prepared in the glass frame. The less distorted arrangement of the atomic groups would be achieved by the introduction of a certain amount of the AA moiety into the polymer chain in the present system studied.

#### 4. Conclusion

Styrene (St)-acrylic acid (AA) copolymer plates were synthesized in the frames made of glass, aluminum (Al) and poly(difluoroethylene) (PDFE).

The critical surface tension ( $\gamma_c$ ) of the prepared copolymer plates increased with the acrylic acid (AA) component. The  $\gamma_c$  value depended on the sort of the frame used, and the increasing order of the  $\gamma_c$  values of the copolymer plates corresponded to those of the used frames, namely, PDFE frame < Al frame < glass frame.

The surface enrichments of the AA contents for copolymer plates with low AA contents were observed.

Estimation of the total and the three components (dispersion force, polar and hydrogen bonding) of the surface free energies of both copolymer plates and frames used enabled to clarify the relationship of the surface properties between the copolymer plates and the used frames.

None of the plots with  $\gamma_s$  vs.  $\gamma_s^d$ ,  $\gamma_s^d$  vs.  $\gamma_s^p$  and so on gave a universal line. It was, therefore, suggested that the surface free energy was not determined merely by chemical composition on the polymer surface.

The surface free energies of the copolymer plates were close to those of the respective used frames. This fact would be attributed to the minimization of the difference in the total surface free energy between the copolymer plate and the used frame. The three components of the surface free energy varied with total surface energy, while the dispersion force component was predominant in the surface.

Orientation of functional groups on the polymer surface was suggested to occur so as to optimize the interfacial free energy between the polymer and the frame.

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#### Authors' address:

Prof. Zenjiro Osawa  
Department of Chemistry  
Faculty of Engineering  
Gunma University  
1-5-1 Tenjin-cho, kiryu-shi  
Gunma 376  
Japan