

# Miscibility of Mixed Stereoregular PMMA/PVCN Monolayers at the Air/Water Interface

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**ABSTRACT:** The mixed monolayer behavior of stereoregular poly(methyl methacrylate) (PMMA) and poly(vinyl cinnamate) (PVCN) was investigated from the measurements of surface pressure–area per molecule ( $\pi$ - $A$ ) isotherms at three different temperatures of  $25 \pm 1$ ,  $32.5 \pm 1$ , and  $40 \pm 1^\circ\text{C}$ . The miscibility and nonideality of the mixed monolayers were examined by calculating the excess area as a function of composition. Positive and negative deviations from ideality were observed. Negative deviations were observed mostly in syndiotactic PMMA (sPMMA) and PVCN blends suggesting the existence of favorable interactions. However, positive deviations in

most isotactic PMMA (iPMMA) and PVCN blends indicated that the existence of unfavorable interactions. Atactic PMMA and PVCN blends demonstrated intermediate deviation behavior to sPMMA and iPMMA blends. On the basis of the results of  $\pi$ - $A$  isotherms, the monolayer miscibility between PMMA and PVCN was in the majority not in agreement with the studies on the same blends in the bulk state. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 333–341, 2012

**Key words:** miscibility; stereoregular; monolayer; PMMA; PVCN

## INTRODUCTION

Polymer blends in the thin film states are of special interest for both fundamental studies and practical applications. There are lots of studies of mixed polymer monolayers spread at the air/water surface.<sup>1–5</sup> In particular, Gabrielli et al.<sup>6–10</sup> have made a significant contribution to the investigation of various mixed polymer films in obtaining information regarding the aspect of their miscibility in the two-dimensional state. One of their vital conclusions is that the miscibility of mixed polymers spread at the air/water interface strongly depends on the interfacial orientation of the polymer chains, such as a predominantly horizontal orientation, with the hydrophobic chains parallel to the interface, and a predominantly vertical orientation, with the hydrophobic chains perpendicular to the interface. The components that show miscibility have the same interfacial orientation, and the immiscible ones have a different orientation. However, the work of Kawaguchi and Nishida<sup>2</sup> seems to demonstrate that the thermodynamic interaction between the two poly-

mers plays an important role besides orientational conditions.

In general, the miscibility of the mixed polymer monolayers is determined from the plot of the mean areas at a constant surface pressure as a function of composition of one component in the binary mixture. If the plot obeys a linear relationship, i.e., the surface areas are additive, the mixed films can be regarded as an ideal mixture or as a completely immiscible mixture. The deviation from the linear relation stems from the contribution of intermolecular interaction between two components. A negative deviation means that the mixtures are considered to be stable and miscible, whereas a positive deviation indicates that the mixtures are less stable than components alone at the interface.

On the other hand, determining the miscibility of two polymers in the bulk state (polymer blends) is one of the central problems in polymer science and engineering. Few pairs of polymers were found to be miscible.<sup>11</sup> Not all polymers form stable films at the air/water interface; therefore, it is not easy to determine good pairs to compare the miscibility in the bulk state with that in a film spread at the air/water interface.

Recently, Wen<sup>12</sup> published an article of network structure control of binary mixed Langmuir monolayers of homopolystyrene (h-PS) and a symmetric diblock copolymer polystyrene-*block*-poly(2-vinyl pyridine) (PS-*b*-P2VP). The results showed that there existed a composition window for mixed

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Langmuir monolayers of h-PS and PS-*b*-P2VP to form necklace-network structure at the air/water interface. The stereocomplex formation between isotactic and syndiotactic poly(methyl methacrylate) (i-PMMA, st-PMMA) in a Langmuir monolayer investigated by surface pressure–area isotherms and atomic force microscopy (AFM) was reported by Aiba et al.<sup>13</sup> Their results indicated that the stereocomplex formation was highly sensitive to the compression rate of the monolayer. Other current references include the molecularly detailed modeling of surface pressure isotherms of poly-L-lactic acid, poly(dimethylsiloxane), PMMA, and poly(isobutylene)<sup>14</sup> and monolayers of poly(styrene)-poly(methyl methacrylate) diblock copolymer<sup>15</sup> at the air/water interface studied by the surface pressure–area isotherms at several temperatures.

Previously,<sup>16</sup> the mixed monolayer behavior of tactic poly(methyl methacrylate) (PMMA) and poly(vinyl phenol) (PVPh) was investigated from the measurements of surface pressure–area per molecule ( $\pi$ -*A*) isotherms. The  $\pi$ -*A* isotherms indicated that isotactic PMMA (iPMMA) and PVPh were miscible at the air/water interface. The miscibility and nonideality of the mixed monolayers were examined by calculating the excess area as a function of composition, and negative deviations from ideality were observed, which suggest that the existence of attractive interactions between iPMMA and PVPh. However, the  $\pi$ -*A* isotherms of mixed syndiotactic PMMA (sPMMA)/PVPh monolayers showed positive deviation from ideality, which might suggest that nonfavorable interactions existing between sPMMA and PVPh.

The  $\pi$ -*A* isotherms of mixed atactic PMMA (aPMMA)/PVPh monolayers exhibited complicated excess area behavior. Both positive and negative deviations from ideality were observed at various surface pressures. These isotherm results of mixed polymers correlate approximately well with the miscibility of the corresponding mixtures in the bulk state. The formation of hydrogen bonding between PMMA and PVPh was substantiated in the bulk state by means of FTIR. Regardless of tacticity, an increase of hydrogen-bonded carbonyl fraction was observed.

In a previous study,<sup>17,18</sup> the miscibility of stereoregular PMMA with poly(vinyl cinnamate) (PVCN) in the bulk state was investigated in this laboratory. Based on the DSC results of the prepared blends,<sup>17</sup> aPMMA was found to be miscible with PVCN on account of single glass transition temperature and transparency detected in the blends. The iPMMA/PVCN blends<sup>18</sup> were also found to demonstrate single glass transition temperature suggesting miscibility between iPMMA and PVCN. However, sPMMA was found to be almost immiscible with PVCN

because of the observation of two glass transition temperatures in the prepared blends.<sup>18</sup> Any marked observation of interaction was not shown by the FTIR spectra. However, the possibility of some degree of hydrogen bonding between C=O of PMMA and OH of PVCN cannot be ruled out.

The aim of this article is to compare the miscibility of stereoregular PMMA with PVCN in the two-dimensional state with that of polymers in the bulk state. The surface pressures of the binary films of stereoregular PMMA/PVCN (the same polymers used in Refs. 17 and 18) were measured. On the basis of the results of  $\pi$ -*A* isotherms, miscibility between stereoregular PMMA and PVCN was investigated in this article. The effect of tacticity and composition of PMMA on its miscibility with PVCN was expounded and reported in detail in this article. It is worth noting the iPMMA in this study had a higher  $T_g$  than pure iPMMA, the monolayer did not show much crystallinity. This point will be discussed more in the “Experimental” section. To the best of our knowledge, there is no systematic and detailed report on the miscibility of mixed stereoregular PMMA/PVCN monolayers at the air/water interface. PVCN could undergo photo<sup>19</sup> and thermal cross-linking by opening its double bonds and therefore PMMA/PVCN monolayers could find potential application in light or temperature sensitive devices.

## EXPERIMENTAL

### Materials

iPMMA, aPMMA, and sPMMA were purchased from Polysciences, Warrington, PA. According to the supplier information, the molecular weights ( $M_w$ ) of iPMMA, aPMMA, and sPMMA are all 100,000 g/mol. The molecular weight ( $M_w$ ) of PVCN obtained from Scientific Polymer Products (Ontario, NY) is also 100,000 g/mol. PVCN was mixed with each tactic PMMA individually to form mixtures in the weight ratios of 1/3, 1/1, and 3/1. The mixtures were designated as PMMA<sub>x</sub>-PVCN<sub>y</sub>. For example, PMMA<sub>3</sub>-PVCN<sub>1</sub> represents PMMA and PVCN were mixed in 3/1 ratio.

The polydispersities ( $M_w/M_n$ ) of the three PMMAs were not measured therefore not reported here. Sutherland et al.<sup>20</sup> reported that molecular weight has a slight effect on the  $\pi$ -*A* isotherms of PMMA and tacticity has a dominant effect on the position of PMMA's isotherms. Therefore, the molecular weight distribution effect is believed to be minimal in this study when compared with the effect of tacticity. We did not characterize the tacticity of PMMA by NMR. Therefore, a simple estimation of the fractions of meso (m) and racemic (r) diads was resorted. The meso diad fractions of PMMA were

computed previously.<sup>21</sup> The *m* and *r* fractions of iPMMA, aPMMA, and sPMMA are 68.7% and 31.3%, 33.8% and 66.2%, and 9.3% and 90.7%, respectively. The error of estimation is 5–8%. Coleman et al.<sup>19</sup> reported that PVCN is actually a copolymer of vinyl alcohol and vinyl cinnamate. According to their estimation of the same product, mole fraction of vinyl alcohol is about 0.24. The glass transition temperatures ( $T_g$ s) of bulk iPMMA, aPMMA, sPMMA, and PVCN were determined to be 75, 103, 122, and 75°C, respectively, with a DuPont 2000 thermal analyzer at a heating rate of 20°C/min. The inflection point of the specific heat jump of the second thermal scan was taken as  $T_g$ .  $T_g$  of iPMMA (75°C) is higher than pure iPMMA (~30–40°C). Brewster angle microscopy (BAM) studies of iPMMA were performed previously,<sup>22</sup> little aggregates were observed in the  $\pi$ -*A* isotherm compression curve. Therefore, aggregation played an insignificant role in the mixed iPMMA/PVCN  $\pi$ -*A* isotherm compression curve.

2-Butanone purchased from Kanto Chemical Co. was used as the spreading solvent for the polymer films. 2-Butanone was chosen to be the same as in Ref. 14 because it produced larger limiting area. Only highly pure water, which was purified by means of a Milli-Q plus water purification system, with a resistivity of 18.2M $\Omega$ -cm was used in all experiments.

### Surface pressure measurements

A model minitrough (M 1200) was purchased from KSV Instruments, Finland. The Teflon trough was 320-mm long and 75-mm wide. Regulation of the trough temperature was controlled by circulating constant temperature water from an external circulator through the tubes attached to the aluminum-based plate of the trough. The trough was placed on an isolated vibration-free table and was enclosed in a glass chamber to avoid contaminants from the air. A computer with an interface unit obtained from KSV instruments was used to control the Teflon barriers. One of the important characteristics of the trough system is that two barriers confining a monolayer at the interface are driven symmetrically during the compression of the monolayer. The surface pressure was measured by the Wilhelmy plate method. The resolution for surface measurement is 0.004 mN/m, and the inaccuracy of surface area regulation is <1%, according to the specifications of the instruments. A  $\pi$ -*A* isotherm was obtained by a continuous compression of a monolayer at the interface by two barriers. Before each isotherm measurement, the trough and barriers were cleaned with an ethanol solution and then rinsed by purified water. The sand blasted platinum plate used for surface pres-

sure measurements was also rinsed with purified water and then flamed before use. In addition, all glassware was cleaned before use in the same manner as the trough and barrier.

For starting the experiment, the freshly cleaned trough was placed into position in the apparatus first, then it was filled with purified water as the subphase with temperatures controlled at 25  $\pm$  1, 32.5  $\pm$  1, and 40  $\pm$  1°C. The clean platinum plate was hanged in the appropriate position for surface pressure measurements. The surface pressure fluctuation was estimated to be <0.2 mN/m during the compression of the entire trough surface area range. Then, the two barriers were moved back to their initial positions. The sample concentration of solution of polymer and solvent was set at 0.5 mg/mL. A 25  $\mu$ L sample containing monolayer-forming polymeric materials was spread on the subphase by using a Hamilton microsyringe to make the deposition of polymer molecules at almost the same condition. At least 30–45 min was allowed for evaporation of the spreading solvent. After the solvent was evaporated, the monolayer was compressed continuously at a rate of 3.5 mm/min to obtain a single  $\pi$ -*A* isotherm. The  $\pi$ -*A* isotherms were often obtained in duplicate. The  $\pi$ -*A* isotherms of our studied polymers are dependent on the compression rate therefore the results were performed at the same compression speed.

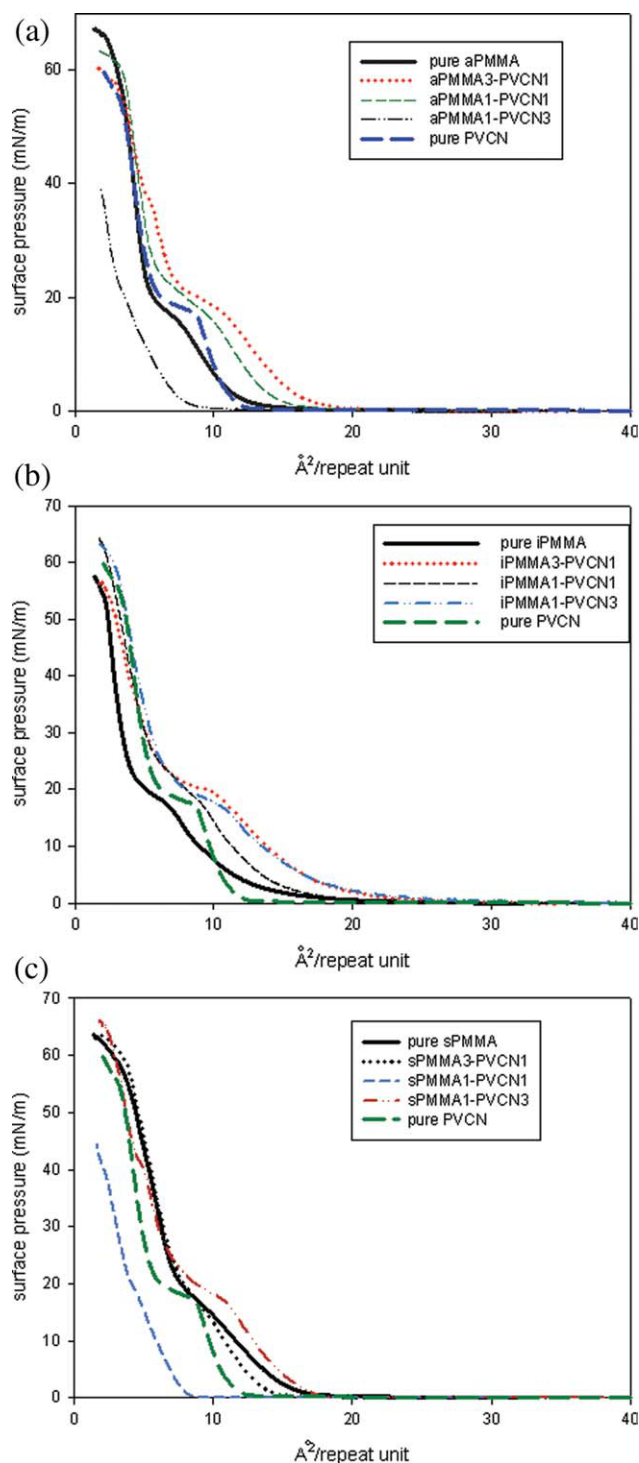
## RESULTS AND DISCUSSION

### Polymers and PMMA/PVCN mixture at 25°C

The  $\pi$ -*A* isotherms of monolayers for the three PMMA stereoisomers and PVCN at 25°C are shown, respectively, in Figure 1(a–c). The discussion for the three stereoisomers at three temperatures was reported previously<sup>23</sup> and therefore omitted here. The results are consistent with those reported by Beredjick.<sup>24</sup>

The  $\pi$ -*A* isotherms of PVCN (presented in Fig. 1) show a smaller lift-off area than PMMA. A clear transition of PVCN was observed at surface pressure slightly lower than 20 mN/m likely because of monolayer transformation into multilayer. The collapse pressure of PVCN is comparable with PMMA stereoisomers.

Figure 1 presents the the  $\pi$ -*A* isotherms of mixed monolayers for (a) aPMMA/PVCN, (b) iPMMA/PVCN, and (c) sPMMA/PVCN at 25°C. For aPMMA/PVCN mixed monolayers [shown in Fig. 1(a)], two  $\pi$ -*A* isotherms of mixed monolayers [aPMMA/PVCN(3/1) and (1/1)] demonstrate larger surface area than either aPMMA or PVCN. However, one mixed monolayer [aPMMA/PVCN(3/1)] isotherms show smaller surface area than PVCN. The mixed monolayer isotherms in Figure 1(b) all



**Figure 1** Surface pressure–area per molecule isotherms for mixed monolayers of (a) aPMMA/PVCN, (b) iPMMMA/PVCN, and (c) sPMMA/PVCN at 25°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

demonstrate larger surface area than iPMMMA or PVCN at the same surface pressure indicating positive deviation. For sPMMA/PVCN mixed monolayers [shown in Fig. 1 (c)], the situation is similar to Figure 1(a). However, one mixed monolayer

[sPMMA/PVCN(3/1)] isotherm is located between sPMMA and PVCN.

### Polymers and PMMA/PVCN mixture at 32.5°C

The  $\pi$ - $A$  isotherms of monolayers for the three PMMA stereoisomers and PVCN at 32.5°C are shown respectively, in Figure 2(a–c). The obvious feature is the PVCN isotherms move to the left of PMMA isotherms. The temperature effect on the isotherms of the studied polymers will be discussed later in this article, therefore omitted here.

Figure 2 presents the  $\pi$ - $A$  isotherms of mixed monolayers for (a) aPMMA/PVCN, (b) iPMMMA/PVCN, and (c) sPMMA/PVCN at 32.5°C, respectively. Since there is a marked isotherm difference between aPMMA and PVCN, the behavior of  $\pi$ - $A$  isotherms of mixed monolayers is determined easily. As shown in Figure 2(a), two mixed monolayers [aPMMA/PVCN(3/1) and (1/1)] demonstrate their isotherms in the middle of aPMMA and PVCN but one mixed monolayer [aPMMA/PVCN(1/3)] isotherm shows smaller surface area than aPMMA or PVCN. Figure 2(b) shows similar characteristic to those in Figure 1(b) at lower temperature. The surface areas of mixed iPMMMA/PVCN monolayers are mostly larger than the average of iPMMMA and PVCN. The sPMMA/PVCN mixed monolayers in Figure 2(c) also demonstrate similar characteristic to Figure 1(c) at lower temperature. Smaller surface area than the average is clearly observed.

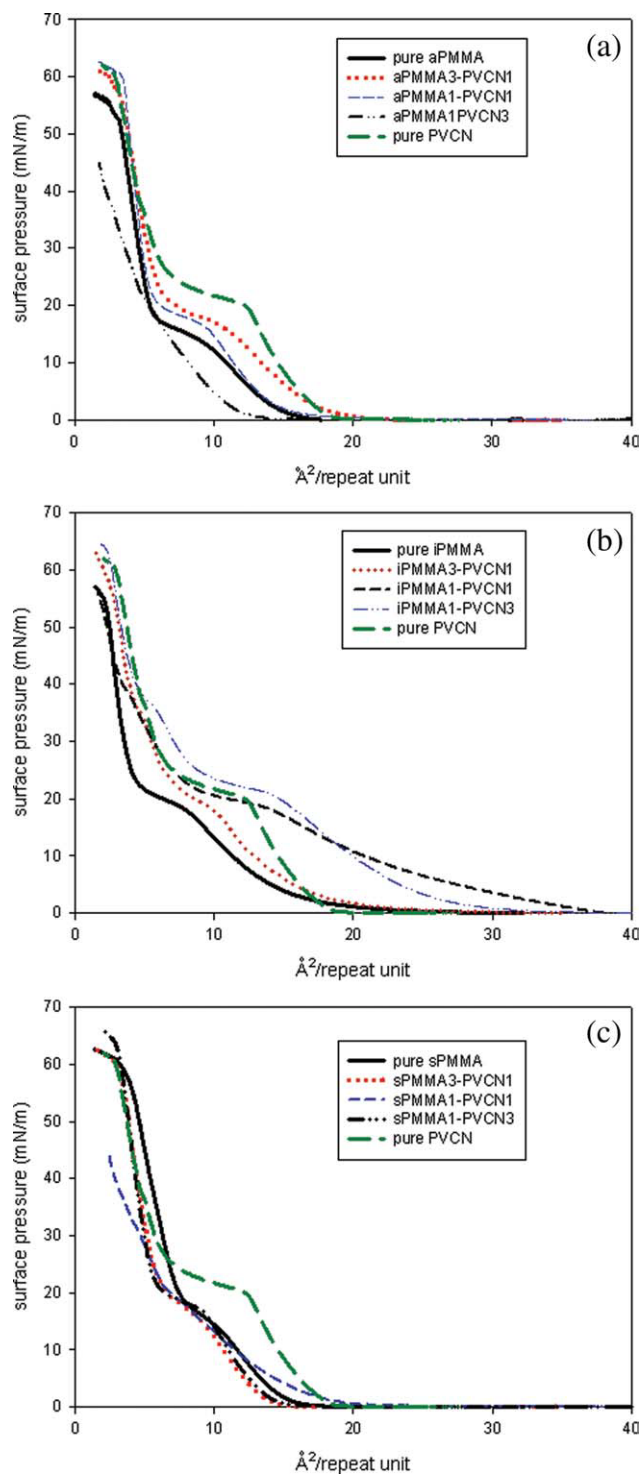
### Polymers and PMMA/PVCN mixture at 40°C

The  $\pi$ - $A$  isotherms of monolayers for the three PMMA stereoisomers and PVCN at 40°C are shown, respectively, in Figure 3(a–c). One thing worth noticing is that surface area of iPMMMA or aPMMA is larger than PVCN.

Figure 3 presents the  $\pi$ - $A$  isotherms of mixed monolayers for (a) aPMMA/PVCN, (b) iPMMMA/PVCN, and (c) sPMMA/PVCN at 40°C, respectively. For aPMMA-PVCN mixed monolayers shown in Figure 3(a), a different behavior from those at 32.5°C is observed. Mostly smaller surface areas of mixed monolayers than aPMMA or PVCN are detected. Figure 3(b) shows similar behavior to those in Figure 2(b). Larger surface areas of mixed iPMMMA/PVCN monolayers than iPMMMA or PVCN at 40°C are observed. For sPMMA/PVCN mixed monolayers shown in Figure 3(c), most  $\pi$ - $A$  isotherms are located in between sPMMA and PVCN.

### Polymers at three different temperatures

The  $\pi$ - $A$  isotherms of monolayers for the three PMMA stereoisomers were presented previously<sup>21</sup>



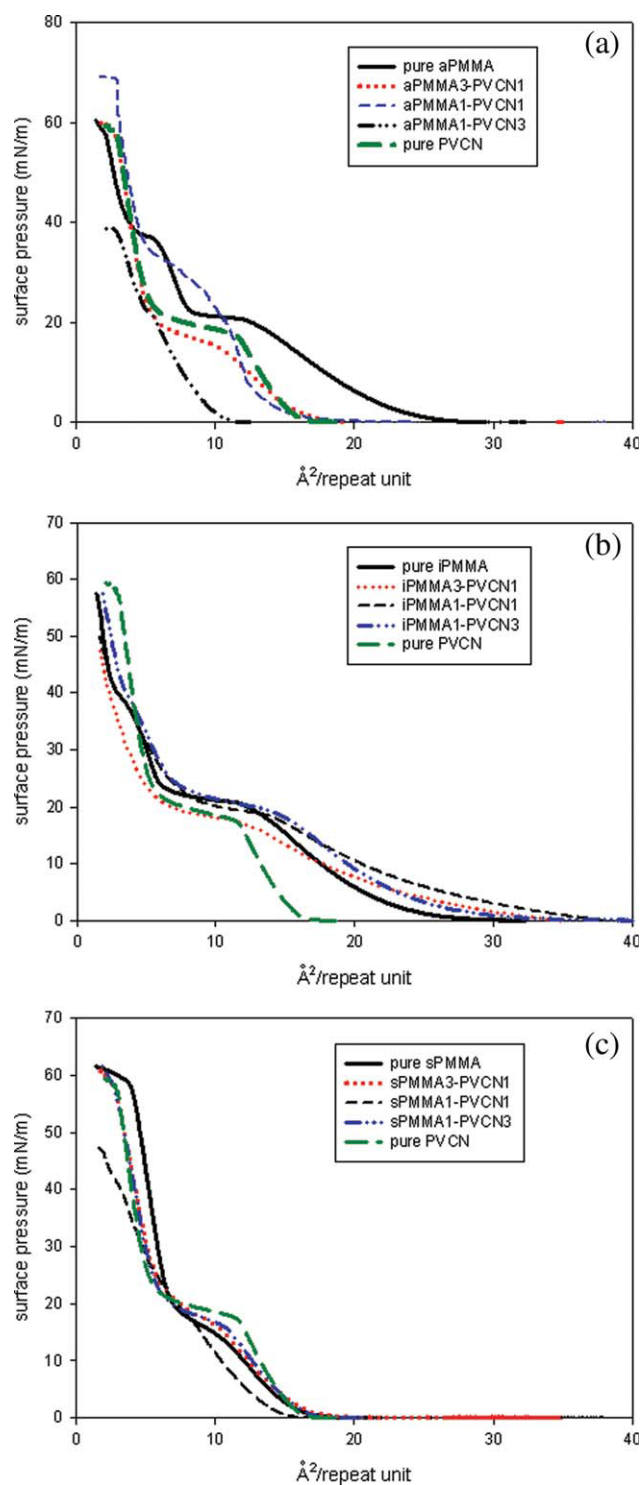
**Figure 2** Surface pressure–area per molecule isotherms for mixed monolayers of (a) aPMMA/PVCN, (b) iPMMMA/PVCN, and (c) sPMMA/PVCN at 32.5°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

at 10, 25, and 40°C, respectively. However, the temperature effect on isotherms was not discussed.

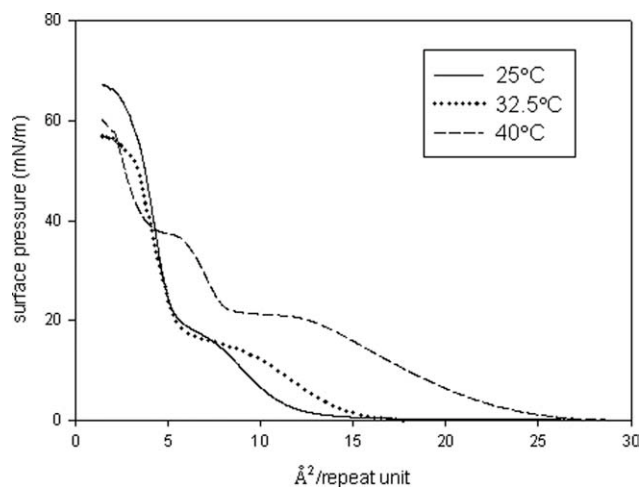
In this section, Figures 4–7 present the  $\pi$ - $A$  isotherms at three different temperatures (25, 32, 5, and

40°C) in the order of aPMMA, iPMMMA, sPMMA, and PVCN, respectively.

Similar temperature dependent behavior of aPMMA and iPMMMA  $\pi$ - $A$  isotherms (shown in

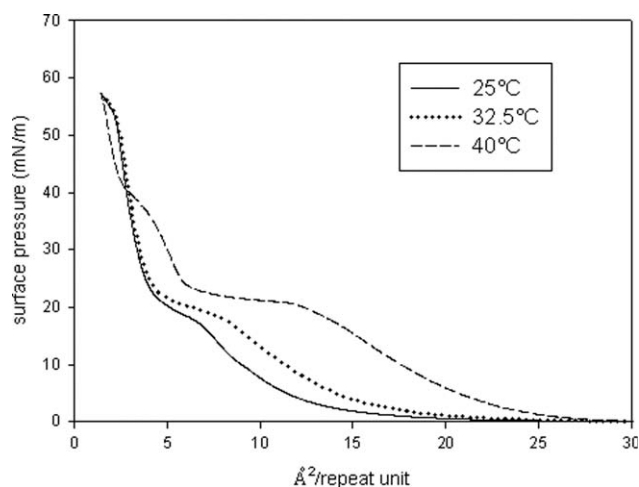


**Figure 3** Surface pressure–area per molecule isotherms for mixed monolayers of (a) aPMMA/PVCN, (b) iPMMMA/PVCN, and (c) sPMMA/PVCN at 40°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

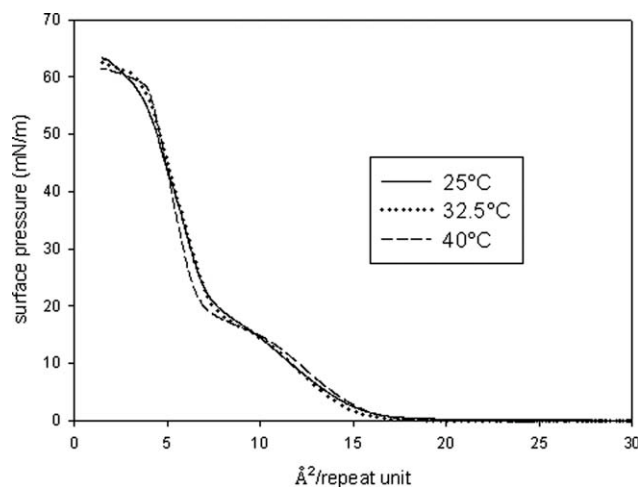


**Figure 4** Surface pressure–area per molecule isotherms of aPMMA at three temperatures.

Figs. 4 and 5) is observed because of similarity in tacticity distribution. aPMMA is shown to have more resemblance with iPMMA than sPMMA according to the  $\pi$ - $A$  isotherms shown in Figure 1(a,b). At higher temperature, the  $\pi$ - $A$  isotherms are above those at lower temperatures. The reason for this is likely predominantly entropic effect. The entropic effect probably results from freer rotation of  $\text{OCH}_3$  groups at higher temperatures. sPMMA  $\pi$ - $A$  isotherms in Figure 6 show little temperature dependence likely because of restricted segmental groups motion. A strong temperature dependence of  $\pi$ - $A$  isotherms (given in Fig. 7) is observed in PVCN monolayer especially at the low surface area region. The entropic effect caused by rotation of cinnamate side chains probably results in the elevation of PVCN  $\pi$ - $A$  isotherms at higher temperatures.



**Figure 5** Surface pressure–area per molecule isotherms of iPMMA at three temperatures.



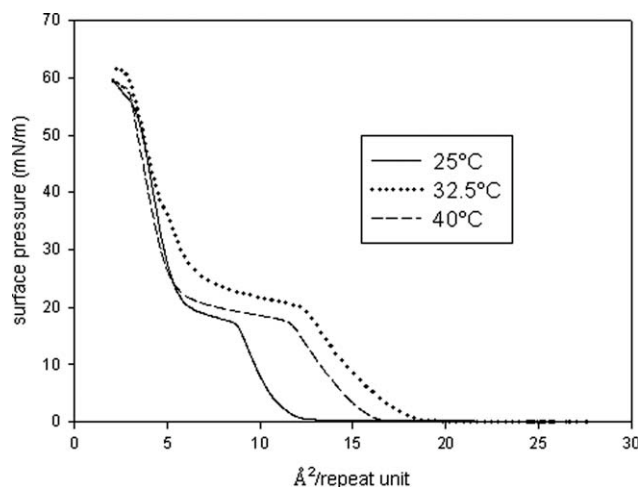
**Figure 6** Surface pressure–area per molecule isotherms of sPMMA at three temperatures.

#### The excess areas of mixture at three different temperatures

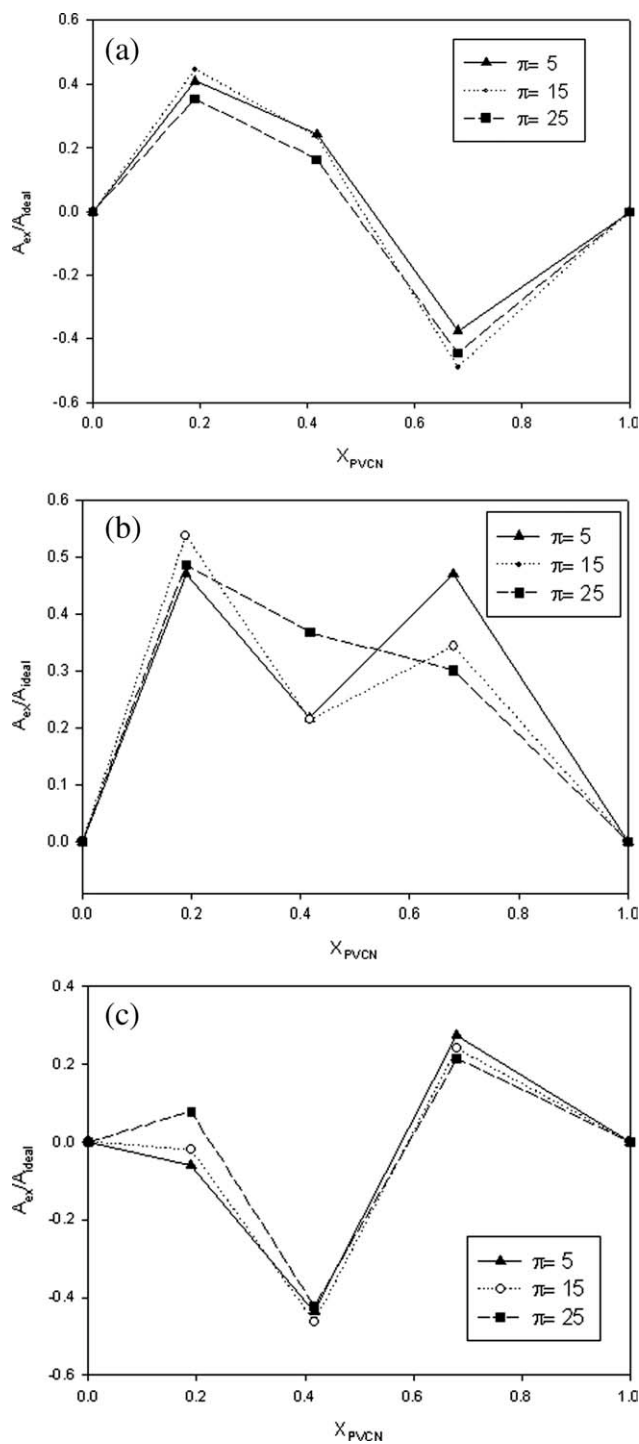
A recent study of Monroy<sup>25</sup> on monolayers of hydrogen-bonded polymer blends indicated that the calculation of the excess Gibbs energy provides a similar result as the excess area. Therefore, in this study only the excess areas were calculated. At a given surface pressure, the excess area is defined as the difference between the average area per molecule of a mixed monolayer consisting of components 1 and 2 and that of an ideal mixed monolayer.<sup>1</sup>

$$A_{\text{ex}} = A_{12} - A_{\text{ideal}} = A_{12} - (X_1 A_1 + X_2 A_2) \quad (1)$$

where  $A_{12}$  and  $A_{\text{ideal}}$  are the mean and ideal areas per molecule of the mixed monolayer at a given surface pressure, respectively,  $X_1$  and  $X_2$  imply the mole fractions of components 1 and 2, respectively, and  $A_1$  and  $A_2$  are the areas per molecule of each



**Figure 7** Surface pressure–area per molecule isotherms of PVCN at three temperatures.

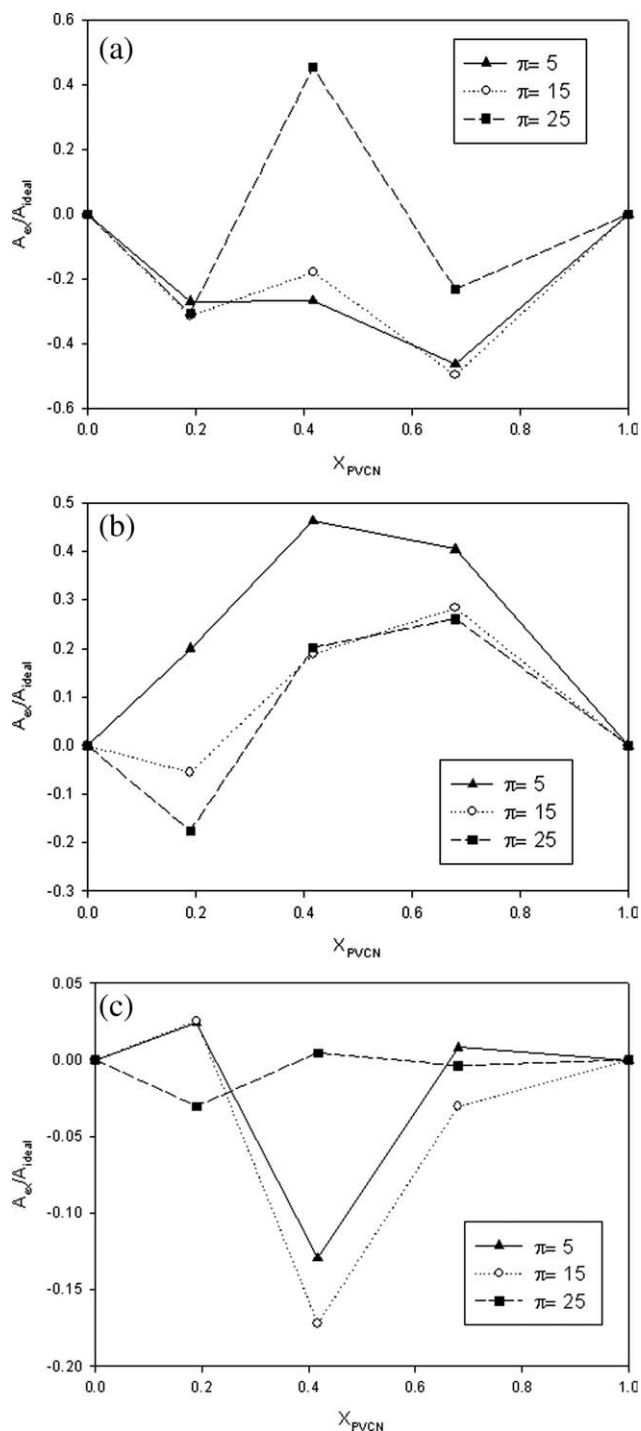


**Figure 8**  $A_{ex}/A_{ideal}$  as a function of composition for mixed monolayers of (a) aPMMA/PVCN, (b) iPMMMA/PVCN, and (c) sPMMA/PVCN at various surface pressures and 25°C (calculated from Fig. 1).

pure monolayer at the same surface pressure. Based on eq. (1), the  $A_{ex}$  values of mixed PMMA/PVCN monolayers can be estimated from the data shown in Figures 1(a-c), 2(a-c), and 3(a-c), individually.

In Figures 8(a-c) and 9(a-c) the estimated normalized quantities,  $A_{ex}/A_{ideal}$  are shown as a function of

PVCN mole fraction and surface pressure at 25°C and 40°C, respectively. Since the repeat unit of PVCN is larger than PMMA, the mole fraction is smaller than the original weight fraction of 0.25, 0.50, and 0.75. The results at 32.5°C are omitted here for brevity. For Figure 8(a), the  $A_{ex}/A_{ideal}$  values are in the majority positive. Positive excess area



**Figure 9**  $A_{ex}/A_{ideal}$  as a function of composition for mixed monolayers of (a) aPMMA/PVCN, (b) iPMMMA/PVCN, and (c) sPMMA/PVCN at various surface pressures and 40°C (calculated from Fig. 3).

TABLE I  
Bulk and Surface Miscibility of the Mixed Monolayers

Blend	PMMA-type	Bulk	Surface	Reference
(1) PMMA/PVPh	Atactic	Miscible	Miscible or partially miscible	14
	Isotactic	Miscible	Miscible	14
	Syndiotactic	Partially miscible or immiscible	Immiscible	14
(2) PMMA/PVCN	Atactic	Miscible	Miscible	15
	Isotactic	Miscible	Partially miscible or immiscible	16
	Syndiotactic	Immiscible	Miscible	16

deviation shows unfavorable interaction between aPMMA and PVCN. Negative excess area deviation only occurs at high PVCN fraction as shown in Figure 8(a). The  $A_{ex}/A_{ideal}$  values shown in Figure 8(b) are always positive indicating probably unfavorable interaction existing between iPMMMA and PVCN. For Figure 8(c), the  $A_{ex}/A_{ideal}$  values are mostly positive. Positive excess area deviation indicates likely unfavorable interaction between sPMMA and PVCN. Negative excess area deviation occurs at mid PVCN composition. The pressure dependence on PMMA/PVCN isotherms at 25°C is not marked.

The elevation of temperature from 25°C to 32.5°C probably causes aPMMA to show more favorable interaction with PVCN. Thus more negative excess areas were observed in the  $\pi$ - $A$  isotherms of aPMMA/PVCN mixed monolayer. For iPMMMA/PVCN mixed monolayers at 32.5°C (not shown), the  $\pi$ - $A$  isotherms still demonstrate positive excess surface area as at 25°C. The interaction between iPMMMA and PVCN is unfavorable. sPMMA/PVCN mixed monolayers at 32.5°C demonstrate more negative excess area because of temperature increase. sPMMA seems to interact favorably with PVCN. Increasing surface pressure is mostly beneficial to more negative excess areas at 32.5°C.

The aPMMA/PVCN mixed monolayers [shown in Fig. 9 (a)] demonstrate in the majority negative excess surface area. Positive surface area occurs at the mid PVCN composition and surface pressure at 25 mN/m. As shown in Figure 9(b), iPMMMA-PVCN mixed monolayers show mostly positive excess surface area similar to the same monolayers at 25°C and 32.5°C. For the sPMMA/PVCN mixed monolayers shown in Figure 9(c), the excess surface area is predominantly close to zero. The negative excess surface areas only occur at the mid PVCN fraction.

It is interesting to make a comparison between the results in monolayers and in the bulk state of PMMA/PVPh and PMMA/PVCN blends as listed in Table I. For the PMMA/PVPh blends, the agreement between the bulk and monolayer states was in the majority observed. For the PMMA/PVCN blends, the following comments were made. Likely because of mainly heterotactic chains in aPMMA,

the results of aPMMA and PVCN are similar to those in the bulk state. Heterotactic chains of aPMMA interact favorably with PVCN either at the air/water interface or in the bulk state. The results for iPMMMA (or sPMMA) and PVCN in the monolayers are different from those in the bulk state. iPMMMA interacts unfavorably with PVCN likely because of the interference of water molecules and likely a low degree of dipole-dipole interaction between iPMMMA and PVCN. However, iPMMMA is miscible with PVCN in the bulk state indicating favorable interaction between iPMMMA and PVCN. Conversely, sPMMA interacts favorably with PVCN at the air/water interface likely because of a high degree of dipole-dipole interaction between sPMMA and PVCN. But sPMMA is found to be immiscible with PVCN in the bulk state.

## CONCLUSIONS

Miscibility deduced from the  $\pi$ - $A$  isotherms of mixed stereoregular PMMA/PVCN monolayers is in the majority different from that for the corresponding polymer blends in the bulk state. The results deduced from the  $\pi$ - $A$  isotherms of mixed stereoregular aPMMA/PVCN monolayers show mostly the negative  $A_{ex}/A_{ideal}$  values in agreement with miscibility between aPMMA and PVCN in the bulk state. Most mixed iPMMMA-PVCN monolayers demonstrate positive  $A_{ex}/A_{ideal}$  values likely because of a low degree of dipole-dipole interaction between iPMMMA and PVCN different from the miscibility between bulk iPMMMA and PVCN. Conversely, sPMMA shows favorable interaction with PVCN in the monolayer state likely because of a high degree of dipole-dipole interaction contrary to the immiscibility found between sPMMA and PVCN in the bulk state.

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