

Molecular Weight Effect of PMMA on Its Miscibility with PS-*b*-PEO at the Air/Water Interface

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ABSTRACT: The mixed monolayer behavior of poly(methyl methacrylate) (PMMA) with different molecular weights and polystyrene-*block*-polyethylene oxide (PS-*b*-PEO) was investigated from the measurements of surface pressure–area per molecule (π -A) isotherms at three different temperatures (10°C, 25°C, and 40°C). The miscibility and nonideality of the mixed monolayers were examined by calculating the excess surface area as a function of composition. The molecular weight of PMMA was demonstrated to have a major effect on its miscibility with PS-*b*-PEO. Negative or close to zero deviations from ideality of

surface areas were observed for PMMA with the lowest molecular weight (12,000 g/mole). Mostly positive deviations were detected in mixed PMMA/PS-*b*-PEO monolayers with higher molecular weights of PMMA. Because of probable mushroom-to-brush transition effect, the miscibility between PMMA and PS-*b*-PEO was found to be the best at 25°C among the experimental temperatures. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1986–1992, 2012

Key words: molecular weight; miscibility; PMMA; PS-*b*-PEO

INTRODUCTION

Polymer blends in the thin film states are of particular interest for both fundamental studies and practical applications. There are a lot of studies of mixed polymer monolayers spread at the air/water surface.^{1–5} In particular, Gabrielli et al.^{6–10} have contributed significantly 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.

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 among many polymer blends were found to be miscible.¹¹ 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. Kawaguchi and co-workers⁵ have performed surface measurements on binary mixtures of poly(methacrylate) (PMA) and poly(vinyl acetate) (PVAc). Since PVAc/PMA mixtures were immiscible, PMA components were squeezed out and their AFM images strongly depend on the mixed ratio of PVAc/PMA.

Recently, Morioka¹² published an article of surface dilatational moduli of poly(vinyl acetate)(PVAc) and PVAc-poly(*n*-hexyl isocyanate)(PHIC) blend films at the air–water interface. PVAc formed a film that was

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looser and also more stable against strain than the PHIC film. The apparent surface dilatational modulus and surface pressure of the blend films were superimposed on the lower concentration of PVAc, irrespective of the composition of PVAc. The stereocomplex formation between isotactic and syndiotactic poly(methyl methacrylate) (it-PMMA, st-PMMA) in a Langmuir monolayer investigated by surface pressure–area isotherms and atomic force microscopy (AFM) was reported by Aiba et al.¹³ 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)¹⁴ and monolayers of poly(styrene)-poly(methyl methacrylate) diblock copolymer¹⁵ at the air/water interface studied by the surface pressure–area isotherms at several temperatures.

There were few studies concerning monolayers of poly(ethylene oxide)(PEO) with PMMA.^{2,3} The results indicated that PEO and PMMA are miscible in the monolayer state. PMMA is known to be immiscible with PS in the bulk state. They are likely to be immiscible in the monolayer state. Poly(styrene)-*block*-poly(ethylene oxide)(PS-*b*-PEO) is a well-studied copolymer^{16–19} forming different patterns of nanostructures (dots, spaghetti, rings, chainlike aggregates etc.) at the air/water interface resulting from the spontaneous copolymer aggregation. The hydrophilic PEO dissolves into the pure water subphase, while the hydrophobic blocks aggregate at the interface during compression. Various morphologies have been detected depending on the relative chain length of the hydrophilic and hydrophobic blocks, the concentration of spreading solution, and the surface pressure. The possible formation of nonequilibrium states when PS-*b*-PEO is spread has a block with a high glass transition temperature (PS in the present case), and another with a relatively low T_g has been pointed out by several authors.^{20–22} PMMA is likely immiscible with PS-*b*-PEO in the bulk state because of repulsive interaction of two pairs (PMMA and PS, PS, and PEO).

Previously,²³ the mixed monolayer behavior of stereoregular PMMA and PS-*b*-PEO was investigated in this laboratory from the measurements of surface pressure–area per molecule (π -A) isotherms at three different temperatures. The miscibility and nonideality of the mixed monolayers were examined by calculating the excess area as a function of composition. Mostly negative deviations from ideality were observed in the mixed monolayers at 25°C and 32.5°C. This is likely because of favorable interaction between PMMA and PEO. The positive deviations occurred at 32.5°C and 40°C with atactic PMMA (or

syndiotactic PMMA) mixed monolayers. Therefore, with confinement in the two-dimensional state, the miscibility between PMMA and PS-*b*-PEO was improved in comparison with the bulk state. In another article,²⁴ poly(methyl methacrylate) (PMMA) monolayers with different molecular weights at the air/water interface were investigated at three different temperatures. The monolayer characteristics of PMMA were studied in terms of surface pressure–area per molecule (π -A) isotherm and isobaric relaxation experiments. The results show that the π -A isotherms of PMMA converge at 40°C regardless of molecular weight. The collapse pressure of PMMA monolayers decreases as the temperature is elevated. It was shown that the area relaxation process of PMMA could be described by a model considering the nucleation and growth mechanisms.

The investigation in this article was extended to explore the molecular weight of PMMA on its miscibility with PS-*b*-PEO. The effects of molecular weights of PMMA, temperature, and PS-*b*-PEO composition on the mixed monolayer was expounded and reported in detail in this article. Because of probable mushroom-to-brush transition effect, the miscibility between PMMA and PS-*b*-PEO was found to be the best at 25°C among the experimental temperatures.

EXPERIMENTAL

Materials

Different molecular weights (12,000 g/mole, 30,000 g/mole, 60,000 g/mole, and 75,000 g/mole) of PMMA were purchased from Polysciences, Inc., Warrington, PA. According to the supplier information, the polydispersity of the aforementioned polymers was 1.04–1.10. The tacticity of PMMA was not indicated by the supplier. It should be classified as atactic. The molecular weight (M_n) of PS-*b*-PEO obtained from Polymer Source, Inc., Montreal, Canada, is about 95,000 g/mole for each block. The polydispersity index is 1.07. According to the supplier information, the glass transition temperatures for the PS block and the PEO block are 89°C and –60°C, respectively. 89°C is reported as the onset point and is, therefore, lower as expected. For the PEO block, the crystallization and melting temperatures are 31°C and 56°C.

2-butanone purchased from Kanto Chemical Co., Inc., was used as the spreading solvent for the polymer films. The solvent was chosen to be the same as a previous study.²⁴ 2-butanone does not dissolve in water and is volatile. Only highly pure water, which was purified by means of a Milli-Q plus water purification system, with a resistivity of 18.2 M Ω cm was used in all experiments. Blank experiments using 2-

butanone were carried out so that there were no surface-active impurities.

Surface pressure measurements

A model minitrough was purchased from KSV Instruments Ltd., 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 Ltd. 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 less than 1%, according to the specifications of the instruments. A surface pressure–area per molecule (π -A) isotherm was obtained by 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 pressure measurements was also rinsed with purified water and then flamed before use. In addition, all glassware was cleaned prior to 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 $10 \pm 0.5^\circ\text{C}$, $25 \pm 0.5^\circ\text{C}$, and $40 \pm 0.5^\circ\text{C}$. The clean platinum plate was hanged in the appropriate position for surface pressure measurements. The surface pressure fluctuation was estimated to be less than 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- μL 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. Then the monolayer was compressed continuously at a rate of 3.5 mm/min to obtain a single π -A isotherm. The π -A isotherms of our studied polymers are dependent on the compression rate; therefore,

the results were performed at the same compression speed. The isotherms were often performed in duplicates to make sure reproducibility.

RESULTS AND DISCUSSION

Polymers and PMMA/PS-*b*-PEO mixture at 10°C, 25°C, and 40°C

Figure 1 presents the π -A isotherms of mixed monolayers for PMMA/PS-*b*-PEO at 10°C in the order of (a) 12,000 g/mole, (b) 30,000 g/mole and (c) 75,000 g/mole, respectively. The results of 60,000 g/mole are similar to 75,000 g/mole and omitted for brevity.

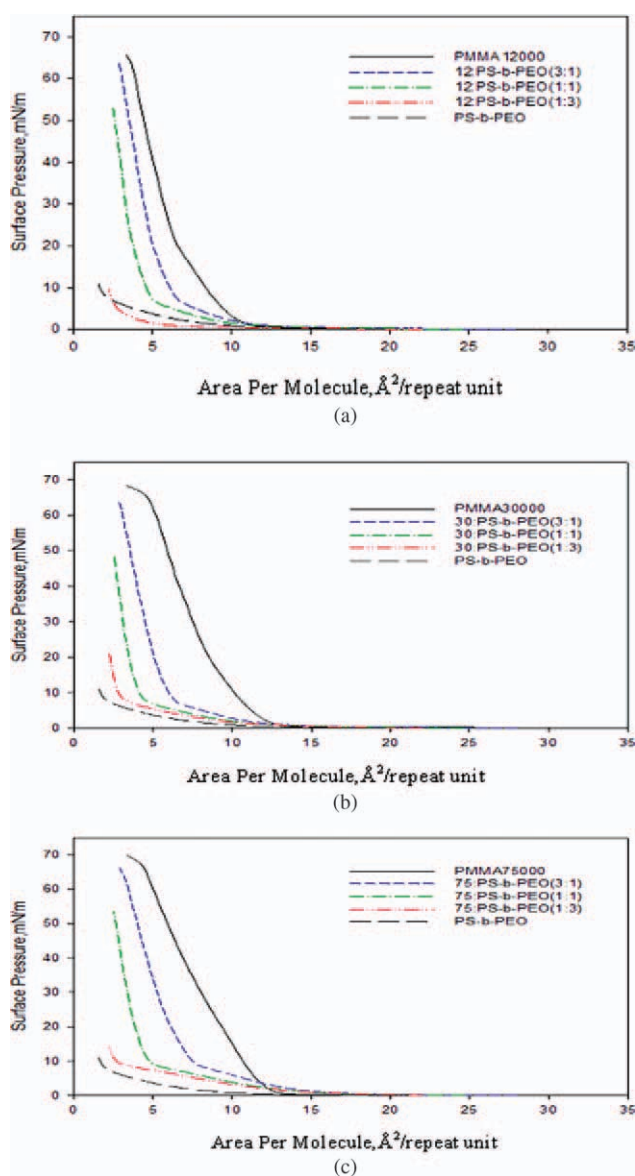


Figure 1 Surface pressure–area per molecule isotherms for mixed monolayers of PMMA/PS-*b*-PEO with different PMMA molecular weights of (a) 12,000, (b) 30,000, and (c) 75,000 at 10°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

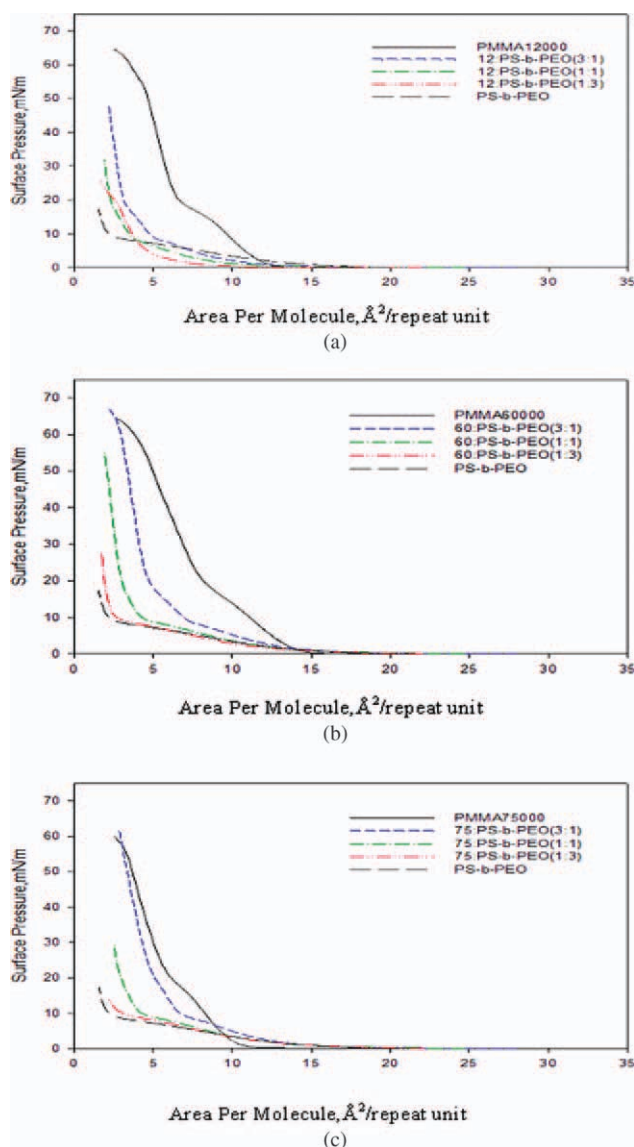


Figure 2 Surface pressure–area per molecule isotherms for mixed monolayers of PMMA/PS-*b*-PEO with different PMMA molecular weights of (a) 12,000, (b) 60,000, and (c) 75,000 at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The π -A isotherms of PS-*b*-PEO (presented in Fig. 1) show a mushroom to brush transition at lower than 10 mN/m similar to the findings of Cox et al.¹⁹ However, the collapse pressure in this study is much smaller. The mixed PMMA/PS-*b*-PEO monolayers in Figure 1(a,c) all demonstrated intermediate behavior between PMMA and PS-*b*-PEO. But one composition (PMMA12000/PS-*b*-PEO(1 : 3)) with the lowest PMMA molecular weight showed even smaller surface area than PS-*b*-PEO monolayer. The collapse pressure of most mixed PMMA/PS-*b*-PEO monolayers in Figure 1 decreases with increasing PS-*b*-PEO composition and is also a symbol of possible miscibility between PMMA and PS-*b*-PEO. There is only one exception, PMMA60000/PS-*b*-PEO (3 : 1)

exhibiting higher collapse pressure than PMMA 60,000(not shown).

Figure 2 exemplifies the π -A isotherms of mixed monolayers for PMMA/PS-*b*-PEO at 25°C in the order of (a) 12,000 g/mole, (b) 60,000 g/mole, and (c) 75,000 g/mole, respectively. The results of 30,000 g/mole are similar to 60,000 g/mole and therefore not reported. The π -A isotherms of PS-*b*-PEO at 25°C show a mushroom-to-brush transition much higher than that at 10°C. The collapse pressure of PS-*b*-PEO at 25°C was found to be higher than that at 10°C. Most of the mixed PMMA/PS-*b*-PEO monolayers in Figure 2(b,c) demonstrated intermediate behavior between PMMA and PS-*b*-PEO. Figure 2(a) showed

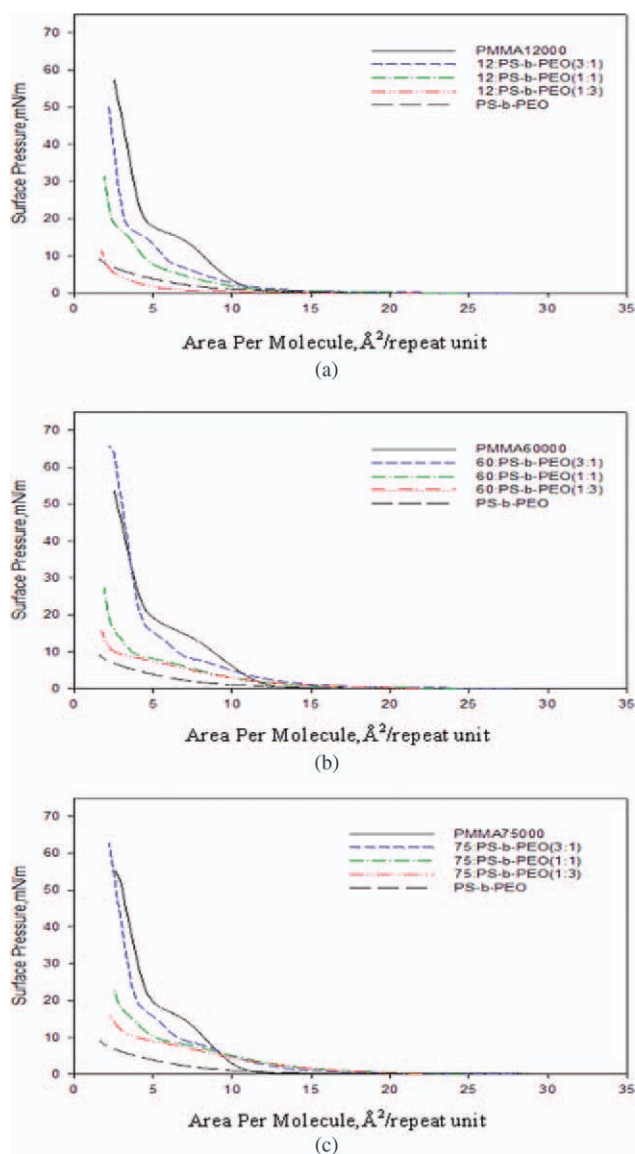


Figure 3 Surface pressure–area per molecule isotherms for mixed monolayers of PMMA/PS-*b*-PEO with different PMMA molecular weights of (a) 12,000, (b) 60,000, and (c) 75,000 at 40°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

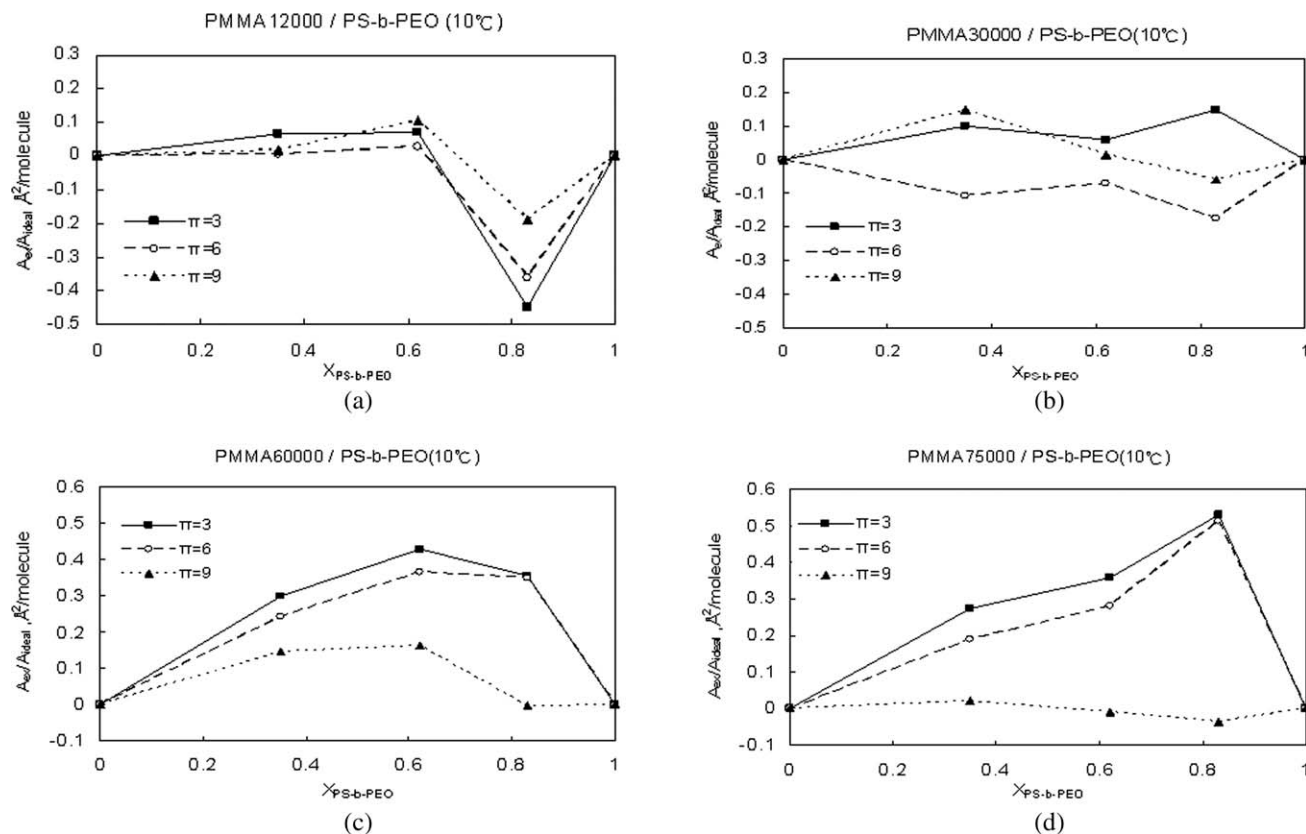


Figure 4 A_{ex}/A_{ideal} as a function of composition for mixed monolayers of PMMA/PS-*b*-PEO with different PMMA molecular weights of (a) 12,000, (b) 30,000, (c) 60,000, and (d) 75,000 at 10°C (calculated from Figure 1).

smaller surface pressure than PS-*b*-PEO in mixed PMMA/PS-*b*-PEO monolayers with the lowest molecular weight of PMMA at low surface pressure region. The collapse pressure of most mixed PMMA/PS-*b*-PEO monolayers in Figure 2 decreases with increasing PS-*b*-PEO composition and is also a symbol of possible miscibility between PMMA and PS-*b*-PEO. There are two exceptions, PMMA60000(or 75000)/PS-*b*-PEO(3 : 1) exhibiting higher collapse pressure than the corresponding PMMA.

Figure 3 illustrates the π -A isotherms of mixed monolayers for PMMA/PS-*b*-PEO at 40°C in the order of (a) 12,000 g/mole, (b) 60,000 g/mole, and (c) 75,000 g/mole, respectively. The results of 30,000 g/mole are omitted. The π -A isotherms of PS-*b*-PEO at 40°C show a transition slightly higher than that at 10°C but lower than 25°C with a lower collapse pressure than 25°C. Most of the mixed PMMA/PS-*b*-PEO π -A isotherms at 40°C in Figure 3 are similar to those at 10°C but different from those at 25°C. The reason will be expounded in the discussion of the excess surface areas. One thing is worth noticing that the lift-off area (defined as the surface area of a monolayer starting to show surface pressure larger than 0) becomes larger in the mixed monolayers than pure PMMA or PS-PEO. The lift-off areas of the mixed monolayers increase with increasing

PMMA molecular weight. The collapse pressure of mixed PMMA/PS-*b*-PEO monolayers at 40°C is similar to the findings at 25°C with dependence on PS-*b*-PEO composition.

The excess areas of mixture at three different temperatures

A study of Monroy et al.²⁵ 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.¹

$$A_{ex} = A_{12} - A_{ideal} = A_{12} - (X_1A_1 + X_2A_2) \quad (1)$$

where A_{12} and A_{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 pure monolayer at the same surface pressure. Based on eq. (1), the A_{ex} values of mixed PMMA/PS-*b*-

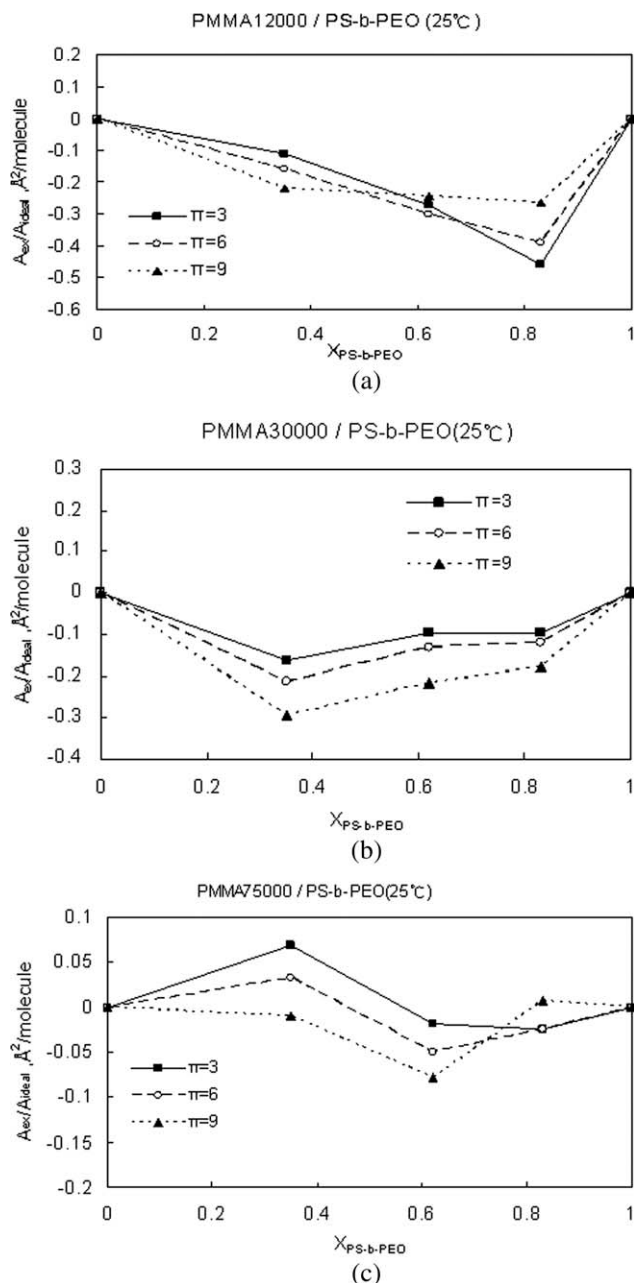


Figure 5 A_{ex}/A_{ideal} as a function of composition for mixed monolayers of PMMA/PS-*b*-PEO with different PMMA molecular weights of (a) 12,000, (b) 30,000, and (c) 75,000 at 25°C (calculated from Fig. 2).

PEO monolayers can be estimated from the data shown in Figures 1–3, individually.

In Figures 4(a,d), 6(a,c), the normalized quantities, A_{ex}/A_{ideal} are shown as a function of PS-*b*-PEO mole fraction and surface pressure at 10°C, 25°C, and 40°C, respectively. Since the average repeat unit of PS-*b*-PEO is smaller than PMMA, the mole fraction of PS-*b*-PEO is larger than the original weight fractions of 0.25, 0.50, and 0.75.

For Figure 4(a), the A_{ex}/A_{ideal} values are slightly positive or negative for PMMA12000 monolayers.

Increasing PMMA molecular weight causes the A_{ex}/A_{ideal} values to be more positive as shown in Figure 4(a,d). Using the A_{ex}/A_{ideal} values as an indicator, the PMMA miscibility order with PS-*b*-PEO at 10°C can be ranked as follows:

$$PMMA\ 12000 > 30000 > 60000 \geq 75000$$

The mixed monolayer miscibility decreases with increasing PMMA molecular weight. At 25°C, the A_{ex}/A_{ideal}

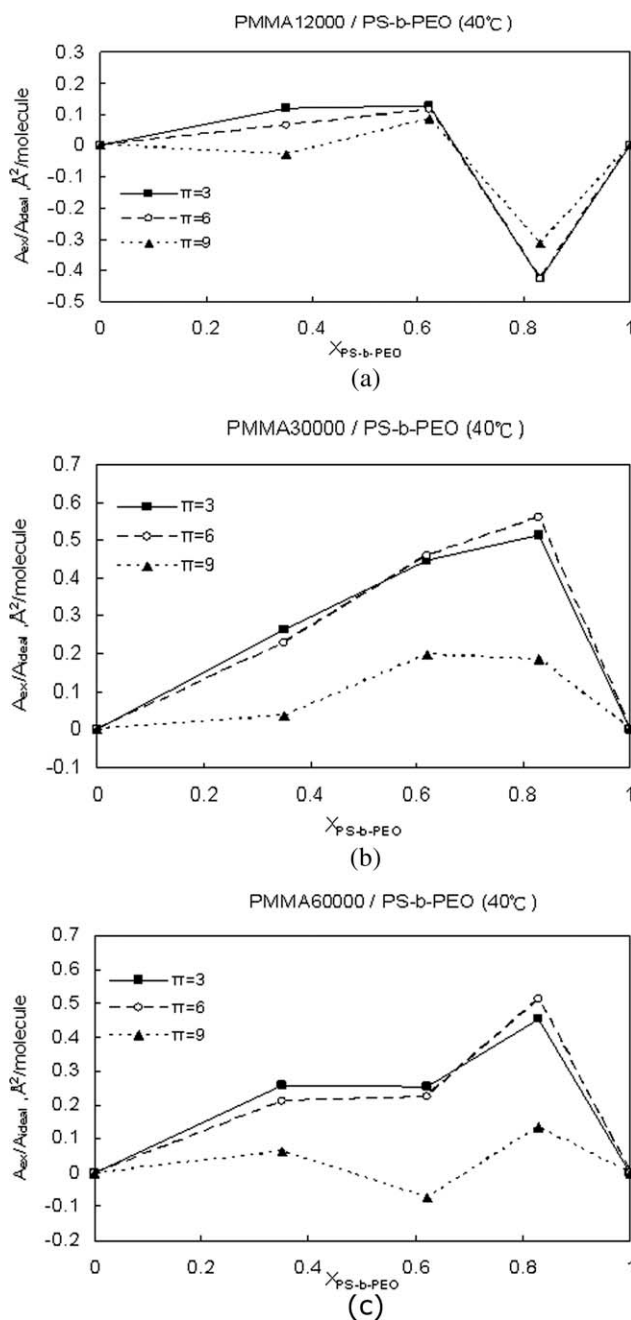


Figure 6 A_{ex}/A_{ideal} as a function of composition for mixed monolayers of PMMA/PS-*b*-PEO with different PMMA molecular weights of (a) 12,000, (b) 30,000, and (c) 60,000 at 40°C (calculated from Fig. 3).

A_{ideal} values are all amazingly negative for PMMA with $M_w = 12,000, 30,000$ [as shown in Fig. 5(a,b)], and 60,000 g/mole (not shown). The possible reason is because of a higher mushroom to brush transition. The studied pressures (3, 6, 9 mN/m) are located below the transition. PMMA likely forms more favorable interaction with PS-*b*-PEO in the mushroom region than the brush region. Only PMMA75000/PS-*b*-PEO showed positive or negative deviation from average surface area as depicted in Figure 5(c). Using the $A_{\text{ex}}/A_{\text{ideal}}$ values as an indicator, the PMMA miscibility order with PS-*b*-PEO at 25°C (almost the same as at 10°C) can be ranked as the following: PMMA 12,000 > 30,000 > 60,000 > 75,000.

The results at 40°C as illustrated in Figure 6(a,c) for 12,000, 30,000, and 60,000 g/mole are similar to those at 10°C and not 25°C. However, the reason for the observation differs. The results of 75,000 g/mole are similar to 30,000 g/mole. Temperature-elevation induced weaker dipole–dipole interaction accounts for probably the results at 40°C. The observations at 10°C likely come from less amorphous PEO segments available for dipole–dipole interaction. The PMMA12000/PS-*b*-PEO monolayers demonstrated slightly positive or largely negative $A_{\text{ex}}/A_{\text{ideal}}$ values. The other mixed monolayers [Fig. 6(b,c)] showed mostly positive deviation from average surface area. Using the $A_{\text{ex}}/A_{\text{ideal}}$ values as an indicator, the PMMA miscibility order with PS-*b*-PEO at 40°C can be ranked as the following:

$$\text{PMMA 12000} > 60000 \geq 30000 > 75000$$

The PMMA miscibility order with PS-*b*-PEO at 40°C is slightly different from two previous temperatures. The reason is likely because of differences in tacticity of samples. According to a previous study,²³ syndiotactic PMMA exhibits a higher collapse pressure than isotactic or atactic PMMA. PMMA 60,000 exhibits a lower collapse pressure than PMMA 30,000 at 40°C. PMMA 60,000 is likely to possess a higher percentage of isotacticity than PMMA 30,000. This higher isotacticity results in more favorable interaction between PMMA 60,000 and PS-*b*-PEO than PMMA 30,000.

Totally speaking, PMMA with the lowest molecular weight (PMMA 12,000) showed most favorable interaction with PS-*b*-PEO. The probable reason is as follows. Lower molecular weight PMMA has more interaction with PEO because of less chain entanglements. The combination of lower molecular weight PMMA and PEO also favors higher entropy. Therefore, the mixing of free energy of lower molecular weight PMMA and PEO is likely to be more negative. The best temperature for miscibility between PMMA and PS-*b*-PEO is 25°C for mostly negative surface area observed.

CONCLUSIONS

Miscibility deduced from the π -A isotherms of mixed PMMA with PS-*b*-PEO correlates probably different from that for the corresponding polymer blends in the bulk state. The results deduced from the π -A isotherms of mixed PMMA 12,000 with PS-*b*-PEO show mostly negative $A_{\text{ex}}/A_{\text{id}}$ values likely because of dipole–dipole interaction and high entropy of mixing between PEO and PMMA. Increasing molecular weight of PMMA causes more positive deviations than average surface area in the mixed PMMA/PS-*b*-PEO monolayers at three temperatures. Mostly negative $A_{\text{ex}}/A_{\text{id}}$ values were observed at mid temperature 25°C likely because of a high mushroom to brush transition effect. The miscibility of most PMMA and PS-*b*-PEO monolayers can be achieved at 25°C.

References

- Gaines, G. L. Jr. *Insoluble Monolayers at Liquid–Gas Interface*; Interscience: New York, 1966.
- Kawaguchi, M.; Nishida, R. *Langmuir* 1999, 6, 492.
- Nagata, K.; Kawaguchi, M. *Macromolecules* 1990, 23, 3957.
- Runge, F. E.; Yu, H. *Langmuir* 1993, 9, 3191.
- Kawaguchi, M.; Suzuki, S.; Imae, T.; Kato, T. *Langmuir* 1997, 13, 3794.
- Gabrielli, G.; Puggelli, M.; Faccioli, R. J. *Colloid Interface Sci* 1971, 37, 213.
- Gabrielli, G.; Puggelli, M.; Faccioli, R. J. *Colloid Interface Sci* 1973, 44, 177.
- Gabrielli, G.; Puggelli, M.; Ferroni, E. J. *Colloid Interface Sci* 1974, 47, 145.
- Gabrielli, G.; Baglioni, P. J. *Colloid Interface Sci* 1980, 73, 582.
- Gabrielli, G.; Puggelli, M.; Baglioni, P. J. *Colloid Interface Sci* 1982, 86, 485.
- Paul, D. R.; Bucknall, C. B. *Polymer Blends*; Wiley: New York, 2000.
- Morioka, T.; Kawaguchi, M. *Langmuir* 2011, 27, 8672.
- Aiba, N.; Sasaki, Y.; Kumak, J. *Langmuir* 2010, 26, 12703.
- Bernardini, C.; Stoyanov, S. D.; Stuart, M. A. C.; Arnaudov, L. N.; Leermakers, F. A. M. *Langmuir* 2010, 26, 11850.
- Seo, Y.; Cho, C. Y.; Hwangbo, M.; Choi, H. J.; Hong, S. M. *Langmuir* 2008, 24, 2381.
- Logan, J. L.; Masse, P.; Gnanou, Y.; Taton, D.; Duran, R. S. *Langmuir* 2005, 21, 7380.
- Devereaux, C. A.; Baker, S. M. *Macromolecules* 2002, 35, 1921.
- Noskov, B. A.; Akentiev, A. V.; Miller, R. J. *Colloid Interface Sci* 2002, 247, 117.
- Cox, J. K.; Yu, K.; Constantine, B.; Eisenberg, A.; Lennox, R. B. *Langmuir* 1999, 15, 7714.
- Baker, S. M.; Leach, K. A.; Devereaux, C. E.; Gragson, D. E. *Macromolecules* 2000, 33, 5432.
- Hosoi, A. E.; Kogan, D.; Devereaux, C. E.; Bernoff, A. J.; Baker, S. M. *Phys Rev Lett* 2005, 95, 037801.
- Monroy, F.; Ortega, F.; Rubio, R. G.; Ritacco, H.; Langevin, D. *Phys Rev Lett* 2005, 95, 056103.
- Hsu, W. P. *Colloid Surf A* 2010, 367, 161.
- Jheng, K. T.; Hsu, W. P. *J Appl Polym Sci* 2011, 120, 2615.
- Monroy, F.; Esquinas, M. J.; Ortega, T.; Rubio, R. G. *Colloid Polym Sci* 1998, 276, 960.