

# Isobaric Relaxation Phenomenon of Mixed PMMA/PS-*b*-PEO Monolayers at Different Temperatures

Kai-Teng Jheng, Wen-Ping Hsu

Department of Chemical Engineering, National United University, Miao-Li, Taiwan 36003, Republic of China

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**ABSTRACT:** The objective of this research was to find out the effect of molecular weight of poly(methyl methacrylate) (PMMA) and temperature on the isobaric relaxation behaviors of mixed PMMA/poly(styrene)-*block*-poly(ethylene oxide) (PS-*b*-PEO) monolayers. Isobaric relaxation experiments of mixed monolayers of PMMA with different molecular weights and PS-*b*-PEO at the air/water interface were investigated at three different temperatures (10, 25, and 40°C). The PS-*b*-PEO monolayer was found to exhibit a fast relaxation curve (i.e., the surface area decreased significantly with increasing time). Addition of PMMA into PS-*b*-PEO slowed the relaxation behavior especially at the

lowest experimental temperature (10°C). It was shown that the area relaxation process of mixed PMMA/PS-*b*-PEO monolayers could be well represented by a model considering the nucleation and growth mechanisms. The characteristic exponent  $x$  values were found to be almost temperature independent. The  $k_x$  values were detected to decrease mostly as a result of temperature elevation regardless of pure or mixed monolayers. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** isobaric relaxation; temperature; PMMA/PS-*b*-PEO; monolayer; molecular weight

## INTRODUCTION

Amphiphilic molecule including polymer can have a stable monolayer existence at the air/water interface because of its hydrophobic groups protruding into the air and its hydrophilic groups anchoring into the water. Monolayer films of polymers have been studied extensively during the past decades,<sup>1,2</sup> but the research efforts have multiplied rapidly because of possible applications in nonlinear optical devices and other fields such as biosensors and microlithography.

Crisp<sup>1,2</sup> was the first to systematically investigate monolayer properties of polymers, especially of polyacrylates and polymethacrylates. He demonstrated that poly(methyl methacrylate) (PMMA) forms patchy structures, composed of condensed islands of PMMA at low-surface coverages. He also proposed conformations for the ester groups in these materials at the air/water interface, on the basis of measurements of the dipole moments. Since then many articles have been published about PMMA monolayers at the air/water surface, such as its monolayer miscibility with low-molecular weight substances and other polymers, the stability and hysteresis that may occur.<sup>3–6</sup>

Very few studies were devoted to the polymer monolayer relaxation behavior. Most literature is focused on the surface pressure-area isotherms of polymers or polymer blends. Morioka and Kawaguchi<sup>7</sup> 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 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 and st-PMMA) in a Langmuir monolayer investigated by surface pressure-area isotherms and atomic force microscopy (AFM) was reported by Aiba et al.<sup>8</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>9</sup> and monolayers of poly(styrene) (PS)-PMMA diblock copolymer<sup>10</sup> at the air/water interface studied by the surface pressure-area isotherms at several temperatures.

In a previous study of our report,<sup>11</sup> 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

Correspondence to: W.-P. Hsu (mjkr.hsu@msa.hinet.net).

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molecule ( $\pi$ -A) isotherm and isobaric relaxation experiments. The results show that the  $\pi$ -A isotherms of PMMA converge at 40°C regardless of molecular weights. The collapse pressure of PMMA monolayers decreases as the temperature is elevated. It was shown the area relaxation process could be described by a model considering the nucleation and growth mechanism. The simulation parameters of area relaxation of PMMA with different molecular weights at 8 mN/m are very similar, indicating similar mechanisms.

Poly(styrene)-*block*-poly(ethylene oxide) (PS-*b*-PEO) is a well-studied copolymer<sup>12-15</sup> 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, whereas 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.<sup>16-20</sup>

To the best of our knowledge, there is no report on the isobaric relaxation behavior of PS-*b*-PEO monolayer. Therefore, no one has reported the results of isobaric relaxation of mixed PMMA/PS-*b*-PEO monolayers. The previous report<sup>11</sup> was focused on  $\pi$ -A isotherm and isobaric relaxation of pure PMMA monolayers. In this article, the isobaric relaxation phenomenon of mixed PMMA and PS-*b*-PEO monolayer was investigated. Effect of temperature and molecular weight of PMMA on the isobaric relaxation behavior of the mixed monolayers was evaluated and discussed in this article. The potential application is the pattern formation of PS-*b*-PEO may be adjusted by the addition of PMMA.

## EXPERIMENTAL

### Materials

PMMA was purchased from Polysciences, Warrington, PA, with molecular weights ( $M_w$ ) of 12,000, 30,000, 60,000, and 75,000 g/mol. The tacticity of PMMA was not indicated by the supplier and should be classified as atactic. The polydispersities ( $M_w/M_n$ ) of each PMMA was estimated to be 1.04–1.10 according to the supplier information. The molecular weight ( $M_n$ ) of PS-*b*-PEO obtained from Polymer Source, Montreal, Canada is about 95,000 g/mol for each block. The polydispersity index is 1.07. The

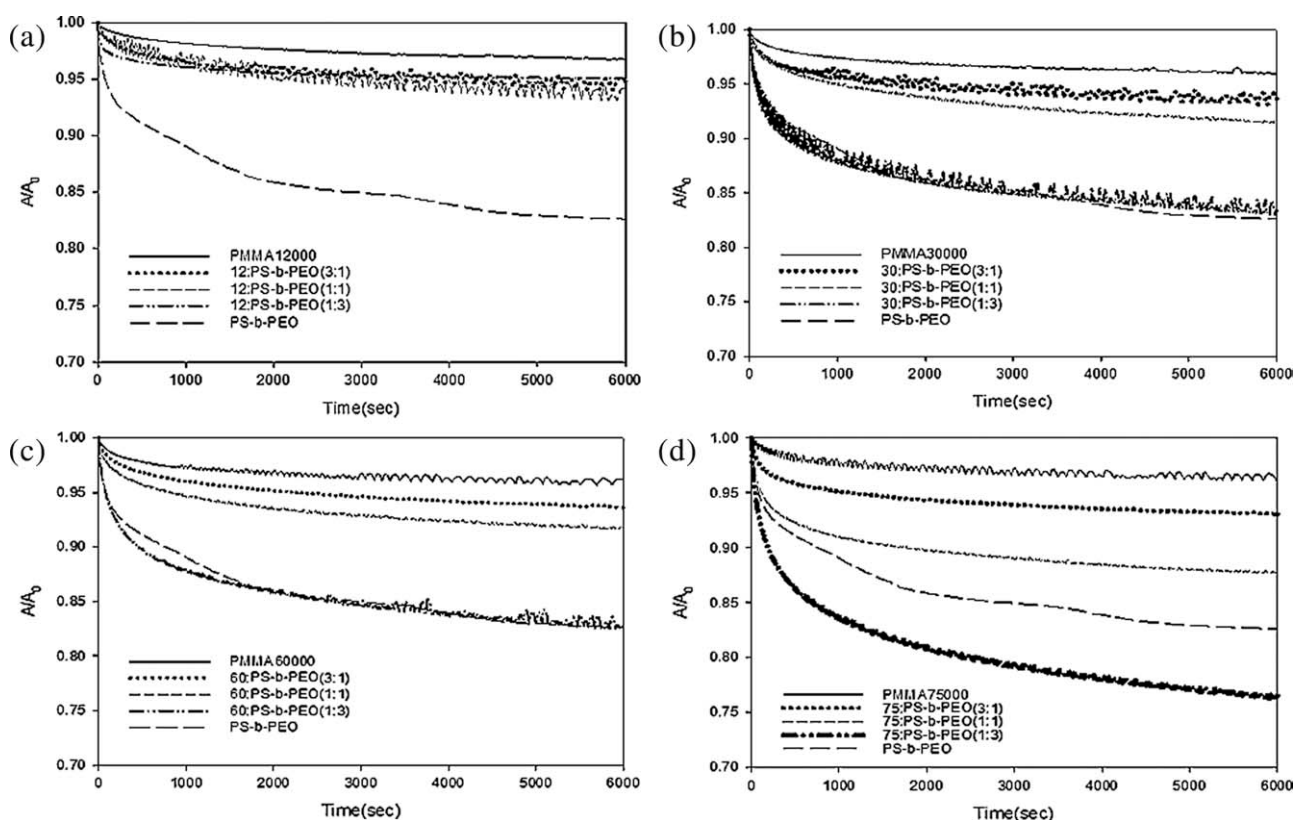
glass transition temperatures for the PS block and the PEO block are 89°C and –60°C, respectively. The temperature 89°C is reported as the onset point, therefore lower as expected. For PEO block, the crystallization and melting temperatures are 31 and 56°C.

2-Butanone purchased from Tedia Company was used as the spreading solvent for the polymer films. The solvent was chosen to be the same as a previous study.<sup>11</sup> 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 $\Omega$  cm was used in all experiments.

### Surface pressure and isobaric relaxation 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 with a controlled speed during the compression of the monolayer. The surface pressure was measured by the Wilhelmy plate method.<sup>19</sup> 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 surface pressure-area per molecule ( $\pi$ -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 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 <0.2 mN/m during the compression of the entire trough surface area range. Then, the two barriers were moved



**Figure 1** Isobaric relaxation curves of mixed PMMA/PS-*b*-PEO at 8 mN/m and 10°C with PMMA molecular weights of (a) 12,000, (b) 30,000, (c) 60,000, and (d) 75,000.

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 materials was spread on the subphase by using a Hamilton microsyringe. 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 [equivalent to 0.3–0.4  $\text{\AA}^2/(\text{molecular min})$ ] to obtain a single  $\pi$ - $A$  isotherm. The  $\pi$ - $A$  isotherms of PMMA<sup>11</sup> and PS-*b*-PEO<sup>20</sup> were reported elsewhere.

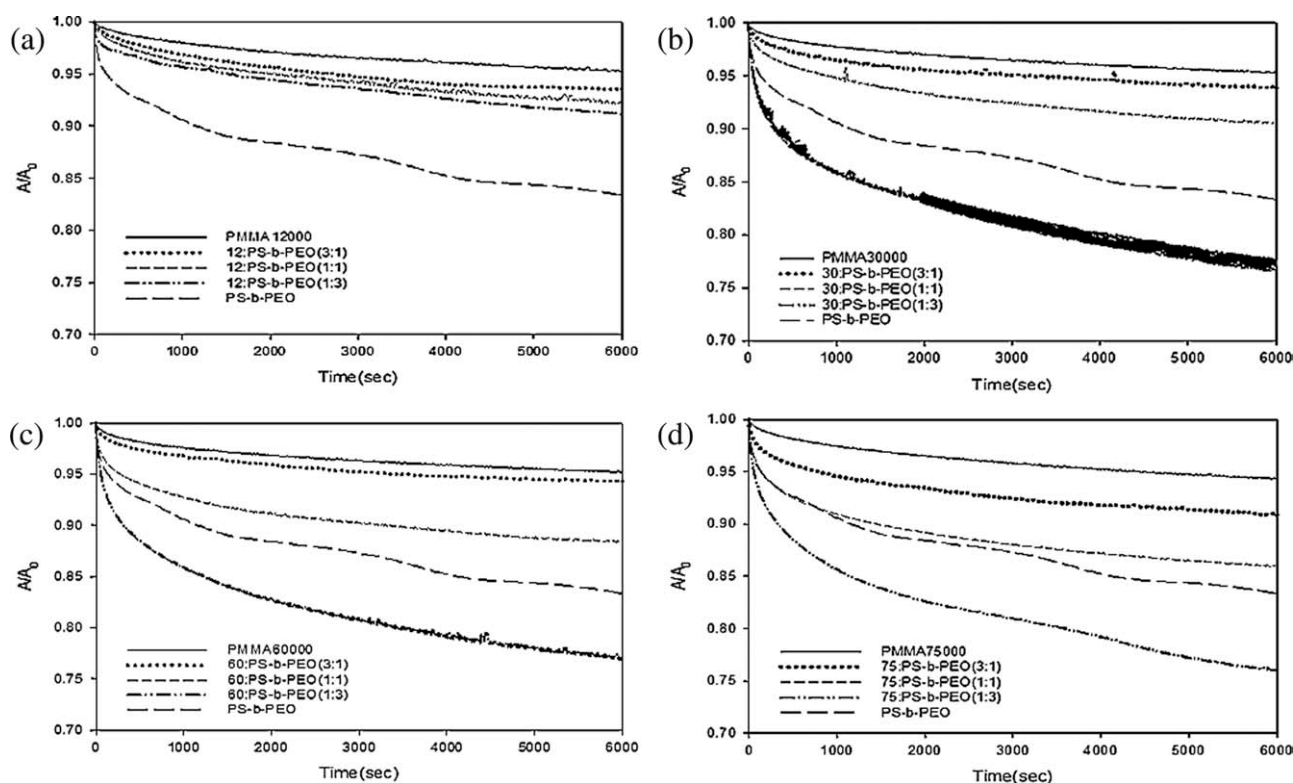
Isobaric relaxation curves of mixed PMMA/PS-*b*-PEO monolayer films were also obtained in the same way as  $\pi$ - $A$  isotherms. The only difference is that when the desired surface pressure was obtained and set as constant. A surface pressure at 8 mN/m was chosen because of the low-collapse pressure of PS-*b*-PEO. Again, the relaxation curves should have some dependence on the original compression rate. Therefore the same compression speed (3.5 mm/min) [equivalent to 0.3–0.4  $\text{\AA}^2/(\text{molecular min})$ ] was used in all the experiments. Then the  $A/A_0$  ratio was monitored as a function of time, where  $A_0$  is the initial surface area occupied by monolayer and  $A$  is the surface area of monolayer at time  $t$ . The initial area ( $A_0$ ) is about 243  $\text{cm}^2$ . The computer will calculate  $A$  automatically with the reduction of area. Nonisobaric relaxation experiments can be carried out. Since both

surface pressure and surface area will likely change with time, the data could not be easily compared. To the best of our knowledge, no report of nonisobaric experiments has been documented. For comparison with our previous results and other literature studies, the relaxation experiments in this article were performed as isobaric.

## RESULTS AND DISCUSSION

### Isobaric relaxation phenomenon

Relaxation curves of mixed PMMA/PS-*b*-PEO at a fixed surface pressure of 8 mN/m and 10°C were given in Figure 1 in the order of (a) 12,000, (b) 30,000, (c) 60,000, and (d) 75,000 g/mol, respectively. The PS-*b*-PEO monolayer exhibited a much faster relaxation curve than PMMA with different molecular weights likely because of hydrophilic PEO segments. PMMA12000 demonstrated the strongest stabilization effect with PS-*b*-PEO among the four molecular weights of PMMA. This is in agreement with lower molecular weight in favor of more dipole-dipole interaction between C=O groups of PMMA and —O— groups of PEO. The stabilization effect of PMMA became weaker with increasing PMMA molecular weight resulting probably from less PMMA-PEO interaction. The mixed PMMA



**Figure 2** Isobaric relaxation curves of mixed PMMA/PS-*b*-PEO at 8 mN/m and 25°C with PMMA molecular weights of (a) 12,000, (b) 30,000, (c) 60,000, and (d) 75,000.

with 75,000 g/mol and PS-*b*-PEO in 1 : 3 ratio showed a even faster relaxation than PS-*b*-PEO likely because of poor miscibility between PMMA75000 and PS-*b*-PEO and self-aggregation of PS-*b*-PEO.

Relaxation curves of mixed PMMA/PS-*b*-PEO at a fixed surface pressure of 8 mN/m and 25°C were given in Figure 2 in the order of (a) 12,000, (b) 30,000, (c) 60,000, and (d) 75,000 g/mol, respectively. Again, PMMA12000 demonstrated the strongest stabilization effect with PS-*b*-PEO among the four molecular weights of PMMA. The stabilization effect of PMMA with PS-*b*-PEO also decreased with its increasing molecular weight. When PMMA was blended with PS-*b*-PEO in 1 : 3 ratio, the surface area of the mixed monolayers decayed even faster than PS-*b*-PEO in the four molecular weights of PMMA except 12,000 one. The probable reason is less favorable PMMA-PEO interaction and more self-aggregation of PS-*b*-PEO at a higher temperature.

Relaxation curves of mixed PMMA/PS-*b*-PEO monolayers at a fixed surface pressure of 8 mN/m and 40°C were given in Figure 3 in the order of (a) 12,000, (b) 30,000, (c) 60,000, and (d) 75,000 g/mol, respectively. The stabilization effect of PMMA with PS-*b*-PEO became less dependent on PMMA molecular weight at this higher temperature. Interesting to notice at the lowest and highest PMMA molecular weights, the mixed monolayers exhibited a greater instability than PS-*b*-PEO when PMMA and PS-

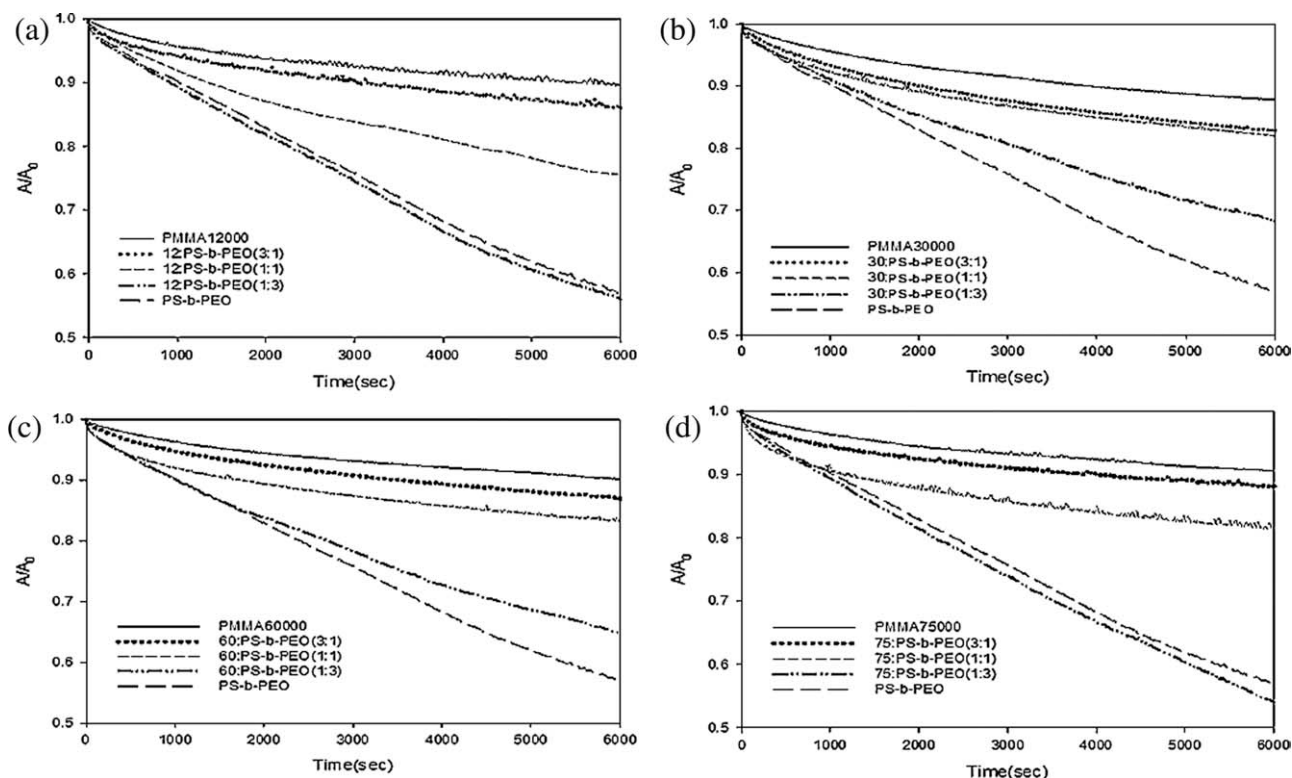
PEO ratio was 1 : 3. The probable reason is because of less favorable PMMA-PEO interaction resulting from the mushroom to brush transition<sup>12–15</sup> effect of PS-*b*-PEO at this temperature.

### Modeling

An attempt was made to interpret our relaxation results in more detail with respect to particle nucleation/growth models. Vollhardt et al.<sup>21–23</sup> presented a series of studies describing the relaxation of stearic acid monolayers in the collapse region. They related the measurable loss of normalized area to the overall growth rate of 3D particles (clusters), considering different rate laws of the initial nucleation (instantaneous or progressive), the geometry of the growing clusters, and the overlap of the grown particles (clusters). Their theory led to a generalized equation for any nucleation model of the form exactly the same as the Avrami equation<sup>24–26</sup>

$$(A_0 - A)/(A_0 - A_\infty) = 1 - \exp(-k_x t^x) \quad (1)$$

where  $A$  is the total surface area at time  $t$ ,  $A_0$  is the initial surface area,  $A_\infty$  is the area at  $t \approx \infty$ , and  $k_x$  is a constant specific for the applied geometry and nucleation model represented by the characteristic exponent  $x$ . The characteristic exponent  $x$  varies from 1.5 to 4 in the Vollhardt's original derivation.



**Figure 3** Isobaric relaxation curves of mixed PMMA/PS-*b*-PEO at 8 mN/m and 40°C with PMMA molecular weights of (a) 12,000, (b) 30,000, (c) 60,000, and (d) 75,000.

In addition to our results<sup>11</sup> of relaxation of PMMA monolayers, the Vollhardt model was utilized successfully in a recent study<sup>27</sup> of relaxation processes of dipalmitoyl phosphatidylcholine monolayers.

The  $A_\infty$  values in this article were obtained first through simulating the whole curves. Second, eq. (1) was converted into a double logarithmic function versus  $\log(\text{time})$  to obtain  $x$  (related to the slope) and  $k_x$  (related to the intercept) values.  $R^2$  is the correlation coefficient of this second step. The estimated  $k_x$  and  $x$  values from data of Figures 1–3 were listed in Tables I–III, respectively. The  $A_\infty/A_0$  values of PS-*b*-PEO are smaller than PMMA because of faster relaxation behavior at three temperatures. The  $A_\infty/A_0$  values of PS-*b*-PEO at 10 and 25°C in Tables I and II are about the same, but the value becomes much smaller at 40°C as listed in Table III. The correlation coefficient in Tables I–III are mostly better than 0.95 indicating a good correlation. The larger  $A_\infty/A_0$  values of PMMA12000/PS-*b*-PEO in Table I in comparison also supported the strongest stabilization effect of PMMA12000 among the four molecular weights of PMMA. The decreasing  $A_\infty/A_0$  values from Table I showed that weaker PMMA stabilization effect on PS-*b*-PEO with higher PMMA molecular weight. The  $A_\infty/A_0$  values in Table II are similar to those in Table I except PMMA/PS-*b*-PEO (1 : 3) showed even smaller  $A_\infty/A_0$  values than PS-*b*-PEO with PMMA molecular weights of 30,000, 60,000,

and 75,000 g/mol. The PMMA monolayers at 40°C (given in Table III) are more unstable in comparison with at 10 and 25°C because of obviously lower  $A_\infty/A_0$  values. The destabilization effect at 40°C probably comes from PS-*b*-PEO aggregation<sup>12–15</sup> and low

**TABLE I**  
Modeling Parameters of Relaxation Phenomenon of Mixed PMMA/PS-*b*-PEO Monolayers at 10°C with PMMA Molecular Weights

	$A_\infty/A_0$	$k_x$	$x$	$R^2$
PMMA12000	0.9684	0.0026	0.8320	0.9799
3 : 1	0.9460	0.0046	0.7563	0.9616
1 : 1	0.9381	0.0056	0.7285	0.9221
1 : 3	0.9506	0.0461	0.5261	0.9304
PS- <i>b</i> -PEO	0.8279	0.0069	0.7305	0.9490
PMMA30000	0.9607	0.0092	0.6811	0.9658
3 : 1	0.9367	0.0092	0.6832	0.9410
1 : 1	0.9155	0.0070	0.7070	0.9432
1 : 3	0.8355	0.0139	0.6478	0.9556
PS- <i>b</i> -PEO	0.8279	0.0069	0.7305	0.9490
PMMA60000	0.9603	0.0099	0.6849	0.9511
3 : 1	0.9368	0.0086	0.6894	0.9446
1 : 1	0.9172	0.0083	0.6946	0.9484
1 : 3	0.8296	0.0165	0.6264	0.9430
PS- <i>b</i> -PEO	0.8279	0.0069	0.7305	0.9490
PMMA75000	0.9645	0.0042	0.7818	0.9632
3 : 1	0.9312	0.0182	0.6095	0.9346
1 : 1	0.8772	0.0237	0.5819	0.9311
1 : 3	0.7644	0.0148	0.6340	0.9426
PS- <i>b</i> -PEO	0.8279	0.0069	0.7305	0.9490

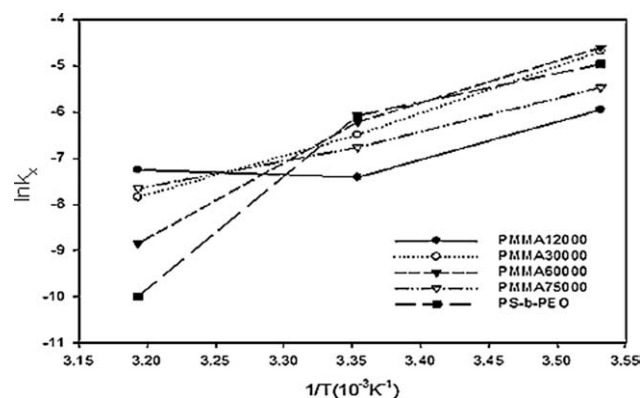
**TABLE II**  
Modeling Parameters of Relaxation Phenomenon of Mixed PMMA/PS-*b*-PEO Monolayers at 25°C with PMMA Molecular Weights

	$A_\infty/A_0$	$k_x$	$x$	$R^2$
PMMA12000	0.9530	0.0006	0.9704	0.9732
3 : 1	0.9348	0.0014	0.8921	0.9589
1 : 1	0.9225	0.0015	0.8655	0.9578
1 : 3	0.9115	0.0012	0.8776	0.9430
PS- <i>b</i> -PEO	0.8331	0.0023	0.8181	0.9538
PMMA30000	0.9533	0.0015	0.8650	0.9587
3 : 1	0.9385	0.0022	0.8301	0.9626
1 : 1	0.9051	0.0052	0.7301	0.9363
1 : 3	0.7709	0.0129	0.6264	0.9182
PS- <i>b</i> -PEO	0.8331	0.0023	0.8181	0.9538
PMMA60000	0.9526	0.0019	0.8388	0.9583
3 : 1	0.9433	0.0037	0.7850	0.9476
1 : 1	0.8832	0.0110	0.6516	0.9299
1 : 3	0.7706	0.0099	0.6656	0.9350
PS- <i>b</i> -PEO	0.8331	0.0023	0.8181	0.9538
PMMA75000	0.9435	0.0012	0.8969	0.9422
3 : 1	0.9101	0.0086	0.6823	0.9291
1 : 1	0.8598	0.0128	0.6403	0.9294
1 : 3	0.7579	0.0034	0.7740	0.9486
PS- <i>b</i> -PEO	0.8331	0.0023	0.8181	0.9538

degree of dipole–dipole interaction between C=O groups of PMMA and —O— groups of PEO. The mixed PMMA/PS-*b*-PEO monolayers in Table III are fairly stable at mid-PMMA molecular weights (30,000 and 60,000 g/mole) likely because of a balance of enthalpic and entropic contributions. The enthalpic contributions probably result mainly from dipole–dipole interaction between PEO and PMMA. Chain arrangements of mixed PMMA/PS-*b*-PEO cause the entropic contributions.

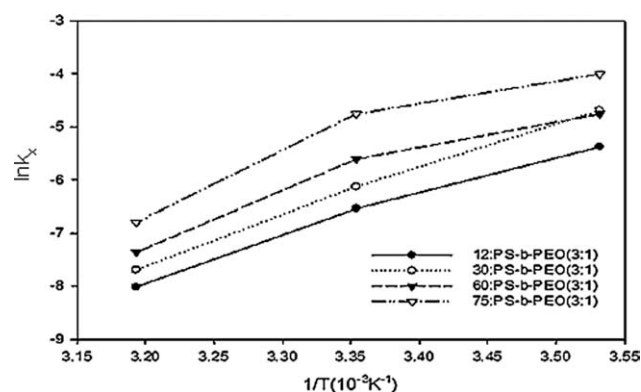
**TABLE III**  
Modeling Parameters of Relaxation Phenomenon of Mixed PMMA/PS-*b*-PEO Monolayers at 40°C with PMMA Molecular Weights

	$A_\infty/A_0$	$k_x$	$x$	$R^2$
PMMA12000	0.8984	0.0007	0.9530	0.9718
3 : 1	0.7545	0.0003	1.0250	0.9682
1 : 1	0.8629	0.0009	0.9109	0.9537
1 : 3	0.5511	0.00005	1.2232	0.9672
PS- <i>b</i> -PEO	0.5612	0.00005	1.2367	0.9666
PMMA30000	0.8779	0.0004	1.0192	0.9708
3 : 1	0.8292	0.0005	1.0042	0.9701
1 : 1	0.8222	0.0008	0.9355	0.9624
1 : 3	0.6799	0.0001	1.1402	0.9676
PS- <i>b</i> -PEO	0.5612	0.00005	1.2367	0.9666
PMMA60000	0.9057	0.0001	1.1438	0.9805
3 : 1	0.8708	0.0006	0.9603	0.9657
1 : 1	0.8344	0.0014	0.8783	0.9577
1 : 3	0.6491	0.00007	1.1958	0.9714
PS- <i>b</i> -PEO	0.5612	0.00005	1.2367	0.9666
PMMA75000	0.9057	0.0005	0.9929	0.9745
3 : 1	0.8829	0.0011	0.9033	0.9618
1 : 1	0.8183	0.0019	0.8414	0.9523
1 : 3	0.5416	0.00005	1.2279	0.9660
PS- <i>b</i> -PEO	0.5612	0.00005	1.2367	0.9666



**Figure 4**  $\ln k_x$  versus  $1/T$  of pure polymers.

The  $k_x$  values of pure polymers were plotted versus the reciprocal of temperature and presented in Figure 4. The  $k_x$  values for most polymers decrease with increasing temperature. However, the  $k_x$  values of PMMA12000 are about the same at 25 and 40°C. The  $k_x$  values of PS-*b*-PEO decrease more drastically when the temperature changes from 25 to 40°C in comparison with 10 to 25°C likely because of its more mushroom to brush transition.<sup>12–15</sup> The  $k_x$  values of the PMMA/PS-*b*-PEO monolayers versus the reciprocal of temperature are illustrated in Figure 5 in the weight ratio of 3 : 1. The other two weight ratios (1 : 1 and 1 : 3) are omitted for brevity. The  $k_x$  values in Figure 5 increase almost exactly with increasing PMMA molecular weight. Higher  $k_x$  values (assuming  $x$  is almost constant) probably indicate higher instability of relaxation curves. The estimated high  $k_x$  values are approximately in agreement with the destabilization effect of PMMA increasing with increasing molecular weight. The molecular weight effect of PMMA on the  $k_x$  values of PMMA/PS-*b*-PEO (1/1) is consistent with Figure 5 only at 25°C. There are no definite trends of the  $k_x$  values of PMMA/PS-*b*-PEO (1/1) at the other two temperatures. When the PMMA and PS-*b*-PEO



**Figure 5**  $\ln k_x$  versus  $1/T$  of mixed PMMA/PS-*b*-PEO in the weight ratio of 3 : 1.

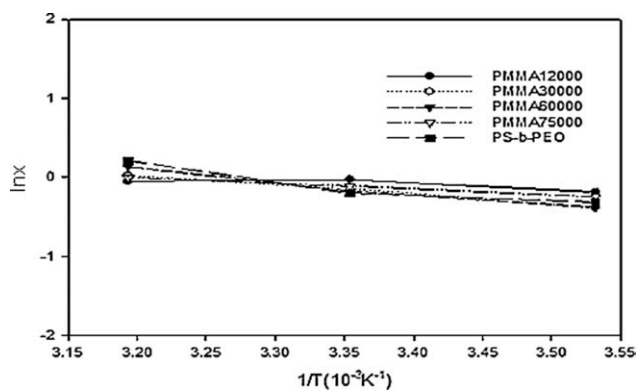


Figure 6  $\ln x$  versus  $1/T$  of pure polymers.

weight ratio is 1 : 3, the  $k_x$  values do not show a definite dependence on PMMA molecular weight.

The  $x$  values of pure polymers were plotted versus  $1/T$  and shown in Figure 6. The  $x$  values are about the same order of magnitude for all the studied polymers. All the PMMAs except PMMA12000 demonstrate that the  $x$  values increase very minutely with temperature. The  $x$  values of PS-*b*-PEO are about the same at 10 and 25°C, but the  $x$  value at 40°C is highest and larger than 1 likely also because of more mushroom to brush transition.<sup>12–15</sup> The  $x$  values of the mixed PMMA/PS-*b*-PEO monolayers are illustrated in Figure 7 in the weight ratio of 3 : 1. The other two weight ratios (1 : 1 and 1 : 3) are omitted for brevity. The  $x$  values in Figure 7 and also PMMA/PS-*b*-PEO (1/1) decrease more or less with increasing PMMA molecular weight. No definite molecular weight dependence of  $x$  values was found in PMMA/PS-*b*-PEO (1/3) when PS-*b*-PEO fraction is higher than PMMA fraction likely because the interaction between PS-*b*-PEO and PMMA was insignificant regardless of PMMA molecular weight.

Totally speaking, PMMA12000 exhibited the strongest stabilization effect with PS-*b*-PEO at 10 and 25°C except at 40°C. The  $A_\infty/A_0$  values of PMMA12000 decrease with increasing temperature. The reduction

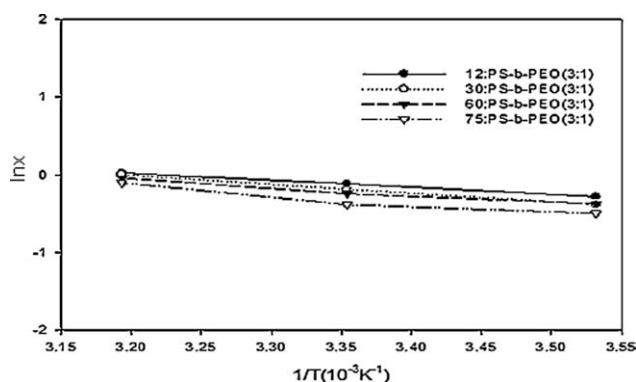


Figure 7  $\ln x$  versus  $1/T$  of mixed PMMA/PS-*b*-PEO in the weight ratio of 3 : 1.

of the  $A_\infty/A_0$  values of PMMA12000 between 25 and 40°C is much larger than that between 10 and 25°C. The  $k_x$  values of mixed PMMA12000/PS-*b*-PEO decrease with the elevation of temperature. The  $x$  values of mixed PMMA12000/PS-*b*-PEO monolayers increase slightly with increasing temperature.

## CONCLUSIONS

On the basis of simulation of isobaric relaxation curves, the Vollhardt model of nucleation/growth mechanism was able to describe the observed relaxation of mixed PMMA/PS-*b*-PEO monolayers. The PS-*b*-PEO monolayer was found to exhibit a fast relaxation curve. Addition of PMMA into PS-*b*-PEO slowed the relaxation behavior especially at the lowest experimental temperature (10°C) because of likely dipole-dipole interaction between PMMA and PEO. The PMMA with the lowest molecular weight was proven to be most effective in stabilization of mixed monolayers as demonstrated in the highest  $A_\infty/A_0$  values. The estimated  $x$  values were found to be almost temperature independent. The molecular weight dependence of PMMA on the  $x$  values was observed when PMMA and PS-*b*-PEO ratios were 3 : 1 and 1 : 1. Increasing PMMA molecular weight caused decreasing  $x$  values. The  $k_x$  values were detected to decrease mostly as a result of temperature elevation regardless of pure or mixed monolayers. Increasing  $k_x$  values with increasing PMMA molecular weight were observed in mixed PMMA/PS-*b*-PEO monolayers when PMMA and PS-*b*-PEO ratio was 3 : 1.

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