Correlation of Relaxation Modeling Parameters of the Studied Polymer Blends at the Air/Water Interface

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Abstract: The main studied mixed monolayers consisting of polyethylene-block-polycaprolactone (PEO-b-PCL) and its component polymers with poly(vinyl phenol). It was shown previously that most of the area relaxation process of mixed monolayers could be well represented by a model considering the nucleation and growth mechanisms. The characteristic exponent x values were found to be slightly temperature dependent. The k_x values were detected to decrease with increasing temperature. When PVPh was added into the most unstable PEO, the mixed monolayer films exhibited a remarkably improved stable relaxation behavior than PCL (or PEO-b-PCL). The characteristic exponent x and k_x values were plotted vesus the A_∞/A_0 values. Mostly increasing characteristic exponent x and k_x values with increasing A_∞/A_0 values were observed. For the PCL and PVPh monolayers, the xk_x values were detected to increase with increasing A_∞/A_0 values. The xk_x values of previously published stereoregular and different molecular weight PMMAs were also demonstrated to become larger with the increasing A_∞/A_0 values.

Keywords: Relaxation, Modeling parameters.

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 [1, 2], but the research efforts have multiplied rapidly because of possible applications in nonlinear optical devices and other fields such as biosensors and microlithography.

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 [3] 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, st-PMMA) in a Langmuir monolayer investigated by surface pressure-area isotherms and atomic force microscopy (AFM) was reported by Aiba *et al*. [4]. 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) [5] and monolayers of poly(styrene)-poly(methyl methacrylate) diblock copolymer [6] at the air/water interface studied by the surface pressure-area isotherms at several temperatures.

The relaxation phenomenon of monolayers of polyethylene oxide-block-polycaprolactone (PEO-b-PCL) and its component polymers with PVPh was published previously [7]. The reason for choosing the system is PEO or PCL forms different degree of hydrogen bonding with PVPh. Iso-baric relaxation experiments of mixed monolayers at the air/water interface were investigated at different temperatures (10℃, 25℃ and 40℃). The temperature was chosen at a 15℃ interval and kept low to minimize water current disturbance. It was shown that most of the area relaxation process of mixed monolayers could be well represented by a model considering the nucleation and growth mechanisms. The characteristic exponent x values were found to be slightly temperature dependent. The k_x values were detected to decrease with increasing temperature. When PVPh was added into the most unstable PEO, the mixed monolayer films exhibited a remarkably improved stable relaxation behavior than PCL(or PEO-b-PCL). The stabilization behavior was likely caused by the PVPh-H_2O-PEO interaction. There were likely less PVPh-H_2O-PCL interaction since PCL interacted with PVPh favorably.

In this article, the objective of this research was to find out the correlation of relaxation of modeling

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parameters of the studied blends at the air/water interface. Iso-baric relaxation experimental data of mixed monolayers at the air/water interface investigated at different temperatures (10℃, 25℃ and 40℃) were used to estimate the modeling parameters.

EXPERIMENTAL

The experimental details can be referred to my previous publication [7].

RESULTS AND DISCUSSION

Modeling

An attempt was made to interpret our relaxation results in more detail with respect to particle nucleation/growth models. Vollhardt *et al*. 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) [8-10].

$$\frac{\left(1-\dfrac{A}{A_0}\right)}{\left(1-\dfrac{A_\infty}{A_0}\right)}=1-\exp(-k_x t^x) \tag{1}$$

where A is the total surface area at time t, A_0 is the initial surface area, A_∞ is the area at t ≈∞, 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.

In addition to the relaxation of stereoregualr and different molecular weight PMMA [11-12] monolayers, the Vollhardt model was utilized successfully in a study [13] of relaxation processes of dipalmitoyl phosphatidylcholine monolayers. The bi-exponential decay equation was used in mixed monolayers of alkylated azacrown ethers and palmitic acid [14]. In a previous study [7], the single exponential decay was proven to be sufficient.

The Sigma-plot software was used in the following simulation. The A_∞ values in this article were obtained first through simulating the whole curves. Secondly, the equation (1) was converted into a double logarithmic function versus log(time) to obtain *x* (related to the slope) and k_x (related to the intercept) values.

The estimated k_x and *x* values of PEO, PCL, PEO-b-PCL and PVPh from a previous study [7] were plotted versus the A_∞/A_0 values in Figures **1** to **4**, respectively. In Figures **1** and **3**, the k_x and *x* values were found to increase with the A_∞/A_0 values. The estimated k_x values increased with the A_∞/A_0 values in Figures **2** and **4**. However, the x values were found to decrease with the A_∞/A_0 values in Figures **2** and **4**.

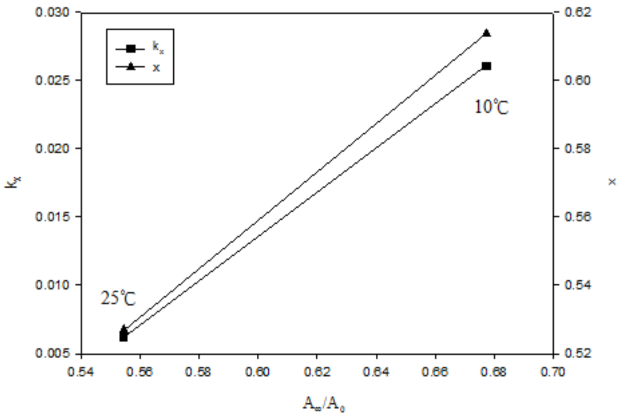

Figure 1: The k_x and x values versus A_∞/A_0 of PEO at the surface pressure of 1.5 mN/m.

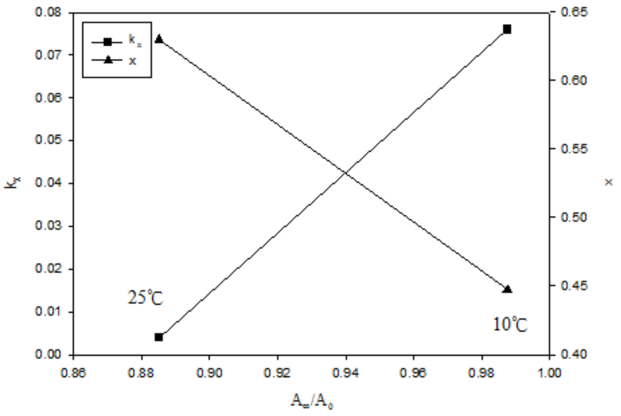

Figure 2: The k_x and x values versus A_∞/A_0 of PCL at the surface pressure of 6 mN/m.

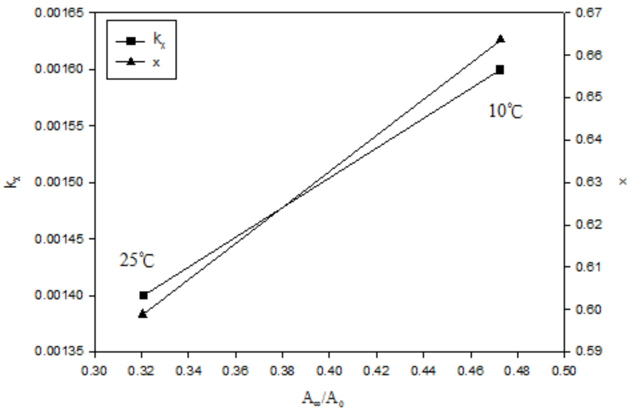

Figure 3: The k_x and x values versus A_∞/A_0 of PEO-b-PCL at the surface pressure of 6 mN/m.

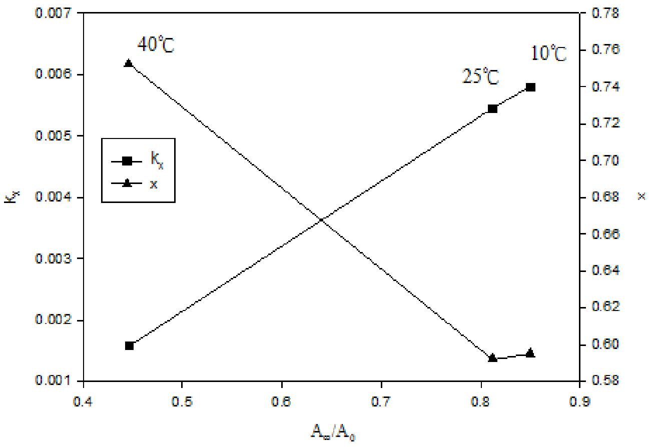

Figure 4: The k_x and x values versus A_∞/A_0 of PVPh at the surface pressure of 1.5 mN/m.

The attempt of trying to combine the two-k_x and *x* values into xk_x as in Figures **2** and **4** was listed in Table **1**. The results can be observed more clearly as demonstrated in Figures **5** and **6**. The xk_x values were found to increase with the A_∞/A_0 values.

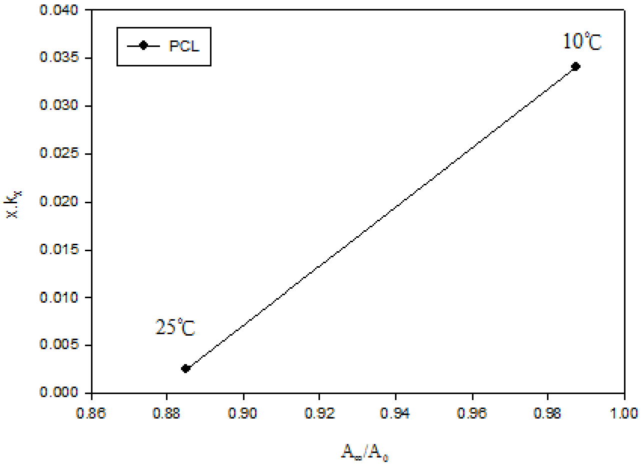

Figure 5: The xk_x values versus A_∞/A_0 of PCL at the surface pressure of 6 mN/m.

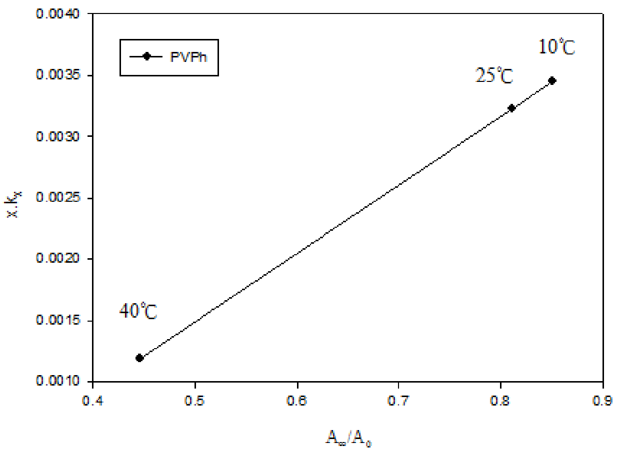

Figure 6: The xk_x values versus A_∞/A_0 of PVPh at the surface pressure of 6 mN/m.

This approach was also applied successfully to the two previous publications [11-12]. The xk_x values of stereoregualr PMMA were found to increase with the A_∞/A_0 values with approximately the largest xk_x values of isotactic PMMA as shown in Figure **7**. For different molecular weight PMMA, the xk_x values also increased with the A_∞/A_0 values as presented in Figure **8**. The xk_x values were found to correlate approximately well with the A_∞/A_0 values.

CONCLUSIONS

The characteristic exponent x and k_x values from the nucleation and growth model were plotted versus the A_∞/A_0 values. Mostly increasing characteristic exponent x and k_x values with increasing A_∞/A_0 values were observed. For the PCL and PVPh monolayers, the xk_x values were detected to increase with increasing A_∞/A_0 values. The xk_x values of previously published stereoregular and different molecular weight PMMAs were also demonstrated to become larger with the increasing A_∞/A_0 values. The xk_x values were found to correlate approximately well with the A_∞/A_0 values.

Table 1: The A_∞/A_0, k_x, x and xk_x Values

	A_∞/A_0	k_x	x	xk_x
PEO(10℃)	0.6773	0.0261	0.6138	0.01602
PEO(25℃)	0.5545	0.0062	0.5269	0.00327
PVPh(10℃)	0.8503	0.0058	0.5952	0.00345
PVPh(25℃)	0.8119	0.0055	0.5922	0.00326
PVPh(40℃)	0.4460	0.0016	0.7526	0.00120

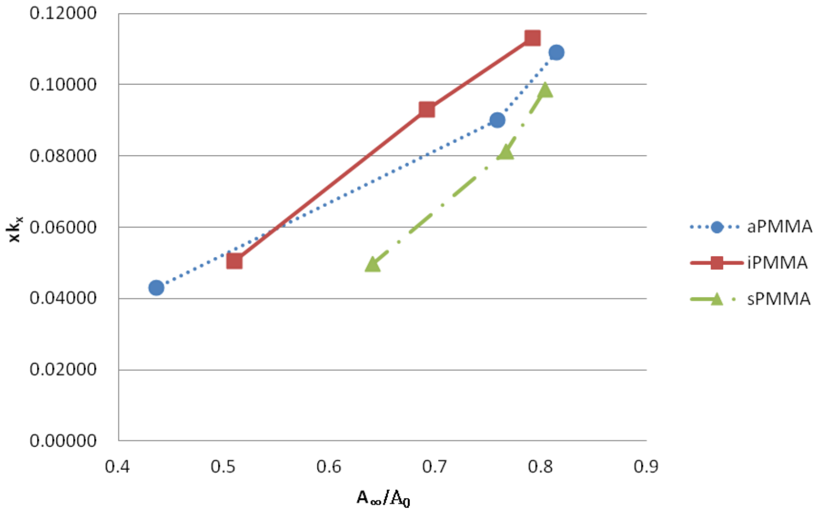

Figure 7: The xk_x values versus A_∞/A_0 of different tactic PMMAs at the surface pressure of 30 mN/m.

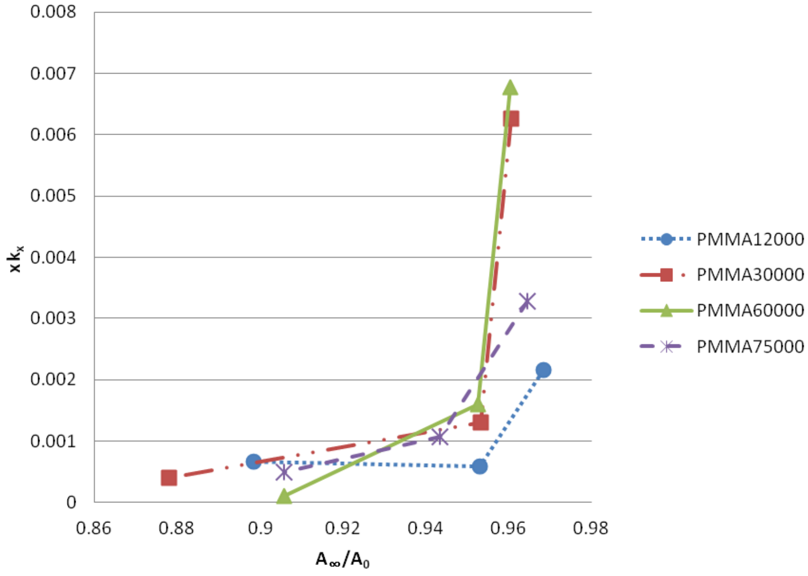

Figure 8: The xk_x values versus A_∞/A_0 of different molecular weight PMMAs at the surface pressure of 8 mN/m.

Using the A_∞/A_0 values as an indicator for xk_x values was proven successful.

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