Journal of Composites and Biodegradable Polymers, 2020, *8*, 17-27

Relaxation Modeling of PEO-b-PCL and its Component Polymers with PVPh at the Air/Water Interface

Hui-Ting Pan and Wen-Ping Hsu*

Department of Chemical Engineering, National United University, Miao-Li, Taiwan 360, R.O.C.

Abstract: The objective of this research was to find out the effects of structure of polyethylene oxide-block-polycaprolactone (PEO-b-PCL) and its component polymers and temperature on the iso-baric relaxation behaviors of mixed monolayers with poly(vinyl phenol). Iso-baric relaxation experiments of mixed monolayers at the air/water interface were investigated at different temperatures (10℃, 25℃ and 40℃). 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.

Keywords: Relaxation, Temperature, PEO-b-PCL, PVPh.

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.

Crisp [1, 2] 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 [3-6].

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 [7] 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*. [8]. 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) [9] and monolayers of poly(styrene)-poly(methyl methacrylate) diblock copolymer [10] at the air/water interface studied by the surface pressure-area isotherms at several temperatures.

In a previous study [11], 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 iso-baric relaxation experiments. The results show that the π-A isotherms of PMMA converge at 40℃ regardless of molecular weights. The collapse pressure of PMMA monolayers decreases as the

---

*Address correspondence to this author at the Department of Chemical Engineering, National United University, Miao-Li, Taiwan 360, R.O.C.;
Tel: (+)886-37-382213; Fax: (+)886-37-382223;
E-mail: mjkr.hsu@msa.hinet.net

E-ISSN: 2311-8717/20

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 [12-15] 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 non-equilibrium 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 [16-20]. The iso-baric relaxation behavior of PS-b-PEO monolayer was published previously [21]. The PS-b-PEO monolayer was found to exhibit a fast relaxation curve (*i.e.* the surface area decreased significantly with increasing time). Two of the recent studies of block copolymer containing poly (ethylene glycol) were reported by Won [22, 23].

The miscibility of PEO-b-PCL and its component polymers with PVPh at the air/water interface was published previously [24]. The mixed monolayer behavior of polyethylene-block-polycaprolactone (PEO-b-PCL) and its component polymers (PEO or PCL) with poly(vinyl phenol)(PVPh) was investigated from the measurements of surface pressurearea per molecule (π-A) isotherms at three different temperatures(10℃, 25℃ and 40℃). The miscibility and nonideality of the mixed monolayers were examined by calculating the excess surface area as a function of composition. Interestingly, PEO and PCL were shown to have different interactions with PVPh at the air/water interface from in the bulk state on the solid substrate. PE O demonstrated mostly positive excess surface area with PVPh. Negative excess surface areas were in the majority observed in the PCL/PVPh monolayers. A scheme of differences in interaction sites between PEO (or PCL) and PVPh at the air/water interface was proposed to explain the negative or positive deviations of surface areas successfully.

In this article, the relaxation phenomenon of monolayers of polyethylene oxide-block-polycaprolactone (PEO-b-PCL) and its component polymers with PVPh was investigated. To the best of our knowledge, the relaxation of PEO-b-PCL has not been reported before. Effect of temperature and molecular structure of PEO-b-PCL and its component polymers on the iso-baric relaxation behavior was evaluated. The relaxation behaviors were quite different from those of the π-A isotherms. The possible cause is discussed. It was found the relaxation stabilization behavior was likely caused by a ternary interaction.

EXPERIMENTAL

Materials

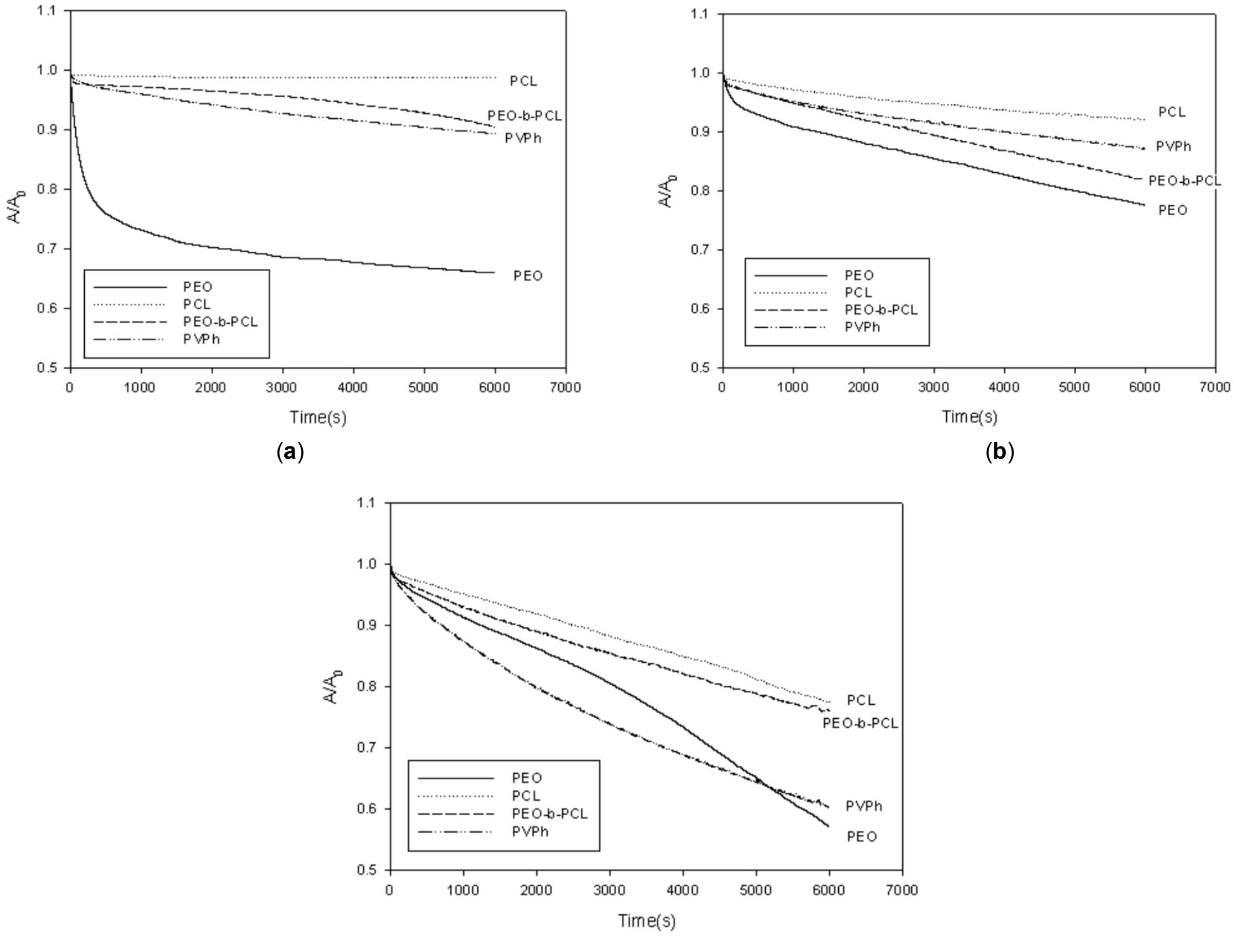
The molecular weight (M_n) of PEO-b-PCL obtained from Polymer Source, Inc., Montreal, Canada is about 5,000 g/mol for each block. The polydispersity index is 1.07. According to the supplier information, the glass transition temperature, melting temperature and crystallization temperature are -71℃, 50℃ and 23℃, respectively. PVPh was purchased from Polysciences, Inc., Warrington, PA with a molecular weight (M_w) of 1500-7000 g/mol. PEO with a M_v = 100,000 g/mol was supplied by Aldrich Chemical Company, Inc. PCL from Scientific Polymer Products, Inc. had a M_w = 120,000 g/mol.

Tetrahydrofuran(THF) purchased from Tedia Company Inc. was used as the spreading solvent for the polymer films. The solvent was chosen to codissolve PEO-b-PCL (or PCL) and PVPh. For PEO/PVPh system, 1 to 1 volume ratio of chloroform and THF was used. Only highly pure water, which was purified by means of a Milli-Q plus water purification system, with a resistivity of 18.2 MΩ-cm was used in all experiments. Blank experiments using THF were carried out that there were no surface-active impurities.

Iso-baric Relaxation Measurements

A model minitrough (M 1200) 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 with a controlled speed 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 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±0.5 ℃, 25±0.5 ℃ and 40±0.5 ℃. 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 materials was spread on the subphase by using a Hamilton microsyringe. At least 40 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 $Å^2$/(molecular min)) to obtain a single π-A isotherm previously.



(a)

(b)

(c)

Figure 1: Relaxation curves of four component polymers at (**a**) 10 ℃ (**b**) 25 ℃ (**c**) 40 ℃.

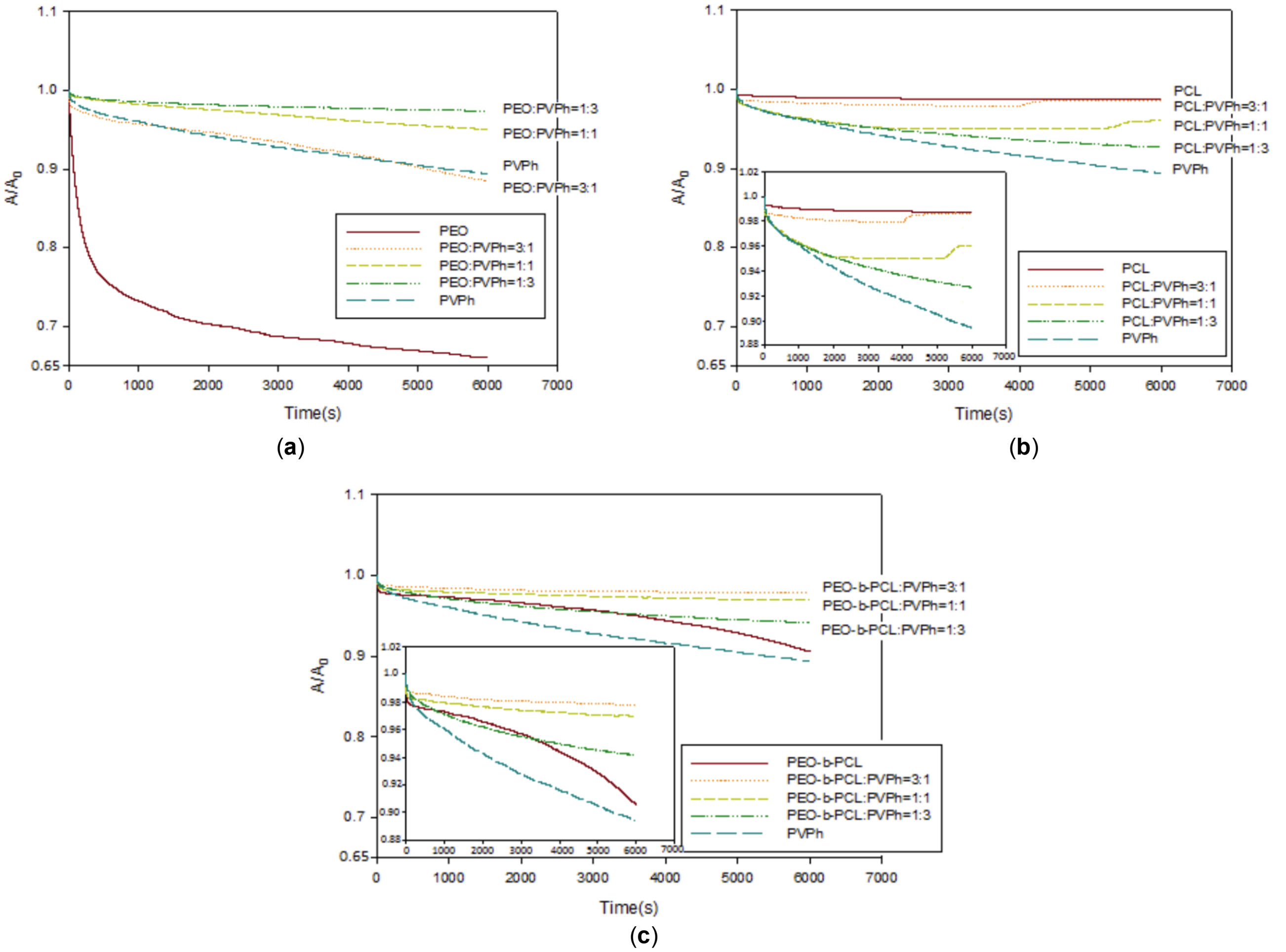
Iso-baric relaxation curves of mixed monolayer films were also obtained in the same way as π-A isotherms. The only difference is that when the desired surface pressure was obtained and set as constant. A surface pressure at 6 mN/m was chosen for most monolayers and a surface pressure at 1.5 mN/m was used for 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 Å^2 /(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 cm^2. The computer will calculate A automatically with the reduction of area.

RESULTS AND DISCUSSION

Iso-baric Relaxation Phenomena

Relaxation curves of the four component polymers were given in Figure **1** in the order of (**a**) 10℃ (**b**) 25℃ and (**c**) 40℃, respectively. For component polymers in Figure **1**(**a**), the PEO monolayer exhibited the fastest relaxation curve likely because of hydrophilic structure. The other three polymers demonstrated similar relaxation behaviors in the order of the A/A_0 values: PCL>PEO-b-PCL>PVPh. For component polymers in Figure **1**(**b**) at 25℃, the relaxation curves of the four component polymers behaved similarly in the order of the A/A_0 values: PCL>PVPh>PEO-b-PCL>PEO. For component polymers in Figure **1**(**c**) at 40℃, the PVPh monolayer exhibited the fastest relaxation curve for most time, however PEO had the lowest A/A_0 values in the end.

Relaxation curves of the mixed monolayers at 10℃ were given in Figure **2** in the order of (**a**) PEO/PVPh (**b**) PCL/PVPh and (**c**) PEO-b-PCL/PVPh, individually. The addition of PVPh into PEO stabilized the mixed monolayers greatly in Figure **2**(**a**) especially at 50% and 75% of PVPh composition. The mixed PCL/PVPh monolayers in Figure **2**(**b**) exhibited typical composition dependent curves. The addition of PEO-b-PCL into



(**a**) (**b**)

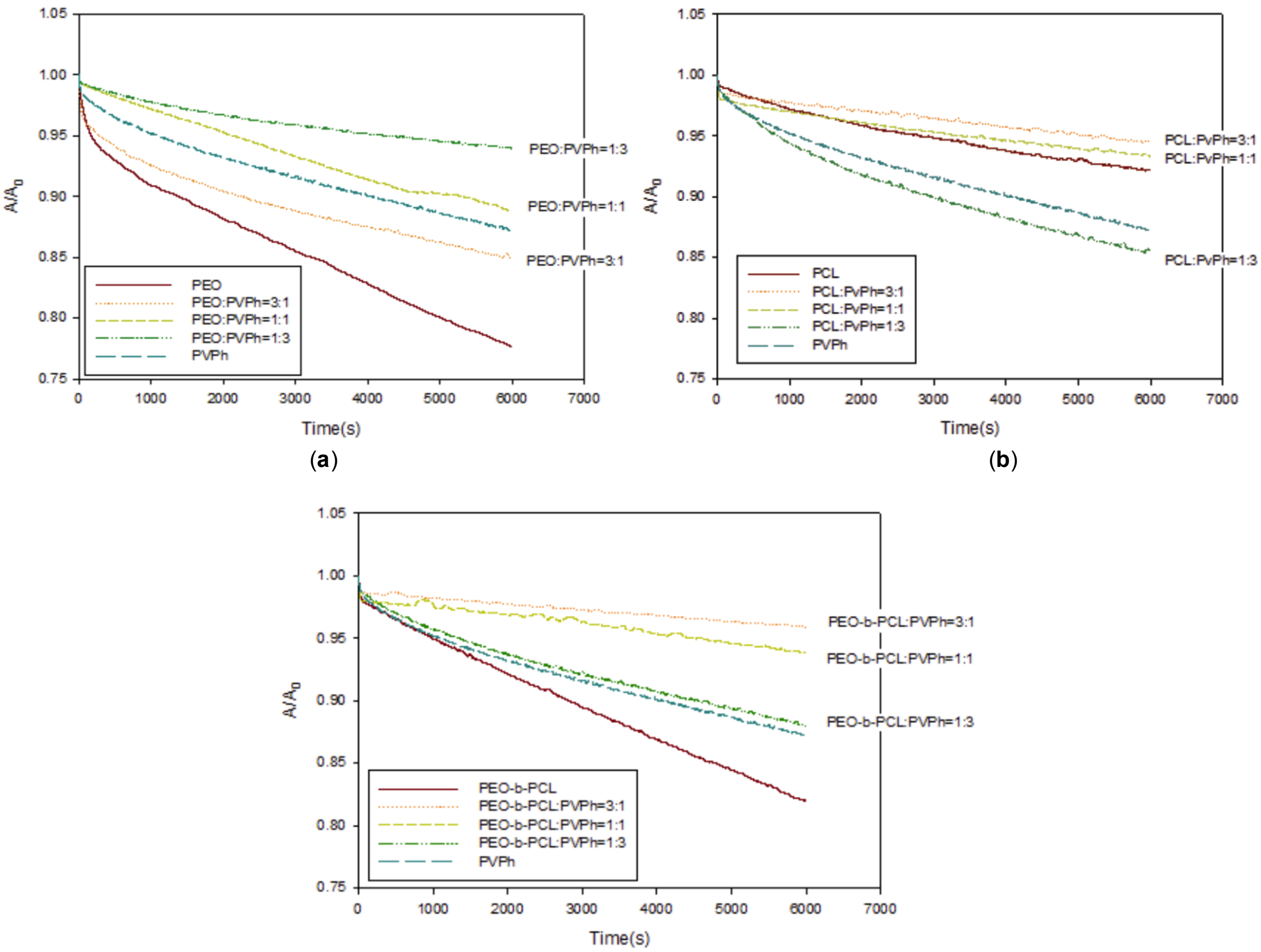
(**c**)

Figure 2: Relaxation curves of mixed monolayers at 10 ℃ (**a**) PEO/PVPh (**b**) PCL/PVPh (**c**) PEO-b-PCL/PVPh.

PVPh increased the stability of the mixed monolayers in Figure **2**(**c**) at the increasing PEO-b-PCL composition. The A/A_0 values of the three mixed monolayers are larger than individual component polymers.

Relaxation curves of the mixed monolayers at 25℃ were given in Figure **3** in the order of (a) PEO/PVPh (b) PCL/PVPh and (c) PEO-b-PCL/PVPh, individually. The addition of PVPh into PEO stabilized the mixed monolayers greatly in Figure **3**(**a**) especially at 50% and 75% of PVPh compositions similar to those in Figure **2**(**a**). The mixed PCL/PVPh monolayers in Figure **2**(**b**) exhibited composition dependent curves with 75% and 50% of PCL composition curves more stable than PCL. The addition of PEO-b-PCL into PVPh increased the stability of the mixed monolayers in Figure **3**(**c**) at the increasing PEO-b-PCL composition. The A/A_0 values of the mixed monolayers are larger than individual component polymers similar to Figure **2**(**c**).

Relaxation curves of the mixed monolayers at 40℃ were given in Figure **4** in the order of (**a**) PEO/PVPh (**b**) PCL/PVPh and (**c**) PEO-b-PCL/PVPh, individually. The mixed PEO/PVPh monolayers demonstrated more stable relaxation behaviors than component polymers with PEO/PVPh(3/1) as the exception having lower A/A_0 values. The mixed PCL/PVPh monolayers in Figure **4**(**b**) exhibited typical composition dependent curves. The addition of PCL into PVPh increased the stability of the mixed monolayers at the increasing PCL composition. The addition of PEO-b-PCL into PVPh as depicted in Figure **4**(**c**) increased the stability of the mixed monolayers at the increasing PEO-b-PCL composition at 25% and 50% of PEO-b-PCL compositions. The A/A_0 values of the three mixed PEO-b-PCL/PVPh(3/1) decreased slowly initially then became smaller in a later stage.

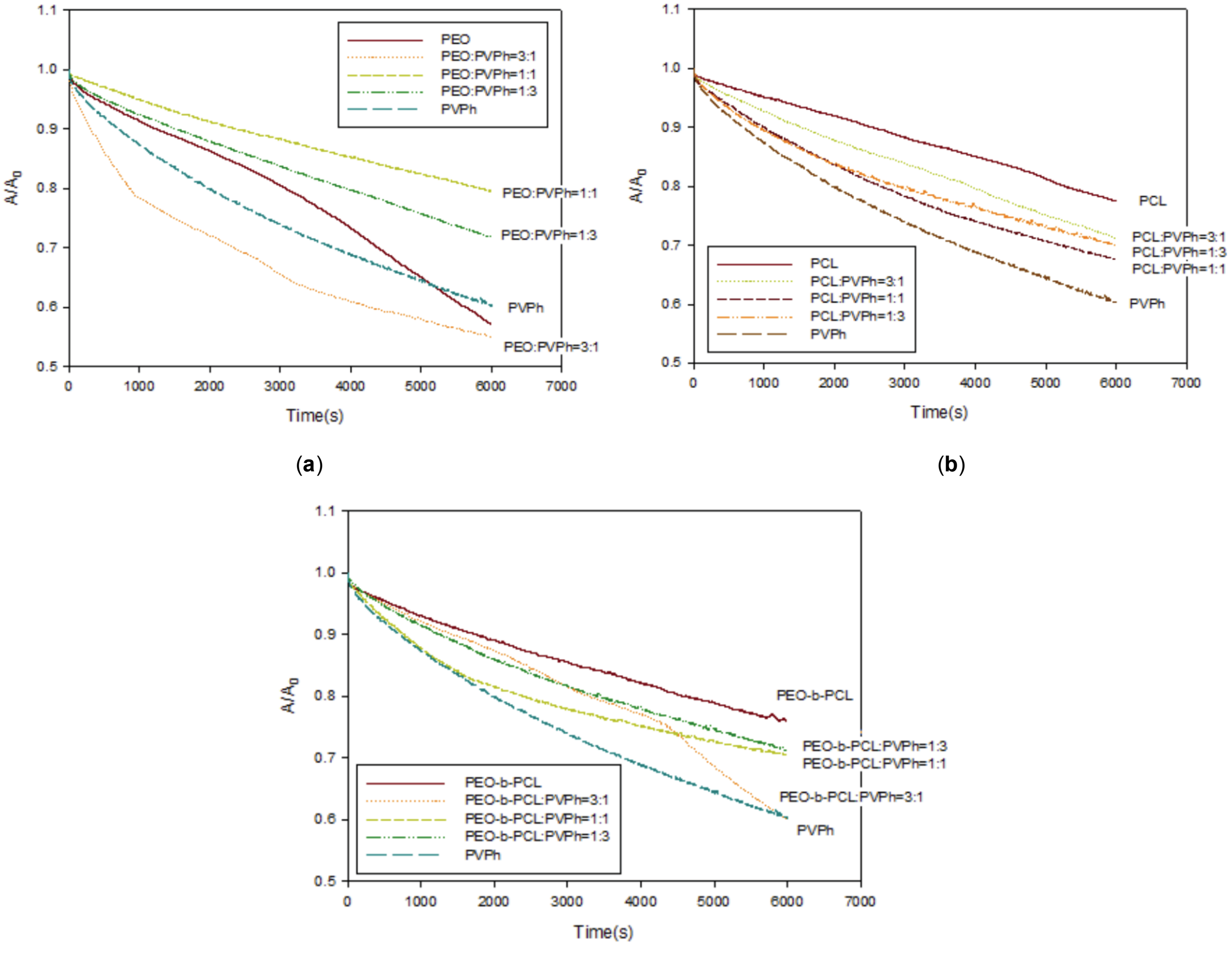


(**a**)

(**b**)

(**c**)

Figure 3: Relaxation curves of mixed monolayers at 25 ℃ (**a**) PEO/PVPh (**b**) PCL/PVPh (**c**) PEO-b-PCL/PVPh.



(**a**) (**b**)

(**c**)

Figure 4: Relaxation curves of mixed monolayers at 40 ℃ (**a**) PEO/PVPh (**b**) PCL/PVPh (**c**) PEO-b-PCL/PVPh.

PCL was found to interact with PVPh favorably than PEO previously [24]. In this study, when PVPh was added into PEO the mixed monolayers demonstrated improved stability due to possible PVPh-H_2O-PEO interaction. OH groups of PVPh can interact with water molecules first, then water molecules can still interact with PEO. There were likely less PVPh-H_2O-PCL interaction since PCL interacted with PVPh favorably.

Modeling

An attempt was made to interpret our relaxation results in more detail with respect to particle nucleation/growth models. Vollhardt *et al*. [25-27] 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 [28-30]

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

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 PMMA [11] monolayers, the Vollhardt model was utilized successfully in a study [31] of relaxation processes of dipalmitoyl phosphatidylcholine monolayers. The bi-exponential decay equation was used in mixed monolayers of alkylated azacrown ethers and palmitic acid [32]. In this study, the single exponential decay was proven to be sufficient.

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. R^2 is the correlation coefficient of this second step.

The estimated k_x and *x* values from data of Figure **2** in 10℃ were listed in Tables **1-3**, respectively. There are four mixed monolayers with poor correlation not tabulated. The reported monolayer demonstrated higher correlation coefficients than 0.95. PEO has the lowest A_∞/A_0 value as predicted by the trend. The estimated k_x and *x* values will be discussed in a later paragraph.

The estimated k_x and *x* values from data of Figure **3** in 25℃ were listed in Tables **4-6**, respectively. There is one PEO-b-PCL/PVPh(1/3) monolayer with poor correlation not tabulated. The reported monolayer demonstrated higher correlation coefficients than 0.95. PEO-b-PCL has the lowest A_∞/A_0 value as simulated by the trend. The estimated k_x and *x* values will be discussed later.

Table 1: Modeling Parameters of Relaxation Phenomenon of Mixed PEO/PVPh Monolayers at 10 ℃

	A_∞/A_0	k_x	x	R^2
PEO	0.6773	0.0261	0.6138	0.9701
PEO：PVPh=3：1	—	—	—	—
PEO：PVPh=1：1	0.8761	0.0049	0.5135	0.9730
PEO：PVPh=1：3	0.9725	0.0181	0.5520	0.9842
PVPh	0.8503	0.0058	0.5952	0.9825

R^2：Coefficient of correlation.

Table 2: Modeling Parameters of Relaxation Phenomenon of Mixed PCL/PVPh Monolayers at 10 ℃

	A_∞/A_0	k_x	x	R^2
PCL	0.9875	0.0761	0.4472	0.9945
PCL：PVPh=3：1	—	—	—	—
PCL：PVPh=1：1	—	—	—	—
PCL：PVPh=1：3	0.9205	0.0152	0.5610	0.9851
PVPh	0.8503	0.0058	0.5952	0.9825

R^2：Coefficient of correlation.

Table 3: Modeling Parameters of Relaxation Phenomenon of Mixed PEO-b-PCL/PVPh Monolayers at 10 ℃

	A_∞/A_0	k_x	x	R^2
PEO-b-PCL	—	—	—	—
PEO-b-PCL：PVPh=3：1	0.9779	0.0854	0.4108	0.9907
PEO-b-PCL：PVPh=1：1	0.9659	0.1101	0.3245	0.9805
PEO-b-PCL：PVPh=1：3	0.9345	0.0135	0.5625	0.9845
PVPh	0.8503	0.0058	0.5952	0.9825

R^2：Coefficient of correlation.

Table 4: Modeling Parameters of Relaxation Phenomenon of Mixed PEO/PVPh Monolayers at 25 ℃

	A_∞/A_0	k_x	x	R^2
PEO	0.5545	0.0062	0.5269	0.9783
PEO：PVPh=3：1	0.8255	0.0168	0.5212	0.9800
PEO：PVPh=1：1	0.7765	0.0010	0.7320	0.9875
PEO：PVPh=1：3	0.9217	0.0045	0.6433	0.9856
PVPh	0.8119	0.0055	0.5922	0.9836

R^2：Coefficient of correlation.

Table 5: Modeling Parameters of Relaxation Phenomenon of Mixed PCL/PVPh Monolayers at 25 ℃

	A_∞/A_0	k_x	x	R^2
PCL	0.8851	0.0040	0.6301	0.9879
PCL：PVPh=3：1	0.5930	0.0053	0.3625	0.9585
PCL：PVPh=1：1	0.8930	0.0225	0.4104	0.9702
PCL：PVPh=1：3	0.8208	0.0036	0.6858	0.9909
PVPh	0.8119	0.0055	0.5922	0.9836

R^2：Coefficient of correlation.

Table 6: Modeling Parameters of Relaxation Phenomenon of Mixed PEO-b-PCL/PVPh Monolayers at 25 ℃

	A_∞/A_0	k_x	x	R^2
PEO-b-PCL	0.3207	0.0014	0.5989	0.9815
PEO-b-PCL：PVPh=3：1	0.8063	0.0111	0.3321	0.9566
PEO-b-PCL：PVPh=1：1	—	—	—	—
PEO-b-PCL：PVPh=1：3	0.8268	0.0043	0.6237	0.9823
PVPh	0.8119	0.0055	0.5922	0.9836

R^2：Coefficient of correlation.

The estimated k_x and *x* values from data of Figure **4** in 40℃ were listed in Tables **7**-**9**, respectively. There are four mixed monolayers with poor correlation not tabulated. The reported monolayer demonstrated higher correlation coefficients than 0.95. PVPh has a slightly lower A_∞/A_0 value than PEO-b-PCL as simulated. The estimated k_x and *x* values will be discussed later.

The logarithmic k_x values were plotted versus the reciprocal of temperature and depicted in Figure **5**. The k_x values were found to decrease with temperature mostly with the exception of PEO-b-PCL having approximately the same values. The mixed monolayers at 75% PVPh composition in Figure **6** demonstrated a quite similar and close trend with decreasing k_x values with elevation of temperature. The k_x values of the mixed monolayers at 25℃ in Figure **7** were found to decrease with increasing PVPh mole fraction while PCL mixed monolayers had the lowest k_x values.

The logarithmic x values of component polymers were plotted versus the reciprocal of temperature and depicted in Figure **8**. The x values were found to increase slightly with temperature mostly with the exception of PEO showing about the opposite trend. The mixed monolayers with 75% PVPh composition in Figure **9** demonstrated a quite similar and close trend with minutely decreasing x values with elevation of temperature. The x values of the mixed monolayers at 25℃ in Figure **10** were found to increase with PVPh

Table 7: Modeling Parameters of Relaxation Phenomenon of Mixed PEO/PVPh Monolayers at 40 ℃

	A_∞/A_0	k_x	x	R^2
PEO	—	—	—	—
PEO：PVPh=3：1	0.5183	0.0029	0.7630	0.9928
PEO：PVPh=1：1	0.5304	0.0006	0.7760	0.9934
PEO：PVPh=1：3	0.1535	0.0009	0.6880	0.9892
PVPh	0.4460	0.0016	0.7526	0.9646

R^2：Coefficient of correlation.

Table 8: Modeling Parameters of Relaxation Phenomenon of Mixed PCL/PVPh Monolayers at 40 ℃

	A_∞/A_0	k_x	x	R^2
PCL	—	—	—	—
PCL：PVPh=3：1	—	—	—	—
PCL：PVPh=1：1	0.5566	0.0015	0.7631	0.9941
PCL：PVPh=1：3	0.6274	0.0020	0.7510	0.9941
PVPh	0.4460	0.0016	0.7526	0.9646

R^2：Coefficient of correlation.

Table 9: Modeling Parameters of Relaxation Phenomenon of Mixed PEO-b-PCL/PVPh Monolayers at 40 ℃

	A_∞/A_0	k_x	x	R^2
PEO-b-PCL	0.4725	0.0016	0.6637	0.9678
PEO-b-PCL：PVPh=3：1	—	—	—	—
PEO-b-PCL：PVPh=1：1	0.6884	0.0019	0.8153	0.9950
PEO-b-PCL：PVPh=1：3	0.5760	0.0012	0.7678	0.9935
PVPh	0.4460	0.0016	0.7526	0.9646

R^2：Coefficient of correlation.

mole fraction with PEO having the highest x values. PCL and PEO-b-PCL had virtually the same x values.

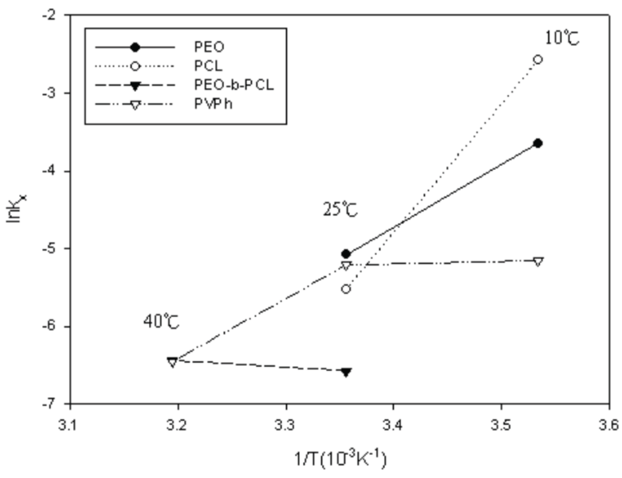


Figure 5: ln k_x versus 1/T of pure polymers.

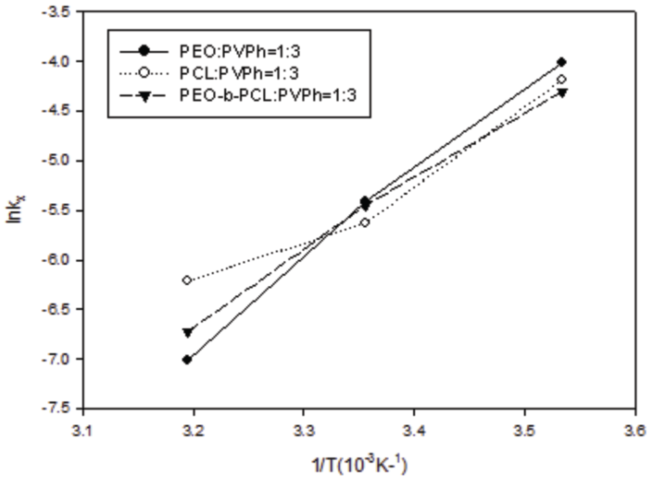


Figure 6: ln k_x versus 1/T of mixed monolayers(1:3).

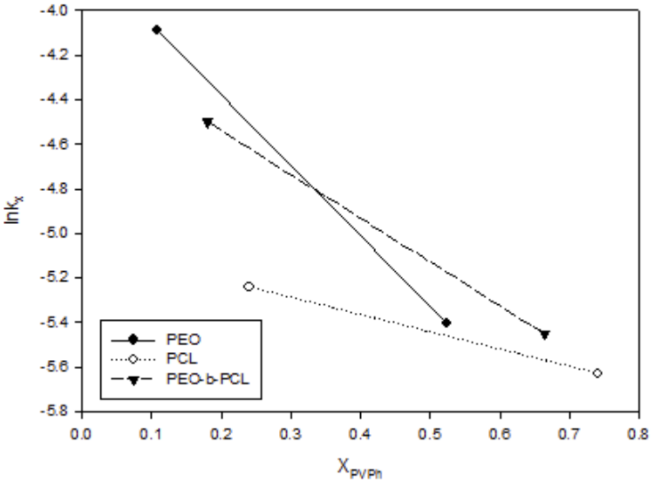


Figure 7: ln k_x versus X_{PVPh} of mixed monolayers at 25 ℃.

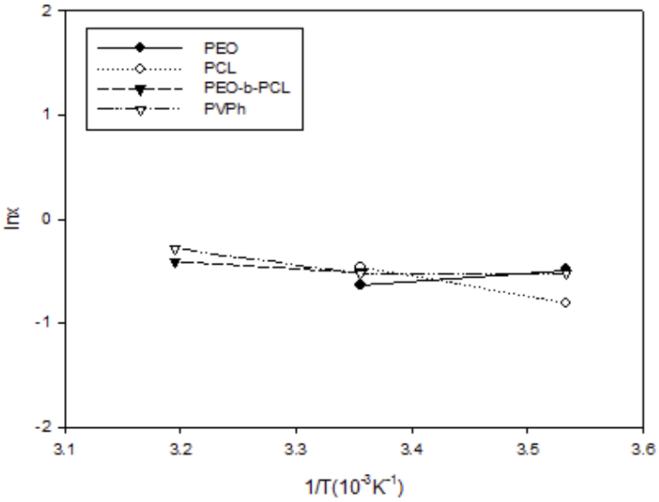


Figure 8: ln x versus 1/T of component polymers.

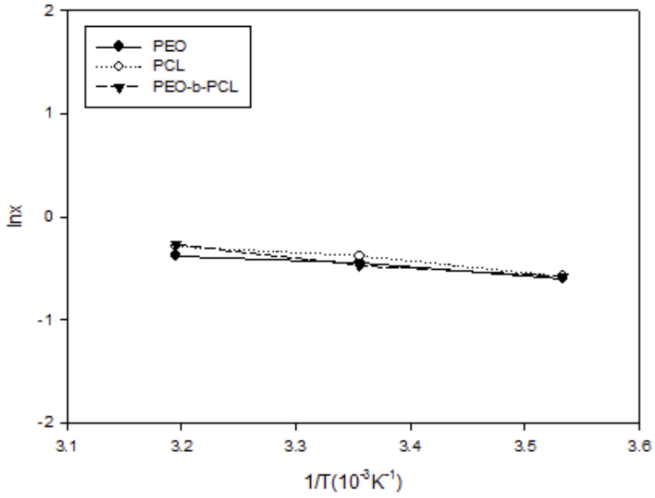


Figure 9: ln x versus 1/T of mixed monolayers (1:3).

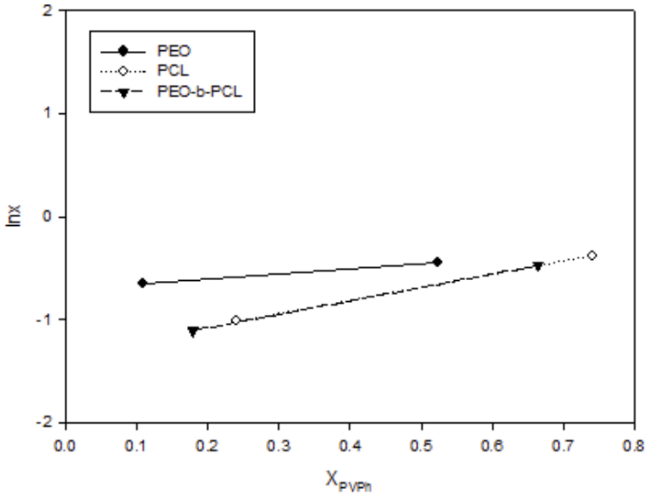


Figure 10: ln x versus X_{PVPh} of mixed monolayers at 25 ℃.

CONCLUSIONS

On the basis of simulation of iso-baric relaxation curves, the Vollhardt model of nucleation/growth mechanism was able to describe most of the observed relaxation of mixed PVPh monolayers. The PEO monolayer was found to exhibit the fastest relaxation curve at 10℃ and 25℃ for the studied polymers. Addition of PVPh into PEO caused the relaxation of mixed PEO monolayers to stabilize mostly. The stabilization behavior was likely caused by the PVPh-H_2O-PEO interaction. The mixed PCL/PVPh and PEO-b-PCL/PVPh did not exhibit such marked stabilization behavior. There were likely less PVPh-H_2O-PCL interaction since PCL interacted with PVPh favorably. The mixed monolayers with 75% PVPh composition at the three studied temperatures demonstrated a quite similar and close trend with decreasing k_x values with elevation of temperature. The mixed monolayers with 75% PVPh composition at the three studied temperatures demonstrated a quite similar and close trend with minutely decreasing x values with elevation of temperature.

REFERENCES

[1] Crisp DJ. J Colloid Sci 1946; 1: 49. https://doi.org/10.1016/0095-8522(46)90006-2

[2] Crisp DJ. J Colloid Sci 1946; 1: 161. https://doi.org/10.1016/0095-8522(46)90014-1

[3] Stroeve P, Srinivasan MP, Higgins BG, Kowel ST. Thin Solid Films 1987; 146: 209. https://doi.org/10.1016/0040-6090(87)90223-9

[4] Baglioni P, Dei L, Puggelli M. Colloid Polym Sci 1985; 283 : 266. https://doi.org/10.1007/BF01415511

[5] Gabrielli G, Puggelli M, Faccioli R. J Colloid Interface Sci 1972; 11: 63. https://doi.org/10.1016/0021-9797(72)90086-0

[6] Gabrielli G, Puggelli M, Baglioni P. J Colloid Interface Sci 1982; 86: 485. https://doi.org/10.1016/0021-9797(82)90094-7

[7] Morioka T, Kawaguchi M. Langmuir 2011; 27: 8672. https://doi.org/10.1021/la201381t

[8] Aiba N, Sasaki Y, Kumak J. Langmuir 2010; 26: 12703. https://doi.org/10.1021/la1018289

[9] Bernardini C, Stoyanov SD, Stuart MAC, Arnaudov LN, Leermakers FAM. Langmuir 2010; 26: 11850. https://doi.org/10.1021/la101003c

[10] Seo Y, Cho CY, Hwangbo M, Choi HJ, Hong SM. Langmuir 2008; 24: 2381. https://doi.org/10.1021/la702745w

[11] Jheng KT, Hsu WP. J Appl Polym Sci 2011; 120: 2615. https://doi.org/10.1002/app.33470

[12] Logan JL, Masse P, Gnanou Y, Taton D, Duran RS. Langmuir 2005; 21: 7380. https://doi.org/10.1021/la050787c

[13] Devereaux CA, Baker SM. Macromolecules 2002; 35: 1921. https://doi.org/10.1021/ma011319m

[14] Noskov BA, Akentiev AV, Miller R. J Colloid Interface Sci 2002; 247: 117. https://doi.org/10.1006/jcis.2001.8121

[15] Cox JK, Yu K, Constantine B, Eisenberg A, Lennox RB. Langmuir 1999; 15: 7714. https://doi.org/10.1021/la9901940

[16] Baker SM, Leach KA, Devereaux CE, Gragson DE. Macromolecules 2000; 33: 5432. https://doi.org/10.1021/ma992029x

[17] Hosoi AE, Kogan D, Devereaux CE, Bernoff AJ, Baker SM. Phys Rev Lett 2005; 95: 037801. https://doi.org/10.1103/PhysRevLett.95.037801

[18] Monroy F, Ortega F, Rubio RG, Ritacco H, Langevin D. Phys Rev Lett 2005; 95: 056103. https://doi.org/10.1103/PhysRevLett.95.056103

[19] Neumann AW, Good PJ. Surface and Colloid Science, Volume II, Plenum, New York, 1979.

[20] Jheng KT, Hsu WP. J Appl Polym Sci 2012; 125: 1986. https://doi.org/10.1002/app.35456

[21] Jheng KT, Hsu WP. J Appl Polym Sci 2012; 126: E267. https://doi.org/10.1002/app.36828

[22] Kim HC, Arick DQ, Won YY. Langmuir 2018; 34: 4874. https://doi.org/10.1021/acs.langmuir.8b00566

[23] Lee J, Pan J, Chun J, Won YY. J Colloid & Interface Sci 2020; 566: 304. https://doi.org/10.1016/j.jcis.2020.01.080

[24] Pan HT; Hsu WP. J Composites and Biodegrad Polym 2019; 7: 8.

[25] Vollhardt D, Retter U. J Phys Chem 1991; 95: 3723. https://doi.org/10.1021/j100162a052

[26] Vollhardt D, Retter U, Sigel S. Thin Solid Films 1991; 199: 189. https://doi.org/10.1016/0040-6090(91)90065-6

[27] Vollhardt D, Retter U. Langmuir 1992; 8: 309. https://doi.org/10.1021/la00037a056

[28] Avrami M. J Chem Phys 1939; 7: 1103. https://doi.org/10.1063/1.1750380

[29] Avrami M. J Chem Phys 1940; 8: 212. https://doi.org/10.1063/1.1750631

[30] Avrami M. J Chem Phys 1941; 9: 177. https://doi.org/10.1063/1.1750872

[31] Qu-Yang W, Weis M, Manaka T, Iwamoto M. J Chem Phys 2011; 134: 154709. https://doi.org/10.1063/1.3581890

[32] Wojciechowski K, Grigoriev D, Ferdani R, Gokel GW. Langmuir 2006; 22: 8409. https://doi.org/10.1021/la0609928

Received on 25-5-2020 Accepted on 15-6-2020 Published on 24-6-2020

DOI: https://doi.org/10.12974/2311-8717.2020.08.3