Characteristics and Iso-Baric Relaxation Phenomenon of PMMA Monolayers with Different Molecular Weights at Different Temperatures

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ABSTRACT: 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 the area relaxation process of PMMA could be described by a model considering the nucleation and growth mechanisms. The simulation parameters of area relaxation of PMMA with different molecular weights at 8 mN/m are very similar, indicating similar mechanisms. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2615–2620, 2011

Key words: isobaric relaxation; temperature; PMMA; monolayer; molecular weight

INTRODUCTION

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] and so on.

Around 1990, Schouten and his coworkers reported extensive studies of thin film behavior of PMMA of varying tacticity,[7] crystallization of isotactic PMMA in mixed monolayers[8] and stereocomplexation of isotactic and syndiotactic PMMA.[9]

In a previous study of our report,[10] relaxation behaviors of isotactic, atactic, and syndiotactic poly(methyl methacrylate) (PMMA) monolayers at the air/water interface were investigated at three different temperatures. The monolayer characteristics of the three stereoisomers were studied in terms of surface pressure-area per molecule (π-A) isotherm, area relaxation and pressure relaxation. The results show that surface pressures at inflection points of π-A isotherms of PMMA decrease with an increase in temperature. The collapse pressure also decreases as the temperature is elevated. It was shown likely for the first time that the relaxation process of PMMA stereoisomers could be described by a model considering the nucleation and growth mechanism. The simulation parameters of area relaxation of the three stereoisomers at 30 mN/m are very similar, indicating similar mechanisms.

In this article, the molecular characteristics and isobaric relaxation phenomenon of PMMA were investigated. Effect of temperature and molecular weight on the PMMA monolayers was evaluated. To the best of our knowledge, there is no systematic and detailed report on the area relaxation of PMMA monolayers with different molecular weights at the air-water interface at three temperatures.

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EXPERIMENTAL

Materials

PMMA was purchased from Polysciences, Inc, 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. It 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.

2-butanone purchased from Tedia Company, Inc. was used as the spreading solvent for the polymer films. 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.

Surface Pressure 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 during the compression of the monolayer. The surface pressure was measured by the Wilhelmy plate method.[11] 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°C, 25 ± 0.5°C, and 40 ± 0.5°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
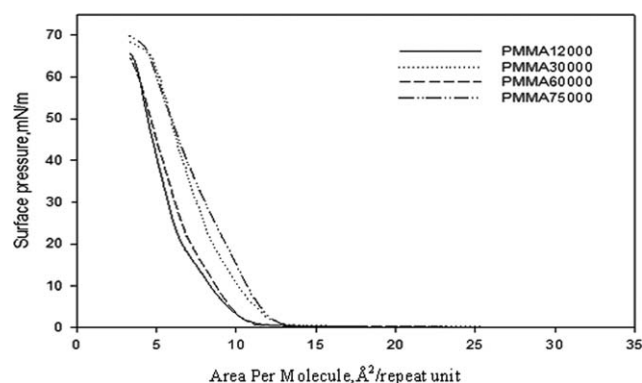
Figure 1 Surface pressure-area per molecule isotherms of PMMA with different molecular weights at 10°C.

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 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.

Iso-baric relaxation curves of 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. Again, the relaxation curves should have some dependence on the original compression rate. Therefore the same compression speed was used for all the experiments for obtaining the desired surface pressure. 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.

RESULTS AND DISCUSSION

π-a isotherms

The π-A isotherms for PMMA with different molecular weights at 10°C are shown in Figure 1. Molecular weight effect on the isotherms was detected. Surface area increased with higher molecular weight slightly. The structural factor for different molecular weight PMMA is almost the same. The reason for the surface area to increase with higher molecular weight is likely because of less enthalpic effect. The carbonyl (C=O) groups of longer PMMA chains are prone to have a lower probability in contact with water. Monolayer characteristics of PMMA in Figure 1 was estimated in terms of solid limiting area, collapse pressure and inflection point and tabulated in Table I. The solid limiting area and collapse pressure follow a similar molecular weight dependence. PMMA75000 demonstrated the largest solid limiting

TABLE I
Monolayer Characteristics of PMMA with Different Molecular Weights at Three Temperatures

		Limiting area (Å^2/repeat unit)	Collapse pressure (mN/m)	Inflection point (mN/m)
10°C	PMMA12000	7.8	65.8	18.4
	PMMA30000	10.8	68.2	21.4
	PMMA60000	8.5	64.9	20.6
	PMMA75000	11.6	69.5	20.3
	aPMMA[a]	10.3	51.0	9.4 16.4
25°C	PMMA12000	7.6	64.0	12.5 20.7
	PMMA30000	9.2	65.1	10.6 18.4
	PMMA60000	10.0	64.3	20.3
	PMMA75000	9.0	63.3	18.1
	aPMMA	8.5	43.0	7.5 16.4
40°C	PMMA12000	5.3	57.5	12.9 18.9
	PMMA30000	5.8	61.6	10.9 17.4
	PMMA60000	5.7	53.7	13.1 20.8
	PMMA75000	5.8	54.8	15.1 20.2
	aPMMA	7.1	41.0	6.5 16.7

[a] Taken from Ref. 10.

area and collapse pressure. One transition of inflection point was observed in the range of 18.4–21.4 mN/m. The results of previous investigation[10] of atactic PMMA (aPMMA) with M_w of 100,000 g/mol at the same temperature are also included in Table I for reference. The limiting area of aPMMA is similar to this study. However, the collapse pressure is smaller.

The π-A isotherms for PMMA with different molecular weights at 25°C are illustrated in Figure 2. Surface area increased with higher molecular weight in the range of 12,000–60,000. However, the π-A isotherms of PMMA75000 were closest to PMMA12000. The reason for the increasing surface area with increasing molecular weight is similar to that at 10°C. Minones[12] reported the π-A isotherms for syndiotactic PMMA with two different molecular weights (M_w = 15,000 and 120,000 g/mol) at 30°C.
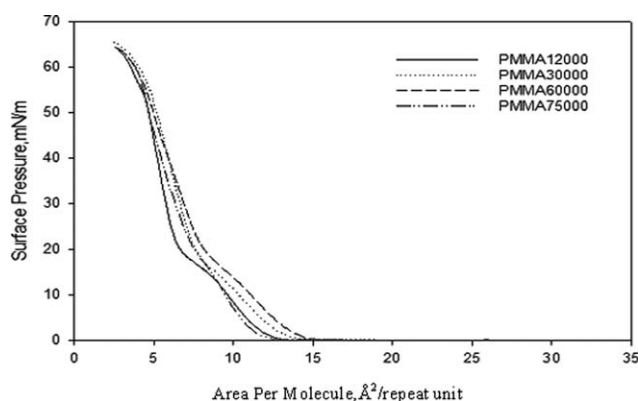
Figure 2 Surface pressure-area per molecule isotherms of PMMA with different molecular weights at 25°C.
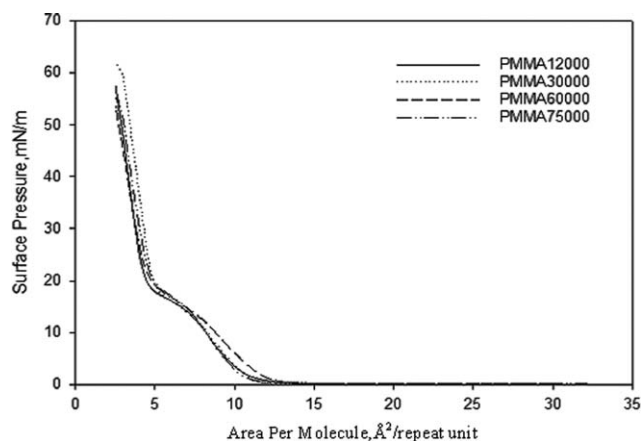
Figure 3 Surface pressure-area per molecule isotherms of PMMA with different molecular weights at 40°C.

At lower surface pressure than 15 mN/m, the syndiotactic PMMA with 15,000 g/mol demonstrated a higher surface area than the 120,000 one. The two syndiotactic PMMA exhibited nearly the same π-A isotherms at surface pressure higher than 15 mN/m. Our results are slightly different from Minones[12] likely because our PMMA samples are atactic not syndiotactic. Monolayer characteristics of PMMA in Figure 2 was calculated and also listed in Table I. The solid limiting areas decreased in comparison with those at 10°C. The collapse pressure reduced slightly from 10 to 25°C. Two inflection points were detected in PMMA12000 and PMMA30000 with similar values. However, one inflection point was detected in PMMA60000 and PMMA75000. aPMMA at 25°C (listed in Table I) again showed similar limiting area as this study.

The π-A isotherms for PMMA with different molecular weights at 40°C are demonstrated in Figure 3. At this temperature, the π-A isotherms of PMMA seemed to converge into a single curve regardless of molecular weight. The reason for conversion is likely because of weaker enthalpic effect at this temperature. The hydrogen bonding between carbonyl groups of PMMA with water decreases with the elevation of temperature resulting in weaker enthalpic interaction. Their monolayer characteristics at 40°C was evaluated and also included in Table I. The limiting area for different molecular weight PMMA was about the same in the range of 5.3–5.8 Å^2/repeat unit. The collapse pressure decreased more from 25 to 40°C in comparison with 10–25°C interval. Two inflection points were observed in all the PMMAs with the first transition at 10.9–15.1 mN/m and the second transition at 17.4–20.8 mN/m. The first transition is likely because of isotactic presence in PMMA.[10] The second transition suggests a process of phase transition to be a bi-layer, α-helix, or β sheet structure.[13]
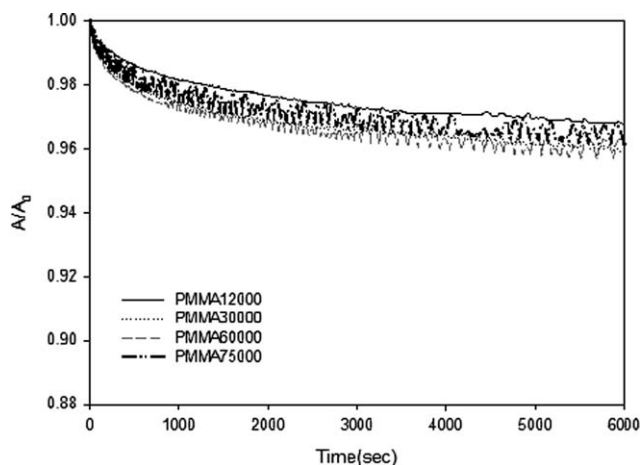
Figure 4 Iso-baric relaxation curves of PMMA at 8 mN/m and 10°C.

aPMMA demonstrated similar but a little larger limiting area. The collapse pressure also decreased in the studied temperature interval (10–40°C).

Iso-baric Relaxation Phenomenon

Relaxation curves of PMMA at a fixed surface pressure of 8 mN/m were given in Figures 4–6 in the order of 10, 25, and 40°C, respectively. On the basis of the observations in Figures 4–6, the area loss of PMMA increased with the elevation of temperature likely because of freer polymer chain movements. The molecular weight did not have an obvious effect on the relaxation curves.

An attempt was made to interpret our relaxation results in more detail with respect to particle nucleation/growth models. Vollhardt et al.[14–16] 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
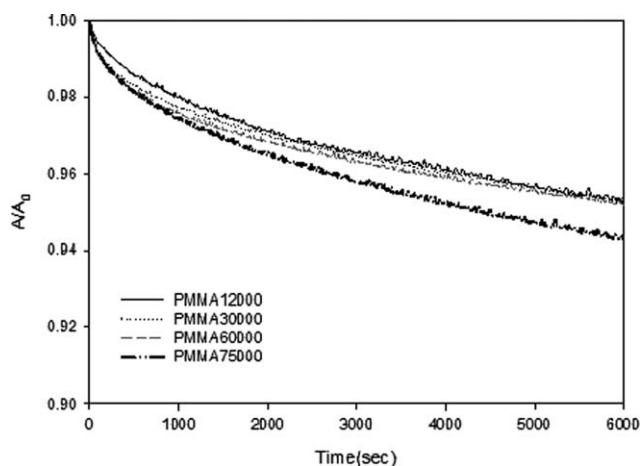

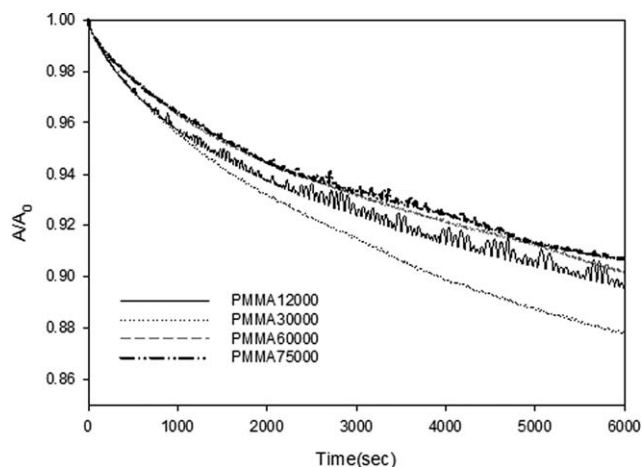**Figure 5** Iso-baric relaxation curves of PMMA at 8 mN/m and 25°C.

Figure 6 Iso-baric relaxation curves of PMMA at 8 mN/m and 40°C.

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[17–19]

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

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.

The estimated k_x and x values from data of Figures 4–6 were listed in Table II in the order of 10, 25, and 40°C, respectively. The A_∞/A_0 values of PMMA at 10°C in Table II are almost the same (0.9603–0.9684) regardless of molecular weight. The k_x values are larger in the mid molecular weights (30,000 and 60,000 g/mol) but with the same order of magnitude. The x values are more or less similar in the range of $\sim$ 0.68 to 0.83.

The A_∞/A_0 values of PMMA are again about the same at 25°C as listed in Table II almost independent of molecular weight. The absolute values of A_∞/A_0 (0.9435–0.9530) decrease minutely from 10 to 25°C. The k_x values at 25°C are smaller in comparison with those at 10°C still larger in the mid molecular weights. The x values at 25°C are larger than those at 10°C and have a range of $\sim$ 0.84 to 0.97.

The temperature effect from 25 to 40°C caused a marked difference on the A_∞/A_0, k_x, and x values as presented in Table II. This corresponds well to the observation of π-A isotherms. The π-A isotherms of PMMA monolayers also demonstrated a marked difference when the temperature is elevated from

TABLE II
(a) Modeling Parameters of Relaxation Phenomenon of PMMA at 10°C; (b) Modeling Parameters of Relaxation Phenomenon of PMMA at 25°C; (c) Modeling Parameters of Relaxation Phenomenon of PMMA at 40°C

	A_∞/A_0	k_X	x	R^2
a				
PMMA12000	0.9684	0.0026	0.832	0.9799
PMMA30000	0.9607	0.0092	0.6811	0.9658
PMMA60000	0.9603	0.0099	0.6849	0.9511
PMMA75000	0.9645	0.0042	0.7818	0.9632
aPMMA	0.8141	0.207	0.7305	0.9964
b				
PMMA12000	0.9530	0.0006	0.9704	0.9732
PMMA30000	0.9533	0.0015	0.865	0.9587
PMMA60000	0.9526	0.0019	0.8388	0.9583
PMMA75000	0.9435	0.0012	0.8969	0.9422
aPMMA	0.7587	0.182	0.495	0.9960
c				
PMMA12000	0.8984	0.0007	0.953	0.9718
PMMA30000	0.8779	0.0004	1.0192	0.9708
PMMA60000	0.9057	0.0001	1.1438	0.9805
PMMA75000	0.9057	0.0005	0.9929	0.9745
aPMMA	0.4359	0.085	0.506	0.9938

25 to 40°C. The A_∞/A_0 values at 40°C are the lowest among the three studied temperatures and have a range of 0.8779–0.9057. The k_x values at 40°C are also the lowest in the range of 0.001–0.007. The x values at 40°C are nearly the same ($\sim$ 0.95 to 1.1).

Previous results of aPMMA are also presented in Table II. The relaxation curves were performed at 30 mN/m for aPMMA much higher than 8 mN/m used in this study. PMMA is in the solid state at 30 mN/m and in this article PMMA is in the liquid expanded or liquid condensed state at 8 mN/m. The lower A_∞/A_0 and higher k_x values of aPMMA are likely because of higher experimental surface pressure. However, the x values of aPMMA are less pressure dependent with similar values to this study.
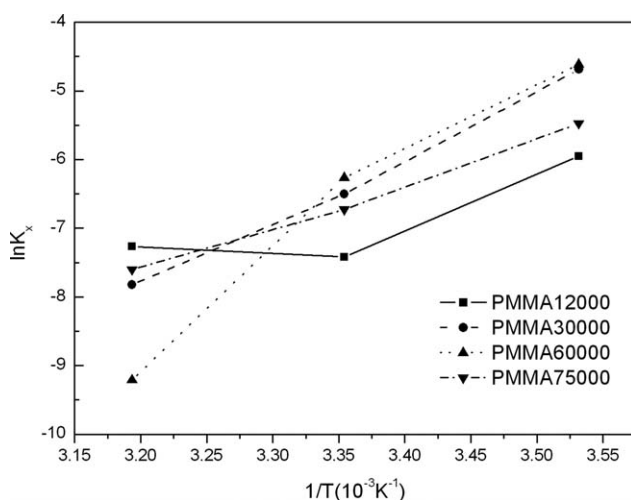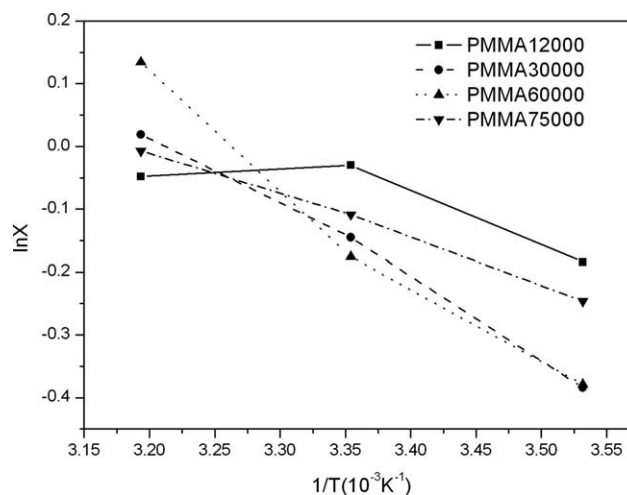

Figure 8 ln x versus $1/T$.

The k_x values were plotted versus the reciprocal of temperature and presented in Figure 7. The k_x values for most PMMAs decrease with increasing temperature. However, the k_x values of PMMA12000 are about the same at 25°C and 40°C. The x values were plotted versus $1/T$ and shown in Figure 8. The x values are about the same order of magnitude for all the studied PMMAs. All the PMMAs except PMMA12000 demonstrate that the x values increase very minutely with temperature. Larger k_x values and smaller x values were estimated for the two mid molecular weight PMMA (30,000 and 60,000 g/mol) at 10°C and 25°C. However, an anomalous molecular weight effect on the k_x values and x values was observed at 40°C. PMMA12000 exhibited the highest k_x values.

CONCLUSIONS

The π-A isotherms of PMMA with different molecular weights were investigated at three different temperatures. The π-A isotherms of PMMA were found to converge at 40°C regardless of molecular weight likely because of less enthalpic interaction between the carbonyl groups of PMMA and water.

On the basis of simulation of isobaric relaxation curves, the Vollhardt model of nucleation/growth mechanism was able to describe the observed relaxation. The x values were found to be almost temperature independent. However, the k_x values decreased as a result of temperature elevation. The k_x values are lower than previous study of aPMMA likely because of experiments performed in a different monolayer state.

Figure 7 ln k_x versus $1/T$.

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