# Size Effects on Miscibility and Glass Transition Temperature of **Binary Polymer Blend Films**

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After determining the size dependent miscibility of binary polymer blend films using molecular dynamics simulation and thermodynamics, the size dependent glass transition temperatures  $T_{e}(w,D)$  of several polymer blend films in miscible ranges are determined by computer simulation and the Fox equation where w is the weight fraction of the second component and D denotes thickness of films. The  $T_g(w,D)$  function of a thin film can decrease or increase as D decreases depending on their surface or interface states. The computer simulation results are consistent with available experimental results and theoretical results for polymer blend films of PPO/PS [poly(2,6-dimethyl-1,4phenylene oxide)/polystyrene] and stereoregular PMMA/PEO [poly(methyl methacrylate)/poly(ethylene oxide)]. The physical background of the above results is related to the root of mean square displacement of thin films in their different regions.

### Introduction

Nowadays, there is much interest in thin polymer films due to their importance in science and technology.<sup>1</sup> The thin films exhibit different thermodynamic, structural, and dynamic properties in comparison with the corresponding bulk materials. These are induced by their large surface/volume ratio and by interface effects when the thin films are deposited on substrates. One of the earliest studies on the thin films is for the thickness dependent glass transition temperature  $T_g(D)$  of polystyrene (PS) with D being the thickness of the film, which was initiated with the PS film coated on a Si wafer that has a slightly favorable interaction with the film.<sup>2</sup> It is found that  $T_g(D)$  decreases with decreasing  $D^2$ . When D < 40 nm, the reduction of  $T_{g}(D)$ , being approximately independent of the molecular weight  $(M_w)$ of samples, was apparent. This phenomenon was suggested to be present due to the presence of a rubbery layer at the film surface, which has been ascertained in various experiments and simulations.<sup>3-6</sup> Up to now, abundant experimental works on  $T_{g}(D)$  of thin polymer films have been widely carried out.<sup>2,5–23</sup> As for the case for the free-standing films and films

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with weak interaction with substrates,  $T_g(D)$  usually decreases with decreasing  $D^{2,5,8,10,12-15,19,20}$  On the other hand, when the film-substrate interaction is very strong,  $T_g(D)$  of thin films could increase as D decreases. 5-7,9,11-13,17-20

To interpret the above phenomena, a thermodynamic consideration has been made based on Lindemann criterion for melting and assumption that the necessary mean square displacement of atoms for melting transition is suitable for glass transition. In terms of the consideration, the  $T_{g}(D)$  function is theoretically modeled as<sup>13</sup>

$$\frac{T_{\rm g}(D)}{T_{\rm g}(\infty)} = \exp\left(-\frac{[2\Delta C_{\rm p}(\infty)/(3R) + 1] - 1}{D/[2c(3-d)\xi] - 1}\right) + \exp\left(-\frac{[2\Delta C_{\rm p}(\infty)/(3R) + 1](e_{\rm s}/e_{\rm i}) - 1}{D/[2c(3-d)\xi] - 1}\right)/2$$
(1)

In eq 1, the subscript s and i denote surface and interface, eshows the bonding strength, R is the ideal gas constant,  $\infty$  denotes the bulk size,  $\Delta C_{\rm p}$  is the heat-capacity difference between glass  $C_{\rm pg}$  and liquid  $C_{\rm pl}$  at  $T_{\rm g}$ . d is the dimension of low-dimensional crystals, d = 0 for a particle, d = 1 for a nanowire, and d = 2for a thin film. c shows the normalized surface (interface) area where the atomic potential differs from that of the interior of the low-dimensional crystal. c = 1 for the free-standing thin films  $(e_i = e_s)$  or a supported thin film with strong interaction between the polymers and the substrates, such as hydrogen bonding; and  $c = \frac{1}{2}$  for a supported thin film with weak interaction between the polymers and the substrates, such as van der Waals force, which is equivalent to the disappearance of this interface from the viewpoint of the chemical bonding.  $\xi$  is the temperature dependent length of the cooperatively rearranging region (CRR)

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at  $T_{g}$ ,<sup>11,13,24,25</sup> where CRR is defined as a sub-ensemble of particles which upon a sufficient fluctuation can be rearranged into another configuration independently of its environment.<sup>24</sup>  $\xi = D$  when  $\Delta C_{\rm p}(D)$  function is extrapolated to  $\Delta C_{\rm p}(D) = 0$ ,<sup>26</sup> or through the Donth's approach, <sup>27,28</sup> namely,  $\xi = [k_b T^2 / \Delta (1/C_v) / \rho \delta T^2]^{1/3}$  where  $k_{\rm b}$  denotes the Boltzmann constant, T the absolute temperature,  $\rho$  the polymer density,  $C_v$  the volume specific heat capacity,  $\Delta$ the difference of  $1/C_v$  between the liquid and the glass, and  $\delta T$ the mean temperature fluctuation. These results give direct evidence that for the glass transition a minimal length scale of cooperativity is relevant with the molecular motions responsible for the glass transition.

In eq 1,  $M_w$ , which affects the  $T_g(D)$  function possibly through  $\xi$ <sup>8,11,25,29</sup> has been neglected for simplicity since this effect is unconspicuous when  $M_w$  is not especially large.<sup>2,3,12,13</sup> With the same purpose, effect of D on  $\xi$  is also ignored although slight effect of D on  $\xi$  has been found when D < 10 nm <sup>30</sup> where the approach of Donth  $^{27,28}$  is used to determine  $\xi$  values as stated above.

The concept of blending two or more existing polymers to obtain new products has been attracting widespread interest in commercial utilization, and the blending or alloying improves many properties of polymer blend systems without sacrificing some attractive properties of each polymer where  $w \neq 0$  or 1 where w is the weight fraction of the second component.<sup>23</sup> However, the realization of the alloying depends on the polymer compatibility, which is determined by the free energy of mixing  $\Delta G_{\rm m}$ .<sup>14</sup> Assuming that the volume change upon mixing is negligible, which is a good first order approximation when the interaction of different polymers is mainly van der Waals force,  $\Delta G_{\rm m}$  for a mixture of polymer 1 and polymer 2 of a molar lattice site is given by modified Flory-Huggins mean theory<sup>31</sup>

$$\frac{\Delta G_{\rm m}}{RT} = \frac{V}{V_{\rm u}} \left( \frac{\varphi_1}{x_1} \ln \varphi_1 + \frac{\varphi_2}{x_2} \ln \varphi_2 + \chi_{12} \varphi_1 \varphi_2 \right) \tag{2}$$

where a mean value of segment volumes of the two polymers  $V_{\rm u}$  is taken for similarity, x is the number of repeat units per molecule,  $\varphi_i = x_i n_i V_u / V$  where  $\varphi$  is the volume fraction with subscript i = 1 or 2 denoting different polymers, n is the polymer chain number in the blend, V denotes the total volume of the blend. When  $\Delta G_{\rm m} \leq 0$ , the two polymers are miscible, which depends on only the sign and the value of the interaction parameter  $\chi_{12}$ , whereas  $\chi_{12}$  itself is a size dependent function through the size dependent cohesive energy density  $E_{\rm c}(D)$  since<sup>10</sup>

$$\chi_{12}(D) = \frac{V_{\rm u}}{RT} [E_{\rm c1}^{1/2}(D) - E_{\rm c2}^{1/2}(D)]^2$$
(3)

where  $E_{c}(D)$  function can be determined by MD simulation, and the detailed simulation process will be shown in the next section.

As for a compatible system, the  $T_g(w,D)$  value is located within the value range of  $T_g(0,D)$  and  $T_g(1,D)$ . The corresponding  $T_g$ -(w,D) function may be determined by the Fox equation, which still holds for thin films of binary polymer blends<sup>14,32</sup>

$$1/T_{g}(w,D) = (1-w)/T_{g}(0,D) + w/T_{g}(1,D)$$
(4)

Equation 4 supplies an easy way to determine  $T_g(w,D)$  function of polymer alloys when  $T_g(0,D)$  and  $T_g(1,D)$  are known from eq 1 (in eq 1, w is neglected where a single polymer with w = 0or w = 1 is considered) although it needs to be confirmed.

A computer simulation with Lennard-Jones (LJ) potential, which denotes van der Waals interactions and is used for single polymer films, shows another way to determine the  $T_{\sigma}(w,D)$ function.<sup>5,21,22</sup> The LJ potential could also be utilized for polymer blends since only van der Waals forces between different polymers decide the interaction and alloying of polymer mixing. The related LJ potential is read as<sup>5,21,22</sup>

$$V_{\rm LJ}(r_{mn}) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r_{mn}} \right)^{12} - \left( \frac{\sigma}{r_{mn}} \right)^{6} \right] : & r_{mn} < 2 \times 2^{1/6} \sigma \\ 0 : & r_{imn} \ge 2 \times 2^{1/6} \sigma \end{cases}$$
(5)

where  $\sigma$  is the site diameter and  $\epsilon$  is the attractive energy between two sites at their equilibrium separation, and  $r_{mn}$  is the distance of sites m and n. Each interaction site represents a persistence length along the polymer backbone.

In this contribution, after checking the validity of eq 1, the size dependences of miscibility of widely studied s-PMMA/ PEO and i-PMMA/PEO systems are first considered. Within the miscibility ranges,  $T_g(w,D)$  functions of s-PMMA/PEO, i-PMMA/ PEO, and PPO/PS blend films are determined using computer simulation in terms of the potential of eq 5, which are confirmed by eq 4 based on eq 1. The both results of theory and computer simulation agree well and are also supported by available experimental evidences.

#### **Simulation Details**

As stated above, when  $M_w$  is not especially large, it hardly affects its  $T_g$  value.<sup>2,3,12,13</sup> To reduce the calculation time and limit computer memory,  $M_{\rm wc}$ s are selected to be 1/4 to 1/11 of  $M_{\rm wes}$  (subscripts c and e denote the computer simulation value and experimental value, respectively). It is assumed that this decrease of  $M_w$  does not lead to evident error in simulations for  $T_{g}$ .

To confirm this assumption,  $T_g$  values of polymer blends of i-PMMA/PEO (w = 0.09) with different  $M_w$  values are simulated with molecular dynamics (MD) method at D = 20 nm. The selected M<sub>w</sub> values for i-PMMA are 35 000 and 8000, whereas for PEO are 400 and 90, respectively. The  $M_{\rm w}$  values of the former are the same of the experimental ones. The obtained results of  $T_g$  are 429 and 425 K, respectively, which has a similar error size of experiments. Thus, in this work,  $M_{\rm wc} = 8000 \ (M_{\rm we})$ = 35 000) for PMMA long chains,  $M_{wc} = 90$  ( $M_{we} = 400$ ) for PEO short chains,  $M_{wc} = 2405$  ( $M_{we} = 244\ 000$ ) for PPO long chains, and  $M_{wc} = 835$  ( $M_{we} = 90\ 000$ ) for PS chains are taken.

With the above  $M_{\rm wc}$  sizes, the polymer blend consisting of PMMA and PEO, and that of PPO and PS, propagate into a simulation cell according to the self-avoiding walk technique33 with the long-range nonbonded interactions described by Theodorou and Suter.34

All simulations have been performed under a periodic boundary condition. For free-standing films, this condition is performed in all directions. For supported films, a wall is placed at the bottom of the simulation box where the polymer can be deposited. This condition is imposed in the x and y directions parallel to the film.<sup>5</sup> The hydrogen bonding is used for the interaction

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**Figure 1.** Temperature dependence of simulated cell volume, v(T), of i-PMMA/PEO (w = 0.09, D = 20 nm) obtained by MD simulation. The intersect point of two straight-line segments marks  $T_g$  value of the film.

between an attractive substrate and a thin film while this is van der Waals force for a passivated substrate. The selection for different chemical bonding determined by distinct interaction potentials is automatically carried out by the software.

The simulation cell is a quadrangular prism with a height longer than the length of the base edges. The procedure is implemented with the Amorphous Cell package of Material Studio software from Accelrys Inc. To get  $T_{g}$ , the simulated dilatometry technique is employed where the simulation cell volume v is determined versus T.<sup>35</sup> The intercept point of the lines joining the two phases, the glassy and the rubbery,  $^{2,7}$  yields the  $T_g$  value. To acquire v at a desired temperature, MD simulations are performed in the NPT statistical ensemble using the modified *pcff* (a polymer consistent force field), i.e., constant numbers of particles N, of pressure P, and of T. P is controlled according to the Parrinello-Raham algorithm,<sup>36</sup> whereas *T* is imposed by the Nosé–Hoover algorithm.<sup>5,21–23</sup> The integration step is 1 fs using the Verlet-leapfrog algorithm.<sup>37</sup> In the present study, configurations at T = 500, 450, 430, 410, 390, 370, 350, 330, 310, 300, 250, and 200 K were kept with 0.1 ns. Configurations are saved every 0.5 ps. The initial configuration for any given T is taken to be the final one for the previous, higher T.

Figure 1 shows an example how to determine the  $T_g(w,D)$  function by MD simulation where a v(T) function of i-PMMA/ PEO blend film (w = 0.09, D = 20 nm) is shown, in which the intersect point of two straight-line segments marks the  $T_g(w,D)$  value. Note that the i-PMMA/PEO blend film at w = 0.09 is miscible both in the bulk and in the thin film geometry, which results in the utility of eq 4.

To get  $\chi_{12}(D)$  function in eq 3,  $E_c(D)$  functions of PMMA and PEO at 300 K are obtained by analyzing the cohesive energy density of configurations of pure PMMA and PEO films at different sizes of *D*.

The root-mean-square displacements of chains (rms) of the blend films in the surface, center, and interface regions of films at 300 K are determined by MD simulation. The chosen set of atoms in the three regions has a thickness of about 0.25 nm in the simulation cell.

#### **Results and Discussion**

Before considering the utility of eq 4, eq 1 should be first confirmed. Figure 2 shows a comparison between the model prediction in terms of eq 1 with different c values determined on the states of surface and interface and experimental results



**Figure 2.**  $T_g(D)$  functions of i-PMMA films supported by an Al substrate and by SiO<sub>2</sub> in terms of eq 1. The related parameters in eq 1 for films supported by Al substrate are  $\Delta C_p(\infty) = 25 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  = 1.667 J·g-atom<sup>-1</sup>·K<sup>-1</sup>,<sup>38</sup>  $T_g(\infty) = 396 \text{ K}$ ,<sup>39</sup>  $c = \frac{1}{2}$ , and  $\xi = 1.6$  nm.<sup>38</sup> The symbol  $\bullet$  denotes the experimental results.<sup>40</sup> For films supported by SiO<sub>2</sub> substrate, the related parameters in eq 1 are  $e_i$  = 18.9 kJ·mol<sup>-1</sup> being the hydrogen bonding strength,<sup>41</sup>  $e_s = 6.3$  kJ·mol<sup>-1</sup> showing the van der Waals force,<sup>41</sup> c = 1. Other parameters are the same as that for films supported by Al substrate. The symbol

for  $T_g(0,D)$  of i-PMMA films supported by Al and SiO<sub>2</sub> substrates obtained by ellipsometry and dielectric spectroscopy measurements,<sup>40</sup> respectively. Note that  $T_g(D)$  function in eq 1 has been substituted by  $T_g(0,D)$  function.

When i-PMMA films supported by an Al substrate with interface interaction of van der Waals force, the film/substrate interface can be neglected and thus c = 1/2. However, when i-PMMA films are supported by a SiO<sub>2</sub> substrate with interface interaction of hydrogen bonding, the thermal vibration of molecules of the thin films on the interface is suppressed. Although the surface of the film has still a tendency to drop the  $T_g$  value of the film, the total effect of the surface and the interface however leads to the decrease of internal energy of the film and thus the increase of  $T_g(0,D)$  as D decreases. As shown in this figure, the model predictions correspond well to the experimental results for both cases. Therefore, based on the results above and on earlier studies,<sup>13</sup> eq 1 is a valid for the  $T_g(0,D)$  function of single polymer films.

The premise of the utility of eq 4 to determine the  $T_{g}(w,D)$ function based on eq 1 is the existence of compatible polymer blends because eq 4 is valid only for miscible systems, which depends on the  $\chi_{12}(D)$  function as discussed above.  $\chi_{12}(D)$ functions of i-PMMA/PEO and s-PMMA/PEO systems at room temperature in terms of eq 3 are shown in Figure 3a. Note that  $E_{\rm c}(D)$  functions of i-PMMA or s-PMMA and PEO in eq 3 are determined by MD simulation. As D increases,  $\chi_{12}$  of the former system increases, whereas that of the latter system decreases, which implies that the compatibility of the system is sizedependent. Based on eq 2, when  $\Delta G_m^R = (\Delta G_m/RT) \le 0$ , a compatible system is present. The  $\Delta G_m^R$  functions with the obtained  $\chi_{12}(D)$  values of i-PMMA/PEO and s-PMMA/PEO systems in light of eq 3 are shown in Figure 3, panels b and c, respectively. The miscibility of PEO in s-PMMA thin films increases as D increases, the corresponding critical value  $w_{\rm c}$ changes from smaller than 0.1 for D = 10 nm to 0.4 for bulk size, whereas the inverse is observed in i-PMMA. When D decreases from bulk to 10 nm, a full range miscibility of PEO

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**Figure 3.** (a)  $\chi_{12}(D)$  of PMMA/PEO blend at room temperature in terms of eq 3 based on the simulated  $E_c(D)$  data of PMMA and PEO with  $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , T = 300 K, and  $V_u = (106.14 + 49.44)/2 \text{ cm}^3\cdot\text{mol}^{-1}$  where 106.14 and 49.44 cm $^3\cdot\text{mol}^{-1}$  are PMMA and PEO segment molar volumes,<sup>42</sup> respectively. Symbols  $\blacktriangle$  and  $\blacksquare$  are  $\chi_{12}(D)$  values of i-PMMA/PEO and s-PMMA/PEO, respectively. The fitted curves guide the eyes. (b) The miscibility range of PEO in i-PMMA films with different D values at room temperature in terms of eq 2. (c) The miscibility range of PEO in s-PMMA films with different D values at room temperature in terms of eq 2.

in i-PMMA thin films, or  $w_c = 1$ , is obtained, which is much larger than  $w_c < 0.2$  when  $D \rightarrow \infty$ .

Since the surface energy and molecular weight of s-PMMA and i-PMMA are similar, they have little effects on the above miscibility changes. The differences in conformation and chain flexibility of various PMMA stereoisomers thus seem to have important effects on the miscibility behavior of their blends. Hamon et al. has found that PEO in bulk s-PMMA and atactic-PMMA (a-PMMA) has a similar miscibility range but PEO in bulk i-PMMA has a much smaller miscibility range.<sup>43</sup> This small

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**Figure 4.**  $T_g(w,D)$  function of PPO/PS blend films supported by a passivated Si (100) substrate in the terms of eqs 4 and 1. To obtain two functions  $T_g(0,D)$  and  $T_g(1,D)$ , respectively, corresponding data of  $\Delta C_{pb0}$ ,  $\Delta C_{pb1}$ ,  $\xi_0$ ,  $\xi_1$ ,  $T_g(0,\infty)$ , and  $T_g(1,\infty)$  are needed, which are  $\Delta C_{pb0} = 27.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 1.591 \text{ J} \cdot \text{g} \text{-atom}^{-1} \cdot \text{K}^{-1}, ^{48} \Delta C_{pb1} = 30.7$  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 1.919 \text{ J} \cdot \text{g} \text{-atom}^{-1} \cdot \text{K}^{-1}, ^{48} \Delta C_{pb1} = 30.7$  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 1.919 \text{ J} \cdot \text{g} \text{-atom}^{-1} \cdot \text{K}^{-1}, ^{12} \xi_0 = 9 \text{ nm}, ^{48} \xi_1 = 5 \text{ nm}, ^{12}$  $T_g(0,\infty) = 483 \text{ K}, ^{14} \text{ and } T_g(1,\infty) = 373.8 \text{ K}, ^{12}$  where subscripts 0 and 1 denote w = 0 and 1, respectively.  $c = \frac{1}{2}$  in eq 1, as the film/ substrate interface is considered to disappear for the passivated Si substrate where the chemical interaction is van der Waals forces being the same within the film. The symbols ▲, ■, and ▼ denote the experiment results, <sup>14</sup> and △, □, and  $\nabla$  show the computer simulation results.

miscibility is ascribed to the specific conformation and high chain stiffness of the isotactic chain segments of i-PMMA, which weaken the interaction with the PEO chains.<sup>44</sup> This may be the reason that miscibility of i-PMMA/PEO thin films increases as *D* decreases where the chain stiffness of i-PMMA located on the film surface drops.

Considering from thermodynamic aspects, there is a relationship between the specific heat difference between the glass and liquid  $\Delta C_p(w,T,D)$  and conformational entropy  $S_c(w,T,D)$  at a given *T* and  $w^{24}$ 

$$S_{\rm c}(w,T,D) = \int_{T_2}^{T} \frac{\Delta C_{\rm p}(w,T,D)}{T} \,\mathrm{d}T \tag{6}$$

where  $T_2$  is the temperature where the configurational entropy of CRR vanishes.<sup>45</sup>

Based on a model for the size dependent melting entropy  $\Delta S(T_{\rm m},D)$  at melting temperature  $T_{\rm m}$ ,<sup>46</sup>  $\Delta S(T_{\rm m},D) = \Delta S(T_{\rm m},\infty) + (3R/2)\ln[T_{\rm m}(D)/T_{\rm m}(\infty)]$ . Since the glass transition is a second-order transition and  $\Delta C_{\rm p}(w,T_{\rm g},D)$  may be given by a generalization of melting entropy in a similar form<sup>47</sup>

$$\Delta C_{\rm p}(w, T_{\rm g}, D) = \Delta C_{\rm p}(w, T_{\rm g}, \infty) + (3R/2) \ln[T_{\rm g}(w, D)/T_{\rm g}(w, \infty)]$$
(7)

the size dependence conformation entropy at  $T_g$ ,  $S_c(w, T_g, D)$ , can be obtained by combining eqs 6 and 7

$$S_{c}(w,T_{g},D) = \int_{T_{2}}^{T_{g}} \frac{\Delta C_{pw}(T_{g},\infty)}{T} dT + (3R/2) \ln[T_{g}(w,D)/T_{g}(w,\infty)] \int_{T_{2}}^{T_{g}} \frac{dT}{T} = S_{c}(w,T_{g},\infty) + (3R/2) \ln[T_{g}(w,D)/T_{g}(w,\infty)] \ln(T_{g}/T_{2})$$
(8)

According to Adam and Gibbs,<sup>24</sup>  $T_g/T_2$  in eq 8 is about 1.30.

<sup>(41)</sup> http://fajerpc.magnet.fsu.edu/Education/2010/Lectures/3\_ Chemical-Bonds.htm.
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**Figure 5.**  $T_g(0.09,D)$  function of PMMA/PEO films in terms of eq 4. The related parameters in eq 1 are  $\Delta C_{p0}(\infty) = 25 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ = 1.667 J·g·atom<sup>-1</sup>·K<sup>-1</sup>,<sup>37</sup>  $\Delta C_{p1}(\infty) = 38.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 5.529$ J·g·atom<sup>-1</sup>·K<sup>-1</sup>,<sup>42</sup>  $\xi_0 = 1.6 \text{ nm}$ ,<sup>36</sup>  $\xi_1 = 1.0 \text{ nm}$ ,<sup>49</sup>  $T_g(0,\infty) = 396 \text{ K}$ ,<sup>39</sup> and  $T_g(1,\infty) = 203 \text{ K}$ ,<sup>39</sup>  $c = 1. e_i = 18.9 \text{ kJ} \text{ mol}^{-1}$  being the hydrogen bonding strength,<sup>41</sup>  $e_s = 6.3 \text{ kJ}\cdot\text{mol}^{-1}$  showing the van der Waals force.<sup>41</sup> The symbols O and  $\Box$  denote the computer simulation results for s-PMMA/PEO and i-PMMA/PEO, respectively. The symbol  $\blacksquare$ is the experimental results of i-PMMA/PEO blend films.<sup>39</sup> The subscripts 0 and 1 denote w = 0 and w = 1, respectively.

Thus,  $S_c(w,T_g,D) \propto \ln[T_g(w,D)/T_g(w,\infty)]$ . As for the case of i-PMMA/PEO blend film supported by a treated Si (111),  $T_g(w,D)/T_g(w,\infty)$  increases as *D* decreases. However, for the case of s-PMMA/PEO blend free-standing films,  $T_g(w,D)/T_g(w,\infty)$  decreases as *D* decreases. These changes are shown in Figure 5. Therefore,  $S_c(w,T_g,D)$  increases for i-PMMA/PEO blend film as *D* decreases, which lowers the free energy of the mixing and increases the miscibility. In the same way, the miscibility changes of s-PMMA/PEO can be discussed.

With the method shown in Figure 1, for completely miscible PPO/PS blend films supported on Si (100),<sup>39</sup>  $T_g(w,D)$  function of eq 4 determined by  $T_g(0,D)$  and  $T_g(1,D)$  functions, which can be obtained by eq 1, MD results in terms of eq 5 and cited experiments results<sup>14</sup> are plotted in Figure 4. A good agreement among them is found.  $T_g(w,D)$  increases as *D* increases and this increase becomes unconspicuous when D > 50 nm, which is similar to the case of a single polymer. On the other side,  $T_{g}(w,D)$  decreases as *w* increases since  $T_g(0,\infty) = 483 \text{ K}^{14} > T_{g}(1,\infty) = 373.8 \text{ K}^{12}$  and the change tendency of  $T_g(w,D)$  with *D* is similar to  $T_g(0,D)^{12}$  and  $T_g(1,D)^{14}$  functions.

 $T_{g}(0.09,D)$  function for PMMA/PEO blend films with different interface states but a fixed w value in terms of eq 4, MD results in terms of eq 5 and cited experiments results  $3\overline{3}$  are plotted in Figure 5. The different sources correspond to each other. For a s-PMMA/PEO blend free-standing film where c = 1, two free surfaces lead to the strongest drop of  $T_g(0.09,D)$  as D deceases. For an i-PMMA/PEO film coated on a treated Si(111) substrate by an argon-water plasma prior to solution deposition where c = 1 with a surface and an interface or a homogeneously hydroxylated high-energy surface,  $T_g(0.09,D)$  increases with D because there are unshared electrons of the oxygen groups in the i-PMMA/PEO blend, which forms hydrogen bonds with the hydroxyl groups at the film/substrate interface. These interactions hinder the mobility of the chain segments of the blend and create a region of low mobility in the vicinity of the polymer-substrate interface.<sup>5,6</sup>

Note the fact that rms of a polymer surface is much larger than that of bulk, which is the theoretical background of eq 1. This phenomenon of Figure 6a confirms that  $T_g$  values at the surface for free-standing blend thin films and thin films deposited on an



Figure 6. Simulation results of rms of blend films in the vicinity of the polymer-substrate interface, center of films and surface region at the room temperature. (a) PPO/PS systems with w = 0.3 and D = 30 nm. (b) i-PMMA/PEO systems with w = 0.09 and D = 10 nm.

inert substrate are much lower than that of the bulk. Thus, the mean  $T_g$  value of a thin film decreases due to the increased surface/volume ratio or decreased *D*. When the chemical interaction is strong at film/substrate interfaces, rms at the interface with the restricted mobility becomes small, which results in a larger  $T_g$  value in the vicinity near the interface. An increased mean  $T_g$  value of the corresponding film could occur when the effect of the interface on the  $T_g$  value is stronger than that of the surface. This is the case of Figure 6b. Since rms is a function of the density of the film,<sup>50</sup> a larger rms is proportional to a lower density  $\rho$  or a larger free volume in a film, the both leads to depression of  $T_g$ .

## Conclusions

In conclusion,  $T_g(w,D)$  functions of PPO/PS and PMMA/PEO blend films with different interface conditions are calculated based on the Fox equation and a model for  $T_g(0,D)$  function in their miscibility ranges where the miscibility of PEO in PMMA thin films is size dependent, which is induced by different conformation and chain flexibility of stereoisomers in distinct PMMA. It is found that as *D* decreases the  $T_g(w,D)$  function of blend films simulated may decrease or increase depending on the interface conditions, which corresponds to known experimental results and the Fox equation with eq 1. Moreover, rms analysis based on MD simulation is given to describe the physical nature of the above phenomena.

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