

Relaxation Behavior of Poly(methyl methacrylate) at a Water Interface

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The relaxation behavior of poly(methyl methacrylate) (PMMA), spin-coated on a silicon wafer, at the water interface was examined by lateral force microscopy as a function of temperature and scanning rate. Even in water, the lateral force peak which was assigned to the segmental motion of PMMA plasticized by water molecules was clearly observed in the temperature domain. The apparent activation energy for the plasticized α_a -relaxation process was much smaller than those for the original α_a -relaxation processes at the intact surface and in the bulk. The depth profile of the glass transition temperature (T_g) of the PMMA film in water was obtained, showing that T_g decreases with proximity to the water phase. The T_g depression observed here was best explained in terms of the water content of the film, rather than a confinement effect.

Introduction

Polymeric materials have been widely used for medical diagnosis and treatment in such applications as DNA arrays, tips for micrototal analysis, and scaffolds for artificial organs.^{1–3} In these applications, the polymer surface is in contact with a water phase. However, despite the importance of detailed knowledge of the fundamental interactions of polymer interfaces with water, such studies are very limited except for those involving water-soluble polymer brushes grafted onto/from a solid substrate.^{4–6} Of course, it is needless to say that the aggregation states and the molecular motion of polymers at liquid interfaces are scientifically important and are still unknown.

Poly(methyl methacrylate) (PMMA) is widely used in many technological applications because of its excellent mechanical, optical, and surface properties. In ophthalmology, for instance, PMMA is an important component in artificial lenses. As an initial benchmark for designing and constructing specialized biomedical surfaces containing this polymer, the adsorption behaviors of lipids and proteins onto PMMA in water should be systematically examined. So far, only a few reports dealing with the issue have been published.^{7–9} A critical difference between other methacrylates, such as poly(2-hydroxyethyl methacrylate),^{10,11} poly(2-methoxyethyl acrylate),^{12–14} and poly-(2-methacryloyloxyethyl phosphorylcholine),^{15–17} and PMMA is that they can be dissolved, or at least swollen, with water on a macroscopic scale, whereas the latter cannot. Nevertheless, PMMA would still be suitable as part of a functionalized biomedical surface if chains of PMMA at the water interface are dissolved into the bulk liquid. This would resemble the excluded volume effect of poly(ethylene oxide) (PEO) chains tethered onto a solid substrate, which prevents the adsorption of proteins onto the substrate.^{18–20}

We have recently studied the density profile of a perdeuterated poly(methyl methacrylate) (dPMMA) film spin-coated on a substrate in water, which is a typical “non-solvent” for dPMMA, along the direction normal to the interface by specular neutron reflectivity (NR) and found that the interface of dPMMA with water was diffuse in comparison with the pristine interface with

air.²¹ This is because a part of the segments is dissolved into the water phase and a swollen layer induced by the penetration of water exists beneath it. Postulating that the difference in the chemical natures of dPMMA and PMMA is insignificant, the molecular motion of PMMA in the interfacial region with water must be different from that at the pristine air surface as well as that in the internal bulk region. Thus, it is timely to uncover the hierarchical molecular motion of PMMA at various time and length scales in the interfacial region with a liquid. If this issue can be solved and the knowledge can be applied to other synthetic polymers, it might be possible to construct highly functionalized materials of use in the medical field using synthetic polymers.

The objective of this study is to investigate the molecular motion of PMMA in the interfacial region with water by lateral force microscopy (LFM). Although the time and temperature ranges for our LFM are too limited to obtain a whole picture of the hierarchical molecular motions, they are sufficient to encompass the segmental motion.

Experimental Section

Monodisperse PMMA with a number-average molecular weight (M_n) of 1.58 M was used, so that the effect of chain ends on the interfacial mobility can be ignored. The bulk glass transition temperature (T_g^b) was determined by differential scanning calorimetry (DSC220, SII NanoTechnology Inc.) at a heating rate of 10 K·min^{−1} under a dry nitrogen purge. Films of PMMA were spin-coated from a toluene solution onto silicon wafers with native oxide layers. The films were dried under the ambient atmosphere at room temperature for more than 24 h, and then annealed under a vacuum at 423 K for 24 h. The film thickness, evaluated by ellipsometry (M-150, JASCO Co., Ltd.), was approximately 460 nm, which was sufficient to avoid any ultrathinning effects on the surface mobility.^{22,23}

The relaxation behavior of PMMA at the water interface was examined by LFM (SPA300HV, SII NanoTechnology Inc.) with an SPI3800 controller. Figure 1 shows a schematic illustration of our experimental setup for LFM measurements in water. The film was fixed on the bottom of a liquid LFM cell, and milli-Q water was poured into the cell before the experiment. Prior to the measurement, the PMMA film was aged in water for 2 h, which was enough to cause swelling in the outermost region of

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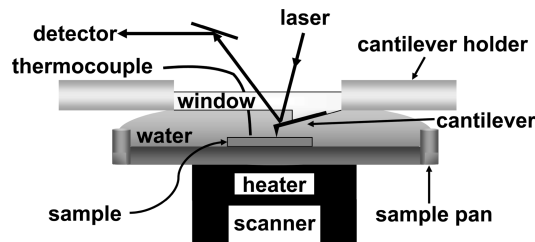


Figure 1. Schematic illustration of the experimental setup for LFM measurement in water.

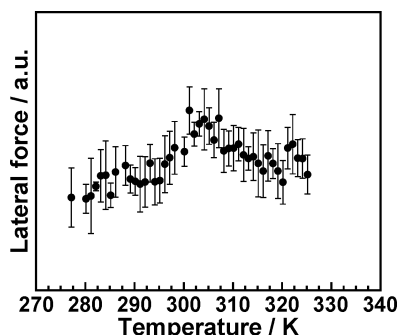


Figure 2. Temperature dependence of lateral force at a scanning rate of $1 \mu\text{m}\cdot\text{s}^{-1}$ for a PMMA film in water.

the film. The temperature of water was recorded with a thermocouple. The cantilever used was made from Si_3N_4 , with both sides uncoated. The spring constant and the tip radius were estimated to be approximately $0.1 \text{ N}\cdot\text{m}^{-1}$ and 11 nm , respectively. The normal force onto the cantilever was set to be ca. 15 nN in the repulsive force region. Lateral force was obtained in a line scan mode.

Results and Discussion

It has been widely accepted that the frictional behavior of polymeric solids is closely related to their viscoelastic properties, especially energy dissipation.^{24,25} Hence, it is reasonable to study local relaxations of polymers at the surface and interfaces by LFM.^{26,27} Figure 2 shows the temperature dependence of the lateral force for the PMMA film in the water at a scanning rate of $1 \mu\text{m}\cdot\text{s}^{-1}$. Under these aqueous conditions, a clear peak was observed with a maximum temperature of 304 K . In this temperature region, no relaxation processes were observed either at the surface or in the bulk.^{27,28} Therefore, it seems reasonable to claim that the LFM peak observed at 304 K is characteristic for PMMA at the water interface.

To confirm whether the LFM peak observed in the temperature domain can be assigned to a relaxation process, LFM measurements were made in rate domains at given temperatures. Figure 3 shows the scanning rate dependence of the lateral force for the PMMA film in water at 296 , 301 , 305 , and 314 K . A clear peak was observed at each temperature. The scanning rate at the peak shifted to higher rate values with rising temperature. These results make it clear that the LFM peak observed here can definitely be assigned to a relaxation process for PMMA at the water interface.

Figure 4 maps the LFM response in temperature and scanning rate for the relaxation process, using data from Figure 3. The abscissa is the inverse of the measurement temperature ($1/T$), and the ordinate is the logarithm of the scanning rate where the lateral force reached a maximum (ν_{max}). The relationship between $(\ln \nu_{\text{max}})$ and T^{-1} seemed to be linear, at least, within the temperature region employed. In other words, the plot can

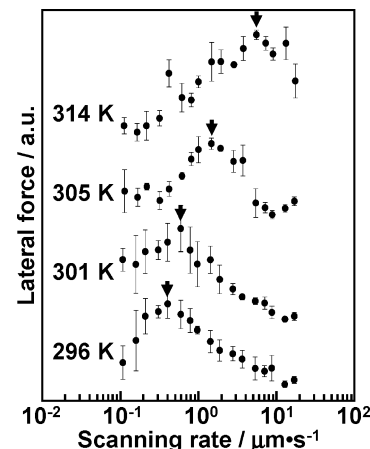


Figure 3. Scanning rate versus lateral force as a function of temperature for the PMMA film in water.

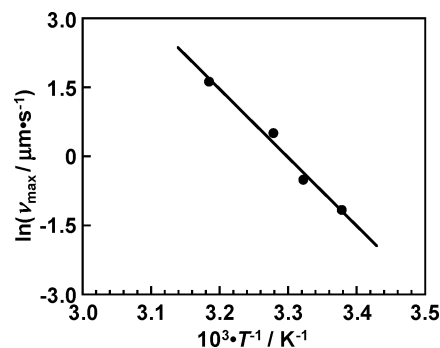


Figure 4. Semilogarithmic plot between the scanning rate at which lateral force reached maximum, versus the reciprocal of the absolute temperature for the relaxation process of PMMA in water.

be regarded as Arrhenius type rather than Vogel–Fulcher type. This is a characteristic feature for relaxation processes in confined spaces such as surface and interface.^{26,29} Then, the following equation was applied to extract the apparent activation energy (ΔH^\ddagger) for the relaxation process:

$$\Delta H^\ddagger = -R \cdot d(\ln \nu_{\text{max}})/dT \quad (1)$$

where R is the gas constant. The ΔH^\ddagger value for the relaxation process was estimated to be $120 \pm 10 \text{ kJ}\cdot\text{mol}^{-1}$. We have previously examined relaxation processes for PMMA, of the same type used here, by LFM in conjunction with dynamic mechanical analysis (DMA). The ΔH^\ddagger values for the surface and bulk α_a -relaxation processes were 230 ± 20 and $660 \pm 60 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. The ΔH^\ddagger value observed here is much lower than either of these. A plausible explanation for this behavior is that the relaxation process observed here arises from the segmental motion accelerated by water molecules.

It is well recognized that sorbed water exhibits a pronounced effect on the relaxation behavior of polymers.^{28,30} When water molecules are sorbed into a matrix polymer, the chain mobility is enhanced and then long-range motions associated with the segmental motion start to take place at lower temperatures than normal. Ceccorulli and Pizzoli investigated the relaxation behavior of PMMA both in dry and wet states by DMA.³⁰ In the case of the wet PMMA, the α_a -relaxation process was observed at a temperature that was 20 K lower than that of the corresponding dry sample. This is simply because sorbed water molecules in PMMA accelerated the segmental motion, the so-called plasticizing effect. As stated in the Introduction, in our case, a swollen layer exists in the outermost region of PMMA

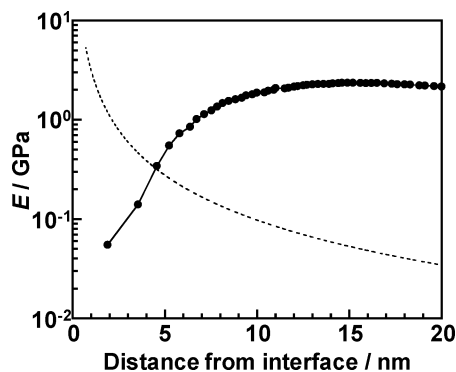


Figure 5. Depth dependence of Young's modulus E for PMMA in water, taken from our previous publication²¹ with some modifications. The dotted curve denotes the relation for PMMA between E and tip penetration depth, taken as being equal to the distance from the interface, was constructed from eq 2.

in water. Taking into account this fact, it seems quite reasonable to claim that what we observe by LFM is the α_a -relaxation process plasticized by water.

The relaxation temperature of the surface α_a -relaxation process for the same PMMA was 360 K at the same scanning rate of $1 \mu\text{m}\cdot\text{s}^{-1}$, which can be simply converted to a deformation frequency of approximately 66 Hz.³¹ This was much lower than the bulk value of 410 K for the same PMMA at a frequency of 70 Hz. Although the reason why the surface mobility is enhanced in comparison with that of the bulk is still under investigation, our tentative explanation for the PMMA used here is mainly based on the discrepancy in the degree of chain conformation between surface and bulk.²⁷ When the PMMA surface is contacted with the water phase, the chain conformation of PMMA is altered.³² Thus, at the moment, it is difficult to decide whether the surface or bulk relaxation temperature should be taken as the origin for the depression of the relaxation temperature at the water interface. In any event, it is necessary to obtain information about the water fraction at the depth to which a tip for LFM measurement reaches under the current experimental condition.

We first estimate the penetration depth of an LFM tip (d) on the basis of simple contact mechanics with the Hertzian model.³³

$$d = [(4/3) \cdot (F_c/R_t^{1/2}) \cdot \{(1 - \mu_{\text{tip}}^2/E_{\text{tip}}) + (1 - \mu_{\text{polymer}}^2/E_{\text{polymer}})\}]^{2/3} \quad (2)$$

where μ , E , R_t , and F_c are Poisson's ratio, Young's modulus, radius of curvature of the tip, and normal force, respectively. Since the tip is much harder than the sample surface, the $1 - \mu_{\text{tip}}^2/E_{\text{tip}}$ term can be ignored. A typical value for μ_{polymer} is 0.33, while R_t was experimentally measured to be 11 nm and F_c was set to be 15 nN. Thus, to obtain the d value, a knowledge of E of PMMA near the water interface is necessary. Fortunately, we could import such data based on the force–distance curve for PMMA in water from our previous publication.²¹

The symbols in Figure 5 show the depth dependence of E for PMMA in water. The value of E decreased with proximity to the water interface because of an increase in the water fraction. The relation between E and the distance from the interface, as described by eq 2, is shown as the broken line in Figure 5, assuming that d is the same as the depth from the interface. Of course, Figure 5 shows that the tip penetrates deeply with decreasing E for PMMA.

The solid and broken lines cross at a depth of 4.5 nm from the interface. In the depth region shallower than the crossing

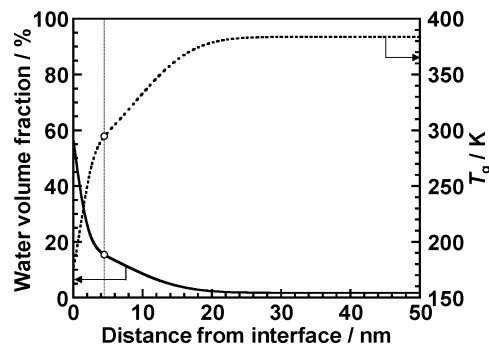


Figure 6. Depth profiles of water volume fraction (solid line) and T_g (dotted line) in PMMA in water.

point, PMMA is too soft to resist the tip penetration. On the other hand, in the region deeper than that point, the tip cannot penetrate because the normal force is too weak for further tip penetration. That is, the pressure induced by the tip is balanced by the hardness of the PMMA interface at this 4.5 nm depth. Therefore, we estimate the penetration depth of the tip to be 4.5 nm under the current conditions.

Previously, we have used NR to examine the density profile of deuterated PMMA film in water.²¹ In this case, assuming that a simple additivity rule for the neutron scattering length density (b/V) between dPMMA and water holds, the water fraction in the dPMMA film (ϕ_{water}) is given by

$$\phi_{\text{water}} = \{(b/V)_{\text{mix}} - (b/V)_{\text{dPMMA}}\} / \{(b/V)_{\text{water}} - (b/V)_{\text{dPMMA}}\} \quad (3)$$

where the mix subscripts correspond to a mixture of dPMMA and water, namely, dPMMA containing some amounts of water. Invoking that the chemical interaction of water molecules with dPMMA is the same as that with PMMA, we can expect the same depth dependence of the water fraction in a PMMA film. The solid line in Figure 6 shows the result. The water content increased closer to the interface, resulting in a swollen layer. Our interest here is to use Figure 6 to estimate the water fraction at a depth of 4.5 nm, and the value is 15 vol %. This value is much larger than the reported bulk value of 2–3 vol %. This is the reason why the plasticization effect on the segmental motion is more striking at the interface than in the bulk.

So far, several equations have been proposed to describe to what extent smaller molecules lower the T_g of the matrix polymer.^{34–37} Kelley–Bueche theory³⁵ predicts T_g for mixtures of glassy polymer and small molecules well, and is expressed as follows:

$$T_g = (\Delta\alpha \cdot \phi_2 \cdot T_{g2} + \alpha_1 \cdot \phi_1 \cdot T_{g1}) / (\Delta\alpha \cdot \phi_2 + \alpha_1 \cdot \phi_1) \quad (4)$$

where ϕ , α , and $\Delta\alpha$ are the volume fraction, cubic expansion coefficient, and change in cubic expansion coefficient for the polymer at T_g . Subscripts of 1 and 2 denote diluent and polymer, respectively. In this study, of course, the diluent is water. The equation has been successfully applied to epoxy/water,³⁸ poly(ether sulphone)/water,³⁹ and PMMA/water⁴⁰ systems. If we accept the postulate that the glass transition is a part of the segmental motion with a likely relaxation time of 100 s,⁴¹ we can here apply the Kelley–Bueche equation to our system. To do so, three constants must be determined: α_1 , $\Delta\alpha$, and T_{g1} . Here, we used the following published values: $8.4 \times 10^{-4} \text{ K}^{-1}$, $2.45 \times 10^{-4} \text{ K}^{-1}$, and 104 K.⁴² The dotted curve in Figure 6 corresponds to the depth dependence of T_g for PMMA in water so obtained and shows that T_g decreased closer to the interface because of increasing water content. The value of T_g at a depth

of 4.5 nm from the interface can be determined from Figure 6 to be 294.5 K.

We now come back to the temperature dependence of lateral force shown in Figure 2. It has been empirically accepted that the onset temperature of the α_a -relaxation process, at which the lateral force starts to increase at $1 \mu\text{m} \cdot \text{s}^{-1}$, corresponds to T_g .^{26,27} Applying this notion to Figure 2, the T_g value of PMMA at the water interface was determined to be 294 K. Interestingly, this value is in excellent accord with the calculated value of 294.5 K. Finally, the following two points should be emphasized. First, since the relaxation process observed in this study can be discussed in terms of the effect of diluents on T_g , this effect is surely assignable to the segmental motion plasticized by water molecules. Second, the enhanced mobility of PMMA observed at the water interface can be rationalized as originating in the amount of water molecules rather than in a confinement effect. Of course, the T_g value of PMMA at the water interface is a strong function of the depth, or the water amount. The interrelationship is clearly demonstrated in Figure 6. The T_g depression observed at the water and air interfaces may not be directly related. We propose that the origin for the depression of the relaxation temperature at the water interface can be best explained in terms of the effect of water content on polymer mobility, even in the bulk.

Conclusions

LFM measurements uncovered a relaxation process of PMMA at the water interface. At a given frequency, the interfacial relaxation temperature was lower than the relaxation temperature for the segmental motion at the surface. The apparent activation energy of the relaxation process at the water interface was lower than those for the surface and bulk α_a -relaxation processes. A plasticizing effect on the T_g value of PMMA induced by sorbed water molecules was deduced from Kelley–Bueche theory. Combining the depth dependence of the water content in the PMMA film with the T_g prediction, the depth dependence of T_g in the PMMA film in the water phase was obtained. This relation reveals that the newly found relaxation process of PMMA at the water interface can be assigned to the segmental motion of PMMA at the interface plasticized by sorbed water molecules.

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