

Interfacial Structure of Deuterated Poly(methyl Methacrylate) with Carbon Dioxide below the Bulk Glass Transition Temperature

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Interfacial structures of deuterated poly(methyl methacrylate) (dPMMA) and polystyrene (dPS) films with gas such as carbon dioxide (CO₂) and nitrogen (N₂) under the pressure of 0.1 MPa were discussed on the basis of neutron reflectivity (NR) measurements. The interface was analyzed using a model that the density of the outermost region of a polymer film was lower than that in the interior region due to the penetration of gas molecules and the profile was expressed by a single exponential equation with a decay length (ξ). The ξ value for the dPMMA films under CO₂ and N₂ atmospheres was larger than that under vacuum at a given temperature, and the extent was more remarkable under CO₂ than under N₂. On the other hand, such a “swollen interfacial layer” was not clearly discerned for the dPS films.

Key words: neutron reflectivity, interface, density profiles, poly(methyl methacrylate), polystyrene

1. INTRODUCTION

Physical properties at surfaces and interfaces of polymers often differ from those in the corresponding bulk ones. In the last two decades, it has been extensively studied, experimentally and theoretically, how and why the presence of surface and interface must alter inherent properties of polymers.¹⁻⁴ Such studies are quite important in fields of photolithography, protective coatings, lubricants, adhesives, permselective membranes, biomaterials and so forth, because the surface and interfacial layers with specific structure and physical properties play crucial roles in the applications. When polymer materials are used for the aforementioned applications, the surface is supposed to be contacted with other phases in reality. That is, the surface turns to be the interface. Therefore, structure and dynamics at the polymer interfaces should be studied after understanding surface structure and properties.

Polymers are often used as key materials for gas separation membranes due to their superior permeability-selectivity balance. In this case, interactions between polymer surface and gas molecules should be understood at first so that the functionality is promisingly improved. While such studies have been widely made at high pressures,⁵⁻⁹ this is not the case under a gentle condition like at an atmospheric pressure. However, to address clearly the interaction, it should be

studied what happens if gas molecules contact with the polymer surface at an ambient atmosphere.

In this study, we chose typical glassy polymers such as poly(methyl methacrylate) (PMMA) and polystyrene (PS), which have been widely used in a variety of technological applications. Then, aggregation states at the (polymer/gas) interface were examined by neutron reflectivity (NR) with a temperature cell. With NR measurement, we gain an access to the density profile of polymers along the direction normal to the surface as well as the film thickness with the depth resolution better than 1 nm.¹⁰⁻¹³

2. EXPERIMENTAL

As materials, monodisperse and perdeuterated PMMA (dPMMA) and PS (dPS) were used. The bulk glass transition temperature (T_g^b), which was determined by differential scanning calorimetry (DSC220, SII NanoTechnology Inc.) at the heating rate of 10 K•min⁻¹ under dry nitrogen purge, was 399 and 377 K, respectively. Polymer films were spin-coated from dilute toluene solutions onto Si substrates. They were dried under the ambient atmosphere at room temperature for more than 24 h, and then, annealed under vacuum at 423 K for 24 h. The film thickness after drying was evaluated to be approximately 110 nm by ellipsometry. As gases, carbon dioxide (CO₂) and nitrogen (N₂) were used. This is because they are regarded as gases with

Table I. (b/V) values for polymers and gases used in this study.

	$b/V \times 10^4 / \text{nm}^{-2}$
dPMMA	6.62
dPS	6.22
CO ₂	0.00491
N ₂	0.00503

Table II. Fitting parameters for (dPMMA/CO₂) at 300 K.

	dPMMA/CO ₂
film thickness [nm]	113.1
roughness [nm]	0.51
ξ [nm]	0.77
χ^2	9.72×10^{-3}

and without a good affinity to PMMA, respectively. Table I shows the scattering length density (b/V) values for polymers and gases used in this study. NR measurement was performed using the advanced reflectometer for interface and surface analysis (ARISA)¹⁴ on the H5 beamline of the Neutron Science Laboratory, High Energy Accelerator Research Organization. Fig. 1 shows the schematic illustration of the experimental set-up in a gas atmosphere. The neutron beam was transmitted through a series of quartz windows in the temperature cell. The gas pressure was regulated to be 0.1 MPa, corresponding to the atmospheric pressure. The NR data were plotted versus the scattering vector (q) which was defined by

$$q = (4\pi/\lambda) \cdot \sin \theta$$

where λ and θ were wavelength and incident angle of the neutron beams, respectively. The incident neutrons wavelength band was 0.05 – 0.4 nm. The reflectivity was calculated on the basis of the scattering length density profile along the depth direction using Parratt32.¹⁵

3. RESULTS AND DISCUSSION

Fig. 2(a) shows the scattering vector dependence of reflectivity for a dPMMA film under CO₂ atmosphere at 300, 333, 373 and 403 K. The data at 333, 373 and 403 K are offset by a decade for the sake of clarity. Solid lines denote the best-fit calculated reflectivity, to the experimental data, on the basis of model scattering length density (b/V) profiles. A typical example of (b/V) profile and fitting parameters are shown in the panel (b) of Fig. 2 and Table II, respectively. Since the calculated curves are in good agreement with the experimental data, it can be claimed that the model (b/V) profiles used well reflect the density profiles of the dPMMA film along the direction normal to the interface.

Fig. 3 shows the enlarged model (b/V) profiles for the (PMMA/CO₂) system at 300, 333, 373 and 403 K.

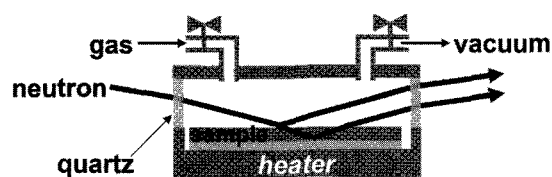


Fig. 1. Schematic illustration of experimental setup for NR measurement.

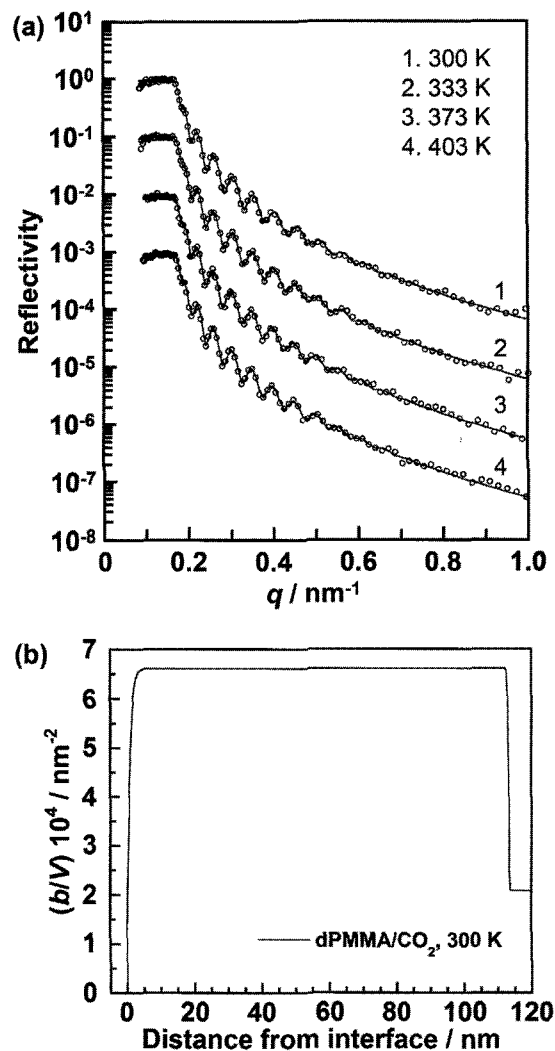


Fig. 2. (a) Neutron reflectivity profiles for a dPMMA film under CO₂ atmosphere of 0.1 MPa at 300, 333, 373 and 403 K. Circles are experimental data, and solid lines depict reflectivity calculated on the basis of model scattering length density profiles. The data is offset by a decade for clarity. (b) A typical model scattering length density profile for a (dPMMA/CO₂) system at 300 K.

The (b/V) value asymptotically reached a constant at the depth of approximately 5 nm for all the cases, although the (b/V) depletion was more prominent at a higher temperature. The (b/V) values for dPMMA and CO₂ were calculated to be 6.62×10^{-4} and $4.91 \times 10^{-7} \text{ nm}^{-2}$, respectively. Hence, it seems most likely that a decrease in the (b/V) value corresponds to an increase in

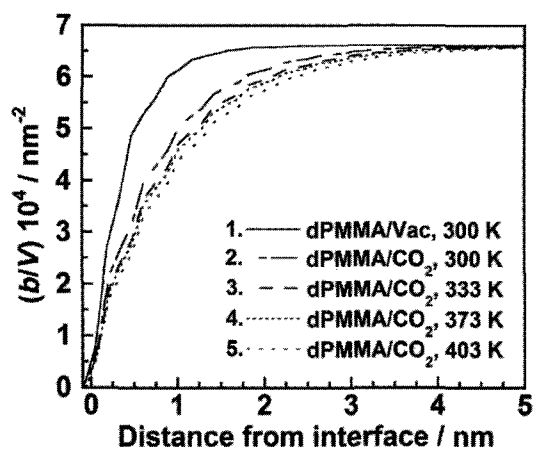


Fig. 3. Enlarged model (b/V) profiles, in the depth range of 5 nm, for a (PMMA/CO₂) system at 300, 333, 373 and 403 K.

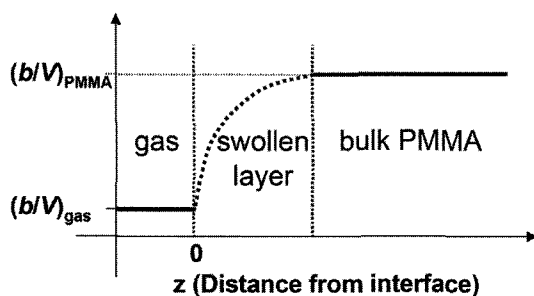


Fig. 4. Schematic illustration of model scattering length density profile for a dPMMA film under gas atmosphere.

the CO₂ fraction in the vicinity of the dPMMA interface. Here, two points should be emphasized. First, the (b/V) in the interfacial region was lower under CO₂ than under vacuum at 300 K. In general, the surface density of a polymer should be higher under the presence of a gas at 0.1 MPa than under vacuum. Nevertheless, the opposite was observed by our experiments. Thus, we may have to think that CO₂ molecules penetrate into the outermost region of the dPMMA film. Second, under CO₂, the (b/V) depletion became more remarkable with increasing temperature. This point will be discussed after Fig. 5.

We here take a model that the density of the outermost region of the dPMMA or dPS film was lower than that in the interior region due to the penetration of gas molecules, and call the depletion layer related to the (b/V) as "swollen interfacial layer". Fig. 4 illustrates the model which can be expressed by a single exponential equation with the decay length (ξ). Thus, the (b/V) value at a given depth of z is given by

$$(b/V) = \left\{ (b/V)_{dPMMA} - (b/V)_{gas} \right\} \cdot \{ 1 - \exp(-z/\xi) \} + (b/V)_{gas}$$

Based on the model, it can be claimed that the ξ is an index of how gas molecules penetrate into the polymer.

Table III. Gas solubility to PMMA and PS.

	solubility $\times 10^3 / \frac{\text{cm}^3(\text{STP})}{\text{cm}^3 \text{cmHg}}$	
	CO ₂	N ₂
PMMA	53.2	1.79
PS	0.33	0.025

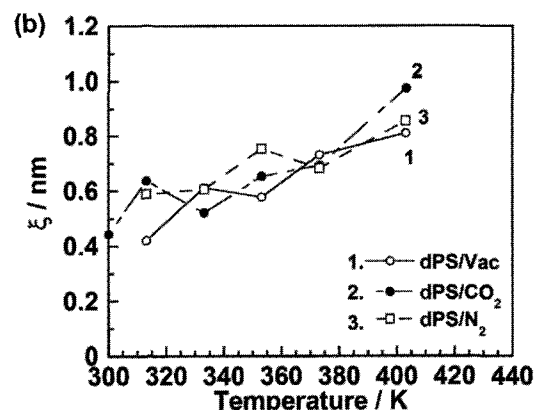
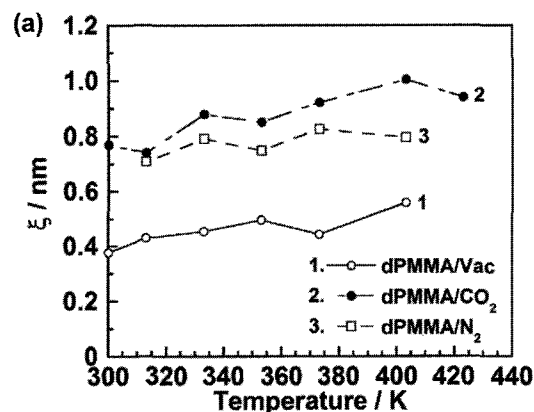


Fig. 5. Temperature dependence of decay length (ξ) for (a) dPMMA and (b) dPS films.

The panels (a) and (b) of Fig. 5 show the temperature dependence of ξ for the dPMMA and dPS films as a function of temperature under three different environments. As a general trend, the ξ value increased with increasing temperature. In the case of the dPMMA films, the ξ value under gas atmosphere was larger than that under vacuum at a given temperature, meaning that the gas molecules penetrated into the outermost region of the films. It is worthy to note that this was the case even for N₂, which has been generally regarded as an inert gas. The extent of the gas sorption was more striking in CO₂ than in N₂. On the other hand, a clear dependence of ξ on environment was not observed for the dPS films, as shown in the panel (b) of Fig. 5. In addition, the ξ value for the dPS films was smaller than that for the dPMMA films at a given temperature upto T_g^b of the PS. These results might be related to the gas solubility into the polymers, as shown in Table III.¹⁶

Here, it is discussed why CO₂ exhibits a good

affinity to dPMMA. Eckert and co-workers have studied, using Fourier transform infrared (FTIR) spectroscopy, an interaction of CO₂ with polymers.¹⁷⁻¹⁹ They have concluded that polymers containing carbonyl groups would act as an electron donor, and that a specific intermolecular interaction between the polymers and CO₂, which behaves as an electron acceptor rather than as an electron donor, is attained.¹⁹ Although a weak electrostatic interaction¹⁹ is possible to be existed between CO₂ and phenyl π -electrons of PS, PS does not show a strong interaction with CO₂ owing to a lack of carbonyl groups. These arguments are consistent with what is seen in Fig. 5.

However, the data shown in Fig. 5 is not so simple to fully understand. For example, the gas solubility to polymers generally decreases with increasing temperature.²⁰ Nevertheless, the ξ here increased with increasing temperature, as shown in Fig. 5, indicating that the gas sorption into polymers increased with increasing temperature. Moreover, to what extent gas molecules were sorbed into polymers was not necessarily consistent with the solubility difference. Thus, it is plausible that the gas sorption process is quite complicated and controlled by not a single factor of the gas solubility but a few or many factors. One candidate for those is molecular motion of polymers. But, further study is necessary to conclude which factor is the most crucial on the gas penetration into the polymers under such a gentle pressure.

4. CONCLUSIONS

It was shown that NR was a powerful tool to examine how gas molecules were sorbed into polymers on sub-nanometer level. CO₂ than N₂ gases could get into the outermost region of the dPMMA films even at 0.1 MPa, being approximately the atmospheric pressure. However, dependence of density depletion layer on environment was not clear for dPS films. Although the gas sorption process was quite complicated, it seems most likely that gas solubility and molecular motion of polymers were responsible in what was seen in our experiments.

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