Effect of interfacial structure on bioinert property of poly(2-methoxyethyl acrylate)/poly(methyl methacrylate) blend films in water


a Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan
b Education Center for Global Leaders in Molecular Systems for Devices, Kyushu University, Fukuoka 819-0395, Japan
c Neutron Science Laboratory, High Energy Accelerator Research Organization, Ibaraki 305-0801, Japan
d Department of Biochemical Engineering, Yamagata University, Yamagata 992-8510, Japan
e International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan

*Authors for correspondence:

Hisao Matsuno
h-matsuno@cstf.kyushu-u.ac.jp

Keiji Tanaka
k-tanaka@cstf.kyushu-u.ac.jp
Composition profile in air. Fig. S1 shows the scattering vector ($q_z$) dependence of neutron reflectivity (NR) for the poly(2-metoxyethyl acrylate (PMEA)/deuterated poly(methyl methacrylate) (dPMMA) blend film with a weight ratio of 50/50 (wt/wt), or a volume ration of 48/52 (v/v) in air. The solid curve in panel (a) was calculated on the basis of the model ($b/V$) profile shown in panel (b), representing the best fit to the experimental data, shown by open circles. Table S1 summarizes the fitting parameters, where $t$ and $\sigma_i$ represent the total film thickness and Gaussian roughness, respectively. According to the mean field approximation, the composition profile of a miscible polymer mixture in the surface region is expressed by an exponential decay function. However, the experimental NR data obtained here could not be well fitted with such a function. Thus, the following ($b/V$) profile was adopted;

\[
(b/V)(z) = \sum_{i=1}^{N} \left( \frac{(b/V)_i - (b/V)_{i+1}}{2} \right) \left\{ 1 + \text{erf} \left( \frac{z - z_i}{\sqrt{2} \sigma_i} \right) \right\}
\]

where $N$ and $z$ are the number of layers and the depth, respectively. Assuming incompressibility of polymer chains, the average ($b/V$) value for the PMEA/dPMMA blend should be $4.20 \times 10^{-4}$ nm$^{-2}$. While the ($b/V)_1$ and ($b/V)_3$ values were much smaller than the average ($b/V$) value, the ($b/V)_2$ value was slightly larger than that value. This means that the PMEA component with a lower ($b/V$) value was enriched both at the air and substrate interfaces.

**Fig. S1.** (a) NR curve for the PMEA/dPMMA blend film in air. Open symbols depict the experimental data, and a solid line is the reflectivity calculated on the basis of (b) the ($b/V$) profile of the blend film in air. (c) A schematic illustration of the three layer model used for fitting. Here, $t$ and $\sigma_i$ represent the total film thickness and Gaussian roughness, respectively.
Table S1. Parameters used to fit the experimental reflectivity for the PMEA/dPMMA blend film in air shown in Fig. S1(a).

<table>
<thead>
<tr>
<th>Film</th>
<th>(b/V) / 10⁻⁴ nm⁻²</th>
<th>t / nm</th>
<th>σ₁ / nm</th>
<th>σ₂ / nm</th>
<th>σ₃ / nm</th>
<th>σ₄ / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMEA/dPMMA</td>
<td>1.10</td>
<td>4.63</td>
<td>1.15</td>
<td>60.0</td>
<td>1.3</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Contact angle measurements. Movie S1 shows the behavior of air bubbles on the PMEA/PMMA blend films (a) before and (b) after being immersed in water for 10 hours.

Fourier transform infrared (FT-IR) spectroscopy. As a sample, a bulk PMEA film was prepared onto an NaCl substrate by a solvent casting method. The film was dried under vacuum for 12 hours at room temperature. FT-IR spectrum of PMEA was recorded in vacuum in a wavenumber region (400 - 4000 cm⁻¹) at the resolution of 1 cm⁻¹ on an FT/IR-620 Fourier transform infrared spectrometer (JASCO Corporation). The obtained spectrum was shown in Fig. S2.

![Fig. S2.](image)

(a) The FT-IR spectrum for a PMEA bulk film. (b) The enlarged spectrum of (a). While both red and blue curves are the curve-fitting results, the red one is the summation of the blue ones.

Reference