

Structural Characterization of Stimuli-Responsive (“Smart”) Surfaces using Neutron Reflectometry

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In past decades, there are many novel areas presently being developed that require so-called “smart biological surfaces,” which can respond to external stimuli such as solvent type, pH, temperature, electric and magnetic fields, etc. Among smart surfaces, thermo-responsive surfaces, which can respond to temperature variation, are some of the most important, since temperature, as a stimulus, can be easily regulated. Recently, a new class of biocompatible thermo-responsive material, namely poly[2-(2-methoxyethoxy)ethyl methacrylate-co-oligo(ethylene glycol) methacrylate] (P(MEO2MA-co-OEGMA)), has attracted much attention. This random copolymer has been shown to have an LCST in water. Knowledge about conformation of the polymer brushes on surface is crucial when designing smart surfaces.

In this work, PEG-based thermo-responsive surfaces were prepared by grafting P(MEO2MA-co-OEGMA) copolymer brushes on silicon wafers via the surface-initiated atom transfer radical polymerization method. NR experiments were carried out at the D3 reflectometer located at the National Research Universal Reactor (Chalk River, ON). The samples were measured both in air and in aqueous solution. PARRATT 32 (BENSC, Berlin) software was employed to interpret the data. In the case of dry samples, a three-layer (SiO₂, initiator monolayer, polymer layer) model was used. For wet samples, a parabolic decay was added to the polymer layer due to the extension of polymer chains into the aqueous environment.

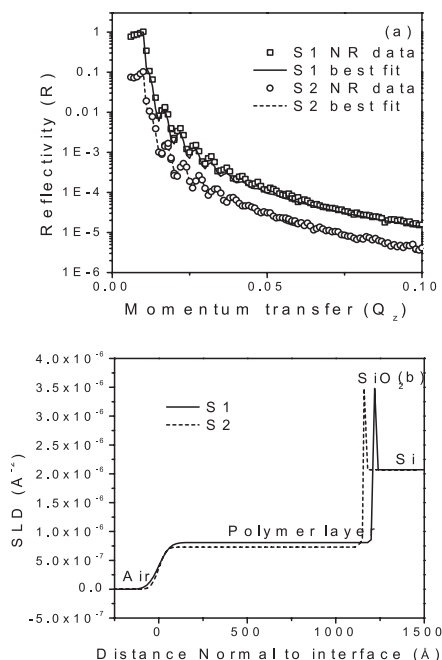


Fig 1. (a) Neutron reflectivity profiles for dry surfaces and the best fits to the data. The curves were offset by arbitrary factors in order to better distinguish the data. (b) SLD profiles of grafts on the silicon substrate.

The samples were measured first in air to obtain the dry thickness of the grafts and the parameters needed to model the wet state. Figure 1a shows the NR profiles for two samples in air.

From the SLD profiles of the grafts (Figure 1b), the polymer layer and SiO₂ layer are clearly discernable. The thicknesses of polymer layers on S1 and S2 are 1185.4 Å and 1131.3 Å, respectively, and are in good agreement with those results obtained by ellipsometry.

The conformations of polymer brushes on S1 in D₂O were measured at different temperatures. The NR profiles and their best fits are shown in Figure 2a.

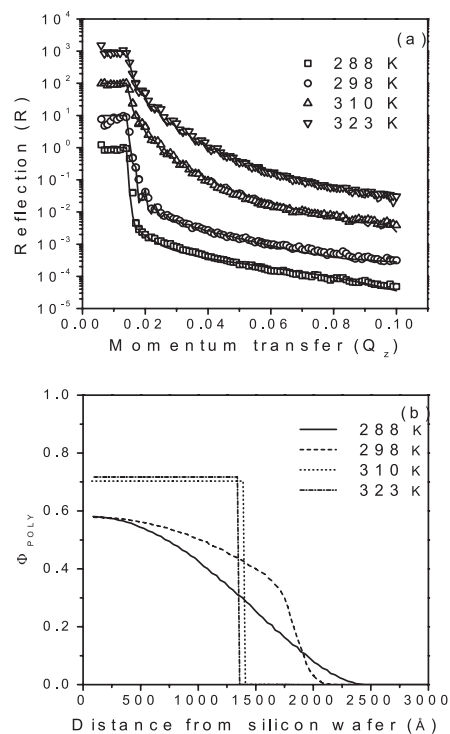


Fig 2. (a) Neutron reflectivity profiles of S1 in D₂O and the best fits to the data. The curves were offset by arbitrary factors in order to better distinguish the data. (b) Volume fraction profiles of polymer brushes.

The SLD profiles of polymer brushes on the surface were determined from the best fits to the data. They were then easily interpreted to polymer volume fraction profiles by assuming that the volumes were additive. At 288 K, the polymer brushes were well extended into water. Compared to the dry state, the swelling ratio of polymer brushes in D₂O was approximately 1.8. OE groups can form hydrogen bonds with water; therefore a hydration layer in which water was combined to the polymer chains by hydrogen bonds was built up surrounding polymer chains. When the temperature was increased to 298

K, the polymer brushes shrank, slightly. This indicates a decrease in the affinity between OE groups and water molecules, affecting the level of hydration around the polymer chains. When the temperature was further increased to 310 K, above the polymer's LCST, the polymer brushes collapsed, excluding much of the water from the polymer layer. When the temperature was increased to 323 K, the polymer layer collapsed further, expelling more water.

Figure 3a shows NR reflectivity data for S2 and the best fits to the data (solid lines) at four different temperatures. The polymer volume fraction profiles are shown in Figure 3b. For S2, its LCST in water was around 321 K, higher than that of S1 (305 K). As shown in Figure 3b, at 298 K the polymer brushes were extended into D_2O , indicating a well-developed hydration layer around the polymer chains.

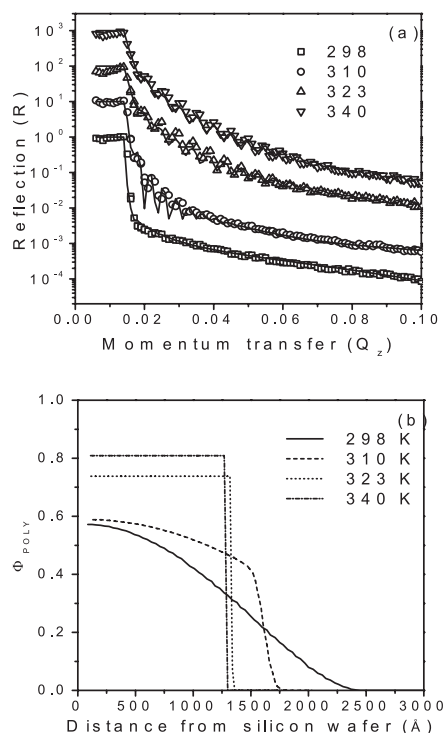


Fig 3. (a) Neutron reflectivity profiles of S2 in D_2O and the best fits to the data. The curves were offset by arbitrary factors in order to better distinguish the data. (b) Volume fraction profiles of polymer brushes.

When the temperature was increased to 310 K, the polymer brushes were obviously compressed and the swelling ratio decreased to around 1.4. An interface formed between the water and polymer layer, which indicated that the hydration layer surrounding the polymer chains was partially destroyed at a temperature close to the LCST.

When the temperature was raised to 323 K, higher than the polymer's LCST, the polymer brushes collapsed onto the surface. The swelling ratio was less than 1.2. When the temperature was 340 K, the polymer layer swelling ratio was only around 1.1, while the water fraction further decreased to around 20%.

In conclusion, PEG-based thermo-responsive surfaces were prepared by grafting P(MEO2MA-co-OEGMA) copolymer brushes on silicon wafers via the surface-initiated ATRP method. The detailed conformation information of the polymer brushes in aqueous solutions as a function of temperature was obtained using the NR method. Polymer conformation changed from the well-extended state to the compressed state, and then to the collapsed state with increased temperature.

References

- [1] Gao, X.; Kučerka, N.; Nieh, M.P.; Katsaras, J.; Zhu, S.; Brash, J. L.; Sheardown, H. Chain Conformation of a New Class of PEG-Based Thermo-Responsive Polymer Brushes Grafted on Silicon as Determined by Neutron Reflectometry. *Langmuir* 2009, (Published online).