2 Introduction

Structure and Graft density of Polymer Brush

"Grafting-to" method
Adhesion of end-functionalized polymers or block copolymers to the substrate.

"Grafting-from" method
Surface-initiated polymerization from the substrate

High graft density: The number of polymer chains at the surface per unit area (chains/nm²)

3 Properties of High-density Polymer Brushes

1. High grafting density (0.1–1.0 chain/nm²)
2. Thickness and molecular weight are controllable.
3. Repulsive force due to osmotic pressure in good solvent

Polymer Brush is expected to show quite different behavior from bulk polymer because of the presence of anchoring point to the substrate.

4 Why Neutron Reflectivity?

Surface-grafted Polymer (Polymer Brush)
Polymer brush is a system formed by densely tethered polymers on a solid surface, of which chains are stretched away from the surface.

The behavior of polymer brushes in solvent has important technological implications for various applications.

However, it is difficult to analyze the interface structure and the thickness of the extended brush because a continuous layer of solvated chains will be formed.

Neutron reflectivity measurements are appropriate for the study of the influence of solvent on polymer brush structure.

5 Neutron Reflectivity Analysis of Swollen Polymer Brush

This Work

Neutron Reflectivity Analysis at the Interface of D₂O / High-density Polyelectrolyte Brush Prepared by surface-initiated ATRP

Effect of salt concentration

What’s going to happen in the high-density polymer brush?

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Surface-initiated Atom Transfer Radical Polymerization

1. Immobilization of Surface Initiator

Hydrophilic Quartz Plate

2. Surface-initiated ATRP

Incident angle = 3.0°

3. Wave length

Apparatus

Incident angle = 1.0°

Incident angle = 0.2°

Scattering length density / 10

Incident Beam

Surface-initiated Atom Transfer Radical Polymerization

Fitting Parameters

Reflectivity

Corresponding Fits

Surface-initiated ATRP

CuCl / PMDETA

Hydrophilic Quartz Plate

Surface-initiated Atom Transfer Radical Polymerization

CuBr / MeOH / 303 K

Parabolic Function

Distance from Surface / nm

Volume fraction

Parabolic fit

Distance from Surface / nm

Volume fraction

(b) Parabolic fit

Distance from Surface / nm

Distance from Surface / nm

-(b) Volume fraction curve

+ (5) Parabolic fit

NR Measurement of PMTAC Brush / NaCl D_2O

Distance from Surface / nm

Reflectivity

Coverage

PMTAC Brush

Mn = 86,000

Thickness = 35 nm (humidity 50%)

Graft density = 0.02 chains/nm^2

PMTAC Brush

Mn = 86,000

Thickness = 46 nm (humidity 50%)

Graft density = 0.06 chains/nm^2

Ionic Strength and Polyelectrolyte

In general, an isolated polyelectrolyte in pure water forms a relatively expanded state due to the electrostatic repulsion of ionic functional groups in the chain, while it would shrink in salt solution by the reduction of electrostatic repulsion between polymer chains.

However, ionic acid cannot be diffused into a high-density polymer brush layer due to the high hydrophilization and high local charge density. Therefore, the thickness of polyelectrolyte brush in solution was hardly changed in 1.0 M NaCl solution.

Neutron Scattering Length
Density Profile

Scattering length density
10^{-4} \text{nm}^{-2}

PMETA Brush
Mn = 86,000
Thickness = 46 nm (humidity = 50%)

PMTAC brush / D_2O

PMETA-Cl brush / 5.6 M NaCl aq

Neutron Reflective Curves and Corresponding Fits

Distance from Surface / nm

5.6 M NaCl
D_2O solution

Scattering length density

Incidence angle = 0.2 ° - 4.5 °
S1 = 1.0 mm, S2 = 0.37 mm, DS = 10 mm

Incidence angle = 1.0 ° - 2.0 °
S1 = 1.5 mm, S2 = 1.31 mm, DS = 10 mm

Incidence angle = 2.0 ° - 3.0 °
S1 = 2.0 mm, S2 = 1.83 mm, DS = 10 mm

PMPC Brush
Mn = 80,000
Thickness = ca. 35 nm (humidity = 50%)


Conclusions

1. Swollen structure PMTAC brush strongly depended on salt concentration. Shrunk brush structure was observed in 5.6 M NaCl solution by NR and AFM, while relatively extended chain structure was formed in 1.0 M NaCl solution.

2. PMPC showed stable swollen structure even in salt solution. This is the unique property of PMPC.
