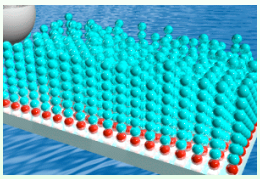
2009/08/05(Wed) 拡大IRT研究会@波紋施設

水界面における高分子電解質ブラシの分子鎖形態のイオン強度依存性



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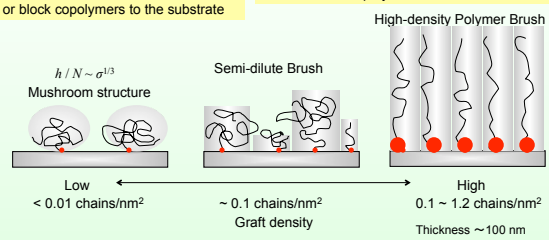
石原一彦[4]，高原淳[1,2]

[1]JST-ERATO, [2]Kyushu University, [3]Kyoto University, [4]The University of Tokyo

2 Introduction

Structure and Graft density of Polymer Brush

"Grafting-to" method	"Grafting-from" method
Adsorption of end-functionalized polymers or block copolymers to the substrate	Surface-initiated polymerization from the substrate

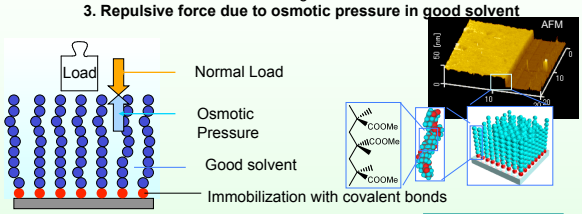


* Chain conformation is a coil dimension
* Large steric hindrance by polymer chains

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 chains/nm²)
2. Thickness and molecular weight are controllable.
3. **Repulsive force due to osmotic pressure in good solvent**



Polymer Brush → **Highly resistant against compression in good solvent due to osmotic pressure.** → **Low-friction Surface**

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

Ref: R. C. Advincula, W. J. Brittain, K. C. Caster, J. Rühe, "*Polymer Brushes* " , Wiley-VCH, Weinheim, (2004).
Adv. Polym. Sci. 197, "Surface-initiated Polymerization I", Springer, Berlin Heidelberg New York, (2006).

4 Why Neutron Reflectivity?

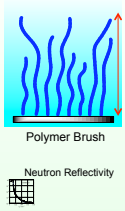
Surface-grafted Polymer (Polymer Brush)

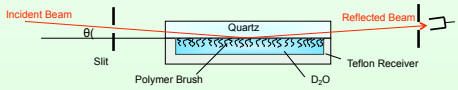
Polymer brush is a system formed by densely tethered polymers on a solid surface, of which chains are stretched away from the surface.

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.

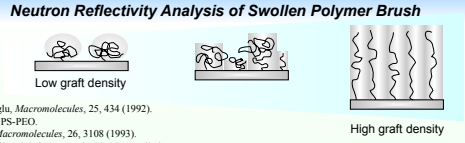
Neutron reflectivity measurements are appropriate for the study of the influence of solvent on polymer brush structure.





・Solvent quality (Good solvent, poor solvent) dependence of brush thickness
・Relationship between brush thickness and graft density

5 Neutron Reflectivity Analysis of Swollen Polymer Brush



C. Toprakcioglu, *Macromolecules*, 25, 434 (1992).
Adsorbed PS-PEO.
G. S. Grest, *Macromolecules*, 26, 3108 (1993).
Scaling of brush height agreed with SCF predictions.
M. Tirrell, *Macromolecules*, 31, 3741 (1998).
P2VP-block-dPS spin cast film, in air, toluene, cyclohexane
R. K. Thomas and S. P. Armes, *Macromolecules*, *32*, 2731 (1999).
PMMA-block-Poly(DMAEMA) in salt solution.
C. Toprakcioglu, *Macromolecules*, 33,1120 (2000).
Structure of PS-b-PEO Brushes under shear flow in a toluene-$_{d8}$
R. Ivkov, *Langmuir*, 17, 2999 (2001).
dPS-$SiCl_3$ grafted-to Si substrate in toluene, cyclohexane.
L. Léger, *Macromolecules*, 34, 8694 (2001).
Absorbed PDMS on Si substrate.
M. Grunze *Langmuir* 2002, 18, 8862 (2001); 19, 2284 (2003); 20, 3848 (2004).
Grafting of alkanethiol-terminated poly(ethylene glycol) on gold.
M. S. Kent, *Macromolecules*, 36, 5244 (2003).
End-tethered PNIPAM Chains in Water.
T. Koga, *J. Polym. Sci. Part B Polym. Phys.*, 42, 3282 (2004).
dPS-*block*-P4VP Brushes in sc-CO_2.
P. D. Gallagher, *J. Polym. Sci. Part B Polym. Phys.*, 42, 4126 (2004).
Swelling of a PS brush (PS-$SiCl_3$) by a poor solvent.
J. L. Brash, *J. Colloid Int. Sci.*, 281, 112 (2005); 296, 520 (2006).
Chemisorption of PEO onto gold. Relationship of layer structure to protein resistance.
G. H. Findenegg, *J. Phys.: Condens. Matter*, 17, S665 (2005).
PEO-PPO-PEO in D_2O.
C. A. Helm, *Langmuir*, 20, 11528 (2004).
PEE212-PEO112 diblock copolymer monolayers at the air/water interface.

J. -P. Chapel, *Macromolecules*, 38, 4296 (2005).
High-density dPS brush on Si wafer in toluene.

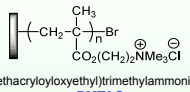
J. L. Brash, *Biointerphases*, 2, 34 (2007)
High-density POEGMA and PMPC brush in D_2O.

A. Takahara, *Soft Matter*, 3, 740 (2007).
High-density poly(MPC) brush in D_2O.

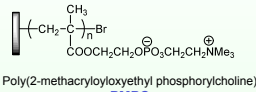
Y. Tran, *Macromolecules*, 41,8721 (2008).
High-density PMETA-I brush in NaCl/D_2O.

6 This Work

Neutron Reflectivity Analysis at the Interface of D_2O / High-density Polyelectrolyte Brush Prepared by surface-initiated ATRP

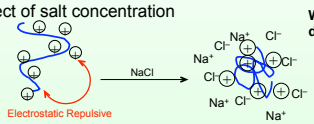


Poly({(2-methacryloyloxyethyl)trimethylammonium chloride} **PMTAC**

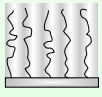


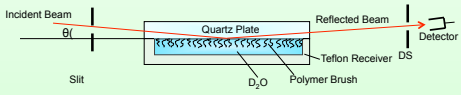
Poly(2-methacryloyloxyethyl phosphorylcholine) **PMPC**

Effect of salt concentration



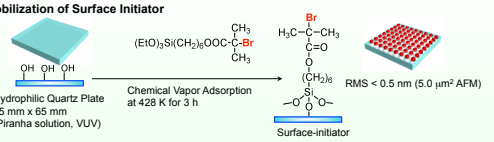
What's going to happen in the high-density polymer brush ?



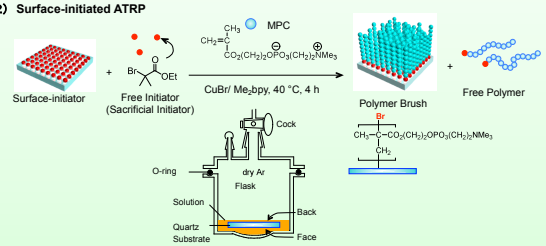


7 Surface-initiated Atom Transfer Radical Polymerization

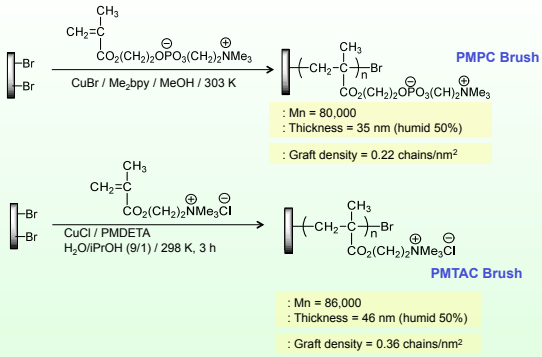
(1) Immobilization of Surface Initiator



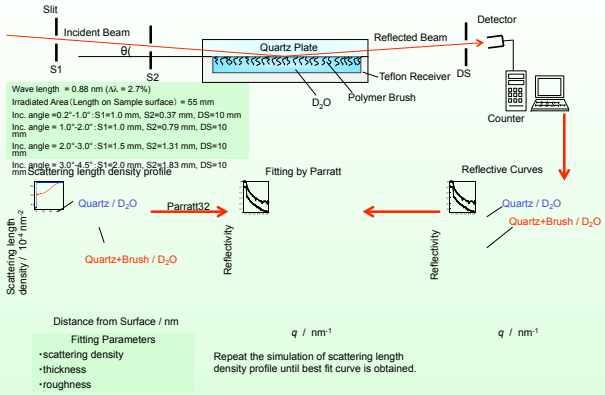
(2) Surface-initiated ATRP



8 Preparation of Polyelectrolyte Brush



9 Neutron Reflectivity (MINE @ JRR3 TOKAI, Japan)



10 Parabolic Function

膨潤ブラシの構造：平均場理論より
ポリマー中のモノマーユニットが媒体中で占める体積分率Φ (z) は以下のようなparabolic関数(1)式と指数関数(2)式で表される。

$$\Phi(z) = \Phi_{\ p}(z) = \Phi_0\{(1-(z/h)^2\}^{\alpha} \quad (z < z_E) \quad (1)$$

$$\Phi(z) = \Phi_{\ T}(z) = M\exp(-\beta z) \qquad (z > z_E) \quad (2)$$

[境界条件 $d\Phi_{\ p}(z_E)/dz = d\Phi_{\ T}(z_E)/dz,\ \Phi_p(z_E) = \Phi_{\ T}(z_E)$]

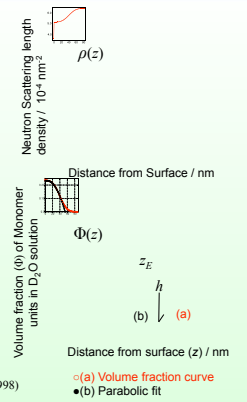
Φ_0：ブラシ／基板界面におけるモノマーユニットの体積分率。
h ：(2)式においてΦ(z) = 0となるz (>0)の値
z_E：体積分率曲線の変曲点に相当する位置
Mとβ：$z = z_E$における境界条件を満たす定数。
指数α：良溶媒中では$\alpha = 1$であり，θ溶媒で$\alpha = 0.5$。

溶媒およびモノマーユニットの中性子散乱長密度をそれぞれ b_{sol}, b_{mon}のとすると，重水中で膨潤したポリマーブラシの中性子散乱長密度ρ(z)は

$$\rho(z) = b_{mon}\Phi(z) + b_{sol}(1-\Phi(z)) \qquad (3)$$

parabolic関数から得られるh値を膨潤膜厚と見なす。

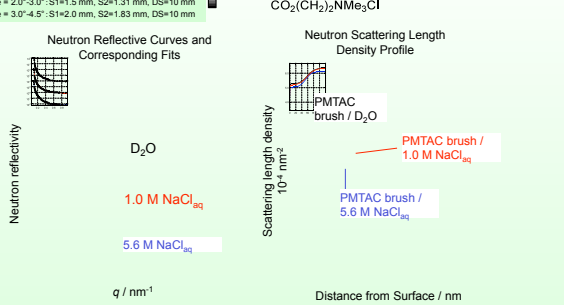
S.T. Milner, T.A. Witten, M.E. Cates *Macromolecules*, 21, 2610 (1998)



11 NR Measurement of PMTAC Brush/ NaCl D_2O

Apparatus : MINE@JRR-3 TOKAI
Wave length λ = 0.88 nm (Δλ = 2.7%), q = (4 π/λ) sin θ
Irradiated Area (Length on Sample surface) = 55 mm
Inc. angle =0.2°-1.0° : S1=1.0 mm, S2=0.37 mm, DS=10 mm
Inc. angle = 1.0°-2.0° : S1=1.0 mm, S2=0.79 mm, DS=10 mm
Inc. angle = 2.0°-3.0° : S1=1.5 mm, S2=1.31 mm, DS=10 mm
Inc. angle = 3.0°-4.5° : S1=2.0 mm, S2=1.83 mm, DS=10 mm

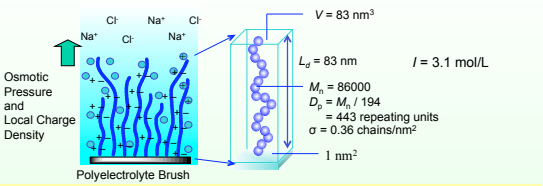
PMTAC Brush
: Mn = 86,000
: Thickness = 46 nm (humidity =50%)



Swollen brush structures were almost same both in pure D_2O and 1.0 M NaCl solution.

M. Kobayashi, Y. Terayama, M. Hino, K. Ishihara, A. Takaharar, *J. Phys.: Conf. Ser.* in-press.

12 Ionic Strength and Polyelectrolyte



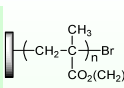
In general, an isolated polyelectrolyte in pure water forms a relatively expanded state due to the electrostatic repulsion of ionic functional groups in the chain, while it would shrink in salt solution by the reduction of electrostatic repulsion between polymer chains.

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

Pincus et al. (*Macromolecules* 1991, 24, 2912-2919)
Klein *et al.* (*Nature* 1994, *370*, 634.)
Ruhe et al. (*Adv. Polym. Sci.* 2004, 165, 79-150)
S. Minko (*J. Macromol. Sci. Part C: Polym Rev.* 2006, 46, 397-420)
Kurihara *et al.*(*Langmuir* 2002, 18, 3932)
Matsuoka *et al.*(*Langmuir* 2004, 20, 6754)

13 NR Measurement of PMTAC Brush/5.6 M NaCl D_2O

Apparatus: MINE@JRR-3 TOKAI
Wave length λ = 0.88 nm (Δλ = 2.7%), q = (4 π/λ) sin θ
Irradiated Area (Length on Sample surface) = 55 mm
Inc. angle =0.2°-1.0°: S1=1.0 mm, S2=0.37 mm, DS=10 mm
Inc. angle = 1.0°-2.0°: S1=1.0 mm, S2=0.79 mm, DS=10 mm
Inc. angle = 2.0°-3.0°: S1=1.5 mm, S2=1.31 mm, DS=10 mm
Inc. angle = 3.0°-4.5°: S1=2.0 mm, S2=1.83 mm, DS=10 mm



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

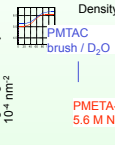
Neutron Reflective Curves and Corresponding Fits

Neutron reflectivity

D_2O

5.6 M NaCl D_2O solution

Neutron Scattering Length Density Profile



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

PMTAC brush / D_2O

PMETA-Cl brush / 5.6 M $NaCl_{aq}$

q / nm^{-1}

Distance from Surface / nm

Brush thickness reduced in 5.6 M NaCl solution.

Molar ratio of [META-Cl]/[D_2O]

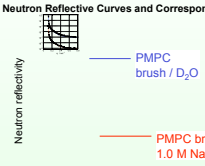
Kyushu University

14 NR Measurement of PMPC Brush at Solution Interface

Apparatus: MINE@JRR-3 TOKAI
Wave length = 0.88 nm (Δλ = 2.7%)
Irradiated Area (Length on Sample surface) = 55 mm
Inc. angle =0.2°-4.5°

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

Neutron Reflective Curves and Corresponding Fits

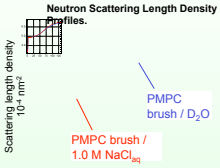


Neutron reflectivity

PMPC brush / D_2O

PMPC brush / 1.0 M $NaCl_{aq}$

Neutron Scattering Length Density Profiles.



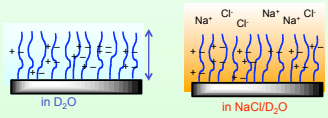
Scattering length density 10^{-4} nm^{-2}

PMPC brush / D_2O

PMPC brush / 1.0 M $NaCl_{aq}$

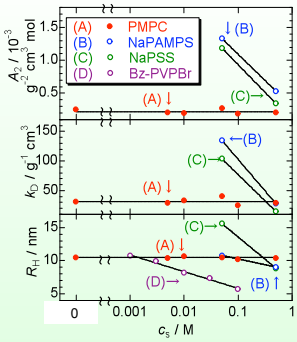
Distance from Surface / nm

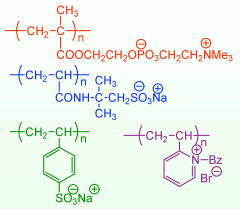
No difference in brush thickness was observed between NaCl solution and pure D_2O



M. Kobayashi, H. Yamaguchi, Y. Terayama, Z. Wang, K. Ishihara, M. Hino, A. Takaharar, *Macromol. Symp.*, 279, 79 (2009).

15 PMPCと他の高分子電解質との比較 （DLS）





水溶液中の塩濃度c_sが増大すると…
一般的な高分子電解質では高分子鎖間の静電反発が弱まるため、A_2、k_Dがは低下する。
高分子鎖内の静電反発が弱まり、高分子鎖が収縮するため流体力学的半径R_Hが減少。

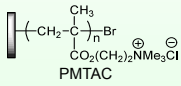
PMPCは分子間相互作用、広がり共に塩濃度にほとんど依存しない極めて特殊な高分子両性電解質と言える。

Y. Matsuda, M. Kobayashi, M. Annaka, K. Ishihara, A. Takahara, *Chem. Lett.* **2006**, *35*, 1310.
Y. Matsuda, M. Kobayashi, M. Annaka, K. Ishihara, A. Takahara, *Langmuir* **2008**, *24*, 8772.

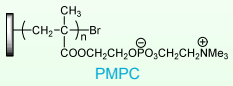
16 Conclusions

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



PMTAC



PMPC

要望など
・S/Nの向上
いかに反射率のBackgroundを低減させるか。1測定に24時間は必要。

Kyushu University