拡大IRT研究会　小角･反射率分科会

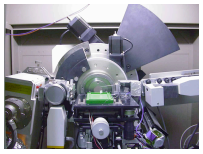
イオン性両親媒性高分子自己組織体

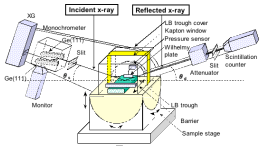
松 岡　秀 樹

京都大学･工学研究科･高分子化学専攻

Air-Water Interface X-ray Reflectometer (XR)

RINT TTR-MA in our laboratory

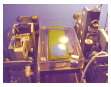


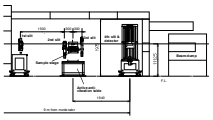


XR ------- Electron Density

Air-Water Interface Neutron Reflectometer (NR)

ARISA at KENS, Japan



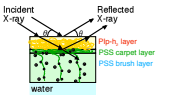


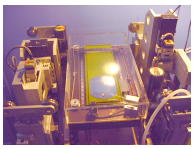
NR ----- Scattering Length Density

Air-Water Interface Neutron Reflectometer (NR)

ARISA-II at J-Parc, Japan

Advanced Reflectometer for Interface and Surface Analysis



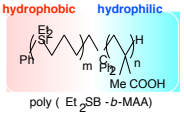


NR ----- Scattering Length Density

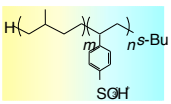
Ionic Amphiphilic Diblock Copolymers for Monolayer Study

Weak Acid　　**Strong Acid**

hydrophobic　hydrophilic

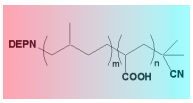


poly (Et_2SB -*b*-MAA)

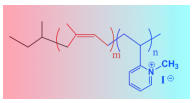


Plp-h-*b*-PSS

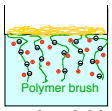
Long hydrophobic chain



Plp-h_2-*b*-PAA



Plp-*b*-PNMe2VP

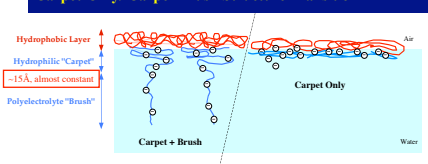


Form insoluble monolayer at air-water interface

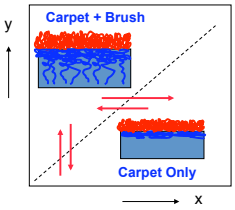
X-Ray,neutron reflectivity

→How different in brush formation mechanism?

Carpet-Only/ Carpe+Brush Structure Transition



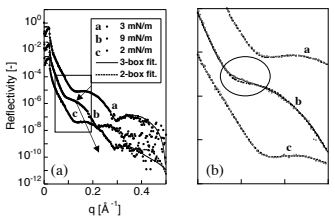
Structure Transition

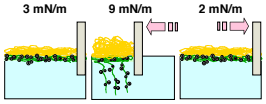


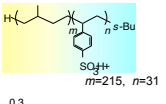
Parameters x, y are…

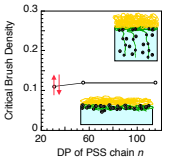
- Hydrophilic Chain Length
  - n = 40 - 50
- Brush Density
- Salt Concentration

Reversibility of Carpet-Only/Carpet+Brush Structure Transition by Compression and Expansion





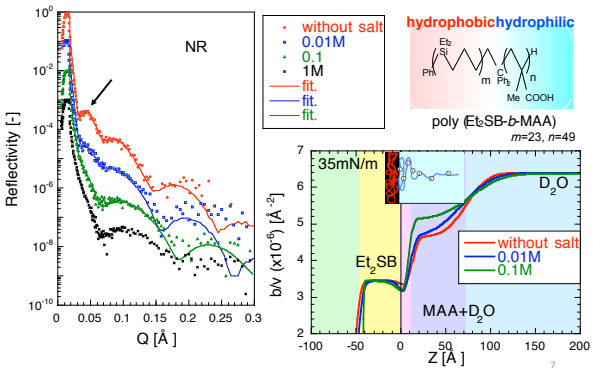




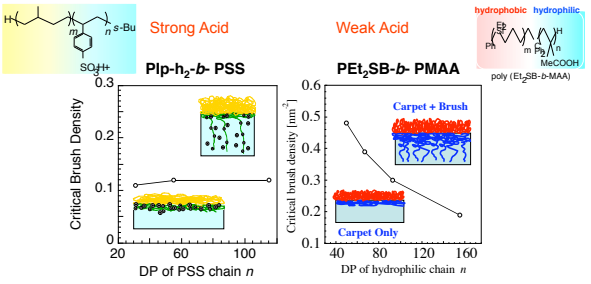
Reversibility was confirmed

Examples of NR data and Scattering Length Density Profile

Comprehensive Use of XR and NR



Hydrophilic Chain Length Dependence of the Critical Brush Density



Important Factor	Electrostatic Repulsion?	Steric Factor? Interface Stabilization?

Brush formation mechanism is different for strong and weak acids?

Critical Salt Concentration

Salt Effect on Strongly Ionic Polyelectrolyte Brush

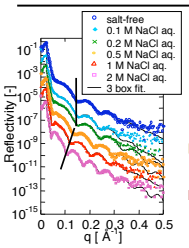
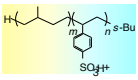
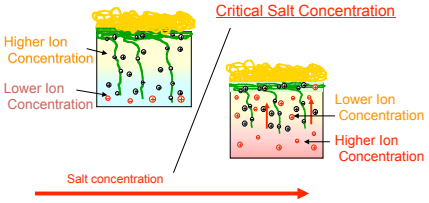


Fig. XR profiles for(lp-h$_3$)$_{220}$ -*b*- (SS)$_{55}$ monolayers on water containing NaCl at various concentrations in subphase at 30mN/m.

Brush nanostructure is not affected by added salt ions because they can not go into the brush layer.

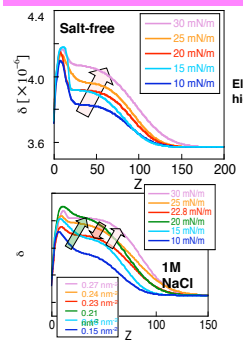




Added small ions go into the brush layer. The brush chains shrink up because the electrostatic repulsion between chain is shielded.

The effective degree of dissociation is ONLY 8%.

Counterion Concentration in Brush Layer During compression

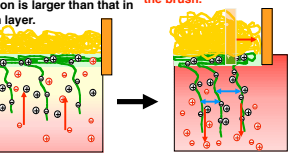


Electron density increased due to high density of PSSNa brush.

Ion concentration in the bulk solution is larger than that in brush layer.

Small Ion Squeezing
Osmotic/Salted Brush Transition by Brush Density

Electron density decreased when salt ions went out of the brush layer and increased again due to high density of the brush.

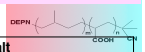


Ion concentration in brush layer became higher then salt ions went out.

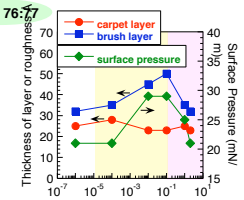
Density profiles for PSSNa layers in salt-free solution (top) and 1M NaCl aqueous solution (bottom).

Salt effect on PAA brush layers

At constant brush density



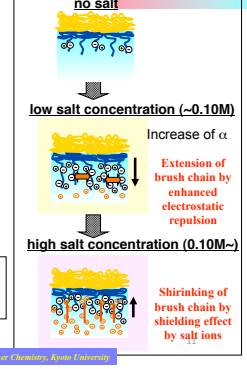
m:*n* = 76:77



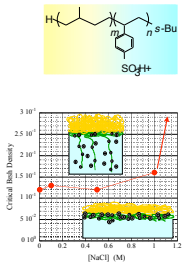
The salt effect on (lp-h$_2$)$_m$-*b*-(AA)$_n$ (*m*:*n* = 76:77) monolayer on the water surface at same brush density(≒0.50 nm^{-2}).

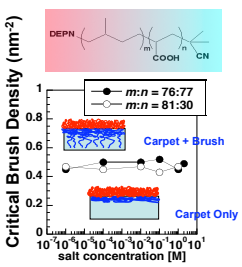
- Constant carpet layer thickness (18~30 Å)
- Brush layer thickness shows maximum at 0.10M
- Surface pressure also shows maximum at 0.10M

→ Change of degree of dissociation α of PAA



Salt concentration dependence of critical brush density





Salt Concentration Dependence --- NR Profiles

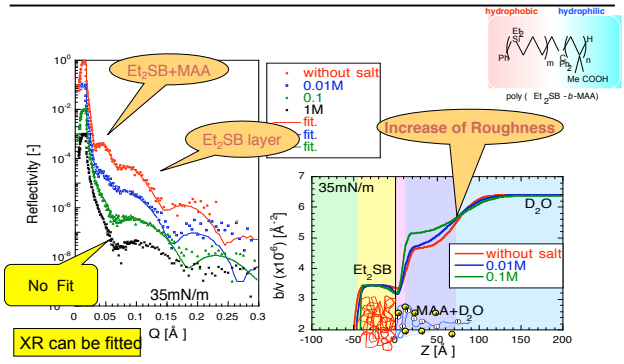
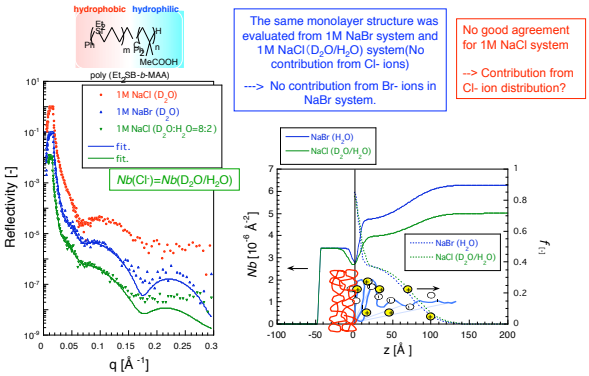


Fig. NR profiles and scattering density profiles for poly(Et_2SB-d_{10})$_{23}$-*b*-poly(MAA)$_{49}$ monolayer monolayer on subphase with different NaCl concentrations at 35mN/m

Contrast-Variation by NR --- Small Ion distribution



The same monolayer structure was evaluated from 1M NaBr system and 1M NaCl (D_2O/H_2O) system(No contribution from Cl- ions)

---> No contribution from Br- ions in NaBr system.

No good agreement for 1M NaCl system

--> Contribution from Cl- ion distribution?

Fig. NR profiles and scattering density profiles for poly(Et_2SB-d_{10})$_{23}$-*b*-poly(MAA)$_{49}$ monolayer monolayer at 35mN/m on various subphase.

Possible Cl- ion Distribution

1M NaCl (D2O) profile was well fitted with taking the Cl- ion distribution into account with the same monolayer structure determined y contrast matching method.

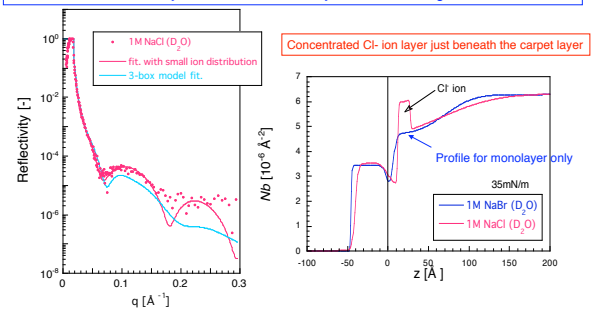
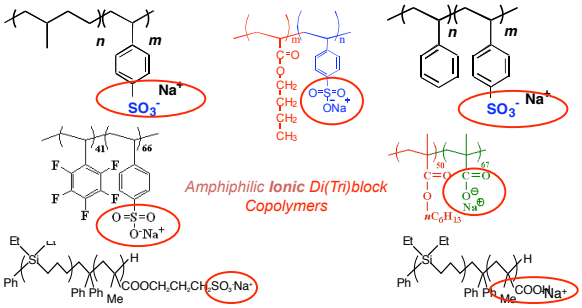


Fig. NR profiles with fitting curve in which Cl- ion distribution is considered. (left)

Scattering length density obtained by the fitting. (right)

These Polymers are Non-Surface Active!

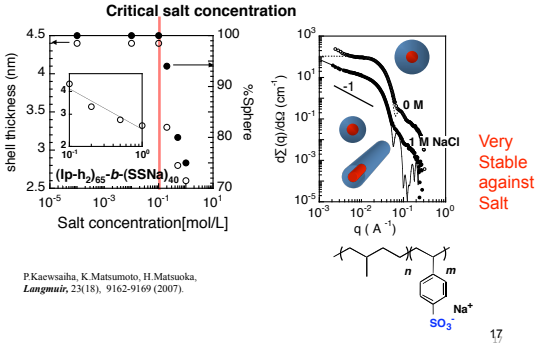
Non-surface active but form micelles in solution



These polymers become "Non-Surface Active" under suitable conditions of m:n and ionic strength

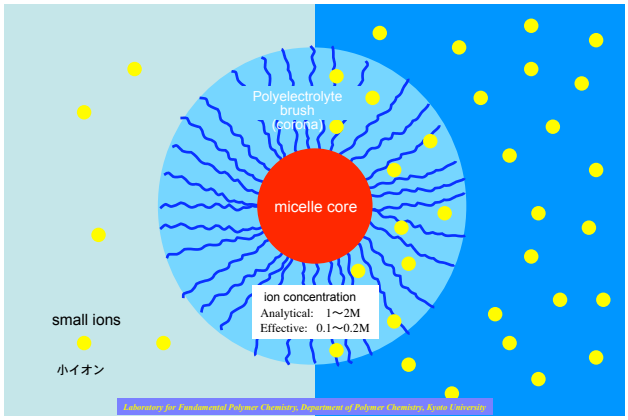
Sphere/Rod Transition and Micelle Structure Parameters

SANS Analysis



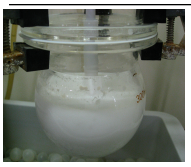
P.Kaewsaiha, K.Matsumoto, H.Matsuoka, ***Langmuir,*** 23(18), 9162-9169 (2007).

Mechanism of High Stability against Salt Addition of Polyelectrolyte Grafted Particles

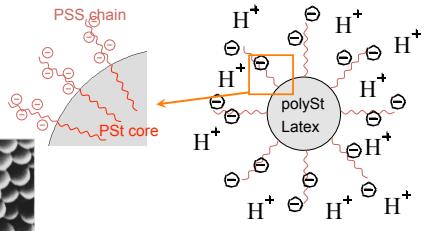


Application as an Emulsifier

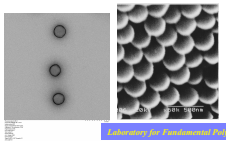
Synthesis of polyelectrolyte grafted colloidal particle



St_{57}-*b*-$SSNa_{59}$ — Styrene, $K_2S_2O_8$, H_2O, 70°C — Dialysis, ion-exchange



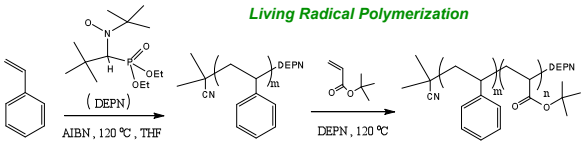
Emulsion Polymerization with no foam

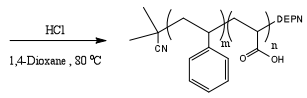


Control of "Non"-Surface Activity

Synthesis of Amphiphilic Diblock Copolymer with Weak Acid

Living Radical Polymerization





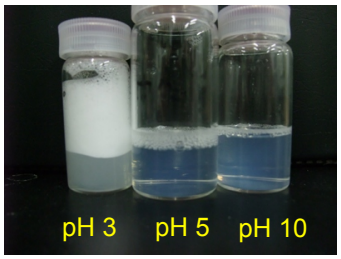
PSt-*b*-PAA

Sample #	m:n	Mw/Mn
1	50:51	1.33
2	27:51	1.32
3	58:142	1.28

Foam Formation Behavior of St_{50}-*b*-AA_{51}

Surface Active ⟷ pH ⟶ Surface "***Non***"-Active

Very Good Foam Formation



Almost No Foam

[polymer]=2.5 mg/ml

今後の予定・展望

- 水面カチオン性ブラシのNR測定
- 水面ポリベタインブラシの NR測定
- 高分子電解質ブラシ中の小イオン分布の評価
- 準弾性（？）NR による高分子電解質ブラシのダイナミクス
- SANSによる界面活性／不活性転移高分子のミセル構造
- iNSEによる高分子電解質コロナのダイナミクス