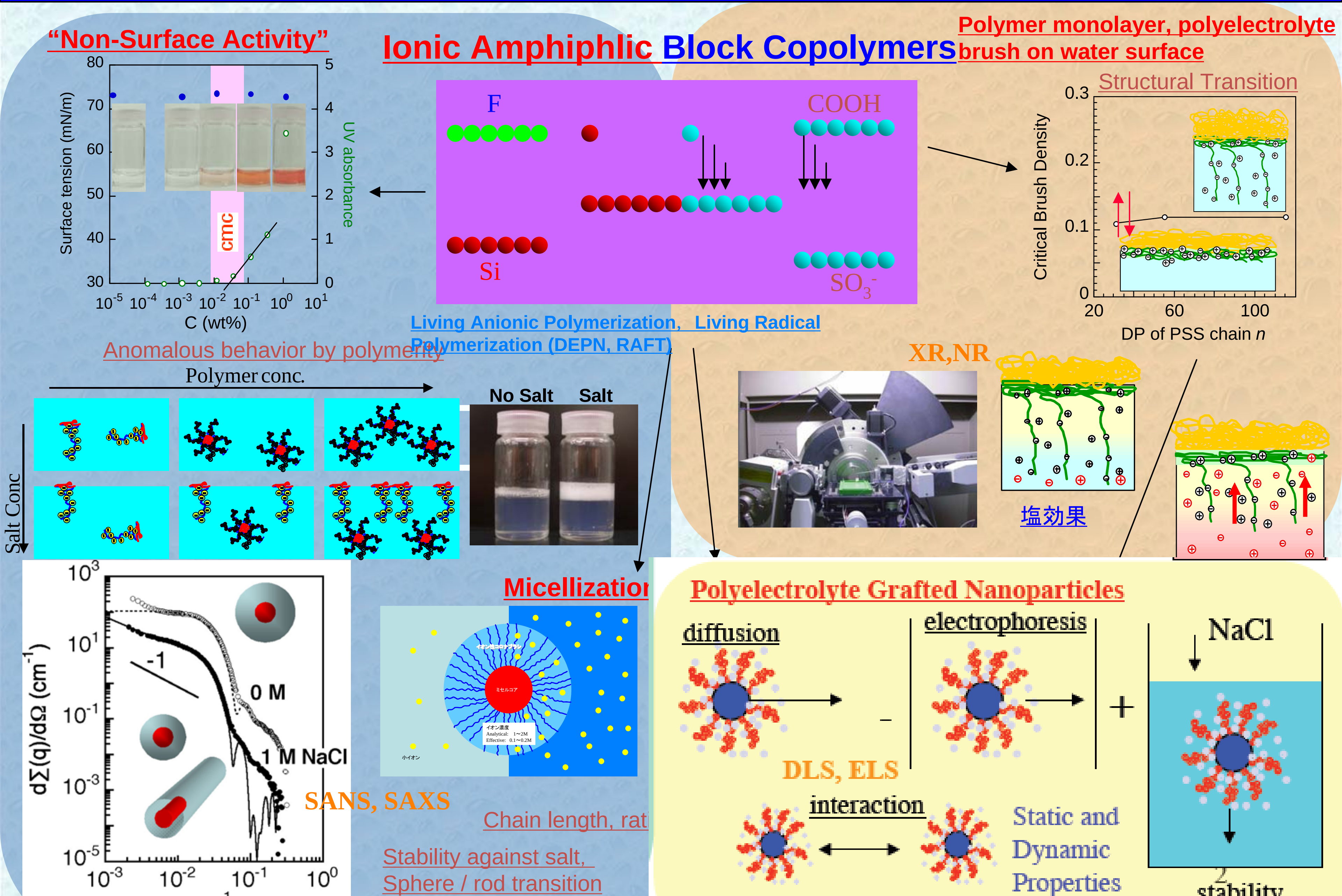
SANS・SAXSによるソフトマター研究

― 高分子ミセルのナノ構造解析を中心として ―

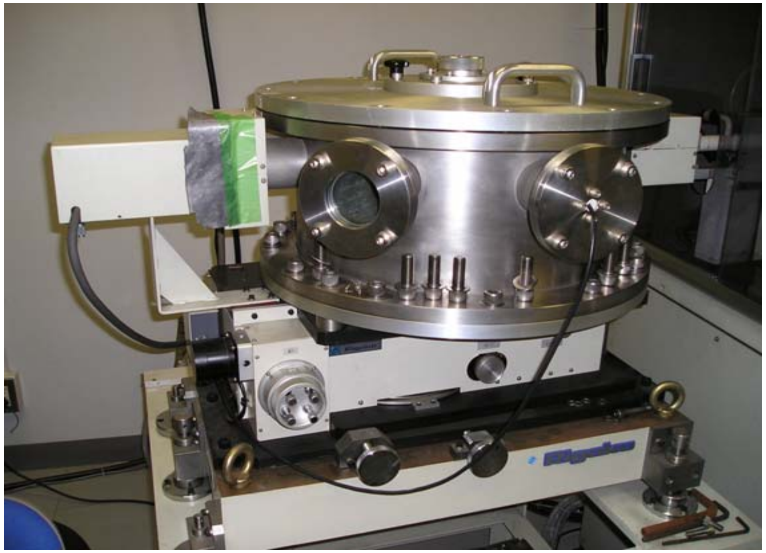
京都大学･工学研究科･高分子化学専攻

松 岡　秀 樹

Research Interests



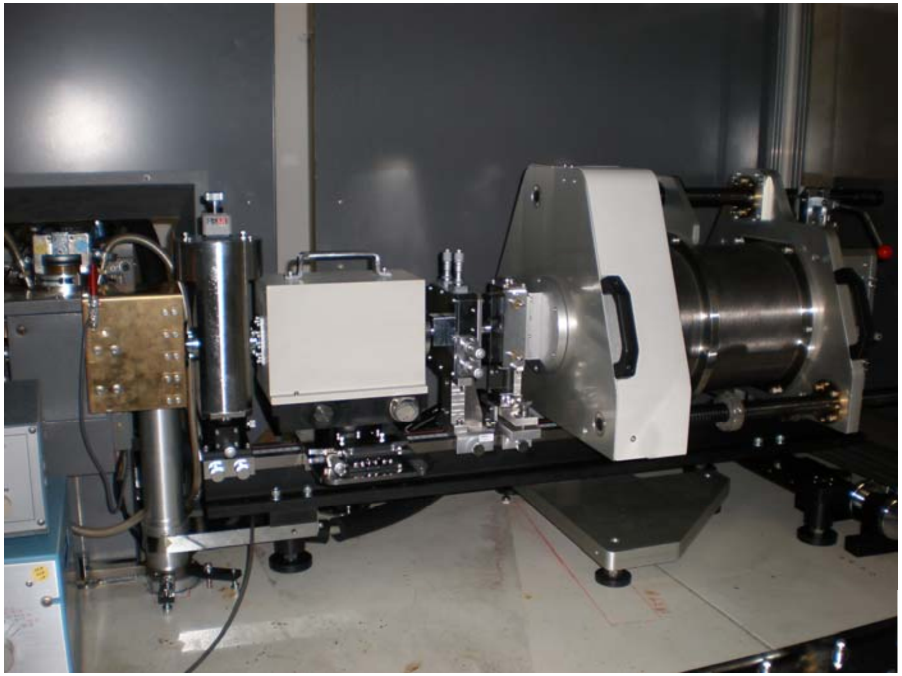
Matsuoka Laboratory, Department of Polymer Chemistry, Kyoto University



超小角 X 線散乱装置
(USAXS)

X 線小角散乱装置
(SAXS)

Upgrade!!



"Ordered" structure in dilute solutions of sodium polystyrenesulfonates as studied by small-angle x-ray scattering[a)]

Norio Ise,[b)] Tsuneo Okubo,[b)] Shigeru Kunugi,[b)] Hideki Matsuoka,[b)] K. Yamamoto,[b)] and Yasuo Ishii[c)]
Department of Polymer Chemistry, Kyoto University, Kyoto and Tochigi Research Laboratories, Kao Corporation, Ichikai-machi, Haga-gun, Tochigi, Japan

3294 J. Chem. Phys. 81 (7), 1 October 1984 0021-9606/84/193294-13$02.10

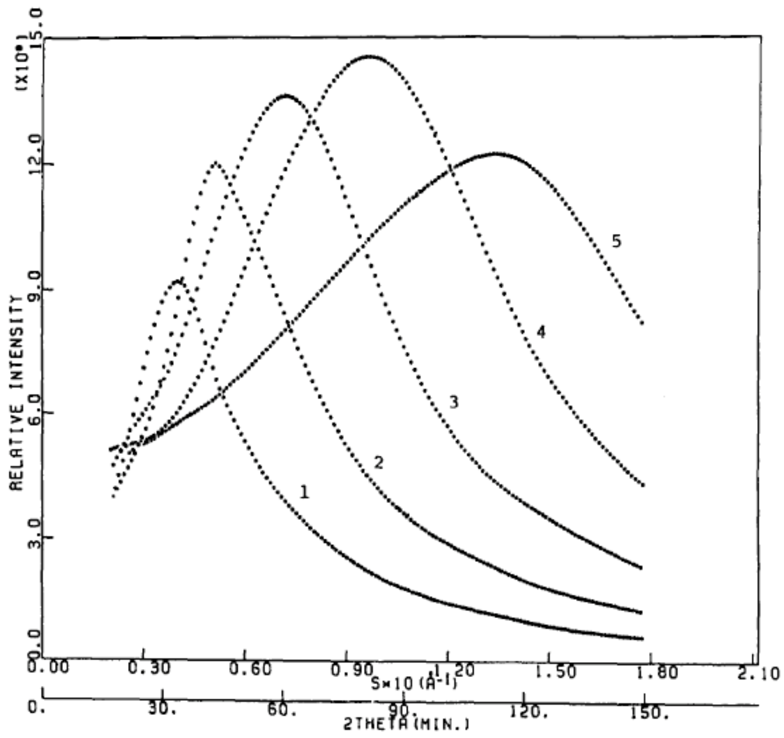
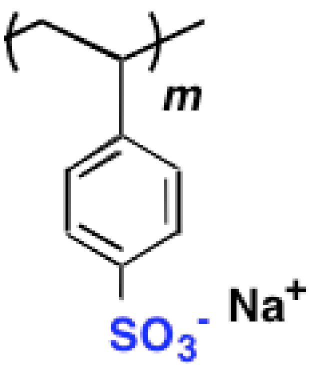


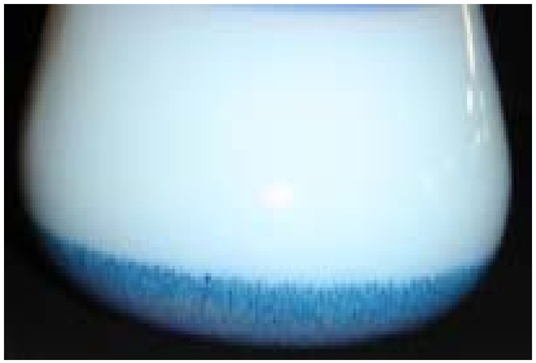
FIG. 6. Concentration dependence of scattering curves of NaPSS. $M_w = 74\,000$, polymer concentration; curve 1:0.01 g/ml, 2:0.02 g/ml, 3:0.04 g/ml, 4:0.08 g/ml, 5:0.16 g/ml.



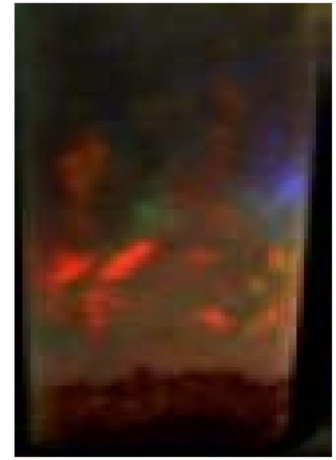
ポリスチレンスルホン酸ナトリウム

Colloidal Crystal of polyelectrolyte grafted latex particles

S2



S2



Colloidal Crystal of polyelectrolyte grafted latex particles

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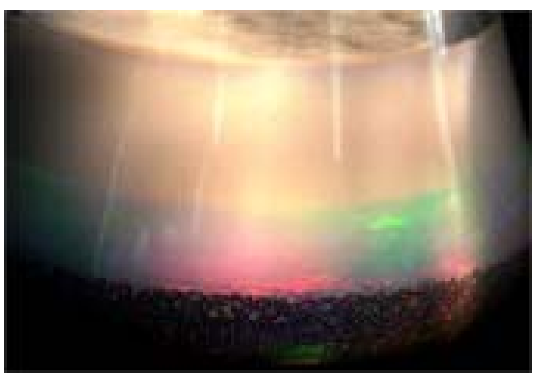
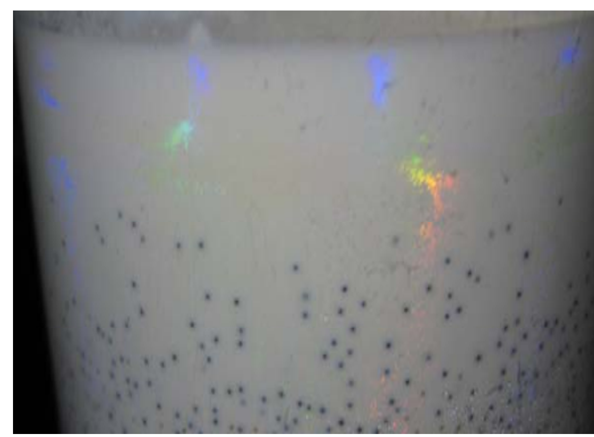
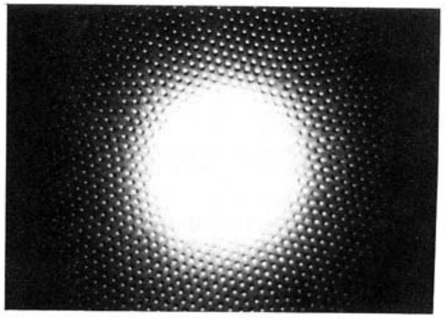


G2



コロイド結晶の解析例



ポリスチレンラテックスが形成する規則構造。六方対称の構造が全面に拡っている。隣接する二粒子の中心間距離は約1000nm。

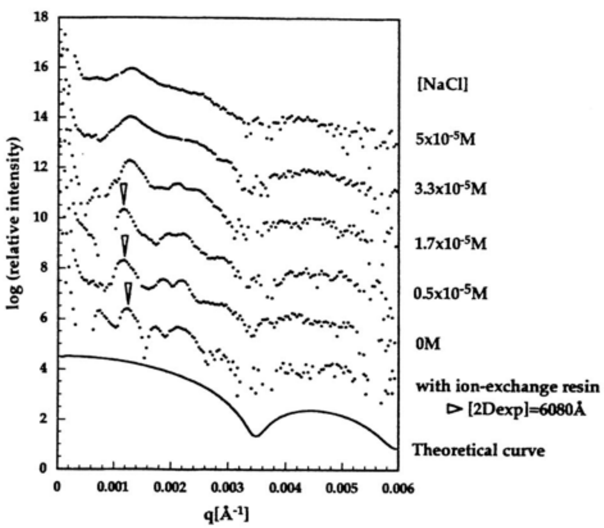


Figure 1. USAXS curves of MS30 latex dispersed in water at various salt concentrations. [Latex] = 4.3 vol %. The ordinate has been shifted by 2 decades to avoid superimposing the data. The solid line (at the bottom) is the theoretical curve for an isolated sphere of diameter 2600 Å with polydispersity 4% which was used for the function $P(q)$.

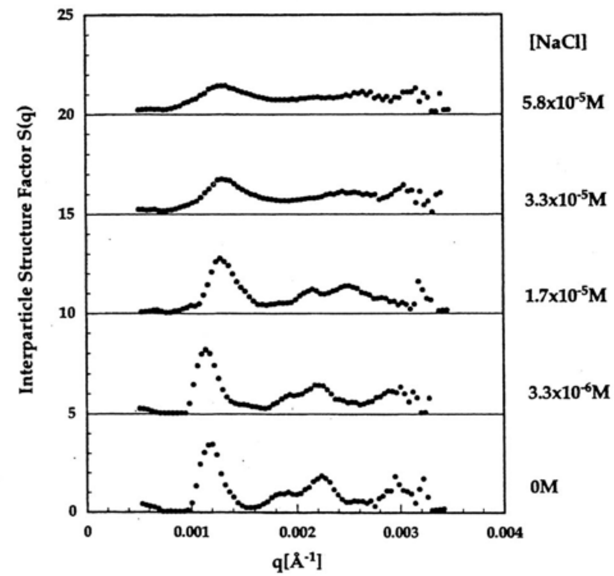
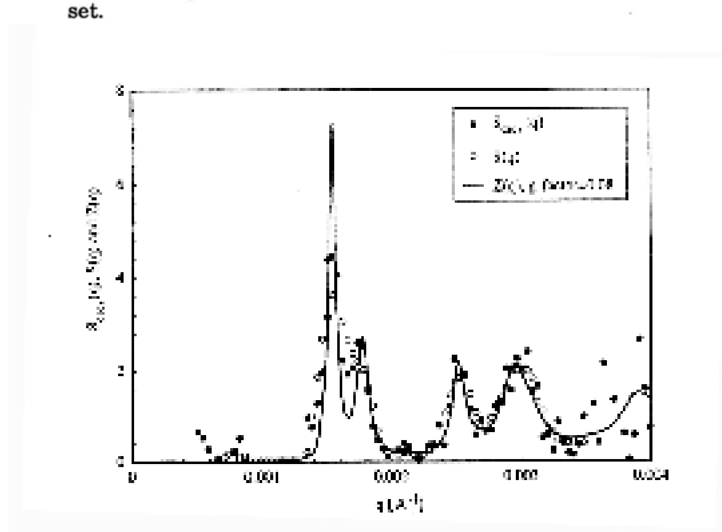


Figure 2. Interparticle structure factor $S(q)$ for an MS-30 latex dispersion ([latex] = 4.3 vol %) obtained from the USAXS profiles shown in Figure 1. The ordinate has been shifted for each data set.



コロイド結晶の三次元パラクリスタル理論による解析

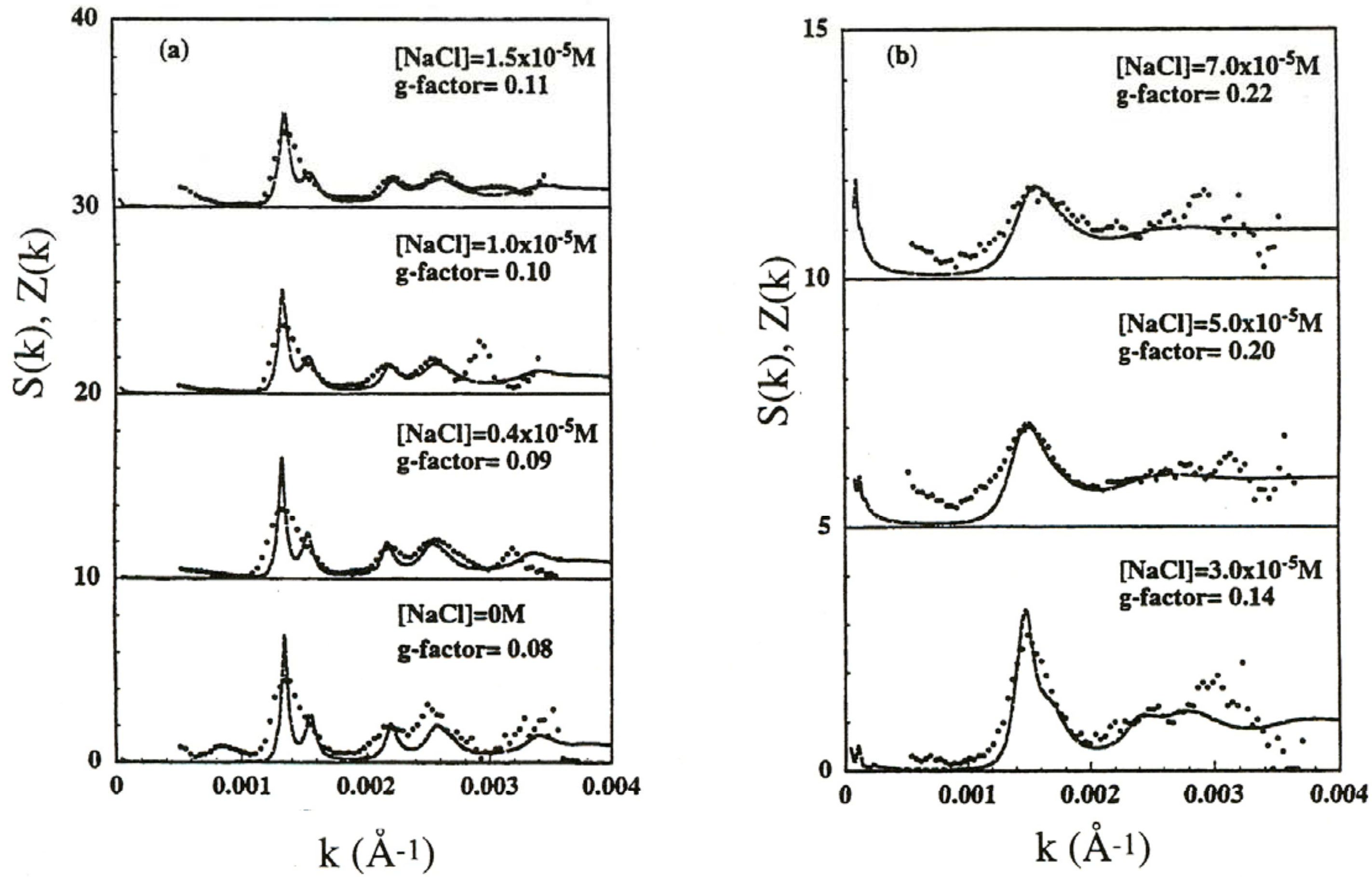


図22　コロイド結晶からのUSAXSデータより得られる粒子間構造因子$S(k)$の三次元パラクリスタル格子因子$Z(k)$でのフィッティング．このフィッティングによりコロイド結晶の種々の条件下での「乱れの程度」が定量できる．[32)]（The interparticle structure factor $S(k)$ for colloidal crystal and fitted results by 3D-paracrystal theory.）

PHYSICAL REVIEW E VOLUME 53, NUMBER 2 FEBRUARY 1996

Evaluation of the counterion distribution around spherical micelles in solution by small-angle neutron scattering

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George D. Wignall
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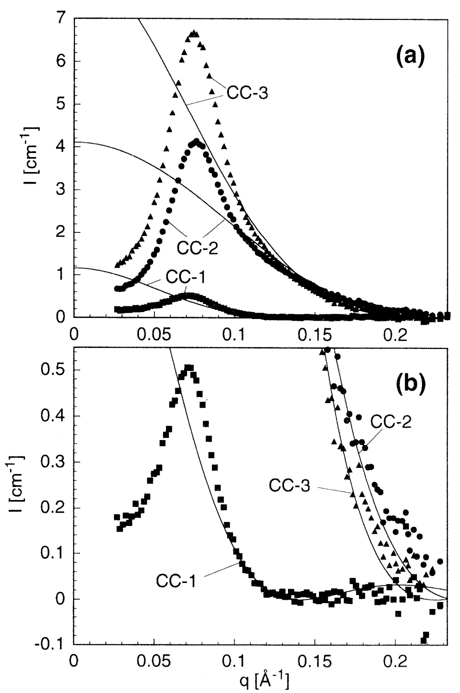


FIG. 1. $I_{\mathrm{expt}}(q)$ (■, ●, and ▲) and $n_p P(q)$ (——, calculated with the CSI model) of 6-vol % samples at three contrast conditions (Table II) plotted against scattering vector q. (a) and (b) are different only in their I scale.

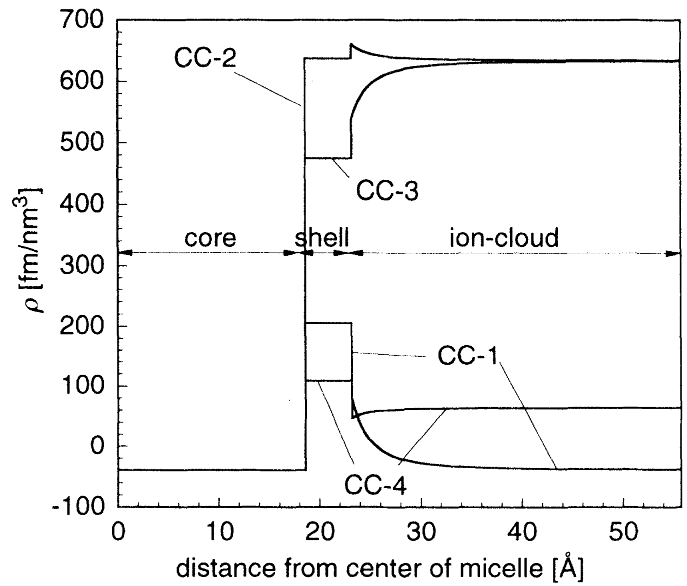
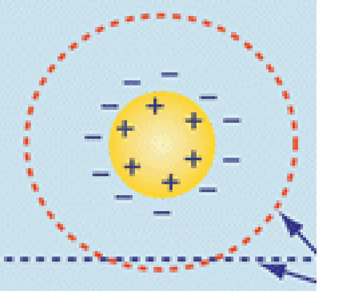


FIG. 4. Scattering length densities ρ of 6-vol % samples in the CSI model as functions of the distance from the center of a micelle r at four contrast conditions (see Table II).



Langmuir **2000**, *16*, 9177−9185 9177

Neutron Spin−Echo Study of the Dynamic Behavior of Amphiphilic Diblock Copolymer Micelles in Aqueous Solution

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Institute für Festkörperforschungs, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

Hideki Seto and Youhei Kawabata

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Neutron Scattering Laboratory, Institute of Solid State Physics, The University of Tokyo,

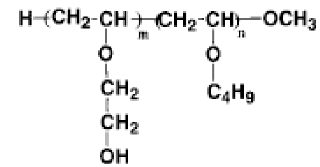


Figure 1. Structure of amphiphilic diblock copolymer used in this study.

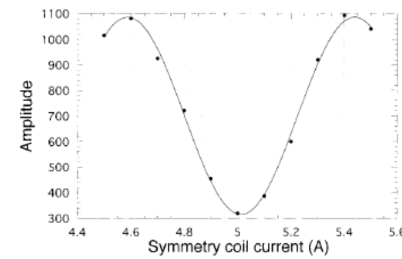
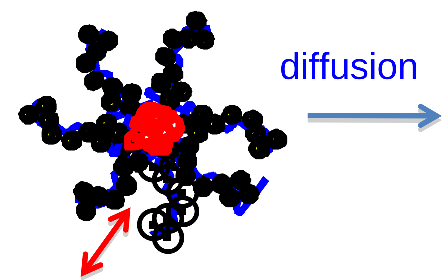


Figure 4. Typical example of echo signal at 21 °C for 5% N496; where q is 0.06 Å^{-1}.



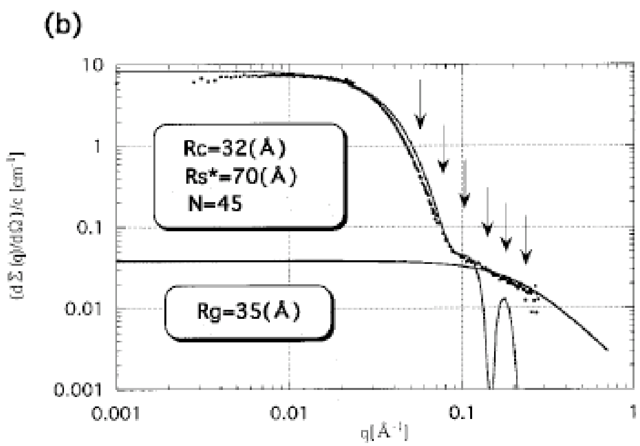


Figure 3. Model fitting of SANS profiles for N496 (a) and N338 (b) in 1 wt % D_2O solutions at 25 °C. The dots are the experimental data, the gray line (upper line in the small q region and with peak in large q region) was obtained by the core−shell spherical model. R_c is the core radius, R_s is the radius of core + shell, and N is the aggregation number (N_{agg} in Table 1). The black line (lower curve in the low q region which shows monotonical decrease) is the fitting curve for a higher q region ($q > 0.1$) by Debye function for the scattering from Gaussian coil. R_g is the radius of gyration of the coil (R_{gGauss} in Table 1).

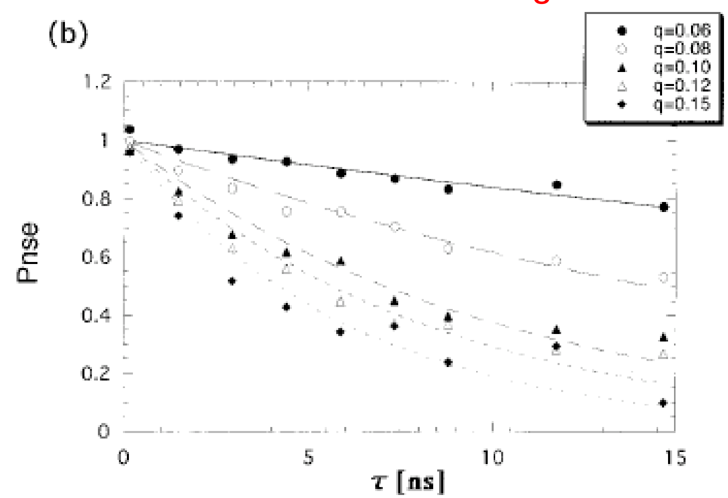
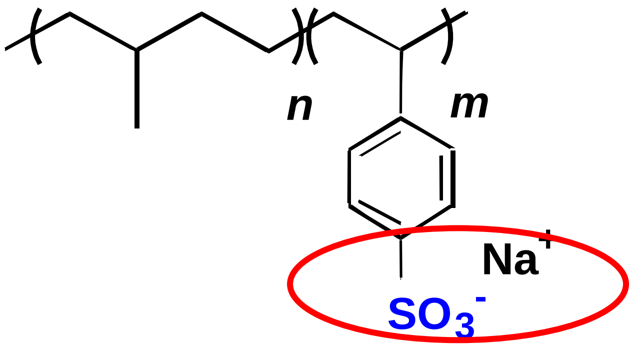
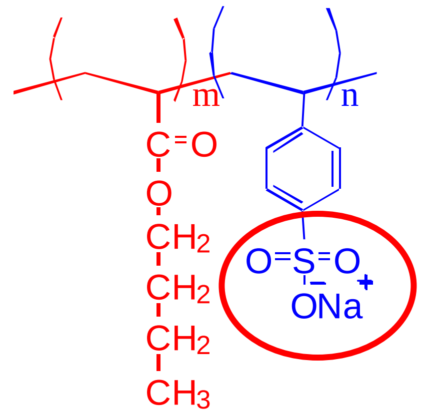


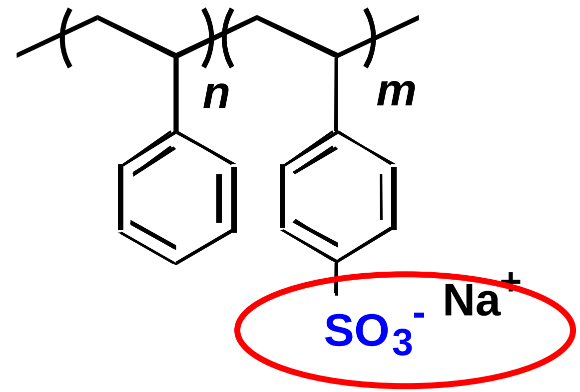
Figure 5. The time correlation function obtained by NSE (P_{nse}) for N496 micelles in 5% D_2O solution at 21 °C (a) and 45 °C (b). The solid and dotted lines show the best-fit curves obtained by single-exponential fitting.

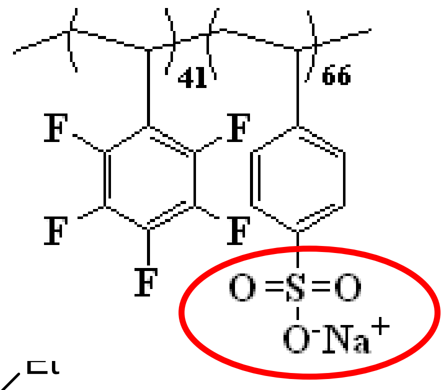
These Polymers are Non-Surface Active!

Non-surface active but form micelles in solution

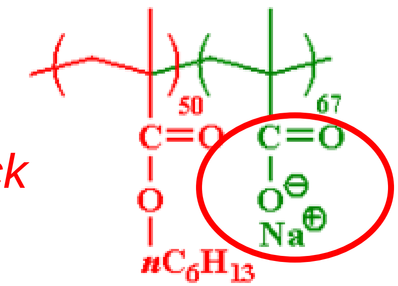


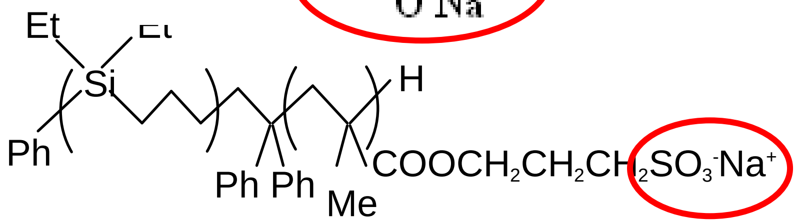


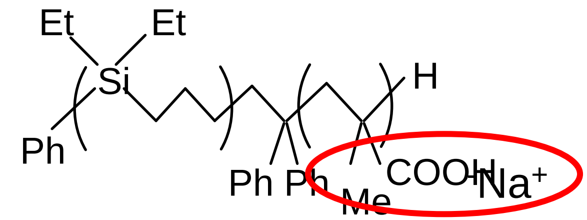




Amphiphilic ***Ionic*** *Di(Tri)block Copolymers*







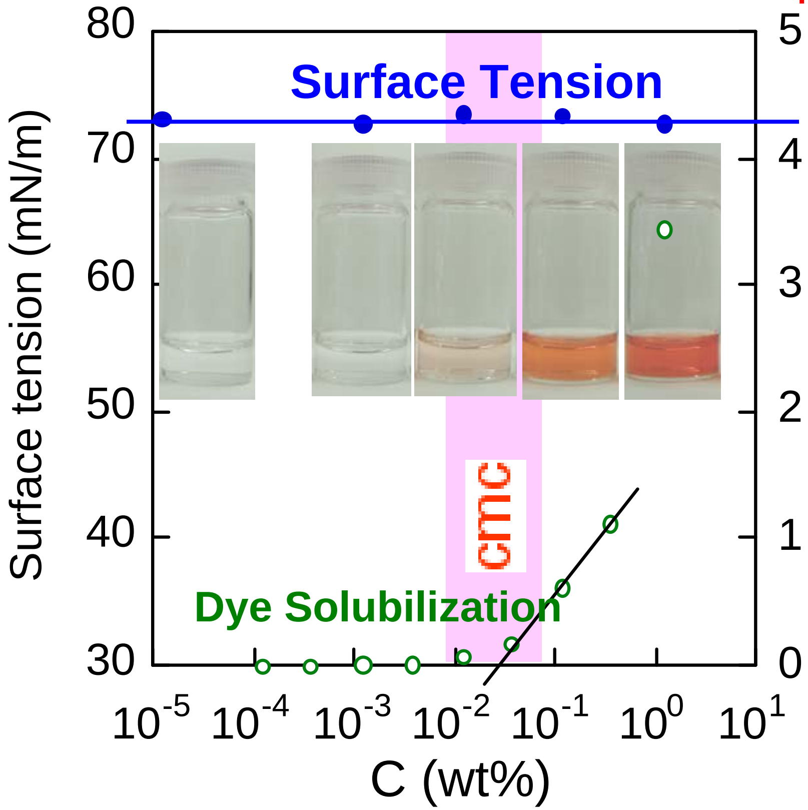
<u>These polymers become “Non-Surface Active” under suitable conditions of m:n and ionic strength</u>

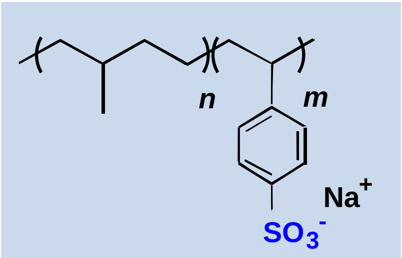
Micelle Formation but No-Adsorption

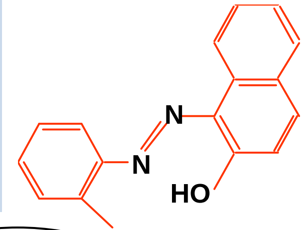
Surface tension does not decrease, but cmc is detected by dye solubilization

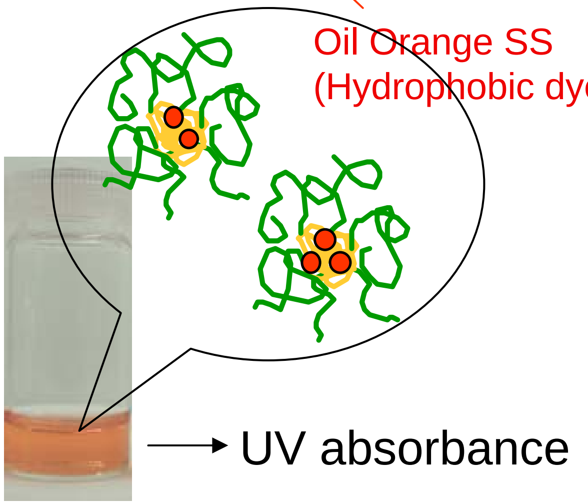
● : surface tension of aqueous solution
○ : UV absorbance of aqueous solution

Surface tension does not reduce.
Very low foam formation activity. (no salt)
However, there are micelles in solution.









Surface tension of $(Ip\text{-}h2)_6$ -*b*-$(SSNa)_{50}$ aqueous solutions and hydrophobic dye adsorption (495 nm) as a function of polymer concentration.

Foam Formation and Salt Effect

Good foam formation by salt addition, which is quite different from "normal surfactant"

Low-molecular weight ionic surfactant

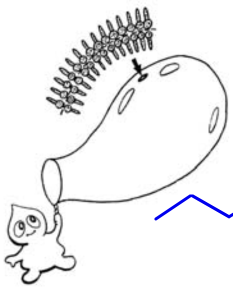
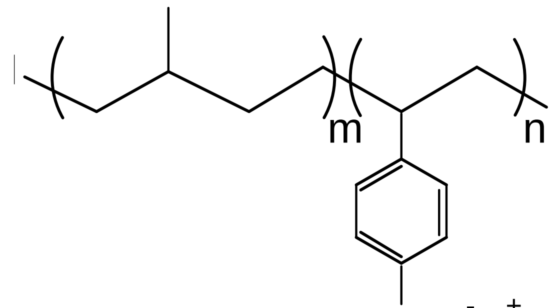
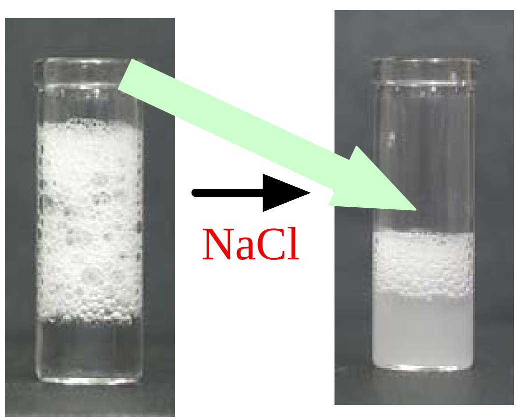
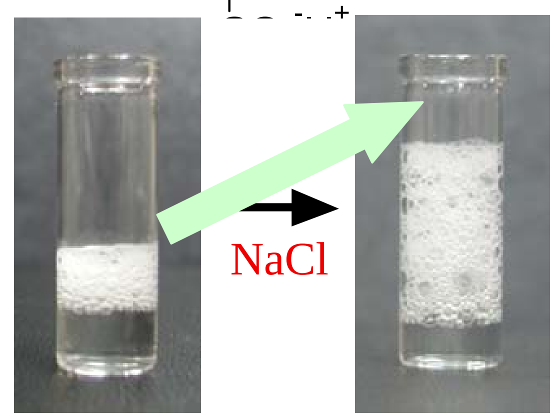


図4.18 シャボン玉の分子膜

Ionic amphiphilic diblock copolymer



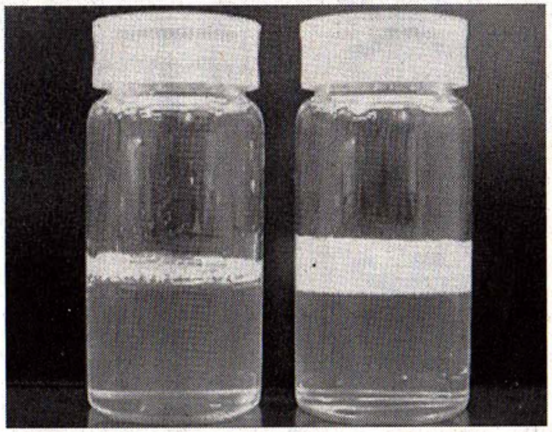




Matsuoka Laboratory, Department of Polymer Chemistry, Kyoto University

京　都　新　聞　　2008年(平成20年)6月28日　土曜日

開発された高分子は水に溶かしても泡立ちにくい(写真左)が、塩(ＮａＣｌ)を入れるとよく泡立つ＝松岡秀樹京大准教授提供



塩水で泡立つが　水では泡立たず

常識破り 高分子

京大准教授ら開発　薬剤体内に運ぶ容器にも

せっけんはイオンを多く含む海水や硬水では泡立たなくなるが、京都大工学研究科の松岡秀樹准教授(高分子化学)らの研究グループが、せっけんとは逆に「水だと泡立たず、塩を入れると泡立つ」不思議な高分子を開発した。常識破りの新物質だが、「せっけんのように、ちゃんと油汚れを落とせる」(松岡准教授)という。

せっけんのように、水になじむ部分(親水基)と油となじむ部分(疎水基)でできている。せっけん分子は親水基が一つだが、この高分子は親水基と疎水基がそれぞれ五十ぐらいずらっと並んでいる。

この独特な構造によって、「鏡像電荷」と呼ばれる界面(表面)からの反発力が強く生じるらしい。反発力が強いため水に溶かしてもせっけん分子のように水面に並ばないが、塩などのイオンがあると反発力が弱まり、水面に分子が並んで泡立つようになると推定される。

疎水基と親水基があるので、分子が集まった会合体(ミセル)が形成され、その中に油汚れもしっかりと取り込むことができる。松岡准教授は「ミセルは非常に安定した構造なので、薬剤を体内に運ぶ容器として使えるかもしれない」という。

塩水で泡立つが水では泡立たず 京大准教授ら開発

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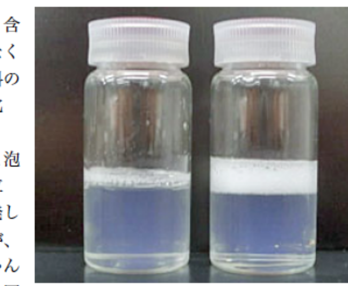

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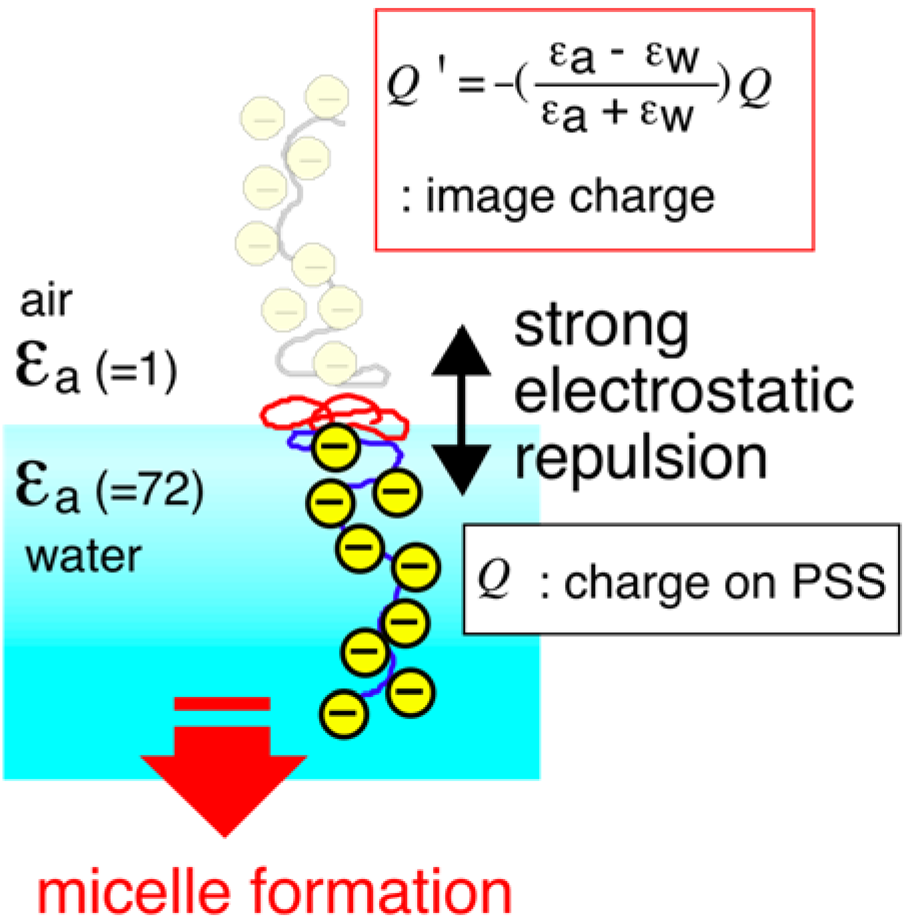
←ひとつもどる

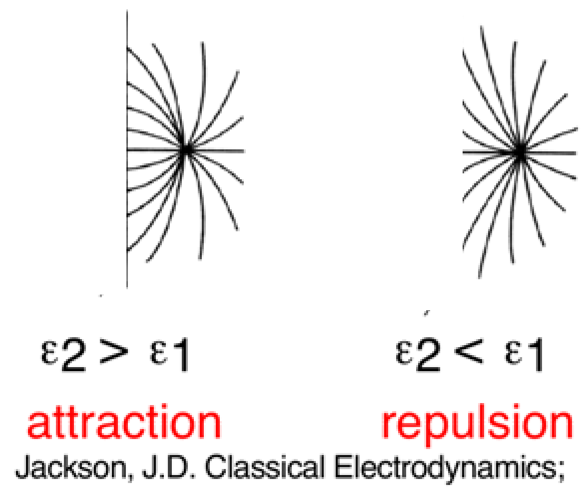
Image Charge at the Interface

----- The Origin of “*Non-Surface Activity*”

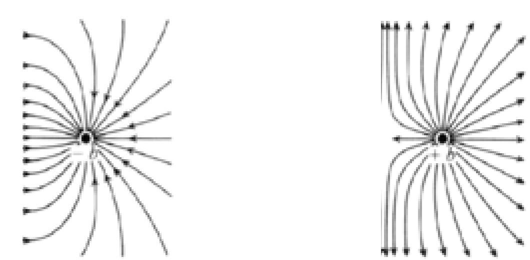
The image charges repulsion prevents polymer adsorption at water surface.



interface between two medea with different dielectric constant ε



in the same medium

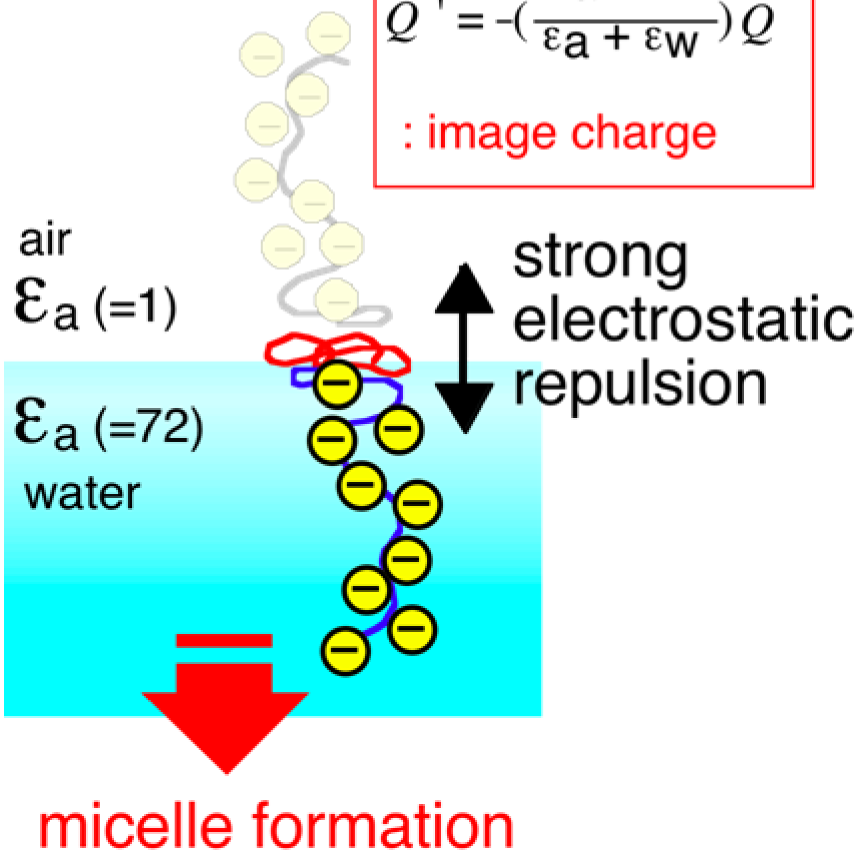


高分子と低分子における鏡像電荷効果

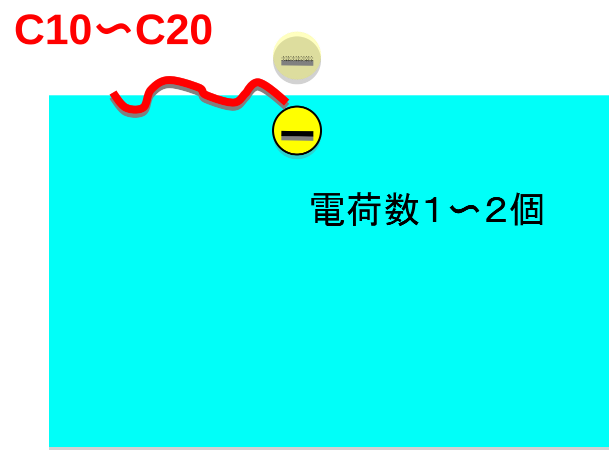
高分子

$$Q' = -\left(\frac{\varepsilon_a - \varepsilon_w}{\varepsilon_a + \varepsilon_w}\right) Q$$

: image charge



低分子

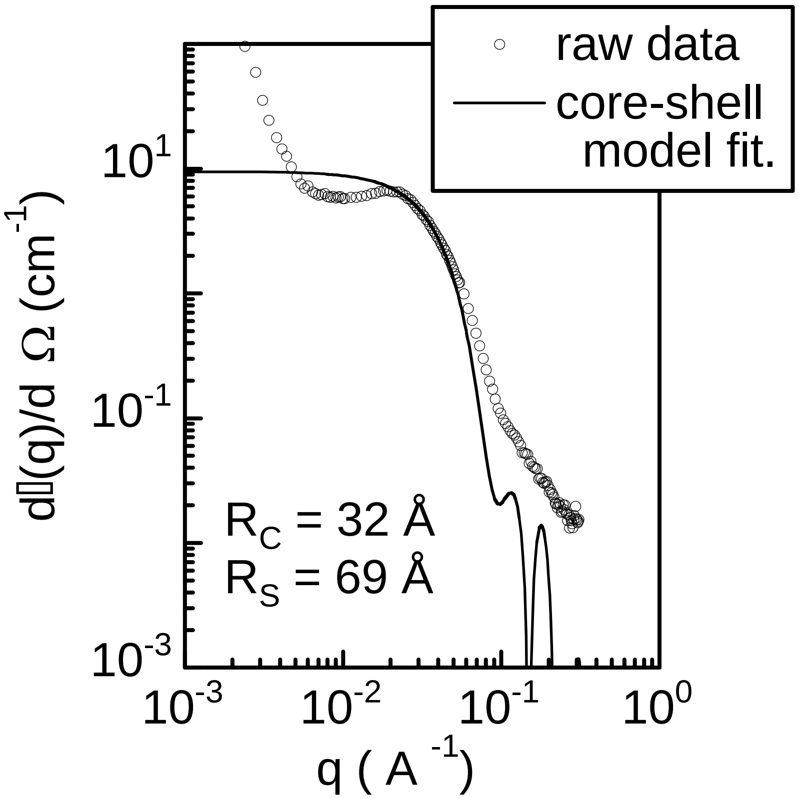


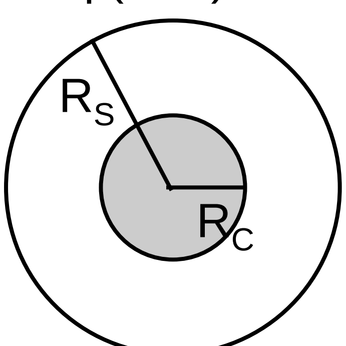
電荷数が多く，疎水吸着に勝る場合がある.

鏡像電荷効果はあるが，疎水吸着が勝る.

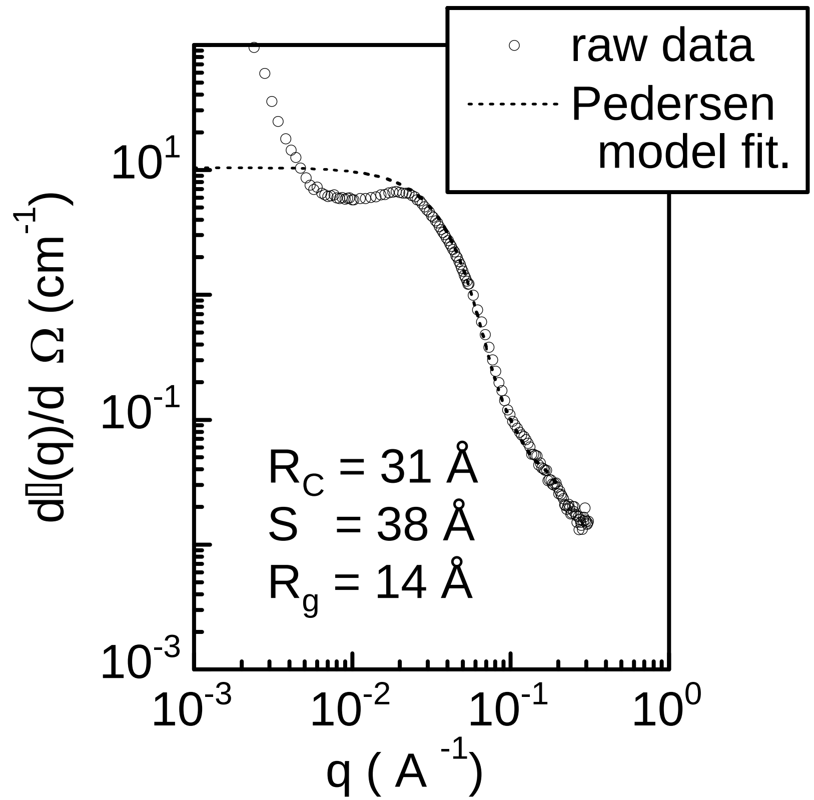
Structure Analysis of Polymer Micelle by SANS

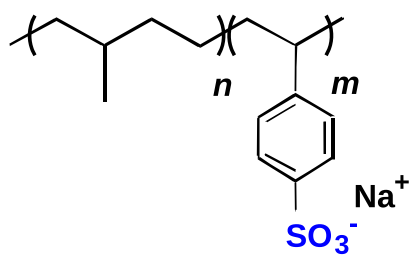
Core-Shell Model



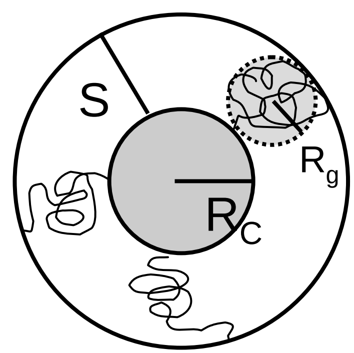


Pedersen Model





(25:40)



Core-Corona Model and Effect of Polydispersity

SAXS

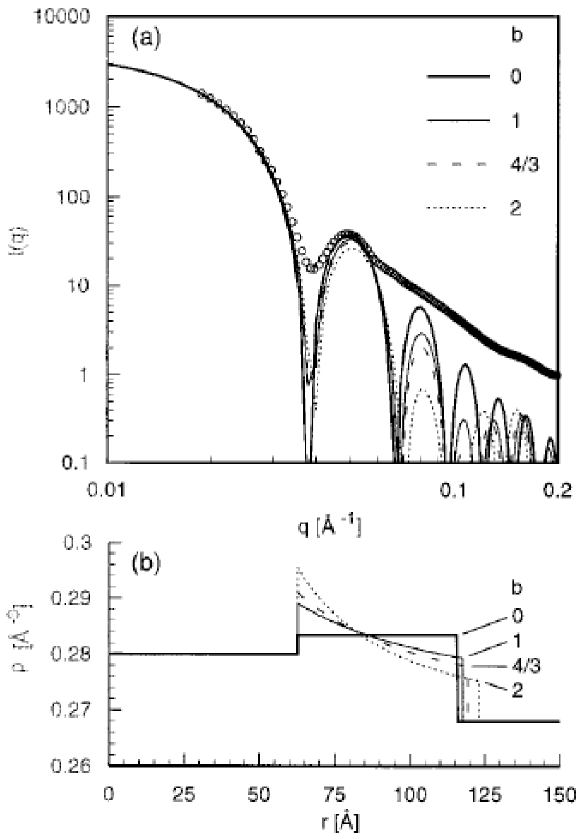


Figure 2. SAXS profile of polymer A (m:n = 26:24) in methanol with theoretical curves of the core−corona model. The curve $b = 0$ corresponds to the simple core−shell model.

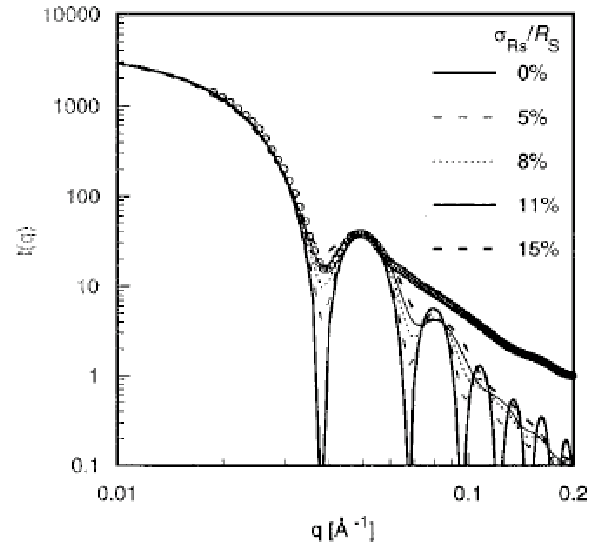
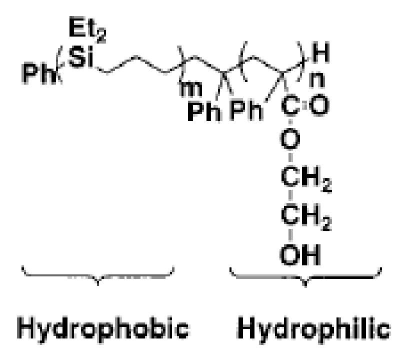
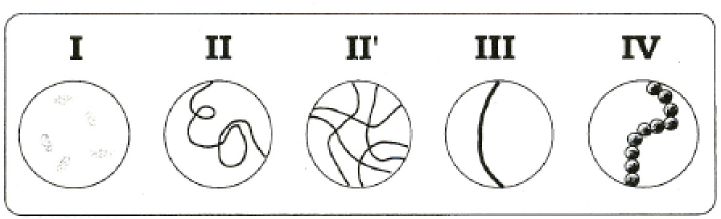


Figure 3. SAXS profiles of polymer A (m:n = 26:24) methanol with theoretical curves of the simple core−shell model, taking the micellar size distribution into consideration.



$$\phi_{\mathrm{HEMA}}(r) = a(r/R_C)^{-b} \quad \text{for } R_C < r < R_S$$

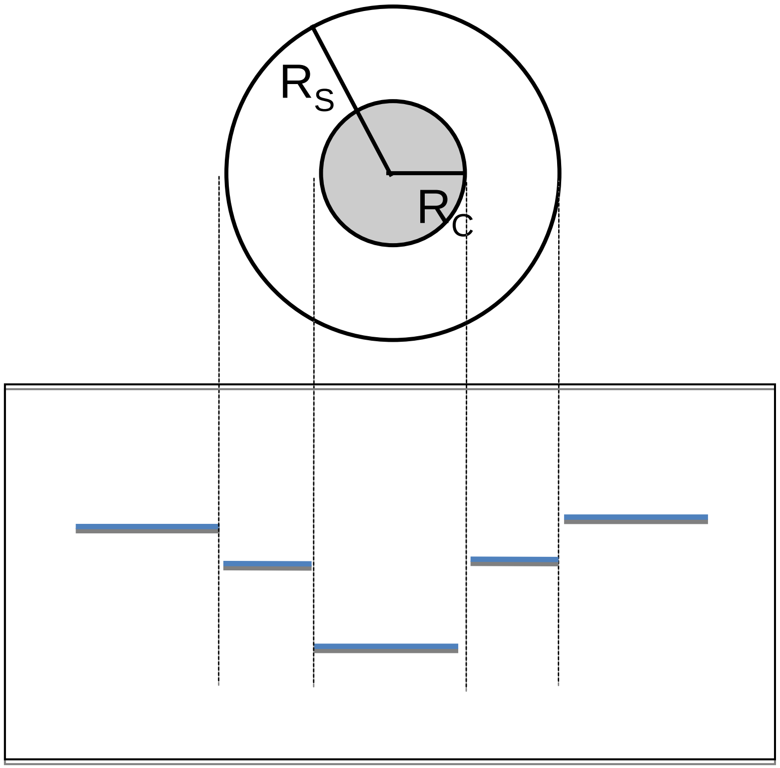
$$\phi_{\mathrm{HEMA}}(r) = 0 \quad \text{for } R_S < r$$



Ref: M.Nakano et al., *Macromolecules* ***1999, 32, 7437-7443***

Structure Analysis of Polymer Micelle by SANS

Core-Shell Model

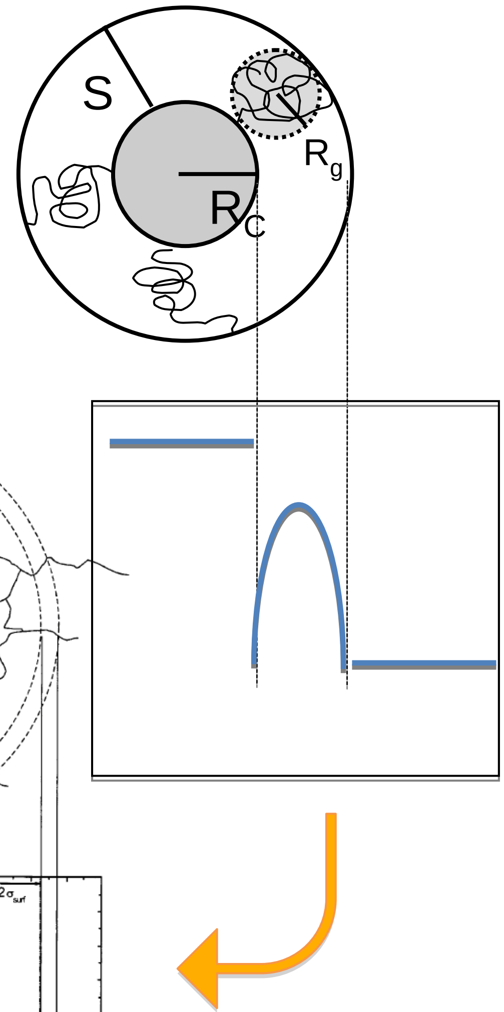


$$P(q)_{\mathrm{sphere}} = \{(\rho_C - \rho_S)V_C F_C(q)_{\mathrm{sphere}} + (\rho_S - \rho_0)V_S F_S(q)_{\mathrm{sphere}}\}^2$$

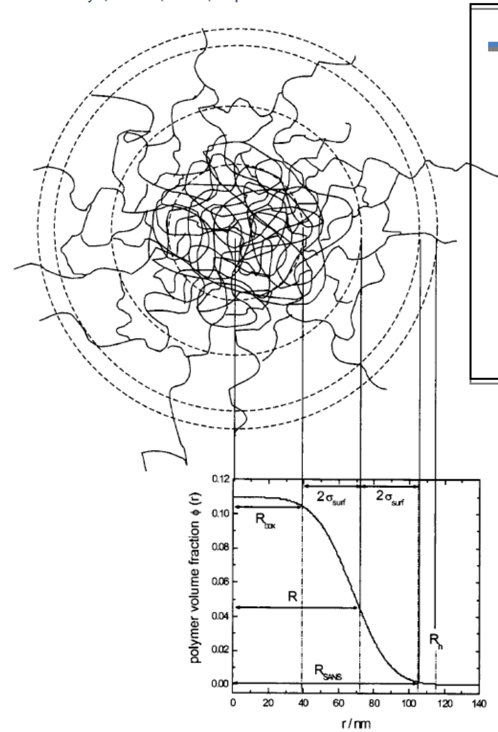
$$F_C(q)_{\mathrm{sphere}} = \frac{3(\sin(qR_C) - qR_C\cos(qR_c))}{(qR_C)^3}$$

$$F_S(q)_{\mathrm{sphere}} = \frac{3(\sin(qR_S) - qR_S\cos(qR_S))}{(qR_S)^3}$$

Pedersen Model



J. Chem. Phys., Vol. 120, No. 13, 1 April 2004



Matsuoka Laboratory, Department of Polymer Chemistry, Kyoto University

Cryo-TEM Image of Polyelectrolyte Grafted Latex Particles

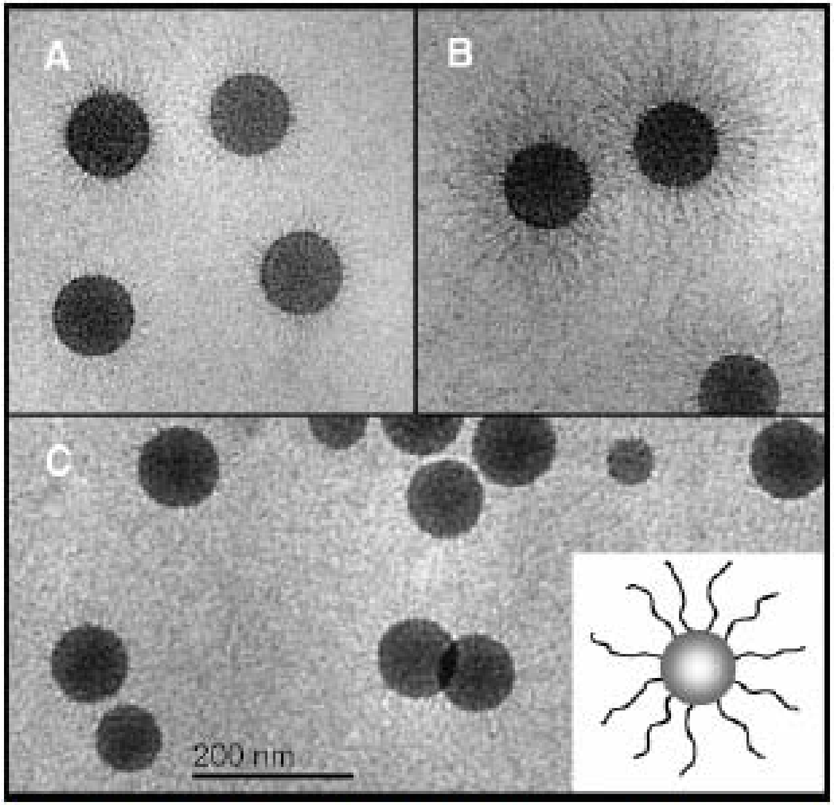
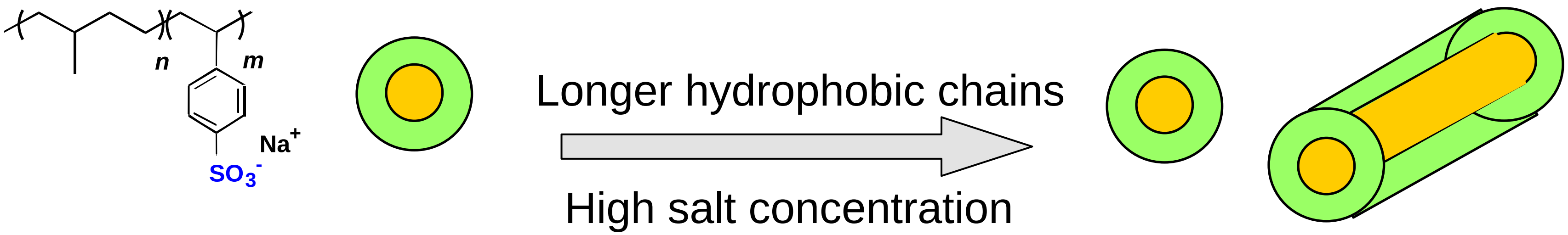


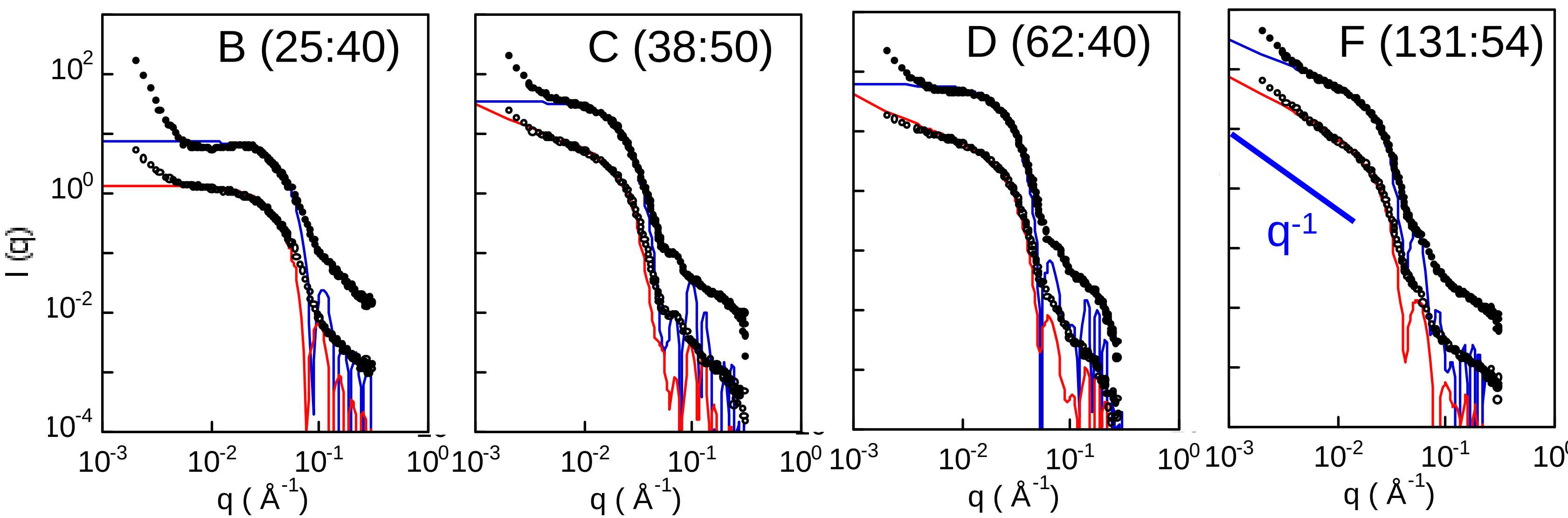
Figure 2. Cryo-TEM images of vitrified 1 wt % SPB suspensions. The contrast is enhanced compared to the original particles (C) by replacing the sodium counterions of the polyelectrolyte chains by cesium ions (A) and, additionally, by BSA molecules (537 mg per g SPB) which are adsorbed in close correlation to the polyelectrolyte chains (B).[10]

***J. Am. Chem. Soc.*, 127, 9688 (2005)**

SANS Profiles for $PIph_2$-*b*-PSSNa Micelles

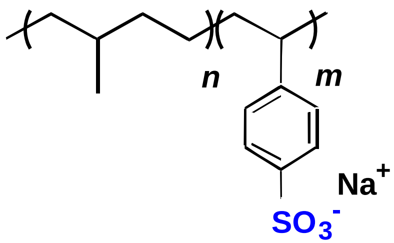
Sphere to rod transition by longer hydrophobic chain and by salt addition



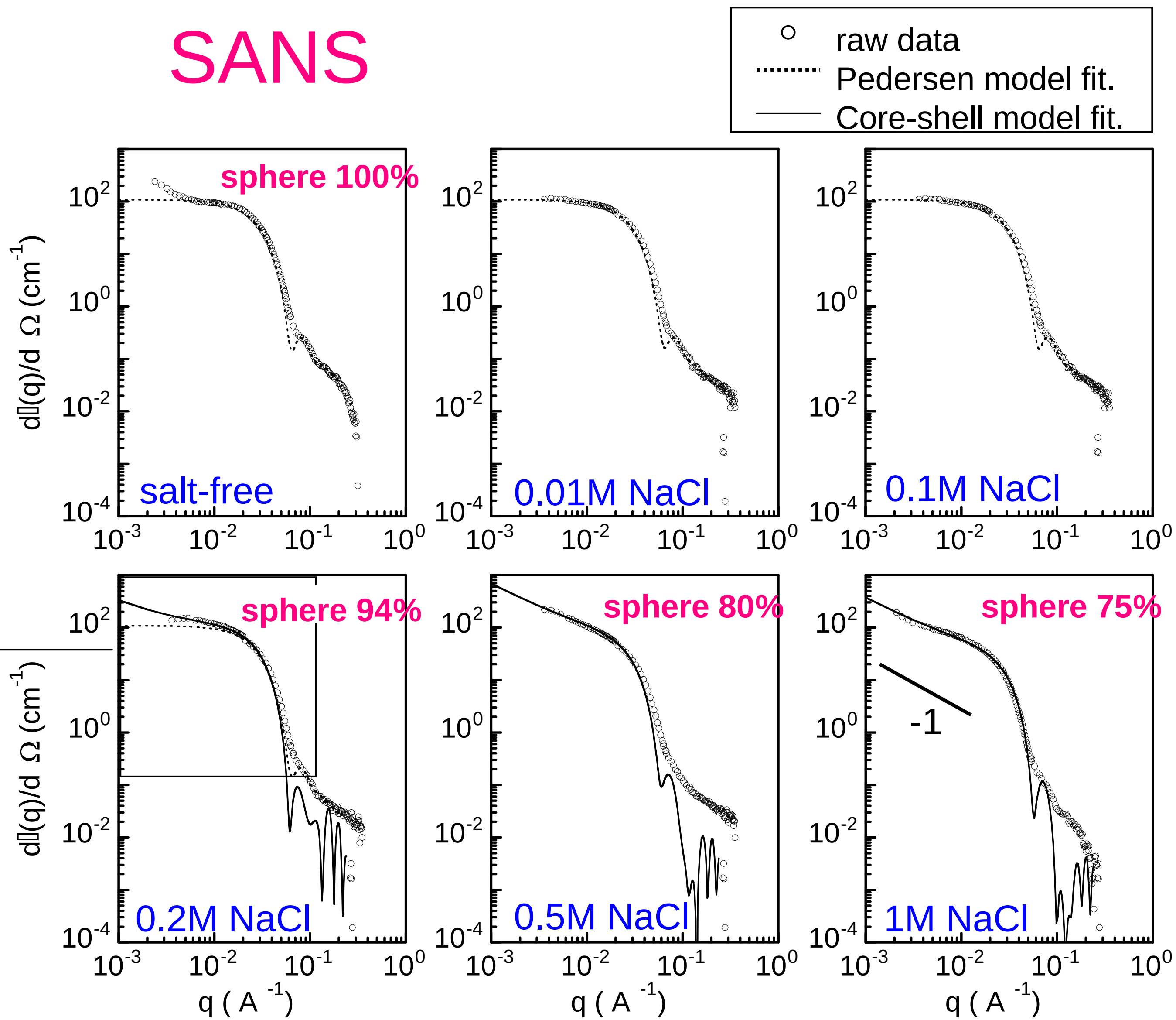


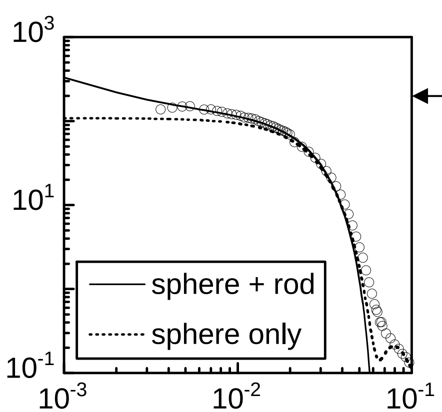
SANS profiles for PIph2-*b*-PSSNa D2O solutions (1 wt %) without salt (filled circle) and with1 M NaCl aq (open circle). Solid lines are fitting curves by a simple core-shell model.

Micelle Structure: Sphere to Rod Transition by Salt Addition



SANS



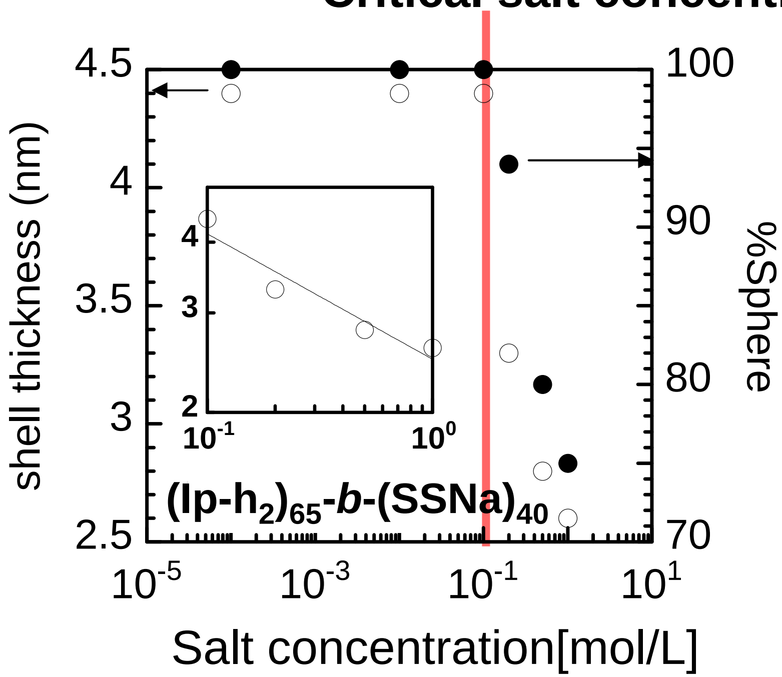


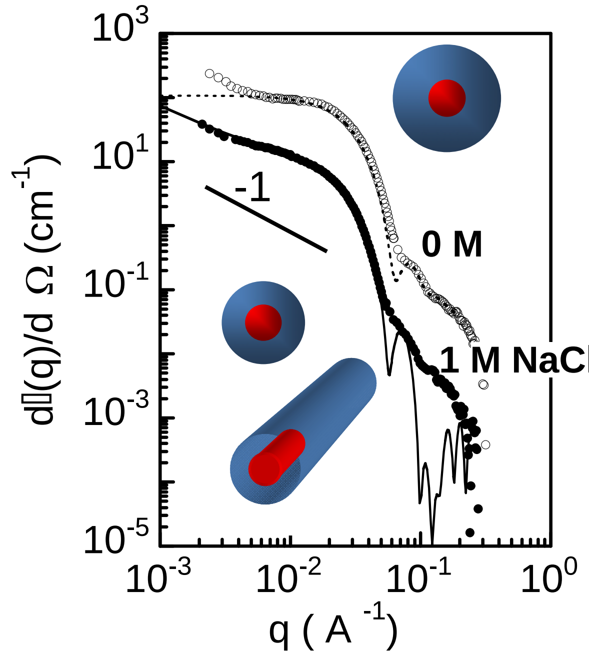
0.2 M NaCl

Sphere/Rod Transition and Micelle Structure Parameters

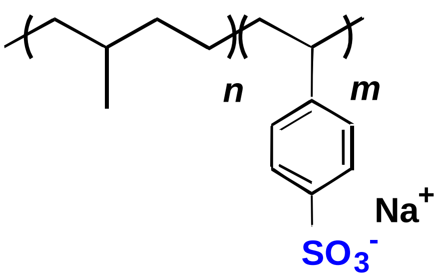
SANS Analysis

Critical salt concentration





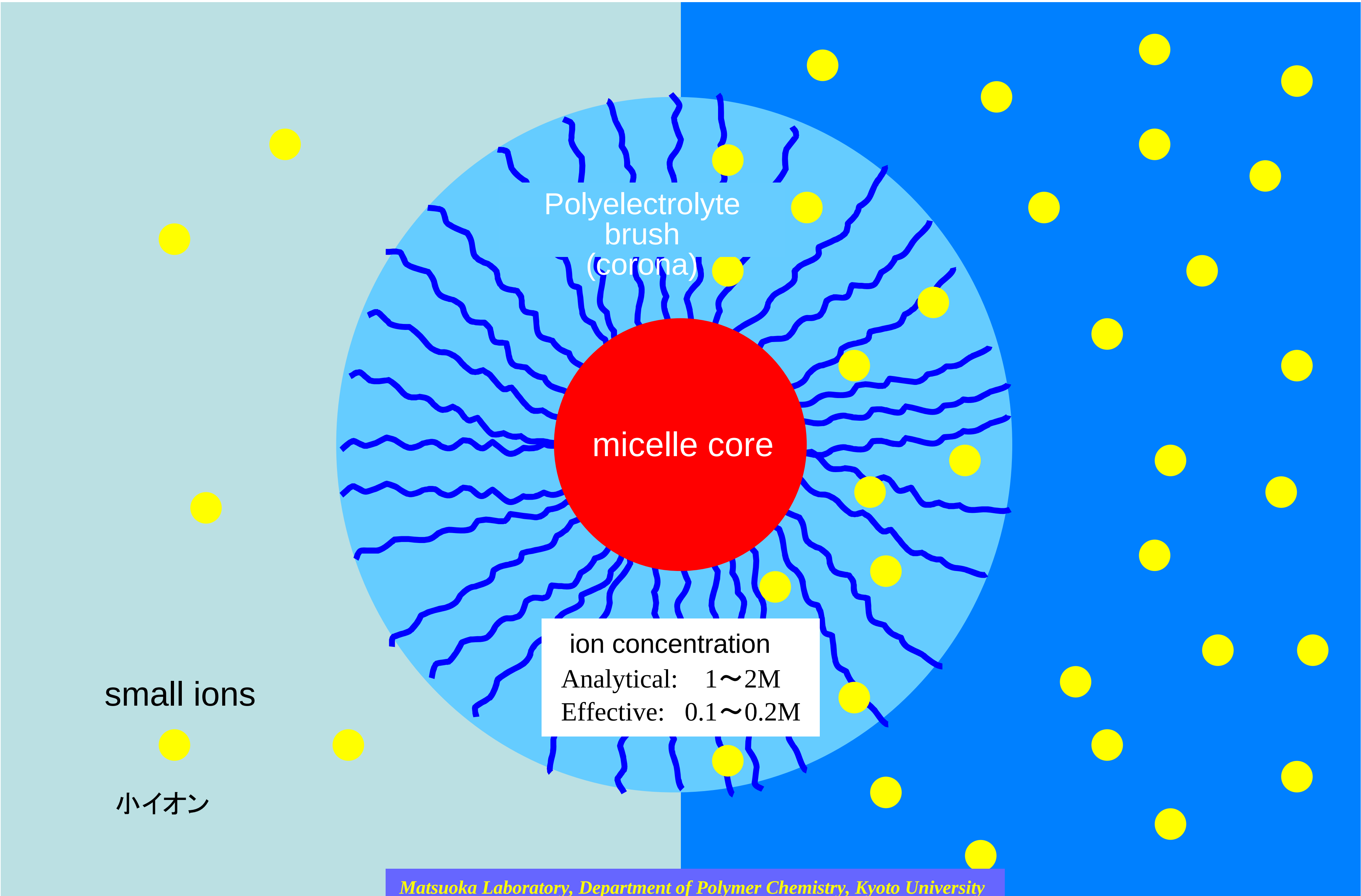
Very Stable against Salt



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

24

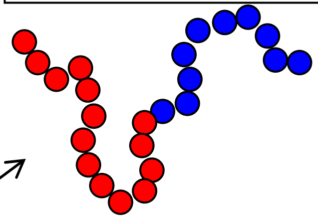
Mechanism of High Stability against Salt Addition of Polyelectrolyte Grafted Particles



Ionic Amphiphilic Diblock Copolymers

Synthesis of block copolymers by living polymerization

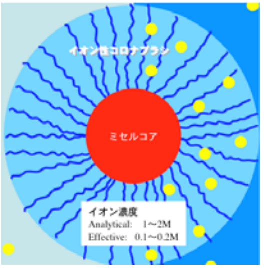
Water soluble



Non-Surface Activity

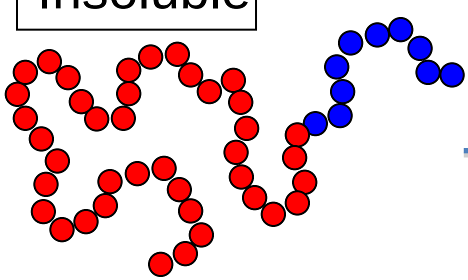
Molecular properties
such as surface activity

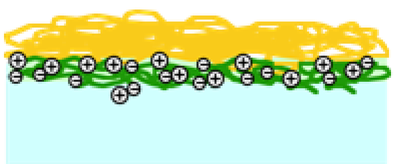
SAXS
SANS



Micelle Formation
Nanostructure Transition

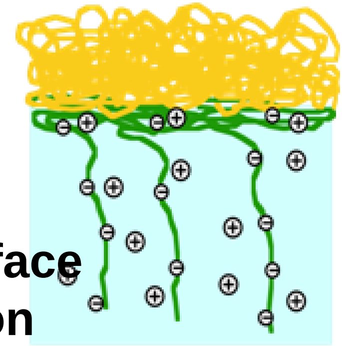
Insoluble





Monolayer on the water surface
Nanostructure and Transition

XR
NR



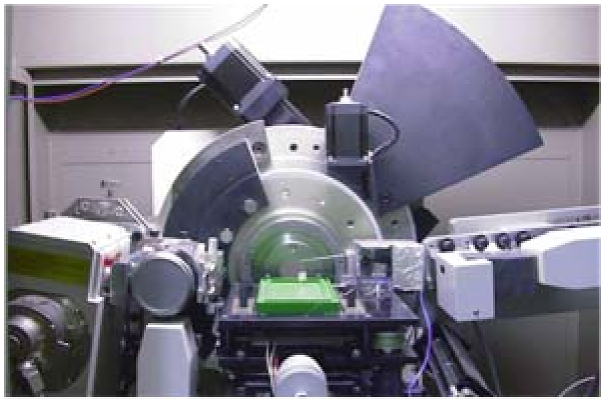
Polyelectrolyte Brush
at the Air/Water Interface

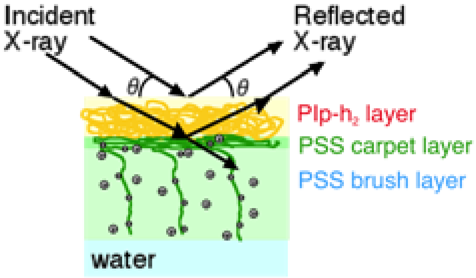
Air-Water Interface X-ray Reflectometer (XR)

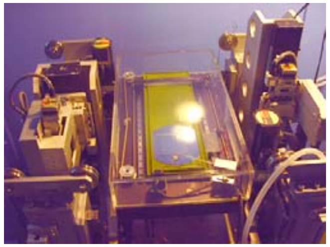
Air-Water Interface Neutron Reflectometer (NR)

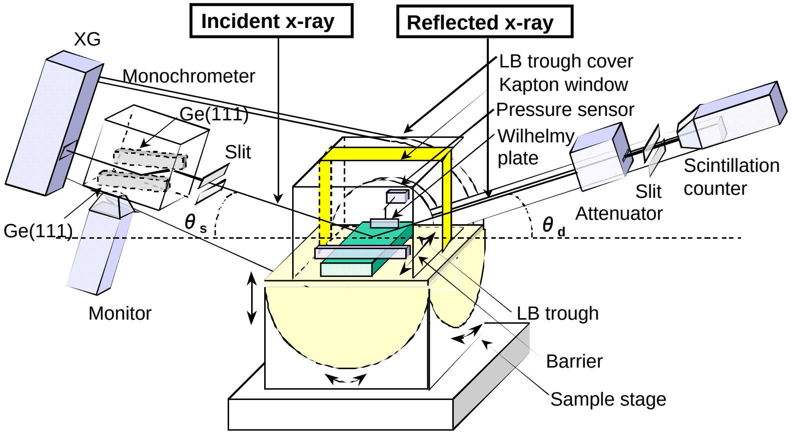
RINT TTR-MA in our laboratory

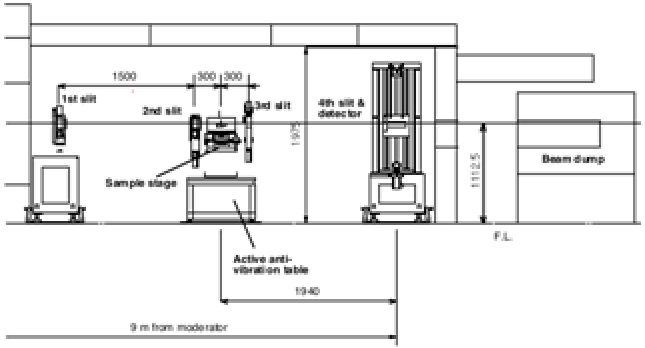
ARISA-II at J-Parc, Japan (formerly at KEK)











XR ------- Electron Density

NR ----- Scattering Length Density

Matsuoka Laboratory, Department of Polymer Chemistry, Kyoto University

Salt Concentration Dependence --- NR Profiles

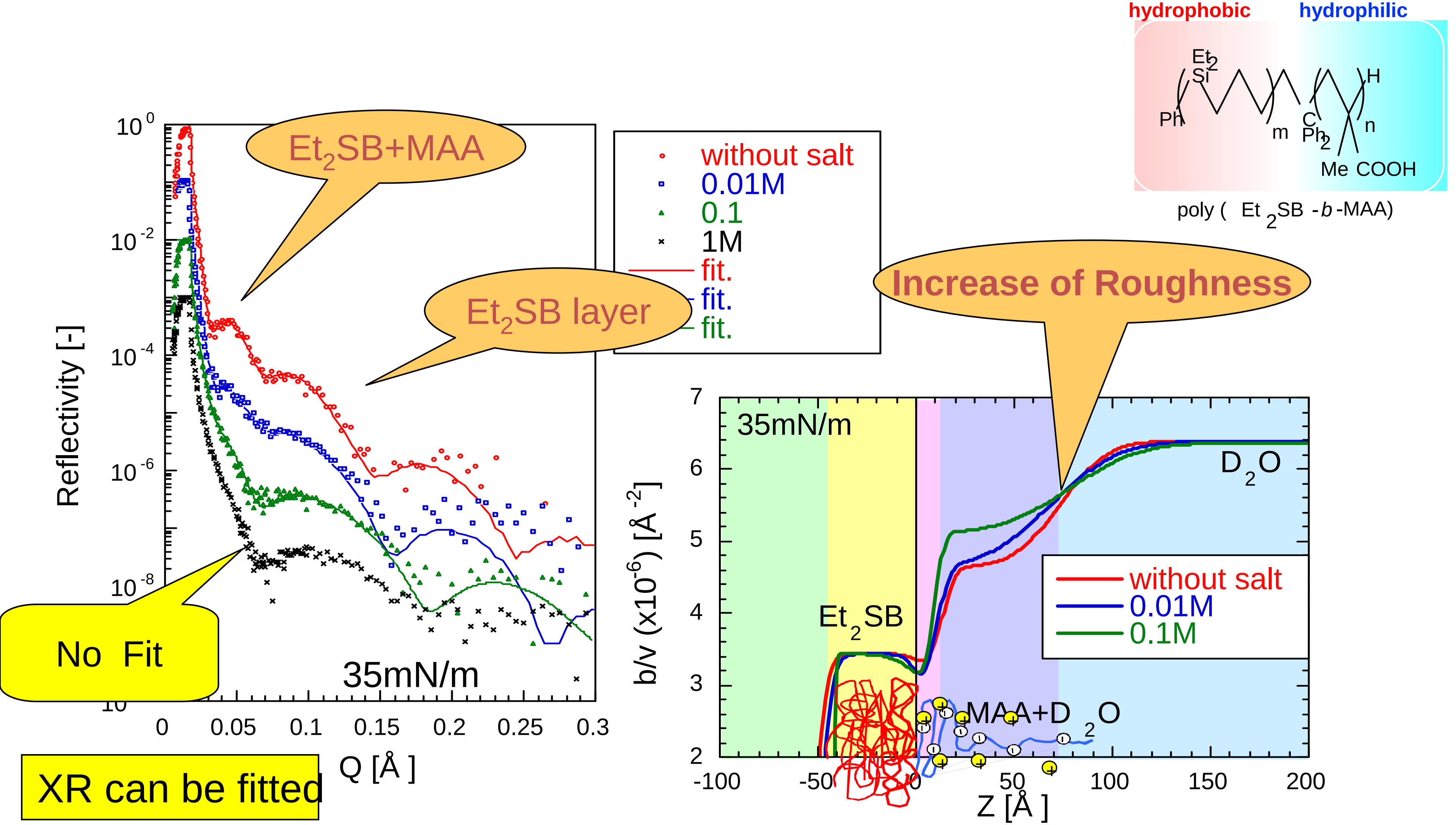


Fig. NR profiles and scattering density profiles for poly(Et_2SB-d_{10})$_{23}$-*b*-poly(MAA)$_{49}$ monolayer monolayer on subphase with different NaCl concentrations at 35mN/m

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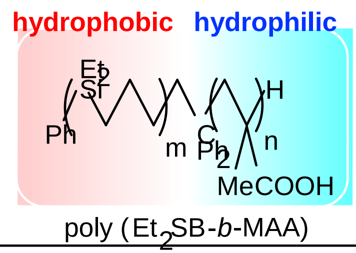
Contrast-Variation by NR --- Small Ion distribution

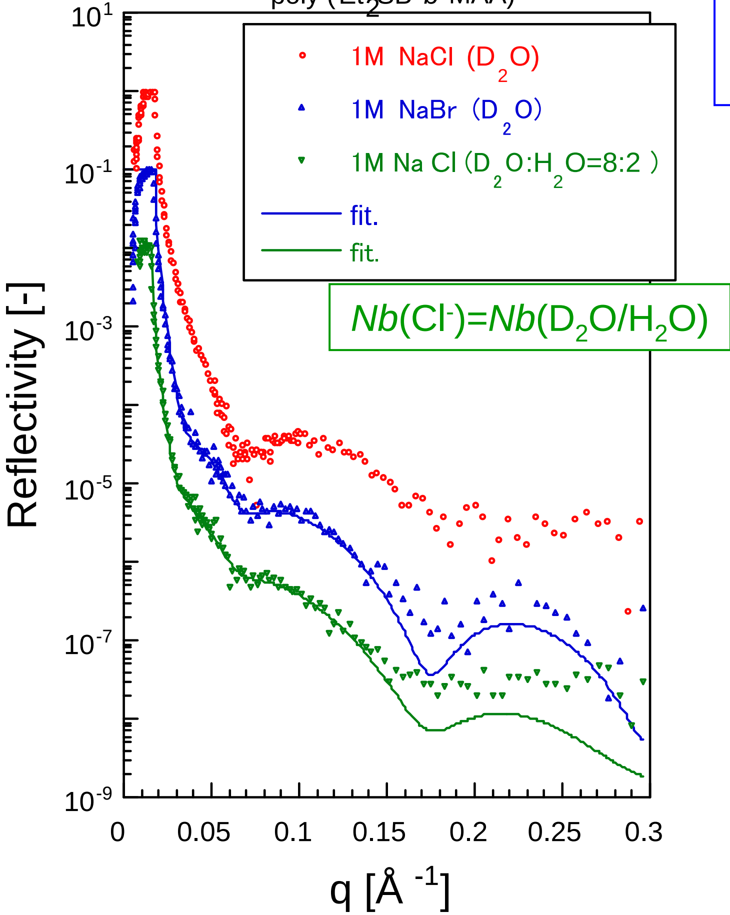


The same monolayer structure was evaluated from 1M NaBr system and 1M NaCl (D_2O/H_2O) system(No contribution from Cl- ions)

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

No good agreement for 1M NaCl system

--> Contribution from Cl- ion distribution?



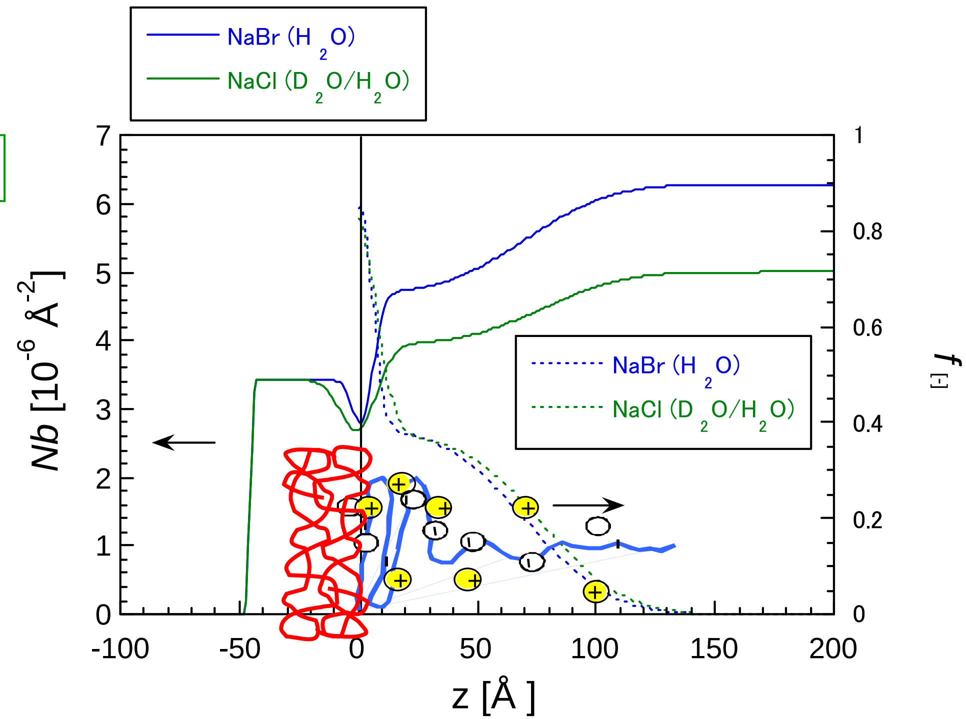


Fig. NR profiles and scattering density profiles for poly(Et_2SB-d_{10})$_{23}$-b-poly(MAA)$_{49}$ monolayer monolayer at 35mN/m on various subphase.

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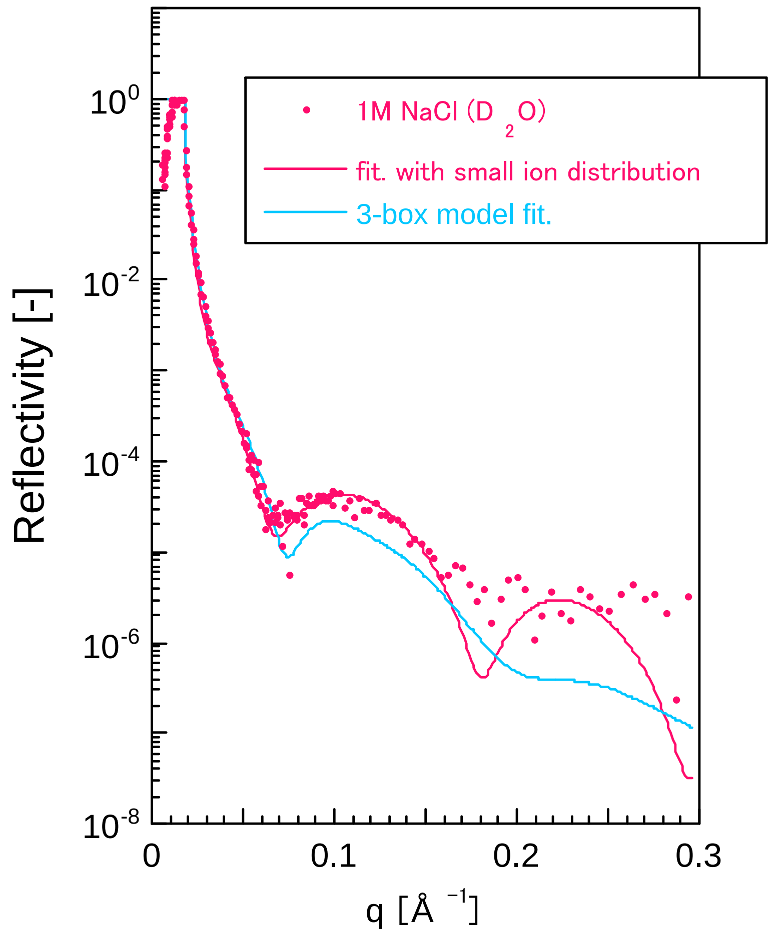
Possible Cl- ion Distribution

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



Concentrated Cl- ion layer just beneath the carpet layer

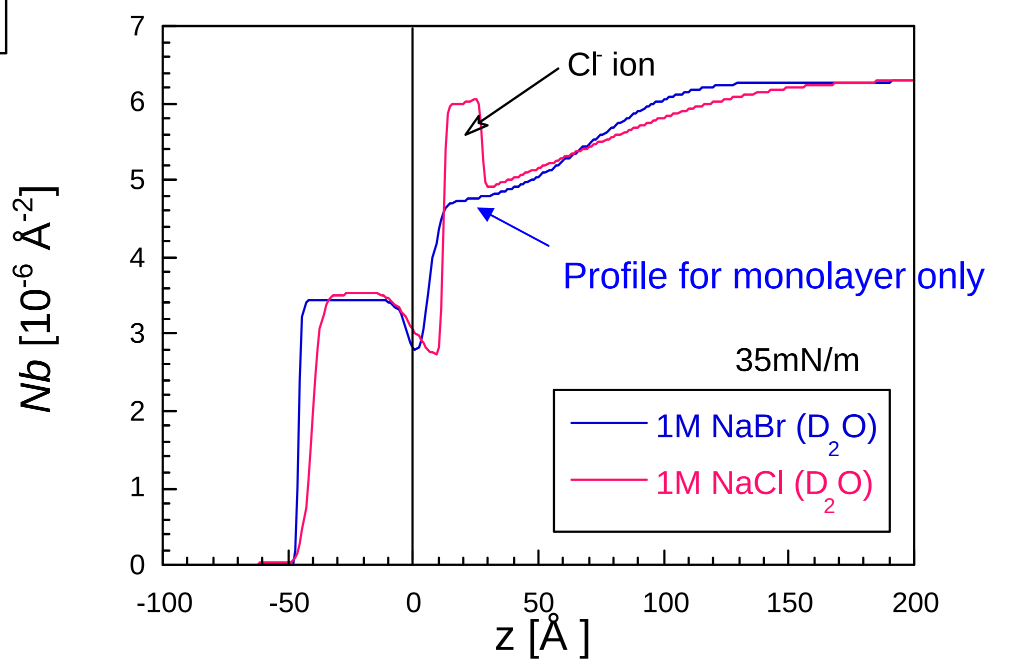


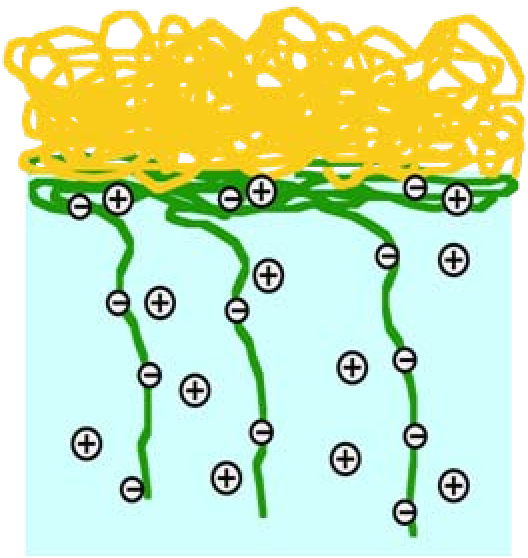
Fig. NR profiles with fitting curve in which Cl- ion distribution is considered. (left)

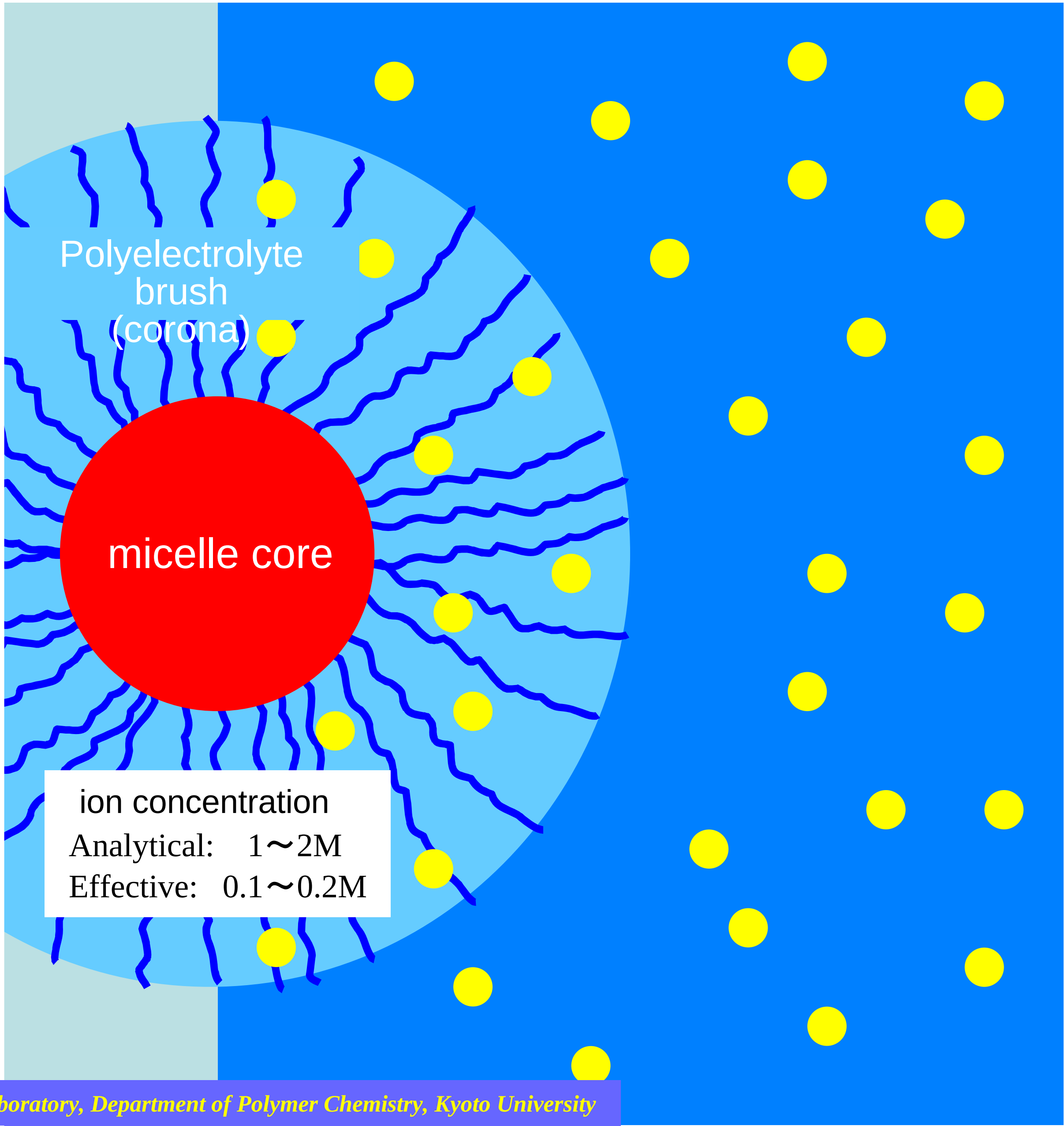
Scattering length density obtained by the fitting. (right)

H. Matsuoka, E. Mouri, P. Kaewsaiha, Y. Furuya, Y. Suetomi, K. Matsumoto, N. Torikai, ***Trans. MRS-J***, 32(1), 297-302 (2007).

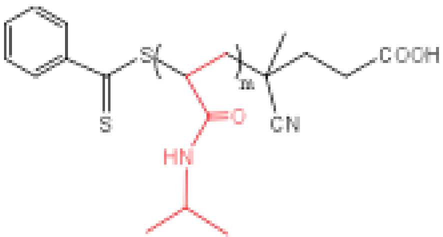
bc(Cl)=9.6, (Br)=6.8)

Counterion and Salt Ion Distribution in the Polyelectrolyte Brush is unknown.

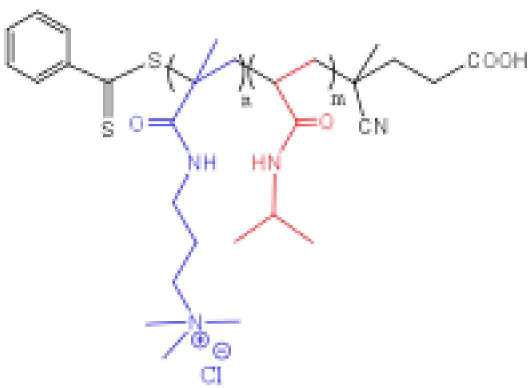




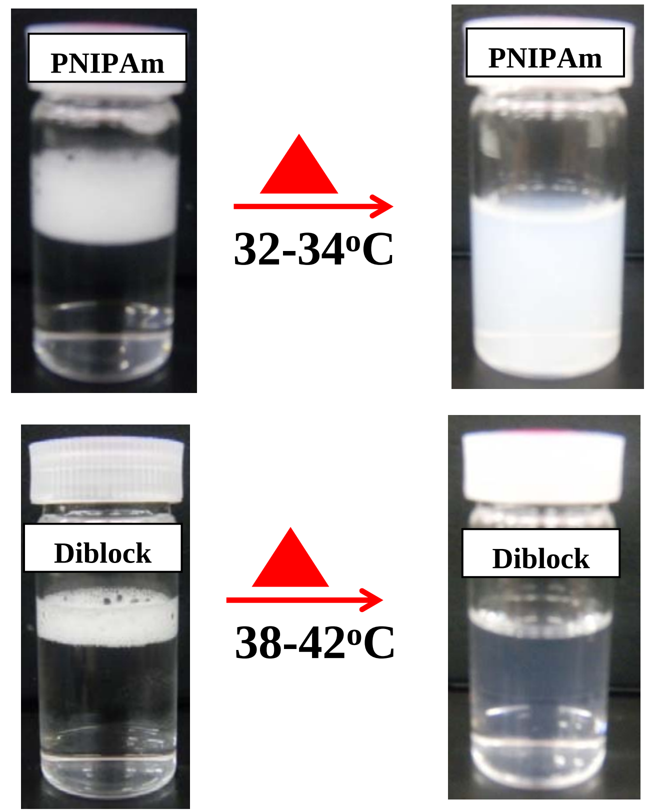
Visual Observation of Phase Transition



PNIPAM

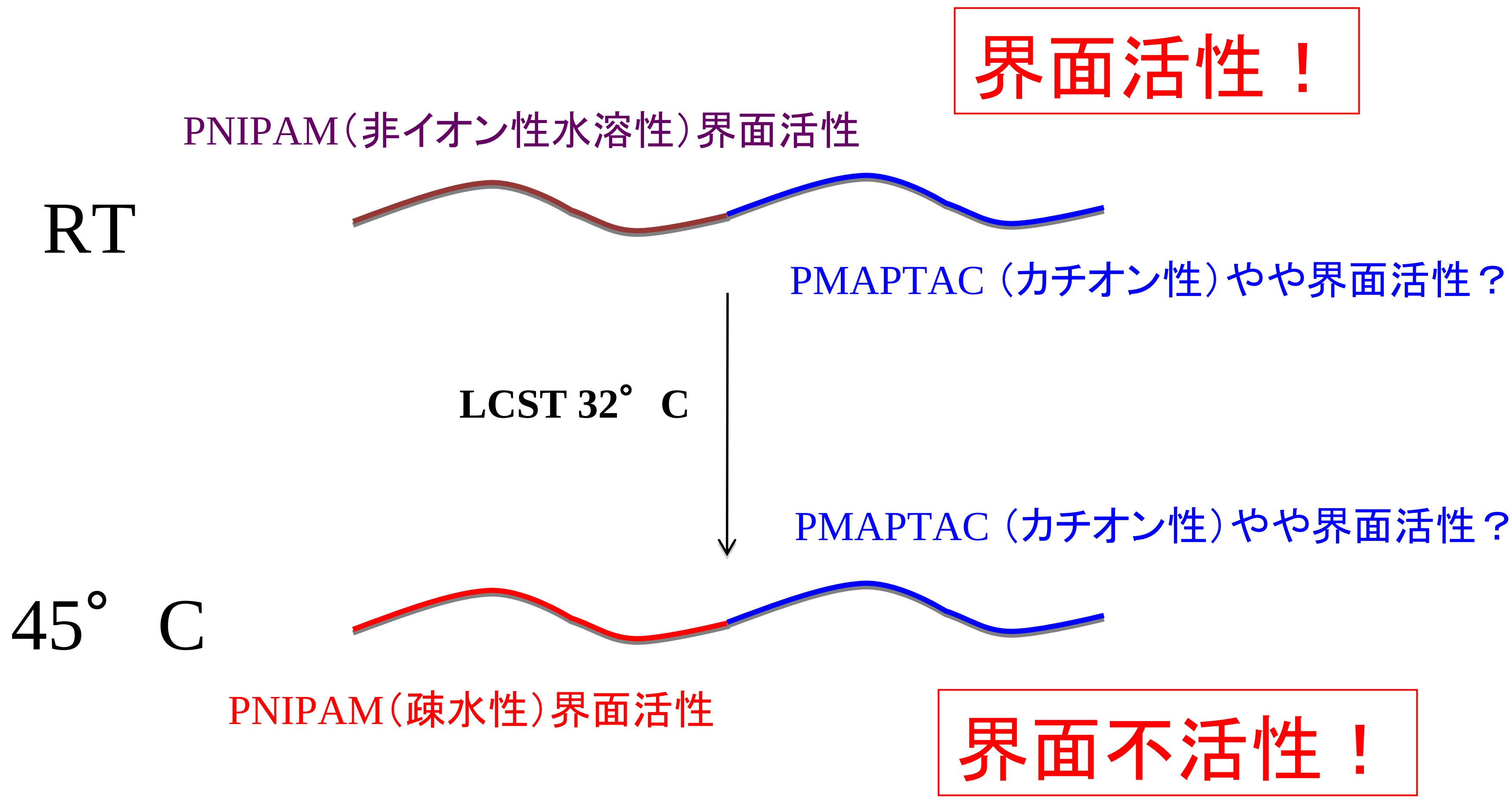


PNIPAM-*b*-PMAPTAC



Conc^{n} 1 mg/ml

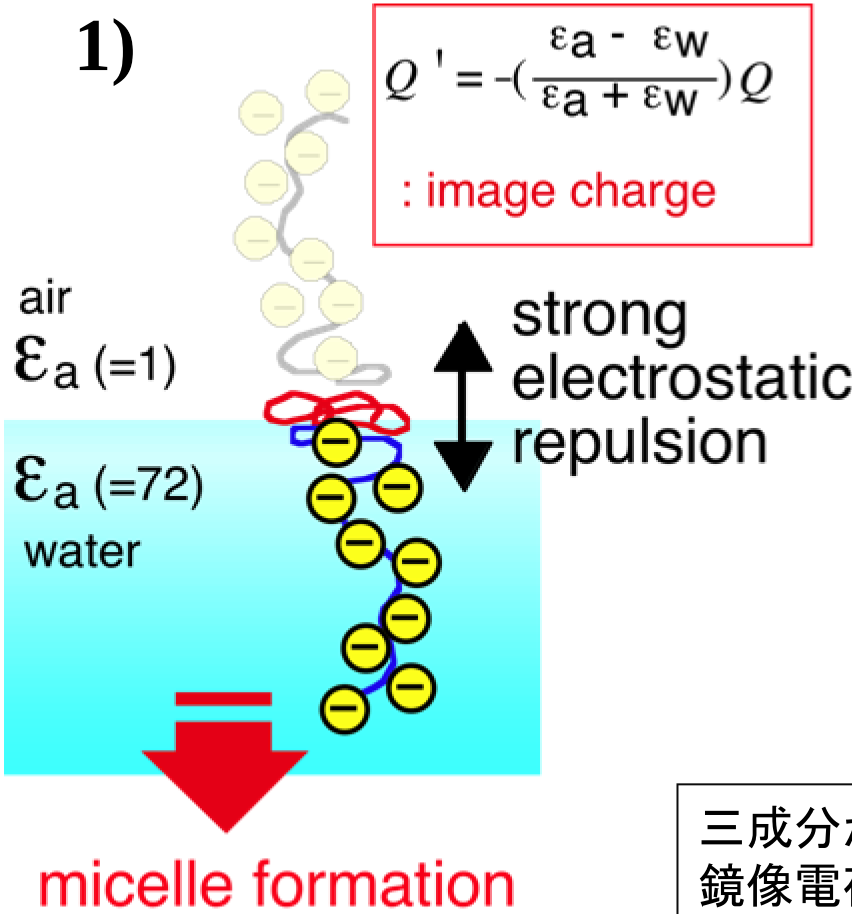
温度による界面不活性／界面活性転移の制御



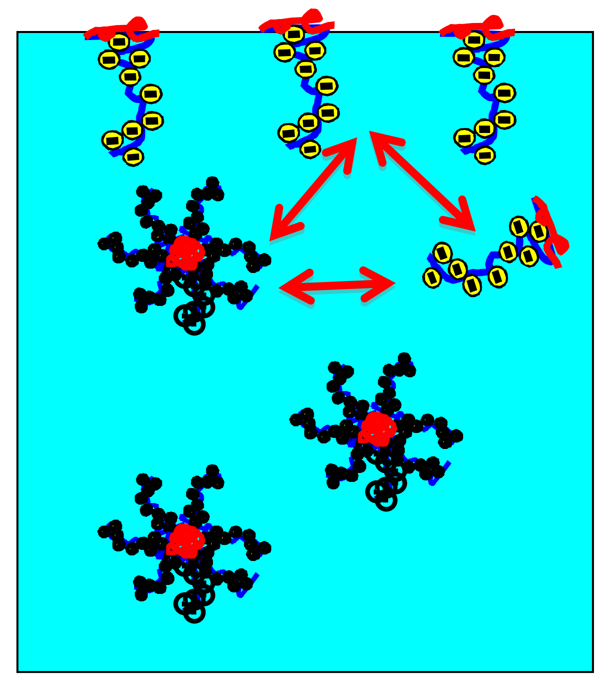
分子が「疎水性」になると，界面「不」活性になる！？

界面不活性性の発現機構

1)



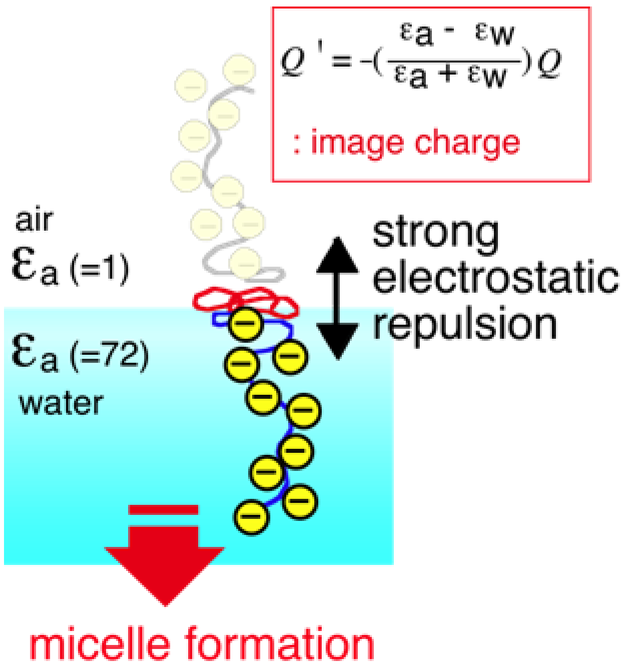
2)



三成分が平衡にある.
鏡像電荷のため，水面での居心地が悪い
→ 界面不活性性+ミセル形成
疎水性増加 → 水面での居心地より
ミセルでの居心地がより良くなる？

水／有機溶媒混合系での界面不活性性とミセル形成挙動

鏡像電荷による静電反発

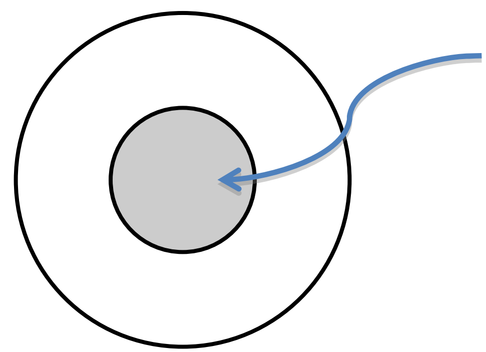


水／有機溶媒混合系を用いる事により誘電率を変化させて界面不活性性およびミセル形成挙動に与える影響の調査

二つのモデル(Core-Shell model)

①コア中に溶媒は存在しない

②コアに有機溶媒だけ取り込まれている



Organic solvent ?

第63回　コロイドおよび界面化学討論会

主催：日本化学会　コロイドおよび界面化学部会

会期：2011年9月7日（水）～9日（金）

会場：京都大学　吉田キャンパス　百周年時計台記念館

工学部・工業化学科講義室

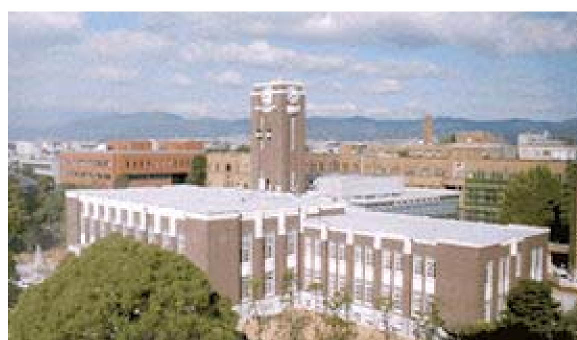
共催：京都大学大学院工学研究科

後援：日本化学会コロイドおよび界面化学部会関西支部

協賛：京都大学・物質ー細胞統合システム拠点

高分子学会，応用物理学会，日本中性子科学会など，
約30の学協会に申請手続中

URL: http:// http://colloid.csj.jp/div_meeting/63th/（2011年4月1日開設予定）



一般セッション

分子集合体の科学と技術	2-(1): 界面活性剤(界面活性剤単独系・混合系、エマルションを含む) 2-(2): 界面活性剤と他物質の相互作用 2-(3): 超分子・高次分子集合体 2-(4): ゲル 2-(5): 高分子溶液 2-(6): その他
組織化膜の科学と技術	3-(1): 単分子膜・LB膜 3-(2): 自己組織化膜 3-(3): 二分子膜(ベシクル・リポソームなど) 3-(4): 界面物性(気ー液、液ー液) 3-(5): その他
微粒子分散系の科学と技術	4-(1): サスペンション 4-(2): 微粒子・ナノ粒子 4-(3): 高分子コロイド 4-(4): 界面電気現象 4-(5): レオロジー 4-(6): その他
固体表面・界面の科学と技術	5-(1): 固体表面構造と物性・機能 5-(2): 吸着と触媒 5-(3): 表面力・トライボロジー・走査プローブ顕微鏡 5-(4): 散乱・回折・分光法 5-(5): ミクロファブリケーション 5-(6): その他
応用・開発セッション	6-(1): 企業開発研究(製品配布可) 6-(2): アカデミアにおける応用研究

シンポジウム

S-1:界面・分散系の新デザイン:サーファクタントフリー分散系と界面吸着粒子の科学と工学

S-2:細胞と粒子の相互作用は,コロイド・界面科学でどこまで理解できるのか？

S-3:液体のクラスター化にともなう新現象

S-4:ソフト界面分子膜科学の新展開

S-5:ナノ細孔物質の新現象・新機能

S-6:界面動電現象の科学と技術ー計測とサイエンス・イノベーション

S-7:蛋白質／水界面の熱力学とATPエネルギー

バイオ関連セッション追加の方針