Antifouling mechanism of hydrophilic polymer brushes

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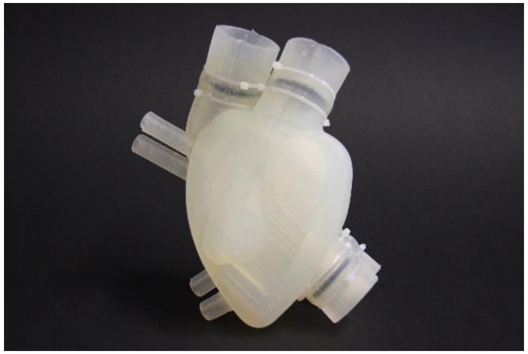
Adsorption of organic matter in water

Ship bottoms

Energy loss

Artificial organs



Thrombus (血栓)

Infection (感染症)

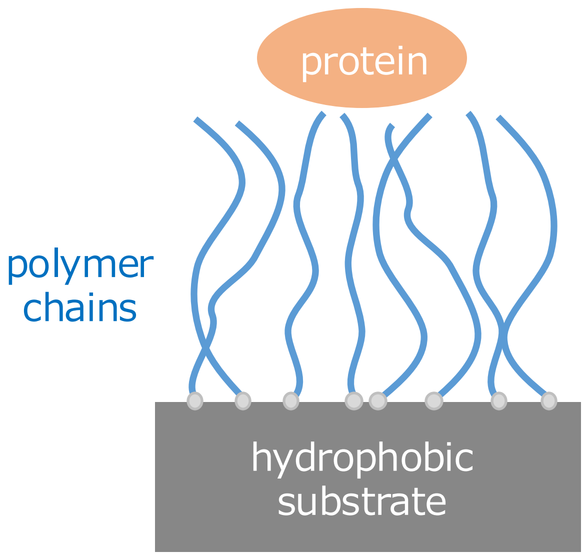
Membranes

Flow reduction

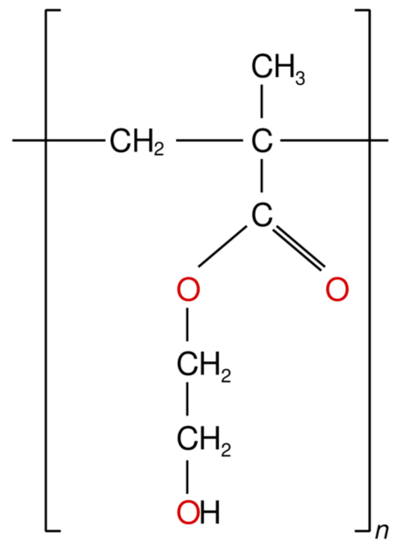
Antifouling surfaces are desired.

https://en.wikipedia.org/wiki/File:Soft_Total_Artificial_Heart_sTAH.jpg
https://upload.wikimedia.org/wikipedia/commons/1/1c/Seepocken%26Miesmuscheln_Galicien2005.jpg
https://upload.wikimedia.org/wikipedia/commons/c/cf/Reverse_osmosis_membrane_coil.jpg

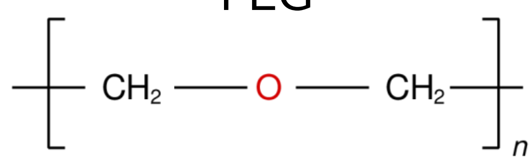
Hydrophilic polymer brushes



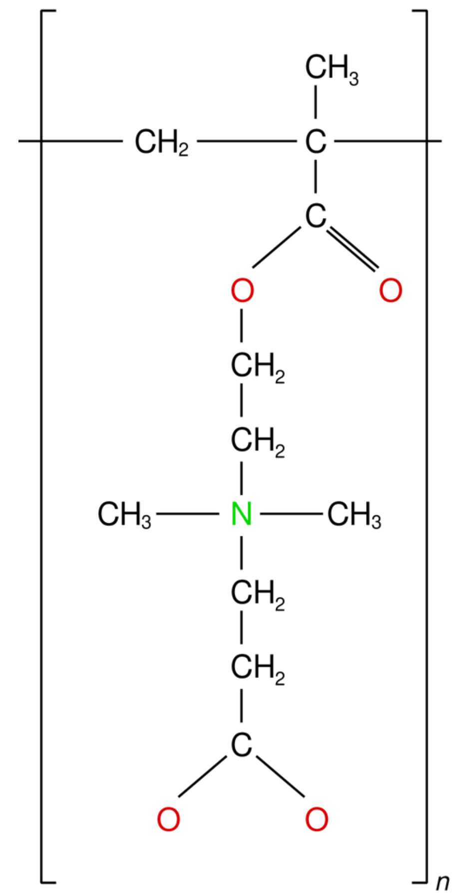
PHEMA



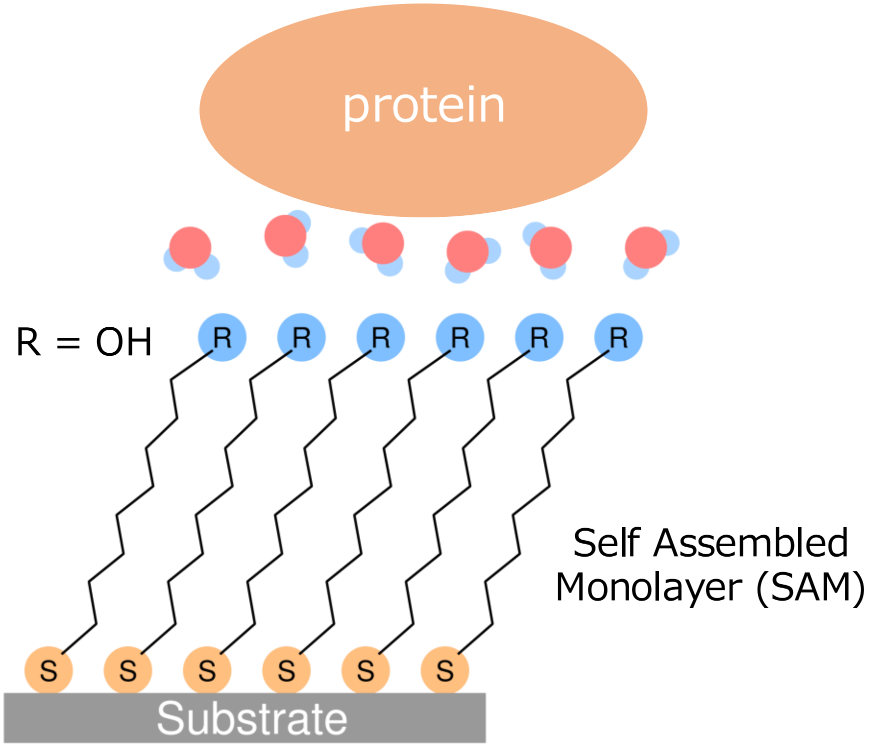
PEG



PCBMA



Antifouling of hydrophilic SAMs



Steric repulsion of bound water molecules

J. Zheng et al., *Biophys. J.* **89**, 158–166 (2005).

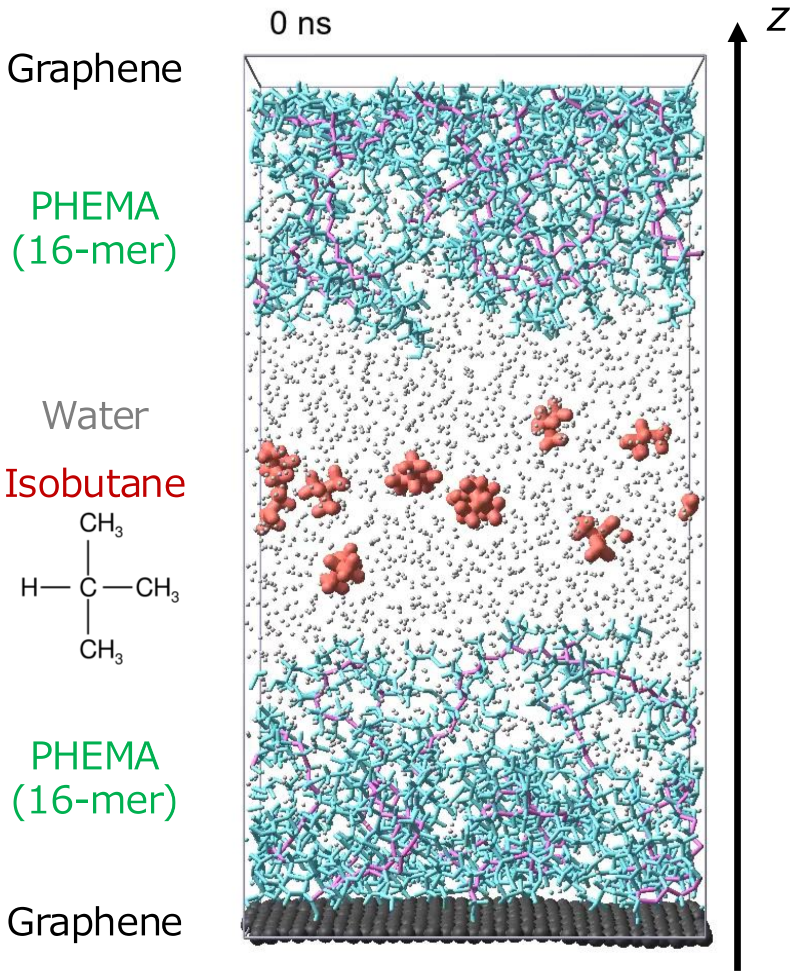
J.I. Monroe et al., *Proc. Natl. Acad. Sci. USA* **118**, e2020205118 (2021).

Water barrier mechanism

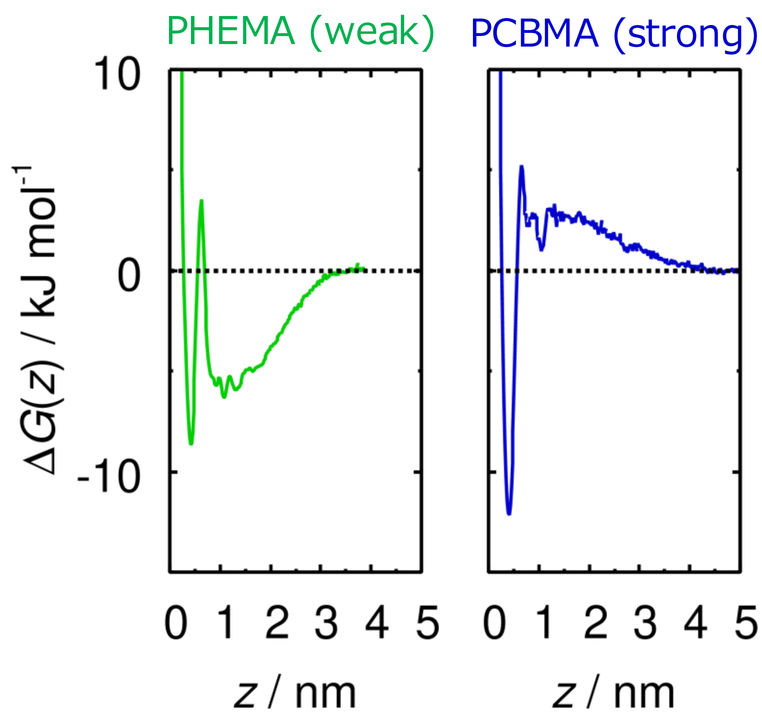
Almost no study for polymer brushes

Is it the only antifouling mechanism?

Polymer brush in water



$$\Delta G(z) = -k_B T \ln \rho(z) - k_B T \ln \rho_{\mathrm{bulk}}$$

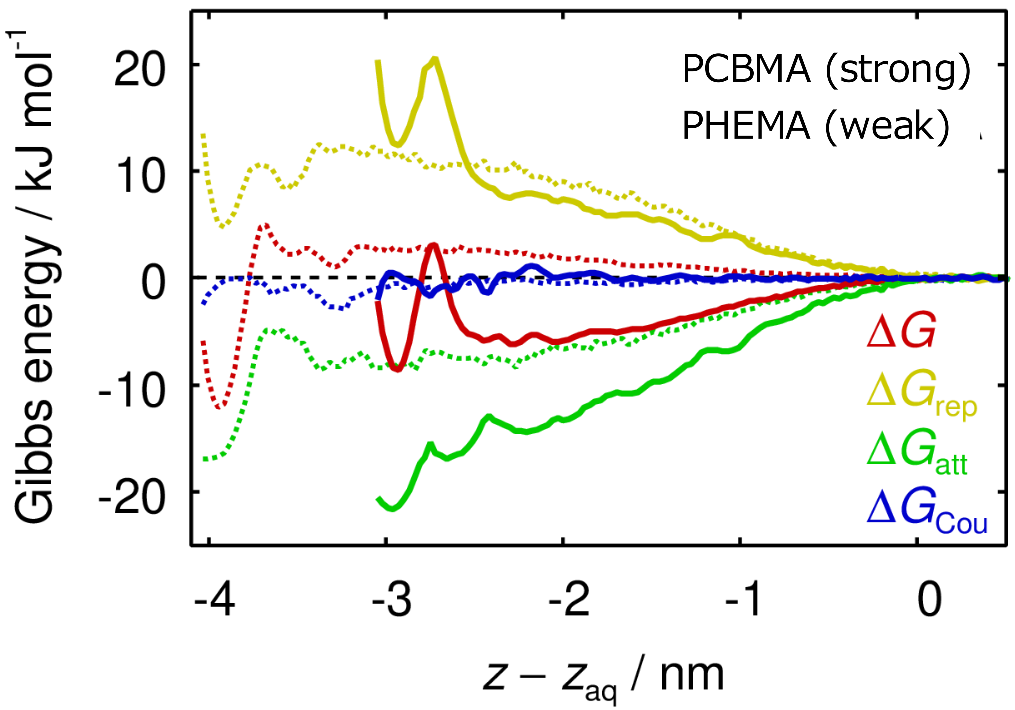


Isobutane binds to PHEMA,

but not to PCBMA.

Components of Gibbs energy

$$\Delta G(z) = \underline{\Delta G_{\mathrm{rep}}(z)} + \underline{\Delta G_{\mathrm{att}}(z)} + \underline{\Delta G_{\mathrm{C}}(z)}$$



$$\Delta G(z) = \Delta G^{\mathrm{np}}(z) + \underline{\Delta G_{\mathrm{C}}(z)}$$

G for the hypothetical nonpolar solute

$$\Delta G^{\mathrm{np}}(z) = \underline{-T\Delta S_{\mathrm{UV}}^{\mathrm{np}}(z)} + \underline{\Delta E_{\mathrm{UV}}^{\mathrm{np}}(z)}$$

Total

Steric repulsion (entropy)

London dispersion (energy)

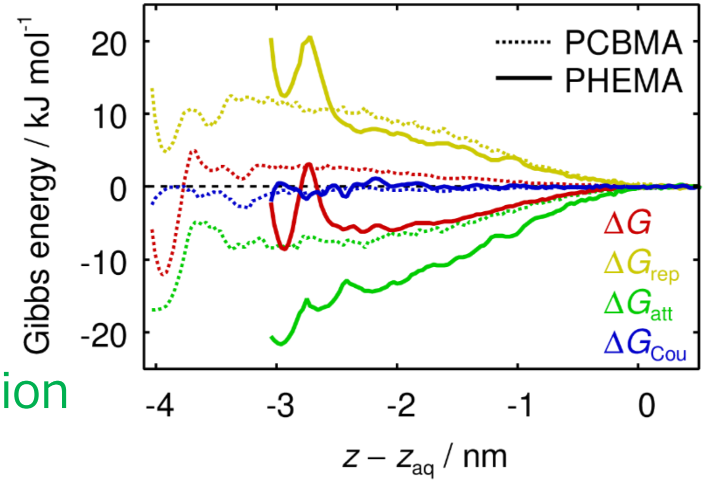
Coulomb (energy)

Steric repulsion is strong (water barrier mechanism)

Stabilization due to London dispersion is small

} in the PCBMA brush

Two roles of water in the brush

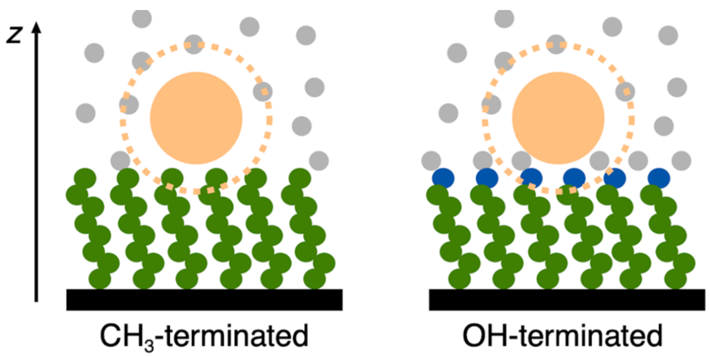


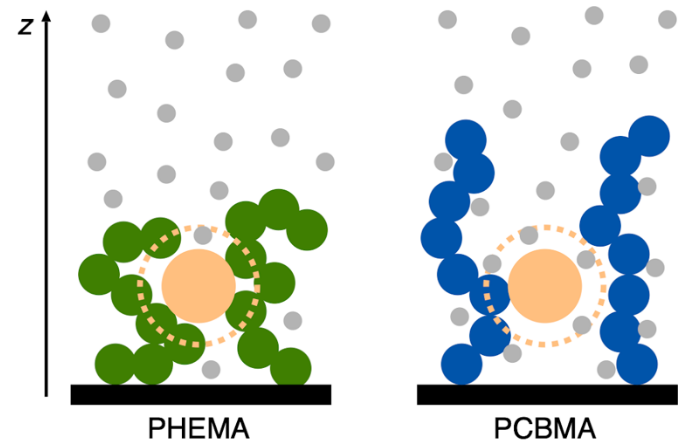
Enhancement of steric repulsion

- Large effective volume due to bound water molecules
- Also observed for SAMs

Reduction of London dispersion interaction

- Not observed for SAMs





Hydrophilic groups

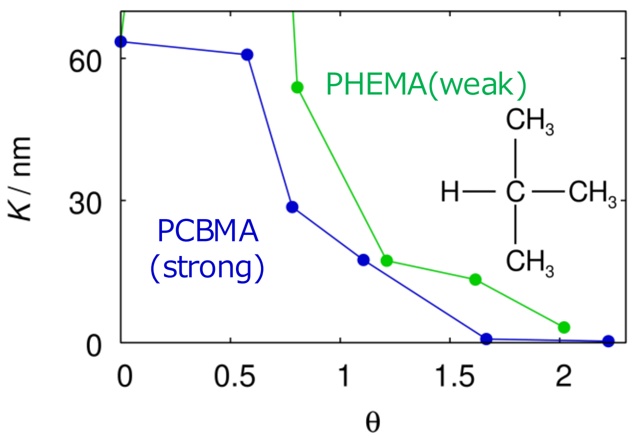
increase

decrease

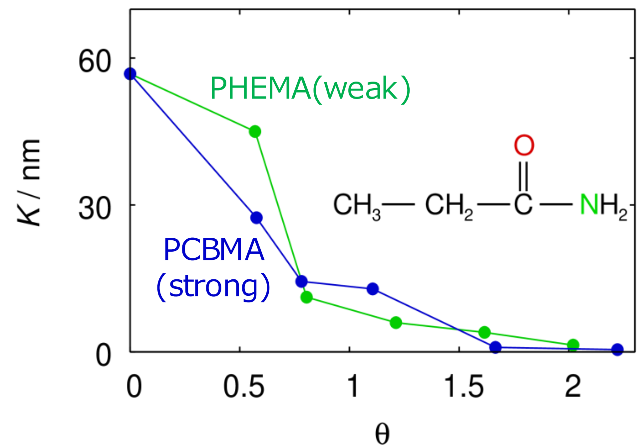
the number of surrounding atoms

Dependence on grafting density

Isobutane (Leu)

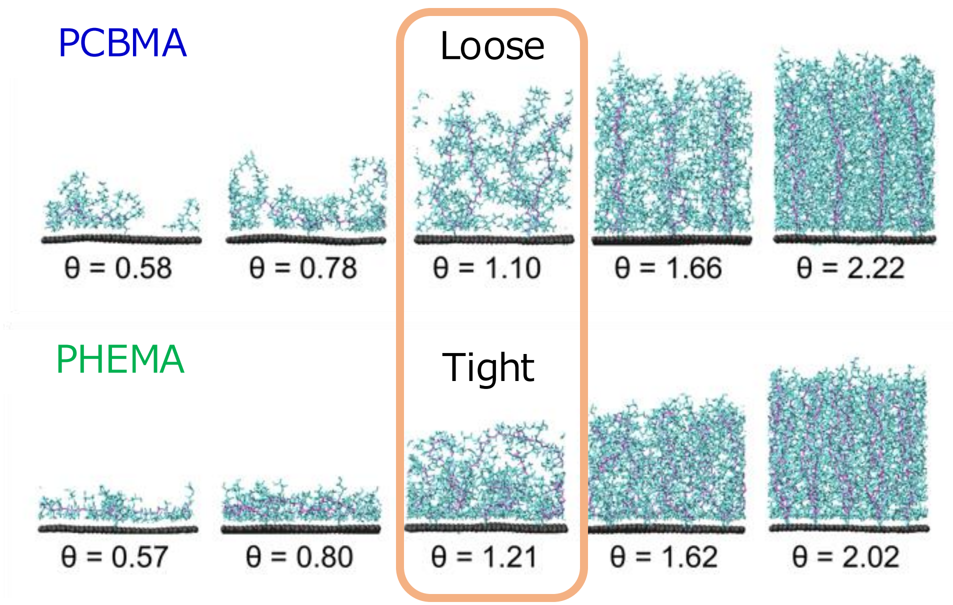


Propionamide (Gln)



Antifouling performance is **better for PHEMA** around θ ~ 1.2!

($\theta = 2R_g/L$)



Adsorbate molecules reach the substrate easily

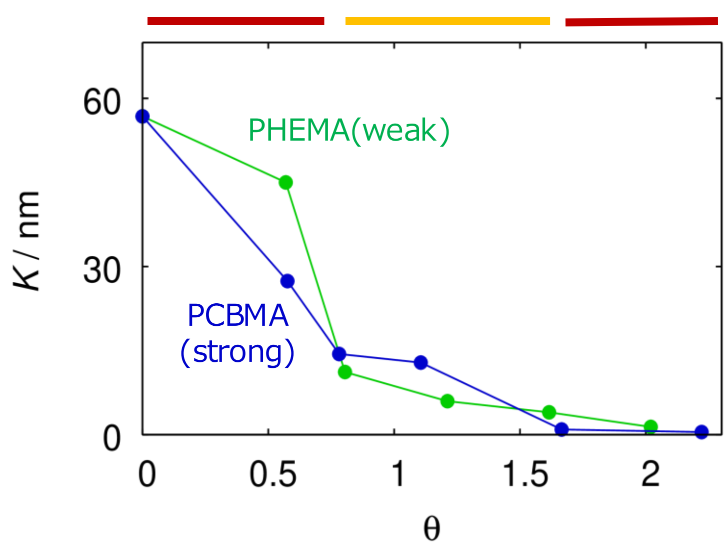
The tight layer blocks the adsorbate molecules

Experimental studies

Better antifouling for more hydrophilic polymers

- C. Zhao et al., *Langmuir* **26**, 17375–17382 (2010).
- W. Zhao et al., *J. Mater. Chem. B* **2**, 5352–5357 (2014).
- B.L. Leigh et al., *Biomacromolecules* **18**, 2389–2401 (2017).
- W. Dai et al., *J. Mater. Chem. B* **7**, 2162–2168 (2019).

High and low surface coverage regimes



Stronger antifouling of less hydrophilic polymers

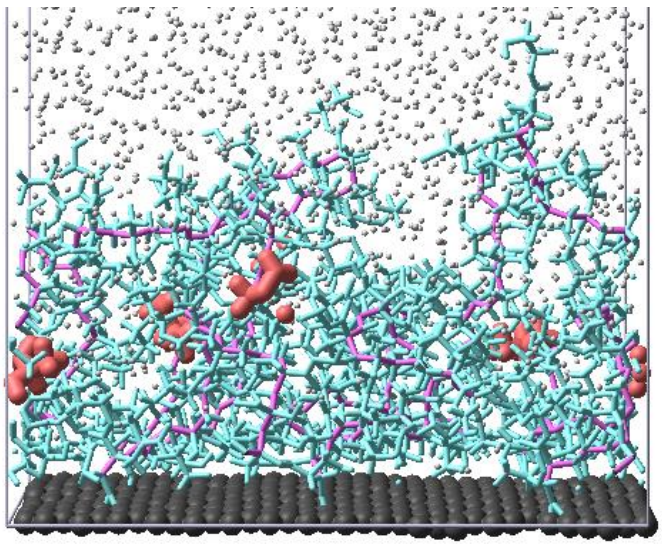
- C. Zhao et al., *Langmuir* **27**, 4906–4913 (2011).
- E. van Andel, et al., *Langmuir* 35, 1181–1191 (2019).

Medium surface coverage regime

No contradiction between the two types of experimental result

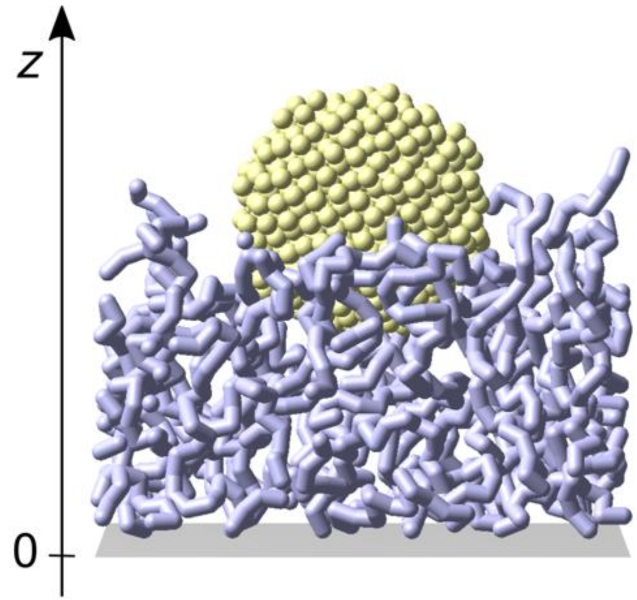
Coarse-grained simulations

All-atom (AA)



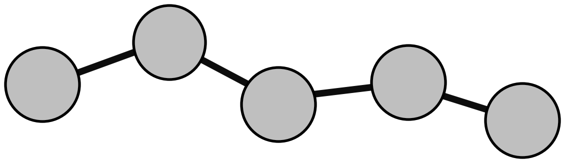
- Small organic molecules
- 16-mer
- Graphene

Coarse-grained (CG)



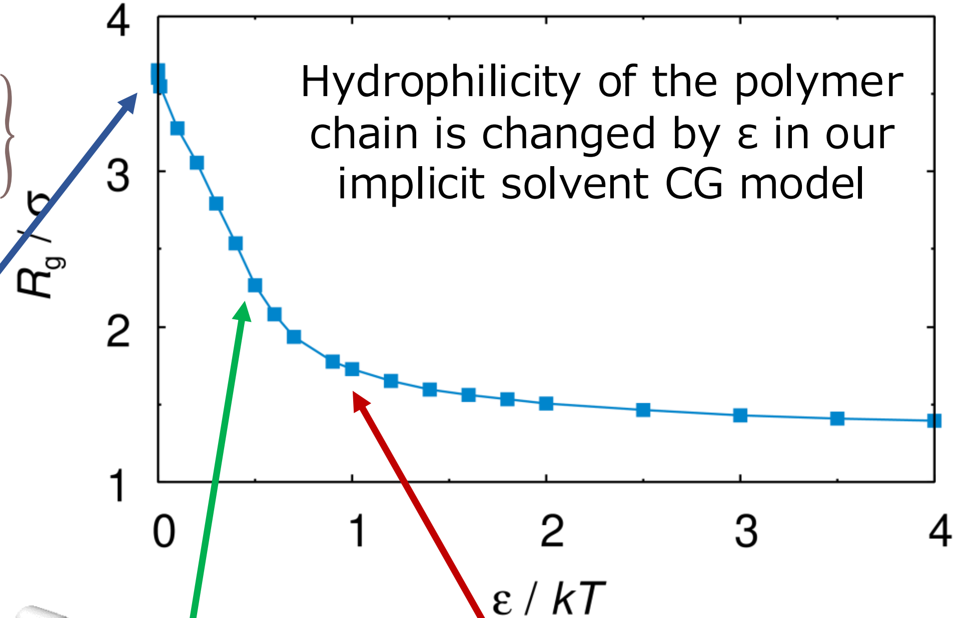
- Proteins
- Long chains
- Various substrates

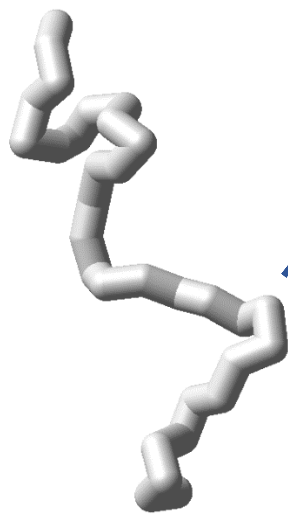
Kremer-Grest type model



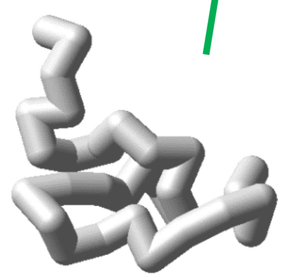
$$V_{\mathrm{FENE}}(r) = -0.5 k_{\mathrm{FENE}} R_0^2 \ln\left\{1 - \left(\frac{r}{R_0}\right)^2\right\}$$

$$V_{\mathrm{LJ}}(r) = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

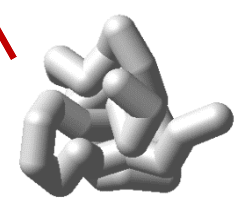




$\varepsilon = 10^{-6}\ kT$
Strongly hydrophilic



$\varepsilon = 0.5\ kT$
Weakly hydrophilic

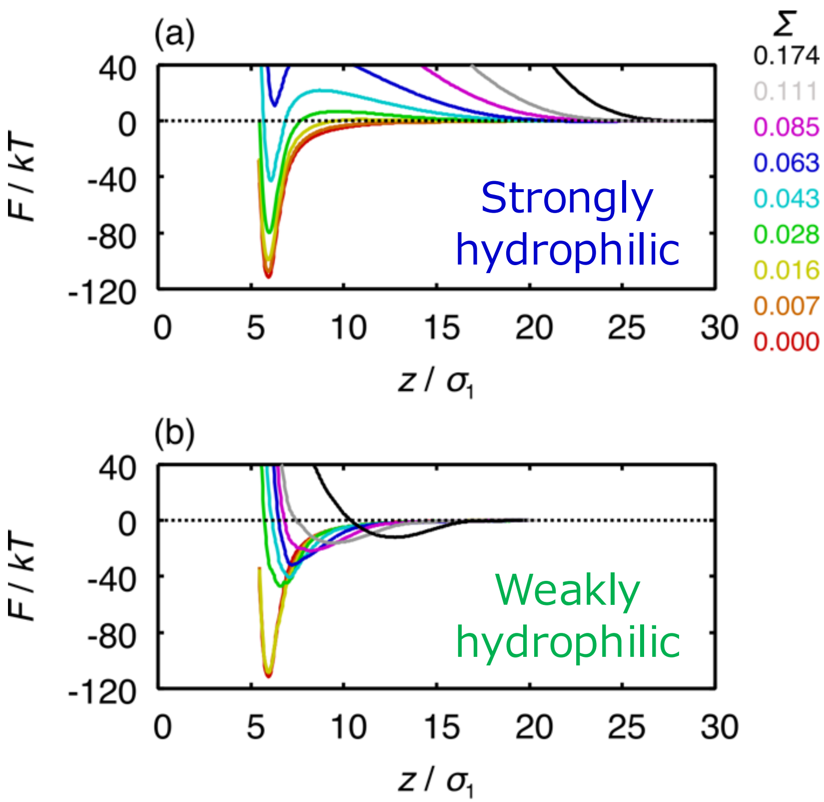


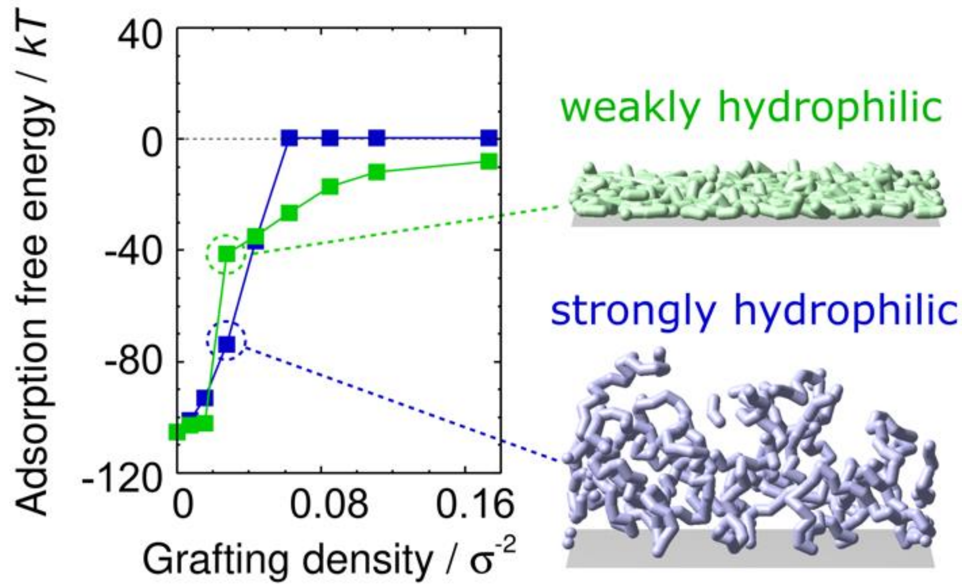
$\varepsilon = 1\ kT$
Hydrophobic

Adsorption free energy

$$F_{\mathrm{ads}} = -kT \ln K$$

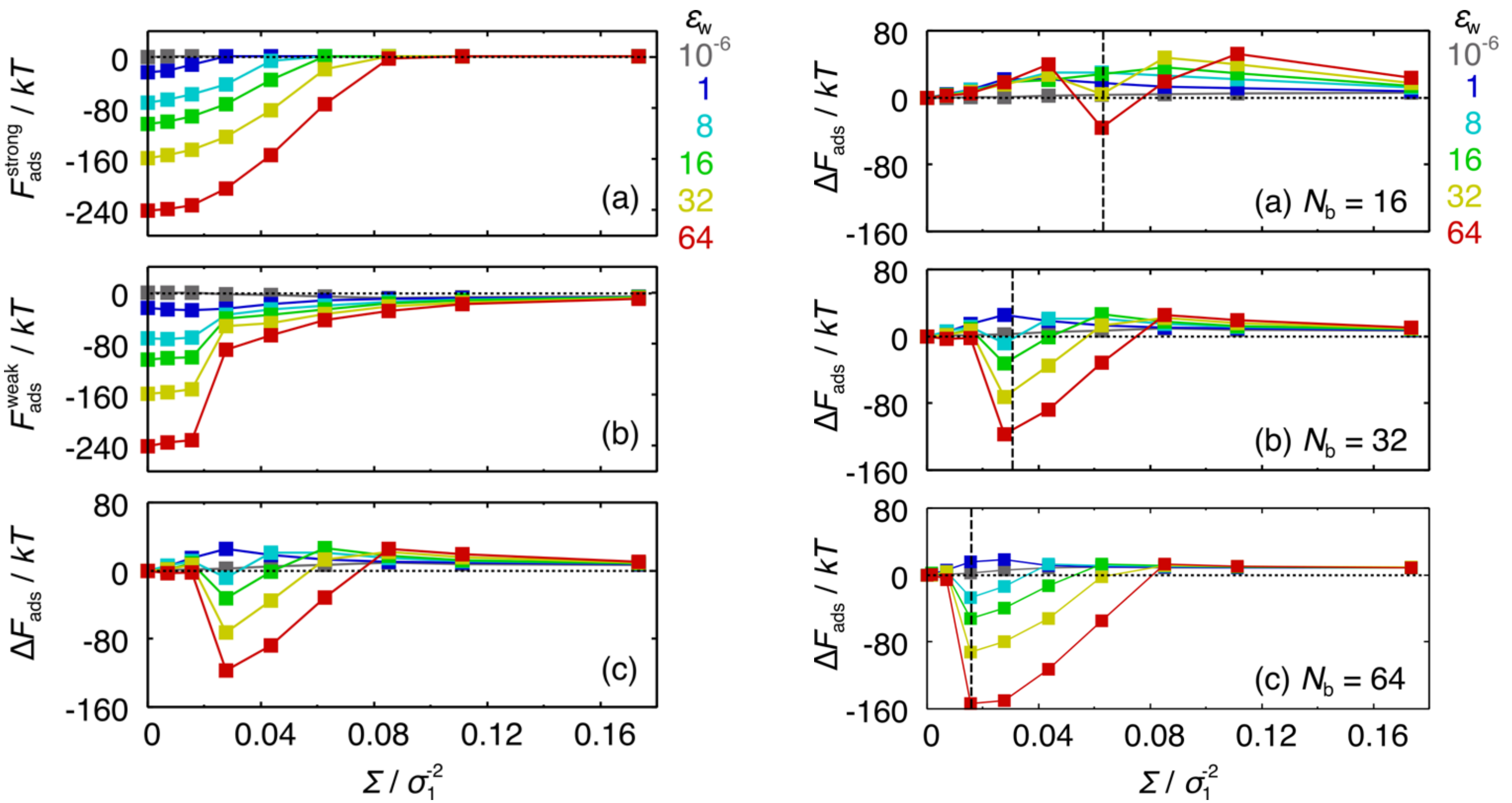
$$K = \frac{1}{\delta}\int_0^{\delta} e^{-F(z)/kT} dz$$





Antifouling performance is better for the less hydrophilic polymer brush in a range of grafting density

Anomalous regime

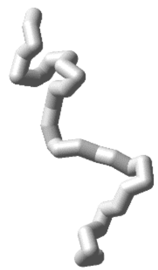


The anomalous behavior is found for $\begin{cases} \text{hydrophobic substrates} \\ \text{long chains} \end{cases}$

Correspondence between CG and AA

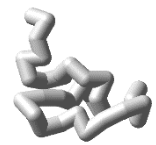
Strongly hydrophilic

$\varepsilon = 10^{-6}\ kT$

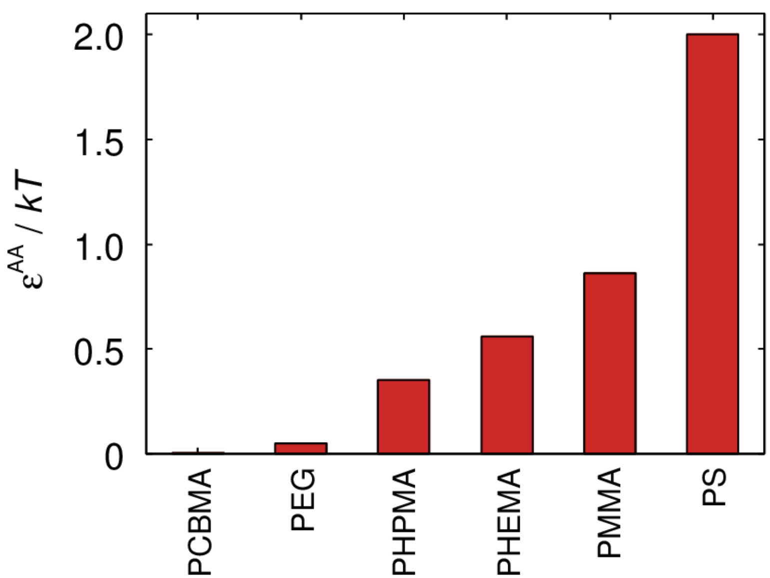


Weakly hydrophilic

$\varepsilon = 0.5\ kT$



Do these two CG models well represent real polymers?



Two equations for CG model

$$R_{\mathrm{g}}^{\mathrm{gs}} = 0.491 N_{\mathrm{b}}^{0.59}\sigma$$

(R_{g} in good solvent)

$$R_{\max} = 0.97 N_{\mathrm{b}}\sigma$$

(maximum chain length)

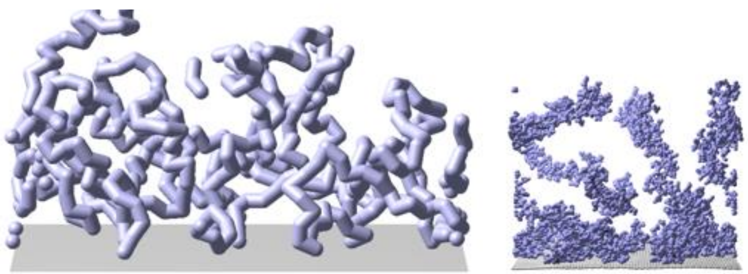
Insert $R_{\mathrm{g}}^{\mathrm{gs}}$ and $R_{\max}$ calculated from AA simulations with $N_{\mathrm{d}} = 98$

σ and N_{b} that reproduce the structure of the AA polymer with $N_{\mathrm{d}} = 98$

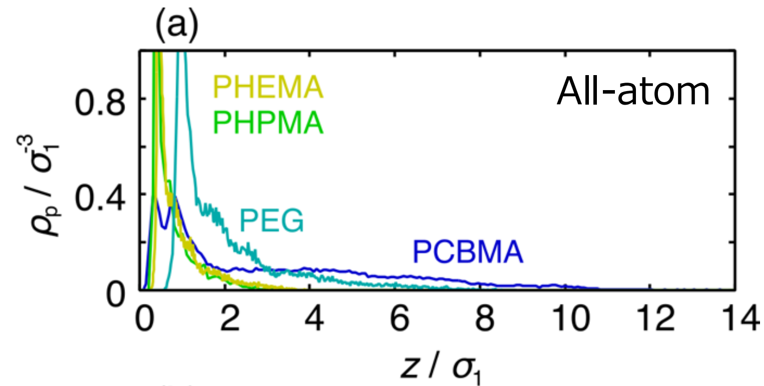
ε is determined by comparison of **R_{g} in water** calculated from CG simulations with AA simulations

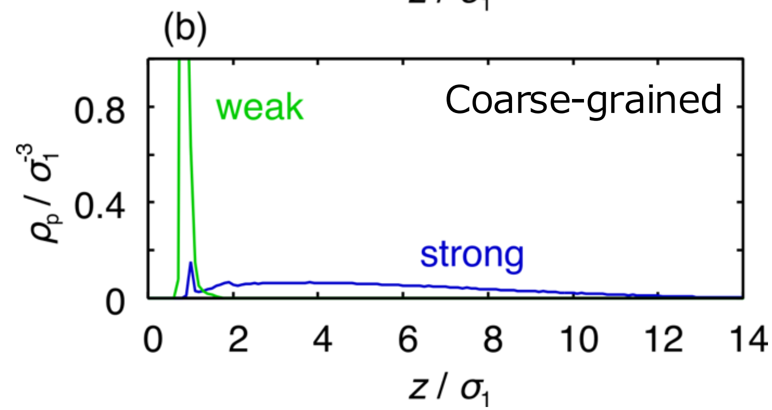
Structures of the CG and AA simulations

$\varepsilon = 10^{-6}\ kT$ PCBMA



$\varepsilon = 0.5\ kT$ PHPMA

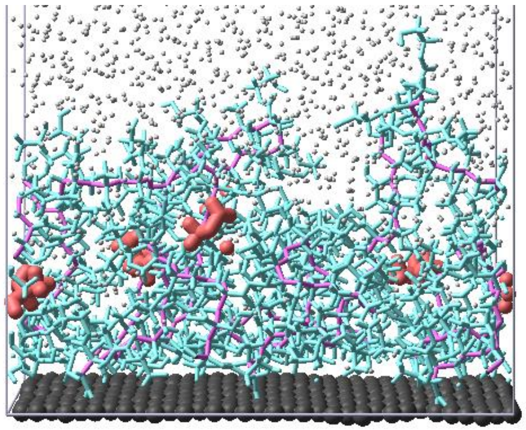




The CG models are structurally similar to the AA models.

Conclusions

All-atom (AA)



PCBMA

vs

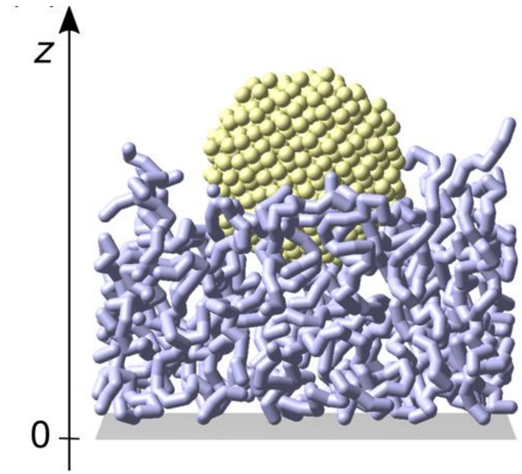
PHEMA

Two roles of bound water

- Enhancement of steric repulsion
- Reduction of London dispersion interactions

Better antifouling performance of the less hydrophilic PHEMA brush

Coarse-grained (CG)



$\varepsilon = 10^{-6}\ kT$

vs

$\varepsilon = 0.5\ kT$

Better antifouling performance of less hydrophilic brushes

- Hydrophobic substrates
- Long chains

Correspondence between CG and AA models

- T. Yagasaki and N. Matubayasi, *Langmuir* **39**, 13158–13168 (2023).
- T. Yagasaki and N. Matubayasi, *Langmuir* **40**, 15046–15058 (2024).

Acknowledgments

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