高分子に閉じ込められた水の水素結合状態と動的性質に対する分子動力学解析

Revealing the hidden dynamics of confined water in acrylate polymers: Insights from hydrogen-bond lifetime analysis

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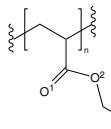
Introduction

✻ Background

PMEA : poly(2-methoxyethyl acrylate)

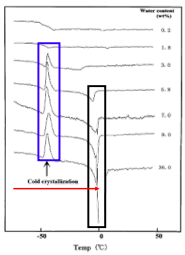


➢ **Blood Compatibility** Polymer

prevents blood clots formation

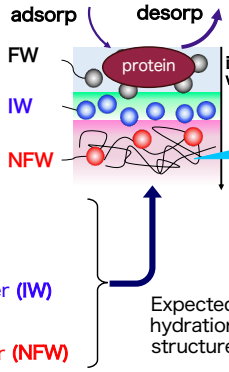
● **Experiments with DSC**

: three kinds of water



- □ : Freeze at **0 ℃**
  → Free water **(FW)**
- □: Freeze at **– 40 ℃**
  → Intermediate water **(IW)**
- **–110 ℃** without freezing
  → Nonfreezing water **(NFW)**

Tanaka, M., *et al.*, *Polymer International*, **49**(12), 1709 (2000)



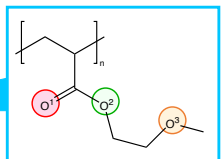
➢ **Hydration structure in PMEA**

- Predictions from thermal experiments
- Water molecule behavior is not organized.

We analyzed the H-bond dynamics in polymer; understand the properties of the water molecules in PMEA by MD simulations.

✻ Simulation systems

● **PMEA**　● **PHEMA**　● **PMC1A**



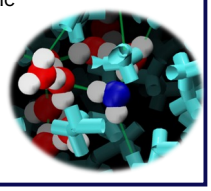
poly(2-methoxy ethyl acrylate)　poly(2-hydroxyethylmeth acrylate)　poly(1-methoxy methyl acrylate)

Only PMEA has **intermediate water**
Saturated moisture content in experiment of PMEA : **9** wt%

- polymer : OPLS-AA Force Field, 50mer, atactic
- water : TIP4P/2005 model

Water molecules inserted into 20 polymers : 3 wt% ~ 90 wt%

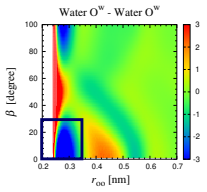
Production run : Max 500 ns (NVT)

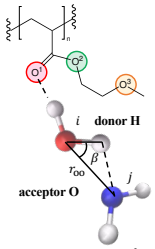


Definition of H-bond

Determined by **free energy surface** :
Distribution of **distance and angle** between water and each oxygen

$$W(r_{oo},\beta) = -k_B T \ln g(r_{oo},\beta)$$

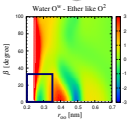




✓ **H-bond region**

$r_{oo} \le 0.35\,\mathrm{nm}$
$0 \le \beta \le 30°$

Ester like oxygen : O^2 does not make H-bond.

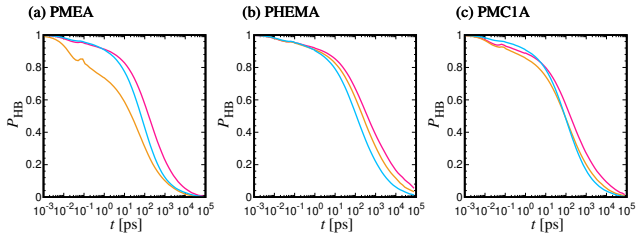


Dynamical properties of water

✻ Time correlation function

$$P_{HB}(t) = \frac{\langle h_{i,j}(t) h_{i,j}(0)\rangle}{\langle h_{i,j}(0)\rangle}$$

Dynamic properties of water molecules in PMEA can be classified according to the acceptor oxygen



✻ H-bond lifetime

$$\tau_{HB} = \int_0^\infty P_{HB}(t)\,dt$$

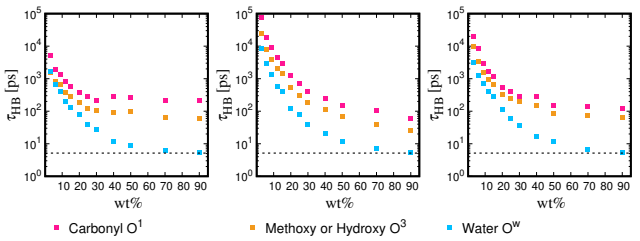
Integration of P_{HB}

= Time constant to break H-bond

➢ Difference of τ_{HB} between each acceptors
➢ Converge to a constant value

Lifetime : O^1 > O^3 > O^w ≈ bulk water

In all systems :
Mobility depends on moisture content



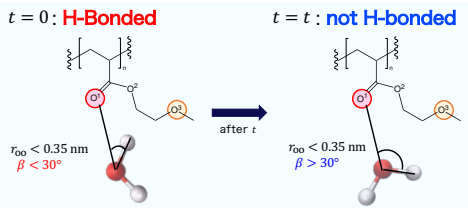
Stability of H-bond and state of water existence

✻ Diffusion of water and H-bond breakage

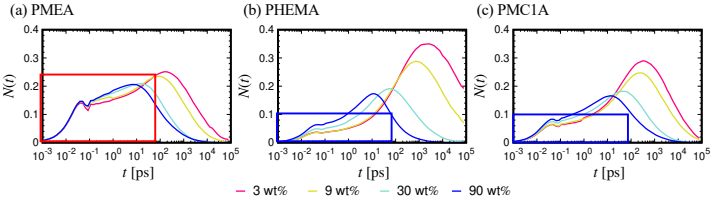
$$N(t) = \frac{\langle h(0)(1-h(t))H(t)\rangle}{\langle h(0)\rangle}$$

$h(t) = \begin{cases} 1 & \text{(H Bond)} \\ 0 & \text{(not H Bond)} \end{cases}$　$H(t) = \begin{cases} 1 & (r_{oo} \le 0.35\text{nm}) \\ 0 & (r_{oo} > 0.35\text{nm}) \end{cases}$

- Long time region : $N(t)$ is decayed, diffused
- Peak near H-bond lifetime



➢ **The conditional probability** of water molecule and acceptor remain **in close** at time t **after H-bond breakage**, given they were **H-bonded at** $t = 0$.

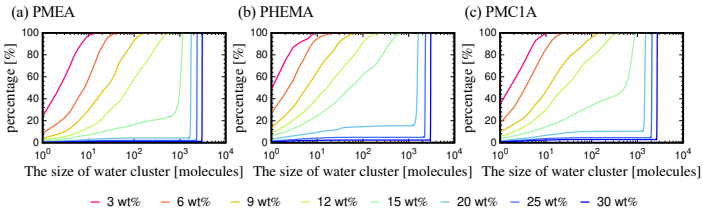


A **unique state** was observed in O^3 at PMEA

In short time region :
PMEA ··· **Large** $N(t)$, no diffusion after H-bonds breakage
Others ··· **Small** $N(t)$, still H-bonding

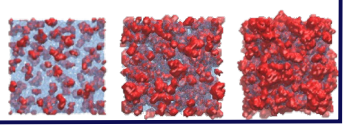
✻ Cluster size

Accumulated percentage of water cluster's size using H-bond length



at 3 wt% : ~ 10 molecules
more than 20 wt% :
almost all water in the system

➢ Small clusters reduce water mobility



Analyzed dynamic properties of water in polymers

- H-bond lifetime can be classified by acceptor oxygen
- Water content governs mobility
- Interaction of PMEA with methoxy oxygen : Intermediate strength interactions

Reference : K. Shikata, *et al.*, *J. Chem. Phys.* **158**, 174901 (2023).