

**ポリアルキルメタクリレート系摩擦調整剤の  
フレキシビリティパターンとコンフォーメーションへの影響**  
Exploring Flexibility Patterns in poly(alkyl methacrylates) Friction Modifiers  
and Influence on Conformations

名大・情（正）\*シェカー ヒマンシュ 名大・情（非）近澤 祐馬 名大・情（正）張 賀東

Himanshu Shekhar\*, Yuma Chikazawa\*, Hedong Zhang\*

\*Nagoya University

## 1. Introduction

Polymeric Friction Modifiers (PFMs) play a crucial role as additives in lubricants to mitigate friction and wear between contacting surfaces.<sup>1)</sup> These modifiers form a protective film upon adsorption onto surfaces, effectively reducing direct contact between surfaces and thereby minimizing friction and wear. The thickness of this boundary film is a critical determinant of PFM performance. PFMs undergo diffusion from the base oil and adopt an extended conformation upon interaction with the surfaces, highlighting the importance of understanding their conformational dynamics during dispersion and adsorption.

Bottlebrush Polymers (BBPs), exemplified in this study by Poly(alkyl methacrylates) (PAMAs), have attracted attention as promising PFMs due to their distinctive molecular architecture.<sup>2,3)</sup> BBPs feature linear side chains extending from a lengthy backbone, offering significant design flexibility to tailor conformation. Molecular parameters such as molecular weight and side chain length, as well as external stimuli like temperature and mechanical stress influence the conformation and flexibility of BBPs, thereby impacting their functional efficacy. Prior studies have shown that side chains in BBPs tend to form clusters around the backbone, with the size and number of these clusters varying based on polymer design parameters and external stimuli.<sup>4)</sup> In this study, we aim to quantify the number of clusters in PAMAs and correlate this clustering phenomenon with polymer flexibility and conformational dynamics.

## 2. Materials and Methods

Atactic PAMA polymers with different side chain lengths, namely Octyl Methacrylate (OC), Lauryl Methacrylate (LA), and Stearyl Methacrylate (ST) were used. Molecular weights of each type of the polymers were varied to approximately 3000, 9000, 12000, and 18000 g/mol. Hexadecane was chosen as the base oil due to its similarity to group III base oils for practical applications. Solid walls confining the polymer solutions were hematite plates with (001) surfaces. All these materials were described with all-atom models combined with the COMPASS II force field.<sup>5)</sup> As represented in Fig. 1, we conducted molecular dynamics (MD) simulations for bulk solutions and shear of the PAMA solutions by solid surfaces. The temperature was set at 298 and 373 K. The concentrations were approximately 2 and 7.4 wt.% for the bulk and shear simulations respectively. The pressure was 0.1 MPa for the bulk simulations. In the shear simulations, the initial configurations of the polymers were the same as the final ones of the bulk simulations, and a normal pressure of 1.0 GPa and shear velocity of 20 m/s were applied to the upper surface while the lower surface remained stationary. MD simulations were performed using LAMMPS<sup>6)</sup> and visualization was facilitated by OVITO.<sup>7)</sup>

Cluster analysis of the polymers was performed using the DBSCAN algorithm,<sup>8)</sup> and conformational analysis was performed by calculating Radius of Gyration ( $R_g$ ) and end-to-end distance ( $R_{ee}$ ) of the polymers.

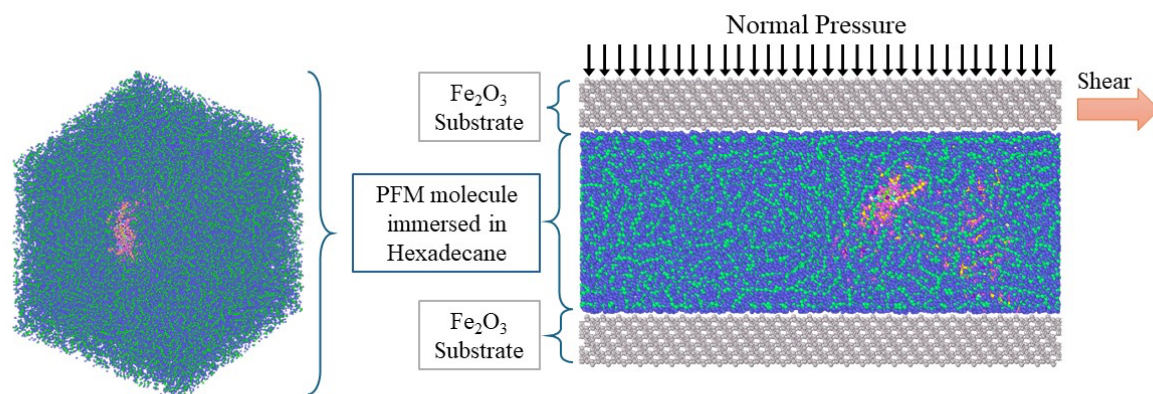


Fig. 1 Model of bulk (left) and shear (right) simulations

### 3. Results and Discussion

Cluster analysis revealed clear patterns in the distribution and arrangement of clusters among these PAMA polymers, with OC manifesting a higher cluster count compared to LA and ST. The schematic depiction of the cluster pattern is shown in Fig. 2. Clusters could be described as accumulations of atoms surrounding the polymer backbone (depicted in blue in Fig. 2), demarcated by regions of low density known as cluster nodes (highlighted in orange in Fig. 2). At the molecular weight of 3000 g/mol, each polymer formed only one cluster, with this count escalating with a reduction in side chain length and an increase in temperature. Kernel Density Estimation (KDE) plots provided insights into the frequency of conformational transitions, which further aided in relating the relationship between cluster arrangement, flexibility, and overall conformation. Notably, for OC, the cluster count remained relatively stable across varying conditions. Also, OC and LA exhibited a transition from a coil to a globule conformation as the temperature increased from 298 to 373 K, accompanied by a change in arrangement of clusters or an increase in cluster count. Examination of KDE plots also suggested that clusters tended to fragment and form nodes at elevated temperatures, attributed to heightened side chain mobility. Shear simulations highlighted the dynamic response of OC to mechanical stress, with significant changes in  $R_{ee}$  attributed to its higher cluster count and flexibility. Examination of the change in conformation of LA and ST revealed that apart from temperature, mechanical stress can also induce formation of nodes between predefined clusters.

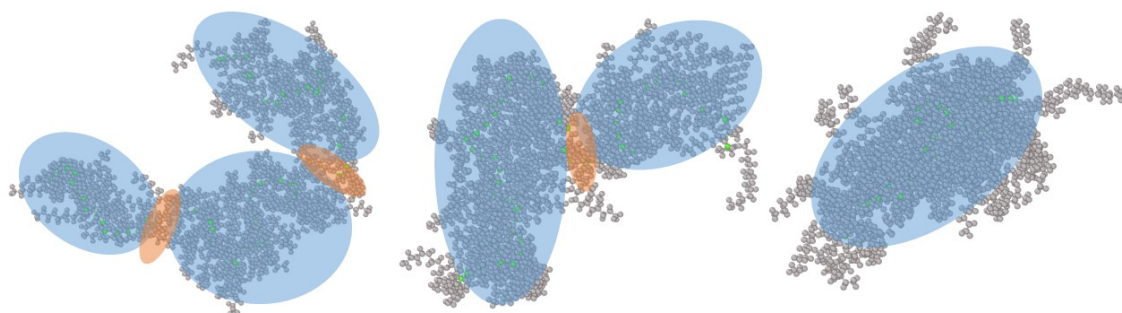


Fig. 2 Random Snapshots taken from bulk simulations of OC (left), LA (center), and ST (right) of molecular weight of approximately 18000 g/mol, showing the wrapping of side chains around the backbone of the polymers to form clusters (blue regions). The clusters are separated by regions of low density (orange regions) referred to as cluster nodes.

### 4. Conclusion

Through bulk and shear MD simulations and cluster analysis, we have demonstrated that the PAMA polymers display characteristics akin to a chain of articulated clusters, and the conformation and flexibility of the polymers is highly correlated with the cluster patterns. These insights provide a foundation for informed design strategies to optimize BBP-based lubricant additives for enhanced friction and wear mitigation in various industrial applications.

### Acknowledgements

This work was supported in part by the JSPS KAKENHI Grants (Nos. 21H01238 and 23H05448). H.S. acknowledges the Japanese Government (MEXT) Scholarship.

### References

- 1) S. Delamarre, G. Tobias, N. D. Spencer & J. Cayer-Barrioz: Polymeric Friction Modifiers: Influence of Anchoring Chemistry on Their Adsorption and Effectiveness, *Langmuir*, 38, 37 (2022) 11451.
- 2) A. Kerr, S. Häkkinen, S. C. L. Hall, P. Kirkman, P. O'Hara, T. Smith, C. J. Kinane, A. Caruana & S. Perrier: Anchor Group Bottlebrush Polymers as Oil Additive Friction Modifiers, *ACS Appl. Mater. Inter.*, 15, 41 (2023) 48574.
- 3) Y. Song, K. Fukuzawa, T. Hirayama, N. Yamashita, N. Yamada, S. Itoh, N. Azuma & H. Zhang: Effects of Polarity of Polymers on Conformation and Lubricating Film Formation of Adsorbed Films, *Macromolecules*, 56, 5 (2023) 1954.
- 4) E. Mohammadi, S. Y. Joshi & S. A. Deshmukh: A Review of Computational Studies of Bottlebrush Polymers, *Comp. Mater. Sci.*, 199 (2021) 110720.
- 5) H. Sun: COMPASS: An ab Initio Force-Field Optimized for Condensed-Phase Applications-Overview with Details on Alkane and Benzene Compounds, *J. Phys. Chem. B*, 102, 38 (1998) 7338.
- 6) A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott & S. J. Plimpton: LAMMPS - a Flexible Simulation Tool for Particle-Based Materials Modeling at the Atomic, Meso, and Continuum Scales, *Comput. Phys. Commun.*, 271 (2022) 108171.
- 7) A. Stukowski: Visualization and Analysis of Atomistic Simulation Data with OVITO—the Open Visualization Tool, *Model. Simul. Mater. Sc.*, 18, 1 (2009) 015012.
- 8) J. Sander, M. Ester, H. P. Kriegel & X. Xu: Density-Based Clustering in Spatial Databases: The Algorithm GDBSCAN and Its Applications, *Data Min. Knowl. Disc.*, 2 (1998) 169.