

# ポリアルキルメタクリレートのせん断下のコンフォメーションに及ぼす側鎖長の影響

## Influence of Side Chain Length on poly(alkyl methacrylate) Conformation under Shear

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### 1. Introduction

Polymeric Friction Modifiers (PFMs) are crucial additives in lubricants, designed to reduce friction and wear between contacting surfaces<sup>1)</sup>. These additives typically consist of long-chain polymers that form an adsorbed layer on surfaces, thereby minimizing solid-to-solid contact and reducing friction. The conformation of these adsorbed molecules is vital in determining the film thickness, making it essential to study their behavior under shear forces to understand their conformation on the substrate.

Bottlebrush Polymers (BBPs), such as poly(alkyl methacrylates) (PAMAs), have garnered interest as effective PFMs due to their unique molecular structure<sup>2)</sup>. BBPs possess linear side chains branching from a central backbone, providing considerable design flexibility to adjust conformation and film thickness. The polymer's molecular architecture can be adjusted by varying the side chain length, which can have complex effects on the adsorbed conformation, especially under mechanical stress. Previous research indicates that BBPs with longer side chains tend to exhibit greater film thickness under static conditions<sup>3)</sup>. This study aims to explore how side chain length affects the conformation of adsorbed polymers under shear stress, to determine whether the polymers maintain a higher film thickness under such conditions.

### 2. Materials and Methods

This study utilized atactic all-atom homopolymer models of PAMAs with varying side chain lengths: poly(octyl methacrylate) (POC-C8), poly(lauryl methacrylate) (PLA-C12), and poly(stearyl methacrylate) (PST-C18) as depicted in Fig. 1(a). These models were constructed with approximate molecular weights of 18,000 g/mol. Hexadecane was selected as the solvent due to its resemblance to Class-III alkane-based base oils. Shear simulations, depicted in Fig. 1(b), were conducted at a temperature of 298 K. Initially, the polymer molecules were equilibrated in bulk hexadecane solution at the target temperature. Subsequently, the equilibrated molecules were mixed again with hexadecane and positioned between two hematite surfaces. The system was then compressed while maintaining the PAMA molecule configuration constant.

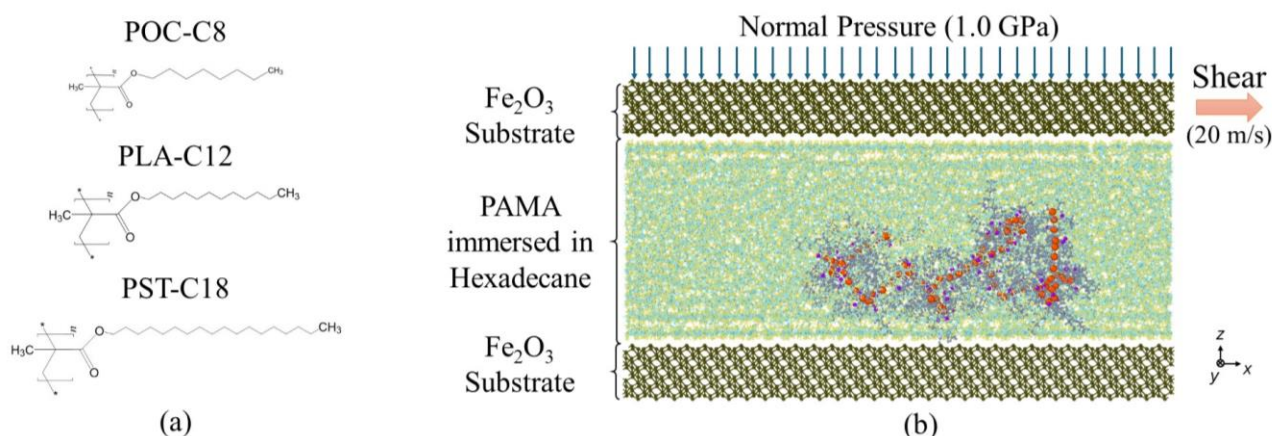


Fig. 1: (a) Molecular structure of three PAMA polymers: poly (octyl methacrylate) (POC-C8), poly (lauryl methacrylate) (PLA-C12), and poly (stearyl methacrylate) (PST-C18). (b) Model of shear simulation system. The polymer backbone is depicted in red; the side chains are depicted in gray and the polar group atoms are depicted in purple.

Following compression, the polymers were subjected to shear between two iron oxide surfaces by moving the upper substrate at a constant velocity of 20 m/s under a normal pressure of 1 GPa. Conformational analysis was performed by measuring the Radius of Gyration ( $R_g$ ) tensor, the ellipsoid flatness of the polymer on the substrate, the number of adsorbed atoms, and the order parameter that defines the rotation of the polymer under shear. Molecular interactions were modeled using the COMPASS force field<sup>4)</sup>, with Molecular Dynamics (MD) simulations executed using LAMMPS<sup>5)</sup> and visualization facilitated by OVITO<sup>6)</sup>.

### 3. Results and Discussion

Conformational analysis reveals distinct adsorption trends that vary with increasing side chain lengths as depicted in Fig. 2. The polymers underwent three phases: initially, they move along the shear direction with low adsorption, followed by a rotational phase, and finally a second translational phase with relatively stable adsorption. The duration and occurrence of these phases differ among polymers due to variations in side chain length. During the first translational phase, the polymers typically adopt a globular conformation, which facilitates rotation by halting flow along the shear direction. This globular form results in a high number of adsorbed atoms within a small area. However, this is not observed for PST-C18, which experiences crowding effects from its long side chains that shield the polar groups near the backbone. Consequently, PST-C18 primarily adsorbs at the terminal ends, where polar groups are more likely to interact with the surface, leading to a vertical adsorption regime. This results in weaker adsorption for PST-C18 compared to other polymers, which achieve stable adsorption after rotation. PLA-C12, with intermediate side chain lengths, shows less stable adsorption compared to POC-C8 after rotation and exhibits stick-slip motion under shear. This highlights the influence of side chain length on adsorption behavior and stability.

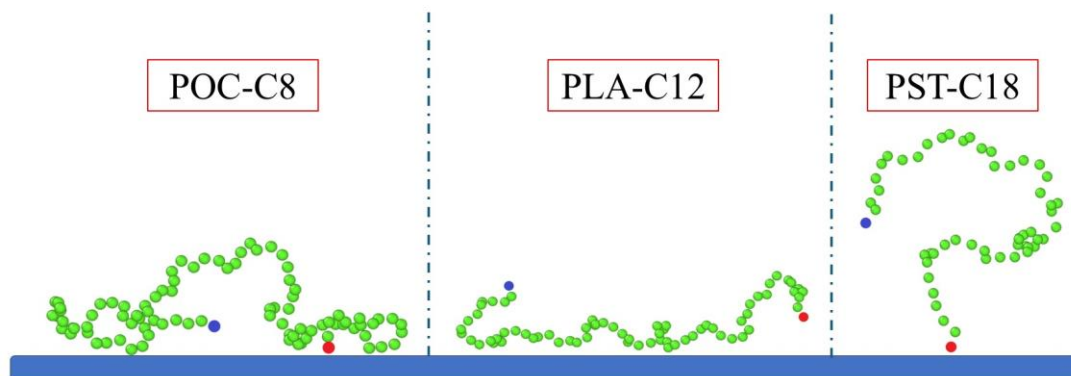


Fig. 2: Snapshots depicting the polymer backbones of POC-C8, PLA-C12 and PST-C18 during adsorption after rotation. The backbone atoms are depicted in green, the terminal atoms are depicted in red and blue colors

### 4. Conclusion

Based on our molecular dynamics simulations, we examined the conformations of PAMA polymeric friction modifiers under shear on a substrate. The results demonstrate distinct adsorption behaviors for each polymer type. The coil-globule transition significantly influences the adsorption process, as polymers with shorter side chains achieve a concentrated distribution of adsorbed atoms during their globular phase. In contrast, polymers with longer side chains exhibit weaker adsorption, primarily at the terminal ends, resulting in a lack of stable adsorption phases post-rotation. This study enhances our understanding of how polymer conformations respond to mechanical stress, highlighting the critical role of side chain length in adsorption stability.

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