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Segmental Dynamics of Poly(Alkyl Methacrylate) Chain in Ultra-Thin Spin-Cast Films

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Abstract : Polymeric materials are often used in a form of thin film such as food wrap and surface coating. In such the applications, polymer films thinner than 100 nm have been often used. The thickness of such the ultra-thin film is less than the unperturbed size of a polymer chain; therefore, the polymer chain in an ultra-thin film is strongly constrained. However, the details on the constrained dynamics of polymer molecules in ultra-thin films are still unclear. In the current study, the segmental dynamics of single polymer chain was directly investigated by fluorescence microscopy. The individual chains of poly(alkyl methacrylate) labeled by a perylenediimide dye molecule were observed by a highly sensitive fluorescence microscope in a defocus condition. The translational and rotational diffusion of the center segment in a single polymer chain was directly analyzed. The segmental motion in a thin film with a thickness of 10 nm was found to be suppressed compared to that in a bulk state. The detailed analysis of the molecular motion revealed that the diffusion rate of the in-plane rotation was similar to the thin film and the bulk; on the other hand, the out-of-plane motion was restricted in a thin film. This result indicates that the spatial restriction in an ultra-thin film thinner than the unperturbed chain dimension alters the dynamics of individual molecules in a polymer system.

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