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Structural Analysis of Polymer Thin Films at Single Macromolecule Level

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Abstract : The properties of a spin-cast film of a polymer material are different from those in the bulk material because the polymer chains are frozen in an un-equilibrium state due to the rapid evaporation of the solvent. However, there has been little information on the un-equilibrated conformation and dynamics in a spin-cast film at the single chain level. The real-space observation of individual chains would provide direct information to discuss the morphology and dynamics of single polymer chains. The recent development of super-resolution fluorescence microscopy methods allows the conformational analysis of single polymer chain. In the current study, the conformation of a polymer chain in a spin-cast film by the super-resolution microscopy. Poly(methyl methacrylate) (PMMA) with the molecular weight of 2.2 x 10^6 was spin-cast onto a glass substrate from toluene and chloroform. For the super-resolution fluorescence imaging, a small amount of the PMMA labeled by rhodamine spiroamide dye was added. The radius of gyration (Rg) was evaluated from the super-resolution fluorescence image of each PMMA chain. The mean-square-root of Rg was 48.7 and 54.0 nm in the spin-cast films prepared from the toluene and chloroform solutions, respectively. On the other hand, the chain dimension in a bulk state (a thermally annealed 10- μm-thick sample) was observed to be 43.1 nm. This indicates that the PMMA chain in the spin-cast film takes an expanded conformation compared to the unperturbed chain and that the chain dimension is dependent on the solvent quality. In a good solvent, the PMMA chain has an expanded conformation by the excluded volume effect. The polymer chain is frozen before the relaxation from an un-equilibrated expanded conformation to an unperturbed one by the rapid solvent evaporation.

Keywords : chain conformation, polymer thin film, spin-coating, super-resolution optical microscopy
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