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Communication

Positioning a fluorescent probe at the core of a glassy star polymer for detection of local dynamics

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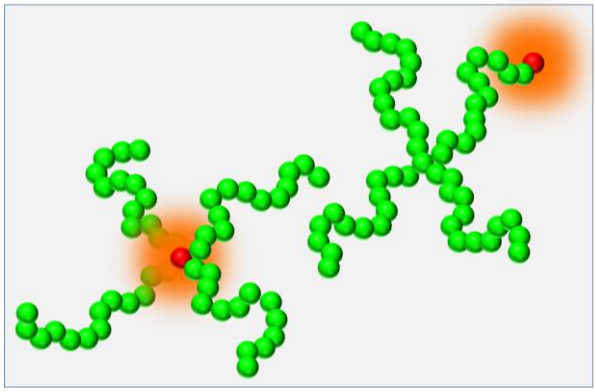
Graphical abstract



By precisely positioning a fluorescent molecule, perylene diimide, at the branch point and the arm's end of a star polymer *via* controlled atom transfer radical polymerization and click-reaction, respectively, the local dynamics is investigated by single molecule defocused fluorescence microscopy. The results expose the vast difference between the local dynamics of these two sites within the star polymer.

ABSTRACT

Accessing local dynamics within a single macromolecule is the key to understand the physical origin of the viscoelasticity and especially the glass transition. In order to extract specific information on the dynamics of the branch point of a star polymer around its glass transition temperature, four-arm star poly (*n*-butyl methacrylate) with a fluorescent core was synthesized using perylene diimide as initiator and polymerization conducted via atom transfer radical polymerization. The process is found to be effective in positioning the fluorophore at the branch point with the fluorophore intact, which allows the successful application of single molecule fluorescence defocus imaging in examining the local site-sensitive dynamics. The power spectra of rotation trajectories, the population of rotating fluorophores as well as the distribution of angular displacement were used to revel the difference in local dynamics between branch point and the arm's end. It is discovered that the local dynamics at the core of the star polymer is much less activated than that at the arm's end. The results demonstrate the strong effect dues to the topological constrain at the branch point and the more free space at the arm's end.

Keywords:Perylene diimide Star polymer Glass transition Fluorescence defocus imaging Local dynamics

Glass transition is one of the most important and challenging research areas in chemical and physical science as well as for the commitment of designing and fabricating advanced materials with high performance [1-3]. Probing local molecular dynamics has long been a key and promising approach to the understanding of glass transition of polymers [2]. For the past decades, tremendous experimental efforts have been made and numerous methods have been applied to access the local segmental dynamics of polymers, related to the glass transition process [4-7]. It is until recently that single molecule fluorescence microscopy has been proved to be a new and effective technique to probe the dynamics of single molecules in different forms of states, such as in the liquid state [8], solid state [9], as well as at the interfaces [10]. Among these ultra-sensitive techniques with excellent spatial resolution, single molecule