

Second-order phase transition behavior in polymer glass transition

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Keywords: Glass Transition; Second-order Phase Transition; Critical Phenomena

Glass transition was primarily considered to be not phase transition. Recent single-molecule spectroscopy (SMS) developments have prompted re-investigating polymer glass transition at the microscopic scale, revealing that glass transition includes phenomena similar to second-order phase transition.¹ They are characterized by microscopic collective polymer motion and discontinuous changes in temperature dependent relaxation times within a temperature window that includes the polymer calorimetric glass transition temperature T_g .

We selected poly(vinyl acetate): PVAC10 (MW 100,000)¹; PVAC50 (MW 500,000) and poly(ethyl methacrylate): PEMA05 (MW 50,000). Viscosity-sensitive fluorescence probe Cy3 used in SMS shows enhanced fluorescence intensity with increased polymer viscosity and *vice versa*. Thus, changes in Cy3 fluorescence intensity report us thermally driven polymer dynamics or relaxation. SMS was carried out with a video microscope equipped with a CCD camera and an image intensifier making it possible observe single molecule Cy3 covalently immobilized on a quartz surface with a polymer overlay. The single molecule Cy3 was irradiated with a CW 532-nm laser using evanescent excitation geometry. Sample temperatures were controlled with a hot plate for microscope use from room temperature (23–25 °C) to 90 °C, within which we evaluated T_g (36.5 for PVAC10, 37.9 for PVAC50, and 65.8 °C for PEMA05) by DSC.

We observed autocorrelation functions $C(\tau)$ and power spectra $J(\nu)$ from individual single Cy3 fluorescence trajectories $I_i(t)$, and then evaluated average relaxation time $\langle\tau_R\rangle$ from 20–30 $C(\tau)$ at the above noted temperatures controlled with a hot plate.

Figure 1 illustrates the key to the present research to contrast it with the conventional idea of glass-forming material relaxations. The present work elucidated enhanced $\langle\tau_R\rangle$ above T_g . This observation looks critical slowing down as a critical phenomenon in the

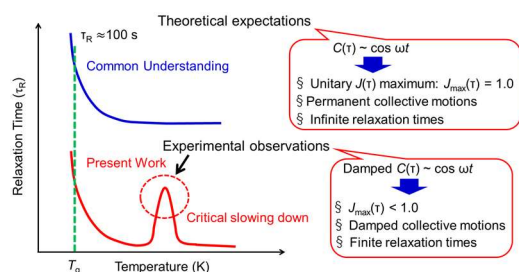


Figure 1. Schematic of the present work summary.

second-order phase transition. Enhanced $\langle\tau_R\rangle$ simultaneously occurred together with oscillatory $C(\tau)$, the latter of which provides evidence for polymer collective motion around single Cy3 molecules. Thus, both enhanced $\langle\tau_R\rangle$ and oscillatory $C(\tau)$ above T_g evidenced second-order phase transition behavior in polymer glass transition.

1) M. Ishikawa et al., *ChemRxiv* **2020**, 12696020.