

The relationship between heterogeneity and the reaction acceleration during bulk polymerization

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The curing of resins is widely used in various applications of polymeric materials, including adhesion, painting, polymer part fabrication, fiber-reinforced plastics, and 3D printing. The liquid resin is eventually converted to a solid glassy polymer via a chemical reaction. Despite the broad application area, the curing behavior, especially around polymerization-induced vitrification, is not fully understood. It is because of the difficulty in monitoring and understanding the drastic change of resins from a liquid to a glassy solid. One widely used chemical reaction is radical polymerization without solvent (i.e., bulk radical polymerization). During bulk radical polymerization, it has long been known that a sudden reaction acceleration may occur. This reaction acceleration is known as the Trommsdorff effect. Despite a long and huge effort in understanding the Trommsdorff effect, the detailed mechanism of the Trommsdorff effect is still under debate. It is explained by the decreased termination rate due to the increased macroscopic viscosity via curing. However, the macroscopic viscosity is insufficient to fully explain the experimental data because the effect occurs so suddenly. One crucial recent observation is the appearance of microscopic heterogeneity at the onset of the Trommsdorff effect detected by a single molecular spectroscopy. Since it has long been assumed a priori that the polymerization solution remains homogeneous, this observation changed the view of polymer curing significantly.

Previously, we applied small-angle neutron scattering (SANS) during the bulk polymerization of methyl methacrylate (MMA) at SANS-U. SANS is suited to see the contrast between deuterium and hydrogen. Therefore, it has been utilized to investigate the miscibility of polymer blends. We gained contrast by dissolving 10, 20, and 30 wt% of corresponding hydrogenated polymer (i.e., PMMA) in

deuterated MMA. We found that the scattering profile discontinuously changes at the vicinity of vitrification, as it has been published in literature [1]. This discontinuous change was correlated with a sudden reaction acceleration.

As a continuous study, we investigate the effect of additives on the polymerization kinetics. It has previously reported that addition of poly(ethylene glycol) (PEG) significantly increases the reaction kinetics of MMA and the onset of the Trommsdorff effect. It is noted that PEG does not chemically react with MMA. We hypothesized that the microscopic heterogeneity changes due to the addition of the PEG. Fig. 1 displays the double-logarithmic plots of the SANS profile during bulk polymerization of MMA in the presence of PEG. After 35 min, a macroscopic phase separation took place. There was a noticeable change in the SANS profile before the macroscopic phase separation. We are analyzing this result in detail to understand the change in reaction kinetics at the molecular level.

[1] Y. Suzuki *et al.*, *Macromolecules* **56**, 3751 (2023).

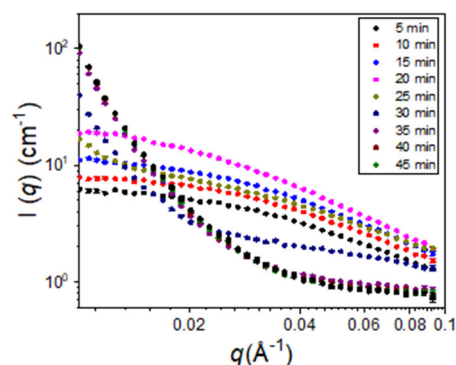


Fig. 1. Double-logarithmic plots of the SANS profile during bulk polymerization of MMA in the presence of pre-dissolved PEG with 40 wt% at different reaction times.