Heterogeneities at the vicinity of polymerization induced vitrification

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Bulk radical polymerization or undiluted polymerization is a polymerization method without a solvent. Typically, a small amount of radical initiator is added to a monomer in a liquid state. As the reaction proceeds, the ratio of monomer and polymer changes continuously. In many cases, the obtained polymer is in a solid state after complete polymerization. In other words, polymerization-induced vitrification or glass transition occurs. This method is advantageous in that pure polymer with high molecular weight can be easily obtained in high yield. Bulk polymerization is widely used for coating applications, dental fillings, and photo- or thermal curing processes. Recently, it is also desired to apply bulk polymerization as a resin for fiber-reinforced plastics and additive manufacturing (3D printing). A huge challenge in using bulk free radical polymerization is the thermal management during the reaction. A sudden temperature increase known as the Trommsdorff effect may occur. Qualitatively, the origin of this effect is attributed to the increased viscosity. The increased viscosity significantly lowers the probability of meeting two radicals and, thus, the termination rate. In comparison to the termination rate, the propagation rate is less affected by the viscosity change. As a result, propagation becomes dominant over termination. While this explanation sounds reasonable, the detailed mechanism of the effect is still under debate.

In order to better understand the microscopic picture at the onset of the Trommsdorff effect, we applied small-angle neutron scattering (SANS) during the bulk polymerization of methyl methacrylate (MMA). SANS is suited to see the contrast between deuterium and hydrogen. Therefore, it has been utilized to investigate the miscibility of polymer blends. In this study, 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 shown in Figure 1. This discontinuous change was correlated with a sudden reaction acceleration. Ornstein-Zernike analysis revealed that the intensity at $q = 0$ ($I(0)$) and the correlation length of concentration fluctuation (ξ) suddenly increases at the discontinuous change of the scattering profile. The obtained data implies that the increased heterogeneity (i.e., microscopic concentration fluctuation) is intimately related to the Trommsdorff effect. For a long time, many scientists have tried to explain the sudden change of the reaction kinetics due to the increased macroscopic viscosity. However, the change in reaction kinetics is so sudden that no mathematical model can predict the behavior. The increased heterogeneity can significantly lower the probability of meeting two radicals (i.e., termination rate) while maintaining the probability of meeting a radical and a monomer molecule (i.e., propagation rate). This may be the origin of Trommsdorff effect.

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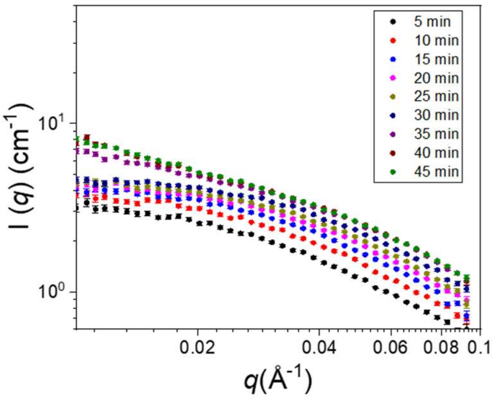

Fig. 1. Double-logarithmic plots of the SANS profile during bulk polymerization of MMA in the presence of pre-dissolved PMMA at different reaction times. The weight percentage of pre-dissolved PMMA is 10 wt %.