Effect of solvent addition on nanoscale heterogeneity during bulk polymerization of methyl methacrylate investigated by small-angle neutron scattering

E. Sasaki, Y. Suzuki

Osaka Metropolitan University

The Trommsdorff effect is a well-known phenomenon in bulk radical polymerization characterized by sudden reaction acceleration. Traditionally, this effect has been explained by increased viscosity and reduced termination rates. However, this picture alone does not quantitatively explain the abrupt change in reaction kinetics. Recent studies have suggested that nanoscale heterogeneity generated during polymerization may play an important role. In our previous studies, small-angle neutron scattering (SANS) measurements revealed that concentration fluctuations rapidly increase at the onset of the Trommsdorff effect during bulk polymerization of methyl methacrylate (MMA). Furthermore, comparison between MMA and styrene suggested that the magnitude of concentration fluctuation growth correlates with the strength of the Trommsdorff effect. In the present study, we further investigated this relationship by systematically weakening the Trommsdorff effect through solvent addition.

Bulk polymerization of deuterated MMA containing predissolved poly(methyl methacrylate) with different amounts of toluene was investigated using the SANS-U instrument installed at JRR-3. Time-resolved SANS measurements were conducted during polymerization while systematically varying solvent concentration. The scattering profiles were analyzed using Ornstein–Zernike analysis to determine the intensity extrapolated to $q = 0$, $I(0)$, and the correlation length of concentration fluctuations, ξ.

Without solvent addition, ξ initially decreased slightly during polymerization, reflecting homogenization of the polymerization solution. At the onset of the Trommsdorff effect, however, ξ increased rapidly, consistent with our previous reports. As the amount of added toluene increased, the reaction acceleration gradually became weaker and the increase in ξ became progressively smaller as shown in Fig.1. The abrupt increase characteristic of bulk MMA polymerization became significantly suppressed when larger amounts of solvent were introduced.

The effect of solvent addition was systematic. Conditions exhibiting stronger Trommsdorff acceleration showed larger increases in concentration fluctuations, whereas conditions with weaker acceleration exhibited only modest changes in ξ. These results indicate that the rapid growth of concentration fluctuations is not unique to neat bulk polymerization but systematically changes together with the magnitude of reaction acceleration.

These findings support the hypothesis that nanoscale heterogeneity plays an important role in changing radical reaction probabilities during bulk radical polymerization. The present results further suggest that concentration fluctuations are not merely a consequence of reaction acceleration but may be intimately related to the emergence of the Trommsdorff effect itself.

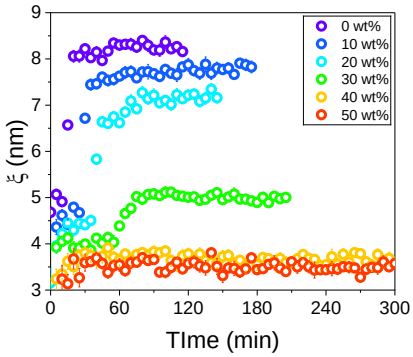

Fig. 1. Correlation length of concentration fluctuations (ξ) during bulk polymerization of MMA with different amounts of added toluene. Increasing solvent concentration suppresses the abrupt increase in ξ associated with the Trommsdorff effect.