Studies on Formation Mechanism of Polymer Particles by Miniemulsion Polymerization

T. Taniguchi1, R. Motokawa2, T. Wakiya3, S. Kitahara4, M. Kohri1, Y. Enomoto1
1Graduate School of Engineering, Chiba University, 2Japan Atomic Energy Agency, 3Sekisui Chemical, 4Sekisui Medical

Miniemulsion polymerization of styrene (St) was carried out by using a conventional cetyltrimethylammonium bromide (CTAB) and a polymerizable surfactant N,N-dimethyl-N-dodecyl-2-methacryloyloxyethylammonium bromide (C12-DMAEMA). A St solution containing polystyrene (PSt) as a hydrophobe was added to the aqueous phase containing the surfactant. The mixture was stirred at room temperature for 10 minutes. The resultant emulsion was then homogenized for 15 min under vigorous stirring by using a SMT UH-300 ultrasonicator operated under pulse-mode at 80% intensity. An ice bath was used to avoid heating during sonication. The miniemulsion was transferred to a four-necked round-bottom flask equipped with a paddle stirrer, a thermometer, a nitrogen inlet, and a reflux condenser. The system was purged with nitrogen for 15 minutes with stirring at 100 rpm to remove oxygen. After injection of a solution of KPS or V50 (when used), polymerization was initiated by heating to 60 - 70 °C with stirring at 200 rpm. After 6 h, the polymer latex formed was filtered through a Spectrum P/N M10S-260-01P hollow fiber membrane by using a Cole-Parmer Master Flex L/S model 7554-90 tubing pump system and purified by repetitive replacement of the aqueous medium with deionized water. The kinetic effect of surfactants on particle formation was quantitatively analyzed from the viewpoint of monomer conversions, molecular weights, compositions, and the interface structures measured by small angle neutron scattering measurement (SANS). SANS profiles revealed that the distribution of monomer droplets in St/C12-DMAEMA/V50 became narrower with progression of polymerization, leading to monodisperse polymer particles. Characteristic interfacial thickness was estimated by SANS profiles. The characteristic interfacial thickness of St/C12-DMAEMA/V50 decreased from 1.8 to 1.3 nm. In the case of St/CTAB/V50, the thickness decreased from 1.2 to 0.6 nm. This difference in interfacial thickness between St/C12-DMAEMA/V50 and St/CTAB/V50 is thought to be due to the maldistribution of copolymerized C12-DMAEMA units on particle surfaces.

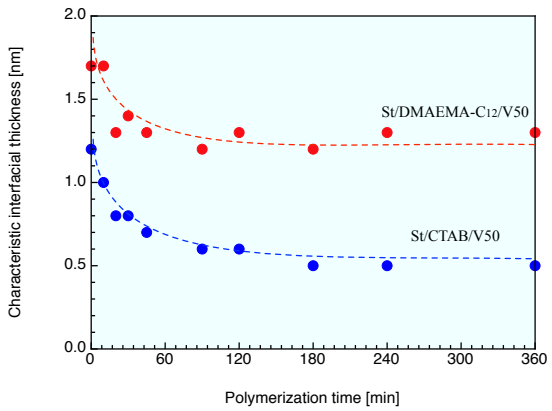

Fig. 1. Plot of characteristic interfacial thickness of St/CTAB/V50 and St/C12-DMAEMA/V50 as a function of polymerization time. Characteristic interfacial thickness is determined from interfacial thickness distribution.