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PREPARATION OF BLOCK COPOLYMER PARTICLES HAVING MULTILAYERED STRUCTURE BY MINIEMULSION ATRP

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Atom transfer radical polymerization (ATRP) is a powerful method for the synthesis of well-defined vinyl polymers of controlled molecular weight and narrow molecular weight distribution [1,2]. In addition, implementation of ATRP in aqueous heterogeneous systems makes it possible to prepare various novel particle morphologies. In our previous work, poly(*i*-butyl methacrylate)-*block*-polystyrene (P*i*BMA-*b*-PS) was successfully prepared by two-step ATRP in an aqueous heterogeneous system [3]. It was demonstrated how this technique can be employed as an alternative to the solvent absorbing/releasing method [4] for the synthesis of composite polymer particles with multilayered morphology.

The purpose of the present work has been to increase the polymerization rate (*R*p) compared to our previous work, as well as to clarify the criteria for synthesis of multilayered particles. The use of activator-generated by electron transfer (AGET) ATRP (using ascorbic acid as reducing agent) enabled synthesis of P*i*BMA-*b*-PS particles at a much higher *R*p. The blocking efficiency, i.e. the number fraction of block copolymer formed in the seeded AGET ATRP, was shown to greatly influence the morphology. If the blocking efficiency is too low (40%), a sea-island morphology is obtained (Fig. 1(a)) Low blocking efficiency was attributed to an excessively high activation rate at the early stage of the seeded AGET ATRP, resulting in extensive bimolecular termination. In order to increase the blocking efficiency, the activation rate was suitably reduced by lowering the polymerization temperature and adjusting the amount of ascorbic acid. In this way, sufficiently high blocking efficiency for formation of multilayered morphology was obtained while maintaining a reasonable high *R*p.

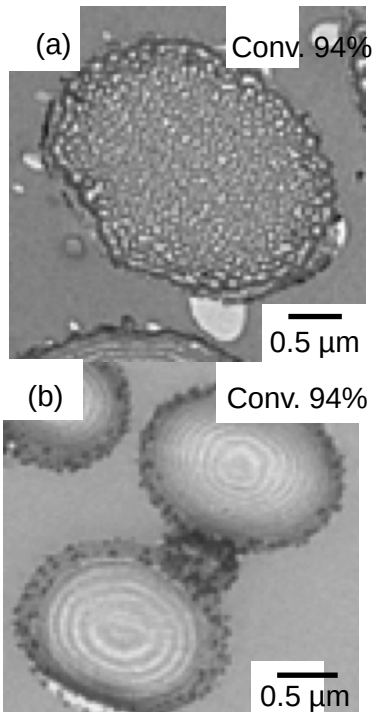

Fig. 1 TEM photographs of ultrathin cross-sections of RuO_4-stained P*i*BMA-*b*-PS particles prepared by seeded AGET ATRP of styrene using P*i*BMA-Br seed particles at 70˚C (a), and at 40˚C for 2 h, followed by at 70˚C (b). $[CuBr_2]/[AsA]$ (Equivalent ratio): (a) 1/1 ; (b) 1/0.8.

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