## PC 03

## ESTIMATION OF DISTRIBUTION OF CARBOXYL GROUPS IN CARBOXYLATED COPOLYMER PARTICLES PREPARED BY BATCH EMULSION COPOLYMERIZATION UNDER DIFFERENT STIRRING CONDITIONS

T. Suzuki, M. Yanagisawa, M. Okubo

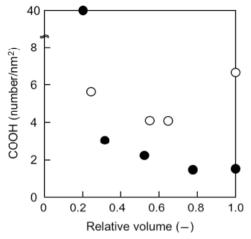
Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan (okubo@kobe-u.ac.jp, http://www.research.kobe-u.ac.jp/eng-cx6/)

Carboxyl groups are generally introduced to polymer particles by emulsion copolymerization with such an unsaturated acid monomer as methacrylic acid (MAA) and acrylic acid in order to confer chemical reactivity onto polymer particles and to improve the stability of polymer emulsion. There has been no satisfactory quantitative method to estimate the distribution state of carboxyl groups within polymer particle yet. In our previous research, the estimation of sulfate groups as initiator fragments at polystyrene particle surfaces was possible even with less than 0.03 g polystyrene particles by isothermal titration calorimetry (ITC), which is one of useful microanalysis can be done by various heat-analysis methods in the biochemical field [1]. Moreover, the semiquantitative estimation of distribution states of carboxyl groups within butyl methacrylate-MAA copolymer particles, which were produced by emulsion copolymerization with different (batchwise and uniform) monomer addition methods was successed [2].

In this presentation, ITC measurement for the estimation of the distribution of carboxyl groups within particles by batchwise emulsion copolymerization of styrene (S) and MAA with nonionic emulsifier in different stirring states will be discussed.

The stirring under the monomer layer which was floating on the aqueous medium, is called "inefficient stirring," and that, under which monomer droplets were dispersed, is called "efficient stirring". ITC measurement (Fig.1) showed that with inefficient stirring, almost all carboxyl groups were distributed inside the particle, while with efficient stirring, carboxyl groups were distributed homogeneously inside the particle. The ITC results were good agreement with the polymerization behaviour.

1) M. Okubo, T. Suzuki, A. Sakauchi, *Colloid Polym Sci*, **277**, 579 (1999), 2) M. Okubo, T. Suzuki, N. Tsuda, *ibid*, **284**, 1319 (2006)



**Fig. 1** Number of carboxyl groups at the surface of P(S-MAA) (MAA 10 mol%) particles prepared by batch emulsion copolymerizations with inefficient ( $\bullet$ ) and efficient (O) stirring as estimated from ITC data