SUPPORTING INFORMATION FOR

THE EFFECT OF SURFACE SEGREGATION OF IONIC END GROUPS ON POLYSTYRENE LATEX EARLY-TIME INTERDIFFUSION

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The Calculation of the Free Energy for Surface Segregation

The adsorption free energy is composed of many factors. Among them, two factors are considered for the first approximation:

(1) The interaction between ionic end-groups and water at a surface.

(2) The interaction between a mer and water at a surface.

Based on the above assumptions, calculations were performed to estimate the surface concentration of carboxyl end-groups in latex particles used for this study.

First, the free energy change due to the interaction between ionic end-groups and water at a surface can be estimated by using the heat of solution of water and carboxyl end-groups. The heat of solution of water and acetic acid[36] is listed as –1.5 kJ/mol, was used to estimate the heat of the solution of water and carboxyl-end-group of polystyrene.

Secondly, the free energy change due to the interaction between a mer and water at a surface was estimated by using interfacial energy. The interfacial energy of water and a styrene mer, γ_{SW}, can be expressed by using the surface energy of water, γ_W, and styrene, γ_S.

$$\gamma_{SW} = \gamma_S + \gamma_W - 2\phi(\gamma_S\gamma_W)^{0.5} \qquad (11)$$

where $\phi = 4(V_sV_w)^{1/3}/(V_s^{1/3}+V_w^{1/3})^2$ and V is a molar volume.

The surface energies of styrene and water[37] are 40.7 x 10^{-3}J/m^3 and 72.8 x 10^{-3}J/m^3, respectively, leading to γ_{SW} = 13 x 10^{-3}J/m^3. To convert this value to a free energy change per mole, the styrene mer was assumed to be confined in a unit cubic cell. If monomer and an end-group are assumed to fit in the same unit cubic cell, the adsorption free energy per mole is (interfacial energy) x (a surface area of a unit cubic cell) x (Avogadro's number). The length, l, of unit cubic cell of styrene mer was calculated to 0.55 nm by the following formulation.

$$l^3 \times \text{density} = \text{mass of a mer} \qquad (12)$$

Therefore, when a mer is replaced by a carboxyl end-group, the free energy change due to the interfacial energy of water and polystyrene mer was -2.4 kJ/mole. Combining this free energy

change with the free energy change due to the heat of solution of water and acetic acid, the total free energy change was estimated to be –3.9 kJ/mole.

References

(36) Parker, V. B. *Handbook of Chemistry and Physics*, 60th ed.; Weast, R. C., M. J., Eds; CRC press, Florida, 1979, p D-118.

(37) Van Krevelen, D. W. *Properties of Polymers*; Elsevier Science Publishers B.V.: Amsterdam The Netherlands, 1990.