

Communications to the Editor

A Simple Structural Model for the Polymer Microsphere Stabilized by the Poly(ethylene oxide) Macromonomers Grafted on Its Surface

Chi Wu,^{*,†} Mitsuru Akashi,[‡] and Ming-Qing Chen[‡]

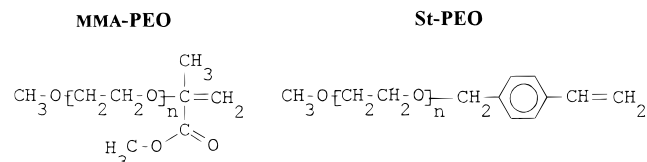
Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong, and Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890, Japan

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Recently, it has been found that water-soluble polymers grafted on the particle surface can stabilize the colloid dispersion.^{1–4} It is generally known that the size of the particles formed in a surfactant-free emulsion polymerization decreases as the fleet ratio (the macroscopic weight ratio of polymer stabilizer to monomer) increases. However, a quantitative relation between the particle size and the fleet ratio has not been well established yet. In our previous studies of the “oil-in-water” microemulsions,⁵ we have shown that the size of spherical microlatex particles can be well predicted using Wu’s plot, namely for a given surfactant/monomer system the average hydrodynamic radius ($\langle R_h \rangle$) of the particles is a linear function of $(W_m + W_s)/W_s$, where W_m and W_s are the macroscopic weights of monomer and surfactant, respectively. Recently, we have extended our studies from the surfactant/monomer microemulsion to the surfactant-free macromonomer/monomer emulsion. A simple structural model is proposed on the basis of our results for both the polystyrene (PS) and poly(methyl methacrylate) (PMMA) microspheres stabilized by low molar mass poly(ethylene oxide) (PEO) macromonomer grafted on the particle surface.

The PEO macromonomers were specially prepared with either one styrene (St) or methyl methacrylate (MMA) molecule attached as the end group, i.e., St-PEO and MMA-PEO. In each case, three different molar masses of PEO ($M_n = 1000, 2000,$ and 4000 for MMA-PEO; and $M_n = 1000, 2000,$ and 5000 for St-PEO) were prepared. Their chemical structures are as follows.



For preparing the microspheres, 5.0×10^{-3} mol styrene or MMA monomer, a proper amount of St-PEO or MMA-PEO macromonomer depending on runs, and 1 mol % of AIBN as the initiator were added in 5 mL of solvent (ethanol/water, the volume ratio is 4:1). After being degassed by freeze-thaw cycles on a vacuum

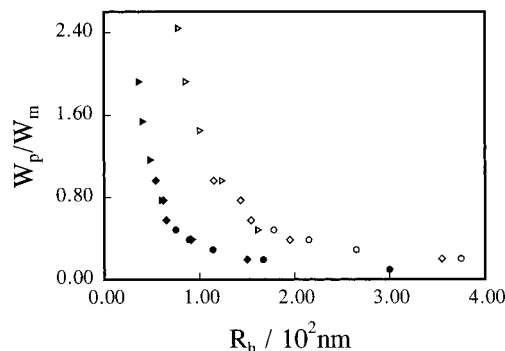


Figure 1. Fleet-ratio (W_p/W_m) dependence of the hydrodynamic radius (R_h) of the microspheres prepared from surfactant-free emulsion polymerization, where W_p and W_m are the macroscopic weights of the PEO macromonomer and monomer, respectively. Key: for St-PEO macromonomers; (Δ), $M_n = 5000$, (\square) $M_n = 2000$, and (\circ) $M_n = 1000$; for MMA-PEO macromonomers, (\blacktriangle) $M_n = 4000$, (\blacksquare) $M_n = 2000$, and (\bullet), $M_n = 1000$.

apparatus, the solution was sealed off and placed in an incubator for 48 h.

Figure 1 shows a typical fleet-ratio-dependence of the average hydrodynamic radius of the resulting microspheres, where the hydrodynamic radius were determined using dynamic laser light scattering (LLS) (both Coulter Instrument, Model N4SD, and a modified research-grade ALV/SP-150 LLS spectrometer with an ALV-5000 time correlator) and Fraunhofer diffraction (Coulter particle size analyzer, LS230). The research-grade LLS spectrometer is capable of doing dynamic LLS in a wide angular range of $6\text{--}154^\circ$. In this study, the accessible small angle ($\theta = 6^\circ$) is particularly useful because of the large size of the particle. The detail of LLS can be found elsewhere.^{6,7} The dispersions used in dynamic LLS were so dilute ($\sim 10^{-7}$ g/mL) that the concentration correction was not necessary. All measurements were done at $25.0 \pm 0.1^\circ\text{C}$. The average line width ($\langle \Gamma \rangle$) and relative distribution width ($\mu_2/\langle \Gamma \rangle^2 = \int G(\Gamma)(\Gamma - \langle \Gamma \rangle)^2 d\Gamma/\langle \Gamma \rangle^2$) was obtained from the cumulants analysis of the measured time correlation function. $\langle \Gamma \rangle$ is related to the average translational diffusion coefficient (D) by $\langle \Gamma \rangle = q^2\langle D \rangle$ where $q = (4\pi n/\lambda_0) \sin(\theta/2)$ with N_A , n , λ_0 , and θ being Avogadro’s number, the solvent refractive index, the wavelength of light in vacuo, and the scattering angle, respectively. Further, $\langle D \rangle$ is related to the average hydrodynamic radius (R_h) (or simply written as R_h) by $R_h = k_B T/(6\pi\eta D)$, where k_B and η are the Boltzmann constant and solvent viscosity, respectively. Our results showed that $\mu_2/\langle \Gamma \rangle^2$ was in the range 0.03–0.08, indicating that all samples were narrowly distributed. The resistivity and viscosity of deionized water used was $18.3 \text{ M}\Omega \text{ cm}$ and 0.894 cp , respectively.

Figure 2 shows a simple structure model for the microsphere stabilized by the PEO macromonomers. The core is consist of either PS or PMMA (and possibly some unreacted monomers). In this model, the average surface area (s) occupied by each PEO molecule has been considered as a fundamental parameter governing the

[†] The Chinese University of Hong Kong.

[‡] Kagoshima University.

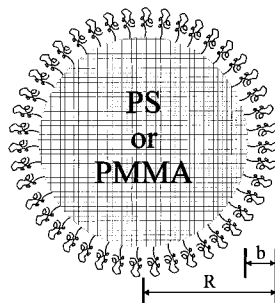


Figure 2. Schematic of a simple model for the poly(methyl methacrylate) (PMMA) or polystyrene (PS) microsphere stabilized by the PEO macromonomers. R and b are the radius and the layer thickness of the PEO macromonomer grafted on the surface of the microsphere, respectively.

particle size. Adding more PEO molecules means more particle surface can be stabilized, which means the decrease of the particle size because for a given mass of monomer the total particle surface increases as the particle size decreases. Qualitatively, this is exactly what we have observed in Figure 1. On the basis of this model, the average surface area (s) occupied by each PEO molecule equals the ratio of the total surface area (A_t) of the core to the total number (N_p) of PEO molecules, i.e., $s = A_t/N_p$. A_t equals the surface area $4\pi(R - b/2)^2$ of one particle multiplied by the number $(W_m + \gamma W_p)/(4/3\pi R^3 \rho)$ of the particles, i.e., $A_t = 4\pi(R - b/2)^2(W_m + \gamma W_p)/(4/3\pi R^3 \rho)$, where W_m and W_p are the macroscopic weights of monomer and the PEO macromonomer, respectively, γ is the weight fraction of the PEO macromonomers grafted on the surface, and ρ is the average density of microspheres. $N_p = N_A(\gamma W_p)/M_p$, where M_p and N_A are the molar masses of the PEO macromonomer and Avogadro's constant, respectively. Thus, we have

$$s = \left\{ \frac{4\pi(R - b/2)^2(W_m + \gamma W_p)}{4/3\pi R^3 \rho} \right\} \left[\frac{N_A \gamma W_p}{M_p} \right] \quad (1)$$

It can be rearranged as

$$\frac{W_m}{W_p} = \gamma \left[s \frac{N_A \rho}{3M_p} \frac{R}{\left(1 - \frac{b}{2R}\right)^2} - 1 \right] \quad (2)$$

If we assume that all PEO macromonomers are grafted on the particle surface, i.e., $\gamma = 1$, we can rewrite eq 2 as

$$\left\{ \frac{RW_p}{W_m + W_p} \right\}^{1/2} = \left[s \frac{N_A \rho}{3M_p} \right]^{-1/2} \left(1 - \frac{b}{2R} \right) \quad (3)$$

It shows that if s is a constant $[RW_p/(W_m + W_p)]^{1/2}$ will be nearly a constant because $b \ll 2R$.

Figure 3 shows such a plot of $[R_h W_p/(W_m + W_p)]^{1/2}$ vs $1/R_h$ on the basis of eq 2 for both the PS and PMMA microspheres. For a given type of the PEO macromonomer, namely a fixed M_p , $[RW_p/(W_m + W_p)]^{1/2}$ is nearly independent of R_h , indicating that s is close to a constant. As for the PEO macromonomers with different molar masses, it was surprised to find that $[R_p/(W_m + W_p)]^{1/2}$ is independent on M_p , which may be explained as follows. If considering that the PEO macromonomers packed on the particle surface behave like in the θ -condition, we will have that $R_{h,p} \propto M_p^{0.5}$, where $R_{h,p}$

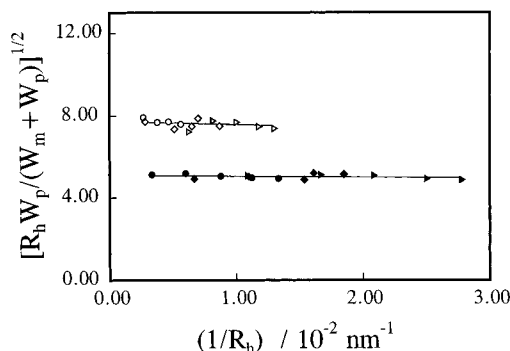


Figure 3. Plot of $[R_h(W_p + W_m)/W_m]$ vs $(1/R_h)$ on the basis of eq 2. The lines represent the least-square fittings of $[RW_p/(W_m + W_p)]^{1/2} = 7.78 - 25.7/R_h$ and $[RW_p/(W_m + W_p)]^{1/2} = 5.11 - 5.57/R_h$ for the St-PEO and MMA-PEO stabilized microspheres, respectively. All symbols are the same as in Figure 1.

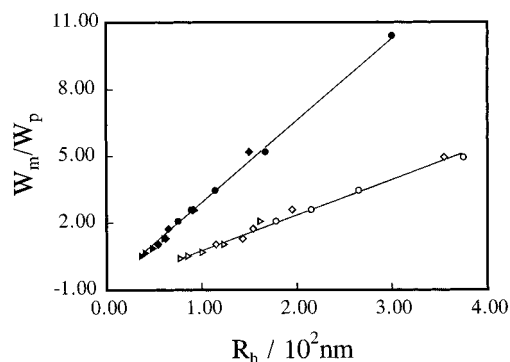


Figure 4. Plot of W_m/W_p vs R_h on the basis of eq 3. The lines represent the least-square fitting of $W_m/W_p = 1.59 \times 10^{-2} R_h - 7.83 \times 10^{-1}$ and $W_m/W_p = 3.78 \times 10^{-2} R_h - 8.67 \times 10^{-1}$ respectively for the St-PEO and MMA-PEO stabilized microspheres. All symbols are the same as in Figure 1.

is the hydrodynamic radius of the PEO macromonomer. On the other hand, s should be proportional to $R_{h,p}^2$, so that $s \propto M_p$ or s/M_p is nearly a constant. We will come back to this point later.

Furthermore, the least-squares fitting of the data in Figure 3 leads to $[RW_p/(W_m + W_p)]^{1/2} = 7.78 - 25.7/R_h$ and $[RW_p/(W_m + W_p)]^{1/2} = 5.11 - 5.57/R_h$ for the PS and PMMA microspheres, respectively. According to eq 2, the intercept and slope differences indicate that on average each PEO macromonomer occupies less surface area, but is more extended, on the PS microsphere than on the PMMA microsphere. The estimated average values of b are in the range 2–4 nm, very close to what we have expected from the molar masses of the PEO macromonomers.⁸ Considering $b \ll 2R$, we can rewrite eq 1 as

$$\frac{W_m}{W_p} \approx \gamma \left[s \frac{N_A \rho}{3M_p} (R + b) - 1 \right] = \gamma s \frac{N_A \rho}{3M_p} R + \gamma s \frac{N_A \rho}{3M_p} b - 1 \quad (4)$$

where we have used the approximation $(1 - (b/2R))^{-2} \approx 1 + b/R$. It shows that the ratio (W_m/W_p) of the macroscopic weights is a linear function of R if s is a constant.

Figure 4 shows the plots of W_m/W_p vs R for the PS and PMMA microspheres, respectively. It clearly shows that W_m/W_p is a linear function of R_h , indicating that s is nearly a constant. The lines represent the least-squares fittings of $W_m/W_p = 1.59 \times 10^{-2} R_h - 7.83 \times 10^{-1}$ and $W_m/W_p = 3.78 \times 10^{-2} R_h - 8.67 \times 10^{-1}$

respectively for the PS and PMMA microspheres. In comparison with eq 4, we have \mathbf{s} (nm^2) = $(7.54 \times 10^{-5}/\gamma)M_p$ and \mathbf{s} (nm^2) = $(1.79 \times 10^{-4}/\gamma)M_p$, respectively, for the PS and PMMA microspheres. It is interesting to notice that for the PMMA microspheres \mathbf{s} is nearly twice larger, indicating that each PEO macromonomer can stabilize a larger surface area when the core is made of PMMA. This is understandable because the acrylate group on MMA is relatively more hydrophilic than the benzene ring on styrene, so that it requires less PEO macromonomer to stabilize the same surface area or each PEO macromonomer can stabilize more surface. Assuming $\gamma \sim 1$, we can estimate that \mathbf{s} is less than 1 nm^2 , which is considered to be too small, but close to what has been found in ref 2. Actually, in the range of $M_p \sim 1000\text{--}5000 \text{ g/mol}$, $R_h \sim 5 \text{ nm}$ and $\mathbf{s} \sim 25 \text{ nm}^2$, so that the rough estimates of γ are 0.1 and 0.2, respectively, for the PS and PMMA microspheres, which is reasonable because it is expected that the reactivity of the styrene or MMA attached at the end of the PEO chain should be much lower than that of free styrene or MMA molecules.

In summary, our results suggest that for a given type of stabilizer and monomer, the surface area (\mathbf{s}) occupied by each PEO macromonomer is nearly a constant. The plot of W_m/W_p reveals that \mathbf{s} is a fundamental parameter for the control of the particle size. In other words, adding more macromonomers can stabilize more particle surface, resulting in smaller microspheres. This simple model is different from what is predicted in the coagulative nucleation theory.⁹ In addition, our results show that \mathbf{s}/M_p is nearly a constant, so that the microspheres

stabilized by the PEO macromolecules with different values of M_p can be scaled into a single line. This will be very useful in practice; namely, for a given monomer/macromonomer system we will be able to predict the size (R_h) of the microspheres from the macroscopic weight ratio, W_m/W_p , if we have a predetermined value of $\gamma\mathbf{s}$, which is similar to what we have found in Wu's plot for microemulsions.⁵

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References and Notes

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