High-Molecular Weight Polymer Segment Distribution in Small Latex Particles

INTRODUCTION

Monomer concentration in the latex particle is of major importance in emulsion polymerization kinetic models. Also, the segment distribution determines various mechanical properties of the material, especially if more than one monomer is employed. Furthermore, in studying the internal morphology of swollen latex particles by SANS, the radial polymer concentration profile in the particle is needed.

In 1947, Debye[1] published his now famous equation expressing the angular, wavelength, and radius of gyration dependence of the form factor for a random polymer coil.

$$\mathcal{P}(x) = \frac{2}{x^2}\{e^{-x} - (1 - x)\} \tag{1a}$$

where $x = K^2R_g^2$, K is the wavevector, and R_g is the radius of gyration. Debye assumed a Gaussian segment distribution

$$\mathcal{C}(s) = \left(\frac{3}{2\pi R^2}\right)^{3/2} \exp\left\{\frac{-3s^2}{2R^2}\right\} 4\pi s^2 \tag{1b}$$

for the polymer chains. Segment distribution indicates the probability that the end mer of the polymer chain is found in a shell of radii between s and $s + ds$ with the beginning of the chain in the center of the sphere of radius R.

By applying a non-Gaussian distribution function other form factors may be generated. The mathematical method to generate other form factors is described properly by Zimm et al.[2]

In 1969, Casassa and Tagami[3] derived a segment density distribution determining the probability that two subchains of m and $n - m$ segments starting at s, inside a spherical cavity of radius a, do not touch the surface.

$$\mathcal{C}_m(s) = \frac{4a^2}{\pi^2 s^2} \sum_{p=1}^{\infty} \sum_{q=1}^{\infty} \frac{(-1)^{p+q}}{pq} \sin\left(\frac{p\pi s}{a}\right) \sin\left(\frac{q\pi s}{a}\right) \times \exp\left\{\frac{-\pi^2 R_g^2}{6a^2}[p^2 m + q^2(n - m)]\right\} \tag{2}$$

Equation (2) is part of Casassa's model to explain the theory of diffusion in spherical voids within a gel permeation column. The important point is that when the polymer chains are the same order of size as the opening in which they are placed, there is a "repulsive wall" effect.[4]

We develop a non-Gaussian segment density distribution from Casassa's foundations, compute a new form factor, and finally compare results with experimental data.

Keywords: latex particles, SANS study of internal morphology of • chain segment distribution of high MW polymer in small sphere • polystyrene in latex spheres, segmental distribution of

THEORY

Introducing $u \equiv m/n$ in eq. (2) so that $0 < u < 1$, we have

$$\mathcal{C}_u(s) = \frac{4a^2}{\pi s^2} \sum_{p=1}^{\infty} \sum_{q=1}^{\infty} \frac{(-1)^{p+q}}{pq} \sin\left(\frac{p\pi s}{a}\right) \sin\left(\frac{q\pi s}{a}\right) \times \exp\left\{\frac{-\pi^2 R_g^2}{a^2}[p^2 u + q^2(1 - u)]\right\} \tag{3}$$

e.g., for the middle segment, $u = 1/2$.

To average $\mathcal{C}_u(s)$ over all segments of the chain $\bar{\mathcal{C}}(s) = \int_0^1 \mathcal{C}_u(s)\, du$

$$\bar{\mathcal{C}}(s) = \frac{4a^2}{\pi s^2} \sum_{p=1}^{\infty} \sum_{q=1}^{\infty} \frac{(-1)^{p+q}}{pq} \sin\left(\frac{p\pi s}{a}\right) \sin\left(\frac{q\pi s}{a}\right) \times \left\{\frac{\exp[-q^2\pi^2 R_g^2/a^2] - \exp[-p^2\pi^2 R_g^2/a^2]}{(p^2 - q^2)\pi^2 R_g^2/a^2}\right\} \tag{4}$$

The sums over p and q cannot be approximated by integrals, but the series converges fairly rapidly for most values of R_g/a of interest. Mathematical analysis, using L'Hospital's rule twice shows that

$$\bar{\mathcal{C}}(s) = \frac{4a^2}{\pi s^2} \sum_{p=1}^{\infty} \sum_{q=1}^{\infty} \mathcal{J}(p, q) \tag{5}$$

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where

$$\mathcal{J}(p, q) = \frac{a^2(-1)^{p+q}\sin\left(\frac{p\pi s}{a}\right)\sin\left(\frac{q\pi s}{a}\right) \times \{\exp[-q^2\pi^2R_g^2/a^2] - \exp[-p^2\pi^2R_g^2/a^2]\}}{(p^2 - q^2)\pi^2R_g^2pq} \quad (6)$$

when $p \neq q$, and

$$\mathcal{J}(p, q) = \frac{1}{q^2}\sin\left(\frac{q\pi s}{a}\right)\exp(-q^2\pi^2R_g^2/a^2) \quad (7)$$

when $p = q$. Thus the sums are easily obtained numerically.

To compare profiles at different values of R_g/a it is necessary to normalize the profiles so that $4\pi \int_0^a s^2\mathcal{C}(s) \times ds = 1$. The normalized $\mathcal{C}(s)$ is therefore,

$$\mathcal{C}(s) = \frac{\bar{\mathcal{C}}(s)}{4\pi \int_0^a s^2\bar{\mathcal{C}}(s)\, ds} \quad (8)$$

The integral in the denominator can be expressed analytically:

$$\int_0^a s^2\bar{\mathcal{C}}(s)\, ds = \sum_{p=1}^{\infty}\sum_{q=1}^{\infty}\mathcal{G}(p, q) \quad (9)$$

where

$$\mathcal{G}(p, q) = \frac{2a^5}{\pi^4R_g^2}\frac{(-1)^{p+q}}{(p^2 - q^2)pq} \times \{\exp[-q^2\pi^2R_g^2/a^2] - \exp[-p^2\pi^2R_g^2/a^2\} \times \left\{\frac{\sin(\pi(p - q))}{(p - q)} - \frac{\sin(\pi(p + q))}{p + q}\right\} \quad (10)$$

when $p \neq q$, and

$$\mathcal{G}(p, q) = \frac{2a^3}{\pi q^2}\exp[-q^2\pi^2R_g^2/a^2] \quad (11)$$

when $p = q$.

Equations (10) and (11), which are components in the segment density distribution [eq. (8)], are functions of R_g^2/a^2. This is contrasted with the Debye relation [eq. (1)], which has a R_g^2 dependence. The new parameter is the particle diameter a, and thus the segment distribution is dependent on R_g^2/a^2, which is shown in Figure 2. As the R_g/a ratio increases the "repulsive wall" effect becomes apparent, there is a region near the profile wall with little or no polymer segment content.

$\mathcal{C}(s)$ in eq. (8) is the normalized concentration distribution profile $w(s)4\pi s^2$ needed to compute numerically the form factor $\mathcal{P}(\kappa)$ for a non-Gaussian distribution function. In detail:

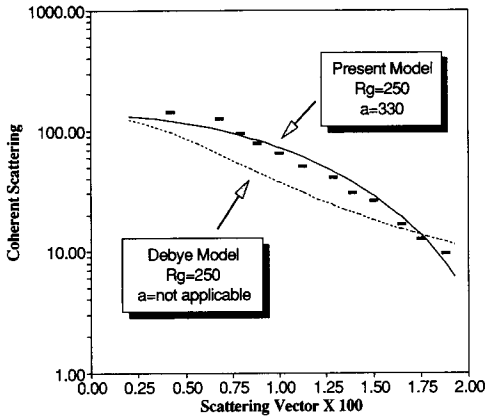

Figure 1. Comparison of the present model with the original Debye model.

$$\mathcal{P}(\kappa) = \frac{\sum_{j=1}^{n}(n + 1 - j)\int_0^{\infty}\frac{\sin[\kappa\sigma r_{\mu\nu}]}{\kappa\sigma r_{\mu\nu}}w(s)4\pi s^2\, ds}{\left(\frac{n(n + 1)}{2}\right)} \quad (12)$$

where n is the number of polymer links, $\sigma = 2\sin(\theta/2)$, θ is the angle between the secondary and primary beam, $\kappa = 2\pi/\lambda$, λ is the wave length as measured in the liquid surrounding the particle, and $r_{\mu\nu}$ is the distance between the emitter μ and another emitter ν.

The main problem is the evaluation of the integral Fourier transform appearing in the numerator of $\mathcal{P}(\kappa)$. This integral was computed numerically in the following way: first, $\bar{\mathcal{C}}(s)$ was determined; then the normalizing factor was computed using standard Monte Carlo techniques to determine $\mathcal{C}(s)$; and finally the Fourier transform was approximated with a higher order (Romberg) integration scheme using an appropriate finite upper limit of integration to obtain convergence (10, 13).

The form factor is proportional to the coherent intensity, $d\Sigma/d\Omega$, measured in a SANS experiment as described by Sperling.[5] Experimental intensities were compared with intensities predicted using the Debye form factor and the present form factor based on a non-Gaussian segment density distribution.

RESULTS AND DISCUSSION

Yang et al.[6] utilized SANS to study polystyrene chain distribution in partly polymerized latexes. Deuterated polymer was used to perform the SANS experiments. They found that for values of R_g/a of the order of unity, significant segregation occurred, resulting in a core-shell ef-

fect. In the following, the experimental results obtained by Yang et al.[6] will be used.

Figure 1 also shows the experimental data of Yang et al.[6] for $R_g/a = 0.68$. It is seen that the data agree better with the present theory than with the original Debye theory. At higher values of the scattering vector, the data deviate from both theories, as then the data yield information about the local structure of the chain.

Figure 2 illustrates the behavior of the normalized segment concentration profiles $\mathcal{C}(s)$ for different values of R_g/a. It can be seen that at low ratios of R_g/a there is a constant distribution of polymer within the particle, diminishing suddenly at the boundary. This case is assumed by most emulsion polymerization kineticists: Russel et al.[7] and Maxwell et al.[8] For larger ratios of R_g/a, the concentration of polymer begins to decline closer to the center of the particle. The polymer chain perceives a repulsive wall effect. There is a monomer-rich shell. This case is assumed by other researches, Wessling and Gibbs.[9]

Most models of emulsion polymerization assume a uniform distribution of chain segments in the particle during polymerization (11, 12). In the past, there has been considerable debate over the presence or absence of core-shell effects. Yang et al.[6] showed that this effect depends on R_g/a, which can be large or small within the attainable ranges of the polymerization. The present derivation shows quantitatively what the segment distribution should look like as a function for R_g/a.

The importance of this data lies in the prediction of the actual segment distribution of polymer chains in an incompletely polymerized latex particle. With an improved knowledge of this distributions, new theories of the kinetics of emulsion polymerization should be possible.

CONCLUSION

Due to a repulsive wall effect in partly polymerized Latex structures, there is a polymer-rich core surrounded by a monomer-rich shell when $0.08 < R_g/a < 1$. In particular, when $R_g/a = 0.68$, the monomer rich layer is about 35 Å thick.

Kinetic models of emulsion polymerization now need to consider that the concentration of polymer segments within the latex sphere varies significantly as a function of R_g/a.

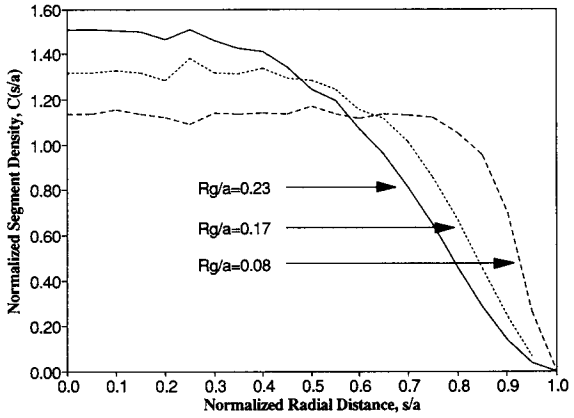

Figure 2. Normalized segment density profiles of polymer chains confined in latex particles.

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REFERENCES AND NOTES

1. P. Debye, *J. Phys. Coll. Chem.*, **51**, 18 (1947).
2. B. H. Zimm, R. S. Stein, and P. Doty, *Polym. Bull.*, **1**, 90 (1945).
3. E. F. Casassa and Y. Tagami, *Macromolecules*, **2**, 14 (1969).
4. P. D. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, NY, 1979, pp. 88–91.
5. L. H. Sperling, *Polym. Eng. Sci.*, **24**(1), (1984).
6. S. Yang, A. Klein, L. H. Sperling, and E. F. Casassa, *Macromolecules* (accepted).
7. G. T. Russel, D. H. Napper, and R. G. Gilbert, *Macromolecules*, **21**, 2133 (1988).
8. I. A. Maxwell, E. D. Sudol, D. H. Napper, and R. G. Gilbert, *Faraday Trans. I*, **84**(9), 3107 (1988).
9. R. A. Wessling and D. S. Gibbs, *J. Macromol. Sci. Chem.*, **A7**(3), 647 (1973).
10. D. Kahaner, C. Moler, and S. Nash, *Numerical Methods and Software*, Prentice Hall, Englewood Cliffs, NJ, 1989.
11. F. Rodriguez, *Principles of Polymer Systems*, 2nd ed., McGraw-Hill, New York, 1982.
12. L. H. Sperling, *Introduction to Physical Polymer Science*, Wiley-Interscience, New York, 1986.
13. S. Wolfram, *Mathematica a System for Doing Mathematics by Computer*, Addison Wesley, Reading, MA, 1988.

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