Communications to the Editor

Experimental Observation of the Onset of Finite Domain Boundaries in a Simple Two-Phase System by Small-Angle X-ray Scattering

Small-angle scattering from domains of constant density and sharp boundaries is known to be proportional to h^{-4} at large values of h, where $h = (4\pi \sin \theta)\lambda$; θ is the Bragg angle and λ is the X-ray wavelength. This limiting behavior of the scattered intensity as given by Porod[1] is

$$\lim_{h \to \infty} I_P(h) = \frac{2\pi S(\rho - \rho_0)^2}{h^4}$$

where I_P is the scattered intensity in the Porod region and S is the total area of the interface between the phase with density ρ and the phase with density ρ_0. Thus the product $I_P(h)h^4$ reaches a constant value at large values of h. Deviations from Porod's law due to finite width of domain boundaries and to the density fluctuations within the domain have been investigated by several workers.[2-7] We present here hydrodynamic and X-ray scattering data obtained from a series of highly monodisperse globular molecules with radii ranging from 0.59 to 4.53 nm and show the negative deviations from Porod's law due to finite domain boundaries in this simple two-phase system. This work is a continuation of our earlier studies,[8,10] and in this report we present supporting evidence for the soft-particle (dense core–soft shell) concept in high molecular weight globular molecules.

The molecules we studied were a series of highly monodisperse *tert*-butyloxycarbonyl (Boc) blocked poly(α,ϵ-L-lysine) molecules dissolved in *N,N'*-dimethylformamide. The polymer was synthesized in stages such that the number of lysine residues increases in a geometric series and the molecular weight approximately doubles at each growth stage from 511 to 233 600.[8] Since the polymer is highly branched, the molecule is expected to be a globular particle. The essential details of hydrodynamic, photon correlation spectroscopy, and small-angle X-ray measurements are given in our previous reports[9,10] and are summarized in Table I along with a description of these molecules. The monodispersity of the macromolecules is expected from their stepwise polymerization procedure; this was confirmed by their hydrodynamic behavior and by the fact that their size exclusion chromatography peaks at half-height were as narrow as the peaks for globular biopolymers and far more narrower than the peaks of "monodisperse" polystyrene.[9]

The hydrodynamic radius, R_H, obtained from viscosity measurements refers to the physical radius of the molecule. The radius of gyration, R_G, obtained from the Guinier approximation to the low-angle X-ray scattering data, $I(h) = I_0 \exp(-h^2 R_G^2/3)$, refers to the second moment of the electron density distribution within the molecule. The ratio of R_G to R_H contains information about the distribution of the electron density within the molecule. Figure 1 shows the values of R_G and R_H plotted against $M^{1/3}$, M being the molecular weight. R_H is proportional to $M^{1/3}$ as expected of globular particles. If the particles behaved as nondraining spheres, then $R_G = (3/5)^{1/2}R_H$, i.e., $R_G = 0.775R_H$,[10] and the R_G values would fall on the line that represents the relation $R_G = 0.775R_H$. If they were free-draining particles, then the R_G values would fall on the line $R_G = 1.143R_H$.[11] The figure shows that while low molecular
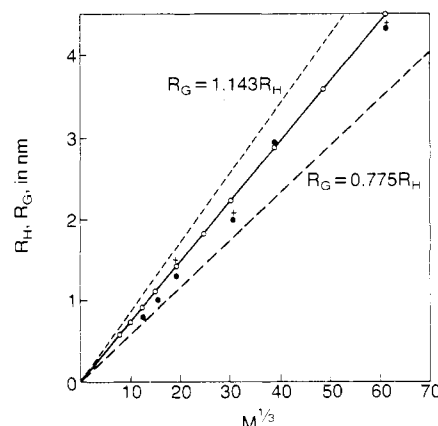

Figure 1. Hydrodynamic radii (O) calculated from viscosity data and radii of gyration (●) plotted against $M^{1/3}$ of Boc-X homologues. Three data points (+) are from dynamic light scattering. The full line is the relation $R_H \propto M^{1/3}$; the broken line $R_G = 0.775R_H$ represents hard spheres (nondraining molecule) and the line $R_G = 1.143R_H$ corresponds to a free-draining molecule.

weight species are close to being hard spheres, the high molecular weight species Boc-H and Boc-K show significant deviations from the hard-sphere model and suggests that Boc-H and Boc-K behave as partially draining spheres, probably on the surface.

One can arrive at similar conclusions by comparing the ratios of volumes calculated by the various methods shown in Table II. Assuming uniform internal density, the theoretical volume V_T is calculated from the molecular weight and the measured density of 1.18 g/cm³ of the dry polymer. Assuming sphericity, the hydrodynamic volume V_H and the Guinier volume V_G were calculated from the hydrodynamic radius R_H and the radius of gyration R_G, respectively. The volume V_P was calculated from the Porod invariant Q by integrating the area under the Ih^2 vs. h curve after extrapolating the curve to the origin and abscissa ($V_P = 2\pi^2 I_0/Q$; the intensity I_0 at $h = 0$ was obtained by extrapolating the Guinier plot to $h^2 = 0$). Although such calculations cannot lead to precise absolute values, they are adequate for relative comparisons. The ratio between V_T and V_H is fairly constant at 0.85. Since V_T is proportional to the molecular weight M, and $V_H \propto M^{1/3}$, this constancy in the V_T:V_H ratio is a simple restatement of the data in Figure 1. The ratio V_T:V_G for the molecules Boc-C through Boc-G is ≈ 0.58, and the volume V_G is considerably higher for Boc-H and Boc-K. This is again a restatement of the data in Figure 1 that the ratio R_G/R_H for Boc-H and Boc-K is considerably different from those for low molecular weight samples. The ratio between the theoretical volume V_T and the volume V_P calculated from the Porod invariant is close to unity for the low molecular weight samples and is considerably smaller than 1 for Boc-H and Boc-K. This suggests that the molecules Boc-H and Boc-K are swollen to a much larger extent than their low molecular weight counterparts.

Data in Table II suggest that the molecules are swollen but do not indicate if the swelling is uniform across the entire radius of the molecule. One suspects that the larger molecules Boc-H and Boc-K might have a core–shell morphology with a dense core and a loose exterior, i.e., resemble a soft particle. This was borne out from the analysis of the Porod plots shown in Figure 2. The data

Table I
Number of Lysine Residues, Molecular Weight, and Radii of Globular Boc-poly(α,ε-L-lysine)

sample code	stage	no. of lysine residues	mol wt	R_H, nm	R_G, nm	R_G/R_H
Boc-A	nucleus	1	511	0.59		
Boc-B	2	3	967	0.73		
Boc-C	3	7	1900	0.91	0.80	0.88
Boc-D	4	15	3700	1.14	1.00	0.88
Boc-E	5	31	7300	1.43	1.29	0.90
Boc-F	6	63	14600	1.80		
Boc-G	7	127	29200	2.26	1.99	0.88
Boc-H	8	255	58400	2.85	2.96	1.04
Boc-I	9	511	116800	3.59		
Boc-K	10	1023	233600	4.53	4.34	0.96

Table II
Comparison of the Theoretical Volume (V_T) with Those
Derived from the Hydrodynamic Radius (V_H), Radius of
Gyration (V_G), and Porod Invariant (V_P)

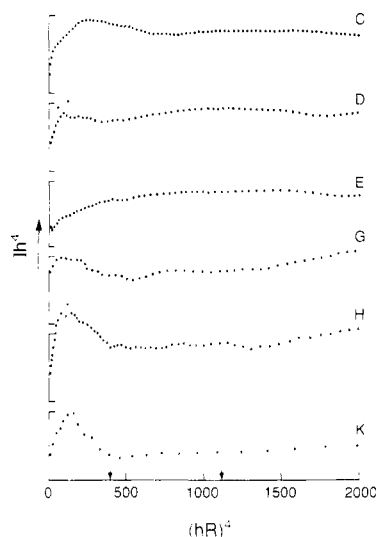| code	V_T/V_H	V_T/V_G	V_T/V_P
C	0.84	0.58	1.11
D	0.84	0.58	1.01
E	0.84	0.53	1.01
G	0.85	0.58	0.98
H	0.85	0.35	0.60
K	0.84	0.45	0.80

Figure 2. Porod-law plots with Ih^4 plotted against $(hR)^4$. R is the hard-sphere radius derived from R_G and is introduced only to normalize the abscissa for all the molecules. The two arrows on the x axis indicate the positions of the first minimum and the second maximum in the scattering curve of a hard sphere.

Figure 3. Theoretical Ih^4 vs. h curves for particles with profiles shown on the right-hand side. h instead of h^4 is used on the abscissa to show a larger range of h values. It is assumed that the electron density changes linearly across the boundary layer. The values of r and Δr (in nm) are (a) 4.0, 0.0; (b) 4.95, 1.15; and (c) 5.27, 2.27. These values keep the volume of the particle constant and equal to that of a hard sphere of radius 4.0 nm.

were obtained from 5% solutions of the Boc molecules, and the data were collected from 20 min to 16 h, depending on the molecular weight. The curves shown in Figure 2 were obtained from smoothed difference (solution–solvent) curves. Molecules Boc-C through Boc-E show a relatively flat Ih^4 vs. h^4 curve at large values of h, thus obeying Porod's law. Boc-H and Boc-K show considerable deviations from Porod's law. Since the molecules are extremely monodisperse,[9] such negative deviations can only be attributed to a boundary layer on the surface of a denser core.[3]

Figure 3 shows the results of some simple calculations carried out to show the effect of finite boundary layer.[4] Broken lines are the calculated values, and the full lines are what one might expect with nonideal spheres, lack of perfect point collimation, and other experimental details and are more appropriate for comparison with experimental data. Curves B and C show that the negative
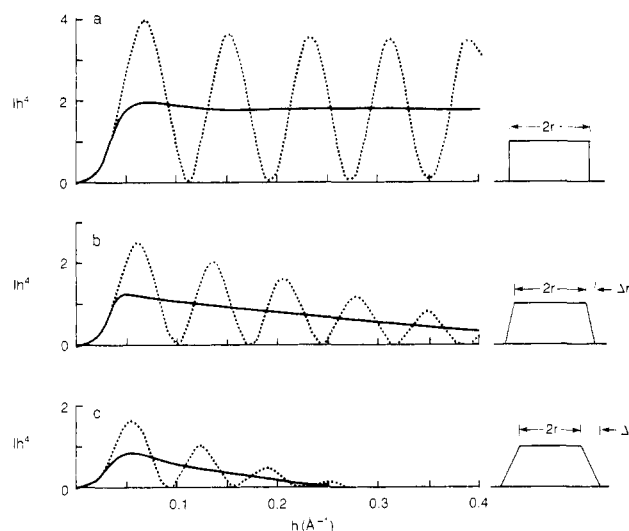
deviations become more and more pronounced as the thickness of the boundary layer increases.

In conclusion, the hydrodynamic and small-angle X-ray scattering data show that while the low molecular weight Boc-poly(α,ε-L-lysine) molecules can be approximated by hard spheres, a soft-sphere model is more appropriate for high molecular weight species. Such soft spheres can give rise to negative deviations from Porod's law.

References and Notes

(1) Porod, G. *Kolloid-Z.* **1951**, *124*, 83; **1952**, *125*, 51, 108.
(2) Ruland, W. *J. Appl. Crystallogr.* **1971**, *4*, 70.
(3) Siemann, U.; Ruland, W. *Colloid Polym. Sci.* **1982**, *260*, 999.
(4) Vonk, C. G. *J. Appl. Crystallogr.* **1973**, *6*, 81.
(5) Todo, A.; Hashimoto, T.; Kawai, H. *J. Appl. Crystallogr.* **1978**, *11*, 558.
(6) Koberstein, J. T.; Morra, B.; Stein, R. S. *J. Appl. Crystallogr.* **1980**, *13*, 34.
(7) Roe, R. J.; Fishkis, M.; Chang, J. C. *Macromolecules* **1981**, *14*, 1091.
(8) Denkewalter, R. G.; Kolc, J.; Lukasavage, W. J. U.S. Patent 4 289 972, Sept 15, 1981.
(9) Aharoni, S. M.; Crosby, C. R., III; Walsh, E. K. *Macromolecules* **1982**, *15*, 1093.
(10) Aharoni, S. M.; Murthy, N. S. *Polym. Commun.* **1983**, *24*, 132.
(11) Tanford, C. "Physical Chemistry of Macromolecules"; Wiley: New York, 1961; pp 306–310, 346–348, 356 ff.

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