What molecular weight polymer is necessary to provide steric stabilization?

The first step is to estimate the thickness of adsorbed polymer layer necessary for steric stabilization. An approximation is:[1]

$$t = \frac{A_{121}d}{48kT}$$

[1]

where t is the necessary polymer thickness, A_{121} is the Hamaker constant for particles of type 1 in a solvent of type 2, d is the particle diameter, and kT is the Boltzmann factor.

The next question is: What molecular weight of polymer will give that adsorbed layer thickness?

A reasonable first approximation is that polymers which are adsorbed and also act as steric barriers are those that are soluble, but barely so. This means that the polymer is in its theta condition, both in solvent composition and temperature. Fortunately, the size of polymers in their theta conditions is well studied. In theta conditions the polymer interacts with itself about the same as it does with the solvent so that it takes on a random configuration (*i.e.*, the second virial coefficient is zero). For many common linear polymers the mean end-to-end distance is given by the expression: [2]

$$\langle r^2 \rangle^{1/2} \sim 0.06 \, MW^{1/2}$$

[2]

Where $\langle r^2 \rangle^{1/2}$ is in nanometers and MW is the polymer molecular weight. Table 1 gives examples.

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[1] Morrison, I.D.; Ross, S. *Colloidal dispersions: Suspensions, emulsions, and foams*; John Wiley & Sons: New York; **2002**, pp 398 - 400.

[2] Napper, D.H. Polymeric stabilization of colloidal disperions; Academic Press: New York; 1983; pp 12 - 13.

Table 1. Typical dimensions of polymer chains of different molecular weights (random coil approximation)[2]

Molecular weight	End-to-end distance (nm) $\langle r^2 \rangle^{1/2}$
1,000	2
10,000	6
100,000	20
1,000,000	60

Numerous theories and Monte Carlo calculations have arrived at the conclusion that, to a reasonable approximation, the mean end-to-end distance from the surface is twice the mean end-to-end length in solution. This makes some sense since the random configurations of a polymer from a surface are hindered by the presence of the surface and so reach further. Therefore the thickness of the adsorbed layer, *t*, is about twice the mean end-to-end distance given in Table 1.

An useful equation is gotten by combining Equation [2] with [1]:

$$MW = \left(\frac{A_{121}}{2.9kT} \right)^2 d^2 \qquad [3]$$

The necessary molecular weight scales as the square of the particle size. In a polydisperse dispersion, only the small particles might be stabilized if the polymer molecular weight is low.

Sophisticated theories are available to estimate the size of a polymer, but for practical applications a productive procedure is to measure the size of the polymer in solution. Once the size of an interesting polymer is known, especially as a function of solvent composition, then more comprehensive ideas can be introduced like the number and strength of attachment points and the flexibility of the polymer chains.

1. Measuring the size of a polymer in solution

The size of a polymer in solution is measured either (or both!) by rheology and by light scattering.

1.1 RHEOLOGY

Two simple rheological methods are used to measure the size of a polymer in solution:

1.1.a From the viscosity of dilute polymer solutions

In 1906 Einstein published an important relation describing the viscosity of a dilute suspension of particles

$$\eta = \eta_0 \left(1 + \frac{5}{2}\Phi + O\left(\Phi^2\right) + ... \right) \qquad [4]$$

where η is the viscosity of the suspension, η_0 is the viscosity of the solvent, and Φ is the volume fraction of particles. The equation has been modified for all kinds of dispersed phases, *e.g.* drops, bubbles, and polymers.[3] But we can make good use of this form of the equation.

Re-arranging Equation [4] gives:

$$\Phi \simeq \frac{2}{5}\lim_{c \to 0}\left(\frac{\eta - \eta_0}{\eta_0} \right) \qquad [5]$$

The relation between volume fraction and mass concentration is:

$$\Phi \simeq \frac{N_0 \left\langle r^2 \right\rangle^{3/2}}{MW} c \qquad [6]$$

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[3] Goodwin, J.W.; Hughes, R.W. *Rheology for chemists: An introduction*; Royal Society of Chemistry: Cambridge; 2000, pp 80 - 84.

Where N_0 is Avogadro's number and c is the mass concentration. Substituting Equation [6] into [5] and re-arranging gives:

$$\left\langle r^2 \right\rangle^{3/2} \simeq \frac{2MW}{5N_0} \lim_{c \to 0} \frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) \qquad [7]$$

or

$$\left\langle r^2 \right\rangle^{3/2} \simeq \frac{2}{5} \frac{MW}{N_0} [\eta] \qquad [8]$$

where $[\eta]$ is the intrinsic viscosity defined by:

$$[\eta] = \lim_{c \to 0} \frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) \qquad [9]$$

The intrinsic viscosity of a polymer is determined by measuring a series of polymer solutions are gradually greater and greater dilution. This is often done with commercial equipment.[4]

1.1.b From the viscosity at polymer concentrations

Intrinsic viscosity is the measure of the size of polymers at concentrations so low that there are no polymer-polymer interactions. At higher concentrations, inter-molecular interactions become important and the viscosity increases faster. At the concentration where the viscosity increases faster than the Einstein limit, the polymer chains are close enough together that they start to interact, a concentration commonly referred to as c^*. A reasonable assertion is that the polymer chains interact when they "fill-space". For our purposes this means that c^* and the intrinsic viscosity are simply related:

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[4] I have used equipment from Viscotek (http://www.viscotek.com/) with good results.

$$c* = \frac{1}{[\eta]} \qquad [10]$$

$c*$ is easy to measure. The viscosity is measured as the polymer concentration is increased. A log-log plot of the data is made and the concentration when the slope of the data becomes greater than one is taken as $c*$. Combining Equation [10] and Equation [8] gives a second approximation for the polymer size in solution:

$$\langle r^2 \rangle^{3/2} \simeq \frac{2}{5} \frac{MW}{N_0 c*} \qquad [11]$$

Therefore there are two methods to estimate the polymer size in solution by viscosity: the first with solutions approaching infinite dilution using intrinsic viscosity and the second using $c*$.

1.1.c From simple polymer theory:

The intrinsic viscosity of a polymer solution is a well-studied physical property. A commonly used relation for polymers is the Flory relation:

$$[\eta] = K \bullet MW^a \qquad [12]$$

where K and a are polymer property from polymer handbooks.[5] MW is the mass average molecular weight. This value of intrinsic viscosity can be used in Equation [8].

Other methods to get the "size" of the polymer are found in Tables in the Polymer Handbook. Chapter VII in the 3rd edition gives *Table D. Calculated unperturbed dimensions of freely rotating chains* and *Table E. Unperturbed dimensions of linear polymer molecules*, whose values are explained in the preceding section in that Chapter.

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[5] *Polymer Handbook*, 4th edition edited by J. Brandrup, E.H. Immergut, E.A. Grulke, A. Abe, and D.R. Block; John Wiley & Sons, New York; 2003, in two volumes. In the 3rd Edition the Chapter is: Viscosity-molecular weight relationships and unperturbed dimensions of linear chain molecules by Kurta, M.; Tsunashima, Y.

1.2 LIGHT SCATTERING

A series of dilute polymer solutions are prepared. The change in refractive index with polymer concentration and the intensity of light scattered as a function of angle are measured. The data is analyzed by means of a Zimm plot and the molecular weight and radius of gyration obtained.[6]

First the concentration dependence of the refractive index at constant temperature and pressure, $\left(\delta n / \delta c\right)_{T,p}^2$, is measured and a parameter, K, is calculated by:

$$K = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_0}\left(\frac{\delta n}{\delta c}\right)_{T,p}^2 \qquad [13]$$

where λ_0 is the light wavelength *in vacuo*, N_0 is Avogadro's number, and n_0 is the refractive index of the solvent. The intensity of light scattered, called the Rayleigh ratio, is measured:

$$R(\theta,c) = r^2 \frac{I}{I_0} \qquad [14]$$

where θ is the scattering angle, r is the distance from the sample to detector, I is the intensity of the scattered light, and I_0 is the intensity of the incident light.

The data reduction is by a method introduced by Zimm[7]. The relevant equations solved are:

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[6] Morrison, I.D.; Ross, S., p 6.

[7] Kerker, M. *The scattering of light and other electromagnetic radiation*; Academic Press: New York; 1969; pp 433 - 437.

$$\frac{Kc}{R(\theta,c)} = \frac{1}{MW}\left[1 + \frac{16\pi^2\langle r_g^2\rangle\sin^2\left(\frac{\theta}{2}\right)}{3\lambda^2}\right] \text{ as } c \to 0 \qquad [15]$$

and

$$\frac{1}{MW} = \lim_{\substack{c\to 0 \\ \theta\to 0}} \frac{Kc}{R(\theta,c)} \qquad [16]$$

which give both the molecular weight, *MW*, and the squared radius of gyration, $\langle r_g^2\rangle$, of the polymer in that solvent at that temperature.

All this can be automated.[8]

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[8] A recommended piece of equipment to make the measurements and calculations automatically is available from Wyatt Technologies (http://www.wyatt.com/).

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