Chemistry C3102-2006: Polymers Section

Dr. Edie Sevick, Research School of Chemistry, ANU

3.0 The size of chains in good and poor solvent conditions

Obviously, the ideal chain is a simple, first approximate model of an isolated polymer chain. It assumes that the chain is intersectable with itself and inert; *i.e.*, it suffers no energetic interactions with itself or with the surrounding solvent. In this section, we are going to lift these assumptions. But we will do so separately for poor solvent and for good solvent conditions. In general, a poor solvent is one in which the solute (in this case the isolated polymer chain) precipitates. A solute precipitates out of solution so as to avoid energetically unfavourable solute-solvent interactions. In such a case the solute-solute interactions are more favourable than the solute-solvent interactions. Thus precipitation in a poor solvent will lower the internal energy ($\Delta U = U_{solute-solute} - U_{solute-solvent} < 0$). In contrast, good solvents are those where the solute-solvent interaction is more favorable than the solute-solute interaction. In this case the solute (or polymer chain) will lower its energy by solubilising in the solvent medium. In this section we ask what effect poor solvent and good solvent have upon the size of a polymer chain.

3.1 A chain in poor solvent

We start here with a FJC chain in a poor solvent. In this case, monomer-monomer interactions are favoured over monomer-solvent interactions. Thus, the chain will adopt a configuration that minimises contact with the poor solvent and maximises self-contact. Very simply, a long, flexible chain will “collapse” upon itself, forming a dense monomer mass that excludes solvent molecules from its interior. In its collapsed state, the chain cannot completely avoid contact with the solvent, but if it adopts a *spherical* collapsed state, then it will minimise its solvent-monomer interactions. In terms of the free energy of the chain, $\Delta F = \Delta U - T\Delta S$, you can see that the collapse of the chain will lower ΔU simply because $U_{monomer-solvent} > U_{monomer-monomer}$. However, what will happen to the chain's entropy? In going from a solvated, fully flexible chain to a collapsed chain with a dense core, the chain will lose entropy, *i.e.*, $\Delta S < 0$. Thus there are two competing effects: the interactions with the solvent will promote collapse (*i.e.*, the interactions contribute to a lowering of the free energy), but the loss of entropy will actually suppress the chain collapse (*i.e.*, entropy contributes to an increase in the free energy). Indeed, the balance of these two effects is determined by the temperature.

Given that the temperature is low so that the chain adopts a collapsed configuration, how does the size of the chain vary with the number of monomers in the chain? The volume of a chain is simply the contour length, Na, times the cross-sectional area of the chain, which is πr^2 where r is the cross sectional radius of the chain. The value of r will be on the order of a, so we can say that the volume of the chain is $V_{chain} \sim Na^3$, where the prefactor depends upon the cross-sectional area of the chain contour. In its collapsed state, a single chain will form a spherical globule of volume $V_{sphere} = (4/3)\pi R^3$ where R is the radius of the sphere. If the chain collapses so as to expel all monomer, then this spherical volume is comprised of polymer only, or $V_{chain} = V_{sphere}$. That is, $Na^3 \sim R^3$, or the size of the collapsed chain scales with the cubed root of the number of monomers:

$$R \sim aN^{1/3} \tag{1}$$

This geometrical argument works fairly well for flexible chains: implicitly, it lifts the simplifying approximation of a self-intersectable chain. If a chain were intersectable, it would intersect itself over and over again to form the smallest volume (smallest surface area) which is a point.

However this analysis does not work for a rigid-rod chain, as it has NO flexibility and will change its shape minimally when in the presence of a poor solvent. What about a semi-flexible chain like DNA? Recall that we said such chains were like a garden hose - imagine collapsing such a hose into a dense ball - it would be very difficult. Indeed, experiments have shown that when subjected to poor solvent conditions, DNA coils up, very much like a neatly wound garden hose, forming a doughnut (or donut), or more mathematically, a torus. This torus is the shape that minimises the solvent contact with the semi-flexible DNA chain.

3.2 A chain in a good solvent

A chain in a good solvent will adopt a configuration that maximises contact with the solvent. That is, the chain will adopt a random walk configuration, with the exception that it will not self-intersect. This is called a self-avoiding random walk or SAW. There are a handful of ways of deriving the scaling relationship for the size of a chain in good solvent. Here we will follow the so-called “Flory” derivation (after Paul Flory, American Chemist and Nobel Laureate). Flory used a simple thermodynamic argument: the chain will adopt an average size that will minimise its free energy:

$$F = U - TS \tag{2}$$

We need to cast each term on the RHS in terms of the chain size. The entropy term is rather straightforward. We said that the solvent-swollen chain is very similar to a random walk chain with the exception that it does not have self-intersections. As you might imagine, the entropy of a SAW of N steps is very similar to a self-intersecting random walk - and consequently, we will simply apply the ideal chain description of entropy that was derived in the previous section for an ideal chain. Thus, the only difference in a Flory good-solvent chain and an ideal chain is ΔU. We can write down a virial expansion of U as

$$U = Vk_BT(\beta\eta^2 + \gamma\eta^3 + \delta\eta^4 + \cdots) \tag{3}$$

where β, γ, $\delta \cdots$ are the second, third, fourth $\cdots$ virial coefficients which are fully determined by the form of the energetic interactions (*e.g.*, Lennard-Jones interactions). We will ignore all but the leading term in this expansion, which represents the energetics of all two-body interactions. Higher order terms represent three-body interactions, four-body interactions, *etc.* If the monomer-monomer interactions are *unfavourable*, or *repulsive*, then the second virial coefficient is positive, $\beta > 0$. If the monomer-monomer interactions are *favourable*, or *attractive*, then $\beta < 0$. For the good solvent case, $\beta > 0$. η is the concentration of statistical monomers, $\eta \equiv N/V$ where V is the volume. Thus, we can recast the free energy in terms as

$$F = k_BT(V\beta\eta^2 + \frac{3R^2}{2Na^2}). \tag{4}$$

This expressions states that the energy of the chain is comprised of all binary interactions amongst the monomers and the ideal elastic contribution of a random walker. We need to get this expression in terms of one variable, say α which we define as the swelling or expansion coefficient,

$$\alpha = \frac{R}{R_0} \tag{5}$$

where R_0 is the natural size of the chain, $R_0 = \sqrt{N}a$. This swelling coefficient becomes larger than unity when the chain exceeds the natural size of an ideal chain, and is smaller than one when the chain collapses to sizes less than that of an ideal chain. We want to know what value α takes on when the solvent is good; clearly α will be greater than 1. The concentration, $\eta = N/V$ is expressed in terms of R and R_0 using $V \sim \alpha^3 R_0^3$. In terms of the swelling coefficient, the free energy is then

$$\frac{F}{k_B T} = \frac{\beta\sqrt{N}}{a^3\alpha^3} + \frac{3}{2}\alpha^2 \tag{6}$$

As you can see from the first term on the RHS, the interactions with the good solvent promote swelling of the chain; *i.e.*, as α becomes larger than 1, the first term becomes smaller and the free energy is thus smaller. On the other hand, a swollen chain has less entropy and therefore the second term on the RHS suppresses swelling; *i.e.*, as α increases beyond 1, the second term becomes larger and the free energy increases. Thus, the energetic interactions with the solvent and the entropic elasticity are in opposition. At low swelling, the free energy will be high due to the energetic interactions, while at high swelling, the free energy will also be high due to the entropic elasticity of the chain. There will be an intermediate or optimal value of swelling at which the two opposing driving energies will be equal and the free energy will then be minimal. You can determine an equation for the optimal swelling coefficient α by solving $dF/d\alpha = 0$, and checking to ensure that $d^2F/d\alpha^2 > 0$. The equation for α at which the free energy is minimal is

$$\alpha \sim (\frac{\beta}{a^3})^{1/5} N^{1/10} \tag{7}$$

which, when inserted into the definition of α, $R = \alpha R_0$, yields

$$R \sim (\frac{\beta}{a^3})^{1/5} N^{3/5} a, \tag{8}$$

or, $R \sim N^{3/5}a$.

This derivation is very simplistic, but the end result is effectively correct. A chain in a good solvent is often referred to as a "Flory chain" after Paul Flory who first wrote down this analysis. Of course, there are several simplifications and Pierre DeGennes (French Physicist and Nobel Laureate) carried out a more precise and very complicated calculation in 1972 and effectively got the same result. The Flory treatment effectively assumes that the only difference between a good solvent chain and an ideal chain is in the incorporation of (repulsive) pairwise interactions. Let's explore this further.

First let us summarise the ideal chain, investigating the occurence of self-intersections with itself. The ideal chain has natural size $R \sim \sqrt{N}a$, the volume circumscribing the chain is $V \sim R^3 = N^{3/2}a^3$, and the volume fraction of segments in that circumscribed volume is $\phi = N\nu/V \sim (\nu/a^3)\sqrt{N}^{-1}$. Now the number of segments on the ideal chain that intersect another segment of the chain is $N \times \phi$ as ϕ is, to first order, the probability of finding a segment at any locations within V. Because $\phi \sim \sqrt{N}^{-1}$, the number of 2-body interactions or single-intersections of the chain scales with $\sqrt{N}$. Thus, the number of intersections increases with the square root of the number of statistical monomers. N is usually large, so the number of binary self-intersections is appreciable. How many intersections are there that are 3-body ior 3-way (*i.e.* the chain self-intersects three times at one point)? That number is $N \times \phi^2 \sim N \times \sqrt{N}^{-2} \sim \mathcal{O}(1)$, and does *not* scale with N, that is, we can find a three-way intersection on the order of once each chain, irrespective of the number of statistical monomers. The number of a four-way intersection is $N \times \phi^3$ and scales as $\sqrt{N}^{-1}$ - and again, as N is usually large, the number of four-body intersection vanishes. So in a random walk or an ideal chain, two-way intersections are frequent, we might find a three-way intersection, but we will not find higher-order intersections.

Now contrast that with the Flory chain. In the Flory chain, an "intersection" corresponds to a close enough approach of the monomers that they feel the (repulsive) monomer-monomer interaction strongly. Whether the monomers intersect or not is determined by the form of the interaction potential. For example, in a Lennard Jones-type interaction, there is a strong repulsion at close distances that prohibits overlap. The size of the good-solvent chain is $R \sim N^{3/5}a$, the volume circumscribing the chain is $V \sim R^3 = N^{9/5}a^3$, and the volume fraction of segments in that volume is $\phi = N\nu/V \sim (\nu/a^3)N^{-4/5}$. The number of 2-way self-intersections is $N \times \phi \sim N^{1/5}$, and the number of three-way intersections is $N \times \phi^2 \sim N^{-13/5}$. For large N, the number of a three-way intersection is vanishingly small, and for higher-order intersection probabilities, it is even smaller.

Consequently, in both the ideal chain and the Flory chain, the occurence of a three-way intersection or interaction is not a dominant contribution to either chain's configuration. However, the probability that a chain intersects itself in a two-way intersection is quite large for an ideal chain, but binary interactions in a Flory chain are smaller in number. Indeed, this we already know: the solvent acts to expand the chain, thereby decreasing the probability that two monomers, on arbitrary locations on the contour, approach closely. We can additionally state that it is these two-body interactions which effectively increase the size of the chain under good solvent conditions.

3.3 θ-solvency conditions

It is important to understand that the sign of the second virial coefficient, β, indicates the type of solvent. If $\beta < 0$, the solvent is poor, if $\beta > 0$, the solvent is good. It is indeed possible for β to take on values that are very close to zero: in that case there is no energetic preference between monomers and solvent molecules and the system has effectively no change in its internal energy, *i.e.*, $\Delta U = 0$. This condition is called "theta" solvency conditions and under these conditions, the chain size does indeed scale as $R \sim \sqrt{N}a$, as predicted by the ideal chain.

EXAMPLE PROBLEMS

• Describe an isolated, single polymer chain in (a) good solvent, (b) theta solvent, and (c) poor solvent conditions.

good solvent: In a good solvent, an isolated chain is swollen by the solvent. Thermodynamically we understand the size of the chain as a balance between the solvent-polymer interactions that promote swelling and the entropy (or stretching penalty) that suppresses swelling. The chain is fluctuating in size and shape. The average size of the chain scales as $R \sim N^{3/5}a$, where N is the number of statistical segments in the chain and a is the size of a statistical segment.

theta solvent In a theta solvent, the monomer-monomer interactions are identical to the monomer-solvent interactions so that the chain is effectively inert to itself and the solvent. The chain is referred to as an ideal chain, as it is similar to the ideal gas model: it can intersect itself and has no interaction energy. We model such a chain as a random walk that can intersect itself. The probability of finding a chain of size R obeys a Gaussian distribution for $R < Na$, and the average size scales as $R \sim N^{1/2}a$.

poor solvent: In poor solvent, the monomer-monomer interactions are far favourable to monomer-solvent interactions, and consequently, the chain will adopt a size and shape to minimise contact with the solvent. That is, the chain will collapse upon itself to expel solvent, forming a dense sphere as a sphere has minimal surface energy and minimal size fluctuations. Thus, the average size of the chain is $R \sim N^{1/3}a$. The chain does not deviate significantly from its spherical shape.

• • From various models, the mean square end-to-end distance of isolated single chains, $\langle R^2 \rangle$, is found to scale with number of monomers in the chain, N, according to various power laws:

For poor solvents or (or solutions where the second virial coefficient, β is negative and monomer-solvent interactions are repulsive), a minimal surface area model yields

$$\sqrt{\langle R^2 \rangle} \sim aN^{1/3}.$$

For theta solvents where $\beta \sim 0$ and monomer-solvent interactions and monomer-monomer interactions are similar and random walk statistics is descriptive,

$$\sqrt{\langle R^2 \rangle} \sim aN^{1/2}.$$

For good solvents described by positive second virial coefficient $\beta > 0$, and monomer-monomer interactions are repulsive, the Flory argument provides

$$\sqrt{\langle R^2 \rangle} \sim aN^{3/5}.$$

Which of these power law descriptions represents the end-to-end distance of a single polymer chain in a melt of identical chains, and why? (A melt is a solution containing only long chains and no solvent).

In a melt, there are no small solvent molecules - only polymer chains. Thus there are only two types of interactions: monomer-monomer interactions within the same chain (intra-chain monomer interactions) and monomer-monomer interactions between different chains (inter-chain monomer interactions). As the chains are identical, the inter-chain interactions are roughly equivalent to the intra-chain interactions (which are akin to monomer-solvent interactions). Consequently, a single chain in a melt has no preference for its own monomers or the monomers of other chains; the inter and intra- chain interactions are balanced and the chain behaves ideally, as in a theta solvent.

- **What happens to the moderately stretched chain if the solvent is changed from a theta solvent to a good solvent?**

The chain extension will not change appreciably, extending only slightly. As an ideal chain is stretched, it will have fewer self-intersections, and non-contiguous monomers will rarely be close. In a good solvent, a chain swells because non-contiguous monomers that are close will feel a repulsion. However, if that chain is stretched and there are few close monomer pairs, then there will be minimal swelling of the chain. You would however see a bigger effect if the solvent was made poor (either through a change of temperature or addition of a co-solvent). The force required to maintain the chain extension will increase in poor solvent.

Partial Summary

We used geometrical reasoning and thermodynamics to explore non-ideal chain, namely chains which interact favourably and unfavourably with their solvent.

- The size of a chain, collapsed upon itself in poor solvent is $R \sim N^{1/3}a$
- The size of a chain, swelled in good solvent, is $R \sim N^{3/5}a$
- As the second virial coefficient decreases from positive values, to zero, then to negative values, the chain is described as being is in a good solvent, theta solvent, and poor solvent, respectively.

3.4 Experimental stretching of single chains in poor solvent

Almost all of the experimental work fo single chain stretching focusses upon chains in good solvent, where the chains are swollen and form loose coils. Under these condition, polymer tails or loops can be “grabbed” by an adsorbing AFM tip. Separation of the AFM tip and the surface produces a tension in the bridging polymer which is measured and characterises the elasticity of the chain. The stretching at weak extensions is purely entropic, but at higher extensions, there is an additional enthalpic penalty. Such stretching profiles obtained from AFM data have been fitted to various models, (including the freely jointed chain FJC, amongst others). These stretching forces increase monotonically with separation until the adsorption site or monomer-surface contact is broken, usually at separations that are of the order of a few hundred Angstroms.

Much less attention has been placed upon the stretching of single chains in poor solvent. The stretching of chains which are collapsed in poor solvent was first studied theoretically by Halperin and Zhulina. They argued that at weak extensions, the globule of chain deforms into roughly an elliptical shape and then into a cylinder, At a critical extension, the polymer undergoes a sharp first-order transition into a "ball-and-string" configurations, shown in figure 1(a). This transition is driven by the high surface tension under poor solvent conditions. In this way, the transition is analogous to the surface tension driven breakup of a column of liquid into a series of droplets, referred to as the Rayleigh-Plateau instability. However, in the polymer case, the applied tension draws out a thin filament rather than a series of disconnected droplets, owing to the constraint on connectivity of the monomers. The force required to pull the chain beyond this critical extension, or to "pull-out" the chain monomer-by-monomer from the collapsed globule, is constant and independent of extension.

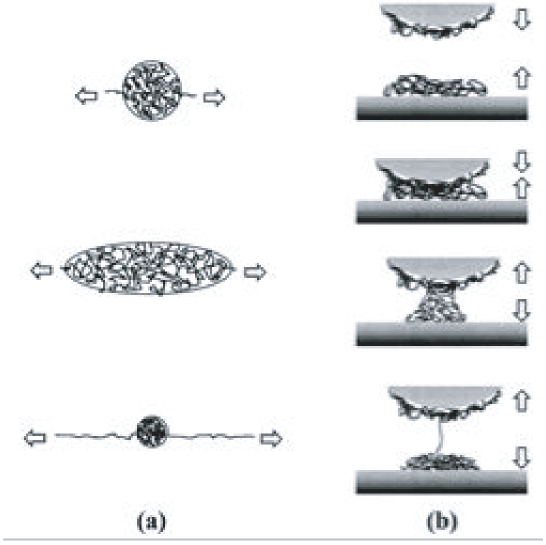

Figure 1: (a) Schematic of the Halperin-Zhulina prediction of a chain, in poor solvent, whose ends are extended. Because the fully-flexible chain is in poor solvent, it is collapsed so as to minimise its surface area or solvent contact. When the ends are extended, the collapsed globule deforms into an elliptical shape, increasing its surface area. However, at a critical extension, the chain forms a "ball-and-string" configuration: this configuration minimises the surface area subject to the constraint of the separation of chain ends. Further extension of the chain simply takes monomer out of the "ball" and into the "string" with a constant energy penalty per monomer; consequently, the force of extension will be constant in the ball-and-string configuration. This theory was nice, but rather impractical: how do you find the ends of the chain in a collapsed globule? (b) Schematic of experimental strategy to demonstrate the "ball-and-string" configuration. Taken from Haupt *et al.*, *Langmuir* 2001..

Haupt, Senden, and Sevick reported the first experimental evidence of the Rayleigh instability of a single chain using AFM. In a simple experiment, they adsorbed polymer onto a flat surface and used the adsorbing tip of an AFM to probe the polymer. This involves repeatedly bringing the surface and AFM tip into contact and separating them again, while simultaneously measuring the force on the tip, as depicted in figure 1(b) This results in chains forming bridges between the two adsorbing surfaces, The resulting force versus separation profiles are often relatively featureless, showing only primary adhesion upon retraction. However, over many separation cycles they find two distinct types of force profiles, depending upon the solvent conditions. The characteristics of the first type of force profile are

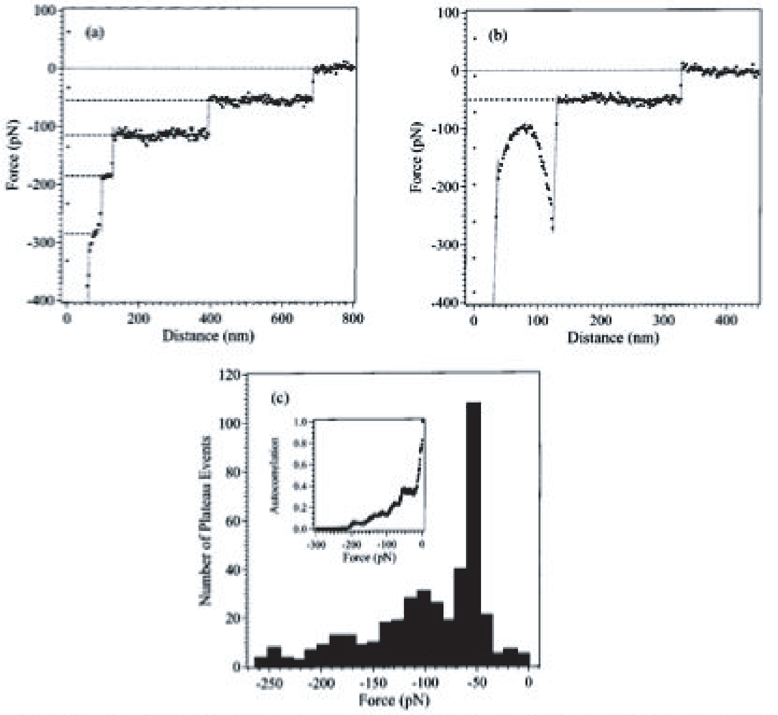

Figure 5. Representative force profiles and histogram summarizing the set of profiles for PEO in 0.45 M K_2SO_4 at 25 °C. The spring constant of the cantilever is 0.040 N m^{-1}, and the rms baseline noise is 22.0 pN. The discontinuities in both force profiles have been connected by gray lines of fixed slope. (a) A force versus distance profile shows 3, arguably 4, Plateau events each highlighted by the dashed lines. We have included the dashed line for the apparent Plateau event which is obscured by primary adhesion. The mean forces associated with each plateau are 285, 185, 115, and 55 pN. These plateaus persist to extension distances of 80, 120, 391, and 679 nm. (b) A force versus distance profile shows simultaneous Langevin and Plateau events. This corresponds to pulling two chains: a chain with two ends fixed to the surfaces, stretched and detached at 120 nm, and a chain with a free end which is pulled out of a surface globule at 330 nm. (c) A histogram shows the frequency of plateau forces. This histogram was constructed from 406 Plateau events in a data set of 600 force profiles. The magnitude of the plateau force is the mean of a Gaussian distribution, fitted to the experimental points of the plateau. The number of Plateau events in the data set peaks at nearly interval steps, suggesting that the plateaus are quantized according to the number of chains in the pulled polymer filament. The bin size of the histogram is 12.0 pN.

Figure 2: From Haupt *et al.* 2001

identical to that observed by previous authors and have been interpreted as the elasticity of various polymers. This characteristic force profile is referred to as a “Langevin” event as it has been fitted to various elasticity models. In poor solvent, we see a new second type of profile. It is characterised by “steps” or plateaus of constant force which extend over separation distances that are comparable to Langevin events. At these separation distances, polymer-solvent contact is minimised by the formation of surface-bound polymer globules at each surface, connected by a polymer filament. This is the analogue of the ball-chain configuration of the polymeric Rayleigh instability. As the surfaces are separated further, monomers are pulled out of the surface-bound globules and incorporated into the lengthening filament. The force of extension of the filament is constant over the separation distance, reflecting the constant rate of monomer extracted from the surface bound globules. This polymer filament may contain several chains, and surface separation can completely pull-out the shorter chains. With each pull-out, the plateau force drops discontinuously in a “step-like” manner, until the last single chain in the filament is pulled out and the force between the surfaces returns to zero. We refer to such constant force events as “Plateau” events after Plateau’s work in instabilities as well as the physical description of the force versus distance profile.