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Biopolymer gelation- exponents and critical exponents

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Summary

The gelation of biopolymer systems has been studied, at least, empirically for many years, but only more recently have the methods of macromolecular science been applied. A number of following studies have tended to concentrate on measuring power law exponents, and have ignored details of the network structure. Biopolymer physical gels are more complicated than "simple" chemically crosslinked systems, which means that approaches designed, for example, for crosslinked melts have to be applied with caution. Consequently, while measuring exponents alone can give some valuable information, and some apparent "universalities" are seen, the details of pre-exponential factors can often prove more significant and useful. In this article we re-examine the mapping of generalised percolation parameters (for example p, p_c) unto either a time or a concentration axis. In this we consider the assumptions behind such an approach, and the applicability of critical exponent treatments in a regime that is typically a long way away from critical, at least when judged in terms of absolute (Ginzburg) criteria.

Introduction

The basic hypothesis of gelation is that of non-linear (f-functional) random step-growth polymerisation, which goes back to the classical work of Flory and Stockmayer in the 1940s [1]. This beautiful model, which in today's terms we would describe as percolation on an infinite dimension, tree-like or Bethe lattice, [2,3] has proved of enormous value even though it neglects many features of relevance to applications, such as the pre-gel formation of intramolecular links (cycles) and the existence of substitution effects. It is also, by its nature, a model that neglects critical fluctuations, and there is a long history of literature in which the applicability, or otherwise of this model close to the critical gel point, here defined simply as:

$$p_c = \frac{1}{f-1} \qquad (\mathbf{1})$$

is discussed [4,5].

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However, it is fair to say that gelation in the absence of intramolecular reaction and other perturbations, such as so-called substitution effects, and outside the critical regime, is well understood in terms of the Flory-Stockmayer theory. Consequently the FS gel point can be used as a reference point for the consideration of the effects of "chemical" perturbations.

At the gel point, the species of infinite molar mass has a tree-like structure permeating through the whole reaction mixture. The critical conversion, p_c, occurs when there is a non-zero probability that a randomly chosen chain continues to infinity. Given the previously mentioned random reaction (or equal reactivity) of like functional groups or sites, the gel point, and properties relating to the gelling system, may be predicted quite generally, in terms of the parameter p, representing the proportion of reacted groups, and this "gel point", p_c. For example many properties can be related back directly to the ratio $p/p_{c,}$ although very close to p/p_c critical fluctuations need to be taken into account. The extent of this critical region is governed by criteria such as that of Ginzburg; evaluation of the extent of the critical domain remains the realm of the theorist. However a practical guide, quoted directly from the excellent review by Stauffer, Coniglio and Adam, [2] and is that the critical regime applies within the region where $10^{-2} <= (p/p_c) - 1 <= 10^{-1}$.

In a chemical step-growth system what is generally monitored is the disappearance of reactants, or equivalently, the appearance of product. It then becomes straightforward to relate p to chemical kinetics, using an appropriate kinetic order equation. In the present article we will begin by considering this, and adopt the simplest assumption relationship possible, i.e. that reaction is governed by second order kinetics with respect to the initial concentration of reactants, and where p_0, at time zero, = 0.

Gelation kinetics

If we do this and provide another relationship, between say the equilibrium shear modulus and p, we can easily generate the observed behaviour, both of the chemical reaction rate of conversion, and the concomitant growth of modulus, G, with respect to time [6]. The latter curve is now generated routinely in many laboratories, because of the ready availability of oscillatory shear rheometers.

Figure 1 illustrates a typical result with the dependence of both p and G on time here plotted on linear time axes, p shows the expected asymptotic behaviour with $p = 1$ attained only at very long times. For convenience (and to comply with usual practice) G is plotted on a log scale.

In practice, non-integral reaction orders are commonly seen, and as has been discussed in detail elsewhere, this is a natural consequence of "wastage" effects [7, 8]. If we assume the simplest case, then step-growth intermolecular reaction of functionalities will involve a binary collision between functionalities on different growing species, with consequent reaction order two in terms of the concentration of reactants. As a consequence of this, intramolecular "ring forming" reactions, must be first order with respect to the same concentration, so the overall order is less than 2, and is concentration dependent.

As illustrated in Figure 1, a specific non-zero gelation time, t_{gel}, at 100 s on the (arbitrary) time scale, becomes evident, and this depends upon the rate constant and the functionality of the step growth model in a simple way. In the above discussion we have already tacitly assumed that the parameter p is readily obtainable experimentally, either from the rate of disappearance of reactant functionalities, or by measuring the

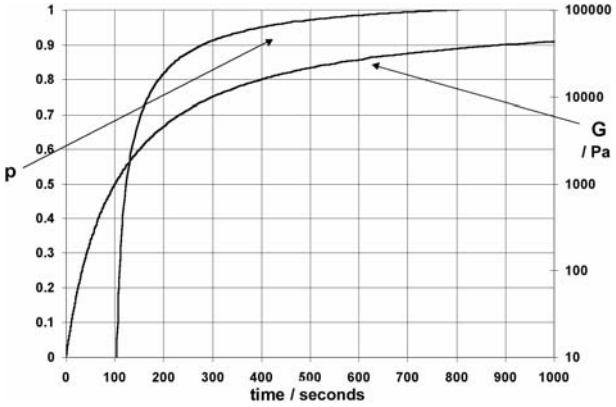

Figure 1. Conversion, *p*, and equilibrium modulus *G* (in units of Pa) plotted against time. Calculation details as in [6].

rate of appearance of product. However, in physical gels, it can be very difficult, if not impossible to determine even the value of *p* directly, and then some further assumptions are required as described below.

Physical versus chemical gels

For the class of systems known as “physical gels”, both inter- (and intra-) molecular bonding is non-covalent [9-12]. The presence of non-covalent crosslinks complicates any physical description of the network properties enormously because, unlike chemical bonds, their number and position can, and does, fluctuate with time and temperature (i.e. such bonds are potentially reversible). In many cases the nature of these physical crosslinks themselves is not known unambiguously, since they often involve a combination of contributions such as hydrophobic, electrostatic and hydrogen bonding interactions.

For biopolymer gels, in particular, non-covalent crosslinks are formed by all of these mechanisms sometimes taking the form of specific and quite complex association phenomena involving extended quasi-crystalline "junction zones" of known, ordered secondary structure [9,10,13,14]. Examples include gelatin and gels from marine and plant polysaccharides, globular and other protein gels. Gels formed from the marine polysaccharide, iota-carrageenan, for example, are traditionally accepted to involve intermolecular double helix formation. The existence of "rogue residues", saccharide units which are in the wrong conformation to allow the helix to propagate, and which therefore terminate the sequence, was established chemically. Then rather than isolated helix pairs being formed, each chain can share portions of ordered helical structure with at least two other chains, an essential condition for branching and subsequent gelation. (We note here that, in general, for gels formed by this mechanism, of which there are a few examples, the helical species form first and associate into networks through higher order aggregation. Consequently, initial helix formation into rods or more complex branched species is just a prelude to a more complex kinetic profile).

Although the molecular structure of physical gels is rather (if not very) different to that of chemical gels, the properties of the underlying "gel state" predominate at the

long distance scales probed by rheological, particularly viscoelastic, measurements. Theoretical approaches originally derived only for chemical gels have therefore had some success in describing the properties of physical gels and networks.
In the case of physical gelling systems the presence of large amounts of a solvent is usually implied, and what is well established is that below a certain critical concentration, usually written as C_0, no gel is formed however long the "reaction" is allowed to proceed, whereas above C_0 the gelation time tends to decrease with increasing concentration. The apparent parallels with p_c in step-growth systems would therefore suggest that we can write:

$$\frac{p}{p_c} \approx \frac{C}{C_0} \approx \frac{t}{t_{gel}} \qquad (\mathbf{2})$$

When the apparent functionality is very large, i.e. the system is in the vulcanisation limit, and measurements are made very close to p_c these equalities may hold. Nevertheless it is certainly not true to suggest this is always the case, and to do so can cause many problems and confusion as we discuss below. The present author and his co-authors have considered some of the more detailed aspects elsewhere [10,15-17].
For the present we will, instead, consider the implications of accepting this equality and explore the consequences in terms of the estimation of appropriate critical exponents. For example if we do so, we can easily write that the modulus G depends upon the measurable parameters for biopolymer gelation (concentration and time) as below:

$$G \approx \left[\left(t / t_c\right) - 1\right]^e \approx \left[\left(C / C_0\right) - 1\right]^e \qquad (\mathbf{3})$$

and close to the gel point, we have assumed that the exponent e will be the same as if we had used the formal percolation expression in terms of p and p_c. Examination of the literature will expose a range of theoretically values for both these exponents, depending upon the precise model and the nature of the underlying percolation lattice graph, but typically values lie in the range 1.7-2.8 [2]. This contrasts with the value of 3, the exact exponent for "classical" percolation on a Bethe (or tree) lattice [3].
What we wish to show in the present article is that even this assumption is flawed, because the measured value of the "critical" exponent is very sensitive to the regime in which it is measured. Of course there is nothing novel, of itself in this assertion, indeed the paper by Gordon and Torkington, for example, published more than 25 years ago, made almost the same point [18]. However it has clearly not been appreciated, because the author continues regularly to have sent to referee papers in which, say, a series of measurements have been made on biopolymer gels, at a range of concentrations. By plotting measured gel modulus versus scaled time or concentration the authors obtain an exponent of say ~2-2.5 and claim this to be a critical exponent, in conformity with the predictions of percolation theory. As we hope to demonstrate below, this conclusion is very often illusory.

Theoretical aspects

To consider this from the theoretical viewpoint, we can generate values of the modulus G, p/p_c and t/t_c by applying the same model used to calculate Figure 1. In doing this, it has to be appreciated we are using the classical model, not always in the appropriate regime. However, despite this limitation, some interesting results appear.

Remembering that the classical model has a critical exponent of exactly 3, we can plot in the usual "critical exponent" manner, log G versus log (p/p_c) as in Figure 2. What is clear, even without the effects of chemical wastage etc., is that this produces a curve rather than a straight line, and crucially that the "measured" critical exponent depends upon the range over which the plot is treated.

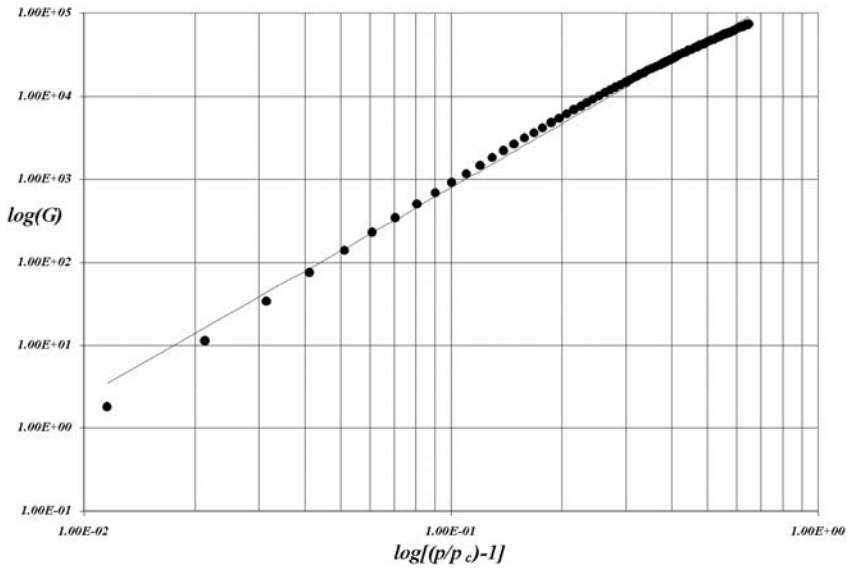

Figure 2. Post-gel data from Fig.1 plotted in "critical exponent" form. The line represents the best regression fit to <u>all</u> the data (cf. Table 1).

To demonstrate what this means in real terms, using all data between G = 0 and G~2x10^4 gives an <u>overall</u> exponent of 2.78. Because this corresponds to (p/p_c)-1 from 0 to 0.33, the highest points are already outside the Ginzburg region, according to the "rule" outlined above, i.e. 10^{-2} <= (p/p_c) -1 <= 10^{-1}. Using data in this more restricted region gives an exponent of 2.88 but, in terms of our kinetic model, requires all data to be collected within the region between 102 and 122 s (remembering that t_{gel} was an arbitrary 100 s)! If we plot the same range of data in terms of (t/t_{gel})-1 we actually obtain an exponent >3, viz. 3.51, so that <u>even in this narrow range</u> the assumption that (t/t_{gel})-1 = (p/p_c)-1 breaks down. This actually not surprising since the relationship of p and t is clearly not linear as we saw in Figure 1, but this particular point seems not to have been appreciated before. We do not, at this stage, extend the calculations still further to consider the mapping of (C/C_0)-1 versus p/p_c, since this depends on a further number of different parameters, and assumptions (see below). However, it is clear that there is no universal equivalence in the form of Equation 2.

Before considering practical aspects in more detail, we feel it is appropriate to extend the argument further. As we saw above, with our, albeit arbitrary, gel time of 100 s, all data needed to be collected in just 20 s of real measurement. What is the implication of measuring totally outside this regime? What is clear from examining the curvature of say Figure 2 is that we will obtain lower exponents, than within the critical regime, but the real question is how much lower?

As an example, if we evaluate the "critical" exponent in the range (p/p_c)-1 = 0.1 to 0.5 we will obtain an overall exponent of 2.39, while the corresponding slope measured for the same range of values of (t/t_{gel})-1 gives an exponent of 2.68. Table 1 shows a more extended set of results - remember that the initial constraint is that the exponent is 3 in terms of (p/p_c)-1, and this remains as an asymptote for this set.

Table 1. The column "slope" represents the exponent calculated from linear regression of a log (G) versus log((p/p_c)-1) regression from its initial value – here 0.0016 - up to and including the value shown.

(p/p_c)-1	slope
$1.6e^{-3}$	-
0.10	2.90
0.23	2.84
0.40	2.75
0.75	2.56
0.95	2.42

Experimental aspects

There are several further issues to be considered, but the first and most significant is that for a number of reasons, it is very difficult, if not impossible, to obtain much reliable data for gelling biopolymer systems in the relevant Ginzburg region. Of course the example above, where t_{gel} was an arbitrary 100 s was somewhat artificial - if we were to make any such measurements, we would attempt to choose conditions such that t_{gel} was say 5000 s, rather than 100, and this would extend our useful time regime to 1000 s. All other factors being equal, this would allow us to take say 20 or more experimental points in the relevant regime. Unfortunately all things are not equal, and physical gels such as these are, very reasonably, far more stress (or strain) sensitive than covalent networks [19]. This requires that tiny mechanical perturbations are made to a very low modulus system, so that the response can be lost in the instrumental noise. Even here, there are further problems, because establishing that these systems are measured in the linear viscoelastic regime may be impossible to establish [20]. Of course this does not preclude optical scattering measurements of G from being made, but then it needs to be established that these are really approximating to the low frequency (nominally equilibrium) value of the modulus predicted by gelation theories. This effect seems not to have been considered either!

In a recent publication [17] we explored some of the (C/C_0)-1 relationships using published data for globular protein heat set gels, from both our own results and those of other workers, in some depth. Exponents were obtained in the range 2.35 - 2.75, although no definitive conclusions were reachable. Indeed, despite these being recent results collected by established groups, very few data (<10%) fell within the Ginzburg regime defined in terms of concentration units. This may explain how and why earlier data, collected at even greater values of the percolation variable, be it in terms of concentration, or time, were often still lower.

A more extensive exploration of the literature again suggests that few, if any of the data published as critical exponents satisfy the, albeit rigorous, criteria of Ginzburg as defined by Stauffer, Coniglio and Adam [2]. Unfortunately experimental agreement with published theoretical predictions is not a guarantee of credibility in this area!

Concentration dependence of gel modulus - non-critical exponents

It has been known for many years that for biopolymer (and other physical gels) if log(G) is plotted versus log(C), near to C_0 a large and variable power law dependence of G on C is observed, whilst at higher concentrations, a constant, and approximately 1.8-2.2 limiting law exponent emerges [10]. Such behaviour has been noted historically, particularly for gelatin gels [9]. In the author's view this has little or nothing to do with the prediction of critical exponents from percolation theory, but is simply a consequence of the gelation kinetics. This is easily asserted since the limit power law is typically seen only for ((C/C_0)-1) >~ 10.

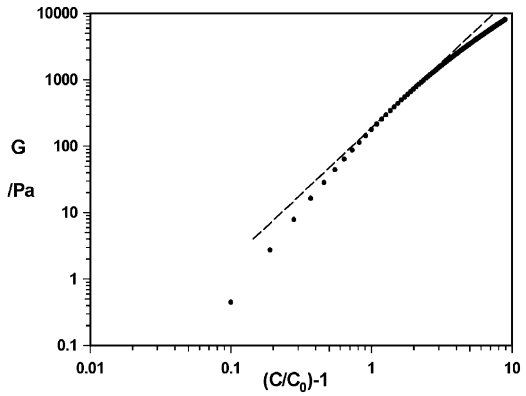

Figure 3. The modulus G plotted versus "critical exponent" scaled concentration showing overall behaviour and the curvature. The dotted line is drawn with a slope (exponent) of 2.

There are several explanations for this, but the simplest is just that any model which asserts a weak reversible binding between "aggregate" and monomer requires some hypothesis for the reaction order between monomer and dimer / higher aggregate species. Accepting this, the simplest conjecture is that monomer to dimer reactions are governed by second order chemical kinetics - just as we assumed at the start of this article. Indeed with very few other postulates, we can model the observed behaviour quite reliably, and reproduce the C^2 behaviour, and even lower exponents using a tree-like model, with initial exponent 3, as illustrated in Fig.3 [10,13].

Conclusion

We suggest that some (perhaps the majority of) publications that claim to have established percolation critical exponents for biopolymer (and synthetic) physical gels have not achieved this objective. This is, of course, not to say all such work is fruitless, indeed this author could hardly claim to have read every single publication. Nor does it suggest that no such experiment would ever achieve this goal: simply that most past work has not. Stauffer's original paper [21] on gelation and percolation is now more than 30 years old, and has continued to stimulate much interest. However, in this area, theory and experiment have rarely run in tandem, and it is fair to say that there is little concordance. As Stauffer himself has said more recently, in this area there is, or appears to be, ".. a failure of co-operation between physics and chemistry.." [22].

References

1. Flory PJ (1953) Principles of Polymer Chemistry. Cornell University Press, New York NY, USA
2. Stauffer D, Coniglio A, Adam M (1982) Adv Polym Sci 44:103
3. Gordon M, Ross-Murphy SB (1975) Pure and Applied Chemistry 43:1
4. de Gennes PG (1979) Scaling Concepts in Polymer Physics. Cornell University Press, Ithaca, NY, USA
5. Stauffer D (1985) Introduction to Percolation Theory. Taylor and Francis, London, England
6. Ross-Murphy SB (2005) Journal of Macromolecular Science - Physics Edition submitted:
7. Ross-Murphy SB, Stepto RFT (1996) in Large Ring Molecules. Semlyen JA, Ed. John Wiley & Sons, Chichester, p.599
8. Dušek K, Gordon M, Ross-Murphy SB (1978) Macromolecules 11:236
9. te Nijenhuis K (1997) Adv Polym Sci 130:1
10. Clark AH, Ross-Murphy SB (1987) Adv Polym Sci 83:57
11. Ross-Murphy SB (2003) in Polymer Gels: Fundamentals and Applications. Bohidar HB, Dubin P, Osada Y, Ed. ACS, Washington DC, p.51
12. Ross-Murphy SB (1998) Ber Bun Gesell Physik Chim 102:1534
13. Clark AH (1996) Current Opinion in Colloid & Interface Science 1:712
14. Picout DR, Ross-Murphy SB (2002) in Polymer Gels and Networks. Osada Y, Khokhlov AR, Ed. Marcel Dekker, Inc., New York, NY, p.27
15. Clark AH (1993) Polym Gels Network 1:139
16. Gosal WS, Clark AH, Ross-Murphy SB (2004) Biomacromolecules 5:2408
17. Gosal WS, Clark AH, Ross-Murphy SB (2004) Biomacromolecules 5:2420
18. Gordon M, Torkington J (1981) Pure and Applied Chemistry 53:1461
19. Kavanagh GM, Ross-Murphy SB (1998) Prog Polym Sci 23:533
20. Rodd AB, Dunstan DE, Ross-Murphy SB, Boger DV (2001) Rheologica Acta 40:23
21. Stauffer D (1976) Journal of the Chemical Society-Faraday Transactions II 72:1354
22. Stauffer D (1998) Ber Bun Gesell Physik Chim 102:1672