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REVIEW ARTICLE

Branched polymers and gels

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Received 14 December 1989

Abstract. We discuss the properties of randomly branched polymers and gels close to the gelation threshold. We first discuss the synthesis of such polymers, with special emphasis on an analogy with percolation. We then discuss the influence of polydispersity on the observed power-law behaviours that are observed in the study of their conformation when these materials are swollen upon addition of a good solvent. The effective exponents that are observed are shown to depend strongly on polydispersity. We also discuss the distribution of relaxation times that is present because of this distribution of molecular weights. Experimental results are given at every stage of this discussion for comparison with theory. Although percolation is shown to be an important universality class, we stress that it is by no means the only one.

1. Introduction

Polymers are a class of materials that have ever-increasing practical importance. They have been synthesised and studied by chemists [1] for a long time. Interest arose in the physics community in the early 1970s when de Gennes [2–5] showed the equivalence between the so-called self-avoiding walk model of a linear polymer in a good solvent and the critical phenomena [6] that occur near the transition temperature of the n -vector model in magnetism in the limit when n goes to zero. Almost equally important was the realisation that it was experimentally possible to observe one polymer among others [7], in a solution of any concentration, by small-angle neutron scattering (SANS) combined with a labelling technique using deuteration, i.e. replacement of hydrogen atoms along the polymer chain by deuterium. This labelling technique avoided the phase separation that normally occurs between polymers of different types, except for very high molecular weights. From the combination of these two events came an explosion in our understanding of the conformation of amorphous polymers. But linear topologies are not the only ones that may exist for polymers. If one considers bifunctional monomers, which may react by only two functionalities, after letting them react for some time, one gets linear chains. On the other hand, if one uses multifunctional units instead, one generates randomly branched structures [1] if reaction takes place for rather short times. A solution of these polymers is called a sol. If the reaction time is larger than a threshold, in addition to the branched macromolecules of the sol, one gets a solid-like structure, called a gel, that has elastic properties, whereas the branched polymers form a viscous solution. The gel is sometimes referred to as the ‘insoluble phase’ for the following reason: usually, in

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order to characterise the product, chemists dissolve it in a good solvent. Two cases may occur. If the reaction time is smaller than the threshold, one gets a solution that may be diluted at will. If the reaction time is larger than this threshold, on the other hand, one gets a gel, which may be swollen to some extent. There is an equilibrium swelling [8] that is reached, which corresponds to a balance between the osmotic and elastic forces. Trying to swell the gel further leads to a phase separation between the swollen gel and a dilute solution containing the sol. An important point that is worth mentioning here and that will be studied further below is that in order to get very large branched polymers one needs to be in the vicinity of the sol–gel threshold. In what follows, we will be interested in the properties of large branched polymers and of a nascent gel, close to the sol–gel transition. We note that the latter is a connectivity transition, where nothing special happens to the free energy. Such a transition has been considered earlier by Flory [1], Stockmayer [9] and others [10, 11], who gave its mean-field theory, in the case when no loops are permitted. Another breakthrough was made in the mid-1970s, when de Gennes [12] and Stauffer [13, 14] independently pointed out the similarity between the sol–gel transition and percolation [15]. As we shall see, this allowed for the knowledge of the distribution of molecular weights in the sol [16]. It stated that it is extremely wide. Thus polydispersity should have important effects. The latter were considered and it was shown that they lead to effective exponents [17] whenever average properties are considered.

In what follows, we will first recall the various ways of getting branched polymers and gels. Among others, we will describe an important case of vulcanisation. This is the case when one crosslinks linear polymers in order to get a gel. It was shown by de Gennes [2, 67] that when this is done in a melt, in the absence of solvent, mean-field theory is valid. Section 2 will sum up the various models that have been proposed so far. Then we shall consider the swelling properties of branched polymers and gels. The dynamic properties will be treated in section 3. Because there is a wide distribution of masses, one may think that there is also a large distribution of relaxation times. This is indeed the case, and the latter may not be reduced to a single time, but to at least two times diverging in a different way as the gel point is approached.

2. Synthesis

In this section, we shall review the various ways of obtaining branched polymers and gels. We will deal only with truly branched macromolecules, where the number of crosslinks is of the order of the total number of monomers. Thus structures like star- or comb-shaped polymers, although interesting in different respects, will be considered as linear chains and will not be discussed here. The polymers that we have in mind are randomly branched structures that are synthesised by a process such as shown in figure 1, borrowed from Gordon and Ross-Murphy [11]. Typically, one starts with a vessel containing multifunctional units. These are monomers that may react by more than two functionalities. Thus, after the chemical reaction has proceeded for some time, one gets polymers with increasing sizes. A property that is common to most of the polymers synthesised this way is that one gets a wide distribution of the molecular weights: the resulting sol is polydisperse. This is the first main difference with linear polymers, where polydispersity is much smaller [1, 18]. As long as the extent of reaction p is smaller than a threshold p_c , finite, eventually very large, molecules are present. They constitute the sol. This is a viscous solution, with diverging viscosity as p approaches p_c . Above the

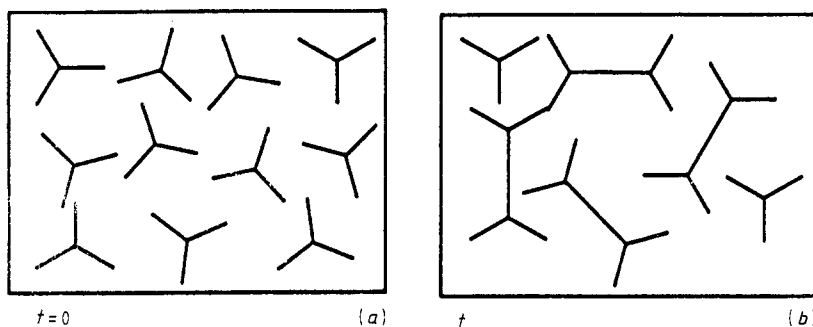


Figure 1. Schematic representation of polyfunctional condensation. (a) At initial time, only three functional monomers are present. (b) For later times, branched polymers are present, with a wide distribution in size. Eventually, an infinite network appears at the gelation threshold.

threshold, in addition to the sol there is an infinite, non-homogeneous network spanning the vessel. This is the gel, which provides an elasticity to the system. Note that when p goes to p_c from above, the elastic modulus vanishes continuously. Although this model system looks simple at first sight, various ways were used to implement it. We mention some of these below.

2.1. Experimental realisations

In *polycondensation*, one basically uses the same monomer, which has a given functionality. This corresponds to figure 1. Usually, however, a mixture of multifunctional and bifunctional monomers is used. Polyurethane [19] is a typical example of this class, which will be our main centre of interest.

In *vulcanisation*, one starts with linear polymer chains either in a melt or in a solution. The chains are permanently crosslinked either by a crosslinking agent or by irradiation. We will discuss the case of polystyrene solutions in cyclopentane crosslinked by irradiation by γ -rays, which was used by the Strasbourg group.

Physical reversible gelation [20–23] takes place when the crosslinks are either hydrogen bonds or local microcrystallites or helices (quenched isotactic polystyrene, gelatin gels). Usually these gels are obtained by decreasing the temperature and are destroyed by heating. An important point here is that the temperatures T_i of gel formation and T_s of destruction are usually different.

Gelation of electrically charged polymers was recently undertaken by Candau and coworkers [24]. The presence of electrical charges considerably changes the properties of the resulting polymers and gels.

In what follows, we will be interested mainly in the first two cases. Physical gels share [22] some properties of the first two classes. But their hysteresis is presently not completely understood.

As mentioned in the introduction, percolation was suggested early in its mean-field approximation to model this transition. More recently, it was recognised that critical rather than classical exponents should be valid in the vicinity of the threshold. Before we come to this model, we wish to recall another one that has appeared even more recently, namely the aggregation model. This is a generalisation of the well known

Table 1. The exponents in cluster–cluster aggregation problem as a function of space dimension d (from [132]).

d	2	3	4	5
D_a	1.42 ± 0.03	1.78 ± 0.05	2.04 ± 0.08	2.3 ± 0.2

Witten–Sander diffusion-limited model [25]. It has been studied by computer simulations and is assumed to describe the formation of rigid particles in a dilute solution, when they have to diffuse towards each other before they can react.

2.2. Theoretical models

2.2.1. Aggregation. The cluster–cluster aggregation model was studied mainly by Meakin [26, 27] and by Botet, Jullien and Kolb [28, 29] using computer simulations. In the crudest version, one starts with a lattice with a small fraction of the sites occupied by atoms. The latter can diffuse freely, with the constraint that they stick irreversibly to each other when they come into contact. The resulting dimer may also diffuse freely, with the same constraint. It is important to note that no relaxation is allowed: the shape of a molecule is quenched until it meets another one and grows. The size of the resulting clusters grows with time. In the limit of vanishing concentrations of initial atoms, one gets ultimately a single cluster that exhibits fractal properties: the number N of atoms is related to its radius R by the usual relation

$$N = (R/l)^D \quad (1)$$

where l is the size of a monomer and D the fractal dimension of the aggregate. The latter was calculated on various lattices for dimensions of space ranging from 2 to 6. The results are shown in table 1 in the case when the diffusion coefficient of the clusters is assumed to be independent of their size. An important result is that, although there is some dispersity in the distribution of sizes for intermediate times, the various clusters appear to have roughly the same size. This was shown by Vicsek and Family [30], who assumed that the distribution $P(N, t)$ of clusters made of N monomers at time t has the scaled form

$$P(N, t) = N^{-x} f(t/N^y) \quad (2)$$

where x and y are two characteristic exponents and $f(z)$ is an unknown function. Because the distribution is normalised, we have, for any time t :

$$\int NP(N, t) dN = 1. \quad (3)$$

Inserting relation (2) in (3) we get

$$t^{(2-x)/y} \sim 1$$

implying $x = 2$. This implies that there is only one characteristic molecular weight in

these systems diverging with time. Calculating the various ratios of successive moments of the distribution homogeneous to a mass gives

$$\int N^2 P(N, t) dN / \int NP(N, t) dN \sim \int N^3 P(N, t) dN / \int N^2 P(N, t) dN \sim \dots \sim t^\nu \quad (4)$$

where \sim is a proportionality sign, ignoring the constants.

For non-vanishing initial concentrations C_0 in atoms on the lattice, gelation occurs in a finite time T , which may be related to C_0 in the following way. For times shorter than T , the same process as above takes place, namely the growth of aggregates. We will neglect polydispersity and assume that at a given time all the clusters have the same radius R . This may be related to time via relations (1) and (4). We will also assume that gelation takes place as soon as the various clusters are in contact. This happens when $C_0 \sim N/R^d$, where d is the dimension of space. Using relations (1) and (4), we get

$$C_0 \sim T^{\nu(1-d/D)}. \quad (5)$$

Because the fractal dimension is smaller than d , one checks easily that gelation time diverges when C_0 vanishes.

It seems that no case has yet been found where the aggregation model describes polymerisation and gelation when microscopic units such as commonly used in chemistry are involved. It is very interesting, however, for aggregation of particles such as the gold particle aggregates studied by the Exxon group [31], for instance, or silica [32] or polystyrene latex [33] particles and more generally for colloidal aggregation. One has, however, to keep it in mind as a model for a rigid polymer that is not dense. This might be the equivalent of the rigid-rod limit of linear polymers. For a more serious and very detailed discussion of this model and its recent generalisations, the reader is referred to the recent reviews by Meakin [27] and Matsushita [34], and to the book by Botet and Jullien [29]. In more conventional cases such as described in section 2.1 above, however, the distribution of molecular weights is very broad and cannot be reduced to a single diverging mass as will be discussed later. This is achieved by the percolation model, which we discuss briefly now.

2.2.2. Percolation. In the opposite limit, when no solvent is present, polycondensation of multifunctional units is modelled by percolation. This is a pure geometrical model that was introduced by Flory and Stockmayer in its mean-field approximation and rediscovered more recently. Its connection with the one-state Potts model, which exhibits a phase transition, was shown by Kasteleyn and Fortuin [35]. In the bond percolation model [14, 15], one considers a lattice where all the sites are present. They model the monomers. The bonds are present at random with probability p (and absent with probability $(1-p)$), as shown on figure 2 for $d=2$. They model the chemical bonds. When p is small, one has small clusters modelling small molecules. As p increases, the size of the clusters increases, and the distribution of sizes widens, as long as p is smaller than a threshold p_c . The resulting mixture of finite, eventually very large, polymers is the sol. Above the threshold, in addition to the sol there is an infinite cluster present, called the gel, with extremely non-homogeneous structure in the vicinity of p_c . From a practical point of view, the sol-gel transition that we are modelling by percolation may be characterised by a divergence of the viscosity of the sol, below the threshold, and by the existence of an elastic modulus above the threshold, as shown on figure 3.

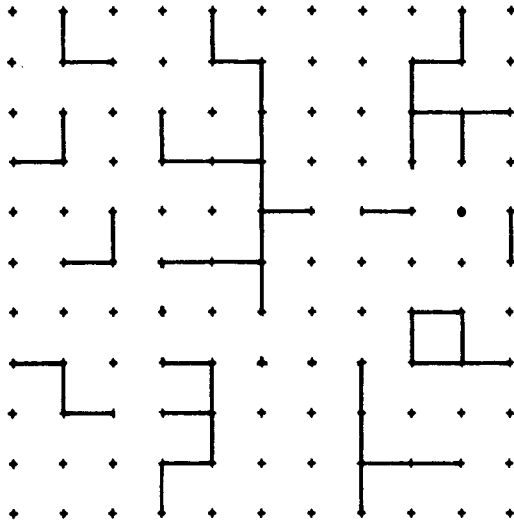


Figure 2. Bond percolation on a square lattice. Below the threshold, only a polydisperse sol is present. Above p_c , in addition to the sol, a gel would also be present.

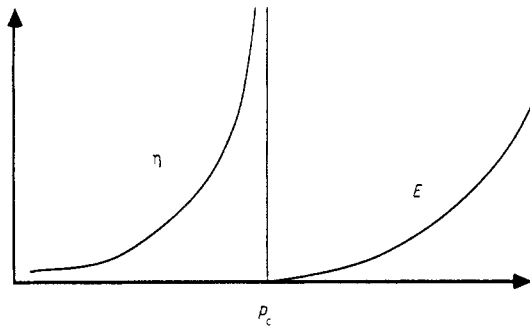


Figure 3. Schematic behaviour of the viscosity η and the elastic modulus E close to the threshold.

We recall briefly the main results of percolation. For further details, the interested reader is referred to the review by Essam [15] and to the book by Stauffer [14].

As discussed above, we may characterise the transition by the following quantities: the viscosity η of the sol diverges below the threshold as

$$\eta \sim \varepsilon^{-s} \quad (p < p_c) \tag{6}$$

and the modulus E of the gel vanishes as

$$E \sim \varepsilon^\mu \quad (p > p_c) \tag{7}$$

where s and μ are exponents to be discussed in section 4.1 below, and $\varepsilon = |p - p_c|$ the distance to the threshold.

The number distribution of clusters, that is the probability $P(N, \varepsilon)$ that a polymer of the sol is made of N monomers, at a distance ε from the threshold is, following Stauffer [13],

$$P(N, \varepsilon) \sim N^{-\tau} f(\varepsilon N^\sigma) \tag{8}$$

with two other exponents τ and σ . Thus the distribution is a slowly decaying power law,

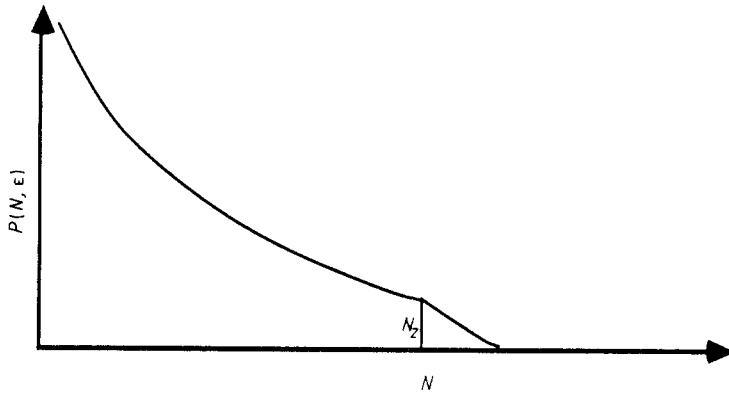


Figure 4. The number distribution of molecular weights decreases as a power law cut off at large masses. The cut-off diverges at the threshold.

which will be discussed further below, cut off by an exponential function $f(x)$ for high molecular weights. It is customary to approximate the latter by a step function cutting the distribution at a characteristic mass $N^* \sim \epsilon^{-1/\sigma}$. As far as the scaling properties are concerned, such an approximation is harmless.

A final definition concerns the characteristic connectivity length ξ , which diverges at the threshold as

$$\xi \sim \epsilon^{-\nu}. \tag{9}$$

This may be interpreted as the radius of the largest polymers in the sol, and as the mesh size of the gel above p_c : the gel is non-homogeneous for distances smaller than ξ and is roughly regular at large distances. Let us stress that these are valid in the reaction bath. When solvent is added, the polymers and the gel swell, as will be discussed later.

The number distribution in relation (9) is shown on figure 4. It is normalised below the threshold: every monomer belongs to a polymer. Above p_c , the difference is the gel fraction G , which is the probability that a monomer belongs to the gel:

$$\int NP(N, \epsilon) dN = 1 - G. \tag{10}$$

Using equations (8) and (10) we get

$$G \sim \epsilon^\beta \tag{11a}$$

with

$$\beta = (\tau - 2)/\sigma. \tag{11b}$$

It is possible to evaluate the next moments of the distribution function, and to define mass averages. The important point here is that two different averages are found, because, as we will see shortly, the exponent τ has values between 2 and 3. By definition of the weight- and Z-average masses, N_w and N_z respectively, we find

$$N_w = \frac{\int N^2 P(N, \epsilon) dN}{\int NP(N, \epsilon) dN} \sim \epsilon^{-\gamma} \tag{12a}$$

and

$$N_Z = \frac{\int N^3 P(N, \varepsilon) dN}{\int N^2 P(N, \varepsilon) dN} \sim \varepsilon^{-1/\sigma} \quad (13)$$

with

$$\gamma = (3 - \tau)/\sigma. \quad (12b)$$

Note that, unlike aggregation, we obtain two characteristic masses, which diverge in different ways when the gelation threshold is approached. Note that the Z-average mass is proportional to the cut-off mass N^* , and is thus characteristic of the largest polymers in the sol.

It is experimentally difficult to define the threshold p_c and thus to determine with the required precision the distance ε . In order to avoid this difficulty, it is useful to express the various quantities that we have just defined in terms of measurable ones. This brings us to define the fractal dimension [36] of the polymers and of the gel in the reaction bath. This is done by relating the mass of the clusters to their radius. Combining relations (9) and (13), we get

$$N_Z \sim \xi^{D_p} \quad (14)$$

with

$$D_p = 1/\nu\sigma. \quad (15a)$$

The fractal dimension D_p may also be calculated in the following simple way. Let us estimate the number of monomers that belong to the gel inside a sphere with radius ξ . The number of sites in the sphere is proportional to its volume, $\Omega \sim \xi^d$. The number of monomers that belong to the gel is $G\Omega$. Using relations (9) and (11a), and comparing with (14), we get

$$D_p = d - \beta/\nu. \quad (15b)$$

Finally, using relations (11b), (12b) and (15b), and the hyperscaling relation $2\beta + \gamma = \nu d$, we get for the exponent τ of the distribution

$$\tau = 1 + d/D_p. \quad (15c)$$

The latter relation is very important because it shows that the distribution function itself is fractal [37]. In order to understand this, let us consider a 'class' of polymers with masses between N and $N + dN$. Let $G(R)$ be the corresponding distribution in radii. We have

$$P(N, \varepsilon) dN = G(R) d \ln R \quad (16)$$

where a logarithmic scale is taken for distance in order to have dimensionless units. Neglecting the exponential tail in the distribution of weights, we have

$$G(R) \sim N^{-\tau} dN/d \ln R.$$

Assuming that all polymers in the distribution have the same fractal behaviour (relation

Table 2. The exponents in the percolation problem as a function of space dimension d (from [46]). Lines 3, 5 and 7 are the Flory approximations, relations (22b), (77b) and (76c).

d	2	3	4	5	6
D_p	1.89	2.52	3.29	3.83	4
D_F	2	5/2	3	7/2	4
\bar{s}	0.98 ± 0.01	0.85 ± 0.04			0
$(6-d)/4$	1	0.75			0
$\bar{\mu}$	0.96	2.2			6
$(5d-6)/4$	1	9/4			6

(14)), i.e. assuming that for all masses N in the distribution the corresponding radius R is similarly related to N ,

$$N \sim R^{D_p}$$

we get

$$G(R) \sim R^{-d}. \quad (17)$$

Relation (17) shows that the polymers of mass N are in a so-called C^* situation, that is they are in contact with each other [38]. Because they are fractal, there are large holes left. Smaller polymers fill these holes, still being in a C^* situation. Thus one may compare the distribution to Russian dolls, with smaller polymers inside the larger ones at every distance scale, in such a way that the total monomer concentration is unity.

2.2.3. Flory approximation. The percolation exponents were calculated in different ways, by renormalisation, computer simulations [39–46] and conformal invariance in two dimensions [47, 48]. Let us mention that a special purpose computer [49, 50] was built at Saclay for calculating the exponents s and μ for percolation. The results are summarised in table 2. As we will use mainly the fractal dimension in what follows, we would like to mention a direct way to estimate it in a closed form, namely Flory's approximation. It was given by Isaacson and Lubensky [51, 52] for gelation. This will also be useful for the discussion of vulcanisation. It is important to give some words of caution. The method is known to be approximate [53]. However, because of some mysterious cancellation in the dominant terms in the free energy, it usually gives an excellent approximation to the fractal dimension for all space dimensions. In the percolation case, however, and in two dimensions, its result is misleading, although it is very close to the exact result: it implies that $d = 2$ is the lower critical dimension.

The free energy of a polymer is written [51, 54] as the sum of elastic and interaction terms. The former is assumed to be quadratic in the actual radius R to be determined,

$$F_{el} = k_B T \frac{R^2}{R_0^2} \quad (18a)$$

where R_0 is the ideal radius when no interaction is present. This was calculated by Zimm and Stockmayer [55, 56]. For a polymer made of N monomers of length l , it is

$$R_0 \sim N^{1/4}l. \quad (19)$$

The interaction term is due to the potential between monomers, which has the form

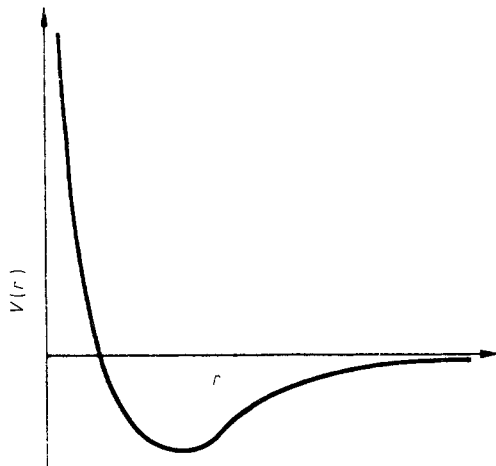


Figure 5. The actual interaction potential $V(r)$ between monomers. In a good solvent, or for high temperature, it is replaced by a point-like pseudopotential $v\delta(r)$, with v the (positive) excluded-volume parameter.

shown in figure 5, with a hard core at short distances preventing the monomers from being on top of each other. For high temperatures, i.e. in a good solvent, this is replaced by a point-like pseudopotential [3, 57], $v\delta(r)$, where $v(T)$ is the excluded-volume parameter and is assumed here to be positive:

$$v = \int [1 - \exp(-V(r)/k_B T)] dr. \quad (20)$$

In the reaction bath, the interaction term reads

$$F_{\text{int}} = k_B T \frac{v}{N_w} \frac{N^2}{R^d} \quad (18b)$$

where the presence of N_w is related to the Edwards screening [57, 58]. As discussed above, in the reaction bath large polymers are penetrated by smaller ones. Because of this the actual interaction between any two monomers of a macromolecule is the sum of the direct interaction and the terms via other monomers belonging to other polymers. This is very similar to what occurs in a solution of electrolytes [59]. As a result there is a screening of the monomer–monomer interaction. It is assumed in relations (18) that we are dealing with large polymers, i.e. that N is of the order of the cut-off mass N_Z . Thus N and N_w are related to each other. In the Flory theory [51, 52], the mean-field approximation to such a relation is assumed:

$$N_w \sim N^{1/2}. \quad (21)$$

Minimising the free energy $F_{\text{el}} + F_{\text{int}}$ with respect to R , and using (21), we get for the fractal dimension D_p of the polymers in the reaction bath:

$$N \sim R^{D_p} \quad (22a)$$

with

$$D_p = (d + 2)/2. \quad (22b)$$

Before we come to the special case of vulcanisation, we will give some experimental evidence of the results we discussed above.

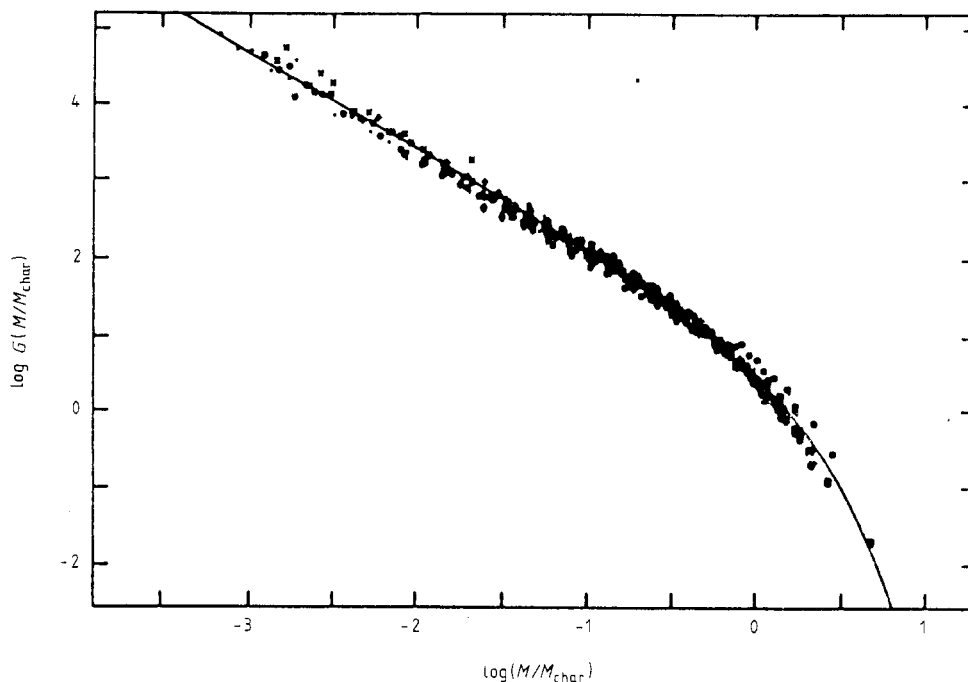


Figure 6. The normalised distribution function measured by coupling light scattering and gel permeation chromatography (from [62]).

2.2.4. Experimental evidence. There is no direct measurement of the fractal dimension itself in the reaction bath as yet. Experiments have focused on the distribution itself and on its second moment, equation (12a). The distribution function was first shown by Leibler and Schosseler [60] to correspond to equation (8). This was achieved by coupling gel permeation chromatography and light scattering on a sample made of irradiated polystyrene solution in cyclopentane. Figure 6 shows the results of Patton *et al*, where $(N^*)^{\tau-1}NP(N, \epsilon)$ is plotted as a function of N/N^* for several extents of reaction ϵ . Their result is $\tau = 2.3 \pm 0.1$, consistent with the results in section 2.2.3. Subsequently, this was also checked with other systems made either by chemical end-linking of polydimethylsiloxane by Lapp *et al* [61], or by bulk condensation polymerisation leading to a polyester by Patton *et al* [62], using the same technique. The resulting estimations for the exponent τ and thus for the fractal dimension D_p , if we accept equation (15c), are consistent with the percolation prediction for these systems synthesised in different ways and therefore show the universality of the percolation results concerning the ‘details’ of the crosslinking procedure.

The weight-average molecular weight N_w was shown first by Adam *et al* [63] to follow relation (12a) by static light scattering measurements on a polyurethane sol. This was confirmed by Candau *et al* [90] on polystyrene systems crosslinked with divinylbenzene, and by the authors cited above on their respective systems. All these measurements lead to a value of the exponent γ in excellent agreement with the best results obtained by renormalisation-group or computer simulations [65, 66] for percolation. One must be cautious, however, in that this does not mean that percolation is the only universal class for gelating systems, although it seems that it is an important one.

2.2.5. Vulcanisation and mean field.

(a) *The melt.* So far we have considered the case when the initial reacting units are small polyfunctional monomers. An important special case is when the former are no longer small, but large linear polymers. In this section, we will consider first a melt of linear chains made of Z monomers. We will assume that they may crosslink at random by any of their monomers. This is achieved experimentally either by a crosslinking agent or by irradiation with γ -rays, for instance. The same phenomena as for small units occur, namely one first gets branched macromolecules when the probability p that two monomers are crosslinked is small. Above a threshold one also gets a gel. The only difference with the previous case lies in the fact that, close to the threshold, the units that one has to consider when one is dealing with the connectivity properties are linear chains with Z monomers instead of small molecules. As we will see now, this has dramatic consequences, and one goes back to mean-field theory because the critical region becomes vanishingly small, as shown by de Gennes [67]. This was also studied by Stauffer and Coniglio [68], who considered the range of interactions in the Potts model. Instead of considering the fluctuations in connectivity as in [67], we will use the Flory approximation [69]. More precisely, we will compare the interaction energy to the thermal energy $k_B T$. We estimate the former, assuming that mean-field theory is valid. When it is smaller than $k_B T$, the interaction term may be neglected, and mean-field theory is valid. Otherwise, one has to compare it to the elastic energy, as we did in section 2.2.3 above. What is important here is that, in the vicinity of the threshold, the units are linear chains with Z monomers each. What we are considering is percolation of such units. Thus we may rewrite equation (18b) in the following form:

$$F_{\text{int}} = k_B T \frac{v}{(N_w/Z)} \frac{(N/Z)^2}{(R/R_L)^d} Z R_L^{-d} \quad (18c)$$

where R_L is the radius of the linear chains. From the literature on the latter [2, 5], we know that, in a melt, a chain with Z monomers has radius

$$R_L \sim Z^{1/2} l. \quad (23)$$

Finally, we know that in the mean-field case, the weight averages are related to the distance ε to the threshold by the following relations:

$$(N_w/Z)^2 \sim N_Z/Z \sim \varepsilon^{-2} \quad (24a)$$

and

$$R/R_L \sim \varepsilon^{-1/2}. \quad (24b)$$

Inserting equations (23) and (24) in (18c), we get

$$F_{\text{int}} \sim Z^{(2-d)/2} \varepsilon^{(6-d)/2} \quad (25a)$$

and, for $d = 3$

$$F_{\text{int}} \sim Z^{-1/2} \varepsilon^{-3/2}. \quad (25b)$$

Thus we find that F_{int} is of order unity when $\varepsilon \sim \varepsilon^* \sim Z^{-1/3}$. When ε is smaller than ε^* , critical exponents are expected. Because we are dealing with large polymer chains, however, Z is very large and this region is very small. Therefore, one is practically in the other regime, $\varepsilon > \varepsilon^*$, where we expect mean-field theory to be valid.

(b) *Semi-dilute solution.* What is the effect of the initial monomer concentration on the above discussion? As we will see now, the width of the critical region increases when

concentration decreases [70]. The easiest way to understand this, following the same lines as above, is to consider a semi-dilute solution of chains in a good solvent. This is an intermediate concentration range, much smaller than unity, where the polymers overlap strongly: $C_L^* \ll C \ll 1$. As in section 2.2.2 above, C_L^* is the overlap concentration of the linear chains. This corresponds to space filling by the chains. Previous studies of this concentration range showed that the chains may be considered as random walks if one chooses the step length carefully. This is the so-called blob model, which may be summarised as follows. In a semi-dilute solution, the chains are locally swollen, for distance scales smaller than a screening length, ξ_L , which is a function of concentration only,

$$\xi_L \sim C^{-3/4}. \quad (26a)$$

This swollen portion of a chain is called a blob and is made of g_L monomers

$$\xi_L \sim g_L^{3/5} \quad (26b)$$

where the exponent in the last relation is the self-avoiding walk exponent and has been approximated by its Flory value.

For larger distance scales, the chain reduces to a random walk if one takes the blob as its unit step. Then the radius of a linear polymer made of Z monomers is

$$R_L^2 \sim (Z/g_L)\xi_L^2. \quad (27)$$

This amounts to assuming that the semi-dilute regime of linear chains reduces to a melt if one renormalises the unit length. The large-scale properties of a semi-dilute solution are very similar to those of a melt. The renormalised step length ensures a smooth crossover to the properties of self-avoiding walks for $C \sim C_L^*$.

We consider now the vulcanisation of such solutions. In order to evaluate the width of the critical region in the Flory approximation, we come back to the interaction free energy as above. The only difference with the previous case is that one now has to consider random chains made of Z/g_L blobs. Thus we have, instead of (18c),

$$F_{\text{int}} = k_B T \frac{v}{N_w/(Z/g_L)} \frac{[N/(Z/g_L)]^2}{(R/R_L)^d} \frac{Z}{g_L} R_L^{-d} \quad (18d)$$

and thus the same equations as (25a) and (25b) with Z/g_L replacing Z . For the three-dimensional case, using relations (26) and (27), this leads to a width ε^* of the critical region

$$\varepsilon^* \sim (Z/g_L)^{-1/3} \sim (ZC^{5/4})^{-1/3}. \quad (28)$$

Note that, for a melt, $C = 1$, we recover the previous results. When the initial monomer concentration is decreased, relation (28) shows that the width of the critical region increases and becomes of the order of unity if the initial concentration is of the order of C^* . The latter result is easily understood, because for such a concentration, the system may be considered as a close-packed ensemble of spheres that may be bonded to a finite number of neighbours. The critical behaviour of semi-dilute solutions of polyacrylamide crosslinked by chromium was studied by Allain and Salome [71, 72]. Finally, let us mention that the vulcanised polystyrene of Leibler and Schosseler [60] was synthesised around C^* , so that the critical exponents are observed with this system.

3. Swelling

So far we have considered the synthesis and the conformation of randomly branched polymers and gels in the reaction bath. Moreover, we assumed that synthesis was carried out in the absence of any solvent. In this section, we will discuss solvent effects. We will assume that the systems we are considering are in equilibrium. Then it is equivalent to carry out the synthesis at a given monomer concentration or to do it in the absence of solvent and then to add solvent in order to bring the system to the required concentration. Clearly, such an assumption neglects the possible influence of diffusion of the various species, including monomers in the reaction bath during the synthesis. In what follows, we will discuss the second case. More precisely, we will assume that the synthesis is quenched, and that the distribution of masses is given. Then a good solvent is added. One has to separate the cases of the sol and the gel. Whereas the former may be diluted at will, the latter only swells up to some extent because of the presence of elastic restoring forces. In the following, we will first discuss dilute solutions of polymers. We will first neglect polydispersity and consider a single mass. Then polydispersity effects will be introduced. Finally, the intermediate semi-dilute concentration range will be discussed.

3.1. The single polymer

Let us first consider a single randomly branched polymer in a good solvent. This corresponds to the so-called lattice animal problem and is in a different universality class [44, 73] than percolation. The question is to determine the average configuration of a polymer made of N monomers with the constraint that it does not cross itself. Note that the statistics of such an animal is different from that of percolation clusters. Whereas all possible configurations of the former have equal probability, the latter has a weight that depends on both the sites that are occupied and the perimeter, that is on the empty sites that are neighbours of an occupied site. Parisi and Sourlas [44] showed an equivalence between the animal problem and an Ising system with quenched random magnetic field. The latter is equivalent to an Ising system in $d - 2$ dimensions. In the following, we will use the Flory approach, which was given by Isaacson and Lubensky [51]. As in the previous section, the free energy is made up of two terms. The elastic contribution is the same as in the reaction bath, relations (18a) and (19) above. The interaction term is different because the solution is now dilute, and there is no screening of the interactions. Thus the total free energy of a polymer is

$$F = k_B T [(R^2/R_0^2) + \nu(N^2/R^d)] \quad (29)$$

with ν the excluded-volume parameter (relation (20)), R_0 the ideal radius (equation (19)) and R the actual radius to be determined. Minimisation with respect to R leads to the fractal dimension of the animals:

$$N \sim R^{D_a} \quad (30a)$$

with

$$D_a = 2(d + 2)/5. \quad (30b)$$

Note that, for $d = 3$, this gives the exact result, known from the Parisi–Sourlas argument.

This implies that the pair correlation function $g(r)$ between any two monomers is

$$g(r) \sim r^{D_a - d}. \quad (31a)$$

Its Fourier transform is proportional to the scattered intensity $S(q)$ in a static light or neutron scattering experiment. Here q is the momentum transfer

$$q = (4\pi/\lambda) \sin \theta/2 \quad (32)$$

where λ is the wavelength of the radiation and θ the scattering angle. Thus we find the usual relation

$$S(q) \sim q^{-D_a}. \quad (31b)$$

3.2. Dilute solutions: polydispersity

Actual solutions are very polydisperse, as discussed previously. Because of this polydispersity, one has to average over the whole distribution $P(N, \varepsilon)$. As we now discuss, this averaging leads to effective exponents that are quite different from the fractal dimension of each polymer and involve the exponent τ of the distribution. In order to show this, we now consider the scattered intensity $I(q)$ by an actual, polydisperse, solution in a light or neutron scattering experiment. Changing notation, let $P(N, N_Z)$ be the number distribution of molecular weights (relation (8)), with N_Z the largest masses in the system (equation (13)). Because the solution is dilute, the normalisation condition is

$$\sum_0^\infty NP(N, N_Z) = C \quad (33)$$

with C the monomer concentration. In a light or neutron scattering experiment, the scattered intensity by such a solution is

$$I(q) = \sum_{i,j,\alpha,\beta} \langle \exp(iq \cdot r_{ij}^{\alpha\beta}) \rangle \quad (34)$$

where the angle brackets are for averaging over configurations and the summation is performed on any pair i, j of monomers belonging to any molecules α, β in the solution. This may be split into two parts corresponding, respectively, to both monomers on the same polymer, and to monomers belonging to different macromolecules:

$$I(q) = \sum_{i,j,\alpha} \langle \exp(iq \cdot r_{ij}^\alpha) \rangle + \sum_{i,j,\alpha \neq \beta} \langle \exp(iq \cdot r_{ij}^{\alpha\beta}) \rangle = I_1(q) + I_2(q). \quad (35)$$

The intra-polymer part $I_1(q)$ corresponds to the scattering by a polydisperse distribution of independent polymers. Choosing a monomer and a polymer at the origin, it may be written as

$$I_1(q) = \sum_N \left[NP(N, N_Z) \left(\sum_i \langle \exp(iq \cdot r_{0i}) \rangle \right) \right] \quad (36)$$

where the second summation is performed on the monomers in the chosen polymer. In the Guinier range, this may be expanded as

$$I_1(q) = \sum_N \left[NP(N, N_Z) \left(\sum_i [1 - q^2 \langle (r_{0i})^2 \rangle] \right) \right] \quad (37)$$

that is

$$I_1(q) = \sum_N NP(N, N_Z)[N - q^2 N \langle R(N)^2 \rangle] \quad (38)$$

where

$$\langle R(N)^2 \rangle = \frac{1}{N} \sum_i \langle (r_{0i})^2 \rangle \quad (39)$$

is the average radius of gyration of a polymer made of N monomers. Dividing both sides of relation (38) by the concentration C and using relation (33), we find

$$I_1(q)/C = N_w(1 - q^2 R_Z^2) \quad (40a)$$

with N_w given in relation (12a) and R_Z^2 given by

$$R_Z^2 = \sum_N N^2 R(N)^2 P(N, N_Z) / \sum_N N^2 P(N, N_Z). \quad (41a)$$

Using relations (8), (12) and (41), we find, following Daoud *et al* [17]

$$R_Z^{D_a(3-\tau)} \sim N_w \quad (41b)$$

and for $d = 3$ in the Flory approximation,

$$R_Z^{8/5} \sim N_w \quad (41c)$$

where we used relations (15c), (22b) and (30b).

More generally, for a dilute solution, following Martin and Ackerson [74] and Teixeira [75], relation (40a) may be written in the scaled form

$$I_1(q)/C = N_w f(qR_Z) \quad (40b)$$

where $f(x)$ is some unknown scaling function with known asymptotic behaviour. For $q \rightarrow 0$, relation (40a) gives the behaviour in the Guinier range. In the intermediate range, $R_Z^{-1} \ll q \ll l^{-1}$, the corresponding behaviour is found by assuming that $f(x)$ has a power-law behaviour: $f(x) \sim x^a$. The exponent a is determined by the condition that in this range the scattered intensity is independent of the mass. Using (8), (12) and (41) we find [74] the generalisation of equation (41b):

$$I_1(q) \sim Cq^{-D_a(3-\tau)} \quad (qR_Z \gg 1) \quad (41d)$$

and for $d = 3$

$$I_1(q) \sim Cq^{-8/5} \quad (qR_Z \gg 1). \quad (41e)$$

Let us now turn to the inter-polymer part $I_2(q)$. Let R_α and R_β be the locations of the centres of mass of polymers α and β and $R_{\alpha\beta}$ their distance. Then we have

$$I_2(q) = \sum_{i,j,\alpha \neq \beta} \langle \exp(iq \cdot r_i^\alpha) \exp(-iq \cdot r_j^\beta) \exp(iq \cdot R_{\alpha\beta}) \rangle \quad (42)$$

where r_i^α and r_j^β are the relative positions of monomers i and j from the respective centre of mass of the polymers α and β to which they belong. In a dilute solution, it is possible to decouple the internal correlations from the correlations between centres of mass of different polymers. Moreover, we will first consider the limit when $q \rightarrow 0$. This will be defined more precisely below. Let us consider distances of the order of, or larger than, the inter-polymer distances. Because the solution is dilute, these distances are much larger than the internal inter-monomer distances in any polymer. Thus the first two

terms in the summation of relation (42) are of order unity, and the expression simplifies to

$$I_2(q \rightarrow 0) \approx \sum_{i,j,\alpha \neq \beta} \langle \exp(i\mathbf{q} \cdot \mathbf{R}_{\alpha\beta}) \rangle \quad (43)$$

that is

$$I_2(q \rightarrow 0) = \sum_{N,M} NP(N)MP(M)g(q, N, M) \quad (44)$$

where $g(q, N, M)$ is the Fourier transform of the pair correlation function between the centres of mass of the different polymers. In the limit $q \rightarrow 0$ that we are considering, this is the virial coefficient between polymers N and M . This was recently considered by Witten and Prentis [76], who showed that for $N > M$, we have

$$g(q \rightarrow 0, N, M) = -A_2(N, M) = -(N/M)R(M)^3. \quad (45)$$

Thus we have

$$I_2(q) \approx - \sum_{N,M} NP(N)MP(M)(N/M)R(M)^3. \quad (46)$$

Using relation (33), we get

$$I_2(q)/C = -N_w \sum_M MP(M)R(M)^3/M \quad (47a)$$

$$= -N_w C \langle R(M)^3/M \rangle_w \quad (47b)$$

$$= -N_w C_p \langle R(M)^3 \rangle_n \quad (47c)$$

with the conventional definitions

$$\langle A \rangle_w = \sum_N NA(N)P(N) / \sum_N NP(N) \quad (48)$$

$$\langle A \rangle_n = \sum_N A(N)P(N) / \sum_N P(N) \quad (49)$$

and where C_p is the total polymer concentration

$$C_p = \sum_N P(N) = \left[\left(\sum_N P(N) \right) / \left(\sum_N NP(N) \right) \right] \sum_N NP(N) \sim C. \quad (50)$$

Using relations (35), (40a) and (47a), we get the scattered intensity by a dilute system at very small angles [77, 78]:

$$I(q)/C = N_w [1 - q^2 R_Z^2 - C \langle R(M)^3/M \rangle_w]. \quad (51)$$

Relation (51) allows us to introduce the second virial coefficient A_2 . It also shows that

we expect the zero-angle scattered intensity to exhibit a maximum [79] at a concentration C^* such that

$$(C^*)^{-1} \sim A_2 \sim \langle R(M)^3/M \rangle_w. \quad (52a)$$

Note that, from relations (47c) and (51), this corresponds to the physical situation of space filling by the polydisperse distribution of polymers:

$$C_p^* \langle R(M)^3 \rangle_n \sim 1. \quad (53)$$

Inserting the percolation distribution for $P(N)$, and using the Flory exponents, we get

$$C^* \sim N_w^{-3/8}. \quad (52b)$$

It is important to note that this correction in concentration to the scattered intensity by dilute solutions corresponds to an (integrated) correlation function between the centres of mass of the various polymers in the solution. As a result, whereas the 'fractal' part $I_1(q)$ is sensitive to mass fluctuations at scales of order q^{-1} , this correction is related to the average distance between the polymers, as shown in equation (47c). In monodisperse distributions [54] this is irrelevant because the same scaling is involved in both parts. As we shall see, this breaks down when polydispersity is too large, which is the case presently. As a conclusion to this section, we may postulate a scaled form for the zero-angle intensity in the following form:

$$I(q=0) = CN_w f(C/C^*). \quad (54a)$$

Using the percolation distribution we get

$$I(q=0) = CN_w f(CN_w^{3/8}) \quad (54b)$$

where $f(x)$ is a scaling function with known limits,

$$f(x=0) = 1 \quad f(x \gg 1) \sim x^{-8/3}$$

leading to

$$I(q=0) \sim C^{-5/3} \quad (C \gg C^*). \quad (54c)$$

This result will be discussed with semi-dilute solutions below. It is interesting to note that the concentration C^* , relation (52b), may be found independently from the calculation of the intrinsic viscosity of a polydisperse solution [17]. The intrinsic viscosity $[\eta(N)]$ corresponding to a given mass is

$$[\eta(N)] = \lim_{C \rightarrow 0} (\eta - \eta_s)/\eta_s C \sim R(N)^3/N \sim N^{1/2} \quad (55)$$

where η and η_s are the viscosities of the solution and of the pure solvent, respectively. We assumed $d=3$ and we used Flory's relation (30b) for the fractal dimension of a single polymer. The average intrinsic viscosity, following Sievers [80] and Marrinan and Hermans [81], is $\langle [\eta] \rangle_w$, with the definition of this average given by equation (48). We find [17]

$$\langle [\eta] \rangle \sim N_w^{3/8} \quad (56)$$

a relation that gives directly the overlap concentration C^* because the cross-over from the dilute to the semi-dilute regimes usually corresponds to the breaking down of the series expansions of the viscosity valid in the dilute range. Relation (56) was also derived recently by Martin *et al* [82] by considering the viscoelastic properties.

3.3. Semi-dilute solutions

The assumption of independent polymers clearly breaks down above the overlap concentration C^* . For higher monomer concentrations, in the semi-dilute regime, smaller polymers interpenetrate the larger, and Daoud and Leibler [78] suggested a blob model to describe this concentration range. As for the linear chains discussed in section 2.2.5(b), one partitions the distance scales into two ranges, with a cross-over distance ξ . The polymers of the distribution corresponding to distances smaller than this screening length are swollen and thus behave as in a dilute solution. The larger polymers are locally swollen and their overall conformation is screened. One is thus led to introduce the size g_b of the largest swollen polymers, with radius ξ . Thus there is a broad distribution of blob sizes. At C^* , this distribution includes all the polymers in the distribution. As C increases, g_b decreases until it becomes of order unity in the melt. All polymers are then assumed to recover the conformation of the percolation clusters in the reaction bath. It is straightforward to determine the variations of the screening length ξ and the average radius R_Z in the intermediate range. This is realised by assuming a homogeneous behaviour of the various lengths. We assume that for the whole concentration range we have

$$R_Z = N_w^{5/8} f(C/C^*). \quad (57)$$

The function $f(x)$ has a power-law behaviour in the semi-dilute regime: $f(x) \sim x^a$. The exponent a is determined by the condition that the N_w variation is the same as in the melt, relations (12a) and (14). Using (52b), we get

$$R_Z \sim N_w^{1/2} C^{-1/3}. \quad (58)$$

The screening length is calculated along the same lines. The condition is that it does not depend on the molecular weight. We find

$$\xi \sim C^{-5/3}. \quad (59)$$

As for linear chains, one may recover the above laws directly by assuming that the large macromolecules have percolation cluster conformations if the blob is taken as unit:

$$R_Z \sim (N_w/g_b)^{1/2} \xi \quad (60a)$$

with

$$\xi \sim g_b^{5/8}. \quad (60b)$$

Assuming power-law dependences on N_w and C for both R_Z and ξ , and using continuity at C^* with the average radius in the dilute regime, relation (41c), one recovers equations (58) and (59).

3.4. Gels

Let us now consider the swelling of a gel [83, 84]. We assume that the initial state is the reaction bath, with no solvent present. Then, excess solvent is added and the gel swells. The main difference between swelling of the sol and of the gel is that the latter cannot be in a dilute regime for obvious connectivity reasons. Thus only the equivalent of the semi-dilute range may be observed in swollen gels. The equilibrium concentration, corresponding to the maximum swelling, may be estimated in a direct way, assuming that it corresponds to a swollen state [85]. From the previous sections, we know the

fractal dimension of the gel in the initial state: the number N of monomers inside a sphere with radius ξ is

$$N \sim \xi^{D_p}. \quad (61)$$

When swelling is completed and equilibrium is reached, the radius ξ has changed to a larger value, ξ_f , corresponding to the same amount of monomers N . Thus we have

$$N \sim \xi_f^{D_a} \quad (62)$$

and thus

$$\xi_f \sim \xi^{D_p/D_a} \quad (63a)$$

with D_p and D_a corresponding respectively to the fractal dimensions of percolation and of the single swollen polymer, relations (22) and (30). Using the latter relations together with (61) and (62), we get, for three-dimensional systems,

$$\xi_f \sim \xi^{5/4}. \quad (63b)$$

Swelling is usually described by the so-called swelling ratio Q , which is the ratio of the final to initial volumes of the gel:

$$Q \sim (\xi_f/\xi)^3 \sim N_w^{3/8}. \quad (64)$$

Note that this relation allows for another estimation of the overlap concentration C^* : the swelling ratio is also the ratio of the initial to final concentrations. Because the initial state is the reaction bath, we find that the final concentration C_f is

$$C_f \sim N_w^{-3/8} \sim C^*. \quad (65)$$

Swelling of vulcanised gels [86–88] was also considered and implies two successive steps, namely disinterpenetration of the multiple infinite networks present in the mean-field case, and swelling of each of these networks [89]. For more details, the reader is referred to [88] and [89].

3.5. Experimental results

Light and neutron scattering experiments have been performed by several teams, with wide agreement in the results. The first set of experiments were performed by Candau *et al* [90], who measured by quasi-elastic light scattering the diffusion coefficient of linear polystyrene crosslinked by divinylbenzene as a function of the weight-average molecular weight N_w . Their result

$$D_Z \sim N_w^{-0.58 \pm 0.06} \quad (66a)$$

is in good agreement with relation (41c) if we accept that the average diffusion coefficient varies as the inverse of the average radius in a dilute solution, a relation that was shown independently [17].

Leibler and Schosseler [91] measured the average radius of polystyrene crosslinked by irradiation by elastic light scattering and found

$$R_Z^2 \sim N_w^{1.16 \pm 0.06}. \quad (66b)$$

Adam *et al* [63] found in polyurethane systems an exponent 0.62 ± 0.03 , by static light scattering measurements, in agreement with the previous results and with equation (41c).

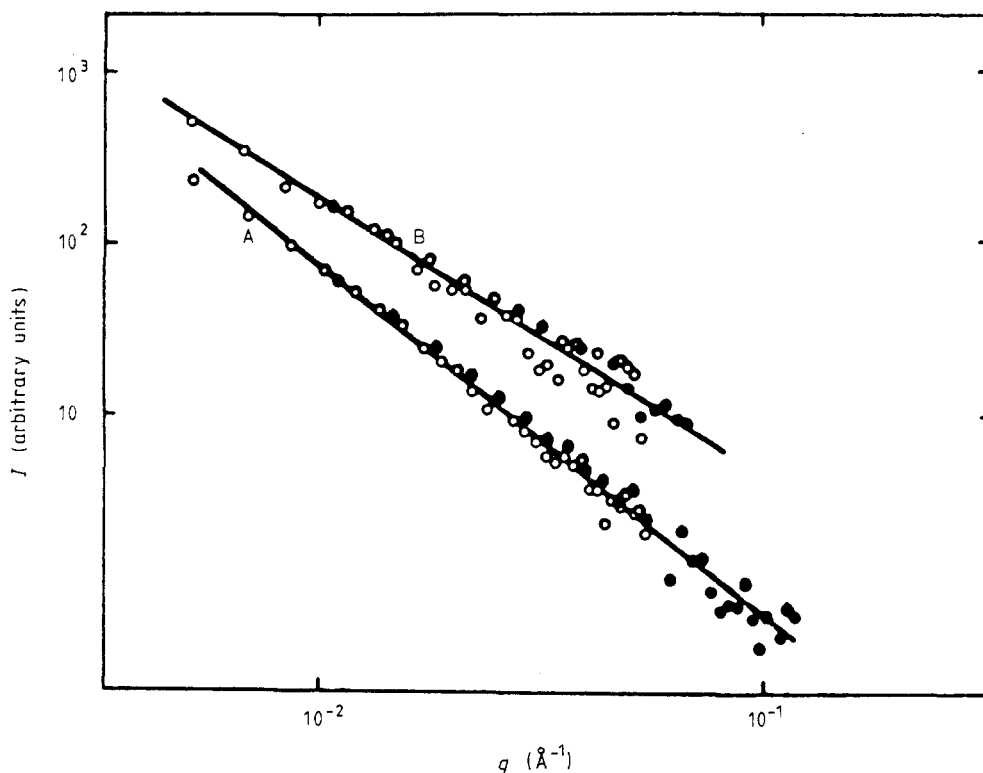


Figure 7. Scattered intensities in a small-angle neutron scattering experiment (from [92]). Curve A corresponds to a fractionated sample and gives the fractal dimension of a polymer. Curve B corresponds to the polydisperse sample and gives an effective dimension.

Finally, Patton *et al* [62] performed both quasi-elastic and elastic light scattering experiments on branched polyesters. Their result is slightly larger but consistent with the previous ones:

$$D_z^{-1} \sim R_z \sim N_w^{0.66 \pm 0.04}. \quad (66c)$$

Two sets of small-angle neutron scattering experiments were performed by Bouchaud *et al* [92] on polyurethane samples. The samples were respectively the natural, polydisperse, distribution as obtained by synthesis, and a fractionated, monodisperse distribution. The results are shown on figure 7 and show the difference between the fractal dimension of a polymer and the effective fractal dimension of the polydisperse sample, relations (31b) and (41d) respectively. From these curves, one finds

$$D_a = 1.98 \pm 0.03 \quad (67a)$$

and

$$D_a(3 - \tau) = 1.59 \pm 0.05. \quad (67b)$$

Combination of the latter two results provides the exponent τ of the distribution of molecular weights:

$$\tau = 2.2 \pm 0.05. \quad (67c)$$

Equation (67b) was also checked by Martin *et al* on silica [93], where they found a value

1.57 for the effective exponent, in agreement with (67*b*). A similar value was also found by Cabane *et al* [94] on a different silica system. Note, however, that silica is much more complicated than other model systems. For instance, Cabane *et al* [94] observe a peak in the scattered intensity in the semi-dilute range, which is not seen in other systems. Above the gelation threshold, depending on the pH of the reaction bath, the fractal dimension may change with concentration. For more details about this important case, the reader is referred to the recent review by Martin and Hurd [93] and to Cabane *et al* [94].

Intrinsic viscosity measurements were performed on polyesters by Patton *et al* [62], who found

$$[\eta] \sim N_w^{0.28 \pm 0.03}. \quad (68a)$$

Combining the results on intrinsic viscosity and radius of gyration led Patton *et al* to the following results,

$$D_a = 2.04 \pm 0.04 \quad (68b)$$

and

$$\tau = 2.26 \pm 0.04 \quad (68c)$$

in very good agreement with the results of Bouchaud *et al* [92], equations (67*a*) and (67*c*). Equation (68*a*) is certainly worth discussing further, because it exhibits the possible limitations of the Flory approximation. Although equations (67) and (68*a*) lead to a numerical value for τ that is in good agreement with the Flory result, $\tau = 11/5$, the slight difference is sufficient to lead to a significant discrepancy between the measured variation of the intrinsic viscosity, relation (68*a*), and the Flory prediction, $[\eta] \sim N_w^{3/8}$, relation (56). Because the overlap concentration C^* varies as the inverse of $[\eta]$, this might have important consequences concerning the concentration dependences of the various observables in the semi-dilute concentration range. These were calculated assuming the Flory approximation for the fractal dimension. In this respect, it will be extremely interesting to have experimental results concerning the screening length ξ , relation (59), in this regime. Assuming $C^* \sim N_w^{-0.28}$, as implied by equation (68*a*), would lead to $\xi \sim C^{-2.23}$, at odds with the Daoud–Leibler [78] prediction $\xi \sim C^{-5/3}$, equation (59), based on the Flory value. Thus the predictions concerning the semi-dilute concentration range might have to be handled with caution because of this slight difference between the Flory prediction and the actual value for the fractal dimension. Thus one should bear in mind this implication of the uncertainty on the exponent τ .

The second virial coefficient A_2 was also measured by Delsanti *et al* [77], by looking at the maximum of the zero-angle scattered intensity as a function of concentration. Their result, $A_2 \sim N_w^{0.345 \pm 0.06}$, is in good agreement with the prediction, relations (51) and (52*b*), and with the Patton *et al* [62] results. The same set of experiments also lead, for high concentrations, to $S_1(q \rightarrow 0, C) \sim C^{-1.35 \pm 0.04}$, again in good agreement with relation (54*c*) above.

We conclude this section by stressing the general agreement between the experimental results and those of the percolation and swelling assumptions. Moreover, the various systems that were used by the different groups tend to show the universality of such behaviour. Thus we can accept the idea that percolation is an important universality class for the synthesis of branched polymers and that, upon addition of a good solvent, the polymers adopt a swollen conformation. In a Flory approximation, the fractal dimension of the swollen polymer is identical to that of a lattice animal. Finally, one

notes the important effects of polydispersity, which lead to effective fractal dimensions that are different from the dimension of each of the macromolecules.

Although percolation is an important class, it is not the only one. The recent results on silica tend to show that the distribution depends on the catalysis and that different classes are present, where polydispersity is not always crucial (see also [33]).

We turn now to the dynamical properties.

4. Dynamics

Because of the wide polydispersity in the molecular-weight distribution, one suspects that there should be a wide distribution of relaxation times in these systems. This is indeed the case, as we now discuss. We shall restrict the following discussion to the reaction bath and to dilute solutions. Intermediate cases, namely semi-dilute solutions and partly swollen gels, correspond to mixtures of these two extreme cases.

4.1. The reaction bath

Let us stress that we assume here that no solvent is present. Because the distribution of times is directly related to the viscoelastic properties, we first discuss the latter. We recall the behaviours of the viscosity and the elastic modulus as the threshold is approached:

$$\eta \sim \varepsilon^{-s} \quad (p < p_c) \quad (69)$$

and

$$E \sim \varepsilon^\mu \quad (p > p_c). \quad (70)$$

Numerous experiments were performed, leading to an extremely wide scatter in the results [95–99], and the situation is still rather confused at this time. The predicted values for the exponents s and μ will be discussed later. Following Efrös and Schklovskii [98–102], Durand *et al* [103] suggested a scaled form for the frequency dependence of the complex modulus $\bar{E}(\omega)$ defined as

$$\bar{E}(\omega) = E + i\omega\eta. \quad (71)$$

At a distance $\varepsilon = p - p_c$ from the threshold, it was assumed that

$$\bar{E}(\varepsilon, \omega) \sim \varepsilon^\mu f(i\omega\varepsilon^{s+\mu}). \quad (72)$$

It is possible to consider the high-frequency range of the modulus. One is then probing regions of space of limited extent. Thus we do not expect any ε dependence of the local modulus, which should be a function of frequency only. Assuming a power-law behaviour for $f(x)$, the exponent in such a power law is determined by the constraint that the modulus is a function of frequency only. This leads to

$$\bar{E}(\varepsilon, \omega) \sim (i\omega)^{-\mu/(s+\mu)}. \quad (73)$$

This implies that the real E' and imaginary E'' parts are proportional,

$$E' \sim E'' \sim \omega^{-\mu/(s+\mu)} \quad (74)$$

and that the loss angle δ is a constant proportional to $\mu/(s + \mu)$,

$$\delta = (\pi/2)\mu/(s + \mu). \quad (75)$$

Relations (73) were checked on polyurethane by Durand *et al* [103] and on polyesters

by Rubinstein *et al* [104], who both found $\mu/(s + \mu) = 0.69 \pm 0.02$, and on epoxy by Martin *et al* [105], who found 0.70 ± 0.05 . Thus all experimental results agree. However, this result was interpreted in different ways by the various authors, with different assumptions about the hydrodynamic interactions.

Durand *et al* [103] and the present authors accepted the percolation set of exponents. The elasticity exponent is, following de Gennes [106] and Kirkpatrick [107],

$$\bar{\mu} = \mu/\nu = d - 2 + \bar{\xi} \quad (76a)$$

where $\bar{\xi}$ is the exponent corresponding to the elastic path [108], and was calculated in a Flory approximation by Coniglio and Family [109] and by Roux [110],

$$\bar{\mu} = d - 2 + D_p/2 \quad (76b)$$

where D_p is the fractal dimension of the polymers in the reaction bath, relations (14) and (15). In a Flory approximation, this leads to

$$\bar{\mu} = (5d - 6)/4 \quad (= 9/4 \text{ for } d = 3). \quad (76c)$$

The viscosity exponent was shown by de Gennes [111] to correspond to the conductivity exponent of a mixture of normal conductors and superconductors in the vicinity of the percolation threshold. It was conjectured by Kertesz [112] and by Coniglio and Stanley [113] that we have

$$\bar{s} = s/\nu = 1 - \bar{\beta}/2 \quad (77a)$$

with $\bar{\beta} = \beta/\nu$. In a Flory approximation, we find

$$\bar{s} = (6 - d)/4 \quad (= 3/4 \text{ for } d = 3). \quad (77b)$$

Note that within the Flory approximation, we find from (76c) and (77b) that $\bar{s} + \bar{\mu} = d$, a relation that was conjectured by Straley [114] some time ago. Using these results, we find $\mu/(s + \mu) = 3/4$, in good agreement with the experimental results.

Another line of interpretation was followed independently by Martin *et al* [105, 115] and by Rubinstein *et al* [104], with different assumptions. Whereas hydrodynamic interactions are assumed to be present via small polymers [116] in the reaction bath in the former approach, the present one assumes that they are screened, so that Rouse [117, 118] type dynamics is valid. The viscosity exponent was calculated by de Gennes [111] and by Stephen [119] in such approximation. Their result is

$$\bar{s} = 2 - \bar{\beta} \quad (77c)$$

and, in a Flory approximation,

$$\bar{s} = (6 - d)/2 \quad (= 3/2 \text{ for } d = 3) \quad (77d)$$

which is exactly twice the percolation value, equation (77b).

The elasticity exponent is assumed by both groups to be

$$\bar{\mu} = d \quad (76d)$$

a result mentioned some years ago by Coniglio and Daoud [120]. Using relations (76d) and (77d), we find $\mu/(s + \mu) = 2/3$, again in good agreement with the experimental results discussed above. Thus these viscoelastic measurements, although showing very clearly the fractal behaviour of the polymers, are unable to differentiate between the two interpretations. So far, direct measurements of the exponents s and μ have also been

unable to settle this point, because of the wide scatter in the experimental results by the various groups [97, 104, 105, 121]. A possible explanation of such scatter is that no such universality exists for the dynamic properties as for the static ones, a situation that has already occurred in other critical phenomena [122].

4.2. The distribution of relaxation times

Leaving aside for the moment this (important) question of the determination of the exponents, it is possible to proceed. The complex viscosity, $\bar{\eta}(\omega) = \bar{E}(\omega)/i\omega$, is directly related [123] to the distribution of relaxation times $H(\tau)$,

$$\bar{\eta}(\omega) = \int \frac{H(\tau)}{1 + i\omega\tau} d\tau. \tag{78}$$

From equations (72) and (78), it is possible to determine the scaled form of the distribution of relaxation times. We find [124]

$$H(\tau) = \tau^{-\mu/(s+\mu)} G_{\pm}(\tau\epsilon^{\mu+s}). \tag{79}$$

Thus the distribution is a slowly decaying power law cut off for large times by an exponential function. It is possible to calculate the normalised moments of this distribution. As mentioned above, we find that two characteristic times are necessary

$$T = \int H(\tau) d\tau / \int (H(\tau)/\tau) d\tau \sim \epsilon^{-s} \sim \eta \tag{80}$$

$$T_Z = \int \tau H(\tau) d\tau / \int H(\tau) d\tau \sim \epsilon^{-s-\mu}. \tag{81}$$

Note that the moment of order (-1) appears in (80) only because of notation: what is used is generally a logarithmic scale for the time distribution. Note also that T_Z is the longest characteristic time and appears in the cut-off function of $H(\tau)$, relation (79), and that the other time is an average time, proportional to the viscosity of the sol. That such a time be present is not a surprise because of the very definition of the shear viscosity, relation (78) with $\omega = 0$. Finally, we note that Martin *et al* [82] and Rubinstein *et al* [104] obtained this result in an independent way by considering the fractal behaviour for local scales.

As a consequence of this distribution of relaxation times, one realises that any relaxation property in the intermediate time or frequency range is not exponential but follows a power law. In order to understand this, let us consider any relaxation process. Any of the modes considered above has an exponential relaxation. As a function of the frequency ω , we have

$$A(\omega, \tau) \sim \exp(-\omega\tau). \tag{82}$$

Thus the total relaxation, being the combination of all modes, is

$$A(\omega) = \int A(\omega, \tau)H(\tau) d\tau \sim \omega^{-s/(s+\mu)} f(\omega T_Z) \tag{83}$$

where we made the assumption of independent modes. A detailed study of the viscoelastic properties was given very recently by Martin *et al* [82] and by Rubinstein *et al* [104].

4.3. Dilute solutions

In the same way as we found a very broad distribution of times in the reaction bath, we also expect a distribution in a dilute solution containing the branched polymers of the sol. This may be found along the same lines as above, following [115]. In the Flory approximation that we discussed above, the intrinsic viscosity of a very dilute solution is given by equation (56) as

$$[\eta] \sim N_w^{3/8}.$$

In these dilute solutions, it is plausible to assume that hydrodynamic interactions are present, so that Zimm dynamics is valid. This implies that the longest characteristic time $T(N)$ of a polymer is

$$T(N_Z) \sim R^d \sim N_Z^{3/2}. \quad (84)$$

Thus we may assume the following scaled form for the frequency-dependent viscosity:

$$[\bar{\eta}(\omega)] \sim N_w^{3/8} f(i\omega N_w^{15/8}). \quad (85)$$

Using the same transformation as above, we get the distribution of relaxation times $H_d(\tau)$ in a dilute solution,

$$H_d(\tau) \sim \tau^{-4/5} h(\tau/N_w^{15/8}). \quad (86)$$

Again this distribution leads to two different characteristic times, defined as above:

$$T \sim N_w^{3/8} \quad (87)$$

$$T_Z \sim N_w^{15/8}. \quad (88)$$

Note that the relation between the distributions of times and masses is not direct, but is through the specific viscosities

$$H(\tau) d\tau = [\eta(N)]NP(N) dN \quad (89)$$

where we assumed a self-similar behaviour of the viscosities in a dilute solution,

$$[\eta(N)] \sim R^3(N)/N \sim N^{1/2}$$

and may be written in the following way:

$$H(\tau) d\tau = P(N)R^3(N) dN.$$

5. Conclusions

This review has focused on the similarity between the distribution of molecular weights in the sol during the synthesis of branched polymers and in the gel, and the distribution of clusters in the percolation problem. Such a similarity has now been widely demonstrated experimentally on many systems with various chemistry involved. Although this establishes percolation as an important universality class in the problem, it would be extremely dangerous to consider it as the only one. We have seen that reversible gelation, in particular, exhibits hysteresis, which suggests a first-order rather than a second-order transition.

Within the analogy with percolation, interesting effects occur, which we tried to discuss, related to the very wide polydispersity: the distribution of molecular weights

decreases as a power law in a diverging range as one approaches the gelation threshold. This implies that, in any experiment, where averages are measured, effective exponents are obtained. They depend on both the actual exponents for one polymer and the exponent that governs the distribution function.

An important problem that is still open in our opinion is the value of the exponents s and μ of the viscosity and the modulus. As these condition all the rheological properties of the reaction bath and concentrated solutions, it is certainly worth having more experimental data on model systems.

Another set of questions is related to the connection with classical rubbers. A first step in this direction was recently made by Bastide and Leibler [125] within the percolation scheme. Another approach was initiated by Edwards [126] and Ball [127] some years ago in a very different context, and should certainly be tested in more densely crosslinked systems.

Finally, let us mention the very interesting experiments that have been performed in order to observe fractons [128, 129] on silica gels. The latter are very different from those we discussed above. More precisely, they are submitted to a thermal process, hypercritical drying, that allows the solvent to be removed and, for some reason unknown to the present authors, have a final fractal dimension of the gel $D = 2.4$ [130]. Thus in these aerogels, all the monomers belong to the fractal structure, whereas we discussed a situation where the gel fraction is vanishingly small. Because no solvent is present, excitations may propagate only along this structure. Rather good support for the existence of fractons [131] was given by this set of experiments.

Acknowledgments

The authors are much indebted to M Adam, B Cabane, R Colby, M Delsanti, D Durand, P G de Gennes, G Jannink, L Leibler, J E Martin, J P Munch, M Rubinstein and Joe Teixeira for related discussions and for keeping them informed of their work.

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