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Randomly Branched Polymers: Semidilute Solutions

M. Daoud*

Laboratoire Leon Brillouin,[†] *C.E.N. Saclay, F-91191 Gif/Yvette Cedex, France*

L. Leibler

E.S.P.C.I., 10 Rue Vauquelin, 75235 Paris Cedex 05, France. *Received July 28, 1987; Revised Manuscript Received October 23, 1987*

ABSTRACT: We study the conformation of randomly branched polydisperse polymers in semidilute solutions. Starting from the dilute case, when the different macromolecules are far apart from each other, we suggest that above a concentration C^*, where the polymers come into contact, a semidilute regime occurs. In this regime, one may separate the distribution of molecular weights into two parts. The smaller molecules behave as in the dilute regime. They penetrate the larger ones and screen out the excluded-volume interaction. Thus large polymers behave as in the reaction bath. As a function of the weight-average molecular weight M_w, we find that the crossover concentration C^* separating the dilute and semidilute regimes is $C^* \sim N_w^{-3/8}$. In the semidilute range, we find $R_z \sim N_w^{1/2}C^{-1/3}$ where C is the total monomer concentration and a screening length $\xi \sim C^{-5/3}$. We also discuss the scattered intensities in small-angle neutron and light scattering experiments in different conditions and the osmotic pressure as a function of concentration.

1. Introduction

There has been recently a renewed interest in polydisperse randomly branched polymers. This originates in the idea proposed by de Gennes[1] and by Stauffer[2] that the synthesis of such macromolecules might be correctly described by percolation. Thus the conformation of these polymers in their reaction bath should be related to percolation. In particular, screening effects are present.[3–5] More recently,[6] it was argued that if one dilutes such a concentrated system and considers a dilute solution made of all the polymers present in the reaction bath, such screening is no longer present. Thus excluded-volume effects are present (and important) and the polymers swell. As a result, the conformational properties of randomly branched polymers are understood in the bulk (reaction bath)[7,8] and in the dilute regime.[9–11] In this paper, we would like to consider the intermediate case of semidilute solutions where the various polymers are no longer far apart from each other but on the contrary interact strongly. Such intermediate concentration range is very important for practical applications of branched polymers, in oil drilling fluids for instance.

Because of the very strong polydispersity in such system, we will first have to define more precisely the semidilute regime. As for linear polymers, we shall see that it is possible in this entire concentration range to bring the question back to the situation in the reaction bath by a suitable change in the scales. Thus we will be led to introduce blobs with size ξ and to distinguish between small distance (or molecular weight) scales and large distance (or molecular weight) scales. The main difference between linear and branched polymers is that whereas linear chains overlap in a concentrated solution, branched macromolecules with similar sizes do not.[12] Therefore the interpretation of the blobs is not the same in both cases. As we shall see, however, for branched polymers as for linear chains, if one considers the blob as a (renormalized) monomer, the large-scale configurational properties of a semidilute solution are the same as those of a melt.

In the following, we will first recall the main results concerning randomly branched polymers in a melt (or rather in the reaction bath) and in a dilute solution in section 2. The model for semidilute solutions will be given in section 3. The last section will deal with some applications, in particular to scattering experiments. All the analysis is made in a Flory approximation.[13,14]

2. The Reaction Bath

Let us consider multifunctional units in a reaction bath and allow them to react. We assume that no solvent is present and that all the functionalities are equally active. Although the latter assumption is crude, we expect it not to alter the basic properties in many systems. Let p be the probability that any functionality is reacted. When p is below a threshold p_c, one gets a sol made of randomly branched polymers, with a very broad distribution of molecular weights. Flory and Stockmayer[13,15] gave a mean-field theory for such a process, when loop formation is neglected. More recently, it was argued that percolation[16] should provide a better description if one takes into account the existence of large loops. Let t be the distance $p_c - p$ to the threshold. The main results may be expressed in terms of the number distribution of molecular weights $P(n,t)$, with n the number of monomers per polymer, proportional to the molecular weight. The latter may be written in a scaled form:[2,7,17]

$$P(n,t) \sim n^{-\tau} f(tn^{\sigma}) \tag{1}$$

Note the normalization for $P(n,t)$:

$$\int P(n,t)\,\mathrm{d}n = 1 \tag{1'}$$

where τ and σ are critical exponents with mean-field values $^5/_2$ and $^1/_2$, respectively.[18] Relation 1 was recently[25] observed on randomly cross-linked polystyrene solutions, with $\tau = 2.2$. Because the exponent τ in percolation is larger than 2, one has to consider two different molecular weight averages:[13,14] The weight-average molecular weight is the normalized second moment of the distribution and diverges with an exponent γ.

$$N_w = \frac{\int n^2 P(n,t)\,\mathrm{d}t}{\int nP(n,t)\,\mathrm{d}t} \sim t^{-\gamma} \tag{2}$$

The z-average molecular weight is the normalized third moment and diverges with an exponent $1/\sigma$.

$$N_z = \frac{\int n^3 P(n,t)\,\mathrm{d}n}{\int n^2 P(n,t)\,\mathrm{d}n} \sim t^{-1/\sigma} \tag{3}$$

Note that the normalization is not the same for N_w and N_z and that the latter is explicitly present in the distribution function

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[†] Laboratoire commun C.E.A.-C.N.R.S.

$$P(n,t) \sim n^{-\tau} f[(n/N_z)^{\sigma}] \qquad (4)$$

and may be interpreted roughly as the largest mass present in the system.

In order to calculate the configuration of the polymers in the reaction bath, Isaacson and Lubensky[5] and de Gennes[4] proposed a Flory theory. For a large macromolecule, the free energy is written in the usual way:

$$F = \frac{R^2}{N^{1/2}} + \frac{v}{N_{\mathrm{w}}} \frac{N^2}{R^d} \qquad (5)$$

with v the excluded-volume parameter, R the actual radius, d the dimension of space, and N the typical mass, to be discussed below, and where the first term is the elastic energy and the second one the interaction contribution. Note that the unperturbed radius is proportional to $N^{1/4}$ instead of $N^{1/2}$ for linear chains. Note also the presence of N_{w} in the second term, related to the screening of the excluded-volume interaction[3] in the reaction bath. In this equation, one considers large polymers with typical mass $N \sim N_z$. In such a Flory approximation, it is assumed[4,5] that the mean-field relation between N_z and N_{w} holds:

$$N_{\mathrm{w}} \sim N_z^{1/2} \qquad (6)$$

Minimizing the free energy with respect to R leads to

$$N \sim R^{D_{\mathrm{p}}} \qquad (7)$$

and

$$D_{\mathrm{p}} = (d + 2)/2 = 5/2 \qquad (d = 3) \qquad (8)$$

Finally, we note that at the percolation threshold the distribution of molecular weights is self-similar in the sense that for every mass in this distribution, the corresponding polymers are in a so-called C^* situation, i.e., are in contact. The resulting structure is somewhat reminiscent of Russian dolls, with smaller polymers filling the empty spaces in larger macromolecules at every scale. This is a consequence of the relation between the exponent τ of the distribution of molecular weights and the exponent D_{p} for the radius ($\tau = 1 + d/D_{\mathrm{p}}$). Such a structure was already noted very recently by Cates.[19]

3. The Dilute Regime

Let us now assume that the polymers have been synthesized as discussed in the previous section and that the molecular weight distribution is quenched. The system is then diluted, and we assume in this section that the resulting solution is dilute: the polymers are far apart from each other. Then, the screening effects discussed above are no longer present, and one may write a Flory free energy for any chain similar to the previous form, but without screening.

$$F = \frac{R^2}{N^{1/2}} + v\frac{N^2}{R^d} \qquad (9)$$

Minimizing with respect to R leads to

$$N \sim R^{D_{\mathrm{a}}} \qquad (10)$$

with

$$D_{\mathrm{a}} = 2(d + 2)/5 \qquad (11)$$

In a scattering experiment, however, what is measured is the z-average radius of gyration.

$$\langle R^2 \rangle_z = \frac{\int R^2(n) n^2 P(n,t) \, \mathrm{d}n}{\int n^2 P(n,t) \, \mathrm{d}n} \sim t^{-2/\sigma D_{\mathrm{a}}} \qquad (12)$$

Eliminating t with relation 2, we get

$$R_z^{\,2} \sim N_{\mathrm{w}}^{2D_{\mathrm{p}}/D_{\mathrm{a}}(2D_{\mathrm{p}}-d)} \sim N_{\mathrm{w}}^{5/4} \qquad (13)$$

Note that in the reaction bath, assuming that all the polymers have the same behavior as the large ones, we get for this same quantity

$$R_z^{\,2} \sim N_{\mathrm{w}}^{2/(2D_{\mathrm{p}}-d)} \sim N_{\mathrm{w}} \text{ (reaction bath)} \qquad (14)$$

With these asymptotic behaviors in hand, let us now turn to the concentration effects.

4. The Semidilute Regime

In the following, we assume that the molecular weight distribution is given and that the only changes that occur are obtained by removing solvent from the solution. Let us start with a dilute solution and increase the concentration C. For very low concentrations, one expects concentration effects to be simple perturbations to relation 13, for instance. Some of these were already calculated.[6,20] In the appendix, we give expressions for the second virial coefficient which can be measured by (light) scattering experiments.[24] For higher concentrations, however, the polymers come into contact, and we assume that more serious deviations to the preceding relations will be present that may not be accounted for by a perturbation expansion. This leads us to define the crossover concentration C^* separating the dilute from the semidilute regimes. It may be defined as the special concentration when the *total volume fraction* occupied by *all* the polymers is of order of unity. Thus at C^*, we have

$$\int R^d(n) P'(n,t) \, \mathrm{d}n = 1$$

where, because of dilution,

$$P'(n,t) = CP(n,t)$$

Thus we find

$$C^* \sim \frac{1}{\int R^d(n) P(n,t) \, \mathrm{d}n} \sim N_z^{-[(d/D_{\mathrm{a}})-(d/D_{\mathrm{p}})]} \qquad (15a)$$

$$C^* \sim N_{\mathrm{w}}^{-3/8} \qquad (d = 3) \qquad (15b)$$

This definition of C^* is merely a generalization of the usual one, taking into account the huge polydispersity present in a diluted sol. Note that this definition implies that, as usual, the various polymers are in contact at C^*. We show in the appendix that C^* is related to the average virial coefficient B_{L} measured by scattering experiments in dilute solutions. Relation 15 was observed very recently by Adam, Delsanti, Munch, and Durand by light scattering experiments.[24]

For concentrations higher than C^*, the solution is semidilute, and we expect dramatic changes in the configurational properties of the macromolecules. Our basic assumption in this regime is that the polymers are going to shrink because the smaller ones penetrate the larger ones. Screening effects are present. Thus in this whole concentration range, the macromolecules occupy the entire volume. The lower part of the mass distribution penetrates the higher part and screens out the excluded-volume interaction as it does in the reaction bath. The main difference with the latter situation comes from the fact that if we consider relation 5 for the free energy of the large chains, the weight-average molecular weight in the screened interaction is now dependent on concentration because only a part of the distribution is actually interpenetrating the large polymers and thus screening the interaction. Thus we are led to partition the distribution of masses in two parts.

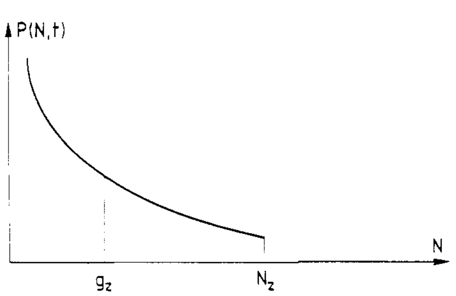

Figure 1. Sketch of the number molecular weight distribution $P(N,t)$ as a function of mass. It decreases as a power law, with an exponential decay above N_z which is neglected here. In the semidilute range, we assume that the smaller polymers ($N < g_z$) are still swollen and screen the excluded-volume interaction in the larger ones. Thus there is a distribution of blob sizes.

First we have the largest masses, which have been penetrated and behave as in the reaction bath. For this part of the distribution, we expect the same screening effects as in the reaction bath, with the restriction on M_w we just mentioned.

The second part is the smaller masses, which are still in contact with each other, as at C^*. In the following, we will assume that they behave as in a dilute solution and that relation 10 for instance is valid for every mass in this part of the distribution. Thus we will introduce "Blobs" in order to distinguish between large distances and smaller ones. But it is very important to keep in mind that for both small and large distance scales, we still have to deal with mass distributions.

Then in the semidilute regime we are led to define a second length, ξ, namely, the z-average radius of a blob. Let g be the weight-average molecular weight of a blob. Because we assume that the smaller molecules are still swollen, we expect a relation between ξ and g analogous to relation 13, in the dilute case.

$$\xi \sim g^{5/8} \tag{16}$$

Moreover, we expect both g and ξ to be functions of concentration only, assuming

$$\xi \sim C^{\alpha} \tag{17a}$$

$$g \sim C^{\beta} \tag{18a}$$

The exponents α and β may be obtained easily by noting that at the crossover C^*, we have

$$\xi(C^*) \sim N_w^{5/8} \tag{17b}$$

$$g(C^*) \sim N_w \tag{18b}$$

Matching the exponents and using relations 13 and 15, we get

$$\xi \sim C^{-5/3} \tag{17c}$$

$$g \sim C^{-8/3} \tag{18c}$$

For the large-mass part of the distribution, it is convenient to make a change in the scales and to take g as a unit mass and ξ as a unit length. With these renormalized units, the configuration of the large macromolecules is identical with what was recalled in section 2. More precisely, we may calculate the average radius, for instance, by assuming that the "average" polymer is made of N/g monomers of length ξ each. We find

$$R_z \sim (N_w/g)^{1/2}\xi \sim N_w^{1/2}C^{-1/3} \tag{19}$$

Note that both relations (17) and (19) may be obtained directly by assuming a scaled form for the distances:

$$L = N_w f(CN_w^{3/8}) \tag{20}$$

with two different power law behaviors for $f(x)$ for large arguments when we consider R_z or ξ. The two exponents are calculated with the requirements that the mass dependence of the radius is the same as in the reaction bath, relation 14, and that ξ depends on concentration only.

Scattered Intensities. It was shown recently that polydispersity changes the exponents of the variation of the scattered intensity with scattering vector in the intermediate range, $l^{-1} \ll q \ll R^{-1}$. For a dilute solution one finds

$$S(q) \sim q^{-D_a(3-\tau)} \sim q^{-8/5} \tag{21}$$

where D_a is the exponent for a single swollen polymer and τ is the exponent of the distribution, relations 10, 11, and 1. Relation 21 is just a reformulation of eq 13. A detailed discussion of polydispersity effects on the scattered intensity in the undiluted case was recently given by Martin and Ackerson.[21] For a semidilute solution, one may define two different scattered intensities, depending on whether one or all the macromolecules are labeled. Let S_1 and S_t be the scattered intensities for these two cases respectively.

(a) One Labeled Macromolecule. In the case where one polymer is labeled, the polydispersity effects mentioned above are not present. Therefore one expects to observe the swelling exponents, relations 7 or 10, directly, depending on the value of the scattering vector. We evaluate the scattered intensity by noting that it is the number of monomers in a volume q^{-3}, with q the scattering vector. Thus we find two regimes.

For $q\xi \gg 1$, as discussed above, the behavior is the same as in a dilute solution. Thus we find

$$S_1(q) \sim q^{-2} \qquad (q\xi \gg 1) \tag{22}$$

For smaller values of the scattering vector, corresponding to larger distances, two different cases have to be considered, depending on the size of the labeled macromolecule.

When the polymer is very large, as discussed before, its behavior is the same as in the reaction bath, if we take the blob as a unit. Thus

$$\frac{S_1(q)}{S_1(\xi^{-1})} \sim \frac{1}{(q\xi)^{-5/2}} \tag{23a}$$

and, using (17) and (22), we find

$$S_1(q) \sim \frac{C^{10/3}}{(q\xi)^{5/2}} \tag{24}$$

When the polymer is smaller, or for very small values of the scattering vector ($qR \ll 1$), one enters in the Guinier range where it is possible to measure the radius of gyration $R(N)$ of the labeled polymer, where N is the mass of the tagged chain. In order to calculate this radius, one has to get back to the distribution of masses. As discussed above, the smaller masses are swollen. What was called the average blob size g corresponds in fact to the weight average of this part of the distribution (See relation 18a for instance). As a consequence, there are larger masses in the distribution which are still swollen. It is easy to evaluate the highest swollen mass. Let g_z be such a mass. The same relation holds between g and g_z as between N_w and N_z, namely,

$$g_z \sim g^{(\beta+\gamma)/\gamma} \sim g^{5/4} \tag{25}$$

In order to calculate the radius of the tagged polymer, one has obviously to compare its mass to g_z and not to g. Thus the number of renormalized monomers in the polymer is N/g_z, of length ξ each.

The radius is

$$R(N) \sim (N/g_z)^{2/5}\xi \sim N^{2/5}C^{-1/3} \qquad (26)$$

(b) All Polymers Labeled. When all the macromolecules are equivalent, one is led again to perform averages over the molecular weight distribution. As mentioned above, this leads to an effective exponent for the dependence of the scattered intensity on scattering vector q in the intermediate range. Here again, we have to divide the q range in several regions.

For large values of the scattering vector ($q\xi \gg 1$), we probe the swollen part of the distribution, and the scattered intensity is similar to what is observed with a dilute solution:

$$S_t(q) \sim Cq^{-8/5} \qquad (27)$$

For smaller scattering vectors ($R_z^{-1} \ll q \ll \xi^{-1}$), one is sensitive to larger distances, where the excluded-volume interaction is screened. As already mentioned, we expect the same intensity as in the reaction bath, if we take the blob as a unit. Thus

$$\frac{S_t(q)}{S_t(\xi^{-1})} \sim \frac{1}{(q\xi)^2} \qquad (28)$$

and, using relations 27 and 17, we find

$$S_t(q) \sim \frac{C^{-5/3}}{1 + q^2\xi^2} \qquad (29)$$

By extrapolation to zero scattering vector, relation 29 gives

$$S_t(0) \sim C^{-5/3} \qquad (30)$$

Scaling arguments for relation 30 are given in the appendix.

Because of polydispersity, the solution is somewhat a multicomponent system, and we cannot[22] relate this intensity to the osmotic pressure. Thus we do not find any power law dependence for the osmotic pressure with concentration in the semidilute range. A plausible conjecture for the osmotic pressure is to assume a scaled form,

$$\Pi = \frac{C}{M_n} f(CN_w^{3/8}) \qquad (31a)$$

with M_n the number-average molecular weight and

$$f(X=0) = 1$$

Because M_n does not diverge, relation 31a does not lead to any special power law behavior for the osmotic pressure in the semidilute regime. It is equivalent to generalize the classical des Cloizeaux[23] relation, eq 32, for monodisperse systems in the following form:

$$\Pi = \frac{1}{\langle R^3 \rangle} f(CN_w^{3/8}) \qquad (31b)$$

with $\langle R^3 \rangle = \int R^3(n)P(n,t)\,dn$ and

$$f(x \rightarrow 0) = x/M_n$$

From both equations (31a) and (31b), we are led to conclude that the osmotic pressure seems to be dependent on the weight-average molecular weight in the semidilute regime.

5. Conclusion

We have considered the static properties of semidilute randomly branched polymers. In order to define the crossover concentration C^*, one has to consider the volume fraction occupied by the macromolecules, taking into account the very large polydispersity of the system. Throughout the paper, we always assumed that the distribution of masses is that of percolation. In the semidilute range, above C^*, we partitioned the distribution in two parts.

First are the smaller masses, which we assumed still have a dilute behavior. This allows us to define a blob with size ξ. An important difference with linear polymers has to be stressed: Whereas for the latter, blobs are basically the same size, this is not the case for randomly branched polymers. One has rather a wide distribution of sizes. At C^*, this distribution covers the entire molecular weight range. Thus one has to be cautious when considering properties of the blobs.

The larger masses overlap the smaller ones. If we take as the renormalized unit the z-average radius of a blob, the z-average radius of the polymers has the same behavior as in the reaction bath, when expressed in normalized units (see relations 17 and 19).

This partitioning allows for the calculation of all the properties of the semidilute solutions. As an example, we looked at the scattered intensity by labeled or unlabeled macromolecules. We stress that all the properties were calculated as a function of the mass concentration C per unit volume. An interesting result concerns the osmotic pressure, relation 31. Because of the polydispersity, the usual scaling relation

$$\Pi R^3 = f(C/C^*) \qquad (32)$$

is no longer valid. With our definitions, we have rather

$$\Pi = \frac{C}{M_n} f\left(\frac{C}{C^*}\right) \qquad (33)$$

All the results quoted above may be checked by light or neutron scattering experiments.

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Appendix: Scattered Intensity in Dilute and Semidilute Solutions

For dilute solutions, the forward scattered intensity, $I(0)$, may be written as

$$\frac{KC}{I(0)} = \frac{1}{M_w} + 2B_L C \qquad (A1)$$

where C is the monomer concentration and B_L denotes the average monomer virial coefficient. In general, for a polydisperse system, this virial coefficient is

$$B_L = (1/M_w^2)\sum_i\sum_j M_i M_j G_{ij} p(i) p(j) \qquad (A2a)$$

$$B_L = (1/M_w^2)[2\sum_{i>j} M_i M_j G_{ij} p(i) p(j) - \sum_i M_i^2 G_{ii} p(i)^2] \qquad (A2b)$$

with G_{ij} denoting the interchain virial, which, according to a blob model, should scale like a volume of a shorter chain, i.e.,

$$G_{ij} = \frac{M_i}{M_j} R_j^3 \qquad (i > j) \qquad (A3)$$

In fact, short chains are expected to penetrate larger ones, and as a result, chains of different sizes do not interact as hard spheres. It can be checked that for polymers prepared by a reaction stopped near the gelation threshold (with $p(i)$ given by eq 1 or 4) the first term in (A2b) dominates, and one finds that B_L scales as

$$B_L \sim M_z^{3/D_a - 2} \sim M_z^{-0.5} \qquad (A4a)$$

or equivalently as

$$B_L \sim M_w^{-5/8} \tag{A4b}$$

From (A1) and in striking analogy with solutions of linear chains, we may write

$$\frac{KC}{I(0)} = \frac{1}{M_w} f(CB_L M_w) = \frac{1}{M_w} f\left(\frac{C}{C^*}\right) \tag{A5}$$

where the crossover function $f(x)$ is analytic in dilute solutions:

$$f(x \ll 1) = 1 + Ax + ...$$

The crossover concentration scales like the overlap concentration C^* (cf. eq 15), i.e.,

$$C^* \sim 1/(B_L M_w) \sim M_w^{-3/8}$$

It is interesting to note that also $C^* \sim 1/[\eta]$ where $[\eta]$ is the intrinsic viscosity.[6]

In the semidilute range the crossover function has a power law behavior

$$f(x) \sim x^a$$

where the exponent a is found by the requirement that $I(0)$ in this regime does not depend on M_w

$$\frac{KC}{I(0)} \sim C^{8/3} \tag{A6}$$

in agreement with eq 30. It should be stressed that the scattered intensity in the semidilute regime falls down much more rapidly than for monodisperse linear chain solutions. This is due to the fact that concentration fluctuations are much smaller in polydisperse interpenetrated systems.

An analogous analysis of a virial expansion for the osmotic pressure confirms that in the semidilute regime the osmotic pressure depends strongly not only on the concentration C but also on the characteristics of the sample (e.g., M_n, ...).

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