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Polydispersity and scaling in linear polymer condensates

M. Daoud (*) and F. Family (**)

(*) LLB/CEN-Saclay (+), B.P. n° 2, 91191 Gif sur Yvette, France
(**) Physics Dept., Emory University, Atlanta, GA30322, U.S.A.

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Abstract. — We consider a linear polymer melt where the chains are made by condensation of bifunctional monomers. In the very large distribution of molecular weights that is obtained one may distinguish typical and very large chains with different behaviours. Screening is effective in the former, which act as a (good) solvent for the latter. The cross-over molecular weight $N^*$ between the two classes is a function of the weight average molecular weight $N_w$. Within a Flory approach, we find $N^* \sim N_w^2$. Chains much larger than $N^*$ are swollen. Typical chains have the same behaviour as in a monodispersed melt.

1. Introduction.

There has been recently a considerable interest in the conformation [1] of linear polymer chains. The analogy [2] between the excluded volume problem [3] and critical phenomena [4] was generalized [5] to describe the properties of more concentrated solutions, in particular the screening [4] of the interactions. This was checked experimentally by Small Angle Neutron Scattering experiments [5, 6] and osmotic pressure measurements [8], among others, on rather monodispersed samples. The influence of polydispersity has been modelled by Flory [3] some time ago, and more recently by de Gennes [9] who considered a melt where one very long chain, made of $N$ segments, is dissolved in a matrix made of shorter chains, with $P$ units of the same chemical species. The monomer was supposed to be a good solvent of the polymer. It was found that when the matrix chains are short ($N > P^2$) the probe chain is swollen. When the matrix is made of longer chains, the melt is conventional ($R_N \sim N^{1/2}$). Note that here there are at least two lengths, corresponding to the radius of gyration $R_g$ and $R_N$ of the matrix and probe chains respectively.

In this paper, we would like to consider one extreme case of polydispersity, namely the case of a melt made by the condensation of bifunctional monomers, and look at the conformation of a chain. As for the bimodal melt, we argue that there is not one but at least two different lengths that one might consider. These are the lengths of a « typical » chain, with molecular weight of the order of the number average molecular weight, and of a « long » chain, much larger than the preceding one : whereas the interaction is screened at small distances, which is the case for typical chains, it is relevant when the polymer is large enough.

2. Conformations in the melt.

Let us consider a melt made initially of bifunctional monomers in a vessel. These monomers are allowed to react with each other, thus leading to a very polydisperse condensate. We suppose that every functional unit has the same chemical reactivity, regardless of the length of the molecule to which it is attached. The distribution of molecular weights in these condensation polymers has been studied a long time ago [13]. If $p$ is the probability that a functional unit has reacted, the probability to have a chain of $N$ elements is

$$P(N) = p^{N-1}(1 - p)^2$$
and the weight fraction of $N$-mers is
\[ \Gamma(N) = N(1 - p)^2 p^{N-1}. \]  
(2)

This distribution as shown in figure 1 has a maximum, and one may calculate the different moments. Here, we need only the number-average and the weight-average molecular weights
\[ \bar{N} = \frac{\sum NP(N)}{\sum P(N)} = \frac{1}{1 - p} \]  
(3)
\[ N_w = \sum N\Gamma(N) = \frac{1 + p}{1 - p}. \]  
(4)

Note that both of them diverge like $(1 - p)^{-1}$ when $p$ goes to unity. Suppose that there is one labelled probe molecule. We now focus on its conformation:

2.1 RADIUS OF GYRATION. — Let us first consider the overall properties of this molecule, and first its radius. For a polydisperse system, it was argued [10, 11] that the Flory free energy of a chain is
\[ \frac{F}{T} = \frac{R^2}{R_0^2} + \frac{\nu N^2}{N_w R^d} \]  
(5)

where the first term is the elastic contribution and the second one the interaction energy. $R_0$ is the unperturbed (Gaussian) radius, $R$ the actual radius and $N_w$ the weight average molecular weight. Its presence is related to the screening of the interaction. Relation 5 supposes that the molecules overlap. Now we argue that two different cases may be considered:

2.1.1 A typical chain, with molecular weight of the order of $\bar{N}$ (or $N_w$). This chain is going to feel the presence of many other chains with roughly the same size, or possibly longer. Note that for this first type of chains, $N$ and $N_w$ are not independent variables, but that there is a relation between them, as can be seen from relations 3 and 4.

\[ N \sim \bar{N} \sim N_w. \]  
(6)

For this first kind of chains, we expect screening to be present. Minimization of the Flory free energy (5) then leads to

\[ R \sim N^{2(d+2)} \]  
(7)

for typical chains where relation 6 has been taken into account.

2.1.2 A very long chain, much larger than the typical one considered above. As in the case of a bimodal distribution [3, 9], this second type will locally feel the presence of the other monomers. On a larger scale, however, the large chain is going to interact with itself and excluded volume effects are present. The other chains act just as a good solvent. Note that in this case, there is no relation between $N$ and $N_w$.

\[ R \sim N^{3/5} N_w^{-1/5} \]  
(8)

Comparing (7) and (8) gives the crossover molecular weight $N^*_c$ between typical and long chains in $d \leq 2$

\[ N^*_c \sim N_w \quad (d \leq 2). \]  
(9)

For $d > 2$, although chains with $N$ larger than $N^*_c$ are long chains, they are not necessarily swollen as can be seen from (8'). In fact, from (8) and (7') we find that long chains become swollen at $N^*_w$ where

\[ N^*_w \sim N_w^{2(d-4)} \quad (4 \geq d \geq 2). \]  
(9')

It is important to realize that in a « melt » made of condensation polymers, both types of macromolecules are present, even if most of the concentration is due to the first type, with only some molecules of the second type being present.

Minimization of the Flory free energy (5) for this case gives

\[ R \sim N^{3/(d+2)} N_w^{-1/(d+2)}. \]  
(8)

Here, the polydispersity effect is trivial and the excluded volume [2, 3] $(n = 0)$ exponent is recovered.

An important remark concerns the critical dimension above which the chains become gaussian : the two types do not have the same critical dimension. Comparing (7) and (8) to the mean field result $R_0 \sim N^{1/2}$

leads to

\[ d^1_c = 2 \quad \text{for typical chains} \]
\[ d^1_l = 4 \quad \text{for long chains}. \]

This result is not surprising and has to be compared with those for monodisperse chains.

For three dimensional chains, our results are then

\[ R \sim N^{1/2} \quad (d = 3) \quad \text{(typical chains)}, \]
\[ R \sim N^{3/5} N_w^{-1/5} \quad (d = 3) \quad \text{(long chains)}. \]

Comparing (7) and (8) gives the crossover molecular weight $N^*_c$ between typical and long chains in $d \leq 2$

\[ N^*_c \sim N_w \quad (d \leq 2). \]  
(9)

For $d > 2$, although chains with $N$ larger than $N^*_c$ are long chains, they are not necessarily swollen as can be seen from (8'). In fact, from (8) and (7') we find that long chains become swollen at $N^*_w$ where

\[ N^*_w \sim N_w^{2(d-4)} \quad (4 \geq d \geq 2). \]  
(9')
Therefore, in $d > 2$ the crossover from typical chains to long chains at $N^*_c$ does not coincide with the swelling of long chains which occurs at $N^*$. Finally, note that for $d \geq 4$ there is no longer any swelling of the chains so that $N^*$ does not exist anymore although one may still distinguish between typical and long chains.

2.2 Correlation Functions. — Let us now consider the monomer-monomer correlation function. We will restrict ourselves to the case when both monomers are on the same polymer.

2.2.1 Typical chain. — We have seen above that in this case there is a screening of the interaction, and that these chains have the same behaviour as in a monodispersed melt. Then we expect the correlation function to be the same as for a Gaussian chain. Its Fourier transform, which is proportional to the intensity in a neutron or light scattering experiment is

$$S(q) \sim q^{-2} \quad (q \xi > 1).$$

where $q$ is the scattering vector.

2.2.2 Long chain. — Although there is locally a screening of the excluded volume interaction, as discussed above, because of the length of this kind of chains, the other (typical) chains act like a good solvent for the global properties such as the radius of gyration. For the correlation function, however, this local screening implies a behaviour very similar to that of typical chains, i.e. an ideal behaviour

$$S(q) \sim q^{-2} \quad (q \xi < 1) \quad (q \xi \gg 1).$$

For larger distances, we recover the excluded volume behaviour

$$S(q) \sim q^{-5/3} \xi^{1/3} \quad (q \xi < 1)$$

where we have introduced a length $\xi$ which we may call an « inverse » screening length : for distances smaller than $\xi$ the excluded volume interaction is screened by the presence of the shorter chains. For distances larger than $\xi$ the interaction is relevant and swells the large chains. This situation is very similar to that of a large chain dissolved in a matrix of monodispersed shorter chains.

We may describe the long chain as made of screened blobs, with $g$ elements and size $\xi$. When the screened blob is taken as statistical unit, the large polymer is swollen :

$$\xi \sim g^{1/2} \quad (d = 3)$$

and

$$\xi \sim N_w \quad (d = 3).$$

A schematic representation of the correlation function is shown on figure 2. Note that both $\xi$ and $R$ depend on $N_w$ which is directly related to the extent of chemical reaction, as shown by equation 4 in a Flory mean field approach, which we expect to be correct for $d = 3$.

When the size $N$ of the probe chain is lowered, it is easy to check that its behaviour crosses over from the swollen to the screened typical behaviour when $N$ becomes of the order of the number $g$ of elements of the screened blob, as already noted above (Eq. 9).

For two dimensional systems, equations 13 to 14' are replaced respectively by

$$R_2 \sim \left( \frac{N}{g} \right)^{3/4} \xi \sim N^{3/4} g^{-1/4} \quad (d = 2).$$

Thus although the experimental set-up is more difficult to realize [12, 13], the cross-over values are easier to get for two dimensional systems.

2.3 Number of Configurations and Distribution of Clusters. — Let us now turn to the number $P(N)$ of configurations of a chain per site. By analogy with the single chain ($n = 0$) problem [1], we assume, for large $N$:

$$P(N) = \mu^N N^{-\theta},$$

where $\mu$ is an effective coordination number, and $\theta$ an exponent which we want to determine. $\theta$ has different values, $\theta_T$ and $\theta_L$ for the typical and long chain problem respectively.

Fig. 2. — Schematic log-log plot of the pair correlation function of a long chain in the « melt ». Screening occurs for distances smaller than $\xi$ ($q$ is the momentum transfer in a scattering experiment). $\xi$ is directly related to the weight average molecular weight (see text).
2.3.1 Typical chain. — We note that because the chains are linear, the normalized number of configurations is just the probability for a chain made of \( N \) elements to be present in the distribution function mentioned above. In the Flory approach, this is proportional to \((1 - \rho)^2\). Taking (3) into account, we find

\[
P(N) \sim N^{-2}
\]

and

\[
\theta_T = 2
\]

which we expect to be valid for space dimensions above \( d_c = 2 \). More generally, using relation 17 for the distribution of chain lengths, one may define a whole set of exponents related to the moments of this distribution [14]. These give us a description of the present chain problem as a « gelation » problem [14, 15] (although the gel point is never reached). The only one we need here is the exponent \( \alpha \), describing the total number of clusters (chains) per unit volume: in order to take into account the whole shape of the distribution function, relation 18 may be generalized for any \( N \) [see Eq. 1]:

\[
P(N) = N^{-\theta_T} f\left(\frac{N}{\bar{N}}\right) \quad (d \leq 2)
\]

where \( \bar{N} \) is the number average and has been defined above and where \( f(x) \sim 1 \) when \( x \leq 1 \). The total number of chains per unit volume \( C_p \) is then obtained by a simple summation:

\[
C_p \sim \bar{N}^{1-\theta_T}
\]

This number is usually defined in terms of \( \rho \) :

\[
C_p \sim \rho^{2-\alpha} \sim \bar{N}^{2-\alpha} \quad (\alpha = 1 - \rho)
\]

from which we get

\[
\theta_T = 1 + \nu d = \frac{3d + 2}{d + 2} \quad (d \leq 2).
\]

Note that (24) may be obtained from the more general equation 19:

\[
P(N) = N^{-\theta_T} f\left(\frac{N}{\bar{N}}\right) \quad (d = 3),
\]

leading to \( m = \theta_T - \theta_L \) and

\[
P(N) \sim \left(\frac{N}{\bar{N}}\right)^{-\theta_L} \sim \left(\frac{N}{\bar{N}}\right)^{-\theta_T}
\]

Note that in \( d = 3 \), \( \bar{N} \) is different from \( N^* \), as we discussed above. Therefore the crossover from typical chains to long chains which occurs at \( \bar{N} \sim N_w \) is different from the crossover between unswollen and swollen large chains which occurs at \( N^* \sim N_w^2 \).

2.4 Diluting the system. — Let us now take the melt that was considered above, and dilute it in a good solvent. We suppose that the system is chemically quenched, so that the distribution of molecular weights remains unchanged. However the system is now dilute, so that the screening effects that were present in the previous section are no longer taking place. Then the radius of any chain is swollen

\[
R \sim N^{2/3}.
\]

What is measured in a light scattering experiment is the \( z \) average radius

\[
\langle R^2 \rangle_z = \frac{\sum N^2 R(N)^2 P(N)}{\sum N^2 P(N)}
\]

where \( R(N) \) is given by (29) and where we are interested now in the average properties of the distribution, and not by the very few chains in the tail of the distribution \( (N \gg \bar{N}^2) \). For the former, then, we have from Flory's result

\[
P(N) = N^{-2} f\left(\frac{N}{\bar{N}}\right)
\]

leading to

\[
\langle R^2 \rangle_z \sim N_w^{2\nu_L}.
\]

It is interesting to note that since hyperscaling is valid here, relation 20 is the same as the one found by Stauffer [17] for a « real » gelation problem - (polycondensation of multifunctional units). In problems where the usual hyperscaling relation \((2 - \alpha = \nu d)\) is not valid, one obtains [14] different relations between \( \nu \) and \( \theta \). Note also that (23) is not valid for \( d = 3 \), where hyperscaling is violated.

2.3.2 Long chain. — We can relate the exponents \( \theta_L \) and \( \nu_L \) for the very long chain in analogy with other polymer systems [14]. From the single chain problem, we know that the total number of configurations of a linear polymer in a good solvent is [1]

\[
P(N) \sim N^{\nu - 1}
\]

where \( \gamma_L \) is the exponent for susceptibility in the \( n = 0 \) problem [2]. Comparing (17) and (24) leads to

\[
\theta_L = 1 - \gamma_L.
\]

It is interesting to note that since hyperscaling is valid here, relation 20 is the same as the one found by Stauffer [17] for a « real » gelation problem - (polycondensation of multifunctional units). In problems where the usual hyperscaling relation \((2 - \alpha = \nu d)\) is not valid, one obtains [14] different relations between \( \nu \) and \( \theta \). Note also that (23) is not valid for \( d = 3 \), where hyperscaling is violated.
the dilute solutions are exactly the same as those of
a monodispersed solution with molecular weight
$N \sim N_w \sim \tilde{N}$.

3. Conclusion.

We have considered a polydisperse melt of linear
chains made by condensation of bifunctional monomers. The distribution of molecular weights depends
on the extent of chemical reaction and has been calculated long ago. In this kind of melt, the main contribution to the density comes from chains with molecular weight of the order of the average molecular weight (here $N_w \sim \tilde{N}$). These act as a good solvent for the very large chains present in the system ($N \gg N^2$).

The properties of the shorter chains are the same as those of a melt of monodisperse polymers with molecular weight $\tilde{N}$. On the other hand, the large chains are swollen for large distance scales. On smaller distances, however, the short chains screen out the excluded volume interaction. We may define a screened blob with size $s_c \sim N_w$ dependent on the extent of reaction. If we now add a good solvent, the total monomer concentration being in the semi-dilute range ($C > N_w^{-4/5}$), we may generalize our results: one has to take as a step length a concentration blob with size $s_c \sim C^{-3/4}$. Then it is easy to show that

$$R_t^2 \sim N_w C^{-1/4}$$

$$R_c^2 \sim N^{3/5} N_w^{-1/5} C^{-3/8}$$

The cross-over between typical and long chain behaviour occurs now for

$$N^* \sim N_w^2 C^{5/4}.$$ 

Again, the situation is very much the same as for a very long chain in a semi-dilute solution with shorter chains of molecular weight $N_w$ [9, 18]. The corresponding experiments may be done by adding some labelled chains-deuterated or heavier for neutron or light scattering respectively to the solution.

A final remark may be done about the viscosity of the melt. This is due to typical chains mainly. We have seen above that the critical dimension for these is $d_c = 2$. This implies that polydispersity effects cannot lead to an anomalous exponent (such as 3.4) for the viscosity, the possible hydrodynamic effects being classical [19].

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