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Bimodal distribution in branched polymer solutions

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1. Introduction. — Consider a melt of randomly branched polymers [1-3] where one molecule is labelled, and has $N$ monomers while all the others are not labelled and have $P$ elements. We will only look at the case when $P$ is smaller than or equal to $N$.

When $P$ and $N$ are the same order, we have a conventional melt, which we studied previously [3]: the structure of the labelled chain is condensed, and its radius of gyration $R$ varies as

$$R \sim N^{1/3} l$$

where $l$ is the step length (we restrict our attention to the case where the dimension of space is 3). On the other hand, when $P$ is of order unity, we have a dilute solution of the large macromolecule in what we suppose to be a good solvent. Then the structure of the chain is swollen, and we have instead of (1)

$$R \sim N^{1/2} l.$$ (2)

In this paper we would like to study the swelling of the large probe chain when the molecular weight of the matrix is decreased.

Another point of interest lies in the interpenetration of the molecules when $P$ is varied. Here again in the two limits considered above one can see very easily that in a conventional melt, as shown by relation (1), there is no interpenetration of the different molecules [2], whereas when $P$ is of order unity the solvent penetrates completely the large chain. So it might be interesting to look at the gradual interpenetration of the chains during the swelling of the probe molecule.

In section 2 we will summarize the properties of solutions of monodispersed branched chains in the more general case when they are made of both bi- and trifunctional units. The parameters then are the monomer concentration $C$ (or rather the volume fraction $\phi = C l^3$) and the activity $A^2$ of the trifunctional units [1, 3]. Section 3 deals with the swelling of a large chain in a melt made of smaller molecules when their size $P$ is decreased. The generalization to a semi-dilute solution, where the matrix is a mixture of small chains and a good solvent is given in section 4.

Throughout the paper by molecule, chain, polymer, ..., unless otherwise specified, we will always mean branched structures.

2. Monodispersed solutions. — In the next two sections, what will be considered as the solvent of the large molecule is itself a solution of shorter chains in a real solvent. So it is useful to recall briefly in this section the properties of a monodispersed solu-
tion of branched chains made of $P$ units. For more
details, the reader is referred to (3).

The molecules we consider are made of both bi-
and tri- (multi)-functional units. We only consider 
randomly branched chains. By this, we mean that the activity $A^2$ of the multifunctional units is held con-
stant during the formation of the molecule [1, 8, 9].
Then it has been shown [1, 8] that the fraction of 
branching units is just $A$. This is turn implies that 
the linear parts between two trifunctional units has 
on average $A^{-1} P$ units.

For a chain in a dilute solution, it has been shown 
recently with a Flory-type approach that in a good 
solvent the radius of gyration behaves as [4]
\[ R \sim P^{1/2} A^{-1/10} l \]  
for the usual three dimensional polymers, to which 
we restrict our attention here. Relation (3) is basic-
ally valid as long as the monomer concentration is 
less than the « contact » concentration $C^*$, when the 
distance between centres of gravity of neighbour 
chains is of the order of the radius of a chain :
\[ C^* \sim \frac{P}{R^3} \sim P^{-1/2} A^{3/10} l^{-3}. \]  
The regimes of interest in this paper are those more 
concentrated than $C^*$.

1) For concentrations between $C^*$ and the overlap 
concentration $C$ (region III in figure 1), there is 
no overlap of the molecules. When $C$ is increased, 
the molecules condense and remain in contact with 
each other. Then we may define three different length 
scales and different behaviours of the chain :
a) Very locally, we have the linear parts, with 
$g_A \sim A^{-1} P$ elements (see above). This is the so called 
linear blob. In this regime, as in a dilute solution, it is swollen :
\[ \xi_L \sim g_A^{3/5} l \sim A^{-3/5} l. \]  

\[ \text{Fig. 1.} \quad \text{The phase diagram of a monodispersed solution :} \]
\[ \text{the different regimes are : I : dilute linear; II : dilute bran-

ched; III : semi-dilute, non overlapping; IV : semi-dilute, 
overlapping; V : semi-dilute, linear.} \]

b) For larger distances, the branched structure is seen, but the concentration effects are not yet impor-
tant. This corresponds to the concentration blob, 
with $g_c$ elements, which has the same behaviour as a 
single chain. In this regime, in contrast to what 
happens for concentrations above $C$, this blob is 
branched. The number of elements $g_c$ may be obtained 
by a generalization of relation (4). We get
\[ g_c \sim \phi^{-2} A^{3/5} \]  
and, from (3)
\[ \xi_c \sim \phi^{-1} A^{1/5} l \]  
where $\phi \equiv C l^3$ is the volume fraction.

\[ \text{Note that at } C^*, g_c \text{ is of the order of } P, \text{ and the} \]
\[ \text{concentration blob is the whole molecule. On the} \]
\[ \text{other hand, when } g_c \sim g_A, \text{ we cross-over to a regime} \]
\[ \text{where the concentration blob is linear : this corres-
ponds to } C \sim C^* \sim A^{4/5} l^{-3}. \]

Finally, the molecule is a condensed ensemble 
of concentration blobs.
\[ R \sim \left( \frac{P}{g_c} \right)^{1/3} \xi_c \sim \left( \frac{P}{C} \right)^{1/3}. \]  
It is easy to check with relation (7) that different 
molecules do not interpenetrate in this regime.

2) For higher concentrations ($C > C^*$), as men-
tioned above, the concentration blob is linear, and 
smaller than the linear blob (region IV in figure 1).
In this regime, the semi-local behaviour (concentration 
blob) is controlled by the linear parts, and there is 
some overlap of the different macromolecules. We 
find three different distance scales with different 
behaviours :
a) Very locally, we find first the concentration 
blob, which is linear in this regime. From what we 
known about linear polymer solutions in a good 
solvent [2, 10], we have
\[ g_c \sim \phi^{-5/4} \]
\[ \xi_c \sim \phi^{-3/4} l. \]  
Inside this blob the behaviour is the same as for a 
single linear polymer.

b) For intermediate distances, inside the linear 
blob with $g_A$ elements, excluded volume effects are 
screened and the behaviour is roughly ideal. This 
leads to
\[ \xi_L \sim A^{-1/2} \phi^{-1/8} l. \]  
c) Finally, the macromolecule is made of a con-
densed ensemble of linear blobs :
\[ R \sim \left( \frac{P}{g_A} \right)^{1/3} \xi_L = P^{1/3} A^{-1/6} \phi^{-1/8} l. \]  
The reader may check easily that there is a significant 
overlap in this regime.
In this brief description, it is supposed that the solvent is a very good solvent of both bi- and multi-functional units. As we are going in next section to look at the case $A = 1$ (only multifunctional units), it is interesting to note that for such polymers, there is no overlap at any concentrations regime III extends from the contact concentration $C^*$ up to the melt (see Fig. 1).

3. Bimodal melt. — Before we look at the general case of solutions in next section, we first study in this part the case when there is no solvent. So we consider a melt made of one large chain with $N$ monomers dissolved in smaller molecules made of $P$ units of the same chemical nature. We look for the configuration of the probe molecule.

3.1 Purely Branched Melts. — 3.1.1 The swelling. — We first restrict our attention to the case $A = 1$. The polymers are thus made of trifunctional units only. When $N \sim P$, the configuration is condensed and has been described above. The radius of gyration is

$$R_N \sim N^{1/3} l \quad (11)$$

and the different molecules do not overlap.

On the other hand, when $P \ll N$, we may consider the short chains as a solvent. We suppose the monomers to be a good solvent of the large chain. For larger solvent molecules, with $P$ monomers, there is a screening of the excluded volume effect. The free energy of the probe molecule may be written \[11, 12, 14\] :

$$F = \frac{R^2}{N^{1/2} l^2} + \frac{N^2}{PR^3} \quad (12)$$

and, minimizing (12) we find for the radius

$$R_N \sim N^{1/2} P^{-1/5} l \quad (13)$$

when the size $P$ of the solvent molecules is increased, there is a deswelling of the probe chain. The cross-over between the dilute behaviour and the melt behaviour is obtained by comparing (11) to (13) : We find a cross-over value for $P$

$$P^* \sim N^{5/6} \quad (14')$$

3.1.2 Local behaviour. — If the small molecules are larger than $P^*$, the excluded volume interaction is screened out, and the behaviour of the probe chain is the same as in a melt (relation (11)). When the solvent chains are smaller than $P^*$ on the other hand, there is a cross-over to a swollen conformation of the large macromolecule. Then we may address the question whether this swelling is valid at any scale on the probe. Let us first suppose that this is true, and that relation (13) may be generalized to any part of the macromolecule containing $n$ elements : the radius of such a part would be

$$r_n \sim n^{1/2} P^{-1/5} l \quad \text{(15)}$$

Then one may ask for the self contribution of the chain to the concentration inside the sphere of radius $r_n$

$$C_s \sim \frac{n}{r_n^3} \sim n^{-1/2} P^{3/5} l^{-3} \quad \text{(15')}$$

This is an increasing function when decreases, equal to $l^{-3}$ when $n \sim N_c$. It is clear that (15') and thus (15) are valid only as long as $n > N_c$. We note that for parts with $N_c$ elements the structure is indeed condensed : from (15) we get

$$\chi \equiv r_{n_c} \sim N_c^{1/3} l \quad \text{(15'')}$$

Thus for distances smaller than $\chi$ we find that the conformation is different from the large scale behaviour. This defines the «condensed» blob with $N_c$ units and size $\chi$ where screening effects are present

$$N_c \sim P^{6/5} \quad (41)$$

$$\chi \sim P^{2/5} l \quad (16)$$

Then for distances smaller than $\chi$, the behaviour is different from the large scale behaviour, and there is no local interpenetration of the long chain by the solvent chains. The probe macromolecule may be represented as a single branched chain in a good solvent [3-7] if we take the condensed blob as unit step :

$$R_N \sim \left(\frac{N}{N_c}\right)^{1/2} \chi \sim N_c^{1/2} P^{-1/5} l \quad (17)$$

3.1.3 Scattering experiments. — This behaviour may be checked by small angle neutron scattering experiments :

- For small values of the scattering vector $q$, $R^{-1} < q < q^*$, where the cross-over occurs around the reciprocal of the blob radius, the scattered intensity, in an experiment where the long chain is labelled, shows the swollen nature of the chain

$$S(q) \sim q^{-2} P^{2/5} (R^{-1} < q < q^*) \quad \text{with} \quad q^* \sim \chi^{-1} \quad (17)$$

- For larger values of $q$, the neutrons probe the interior of a blob. Depending on the exact shape of the density inside the blob, one may get either a $q^{-4}$ law if the density profile is sharp, or a $q^{-3}$ intensity if the profile is smooth. In both cases, there is a significant difference between the two regimes, above and below $q^*$ which can be seen very easily in a neutron scattering experiment. Moreover, it would be very interesting to know the scattered intensity at large values of $q$ ($q > q^*$) in order to have a more precise idea about the density profile inside a blob.

Note that these experiments are much easier to perform than the equivalent ones on linear polymer chains. In the latter case, the cross-over length $P^*$ varies as $N^{1/2}$ [13, 14] instead of $N^{5/6}$ here, so that one has to use huge probe molecules to be sure that
the short $P$ chains are still macromolecules. This difficulty is much less dramatic for branched chains.

3.2 General case : $A < 1$. — We generalize the preceding discussion to the more general case where the branched chains are made of both bi- and trifunctional units : we suppose that the activity of the multifunctional units is less than unity. As we will see, there are two different mechanisms (at least) depending on the branching of $P$ : we know that we have linear blobs with $g_A \sim A^{-1}$ elements. Thus if $P$ is larger than $A^{-1}$, the matrix molecules are branched. Then we can reduce the problem to that studied in the preceding section. On the other hand, when $P$ is smaller than $A^{-1}$, the matrix is in fact made of linear chains. Then the question is in fact the screening of the linear blobs by the solvent chains, which has already been studied by Flory [13] and de Gennes [14].

Let us stress again at this point that we suppose that the matrix molecules and the probe chain are the same chemically : there is only one value for $A$ for both constituents.

3.2.1 Branched solvent chains. — In the following we will suppose that the size $N$ of the large molecule is fixed and that we vary the size of the matrix polymers. Let us first suppose that $P$ is of the order of $N$ : we are dealing with a monodisperse melt. We may define a linear blob which is ideal

$$\xi_L \sim g_A^{1/2} l \sim A^{-1/2} l.$$  \hfill (18)

We have seen in section 1 that the probe chain is condensed if we take the linear blob as statistical unit :

$$R_N \sim \left( \frac{N}{g_A} \right)^{1/3} \xi_L \sim N^{1/3} A^{-1/6} l.$$  \hfill (19)

In fact, the whole problem reduces to the one studied in 2.1. If we take the linear blob as statistical unit. This is done by replacing $N$, $P$ and $l$ by $N/g_A$, $P/g_A$ and $\xi_L$ respectively. We summarize the results : there is a cross-over between the melt behaviour described above (relation (19)) and a swollen regime. The cross-over occurs for

$$N \sim P^{6/5} A^{1/5}.$$  \hfill (20)

When the matrix chains are too short ($P < P^*$), the large chain is swollen at large distance scales

$$R_N \sim N^{1/2} P^{-1/5} A^{-1/5} l.$$  \hfill (21)

3.2.2 Linear solvent chains. — The analysis given above does not hold any longer when the short chains are not branched, i.e. when $P$ becomes smaller than $A^{-1}$. Thus when $P \sim A^{-1}$, if we consider the number of elements in the condensed blob, we find that $N_c \sim A^{-1}$ : the blob becomes itself linear :

$$\chi \sim P^{2/5} A^{-1/10} l.$$  \hfill (22)

For distances smaller than $\chi$ the structure is condensed.

Note that in both regimes the short chains are branched, as are the condensed blobs : in both cases the radius of the short chains is

$$R_p \sim P^{1/3} A^{-1/6} l.$$  \hfill (23)

More locally, there is a condensed blob made of $N_c \sim P^{6/5} A^{1/5}$ units, with radius

$$\xi_L \sim g_A^{1/2} l \sim A^{-1/2} l.$$  \hfill (24)

Note that in this regime, the size of the large chain is exactly the same as if there were no linear parts inside.

Finally, when $P < A^{-1/2}$, the linear blob itself is swollen

$$\xi_L \sim g_A^{3/5} P^{-1/5} l$$  \hfill (25)

and the radius of the large chain is

$$R_N \sim \left( \frac{N}{g_A} \right)^{1/2} \xi_L \sim N^{1/2} A^{-1/10} P^{-1/5} l.$$  \hfill (26)

When $P$ becomes of order unity, we get back the usual relation for a branched chain in a good solvent. Note also that when $N \sim A^{-1}$, we get the correct cross-over to the linear chain behaviour. The different regimes are summarized in table I.

<table>
<thead>
<tr>
<th>$P$</th>
<th>$R_N$</th>
<th>$\chi$</th>
<th>$R_P$</th>
<th>$\xi_L$</th>
</tr>
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<tbody>
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<td>$P &gt; P^*$</td>
<td>$N^{1/3} A^{-1/6}$</td>
<td>$P^{1/3} A^{-1/6}$</td>
<td>$A^{-1/2}$</td>
<td></td>
</tr>
<tr>
<td>$A^{-1} &lt; P &lt; P^*$</td>
<td>$N^{1/2} P^{-1/5} A^{-1/5}$</td>
<td>$P^{1/3} A^{-1/6}$</td>
<td>$A^{-1/2}$</td>
<td></td>
</tr>
<tr>
<td>$A^{-1/2} &lt; P &lt; A^{-1}$</td>
<td>$N^{1/2}$</td>
<td>$P^{1/2}$</td>
<td>$A^{-1/2}$</td>
<td></td>
</tr>
<tr>
<td>$P &lt; A^{-1/2}$</td>
<td>$N^{1/2} A^{-1/10} P^{-1/5}$</td>
<td>$A^{-3/5} P^{-1/5}$</td>
<td>$A^{-1/2}$</td>
<td></td>
</tr>
</tbody>
</table>

Table I. — Different behaviours in a bimodal melt for a fixed value of $N$ and a varying length $P$ of the matrix polymers.
4. **Bimodal solutions.** — We turn now to the case of semi-dilute solutions. In the following, we suppose that we have one large probe chain dissolved in a mixture of a good solvent and shorter chains. The monomer concentration is above the contact concentration $C^*$

$$C^* \sim p^{-1/2} A^{3/10} l^{-3}.$$  

(4)

As can be seen on figure 1, we may consider either the overlapping or the non overlapping regime. We stress that this is specific to the short $P$ chains. The basic difference between a semi-dilute solution and a melt lies in the existence, for short distances, of a concentration blob. This may be either linear (region IV in figure 1) or branched (region III). This remark tells us how to proceed: a change of scales where we take the concentration blob as a "renormalized" unit leads us back to a melt that was studied in sections 3.2 and 3.1 respectively and takes care of the solvent effects.

4.1 **Non overlapping regime** : $C^* \leq C \leq \bar{C}$. —

Let us first consider the case when the solution is represented by a point in region III on figure 1. The main characteristics of this region are summarized in section 2. The large chain may be described as a condensed ensemble of branched blobs, which may be taken here as statistical units:

$$R_N \sim \left( \frac{N^*}{g_e} \right)^{1/3} \xi_e \sim \left( \frac{N}{C} \right)^{1/3}$$  

(27)

where $g_e$ and $\xi_e$ are the number of elements and the size of a concentration blob (relations (6)). In fact, the only difference between this case and the one studied in section 3.1 lies in the nature of what is taken as a statistical unit. Whereas in last section, it was the monomer, here it is rather the concentration blob with size $\xi_e$ that has to be used as a renormalized segment [3]. Once this has been recognized, one has just to generalize the results of section 2.1. For instance the cross-over between the swollen and condensed regimes is found from relation (14):

$$\left( \frac{N^*}{g_e} \right) \sim \left( \frac{P}{\phi_e} \right)^{6/5}$$

and thus the cross-over length above which the probe chain is swollen is, using relation (6')

$$N^* \sim p^{6/5} \phi^{2/5} A^{-3/25}.$$  

(28)

All the results in section 2.1 may be generalized in the same straightforward way. We summarize them.

When the size of the probe chain is large ($N \gg N^*$), the molecule is swollen at large distance scales. Its radius is

$$R_N \sim N^{1/2} \phi^{-1/5} A^{1/50} l (\phi_e \leq \phi \leq \bar{\phi}).$$  

(29)


\[ \text{Fig. 2. — Schematic representation of the different behaviours for different scales of a large probe chain dissolved in a non overlapping semi-dilute solution of shorter chains. The different behaviours are as follows: I: linear, swollen; II: branched, swollen; III: branched, condensed; IV: branched, swollen.} \]

For smaller scales (1) the configuration becomes more dense. We may define a condensed blob, with $N_e$ elements

$$N_e \sim p^{6/5} \phi^{2/5} A^{-3/25}$$  

(30)

and a size

$$\chi \sim p^{2/5} \phi^{-1/5} A^{-1/25} l.$$  

(31)

The conformation of the large macromolecule is given schematically on figure 2 in this regime: the swollen chain is made of condensed blobs with size $\chi$. The more local conformation is the same as described in section 2.

One way to have a formal check of the above analysis is to suppose now that $N$ is fixed and that $P$ is decreased. Starting from the « condensed » conformation of the probe chain, there is first the cross-over to the swollen behaviour described above. The corresponding cross-over value for $P$ is obtained directly from relation (28). If we keep on decreasing $P$, relation (4) shows that the contact concentration $C^*$ increases. There comes a point when

$$C \sim C^* \sim P_{\downarrow}^{-1/2} A^{3/10} l^{-3} \quad \text{i.e.} \quad P_{\downarrow} \sim \phi^{-2} A^{3/5}$$

and there is a cross-over to a dilute regime. We may check on relation (29) that for such a value of $P$, the radius of the probe chain

$$R \sim (P_{\downarrow}) \sim N^{1/2} A^{-1/10} l,$$

crosses-over to what is expected in a dilute regime. Note also that the condensed blob has then a size $\chi$ of the order of the concentration blob and crosses-over to the size of the solvent chain

$$\chi(P_{\downarrow}) \sim \xi_e(P_{\downarrow}) \sim P_{\downarrow}^{1/2} A^{-1/10} l.$$  

4.1.1 **The overlap.** — We discuss briefly the overlap of the different chains. Clearly, the short chains are not concerned since their overlap properties are governed only by the values of $C$ and $A$ [15]. When $N \sim P$, the short chains do not overlap the probe molecule. This holds true as long as $N \lesssim N^*$. When $N$ is very large, $N > N^*$, the self contribution of the

(1) Larger than the size $\xi_e$ of the concentration blob.
large polymer to the concentration inside the sphere of radius $R_N$ is
\[
\phi_s \sim \frac{N}{R_N^3} \sim N^{-1/2} P^{3/5} \phi^{6/5} A^{-3/50}
\]  
and is smaller than the total concentration. So there is an overlap with the shorter chains in order to keep the concentration constant. The number $p$ of small macromolecules in the sphere is
\[
p \sim \frac{N}{P} \left( \frac{C}{C_s} - 1 \right)
\]
and becomes large when $N \gg N^*$
\[
p \approx C \frac{R_N^3}{P} \sim \frac{N}{P} \left( \frac{N}{N^*} \right)^{1/2}
\]  

4.2 Overlapping regime : $C \geq \tilde{C}$. — We turn now to more concentrated — or less branched — solutions with $C \geq \tilde{C}$. Then there is an overlap of the short chains, but the conformation of the chains is still condensed (see section 2 and reference [3]). The properties of the chains in this regime can be reduced to those of a melt with $L < 1$ if we take the linear concentration blob as a statistical unit. For instance, the radius of the probe chain is
\[
R_N \sim \left( \frac{N}{g_c} \right)^{1/3} \left( \frac{a_c}{g_c} \right)^{1/6} \xi_e
\]
where $g_c$ and $\xi_e$ are given now by relations (8), and thus
\[
R_N \sim N^{1/3} A^{-1/6} \phi^{-1/8} l.
\]
Taking then the concentration blob as basic scale leads us back to the bimodal melt studied in section 3.2. It is then straightforward to make the generalization. We just give the results.

4.2.1 Branched short chains. — Starting with $N$ and $P$ of the same order, we keep $N$ fixed and decrease $P$. The cross-over to a swollen behaviour for the probe chain occurs for a value $P^*$ given by
\[
N \sim P^{6/5} A^{1/5}.
\]
When $P$ is smaller than $P^*$, the large chain is swollen at large distances. Its radius is
\[
R_N \sim N^{1/2} P^{-1/5} A^{-1/5} \phi^{-1/8} l.
\]
Note that when $\phi$ goes to unity we recover the results we obtained above (cf. relation (21)) in the melt.

For small scales we may define a condensed blob with $N_c$ units
\[
N_c \sim P^{6/5} A^{1/5}
\]
and with radius
\[
\chi \sim N_c^{1/3} A^{-1/6} \phi^{-1/8} l.
\]
Let us recall that this blob has a branched structure. The reader may also check that relations (36), (37) cross-over smoothly to (30) and (32) respectively in the non overlapping regime, for $\phi \sim \phi (\sim A^{4/5})$.

We come back to the condensed blob. It is branched as long as
\[
N_c A \gg 1 \text{ i.e. } (PA)^{6/5} \gg 1
\]
i.e. as long as the short chains are.

4.2.2 Linear short chains. — When $PA < 1$, the solvent chains are linear, and they may have an effect on the behaviour of the linear blob. The latter is ideal as long as $[14] P > A^{-1/2} \phi^{-5/8}$. Thus there is a regime, when $A^{-1} > P > A^{-1/2} \phi^{-5/8}$ where the linear blob is ideal, and where the local condensed blob described just above (Eq. (37)) is no longer present : one may check that for $P \sim A^{-1}$, the condensed and linear blobs coalesce
\[
\chi(P \sim A^{-1}) \sim \xi_L \sim A^{-1/2} \phi^{-1/8} l.
\]
Then the radius of the probe chain may be written
\[
R_N \sim \left( \frac{N}{g_A} \right)^{1/2} \xi_L \sim N^{1/2} \phi^{-1/8} l.
\]
In this range for $P$, there is no equivalent for the condensed blob : as the short chains are linear (and small), they have no influence on a scale larger than the distance between trifunctional units. When $P$ becomes less than $A^{-1/2} \phi^{-5/8}$, the linear blob itself swells [12, 17]. Its radius is
\[
\xi_L \sim A^{-3/5} P^{-1/5} \phi^{-1/4} l \quad (P \ll A^{-1/2} \phi^{-5/8})
\]
and the probe chain is swollen :
\[
R_N \sim \left( \frac{N}{g_A} \right)^{1/2} \xi_L
\]
\[
\sim N^{1/2} P^{-1/5} \phi^{-1/4} A^{-1/10} l.
\]
This is the only regime where we can look at the cross-over to linear chain behaviour of the probe chain : in order for the latter to become linear ($AN \sim 1$), the shorter $P$ chains have to be already linear. Clearly when $A N \sim 1$, relation (40) crosses-over smoothly to the linear behaviour [14, 17].

4.2.3 Local behaviour. — On a smaller scale, we may define an ideal linear blob with $n_e$ elements
\[
n_e \sim P^2 \phi^{5/4}
\]
and size
\[
\chi \sim n_e^{1/2} \phi^{-1/8} l.
\]
It is of interest to look at the limit when this blob becomes of the order of the concentration blob $\xi_e$. Comparison of (41) and (8) gives
\[
P \sim \phi^{-5/4}
\]
which is the overlap concentration for the solvent chains. As we were decreasing $P$, the concentration $C^*$ increased, and if we keep decreasing $P$, the solution would become dilute. Note that when (42) holds, $\chi$ and $\xi_c$ become of the order of the radius $R_p$ of the solvent chains. Note also that the radius of the probe chain, cf. relation (40), crosses-over to the dilute chain limit, relation (3) (with $N$ replacing $P$).

5. Conclusion. — We have studied a particular bimodal branched polymer solution where one (or some) large chains are dissolved in a solution of shorter macromolecules in a good solvent. All the chains are branched and are of the same chemical species: by this we mean that the fraction $A$ of branch points is the same for both. We find basically two regimes depending on the lengths of the macromolecules: whereas when $N$ and $P$ are the same order, the large chains are condensed ($R_N \sim N^{1/3}$), there is a swelling of the probe chain ($R_N \sim N^{1/2}$) when the molecular weights differ significantly. For a fixed value for $P$ the cross-over value for $N$ varies as

$$N^*_B \sim P^{6/5}. \quad (43)$$

This can be compared with the Flory-de Gennes result for linear chains [13, 14]: in the equivalent problem for linear polymers, the cross-over value for $N$ between a swollen and an ideal behaviour varies as

$$N^*_I \sim P^2. \quad (44)$$

Thus from an experimental point of view, it is much easier to reach the cross-over with branched polymers than with linear chains [18]. On the other hand, because the exponent in relation (43) is close to 1, the domain where the chain is condensed when $N$ and $P$ are close to each other is rather small, and it is probably not easy to study. But the region where the probe chain is swollen is very large, and thus very easy to investigate. Thus for these branched systems, it should be easier to look at the regime where the chains are swollen and to check both the radius of gyration of the probe chain and the monomer correlation functions by light and neutron scattering experiments on purely branched polymers ($A = 1$).

For randomly branched macromolecules with a finite fraction of trifunctional units ($A < 1$), different regimes may be found, and it would be interesting to check these different behaviours. Of particular interest is the case when the long branched chain is dissolved in small linear chains ($P < A^{-1}$) and a good solvent. Then the solvent chain molecules are predicted to have an influence only on the linear parts of the probe chain but not on the branched structure. There results a typical law for the radius, relation (38), which may also be checked by small Angle Neutron scattering experiments.

Finally, the above results suggest one possible difficulty about experiments on monodisperse melts: usual distributions are always polydisperse. Because of the small value of the exponent in relation (43), there is a part of the molecules which are below $N^*$ and are thus good solvents of any labelled molecule. This could lead to possible difficulties in the interpretation of some experimental results, for instance if the labelled chains belong to the high molecular weight part of the distribution.

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References

[15] Except when $P$ is smaller than $A^{-1}$, where they do overlap, We do not consider this case.
[16] The basic difference between the branched and linear chains is that the screening effects make the chain ideal for the latter, whereas the ideal Zimm-Stockmayer behaviour cannot be reached for $d = 3$ and the deswelling stops at the condensed state with $R \sim N^{1/3}$.