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Phase Separation in Branched Polymer Solutions

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ABSTRACT: For low space dimensions, the conventional Flory–Huggins theory fails to describe accurately the phase separation that occurs at low temperatures in polymer solutions. Two-dimensional linear chains and three-dimensional randomly branched polymers belong to this category. We give a scaling approach to the collapse of a single polymer chain and to the phase separation for both cases. The results differ drastically from the classical results: For the critical point we find for two-dimensional linear chains $\tau_c \sim N^{-2/3}$ and $C_c \sim N^{-1/3}$ and for three-dimensional branched chains $\tau_c \sim N^{-11/16}$ and $C_c \sim N^{-5/16}$, where N is the molecular weight, C the monomer concentration, and τ the reduced temperature, $|(T-\Theta)|/\Theta$. A law of corresponding states is obtained for systems with different molecular weights. On the high-concentration side of the coexistence curve we find $C \sim \tau^{1/2}$ and $C \sim \tau^{5/11}$ for the two cases quoted above. We also study the crossover between the "branched" and "linear" behavior for branched chains made of both bi- and trifunctional units when the fraction of branch points is varied.

I. Introduction

There has recently been renewed interest in the configurational properties of large randomly branched polymers.[1–7] The conformation of a single such macromolecule in a good solvent has been worked out[2–5] with a Flory-type theory and ϵ expansion, where $\epsilon = 8 - d$ (d, *dimension of* space), giving results in good agreement with computer simulations and an exact result derived by Parisi and Sourlas[7] for $d = 3$. The Flory theory has also been applied to Θ solvents. Here, the temperature Θ is defined[19] as the limit as the number N of units tends to infinity of the temperature where the second virial coefficient vanishes. An alternative definition is the limit of the temperature of the critical point of the phase separation curve, in the same $N \to \infty$ limit.

For good and Θ solvents, the classical results, derived earlier by Zimm and Stockmayer,[8] are recovered only for d larger than or equal to 8 and 6, respectively.

For lower quality solvents, as for any binary mixture, we expect a phase separation to occur. The aim of this paper is to study this demixing. From what has been said above concerning the Θ point, we expect that there should be large deviations from a Flory–Huggins[9] type of approach. The reasons lie in the approximations involved in such a theory: (i) The polymers are supposed to overlap very strongly in the concentrated regime. (ii) Fluctuations are neglected and the results are on the level of a mean field theory.

Branched polymers do *not* overlap strongly in the concentrated regime for d less than 4,[5] which are of interest. Moreover, because the critical dimension in the Θ regime is 6, we can expect fluctuations to be important for actual systems. For $d = 6$, the Flory–Huggins approach should be adequate.

At this point, we note that a similar situation occurs for *linear* chains in two dimensions. In this case, it was pointed out recently that a polymer has its ideal Gaussian configuration only for space dimensions at least equal to 3.[10] So we expect fluctuations to be important for $d = 2$. Further,[15] concentrated linear-chain solutions in two dimensions do not interpenetrate strongly. Again, as for branched polymers, we expect the phase separation curve for two-dimensional linear systems to be different from the Flory–Huggins predictions.

In this paper, our aim is to give a description of the phase separation at the level of a Flory-type theory. It turns out that knowledge of the behavior of a *single* polymer chain, linear or branched, in solution is sufficient to provide both the location of the critical point of the coexistence curve and a law of corresponding states relating different molecular weights.[11] For the single-chain problem we will use the Flory approach to provide the various exponents required. Then a scaling theory is constructed for the phase separation curve. While we do not expect the exponents to be exact, we expect them to be sufficiently accurate[12] to provide *a fair description* of the coexistence curve and of the collapse of a chain.

In section II, we briefly recall the properties of branched chains in good and in Θ solvents. Section III is devoted to the phase separation at low temperatures. Finally, in the last section, we consider the more general case of a polymer made of both bi- and trifunctional units. This allows us to look at the crossover to linear-chain behavior when the fraction of branching units becomes very small.

Note that throughout the paper, the free energy will always be expressed in units of k_BT.

II. Swelling of Branched Polymers

(1) Purely Branched Chains. Consider a randomly branched polymer made of N identical tri(multi)functional flexible units of length l (which may or may not be saturated). The statistics of such an "animal"[13] has been worked out by one of us[8] in the case when no interaction is present between units. The result for the radius of gyration is

$$R_0 \sim N^{1/4} l \tag{1}$$

For the large polymers we consider here and for usual dimensions d of space, this unperturbed radius is too small, i.e., the monomer density diverges as $N^{(4-d)/4}$, and one has clearly to take into account the interactions between segments.

(a) Good Solvents. Let us then introduce the excluded volume parameter[9,14] $v(T)$. We may write a Flory-type free energy for the chain:[9,15]

$$F = \frac{R^2}{R_0^2} + v\frac{N^2}{R^d} \tag{2}$$

where the first term is the elastic contribution and the second the excluded volume interaction. R_0 and R are the

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unperturbed and actual radii, respectively. Minimizing with respect to R, we find

$$R \sim N^{\nu} l \tag{3}$$

where

$$\nu = 5/[2(d + 2)] \tag{3'}$$

This agrees with the $^1/_4$ exponent of the classical theory[8] for large values of d ($d \geq 8$). This result is in good agreement with computer simulations[3] and is exact for $d = 3$, where an equivalence with an exactly soluble problem[7] has been found. For completeness, we note that a similar approach applied to *linear* chain (i.e., $R_0 \sim N^{1/2}$ instead of $N^{1/4}$) leads to the usual Flory exponent for linear chains:

$$\nu^{\mathrm{L}} = 3/(d + 2) \tag{4}$$

(b) Θ Solvent. Let us now consider the case when the excluded volume parameter vanishes: $v(\Theta) = 0$. This corresponds to a Θ solvent. One has then[26,27] to take into account the three-body interaction. The free energy may be written as

$$F = \frac{R^2}{R_0^2} + w\frac{N^3}{R^{2d}} \tag{5}$$

where w is a positive constant. Minimization leads to

$$R \sim N^{\nu_\Theta} l \tag{6}$$

$$\nu_\Theta = 7/[4(d + 1)] \tag{6'}$$

Now the classical behavior is recovered only for space dimensions larger than $d = 6$. Note that for linear chains this leads to

$$\nu_\Theta{}^{\mathrm{L}} = 2/(d + 1) \tag{7}$$

Relation 7 implies a power law dependence for two-dimensional systems in the Θ regime that appears to differ from some recent computer simulations.[16] It would be very interesting to check this value experimentally, for instance, by osmotic pressure measurements in the semidilute range.

We conclude this part by noting that we expect large deviations from mean field results both for actual branched polymer solutions ($d = 2, 3$) and for two-dimensional linear-chain solutions.

(2) General Case. As we will consider the crossover from purely branched to linear chains for the coexistence curve, let us consider now the behavior of a more general chain made of both bi- and trifunctional units.[5] Let Λ^2 be the activity of the branching points during the formation of the polymer. We suppose it remains constant during the whole process. Then the fraction of branching points in the chain has been shown[8,17,18] to be Λ. The average number of bifunctional units between two branch points is Λ^{-1}.[5] Then for this general case, we define linear blobs, made of $g_\Lambda \sim \Lambda^{-1}$ elements. Taking these blobs as step length allows us to recover to the purely branched case we considered above. Let ξ_{L} be the radius of a linear blob. The radius of the polymer is

$$R \sim (N/g_\Lambda)^{\nu} \xi_{\mathrm{L}} \tag{8}$$

where ξ_{L} is related to g_Λ by the usual relations for linear chains. In all the following wherever we discuss this kind of polymer, we shall *always* suppose that the linear and branched parts have the *same* Θ point. This will make our expressions simpler without altering the essential physics. The results are, for a good and a Θ solvent

$$R \sim N^{\nu} \Lambda^{-1/[2(d+2)]} \qquad (d \leq 4) \tag{9}$$

$$R_\Theta \sim N^{\nu_\Theta} \Lambda^{-1/[4(d+1)]} \qquad (d \leq 3) \tag{10}$$

where ν is given by eq 3′ and ν_Θ by eq 6′.

Note that these relations are valid for dimensions less than 4 and 3, respectively, when the linear chains are swollen. For larger dimensions, which we do not consider here, the linear parts are ideal, and one has to get back to relation 8. Note also that relations 9 and 10 have the right crossover to the linear-chain behavior (within a Flory approach) when $\Lambda N \sim 1$. These relations will be helpful when we consider the crossover to linear chains for the demixing problem in section IV.

III. Collapse and Phase Separation

For temperature below[19] Θ, we expect first a Θ regime, the width of which decreases with increasing N, and then a regime of phase separation. We first consider linear-chain solutions.

(1) Two-Dimensional Linear Chains. The following considerations are quite general. But as we shall see, they lead to predictions widely different from the classical Flory–Huggins results only for two-dimensional systems. What we wish to do is provide a scaling approach to the phase separation process. Of course, this will not allow us to give a precise form for the phase separation curve. But we can locate the critical point, give a universal form for the curve when the molecular weight is varied, and predict its shape in the high-concentration region. In order to do this, we need to know how the chain crosses over from the Θ regime to either the collapsed or the swollen state.

(a) Collapsed State. Let us start with a single chain at the Θ temperature. Thus its radius is given by relations 6 and 7. If we now cool the system down, thus making an *attractive* segment–segment interaction $v(T)$, the polymer eventually collapses. We argue that the crossover from the Θ regime to the collapsed one occurs when attractive interaction of the chain is of order $k_{\mathrm{B}}T$. (As long as this is not realized, the attractive interaction may be considered as a perturbation, and the size of the chain is—apart from corrections—basically its Θ radius). Let v_{c} be that value of the excluded volume parameter for which the crossover occurs. As we will be interested only in temperatures below Θ, we will put

$$-v(T) \simeq l^d(\Theta - T)/\Theta \equiv \tau l^d \tag{11}$$

we find

$$\tau_{\mathrm{c}} \sim N^{-\phi} \tag{12}$$

where

$$\phi = 2 - \nu_\Theta{}^{\mathrm{L}} d \tag{12'}$$

and, using relation 7 for $\nu_\Theta{}^{\mathrm{L}}$

$$\phi = 2/(d + 1) \qquad (d \leq 3) \tag{12''}$$

which is one of our central results. This gives $\tau_{\mathrm{c}} \sim N^{-1/2}$ for $d = 3$, in agreement with previous results.[9,11] For $d = 2$, we find

$$\tau_{\mathrm{c}} \sim N^{-2/3} \tag{12'''}$$

It may be observed that in the derivation of eq 12″, we used the conventional procedure, which amounts to neglecting completely the effect of the attractive interaction before the crossover, thus extrapolating the unperturbed value for the radius at the Θ point—cf. eq 7—until the crossover. The crossover itself is determined by the importance of the attractive term that is neglected. The latter is supposed to take over beyond the crossover point. Thus the whole procedure amounts to extrapolating the asymptotic behaviors—Θ and collapsed—from both sides to determine a crossover point lying approximately in the middle of the crossover region.

For temperatures below τ_c, the chain is collapsed. In order to get its radius, we may use a scaling approach. The radius may be written in the general form

$$R \sim lN^{2/3}f(\tau N^{2/3}) \qquad (d = 2) \tag{13}$$

When its argument is large, $f(x)$ behaves as a power law

$$f(x) \sim x^{\alpha} \qquad (x \gg 1) \tag{14}$$

where α is determined by the requirement that the chain is collapsed:

$$R \sim lN^{1/2} \tag{15}$$

Combining (13)–(15) we get

$$R \sim N^{1/2}\tau^{-1/4}l \tag{16}$$

This might be checked by measuring the second virial coefficient in surface pressure experiments.[20]

An analysis in terms of blobs[21,22] provides a more detailed description: For temperatures not too far below Θ, we argue that the monomers are locally unperturbed by the υ interaction. The perturbation is substantial only for a "blob" of g monomers such that

$$|\upsilon|g^{2-\nu_{\Theta}^{\mathrm{L}}d} \sim 1$$

$$g \sim \tau^{-3/2} \tag{17}$$

Each blob has a Θ behavior; its size is given by relation 7:

$$\chi \sim g^{2/3}l \sim \tau^{-1}l \tag{18}$$

The linear chain itself is a condensed ensemble of blobs:

$$R \sim (N/g)^{1/2}\chi \tag{19}$$

Replacing g and χ by their expressions leads back to relation 16

$$R \sim N^{1/2}\tau^{-1/4}l$$

We finally note that ϕ is in rather good numerical agreement with ϵ expansion.[25]

(b) Phase Separation. Let us turn now to the coexistence curve when we lower the temperature in a solution with a monomer concentration C. As long as we are not too far from the Θ point, we may write a scaling form for the free energy. For two-dimensional systems it is, per unit volume

$$F = N^{-4/3}f[CN^{1/3},\tau N^{2/3}] \tag{20}$$

where f is an unknown function and the powers of N in its argument are just the values of the overlap concentration in the Θ regime and the crossover value υ_c calculated above. Similarly, the "osmotic" pressure may be written as

$$\pi = \frac{C}{N}g[CN^{1/3},\tau N^{2/3}] \tag{21}$$

The expressions above are the most general and are valid in all regimes. The spinodal curve and the critical point are obtained by differentiating either of these expressions.

For the critical point, we get two relations

$$h(CN^{1/3},\tau N^{2/3}) = 0 \tag{22}$$

$$i(CN^{1/3},\tau N^{2/3}) = 0 \tag{22$'$}$$

where $h(x,y)$ and $i(x,y)$ are unknown functions. For our purpose here, those two equations are sufficient to determine the location of the critical point, within some multiplicative constant of order unity:

$$C_c \sim N^{-1/3} \tag{23}$$

$$\tau_c \sim N^{-2/3} \tag{23$'$}$$

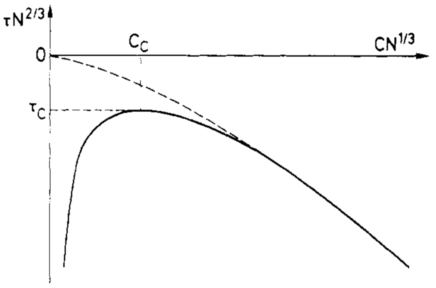

Figure 1. Coexistence curve for a solution of two-dimensional linear chains. Note that the coordinates are very different from the $(CN^{1/2},\tau N^{1/2})$ corresponding to the Flory–Huggins theory. The high-concentration part of the curve is parabolic: $\tau \sim C^2$.

Note that these expressions differ widely from what would be expected in a Flory–Huggins theory, where one would get $C_c \sim \tau_c \sim N^{-1/2}$ in any number of dimensions.

Relation 22 also allows us to provide a scaling form for the coexistence (or to the spinodal) curve.

$$CN^{1/3} = F(\tau N^{2/3}) \tag{24}$$

This suggests that using the above coordinates, $CN^{1/3}$ vs. $\tau N^{2/3}$ should lead to a master curve for a given polymer–solvent system, regardless of its molecular weight.

An important property may be derived from our universal form, eq 24, concerning the shape of the coexistence curve in the high-concentration regime. In this region, it has been argued[11] that this shape should be independent of the molecular weight of the chains (see also eq 53 and discussion). This suggests that in (24), the right-hand side has a power law behavior

$$F(x) \sim x^{\beta} \tag{25}$$

the exponent being determined by the requirement that the coexistence curve is independent of N. This leads us to predict

$$\tau \sim C^2 \tag{26}$$

in this high-concentration regime. The resulting curve is shown in Figure 1.

Again, we may note the difference with a Flory–Huggins approach, which would give a *linear* relationship between τ and C in the high-concentration range. We conclude this section by emphasizing the differences we obtain with the classical approach. The location of the critical point is very different, leading to a very different conjecture about the universal coordinates to be used for the coexistence curve. The shape of this curve is parabolic rather than linear.

(2) Branched Chains. As discussed in the Introduction, the situation for actual branched polymers (d = 2, 3) is very much the same as that discussed above for linear chains in two dimensions: mean field theory is valid only when d = 6, or above, and we expect large deviations for usual space dimensions. We use the same scaling approach for the description of the coexistence curve. In order to do this, we need the crossover values for the concentration, C_{Θ}^*, and the excluded volume parameter υ_c. The overlap concentration is obtained from relation 6, giving the radius of the polymer at the Θ point:

$$C_{\Theta}^* \sim N^{1-\nu_{\Theta}d} \approx N^{(4-3d)/[4(d+1)]} \tag{27}$$

The crossover value for the interaction parameter is described by the crossover exponent ϕ

$$|\upsilon_c| \sim N^{-\phi} \tag{28}$$

which we evaluate in the same way as for linear chain above.

(a) Collapsed Branched Chain. Let us start with a single chain in a Θ solvent and lower the temperature. The free energy is, in the Flory approximation

$$F = \frac{R^2}{N^{1/2}l^2} + v\frac{N^2}{R^d} + w\frac{N^3}{R^{2d}} \tag{29}$$

where $v(\Theta) = 0$, leading to eq 6 for the radius. When v becomes negative, there is a growing attractive interaction, which makes the chain eventually collapse. Our argument, as before, is that this happens when the attractive term, evaluated in a consistent way, becomes of the order of the thermal energy:

$$|v_c|\frac{N^2}{{R_\Theta}^d} \sim 1 \tag{30}$$

leading to

$$\tau_c \sim N^{-(8+d)/[4(d+1)]}l^d \tag{31}$$

and thus

$$\phi = \frac{8 + d}{4(d + 1)} \tag{32}$$

In the following, we will restrict our discussion to the case of usual ($d = 3$) branched polymers. From (31) we get

$$-v_c \sim N^{-11/16}l^3 \tag{33}$$

and, supposing $-v = -[(T - \Theta)/\Theta]l^3 \equiv \tau l^3$, this becomes

$$\tau_c \sim N^{-11/16} \tag{34}$$

When the temperature is not too far from Θ, $\tau \ll 1$, we may write a scaling form for the radius of the chain:

$$R = N^{7/16}f[\tau N^{11/16}]l \tag{35}$$

where the unknown function $f(x)$ has a power law behavior for large x

$$f(x) \sim x^\alpha \qquad (x \gg 1) \tag{36}$$

The exponent is obtained by the requirement that in this regime the chain is collapsed:

$$R \sim N^{1/3}l \tag{37}$$

Combining eq 35–37 we get

$$R \sim N^{1/3}\tau^{-5/33}l \tag{38}$$

As for linear chains, we may define a local-thermal blob with g elements and size χ. The behavior inside such a blob is the same as in the Θ regime:

$$\chi \sim g^{7/16}l \tag{39}$$

Both χ and g are obtained by a generalization of eq 30: For $|v|$ much larger than $|v_c|$, the energy of a blob is of order kT, or

$$v\frac{g^2}{\chi^3} \sim 1 \tag{40}$$

Taking (39) into account, we get

$$g \sim \tau^{-16/11} \tag{41}$$

$$\chi \sim \tau^{-7/11} \tag{42}$$

The polymer chain is a collapsed ensemble of blobs:

$$R \sim (N/g)^{1/3}\chi$$

These predictions, (38) and (42), might be checked by neutron scattering experiments on deuterated polymers. The above analysis also implies that the scattered intensity in the intermediate range, $l^{-1} > q = (4\pi/\lambda)\sin(\theta/2) > R^{-1}$ should exhibit a crossover:

$$S(q) \sim q^{-16/7} \qquad l^{-1} < q < q^* \tag{43}$$

$$S(q) \sim q^{-3} \qquad q^* < q < R^{-1} \tag{43'}$$

with

$$q^* \sim \chi^{-1} \tag{44}$$

(b) Coexistence Curve. In order to describe the phase separation that occurs when the concentration is not vanishingly small, one might use, for instance, a virial expansion for the free energy. The important point then is to use a *renormalized* interaction parameter taking into account the crossover exponent ϕ discussed above:[23]

$$F = \frac{C}{N}\log C + \tilde{v}R^d\left(\frac{C}{N}\right)^2 + \tilde{w}R^{2d}\left(\frac{C}{N}\right)^3 \tag{45}$$

where R is the radius of a chain in the Θ regime, relations 6 and 6′, $\tilde{v} = vN^\phi$ is the renormalized interaction parameter, and $\tilde{w}$ is the renormalized three-body interaction, which is a positive constant. For the usual three-dimensional linear chain, $\tilde{v}$ is just the Fixman expansion parameter[25] z. The coexistence curve may be obtained from eq 45. Here, as for linear chains, we use a scaling approach. The free energy per unit volume may be written as

$$F = N^{-\nu_\Theta d}f\left[\frac{C}{{C_\Theta}^*}, vN^\phi\right] \tag{46}$$

where C^* is given by relation 27 above. The reader may easily check that eq 45 has indeed the form given above. The coordinates of the critical point are obtained by successive differentiations of eq 46.

$$\frac{\partial^2 F}{\partial C^2} = 0 = g\left(\frac{C}{{C_\Theta}^*}, vN^\phi\right) \tag{47}$$

$$\frac{\partial^3 F}{\partial C^3} = 0 = h\left(\frac{C}{{C_\Theta}^*}, vN^\phi\right) \tag{48}$$

where eq 47 is the equation for the spinodal curve. Note that any condition on the free energy will result in an equation similar to (47) or (48). Thus we expect the phase separation curve to be also of the same type:

$$S\left(\frac{C}{{C_\Theta}^*}, vN^\phi\right) = 0 \tag{47'}$$

From these equations, one gets easily the coordinates of the critical point. For three-dimensional systems, they are

$$C_c \sim {C_\Theta}^* \sim N^{-5/16}l^{-3} \tag{49}$$

$$|\tau_c| \sim N^{-\phi} \approx N^{-11/16} \tag{50}$$

Note that again these results are very different from those of a classical Flory–Huggins approach ($C_c \sim \tau_c \sim N^{-1/2}$).

The coexistence curve, or equally well the spinodal curve, is given by eq 47, which may be written as

$$CN^{5/16} = K(\tau N^{11/16}) \tag{51}$$

So, for a given polymer–solvent system, the above coordinates should give a universal curve with a shape independent of the molecular weight of the solute polymer. Further, the high-concentration part of the curve should be independent of the molecular weight of the polymer in a (τ, c) diagram. This is obtained from relation 51 by supposing that $K(x)$ has a power law behavior for large x. We find

$$\tau \sim C^{11/5} \tag{52}$$

Equation 52 may also be recovered by the following simple argument: In the dilute regime, where the chains do not overlap, the volume fraction occupied by the chain is

$$f = (C/N)R^d \tag{53}$$

The phase separation occurs when f reaches some constant, independent of N and τ. Taking (38) into account for the radius of the chain gives relation 52 for the high-concentration part of the coexistence curve.

(3) General Case. Let us now consider the more general case when the polymer is made of both bi- and trifunctional units. The total number of units is N and the fraction of branching points is Λ. The size of the polymer is given by relations 7 and 8. One important hypothesis we make is that both linear and branched parts have the same Θ temperature (Θ being always defined in the limit of infinitely large chains). The overlap concentration is obtained from relation 8:

$$C^* l^d \sim N^{(4-3d)/[4(d+1)]}\Lambda^{d/[4(d+1)]} \qquad (d \le 4) \tag{54}$$

which crosses over smoothly from relation 27 when $\Lambda = 1$ to the proper expression for linear chains in a Θ solvent when $\Lambda N \sim 1$:

$$C_{\mathrm{L}}^* l^d \sim N^{(1-d)/(1+d)}$$

(a) Collapse of a Single Chain. It is important to realize that although they have the same Θ temperatures, the linear and branched parts of the chain *do not* have the same sensitivity to υ. This is simply due to the fact that the crossover to the collapsed state depends on the length of the chain. The branched parts crossover first for a value of υ that is obtained by generalizing relation 30:

$$-\upsilon_{\mathrm{c}} \sim \frac{R^d}{N^2} \sim N^{-(8+d)/[4(d+1)]}\Lambda^{-d/[4(d+1)]} l^d \tag{55}$$

The linear parts collapse for a higher value, related to their average length

$$-\upsilon_{\mathrm{c}}^{\mathrm{L}} \sim \frac{\xi_{\mathrm{L}}^{\,d}}{g_\Lambda^{\,2}} \sim \Lambda^{+2/(d+1)} l^d \tag{56}$$

where ξ_{L} and g_Λ are given by relation 8 and are respectively the size and the number of elements in a linear blob. Note that (55) and (56) coalesce when $\Lambda N \sim 1$, when we recover the linear-chain behavior. A blob analysis may give some further insight: Once the molecule starts condensing we may define a *thermal* blob as above, where the local behavior is Θ-like. The number g of elements in such blob is obtained by generalizing eq 55, as was done in eq 17:

$$g \sim (-\upsilon)^{-4(d+1)/(8+d)}\Lambda^{-d/(8+d)} \tag{57}$$

and its size

$$\chi \sim (\Lambda g)^{7/[4(d+1)]}\xi_{\mathrm{L}} \tag{57$'$}$$

where ξ_{L} is the size of the *linear* blob:

$$\xi_{\mathrm{L}} \sim \Lambda^{-2/(d+1)}$$

The chain is a condensed ensemble of temperature blobs:

$$R \sim (N/g)^{1/d}\chi \tag{58}$$

The above analysis is valid below υ_{c}, eq 55, as long as the thermal blob is larger than the linear blob. The limit for this is reached when both have the same number of elements:

$$g \sim g_\Lambda \sim \Lambda^{-1}$$

leading to

$$\tau \sim \tau_{\mathrm{c}}^{\mathrm{L}} \sim \Lambda^{2/(d+1)}$$

For values of τ larger than $\tau_{\mathrm{c}}^{\mathrm{L}}$, the linear blob is also collapsed and the temperature blobs are now *linear*. Relation 58 then becomes

$$R \sim (N/g_\Lambda)^{1/d}\xi_{\mathrm{L}} \tag{59}$$

and

$$\xi_{\mathrm{L}} \cong (g_\Lambda/g)^{1/d}\chi \tag{59$'$}$$

$$\chi \sim g^{2/(d+1)}$$

$$g \sim \tau^{-(d+1)/2}$$

Note that combining (59) and (59′) leads to the same relation as for a *linear* polymer: For temperature below $\tau_{\mathrm{c}}^{\mathrm{L}}$, the radius is the same as for a linear polymer chain. This will have consequences on the phase separation curve, as shown below.

(b) Coexistence Curve. It is not possible for the general case to give a simple universal law for the coexistence curve. The reason is that we have an extra variable, Λ, to take into account. Thus, the free energy per unit volume is of the form

$$F = N^{-\nu_\Theta{}^{\mathrm{L}} d} f[\Lambda N, CN^{\nu_\Theta{}^{\mathrm{L}} d-1}, \tau N^{2-\nu_\Theta{}^{\mathrm{L}} d}] \tag{60}$$

where $\nu_\Theta{}^{\mathrm{L}} = 2/(d+1)$ is the Θ exponent for linear chains. When $\Lambda N \rightarrow 0$, the above expression reduces to that for linear chains, i.e., eq 20 above, in the two-dimensional case. When $\Lambda = 1$, on the other hand, relation 60 goes to that for purely branched chains, eq 46. In the more general case, we have three variables instead of two before. Thus the equation for the coexistence curve may be written as

$$G(\Lambda N, CN^{\nu_\Theta{}^{\mathrm{L}} d-1}, \tau N^{2-\nu_\Theta{}^{\mathrm{L}} d}) = 0 \tag{61}$$

which is very general, but of limited use. However, for large values of ΛN, it takes a simpler form:

$$F = N^{-\nu_\Theta d}\Lambda^{-(\nu_\Theta-\nu_\Theta{}^{\mathrm{L}})d} f[CN^{\nu_\Theta d-1}\Lambda^{(\nu_\Theta-\nu_\Theta{}^{\mathrm{L}})d}, \tau N^{2-\nu_\Theta d}\Lambda^{(\nu_\Theta{}^{\mathrm{L}}-\nu_\Theta)d}] \tag{62}$$

which reduces to eq 46 for purely branched chains when $\Lambda = 1$, leading to an expression for the phase separation curve:

$$CN^{\nu_\Theta d-1}\Lambda^{(\nu_\Theta-\nu_\Theta{}^{\mathrm{L}})d} = g[\tau N^{2-\nu_\Theta d}\Lambda^{(\nu_\Theta{}^{\mathrm{L}}-\nu_\Theta)d}] \tag{63}$$

In the above expressions, ν and ν_Θ are the Θ exponents for the linear and branched chains, respectively. The reader may convince himself that there is an important restriction to the use of the above relations: They are valid only if C and τ are small enough; namely, as can be seen on eq 61, for instance

$$\tau < \Lambda^{2-\nu_\Theta{}^{\mathrm{L}} d} \sim \tau_* \tag{64}$$

$$C < \Lambda^{\nu_\Theta{}^{\mathrm{L}} d-1} \sim C_* \tag{64$'$}$$

Let us first consider the critical point, where (63) is valid when Λ is large enough. Then, we get directly the coordinates of the critical point. Replacing $\nu_\Theta{}^{\mathrm{L}}$ and ν_Θ by their expressions, eq 7 and 6′, respectively, we get

$$C_{\mathrm{c}} \sim N^{(4-3d)/4(d+1)}\Lambda^{d/[4(d+1)]} l^d \tag{65}$$

$$\upsilon_{\mathrm{c}} \sim N^{-(d+8)/[4(d+1)]}\Lambda^{-d/[4(d+1)]} l^d \tag{66}$$

Note that for $\Lambda = 1$ and $\Lambda \sim N^{-1}$ we recover the branched polymer and linear-chain behaviors, respectively (cf. eq 49 and 50 for $d = 3$, $\Lambda = 1$, and eq 23 and 23′ for $d = 2$, $\Lambda \sim N^{-1}$).

The shape of the coexistence curve for concentrations larger than C_{c} may be obtained as in the previous sections.

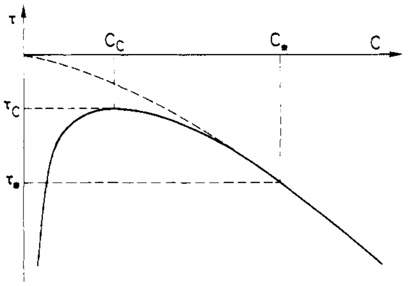

Figure 2. Coexistence curve for a polymer solution ($d = 3$) where the chains are made of both bi- and trifunctional units. The curve may be divided into two parts. The higher part exhibits the branched nature of the polymer, while the lower part reflects the local linearity. The relative importance of the two parts is governed by the fraction Λ of branch points: $C_* \sim \Lambda^{1/2}$, $\tau_* \sim \Lambda^{1/2}$ (for $d = 3$). The higher part of the curve is almost parabolic: $\tau \sim C^{11/5}\Lambda^{-3/5}$, while the lower part is linear.

However, because of the successive condensations of the global branched structure and then of the local linear structure, we expect a change in the shape when relations (64) are no longer fulfilled.

When (64) are valid, we may get the high-concentration part of the curve by using eq 63 for the coexistence curve. We obtain

$$C \sim \tau^{(3d-4)/(d+8)}\Lambda^{d/(d+8)} \qquad (\tau < \tau_*) \tag{67}$$

This equation is valid until τ_* only. For lower temperatures or larger τ, the linear parts collapse, and the coexistence curve should become also independent of Λ, which is related to the length of these linear parts. It is easy to check that when $\tau \sim \tau_*$, $C \sim C_*$, from eq 67:

$$C(\tau_*) \sim \Lambda^{(d-1)/(d+1)} = C_* \sim \tau_*^{(d-1)/2} \tag{68}$$

and for concentrations higher than C_*

$$C \sim \tau^{(d-1)/2} \qquad (C > C_*)$$

exhibiting the fact the linear parts are collapsed. The resulting curve is shown in Figure 2 for $d = 3$. Note that when Λ is varied, both C_c and C_* vary. When Λ is decreased, C_* decreases faster than C_c, and both eventually coalesce when $\Lambda N \sim 1$. Then the whole coexistence curve exhibits only the linear-chain "behavior".

IV. Conclusion

We have studied the collapse of a chain and the phase separation curve for a polymer solution below the Θ temperature. The classical Flory–Huggins theory is valid for usual ($d = 3$) linear chains. It is also valid for branched chains for high space dimensions ($d \geq 6$). In general, it is valid whenever Θ chains are ideal. For usual ($d = 3$) highly branched polymer solutions or for two-dimensional linear chains, the classical theory *does not* work, and one has to use another approach. A possible way is to use a virial expansion for the free energy. One has then to use *renormalized* virial coefficients. In this paper, we followed a scaling approach. A crucial parameter is the crossover exponent ϕ describing the collapse of a single polymer chain: Starting from a Θ solution and decreasing the excluded volume parameter, the collapse occurs around a value

$$\tau_c \sim N^{-\phi}$$

We have estimated this exponent within the Flory theory

$$\phi = -\nu_\Theta d + 2$$

where ν_Θ is the exponent for the molecular weight dependence of the radius of gyration in the Θ regime. For space dimensions higher than 3 or 6 for the linear or branched polymers, respectively, we recover the classical value $\phi = {}^1/_2$ of the Flory–Huggins theory. Below these dimensions, we get the following results:

(1) The coordinates of the critical point are

$$\tau_c \sim N^{-\phi}$$

$$C_c \sim N^{-(\nu_\Theta d - 1)}$$

with $\phi = {}^2/_3$ and ${}^{11}/_{16}$ for two-dimensional linear chains and three-dimensional branched polymers, respectively, and $-1 + \nu_\Theta d = {}^1/_3$ and ${}^5/_{16}$ for both cases.

(2) We suggest a law of corresponding states for solutions with different molecular weights:

$$C = C_c f(\tau/\tau_c)$$

where C_c is defined above and where we have supposed that the excluded volume parameter v has a linear dependence on temperature: $v \approx (\mathrm{T} - \Theta)/\Theta \equiv \tau$. Here, as usual, Θ may be defined as the limit when N goes to infinity of the critical point of the phase separation curve.

(3) The high-concentration part of the coexistence curve should not show any dependence on molecular weight. This leads to

$$\tau \sim C^{\phi/(\nu_\Theta d - 1)}$$

for this high-concentration branch. This has been checked for linear chains in three dimensions, where $\phi = -\nu_\Theta d + 2 = {}^1/_2$, leading to a linear dependence.

This also leads to

$$\tau \sim C^2$$

and

$$\tau \sim C^{11/5}$$

for linear chains in two dimensions and branched chains in three dimensions, respectively.

(4) For the more general case of a randomly branched polymer made of both bi- and trifunctional units, in the limit of high branching, the critical point is governed by the branched points:

$$C_c \sim N^{-5/16}\Lambda^{3/16}$$

$$\tau_c \sim N^{-11/16}\Lambda^{-3/16}$$

for three-dimensional systems. Note that these values crossover smoothly to the usual Flory–Huggins estimates when $N\Lambda \sim 1$, where we recover the linear-chain behavior. (For $d = 3$ and for linear chains, the Flory–Huggins results are valid, as we said above.)

The high-concentration branch of the coexistence curve may be divided into two parts, depending on whether the linear part of the macromolecule have collapsed or not.

For small values of τ, the linear blobs still have their Θ behavior. This leads to

$$C \sim \tau^{5/11}\Lambda^{3/11}$$

which is valid as long as $|\tau| < |\tau_*| \sim \Lambda^{1/2}$.

For larger values of τ, the linear parts collapse, and the high-concentration part of the coexistence curve is

$$C \sim \tau$$

The importance of these two parts depends on Λ. When $\Lambda = 1$, the latter part does not exist. When $\Lambda N \sim 1$, τ_* is of the order of τ_c and the former part does not exist anymore.

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New Approach to Probing Polymer and Polymer Blend Structure Using Electronic Excitation Transport

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ABSTRACT: A theoretical study of electronic excitation transport in polymer systems is presented. $G^s(t)$, the time-dependent ensemble-averaged probability that the excitation is on the originally excited chromophore, is calculated by using an approach involving a density expansion. It is shown that this quantity is a direct observable in a time-resolved fluorescence depolarization experiment. The effects of the finite volume associated with a single polymer coil or a small aggregate in a polymer blend are considered explicitly. Calculations are presented for systems having a Gaussian ensemble-average segmental distribution. The influences of density, volume, and aggregation are illustrated. $G^s(t)$ can yield reliable information about the local chromophore distribution of systems for which a lack of knowledge of the number of excimer traps prevents quantitative application of trapping experiments. The approach described here should be particularly valuable in obtaining structural information about very low concentration guest polymers in polymer blends and solutions.

I. Introduction

In recent years there has been considerable work devoted to understanding electronic excitation transport processes in polymer systems.[1] Because of their sensitivity to the spatial separation and orientation of chromophores in a polymer system, excitation transport observables contain detailed information about structural properties, e.g., coil configuration and the degree of coil extension. This information is of key importance in understanding the microscopic interaction of a polymer with its environment, and thus the macroscopic properties of polymers and polymer blends.

Recent theoretical and experimental advances have provided a detailed picture of incoherent excited-state transport among molecules distributed randomly in solutions or molecular crystals. Accurate theoretical treatments have been developed that are able to quantitatively predict experimental observables for single-component systems (donor-donor transport only) and two-component systems (donor-donor transport with donor-to-trap transfer).[2-4] Similar success in understanding energy-transport processes in polymer systems has not yet been achieved, due to the increased theoretical difficulty of including polymer structure in the problem.

Chromophores attached to an isolated polymer coil differ from independent chromophores in solution in at least two important respects. Chromophores in polymer systems are not in general randomly arranged but are correlated by the covalent bonds that join them. In addition, the finite extent of an isolated polymer coil effectively limits the number of possible sites that the excitation can sample. Therefore previous theoretical approaches that involve the thermodynamic limit,[2,3] i.e., the limit of an infinite number of sites distributed in an infinite volume, cannot be applied in many cases of interest.

Excitation transport among coil chromophores depends both on local molecular structure and on thermodynamic interactions of the coil with its environment. If an individual coil with closely spaced chromophores is dissolved in a good solvent, it will assume an extended configuration. Then, on the average, the only chromophores near the originally excited chromophore will be those most closely linked to it along the polymer backbone. The extended geometry makes the probability *small* that a chromophore from a polymer segment far removed along the backbone is in spatial proximity to the initial excitation. Thus ex-