Scaling Theory for Mixtures of Randomly Branched and Linear Polymers in the Melt

F. Roby and J.-F. Joanny*

Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg Cedex, France

Received July 12, 1990; Revised Manuscript Received September 27, 1990

ABSTRACT: We study theoretically mixtures of linear and branched chains in the melt using a Flory theory and scaling concepts. For one isolated branched chain immersed in a melt of linear chains we find three possible behaviors. If the molecular weight of the branched chain is large enough, it has the same behavior as in a monomeric solvent. If the branched chain has a smaller weight than the linear chains, it takes a compact conformation when the branching fraction is large and displays the Zimm–Stockmayer ideal statistics if the branching fraction is small. The statistics of semidilute solutions of branched chains in a polymeric solvent is deduced from the single-chain behavior with the help of a blob model. The important results is that in most regimes different branched chains do not interpenetrate. Above a critical value of the Flory interaction parameter, branched and linear chains phase separate: the phase separation is well described by the classical Flory theory for a small branching fraction. At higher branching fraction the classical theory is inappropriate and the critical demixing concentration is the overlap concentration of the branched chains in the linear-chain melt.

I. Introduction

A general feature of polymer blends is that polymers of different chemical nature are incompatible.[1] There is, however, a big practical interest to combine properties of different polymers by mixing them to make new materials, and polymer metallurgy is a field of major industrial importance. From the theoretical side, the thermodynamics of linear polymer mixtures is qualitatively well described by the classical Flory–Huggins theory. This theory is based on a lattice fluid model in which the polymer chains are distributed randomly on the lattice; it thus implicitly assumes that the polymer chains interpenetrate freely and retain ideal Gaussian statistics. The interaction between different monomers is described in a mean-field manner by the Flory interaction parameter χ. If the interaction energy between monomers i and j is ϵ_{ij}, the Flory parameter is defined as

$$\chi = \frac{1}{k_{\mathrm{B}}T}\left(\epsilon_{\mathrm{AB}} - \frac{\epsilon_{\mathrm{AA}} + \epsilon_{\mathrm{BB}}}{2}\right)$$

In the original version of Flory theory χ is inversely proportional to T and does not depend on the composition of the mixture. We use here χ as a phenomenological parameter that is a function of temperature only. In this approximation we neglect the concentration dependence of χ that should be included in a more refined theory.[2,3]

The polymers segregate at a critical value of the Flory parameter equal to $2/N$ where N is the degree of polymerization (supposed to be equal for the two polymers). Apart from a few exceptions (of academic interest) for which the two components of the blend are chemically very similar (mixtures of deuterated and hydrogenated chains[4] where χ can be as low as 10^{-4}) and a few cases where χ is negative[5] (polystyrene/poly(vinyl methyl ether)), the Flory–Huggins theory always predicts a phase separation in the limit of high molecular weights and explains the observed incompatibility of polymers of different chemical nature.

Mixtures of branched polymers and linear polymers have some industrial importance in the field of resin reinforcement.[6] The mechanical properties of brittle thermoset resins are often improved by addition of elastomeric components, a typical example being the toughening of epoxy resins by carboxyl-terminated butadiene–acrylonitrile random copolymers.[7] Before polymerization, the linear elastomer is miscible with the resin monomer. As the polymerization proceeds, the resin forms larger and larger branched structures that become incompatible with the elastomer.

The thermodynamics of the phase separation between the branched resin and the elastomer has been analyzed,[6] in the framework of the Flory–Huggins theory. This, however, ignores the specific behavior of the branched polymer and might in some cases be a very rough approximation.

In this paper we want to address this point in more detail in the idealized case of a mixture of monodisperse linear A chains with a degree of polymerization P and monodisperse randomly branched B chains with a degree of polymerization N. Although in the "gelling" resins the branched chains have an intrinsic broad polydispersity, this simplification seems a necessary step toward the detailed understanding of their properties.

The branched chains are supposed to be made of bifunctional and multifunctional units reacted at random. Following ref 8, the fraction of branched units is measured by an activity Λ (sometimes called branching fraction below); the average number of branching points is ΛN. If $\Lambda = 1$, the chain is fully branched; if Λ is of order N^{-1}, there is about one branching point per chain and the chain may be considered as linear. For intermediate values of Λ the branched polymer is made of linear parts with Λ^{-1} monomers, on average, randomly branched to each other.

We first discuss the conformation of one branched B chain of N monomers in a polymer solvent made with the linear A chains of P monomers both when this solvent is a good or a Θ solvent, in particular emphasizing the role of the interpenetration between branched and linear chains. We then discuss the concentration effect and the structure of semidilute solutions of the branched chains. Finally we discuss the demixing transition between branched and linear chains.

II. Conformation of a Single Chain

II.1. Flory Theory. We consider here a single branched polymer in a melt of linear polymers and study

0024-9297/91/2224-2060$02.50/0

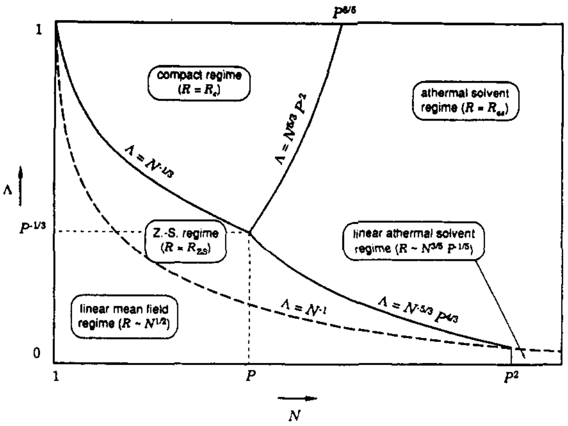

Figure 1. Different regimes for an isolated randomly branched molecule of degree of polymerization N and branching fraction Λ in an athermal linear solvent of P monomers. Note that both compact and Zimm–Stockmayer regimes disappear when $P \to 1$: their existence is due to the screening effect of the polymeric solvent.

its radius of gyration. As our starting point, we use in our calculations the basic result obtained by Zimm and Stockmayer,[9,10] which is now recalled. These authors calculated the radius R_{ZS} of a randomly branched chain of N monomers of size a and of branching fraction Λ, when the monomers do not interact. The result is

$$R_{ZS} \sim N^{1/4}\Lambda^{-1/4}a \tag{1}$$

This clearly is a nonrealistic result when $\Lambda = 1$, for the radius $R_{ZS} \sim N^{1/4}a$ would be smaller than the radius of a close packing of monomers, $R_c \sim N^{1/3}a$. Equation 1 is thus meaningful only when the branching ratio Λ is smaller than $N^{-1/3}$. Still, R_{ZS} can be regarded, even in the high branching limit, as an abstract radius corresponding to the maximum entropy of the chain, all the constraints acting on the monomers being released. It is the equivalent of the Gaussian radius for a linear chain and will enter the entropic part of the free energy. We sometimes call a chain with the Zimm–Stockmayer statistics an ideal chain.

Even though the calculations are not much more complicated in the general case, for pedagogical purposes we beging with the athermal solvent case, where A monomers and B monomers are chemically identical ($\chi = 0$).

The free energy F corresponding to the volume occupied by the branched chain may be written as

$$\frac{F}{T} = \frac{R^2}{{R_{ZS}}^2} + R^3\frac{F_{mix}}{T} \tag{2}$$

where T is the absolute temperature on a scale where the Boltzmann constant is $k_B = 1$. The first term is the entropic part of the free energy and has been derived in refs 11 and 12. Note that it has the same structure as for a linear chain and that it is meaningful for swollen chains (we do not consider situations where $R < R_{ZS}$). The second term represents the mixing free energy of the linear chains with the branched chain. R^3 is the volume of the branched chain, and F_{mix} is the mixing free energy per unit volume

$$a^3\frac{F_{mix}}{T} = \frac{1-c}{P}\ln(1-c) \tag{3}$$

where $c \equiv a^3N/R^3$ is the dimensionless concentration (or volume fraction) of B monomers inside the branched chain. Here, the mixing free energy reduces to the change in the entropy of the linear chains, since monomers A and B are chemically identical ($\chi = 0$).

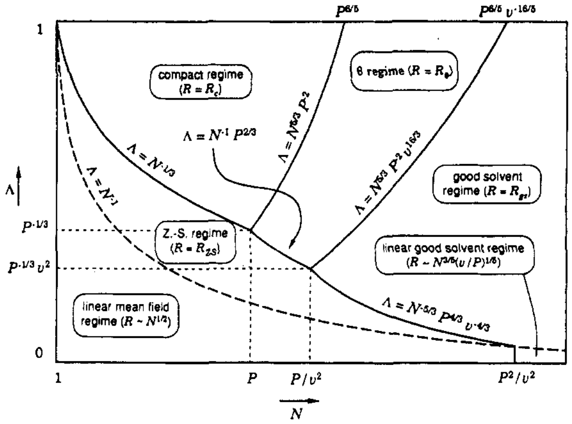

Figure 2. Different regimes for an isolated randomly branched molecule of degree of polymerization N and branching fraction Λ in a "rather good" ($0 < \upsilon < 1$) linear solvent of degree of polymerization P. Note that a Θ regime still exists; it shrinks when υ increases and disappears at $\upsilon = 1$.

When the radius R is eliminated, the free energy may be written as a function of the volume fraction c:

$$\frac{F}{T} = \frac{N}{P}\left(\frac{P\Lambda^{1/2}}{N^{5/6}}c^{-2/3} + \frac{1-c}{c}\ln(1-c)\right) \tag{2'}$$

The equilibrium value of the volume fraction is obtained by minimization of the free energy. This leads us to distinguish two different regimes according to the value of the dimensionless parameter $\alpha = P\Lambda^{1/2}/N^{5/6}$:

(1) If $\alpha \gg 1$, the minimum of the free energy corresponds to a volume fraction $c = 1$; the branched chains are compact with a radius

$$R_c \sim N^{1/3}a \tag{4}$$

There is thus a critical value of the degree of polymerization $N_c \sim P^{6/5}\Lambda^{3/5}$ such that if N is smaller than N_c there is no interpenetration between linear and branched chains.

(2) If $\alpha \ll 1$, the linear chains penetrate the branched chain, the equilibrium value of c is close to zero and we can expand the logarithm in the free energy in powers of c:

$$\frac{F}{T} = \frac{N}{P}\left(\frac{P\Lambda^{1/2}}{N^{5/6}}c^{-2/3} - 1 + \frac{c}{2} + \frac{c^2}{6} + o(c^3)\right) \tag{5}$$

The volume fraction in an athermal solvent c_{as} is

$$c_{as} \sim N^{-1/2}\Lambda^{3/10}P^{3/5} \tag{6}$$

and therefrom the radius in an athermal solvent $R_{as} \sim (N/c)^{1/3}a$ is

$$R_{as} \sim N^{1/2}\Lambda^{-1/10}P^{-1/5}a \tag{7}$$

In the limit where $P = 1$ we recover the known result for a branched polymer in a good solvent.[13,14]

The free energy of one chain given by eq 2 or 2′ only includes effective repulsive interactions; the equilibrium radius must thus be larger than the ideal Zimm–Stockmayer radius R_{ZS}. If this is not the case, the repulsive interactions are not relevant and the chain has a radius R_{ZS}. This gives the following conditions to observe a nonideal radius of the chain:

$$\begin{aligned} &\Lambda > N^{-5/3}P^{4/3} \quad \text{if } \Lambda < N^{5/3}P^{-2}\ (\alpha \ll 1) \\ &\Lambda > N^{-1/3} \quad \text{if } \Lambda > N^{5/3}P^{-2}\ (\alpha \gg 1) \end{aligned} \tag{8}$$

All the results are summarized on the diagram of Figure 1 where for a fixed value of P we display the various regimes in a (Λ,N) plane. We have also drawn the curve $\Lambda = 1/N$, below which branching becomes irrelevant and the chains may be considered as linear. These linear chains have Gaussian statistics ($R \sim N^{1/2}a$) if $N < P^2$, and they are swollen ($R \sim N^{3/5}a$) if $N > P^2$.[15] Notice that this crossover between swollen and ideal chains corresponds to the intersection between the curves $\Lambda = N^{-1}$ and $\Lambda = N^{-5/3}P^{4/3}$, ensuring thus a smooth crossover between the statistics of branched and linear chains.

The generalization to chemically different chains is straightforward. The chemical difference between A and B monomers is taken into account through an effective Flory interaction parameter $\chi(>0)$. The free energy of the branched chain is

$$\frac{F}{T} = \frac{N}{P}\left(\frac{P\Lambda^{1/2}}{N^{5/6}}c^{-2/3} + \frac{1-c}{c}\ln(1-c) + P\chi(1-c)\right) \quad (9)$$

or for $c \approx 0$

$$\frac{F}{T} = \frac{N}{P}\left(\frac{P\Lambda^{1/2}}{N^{5/6}}c^{-2/3} - 1 + \frac{c}{2}(1-2P\chi) + \frac{c^2}{6} + o(c^3)\right) \quad (9')$$

Notice that the interaction term might no longer be acceptable when c is close to unity; however, it has a small contribution in this case and we expect that this should not alter dramatically the validity of the free energy when the branched chain is compact. The term that is linear in c corresponds to a two-body interaction—if F were expressed as an energy per unit volume, it would be quadratic in c—and we call the quantity $1 - 2P\chi \equiv \upsilon$ the excluded-volume parameter. This allows the definition of an effective Θ point when $\upsilon = 0$ or $\chi = 1/2P$.

As before, there is a regime where $c \approx 1$ for $P\Lambda^{1/2}/N^{5/6} \gg 1$, but we can define now two different regimes when c is close to zero:

(1) When the two-body interactions are negligible with respect to the three-body interactions, we say that we are in a Θ regime. The corresponding radius R_Θ is calculated by dropping the $(c/2)\upsilon$ term in the free energy:

$$R_\Theta \sim N^{7/16}\Lambda^{-1/16}P^{-1/8}a \quad (10)$$

This gives back the radius of branched polymers in a Θ solvent when $P = 1$.[11]

(2) On the contrary, when the two-body interactions are predominant, we are in a good solvent regime (we consider here only positive values of υ) and the radius reads

$$R_{\text{gs}} \sim N^{1/2}\Lambda^{-1/10}(\upsilon/P)^{1/5}a \quad (11)$$

which recovers the athermal solvent radius when $\upsilon = 1$.

The crossover between good and Θ solvent occurs when $R_{\text{gs}} = R_\Theta$ or

$$\Lambda = N^{5/3}P^{-2}\upsilon^{16/3} \quad (12)$$

The values of the radius in the good solvent and Θ solvent regimes will actually be observed if the radii are larger than the Zimm–Stockmayer radius:

$$\Lambda > N^{-1}P^{2/3} \quad \Theta \text{ solvent}$$

$$\Lambda > N^{-5/3}P^{4/3}\upsilon^{-4/3} \quad \text{good solvent} \quad (13)$$

In the other limit the chains have a radius R_{ZS}.

The results can be summarized on a diagram similar to that of Figure 1. As an example, we show on Figure 2 such a diagram for an excluded-volume parameter υ such that $0 < \upsilon < 1$.

II.2. Blob Description. The previous results for the radius of a branched chain in a melt of linear chains may be given a simple geometrical interpretation in terms of blobs. This is equivalent to the above Flory approach, but it also gives information on the local structure of the chain and allows thus the determination of the structure factor $S(q)$ at a wave vector q in the intermediate range ($a < q^{-1} < R$). The structure factor is the quantity directly measured experimentally in scattering experiments.

As an example of the blob description, we consider a branched chain with a branching ratio $\Lambda > P^{-1/3}$ in a good solvent where the excluded-volume parameter is such that $0 < \upsilon < 1$. Our results for the radius of the chains are summarized in Figure 2 in this case.

The basis of the blob model[16] is that a small part of the chain containing g monomers has the same statistics as a small chain containing the same number g of monomers. This property is certainly true as soon as we do not consider the Zimm–Stockmayer regime, i.e., as soon as we do not build a molecule with blobs that are overlapping. In the Zimm–Stockmayer regime, however, the interactions between monomers are irrelevant and the statistics is the same at all length scales.

At small length scales branching is irrelevant as soon as $g < \Lambda^{-1}$. We thus group the monomers into linear blobs of $g_{\text{lin}} = \Lambda^{-1}$ monomers with a size

$$\xi_{\text{lin}} \sim g_{\text{lin}}{}^{1/2}a = \Lambda^{-1/2}a \quad (14)$$

At larger length scales branching becomes relevant, but the chains are still "ideal". This remains true if the number of monomers is smaller than the value of the crossover to the compact regime on Figure 2. We thus group the linear blobs into Zimm–Stockmayer ideal blobs with $g_{\text{ZS}} = \Lambda^{-3}$ monomers. Their size is

$$\xi_{\text{ZS}} \sim (g_{\text{ZS}}/\Lambda^{-1})^{1/4}\Lambda^{-1/2}a \sim \Lambda^{-1}a \quad (15)$$

The ideal blobs overlap to make the compact blobs, inside which the branched polymer volume fraction is $c = 1$. The number of monomers in the compact blobs is given by the crossover between eqs 4 and 10: $g_{\text{c}} = \Lambda^{3/5}P^{6/5}$. The size of the compact blobs is

$$\xi_{\text{c}} \sim (g_{\text{c}}/\Lambda^{-3})^{1/3}\Lambda^{-1}a \sim \Lambda^{1/5}P^{2/5}a \quad (16)$$

At larger length scales the chain may be considered as a purely branched chain in a Θ solvent for which the compact blobs would be renormalized monomers. If the molecular weight is not too large, it has Θ statistics. For larger chains we group the monomers into Θ blobs; the number of monomers in these Θ blobs is given by $g_\Theta = \Lambda^{3/5}P^{6/5}\upsilon^{-16/5}$ and therefrom the size of the Θ blobs

$$\xi_\Theta \sim (g_\Theta/\Lambda^{3/5}P^{6/5})^{7/16}\Lambda^{1/5}P^{2/5}a \sim \Lambda^{1/5}P^{2/5}\upsilon^{-7/5}a \quad (17)$$

Finally, if the degree of polymerization is larger than g_Θ, we recover the pure good solvent behavior for a fully branched chain of Θ blobs:

$$R \sim (N/g_\Theta)^{1/2}\xi_\Theta \sim N^{1/2}\Lambda^{-1/10}(\upsilon/P)^{1/5} \quad (18)$$

The description in terms of blobs allows the determination of the structure factor $S(q)$ by noting that $S(q)/c$ is the number of monomers in a volume of size q^{-1}.

At large values of q ($q\xi_{\text{c}} \gg 1$) the structure of the compact blob is probed, and one should observe the scattering by "hard spheres" of volume ξ_{c}.

At smaller wave vectors ($\xi_{\text{c}} < q^{-1} < \xi_\Theta$) a scattering experiment probes the internal structure of the Θ blobs:

$$S(q) \sim cg_{\text{c}}/(q\xi_{\text{c}})^{16/7} \sim \Lambda^{1/7}P^{2/7}c\, q^{-16/7} \quad (19)$$

At smaller wave vectors ($\xi_\Theta < q^{-1} < R$) one probes the good solvent statistics:

$$S(q) \sim c g_\Theta/(q\xi_\Theta)^2 \qquad (20)$$

Finally at very small values of $q(qR \ll 1)$, in the Guinier range

$$S(q) \sim Nc(1 - q^2 R_g^{\,2}/6) \qquad (21)$$

This straightforward "blob" analysis can be carried out for the other values of the parameters Λ or v, and we do not give the corresponding results here for the sake of simplicity.

The blob model also allows a more detailed description of the compact regime. Up to now we have considered a compact chain or a compact blob as a dense sphere of branched monomers impenetrable by the linear chains. The interface between the sphere and the linear chains is not, however, infinitely sharp and its width may be inferred from the blob model: g monomers of the compact chain do not form a close packing if $g < g_{ZS}$. It does not mean, however, that the chain is not compact; other monomers than the ones we consider fill the spaces in between them and adjust the concentration to 1. This suggests that on the surface of the compact chain there is a layer of thickness $t \sim \xi_{ZS} \sim \Lambda^{-1}a$ where interpenetration of the linear chains and the branched chain is possible. This argument for the penetration thickness t is purely geometrical and involves no thermal energy since there is no energy scale either in the Zimm–Stockmayer or in the compact regimes.

III. Semidilute and Concentrated Branched Chains

We study in this section the conformation of branched molecules when their concentration in the melt of linear chains is higher than their overlap concentration $c^* \equiv N/R^3$. We first consider a melt of branched chains ($c = 1$) and then the semidilute regime $c^* \ll c \ll 1$ both in Θ and good solvents.

III.1. Melt of Branched Chains. In order to describe the conformation of polymer chains in the melt, we use the same Flory approach as in section II. The only difference is that all the other chains surrounding or penetrating the test chain are not linear chains but similar branched chains.

The test chain free energy is written as

$$\frac{F}{T} = \frac{R^2}{R_0^{\,2}} + R^3\left(\frac{1-c}{N}\ln(1-c)\right) \qquad (22)$$

Replacing R by $(N/c)^{1/3}$ in this equation, we may express F as a function of c only:

$$\frac{F}{T} = N^{1/6}\Lambda^{1/2}c^{-2/3} + \frac{1-c}{c}\ln(1-c) \qquad (22')$$

Whenever $N\lambda^3 \gg 1$, the minimum of the free energy is obtained for $c \approx 1$; the branched chains are compact and do not interpenetrate.

If $N\Lambda^3 \ll 1$, the free energy has a minimum at a value of c close to zero ($c = N^{1/10}\Lambda^{3/10}$), but the corresponding radius is smaller than the "ideal radius", and, as argued earlier, the actual radius of the chain is the Zimm–Stockmayer radius. In this limit different chains interpenetrate. The radius of a branched chain in the melt is thus

$$R_{ZS} \sim N^{1/4}\Lambda^{-1/4}a \qquad \text{if } \Lambda < N^{-1/3}$$
$$R_c \sim N^{1/3}a \qquad \text{if } \Lambda > N^{-1/3} \qquad (23)$$

The transition between these two regimes when $\Lambda = N^{-1/3}$ is the same as that found for a single branched chain for the crossover between the Zimm–Stockmayer regime and the compact regime as could be expected; it occurs when the density in an ideal chain is equal to 1.

Notice also that these results are different from those proposed in ref 11 where the ideal state has not been considered.

III.2. Semidilute Branched Chains. We consider a dilute solution of branched chains in a polymeric solvent of degree of polymerization P and increase the concentration of branched chains c/N until they overlap. The overlap concentration c^*[16] depends on the configuration of the isolated chain:

$$c^*_{gs} \equiv N/R_{gs}^{\,3} \sim N^{-1/2}\Lambda^{3/10}(v/P)^{-3/5} \qquad (24)$$

$$c^*_\Theta \equiv N/R_\Theta^{\,3} \sim N^{-5/16}\Lambda^{3/16}P^{3/8} \qquad (25)$$

$$c^*_{ZS} \equiv N/R_{ZS}^{\,3} \sim N^{1/4}\Lambda^{3/4} \qquad (26)$$

$$c^*_c \equiv N/R_c^{\,3} \sim 1 \qquad (27)$$

The compact regime case is trivial: since the concentration inside the compact chain is that of a melt, there is no semidilute solution.

As there is no energy scale in the Zimm–Stockmayer regime, semidilute ideal chains are also quite simple to describe: when the concentration c goes beyond c^*_{ZS}, the different chains simply interpenetrate; their radius remains the "ideal radius" $R_{ZS} \sim N^{1/4}\Lambda^{-1/4}a$ until $c = 1$.

The good solvent and the Θ regimes lead to "ordinary" semidilute solutions, which can be described using concentration blobs; at short length scales inside the concentration blobs the configuration is that of an ideal chain that has been discussed in section II. At length scales larger than the blob size ξ, the solution behaves as a melt of these concentration blobs. The blob size ξ is the correlation length of the solution and could be measured in scattering experiments. We now discuss in more details the correlation length ξ and the radius of labeled chains both in Θ and good solvents.

III.2.1. Semidilute Solution in a Θ Solvent. In a semidilute solution obtained from dilute Θ chains, the correlation length ξ is equal to R_Θ at $c = c^*_\Theta$ and obeys the scaling law

$$\xi \sim R_\Theta f(c/c^*_\Theta) \qquad (28)$$

with the requirement that the scaling function $f(x)$ goes to 1 when x goes to zero and that when $x \gg 1$ $f(x)$ is a power law such that ξ is independent of N following ref 6 so that

$$\xi \sim c^{-7/5}\Lambda^{1/5}P^{2/5} \qquad (29)$$

One blob being equivalent to an isolated molecule of g monomers, the number of monomers per blob is

$$g \sim c^{-16/5}\Lambda^{3/5}P^{6/5} \qquad (30)$$

In the limit of a monomeric solvent, P is equal to 1, and these results reduce to those of ref 11. Equations 29 and 30 are valid as long as the concentration blob stays in the Θ regime, i.e., as long as the concentration is not too high. At larger concentrations, the concentration blobs become compact if $\Lambda > P^{-1/3}$ or ideal if $\Lambda < P^{-1/3}$.

If $\Lambda > P^{-1/3}$, the blob becomes compact when the volume fraction inside the blob is of order 1; the blobs forming a close packing, this corresponds to an overall concentration

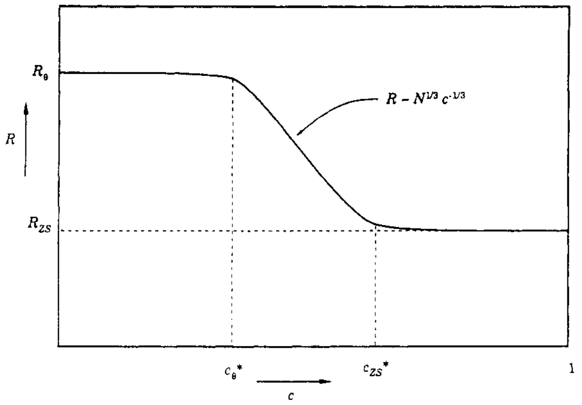

Figure 3. Radius of the branched chains versus concentration (log-log plot) for a small branching fraction $\Lambda < N^{-1/3}$. The diagram corresponds to chains exhibiting a Θ radius in the dilute solution.

of order 1 and eqs 29 and 30 are thus valid in the whole concentration range $c^* \ll c \ll 1$.

If $\Lambda < P^{-1/3}$, the concentration blob reaches the Zimm–Stockmayer regime when $g_\Theta \sim \Lambda^{-1}P^{2/3}$ (eq 13), which corresponds to a concentration

$$c_\Theta^{ZS} \sim \Lambda^{1/2}P^{1/6} \tag{31}$$

At this concentration, the semidilute solution is a close packing of "blobs", inside which the chain obeys Zimm–Stockmayer statistics, but above this concentration, we cannot use any longer the notion of concentration blobs; as we already mentioned for a semidilute solution obtained from isolated chains in the Zimm–Stockmayer regime, the different parts of the molecule that have reached the Zimm–Stockmayer regime interpenetrate when the concentration is increased further.

We now calculate the radius of a test chain in the semidilute solution when c increases from c^*_Θ to 1 in these two limits.

(a) $\Lambda > P^{-1/3}$. In the whole concentration range the test chain may be viewed as a close packing of Θ concentration blobs and different chains do not interpenetrate. Each chain forms thus a close packing of blobs of size ξ with a radius

$$R \sim (N/c)^{1/3}a \tag{32}$$

(b) $\Lambda < P^{-1/3}$. When $c^*_\Theta < c < c_\Theta^{ZS}$, the blobs have Θ solvent statistics, and the same argument leads to the radius given by eq 32. At the concentration c_Θ^{ZS}, the excluded-volume interaction leading to the Θ behavior is completely screened and locally the chain has ideal statistics. As the concentration is increased these different Zimm–Stockmayer regions overlap progressively and the chains remain ideal over larger and larger length scales. Different chains do not interpenetrate if the size of the ideal regions remains smaller than the radius of one chain. This is always the case if $\Lambda > N^{-1/3}$ and the test chain radius is given by eq 32. If $\Lambda < N^{-1/3}$, when the overlap concentration of ideal chains $c^*_{ZS} \sim N^{1/4}\Lambda^{3/4} \ll 1$ is reached, the chain becomes ideal at all length scales and the radius is the Zimm–Stockmayer radius independent of concentration.

On Figure 3 we plot the radius of the test chain in a semidilute Θ solvent as a function of concentration in the case where $\Lambda < N^{-1/3}$. The plot would be similar if $\Lambda > N^{-1/3}$ but $c^*_{ZS} \gg 1$ and the ideal regime $c > c^*_{ZS}$ does not exist.

The various possible regimes for the radius of a chain are displayed on Figure 4 in a (Λ,c) plane for given values of N and P such that $N > P^{6/5}$.

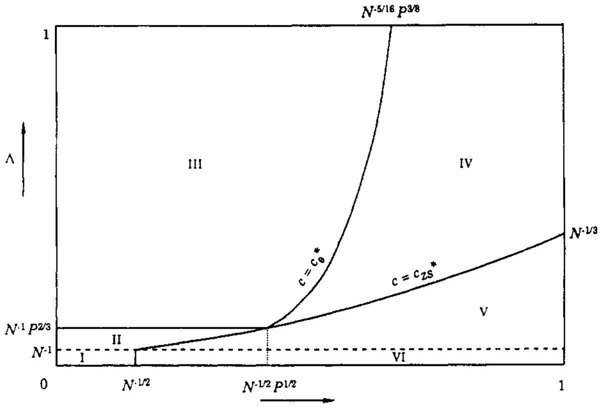

Figure 4. Different regimes for branched chains of N monomers in a melt of linear chains of P monomers, when $\upsilon = 0$ ($N > P^{6/5}$): I, dilute ideal linear chains ($R \sim N^{1/2}$); II, dilute Zimm–Stockmayer branched chains ($R \sim N^{1/4}\Lambda^{-1/4}$); III, dilute Θ branched chains ($R \sim N^{7/16}\Lambda^{-1/16}P^{-1/8}$); IV, semidilute nonoverlapping chains ($R \sim N^{1/3}c^{-1/3}$); V, semidilute overlapping chains ($R \sim N^{1/4}\Lambda^{-1/4}$); VI, semidilute ideal linear chains ($R \sim N^{1/2}$).

III.2.2. Semidilute Solutions in a Good Solvent.

The properties of semidilute solutions in a good solvent may be described with a blob model very similar to that used for the Θ solvent. The size of the good solvent blobs ξ and the number of monomers in a blob g are obtained by the standard arguments

$$\xi \sim c^{-1}\Lambda^{1/5}(\upsilon/P)^{-2/5}$$

$$g \sim c^{-2}\Lambda^{3/5}(\upsilon/P)^{-6/5} \tag{33}$$

As the concentration is increased, the blob no longer has branched good solvent statistics when g reaches one of the boundaries of the good solvent regime in Figure 2.

(a) If $\Lambda > P^{-1/3}\upsilon^2$, the blobs show Θ statistics when $g \sim \Lambda^{3/5}P^{6/5}\upsilon^{-16/5}$, i.e., at a concentration $c \sim \upsilon$.

(b) If $P^{-2}\upsilon^2 < \Lambda < P^{-1/3}\upsilon^2$, the blobs become ideal when $g \sim \Lambda^{-3/5}P^{4/5}\upsilon^{-4/5}$, i.e., at a concentration $c \sim \Lambda^{3/5}(\upsilon/P)^{-1/5}$.

(c) If $\Lambda < P^{-2}\upsilon^2$, the concentration blob becomes a linear swollen blob when $g \sim \Lambda^{-1}$ at a concentration $c_1 \sim \Lambda^{4/5}(\upsilon/P)^{-3/5}$.

In the first two cases, a further increase in concentration leads to a behavior exactly similar to that discussed for a Θ solvent. We only need to discuss the last regime that gives a new behavior. We thus focus on the case $\Lambda < P^{-2}\upsilon^2$ for a chain where $N > P^2\upsilon^{-2}$ (branching being irrelevant for smaller chains).

Above the concentration c_1 the solution is locally similar to a solution of linear macromolecules in a polymeric solvent,[16] for which

$$\xi \sim c^{-3/4}(\upsilon/P)^{-1/4} \tag{34}$$

$$g \sim c^{-5/4}(\upsilon/P)^{-3/4} \tag{35}$$

We may then consider the branched polymer as a branched chain of these linear blobs with an effective branching ratio $\Lambda_{\text{eff}} = \Lambda g$.

If the concentration is small enough, different chains do not interpenetrate and the radius is $R \sim (N/c)^{1/3}$. At higher concentrations the branched chain of blobs becomes ideal and has a radius

$$R \sim \left(\frac{N}{g}\right)^{1/4}\frac{1}{\Lambda_{\text{eff}}^{1/4}}\xi \sim N^{1/4}\Lambda^{-1/4}c^{-1/8}(\upsilon/P)^{1/8} \tag{36}$$

The crossover between these two regimes occurs at a

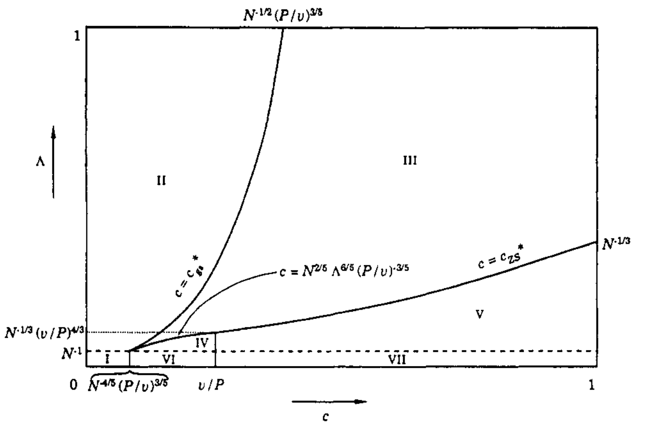

Figure 5. Different regimes for branched chains of N monomers in a melt of linear chains of P monomers, when $0 < \upsilon < 1$ and $N > P^2\upsilon^{-2}$: I, dilute swollen linear chains ($R \sim N^{3/5}(\upsilon/P)^{1/5}$); II, dilute swollen branched chains ($R \sim N^{1/2}\Lambda^{-1/10}(\upsilon/P)^{1/5}$); III, semidilute nonoverlapping branched chains ($R \sim N^{1/3}c^{-1/3}$); IV, semidilute overlapping branched chains with local swelling of linear parts ($R \sim N^{1/4}\Lambda^{-1/4}c^{-1/8}(\upsilon/P)^{1/8}$); V, semidilute overlapping branched chains without local swelling of linear parts ($R \sim N^{1/4}\Lambda^{-1/4}$); VI, semidilute linear chains with local swelling ($R \sim N^{1/2}c^{-1/8}(\upsilon/P)^{1/8}$); VII, semidilute linear chains without local swelling ($R \sim N^{1/2}$).

concentration

$$c_{ZS}{}^{b} \sim N^{2/5}\Lambda^{6/5}(\upsilon/P)^{-3/5} \tag{37}$$

At even higher concentrations the blobs themselves are no longer swollen and the chain is ideal at all length scales. This occurs when $g = (P/\upsilon)^2$ for a concentration

$$c \sim \upsilon/P \tag{38}$$

The correlation length is then that of a linear semidilute solution in a Θ solvent ($\xi \sim c^{-1}$),[16] and the chain radius is the "ideal radius" R_{ZS}. Note that the intermediate regime of eq 36 exists only if $c_{ZS}{}^{b} < \upsilon/P$ or

$$\Lambda < N^{-1/3}(\upsilon/P)^{4/3} \tag{39}$$

All these results are summarized in Figure 5 where the various regimes for the radius R are displayed in a (Λ, c) plane. When $\upsilon = 1$ and $P = 1$, the plot of Figure 5 should reduce to Figure 4 of ref 11. This is not, however, the case. As we already mentioned, the ideal behavior of branched chains was not considered in this paper and this diagram is erroneous.

IV. Phase Separation

Phase separation in branched polymer solutions has already been studied by Daoud et al.[17] for a monomeric solvent. We use here a similar approach to determine the critical point and the shape of the coexistence curve when the solvent is a linear polymer of length P. For phase separation between linear and branched molecules to occur, the effective interaction υ between B monomers must be attractive; i.e., υ must be negative. Phase separation is achieved when this attraction is large enough to exceed the entropic part of the free energy that favors mixing. In polymer mixtures, the large number of monomers per molecule greatly reduces the entropic contribution compared to monomeric mixtures, and a very small attraction is sufficient to induce phase separation: the critical point is very close to the Θ point ($\upsilon = 0$). It is, therefore, legitimate to use a free energy corresponding to chains in a Θ solvent as a starting point to study phase separation: at least at small length scales the chains have the same statistics as at the Θ point.

We have already shown that dilute branched chains in a solvent of length P exhibit three different regimes. We must consider these regimes separately to discuss the phase separation properly.

(1) **Compact Regime.** This regime is somewhat special because it does not allow semidilute solutions to exist. Branched chains do not "see" each other as long as they are dilute, and they are dilute in the whole range of concentration since they are compact. From a scaling point of view, the only result we can give is trivial: the critical concentration c_K is close to 1. To determine the critical excluded-volume parameter υ_K, one would have to use a much more refined model; this is beyond the scope of this paper.

(2) **Zimm–Stockmayer Regime.** We have stated above that branched chains are ideal when all correlations between monomers can be neglected. We expect therefore that a mean-field free energy should be appropriate to describe phase separation in this limit. As the mean-field approach for a binary polymer system is classical and has been extensively developed,[1] we only quote the results here. The free energy is written in a Flory manner as

$$\frac{F}{T} = \frac{c}{N}\ln c + \frac{1-c}{P}\ln(1-c) + \chi c(1-c) \tag{40}$$

The coordinates of the critical point are

$$c_K = \frac{P^{1/2}}{N^{1/2} + P^{1/2}}$$

$$\chi_K = \frac{1}{2}\frac{(N^{1/2} + P^{1/2})^2}{NP} \tag{41}$$

or equivalently

$$\upsilon_K \equiv 1 - 2P\chi_K = -\frac{P^{1/2}}{N}[2N^{1/2} + P^{1/2}]$$

For large branched molecules compared to the linear chains, $N \gg P$, this reduces to

$$c_K \sim N^{-1/2}P^{1/2}$$

$$\chi_K = \frac{1}{2P}\left(1 + \frac{P^{1/2}}{N^{1/2}}\right) \tag{42}$$

$$\upsilon_K \sim -N^{-1/2}P^{1/2}$$

We see that both c_K and υ_K are very small and have the same scaling form. The excluded-volume interaction being strongly screened, the critical demixing concentration is much higher than the overlap concentration c^*. When eq 40 is used, the coexistence curve may be obtained by equating the chemical potentials and the osmotic pressures in the two phases at equilibrium. The coexistence curve has not, in general, a simple algebraic expression.

(3) **Θ Regime.** We know that the phase separation must occur in the semidilute regime, because branched chains do not "see" each other when they are dilute. If υ were exactly equal to zero, the free energy per unit volume of the solution would be that of a Θ solution

$$\frac{F}{T} = a^{-3}\frac{c}{N}\ln c + \frac{1}{\xi^3} \tag{43}$$

where the first term represents the entropy of mixing of the chains and the second one the energetic contribution: each blob, of size ξ, has an energy T.

Now, if v is slightly negative, one must add an attractive binary interaction term. Following the work of Daoud et al.,[17] we use a mean-field approximation for this term and write the attraction energy $(1/2)(v/P)c^2$. The free energy of the blend in a poor solvent thus becomes

$$a^3\frac{F}{T} = \frac{c}{N}\ln c + \frac{1}{2}\frac{v}{P}c^2 + \Lambda^{-3/5}P^{-6/5}c^{21/5} \tag{44}$$

The critical point is the point where the second and third derivatives of F with respect to the concentration vanish:

$$c_K \sim N^{-5/16}\Lambda^{3/16}P^{3/8} \tag{45}$$

$$v_K \sim -N^{-11/16}\Lambda^{-3/16}P^{5/8} \tag{46}$$

The critical volume fraction c_K has here the same scaling form as the overlap concentration c^*_Θ. In the limit where $P = 1$, we recover the results of ref 17. To determine the shape of the coexistence curve in the phase dense in branched polymer for $c \gg c^*_\Theta$, we write that in the two phases at equilibrium the osmotic pressure is very small. This amounts to writing that the scaling behavior of the two interactions is the same: $(v/P)c^2 \sim \Lambda^{-3/5}P^{-6/5}c^{21/5}$ or

$$v \sim c^{11/5}\Lambda^{-3/5}P^{-1/5} \tag{47}$$

The curve is almost parabolic $(11/5 \approx 2)$, but eq 47 is not valid for all concentrations above c^*_Θ; when the concentration blobs enter the Zimm–Stockmayer regime, the free energy (eq 44) is no longer correct. This happens at $c = c_\Theta^{ZS}$ (eq 31); for higher concentrations we expect the phase diagram to be well described by the mean-field Flory–Huggins theory. At this concentration $c = c_\Theta^{ZS} = \Lambda^{1/2}P^{1/6}$, the excluded-volume parameter is

$$v \sim (\Lambda^{1/2}P^{1/6})^{11/5}\Lambda^{-3/5}P^{-1/5} \sim \Lambda^{1/2}P^{1/6}$$

which corresponds to the result obtained by Daoud et al. for $P = 1$.

The crossover between the ideal regime and the Θ regime for the chains in dilute solutions occurs for $\Lambda = N^{-1}P^{2/3}$ $(N > P)$. One easily checks that at this point the phase diagram in the Θ regime crosses over smoothly to the mean-field phase diagram of the previous section.

V. Concluding Remarks

We have studied the properties of mixtures of linear and randomly branched chains in the melt using a Flory theory and scaling arguments. Even for a single isolated branched chain in a melt of linear chains the number of control parameters (Λ, N, P, v) is large, and several possible regimes have been identified in the space of these parameters. If the branched chain has a sufficiently high molecular weight, its conformation is qualitatively the same as that in a monomeric solvent. If the branched chain has a lower molecular weight, two new types of behaviors are observed. When the branching fraction is large, the linear chains do not penetrate the branched chain, which forms a compact sphere in the polymeric solvent. When the branching fraction is small, the branched chain becomes ideal in the sense that it obeys the Zimm–Stockmayer statistics. This very rich variety of behaviors compared to what is expected for blends of linear chains in the melt is due to the fact that the space dimension $d = 3$ is smaller than the upper critical dimension for molten branched chains $d_c = 4$. Similar effects would be expected for linear chains in spaces of dimensions lower than 2 (not physical).

When blob arguments are used, the structure of semidilute solutions stems from that of a single branched chain; for high branching fractions, different chains do not interpenetrate and an increase of the branched chain concentration contracts these chains; for lower branching fractions, the branched chains interpenetrate at high concentration and show ideal behavior at large length scales.

If the Flory interaction parameter is large enough, in a poor solvent, branched and linear chains phase separate; three regimes have been identified. If the branched chains are compact, no semidilute solution exists and the phase separation occurs for volume fractions of branched chains close to 1; our Flory-like theory is not then appropriate to discuss it quantitatively. This raises the question of the phase separation between a polymer melt and small hard spheres that does not seem to have received any theoretical attention. If the branched chains are ideal, the phase separation is well described by the classical Flory–Huggins theory. Finally, for very long branched chains the critical concentration for demixing is the overlap concentration. This is at variance with the behavior of the mixture of linear chains where the critical concentration is always higher than the overlap concentration of the larger chains. In general, due to the more compact structure of branched chains, we expect branched and linear chains to be more compatible than chemically different linear chains.

Our approach is based on a Flory theory that is known not to give exact exponents in most cases. We believe, however, that the general trends that we just summarized are correct; a use of more exact theory would only modify the precise values of the exponents. Another limitation of the Flory approach is the description of the interactions by a Flory parameter χ independent of concentration. More generally, one should introduce an effective Flory parameter that is concentration-dependent; its variation with concentration is, however, not well understood. Finally, we also note that the Flory theory is not entirely consistent: in the Θ regime, the critical value of the excluded-volume parameter scales as $v_c \sim N^{-\phi}$ where ϕ is the crossover exponent of the Θ fixed point. The results of section IV are consistent with $\phi = {}^{11}/_{16}$. The exponent ϕ could also be extracted from the crossover between the good solvent and the Θ solvent radius of isolated chains. This gives a different value $\phi = {}^{5}/_{16}$.

Experimentally, the best way to obtain randomly branched polymers is to induce a reaction between difunctional and trifunctional units. This, however, creates polymers with a broad polydispersity, which is obviously relevant for the phase separation. This polydispersity should be included in the theory to allow comparison with existing experiments; we hope to do that in a future work. Experimentally there is also often a competition between demixing transition and a gelation transition.[18]

A more direct comparison between the present scaling theory and experiments could be made by forming monodisperse fractions of branched chains and mixing them with linear chains. In order to achieve at least partial compatibility between the polymers, one, however, needs a small interaction parameter χ. This is necessary to determine the structure of the branched chains (e.g., by neutron scattering) and the phase diagram.

Acknowledgment. F.R. thanks the French company Rhône-Poulenc for financial support. We also want to thank Dr. G. Schorsch (Rhône-Poulenc) for suggesting this problem and Dr. J.-P. Pascault (INSA Lyon) for interesting discussions on thermoset resins.

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(2) Pesci, A.; Freed, K. *J. Chem. Phys.* **1989**, *90*, 2003, 2017.

(3) Schweitzer, K.; Curro, J. *Phys. Rev. Lett.* **1988**, *60*, 809. Curro, J.; Schweitzer, K. *J. Chem. Phys.* **1988**, *88*, 7242.

(4) Bates, F. S.; et al. *Phys. Rev. Lett.* **1985**, *55*, 2425. Bates, F. S.; et al. *Macromolecules* **1986**, *19*, 1938.

(5) Paul, D. R., Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1978; Vols. 1 and 2.

(6) Verchère, D.; et al. *Miscibility of epoxy monomers with carboxyl-terminated butadiene–acrylonitrile random copolymers*; preprint, 1990.

(7) Riew, C. K., Gillham, J. K., Eds. *Rubber Modified Thermoset Resins*; Advances in Chemistry Series 208; American Chemical Society: Washington, DC, 1984.

(8) de Gennes, P.-G. *Biopolymers* **1968**, *6*, 715.

(9) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.

(10) Dobson, G. R.; Gordon, M. *J. Chem. Phys.* **1964**, *41*, 2389.

(11) Daoud, M.; Joanny, J. F. *J. Phys.* (*Paris*) **1981**, *42*, 1359.

(12) Cates, M. E. *Phys. Rev. Lett.* **1984**, *53*, 926. Cates, M. E. *J. Phys.* (*Paris*) **1985**, *46*, 1059.

(13) Isaacson, J.; Lubensky, T. C. *J. Phys., Lett.* **1980**, *41*, 469.

(14) Parisi, G.; Sourlas, N. *Phys. Rev. Lett.* **1981**, *46*, 871.

(15) de Gennes, P.-G. *J. Polym. Sci., Polym. Symp.* **1977**, *61*, 313. Joanny, J.-F.; et al. *J. Phys.* (*Paris*) **1981**, *42*, 1045.

(16) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(17) Daoud, M.; Pincus, Ph.; Stockmayer, W. H.; Witten, T., Jr. *Macromolecules* **1983**, *16*, 1833.

(18) de Gennes, P.-G., preprint, 1990.