Abstract

The radius of gyration of a polymer chain immersed in a low molecular weight solvent is known to vary monotonically with the solvent quality. Here, we consider the behavior of a chain immersed in a high molecular weight solvent (polymer melt). Unsurprisingly, we find that, as the incompatibility between the chain and the polymer melt is increased, the two limiting conformations of the chain are the ideal random coil \( R \approx aN^{1/2} \) and the dense globule \( R \approx aN^{1/3} \). We show, however, that between these two limits the radius of gyration of the chain presents a hysteretic behavior.

Introduction

The behaviour of an isolated linear chain (with degree of polymerization \( N \)) dissolved in a solvent of low molecular weight is well understood \([1, 2, 3]\). The
effective interaction between two monomers may be described in terms of the Flory parameter $\chi$, which, in most cases, is positive. For $0 \leq \chi \leq \frac{1}{2}(1 - \frac{1}{\sqrt{N}})$, the chain is swollen and its radius, $R$, is given by $R \simeq aN^{3/5}(1 - 2\chi)^{1/5}$ where $a^3$ is the monomer volume. For $\frac{1}{2}(1 - \frac{1}{\sqrt{N}}) \leq \chi \leq \frac{1}{2}(1 + \frac{1}{\sqrt{N}})$, the chain can be described as a random walk and $R \simeq aN^{1/2}$. For $\frac{1}{2}(1 + \frac{1}{\sqrt{N}}) \leq \chi \leq 1$, the chain is collapsed and its radius is given by $R \simeq aN^{1/3}(-v/a^3)^{2/3}$. For $\chi$ larger than unity, $R$ is given by $R \simeq aN^{1/3}$. The radius of the chain therefore decreases monotonically when $\chi$ increases, that is when the quality of the solvent (described by the excluded volume parameter $v = a^3(1 - 2\chi)$) decreases, and no hysteresis in the chain conformation is expected as $\chi$ is varied [4].

Consider now an isolated linear chain, with degree of polymerization $N$, dissolved in a melt of chemically identical chains with degree of polymerization $P$. This situation is also well understood [1, 2, 3]. The bare monomer-monomer interaction of the $N$-chain, described by the excluded-volume parameter $a^3$, are screened out by the $P$-chains, and the effective excluded volume parameter is given by $a^3/P$ [5, 6]. Consequently, the $N$-chain remains ideal (i.e. $R \simeq aN^{1/2}$) as long as $N \leq P^2$. However, for $N > P^2$, the chain is swollen and its radius is given by $R \simeq aN^{3/5}P^{-1/5}$ [7, 8, 9, 10].

In the present article, we generalize this analysis to the case where the $N$-chain and the $P$-chains are chemically different (see the work of Joanny and Brochard [11]). Consider for instance the limit $P \to \infty$. For $\chi = 0$, the chain
radius is given by $R \simeq aN^{1/2}$ while for large values of $\chi$ (i.e. $\chi \gg 1$), we expect $R$ to be given by $R \simeq aN^{1/3}$. We here investigate the whole range of incompatibilities, both for $P \to \infty$ and for finite $P$.

**Free energy**

Consider a chain ($N$ monomers of size $a$) immersed in a melt of chemically different chains ($P$ monomers, Flory interaction $\chi$ between both types of monomers). The Flory free energy [5] of the system can be expressed as:

$$F = \frac{R^2}{Na^2} + \frac{Na^2}{R^2} + N\chi \left(1 - \frac{Na^3}{R^3}\right) + \frac{N^2a^3}{PR^3} + \frac{N^3a^3}{PR^6}$$ (1)

The first and second terms are the classical elastic and confinement terms. The third term corresponds to enthalpic interactions between the $N$-chain and the $P$ chains: for each monomer of the $N$-chain, these interactions amount to $\chi kT$ per contact with a melt monomer (probability $1 - \phi_N$, where $\phi_N = Na^3/R^3$ is the volume fraction of the $N$-chain). The last two terms describe the screened excluded volume interactions [6] (see Introduction). The radius of the chain is obtained by minimizing the free energy, along with the condition $R \geq aN^{1/3}$. For the moment, we consider the limit of high melt molecular weights ($P \to \infty$) and therefore neglect the last two terms on the r.h.s. of eq. (1).

The general shape of the above free energy, as a function of the radius of gyration $R$, depends on the degree of incompatibility: three different regimes...
arise, depending on the value of the Flory interaction parameter $\chi$ compared to the following values:

$$\chi_- \equiv N^{-2/3} \quad (2)$$

$$\chi_+ \equiv N^{-1/2} \quad (3)$$

In the intermediate regime $\chi_- < \chi < \chi_+$, the free energy has two different minima (see Fig 1): one that corresponds to a Gaussian chain ($G$, radius of gyration $aN^{1/2}$), and one that corresponds to a dense globule ($D$), whose radius of gyration is very close to $aN^{1/3}$. In the weak and strong incompatibility regimes, conversely, there is only one minimum: the chain is unperturbed ($G$) if the incompatibility is weak ($\chi < \chi_-)$, and it is collapsed into a dense globule ($D$) in the reverse case ($\chi > \chi_+$).

We now focus on the intermediate regime ($\chi_- < \chi < \chi_+$), where two conformations are possible, and we discuss their relative stabilities. The more stable conformation is the dense globule $D$ (except when $\chi$ approaches $\chi_-)$). However, since $\chi < \chi_+$, the amplitude of the barrier $\Delta F \simeq kT/(N\chi^2)$, is large compared to thermal fluctuations and the chain retains a Gaussian conformation. It is in fact necessary to go into some more detail in order to fully justify the above statement. Indeed, the above Flory approach is global (mean field). Hence, the sole consideration of equation (1) only shows that the monomers of the chain have no tendency to collapse in a collective manner. But one can wonder whether the chain could tend to collapse locally, which would progressively lead to the dense collapsed state $D$, possibly
without any need for passing high energy barriers. One can easily show that this is not the case. Indeed, the barrier $kT/(m\chi^2)$ for a subchain containing $m$ monomers ($m < N$) is even higher than the barrier for the whole chain: there is no tendency towards any local collapse of the chain. The global, Flory approach is thus sufficient.

Since the amplitude of the barrier in the intermediate regime is high (except near $\chi_-$ or $\chi_+$), the radius of gyration of the chain presents an hysteretic behavior as the incompatibility $\chi$ is varied. If we start from a low value of $\chi$ ($\chi < \chi_-$) and progressively increase $\chi$, the chain remains Gaussian ($R \simeq aN^{1/2}$) as long as $\chi < \chi_+$. For $\chi > \chi_+$, the chain collapses and reaches its equilibrium conformation, namely that of a dense globule ($R \simeq aN^{1/3}$). If, on the other hand, we start from a high value of $\chi$ ($\chi > \chi_+$) and progressively decrease $\chi$, the chain remains collapsed as long as $\chi > \chi_-$ and recovers its Gaussian conformation only for $\chi < \chi_-$. The fact that both antagonistic transitions (collapse and swelling) take place for different degrees of incompatibility ($\chi_+ \neq \chi_-$) constitutes a hysteretic behavior.

**Interpretation of the hysteresis**

The above Flory approach describes the hysteretic behaviour of the system. To understand the physical origin of the hysteresis, we present below two alternative interpretations. The first one is an analogy with adsorption (the collapse of the $N$-chain is analog to self-adsorption). The second interpreta-
tion is based on the fact that the melt chains may or may not penetrate the
volume pervaded by the $N$-chain, depending on the degree of incompatibility.

Let us start with the first interpretation. In the classical scaling theory of
polymer adsorption \cite{2}, each adsorbed blob ($g$ monomers) gains an enthalpy
$n\epsilon$ through the contact of $n$ of its monomers with the surface (typically
$n = g^{1/2}$ for a Gaussian blob). This energy gain is balanced by a free energy
loss (confinement entropy) of the order of $kT$ per blob. Hence, the number
of monomers per blob is given by $n\epsilon = kT$, which reads: $g = (kT/\epsilon)^2$. The
gain in free energy that results from this balance is of order $kT$ per blob.
Therefore, for the chain to adsorb, it has to contain at least one blob, \textit{i.e.}
$N \geq (kT/\epsilon)^2$.

Consider now the present situation of one $N$-chain immersed in an incom-
patible melt. The equilibrium conformation of a confined chain ($R \leq aN^{1/2}$)
can be described in terms of $N/g$ superimposed blobs, each containing $g$
monomers (with $R = a g^{1/2}$). Typically, the number of contacts between one
blob and other monomers of the chain is $n = g\phi$, where $\phi = Na^3/R^3$ is the
overall chain volume fraction. If the confinement of the chain results from
the incompatibility with the $P$ melt, its equilibrium conformation can be
seen in terms of self-adsorption: if the incompatibility (measured by $\chi$) is
strong enough and if the volume fraction is sufficiently high, the contacts
between monomers of the chain provide a sufficient enthalpic gain to yield a
certain blob dimension (\textit{i.e.}, radius of gyration). Whereas if $\chi$ is small, the
corresponding blob dimension is too large \((g > N)\), and the chain is then Gaussian. Following the analogy with the problem of an adsorbed chain on a surface and noticing that here, \(\epsilon = \chi kT\), the equilibrium between enthalpy gain and confinement entropy can be written as \(n\chi kT = kT\), i.e.,

\[
g\phi \chi = 1
\]

The fact that the above criterion depends on the chain volume fraction \(\phi\) is the very reason for the existence of the hysteresis. Indeed, it causes the corresponding adsorption thresholds for the Gaussian conformation and for the dense globule to be different. For the Gaussian chain, for instance, the blob is the whole chain \((g = N)\) and the volume fraction is small \((\phi = N^{-1/2})\). The corresponding incompatibility threshold is \(\chi = \chi_+ = N^{-1/2}\). Hence, as long as \(\chi < \chi_+\), the chain is not self-adsorbed (Gaussian conformation). Once it reaches \(\chi_+\), it starts to self-adsorb. The volume fraction correspondingly increases, which in turn reinforces the tendency towards self-adsorption. This process only stops when steric hindrances prevent the chain any from further collapse, namely when \(R \simeq aN^{1/3}\).

Conversely, when the chain is a collapsed globule, its volume fraction \(\phi\) is equal to unity, and the blob corresponds to \(g = R^2/a^2 = N^{2/3}\) monomers. The corresponding threshold is \(\chi = \chi_- = N^{-2/3}\) (which is lower than the Gaussian threshold \(\chi_+\)). Hence, if \(\chi\) is above \(\chi_-\), the globule is stable. If \(\chi\) becomes lower than \(\chi_-\), however, the chain cannot continue to remain self-adsorbed. It therefore starts to swell. This reduces its volume fraction,
which in turn enhances its swelling, until the chain reaches its equilibrium, ideal, Gaussian conformation.

An alternative derivation of equation (4) is based on the behaviour of the melt chains. If the incompatibility is strong, entering the volume pervaded by the $N$-chain is too unfavourable for the $P$ chains, and they rather go back into a pure melt region. This can be described more quantitatively as follows. For a $P$ chain, assuming that it remains Gaussian, penetrating the $N$ region of extension $R$ takes up roughly $p = (R^2/a^2) = g$ monomers, among which a fraction $\phi$ are in contact with the $N$-chain (where $\phi \simeq Na^3/R^3$ is still the volume fraction of the $N$-chain). If the corresponding enthalpy $p\phi\chi kT$ is higher than $kT$, then the $P$ chain rather goes back into the melt, thus suffering an entropy loss of order $kT$. This criterion again yields equation (4). Note that in the case of the globular conformation ($\phi = 1$), where the melt chains rather turn back into the melt after $p$ monomers have penetrated the $N$ region ($p < g = R^2/a^2$), it is possible to estimate the width $\lambda \simeq a^1/\chi$ of the interface between the globule and the melt (see references [12, 13] for the similar problem of the interface between two melts). The interface width increases when the incompatibility $\chi$ is reduced. One can check that the transition from the globule to the Gaussian conformation ($\chi \simeq \chi_-$) corresponds to the point where the interface has invaded the whole globule ($\lambda \simeq R$).

We have shown that the consideration of equation (4) obtained through
the analogy with adsorption or alternatively through the consideration of the melt chains, proves that the chain conformation has a hysteretic behaviour when the Flory parameter $\chi$ is tuned. It thus provides a simple physical interpretation for the hysteresis obtained initially through the Flory approach.

**Shorter melt chains**

The above considerations show that the radius of gyration of the $N$-chain has a hysteretic dependence on the Flory parameter $\chi$ in the limit of very long melt chains ($P \rightarrow \infty$). In the opposite limit (low molecular weight solvent with $P = 1$), the radius of gyration is known to be a single-valued function of $\chi$. In the following, we consider a melt with finite chain length $P$ in order to investigate the crossover between hysteretic and non-hysteretic behaviours.

The essential point is that when the melt chain length is decreased, the translational entropy of the molecules becomes comparatively more important. When $P < \chi^{-1}$, the two-body term in the Flory free energy (equation 1) exceeds the enthalpic term. As a result, the free energy has now only one minimum, and the variations of the radius of gyration with the degree of incompatibility are then similar to the case of a low molecular weight solvent. The corresponding phase diagram for the $N$-chain for all values of $P$ is depicted on Fig. 3. In the swollen regime (S), the radius of gyration is given by $R \simeq aN^{3/5}P^{-1/2}(1 - 2\chi)^{1/5}$ [7]. For $P \simeq 1$, we recover the known bad-to-good solvent transition which includes the $\theta$-solvent regime
for $\chi$ of order unity ($\chi = 1/2$ in the classical description by Flory recalled in the Introduction). When $P \leq N^{1/2}$, as was shown by J.-F. Joanny and F. Brochard [11], a hysteresis is present between $\chi = (P^{-1} - N^{-1/2})/2$ and $\chi = (P^{-1} - N^{-1/2}P^{-1/4})/2$ (this zone appears only as a double line in the Log-Log diagram of Figure 2). For $N^{1/2} \leq P \leq N^{2/3}$, the width of the hysteresis range for $\chi$ increases with the melt molecular weight $P$ (since $\chi_- \simeq P^{-1}$ and $\chi_+ = \text{const}$ in that regime). For $P \geq N^{2/3}$, the width is constant (equations 2 and 3).

**Conclusion**

A polymer chain immersed in a melt of long, chemically different molecules, adopts either a Gaussian conformation, or a dense, collapsed conformation. The transition between both situations was shown to be hysteretic when the degree of incompatibility is tuned (this can be achieved for instance by varying the system temperature). In practice, this effect will be more easily observed at an interface, with scarcely grafted $N$-chains. For such a polymer brush, the hysteretic behaviour should combine with the tendency to in-plane micellization [14] to yield a rich temperature dependence. The transition could be used for tuning the interpenetration between a brush and a matrix. The hysteresis would then prove very useful for designing a system that could be insensitive to weak temperature fluctuations, while it could be switched between both states through larger temperature changes. In
order to obtain a good coupling between the interfacial chains and the matrix, large molecular weights are usually required. This corresponds to rather small values of $\chi_-$ and $\chi_+$. Such values can be obtained for instance by using protonated $P$-chains and deuterated $N$-chains (or vice-versa) [13]. Another possibility would be to use a homopolymer melt ($P$-chains) and an $N$-chain made of mainly the same monomer species as the $P$-chains, copolymerized with a very small fraction of chemically different monomers (the number of comonomers and their incompatibility must be small, in order to avoid microphase separation). Kinetical aspects of the transition at $\chi \approx \chi_-$ and $\chi \approx \chi_+$ would require a separate development. In the case of a simple solvent, many studies have been devoted to this subject [16, 17]. Various intrachain effects may take place, such as a glass transition or physical crosslinking in the globule, or such as the formation of tight knots [18] through sudden tension in a swelling entangled chain. In a hypothetical system where none of these effects would be dominant, we expect the kinetics to be governed by diffusion of the molecules: in the present case of a high molecular weight solvent, the typical time-scale would therefore be the therefore the reptation time of the shorter chains ($N$ or $P$).

**Acknowledgments.** We thank P.-G de Gennes and T. Waigh for useful discussions, and Ludwik Leibler for indicating reference [11] to us.
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Figure Captions.

**Figure 1.** Flory free energy of a linear polymer molecule ($N$ monomers) immersed in a melt of very long, chemically different chains, in the case of an intermediate degree of incompatibility ($N^{-2/3} < \chi < N^{-1/2}$). $R$ is the radius of gyration of the chain. One minimum of the free energy corresponds to a dense globule. The other one corresponds to a Gaussian conformation.

**Figure 2.** If the melt chains ($P$ monomers) are long, the $N$-chain displays a hysteretic behavior when the degree of incompatibility is varied. If the melt chain are shorter, their translational entropy enhances interpenetration with the $N$-chain: there is no more hysteresis when $P < N^{1/2}$. For a simple solvent ($P = 1$), we recover the good, theta and bad solvent regimes.
\[ R = aN^{1/2} \Rightarrow aN^{1/2} \quad (G) \]

or

\[ (D) \ aN^{1/3} \Rightarrow R = aN^{1/3} \]

\[ R = aN^{3/5}P^{-1/5} \quad (S) \]