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Single-Chain Collapse or Precipitation? Kinetic Diagram of the States of a Polymer Solution

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ABSTRACT: Relaxation of a dilute polymer solution after an abrupt cooling from good- or Θ-solvent to poor solvent is considered. Four processes are involved in relaxation, namely, single unknotted chain crumpling, single-chain knotting, interchain aggregation, and interchain entanglement formation. Five different regimes are described depending on the relaxation times of these stages; they are presented on a *T–c* diagram of the solution. The interpretation of recent experiments of Chu et al.[1] on the kinetic study of a coil-to-globule transition is discussed.

1. Introduction

Single polymer chain collapse, or coil-to-globule phase transition, has been investigated extensively, both theoretically and experimentally (see ref 2 and references therein). It has implications both for biological and synthetic polymers[3,4] and is of great importance for general concepts in the field of polymer physics. Although the single-chain regime seems the most fundamental for both chemical and biological applications, its observation is extremely difficult mainly because of the strong tendency toward segregation in a poor solvent. Using our quantitative theory of coil-to-globule transition,[2] we concluded in ref 5 that true equilibrium single-chain collapse has not been observed yet (for simple uncharged homopolymers without mesogenic groups).

To avoid the problems with aggregation, a kinetic study was performed recently[1] to observe collapse before precipitation. A two-stage kinetics reported in that work was corresponded with the theoretically predicted[6,7] two-stage kinetics of a single-chain collapse process, where fast crumpling of the unknotted chain and slow knotting of the collapsed polymer are the first and second stages, respectively.

In principle, however, there are three or even four kinetic processes, which have to be distinguished: (i) crumpling of macromolecules in the single-chain regime, (ii) knotting of crumpled macromolecules in the single-chain regime, (iii) polymer aggregation, and (iv) mutual entanglement of aggregated chains. Accordingly, many different scenarios can be realized in the system depending on the characteristic relaxation times of the processes listed above. The main task of the present paper is to describe all these scenarios systematically. It is done on the *T–c* diagram shown in Figure 1.

For experiments, the following questions can be discussed using our results in Figure 1:

(i) Is it possible to reach the globular state of chains in an unequilibrium polymer solution before precipitation?

(ii) What type of globular state can be realized under unequilibrium conditions? Is it the crumpled globule or the knotted one?

(iii) What is the dynamics of a dilute polymer solution initiated by fast cooling from good-solvent temperature?

In particular, the results of ref 1 seem to be interpreted quite naturally.

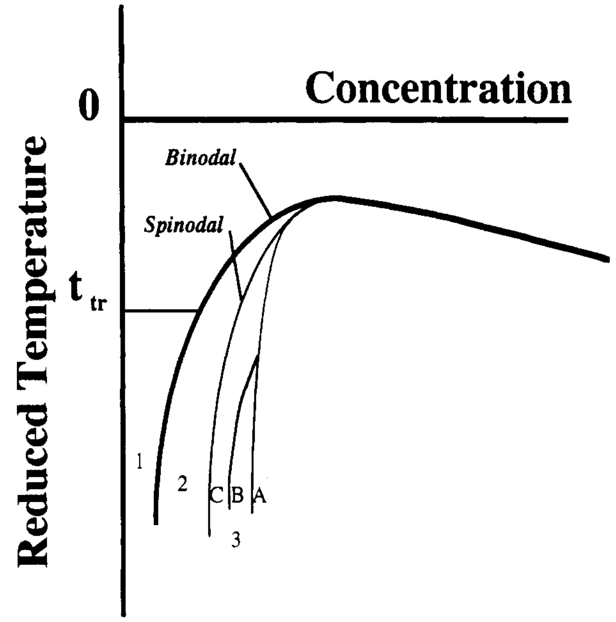

Figure 1. Schematic form of the kinetic phase diagram of a polymer solution. t_{tr} is the temperature of the coil-to-globule transition; other comments are in the text.

2. Region of a Stable Dilute Polymer Solution

To begin with, we will reproduce the main ideas of ref 7. Consider a single polymer chain in a good solution. With overwhelming probability, this swollen coil does not contain any knots (whatever it means for a linear chain). After an abrupt decrease of the temperature from good solvent conditions, the single polymer chain forms a crumpled globule. The relaxation time of this process is on the order of N^2 (N stands for the number of chain links, $N \gg 1$) or, more completely,

$$\tau_{\mathrm{crum}} \sim \eta \frac{|B| N^2}{\Theta} \frac{a^6}{C} \left[1 + \frac{\mathrm{const}}{N_e} \frac{a^6}{C} \right] \qquad (1)$$

Here η is the solvent viscosity, a is the link size, B and C are two- and three-body interaction constants of quasi-monomers, Θ stands for the Flory Θ-temperature (in energetic units), and N_e is the usual phenomenological parameter, which means the number of links along a chain between neighboring topological constraints. At this first stage the polymer still does not have any chain knots. We believe the knots are tied in the course of chain relaxation toward the state of the equilibrium globule, and this process is of reptational character. The relaxation time of knotting of an individual chain is, therefore, essentially more than τ_{crum} and is proportional to N^3 since this process is of the

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reptation type

$$\tau_{\mathrm{eq}} \sim \eta \frac{N^3}{\Theta} \frac{a^6}{C} \frac{(na^3)^2}{N_{\mathrm{e}}} \gg \tau_{\mathrm{crum}} \tag{2}$$

where $n \sim |B|/C$ is the globule density.

Let us comment here on the reason why we believe the chain starts with collapse in the unknotted state and forms knots during the relaxation in a collapsed state only. There are several works showing by computer simulation,[8,9] experimentally[10] and theoretically,[11,12] that the probability of a nontrivial knot grows very dramatically with polymer compaction. Therefore, we assume the situation to be as follows: at the first stage of the process, knots remain the same as in the Gaussian state; i.e., they are very weak and negligible compared to the heavily knotted equilibrium globule.

The reviewer suggested that we address the following question: what is the driving force for the knotting process in a compressed state? This force is of an entropic nature, and it is associated with entropy gain due to the fact that there are a lot of different knotted conformations for a compressed polymer and a remarkably smaller amount for a Gaussian chain. It can also be illustrated with the everyday experience of dealing with ropes: it is known that a crumpled rope becomes heavily knotted, and not an extended one. This fact is more rigorously analyzed in ref 12.

Let us now take a real dilute polymer solution of some nonzero concentration in good- or Θ-solution and cool it very quickly. What happens to our solution? If the system does not cross the coexistence curve on the phase diagram and stops at some point in region I (Figure 1), then the dissolved knotted globules represent the equilibrium state of the solution, so that formation of equilibrium globules is the last stage of the process.

Most experimenters believe that they work in this very regime. It is true, however, mainly very near the collapse temperature, just inside the transition range, where one actually cannot distinguish between the slightly contracted coil and the real globule. In reality, however, the dilute branch of the coexistence curve lies at very small concentrations at any temperature below the range of the coil-to-globule transition. Practically, it cannot be observed with modern instrumentation and the sample preparation technique at this time. The phase diagram in Figure 1 is presented in schematic form; the quantitative phase diagram was calculated in ref 5 for polystyrene in a cyclohexane solution (see Figure 4 in ref 5), where the smallness in the concentration is very obvious.

3. Region of Instability of Dilute Polymer Solution

What happens in real experiments at concentrations not so small? At first we suppose, that our solution has crossed not only the coexistence curve (binodal) but also the spinodal curve (region III in Figure 1). It is natural to expect fast aggregation here. However, it cannot be faster than the mean time interval between polymer–polymer collisions in a dilute solution:

$$\tau_{\mathrm{collis}} \sim s^2/D \tag{3}$$

Since the mean distance between the polymer chains in solution scales as $s \sim c^{-1/3}$ (c is the number of chains per unit volume) and the diffusion coefficient is $D = T/6\pi\eta R$ (T stands for temperature in energetic units, R is the chain hydrodynamic radius), one obtains

$$\tau_{\mathrm{collis}} \sim \eta \frac{N^{1/3} C^{1/3}}{|B|^{1/3} c^{2/3}} \tag{4}$$

In region III of the phase diagram (Figure 1) this collision interval corresponds roughly to a characteristic time of the precipitation process, because each collision leads to a chain–chain aggregation. What is the state of the individual polymer chains after the period τ_{collis} from the start of the process? It depends on the relations between the characteristic times τ_{crum}, τ_{eq}, and τ_{collis}.

If $\tau_{\mathrm{collis}} < \tau_{\mathrm{crum}} < \tau_{\mathrm{eq}}$ (region III-A in Figure 1), we will have naturally a fast aggregation of coils.

On the other hand, if $\tau_{\mathrm{crum}} < \tau_{\mathrm{collis}} < \tau_{\mathrm{eq}}$ (region III-B), then fast crumpling of the individual chains will be the first step of relaxation and aggregation will deal with crumpled (but unentangled) globules rather than coils.

At last, in region III-C, corresponding to $\tau_{\mathrm{eq}} < \tau_{\mathrm{collis}}$, the process will have four stages, including crumpling of individual chains (i), knotting of individual chains (ii), and then aggregation of equilibrium knotted globules (iii). We would like to stress that these globules, even aggregated, remain to be unentangled with each other, so that mutual reptation in this precipitate is the last (iv) stage of relaxation; at this very stage individual chains become Gaussian according to the Flory theorem.

Using eqs 1, 2, and 4, it is easy to determine the crossover curves between these three regions A–C. The A–B line is given by $\tau_{\mathrm{collis}} = \tau_{\mathrm{crum}}$ or

$$cR_{\mathrm{id}}^{\;3} \sim |t|^{-2} \left[\frac{C^{1/2}}{a^3}\right]^3 \left[1 + \frac{\mathrm{const}}{N_{\mathrm{e}}} \frac{a^6}{C}\right]^{3/2} \tag{5}$$

and for the B–C line at $\tau_{\mathrm{collis}} = \tau_{\mathrm{eq}}$ we have

$$cR_{\mathrm{id}}^{\;3} \sim |t|^{-5} \left[\frac{C^{1/2}}{a^3}\right]^{15/2} N_{\mathrm{e}} \tag{6}$$

Here $R_{\mathrm{id}} \sim N^{1/2}a$ is the ideal (Gaussian) coil dimension, and $t \equiv BN^{1/2}/C^{1/4}(a^2/6)^{3/4} \sim N^{1/2}(T-\Theta)/T$ is the reduced temperature used in this form in ref 2. We remind the reader that the value of $C^{1/2}/a^3$ plays the role of a chain stiffness parameter and the quantitative theory[2] is a three-parametric one, based on R_{id}, t, and $C^{1/2}/a^3$. One more parameter, namely, N_{e}, appears important in the present kinetic study.

The difference between crumpled and equilibrium states is relevant for contracted enough chains, or low enough temperatures, and becomes irrelevant near the coil-to-globule transition region. Accordingly, the two lines A–B and B–C cross each other; the cross point can be found using eqs 5 and 6:

$$|t_{\mathrm{cross}}| \sim \left[\frac{C^{1/2}}{a^3}\right]^{3/2} N_{\mathrm{e}}^{\;1/2} \left[1 + \frac{\mathrm{const}}{N_{\mathrm{e}}} \frac{a^6}{C}\right]^{-1/2}$$

$$c_{\mathrm{cross}} R_{\mathrm{id}}^{\;3} \sim N_{\mathrm{e}}^{\;-1} \left[1 + \frac{\mathrm{const}}{N_{\mathrm{e}}} \frac{a^6}{C}\right]^{5/2} \tag{7}$$

At $t > t_{\mathrm{cross}}$ the difference between regions B and C disappears and, if the cross point lies below the spinodal curve, only the A–B line (eq 5) has to be continued from this point (see Figure 1).

4. Metastable Region of Dilute Polymer Solution

Now we deal with the intermediate region II in Figure 1 between the two regimes discussed above. This region is limited by the coexistence curve and the spinodal curve. The quantitative description of the coexistence curve for a dilute polymer solution in the globular range was presented in ref 5. As for the spinodal conditions, the following delicate feature has to be stressed. A usual definition of the spinodal curve is based on the equation of the type

$$\partial^2 f_{\text{pol}}/\partial c^2 = 0 \qquad (8)$$

where f_{pol} is the polymer–solvent system free energy per unit volume. In ref 5 we have calculated the function f_{pol} in the second virial approximation and solved the spinodal eq 8. Since our calculations were based on a standard statistical approach, the equilibrium conditions for both individual and interacting chains were actually supposed. It means that the chains were supposed to be phantom ones, so that knots and entanglements relax immediately. In fact, however, the uniform state of the solution may become absolutely unstable even in the situation when chain–chain aggregation is favorable without interchain entanglements. In some sense, an aggregate of two unentangled chains is similar to an unknotted single-chain crumpled globule. The real physical spinodal of the polymer solution corresponds to this very regime. This spinodal represents the borderline of region III-C in Figure 1. Although its deviation from the "equilibrium" spinodal calculated in ref 5 is important physically, it can be shown to be rather small quantitatively in the sense that it depends in the same way on parameters T–c and t, differing in numerical coefficients only. Accordingly, we can use our results[5] for both coexistence and spinodal curves.

What happens at this region II of the phase diagram (Figure 1) under the fast cooling of the solution? The two initial stages are the same as in regions I and III-C, namely, fast crumpling of the individual chains and knotting of the individual chains, i.e., formation of single-chain equilibrium globules. Chain–chain aggregation is the third stage, but, unlike region III-C, here the aggregation is accompanied by a formation of interchain entanglements. Aggregation begins just in the course of the knotting process of the individual chains, because these processes are both of the reptation type, and, accordingly, the correspondent relaxation times are nearly the same.

Our theoretical conclusions for the metastable region II seem closely correlated with the experimental results for the kinetic study of the coil-to-globule transition as observed in ref 1. We remind the reader that the following two-stage kinetics was observed: fast collapse of the individual chains was the first stage, and the second one, taking a time on the order of an hour, includes two simultaneous processes, namely, formation of aggregates and further collapse of the individual chains. These results are naturally interpreted in the terms of the present work; the first stage is identified with the crumpling process of individual macromolecules, while the second one includes both aggregation caused by interchain entanglements and intrachain knotting.

The following argument also supports our interpretation of the data.[1] These data were presented in the form of a master curve $\alpha^3\tau M^{1/2}$ versus $\tau M^{1/2}$ ($\tau = (T-\Theta)/T$, α is an expansion factor, and M is the chain molecular mass). According to theoretical prediction,[2] this curve has to be of the nonmonotonic type: $\alpha^3\tau M^{1/2}$ grows at small $\tau M^{1/2}$, then reaches a maximum, and goes down to some asymptotic constant value, which corresponds to the well-formed equilibrium globule. Only the growing part of the master curve was observed in previous experiments.[13] The second stage of individual chain collapse observed in ref 1 leads really to the values of $\alpha^3\tau M^{1/2}$ which are essentially smaller than the ones observed earlier, so that the master curve has the predicted nonmonotonic character. This fact supports the hypothesis that the result of the second stage of observed relaxation of the individual chain has to be interpreted in terms of an equilibrium rather than crumpled globule.

Following our interpretation of the data,[1] we can try to estimate roughly the value of parameter N_e, which appears in the present kinetic study together with three static parameters R_{id}, t, and $C^{1/2}/a^3$. Comparing the observed values of α for crumpled and equilibrium globules (i.e., using the data for individual chains after the first and second stages of relaxation, respectively) and taking into account the theoretical prediction,[7] which can be written as

$$\alpha_{\text{crum}} = \alpha_{\text{eq}}\left[1 + \frac{\text{const}}{N_e}\frac{a^6}{C}\right]^{1/3}$$

and an estimation of $C^{1/2}/a^3 = 0.15 \pm 0.04^2$ for the polystyrene–cyclohexane solution, one obtains $N_e/\text{const} \approx 6 \pm 3$, the value which appears to be reasonably consistent with known estimations of N_e.

In conclusion, we mention the recent work,[14] where the dynamics of polymer chain collapse is studied by means of computer simulation.

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