Dynamics of irreversible uncoiling of a polymer chain

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Using a simple dynamic model, the growth of rigidity and of the mean size of the polymer chain induced by a chemical reaction irreversibly fixing extended conformations of units has been investigated. When the reaction rate is controlled by the rotational diffusion of segments, the change in the mean length of a rigid segment and mean radius of gyration of the chain with time are described by power dependencies. For a macromolecule in a constant viscosity medium, the time needed to complete the reaction (i.e. to transform the coil into an extended rigid rod) is $t_{\mathrm{comp}} \sim N^3$, where N is the initial number of segments in the chain. The cases of a kinetically controlled reaction and a mixed type of reaction have also been considered. The slowing down of the reaction caused by increasing the viscosity of the reaction medium has been evaluated, giving $t_{\mathrm{comp}} \sim N^7$.

(Keywords: large-scale chain dynamics; irreversible uncoiling; intramolecular reaction kinetics)

INTRODUCTION

Uncoiling of a macromolecule as a result of increasing its effective rigidity can be involved in a variety of phenomena occurring in polymer systems. It may be caused by a chemical reaction irreversibly fixing the extended conformations of the statistical units. Some examples are the imidization of some polyamidoacids producing polyarimides without hinge atoms[1] or the elimination reactions in substituted polymers (poly(vinyl alcohol), poly(vinyl chloride) etc.) leading to double bond formation. A macromolecule capable of undergoing the helix–coil transition will uncoil when placed in a spiralizing solvent. If the process occurs far beyond the helix–coil transition point, it is possible to neglect the effect of the reverse despiralization reaction and to consider chain uncoiling as irreversible. A similar picture may also be observed when the polymer system passes from the isotropic to the nematic phase. Recently, a coil-to-rod transition in polydiacetylenes was reported to occur with the change in solvent quality[2]. In all these cases, provided the stiffening process is not accompanied by collapsing or aggregation of chains, the mechanisms of chain uncoiling and consequently the main features of large scale dynamics should be basically the same.

The purpose of this paper is to describe the time dependence of the mean length of the rigid segment and mean-square radius of gyration of the chain and to establish the molecular weight dependence of characteristic times of the chain uncoiling process.

DESCRIPTION OF THE MODEL

The present work considers a simple dynamic model for a macromolecule undergoing irreversible uncoiling induced by a chemical reaction, see *Figure 1*. A macromolecule of contour length L in a homogeneous viscous medium is considered. Initially it consists of N freely jointed segments ($N > 1$). A chemical reaction occurs in the macromolecule resulting in the immobilization of the extended conformation of two adjacent segments and in locking the joint between them. The reaction can proceed when two segments adopt the extended conformation in the course of their Brownian motion, and this implies that the angle θ between these segments is smaller than a certain predetermined value:

$$\theta \leqslant \Delta\theta \qquad (1)$$

After the reaction has taken place at a given location, this pair of segments remains in a completely extended conformation and is treated as a single rigid segment of summary length. We consider first the simple case when the macromolecule is an ideal Gaussian coil without volume interactions. In the initial state, its mean-square radius of gyration is given by:

$$R_0 = \left(\frac{1}{6} N A_0^2\right)^{1/2} \qquad (2)$$

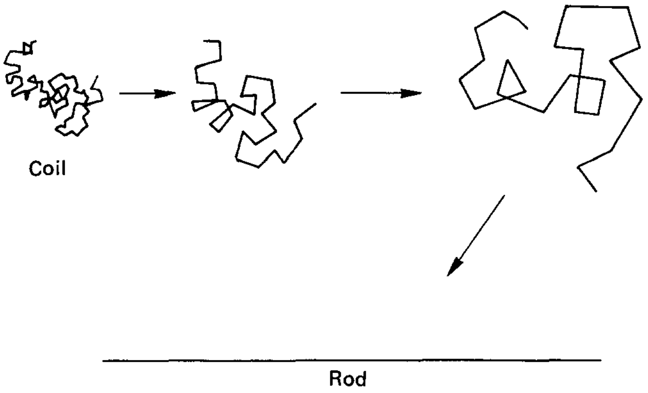

Figure 1 Uncoiling of a macromolecule due to increase in chain rigidity

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where $A_0 = L/N$ is the initial segment length. The reaction stops completely when the macromolecule is transformed into an extended stiff rod with the radius of gyration: $R_{\rm rod} = 1/\sqrt{12}L$; $R_{\rm rod}/R_0 = (N/2)^{1/2}$.

We will investigate the time dependence of both local and global chain characteristics, namely the mean length of rigid segments $A(t)$ averaged along the chain and the non-equilibrium radius of gyration $R(t)$. The mean segment length $A(t)$ can be expressed as:

$$A(t) = \left\langle \frac{1}{\hat{n}(t)+1} \sum_{R=1}^{\hat{n}(t)+1} \hat{A}_k(t) \right\rangle = L \left\langle \frac{1}{\hat{n}(t)+1} \right\rangle \tag{3}$$

Here $\{\hat{A}_k\}$ and $\hat{n}$ are stochastic dynamic variables giving the instantaneous lengths of all the segments and the number of flexible joints, correspondingly, and $\langle \ldots \rangle$ denotes averaging over the stochastic configuration space trajectories as well as over random initial conformations of the coil. We will use the approximation in which $\langle (\hat{n}(t)+1)^{-1} \rangle \simeq \langle \hat{n}(t)+1 \rangle^{-1} \simeq \langle \hat{n}(t) \rangle^{-1}$, so that $A(t) = L/n(t)$, $n(t)$ being the mean number of flexible joints at time t from the reaction start.

KINETIC EQUATIONS

Treating the problem rigorously one can begin by stating that the probability $\mathrm{d}P_i(t)$ for the reaction to occur at the ith joint in the time interval t, $t+\mathrm{d}t$ is given by:

$$\mathrm{d}P_i(t) = [1 - P_i(t)] W_i \, \mathrm{d}t, \qquad i = 1, \ldots, N-1 \tag{4}$$

where $[1 - P_i(t)]$ is the probability that the ith joint remains flexible by time t and W_i is the corresponding reaction rate. Generally W_i depends on all the details of the chain conformation, particularly on the actual sequence of rigid segment lengths along the chain, at the moment t. Thus closing of the set of equations (3) would require the detailed analytical description of internal dynamics for the chain consisting of rigid segments, which is far beyond the capability of present theory.

In order to obtain the analytical solution of the problem a simplified approach is used. Summing equation (4) over i and noting that:

$$\sum_{i=1}^{N-1} [1 - P_i(t)]$$

gives the average number of flexible joints $n(t)$ at the moment t from the reaction start, we obtain:

$$\frac{\mathrm{d}n(t)}{\mathrm{d}t} = -n(t) W \tag{5}$$

where

$$W = \left\{ \sum_{i=1}^{N-1} [1 - P_i(t)] \right\}^{-1} \sum_{i=1}^{N-1} W_i [1 - P_i(t)]$$

is the average reaction rate at time t. We assume that W depends only on the average chain characteristics $A(t)$ and $R(t)$. To evaluate this dependence we consider a reference chain consisting of identical rigid segments of the same length $A(t)$, their number being $n(t) = L/A(t)$. With the course of the reaction, the number of flexible joints in the reference chain decreases, whereas the length of each rigid segment increases. The accuracy of this approximation will be evaluated below when the analytical solution is compared with the results of computer simulation.

First, a diffusion-controlled reaction will be considered. In this case, W is the average rate at which two neighbouring segments adopt the extended conformation as a result of mutual rotational diffusion. It can be shown that for a diffusion-controlled reaction the rate W depends logarithmically on the parameter $\Delta\theta$ (see equation (1)) under the condition $\Delta\theta < 1$. For the freely jointed chain, in the equilibrium coiled state we have:

$$W \sim \tau_{\rm rot}^{-1} \sim \frac{kT}{\eta A^3}$$

and hence

$$W(t) = w_0 \left(\frac{A_0}{A(t)} \right)^3 \tag{6}$$

where T is the temperature, k is the Boltzmann's constant, $\tau_{\rm rot}$ is the characteristic time of the rotational diffusion of a rigid rod of length A, η is the local viscosity of the medium and w_0 is the initial reaction rate at $t = 0$.

Initially, the coil has the equilibrium size R_0 (see equation (2)). Subsequently, the length of the rigid segment increases and so does the equilibrium (or to be more precise, quasi-equilibrium) mean value:

$$R_{\rm eq}(t) = \left[\frac{1}{6} n(t) A^2(t) \right]^{1/2} \tag{7}$$

so that the non-equilibrium value of the radius of gyration $R(t)$ becomes lower than $R_{\rm eq}$. Since the coil is in the non-equilibrium state with $R < R_{\rm eq}$, the reaction rate W generally depends on R. It may be shown that for a compressed coil, e.g. by external field, the value of $\tau_{\rm rot}$ remains virtually invariable with decreasing $R/R_{\rm eq}$ while $R \gg A$. However, when the radius of gyration of chain approaches that of a single rigid segment

$$r_s = \frac{1}{\sqrt{12}} A$$

(this situation corresponds to a completely folded chain conformation) the probability of the appearance of stretched conformations of neighbouring segments should drastically decrease. In order to take this effect into account, an additional cutting-off factor $f(A/R)$ will be introduced into the expression for W having the following properties: $f \simeq 1$ if $A \ll R$ and $f \to 0$ if $R \to r_s$. Its specific form is not important since, as will be shown below, $A(t)$ never tends to exceed $R(t)$ so that f is always of the order of unity.

During the entire reaction, the coil is in the non-equilibrium compressed state. As a result, a driving force appears which tends to expand the coil to the dimension $R_{\rm eq}$. This force is due to the increase ΔF in the free energy of a compressed coil compared to its free state (see discussion in ref. 3). For chains without volume interactions ΔF is of purely entropic nature and under the condition $R \ll R_{\rm eq}$ it is given by:

$$\Delta F = \gamma k T \left(\frac{R_{\rm eq}^2}{R^2} + \ln \frac{R^2}{R_{\rm eq}^2} \right) \tag{8}$$

where γ is the numerical coefficient of the order unity[4].

The evolution of the average radius of gyration R of the coil in the simplest approximation, when R is treated as an independent dynamic variable[5,6] is governed by the equation:

$$\zeta\frac{dR}{dt}+\frac{\partial\Delta F}{\partial R}+0 \tag{9}$$

where ζ is a friction coefficient related to the large scale expansion of the coil as a whole. In order to evaluate ζ, a free draining model and a completely non-draining model for the coil will be considered. In the case of a draining coil, which occurs for relatively concentrated solutions or melts under the condition that the entanglement network is not yet manifested, the friction coefficient ζ is proportional to ηL and is independent of chain conformation.

In the case of a non-draining coil (the chain in a dilute solution) according to Stokes equation, the friction coefficient is proportional to the coil size $\zeta \sim \eta R$.

Finally, the evolution of the mean number of flexible joints in the chain $n(t)$, and its radius of gyration $R(t)$ is described by a system of equations:

$$\frac{dn}{dt}=-nw_0\left(\frac{A_0 n}{L}\right)^3 f\left(\frac{A}{R}\right) \tag{10}$$

$$\frac{dR}{dt}=2kT\gamma\zeta^{-1}R^{-1}\left(\frac{L^2}{6nR^2}-1\right) \tag{11}$$

In order to obtain an analytical solution, two assumptions will be made, the self-consistency of which is confirmed by the analysis of the solution.

(a) At any time, except a small initial interval, $R^2 \ll R_{eq}^2$, so that it is possible to neglect unity in equation (11) in comparison with $L^2/6nR^2 = R_{eq}^2/R^2$.

(b) The factor $f(A/R)$ changes little with time and may be considered to be a constant of the order of unity.

It should be noted that both equations (10) and (11) and conditions (a) and (b) are valid only when $n \gg 1$, i.e. they do not describe the latest reaction stage in which the number of chain segments becomes small.

If the above assumptions are taken into account, equations (10) and (11) are simplified to:

$$\frac{dn}{dt}=-w_0 f N^{-3} n^4 \tag{12}$$

$$\frac{dR}{dt}=\beta w_0 N^{-3} L n^{-1}\left(\frac{L}{R}\right)^{3+p} \tag{13}$$

where β is the numerical coefficient of the order of unity, $p=0$ for a draining coil and $p=1$ for a non-draining coil. Equation (12) is easily integrated to give the dependence $n(t)$ which is used for the solution of equation (13). The solution of equations (12) and (13) for the initial conditions $n/_{t=0}=N$; $R/_{t=0}=R_0$ is given by:

$$n(t)=N(1+3fw_0t)^{1/3} \tag{14}$$

$$R(t)=L\left\{\left(\frac{R_0}{L}\right)^{4+p}+\frac{\beta(4+p)}{4f}\times N^{-4}[(1+3fw_0T)^{4/3}-1]\right\}^{1/(4+p)} \tag{15}$$

ANALYSIS OF THE SOLUTION

It follows from equation (14) that the number of segments in the chain begins to decrease markedly starting with time t of the order of $w_0^{-1} \sim \tau_{rot}$ (local relaxation time of the initial chain segment). In the entire time range from w_0^{-1} to the end of the reaction, the number of flexible joints exhibits a power law dependence on time $n \sim N(w_0t)^{-1/3}$. The mean length of the rigid segment increases with time as $A(t) \sim A_0(w_0t)^{1/3}$ (see *Figure 2*).

The dynamics of change in the radius of gyration R exhibit two stages, each being relatively long compared to the characteristic time scale w_0^{-1}. At times t smaller than a certain value τ_R, the first term in equation (15) is dominant, and in this time range the relative change in R is small: $R(t) \simeq R_0$. The value of τ_R scales as:

$$\tau_R \sim w_0^{-1}N^{[3(4-p)]/8} \tag{16}$$

For a draining coil, we obtain $\tau_R \sim N^{3/2}$, and for a non-draining coil, we have $\tau_R \sim N^{9/8}$.

Beginning from the time $t \sim \tau_R$ the second term in equation (14) dominates, and in this case R has a power law time dependence:

$R(t) \sim A_0 N^{1/5}(W_0t)^{4/15}$ for a non-draining coil

$R(t) \sim A_0(w_0t)^{1/3} \sim A(t)$ for a draining coil.

The crossover between two dynamic regimes of changes in R takes place at $t \sim \tau_R$.

The time of completion of the reaction t_{comp}, when the chain is completely uncoiled (A acquires the order of L), is proportional to the cube of the initial number of chain segments: $t_{comp} \sim w_0^{-1}N^3$.

The time dependences of the mean segment length A, of the non-equilibrium radius of gyration R, and of the equilibrium mean value of the radius of gyration R_{eq} for a chain with the given segment length A are compared in *Figure 2*. It is clear that the assumption that $R \ll R_{eq}$ made for the simplification of kinetic equations is valid for $N \gg 1$ in the time range $w_0^{-1} \ll t \ll t_{comp}$. At $t < \tau_R$ we have $R^2/R_{eq}^2 \sim (w_0t)^{-1/3}$, and at $\tau_R < t$ we have

$$R^2/R_{eq}^2 \sim \left(\frac{t}{t_{comp}}\right)^{(4-p)/[3(4+p)]}$$

In the range $t \sim \tau_R$, the difference between R_{eq}^2 and R^2 is at a maximum and is:

$$R^2/R_{eq}^2 \sim N^{-(4-p)/16}$$

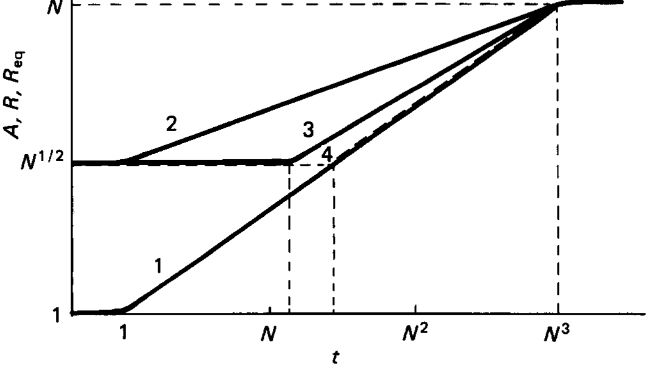

Figure 2 Time dependence of chain rigidity and size for the case of a diffusion-controlled reaction. Curve 1, mean length of a rigid segment A; curve 2, equilibrium mean-square radius of gyration R_{eq} for a chain of given segment length A; curves 3 and 4, non-equilibrium mean radius of gyration for the cases of non-draining and free-draining chains, respectively. Values having the dimensionality of length are referred to A_0 and time is referred to w_0^{-1}. Scale on both axes is logarithmic

The ratio of the radius of gyration R to the segment length A also satisfies the assumption made above. Even when the cutting-off factor in equation (12) is absent, the ratio A/R always remains small, $A/R \ll 1$, and correspondingly $f \simeq 1$, except for the case of a free-draining coil at $t > \tau_R$. In this case, the ratio A/R remains a constant of the order of unity and may be self-consistently determined from equations (14) and (15) for any particular form of the cutting-off factor $f(A/R)$.

COMPARISON WITH RESULTS OF COMPUTER SIMULATION

In order to verify the validity of the assumption that the kinetics of the reaction can be described by a single time-dependent reaction rate (see equations (5) and (6)) an attempt has been made to perform computer simulation on the basis of a more rigorous approach. The main point of the simulation was to account for the distribution of segment lengths which appear in the course of the reaction resulting in a spectrum of local reaction rates.

Starting from equation (4), we note that, for a diffusion-controlled reaction, W_i is the rate of local rearrangement of ith and $(i+1)$th segments adjacent to the ith joint. In the simplest approximation, W_i depends only on the properties of ith and $(i+1)$th segments, the effect of more distant neighbours being neglected:

$$W_i \sim \frac{1}{\tau_{\mathrm{rot}}^{(i)}} + \frac{1}{\tau_{\mathrm{rot}}^{(i+1)}}$$

Hence, we have

$$W_i = w_0 \frac{1}{2}\left(\frac{A_0^3}{A_i^3} + \frac{A_0^3}{A_{i+1}^3}\right) \tag{17}$$

where A_i is the length of ith segment at time t, $\tau_{\mathrm{rot}}^{(i)}$ is the characteristic time of its rotational diffusion.

The kinetics of the increasing chain rigidity described by equations (4) and (17) were simulated by the Monte-Carlo method. The spatial motion of chain segments and the resulting change in the chain radius of gyration were not considered. In the initial state, the chain consisted of $N=200$ segments of length $A_0=1$. The reaction was followed sequentially, with a time step Δt. During one step each pair of neighbouring segments could be united into a single segment (its length being a sum of their lengths) with the probability $\Delta P_i = 1-\exp(-W_i\Delta t)$. The step was chosen to be sufficiently small to neglect the probability of uniting three or more neighbouring segments simultaneously. The simulation was over when all the segments became a single rigid segment of the length $A=NA$. The time dependence of the mean segment length $A(t)$ was averaged over 100 random 'trajectories'.

Over almost the entire time range, $w_0^{-1} < t < t_{\mathrm{comp}}$, the dependence $A(t)$ is adequately approximated by the power function $A(t) = A_0(3\tilde{w}t)^{1/3}$ with the exponent 1/3 derived from the analytical theory (*Figure 3*). The effective frequency $\tilde{w}$ is found to be higher than w_0, with $\tilde{w}/w_0 \approx 3$. For a pair consisting of a short and a long segment, the rate of conformational rearrangement is mainly determined by the mobility of the short segment, rather than by that of a segment of mean length. This result may be illustrated taking as an example a pair of segments with a fixed mean length. For identical segments we have $W = w_0(A_0/A)^3$ and for segments of lengths $A(1+\delta)$ and $A(1-\delta)$ we have $W = \tilde{w}(A_0/A)$ where:

$$\tilde{w} = w_0\left[\frac{1}{2(1+\delta)^3} + \frac{1}{2(1-\delta)^3}\right]$$

The ratio $\tilde{w}/w_0 = 3$ is obtained at $\delta = 0.43$, which gives the estimate of the width of the segment length distribution appearing in the chain model under consideration.

Hence, the analytical theory based on the approximation of the equal segment lengths gives the correct description of the character of the kinetics of increasing rigidity. The segment length distribution appearing in the chain during the reaction leads only to the renormalization of the initial reaction rate.

GENERALIZATIONS OF THE MODEL

The simple model suggested in this work assumes several natural generalizations, some of which are described below.

Chain in a good solvent (evaluation of excluded volume effects)

The kinetics of the reaction are described by equation (10), but the equation of motion of the chain radius of gyration changes. Using Flory's method[4,7] we can represent the coil free energy as

$$\Delta F = \Delta F_0 + \Delta F_c \tag{18}$$

where the entropy contribution ΔF_0 under the conditions $R \ll R_{\mathrm{eq}}$ is described by equation (8).

The energy of pair interactions of segments in the mean-field approximation, ΔF_c is given by $\Delta F_c = \frac{1}{2}kTn^2a^3\varepsilon R^{-3}$, where a is the chain thickness (it will be assumed that $a = A_0$), and $\varepsilon = (T-\theta)/T$ is the parameter of the thermodynamic quality of the solvent proportional to the deviation from the θ temperature. The contribution of ternary interactions at $R \geqslant R_0$ is small. In this approximation, ΔF_c is independent of the mean segment length A. The equation of motion for R becomes:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{kT}{\eta R^2}\left[2\gamma\left(\frac{L^2}{6nR^2} - 1\right) + \frac{3\varepsilon L^2 A_0}{2R^3}\right] \tag{19}$$

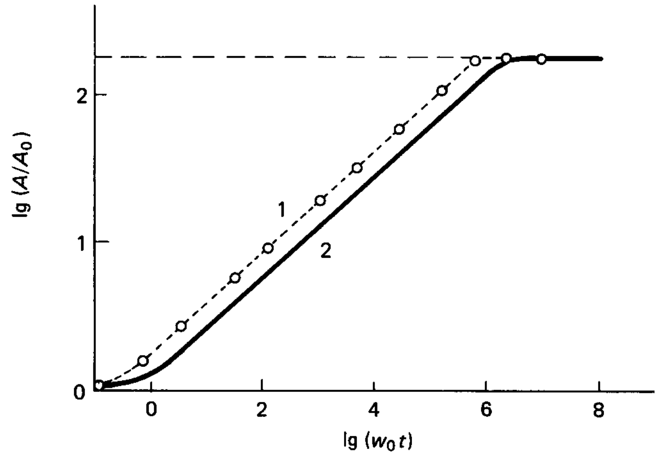

Figure 3 Time dependence of the mean length of a rigid segment. Curve 1, Monte-Carlo simulation ($N=200$); curve 2, analytical theory. Values having the dimensionality of length are referred to A_0 and time is referred to w_0^{-1}

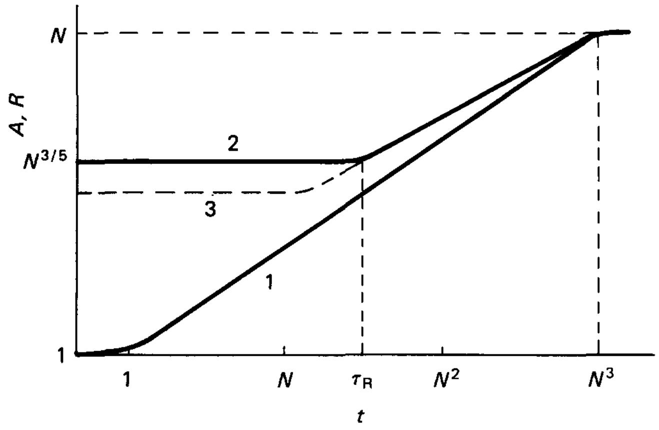

Figure 4 Time dependence of chain rigidity and size for a chain with excluded volume interactions (parameter of solvent quality $\varepsilon \sim 1$). Curve 1, $A(t)$; curve 2, $R(t)$; curve 3, the dependence $R(t)$ for an ideal chain given for comparison. Values having the dimensionality of length are referred to A_0 and time is referred to w_0^{-1}

Here the hydrodynamic model for the non-draining coil is used.

The expanding force related to volume interactions will dominate if:

$$\frac{\varepsilon A_0}{R} \geqslant \frac{1}{n}$$

In the framework of the Flory method used we have $R_0 \simeq A_0 \varepsilon^{1/5} N^{3/5}$. Taking into account equation (14) one can see that this force dominates only at $t < t^*$, where $t^* \sim w_0^{-1} \varepsilon^{12/5} N^{6/5}$. During this time R cannot change greatly: $R(t^*) \simeq R_0$, since characteristic time τ_R of the global chain swelling for a non-draining chain is given by $\tau_R \sim w_0^{-1} \varepsilon^{3/4} N^{3/2} \gg t^*$. At $t \gg t^*$, the evolution of R is governed by the entropic force, just as in the case of an ideal chain (*Figure 4*).

The free energy of the chain in the presence of excluded volume interactions may be determined more rigorously[8,9]. It is known that there are different regimes in the temperature–concentration diagram for semi-flexible chains. For sufficiently flexible chains in good solvent, free energy per chain is given by scaling theory formula:

$$\Delta F = R^3 \varphi^{9/4} \left(\frac{A\varepsilon}{a}\right)^{3/4} \sim N^{9/4} \left(\frac{A_0}{A}\right)^{3/4} \varepsilon^{3/4} R^{-15/4} \quad (20)$$

where $\varphi = Na^3/R^3$ is the mean volume fraction of units in the coil. In the case of poorer solvents and stiffer chains the free energy of the coil is given adequately by the mean-field approximation in equation (18). The cross-over from the scaling to the mean-field regime takes place at:

$$\frac{A}{a} \sim \left(\frac{\varepsilon}{\varphi}\right)^{1/3}$$

In our case we start from the flexible chain, its free energy being given by equation (20). If this relation held for the chain under consideration through the entire reaction time, excluded volume interactions would determine essentially the expansion rate giving the characteristic time $\tau_R \sim N^{36/25} \varepsilon^{12/25}$. However, the mean length of rigid segment exceeds the value of $A_0(\varepsilon/\varphi)^{1/3}$ much earlier (beginning from $t \sim n^{4/5} \varepsilon^{8/5}$) and thereafter the mean-field approximation for the free energy of the coil is adequate. Thus we come again to the estimates $t^* \sim w_0^{-1} \varepsilon^{12/5} N^{6/5}$; $\tau_R \sim w_0^{-1} \varepsilon^{3/4} N^{3/2} \gg t^*$ and conclude that excluded volume interactions do not significantly alter the dynamics of coil expansion.

Consequently the change in solvent quality (or in temperature at $T \geqslant \theta$) should lead only to small changes in the character of the irreversible chain uncoiling.

Kinetically controlled reaction

The reaction leading to increasing chain rigidity is diffusion controlled if the rate constant K of the chemical reaction fixing the extended position of the neighbouring segments (provided they have adopted suitable conformation given by equation (1)) obeys the condition $1/4\,(\Delta\theta)^2 K \gg w_0$. The factor $1/4\,(\Delta\theta)^2$ at $\Delta\theta \ll 1$ represents the equilibrium fraction of segments in the extended conformation. In the opposite case, when $K_c \equiv 1/4\,(\Delta\theta)^2 K \ll w_0$, the reaction, at least initially, is kinetically controlled.

Let $w_0 \gg K_c \gg w_0 N^{-3}$. Then a characteristic segment size $A^* = A_0 (w_0/K_c)^{1/3}$ exists, so that $K_c = w_0 (A_0/A^*)^3$.

Chain uncoiling follows two-stage kinetics. In stage 1, the reaction is kinetically controlled and is described by the equation:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -K_c n \quad (21)$$

where K_c is independent of time. The number of flexible joints in the chain decreases exponentially, $n(t) = N\exp(-K_c t)$, until it obtains the value of $n^* = N(K_c/w_0)^{1/3}$. Subsequently at:

$$t \geqslant t^* = \frac{1}{3} K_c^{-1} \ln\left(\frac{w_0}{K_c}\right)$$

the character of the reaction changes. In stage 2 it becomes diffusion controlled and is described by equation (12) with the initial condition $n(t^*) = n^*$.

The analysis of the solution of kinetic equations gives the following results. For brevity, only the case of an ideal non-draining chain will be considered. If $\tau_c < \tau_R$ where $\tau_c \equiv 1/K_c$ then the kinetically controlled reaction stage does not affect the dynamics of changes in chain size (*Figure 5a*). If the value of τ_c is such that $\tau_R < \tau_c < w_0^{-1} N^3$, it is possible to single out three different regimes of changes in $R(t)$. At $t \ll \tau_c$, the radius of gyration virtually remains constant, $R \simeq R_0$. In the vicinity of $t = \tau_c$, a relatively narrow range of exponential growth exists, $R(t) \sim A_0 (N w_0 \tau_c)^{1/5} \exp(t/5\tau_c)$. These two regimes correspond to the first kinetically controlled reaction stage. Finally, at $t \gg t^*$ we have $R(t) \sim A_0 N^{1/5} (w_0 t)^{4/15}$ as for the case for a completely diffusion-controlled reaction (*Figure 5b*, curve 3).

When $K_c \ll w_0 N^{-3}$, the irreversible chain uncoiling is determined from the beginning to the end by a kinetically controlled chemical reaction. Equation (11) describes relaxation of R only under the condition $R \ll R_{eq}$, but for the case being considered it will have the form:

$$\zeta \frac{\mathrm{d}R}{\mathrm{d}t} + E[R - R_{eq}(t)] = 0 \quad (22)$$

where $E \sim kT/R_{eq}^2(t)$ is the coefficient of coil elasticity for small deviations from the equilibrium. Since $K_c \ll w_0 N^{-3} \leqslant E/\zeta$, the reaction proceeds so slowly that the coil radius of gyration changes in a quasi-equilibrium

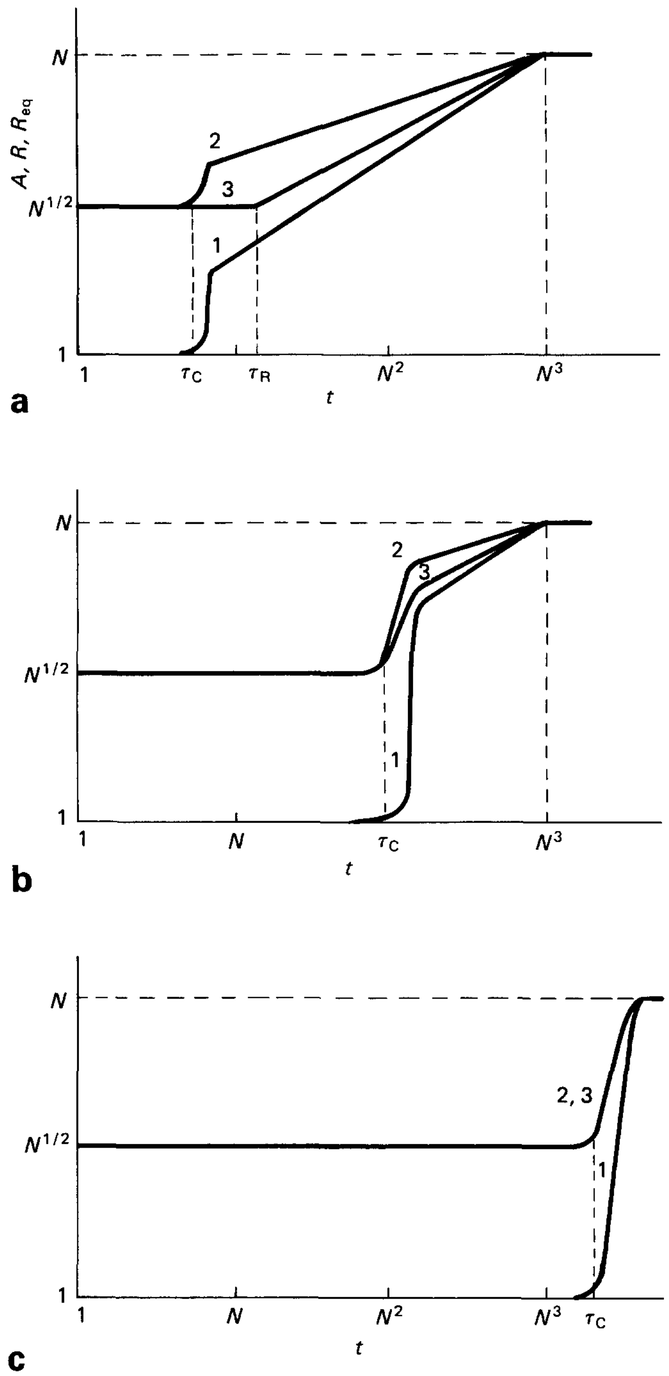

Figure 5 Time dependence of chain rigidity and size for the case when the initial reaction stage (a) and (b) or the whole reaction (c) is controlled by chemical kinetics. The time constant τ_c increases from (a) to (c). Values having the dimensionality of length are referred to A_0 and time is referred to w_0^{-1}. See *Figure 2* for the description of curves 1–3

manner, $R(t) \simeq R_{eq}(t) = R_0 \exp(\frac{1}{2}K_c t)$ (*Figure 5c*, curve 2, 3). If the chemical reaction is induced by sample irradiation, then by changing its intensity the value of K_c may be varied over a wide range. In this case the dynamics of chain stretching should change as shown in *Figure 5a–c*.

Effect of viscosity change during the reaction

So far we have considered only the uncoiling of the polymer chain in a medium with a constant viscosity η. If the chemical reaction proceeds in a condensed polymer system, relatively concentrated solution or melt, and the increase in the length of rigid segments proceeds in all polymer chains and not only in one 'labelled' macromolecule, then in the course of the reaction the viscosity of the system increases. It is known that the effective viscosity controlling the rotational mobility in relatively concentrated solutions of rigid rods is $\eta \sim \eta_0(cA^3)^2$ where η_0 is the solvent viscosity, c is the number of rods in unit volume and A is the rod length[10,11]. This relationship is valid at concentrations $A^{-1}a^{-2} \gg c \gg A^{-3}$. Here, and in the following discussion, the system is assumed to be isotropic and the possibility of liquid crystalline ordering is not considered. The problem of the effective viscosity controlling the local orientational mobility in a concentrated solution of chains consisting of rigid segments is intricate, there being no rigorous theory at present. It is reasonable to assume that this viscosity is not lower than that in a solution with the same concentration of rods not joined into a chain. We conjecture that η scales as $\eta \sim \eta_0(cA^3)^\alpha$, and $\alpha = 2$ will be used as the lower estimate. In the simplest approximation, it will also be assumed that the same value of η controls a larger scale relaxation of the coil radius of gyration R. This implies that the reptation of the chain as a whole is not taken into account.

At a constant chain concentration in the system, the concentration of segments c decreases with increasing mean length of the segment:

$$c = c_0 \frac{A_0}{A}$$

Hence, the viscosity η changes as $\eta \sim \eta_0(A/A_0)^{2\alpha}$ where η_0 is the local viscosity of the system at the beginning of the reaction.

The kinetic equations (10) and (11) retain their form, but an additional factor, $\eta_0/\eta = (n/N)^{2\alpha}$, appears on their right-hand sides. By this factor, the retardation of all relaxation processes due to increasing viscosity is taken into account. As will be shown below, the conditions:

$$R^2 \ll R_{eq}^2; \qquad f(A/R) \sim 1 \tag{23}$$

are still valid, as in the case $\eta = $ const. Hence, it is possible to pass to simpler kinetic equations:

$$\frac{dn}{dt} = -w_0 f N^{-3} n^4 (n/N)^{2\alpha} \tag{24}$$

$$\frac{dR}{dt} = w_0 \beta N^{-3} n^{-1} L (L/R)^{3+p} (n/N)^{2\alpha} \tag{25}$$

Excluding time t from equations (24) and (25) we obtain the relationship between $A = L/n$ and R:

$$R = L\left[\left(\frac{R_0}{L}\right)^{4+p} + \beta\frac{4+p}{4f}\,\frac{A^4 - A_0^4}{L^4}\right]^{1/(4+p)} \tag{26}$$

This equation is valid regardless of whether the viscosity changes or not during the reaction under the condition that the orientational rearrangement of segments and the relaxation of chain radius of gyration are controlled by the same value of viscosity. Hence, the validity of inequalities (23) relating the values of R and A, being established for the $\eta = $ const, is also retained in the case when viscosity increases during the reaction.

Equation (24) shows that the mean length of the segment A increases with time as:

$$A = A_0[1 + f(3 + 2\alpha)w_0 t]^{1/(3+2\alpha)}$$

Taking into account the fact that $\alpha \geqslant 2$ we obtain a very marked retardation of the rigidity growth with time $A(t) \leqslant A_0(w_0 t)^{1/7}$. The time of the completion of the reaction is found to be very strongly dependent on the degree of polymerization of the chain $t_{\mathrm{comp}} \sim N^{3+2\alpha} \geqslant N^7$. In practice, this means that in a given system the reaction is frozen in a certain stage, and it may prove to be impossible to observe complete uncoiling of long chains in the experiment.

For this case the form of the dependencies $A(t)$ and $R(t)$ is similar to those in *Figure 2* (curves 1, 2 and 4), but the logarithmic scale along the axis t changes: at $\alpha = 2$ we have $\tau_{\mathrm{R}} \sim w_0^{-1} N^{7/2}$; $T_{\mathrm{comp}} \sim w_0^{-1} N^7$.

The above qualitative evaluations show that the increasing viscosity of the medium during the reaction leading to the increasing of chain rigidity can profoundly affect both the kinetics of local stiffening and the rate of global chain swelling.

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