

CHAPTER I

INTRODUCTION

1.1 Introduction

Analytical rheology is a tool for predicting polymer molecular properties from rheological properties or vice versa. Determination of molecular weight distribution from linear viscoelastic data is the major interest and of economic importance. The study of the effect of molecular weight distribution on the rheological properties of a polymer melt is one of the central concerns in macromolecular science. The knowledge contributes towards the optimization of material formulations.

The use of melt rheology to characterize the molecular weight distributions and number of chain atoms between entanglement of polymers can yield further insight on the relationship between the unique properties of polymer and the chemical structure. In the case of low molecular weight compounds, it is possible to determine molecular weight by analyzing the X-ray diffraction pattern. But for a macromolecule, it is impossible to use this method. Traditional methods such as light scattering from a dilute solution, dilute solution viscosity, dilute solution osmotic pressure, and rate of elution from a porous medium (gel permeation chromatography, GPC) have been developed for characterizing the size of high molecular weight polymers. These traditional methods require a polymer that is soluble in a suitable solvent but many important polymers are often insoluble in any suitable solvents and therefore the molecular weight distribution cannot be measured by these methods. In addition, solvents used in the traditional methods are very expensive and the traditional methods are time consuming.

On the other hand, viscoelastic properties can be easily measured and used to determine the molecular weight distribution. The reptation theory by

de Gennes and the development of rheological constitutive equation by Doi and Edwards can be used to determine the molecular weight distribution on the basis of viscoelasticity. From these concepts, it is possible to develop a method in which polymer molecular weight and its distribution can be obtained from the rheological properties according to the dynamic theories.

This work focuses on the prediction of rheological data from a molecular weight distribution, for several commercial polymers such as high density polyethylene (HDPE), low density polyethylene (LDPE) and polystyrene (PS), using the double reptation theory (des Cloizeaux, 1988) and the dual constraint theory (Mead and Van dyke, 2000). Later, comparison between the predicted rheological properties and the experimental data is made.

1.2 Theoretical Background

1.2.1 Molecular Weight

We can define several measures of polymer molecular weight:

$$\text{Number average molecular weight: } \bar{M}_n = \frac{\sum_{i=1}^x M_i N_i}{\sum_{i=1}^x N_i} \quad (1.1)$$

$$\text{Weight average molecular weight: } \bar{M}_w = \frac{\sum_{i=1}^x M_i^2 N_i}{\sum_{i=1}^x M_i N_i} \quad (1.2)$$

where M_i is the molar mass of the i^{th} polymer chain, and N_i is the number of chains with that mass.

The ratio \bar{M}_w / \bar{M}_n , called the polydispersity, is a useful measure of the breadth of molecular weight distribution. Larger values of \bar{M}_w / \bar{M}_n indicate a very wide spread in weight and size. For $\bar{M}_w / \bar{M}_n = 1$,

monodisperse polymer, all polymer chains have exactly the same mass, and therefore the number and weight average molecular weights are equal. In reality, monodisperse polymer distributions do not exist (Sun, 1994).

1.2.2 Rouse Theory

Rouse (1953) developed a molecular theory for dilute polymer solutions in which a polymer molecule is modeled as a chain of N consecutive segments submolecules that act as Hookean springs. Since the origin of the spring force is Brownian motion, the spring constant is proportional to the absolute temperature. These segments are connected by beads in which the mass of the molecule is assumed to be concentrated as shown in Figure 1.1. The motion of the beads through the solvent gives rise to a viscous resistance. The combination of the elastic spring and the viscous resistance gives rise to a viscoelastic behavior (Dealy and Wissbrun, 1990).

The Rouse theory predicts that the viscosity should be directly proportional to the molecular weight, which is only true up to the entanglement M_c , beyond which the viscosity becomes proportional to the molecular weight to the power of 3.4. This is because in the Rouse model each chain is considered to be moving independently, so entanglements are neglected (Painter, 1997).

In Rouse's model, there is no "hydrodynamic interaction". This means that the resistance to bead motion due to the solvent is that of a particle moving in a liquid when there are no other particles. In reality, the flow pattern in the solvent caused by the motion of one bead has an influence on the resistance of the solvent to the motion of other beads, even of other beads on the same chain. Thus, the Rouse theory is not correct even for an infinitely dilute solution (Dealy and Wissbrun, 1990).

Ferry (1980) modified the Rouse theory by using Bueche's hypothesis (1952) which suggested that for low molecular weight molten

polymers in which there is no entanglement of molecules. The Rouse dilute solution theory can be used with rather minor modification to account for the fact that a polymer molecule is surrounded by not only solvent but other polymer molecules. This modification of Rouse theory can predict several important features of the behavior of molten linear polymers in which there are no entanglements. In case of entangle coupling, it is a rather sharp change in the dependence of viscosity on molecular weight. Whereas the modified Rouse theory predicts that η_0 is proportional to M in the neighborhood of a certain molecular weight, M_c , which depends on the chemical structure of the polymer, the viscosity starts to increase rapidly with molecular weight (Dealy and Wissbrun, 1990).

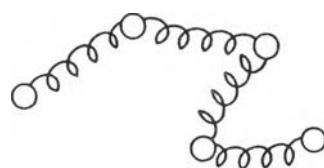


Figure 1.1 The Rouse beads and springs model for a polymer molecule.

1.2.3 Reptation Theory

Since the Rouse model does not predict the correct relaxation spectrum of a high molecular weight polymer melt where entanglements exist, another theory was needed.

For polymers that have molecular weights above the critical molecular weight, M_c , entanglements begin to form. Then the two distinct relaxation processes are readily seen. Consider the stress relaxation of high molecular weight polymer. Figure 1.2 shows two graphs of $\log G(t)$ versus $\log t$, and $\log G'(\omega)$ versus $\log \omega$. The region where the slope in Figure 1.2 is nearly zero is the plateau region G_n^0 . The relaxations in this region are

associated with entanglements time scale τ_e . The other region of importance for melt rheology is the terminal region, which corresponds to relaxation of the entire chain with a time scale τ_d . The model that best describes the rate dependence of the material functions of linear homogeneous polymer melts is the *Reptation Tube Model*. For short relaxation times, $t < \tau_e$, the dynamics of the Rouse model are active. However, at longer relaxation times $t > \tau_e$, the Rouse model is restricted by tube constraints (Rohn, 1995).

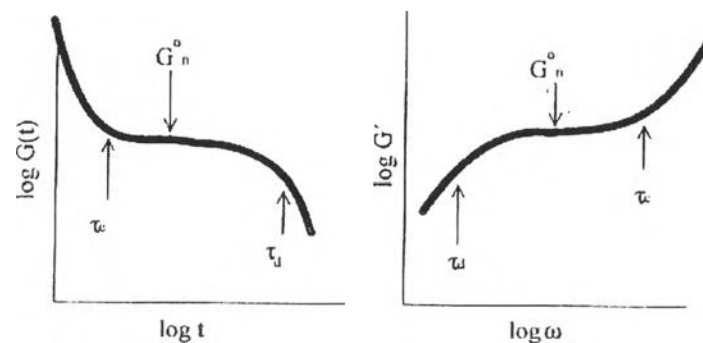


Figure 1.2 Left graph shows the stress relaxation curve and the right graph shows the frequency dependent shear storage modulus curve. The location of the characteristic relaxation times for the entanglement spacing τ_e and contour length τ_d of the polymer chains are located on the curves. Also, the plateau modulus G_n^0 is indicated.

Entanglements place topological constraints on the number of degrees of freedom of a polymer chain. This will have an effect on the entropy of the system. When a chain becomes deformed, it can only translate along its axis. The allowed conformations of the chain are confined in a tube-like region. Figure 1.3 shows a chain in a tube. The length of the tube defines the shortest path connecting the two ends of the chain. The diameter of the tube corresponds to the topological constraints. A primitive path is defined as a group of chain conformations that are allowed by the topological constraints. The contour length of the chain is longer than the tube. Therefore, the chain is

not fully extended and contains some slacks. The slacks will constitute a series of defects. de Gennes (1971) visualized that parts of the tube will form and disappear as the chain translates. This type of motion was called reptation by de Gennes. As the polymer chain moves along the tube, the moving front of chain may continue to form a new tube section and the trailing tube end may disappear. This process is called reptation as shown in Figure 1.4 (Rohn, 1995).

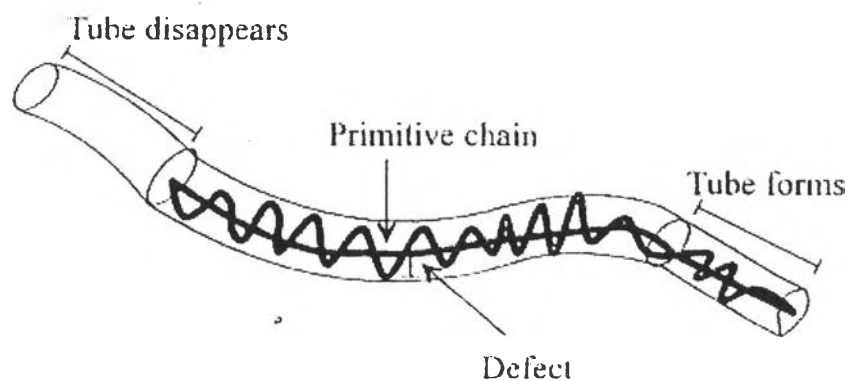


Figure 1.3 Polymer chain reptating through an imaginary tube.

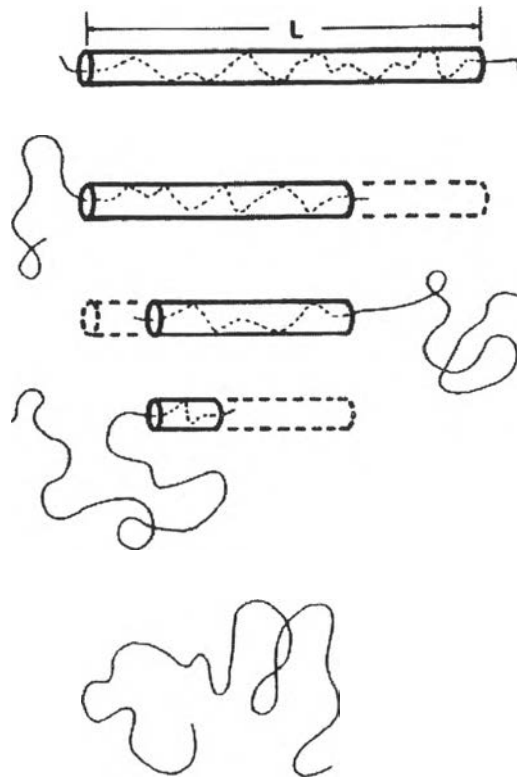
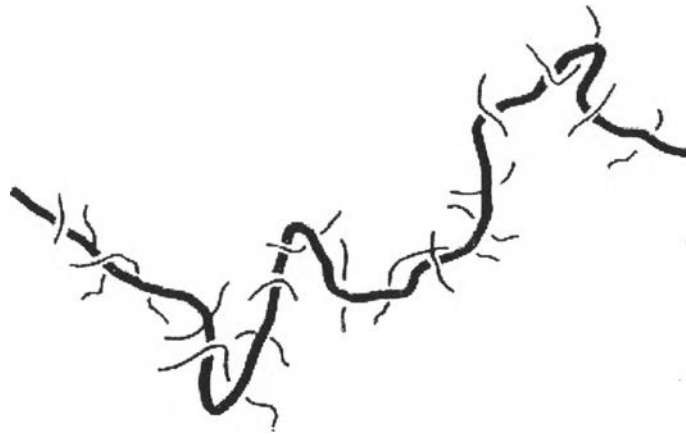


Figure 1.4 Reptative diffusion of a polymer molecule out of its tube.

1.2.4 The Doi-Edwards Theory

Doi and Edwards (1978) have developed the molecular theory of viscoelasticity for molten, high molecular weight polymers that makes use of the reptation concept. They started with the Rouse segmented chain model for a polymer molecule. Because of the presence of neighboring molecules, there are many places along the chain where lateral motion is restricted, as shown in Figure 1.5. To simplify the representation of these restrictions, Doi and Edwards assumed that they are equivalent to placing the molecule of interest in a “tube”, as shown in Figure 1.6. This tube has a diameter d and a length L . Because the model does not refer to specific points of entanglement, the molecular weight between entanglements, M_e , does not appear as a parameter. However, there is some basis for associating the number of entanglements, M/M_e , with the ratio, L/d .



、 **Figure 1.5** Sketch showing one entire molecule together with the segments of other molecules that are located near to it and restrict motions.

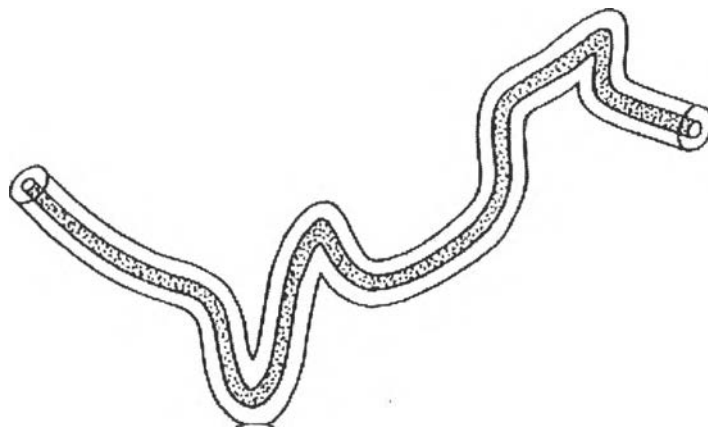


Figure 1.6 Sketch showing the hypothetical tube as assumed by Doi and Edwards to be equivalent in its effect to the segments shown in Figure 1.5.

Doi and Edwards (1986) examined the ways in which the chain can respond to a change in the configuration of its tube. At very short times, the only reaction that occurs within the tube is the redistribution of extensions among the segments between the points where topological constraints

(entanglements) are present. The theory predicts that this rapid relaxation process has a characteristic time, λ_e , called the equilibration time. Once this process is completed only additional mechanism available for the molecule to further relieve the stress is disengagement. This is a relatively slow process with a characteristic time of λ_d , which is a diffusion time. For long chain, $\lambda_d \gg \lambda_e$. Another relaxation process that can occur in entangled melts is relaxation of the contour length, i.e., the retraction of the molecule within its tube. However, this process makes no significant contribution to linear viscoelastic properties.

In this way the theory accounts for the two distinct groups of relaxation times that are observed for high molecular weight, monodispersed, linear polymers. For times $t < \lambda_e$, the theory predicts the same result as is given above for the modified Rouse theory. Even though the model does not predict a flat plateau, the decrease in G in the plateau-like region is only about 20%. Doi and Edwards identified the plateau modulus with the value of $G(t)$ at $t = \lambda_e$

$$G_N^0 \approx G(\lambda_e) \quad (1.3)$$

With this approximation, for $t \leq \lambda_e$ the model predicts:

$$G(t) = G_N^0 (\lambda_e/t)^{1/2} \quad (1.4)$$

In the plateau and terminal zones, the model predicts:

$$G(t) = G_N^0 \frac{8}{\pi^2} \sum_{p \text{ odd}}^N \frac{1}{p^2} e^{-p^2 t / \lambda_d} \quad (1.5)$$

Because of the $1/p^2$ factor, this result is quite close to a relaxation with a single relaxation time, i.e., the term with $p = 1$. This implies that the relaxation spectrum is quite narrow compared with the Rouse spectrum.

The longest relaxation time, λ_d , is:

$$\lambda_d = \frac{a^2 \zeta M^3}{M_e M_o^2 \pi^2 kT} \quad (1.6)$$

where a is a tube diameter, ζ is the monomeric friction coefficient, M is molecular weight, M_e is molecular weight between entanglement, M_o is monomer molecular weight, k is Boltzmann's constant and T is absolute temperature.

Grassley (1980) has derived expressions for another linear properties predicted by the model:

$$\eta_o = \frac{1}{15} \frac{\rho N_o a^2 \zeta M^3}{M_e^2 M_o^2} = \frac{\pi^2}{12} G_N^o \lambda_d \quad (1.7)$$

$$J_s^o = \frac{3M_e}{\rho RT} = \frac{6}{5G_N^o} \quad (1.8)$$

where ρ is density, N_o is equal to M/M_o , and J_s^o is complex compliance.

Making use of these expressions, the longest relaxation time, λ_d , can be written in terms of rheological properties:

$$\lambda_d = \frac{15M_e \eta_o}{\pi^2 \rho RT} = \frac{10}{\pi^2} \eta_o J_s^o \quad (1.9)$$

where η_o is shear viscosity.

Comparing these results with experimental observations for linear, monodispersed, entangled polymers, the following general statements can be made. The very strong effect of M on the viscosity is in qualitative agreement with observation, but the value of 3 for the exponent is somewhat below the experimentally observed value of about 3.4. The steady state compliance is predicted to be independent of molecular weight for a given polymer. This is in agreement with observation for high molecular weight melts, and it is in a sharp contrast with the prediction of the modified Rouse theory, for

unentangled melts, that J_s^0 is proportional to molecular weight. It is predicted that $J_s^0 G_N^0 = 6/5$, whereas the observed value is often about 2.

The predicted relaxation modulus by the Doi and Edwards theory at short times and the storage and loss moduli at high frequencies are not in accordance with observation, falling below the experimental curves, especially in the case of $G''(\omega)$. These results reflect the very narrow relaxation spectrum predicted by the theory.

The Doi-Edwards theory is a major step forward from the modified Rouse theory in its ability to predict the most prominent effects of entanglement in high molecular weight, linear, monodispersed polymers. However, it is deficient in its ability to make accurate quantitative predictions of most phenomena. In an effort to preserve the basic tube model while improving quantitative predictions, several modifications of the theory have been proposed. For example, consideration of an additional relaxation mechanism due to contour length fluctuation leads to significant improvements in the shape of the spectrum, the dependency of η_0 on m and the value of J_s^0 .

A central hypothesis of Doi-Edwards theory is that the “tube” retains its identity throughout the disengagement time for an individual molecule. For a monodispersed system estimates of the time required for the tube to lose its identity through Brownian motion (diffusion) of the molecules comprising the tube is much larger than λ_d , and the hypothesis is thus valid. However, in a polydispersed system, this is no longer true, as some of the molecules making up the tube have a much lower M_w than the longest molecules in the system. In this case, “tube renewal” provides an additional mechanism for relaxation and thus speeds up the process.

The presence of long chain branching leads to significant theoretical complications. Reptation is no longer possible, and relaxation

occurs primarily through the mechanism of contour length fluctuation (Dealy and Wissbrun, 1990).

1.2.5 Double Reptation Model

In a polymer melt, at a stress point P , two polymers are entangled and we shall assume that such stress points are distributed at random on the polymers. The stress at P will disappear if one end point of A or B reptates through the motionless point P (des Cloizeaux, 1988).

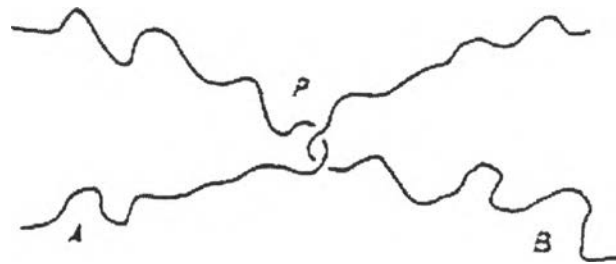


Figure 1.7 The polymers A and B are entangled and there is a point at P . The stress disappears if either A or B reptates entirely through P .

The constitutive equation of double reptation theory is:

$$m_d(t) = \sum_A \sum_B w_A w_B p_A(t) p_B(t) = \left[\sum_i w_i p_i(t) \right]^2 \quad (1.10)$$

where $m_d(t)$ is the fraction of unrelaxed stress at time t and w_i is volume fraction of chain i . p_i is the tube survival probability of chain i at time t calculated from the original theory of Doi and Edward with a single relaxation time by

$$p_i(t) = \sum_{k=\text{odd}}^{\infty} \frac{1}{k^2} \exp[-k^2 t / \tau_{\text{rep},i}] \sim \exp[-t / \tau_{\text{rep},i}] \quad (1.11)$$

where $\tau_{\text{rep},i}$, the longest relaxation time of chain i , is obtained from an empirical dependence on molecular weight:

$$\tau_{\text{rep},i} = K' \left(\frac{M_{w,i}}{M_e} \right)^{3.4} = KM_{w,i}^{3.4} \quad (1.12)$$

where $M_{w,i}$ is the weight-average molecular weight of chain i , M_e is the molecular weight between entanglements, and K is the empirical parameter which equals $K'/M_e^{3.4}$.

The stress-relaxation modulus $G_{\text{total}}(t)$ is directly proportional to $m_d(t)$

$$G_{\text{total}}(t) = G_N^0 m_d(t) = G_N^0 \left[\sum_i w_i p_i(t) \right]^2 \quad (1.13)$$

For monodisperse polymers, η_0 , the zero-shear viscosity, is simply related to τ_{rep} by

$$\frac{\eta_0}{G_N^0} = \frac{\tau_{\text{rep}}}{2} = \frac{K}{2} M_w^{3.4} \quad (1.14)$$

The parameters for this model are the plateau modulus G_N^0 , and the empirical parameter K .

The stress-relaxation modulus $G_{\text{total}}(t)$ from the model can convert to the storage modulus (G') and the loss modulus (G'') by

$$G'(\omega) = \omega \int_0^{\infty} G_{\text{total}}(t) \sin(\omega t) dt \quad (1.15)$$

and

$$G''(\omega) = \omega \int_0^{\infty} G_{\text{total}}(t) \cos(\omega t) dt \quad (1.16)$$

1.2.6 Modified Dual Constraint Model

The dual constraint model combines two forms of constraint release into the dynamics of entangled polymers. The first form of constraint release is ‘double diffusion’ which augments ‘double reptation’ by inclusion of primitive path fluctuation as a mechanism of constraint release. This first mode of constraint release has been found successfully for the effects of polydispersity on the relaxation of polydispersed linear chains in most cases. The second form of constraint release is ‘dynamic dilution’ which describes the self-consistent time-dependent loosening of the effective entanglement network, or widening of the tube, that is realized when the relaxation of monodispersed star polymers is considered on ever longer time-scales. This second form of constraint release is required for stars, because even a monodispersed star has such a wide range of relaxation times that over the time-scale required for the last interior part of an arm to relax, the tip of that arm has relaxed so many times that it acts more like a solvent than a real obstacle to motion of other chains (Pattamaprom *et al.*, 2000).

a) Reptation and fluctuation in a fixed matrix

The linear viscoelastic constitutive equation for highly entangled polymers proposed here is based on the tube model of Doi and Edwards. For an oscillatory deformation at low and moderate frequencies, the major relaxation mechanisms for linear polymers are reptation, contour-length fluctuation, and constraint release. For star polymers, the arms are joined together, preventing reptation. Thus, contour-length fluctuation and constraint release are the only relaxation mechanisms for stars at low and moderate frequencies. At high frequencies, Rouse processes are important for both architectures.

Reptation can be thought of as the diffusion of a chain out of a tube; therefore, it can be represented by a diffusion equation for the tube-

survival probability. Contour-length fluctuation is a relaxation process induced by the thermal fluctuation of the tube length with time. Including both reptation and contour-length fluctuation, the diffusion equation for linear polymers subjected to a small step strain at time $t = 0$ is (Mead, Van Dyke et al., 2000):

$$\frac{\partial p_i^*(s_i, t)}{\partial t} = \frac{D_i}{L_i^2} \frac{\partial^2 p_i^*(s_i, t)}{\partial s_i^2} - \frac{p_i^*(s_i, t)}{\tau_{\xi, i}^*(s_i)} \quad (1.17)$$

The initial and boundary conditions are $p_i^* = 1$ at $t = 0$, and $p_i^* = 0$ at the chain end. The first term on the right of Equation (1.17) represents the reptation mechanism and the second term is for the contour-length fluctuation. The equation is the same for star polymers except for the reptation term is removed. The subscript i denotes a linear chain of molecular weight M_i or the arm molecular weight for a star polymer. In Equation (1.17), $p_i^*(s_i, t)$ is the survival probability of a tube segment occupied by a chain of type i as a function of time t and contour distance s_i , where s_i ranges from 0 at the center of a linear polymer chain or the branch point of a star to $1/2$ at the chain end of a linear, or to 1 at the chain end of a star. D_i , the curvilinear diffusion coefficient, can be calculated by

$$D_i = \frac{L_i^2}{\tau_{d, i} \pi^2} \quad (1.18)$$

where L_i is the average contour length of the tube and $\tau_{d, i}$ is the reptation time constant. L_i equals $N_i b^2/a$, where a is the tube diameter, b is the effective polymer statistical segment length, and N_i is the number of monomers composing a chain of type i . The relationship between a and b is given by $b = a(M_0/M_e)^{1/2}$, and N_i can be written as M_i/M_0 , where M_0 is the monomer molecular weight and M_e is the molecular weight between two entanglements.

$\tau_{d,i}$ is given by $\tau_{d,i} = (\zeta N_i^3 b^4) / (\pi^2 k_b T a^2)$ where ζ is the monomeric friction coefficient, k_b is the Boltzmann constant and T is the absolute temperature.

The second term represents contour-length fluctuations. The relaxation time for contour-length fluctuations, $\tau_{\xi,i}$, which is the time constant for contour length fluctuations in the presence of constraint release for shallow ($\tau_{\text{early},i}$) and deep ($\tau_{\text{late},i}^*$) fluctuations which can be expressed by

$$\tau_{\text{early},i}(s_i) = \frac{225}{256} \pi^3 \frac{\tau_{R,i}}{c^2} (1 - cs_i)^4 \left(\frac{N_{\text{en},i}}{c} \right)^2 \quad (1.19)$$

and

$$\tau_{\text{late},i}^*(s_i, t) = \frac{\tau_{R,i}}{c^2} \exp(U_{(s_i)}^*) \quad (1.20)$$

where c is a prefactor which equals 2 for linear polymers (linear polymer has two fluctuating chain ends), and 1 for star polymers. $N_{\text{en},i}$ is the number of entanglements per chain, which equals M_i/M_c . M_i is the weight-average molecular weight of chain i . $\tau_{R,i}$ is the longest Rouse stress relaxation time of chain i defined by $\tau_{R,i} = \zeta N_i^2 b_i^2 / 6\pi^2 k_b T$, which is smaller than the rotational relaxation time τ_r from Doi and Edwards by a factor of two, so $\tau_{R,i} = \tau_{d,i} / (6N_{\text{en},i})$.

$U^*(s_i)$ is the activation energy for chain retraction given by

$$U^*(s_i) = \frac{15}{8} \frac{N_{\text{en},i}}{c} (1 - cs_i)^2 \quad (1.21)$$

The quick fluctuation mode of chain ends (s_i close to 1) is controlled by $\tau_{\text{early},i}$ and gradually changes to the normal activation mode $\tau_{\text{late},i}^*$ toward the center (s_i close to 0). Therefore, $\tau_{\xi,i}^*$ in Equation (1.17) equals $\tau_{\text{early},i}$ for large s_i and $\tau_{\text{late},i}^*$ for small s_i . It was proposed (Pattamaprom *et al.*, 2000) here a simple

crossover function that splices these two functions together with a transition zone over which a geometric average of the two is used. The crossover function from $\tau_{\text{early},i}$ to $\tau_{\text{late},i}^*$ along the chain follows the solid line in Figure 1.8, which is given by

$$\begin{aligned} \tau_{\xi,i}^* &= \tau_{\text{early},i} && \text{when } (1-s_i) < C_1^* \\ \tau_{\xi,i}^* &= \tau_{\text{early},i} * \tau_{\text{late},i}^* && \text{when } C_1^* < (1-s_i) < C_2^* \\ \tau_{\xi,i}^* &= \tau_{\text{late},i}^* && \text{when } (1-s_i) > C_2^* \end{aligned} \quad (1.22)$$

where C_1^* is the first crossover position of $\tau_{\text{early},i}$ and $\tau_{\text{late},i}^*$ close to the chain end, and C_2^* is the second crossover point deeper inside the tube. Close to the chain end where $(1-s_i) < C_1^*$, $\tau_{\xi,i}^*$ takes the value of $\tau_{\text{early},i}$ and deep inside the tube where $(1-s_i) > C_2^*$, $\tau_{\xi,i}^*$ is controlled by $\tau_{\text{late},i}^*$. For the tube segments between C_1^* and C_2^* , $\tau_{\xi,i}^*$ is taken to be the geometric average of the two functions of s_i .

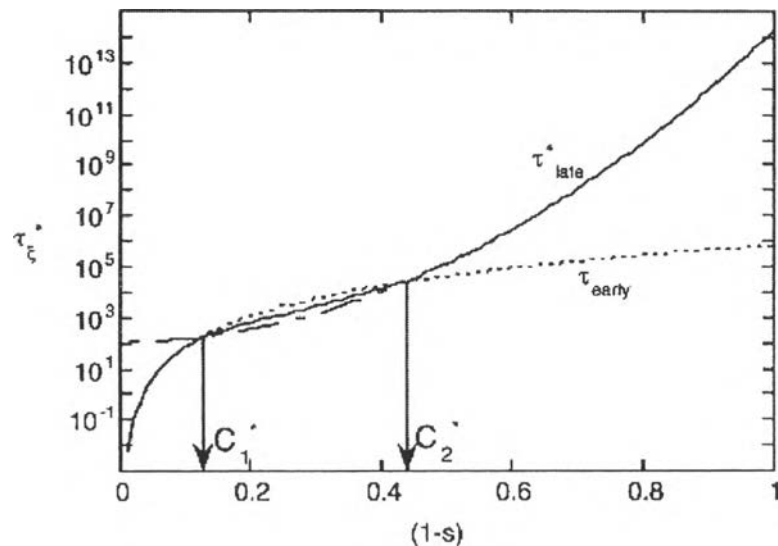


Figure 1.8 The crossover function (solid line) from τ_{early} (dotted line) to $(\tau_{\text{late},i}^*)$ (dashed line) with no constraint release ($\phi^* = 1$) for a linear polymer with 30 entanglements per chain or for a star with 15 entanglements per arm. The crossover points are indicated by C_1^* and C_2^* . The x-axis $(1-s)$ is the

distance from the chain end ($1 - s = 0$) toward the branch point of the star or the center of the linear chain ($1 - s = 1$).

The overall survival probability $\psi_i^*(t)$ of a tube occupied by chain i can then be calculated from $p_i^*(s_i, t)$ by

$$\psi_i^*(t) = \int_0^1 p_i^*(s_i, t) ds_i \quad (1.23)$$

and the average tube survival probability $\psi^*(t)$ of all chains is

$$\psi^*(t) = \sum w_i \psi_i^*(t) \quad (1.24)$$

where w_i is the weight fraction of the chains of length L_i . $\psi^*(t)$ can be obtained numerically by solving for $p_i^*(s_i, t)$ using the Crank-Nicolson method, and then converting to $\psi_i^*(t)$ and $\psi^*(t)$ by means of Equation (1.23) and (1.24), respectively. $\psi^*(t)$ is calculated when constraint release is not present.

The approximate constraint release Rouse process is then activated when $\psi^*(t)$ decreases faster than a Rouse relaxation process would permit. The constraint release Rouse relaxation permits relaxation no faster with time than

$$\psi_R(t) = \psi^*(t_0) \left(\frac{t}{t_0} \right)^{-1/2} \quad (1.25)$$

where t_0 is the time when $\psi^*(t)$ starts to drop faster than $t^{-1/2}$.

At time near zero, when the majority of the entanglement constraints still exist, the average survival probability of the chains $\phi_{(t)}^*$ equals $\psi_{(t)}^*$ and remains so until some time $t = t_0$, at which $\phi_{(t)}^*$ switches to $\psi_R(t)$. at some later time t , if $\psi_R(t)$ drops below $\psi_{(t)}^*$, $\phi_{(t)}^*$ then switches back to $\psi^*(t)$. whenever $\psi^*(t)$ drops faster than $t^{-1/2}$ again, the constraint release Rouse

process will be activated and $\psi_{R(t)}$ from Equation (1.25) with a new t_0 will be used for $\phi^*(t)$. the expression for $\phi^*(t)$ can therefore be written as

$$\begin{aligned}\phi^*(t) &= \psi^*(t) \quad \text{when } \psi^*(t) > \psi_R(t) \\ \phi^*(t) &= \psi_R(t) \quad \text{when } \psi^*(t) < \psi_R(t)\end{aligned}\tag{1.26}$$

The average survival probability of the chains $\phi^*(t)$ will be used as the dilution factor in the fluctuation term in the next part.

b) Reptation and fluctuation with constraint release

In general, constraint release manifests itself both in a local relaxation of an entanglement constraint and in a global loosening of the entanglement network. These modes of constraint release are called “tube reorganization” and “tube dilution”, respectively (Viovy *et al.*, 1991). While the local relaxation of entanglement constraints will be combined later in the final relaxation modulus, the time-dependent loosening of the entanglement network or tube widening, known as “dynamic dilution” (Ball and McLeish, 1989), is included in the activated fluctuation term.

Dynamic dilution takes into account the large differences in time-scales between fast and slow relaxation processes by allowing the accumulation of constraint release events to reduce the activation energy for deep-chain fluctuations. This reduction results in faster relaxation of the test chain. The dynamic dilution mechanism is incorporated into the dual constraint model by using the reduced activation energy, $U_{eff}(s_i, t)$, instead of $U^*(s_i)$, to calculate $\tau_{late,i}$. While this makes $\tau_{late,i}$ time dependent, $\tau_{early,i}$ remains the same as in part a) the expression for $\tau_{early,i}$ and $\tau_{late,i}$ with dynamic dilution can be written as

$$\tau_{early,i}(s_i) = \frac{225}{256} \pi^3 \frac{\tau_{R,i}}{c^2} (1 - cs_i)^4 \left(\frac{N_{en,i}}{c} \right)^2\tag{1.27}$$

and

$$\tau_{\text{late},i}(s_i, t) = \frac{\tau_{R,i}}{c^2} \exp(U_{\text{eff}}(s_i, t)) \quad (1.28)$$

where $U_{\text{eff}}(s_i, t)$ is obtained by multiplying U^* by the dilution factor $\phi^*(t)$ calculated from Equation (1.26) giving

$$U_{\text{eff}}(s_i, t) = \frac{15}{8} \frac{N_{\text{en},i}}{c} \phi^*(t) (1 - cs_i)^2 \quad (1.29)$$

As shown in Figure 1.9, although $\tau_{\zeta,i}$ behaves similarly to that in part a), the crossover locations, C_1 and C_2 , are now changing with time due to the time dependence of $\tau_{\text{late},i}$. Hence, $\tau_{\zeta,i}$ along the tube position s_i is described by Equation (1.22) with $\tau_{\text{late},i}^*$ replaced by $\tau_{\text{late},i}$.

$$\begin{aligned} \tau_{\xi,i} &= \tau_{\text{early},i} && \text{when } (1-s_i) < C_1 \\ \tau_{\xi,i} &= (\tau_{\text{early},i} \tau_{\text{late},i})^{1/2} && \text{when } C_1 < (1-s_i) < C_2 \\ \tau_{\xi,i} &= \tau_{\text{late},i} && \text{when } (1-s_i) < C_2 \end{aligned} \quad (1.30)$$

where C_1 and C_2 are the crossover points.

This new expression for $\tau_{\xi,i}$ is now incorporated into the diffusion equation as follows:

$$\frac{\partial p_i(s_i, t)}{\partial t} = \frac{D_i}{L_i^2} \frac{\partial^2 p_i(s_i, t)}{\partial s_i^2} - \frac{p_i(s_i, t)}{\tau_{\xi,i}(s_i)} \quad (1.31)$$

where $p_i(s_i, t)$ and $\tau_{\xi,i}$ are the tube segment survival probability and the time constant for contour length fluctuation, respectively, in the presence of constraint release by dynamic dilution (Equation 1.30).

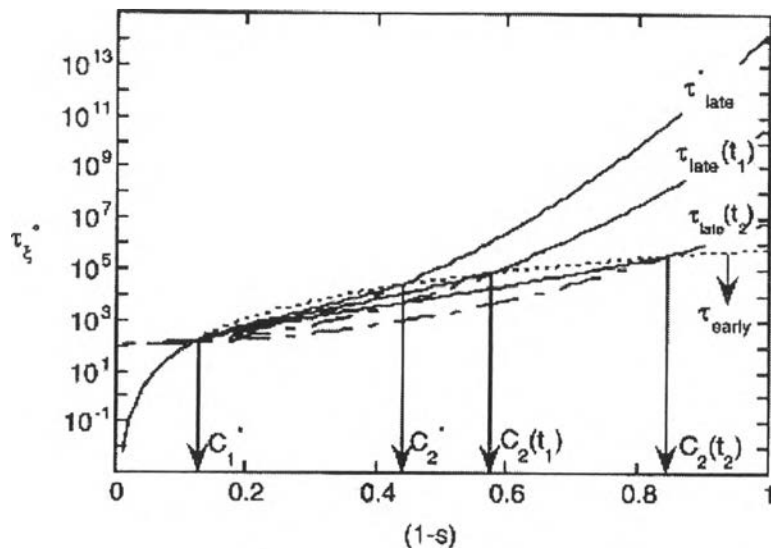


Figure 1.9 The crossover function from τ_{early} to τ_{late} with constraint release ($\phi^*(t) = 1.0, 0.7, \text{ and } 0.4$) for the polymer of Figure 1.8. The crossover points C_1 and C_2 change with $\phi^*(t)$, which decreases with time.

The overall survival probability $\phi_i(t)$ of a tube occupied by chain i can then be calculated from $p_i(s_i, t)$ by

$$\phi_i(t) = \int p_i(s_i, t) ds_i \quad (1.32)$$

and the average survival probability of all tube is

$$\phi(t) = \sum w_i \phi_i(t) \quad (1.33)$$

$\phi(t)$ can be obtain numerically by solving for $p_i(s_i, t)$ using the Crank-Nicolson method, (using logarithmic time) then converting to $\phi_i(t)$ and $\phi(t)$ by means of Equations (1.32) and (1.33), respectively.

So far, it has only accounted for “global” constraint release effects that accelerate contour length fluctuations via the dilution factor $\phi^*(t)$, which is used in the fluctuation potential U_{eff} . It can describe local constraint release events using the double-diffusion mechanism, developed as an

extension of double reptation (des Cloizeaux, 1988). This theory considers the survival probability of a binary topological interaction of a test chain with a surrounding chain. This mechanism accounts for the effect of the surrounding chains on the overall relaxation process by multiplying the average survival probability of the test chain by that of the constraints surrounding the chain. Without the constraint release Rouse process, the multiplication would be $\phi^2(t)$. However, after including constraint release Rouse processes, the fraction of constraints $\phi'(t)$ that block motion of a test chain at time t can differ from the fraction of tube segment $\phi(t)$ that are still occupied at time t . Thus

$$\begin{aligned}\phi'(t) &= \phi(t) & \text{when } \phi(t) > \phi_R(t) \\ \phi'(t) &= \phi_R(t) & \text{when } \phi(t) < \phi_R(t)\end{aligned}\tag{1.34}$$

where $\phi_R(t) = \phi(t_0)(t/t_0)^{-1/2}$, t_0 is the time when $\phi(t)$ begins to drop faster than $t^{-1/2}$, and $\phi(t_0)$ is the average survival probability at t_0 . The activation of constraint release Rouse processes for the fraction of local constraint $\phi'(t)$ in Equation (1.34) is identical to that for the dilution term $\phi^*(t)$ in Equation (1.26). That is, at time near zero, $\phi'(t)$ equals $\phi(t)$. After that, at each time t , $\phi'(t)$ is assigned the greater of the values of $\phi(t)$ and $\phi_R(t)$.

Thus, the overall survival probability of the binary interactions between the test chains and the surrounding chains becomes

$$\Phi(t) = \phi(t)\phi'(t)\tag{1.35}$$

The relaxation modulus $G(t)$ from the contributions of reptation, contour length fluctuations, and constraint release can be obtained by multiplying $\Phi(t)$ by the plateau modulus G_N^0 :

$$G(t) = G_N^0 \Phi(t) = G_N^0 \phi(t)\phi'(t) \quad (1.36)$$

The final relaxation mechanism is high frequency Rouse relaxation within the tube. High frequency Rouse relaxation includes stress relaxations of segments of the test chain at time-scales both shorter than τ_e , the time at which the chain segments first feel the constraint imposed by the conceptual tube, and longer than τ_e , during which only the longitudinal Rouse modes along the tube are available. The “equilibrium time” τ_e is the Rouse relaxation time for an entanglement segment of a chain and is independent of chain length, i.e., the molecular weight of the polymer. τ_e is related to $\tau_{R,i}$ by $\tau_e = 2\tau_{R,i}/N_{en,i}^2$ which implies that τ_e is related to $\tau_{d,i}$ as $\tau_e = \tau_{d,i}/3N_{en,i}^3$. The division of spatial scales separating Rouse processes with time-scales less than τ_e from those with time-scales greater than τ_e has been represented by Milner and McLeish (1998) using an approximate “fragmented Rouse” spectrum to calculate the Rouse relaxation modulus of chain i ($G_{R,i}$):

$$G_{R,i}(t) = \frac{1}{3} G_N^0 \sum_{k=1}^{N_{en,i}} \exp\left(\frac{-k^2 t}{\tau_{R,i}}\right) + G_N^0 \sum_{k=N_{en,i}}^N \exp\left(\frac{-k^2 t}{\tau_{R,i}}\right) \quad (1.37)$$

Here, the first term accounts for the slow longitudinal modes which are confined by the tube to one dimension rather than three as in the ordinary Rouse theory, so their magnitude is reduced by a factor of three. The second term represents fast three-dimensional relaxation of portions of the chain within a single tube segment.

Finally, the full stress-relaxation modulus (G_{total}) combines $G(t)$ from Equation (1.36) with the contribution from Rouse processes giving

$$G_{total}(t) = G(t) + \sum_i w_i G_{R,i}(t) \quad (1.38)$$

The stress-relaxation modulus can then be converted to the storage modulus (G') and the loss modulus (G'') by

$$G'(\omega) = \omega \int_0^{\infty} G_{\text{total}}(t) \sin(\omega t) dt$$

and

$$G''(\omega) = \omega \int_0^{\infty} G_{\text{total}}(t) \cos(\omega t) dt$$

(1.39)