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Tight Knots†

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ABSTRACT: We present a conjectural explanation for long-time memory effects in melts of crystallizable, linear polymers. During a crystallization process, chains that are knotted, and that are reeled in from *both ends*, might make very tight knots. These knots are expected to be very stable and to persist for long times after the sample is heated above the melting temperature. The density and the lifetime of tight knots should be sensitive functions of the original quenching temperature. Tight knots could also be generated, in the absence of any crystallization process, by strong longitudinal shear of a solution—especially with poor solvents.

I. Introduction

The natural time unit for entangled polymer melts of high molecular weight is the terminal time τ measured from viscoelastic data.[1,2] This time is a rapidly increasing function of the molecular weight M ($\tau \sim M^{3.3}$) and can become rather large (minutes) for high polymers ($M > 10^6$) even when they are well above their glass temperatures. A partial picture for τ has been provided by the reptation model.[3,4]

However, some strange things still happen at times $t \gg \tau$.

(a) The T_2 relaxation or protons in melts displays two distinct fractions associated respectively with fast or slow relaxation. The relative weight of the two fractions in a polyethylene melt appears to depend on the thermal history of the sample.[5] Memory effects are present after melting for many hours, in samples where the terminal time is smaller than 1 min.

(b) One can probe the organization of chains in a crystallizable melt by a rapid quenching below the crystallization temperature, followed by a measurement of the repeat period of the lamellae.[6,7] This again shows remarkably long relaxation times θ in the melt: θ is a rapidly increasing function of M, as is τ, but θ is considerably larger than τ; naive reptation cannot account for the long memory times.

In the present paper, we propose an explanation for the long times θ based on tight knots (section II). This is very tentative but may stimulate certain relevant experiments: we discuss them in section III.

II. Kinks and Knots

Figure 1 shows a tight knot made with a flexible aliphatic chain, preserving the tetrahedral carbon coordinations and forbidding overlap between neighboring C or H atoms but allowing for local conformations that can be neither trans nor gauche (arbitrary dihedral angles). With that set of constraints the minimal number N_m of carbon atoms required to make the knot is $\sim$38. Imposing strict trans or gauche conformations, by applying the chain on a diamond lattice, we find a rather similar figure ($N_\mathrm{m} \sim 36$).

Our first aim is to estimate the statistical weight for such a tight knot. We shall use a very qualitative approach based on the kink model, which was used as an image in early reptation work.[3] We picture a flexible thread with a certain average number ρ of kinks per monomer and a *stored length b* per kink. What characterizes the knot region is primarily the absence of kinks, or of stored length. Thus the probability P of finding a sequence of monomers $n, n+1, ..., n+N_\mathrm{m}$, in a tight knot may be estimated by the Poisson law

$$P = P_0 e^{-\rho N_\mathrm{m}} \tag{1}$$

where P_0 is an unknown prefactor of order unity.

In a conventional melt of flexible chains, we expect $b \sim a$ (a being the monomer length) and $\rho \sim 1$. Then the probability P is exponentially small and tight knots are probably unobservable.

In a quenched system that is undergoing crystallization,[8] some chains may start to crystallize at two (or more) different points A and B. At each crystallization point the chain is reeled in with a certain tension ζ, which is simply related to the thermodynamics of undercooling

$$\zeta = \frac{\Delta F}{a} \simeq \frac{\Delta H}{a}\,\frac{T_\mathrm{m} - T_\mathrm{Q}}{T_\mathrm{m}} \tag{2}$$

where ΔF is the free energy difference between crystal and melt and ΔH is the enthalpy of transition (per monomer). T_m is the melting point and T_Q is the quenching temperature. In steady state the tension ζ is applied all along the flexible portion AB. (In transient states some regions of the AB chain do not yet feel the tension, but we omit this complication in what follows.) We conclude that the density of kinks must be drastically reduced in the AB portion

$$\rho = \rho_0 \exp\left(-\frac{b\zeta}{kT_\mathrm{Q}}\right) \tag{3}$$

$b\zeta$ being the work performed to destroy one kink. If we insert (3) in (1), we find a "doubly exponential" form, giving a very abrupt increase in P when $\zeta \sim kT_\mathrm{Q}/b$.

When a tight knot is made, it becomes extremely difficult to undo even after melting and returning to $\zeta = 0$. The knot can disappear only through entry (in the knot region) of a certain amount of stored length; when this is provided, the usual reptation processes can start to work. We all know, from experience with macroscopic strings, that the insertion of some stored length in a tight knot is difficult to perform. Here, stored length will probably not enter in the form of a sharp kink, but rather by some very progressive distortion of many bonds. The activation energy E for this process is expected to be high and to be a rapidly increasing function of the original tension ζ. The calculation of $E(\zeta)$ will require a considerable effort of numerical analysis. But, at the present zero-order level, it may be plausible to think that the activation energy is linear in ζ

$$E(\zeta) = b'\zeta \tag{4}$$

where b' is another length comparable to a monomer size. The lifetime of the knots in the melt is expected to be of order

$$\theta = \tau \exp[E(\zeta)/kT] \gg \tau \tag{5}$$

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† In spite of its obvious imperfections, we dedicate this work to Walter Stockmayer, whose advice, encouragement—and living example—have been a major help to our group during the past 15 years.

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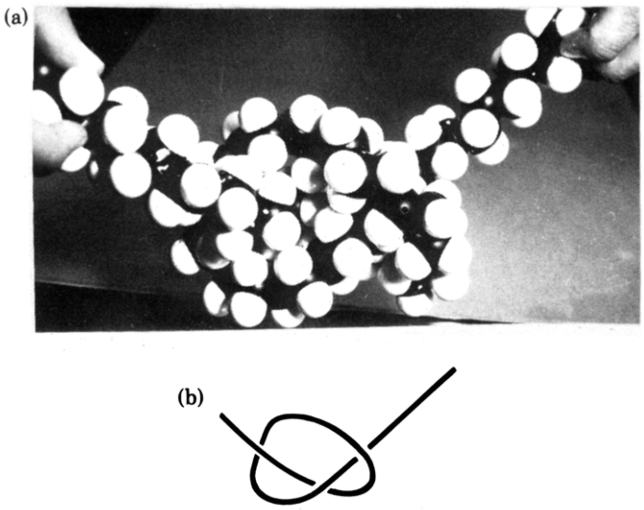

Figure 1. (a) Typical conformation for the simplest tight knot made with an aliphatic chain. The number of carbons involved in the "active" region is ~36–38. (b) Topology of the knot in (a).

For polyethylene quenched at room temperature,[14] eq 2 leads to $E(\zeta) \sim 0.5kTb'/a$. The precise value of b'/a is thus crucial, because it enters in eq 5 through an exponential. To explain the observed values of θ we need $b'/a > 10$. I do not have any precise argument for these high values of b'/a. I tend to believe that they reflect the *cooperativity* of a tight knot: to loosen it at one point requires extra freedom in another loop.

III. Concluding Remarks

(1) If they are high enough, the line tensions ζ present during a crystallization process may favor the formation of tight knots. These knots can be simple self-knots such as the one shown in Figure 1, but they can also be more complex objects involving two (or more) chains.

(2) Both the number of knots (eq 1 and 3) and the lifetime of the knots (eq 4 and 5) are expected to be strongly dependent on ζ and thus on sample history.

(3) Cumulative effects may occur: successive quench–melt cycles during time intervals smaller than θ could lead to rather high knot densities.

(4) The presence of one tight self-knot may slow down the opening of another knot on the same chain: there may be corrections to eq 5 describing knot/knot interactions.

(5) Apart from (4), a self-knot has few physical effects (it may reduce the crystallinity slightly). On the other hand, a tight knot of two chains transforms them into a star, with strongly enhanced relaxation times. A single star in a matrix of linear chains of comparable molecular weight is expected to display a mechanical relaxation

$$\tau_s \simeq \tau(N/N_e)^2 \qquad (6)$$

where N is the degree of polymerization and N/N_e is the number of entanglements per molecule.

(6) Tight knots may be generated, in the absence of any crystallization process, by *strong shear flows*. Consider, for instance, a single, flexible chain undergoing a coil–stretch transition in a longitudinal shear flow.[9,10] In the fully extended state the tensions in the middle of the chain (obtained by integrating the local friction forces along the whole chain length) are of order

$$\zeta \simeq \frac{kT}{a}\tau_R\dot{\gamma} \qquad (7)$$

where τ_R is the Rouse relaxation time (proportional to M^2) and $\dot{\gamma}$ is the shear rate. The tension ζ is often sufficiently strong to induce polymer degradation.[11] For our purposes, assume that the original coil carried a loose knot before stretching: then it may end up with a tight knot after stretching. Loose self-knots are probably rare in good solvents but more frequent in Θ solvents.[12,13] Thus this process may become important in poor solvents. Comparing (7), (3), and (1), we see that the minimal shear rate $\dot{\gamma}_m$ required to generate tight knots is of order

$$\dot{\gamma}_m \sim \frac{1}{\tau_R}\ln N_m \qquad (8)$$

(We usually expect $\dot{\gamma}_m < \dot{\gamma}_c$, where $\dot{\gamma}_c$ is the threshold for chemical degradation).

(7) We might also generate tight interchain knots in *semidilute* solutions (even with good solvents) under strong longitudinal shear flows: this may have interesting rheological consequences.

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