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Kinetics of the Unfolding of Collapsed Polystyrene Chains above the Glass Transition Temperature[1]

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ABSTRACT: Monodisperse polystyrenes with three molecular weights were doubly labeled with phenanthrene and anthracene and dissolved with a large excess of unlabeled polystyrene in benzene keeping the polymer concentration below the critical c^* value for chain overlap. After rapid freezing of the solution, the solvent was sublimed so that the individual chain molecules collapsed into compact globules. Pellets pressed from this material were heated above T_g and the expansion of the doubly labeled chains into the unlabeled matrix was monitored by the change in the emission spectrum due to a decreasing energy transfer from phenanthrene to anthracene with an increasing donor–acceptor separation. The kinetics of the process were characterized by $R_s^2/t_{1/2}$ or by $(\Delta R_g)^2/t_{1/2}$ where R_s was the radius of the globule, ΔR_g the difference between the radius of gyration of the unperturbed molecular coil and the globule, and $t_{1/2}$ the time required for the ratio of the acceptor and donor emission intensity to decay halfway from its initial value to the equilibrium value observed in films cast from a mixture of doubly labeled and unlabeled polystyrene. The dependence of these parameters on the molecular weight of the doubly labeled polymer, on temperature, and on the molecular weight of the unlabeled matrix was compared with the dependence of the self-diffusion coefficient on these variables.

Introduction

The diffusion of long chain molecules in polymer melts has been a subject of intense study in recent years. Since theory predicts[2,3] that the self-diffusion coefficient D is inversely proportional to the square of the chain length, an experimentalist concerned with polymers of high molecular weight is faced with the problem of characterizing extremely small D values. With $D = \langle x^2 \rangle / 2t$, where $\langle x^2 \rangle$ is the mean square displacement in a given direction in time t, the determination of such small D within a reasonable time requires the development of experimental techniques allowing a very high spatial resolution. A number of such techniques have been reported,[4] some allowing measurements of D as small as 10^{-16} cm^2 s^{-1}.

In a previous communication from this laboratory[5] it was suggested that the rate at which collapsed polymer chains interdiffuse to approach conformational equilibrium might yield data from which the self-diffusion coefficient could be estimated. Samples were prepared by rapid freezing of dilute solutions of mixtures of poly(ethyl methacrylate) labeled with donor and acceptor fluorophores, respectively. After sublimation of the frozen solvent, this procedure is known to lead to a collapse of the individual chain molecules into compact globules.[6] When a pellet pressed from donor and acceptor (D and A) globules was irradiated in the donor absorption band, the emission spectrum was characterized by little nonradiative energy transfer[7] since the donor and acceptor fluorophores are segregated in different globules so that only in areas where the A and D globules are in contact with one another the donor–acceptor distance is sufficiently close for energy transfer. However, when the pellet was heated above the glass transition temperature, the interdiffusion of the chain molecules brought the donor and acceptor fluorophores closer to one another and this was reflected in a gradual increase of I_A/I_D, the ratio of the acceptor and donor emission intensities. It was conjectured that $d^2/t_{1/2}$, the ratio of the square of the globule diameter and the time required for I_A/I_D to move halfway to its equilibrium value, might be proportional to D, and because the change in the emission spectrum involves motions of the order of only a few nanometers, it was hoped that very small diffusion rates could be characterized. In fact, poly(ethyl methacrylate) with a molecular weight as high as 5×10^5 was found to expand within a few hours from the collapsed to the equilibrium state.

These first experiments were designed only to demonstrate the feasibility of the method, and since they utilized polydisperse polymers, they did not lend themselves to reliable interpretation. We have used, therefore, in the present study monodisperse polystyrene samples. We modified our procedure also in another important respect. A random mixing of D and A globules leads to D–D, A–A, and D–A contacts, rendering a description of the distribution of donor–acceptor distances rather complex. We employed, therefore, polymers doubly labeled with donor and acceptor fluorophores mixed with a large excess of unlabeled polymers.[8] This leads to a gradual decrease in nonradiative energy transfer as the labeled polymer globules expand into the unlabeled matrix. Although we did not attempt to derive from the fluorescence data the extent of chain expansion, the spherical symmetry of the label densities makes such an analysis in principle accessible.

Here we report data obtained with polystyrenes of three molecular weights over a range of temperatures. Parameters obtained from the kinetics of the unfolding of collapsed polymer chains are then compared with polystyrene diffusion coefficients.

Experimental Section

Materials. 9-Anthracenemethanol (Aldrich) was twice recrystallized from ethanol (mp 163 °C). 9-Phenanthrenemethanol was prepared by the reduction of 3.1 g of 9-phenanthrenealdehyde (Aldrich) with 0.31 g of $NaBH_4$ in methanol solution at 0 °C for 1 h and at room temperature for 3 h. It was recrystallized from a 1:5 mixture of dioxane and methanol (mp 143.5–144 °C). The "monodisperse" polystyrene samples (Polysciences) were specified to have molecular weights of 3×10^4, 1×10^5, and 3×10^5 with $M_w/M_n = 1.06$. Intrinsic viscosities of these samples in benzene at 25 °C were 0.20, 0.47, and 1.02 dL/g, corresponding to viscosity-average molecular weights[9] of 3.1×10^4, 9.8×10^4, and 2.8×10^5, and we shall use these values in interpreting our results.

Polymer Labeling. To a 5% solution of polystyrene in CCl_4 were added 5 vol % chloromethyl methyl ether and 5 vol % $SnCl_4$ under nitrogen. After 40 min at 30 °C, the reaction was stopped by the addition of methanol. The lightly chloromethylated polymer was precipitated into methanol, washed, and dried. A dimethylformamide solution containing the potassium salt of 9-phenanthrenemethanol and 9-anthracenemethanol was added to the chloromethylated polystyrene in the same solvent, and the reaction was allowed to proceed for 10 h at 30 °C before stopping it by methanol addition. The labeled polystyrene was dissolved and precipitated at least four times. A constant absorption at 298 nm and at 365 nm ensured absence of free chromophores trapped in the polymer. The content of the labels in the polymer

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Table I
Labeled Polystyrenes Used in This Study

viscosity av mol wt	phenanthrene content,[a] mol %	anthracene content,[a] mol %
3.1×10^4	0.22	0.28
9.8×10^4	0.33	0.36
28×10^4	0.28	0.28

[a] Based on the concentration of styrene residues in the labeled polystyrenes.

was determined by UV spectroscopy assuming that the extinction coefficient (11 900 cm^{-1} M^{-1} for phenanthrene at 298 nm and 8600 cm^{-1} M^{-1} for anthracene at 365 nm) was the same as in the 9-methanol derivatives. Table I lists the characteristics of the labeled polystyrenes.

Sample Preparation. Benzene solutions of monodisperse polystyrene, 5% of which was doubly labeled, were prepared. Unless stated othewise, the doubly labeled and the unlabeled polystyrene had the same molecular weight. The product of concentration and intrinsic viscosity, $c[\eta]$, was 0.69 ± 0.02, well below $c^*[\eta] \geq 1$ characteristic of the critical overlap concentration c^*.[10] The solution was rapidly rotated in a round-bottom flask while it was immersed in liquid nitrogen, so that it froze within a fraction of a second. The frozen solvent was sublimed between −15 °C and −10 °C at 10^{-3} Torr for 24 h, and any residual benzene was removed by applying this vacuum at room temperature for an additional 24 hours. The fluffy polystyrene foam was stored under nitrogen before being pressed at 5.3 kilobars into partially transparent pellets. The same mixture of doubly labeled and unlabeled polystyrene was used for film casting from 10% benzene solutions on Teflon plates. After drying in a slow stream of nitrogen the films were kept for 24 h under 10^{-3} Torr at room temperature before fluorescence measurements.

Kinetics Measurements. Pellets prepared from the freeze-dried material placed on a copper holder (diameter 2.1 cm, height 9 mm) were inserted into a copper cylinder which was immersed, after three evacuations and flushing with oxygen-free argon, in a silicone oil bath thermostated to within ±0.5 °C. After the sample was heated for a given time under argon, the cylinder was immersed in ice water before the fluorescence spectrum of the sample was recorded. The inner surface of the cylinder was found to reach the oil bath temperature within 2 minutes and to fall below room temperature during 1 min after being quenched in ice water. Reflectance fluorescence spectra, as previously described,[11] were recorded using excitation at 298 nm, the absorption maximum of the phenanthrene donor. The emission spectra were characterized by the ratio of the anthracene emission intensity at 415 nm, I_A, and the phenanthrene emission intensity at 355 nm, I_D. Eight spectra were taken to obtain an average I_A/I_D, with the standard deviation of this ratio less than 5%.

Results

Properties of the Fluorescent Labels. Our study required the use of fluorescent labels that would remain stable when heated for prolonged periods under argon at temperatures such as used in this investigation. The pyrene donor, used previously,[5] was found to be unsatisfactory, but styrene labeled with phenanthrene and anthracene exhibited an unchanged emission intensity after being heated for 24 h at 150 °C. Use of the phenanthrene donor was also favorable because its extinction coefficient at 298 nm was a 100 times higher than that of the anthracene acceptor, so that the anthracene emission intensity depended almost entirely on the efficiency of nonradiative energy transfer.

The efficiency E of nonradiative energy transfer is given by[7,12]

$$E = R_0^6/(R_0^6 + r^6)$$

$$R_0^6 = (8.8 \times 10^{-25}) J n^{-4} \kappa^2 \phi_D^0 \qquad (1)$$

where r is the distance between donor and acceptor, J is the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor, n is the refractive index, κ^2 is a factor which depends on the mutual orientation of the donor and acceptor transition moments, and ϕ_D^0 is the fluorescence quantum yield of the donor in the absence of the acceptor. We found $J = 7.0 \times 10^{-15}$ cm^2 mol^{-1}, and using $n = 1.59$, $\kappa^2 = 0.47$ (corresponding to a random orientation of donors and acceptors in a medium of high viscosity[13]), and $\phi_D^0 = 0.13$ (reported for unsubstituted phenanthrene[14]), we obtained $R_0 = 2.0$ nm, close to the value 2.3 nm reported for the phenanthrene–9-methylanthracene pair.[15]

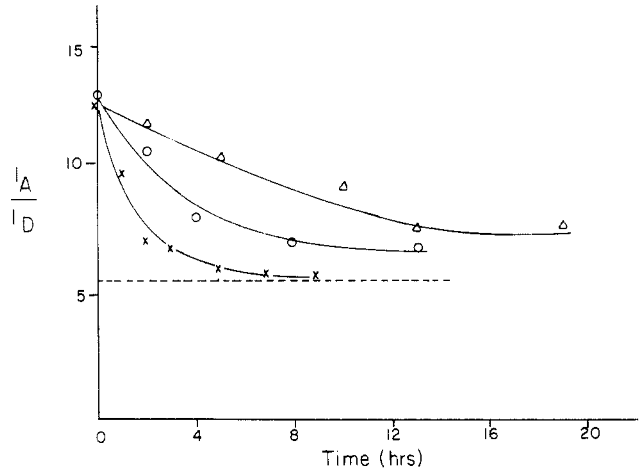

Figure 1. Unfolding of collapsed polystyrene chains, $M = 3.1 \times 10^4$. Temperature: (△) 130 °C; (○) 140 °C; (×) 150 °C.

The label concentration on the polymer should be chosen so as to maximize the change in the nonradiative energy transfer when the collapsed chain molecules expand to their equilibrium conformation.[25] With 0.28 mol % anthracene label in the polymers with molecular weights 3.1×10^4 and 28×10^4 and 0.36 mol % of the anthracene label in the polymer with a molecular weight of 9.8×10^4, the average acceptor concentration in the collapsed globules was $0.043M$ and $0.055M$, respectively, as compared to a characteristic concentration $c_A = 0.052M$ corresponding to a system in which an acceptor molecule is on the average within a sphere of radius R_0. With this density of acceptor labels, the initial I_A/I_D was 12.5, 11, and 10.4 for pellets from freeze-dried polystyrenes with molecular weights of 3.1×10^4, 9.8×10^4, and 28×10^4, respectively. The I_A/I_D ratio corresponding to the conformational equilibrium of the chains was determined on films cast from mixtures of doubly labeled and unlabeled polymers. For the above molecular weights, these I_A/I_D were 5.5, 5.1, and 3.0. The decrease of this value with an increasing molecular weight of the polymer, M, is expected since the average polymer segment density within the unperturbed polymer coil decreases as $M^{-1/2}$ leading to a corresponding increase in the average spacing between the donor and acceptor labels.

The Kinetics of Chain Unfolding. The pellets obtained by the compression of the freeze-dried mixture of doubly labeled and unlabeled polystyrene contained some voids, and their removal when the pellet was annealed at a temperature in the neighborhood of the glass transition resulted in a substantial increase in the measured I_A/I_D. For instance, with the polymer with the molecular weight 3.1×10^4, I_A/I_D increased from 8.1, approaching a constant value of 12.5 in 10 min.

At temperatures much higher than T_g, I_A/I_D decreased gradually, as shown in Figures 1–3, toward the value observed in cast films (indicated by dashed lines), which may

Table II
Characteristic Parameters for the Unfolding of Polystyrene Chain Molecules

$10^{-4}M$	temp, °C	R_s, nm	R_{gs}, nm	R_{gc}, nm	$10^{-4}t_{1/2}$, s	$10^{18}R_s^2/t_{1/2}$, cm^2/s	$10^{18}(\Delta R_g)^2/t_{1/2}$, cm^2/s
3.1	130	2.3	1.9	4.9	3.0	1.8	3.0
3.1	140	2.3	1.9	4.9	1.2	4.4	7.5
3.1	150	2.3	1.9	4.9	0.47	11	19
9.8	150	3.4	2.9	8.8	9.7	1.2	3.6
9.8	170	3.4	2.9	8.8	0.40	29	87
9.8	180	3.4	2.9	8.8	0.14	83	250
28	170	4.8	4.0	14.8	11	2.1	11
28	180	4.8	4.0	14.8	3.1	7.4	38
28	185	4.8	4.0	14.8	2.0	12	58

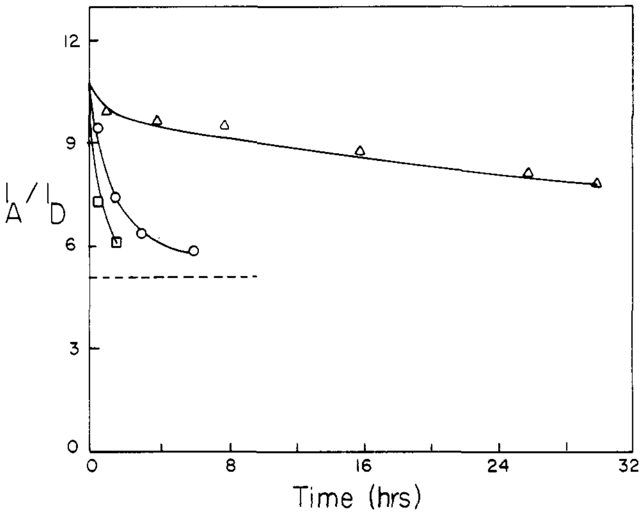

Figure 2. Unfolding of collapsed polystyrene chains, $M = 9.8 \times 10^4$. Temperature: (△) 150 °C; (○) 170 °C; (□) 180 °C.

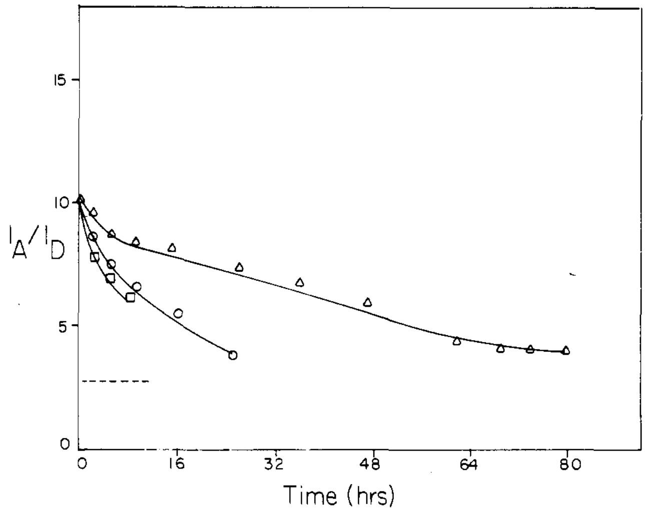

Figure 3. Unfolding of collapsed polystyrene chains, $M = 28 \times 10^4$. Temperature: (△) 170 °C; (○) 180 °C; (□) 185 °C.

be assumed to characterize the equilibrium condition with the doubly labeled and the unlabeled polystyrene chains randomly intertwined.

It seemed reasonable to assume that the diffusional process resulting in the unfolding of the collapsed polymer chains could be characterized by a parameter with the dimensionality of L^2/t, like the diffusion coefficient. We used for the characteristic time t the time $t_{1/2}$ required for I_A/I_D to decay halfway from its initial value to the value observed in the cast film. For the characteristic length L we made two choices:

(a) In the first choice, $L = R_s$, the radius of the compact globule to which the polymer chain collapsed during the freeze-drying. To calculate R_s, the specific volume of polystyrene was taken as $(0.913 + 5.5) \times 10^{-4}T + 53/M$[16] where M is its molecular weight.

(b) In the second choice, $L = \Delta R_g$ where $\Delta R_g = R_{gc} - R_{gs}$ with R_{gc} the radius of gyration of the polymer coil in its equilibrium conformation and R_{gs} the radius of gyration of the spherical globule, $R_{gs} = (^3/_5)^{1/2}R_s$. To obtain R_{gc}, we used the characteristic ratio $C_\infty = 10$[17] neglecting its small temperature coefficient. This led to $R_{gc} = 0.028M^{1/2}$ nm.

Table II gives a summary of the $R_s^2/t_{1/2}$ and $(\Delta R_g)^2/t_{1/2}$ for the polystyrenes of the three molecular weights over a range of temperatures. The following features are of interest:

(a) The value $R_s^2/t_{1/2} = 83 \times 10^{-18}$ and $(\Delta R_g)^2/t_{1/2} = 250 \times 10^{-18}$ cm^2 s^{-1} for polystyrene with $M = 9.8 \times 10^4$ at 180 °C may be compared with the self-diffusion coefficient obtained by Antonietti et al.[4d] With use of their Figure 6 giving D at 177 °C and their reported activation energy of 167 kJ/mol, D for this molecular weight at 180 °C may be estimated as close to 10^{-12} cm^2 s^{-1}. Thus $R_s^2/t_{1/2}$ and $(\Delta R_g)^2/t_{1/2}$ are smaller than D by 4 orders of magnitude.

(b) The $R_s^2/t_{1/2}$ parameter is inversely proportional to the 1.9, 2.5, and 2.3 power of the molecular weight of the polymer at 150, 170, and 180 °C, respectively. The $(\Delta R_g)^2/t_{1/2}$ vary as the −1.5, −2.0, and −1.8 power of the molecular weight at these temperatures. Since these dependencies are based on only two molecular weights at each temperature, their significance is uncertain. They compare with $D \approx M^{-a}$ where $a = 2.2$ at 177 °C.[4d]

(c) The activation energy based on the $R_s^2/t_{1/2}$ data is 130, 220, and 200 kJ/mol for the temperature intervals 130–150, 150–180, and 170–185 °C, respectively. The corresponding values for the $(\Delta R_g)^2/t_{1/2}$ are 130, 230, and 190 kJ/mol. Because of the steep dependence of $t_{1/2}$ on the chain length of the polymer, we could only study a single polymer over each of these temperature intervals, and we do not know, therefore, whether these activation energies vary with the molecular weight of the polystyrene. The above values compare with an activation energy for the self-diffusion of polystyrene of 167 kJ/mol in the neighborhood of 177 °C.[4d] According to the reptation theory of polymer self-diffusion,[2,3] the temperature dependence of D/T should depend on $T - T_g$ in a similar manner as the temperature dependence of viscous flow,[18,19] i.e., as predicted by the WLF shift factor[20] $\log a_T = c_1(T - T_g)/[c_2 + (T - T_g)]$ where c_1 and c_2 are constants, slightly different for D/T and viscosity, depending on the type of polymer. Such a behavior has, in fact, been observed by Green and Kramer for polystyrene,[19] and it leads to a decreasing $\mathrm{d}\ln(D/T)/\mathrm{d}T$ as $T - T_g$ is increased. This contrasts with the sharp increase in $\mathrm{d}\ln(R_s^2/Tt_{1/2})/\mathrm{d}T$ and $\mathrm{d}\ln[(\Delta R_g)^2/Tt_{1/2}]/\mathrm{d}T$ with increasing $T - T_g$. For instance, $\mathrm{d}\ln(R_s^2/Tt_{1/2})/\mathrm{d}T = 0.088$ (K)$^{-1}$ for polystyrene, $M = 3.1 \times 10^4$ (T_g = 94 °C[16]) in the temperature range 130–150 °C and 0.14 (K)$^{-1}$ for $M = 9.8 \times 10^4$ (T_g = 98 °C[16]) in the range 150–180 °C.

The effect of the size of the unlabeled globules in the surounding matrix on the unfolding rate of the doubly labeled polystyrene with $M = 3.1 \times 10^4$ was determined at 150 °C. As the matrix molecular weight was increased from 3.1×10^4 to 9.8×10^4 and 28×10^4, $t_{1/2}$ increased by factors of 3 and 7. This may be compared with recent results of Green and Kramer[4g] on the dependence of the diffusion coefficient of polystyrene chains on the molecular weight of the surrounding matrix. For $M = 5.5 \times 10^4$ of the diffusing chains D decreased, as the matrix of the same molecular weight was replaced by a matrix of longer chains, leveling off for $M = 3 \times 10^5$ of the matrix with D reduced by a factor of about 3.

Discussion

The interpretation of results obtained in this study is based on the assumption that the rapid freezing of a polymer solution well below the critical overlap concentration c^*, followed by sublimation of the frozen solvent, leads to a collapse of the individual molecular chains into compact spherical globules with no significant chain entanglement. This concept is based not only on electron microscopic evidence,[6] but also on a previous study in this laboratory[10a] in which it was shown that such freeze-drying of a mixture of donor- and acceptor-labeled polystyrene led to samples with I_A/I_D values independent of the original solution concentration, c, and independent of the nature of the solvent as long as $c < c^*$, while for $c > c^*$ the emission spectrum reflected an increasing intertwining of the chain molecules. Freeze-drying from dilute polymer solution has also been used to investigate the effect of a reduced chain entanglement on the rheology of the material, although no attempt was made in that study to determine the extent to which such entanglements were eliminated.[21] On the other hand, another study concerned with the same problem used samples obtained by rapid precipitation of dilute polymer solutions to reduce chain entanglement,[22] and we tried to assess the efficiency of this procedure. Precipitating a benzene solution of doubly labeled and unlabeled polystyrene ($M = 3.1 \times 10^4$) of the same concentration as used for freeze-drying into a large excess of methanol, we obtained after drying the material, pressing it into a pellet and annealing it, an emission spectrum with $I_A/I_D = 7.5$, much closer to $I_A/I_D = 5.5$ observed with the cast film than to $I_A/I_D = 12.5$ characterizing the freeze-dried samples. We must conclude that precipitation from dilute solution is a rather inefficient procedure for producing samples with reduced chain entanglement.

During the collapse of a polymer chain into a compact globule, the probability must be high that the chain ends will be occluded in the interior of the particle. Yet, as long as no chain ends lie at the interface between two such globules, no interdiffusion by the reptation mechanism can be envisaged and any interpenetration of chain loops must be a very difficult process. Thus, we must assume that the expansion of the doubly labeled chains into the unlabeled matrix becomes significant only after the diffusion of a chain end to the surface of one of the particles in contact with each other. Once such a contact between a chain end and a chain loop at the surface of a neighboring globule has been established, the diffusional process should have features similar to those characterizing diffusion between linear and cyclic polymer chains. Such diffusion has been treated theoretically by Klein[23] whose model of the polymer melt contained cyclic chains part of which were "threaded" by linear chains. A detailed experimental study of the diffusion of cyclic polystyrene of varying size into linear polystyrene of a range of chain lengths, published recently by Mills et al.,[24] used a bilayer of films containing the cyclic and the linear species, respectively. The authors of this study stressed the need of a corresponding study of the reverse process, i.e., the diffusion of the linear into the cyclic chains. We should like to emphasize that any study of self-diffusion treats a system in conformational equilibrium while our experiments were concerned with the approach to this equilibrium.

In conclusion it may be stated that the kinetics of the unfolding of collapsed chains in a polymer melt are related to self-diffusion processes but that characteristic features of the chain unfolding make it unlikely that a parameter derived from the unfolding process can be used to estimate the self-diffusion coefficient.

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