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Diffusion by Constraint Release in Branched Macromolecular Matrices†

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ABSTRACT: Tracer diffusion coefficients of linear, deuterated polystyrene chains in three-arm symmetric and asymmetric star-branched polystyrene matrices were measured by forward recoil spectrometry. The stars are molecules that have a single branch extending from a longer linear segment. Increases in the diffusion coefficients for the lower matrix molecular weights were used to extract τ_W, the lifetime of a lateral constraint on a diffusing molecule. Comparison of τ_W for linear and branched matrices indicates that τ_W depends on the molecular weight of the longest linear span of the matrix chains and not on the total matrix molecular weight. These results indicate that polymer chain branching does not affect the relaxation of a polymer melt for branch molecular weights up to at least 4 times the entanglement molecular weight.

Introduction

The rheological properties of polymer melts are determined by the rate at which polymer molecules can rearrange their configurations. There is a critical molecular weight beyond which the rate of this molecular reorientation is limited by the presence of physical entanglements that impose constraints on the lateral motion of individual polymer chains.[1] The lifetime of these constraints, τ_W, and the average spacing between them, **a**, are fundamental parameters that must be included in any entanglement theory. These are phenomenological parameters that depend on the molecular weight, chemical structure, and topological structure of the polymer melt. The entanglement picture is simplified for high molecular weight polymer melts where **a** reaches a plateau value and τ_W can be considered to be infinite. Relaxation processes in this high molecular weight regime can be understood in terms of the behavior of a single chain in a lattice of fixed obstacles, where the spacing between these obstacles is known. The chain relaxation in this regime can be modeled as a single-chain property that is independent of the matrix molecular weight and topology. The tracer diffusion coefficient of a polymer chain in a cross-linked network is an example of such a matrix-independent quantity, as is the self-diffusion coefficient of a very high molecular weight linear chain melt.

The release of lateral constraints will contribute significantly to the polymer chain relaxation when τ_W is sufficiently low, giving rise to a matrix-dependent "constraint release" contribution to this relaxation.[2,3] Rheological properties such as the zero shear rate viscosity of a polymer melt will often have such a constraint release contribution. It is very difficult, however, to relate these rheological properties to τ_W because of the complexities of the molecular processes involved. Diffusion is a simpler process, and constraint release models have been particularly successful in describing the matrix-dependent contribution to the tracer diffusion coefficient of linear polymers in linear chain matrices.[4]

Additional constraints are placed on the motion of branched polymer chains by the connectivity of several polymer chain segments at a common junction. The effects of these constraints are poorly understood, in spite of the fact that many practical polymers are branched. Star-branched polymers have been used extensively as model systems for studying the effects of chain branching because the branch points have a well-defined structure and are easily characterized. Here we use the diffusion of linear polymer chains in three-arm symmetric and asymmetric star-branched matrices as a probe for studying the relaxation of branched polymer melts.

Experimental Section

Three different types of three-arm star-branched polystyrene (PS) molecules were synthesized by anionic polymerization. Symmetric stars were synthesized by terminating a "living" solution of linear precursor chains with a trifunctional linking agent as described previously.[5] Two different types of asymmetric stars were synthesized by carrying out the linking reaction in two separate stages. In the first stage, linear chains of a given molecular weight, P_a, react with two of the three active sites on a given linking molecule. In the second stage, linear chains of a different molecular weight react with the third active site. Short-arm stars were produced by using linear chains with a molecular weight of $P_a/2$ in this second stage, and long-arm stars were produced by using linear chains with molecular weights of $2P_a$ in this second stage. The detailed procedure for carrying out the linking reaction in two stages has been described elsewhere, as has the characterization of the short-arm and long-arm stars.[6] The polydispersity index is less than 1.1 for all polymers used in this study.

An important characteristic of a given matrix melt is the span molecular weight, P_s, defined as the longest linear segment that can be constructed from a given polymer chain. The branch molecular weight, P_b, is then defined as the molecular weight of the segment not contained in this longest linear span. For symmetric stars, $P_s = 2P_a$ and $P_b = P_a$. Short-arm stars have $P_s = 2P_a$ and $P_b = P_a/2$, whereas long-arm stars have $P_s = 3P_a$ and

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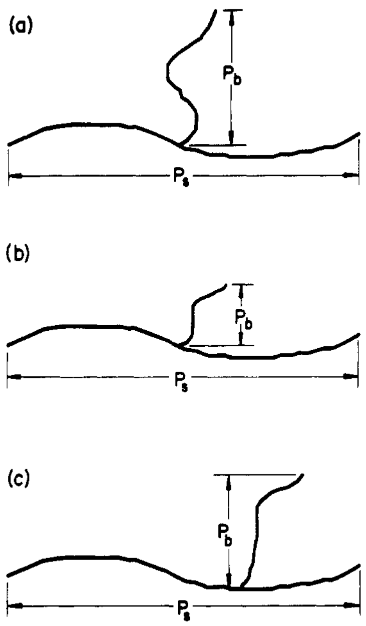

Figure 1. Schematic representations of the different branched polymer chains, showing the significance of P_s, the span molecular weight, and P_b, the branch molecular weight: (a) symmetric stars; (b) short-arm stars; (c) long-arm stars.

Table I
Characterization of the Star-Branched Molecules (from Low-Angle Laser Light Scattering)[a]

P	P_s	P_b
	Symmetric Stars	
24 000	16 000	8 000
57 000	38 000	19 000
99 000	66 000	33 000
165 000	110 000	55 000
750 000	500 000	250 000
	Short-Arm Stars	
71 000	58 000	13 000
105 000	84 000	21 000
113 000	90 000	23 000
153 000	124 000	29 000
229 000	186 000	43 000
334 000	268 000	66 000
	Long-Arm Stars	
23 000	18 000	5 000
32 000	25 000	7 000
48 000	37 000	11 000
67 000	50 000	17 000
84 000	63 000	21 000
97 000	71 000	26 000
154 000	116 000	38 000
222 000	171 000	51 000
289 000	216 000	73 000

[a] All polydispersities < 1.1.

$P_b = P_s$. The stars therefore behave as linear chains to which a single branch has been added, as illustrated schematically in Figure 1. Symmetric stars and short-arm stars are similar in that the branch is placed at the midpoint of the linear chain that makes up the longest span. Long-arm stars, however, have a branch that is offset from the midpoint of the longest span. Together, these three star types form an ideal set of molecules for looking at the effects of a single branch on the dynamics of an otherwise linear polymer chain. The span and branch molecular weights for the star molecules used in this study are listed in Table I.

Tracer diffusion coefficients of linear deuterated polystyrene (dPS) chains in matrices of the various three-arm star-branched PS molecules were measured by forward recoil spectrometry. Details of this technique are described elsewhere.[7,8] Diffusion couples were made by spin casting 2-μm-thick layers of star-branched PS onto polished silicon substrates from PS/toluene solutions. Thin, 200-Å layers of linear dPS were then spun from dPS/toluene solutions onto glass slides, floated onto a water bath, and picked up on top of the various star matrix layers. The diffusion couples made in this way were allowed to dry and were subsequently annealed in a vacuum oven at temperatures ranging from 138 to 178 °C for times required to give diffusion distances of ca. 4000 Å. Diffusion coefficients were obtained by comparing the experimentally determined dPS volume fraction vs depth profiles to those generated from the following solution to the diffusion equation:

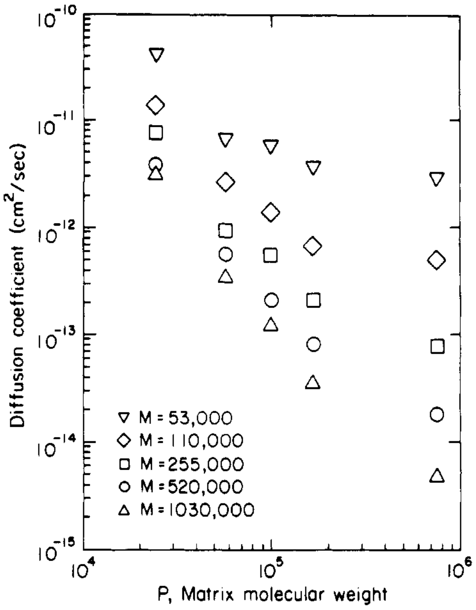

Figure 2. Diffusion coefficients at 178 °C for linear tracer chains as a function of the total molecular weight of symmetric star matrices.

$$\phi(x) = 0.5\left\{\operatorname{erf}\left[\frac{h-x}{(4D^*t)^{0.5}}\right] + \operatorname{erf}\left[\frac{h+x}{(4D^*t)^{0.5}}\right]\right\} \qquad (1)$$

where h is the thickness of the tracer layer, t is the annealing time, x is the depth from the surface of the diffusion couple, and D^* is the tracer diffusion coefficient. Diffusion coefficients for several linear dPS polymers in linear PS matrices were also measured so that the results for star and linear matrices could be compared directly.

Results

The measured diffusion coefficients of the linear chain molecules in the symmetric star matrices are plotted in Figure 2 as a function of P, the total matrix molecular weight. Figures 3 and 4 are similar plots for matrices of short-arm stars and long-arm stars, respectively. Measurements made at different temperatures were scaled to an equivalent temperature of 178 °C by multiplying the diffusion coefficients by an experimentally determined conversion factor, given by the ratio of the diffusion coefficient of 110 000 molecular weight linear dPS polymer in high molecular weight PS matrix at 178 °C to the value of this diffusion coefficient at the temperature of interest. The limiting diffusion coefficients in very high molecular weight linear matrices were also measured and were found to be equal to the values for the highest molecular weight symmetric star matrix. These values correspond to $D_{\text{ind}}(M)$, the matrix-independent values of the tracer diffusion coefficient obtained in the limit of infinite τ_W, and are shown as the filled symbols in Figures 3 and 4.

The matrix-independent diffusion mechanism for linear chains is reptation, with the diffusion coefficient given as follows:[3]

$$D_{\text{rep}} = D_0^{\text{rep}} M^{-2} \qquad (2)$$

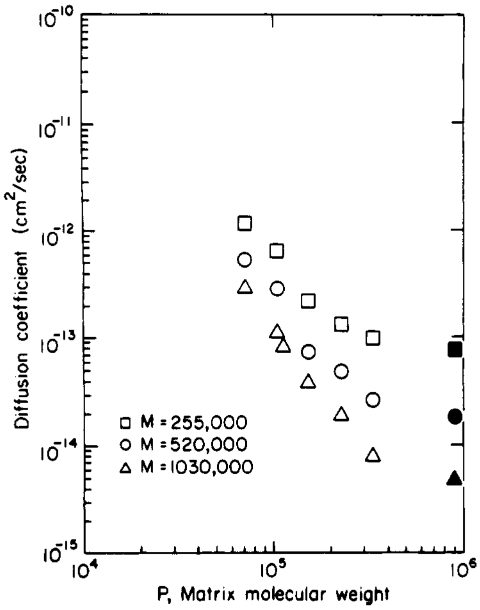

Figure 3. Diffusion coefficients at 178 °C for linear tracer chains as a function of the total molecular weight of short-arm star matrices. The filled symbols represent the reptative diffusion coefficients characteristic of diffusion in very high molecular weight matrices.

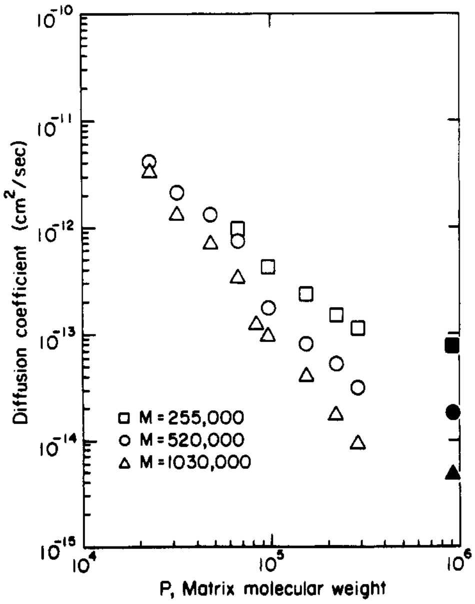

Figure 4. Diffusion coefficients at 178 °C for linear tracer chains as a function of the total molecular weight of long-arm star matrices. The filled symbols represent the reptative diffusion coefficients characteristic of diffusion in very high molecular weight matrices.

where D_0^{rep} is given by

$$D_0^{\text{rep}} = \frac{4M_eM_0k_BT}{15\zeta_0} \qquad (3)$$

Here, M_e is the entanglement molecular weight, M_0 is the monomer molecular weight, and ζ_0 is the average monomeric friction coefficient. The diffusion coefficient for long linear chains in high molecular weight matrices scales as M^{-2} indicating that ζ_0 approaches a constant value for these high molecular weights.[9]

Matrix-dependent diffusion corresponding to finite values of τ_W gives rise to the increase in the diffusion coefficient of the linear chains with decreasing P. The constraint release models of Klein[2] and Graessley[3] are attempts to describe these matrix effects within the context of a simple entanglement picture. We use Graessley's formulation in which τ_W and $\mathbf{a}$ are the central quantities. The entanglement spacing, $\mathbf{a}$, can be determined from known molecular parameters:[3]

$$\mathbf{a} = (4KM_e/5)^{1/2} \qquad (4)$$

Here, M_e is the entanglement molecular weight as determined from measurements of the plateau shear modulus[1] and K is the ratio of the mean-squared end-to-end distance to the molecular weight for a linear polymer chain in the melt. The constraint release diffusion coefficient is obtained from the general relation $D = \Gamma b^2/6$, where b is the center of mass displacement which occurs with a frequency Γ. A tracer chain of molecular weight M contains N entanglement spacings, where N is given by[10]

$$N = 5M/4M_e \qquad (5)$$

Graessley made the assumption that one of these segments has a 50% chance of moving a distance $\mathbf{a}$ after time τ_W.[3] The jump frequency and jump distance are therefore given by $N/2\tau_W$ and $\mathbf{a}/N$, respectively, and the constraint release diffusion coefficient, D_{cr}, is given by

$$D_{cr} = \frac{a^2}{12N\tau_W} = \frac{4KM_e^2}{75M\tau_W} \qquad (6)$$

As τ_W approaches infinity the constraint release diffusion coefficient vanishes and the tracer diffusion coefficient is given by the matrix-independent component. The diffusion coefficients for linear chains in 750 000 molecular weight symmetric star matrices are equal to the reptation values because τ_W for this matrix is very large and D_{cr} is much less than the reptation diffusion coefficient. The transition region between reptation and constraint release can be approximated by assuming that these two diffusion mechanisms are operating independently. The measured tracer diffusion coefficient, D^*, is therefore given by the sum of these two different diffusion coefficients:

$$D^* = D_{cr} + D_{ind} \qquad (7)$$

where D_{ind} is the matrix-independent diffusion coefficient, which for linear tracer chains is the reptation value given by eqs 2 and 3. Equations 6 and 7 can be combined to obtain the following expression for τ_W:

$$\tau_W = \frac{4KM_e^2}{75M(D^* - D_{ind})} \qquad (8)$$

For high molecular weight linear polystyrene, M_e = 18 000 g/mol[1] and $K = 4.3 \times 10^{-17}$ (cm^2 mol)/g.[11] By assuming that these values also characterize the star matrices studied here, we arrive at the values of τ_W shown in Figures 5 and 6. Figure 5a shows the results for linear matrices, where the symbols represent values measured at 178 °C as part of this investigation and the line is the best fit to the $P^{2.7}$ dependence that has been established by previous experimental studies.[4,12] The self-diffusion coefficient of a three-arm star with P = 165 000 is entirely dominated by constraint release,[5] and the value of τ_W derived from this diffusion coefficient is also included in Figure 5b. Figure 6 includes plots of τ_W as a function of P for the short-arm and long-arm star matrices, with similar comparisons to the data from the linear chain matrices. In all cases we have only included values where $D^*/D_{ind} > 2.5$ in order to minimize errors associated with our simple description of the transition region between matrix-independent and matrix-dependent diffusion.

The constraint release picture is valid only when the matrix molecules are long enough to form entanglements

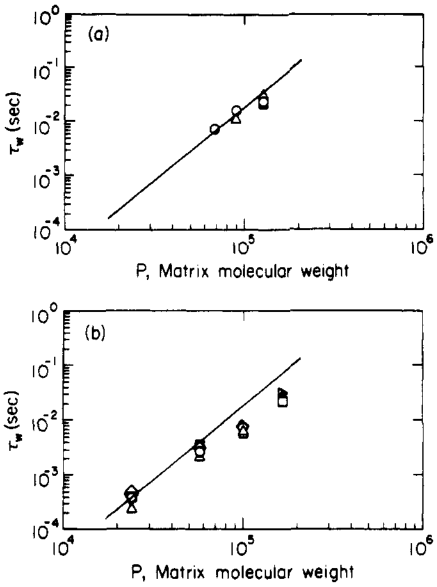

Figure 5. Measured values of τ_W as a function of matrix molecular weight: (a) linear chain matrices (symbols) with the best fit to a $P^{-2.7}$ dependence (line); (b) symmetric star-branched matrices (symbols) as compared to the values obtained for the linear chain matrices (line). Symbols have the same meaning as described in Figure 2, with the addition of a point obtained from the self-diffusion coefficient of a star (▷).

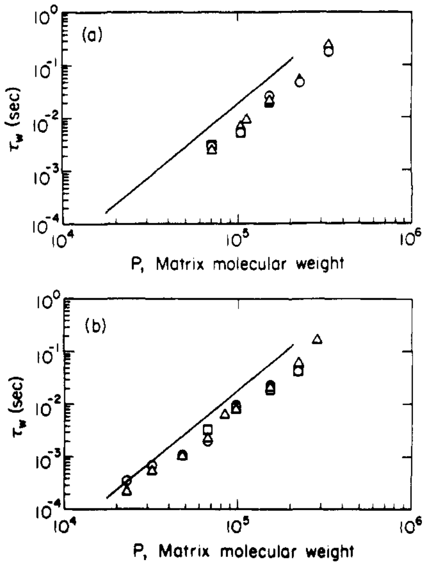

Figure 6. Measured values of τ_W as a function of matrix molecular weight: (a) short-arm star matrices; (b) long-arm star matrices. The lines represent the best fit to the data for linear chain matrices as shown in Figure 5a. Symbols have the same meaning as described in Figures 3 and 4.

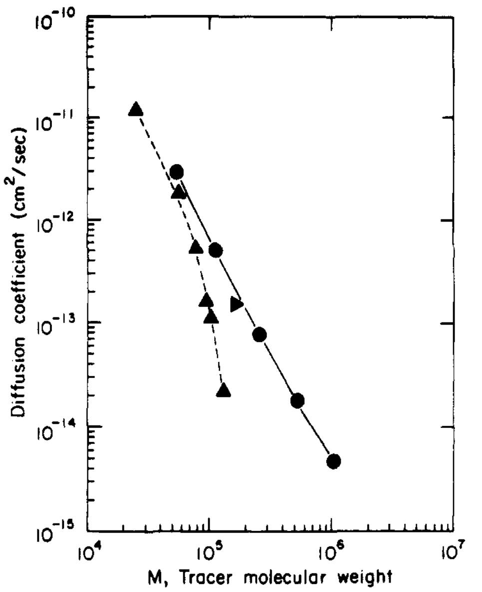

Figure 7. Matrix-independent diffusion coefficients at 178 °C for linear polystyrene chains (●) and 3-arm star-branched polystyrene chains as reported in ref 5 (▲). The self-diffusion coefficient of a symmetric 3-arm star is also included (▶).

with each other. As discussed in ref 4, hydrodynamic interactions between segments of a diffusing tracer chain are screened by these matrix entanglements, giving rise to the M^{-1} scaling of the constraint release diffusion coefficient. Hydrodynamic interactions are not screened when the matrix polymer is unentangled, and the tracer diffusion coefficient varies inversely with the hydrodynamic radius of the diffusing tracer chain. This hydrodynamic radius scales as $M^{0.5-0.6}$, so MD^* is not a constant for unentangled matrices. Our estimation of τ_W is therefore strictly valid only for the higher molecular weight star matrices, where D_{cr} scales as M^{-1}. The most striking feature of the data shown in Figures 5 and 6 is that τ_W for the entangled star-branched matrices is actually lower than τ_W for entangled linear chain matrices of the same total molecular weight.

Discussion

Matrix-dependent contributions to the overall relaxation of branched polymers are significant.[5,13] Branched polymer chains cannot relax by reptation because the chains do not have a linear configuration. The matrix-independent relaxation mode for entangled star-branched chains is arm retraction where relaxation occurs by retraction of the arms toward the branch point. Linear chains are two-arm stars in this sense, and arm retraction corresponds to a fluctuation in the length of the "primitive path" of a linear polymer chain. Diffusion by arm retraction is a very slow process, and this mechanism contributes very little to the matrix-independent diffusion coefficient of linear reptating chains. Figure 7 shows the measured matrix-independent diffusion coefficients at 178 °C for linear PS chains and three-arm symmetric PS stars as a function of the total tracer molecular weight. The values for the linear tracer chains correspond to the values measured in star-branched matrices with $P = 750\,000$, and the values for the star-branched chains are from ref 5. The matrix-independent diffusion coefficient for star molecules begins to diverge from the matrix-independent diffusion coefficient for linear molecules for $M_a/M_e \approx 1$. Star arms with $M_a/M_e > 1$ entangle with the matrix chains so that the matrix-independent diffusion coefficient is determined by the much smaller arm retraction contribution. Klein et al. have found a similar decrease in the matrix-independent diffusion coefficient of asymmetric stars as the branch molecular weight approaches M_e.[14]

The self-diffusion coefficient as reported in ref 5 for a symmetric three-arm star melt with $M = 165\,000$ is also shown in Figure 7. This diffusion coefficient is much greater than the arm retraction diffusion coefficient for the stars, indicating that the self-diffusion coefficient is essentially equal to the constraint release component. Constraint release, as characterized by τ_W, therefore plays a central role in the relaxation of branched polymer melts which have $P_b > M_e$. Our result that τ_W is lower for star-branched polymers than it is for linear chain melts of the same total molecular weight is consistent with other measurements of polymer chain relaxation. For example,

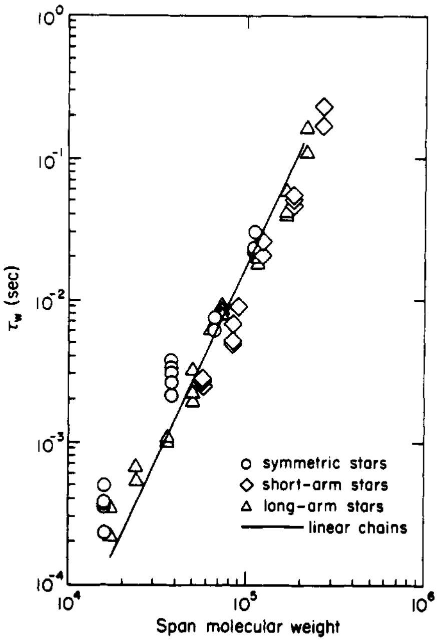

Figure 8. Measured values of τ_W as a function of the span molecular weight for linear chains and for the three different types of branched matrices.

the zero shear rate viscosity of symmetric star melts with $P_b/M_e < 4$ is less than the zero shear rate viscosity of linear chains of the same total molecular weight.[15,16] In addition the dielectric relaxation time for symmetric *cis*-polyisoprene stars is less than the dielectric relaxation time for linear chains of the same total molecular weight for P_b/M_e up to at least 4.5.[17] The dielectric relaxation time in this entanglement regime is found to scale with the span molecular weight.[18]

Figure 8 indicates that in the entanglement regime probed by our measurements, τ_W also scales with the span molecular weight. We expect that this simple scaling will not work for values of P_b/M_e that are considerably greater than the maximum value of 4 for which we were able to measure τ_W. Bartels et al. have measured self-diffusion coefficients of symmetric, three-arm hydrogenation polybutadiene stars having $6.1 < P_b/M_e < 40$.[13] The self-diffusion coefficient for the star melt with $P_b/M_e = 6.1$ is only slightly lower than the self-diffusion coefficient of a linear chain melt of the same total molecular weight. At higher values of P_b/M_e, the star self-diffusion coefficients are significantly lower than the corresponding linear chain diffusion coefficients. The decrease in the self-diffusion coefficient for higher molecular weights can be attributed to an increase in τ_W. Taken together, these results show that there is an entanglement regime extending from $P_b/M_e \approx 1$ to $P_b/M_e \approx 4$–6 where the diffusion is dominated by constraint release but where τ_W is not affected by the branching.

Conclusions

The matrix-dependent, constraint release contribution to the diffusion of linear tracer chains can be used to extract τ_W, the lifetime of a lateral constraint on a tracer molecule. The relaxation of branched polymer melts with branch molecular weights greater than M_e is governed by constraint release. The relaxation of these melts is therefore related in some fundamental way to τ_W. We find that τ_W is not affected by chain branching for branch molecular weights up to at least $4M_e$. In this entanglement regime τ_W is determined by the length of the longest span that can be constructed from a given matrix molecule. This finding is consistent with other results that indicate that branching slows down the relaxation of polymer melts only for branch molecular weights greater than at least $4M_e$.

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