3300 *Macromolecules* 1991, *24*, 3300–3303

Reptation and Constraint Release in Linear Polymer Melts. An Experimental Study

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Received August 20, 1990; Revised Manuscript Received October 30, 1990

ABSTRACT: Self-diffusion and tracer diffusion of hydrogenated and deuterated polybutadienes, both above the entanglement molecular weight (M_e), were investigated over a broad range of molecular weight ($1 \le M_W/M_e \le 253$) by scanning infrared microscopy (SIRM). Experimental evidence was found that constraint release influences the self-diffusion in the region $M_e < M_w < 10M_e$. The self-diffusion coefficients could quantitatively be described by Graessley's model of constraint release. In the case of tracer diffusion the polymer chains moved above a critical matrix molecular weight, P^*, in a tube; P^* is dependent on the molecular weight of the tracer chain. Below P^*, constraint release influenced the polymer diffusion. The experimental data showed that constraint release should be considered in a wider sense allowing for nonreptative removal of barriers to lateral chain motion.

I. Introduction

In the reptation model,[1-3] any lateral motion of polymer chains is blocked by topological constraints forming a tube. For the special case of self-diffusion, in which M equals P (M = molecular weight of the diffusant, P = molecular weight of the matrix), the assumption of purely curvilinear motion leads to

$$D_{\text{self}} = D_0 M^{-2} \tag{1}$$

Here D_0 is a temperature-dependent parameter, which also depends on the polymer entanglement molecular weight (M_e) and the monomeric friction coefficient (ζ_0).

For tracer diffusion, or equivalently the interdiffusion coefficient in the limit of nearly infinite dilution of the diffusant in a matrix, it has been suggested[4,5] that

$$D^*(M,P) = D_0 M^{-2} \quad \text{for } P \gg M_c \tag{2}$$

$$D^*(M,P) = D_0 M^{-1} P^{-1} \quad \text{for } P < M_c \tag{3}$$

There exists a number of measurements of diffusion in molten polyethylene (PE)[6-12] in accordance with these predictions both above and below the critical molecular weight for entanglement coupling (M_c).

In an entangled homopolymer melt the topological constraints are formed by the neighboring chains, which also undergo reptation. Thus, some of the constraints forming the tube will reptate away during the residence time of the diffusing tracer chain in this tube. This mechanism, referred to as "constraint release", allows additional molecular mobility of the chain of interest by permitting the topological environment to vary due to reptation of the surroundings, i.e., the other chains. On the basis of the lattice theory, Graessley[13] derived the following equation for the constraint release diffusion coefficient

$$D_{\text{cr}}(M,P) = \alpha_{\text{cr}} D_0 M_e^2 M^{-1} P^{-3} \tag{4}$$

with $\alpha_{\text{cr}} = (48/25)z(12/\pi^2)^{z-1}$ where z is the number of "suitably situated constraints" per cell. Under the assumption that constraint release and reptation are independent, the tracer diffusion coefficient varies as

$$D^*(M,P) = D_0 M^{-2}(1 + \alpha_{\text{cr}} M_e^2 M P^{-3}) \tag{5}$$

In the self-diffusion limit ($M = P$), eq 5 becomes

$$D_{\text{self}} = D_0 M^{-2}(1 + \alpha_{\text{cr}} M_e^2 M^{-2}) \tag{6}$$

An alternate approach adopted by Klein[14] yields a slightly different dependence of D_{cr} on P. The tracer chain is also treated as a Rouse chain with M/M_e independent submolecules. The total number of constraints per M_e is treated as one effective constraint. In the Graessley model the constraints are assumed to be independent. Klein argues that only a fraction of these constraints are in fact independent since it is likely that different segments on the same matrix chain provide constraints at different points along the tracer chain. For this nonindependent constraint release (nicr) mechanism the diffusion coefficient scales as

$$D_{\text{nicr}}(M,P) \approx M_e^{3/2} M^{-1} P^{-5/2} \tag{7}$$

By including an unspecified parameter K and the assumption that reptation and constraint release are independent, we expect the following equation

$$D^*(M,P) = D_0 M^{-2}(1 + K M_e^{3/2} M P^{-5/2}) \tag{8}$$

Most recently, Hess[15,16] attempted a microscopic derivation of chain motion using a many-body approach. The polymer segments are assumed, in this case, to be Brownian particles with the possibility of random motion. The phenomenological tube concept is replaced by the translational invariance of the interaction potential for curvilinear displacement of the segments. Chain motion is also reduced on the basis of interactions between polymer segments. His mathematical approach was the Fokker–Planck equation for the phase-space distribution of polymer segments. A remarkable result of Hess' theory is a much stronger contribution of constraint release to diffusion, even in the highly entangled regime. The scaling law of the reptation theory (eq 2) is reached only if $P/M_c > 1000$. Furthermore, the crossover region between unentangled and entangled behavior in Hess' model is more extended than predicted by the phenomenological theories.

These models differ in their conclusions of the molecular weight dependence of tracer diffusion coefficients.

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0024-9297/91/2224-3300$02.50/0

Table I
Molecular Characteristics of Polymers[a]

sample	M_w, g/mol	M_w/M_n	M_w/M_e
h-PB19, d-PB19	1 250	1.05	1.04
h-PB37, d-PB37	1 760	1.06	1.47
h-PB70, d-PB70	3 270	1.04	2.73
h-PB207, d-PB207	12 000	1.05	10.0
h-PB555, d-PB555	45 200	1.03	37.67
h-PB1849, d-PB1849	145 800	1.03	121.5
h-PB7395, d-PB7395	303 600	1.03	253.0

[a] The molecular weights of the deuterated and hydrogenated polybutadienes were measured by the corresponding polybutadiene: M_w/M_n by GPC, M_n by osmometry, M_w was calculated from the experimental data of GPC (M_w/M_n) and osmometry (M_n). The molecular weight of entanglement is taken as M_e = 1200 g/mol.

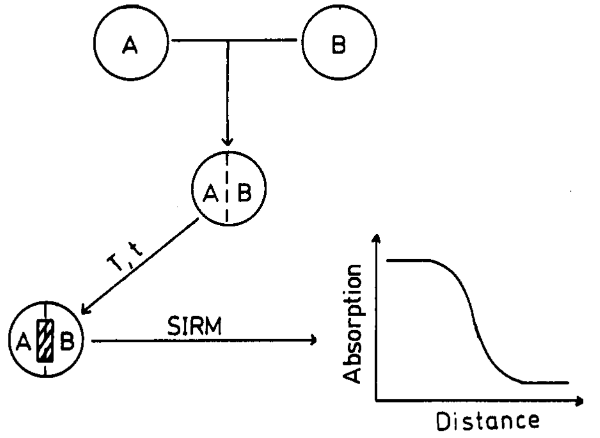

Figure 1. Schematic representation of sample preparation and measurement of the interface profile.

Thus, to examine the different theoretical approaches, it is desirable to obtain experimental diffusion data for a broad range of tracer and matrix molecular weight, e.g., $1 \leq M_w/M_e \leq 253$.

In the present study we have investigated the tracer diffusion of linear deuterated polybutadienes (d-PB) in linear hydrogenated polybutadiene matrices (h-PB). These polymers are equivalent to linear PE. The phase profiles and the diffusion coefficients were determined by IR microdensitometry (IRM)[17] where improved instrumentation and sample preparation resulted in a spatial resolution of ≈10 μm.[18] In section II the experiments and investigated materials are described in detail, and in section III results are presented and compared with theoretical predictions.

II. Materials and Methods

As precursors, polybutadienes were anionically polymerized[19] with narrow molecular weight distributions (M_w/M_n < 1.06). They were then reacted with either H_2 (to form h-PB) or D_2 (to form d-PB) at 70 °C and 500 psi in a cyclohexane solution over a Pd catalyst supported on $CaCO_3$.[20] Measurements by Graessley et al.[20,21] and our own FT-IR and viscosity measurements have shown that this process is quantitative and without side reactions that alter the molecular structure. Deuterium substitution in the d-PB was approximately 35% in all samples. 2% of the C atoms in h-PB and d-PB carrier on ethyl side group from 1,2-addition of butadiene. Sample designation and characterization data are summarized in Table I.

A schematic representation of the sample preparation and the measurement procedure is given in Figure 1. Disks (diameter = 14 mm, thickness = 0.15 mm) were formed by gently pressing the polymers for 5 min at 140 °C in a hydraulic press. The disks were then carefully halved with a hot knife. Two of these divided discs (one of them containing a maximum of 5% wt d-PB) were placed side by side in a close-fitting PTFE frame. The combination was pressed between PTFE sheets to form a "diffusion cell". Each cell was annealed in a vacuum oven at selected temperatures and for a specific length of time. The sample was quenched in liquid air and removed from the frame. Following the preparation steps the diffusion cell was placed under an FT-IR microscope equipped with a computer-controlled movable table. To obtain the concentration profile, the hatched area of the A/B pellet was scanned along the diffusion axis with an IR beam spot of 10 mm. In this way usually 40–50 complete FT-IR spectra were taken along the interface of the diffusion cell. From the absorbance of the carbon–deuterium vibrations of the different IR spectra and the corresponding x-coordinates, the concentration profiles were obtained directly. A typical concentration–distance profile is given in Figure 2. The circles indicate the initial broadening and the squares represent the interface profile after thermal treatment. For the quantitative evaluation of diffusion coefficients, the experimental concentration–distance profiles were deconvoluted for the initial broadening of the interface.[22] A more detailed description of the procedure has been given in detail elsewhere.[18]

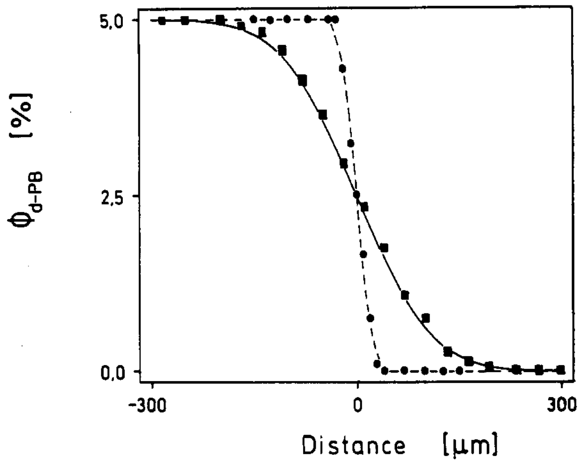

Figure 2. Concentration–distance profile of a diffusion cell. One side is 5 wt % d-PB and 95 wt % h-PB; the other side is h-PB. (●) Measurement taken immediately after creation of the step function. (■) Interface profile at t = 2 h and T = 170 °C.

III. Results and Discussion

Self-Diffusion. In the tube model reptation will dominate polymer motion, in the case of self-diffusion, even below the critical molecular weight M_c ($M_{c,PE}$ = 3800 g/mol).[23] Thus the self-diffusion coefficient, D_{self}, should vary like M^{-2} (eq 1). In highly entangled PE melts the reptation equation is well established.[7,8,10,11] However, diffusion studies on polystyrene (PS)[24] and poly(propylene oxide) (PPO)[25] and an analysis of self-diffusion data for PS[26] showed that reptation could not describe the diffusion entirely in the limit of $M_e < M < 10M_e$.

In Figure 3 self-diffusion coefficients versus the molecular weight are shown. The circles represent the experimental diffusion coefficients at T = 170 °C. The experimental data are in excellent agreement with self-diffusion data of d-PB in h-PB matrices measured by other methods, e.g., small angle neutron scattering (SANS),[8] scanning infrared microscopy (SIRM),[27] and forward recoil spectroscopy (FRES).[28] The line is a least-square fit according to Graessley's model with α_{cr} = 9.7; that is, z = 3.25 (eq 6). The long dotted line was calculated on the basis of the tube model (eq 1) with D_0 = 0.54 and the small dotted line is the Hess model prediction, $D^* = 1D_0M^{-2}$.

From Figure 3 one can infer that self-diffusion can be described by Graessley's derivation of constraint release. Above a critical molecular weight of $M = 10M_e$ reptation is the dominant mechanism. Below $M = 10M_e$ one has to consider lateral chain motion on the basis of constraint release. For the diffusion of d-PB in h-PB matrices, 3.25 barriers per cell, on average, will reptate away and thus the primitive path of the polymer chain of interest is changed. The consequence is a lateral motion of the polymer chain.

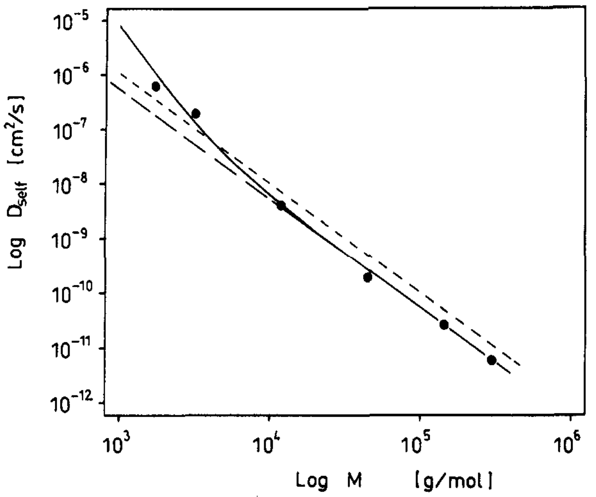

Figure 3. Self-diffusion coefficient of deuterated polybutadiene versus molecular weight of hydrogenated polybutadiene at 170 °C. The circles are the experimental data. The line was calculated according to Graessley's model (eq 4) with $z = 3.25$; the long dotted line corresponds to reptation (eq 2) and the small dotted line is the prediction of the Hess model.

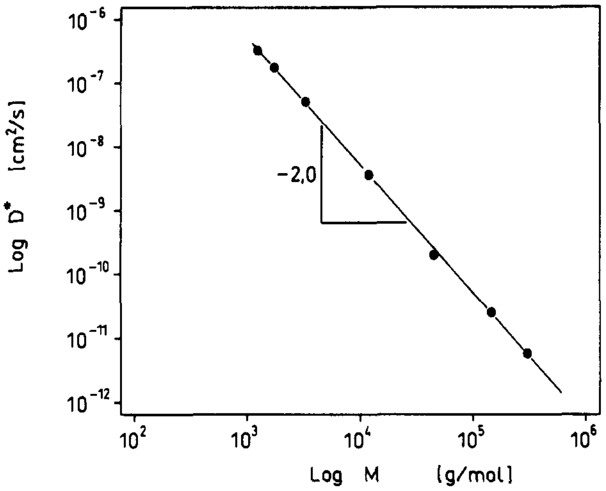

Figure 4. Tracer diffusion coefficients of deuterated polybutadiene as a function of tracer chain molecular weight, M, in matrices of highly entangled hydrogenated polybutadienes ($P/M_e > 38$) at 170 °C. The circles represent the experimental data. The line is a least-square fit according to eq 2 with $D^* = (0.54 \pm 0.008)M^{-2\pm0.02}$.

The prediction of Hess' model failed completely over the entire range of molecular weight. In highly entangled polymer melts the Hess model overestimates the self-diffusion. Below $10M_e$ the model underrates the influence of constraint release.

Tracer Diffusion. The self-diffusion has shown that below a critical molecular weight constraint release will influence chain motion. For this reason we have investigated the molecular weight dependence of tracer diffusion in the crossover region to further investigate constraint release and its mechanism in detail.

In Figure 4, tracer diffusion coefficients in highly entangled h-PB matrices are shown ($P/M_e > 38$). The circles represent the experimental diffusion coefficients at $T = 170$ °C and the line is a least-square fit according to eq 2 ($D^* = (0.54 \pm 0.008)M^{-2\pm0.02}$). For the diffusion of d-PB in h-PB matrices with molecular weights higher than $P/M_e = 38$, the tube model was verified. Figure 5 shows all experimental tracer diffusion coefficients as a function of matrix molecular weight, P, at $T = 170$ °C. The lines are least-squares fits with different z values (eq 5). The four lower curves ($10 \leq M_w/M_e \leq 253$) were fitted with $z = 4.68$, which is still consistent with the lattice model. Green and Kramer[24] studied the tracer diffusion of PS. In the range $3.1 \leq M_w/M_e \leq 110$ the data could be described with Graessley's model and a z value of 3.5. The difference between the z values of d-PB in this work (4.68) and PS (3.5) is probably insignificant. For the three shorter chains (where $M_w/M_e = 2.8$, 1.5, and 1.0) z equals 3.5, 2.3, and 2.0, respectively. The dashed line at P^* in Figure 5 separates the "plateau regime" where the influence of constraint release upon chain diffusion is negligible ($D_{CR} \leq 0.2D_{rep}$). In the plateau regime reptation is the dominant diffusion process. At lower values than P^* constraint release is more important.

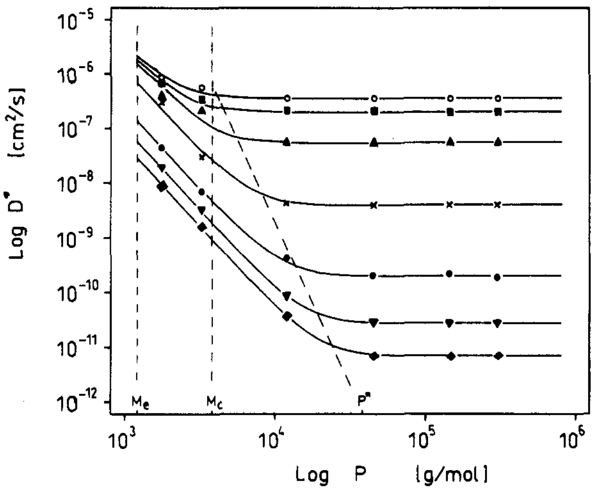

Figure 5. Tracer diffusion coefficients of deuterated polybutadiene versus the matrix molecular weight, P, at $T = 170$ °C. Tracer chain molecular weights (M_w/g mol^{-1}): 1250 (○); 1760 (■); 3270 (▲); 12 000 (×); 45 200 (●); 145 800 (▼); 303 600 (◆). The lines correspond to Graessley's model (eq 4) with different z values. $M_e = 1200$ g/mol; $M_c = 3800$ g/mol; $P^* = 38\,000$ g/mol.

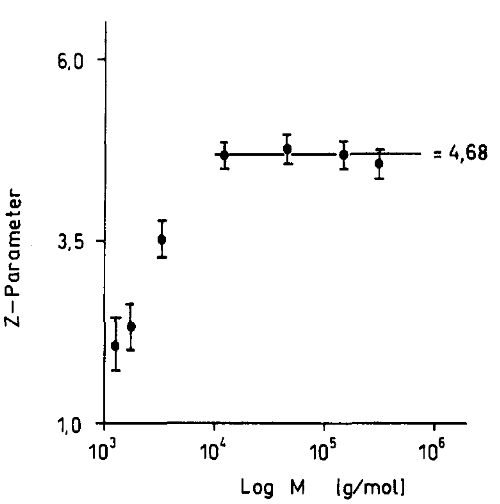

Figure 6. z parameters of Figure 5 as a function of tracer molecular weight.

As mentioned above, the z value decreases above a certain molecular weight of the tracer chain. The dependence of z on the tracer molecular weight is shown in Figure 6. In the plateau regime, 4.68 ± 0.07 constraints per cell on average will reptate away. Below $M = 10M_e$, z decreases. If the Graessley model can describe the molecular weight dependence of the tracer chain mobility, D^* should vary like P^{-b} with $b = 3$. Following eq 4 we have examined this power law. For d-PB with $M_w/M_e \geq 10$ (or the four lower curves in Figure 5) we have obtained a scaling factor $b = 2.83 \pm 0.19$. For the tracer chains with $M_w/M_e = 2.7$, 1.5, and 1.0 we calculated $b = 1.1$, 1.2, and 0.6, respectively. For the determination of the scaling factor

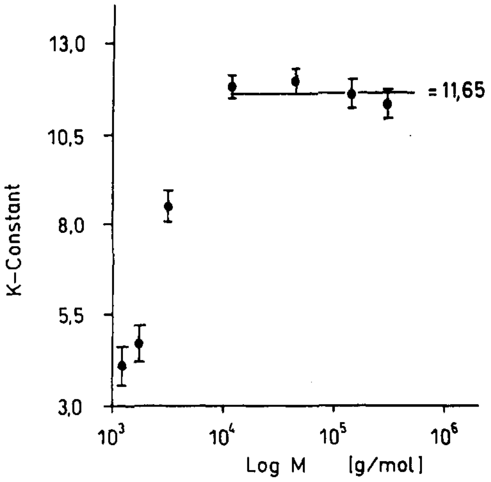

Figure 7. K constants of the Klein model (eq 8) versus tracer molecular weight.

b, we could use only three values. A considerable deviation in the absolute b values is to be expected. However, the tendency of b is very clear: the mobility of the three shorter tracer chains with $M_w/M_e \leq 2.7$ is affected least by the matrix molecular weight, P. This means that the tracer diffusion coefficients of the tracer chains are greater as predicted by the Graessley model of constraint release.

With K of the Klein model (eq 8) as a fit parameter, equally acceptable fits are obtained. Like the z parameter in Greassley's model, K decreases at a certain tracer molecular weight, as seen in Figure 7.

Due to the decrease of the z values and the scaling factor b, constraint release by reptation of neighboring chain is not the only mechanism allowing for lateral chain motion. The tube can be deformed or move cooperatively carrying the chain inside in any direction. In a broader sense, all motions within the environmental matrix of a diffusing tracer chain can be termed constraint release as they remove constraints to lateral motion.

However, the Hess model, where constraint release has a much larger influence upon chain diffusion, can be safely eliminated.

These results agree with recent measurements[29] of the diffusion of PS chains in matrices of star-branched PS, which suggest that constraint release by star molecules is as fast as for the corresponding linear matrix of PS chains. This diffusion data could not be explained by the original constraint release model of Graessley.

IV. Conclusion

In this study the molecular weight dependence of self-diffusion and tracer diffusion of deuterated polybutadienes in matrices of hydrogenated polybutadienes was investigated with an improved scanning infrared microscopy technique.

For self-diffusion, reptation is the dominant mechanism above a molecular weight of $10M_e$. Below $10M_e$ constraint release predominantly influences chain motion. In agreement with other investigations[24] we have obtained a z value of 3.25 for d-PB. This z value indicates that, on average, 3.25 barriers per cell will reptate away and as a consequence the primitive path of the polymer of interest is changed.

The tracer diffusion is also affected by constraint release below a certain matrix molecular weight. If $D_{cr} \leq 0.2D_{rep}$ (eq 4), the influence of constraint release upon chain diffusion is negligible. For tracer molecular weights above $10M_e$, we obtained a constant z value of 4.68 ± 0.07. For tracer chains of $2.8M_e$, $1.5M_e$, and $1.0M_e$ the z values decrease respectively. In this region reptation cannot be explained as a mechanism for the barriers, as assumed in Graessley's model. Thus we conclude that constraint release should be considered in a wider sense, allowing for nonreptative removal of constraints to lateral chain motion.

Acknowledgment. J. von Seggern is very grateful to Prof. Dr. H. Sillescu for helpful and stimulating discussions leading to the interpretation of the diffusion data. J. von Seggern also thanks the Graduiertenkolleg Polymerwissenschaften at the University of Freiburg and the Bundesministerium für Forschung und Technologie (BMFT) for financial support.

List of Symbols

M	molecular weight of the diffusant (tracer)
M_e	molecular weight of entanglement
M_c	critical molecular weight by melt viscosity ($M_c \approx 2M_e$)
P	molecular weight of the matrix
P^*	critical molecular weight of a matrix, in which the transition to reptation takes place
D^*	trace diffusion coefficient
D_{self}	self-diffusion coefficient
z	number of "suitably situated constraints" per cell
K	unspecified fit parameter

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