$$\tau_{n*}(N_a) = 2\tau_w \qquad \text{(A-4)}$$

The waiting time for constraint release in a matrix of star polymers is given by eq 31, which we now rewrite as

$$\tau_w = (S_3(z)/zN_a^{z})\tau_0(N_a) \qquad \text{(A-5)}$$

Combining eq A-2, A-4, and A-5, we determine that the crossover for star self-diffusion occurs when the equation

$$\alpha_n^* = 2S_3(z)/zN_a^{a} \qquad \text{(A-6)}$$

is satisfied. This relationship permits evaluation of the parameter $\lambda = 3(1 + n^*)$, which appears in eq 32 for D_{CR}. The following table presents λ as a function of N_a, calculated for $z = 3$ and $S_3(z) \sim 1.5^{22}$ with eq A-5–A-7 with $q = 6$ in eq A-3.

N_a	n^*	λ
3.2	2	9
8.6	4	15
21.4	6	21
52.1	8	27

The results in this table suggest that λ changes rather slowly with branch length over the range covered by our experiments ($7.5 < N_a < 33$, using $N_a = (5/4)M_a/M_e$ from eq 7). Taking the tabulated values literally, as well as $S_3(3) = 1.5$ and $\Gamma = 1$ (from the comparison of simulation and theory in Figure 1), we estimate values of $\beta(z)$ (eq 39) ranging from 0.025 to 0.04 ($z = 3$) for our polymers. Aside from reservations about the correctness of these magnitudes, which clearly rely excessively on model details, the variation of $\beta(z)$ with arm molecular weight is certainly weak compared with the power law and exponential dependences of the other quantities in eq 38. It thus seems sensible to treat $\beta(z)$ as a constant for the purpose fitting data, such as done in Figure 11.

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Diffusion of Linear Polystyrene Molecules in Matrices of Different Molecular Weights

Markus Antonietti, Jochen Coutandin, and Hans Sillescu*

Institut für Physikalische Chemie der Universität Mainz, D-6500 Mainz, West Germany.

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ABSTRACT: A holographic grating technique has been used to measure diffusion coefficients D of photolabeled polystyrene (PS) molecules having molecular weights in the range $18000 \leq M \leq 100000$ in PS matrices of $4000 \leq M' \leq 220000$ and a matrix of intra-cross-linked PS ($M' \rightarrow \infty$) at 212 °C. Self-diffusion coefficients ($M = M'$) have been determined in PS and poly(methylstyrene) (PMS), a random copolymer of 60% 3-methylstyrene and 40% 4-methylstyrene ($23000 \leq M \leq 425000$). A fit to the power law $D \sim M^{-\alpha}$ yields α between 2.4 and 2.5 in a range $30000 \lesssim M \lesssim 150000$, and $\alpha = 2$ for higher M values. The matrix dependence and the increased α values are explained by considering "tube formation" effects which should influence diffusion in a certain range above the entanglement spacing M_e in the Doi–Edwards reptation model.

Introduction

Recent studies of polymer-chain diffusion in entangled systems[1-7] have accumulated considerable support for the polymer law $D = D_0M^{-\alpha}$ relating the diffusion coefficient D with the molar mass M by an exponent $\alpha = 2$, as predicted by the reptation model.[8] The same model predicts

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an exponent 3 for the corresponding power law of the zero shear gradient viscosity η_0, whereas the value 3.4 has been found in a large number of experimental studies.[9] Modified reptation models[2,10-13] explain the difference of 0.4 in a certain range above the critical entanglement molecular weight M_c where most experimental studies have been performed. However, the additional 0.4 does not carry over to the diffusion exponent α in the reptation models which consider tube-length fluctuations, whereas the assumption of a particular defect diffusion mechanism causing chain reptation[13] has led to $\alpha = 2.4$ for diffusion.

In our previous studies of polystyrene (PS) chain diffusion[14,15] we have found deviations from the reptation value $\alpha = 2$. However, we have also been able to simulate the conditions of a "fixed-obstacle" tube system by measuring diffusion coefficients of PS chains in PS networks.[16] In addition to providing the expected exponent $\alpha = 2$ these experiments have revealed that the linear PS matrix of $M'_w = 110\,000$ used before[14,15] causes an increase of the diffusion coefficient and an exponent $\alpha > 2$ in a diffusant molecular weight range between $M_c = 32\,000$ and $M = 160\,000$. Since shorter matrix chains should have an even larger influence, we have no doubt that the self-diffusion coefficient in a matrix having the same chain length as the diffusant must scale with an exponent $\alpha > 2$ in this M range. The term *self-diffusion* is preserved for the condition $M' = M$ throughout this paper where M' and M denote the matrix and the diffusant molecular weight, respectively.

The possibility of matrix variation is an advantage of diffusion in comparison with dynamic mechanical measurements where studies in blends[9] encounter the problem of separating the contributions from different molecular weights. We can readily subtract the reptative contribution to chain diffusion obtained at large M' or in a network and compare the nonreptative contributions with predictions from theoretical considerations. In the following paper,[17] we will discuss the diffusion of intra-cross-linked PS molecules, which cannot move by reptation, and the diffusion of 3-arm branched PS stars where molecular motion occurs by reptative arm retraction[8] or by environmental and cooperative models, depending on the structure of the environmental matrix. We vary the topological structure of the diffusant as well as the matrix molecules in a rather broad range in order to obtain quantitative information upon the different contributions to motion in molten polymers.

Experimental Section

Photolabeled PS chains were prepared as before[14,18] from anionically polymerized PS, terminated with *p*-dichloroxylylene, and reacted with the Cs salt of 2-nitro-4-carboxy-4′-(dimethylamino)stilbene. The poly(methylstyrene) (PMS) samples were prepared by anionic polymerization in the same fashion as the PS samples. The monomer was an isomer mixture of about 60% 3-methylstyrene and 40% 4-methylstyrene obtained from Merck (Darmstadt). The polymerization was performed in tetrahydrofuran solution at −78 °C initiated with cumenyl potassium and terminated with dichloroxylylene. The samples were characterized by GPC using the universal calibration method.[19] The results are listed in Table I along with those of the PS samples. The glass-transition temperature of PMS is close to that of PS; we determined 94 °C for a high M_w sample. For the PS matrix we used commercial standard samples ($M_w/M_n < 1.1$) obtained from the Pressure Chemical Co. and Polymer Laboratories. The labeled and unlabeled samples were mixed in benzene solution which was filtered through a 0.45-μm Millipore filter, freeze-dried, and pressed into pellets of 0.75-mm thickness and 8.5-mm diameter as described previously.[14] In high molecular weight samples ($M_w > 2 \times 10^5$) were observed viscous flow phenomena that interfere with diffusion and cause forced Rayleigh scattering decay curves incompatible with eq 1 of ref 14. The viscous flow could be relaxed by annealing the samples for some days in an evacuated drybox at the diffusion temperature. The diffusion coefficients were measured by the holographic grating technique as described previously.[14,15] The grating distance was 0.3 μm for an intersecting angle $\theta = 90°$ of the coherent light beams and between 2 and 10 μm in the range of small θ. No θ dependence of the results was detected. As before,[14,15] we have corrected the diffusion coefficients for the small polydispersity of our samples and believe that the corrected D values have an accuracy of about ±5%.

Table I
Characterization of Polystyrene and Poly(methylstyrene) Samples

M_w	M_w/M_n	M_n (labeled)[a]	M_w	M_w/M_n	M_n (labeled)[a]
Polystyrene			Poly(methylstyrene)		
3 850	1.09		24 800	1.06	23 000
7 280	1.08		33 600	1.06	30 000
16 640	1.04		46 000	1.06	44 800
21 000	1.06	18 400	51 700	1.05	49 000
34 500	1.06	31 200	65 000	1.05	63 100
35 400	1.03		86 400	1.05	86 100
45 900	1.03		126 000	1.06	125 100
64 200	1.06	59 500	207 100	1.09	
100 400	1.04		348 100	1.12	342 200
106 300	1.06	99 800	416 500	1.13	424 800
223 600	1.03				

[a] Number average of end-group-labeled molecules with $M_w/M_n \leq 1.02$.

Results and Discussion

In our previous diffusion measurements[15] of M chains in a matrix of $M' = 110\,000$, we have found that the M exponent α had the reptation value 2.0 at 208 °C but increased to 2.4 at temperatures below 170 °C. This reflects an increased matrix influence at lower temperature and smaller M'. These results obtained with fluorescein-labeled PS have been confirmed[20] with the *o*-nitrostilbene (ONS) labeled used in the present paper, except for the smallest M chain ($P_n = 177$) where D was found increased by 40% with ONS-labeled PS. In order to minimize the matrix influence related with the end group free volume effects close to the glass transition (see below), we have measured D of labeled M chains in M' chains at the relatively high temperature of 212 °C. The results are shown in Figure 1 as a function of the matrix number-average degree of polymerization P'_n ($= M'_n/104$) and in Figure 2 as a function of the diffusant chain length P_n. The diamonds in Figure 1 denote the D values measured in a matrix[17] of intra-cross-linked PS having a molecular weight of 233 000 and an average of 33 monomers between cross-links. We have verified in a control experiment with $P_n = 70$ that D is still somewhat smaller in the cross-linked matrix than in the linear matrix with $P'_n = 960$. Thus, the lowest curve in Figure 2 bends over to a smaller slope at $P_n < 177$.

It is apparent from Figure 1 that a matrix influence is observable up to $M' \sim 200\,000$. We demonstrate below that the matrix effect in the M and M' range covered by our experiments cannot be explained by the model of "tube renewal" or "constraint release" where the M chain motion is caused by reptating away of the tube-forming M' chains.[8,12,21] This model predicts

$$D_{CR} = D_0 M^{-1} M'^{-3} \qquad (1)$$

and should only be able to compete with reptation in the limit[8] $M'_c < M' \ll M$. Green et al.[7] have recently published PS diffusion coefficients in a diffusant range of $50\,000 \leq M \leq 900\,000$ and a matrix range of $2 \times 10^3 \leq M' \leq 2 \times 10^7$.

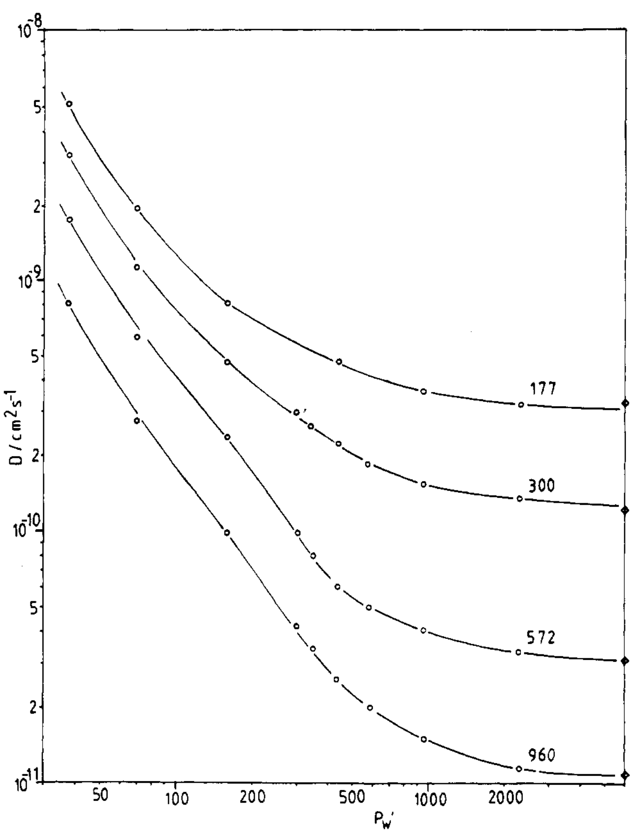

Figure 1. Diffusion coefficients of PS with number-average degree of polymerization P_n = 177, 300, 572, 960, respectively, drawn as a function of the matrix weight-average degree of polymerization P'_w at 212 °C. The diamonds refer to a matrix of intramolecular cross-linked PS.

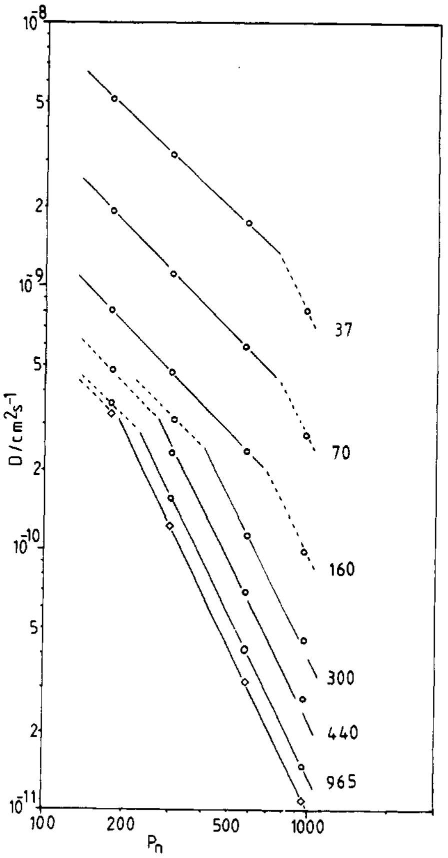

Figure 2. Part of the diffusion coefficients of Figure 1 redrawn as a function of the diffusant degree of polymerization P_n. The numbers indicate the matrix P'_w. See legend of Figure 1 for diamonds. The slopes of the full lines are α = 1 or 2, respectively.

The authors have reduced the measured D values to constant free volume ($T - T_g = 74$ K) using an appropriate WLF shift procedure.[9] In a range of M' values above $M_c' \approx 32000$ but below a crossover value $M'^*(M)$ of about 100000 they found good agreement of their data with the sum $D_R + D_{CR}$ where $D_R \sim M^{-2}$ is the contribution from M chain reptation and D_{CR} is given by eq 1. Thus, they were able to attain the constraint-release regime, whereas our data, being restricted to $M \leq 100000$, have a weaker M' dependence, $D \sim M'^{-1}$, if properly corrected for free-volume effects (see below). It should be noted that our D values agree with those of Kramer and collaborators[7] in the ranges covered by both investigations.

We have redrawn our data in Figure 2 in order to exhibit the M dependence at constant M'. We find a crossover behavior as the matrix degree of polymerization P'_n varies from 160 to 430, which is close to the critical value for the zero shear gradient viscosity,[9] $P_c(\eta_0) = 310$. The P_n exponent ($D \sim P_n^{-\alpha}$) agrees with the reptation value $\alpha = 2$ for diffusant chains in long-chain matrices provided $P_n \gtrsim 200$ which is close to the critical entanglement length $P_e = 174$ obtained from the plateau modulus determined in dynamic mechanical measurements.[9] In short-chain matrices we find $\alpha = 1$ for $P_n \lesssim 600$. Although we cannot be sure whether the increase of α for $P_n > 600$ originates from the interaction of diffusant chains in our relatively concentrated solutions (see below), it is apparent that the onset of reptative diffusion ($\alpha = 2$) depends upon the matrix chain length. We suggest that the critical value $P_c(\eta_0) = 310$ marks the onset of *tube formation* in the sense of the Doi–Edwards model[22] where the step length of reptative motion is given by the root mean square average distance of entanglements. Of course, most assumptions of this model are no longer applicable if the tube consists of only one or a few steps. Thus, experimental deviations from the Doi–Edwards model found in PS in a range of $M_e \lesssim M \lesssim 100000$ could very well originate from the dynamics of tube formation rather than from tube-length fluctuations[2,10–13] or "chain slippage through entanglement links".[23] An alternative view of tube formation results from the assumption of enhanced chain-end mobility which was considered in Kimmich's model[2] and is also seen in recent numerical simulations of chain motion in a tube confinement.[24] The Doi–Edwards model also implies that a chain of N beads ($M = NM_e$) has two end beads of length M_e characterized by Rouse type motion which dominates for small N.

The diffusion coefficients measured in short M'-chain matrices depend to some extent upon the finite concentration of the labeled M chains, which was determined by the limited sensitivity of our present experimental setup requiring about 1 label per 10^4 monomer units of PS. Therefore, the concentration was chosen as 3, 5, 8, and 12 wt % of the labeled PS with P_n of 177, 300, 572, and 960, respectively. In order to obtain an estimate of the concentration dependence in short-chain matrices, let us compare with diffusion in PS–benzene solutions.[25] Here a 3% PS solution of P_n = 177 is almost at the infinite dilution limit, whereas a 12% solution of P_n = 960 is well in the semidilute regime with a D value down by a factor of 5 from the infinite dilution limit. Though we expect a reduction[26] by a factor of less than 2 for our 12% solution of P_n = 960 in a matrix of P'_n = 37, we should be prepared for a considerable change in the upper curves of Figure 2 after D values in more dilute solutions become available. Accordingly, we may find a slope $\alpha < 1$, and the change to a higher slope for long M chains should vanish in a dilute very short M'-chain solution. In this case, the Zimm

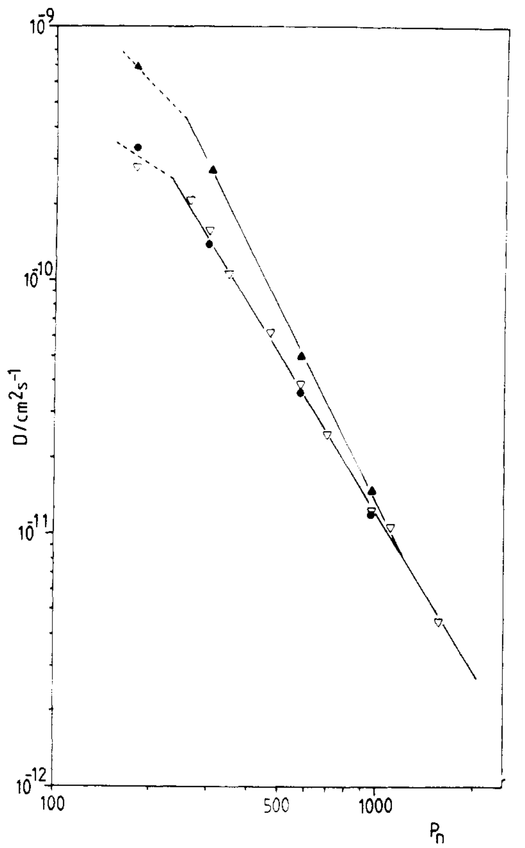

Figure 3. Self-diffusion coefficients D of PS (full triangles) at 212 °C. For comparison, the D values in a matrix of $P_w = 2150$ are shown (full circles) along with values from ref 15 (open triangles) shifted by small corrections due to the different temperature (208 °C) and matrix.

model should be applicable, which yields in the non-free-draining limit[27]

$$D_{\mathrm{Zimm}} = 0.196kT/\eta_0\langle R^2\rangle_0{}^{1/2} \qquad (2)$$

If we use the unperturbed dimension[27] $\langle R^2\rangle_0 = 4.9 \times 10^{-16}$ m^2 for the $P_n = 960$ PS molecule and $\eta_0 \approx 0.4$ Pa·s from the viscosity data of Allen and Fox[28] at 212 °C, we obtain $D_{\mathrm{Zimm}} = 1.5 \times 10^{-9}$ cm^2 s^{-1}. This is indeed above our value of 0.45×10^{-9} cm^2 s^{-1} measured in the 12% solution in the $P'_n = 37$ matrix. It should be noted that de Gennes[8] has used the estimate

$$D_{\mathrm{Stokes}} = kT/6\pi\eta_0\langle R^2\rangle_0{}^{1/2} = 0.27D_{\mathrm{Zimm}}$$

Though more quantitative considerations must await the results of future experiments in dilute solutions, we conclude that the diffusion of long M chains in short M' chains is characterized by a large contribution from Stokes–Einstein diffusion.

Free-volume effects can also lead to increased diffusion coefficients in short-chain matrices.[9,14] We have estimated this effect by taking into account the reduced glass temperature of short M' chains in the WLF equation (see eq 2 in ref 14). Using the WLF parameters of Allen and Fox,[28] we obtain an increase of D by a factor of ~3.5, 2.1, and 1.4 for $P'_n = 37$, 70, and 160, respectively. Thus, free-volume corrections lead to a downward shift of the three upper curves in Figure 2 with a marginal slope change caused by the finite concentration of the diffusant chains in our systems. The corrections do not alter our main conclusion that tube formation depends upon *M and M'* in a plausible manner, resulting in reptative motion of relatively short M chains ($M > M_e$) provided $M' > M_c(\eta_0)$ and Rouse or Zimm type motion of large M chains if $M' < M_c(\eta_0)$.

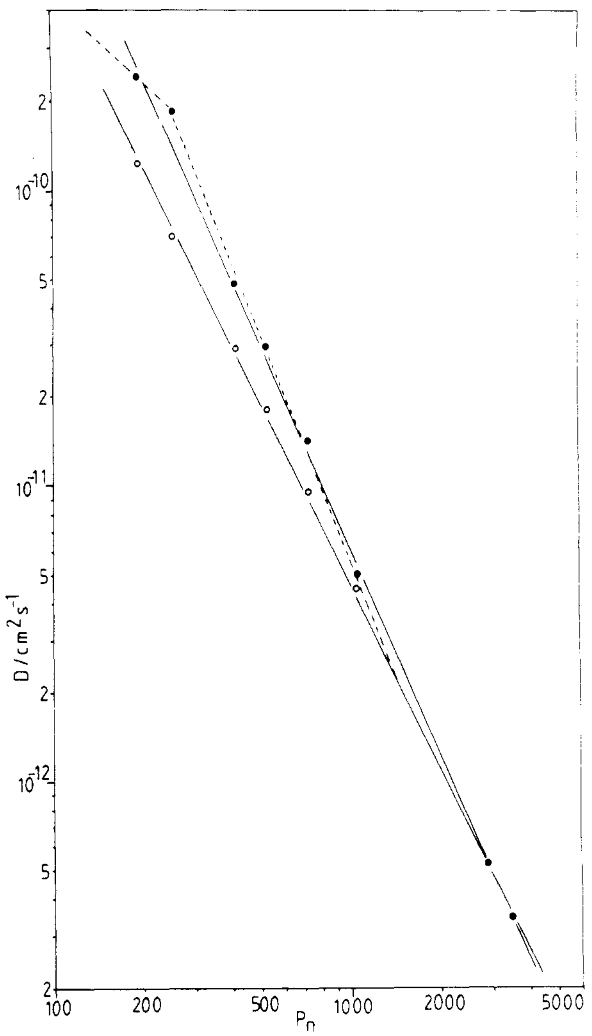

Figure 4. Self-diffusion coefficients D of poly(methylstyrene) (full circles) and D values in a matrix of $P_w = 1750$ (open circles) at 194 °C. See text for full and dashed lines.

We can infer from Figure 1 that *self-diffusion* ($M = M'$) is a complex phenomenon in the regime of $M < 200\,000$ where "matrix effects" influence the diffusion coefficients. This is confirmed by the results shown in Figures 3 and 4. For PS, the D values for $P_n = 300$, 572, and 960 are particularly accurate since they are obtained by interpolation from the measurements in different matrices (Figure 1). We believe that the slope $\alpha = 2.45$ determined from Figure 3 is accurate to ±0.05. For comparison, we have shown in Figure 3 the D values determined[15] in a matrix of $P_w = 2150$ having a slope of $\alpha = 2$ and merging with self-diffusion at a P_n value between 1000 and 2000. A similar behavior can be inferred from Figure 2 of ref 7 where $\alpha = 2$ for M between 255 000 and 915 000, whereas $\alpha > 2$ for smaller $M = M'$. Pulsed gradient NMR measurements of D in PS yield $\alpha = 2$ for $1000 \leq M \leq 40\,000$.[2,3] However, it has been noted that a smaller slope should result after correcting for the effect of end-group free volume.[3] Our D value for $P_n = 177$ may also be affected somewhat by free volume and labeling influences. Further experiments in the regime $P_n < 300$ are necessary in order to study the onset of Rouse type motion. In Figure 4, self-diffusion is compared with diffusion in a high M' matrix for poly(methylstyrene) at 194 °C. The slope $\alpha = 2.07$ for the latter is close to the reptation value, whereas a straight line through all self-diffusion values yields $\alpha =$

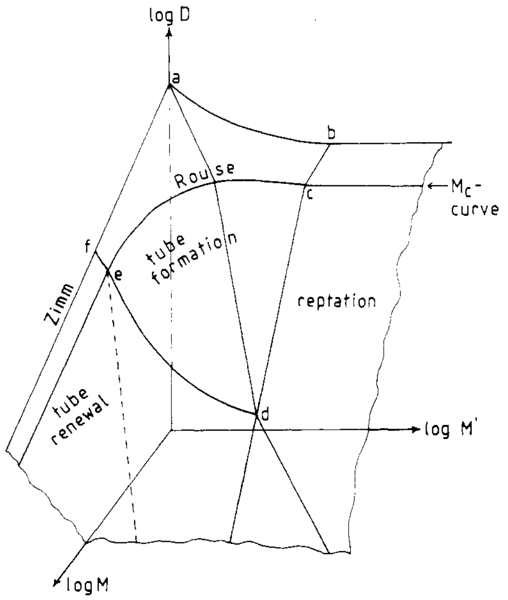

Figure 5. Schematic drawing of diffusion coefficient regimes as a function of the diffusant and matrix molecular weights M and M', respectively. See text.

2.32. A better fit is obtained with the dashed line, where $\alpha = 2.52$ for $250 \leq P_n \leq 1500$ and $\alpha = 2$ for longer chains. In polyethylene, all published diffusion data[1-5] comply with the slope $\alpha = 2$ in a wide range $500 \leq M \leq 200\,000$. However, the low accuracy of the results allows for deviations due to "tube formation" in a certain range above $M_c = 2000$. We also find by inspecting a summary of recent zero shear viscosity data of PS[29] that a crossover from the slope 3.4 to the reptation value 3.0 at high M cannot be excluded in view of the limited experimental accuracy. In conclusion, the data shown in Figures 3 and 4 indicate that a slope increase by 0.4 may be common to self-diffusion *and* shear viscosity in a certain range above M_c.

Let us discuss the different regimes of diffusive behavior in terms of Figure 5, which summarizes our results. If we start from point a in a region of very short M and M' and follow the line (M = const) to b, there must be a decrease of D due to the decrease of *local* mobility in the matrix, which becomes constant for M' values above some $M_c^* \sim 200\,000$ at "b". If we follow the M dependence at M' = const along the line b–c–d, there should be a crossover from Rouse type motion to reptation at point c, which marks the M_c curve. There must be a large increase of D along line d–e–f (M = const) since we have to connect the reptation line c–d ($\alpha = 2$) with the Zimm line a–f ($\alpha < 1$). This means in terms of the power law

$$D = D_0 M^{-\alpha} M'^{-\beta} \qquad (3)$$

that the connectivity of the line a–b–c–d–e–f–a enforces a large exponent β for large M if we accept that α varies from the reptation value 2 to the Zimm value below 1. This is just a different approach to the tube-renewal regime where $\beta = 3$, cf. eq 1. However, we have seen above that tube renewal is not effective for shorter M' in the tube-formation regime where we find $\beta \approx 1$. We have tentatively indicated by the dashed line a crossover between tube formation and tube renewal. Inspection of the M_c curve shows that M_c increases as M' is lowered and becomes infinite for very short M' chains where even very long M chains show Stokes–Einstein diffusion of the non-free-draining Zimm limit. It is possible that the asymptotic limit of M_c for large M' approaches the entanglement value $M_e = 18\,000$, whereas $M_c = M_c(\eta_0) \approx 32\,000$ for $M = M'$. For self-diffusion, eq 3 yields $D = D_0 M^{-(\alpha+\beta)}$. Since $\beta > 0$ for $M' < M_c^*$ below the line b–c–d, we obtain $\alpha + \beta > 2$ if $\alpha = 2$ for M-chain reptation. Thus, further modification[10-13] of the tube model is not necessary if one accepts that "tube formation" is important for $M' < M_c^*$. It should be noted that $M_c^* \sim 200\,000$, as inferred from Figure 1, is of the order of the value 130 000, which separates the plateau and terminal zones in dynamic mechanical measurements in PS.[9]

Conclusions

The diffusion coefficients of PS chains with molecular weight M in matrices of different chain length M' have been interpreted in terms of "tube-formation" effects in a range between the entanglement spacing $M_e \approx 18\,000$ and a value M_c^* that is close to the crossover at $\sim 130\,000$ between the plateau and terminal zones of dynamic mechanical measurements.[9] In this range, we find $D \sim M^{-2}$ for relatively long matrix chains (Figure 2), and approximately $D \sim M'^{-1}$ for long M chains and $M' \lesssim 30\,000$ (Figure 1). This matrix influence cannot be described in terms of tube renewal by reptating away of tube forming chains,[8,12,21] which predicts the power law $D \sim M^{-1}M^{-3}$. In the regime $M' \lesssim M_c^*$ the power law $D \sim M^{-\alpha}$ for self-diffusion (M v M') yields α values between 2.4 and 2.5 for PS and poly(methylstyrene) which may be related with the exponent 3.4 of the corresponding viscosity power law. Whereas tube length fluctuation models[10,11] yield the incremental 0.4 only for the viscosity exponent, tube formation affects both transport processes in the same fashion.

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Diffusion of Intramolecular Cross-Linked and Three-Arm-Star Branched Polystyrene Molecules in Different Matrices

Markus Antonietti and Hans Sillescu*

Institut für Physikalische Chemie der Universität Mainz, D-6500 Mainz, West Germany.
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ABSTRACT: Diffusion coefficients D of photolabeled nonlinear polystyrene (PS) molecules in different PS matrices have been measured by using a holographic grating technique. Intramolecular cross-linked PS molecules (microgels) were prepared by Friedel–Crafts cross-linking with *p*-dichloroxylylene in dilute solution in a molecular weight range $25\,000 \le M_{\rm w} \le 160\,000$ with average number of monomers between cross-links $P_{\rm c} = 10, 20, 30$, and 40. The D values of microgels in microgel matrices decrease as the degree of cross-linking and the size of diffusant microgels are increased. At 194 °C, $D = 9.0 \times 10^{-14}$ cm^2 s^{-1} for $M_{\rm w} = 160\,000$ and $P_{\rm c} = 20$, as compared with 1.9×10^{-12} cm^2 s^{-1} for the corresponding linear PS. D of microgels ($P_{\rm c} = 20$) in linear matrices ($16\,400 \le M'_{\rm w} \le 160\,000$) is proportional to $M'_{\rm w}{}^{-1}$ for $M'_{\rm w} \lesssim 40\,000$. D of small microgels becomes constant for larger $M'_{\rm w}$ and approaches the limit of a microgel matrix. For large microgels, D is found to be approximately $\sim M'_{\rm w}{}^{-3}$ for $M'_{\rm w} \ge 40\,000$, but has a weaker $M'_{\rm w}$ dependence for large $M'_{\rm w}$. For three-arm-star PS in a microgel matrix D is proportional to $\exp(-\alpha M_{\rm w})$ over a D range from 3×10^{-11} to 8.7×10^{-14} cm^2 s^{-1} for arm lengths from 80 to 420 monomer units at 194 °C. In PS chain and star matrices, increased D values are obtained for diffusant molecular weights $M_{\rm w} \gtrsim 100\,000$. The results are discussed in relation with current theories of polymer diffusion.

Introduction

Our diffusion studies in bulk polystyrene (PS) aim at separating different contributions to polymer motion by varying the topological structure of diffusant and matrix molecules. We have isolated the reptation contribution by dissolving PS chains in networks,[1] and we have shown that reptation dominates chain motion in a matrix of long chains. Deviations found in short-chain matrices[2] have been attributed to "tube formation" in a certain range above the entanglement spacing $M_{\rm e}$. No reptation should be possible for ring-shaped macromolecules. In a previous study[3] we have found PS ring diffusion surprisingly rapid, except for one sample that was probably heterogeneous.[4] A recent investigation[5] of PS ring diffusion in blends with PS chains also yields relatively rapid motion of small rings, whereas large rings diffuse much more slowly. The authors conclude that a mechanism other than reptation or constraint release is required to account for the diffusion of rings.

Intramolecular cross-linking introduces further constraints upon chain mobility. We have recently shown[1] that Friedel–Crafts cross-linking with *p*-dichloroxylylene provides highly flexible cross-links which preserve the local mobility up to very high cross-link densities. Thus, molecular *microgels* have become available that can neither reptate nor entangle with their neighbors, as no interpenetration is possible. Since the large bulk size of the microgels precludes usual vacancy mechanisms, the only possibility left for diffusion is through cooperative motion. Microgel diffusion in blends with linear PS should reveal to what extent the interpenetration of large chains affects motional freedom. We have shown previously[1] that chains reptate with the same diffusion coefficient through highly cross-linked microgel and continuous networks. In a forthcoming neutron diffraction study the swelling of microgels by interpenetrating chains will be determined quantitatively. However, the interpenetration of chains may have less influence upon microgel or ring diffusion than the effect of entanglements. Klein[6] has estimated that for ring lengths up to about ten entanglement lengths a large fraction of rings may diffuse by reptative motion since they are "non-obstacle-enclosing" in the sense that only entanglements are counted as obstacles forming the tube of the reptation model. In the present paper, the questions of what is an entanglement and how it is related with cooperative motion and tube formation will be dealt with primarily from the point of view of an experimentalist who contributes new experimental data. Thus, we have varied the size and the cross-link density of the microgels and have measured self-diffusion coefficients as well as diffusion coefficients in blends with linear PS as a function of the chain length. Furthermore, we have measured self-diffusion coefficients as well as diffusion coefficients in blends with linear PS as a function of the chain length. Furthermore, we have measured diffusion coefficients of three-arm-star branched PS in chain, star, and microgel matrices in order to investigate the influence of cooperative motion, arm retraction, and tube renewal.

Experimental Section

1. Intramolecular Cross-Linked Polystyrene. Molecular microgels were prepared by Friedel–Crafts cross-linking of linear PS with *p*-dichloroxylylene in dilute dichloroethane solution, as described in ref 1. This Friedel–Crafts reaction was also applied in order to prepare loop-shaped PS molecules from PS chains carrying a chloromethylbenzene end group introduced in the termination step of the anionic polymerization. Although one cannot be sure whether this "backbiting" reaction occurs in a random manner, we have estimated the loop size from the random walk in a good solvent[7] and have obtained[8] the number- and weight-average ring sizes of 65 and 385 monomers, respectively,

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