(4) Akcasu, A. Z.; Gurol, H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1.
(5) Kirkwood, J. G. *J. Polym. Sci.* **1954**, *12*, 1. Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(6) Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3831.
(7) Burchard, W.; Schmidt, M.; Stockmayer, W. H. *Macromolecules* **1980**, *13*, 580.
(8) Fisher, M. E. *J. Chem. Phys.* **1966**, *44*, 616.
(9) (a) des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1980**, *41*, 223; (b) *Phys. Rev. A* **1974**, *10*, 1665.
(10) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(11) Redner, S. *J. Phys. A: Math., Nucl. Gen.* **1980**, *13*, 3525.
(12) Benmouna, M.; Akcasu, A. Z. *Macromolecules* **1978**, *11*, 1187; **1980**, *13*, 409.
(13) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(14) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276. Their formula (eq 28) yields $R_G/R_H = 1.807$ if one uses $\nu = 0.588$ instead of $\nu = {}^3/_5$.
(15) Barrett, A. J. *Macromolecules* **1984**, *17*, 1561, 1566. According to the treatment of ref 3, the set of $l = t$ and $\nu = {}^3/_5$ gives $l = t = (1-\nu)^{-1} = 2.5$.
(16) Wang, S.-Q.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1986**, *85*, 3674.
(17) Oono, Y.; Kohmoto, M. *J. Chem. Phys.* **1983**, *78*, 520. The reported value 1.56 and 1.24 for $R_G/R_H$ in good and Θ states, respectively, were revised as described in the text since simple mathematical errors were found in the article.
(18) Oono, Y. *Adv. Chem. Phys.* **1985**, *61*, 301.
(19) Tanaka, G.; Stockmayer, W. H. *Proc. Natl. Acad. Sci. U. S. A.* **1982**, *79*, 6401.
(20) Wang, S.-Q.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 1346.
(21) Tsunashima, Y.; Hirata, M.; Nemoto, N.; Kurata, M. *Macromolecules* **1987**, *20*, 2862.
(22) Zimm, B. H. *Macromolecules* **1980**, *13*, 592.
(23) Freire, J. J.; Rey, A.; Garcia de la Torre, J. *Macromolecules* **1986**, *19*, 457.
(24) Fixman, M. *J. Chem. Phys.* **1986**, *84*, 4080, 4085.

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# Diffusion of Macromolecular Stars in Linear, Microgel, and Network Matrices

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ABSTRACT: Tracer diffusion coefficients for star-branched polystyrene diffusing into linear, intramolecularly cross-linked (microgel), and intermolecularly cross-linked (network) polystyrene matrices were measured by forward recoil spectrometry. The diffusion behavior can be modeled by assuming that constraint release and arm retraction mechanisms are both operating. Microgels and networks behave as if they are linear chains of infinite molecular weight, so that only the arm retraction contribution is measured. It is found that, for a given arm molecular weight, four- and eight-arm stars diffuse about as quickly as three-arm stars in microgel matrices. A simple arm retraction mechanism is proposed whereby diffusive steps occur each time a single arm retracts, giving rise to a relatively weak dependence of the diffusion coefficient on the number of arms of the star.

## Introduction

Star-branched polymers are frequently used as model systems for studying the effects of branching on rheological properties. In the Doi–Edwards tube model,[1-3] stress relaxation occurs as molecules withdraw from the tube within which they were originally confined. For star molecules, this process requires the retraction of arms to the branch point. The time scale for arm retraction is predicted to depend exponentially on the length of the arms.[4] Viscoelastic properties are not expected to depend on the number, *f*, of arms joined at the branch point, since conformational adjustment can take place by the independent retraction of different arms. Experimental studies have confirmed this expectation.[5,6] The diffusion of stars in a network requires a net translation of the center of mass, so the situation here is somewhat different. Current theoretical treatments assume that the branch point is fixed by network constraints unless all but two of the arms retract simultaneously. An arm retraction contribution to the tracer diffusion coefficient is obtained which has the following form:[7,8]

$$D_{\mathrm{ar}} = D_0^{\mathrm{AR}} M_{\mathrm{a}}^{-\beta} e^{-\alpha(f-2)M_{\mathrm{a}}} \tag{1}$$

Here $\alpha$, $\beta$, and $D_0^{\mathrm{AR}}$ are model-dependent constants and $M_{\mathrm{a}}$ is the molecular weight per arm. Experimental evidence for the exponential $M_{\mathrm{a}}$ dependence for three-arm stars has been obtained.[9,10]

The constraints which define the Doi–Edwards tube in a linear polymer melt (as opposed to those of a network) are not necessarily fixed, so diffusion of a star macromolecule can take place by the motion of the tube itself. The relevant time scale for this constraint release mechanism is determined by the relaxation time, $\tau_{\mathrm{e}}$ of the molecules defining the constraints. The relaxation time for linear molecules scales as the cube of the molecular weight, and most theories of constraint release give the following form for the diffusion coefficient:[8]

$$D_{\mathrm{cr}} = D_0^{\mathrm{CR}} M^{-1} P^{-3} \tag{2}$$

Here *M* is the total molecular weight of the diffusing species, and *P* is the molecular weight of the matrix chains. If diffusion by arm retraction and by constraint release are independent processes, the total tracer diffusion coefficient for a star molecule in a matrix of linear chains will be given by the sum

$$D^* = D_{\mathrm{cr}} + D_{\mathrm{ar}} \tag{3}$$

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**Table I**
**Characterization of the Four-Arm and Eight-Arm Stars**

| $M_a$ (GPC) | $M$ (light scattering) | $M/M_a$ |
|---|---|---|
| 18 000 | 71 000 | 3.9 |
| 40 000 | 169 000 | 4.2 |
| 60 000 | 488 000 | 8.1 |

## Experimental Section

In an effort to test these ideas, we have made measurements of the tracer diffusion coefficients of three-, four-, and eight-arm polystyrene stars in linear, microgel, and network polystyrene matrices. The microgels are intramolecularly cross-linked molecules with an average of 20 monomers between cross-links. Self-diffusion of the microgels is very limited, and we assume that there is no constraint release contribution for stars diffusing in the microgel matrices. Intermolecularly cross-linked networks were used as matrices in order to rule out any possibility of constraint release. Networks were formed by exposing thin films of high molecular weight (MW = $10^6$) polystyrene to $1.5 \times 10^8$ rad of $\gamma$ radiation. The resulting gel fraction was approximately 90%. Diffusion coefficients for the three-arm stars in microgel matrices were measured at 194 °C by using a holographic grating technique. These results have been published previously, along with a description of the synthesis and characterization of the three-arm stars.[10]

The four- and eight-arm stars were synthesized by terminating an anionic polymerization with an excess of tetravinyllead or divinylbenzene, respectively. Star functionality is determined by steric hindrance to the addition of multiple arms. A small amount of the linear precursor was removed prior to termination for characterization by gel permeation chromatography (GPC). The star macromolecules were purified by fractional precipitation. Analysis of the purified star polymers by GPC shows only trace amounts of the linear precursor. The total (weight-average) molecular weights of the stars were determined by light scattering. Comparison to the arm molecular weights gave a weight-average star functionality, $f$. These results are summarized in Table I.

Forward recoil spectrometry was used to measure tracer diffusion coefficients of the four- and eight-arm h-PS stars at 178 °C into d-PS matrices, either linear, microgel, or network. Details of this technique are described elsewhere.[11-13] Where more than one measurement was made, diffusion coefficients were found to be independent of star concentration and annealing time, indicating that the measured diffusion coefficients are true tracer diffusion coefficients. The monodisperse d-PS polymers used as linear matrices had molecular weights ranging from $5 \times 10^4$ to $10^6$ g/mol. Diffusion coefficients which were greater than $10^{-12}$ cm$^2$/s at 178 °C were measured at 138 °C and scaled to 178 °C by using the WLF equation. The WLF parameters used are known to be valid for both linear and star-branched polystyrenes.[5,14]

## Results and Discussion

In Figure 1 the measured diffusion coefficients for the four- and eight-arm stars are plotted versus the molecular weight, $P$, of the linear d-PS matrix chains. The microgels behave just as the networks do, simulating chains of infinite molecular weight as reported elsewhere.[15] The $P$ dependence of the diffusion coefficient is due to constraint release and goes as $P^{-2.5}$, whereas eq 2 predicts a stronger ($P^{-3}$) dependence. Klein arrives at a $P^{-2.5}$ dependence for the constraint release contribution to diffusion by assuming that the number of constraints defined by a single $P$ chain varies as the spatial extent of the $P$ chain.[7] The solid lines of Figure 1 are fits to eq 3, assuming that the constraint release contribution varies as $P^{-2.5}$.

The actual cause of the decreased $P$ dependence for constraint release is probably somewhat more complicated. As described by Bartels et al.,[16] not all constraints along the star are equivalent. Consider a constraint which lies midway along one of the arms. Constraint release will dominate at this point only if the time required for a matrix chain to renew its configuration, $\tau_e$, is less than the time required for the arm to retract to this point. The arm retraction time increases exponentially toward the branch point, so constraint release is controlled by a central core of the star. Arms move around constraints at the outside of the star much more quickly by arm retraction. As $P$ increases, $\tau_e$ increases and arm retraction dominates for a larger fraction of the star. The net result can be modeled with eq 2 but with an effective $M$ decreasing with increasing $P$, leading to a diffusion coefficient with a weakened $P$ dependence. At very high $P$'s, arm retraction is totally dominant, whereas at very low $P$'s constraint release operates over the entire star. The transition region between these two extremes is very broad and can easily lead to the type of $P$ dependence seen here.

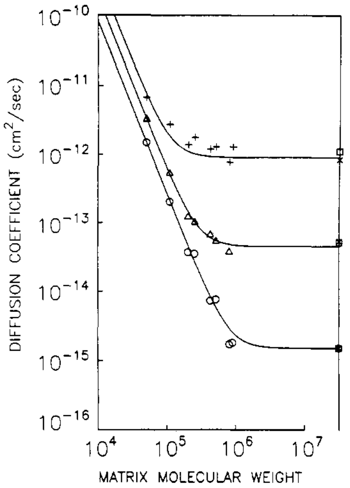

**Figure 1.** Tracer diffusion coefficients at 178 °C for star-branched molecules plotted against the molecular weight of linear matrix chains: crosses, $f = 4$, $M_a = 18000$; triangles, $f = 4$, $M_a = 40000$; circles, $f = 8$, $M_a = 60000$. The ×'s represent diffusion into microgels, and the squares represent diffusion into networks. The solid lines are empirical fits to eq 3, with $D_{cr}$ proportional to $P^{-2.5}$.

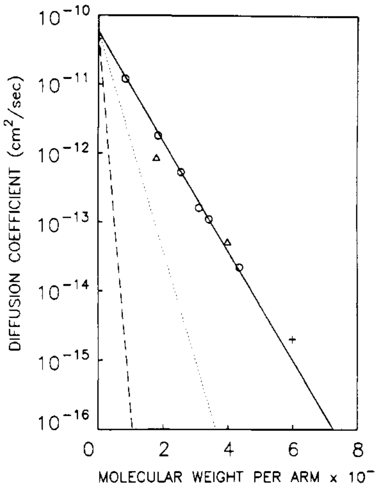

**Figure 2.** Diffusion coefficients for various star-branched molecules in microgel matrices, plotted as a function of $M_a$, the molecular weight per arm: circles, three-arm stars; triangles, four-arm stars; cross, eight-arm star. The solid line is the prediction of eq 1 for $f = 3$, the dotted line for $f = 4$, and the dashed line for $f = 8$, with $\beta = 0$, $D_0^{AR} = 5.8 \times 10^{-11}$ cm$^2$/s, and $\alpha = 1.83 \times 10^{-4}$.

Diffusion coefficients for all of the stars in microgel matrices are plotted in Figure 2. The diffusion coefficients for the three-arm stars were scaled from 194 to 178 °C by using the same WLF parameters as before.[5,14] The solid line in Figure 2 represents the predicted diffusion coefficients from eq 1 for three-arm stars, using $D_0^{AR} = 5.8 \times 10^{-11}$ cm$^2$/s, $\alpha = 1.83 \times 10^{-4}$, and $\beta = 0$, whereas the dotted and the dashed lines represent the prediction from eq 1 for four-arm and eight-arm stars, respectively, using the same values of the constants. The diffusion coefficients for the four- and eight-arm stars are much greater than predicted by the $f - 2$ dependence in the exponential of eq 1. For example, the predicted value of $D^*$ for the four-arm star with $M_a = 40\,000$ is $2.5 \times 10^{-17}$ cm$^2$/s, while the measured value is $5 \times 10^{-14}$ cm$^2$/s. The comparison of $D^*$'s for the eight-arm star with $M_a = 60\,000$ is even worse, $1.4 \times 10^{-39}$ cm$^2$/s predicted versus $2 \times 10^{-15}$ cm$^2$/s measured. In contrast, the tracer diffusion coefficients of all the star molecules in microgels are described approximately by a single-exponential law, which is independent of the number of arms on the star. We conclude from this result that diffusion of a star-branched molecule by arm retraction does not require simultaneous retraction of more than one arm. Diffusive steps may occur by retraction of one arm at a time.

While we have been able to rule out very large differences in the diffusion coefficient as a function of $f$, it is expected that a weaker dependence must remain. An intuitive understanding can be gained by assuming that individual arm retractions are uncorrleated and that the branch point moves a distance proportional to $1/f$ each time a single arm retracts. This assumption leads directly to a diffusion coefficient which scales as $1/f$. A detailed model which gives a similar result has been proposed by Rubinstein.[17] This relatively weak dependence is certainly within the range of uncertainty of our data.

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## References and Notes

(1) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789.
(2) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1802.
(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1818.
(4) deGennes, P.-G. *J. Phys.* **1975**, *36*, 1199.
(5) Graessley, W. W.; Roovers, J. *Macromolecules* **1979**, *12*, 959.
(6) Pearson, D. S.; Helfand, E. *Macromolecules* **1984**, *17*, 888.
(7) Klein, J. *Macromolecules* **1986**, *19*, 105.
(8) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(9) Klein, J.; Fletcher, D.; Fetters, L. J. *Nature (London)* **1983**, *304*, 526.
(10) Antonietti, M.; Sillescu, H. *Macromolecules* **1986**, *19*, 798.
(11) Green, P. F.; Mills, P. J.; Palmstrøm, C. J.; Mayer, J. W.; Kramer, E. J. *Phys. Rev. Lett.* **1984**, *53*, 2145.
(12) Mills, P. J.; Green, P. F.; Palmstrøm, C. J.; Mayer, J. W.; Kramer, E. J. *Appl. Phys. Lett.* **1984**, *45*, 957.
(13) Green, P. F.; Mills, P. J.; Kramer, E. J. *Polymer* **1986**, *27*, 1063.
(14) Green, P. F. Ph.D. Thesis, Cornell University, 1985.
(15) Antonietti, M.; Coutandin, J.; Sillescu, H. *Macromolecules* **1986**, *19*, 793.
(16) Bartels, C. R.; Crist, B.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1986**, *19*, 785.
(17) Rubinstein, M. *Phys. Rev. Lett.* **1986**, *57*, 3023.

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# Mutual Diffusion in the Miscible Polymer Blend Polystyrene/Poly(xylenyl ether)

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ABSTRACT: We have used forward recoil spectrometry to measure the mutual diffusion and tracer diffusion coefficients, $D$ and $D^*$, in the miscible polymer blend of deuteriated polystyrene (d-PS)/poly(xylenyl ether) (PXE) containing a volume fraction $\phi = 0.55$ of d-PS. In this blend, $D^*$ of the faster diffusing PS molecules of degree of polymerization $N_{\mathrm{PS}}$ decreases as $N_{\mathrm{PS}}^{-2}$ as expected from reptation. On the other hand $D$ decreases as $N_{\mathrm{PS}}^{-1}$, an observation in strong support of the "fast theory" of mutual diffusion which predicts that $D$ is controlled by the $D^*$ of the faster moving species, i.e., $D = 2\phi(1 - \phi)D_{\mathrm{T}}(\chi_{\mathrm{S}} - \chi)$, where $\chi$ and $\chi_{\mathrm{S}}$ are the Flory interaction parameter of the blend and its value at the spinodal and $D_{\mathrm{T}}$ is the transport coefficient given by $D_{\mathrm{T}} = (1 - \phi)D^*_{\mathrm{PS}}N_{\mathrm{PS}} + \phi D^*_{\mathrm{PXE}}N_{\mathrm{PXE}}$. While at low temperatures (e.g., 200 °C), $D$ is much larger than $D^*$, the difference between $D$ and $D^*$ diminishes with increasing temperature until finally at the highest temperatures (e.g., 310 °C) $D$ is less than $D^*$. This change in the relative values of $D$ and $D^*$ is due to the temperature dependence of $\chi$. Using the measured values of $D^*$ and $D$, we find that $\chi(T) = 0.112 - (62/T)$. The $D$ and $D^*$'s were also measured as a function of composition in d-PS/PXE blends ranging from $\phi = 0.0$ to $\phi = 1.0$ at a temperature 66 °C above the glass transition temperature of each blend. Under these conditions $D$ is much larger than the $D^*$'s, an increase predicted quantitatively by the "fast theory" using the same $\chi(T)$ determined for the $\phi = 0.55$ blend.

## Introduction

Mutual diffusion or interdiffusion in miscible polymer blends, aside from its practical importance in the control of phase separation and homogenization, is of great interest for testing the relationship between the thermodynamics of such blends and their diffusion behavior.[1-13] de Gennes[14] was the first to point out that because the combinatorial entropy of mixing of polymers is so small, scaling as $N^{-1}$

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