However, in our previous work we have found that in PMMA the $\xi(\mathrm{CQ})/\xi(\mathrm{CQP})$ ratio is equal to 1.03, and in polycarbonate[14] it is equal to 1.34. These results thus demonstrate that the ξ value and hence for the critical molecular volume V_d^* of the dye dependents on the nature of the polymer host.

Using eq 6, we find that above T_g the effective activation energy

$$E_D = RT^2\left(\frac{\partial \ln D}{\partial T}\right)_p = RT + \frac{2.3\xi C_1C_2RT^2}{(C_2 + T - T_g)^2} \qquad (10)$$

Equation 10 indicates that the effective activation energy increases rapidly as T is decreased toward T_g. Furthermore, one notes that E_D is linearly proportional to ξ. Thus, given the same polymer environment, the rate of dye diffusion in a polymer is strongly affected by the size of the dye molecule.

In conclusion, we have carried out diffusion measurements of a trace amount of CQ in PEEK as a function of temperature. We have shown that the diffusion coefficient of CQ in PEEK is closely associated with the viscoelastic property of PEEK. The main-chain segmental motion that affects the dynamic shear modulus data also dominates the diffusion process of camphorquinone and its photoproduct in PEEK.

Acknowledgment. This work is financially supported by ONR and by the Polymer Program (DMR-8606884) of the National Science Foundation.

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Chain Architecture in the Hydrodynamic Scaling Picture for Polymer Dynamics[†]

George D. J. Phillies

Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

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ABSTRACT: The hydrodynamic scaling picture of polymer dynamics is extended to treat the consequences of chain architecture on tracer diffusion by linear and star polymers in a matrix of linear polymers. From hydrodynamic scaling, one clearly predicts: (i) whereas in comparing linear and many-armed star polymers of equal *total* molecular weight, a given large concentration of matrix polymer is modestly more effective (smaller D/D_0) at retarding a linear polymer than at retarding a star polymer; (ii) with linear and star polymers of equal *arm* molecular weight, a large concentration of matrix polymer is far more effective at retarding a star than at retarding a linear polymer. Contrary to the claims of their authors, recent experiments of Lodge, Wheeler, et al. (*Macromolecules* 1989, *23*, 3409) on tracer diffusion of linear and star polystyrenes in poly(vinyl methyl ether) matrices are consistent with predictions of the hydrodynamic scaling model.

Introduction

Wheeler, Lodge, and Markland[1,2] have recently reported an extensive experimental study on the tracer diffusion coefficient D of linear and star polystyrenes (PS) through poly(vinyl methyl ether) (PVME)/*o*-fluorotoluene, comparison being made with the reptation-scaling,[3] reptation-Mori,[4,5] dynamic entanglement,[6,7] and hydrodynamic scaling[8-10] models of polymer dynamics. Lodge et al.[2] concluded "...star-branched polymers are retarded significantly relative to linear polymers...the observation that branched polymers move less rapidly is consistent only with the reptation-based picture." A reader might reasonably conclude from the latter phrase that Lodge et al.[2] viewed their findings to be *inconsistent* with the hydrodynamic scaling[8-10] and dynamic entanglement[6,7] models. Since neither of these models had hitherto been

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extended to treat influences of chain architecture on D, it was clearly erroneous to assert that *any* finding on chain versus star diffusion could be inconsistent with either hydrodynamic scaling or with dynamic entanglement, at least as those models existed when refs 1 and 2 were written.

The objective of this note is to report the incorporation of chain architecture effects into the hydrodynamic scaling model. It will be shown that Lodge, Wheeler, et al.'s[1,2] experiments on D of linear (D_l) and star (D_*) polymers are in reasonable agreement with hydrodynamic scaling. At the present level of sophistication of theory and experiment, comparison of D_l and D_* does not distinguish between hydrodynamic scaling, dynamic entanglement, and some reptation-based pictures of chain dynamics.

The primary experimental data are studies of tracer diffusion by dilute ("probe") polymer chains through solutions containing a background ("matrix") polymer; the matrix polymer may be concentrated. If the probe and matrix polymers are chemically identical, tracer diffusion becomes self-diffusion. Experimental findings on tracer diffusion in polymer solutions have recently been reviewed.[11] Polymer melts are an unrelated issue not considered treated here. Wheeler et al.[1,2] report a detailed study of tracer diffusion, varying in particular the architecture of their probe chains. Their major experimental findings were as follows:

(i) D_l and D_* of tracer polystyrenes fall with increasing concentration c of the PVME matrix polymer, the concentration dependence following the stretched-exponential (so-called[1] "Phillies") form

$$D = D_0 \exp(-\alpha c^{\nu}) \tag{1}$$

with α and ν as scaling parameters, c being the matrix concentration. D_0, if treated as a free parameter, is somewhat larger than the low-c limit of D. α and ν depend on probe M and on chain architecture.

(ii) Linear and star PS species have different concentration dependences. Comparing polymers of the same *total* molecular weight M, at large matrix c many-armed star polymers are *less* retarded (larger D/D_0) by the matrix than are linear polymers. For 12-arm stars and linear (2-arm star) polymers of equal M, $[D_*/D_{0,*}]/[D_l/D_{0,l}]$ reaches a largest value of 2 for $c \sim 100$ g/L. Above 100 g/L, $[D_*/D_{0,*}]/[D_l/D_{0,l}]$ falls with increasing c. On the other hand, with polymers having equal *arm* molecular weight M_a (a linear polymer being a 2-arm star), $[D_*/D_{0,*}]/[D_l/D_{0,l}]$ falls rapidly with increasing c. At large matrix concentrations, the retardation of a star polymer by a matrix may be an order-of-magnitude larger than the retardation of a linear polymer having the same M_a.

(iii) R_g of linear and star polymers, as obtained from static light scattering, falls substantially with increasing c.

These experimental data may be compared with four major families of models of polymer solution dynamics. In the reptation models, a concentrated polymer solution is described as a meshwork ("pseudogel lattice"), in which polymer chains have cross-link ("entanglement") points which constrain polymer chains to diffuse parallel to their own contours. Reptation models may be divided between reptation-scaling models,[3] in which variables are assumed to be related by power-law ("scaling") relations, and nonscaling models, in which reptation is supplemented by dynamic equations such as the eq 4 of the Mori–Zwanzig projection formalism. The reptation models are here collectively described as "static entanglement" models because in these models the entanglement points appear and disappear but do not move relative to the solution volume.

Table I
Dependence of the Dilute-Solution D_o of 2-, 3-, and 12-Arm Star Polymers on Polymer Molecular Weight M, As Described by Eq 2[a]

f	D_{Mf}	g	% rmse[b]
2	2320	0.538	2.4
3	2717	0.552	~0
12	3078	0.551	5.4

[a] A 2-arm star is a linear polymer; M is in Da. [b] rmse = root-mean-square error.

A third family of models, such as Einaga's "noodle" picture[12] and Skolnick et al.'s[6,7] phenomenological picture, resembles the reptation models in that chain entanglements dominate interpolymer interactions. These models differ from the reptation models in that entanglements are dynamic and move through solution on significant time scales. In these "dynamic entanglement" models, polymer chains are constrained by entanglements. However, dynamic entanglements move, so chains can diffuse both parallel and perpendicular to their own contours. Dynamic entanglement models have received extensive support from elaborate on-lattice computer Monte Carlo dynamics calculations.[6,7]

A fourth model of polymer solution dynamics is this author's hydrodynamic scaling picture,[8-10] in which the dominant force between polymer chains is assumed to be hydrodynamic in nature, moderated by a Newtonian solvent filling the spaces between the polymer chains. A self-similarity approximation for multiple-chain interactions is used to bootstrap the computation from dilute solution to large concentrations, yielding stretched-exponential concentration dependences. Since this model fills the space between polymer chains with a Newtonian fluid, it does not (in its present form) describe polymer melts.

Effects of Chain Architecture

This section treats considers the effect of chain architecture on a chain's self-diffusion coefficient. The following analysis is based on the universal scaling law (eq 1) for D. The hydrodynamic scaling model is used to estimate α, ν, and D_0 for chain and star polymers. A change in chain architecture is predicted to have a substantial effect on α but only a weak effect on ν.

How does chain architecture influence chain dimensions? Wheeler, Lodge, et al.'s data[1,2] on D_0 of linear polymers, 3-armed stars, and 12-armed stars is fit well by

$$D_0 = D_{Mf} M^{-g} \tag{2}$$

D_{Mf} and g are given in Table I, separate values of D_{Mf} and g being required for different numbers (f) of arms. From Table I, D_{M2}:D_{M3}:D_{M12} = 1:1.17:1.33. g of a 2-arm star is slightly less than g of 3- and 12-arm stars, so, for a polymer having a nominal $M = 1 \times 10^6$ Da, D_0 of a linear chain is larger than D_0 of a 3-armed star but is less than D_0 of a 12-arm star. From eq 2 and Table I, for polymers with $M = 1 \times 10^6$ the infinite-dilution hydrodynamic radii r_{hf} are in the ratio r_{h2}:r_{h3}:r_{h12} = 1:1.04:0.91.

Chain size can also be described with the radius of gyration. For an f-armed star polymer of arm molecular weight M_a, Grest and Kremer note[15]

$$R_{g,f}^{\;2} \sim M_a^{\;1.18} f^{\,0.41} \tag{3}$$

Since $M_a = M/f$, for chains of total molecular weight M

$$R_{g,f}^{\ 2} \sim M^{1.18} f^{-0.77} \tag{4}$$

In a Θ solvent, $R_g^2 \sim M^1$. Lodge et al.[2] report R_g measurements from static light scattering by linear and star polymers. Their experimental results are compared with eq 4 in Table II. Equation 2 was used to transform measured R_g values to a single M, the same for all f. Agreement of f dependence between experiment and theory is excellent.

The universal scaling law eq 1 has previously been derived[9,10] from a treatment of hydrodynamic interactions between two polymer chains, both chains being described at the Kirkwood–Risemann bead–spring level. The detailed order of bonds between the beads plays no role in the calculation. Instead, each chain is treated as having a radially symmetric density $g(s)$ of beads, $s = 0$ being the chain's hydrodynamic center. At this level of approximation, for a probe a in a matrix b

$$\alpha = C R_{ga} R_{gb}^{\ 3}/M_b \tag{5}$$

C being a constant which is independent of the molecular weight of the polymer.

Suppose in this[9,10] derivation that a linear probe (a 2-armed star) were to be replaced by a star polymer (an f-armed star) having the same M. The number of polymer beads in the linear probe and the star probe would be equal. The list of bead–bead interactions between pairs of chains is independent of f. There is one point in the derivation of eq 1 at which f is important, namely, the moment at which R_{ga} of eq 5 is evaluated for chains having the same M but different f. Noting that R_{gb} and C are both independent of probe f, while a concentrated system approximates Θ conditions

$$\alpha_f \sim M^{0.5} f^{-0.38} R_{gb}^{\ 3}/M_b \tag{6}$$

or

$$\alpha_f \sim M_a^{\ 0.5} f^{0.2} R_{gb}^{\ 3}/M_b \tag{7}$$

α is implicitly dependent on c because $R_g^2 \sim c^{-x}$ with $x \approx {}^1/_4$,[16] so $\alpha \sim c^{-2x}$. In terms of eq 1, ν and x are related via $\nu = 1 - 2x$. It is possible (adequate data appear to be lacking) that ν should be predicted to depend on f. Namely, as f is increased, the core of the star polymer becomes increasing dense and hence resistant to compression by neighboring polymer molecules. With increasing f, x might therefore tend to 0, in which case one would find $\nu \rightarrow 1$ as $f \rightarrow \infty$. For fixed M_a, Lodge et al.[2] in fact note that ν increases slightly (by perhaps 0.1) between $f = 2$ and $f = 12$.

The above considerations lead to qualitative predictions as to the relative D_s of linear and star polymers. The behavior of D_f of f-armed stars is well-described by the parameter

$$K_{f,2} = \frac{D_f/D_{0,f}}{D_2,D_{0,2}} \tag{8}$$

introduced by Lodge et al.[2]

To facilitate graphing the behavior of polymers of equal M, Lodge et al.'s data on 1.05×10^6 Da linear probes in a 1.3×10^6 Da matrix are used as a reference system. For this reference system, $\alpha = 0.645$ (with c in mg/mL) and $\nu = 0.525$. Equation 6 predicts, for a $1.05 \times 10^6 \times$ Da 12-armed star probe in the same 1.3×10^6 Da matrix, that $\alpha = 0.33$. If ν is the same for 2-armed and 12-armed stars, the qualitative prediction of the hydrodynamic scaling model is shown by Figure 1, line a. Over most of the accessible concentration range, $K_{12,2}$ gradually increases from 1.0 to 2.0. For polymers of equal total molecular weight, the hydrodynamic scaling model thus predicts that linear chains are slightly more retarded than are 12-armed stars by a polymeric matrix.

Table II
Theoretical[15] and Experimental[2] Radii of Gyration of f-Armed Stars, Reduced to Constant M, in Units of $R_{g,2}$

f	$(R_{g,f}/R_{g,2})_{\text{theo}}$	$(R_{g,f}/R_{g,2})_{\text{exptl}}$
2	1	1
3	0.85	0.87
12	0.50	0.51

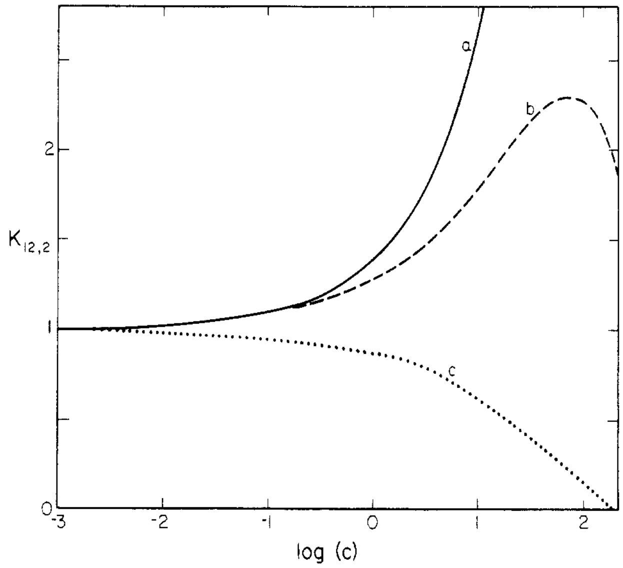

Figure 1. Hydrodynamic scaling predictions of $K_{12,2} = (D_{12}/D_{0,12})/D_2,D_{0,2}$ for 2- and 12-armed probes having equal total molecular weight (solid line) and equal arm molecular weight (dotted line). Dashed line (see text) shows how small parametric adjustments can yield excellent agreement between experiment and eq 1.

The details of the retardation are quite sensitive to the numerical parameters used to compute $K_{12,2}$. Line b of Figure 1 shows how $K_{12,2}$ is changed if α_{12} and ν are each slightly increased, namely, to their experimental values (0.39 and 0.608, respectively) for a 1.11×10^6 Da 12-armed star in the matrix polymer solution of the previous paragraph. With this small change in parameters, $K_{12,2}$ at first gradually increases (to ≈2.0) and then falls again.

In contrast to behavior at constant total molecular weight, one may consider behavior at constant arm molecular weight M_a. The experimental reference system is taken to have 1.11×10^6 Da 12-armed stars as probes in a 1.3×10^6 amu matrix. For this reference system, experiment finds $\alpha = 0.390$ and $\nu = 0.608$. From eq 7, the corresponding 2-armed star is predicted to have $M = 2 \times 10^5$ Da, $\nu = 0.608$, and $\alpha = 0.273$. For 2- and 12-armed stars of equal M_a, $K_{12,2}$ is described by line c of Figure 1. At constant arm molecular weight, the hydrodynamic scaling model is seen to predict that a concentrated matrix polymer solution is much more effective—by an order of magnitude or more at large c—at retarding star polymers than at retarding linear polymers.

Lodge et al.[1,2] give data on 3- as well as 12-armed stars. From ref 2, Table VIII, and applying $R_g \sim M^{1/2}$, R_g of polymers having the same M differs by perhaps 13% between 2- and 3-armed stars, implying that α of 2- and 3-armed stars also differs by 13% or so. For stars having equal M and ν, at elevated c $K_{3,2}$ would therefore be expected to be slightly larger than 1. For reasons not presently completely understood (though see below), ν

Table III
Values of α and ν from Lodge et al.[2] for Systems Having $M \approx P$

matrix M	probe M	α	ν
	$f = 2$		
1.3×10^6	1.05×10^6	0.645	0.525
6.3×10^5	4.22×10^5	0.312	0.589
1.4×10^5	1.79×10^5	0.140	0.663
	$f = 3$		
1.19×10^6	1.3×10^6	0.657	0.657
3.79×10^5	6.3×10^5	0.179	0.681
3.79×10^5	1.4×10^5	0.139	0.679
	$f = 12$		
1.3×10^6	1.69×10^6	0.413	0.617
1.3×10^6	1.11×10^6	0.390	0.608
1.4×10^5	4.67×10^5	0.164	0.666
1.4×10^5	5.5×10^4	0.0638	0.757

Table IV
Fits of α (Table III) to $\alpha = a_M M^g$ and Root-Mean-Square Errors (Rmse) in These Fits

f	a_M	g	% rmse
2	1.59×10^{-5}	0.756	6
3	1.05×10^{-5}	0.756	17
3	3.87×10^{-5}	0.657	11
12	1.11×10^{-5}	0.756	29
12	7.67×10^{-7}	0.96	26

differs slightly between different probe:matrix systems. The consequences of a 13% change in α between $f = 2$ and $f = 3$ can be swamped by changes in ν between linear polymers and simple stars. The effect on $K_{12,2}$ of the large change between $f = 2$ and $f = 12$ would be much more difficult to mask by changing ν, so the above discussion has emphasized $K_{12,2}$.

The hydrodynamic scaling model directly predicts α, not $K_{f,2}$, the direct test of the hydrodynamic scaling model being compared to eq 6 with α_f. The self-similarity approximation implicitly assumes that the probe and matrix polymers are largely identical. This is a reasonable approximation if the matrix and probe molecular weights M and P are equal, but the approximation presumably deteriorates if $M \ll P$ or $M \gg P$. Examination of measured α's is limited to those of Lodge et al.'s systems[2] with $M \approx P$, as listed in Table III. Table IV gives results from fits (at fixed f) of these data to the form

$$\alpha = a_M M^g \tag{9}$$

For 2-armed stars $g = 0.756$ in the best fit. For 3- and 12-armed stars, Table IV includes fits using both a_M and g as free parameters and also fits to a_M made while holding g at its best value for $f = 2$.

Figure 2 plots α from Table III against $(MP)^{1/2}$. The solid line represents the best fit to α for systems with $f = 2$. The dashed and dotted lines (which refer to $f = 3$ and 12, respectively) are drawn parallel to the solid line, using eq 6 to fix the ratio of the y intercepts. The hydrodynamic scaling model correctly predicts that α_3 and α_{12} are both less than α_2, α_3 being somewhat scattered, while experimentally α_{12} is typically slightly larger than predicted.

Discussion

As shown above, the hydrodynamic scaling model is successful at reproducing the major *qualitative* features of chain and star diffusion through matrix polymer solutions. Quantitative agreement with the simplified calculation of ref 9 is not perfect. Comparing probes of equal *total* molecular weight, the model correctly predicts that a concentrated matrix polymer is more somewhat effective at retarding a linear chain that a retarding a many-armed star. Comparing probes of equal *arm* molecular weight, the model correctly predicts that a concentrated matrix polymer is substantially more effective at retarding a many-armed star than at retarding a linear chain. Experimental measurements of D_l and D_* thus do not, at the present stage of experimental and theoretical development, serve to distinguish between hydrodynamic and entanglement-based pictures of polymer dynamics.

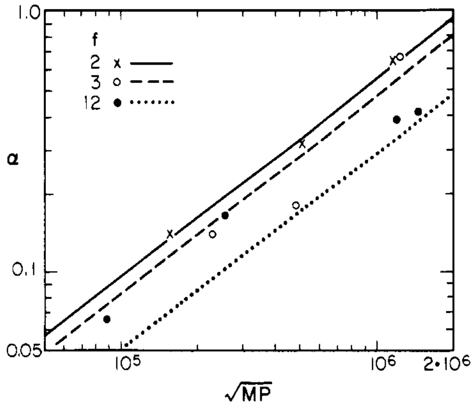

Figure 2. Dependence of α on $(MP)^{1/2}$ for 2-, 3-, and 12-armed stars. Solid line is a best-fit. Dashed and dotted lines had their vertical shifts determined by eq 6.

In refs 1 and 2, several other criticisms of the hydrodynamic scaling model were advanced. In particular, in Wheeler and Lodge's fits of eq 1 to their data, D_0 was alternatively used as a fitting parameter and as the $c \rightarrow 0$ limit of $D(c)$. The $c \rightarrow 0$ limit of D_0 was consistently smaller than the corresponding D_0 from a three-parameter fit to $D(c)$, especially for large-M probes in large-M matrices. The difference between fitted and measured D_0 has been attributed[17] to probe coil contraction (which increases D) with increasing c. Wheeler and Lodge[1] argue that the difference in the D_0's is not due to coil contraction because "the derivation of the stretched exponential advanced by Phillies already incorporates the probe coil contraction, and thus it should not be incorporated twice". A careful examination of the derivation of the universal scaling equation[10] shows, contrary to Wheeler and Lodge, that self-consistency requires including the consequences of probe coil contraction both in D_0 and in the exponential. A brief sketch of the universal scaling law's derivation should clarify this consistency requirement.

The extant derivation of the universal scaling law treats the drag coefficient $f(c,a)$ of a polymer coil of hydrodynamic radius a immersed in a polymer solution having concentration c. $f(c,a)$ and the self-diffusion coefficient are linked by the Einstein diffusion equation $D_s = k_B T / f(c,a)$. For a small concentration increment δc

$$f(c + \delta c, a) = f(c,a) + \left(\frac{\partial f}{\partial c}\right)_a \delta c + \left(\frac{\partial f}{\partial a}\right)_c \frac{da}{dc} \delta c \tag{10}$$

Since a depends but weakly on c, the final term is negligible by comparison with its neighbors. Equation 10 is integrated by imposing a self-similarity assumption (written here for the case that the matrix and probe polymer are the same species)

$$\left(\frac{\partial f}{\partial c}\right)_a = K(a) f(c,a) \tag{11}$$

Physically, eq 11 implies that the ability of an additional matrix polymer to retard the motion of the probe coil is proportional to the matrix polymer's hydrody-

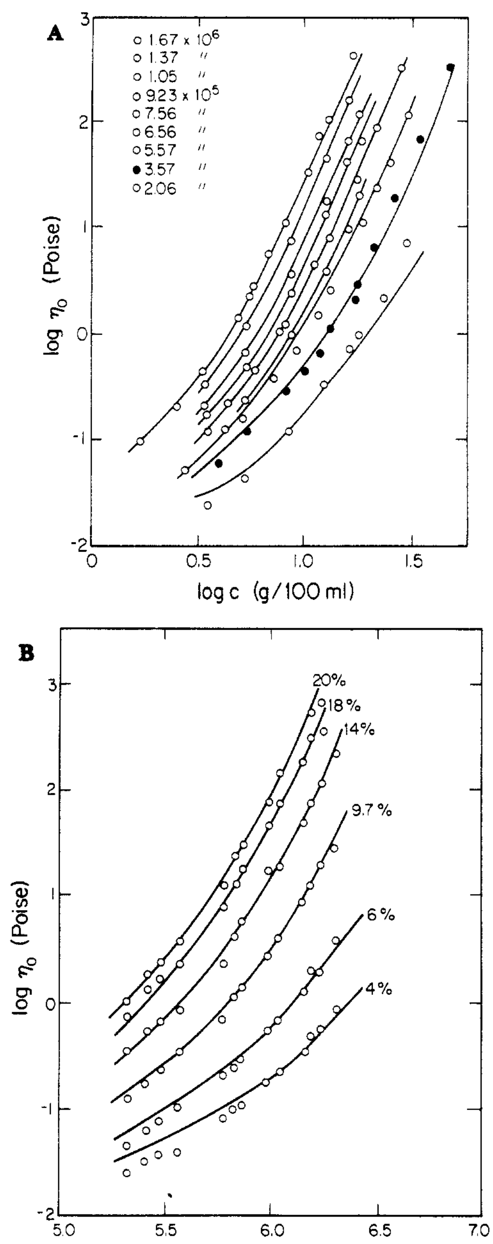

Figure 3. A. Zero-shear viscosity against concentration for polystyrene: toluene at 40 °C, based on measurements of Onogi et al.,[13] as presented by Doi and Edwards.[14] Solid lines: fits to the stretched exponential of eq 18, lines representing surfaces of constant M. B. Zero-shear viscosity against polymer molecular weight for polystyrene: toluene, 40 °C, based on Onogi et al.,[13] from Doi and Edwards.[14] Solid lines: fits to the stretched exponential of eq 18, lines representing surfaces of constant c.

namic interaction with the solvent, i.e., to the matrix polymer's drag coefficient f at concentration c. The integral of eq 10, under the approximation $\mathrm{d}a/\mathrm{d}c \approx 0$, is

$$f(c,a) = f_0 \exp\left(\int_0^c K \,\mathrm{d}c\right) \tag{12}$$

To apply eq 12, a form is needed for K. K is assumed to be dominated by the hydrodynamic interactions between pairs of nearby polymer chains. The effects of three-body chain–chain–chain interactions are approximated by the self-similarity assumption (eq 11); three-body interactions contribute to the difference between $f(c,a)$ and $f(0,a)$.

For an isolated polymer coil in solvent, $f_0 = 6\pi\eta a$, a being the hydrodynamic radius of the polymer and η being the solvent viscosity. The effect of a second polymer chain on the probe chain is best stated in terms of the polymer probe's mobility $\mu = 1/f$. For polymer chains whose hydrodynamic centers are separated by $\mathbf{R}$, a series expansion in a/R (where $R = |\mathbf{R}|$) gives[10] to lowest nonzero order

$$\mu = \mu_0\left(\mathbf{I} - \frac{9a^4\hat{\mathbf{R}}\hat{\mathbf{R}}}{8R^4}\right) \tag{13}$$

$\mathbf{I}$ being the identity matrix and $\hat{\mathbf{R}}$ denoting the unit vector. For one probe in a solution containing N other chains

$$\mu = \mu_0\left(\mathbf{I} - \sum_{j=1}^{N} \frac{9a^4\hat{\mathbf{R}}_j\hat{\mathbf{R}}_j}{8R_j^4}\right) \tag{14}$$

$\mathbf{R}_j$ being the vector separating the hydrodynamic centers of the probe and matrix polymer j. In this equation, μ is implicitly concentration-dependent because the polymer hydrodynamic radius a depends on c, namely, $a^2 \sim Mc^{-x}$ (except at very small c, where $x \approx 0$). Thus, $a^4 \sim c^{-2x}$. Furthermore, μ_0 refers to the actual hydrodynamic radius of the first polymer chain, not to the radius of the probe chain in the absence of the matrix chains, so μ_0 is weakly concentration-dependent through its inverse proportionality to a. In other words, μ_0 is the mobility (and $D = \mu_0 k_B T$ is the diffusion coefficient) which the polymer chain would have at infinite dilution, if at infinite dilution the chain had the same hydrodynamic radius which the chain has at the concentration c.

Polymers in solution do not occupy fixed relative positions, so eq 13 is properly averaged over the $\mathbf{R}_j$. Comparing eqs 10, 11, and 13

$$K(a) = Ca^4 \tag{15}$$

C being a concentration-independent constant embodying the hydrodynamic series expansions and ensemble averages described in ref 10. It follows that

$$m(c,a) = \mu_0 \exp\left(-\int_0^c Ca^4 \,\mathrm{d}c/M\right) \tag{16}$$

M is the polymer molecular weight, appearing here because the summation variable j has been replaced by the mass concentration c. In eq 16, μ_0 refers to the probe chain as it behaves in the presence of the other chains. μ_0 is still proportional to a^{-1}, so μ_0 is weakly concentration-dependent. Thus, in applying eq 16 or its diffusional equivalent

$$D \equiv k_B T\mu(c,a) = D_0 \exp\left(-\int_0^c Ca^4 \,\mathrm{d}c/M\right) \tag{17}$$

D_0 and a should both be interpreted to be c-dependent.

Wheeler and Lodge[1,2] further argue that the hydrodynamic scaling model has not received universal acceptance because (among other reasons) the model does not account for all features of the viscoelastic properties of concentrated solutions, such as the plateau modulus. The model's prediction of stretched-exponential c and M dependences does, however, describe measurements of the zero-shear viscosity η of random-coil polymers. For example, parts A and B of Figure 3 show data of Onogi et al.[13] on η of polystyrene:toluene at 40 °C, as presented by Doi and Edwards.[14] Doi and Edwards[14] describe Figure 3B as confirming $\eta \sim M^x$ with $x \approx 3.4$, the result $\eta \sim M^x$ with $x = 3.0$ being a major prediction of the reptation-scaling model. The data in parts A and B of Figure 3 are in fact well-described by stretched exponentials, solid lines in these figures representing

$$\eta = \eta_0 \exp(-\alpha c^\nu M^\gamma) \tag{18}$$

Table V
Nonlinear Least-Squares Fits of Stretched Exponentials of η of Polystyrene/Toluene (40 °C) Using Data of Onogi et al.[13] As Given by Doi and Edwards[14]

Part I

M, kDa	α_c	ν	% rmse
206	0.634	0.676	11
357	1.13	0.603	13
557	1.34	0.594	10
656	1.44	0.606	6.3
756	1.65	0.580	16
923	1.77	0.583	17
1050	1.78	0.606	12
1370	2.06	0.589	10
1670	2.29	0.578	13

Part II

c, g/100 mL	α_M	γ	% rmse
4	0.932	0.502	7.1
6	0.814	0.467	10
9.7	0.679	0.44	7.5
14	0.586	0.425	13
18	0.517	0.388	11
20	0.493	0.392	13

Part III

	α_M	ν	γ	% rmse
Figure 3A	1.79	0.590	0.426	18
Figure 3B	1.66	0.597	0.415	18

[a] Part I of this table uses eq 19 to fit points from Figure 3A at fixed M; part II of this table uses eq 20 to fit points from Figure 3B at fixed c; part III of the table describes fits of eq 18 to all the data in parts A and B of Figure 3. α, ν, and γ are for units: c in g/100 mL, $M = 1$ for a 100 000 Da polymer.

where $\eta_0 = 0.471$ cP is the solvent viscosity. For all the data in Figure 3A, a nonlinear least-squares fit to eq 18 with α, ν, and γ as free parameters obtains $\alpha = 1.788$, $\nu = 0.590$, and $\gamma = 0.426$. For all the data in Figure 3B, the same process obtains $\alpha = 1.664$, $\nu = 0.597$, and $\gamma = 0.415$. The root-mean-square error between either fit and its data set was approximately 18%. Parts A and B of Figure 3 represent largely overlapping sets of measurements, so the differences between α, ν, γ from these two parts are a robust estimator of the experimental error in determining the parameters. Hence, ν and γ are obtained with an error of ±1% or so, while α was obtained with an error of ±4%. As noted elsewhere[18] it is easier to determine ν than to determine α.

Table V shows results from nonlinear fits to obtain α, ν, and γ for individual values of M (Figure 3A) or c (Figure 3B). If data from Figure 3A (which gives η against c) for fixed M are fit to

$$\eta = \eta_0 \exp(-\alpha_c c^{\nu}) \tag{19}$$

one finds that ν falls with increasing M, ranging from $\nu = 0.675$ at $M = 2 \times 10^5$ to $\nu = 0.578$ at $M = 1.67 \times 10^6$. If data from Figure 3B (which gives η against M) for fixed c are fit to

$$\eta = \eta_0 \exp(-\alpha_M M^{\gamma}) \tag{20}$$

one finds that γ falls with increasing c, ranging from $\gamma = 0.502$ at $c = 4\%$ to $\gamma = 0.388$ at $c = 18\%$. The analytic form (eq 18) predicted by the hydrodynamic scaling model thus does give a good account of the dependence of η on polymer concentration and molecular weight. Equation 18 (with constant exponents) becomes increasingly reliable at large M and c.

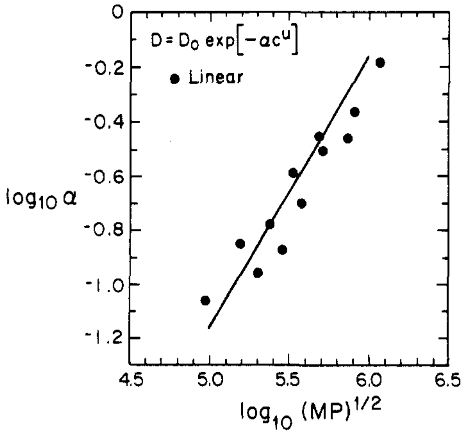

Figure 4. α against M for all of Wheeler and Lodge's data using linear probes, showing good agreement with $\alpha \sim (MP)^{1/2}$.

Wheeler and Lodge[1] advance the argument that "the stretched exponential is rather sensitive to changes in α ... the uncertainty in the experimental data is generally much too small to generate noticeable error bars on values of α ... Thus the wide scatter seen (in ref 2, Figure 17) in values of α ... must arise from inadequacies in the theory ...". First, in their Figure 17, Wheeler and Lodge include results on 2-, 3-, and 12-armed stars. Even if

$$\alpha = k(MP)^{1/2} \tag{21}$$

for each type of star separately, there is no reason to suppose that k will be the same for $f = 2, 3$, and 12. Indeed (cf. Figure 2), the hydrodynamic scaling model predicts that k depends on f. An appropriate test of eq 21 involves only one type of star at a time, not the three different types included in ref 2, Figure 17. Figure 4 shows an appropriate comparison of α measurements, plotting Lodge and Wheeler's α against M for PS with a single f, viz. $f = 2$. Most points are within 10% of a line slope 1. The scatter in values of α is not large, just as expected if the hydrodynamic scaling theory and its prediction $\alpha \sim (MP)^{1/2}$ were basically adequate to treat diffusion. Second, with respect to their argument that α should not be scattered, note Table V.iii. Between parts A and B of Figure 3, there is a 7% change in α, even though the two parts include many of the same data points. The random noise in determining α, even with good data, is large.

Finally, Wheeler and Lodge[1,2] argue that their comparison of ν and M (ref 2, Figure 18) does not show the predicted transition from the small-M, $\nu = 1$ limit to the large-M, $\nu = {}^1/_2$ limit. Their figure tends to obscure the transition apparent in their data. Namely, within the hydrodynamic scaling model, this predicted transition is driven by the change from small-M to large-M chain contraction. While large linear chains and large stars all contract with increasing matrix concentration, for fixed polymer molecular weight the exact degree of contraction (as measured by x of the scaling law $R_g \sim c^x$) is expected to be sensitive to the number of arms and to the relative molecular weights of probe and matrix polymers. For each f and M/P, ν should show a clean dependence on polymer size. The transition need not occur at the same P for each f. Indeed, as noted in ref 2, u is larger for stars than for linear polymers, as would occur of the transition required a larger M for star polymers than for linear polymers. Combining ν values for different f and M/P, as done in ref 2, Figure 18, therefore tends to mask the transition.

It is not here claimed that the hydrodynamic scaling picture is in all respects complete. As presently developed, the model does not include detailed consequences of chain rigidity, short-range hydrodynamic interactions, polymer internal modes, or the detailed form of the chain–chain correlation hole. Nor has the model yet been extended to treat other solution transport properties, such as probe diffusion, sedimentation, or the plateau modulus. A rigorous justification of the self-similarity approximation—one capable of predicting correction terms in a systematic way—is presently lacking.

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Enantioselective Permeation of α-Amino Acid Isomers through Poly(amino acid)-Derived Membranes

Atsushi Maruyama,* Noriyuki Adachi, Takehisa Takatsuki, Masanori Torii, Kohei Sanui, and Naoya Ogata

Department of Chemistry, Faculty of Science and Technology, Sophia University,
7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan

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ABSTRACT: Poly(L-glutamates) having amphiphilic side chains of (*n*-nonylphenoxy)oligo(oxyethylene) (NON*x*-PLG) were observed to possess potential properties as membrane materials for resolving optical isomers of α-amino acids. Permeation rate ratios of >8.0 for the D isomer to L isomer of tyrosine and tryptophan were achieved. Permeation of amino acids for times >500 h did not cause any drop in selectivity. Operating temperature considerably affected the permselectivity of the isomers. Since NON*x*-PLG adopted mainly an α-helical structure in its cast film and formed a liquid crystalline (nematic) type mesophase, this ordered structure of poly(amino acid) derivatives was considered to be the reason for the enantioselectivity of the membrane.

Introduction

With the rapid production of novel specialty (highly functional) materials such as pharmaceutics, bioactive substances, and liquid crystals, improvement of preparative separation methods for geometrical isomers including optical isomers is currently demanded. Although the membrane separation process has marked advantages in production such as ease of handling, instrumental simplicity, and efficiency in energy as compared to the chromatographic separation process, a practical membrane having the capability of separating optical isomers has not yet appeared except in the form of liquid membranes. These are triphasic systems composed of aqueous–organic–aqueous solutions utilizing optically active crown ethers, originally demonstrated by Cram et al.[1]

The permeation of substances through a membrane is determined by the partitioning behavior of the substances with respect to the membrane and their diffusibility (or mobility) in the membrane. Thus, to improve enantioselectivity of a membrane, considerable effort should be made to optimize these two factors. The partitioning behavior of optical isomers is largely influenced by the structure and number of recognition sites in the membrane. However, diffusibility is difficult to control because optical isomers have identical molecular sizes.

To refine the selectivity of polymeric membranes, we paid particular attention to the microenvironmental nature in the vicinity of the recognition sites as well as the distribution (or assembling) mode of the recognition sites.

Aqueous liquid membranes with amphiphilic substances such as surfactants were reported to discriminate geometric isomers of amphiphilic substances or of hydrocarbons in terms of their permeation or partitioning behavior based on the differential solubilizing effect.[2] In this case, the hydrophilic–hydrophobic balance of amphiphilic substances was considered to play a significant role. Colonna et al.[3] reported the successful asymmetric oxidation of electron-poor olefins such as chalcones to optically active oxiranes in the triphase system (water/organic solvent–poly(amino acid)). In this case, the poly(amino acid), which provides the stereoselectivity of the reaction, was placed at the interface of an emulsion of the organic phase in the aqueous phase. The hydro-

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* To whom correspondence should be addressed.

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