lhs and rhs of (A) are completely different. Hence, even in the linear $c$-dependence regime (A) is false. The main objective of this theory was to have a theory beyond this regime, but in the nonlinear $c$-dependence regime there is no way to equate $Q$ and $cAp^{-\kappa}$. If we were to accept (A) there, we would have another bad contradiction, because (A) is not correct in any regime.
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# The Ubiquity of Stretched-Exponential Forms in Polymer Dynamics[†]

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ABSTRACT: Literature results on the zero-shear viscosity $\eta$, rotational diffusion coefficient $D_R$, and sedimentation coefficient $s$ of polymers in good, $\Theta$, and marginal solvents are reanalyzed in terms of the universal scaling equation $A = A_0 \exp(-ac^{\upsilon})$, where $A$ is a transport coefficient, $c$ is the polymer concentration, and $a$ and $\upsilon$ are scaling constants. This equation gives reasonably good descriptions of almost all results on $\eta$, $D_R$, and $s$, a single pair of parameters $(a,\upsilon)$ sufficing for results from all concentrations. There is apparently no qualitative change in transport behavior between the dilute ($c < c^*$) and semidilute ($c \gg c^*$) regimes.

## Introduction

The entire modern (through early 1986) literature on polymer self-diffusion was recently reexamined,[1,2] finding that the dependence of $D_s$ on polymer concentration is described by a stretched exponential

$$D_s = D_0 \exp(-ac^{\upsilon}) \qquad (1)$$

$D_0$ being the diffusion coefficient at infinite dilution. $\upsilon$ and $a$ are constants that differ from system to system but are independent of $c$, with no change between the meltlike, semidilute, and dilute concentration regimes. (Recent data of Lodge et al.[3] reveals a change in $D_0$ at $c > 0$; the change correlates well with changes in $R_g$ at the same concentrations[4]). The stretched-exponential form affords a description of polymer and protein self-diffusion which, while in good agreement with experiment, is at variance with some[5-9] scaling-law descriptions for polymer solution dynamics.

A heuristic picture—the hydrodynamic scaling model—which predicts eq 1 was recently presented.[2] The model predicts how $D_0$, $\upsilon$, and $a$ depend on polymer molecular weight $M$, namely, $D_0 \approx M^{-1/2}$ and $a \approx M^1$, with $\upsilon = 1$ at small $M$ and $\upsilon = {}^1/_2$ at large $M$. Physically, $a$ is determined by the strength of whole-chain–whole-chain hydrodynamic interactions, i.e., $a$ increases with increases in chain size. $\upsilon$ is determined by chain contraction. Unlike small chains, large chains shrink at high $c$, so $\upsilon$ is not the same for big as for small polymers.

A major positive contribution of the reptation/scaling models of polymer dynamics is the idea that different transport properties are interrelated,[5] so that fixing the $c$ and $M$ dependences of $D_s$ constrains the $c$ and $M$ dependences of the zero-shear viscosity $\eta$, entanglement relaxation time $T_R$, rotational diffusion coefficient $D_R$, and sedimentation coefficient $s$. If $\eta$ and $D_s$ are determined by the same polymer motions, their $c$ and $M$ dependences should be related. It might appear incongruous that eq 1 describes $D_s$, while an incompatible scaling equation

$$A \approx c^x M^y \qquad (2)$$

has been said[5-9] to describe $\eta$, $D_R$, and $s$. This paper reexamines published studies on polymer transport, showing that the apparent incongruity is illusory. Experimental results on $\eta$, $D_R$, $s$, and $D_s$ are consistent, a stretched exponential providing a good description for each of these parameters.

The next three sections review literature studies on viscosity, rotational diffusion, and sedimentation, com-

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**Table I**
**Comparison of Viscosity Measurements with the Stretched Exponential $\eta = \eta_0 \exp(ac^v)$ $\eta_0$ Being the Solvent Viscosity and $a$ and $v$ Being Fitting Parameters, with $c$ in g/L[a]**

| material + solvent, $M$ in kD | $a$ | $v$ | % rmse |
|---|---|---|---|
| polystyrene:THF[15] | | | |
| 390 | 0.279 | 0.63 | 11 |
| 600 | 0.37 | 0.62 | 7 |
| 1800 | 0.70 | 0.57 | 16 |
| 7800 | 1.27 | 0.59 | 17 |
| poly($\alpha$-methylstyrene):[12-14] + toluene[13] | | | |
| 1120 | 0.51 | 0.59 | 9 |
| 332 | 0.217 | 0.65 | 5 |
| 146 | 0.115 | 0.71 | 10 |
| + *trans*-decalin[13] | | | |
| 1120 | 0.22 | 0.82 | 13 |
| 332 | 0.087 | 0.88 | 7 |
| 146 | 0.049 | 0.92 | 7 |
| + $\alpha$-chloronaphthalene[13] | | | |
| 1650 ($\eta$ < 250 P) | 0.60 | 0.60 | 4 |
| 1650 (all data) | 0.74 | 0.55 | 18 |
| + $n$-butyl benzylphthalate[13] | | | |
| 1650 ($\eta$ < 250 P) | 0.088 | 1.13 | 8 |
| 1650 (all data) | 0.19 | 0.91 | 32 |
| 440 ($\eta$ < 250 P) | 0.058 | 1.01 | 10 |
| 440 (all data) | 0.096 | 0.90 | 25 |
| + undecyl anisitate[12] | | | |
| 870 (3-arm star) | 0.027 | 0.82 | 0.1 |
| 3570 (3-arm star) | 0.050 | 0.83 | 16 |
| 440 | 0.010 | 0.93 | 4 |
| 1820 | 0.00217 | 1.33 | 7 |
| + $\alpha$-chloronaphthalene[12] | | | |
| 870 (3-arm star, $T$ = 50 °C) | 0.27 | 0.67 | 10 |
| 870 (3-arm star, $T$ = 20 °C) | 0.50 | 0.57 | 4 |
| 3570 (3-arm star) | 0.81 | 0.55 | 3 |
| + $\alpha$-chloronaphthalene[14] | | | |
| 146 | 0.10 | 0.74 | 2 |
| 1120 | 0.46 | 0.62 | 4 |
| + *trans*-decalin[14] | | | |
| 146 | 0.07 | 0.82 | 19 |
| 1120 | 0.16 | 0.90 | 26 |
| + $n$-undecyl anisitate[14] | | | |
| 60 | 0.011 | 1.13 | 9 |
| 146 | 0.041 | 0.97 | 5 |
| schizophyllan:$H_2O$[11] | | | |
| 128 | 0.107 | 0.80 | 11 |
| 220 | 0.323 | 0.69 | 18 |
| 340 | 0.567 | 0.65 | 23 |
| 460 | 0.815 | 0.67 | 21 |
| 960 | 1.68 | 0.58 | 33 |
| 1730 | 2.40 | 0.64 | 20 |
| 4300 | 3.37 | 0.64 | 31 |

[a] % rmse = % root-mean-square error.

paring data with stretched exponentials akin to eq 1. Our interest is in polymer solutions, not polymer melts. Calculations used a nonlinear least-squares fitting program[10] based on the simplex method. The error measure being minimized was the mean-square fractional difference between data and theory, relative to the actual data.

## Viscosity

As representative samples of a large literature, we analyzed measurements of zero-shear viscosity by Enomoto et al.[11] on schizophyllans, by Kaijura et al.,[12] Isono and Nagasawa,[13] and Takahashi et al.[14] on poly($\alpha$-methylstyrenes), and by Jamieson and Telford[15] on polystyrene–tetrahydrofuran. All polymers were highly monodisperse and were studied over substantial ranges of concentration and molecular weight. Data were compared with

$$\eta = \eta_0 \exp(ac^v) \tag{3}$$

$\eta_0$ being the viscosity at $c = 0$. In some cases, results were also compared with a scaling-law $\eta \approx c^x$. The analysis is

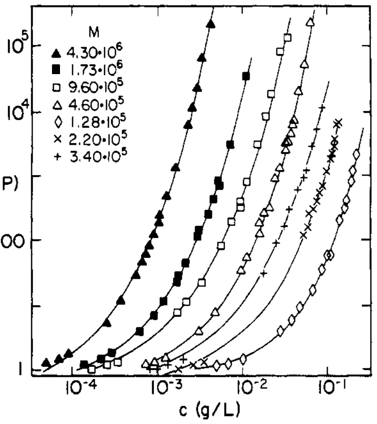

**Figure 1.** Viscosity of aqueous monodisperse schizophyllans[11] and fits (lines) to the scaling-law form. The curves, which for legibility are omitted at small $\eta$, extrapolate to the viscosity of pure water at $c = 0$.

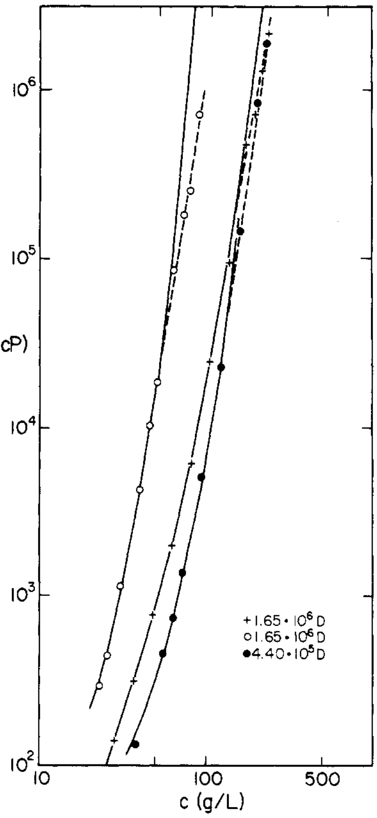

**Figure 2.** Visocity of poly($\alpha$-methylstyrenes)[14] of several molecular weights in $\alpha$-chloronaphthalene and $n$-butyl benzylphthalate, showing the transition from stretched-exponential forms (solid lines) to power-law behavior (dashed lines) above 200 P. Note the failure of a stretched exponential to follow the power-law behavior, showing the lack of arbitrary flexibility of the stretched-exponential form.

summarized by Table I, Figures 1–3, and supplementary Table S1 and Figure V1.

Enomoto et al.[11] studied the triple-helical polysaccharide schizophyllan in aqueous solution, using monodispersed materials with $M$ ranging from 128 kD to 4.3 MD. Over the region $0.18 < c < 205$ g/L, schizophyllan solutions attain viscosities as high as $10^5$ cP. Schizophyllans are highly rigid, with a liquid–liquid crystal phase transition at concentrations above those included in this study. Figure 1 shows that $\eta$ follows fairly well (10–20% root-mean-square error) a stretched exponential. Curves represent fits with $\eta_0$ held fixed; near $c = 0$ the calculated curves (omitted at small $c$ for legibility) go to the viscosity

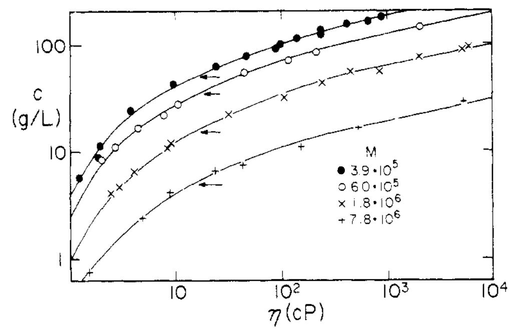

**Figure 3.** Viscosity[15] of monodisperse polystyrenes in tetrahydrofuran and fits (lines) to the scaling law of eq 3. One function with fixed parameters describes $\eta$ at all polymer concentrations, there being no indication of a discontinuity near $c^*$ (arrows).

of pure water. Three-parameter fits which take $\eta_0$, $a$, and $\upsilon$ as fitting parameters cannot readily be distinguished from the two-parameter fits seen in the figure. As seen in Table I, a increases substantially with increasing $M$. Except for the lowest-molecular-weight polymer, $\upsilon \approx 2/3$.

Nagasawa and collaborators[12-14] studied poly($\alpha$-methylstyrenes). Analyses of their results appear in Figures 2 and V1 and Table I. In chronological order:

Kajiura et al.[12] studied star and linear poly($\alpha$-methylstyrenes) in *n*-undecyl anisitate ($\Theta$ solvent) and $\alpha$-chloronaphthalene (good solvent), observing solutions with $\eta$ in the range 2–1370 P. Fits with $\eta_0$ fixed agree well with eq 3 with root-mean-square errors of 0.1–16%.

Isono et al.[13] examined linear polymers in toluene and $\alpha$-chloronaphthalene (good solvents) and in *trans*-decalin and *n*-butylbenzyl phthalate (poor solvents); $c$ extended up to 220 g/L. Polymer molecular weights ranged from 146 kD to 1.65 MD. Supplementary Figure V1 shows good fits to stretched exponentials. In Figure 2, for $\eta < 250$ P $\eta$ is well-described by eq 3. Above 250 P, there is a transition from stretched exponential (solid lines) to power-law behavior (dashed lines). Numerical analysis (supplementary Table S1) on data with $\eta > 250$ P finds power-law exponents $\upsilon$ in the range 5–7. Efforts to force-fit stretched exponentials through the high-viscosity points of Figure 2 failed, root-mean-square errors being 3–4 times larger than those of fits confined to lower viscosity data. Stretched exponentials are thus seen not to be arbitrarily malleable; they cannot describe power law behavior accurately.

Takahashi et al.[14] used a wide variety of solvents. Their data on 146 kD and 1.12 MD polystyrene in $\alpha$-chloronaphthalene is described well (root-mean-square errors 2–4%) by eq 3. Their results on *trans*-decalin solutions, given only for very high concentrations ($c > 230$ g/L, $\eta > 6500$ cP), are not described as well by a stretched exponential. In both solvents, $\upsilon$ depends but weakly on $M$, while $a$ increases substantially with increasing $M$.

Jamieson and Telford[15] obtained $\eta$ for polystyrene–tetrahydrofuran for $0.75 < c < 183$ g/L. In this concentration range, $\eta$ increases to more than 6000 cP. Figure 3 compares their data with fits to eq 3. $\eta_0$ was fixed at the solvent viscosity. Agreement with eq 3 is visibly good. As seen in Table I, $\upsilon$ is virtually independent of $M$, while $a$ increases from 0.28 to 1.27 with increasing $M$.

Jamieson and Telford[15] interpreted their data in terms of scaling laws, proposing $\eta \approx c^4$ for $c > c^*$. Table S1 repeats this analysis, finding a scaling exponent $x$ between 3.5 and 4.0. Fits to the power law are no better than fits to eq 3, even though the power law only applies to those measurements with $c > c^*$. From Figure 3, eq 3 with constant parameters describes all the data, with no transition in rheological behavior between dilute ($c < c^*$) and semidilute ($c \gg c^*$) regimes.

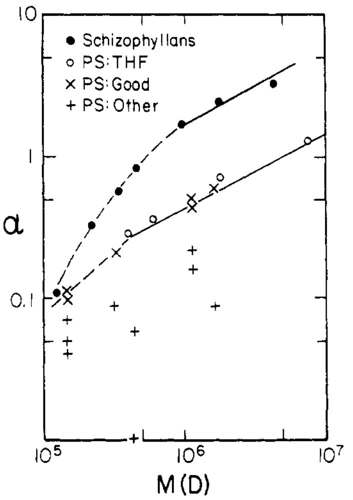

**Figure 4.** Dependence of the scaling parameter $a$ on polymer molecular weight. Solid lines have a slope of $^1/_2$; dashed lines are guides to the eye. Abbreviations: PS, polystyrene; THF, tetrahydrofuran; good, in good solvents; other, in poor or $\Theta$ solvents.

Figure 4 correlates log $a$ and log $M$ for the above systems. Values of $a$ for high-molecular-weight polystyrenes and polystyrene derivatives in good solvents fall on a single line of slope $\sim ^1/_2$. Equation 3 thus serves to correlate data on a series of different systems. The hydrodynamic scaling model indicates that $a$ is determined by polymer size. Reducing the solvent quality reduces $R_g$, so transferring a polymer from a good to a poor solvent should reduce $a$, as confirmed by the figure. The hydrodynamic scaling model also interprets the schizophyllan results. The four lower molecular-weight schizophyllans are expected to be rodlike, while the larger schizophyllans are coil-like.[11] $a$ of the larger schizophyllans lies near a line of slope $\sim ^1/_2$, which is the same as the slope for other random-coil polymers in good solvents. Since $a$ is determined by $R_g$, for polymers of fixed $M$ $a$ should increase with increasing polymer persistence length. Relatively rigid schizophyllans should then have a larger $a$ than random-coil polystyrenes of the same $M$, as is observed. For small, rodlike schizophyllans, Figure 4 gives $a \approx M^g$ for $g$ between 1.5 and 2. These materials may not be totally rigid, so the limiting slope for true rigid rods could be larger than 2.

## Rotational Diffusion

Rotational diffusion coefficients $D_R$ of rodlike polymers can be obtained from dynamic depolarized light scattering (DDLS) or from the field-free relaxation of transient electric birefringence (TEB). Published studies of $D_R$ at large $c$ were made on a single concentrated species, not a probe species in a matrix. DDLS data therefore represents the pair (two-body) rotational diffusion coefficient $D_{R2}$, not the self rotational diffusion coefficient $D_R$. If orientation correlations between nearby rods are relatively weak, as is often assumed, $D_{R2}$ and $D_R$ would be nearly equal.

Literature measurements of $D_R$ were fit to

$$D_R = D_{R0} \exp(-ac^{\upsilon}) \qquad (4)$$

$D_{R0}$ is $D_R$ in the limit $c \rightarrow 0$. We analyzed (Table II) Mori et al.'s results[16] (as described by Teraoka et al.[17]) on poly($\gamma$-benzyl-L-glutamate) (PBLG) in *m*-cresol, Maguire et al.'s work[18] on M - 13 virus in 10 mM KCl, Statman and Chu's[19] findings on poly(*n*-butyl isocyanate) in $CCl_4$, and Zero and Pecora's[20] data on PBLG in 1,2-dichloroethane. The first two studies used TEB; others relied on DDLS.

**Table II**
**Comparison of Rotational Diffusion Measurements with the Form $D_R = D_{R0} \exp(-ac^{\nu})$, $D_{R0}$ Being Kept Fixed**[a]

| $M$, kD | $D_{R0}$, $s^{-1}$ | $a$ | $\nu$ | % rmse |
|---|---|---|---|---|
| poly($\gamma$-benzyl-L-glutamate):*m*-cresol | | | | |
| 73 | (-) | 17.8 | 0.93 | 9 |
| 97 | (-) | 26 | 0.77 | 6 |
| 150 | (-) | 148 | 0.78 | 12 |
| poly($\gamma$-benzyl-L-glutamate):$(CH_2Cl)_2$ | | | | |
| 150 | 15 500 | 131 | 1.23 | 12 |
| 170 | 11 200 | 523 | 1.56 | 15 |
| 210 | 6 250 | 18200 | 2.43 | 4 |
| M - 13:0.01 M KCl | | | | |
| M - 13 - WT ($L$ = 8920 Å) | (-) | 71 | 0.69 | 8 |
| M - 13 - $T_n$3 - 15 ($L$ = 15 750 Å) | (-) | 52 | 0.59 | 10 |
| poly(*n*-butyl isocyanate):$CCl_4$ | | | | |
| 75 | 12 500 | 2.82 | 0.37 | 3 |

[a] % rmse = percent root-mean-square error. (-) = data reported as $D_R/D_{R0}$. $L$ = length. $a$ matches concentration of g/L.

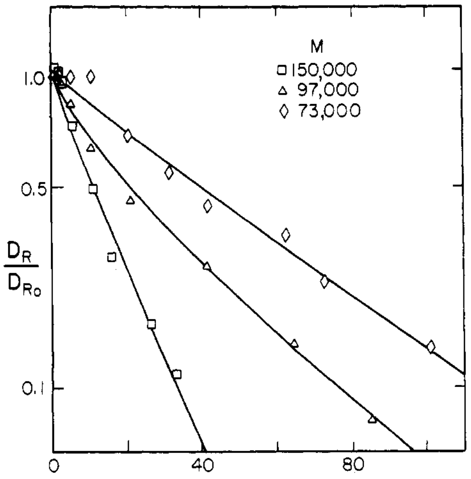

**Figure 5.** Rotational diffusion coefficients(19,20) of poly($\gamma$-benzyl-L-glutamate) in *m*-cresol, as compared with stretched exponentials.

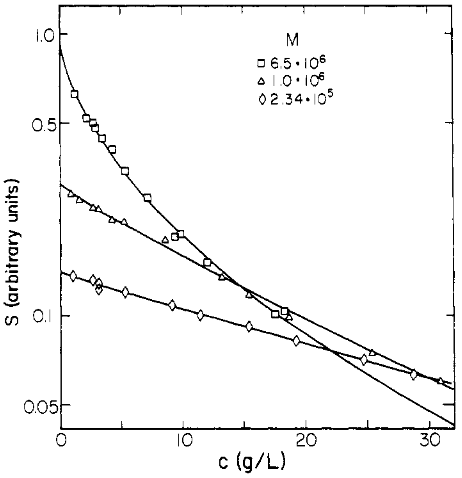

**Figure 6.** Sedimentation coefficients of poly($\alpha$-methylstyrenes) in cyclohexane (after ref 32) under $\Theta$ conditions and three-parameter fits to eq 9. $s$ was rescaled[25] by an arbitrary constant.

In all systems $D_R$ is consistent at the 10% level with eq 4. $a$ (Table II) increases very sharply with increasing $M$. Figure 5 shows Mori et al.'s[19,20] data. The points appear to be scattered randomly around the fitted curves (solid lines); root-mean-square errors were 6–12%.

Several of these experiments were intended to test the Doi–Edwards[21-23] theory of rod diffusion in semidilute solution. Such experiments had no reason to obtain extensive data at low concentration, so fits to $D_R$ are less reliable than were fits to $\eta$ or $D_s$. The available measurements of $D_R$ are consistent with the supposition that eq 4 is a good approximation.

## Sedimentation

For consistency with the universal scaling law,[24] the sedimentation coefficient $s$ should obey

$$s = s_0 \exp(-ac^{\nu}) \tag{5}$$

where $s_0$ is the sedimentation coefficient at zero concentration. We tested eq 5 against a wide variety of sedimentation measurements, including those reviewed by Nystrom and Roots,[25] Roots and Nystrom's results[26,27] on polystyrenes in good and marginal solvents, and Nystrom and Bergman's work[28] on hydroxypropylcellulose–water. Nystrom and Roots[25] reviewed on polymer sedimentation in good and $\Theta$ solvents. Polymers included linear and branched polystyrene,[29-31] poly($\alpha$-methylstyrene),[32] poly(2-(triphenylmethoxy)ethyl methacrylate) (TEM),[33] poly(methyl methacrylate),[33] and polyisobutylene.[34,35] $\Theta$ solvents were cyclopentane,[29] cyclohexane,[30,31] and *trans*-decalin,[28,32] good solvents included benzene,[28] toluene,[28,30,33] and octane,[34,35] for a total of 27 polymer–solvent pairs. For each pair, eq 5 was fit to the data in three ways. (For full details, see supplemental material Table S3 and Figures S1–S12.) A three-parameter fit retained $s_0$, $a$, and $\nu$ as fitting parameters. A two-parameter fit was obtained by constraining the curve to pass through the lowest concentration datum. Figures S5, S6, S7, S8, S11, and S12 compare these two fits. Another two-parameter fit was performed by making a linear fit to the first few data points, extrapolating to $c = 0$ to find $s_0$ and using the linearly extrapolated $s_0$ in eq 5. In $\Theta$ solvents, these three approaches gave similar results. In good solvents, complications arose, perhaps because the linear extrapolations to $c = 0$ did not yield good values for $s_0$.

Figure 6, based on work of Mijnlieff and Jaspers[32] on poly($\alpha$-methylstyrenes), is representative of results on polymers in $\Theta$ solvents. Stretched-exponential forms describe the data well. The figures show three-parameter fits, with root-mean-square errors under 6%. Two-parameter fits through the first data point give curves that are practically indistinguishable from those in the figures. Supplementary Figure V2 shows very similar data of Nystrom et al.[29]

The effect of $M$ on $s$ is smaller at large $c$. The reptation/scaling models predict $s$ to be independent of $M$ for $c > c^*$. The calculated curves in Figure 6 do not converge; instead, they cross and continue on their separate ways. Note in Figure 6 that the 6.5 MD points stop when they reach the 1 MD curve, with no measurements on the 6.5 MD material for $c > 20$ g/L. The 1.0 MD points similarly

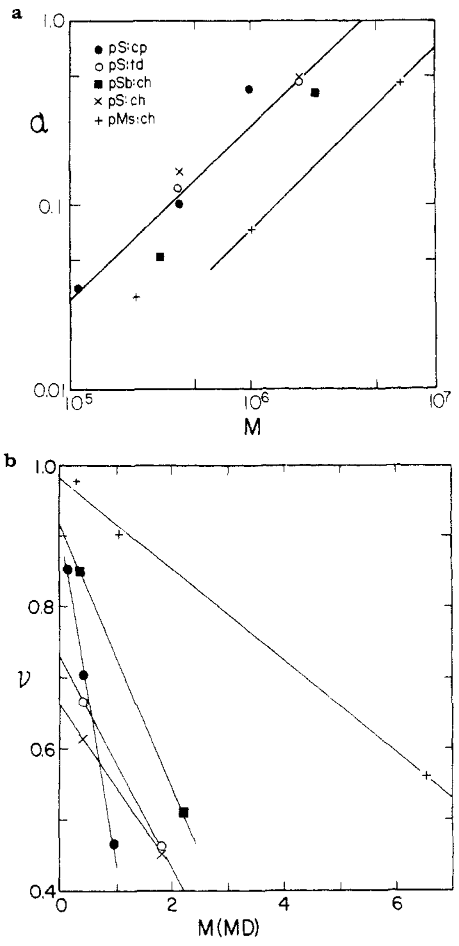

**Figure 7.** (a) $a$ against polymer molecular weight for ps–cp[29] (polystyrene–cyclopentane), ps–td[30,31] (polystyrene–*trans*-decalin), pSb[28] (branched polystyrene), pS[28] (linear polystyrene), and pMS[32] (poly($\alpha$-methylstyrene)) in ch (cyclohexane). (b) $v$ against $M$, using the symbols of Figure 7a.

stop on reaching the 234 kD data. Without data at concentrations beyond the crossing points of the curves, Figure 6 does not reveal if $s$ is independent of $M$ at large $c$.

Molecular weight dependences of $s$, $a$, and $v$ are qualitatively similar for all polymer–Θ solvent combinations. In each system, $d^2 \log s/dc^2$ increases with increasing $M$, especially at low $c$. As seen in parts a and b of Figure 7, with increasing $M$ $a$ increases and $v$ decreases, in agreement with the qualitative predictions of the hydrodynamic scaling model. The narrow range over which $M$ was varied, and the small number of different molecular weights studied for each polymer, makes it difficult to form generalizations. Additional data on a single polymer over a wide range of molecular weights would be desireable.

Sedimentation in a good solvent is represented by Figure 8, which shows results on TEM–toluene from Nystrom et al.,[33] and supplementary Figure V3, which shows $s$ of poly($\alpha$-methylstyrene).[32] Stretched exponentials describe well the behavior of $s$. The $M$ dependence of $s$ is substantially less in good solvents than in Θ solvents. Relative to polymers under Θ conditions, $(ds/dc)/s$ of polymers in good solvents increases rapidly as $c \to 0$. At concentrations below those for which measurements were made, the calculated stretched-exponential curve increases very sharply. It is not clear if this effect is real or if $s$ deviates from eq 5 at extremely small $c$.

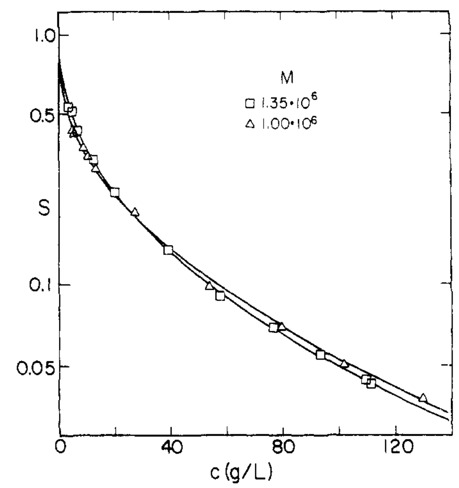

**Figure 8.** Sedimentation coefficients (in arbitrary units) of branched poly(2-(triphenylmethoxy)ethyl acrylate) (after ref 33) in the good solvent toluene at 25 °C and three-parameter fits of the data to eq 5.

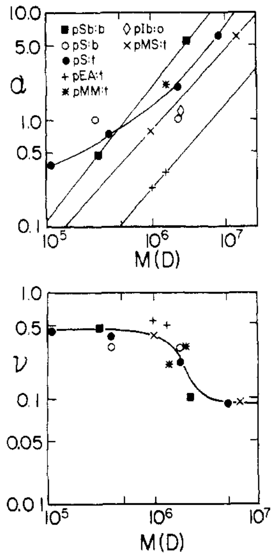

**Figure 9.** (a) $a$ against polymer molecular weight for branched polystyrene[28] (pSb), linear polystyrene[28,30] (pS), poly(2-(triphenylmethoxy)ethyl acrylate)[33] (pEA), poly(methyl methacrylate)[33] (pMM), polyisobutylene[34,35] (pIB), and poly($\alpha$-methylstyrene)[32] (pMS) in the good solvents benzene (b), toluene (t), and octane (o). (b) $v$ against polymer molecular weight for polymers in good solvents, using the systems and symbols of Figure 10a.

Parts a and b of Figure 9 give fitting parameters for all of the polymer–good solvent combinations. The available data are largely consistent with $a \approx M^1$, though more data on a single polymer is needed. At low $M$, $v$ is $\sim{}^1/_2$; at large $M$, $v$ falls to ~0.1 or less. This drop in $v$ between small and large $M$ occurs at the same molecular weights as the low-to-high $M$ crossover previously found[1,36] for $D_s$ of polymers in good solvents.

Roots and Nystrom[26,27] compared $s$ of polystyrenes ($M$ up to 20.6 MD) in toluene (good solvent) and butan-2one (marginal solvent). Results of three-parameter fits to their data appear in Table S2 and as Figures S13–S22 of the supplementary material. The fits have root-mean square errors of 2–5%. Figure 10 shows for these systems that $a$ increases and $v$ falls with increasing $M$. The hydrodynamic scaling model predicts $a$ to be proportional to polymer size. As expected from this prediction, $a$ is substantially (3–8 times) larger for a given polymer in a good solvent than in a marginal solvent. For the largest polymers, extrapolation of $s$ to $c \to 0$ yields unreasonably big values of $s_0$, implying that eq 5 is not always adequate in extremely dilute solution.

Nystrom and Bergman[28] measured $s$ of hydroxypropyl

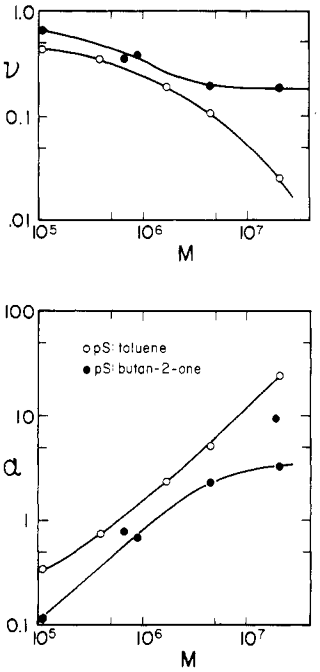

**Figure 10.** Comparison of (a) $a$ and (b) $\upsilon$ for polystyrenes in the good solvent toluene and the marginal solvent butan-2-one, based on fits of eq 5 to the data of Roots and Nystrom.[26,27]

cellulose (HPC) in water for $0 < c < 93$ g/L. The temperature was varied from 25 °C (good solvent conditions) to 40 °C, the $\Theta$ temperature being 41 °C. Three-parameter fits to the data are in the supplementary material as Table S2 and Figures S23–S27. As previously noted with polystyrenes, transferring HPC from good to theta conditions increases $\upsilon$ slightly and reduces $a$ by more than 50%. From Figures S23–S27, eq 5 may overestimate $ds/dc$ at large $c$.

## Discussion

Our primary objective was to show that $\eta$, $D_R$, and $s$ all depend on $c$ via stretched exponentials. Just as the reptation/scaling models[4-8,36] predict an internal consistency in the $c$ and $M$ dependences of polymer transport coefficients, the universal scaling law[1,2,36] of eq 1 reveals a consistent form (eq 1 and 3–5) for the major transport coefficients, including $D_s$, $\eta$, $D_R$, and $s$. Even data that were previously found to have a power-law dependence on $c$ were here shown to fit stretched exponentials, over concentration ranges wider than those over which the power law was valid.

In almost all cases, fixed values of $\upsilon$ and $a$ sufficed to describe data at all concentrations at which measurements were made. No transition is apparent between dilute and semidilute regimes. At very large viscosities, $\eta$ changes from a stretched-exponential to a power law dependence on $c$. This transition (seen for a 440 000 D polymer at $c > 100$ g/L) occurs at $c \gg c^*$ and may mark the transition from semidilute to concentrated solution. In concentrated poly(acrylic acid), a similar transition in the $c$ dependence of $\eta$ is accompanied by a change in the solution's optical probe spectrum,[37] from a single- to a multi-exponential form.

The hydrodynamic scaling model of polymer self-diffusion[1,2,36] predicts relations between $\upsilon$, $a$, and $M$. Experiment confirms these predictions. Simple correlations between $\upsilon$, $a$, and $M$ were similarly found here for $\eta$, $D_R$, and $s$. To first approximation, we find $\alpha \approx M^g$. In viscosity studies, $g$ is about $^1/_2$ for random-coil polymers, but 1.5–2 for rigid-rod materials. For sedimentation in either $\Theta$ or good solvents, $g$ is approximately unity, close to the $g = 1$ found for self-diffusion.

$\upsilon$ can also be correlated with $M$. For self-diffusion, $\upsilon$ is near unity for small polymers, but $\upsilon \approx {}^1/_2$ for large polymers. For polymer sedimentation in good solvents, $\upsilon$ declines with increasing $M$, changing from $\sim{}^1/_2$ at small $M$ (100 kD) to to $\sim$0.1 or less at large $M$ (>2 MD). In $\Theta$ solvents, $\upsilon$ falls from 1 with small polymers to roughly 0.5 with large polymers. The molecular weight regimes in which $\upsilon$ changes from its small $M$ to its large $M$ limit are the same for $D_s$ and for $\eta$.

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**Registry No.** PMM, 9011-14-7; pIB, 9003-27-4; pS, 9003-53-6; pMS, 25014-31-7; pEA, 111026-46-1; poly($\gamma$-benzyl-L-glutamate) (copolymer), 25014-27-1; poly($\gamma$-benzyl-L-glutamate) (SRU), 25038-53-3; poly($n$-butyl isocyanate), 25067-04-3; schizophyllan, 9050-67-3.

**Supplementary Material Available:** Table S1, comparison of viscosity measurement, Table S2, sedimentation of polystyrene, Table S3, sedimentation of polymers in $\Theta$ and good solvents, Figure V1, viscosity of poly($\alpha$-methylstyrenes), Figure V2, sedimentation coefficients of polystyrene, Figure V3, sedimentation coefficients of poly($\alpha$-methylstyrene), Figures S1–S22, log $s$ against $c$ for polystyrene in various solvents at various temperatures, and Figures S23–S27, log $s$ against $c$ for hydroxypropylcellulose–water (21 pages). Ordering information is given on any current masthead page.

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# Thermodynamic Studies on Poly[*N*-(*n*-octadecyl)maleimide] (PMI-18)/Solvent Systems by Inverse Gas Chromatography with Capillary Columns[†]

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ABSTRACT: An open tubular column (capillary) coated with poly[*N*-(*n*-octadecyl)maleimide] (PMI-18) has been used above its glass transition temperature for estimating polymer–solvent interaction parameters by means of inverse gas chromatography (IGC). Experimental retention volumes corrected to zero flow rate $V_g^0$ are reported for nonpolar ($C_n$ *n*-alkanes, $n$ = 9–13) and polar ($C_n$ *n*-alkyl alcohols, $n$ = 6–8 and 10) solute probes. Activity coefficients $(a_1/\omega_1)^\infty$, the Flory–Huggins parameter $\chi$, and mixing functions were derived and discussed with respect to the chain length and polarity in the solute molecules. The heat of mixing at infinite dilution $\Delta\bar{H}_1^\infty$ taken at the midpoint, 143 °C, is in the range of 60 to 160 J/g. These values are interpreted as indicative of some fitting of a cooperative orientational order between neighboring *n*-alkyl side chains of a comb structure and the *n*-alkyl side of the probe molecules. The heats of vaporization of solute molecules, $\Delta H_v$, are in quantitative agreement with those calculated from vapor pressures by means of the Clausius–Clapeyron equation. The apparent glass transition temperature, $T_g$, estimated by IGC was found to be dependent on the chemical nature of the probe and the number of methylene groups in the *n*-alkyl chain. This dependence is explained within the framework of the theory of free volume and the difussion coefficient of the probe molecules into the polymer by an equation of the Fujita type. An expression has been derived from the free volume theory which relates the self-diffusion coefficient of the probes in the gaseous state to the apparent glass transition temperature of the PMI-18 estimated by IGC.

## Introduction

A few years ago, Lichtenthaler and Prausnitz[1,2] reported the use of open tubular capillary columns to measure polymer–solute interaction parameters by inverse gas–liquid chromatography (IGC). The only reason given by these authors[1,2] for the employment of open tubular (capillary) over packed columns was to provide an increase in film thickness, thus simulating the conditions prevailing in the bulk material. Since then very little attention has been paid to the study of IGC by means of open tubular columns. Latter, Braun and Guillet[3] concluded that the film thickness in packed columns may be only an order of magnitude less than for capillary columns. They also claimed that due to high linear velocities of carrier gas and thick polymer films, the retention data in the case of capillary columns must be obtained from lengthy and necessarily less precise extrapolation procedures.[3] However, they did not present any experimental fact in favor of their arguments.

Interlaboratory comparison of retention data obtained on packed columns has indicated that column packing procedures may be of fundamental importance.[4] However, very recently, Card, Al-Saigh, and Munk[5] carried out a detailed study on the role played by the very often termed "*innert support*" by studying retention volumes of nonpolar as well as moderately and strongly polar probes. They concluded that to obtain meaningful data for the retention of the probes and the thermodynamic parameters derived from the retention volumes, the data measured on the uncoated column support had to be subtracted from the corresponding data of the coated column support.

In addition, open tubular columns have rarely been used for thermodynamic measurements. The data on the Flory–Huggins parameter $\chi$ obtained from a packed column according to Lichtenthaler et al.[1] are lower than static data. However, the differences are less if the comparison is made between data from static experiments and those from capillary columns.

In the present paper we have focused our main interest on the three following points: (i) We explored the validity of the data obtained by using open tubular columns coated on the inner wall with a polymer above its glass transition temperature and extrapolated the retention volume to zero flow rate. (ii) The study of the influence of a comb structure such as the poly[*N*-(*n*-octadecyl)maleimide] by using both nonpolar (*n*-alkanes) and polar (*n*-alkyl alcohols) substances as probes on the thermodynamic properties of mixing was conducted. In linear polymers these thermodynamic functions are determined by interactions between the solvent molecule and short sequences within the polymer chain. A thermodynamic study of polymer–probe interactions can lead to an understanding of the specific interaction between the probe molecules and the polymer structure. (iii) We examined the dependence of the glass transition temperature determined by IGC on the structural properties and dimensions of *n*-alkyl derivatives used as probes.

## Experimental Section

The experimental framework of IGC is mainly in the literature, so that only the significant details will be covered here. Experimental procedures on IGC in general[5-9] and open tubular columns in particular[1,2,10] will be used.

**Materials.** A fractionated sample of PMI-18 of $\bar{M}_n = 1.90 \times 10^5$ and $\bar{M}_w/\bar{M}_n$ = 1.74, as estimated from measurements by

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[†] Dedicated to Professor Dr. A. P. Masiá on the occasion of his 63rd birthday.

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