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Thermal Diffusion of Dilute Polymer Solutions: The Role of Chain Flexibility and the Effective Segment Size

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ABSTRACT: We have investigated the influence of the chain length and the size of the Kuhn segment on the thermal diffusion coefficient D_T of dilute solutions of polymers in organic solvents. For oligomers and short polymer chains, D_T increases with molar mass M and reaches a molar mass independent constant plateau value. A similar increase and plateau is observed for high polymers with increasing chain stiffness. For chains with Kuhn segments above 1 kg/mol, the plateau value is independent of the polymer and inversely proportional to the solvent viscosity. The thermal diffusion coefficient of such a polymer can be estimated to be $D_T \approx 0.6 \times 10^{-14}$ Pa m^2 K$^{-1} \times \eta^{-1}$. No simple relation holds for short chains and flexible high polymers.

1. Introduction

Within the framework of linear nonequilibrium thermodynamics, diffusion processes in multicomponent liquid mixtures are considered to be driven by generalized thermodynamic forces. These forces are related to the gradient of the chemical potential (Fickian diffusion), the gradient of the temperature (thermal diffusion, thermodiffusion, or Soret effect), and the pressure gradient (barodiffusion). The latter is usually negligible in typical laboratory experiments sufficiently away from a critical point.[1] By restricting ourselves to binary mixtures and introducing suitable diffusion coefficients D and D_T for Fickian and thermal diffusion, respectively, the total diffusion current can be expressed as[2]

$$\vec{j} = \vec{j_D} + \vec{j_T} = -\rho D \nabla c - \rho c (1-c) D_T \nabla T \qquad (1)$$

Because of mass conservation, there is only one independent component of weight fraction, c. ρ is the density of the mixture.

In dilute polymer solutions, the Fickian or mass diffusion coefficient, D, of a single polymer chain can be expressed by the well-known Stokes–Einstein relation $D = k_B T (6\pi\eta R_h)^{-1}$. R_h is the hydrodynamic radius of the polymer chain, η is the viscosity of the solvent, and $k_B T$ is the thermal energy. Mass diffusion and sedimentation of a particle in a viscous fluid are characterized by stick boundary conditions for the fluid at the particle surface and flow fields that decay inversely proportional to the distance, r, from the particle. These long-ranged flow fields lead to hydrodynamic coupling between the beads of a polymer chain. The effective hydrodynamic radius, R_h, of the polymer scales with the molar mass, M, according to $R_h \propto M^\nu$, where $\nu = 0.5$ to 0.6 in the case of theta and good solvents, respectively.

Thermal diffusion is a phoretic motion, where no net force and torque act on a volume element containing a particle and some surrounding fluid. A treatment based on slip instead of stick boundary conditions yields short-ranged hydrodynamic flow fields that decay like r^{-3}.[3] As first recognized by Brochard and de Gennes,[4] there is no hydrodynamic coupling, and long-ranged interactions between the individual beads of a polymer chain are absent. As a consequence, the thermal diffusion coefficient, D_T, of long chains does not depend on the molar mass of the polymer. Chains of a certain polymer in a given solvent all move with the same thermophoretic velocity, $\vec{v}_T = -D_T \nabla T$, irrespective of their degree of polymerization. This initially surprising molar mass independence of D_T for high polymers has been observed in a number of experiments[5−10] and could also be confirmed in reverse nonequilibrium molecular dynamics simulations (RNEMD).[11]

A comparison between theoretical models of Brenner (ref 12 and refs 38 and 39 therein), Khazanovich and Bender,[13,14] Semenov and Schimpf,[15] and experimental data for polystyrene (PS) in seven different solvents revealed that the viscosity is the predominant solvent property that determines D_T.[12] Such a simple correlation is quite different from solutions of small molecules, where Soret and thermal diffusion coefficients are hardly predictable.

Systematic studies of the molar mass dependence of D_T of PS in various solvents showed that D_T becomes chain-length-dependent for oligomers and shorter polymer chains.[16,17] Although it is molar-mass-independent in the long chain limit, the thermal diffusion coefficient is not a monomer property. The relevant entities for the Soret effect are more likely segments or beads of a size comparable to the Kuhn segment. Monomers are correlated within these segments but not over significantly longer distances.[11]

Starting with the effective monomer ethylbenzene, which is of the same size as a typical solvent molecule, a plot of the product ηD_T versus molar mass for PS in various solvents revealed two distinct features.[16] First, the data show the typical broad variation without any systematic dependence on the solvent for very short chains, where even different signs of D_T can be observed. Increasing chain length consistently makes the polymer more thermophobic, corresponding to an increase in D_T. Second, D_T levels off and reaches a molar-mass-independent plateau for polymer molar masses somewhere between 1 and 10 kg/mol, corresponding to a few Kuhn segments. When plotted as ηD_T, this plateau value is not only independent of the molar mass but also independent of the type of solvent.

The increase in D_T with the degree of polymerization of the short chains has been rationalized in terms of an increasing thermophobicity due to the growing size and mass of the thermodiffusing entities. In the case of PS, the mass of a Kuhn segment is approximately one order of magnitude larger than the

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Table 1. Weight-Average Molar Mass (M_w) and Polydispersity M_w/M_n of Polymer Samples

polymer	M_w (kg/mol)	M_w/M_n
PDMS	23.2	2.7
PMMA	23.2	1.03
PtBMA	42	1.02

Table 2. Molecular Formulae, Viscosities and Molar Masses of Solvents Investigated at $T = 295$ K[a]

solvent	formula	η (10^{-3} Pas)	M (kg/mol)
chloroform	$CHCl_3$	0.552	0.118
cyclohexane	C_6H_{12}	0.947	0.084
cyclohexanone	$C_6H_{10}O$	2.127	0.098
cyclooctane	C_8H_{16}	2.418	0.112
ethyl acetate	$C_6H_8O_2$	0.440	0.088
ethylbenzene	C_8H_{10}	0.661	0.106
MEK	C_4H_8O	0.391	0.072
toluene	C_7H_8	0.573	0.092
THF	C_4H_8O	0.477	0.072

[a] Data from ref 16 and references therein and from ref 38 (cyclohexanone, chloroform).

Table 3. Polymer Parameters: Characteristic Ratio $C_\infty = \langle R^2\rangle/(Nl^2)$ according to refs 12, 25 and 39 (PE) and 26 and 27 (PtBMA), monomer mass (M_m), and Kuhn Mass ($C_\infty M_m$.)[a]

polymer	C_∞	M_m (kg/mol)	$C_\infty M_m$ (kg/mol)
PE	8.3	0.028	0.23
PI	5.8	0.068	0.39
PDMS	5.7	0.074	0.42
PMMA	8.8	0.100	0.88
PS	9.9	0.104	1.03
PαMS	10.5	0.118	1.24
PtBMA	12.1	0.142	3.38

[a] All values for approximately room temperature.

Table 4. Thermal and Mass Diffusion Coefficients of PS in Various Solvents in the Dilute Limit ($c_{PS} \rightarrow 0$)[a]

system	$D_T/[10^{-12}$ m^2/(sK)]	$D/[10^{-10}$ m^2/s]
PS23800/chloroform	5.59 ± 0.40	1.20 ± 0.06
ethylbenzene/cyclooctane	-4.48 ± 1.08	7.53 ± 1.78
PS162/cyclooctane	-1.32 ± 0.98	4.20 ± 1.09
PS266/cyclooctane	0.46 ± 0.14	3.54 ± 1.06
PS370/cyclooctane	1.24 ± 0.16	2.63 ± 0.23
PS725/cyclooctane	1.70 ± 0.17	1.80 ± 0.13
PS1560/cyclooctane	2.14 ± 0.18	1.04 ± 0.02
PS10300/cyclooctane	2.66 ± 0.24	0.40 ± 0.01
ethylbenzene/THF	-3.08 ± 0.63	20.97 ± 4.00
PS162/THF	-1.33 ± 0.68	13.25 ± 5.70
PS266/THF	6.50 ± 0.39	11.97 ± 0.91
PS370/THF	7.07 ± 0.74	12.32 ± 0.78
PS1560/THF	9.98 ± 1.46	5.23 ± 0.62
ethylbenzene/ethyl acetate	4.38 ± 1.11	35.40 ± 14.00
PS162/ethyl acetate	1.17 ± 0.99	17.52 ± 10.06
PS266/ethyl acetate	8.15 ± 0.38	13.02 ± 0.78
PS370/ethyl acetate	9.40 ± 0.67	10.11 ± 0.76

[a] Numbers indicate the molar mass of the polymer (e.g., PS23800 refers to PS with $M_w = 23\,800$ g/mol).

mass of a typical solvent molecule. In this case, details of the polymer–solvent interaction seem to become less important, and only the solvent viscosity remains as dominating factor.

The above results have been obtained for PS, and it has not been clear whether experiments with other polymers would yield similar results. In particular, questions concerning the behavior of polymers with shorter and larger Kuhn segments remained unanswered. There was only a hint based on a few literature data in ref 12 that more chain flexibility might result in lower plateau values of D_T.

In the present work, we extend previous studies in a systematic way to polymers other than PS to investigate the influence of the chain stiffness and hence the size of the correlated segments on the plateau value of the thermal diffusion coefficient. For this purpose, we have performed measurements on dilute solutions of poly(methyl methacrylate) (PMMA), poly(*t*-butyl methacrylate) (PtBMA), and poly(dimethyl siloxane) (PDMS) in the high polymer limit. Additionally, we have studied the influence of increasing chain length for a series of *n*-alkanes, which can be considered to be oligomers of the very flexible polymer polyethylene (PE).

2. Experimental Section

Measurements have been performed by means of the transient holographic grating technique of thermal diffusion forced Rayleigh scattering (TDFRS), as described in detail in previous works.[16,18,19] With this technique, periodic temperature gradients are created on a micrometer length scale by optical heating. Diffusion processes are monitored by optical readout of the resulting phase grating. For a quantitative analysis, the contrast factors $(\partial n/\partial T)_{p,c}$ and $(\partial n/\partial c)_{p,T}$ must be known and have been measured separately as described in ref 18. $n = n(p,c,T)$ is the refractive index of the solution. Such experiments directly yield D, D_T, the Soret coefficient $S_T = D_T/D$, and the thermal diffusivity D_{th}.

The polymers PtBMA and PMMA have been obtained from Polymer Standard Service GmbH (Mainz), and PDMS has been obtained from ABCR GmbH (Karlsruhe). The molar mass distribution of PDMS has been determined by size exclusion chromatography at the Max Planck Institute for Polymer Research in Mainz. The characteristic polymer properties are summarized in Table 1. The polydispersities of PMMA, PtBMA, and the here referenced PS are not > 1.03 and can be neglected. The polydispersity of PDMS of $M_w/M_n = 2.7$ has been accounted for by a cumulant expansion, as described in ref 20.

Alkane solutions have been prepared using *n*-eicosane (>99.8%, Fluka), *n*-hexadecane (>98%, Fluka), *n*-pentadecane (>99%, Aldrich), *n*-dodecane (>99%, Aldrich), *n*-decane (>98%, Fluka), *n*-octane (>99%, Merck), and *n*-hexane (>95%, Fluka). As solvents, we used cyclohexane (p.a., >99.5%, Acros), cyclohexanone (>99%, Fluka) cyclooctane (>99%, Aldrich), ethyl acetate (>99%, Merck), ethylbenzene (>99%, Fluka), methyl ethyl ketone (MEK, >99.5%, Merck), tetrahydrofuran (THF, >99%, Aldrich), and toluene (>99.9%, Merck). The solvent viscosities can be found in Table 2. All coefficients discussed in the following sections were measured at a number of finite concentrations and have been extrapolated back to a concentration $c = 0$. The temperature for all experiments was $T = 295$ K.

3. Results and Discussion

The measured thermal diffusion coefficients, D_T, and mass diffusion coefficients, D, extrapolated to zero concentration from a number of measurements at finite concentrations, are summarized in Tables 4 (PS), 5 (alkanes), and 6 (PDMS, PMMA, PtBMA). Soret coefficients can be obtained as $S_T = D_T/D$.

3.1. Chain Length Dependence. The existence of a molar-mass-independent plateau value of D_T in the high polymer limit has been observed in many experiments,[5,6,9] but data for the transition from the polymer to small molecules exist only for polystyrene.[17,16]. Because in ref 12 it has been observed that the plateau value of D_T is significantly smaller in the case of flexible polymers, our first aim was to investigate the molar mass dependence of D_T for a highly flexible polymer. As we intended to go down to very short chain lengths with well-defined oligomers and narrow molar mass distributions, the availability of suitable polymers turned out to be rather limited. We choose polyethylene (PE) because of its flexibility in combination with a very light repeat unit and the availability of well-defined oligomers, the *n*-alkanes. The

Table 5. Thermal and Mass Diffusion Coefficients of Alkanes (1st Component) in Various Solvents in the Dilute Limit

system	$D_T/[10^{-12}\ m^2/(sK)]$	$D/[10^{-10}\ m^2/s]$
hexane/cyclooctane	-12.59 ± 1.18	8.55 ± 0.34
octane/cyclooctane	-9.38 ± 3.73	7.15 ± 0.18
decane/cyclooctane	-9.99 ± 1.23	6.82 ± 0.37
dodecane/cyclooctane	-6.93 ± 0.33	5.13 ± 0.38
pentadecane/cyclooctane	-6.34 ± 0.43	4.66 ± 0.12
hexadecane/cyclooctane	-7.42 ± 6.68	5.19 ± 0.37
eicosane/cyclooctane	-4.03 ± 6.42	3.66 ± 0.21
hexadecane/cyclohexanone	-10.11 ± 1.34	5.69 ± 0.55
hexadecane/ethyl acetate	-3.39 ± 0.60	13.49 ± 1.59
hexane/ethylbenzene	-14.06 ± 0.51	22.23 ± 0.54
hexadecane/ethylbenzene	-5.52 ± 0.47	12.82 ± 1.04
hexane/THF	-24.02 ± 4.01	26.60 ± 3.50
hexadecane/THF	-4.72 ± 1.28	10.71 ± 2.76
hexane/toluene	-19.57 ± 1.51	24.92 ± 1.77
octane/toluene	-14.16 ± 1.65	23.56 ± 1.73
decane/toluene	-8.44 ± 0.61	18.01 ± 1.04
dodecane/toluene	-7.01 ± 0.58	15.45 ± 1.04
pentadecane/toluene	-7.37 ± 0.82	13.52 ± 1.43
hexadecane/toluene	-7.56 ± 1.72	15.96 ± 2.80
eicosane/toluene	-5.14 ± 3.37	12.91 ± 6.09

Table 6. Thermal and Mass Diffusion Coefficients of PDMS, PMMA, and PtBMA in Various Solvents in the Dilute Limit[a]

System	$D_T/[10^{-12}\ m^2/(sK)]$	$D/[10^{-10}\ m^2/s]$
PDMS23153/cyclooctane	-1.22 ± 0.26	0.43 ± 0.01
PDMS23153/ethylbenzene	2.28 ± 0.31	1.07 ± 0.22
PDMS23153/toluene	2.39 ± 0.40	1.44 ± 0.20
PDMS23153/ethyl acetate	2.57 ± 1.32	1.69 ± 0.92
PMMA23200/cyclohexanone	3.58 ± 0.77	0.32 ± 0.02
PMMA23200/toluene	12.00 ± 4.97	1.24 ± 0.14
PMMA23200/THF	12.27 ± 1.05	1.45 ± 0.06
PMMA23200/ethyl acetate	11.57 ± 1.87	1.63 ± 0.04
PMMA23200/MEK	22.86 ± 1.87	1.80 ± 0.05
PtBMA42000/cyclohexanone	3.24 ± 1.15	0.28 ± 0.02
PtBMA42000/THF	10.74 ± 1.00	1.25 ± 0.07
PtBMA42000/ethyl acetate	13.76 ± 1.14	1.36 ± 0.04
PtBMA42000/MEK	18.14 ± 1.75	1.52 ± 0.03

[a] Numbers indicate the molar mass of the polymer (e.g., PDMS23153 refers to PDMS with $M_w = 23\,153$ g/mol).

approximate mass of the Kuhn segment, $C_\infty M_m$, of PE is only 230 g/mol (Table 3). On the downside, the solubility for longer chain length is poor, and the polymer is completely insoluble at room temperature in all common solvents. Therefore, the high molar mass limit was set by *n*-eicosane ($C_{20}H_{42}$, $M = 282$ g/mol), which is just slightly more than the Kuhn segment. The shortest chain we have investigated is *n*-hexane.

Figure 1 shows the results for the linear alkanes plotted in comparison with a subset of the PS values from ref 16 that were measured in the same solvents as the alkanes. The most striking feature is the thermophilic behavior of the alkanes in all solvents as expressed by the negative thermal diffusion coefficients. With increasing chain length, a similar trend as in case of PS is observed: D_T monotonously increases, and longer alkane chains become less thermophilic (more thermophobic). A similar trend of increasing thermophobicity with increasing molar mass has been observed by Blanco et al. for equimolar mixtures of *n*-alkanes.[21] Leahy-Dios and Firoozabadi investigated mixtures containing equal mass fractions of different alkanes and *n*-decane.[22]

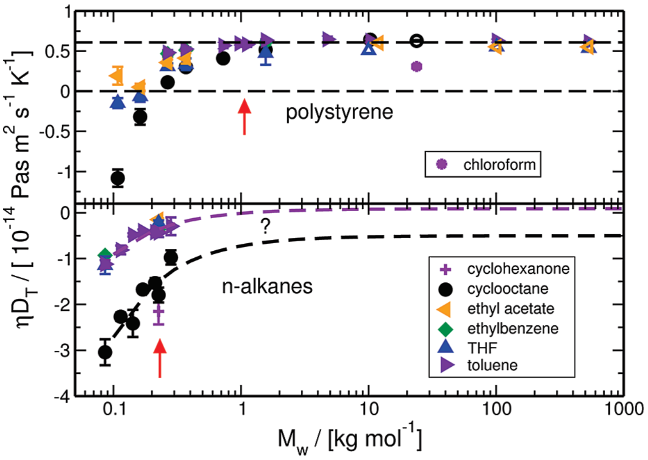

Figure 1. Product ηD_T for PS (top) taken from ref 16 and references therein and linear alkanes (bottom) in different solvents. The dashed lines are fits of eq 2 with $\alpha = 1$. A common plateau is not reached for the alkanes. The question mark indicates the somewhat speculative extrapolation to the plateau values. The arrows mark the approximate molar masses of the Kuhn segments.

In refs 16 and 17, we studied the molar mass dependence of the thermal diffusion coefficient of PS in various solvents. The data measured in the same solvents as the alkanes are shown in the upper part of Figure 1. The main result of these investigations was the proportionality of the high polymer plateau value of D_T to the inverse solvent viscosity, η, and the pronounced decrease in D_T for short chains. For certain solvents even a sign reversal could be observed. A reasonable phenomenological parametrization of all PS data could be obtained by an equation of the form

$$D_T = \frac{\Delta_T}{\eta} - \frac{a}{M^\alpha} \tag{2}$$

where Δ_T is a constant that is characteristic for the polymer but, interestingly, independent of the solvent. The second term in eq 2 describes the decrease in D_T for short chains. Contrary to Δ_T, the amplitude factor, *a*, of the chain-length-dependent part varies for different solvents. In THF, cyclohexane, and cyclooctane, this second term is sufficient to revert the migration direction in the case of the two "effective monomers" ethylbenzene and 3,3′-dimethyl-butylbenzene. Whereas long PS chains are always thermophobic and migrate toward the cold side, the monomer in, for example, cyclooctane behaves thermophilic. The exponent α is on the order of unity, and $\alpha = 1$ yields a good parametrization. The comparison with the Soret coefficient, S_T,[16] and a recent theoretical model by Würger[23] suggest to identify α with the exponent for the hydrodynamic radius, R_h. The latter scales in the limit of long polymer chains such as $R_h \approx M^\nu$ with the Flory exponent $\nu \approx 0.6$ under good solvent conditions and $\nu = 0.5$ under theta solvent conditions. For short chains and oligomers, the asymptotic scaling law is not reached, and the molar mass dependence of R_h is more complicated. A fit of eq 2 to the PS data, where α is treated as a free parameter, yields values of $\alpha \approx 1$. A fit with $\alpha = 0.5$ to 0.6 shows only a poor agreement with the data. Therefore, $\alpha = 1$ will be kept fixed in the following.

Although the asymptotic molar mass independent plateau value is not fully reached in the case of the alkanes, the data are reasonably well described by eq 2 with $\alpha = 1$. Nevertheless, the extrapolated plateau remains somewhat speculative and, other than in the case of PS, it appears to depend on the solvent.

The fit parameters obtained from the fits of eq 2 to the PS and alkane data are summarized in Table 7. In Figure 2, all molar-mass-dependent data from Figure 1 and the remaining PS data from ref 16 have been included in a common master plot after rescaling the measured values

Table 7. Fit Parameters As Obtained from Fits of Equation 2 to the PS and Alkane Data

system	$\Delta_T/[10^{-15}$ N/K]	$a/[10^{-13}$ kg m^2/s K mol]
PS/cyclooctane	6.87	7.37
PS/cyclohexane	6.93	12.70
PS/ethyl acetate	5.52	11.75
PS/MEK	6.38	13.27
PS/THF	5.38	16.55
PS/toluene	6.35	7.02
alkane/cyclooctane	−5.03	9.15
alkane/toluene	0.87	17.35

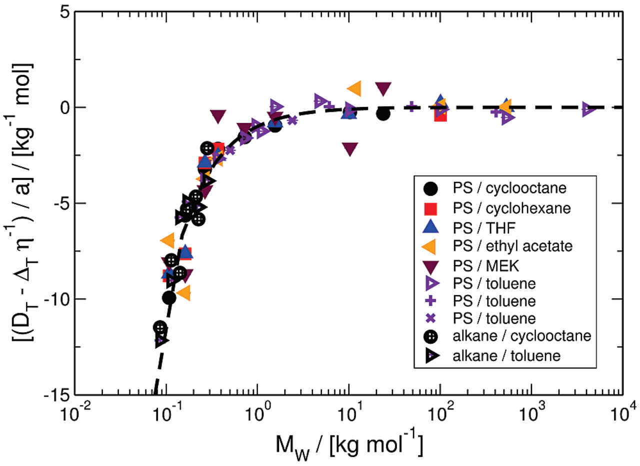

Figure 2. D_T of PS and *n*-alkanes in different solvents plotted after rescaling according to eq 3. For the *n*-alkanes, only solvents with sufficient data points (toluene, cyclooctane) have been included.

according to eq 2 with the two fit parameters Δ_T and a in the form

$$y = \frac{1}{a}\left(D_T - \frac{\Delta_T}{\eta}\right) \tag{3}$$

The results for PS in MEK, which is a poor solvent where the polymer is sometimes difficult to dissolve completely, scatter considerably, but all other data nicely collapse onto a single master curve that corresponds to an M^{-1} dependence of the deviation from the asymptotic plateau value of D_T.

3.2. Chain Stiffness. Besides the chain length dependence, we have investigated the influence of chain stiffness on the plateau value of D_T in the high polymer limit. It has already been observed in ref 12 that D_T can tentatively be expressed by the first term of eq 2 for high molar masses. Except for PS, there were only few literature data available, and the conclusion was still rather speculative for polymers other than PS. There was, however, a clear tendency toward smaller values of Δ_T and hence D_T for highly flexible polymers like polyisoprene (PI) and PDMS, although only a single data point, measured in toluene, was available for the latter.

For our new systematic investigations, we have chosen three polymers with different degrees of stiffness: PMMA, PDMS, and PtBMA. The relevant parameters are summarized in Tables 1 and 3. PMMA has a Kuhn segment comparable to the one of PS. There are a few literature data on PMMA in benzene, toluene, THF, and MEK. These were already included in the discussion in ref 12, but they showed a strong scatter. PDMS is an example of a very flexible polymer with a Kuhn segment of only half the mass of the one of PS and PMMA. Polymers with large Kuhn segments are represented by PtBMA.

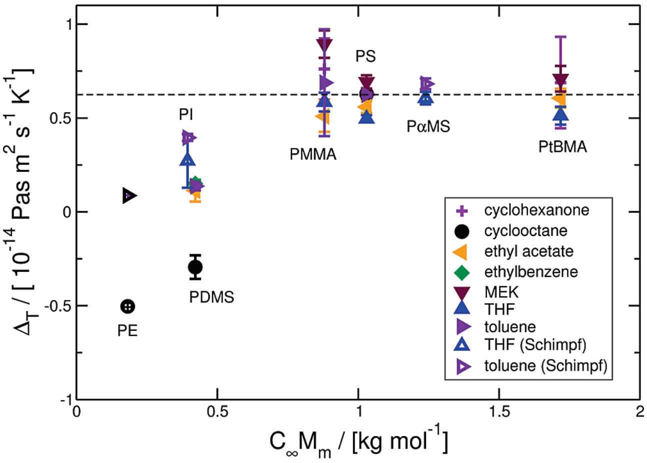

Figure 3. Plateau value $\Delta_T = \lim_{M\to\infty}(\eta D_T)$ in the high polymer plotted versus the mass of the Kuhn segment $C_\infty M_m$. Data for PI and PαMS labeled with "Schimpf" are from ref 5. Data for PS[12,16] have previously been measured in our group. PE refers to the extrapolated plateau values of *n*-alkanes from Figure 1.

The length l_K and the molar mass M_K of the Kuhn segment are given by $l_K = C_\infty l/\cos(\theta/2) \approx C_\infty l$ and $M_K \approx C_\infty M_m$ if the effect of the fixed bond angle, $\theta \approx 68°$, on the contour length is neglected.[12] M_m and l are molar mass and length of a monomer, respectively. The characteristic ratio in the limit of infinite degree of polymerization, N

$$C_\infty = \lim_{N\to\infty} \frac{\langle R^2\rangle}{Nl^2} \tag{4}$$

with $\langle R^2\rangle$ being the mean square end-to-end vector, serves as a measure for chain stiffness. There are different values for the characteristic ratio of PtBMA in the literature. In ref 24, a value of 23.8 is assumed. Newer publications, however, report a value between 11.8[25,26] and 12.2[27]. In ref 27, the author corrects his previous value of 23.8[28] down to the newly measured value of 12.2. We therefore take $C_\infty = 12.1$ to be the average for the characteristic ratio of PtBMA.

Figure 3 shows the high molar mass plateau values $\Delta_T = \lim_{M\to\infty}(\eta D_T)$ (eq 2) of ηD_T plotted as a function of the molar mass of the Kuhn segment $C_\infty M_m$. The Figure contains the new data for the polymers with increasing stiffness, PDMS, PMMA, and PtBMA. Also included are data for PS[12,16] in a large number of solvents and data for PαMS and PI measured by Schimpf and Giddings with the thermal field flow fractionation technique.[5] The values for PE have been extrapolated to infinite molar mass by means of the fits to the *n*-alkanes in Figure 1.

The general shapes of the data in Figures 1 and 3 look surprisingly similar. There is a horizontal plateau value of ηD_T at high and a bending down toward low masses. In either Figure, the bending down at low masses is accompanied by a fanning-out of the data. Note, however, the different "masses" along the x axis. Whereas the data have been plotted as a function of the overall molar mass in Figure 1, Figure 3 shows the data for long chains as a function of the mass of the Kuhn segment.

From our experiments and the literature data cited, we can develop the following picture: Single monomers or very short oligomers behave essentially like small molecules, for which no simple rule exists and a prediction of D_T is hardly feasible. Depending on the solvent, positive and negative values of D_T can be observed. When more monomers are added together, the size and mass of the molecules, which may now be called oligomers, grow. The thermal diffusion coefficient of these larger entities increases, and they become more thermophobic. Such an increase in thermophobicity with increasing molecular mass has also been observed for other situations, such as the isotope effect of cyclohexane and benzene[29,30] and the nonequilibrium molecular dynamics simulations of simple Lennard-Jones liquids[31] and, most noticeably, of polymer chains of varying length.[11] Once the chains have reached a certain length, D_T does not increase any longer, and it assumes a stationary molar-mass-independent plateau value. At least in the case of PS, where data for the entire molar mass range exist, the transition occurs at a chain length that is on the order of a Kuhn statistical segment. These effective segments define the entities that are relevant for thermodiffusion. Because of the short-ranged hydrodynamic flow fields, which decay like r^{-3} in the case of phoretic motion as compared with r^{-1} in the case of Fickian diffusion or sedimentation, there is no hydrodynamic coupling between the segments.[3,4] As a consequence, D_T becomes molar-mass-independent once the chain length exceeds a few Kuhn or persistence lengths, a behavior that has also been observed in RNEMD simulations.[11] Approximately at the same chain length where the plateau value is reached, the product ηD_T of PS also becomes independent of the solvent (Figure 1 and ref 16). In case of the alkanes, the polymer plateau is not reached, and longer chains cannot be investigated because of solubility problems. As in case of polystyrene, different ηD_T values are measured for short chains in different solvents. Whether an extrapolation to infinite chain length would result in a common molar-mass-independent plateau value cannot be decided without ambiguity, but an extrapolation based on eq 2 results in molar-mass-dependent plateaus.

As can be seen in Figure 3, an approximately solvent-independent plateau value of ηD_T is also reached for the other polymers (PMMA, PαMS, PtBMA) provided that the correlated units (the Kuhn segments) are sufficiently large. For more flexible chains (PDMS, PI, PE), the plateau remains solvent-dependent and, as in case of the short oligomers, smaller correlated units result in smaller values of ηD_T. For the stiffer polymers, the plateau is not only solvent-independent but, surprisingly, also independent of the type of polymer. To observe this both solvent- and polymer-independent asymptotic value of $\eta D_T \approx 0.6 \times 10^{-14}$ Pa m ^{2}K^{-1}, the requirement seems to be that the thermodiffusing entities are at least one order of magnitude larger than the solvent molecules. Note that in all three plots (Figures 1, 2, and 3) the transition occurs at a molar mass of ~1 kg/mol, no matter whether the units are short chains, which are single molecules, or Kuhn segments within very long chains. The molar masses of the solvents are on the order of 0.1 kg/mol and summarized in Table 2. Increasing the Kuhn mass above roughly 1 kg/mol does not lead to a further increase in the thermal diffusion coefficient.

Before coming to the conclusion, a few critical remarks shall be added with respect to difficulties encountered when defining the crossover chain length. When talking about the size of the Kuhn segment, we have not always distinguished between the mass and the length. For our purposes, either quantity can be used to characterize the Kuhn segment, and comparable results are obtained because mass and length are strongly correlated; a light Kuhn segment is also short. From a theoretical point of view, it is not quite clear whether length or mass is more relevant. Experiments on isotopic systems[30,29] and molecular dynamics simulations[32,33,31], however, support the notion of heavier molecules being more thermophobic.

There are some fundamental problems related to the determination of the crossover of D_T from the short chains to the molar-mass-independent plateau characteristic for high polymers. Although it appears to be clear from a visual inspection of Figure 1 that the plateau is reached for a molar mass approximately corresponding to the Kuhn segment, it is difficult to define this transition in a mathematically clean way. The reason is that the parametrization of the data according to eq 2 with a power law $\propto M^{-1}$ for the deviation from the plateau does not contain an intrinsic length scale. Therefore, a crossover molar mass (or chain length) can be defined only by comparing the absolute value of the deviation with some characteristic value of D_T, which can be the plateau value Δ_T/η or the maximum deviation observed for the shortest chains investigated. Then, the crossover can be defined for a molar mass where only say 10% of the deviation is left over. Such a procedure roughly corresponds to what is done when judging with the eye. On the basis of this reasoning and considering the broad logarithmic M axis, the transition can be located around $M \approx 1$ kg/mol in the case of PS. For the alkanes, the crossover seems to be shifted toward lower M, but the data are not sufficient to make a clear distinction and unambiguously determine a crossover molar mass. It should be emphasized, however, that this problem affects the determination of only the transitions in Figures 1 and 2 but not the plateau values plotted in Figure 3.

4. Conclusions

On the basis of the results presented here, which have been derived from measurements on seven different polymers and eight different nonpolar or only weakly polar solvents, the following hypothesis can be derived:

For sufficiently large cooperative units undergoing thermodiffusion, which can either be rigid single molecules (oligomers) or correlated segments within a polymer chain, the thermal diffusion coefficient, D_T, becomes independent of the chemical nature of the molecule or polymer. The solvent dependence is only via the solvent viscosity, and the quantity $\Delta_T = \lim_{M\to\infty}(\eta D_T)$ assumes a universal value of $\Delta_T \approx 0.6 \times 10^{-14}$ Pa m^2 K^{-1}. In particular, high polymers with a Kuhn segment of at least 1 kg/mol have a thermal diffusion coefficient of

$$D_T \approx 0.6 \times 10^{-14}\ \mathrm{Pa\ m^2\ K^{-1}} \times \eta^{-1} \qquad (5)$$

in a solvent of viscosity η.

The above hypothesis is surprising, and currently, we do not have a theoretical model that could explain it. Nevertheless, qualitative aspects of our experimental findings, such as the increase in D_T with increasing degree of polymerization and the well-known constant molar mass independence in the high polymer limit, have already been predicted or reproduced by theoretical models or RNEMD simulations.[23,3,11,4] The viscosity dependence in eq 5 is easily understood and may be regarded to be a trivial factor because any motion that is unavoidably associated with a displacement of solvent is expected to depend inversely on η in the linear regime. This holds for the thermal diffusion coefficient in polymer solutions, even close to a glass transition, where the viscosity increases by many orders of magnitude.[10,34]

For the sake of simplicity, we have identified the cooperative units that are relevant for thermal diffusion with the Kuhn segments, which might be an oversimplification. In reality, the Kuhn segment is, like the persistence length, a static correlation length determined by the local chain stiffness. Dynamic correlation lengths may be different,[35,36] but until now, the available data do not allow for such a distinction.

More experiments are needed with possibly more "exotic" systems to discover the limits where the rule breaks down. First hints may possibly be obtained from a single measurement that has been performed on PS in chloroform, where the plateau value of D_T is only slightly more than half of the universal value of eq 5 (Figure 1). There is also the need for further theoretical developments. Schimpf and Semenov have predicted an increase in D_T with increasing segment size[37] but no leveling off. Although the theoretical model of Würger[23] nicely predicts an increase in D_T with increasing chain length and a molar mass independent contribution for long chains, the molar-mass-dependent part in this model should scale like $R_h^{-1} \approx M^{-0.5 \text{ to } 0.6}$, whereas the experiments are better describe by an exponent of $\alpha = 1.0$, as shown by the dashed line in Figure 2.

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References and Notes

(1) Hicks, F. B.; Franck, C. *Phys. Rev. E* **1998**, *58*, 4582.
(2) de Groot, S. R.; Mazur, P. *Non-Equilibrium Thermodynamics*; Dover Publications: New York, 1984.
(3) Würger, A. *Phys. Rev. Lett.* **2007**, *98*, 138301.
(4) Brochard, F.; de Gennes, P.-G. *C. R. Acad. Sci. Paris, Ser. II* **1981**, *293*, 1025.
(5) Schimpf, M. E.; Giddings, J. C. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 1317.
(6) Meyerhoff, G.; Nachtigall, K. *J. Polym. Sci.* **1962**, *57*, 227.
(7) Schimpf, M. E.; Giddings, J. C. *Macromolecules* **1987**, *20*, 1561.
(8) Wiegand, S. *J. Phys.: Condens. Matter* **2004**, *16*, R357.
(9) Chan, J.; Popov, J. J.; Kolisnek-Kehl, S.; Leaist, D. G. *J. Solution Chem.* **2003**, *32*, 197.
(10) Rauch, J.; Köhler, W. *J. Chem. Phys.* **2003**, *119*, 11977.
(11) Zhang, M.; Müller-Plathe, F. *J. Chem. Phys.* **2006**, *125*, 124903.
(12) Hartung, M.; Rauch, J.; Köhler, W. *J. Chem. Phys.* **2006**, *125*, 214904.
(13) Khazanovich, T. N. *J. Polym. Sci., Part C: Polym. Lett.* **1967**, *16*, 2463.
(14) Bender, M. *Macromolecules* **1995**, *28*, 1309.
(15) Semenov, S.; Schimpf, M. *Phys. Rev. E* **2004**, *69*, 011201.
(16) Stadelmaier, D.; Köhler, W. *Macromolecules* **2008**, *41*, 6205.
(17) Rauch, J.; Köhler, W. *Macromolecules* **2005**, *38*, 3571.
(18) Wittko, G.; Köhler, W. *Philos. Mag.* **2003**, *83*, 1973.
(19) Köhler, W. *J. Chem. Phys.* **1993**, *98*, 660.
(20) Rossmanith, P.; Köhler, W. *Macromolecules* **1996**, *29*, 3203.
(21) Blanco, P.; Bou-Ali, M. M.; Platten, J. K.; Urteaga, P.; Madariaga, J. A.; Santamaria, C. *J. Chem. Phys.* **2008**, *129*, 174504.
(22) Leahy-Dios, A.; Firoozabadi, A. *J. Phys. Chem. B* **2007**, *111*, 191.
(23) Würger, A. *Phys. Rev. Lett.* **2009**, *102*, 078302.
(24) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989.
(25) *Polymer Handbook*, 4th ed.; Brandup, J., Immergut, E. H.,Grulke, E. A., Abe, A., Bloch, D. R., Eds.; Wiley: New York, 1999.
(26) Karandinos, A.; Mays, J. W.; Hadjichristidis, N. *Polym. Bull.* **1990**, *24*, 251.
(27) Wu, S. *Polym. Eng. Sci.* **1992**, *32*, 823.
(28) Wu, S. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 723.
(29) Debuschewitz, C.; Köhler, W. *Phys. Rev. Lett.* **2001**, *87*, 055901.
(30) Wittko, G.; Köhler, W. *J. Chem. Phys.* **2005**, *123*, 014506.
(31) Reith, D.; Müller-Plathe, F. *J. Chem. Phys.* **2000**, *112*, 2436.
(32) Artola, P.-A.; Rousseau, B.; Galliero, G. *J. Am. Chem. Soc.* **2008**, *130*, 10963.
(33) Polyakov, P.; Zhang, M.; Müller-Plathe, F.; Wiegand, S. *J. Chem. Phys.* **2007**, *127*, 014502.
(34) Rauch, J.; Köhler, W. *Phys. Rev. Lett.* **2002**, *88*, 185901.
(35) Ding, Y.; Sokolov, A. P. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 3505.
(36) Ding, Y.; Kisliuk, A.; Sokolov, A. P. *Macromolecules* **2004**, *37*, 161.
(37) Schimpf, M. E.; Semenov, S. N. *J. Phys. Chem. B* **2000**, *104*, 9935.
(38) Marcus, Y. *The Properties of Solvents*, Wiley: Chichester, U.K., 1998.
(39) Fetters, J. L.; Lohse, D. J.; Colby, R. H. Chapter 25. In *Physical Properties of Polymers Handbook*; Springer: New York, 2007; p 447.