From Small Molecules to High Polymers: Investigation of the Crossover of Thermal Diffusion in Dilute Polystyrene Solutions

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Received April 22, 2008; Revised Manuscript Received June 19, 2008

ABSTRACT: We have studied the crossover from small-molecule to polymer behavior in the Soret effect of dilute solutions of polystyrene in seven different solvents. The molar masses range from the monomer to $M \approx 10^6$g/mol. The thermal diffusion coefficient D_T is molar mass independent in the high polymer regime, and the quantity ηD_T is approximately constant and independent of the solvent. For shorter chains below $M \approx 10$ kg/mol, D_T decreases monotonously with M and ηD_T does no longer follow a common master curve. For the two "monomers" ethylbenzene and 3,3′-dimethylbutylbenzene there is even a sign change in several solvents. We conclude that the thermal diffusion coefficient, albeit being molar mass independent in the high polymer limit, is not a property of the monomer but rather of correlated segments of the order of the Kuhn segment. Hydrodynamic interactions dominate the behavior of the Soret coefficient for sufficiently long chains, where swelling due to excluded volume interactions becomes important. For a given molar mass the Soret coefficient depends only on the effective hydrodynamic radius of the polymer coil and, hence, on the solvent quality.

1. Introduction

The question of how polymer properties emerge and how the transition from monomers and oligomers to polymers occurs has recently attracted new interest. Ding et al. employed depolarized light scattering and derived a so-called random step size of ∼5 kg/mol for polystyrene. True polymer behavior is reached only for chains of at least 10 times this length.[1,2] Kariyo et al. followed the path from a simple liquid to a polymer melt as characterized by the transition from glassy to Rouse and reptation dynamics by means of field cycling NMR.[3] In this contribution, we discuss the interplay between isothermal and nonisothermal diffusion in dilute polymer solutions. These diffusion phenomena are of particular interest in the context of the emergence of polymer properties, since isothermal diffusion coefficients are known to depend on the chain length, whereas thermal diffusion has traditionally been regarded as being molar mass independent and, hence, more a monomer than a polymer property.

Isothermal diffusion in polymer solutions has extensively been studied, and there exists a well-established picture for the interpretation of the collective diffusion coefficient D in terms of polymer properties. According to Fick's first law, the associated diffusion current is $\vec{j}_D = -\rho D \nabla c$, where ρ is the density of the solution and c the polymer concentration in mass fractions. Dynamic light scattering is the experimental method of choice for quick and easy measurements even in routine polymer characterization work. D shows a pronounced concentration dependence for finite concentrations and loses its molar mass dependence in the semidilute regime above the overlap concentration. In the dilute limit hydrodynamic interaction between the segments of a polymer chain plays a dominant role and, according to the Zimm model, leads to a characteristic molar mass dependence $D \propto M^{-\nu}$. The scaling exponent ν depends on the solvent quality and ranges from $\nu = 0.5$ for an ideal chain under theta conditions to $\nu \approx 0.6$ for an expanded chain in a good solvent.[4]

Under nonisothermal conditions there is an additional thermal diffusion current $\vec{j}_T = -\rho c(1 - c) D_T \nabla T$, which is driven by a temperature rather than a concentration gradient. D_T is the thermal diffusion coefficient. Experiments are not as easily performed as in case of isothermal diffusion, but Soret cells with optical readout,[5−7] thermal field flow fractionation,[8] thermogravitational columns,[9] and transient holographic gratings[10,11] have successfully been employed.

While there is still only very little known about this so-called Soret effect in semidilute and concentrated polymer solutions,[6,12−14] more results have been accumulated for the dilute case by a number of different authors. The most surprising finding has been the molar mass independence of D_T, which has been reported by Meyerhoff and Nachtigall already in 1962[5] and later by e.g. Giddings and co-workers,[8,15] by Wiegand,[16] and by Chan.[9]

A first theoretical explanation has been given by Brochard and de Gennes[17] based on the absence of long-range interactions between distant monomers in a chain. Würger has analyzed thermophoresis in colloidal suspensions as originating from Marangoni forces.[18] Assuming slip boundary conditions, he obtained a flow field that does not give rise to hydrodynamic interactions between different particles. By treating a polymer chain as a chain of spheres, he concluded that D_T should be both independent of molar mass and concentration.

Zhang and Müller-Plathe investigated polymer thermal diffusion by means of reverse nonequilibrium molecular dynamics simulations[19] and found a molar mass independent D_T for sufficiently long polymer chains exceeding a few persistence lengths. They interpreted their results as being in qualitative agreement with predictions by Schimpf and Semenov of a proportionality between D_T and the segment size.[20]

Prior to the theoretical work of Zhang, we experimentally investigated thermal diffusion of dilute polystyrene (PS) in toluene not only in the high polymer limit but also for short chains down to the dimer.[21] We observed that D_T is constant for sufficiently long chains but monotonically decreases with decreasing chain length below $M \approx 10$ kg/mol. We tentatively interpreted this deviation from the so far observed molar mass independence as being due to an end-group effect, but especially in the light of the work of Zhang and Müller-Plathe, an interpretation in terms of an effective segment size being responsible for thermal diffusion might be more reasonable.

In this contribution we report on a systematic study of the molar mass and solvent dependence of the thermal diffusion

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10.1021/ma800891p CCC: $40.75
Published on Web 07/22/2008

Table 1. Weight-Average Molar Mass M_w and Polydispersity M_w/M_n of Polystyrene Samples

name	M_w (kg/mol)	M_w/M_n
ethylbenzene	0.106	1.0
PS162	0.162	1.0
PS266	0.266	1.0
PS370	0.370	1.0
PS725	0.725	1.09
PS1560	1.56	1.06
PS10300	10.3	1.03

and the Soret coefficient of PS in the dilute limit. The work was partly motivated by the request for experimental data on the effect of different solvents and end groups raised by Zhang and Müller-Plathe.[19] When designing the experiments, we were guided by the following main questions:

First, is it possible to identify characteristic polymer properties in thermal diffusion, and can they clearly be distinguished from the respective properties of small molecules? How does the transition from the monomer to the polymer occur? Is there a correlated effective segment relevant for thermal diffusion, and if so, what is its size? Second, the stationary Soret effect results from a subtle interplay between a diffusion process with hydrodynamic interactions between the chain segments and one without. As a consequence, there are two different friction mechanisms appearing in the Soret coefficient S_T, which should lead to characteristic properties.

2. Experimental Section

All transport coefficients have been measured with the transient holographic grating technique of thermal diffusion forced Rayleigh scattering (TDFRS). Thermal gratings with a spatial period of the order of 10 μm are written into the sample by means of an argon ion laser (514.5 nm). A small amount of quinizarin is added for optical absorption. The diffraction efficiency of the phase grating, which contains contributions due to both thermal expansion of the solution and composition shifts due to the Soret effect, is detected using a HeNe laser (632.8 nm). The heterodyne diffraction efficiency is fitted by the working equation

$$\zeta_{het}(t) = 1 - e^{-t/\tau_{th}} - \left(\frac{\partial n}{\partial c}\right)_{p,T}\left(\frac{\partial n}{\partial T}\right)_{p,c}^{-1} S_T c_0(1-c_0)(\tau-\tau_{th})^{-1} [\tau(1-e^{-t/\tau}) - \tau_{th}(1-e^{-t/\tau_{th}})] \quad (1)$$

where τ_{th} and $\tau = 1/(Dq^2)$ are the temperature and mass diffusion time constants, respectively. c is the polymer mass fraction. The contrast factors $(\partial n/\partial c)_{p,T}$ and $(\partial n/\partial T)_{p,c}$ have been measured with an Abbe refractometer and an interferometer. Details of the experimental setup and data evaluation can be found in ref 22.

Anionically polymerized polystyrene of various degrees of polymerization and narrow molar mass distribution (Table 1) was obtained from Polymer Standards Service GmbH (Mainz). Ethylbenzene is a model compound for the repeat unit of PS. 3,3′-Dimethylbutylbenzene (PS162) is effectively a PS oligomer with degree of polymerization of unity, including the *tert*-butyl end group (Figure 1). The solvents were cyclooctane (>99%, Aldrich), cyclohexane (p.a., >99.5%, Acros), toluene (>99.9%, Merck), tetrahydrofuran (THF, >99%, Aldrich), ethyl acetate (>99%, Merck), and methyl ethyl ketone (MEK, >99.5%, Merck). The effective monomer ethylbenzene (>99%, Fluka) has also been used

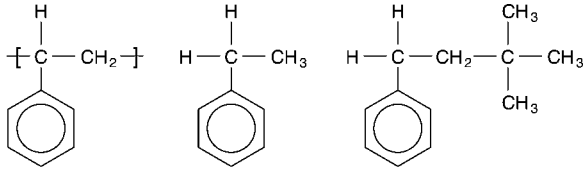

Figure 1. Repeat unit of the PS chain (left), ethylbenzene (middle), and 3,3′-dimethylbutylbenzene (PS162) (right).

Table 2. Solvents Investigated at $T = 295$ K; Viscosities from Refs 33 and 34 (Cyclooctane)

solvent	η (10^{-3} Pa s)	solvent	η (10^{-3} Pa s)
cyclohexane	0.947	MEK	0.391
cyclooctane	2.418	toluene	0.573
ethyl acetate	0.440	THF	0.477
ethylbenzene	0.661		

as solvent from the dimer on. The viscosities are shown in Table 2. The temperature for all experiments was $T = 295$ K.

3. Results

All coefficients discussed in the following were measured at a number of finite concentrations and have been extrapolated back to $c = 0$. For the sake of simplicity, we do not explicitly indicate these infinite dilution values with a subscript 0. In this dilute limit the solution viscosity η is identical to the viscosity of the pure solvent.

The thermal diffusion coefficient D_T of PS in six different solvents is plotted as a function of molar mass in Figure 2. The range extends from the high polymer limit down to ethylbenzene, the effective repeat unit of PS with a molar mass of 106 g/mol. Common to all solutions are a constant molar mass independent plateau value D_T^∞ in the high polymer limit and a progressive bending down of all curves below $M \approx 10$ kg/mol. For ethylbenzene and PS162 (162 g/mol) there is even a sign reversal in THF, cyclohexane, and cyclooctane. In these solvents both "monomers" are thermophilic—they migrate to the warm side—whereas all higher oligomers and polymers behave thermophobic in all solvents investigated.

We have shown in ref 23 that the high molar mass plateau value of the thermal diffusion coefficient, D_T^∞, is to a good approximation inversely proportional to the solvent viscosity: $D_T^\infty = \Delta_T^\infty/\eta$. The proportionality constant Δ_T^∞ only depends on the polymer and not on the solvent. This proportionality suggests to plot ηD_T as shown in Figure 3.

As expected, all curves collapse onto a common plateau for large M. For short chains this universality gets lost completely. Although all curves show a similar functional form for their bending down from the plateau value, they terminate in completely different end points for the monomer. As already known from other mixtures of small molecules, there is no simple theory to predict D_T (or ηD_T), except for some phenomenological rules like the more pronounced thermophobic behavior of heavier and more strongly interacting molecules.[24–28]

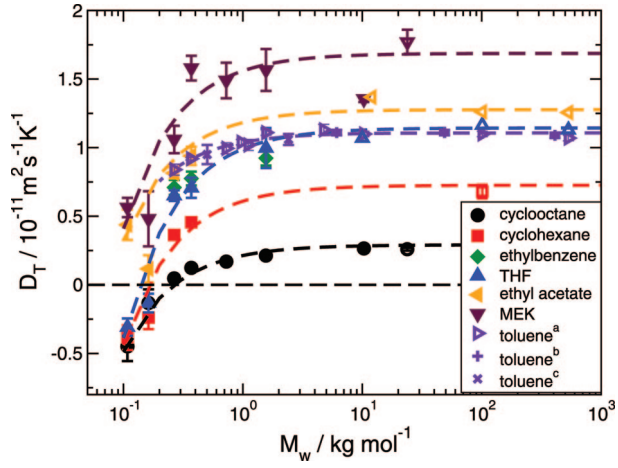

Figure 2. Thermal diffusion coefficient D_T as a function of molar mass for PS in different solvents. $T = 295$ K. The lines are phenomenological fits of $D_T = D_T^\infty - a_1/M$.[21] D_T^∞ and a_1 are fit parameters. Included are data from refs 21 (a), 35 (b), and 36 (c).

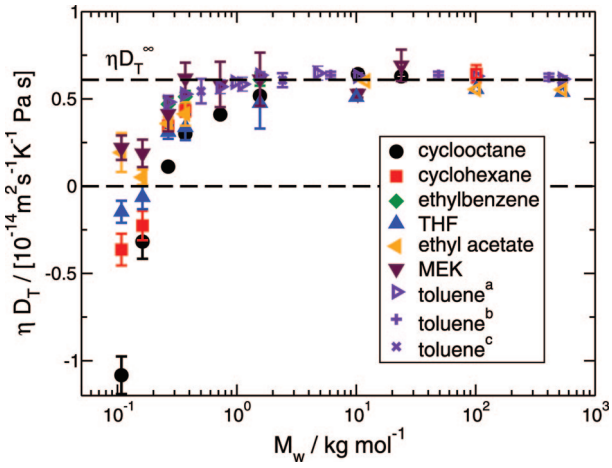

Figure 3. Data from Figure 2 replotted as ηD_T.

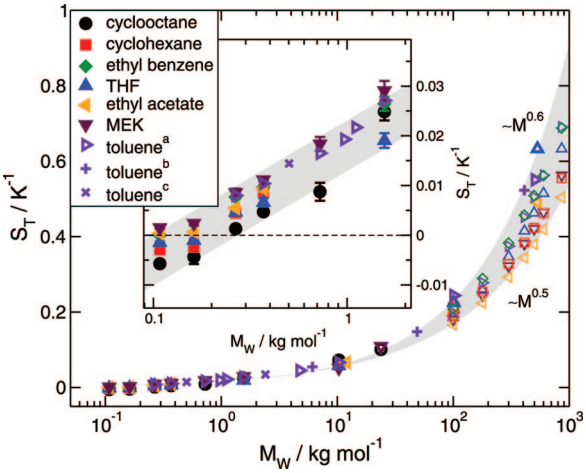

Figure 4. Soret coefficient S_T as a function of molar mass for PS in different solvents. $T = 295$ K. Included are data from the literature: ref 21 (a), ref 35 (b), ref 36 (c). Thin open symbols from ref 8 (computed from D and D_T, $T = 298$ K). Thick open symbols from ref 37.

More insight is obtained when looking at the Soret coefficient plotted in Figure 4. Again, two distinctly different regimes can be identified.

As shown in the enlarged insert, S_T increases approximately logarithmically with M for oligomers and short polymer chains up to a few kg/mol. Remarkably, the slope of $S_T(\log M)$ is constant, and a change of the solvent always leads to approximately the same change of S_T, as indicated by the gray band. A similar additivity of the Soret coefficient has already been observed for other mixtures consisting of small molecules[29] and, in particular, for isotopic substitutions of one of the two components.[28,27] Both the absolute values of S_T and the width of the band are of the order of 10^{-2} K^{-1} and, hence, of the magnitude usually observed for small molecules. The sign change of S_T does not change this general behavior and does not appear as anything special in Figure 4. Interestingly, this molar mass range up to a few kg/mol with the simple and predictable behavior of S_T corresponds exactly to the range where both D_T (Figure 2) and ηD_T (Figure 3) depend on M and the type of solvent in a complicated manner.

For molar masses above 10 kg/mol, where D_T has reached its constant plateau value, the solvent dependence of S_T becomes more pronounced. As indicated by the shaded area in the main part of Figure 4, all values now fall into a region whose boundaries are defined by power laws M^ν with the exponents $\nu = 0.5$ and $\nu = 0.6$. At $M \approx 10^3$ kg/mol the change of S_T for different solvents already spans 0.4 K^{-1}, which is 40 times the value found for short chains and oligomers.

4. Discussion

Since a quantitative theoretical model for the Soret and thermal diffusion coefficient is still missing, we will attempt to develop some phenomenological description that takes well-known scaling properties of polymers into account. Let us first consider the same polymer in two different solvents s and s' in the dilute limit. The two solutions are characterized by the diffusion, thermal diffusion, and Soret coefficients D, D_T, S_T and D', D_T', S_T', respectively. Let us further assume that a change of the solvent from s' to s changes the Soret coefficient by δS_T:

$$S_T = S_T' + \delta S_T \tag{2}$$

The observed constant vertical shift in the inset of Figure 4, irrespective of the initial value of S_T, motivates such an additive approach.

The diffusion coefficient of the polymer can be expressed by the well-known Stokes−Einstein relation $D = k_B T/(6\pi\eta R_h)$, where η is the solvent viscosity and R_h the effective hydrodynamic radius of the polymer chain. Exchange of the solvent leads to a change of the diffusion coefficient

$$D = D' \frac{\eta' R_h'}{\eta R_h} \tag{3}$$

R_h' is the hydrodynamic radius of the polymer in solvent s' of viscosity η'.

Combining eqs 2 and 3, the thermal diffusion coefficients in s and s' are related by

$$D_T = S_T D = D_T' \frac{\eta' R_h'}{\eta R_h} + \delta S_T D \tag{4}$$

In the following we will discuss the case of short chains down to the monomer and the high polymer limit separately.

4.1. Monomers, Oligomers, and Short Chains. Polymer molar masses $M \leq 10$ kg/mol define the regime where δS_T does not depend on M and is only a function of the solvents considered. Swelling of the polymer chains due to excluded volume interaction is not yet effective and the hydrodynamic radius of a given polymer chain is independent of the solvent, $R_h = R_h'$. In this case, eq 4 reduces to

$$\eta D_T = \eta' D_T' + \delta S_T \frac{k_B T}{6\pi R_h} \tag{5}$$

Equation 5 reflects the scenario plotted in Figure 3. For higher molar masses, but still below $M = 10$ kg/mol, the second term vanishes like $1/R_h$ and the left and right side become equal ($\eta D_T = \eta' D_T'$). For shorter chains with $M \ll 10$ kg/mol, however, the second term becomes increasingly important and eventually dominates D_T of oligomers and the two effective monomers.

4.2. High Polymers. As already mentioned, the high polymer limit for $M > 10$ kg/mol is characterized by a molar mass independence of $D_T = D_T^\infty$ and by a molar mass and solvent independent value of $\eta D_T^\infty \equiv \Delta^\infty$. On that condition, together with eq 3, the ratio of the Soret coefficients in solvent s and s' becomes

$$\frac{S_T}{S_T'} = \frac{D_T}{D_T'} \frac{D'}{D} = \frac{\eta'}{\eta} \frac{\eta R_h}{\eta' R_h'} = \frac{R_h}{R_h'} \tag{6}$$

This remarkable result tells us that the ratio of the Soret coefficients of a high polymer in two different solvents should only depend on the ratio of the respective hydrodynamic radii. The hydrodynamic radius of a flexible polymer follows a scaling

law $R_h \propto M^\nu$. The exponent ν is determined by the quality of the solvent. $\nu = 0.5$ characterizes ideal chains in a Θ solvent, and $\nu \approx 0.6$ is typical for chains expanded by excluded volume interaction in a good solvent.

Figure 4 shows that above relation is fulfilled to good approximation. The shaded area indicates the range between the two limiting scaling laws corresponding to exponents of 0.5 and 0.6. Since chain expansion is only effective in the high polymer limit, the prefactor has arbitrarily been chosen such that both curves start with a common value at $M = 10$ kg/mol. All Soret coefficients for high molar masses fall into this region. As expected, good solvents like toluene and THF can be found closer to the upper limit, corresponding to more chain expansion. Marginal and Θ solvents like ethyl acetate and cyclohexane tend toward the lower boundary defined by $\nu = 0.5$.

4.3. Crossover from the Monomer to the Polymer. In a previous work we investigated the molar mass dependence of D_T of PS in toluene[21] and interpreted the bending down for low M, which parallels the behavior of other quantities like the refractive index and the glass transition temperature, as being due to an end-group effect. This conclusion was reached by the assumption of a linear mass-weighted superposition of the thermal diffusion coefficients of the repeat unit (C_8H_8, $M = 104$ g/mol) and of the end groups, consisting of a *tert*-butyl group on one and a hydrogen on the other end ($M = 58$ g/mol). The idea of a linear superposition goes back to the work of Schimpf and Giddings, who showed that such a relation holds in case of copolymers.[30]

The shortest oligomer investigated in ref 21 was the dimer, consisting of two C_8H_8 repeat units and a butyl end group. In the present work we have extended our investigations not only to a large number of different solvents but also have included ethylbenzene and PS162 on the "polymer" side. Ethylbenzene (C_8H_{10}), which could not be measured in toluene because of the almost identical refractive indices, corresponds, except for two terminating hydrogens, to the effective repeat unit of PS. PS162 ($C_{12}H_{18}$) is a PS with a degree of polymerization of unity, including the correct butyl end group. Since the linear superposition in ref 21 resulted in $D_T = 1.11 \times 10^{-7}$ cm^2/(s K) for the repeat unit and in $D_T = -0.1 \times 10^{-7}$ cm^2/(s K) for the end group, a significantly smaller thermal diffusion coefficient would have to be expected for PS162 than for ethylbenzene. As can be seen from Figures 2 and 3, this is obviously not the case and D_T of PS162 is almost identical to D_T of ethylbenzene in all solvents investigated.

In addition, Zhang and Müller-Plathe found a saturation of D_T for chains exceeding a few persistence lengths in their recent reverse nonequilibrium molecular dynamics simulations.[19] On the basis of this finding and on our new results with a continuous increase of D_T with increasing M for short chains, including the two monomers, we come to the conclusion that an end-group model with a linear superposition does not yield an adequate description.

Starting with ethylbenzene, the systematic increase of both D_T and S_T must be attributed to the increasing mass and/or size of the molecules. As long as the PS chains are shorter than the Kuhn segment, they may be regarded as rigid units. This increase of D_T is in accordance with the observation that heavier species are more thermophobic[24,28,27] than lighter ones. The Kuhn segment of PS comprises 8−10 monomers,[2] corresponding to a molar mass of $M = 1$ kg/mol. Indeed, a small number of such Kuhn segments defines the range between 1 and 10 kg/mol where the high polymer plateau value of D_T is reached in Figures 2 and 3. A further increase of the chain length does not lead to a further increase of D_T. Hence, the molar mass independence of D_T observed in the high polymer limit does not imply that the thermal diffusion coefficient is a monomer property. From our data it rather follows that there are units of the size of the Kuhn segment that are the relevant entities for thermal diffusion. Within these segments the monomers are correlated and act cooperatively. Over length scales significantly exceeding the Kuhn length this correlation gets lost. This idea is sketched in Figure 5. Starting with the smallest molecule ethylbenzene (a), the molecular mass increases by the addition of C_8H_8 repeat units, resulting in larger but still rigid entities (b). Eventually, the size of a correlated segment is reached (c). Longer polymer chains (d) are composed of such segments, which act independently with respect to thermal diffusion but cooperatively with respect to Fickian diffusion. The transition from (c) to (d) is not sharp but gradual. It must be kept in mind that thermal diffusion is a dynamic nonequilibrium process, whereas the Kuhn segment is derived from static quantities. Hence, without a detailed microscopic model, it is impossible to say whether the correlated segment relevant for thermal diffusion is identical to the Kuhn segment.

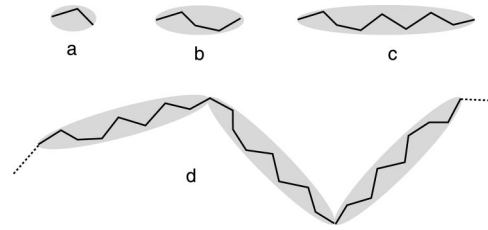

Figure 5. Increasing molecular mass of unit undergoing thermal diffusion starting from ethylbenzene (a) over short oligomers (b) to the correlated segment (c) and the polymer chain (d) consisting of independent segments. The solid lines indicate the C−C backbone of the polymer.

The range $M < M_s$, M_s being the molar mass of such a correlated segment, is not only characterized by a monotonous increase of D_T and S_T. Since the absolute variation of S_T stays constant, its relative variation decreases (Figure 4). Tentatively, this behavior is similar to the one observed in case of isotopic substitution. For cyclohexane/benzene mixtures it could be shown that S_T can be split into additive contributions. One contribution results from differences in mass and moment of inertia, and the other depends on the different chemical nature of the two components.[28,27] Within this line of arguments, adding more monomers to the polymer does not change its chemical nature but increases its mass and moment of inertia. This leads to an increase of S_T. Replacing the solvent, on the other hand, always results in the same change δS_T, irrespective of the mass of the polymer. According to eq 5 this directly leads to the almost constant asymptotic value of ηD_T. The merging of the curves $\eta D_T(M)$ stops when the polymer has reached the size of the correlated segment. Possibly, the remaining deviations from the common plateau value in Figure 3 would be even smaller in case of a larger correlated segment size.

Remarkably, for the systems investigated here, the high polymer value of ηD_T is even independent of the solvent quality and, thus, independent of the interaction strength between solvent and polymer. However, the solvent quality determines the swelling of long polymer chains and, due to hydrodynamic coupling between the polymer segments, the effective hydrodynamic radius. Since hydrodynamic interactions with a long-ranged flow field ($\propto r^{-1}$) are only effective for Fickian diffusion but not for thermal diffusion, where the flow field around a monomer decays like r^{-3},[18] a dependence on the solvent quality is introduced in $S_T = D_T/D$ according to eq 6 for higher molar masses.

5. Summary and Conclusion

Summing up, we have studied the crossover from small molecules to high polymers for the thermal nonequilibrium

transport effect of thermal diffusion. In order to observe the emergence of polymer properties, we have investigated thermal diffusion of polystyrene in a number of different solvents in the dilute limit. The thermal diffusion coefficient of high polymers above $M \approx 10$ kg/mol is independent of molar mass and inversely proportional to the solvent viscosity. As a consequence, the quantity ηD_T is constant for all solvents and all degrees of polymerization in the high polymer limit.

For shorter chains there is a systematic decrease of D_T with decreasing molar mass, and $\eta D_T(M)$ no longer follows a common master curve for different solvents. Comparison of ethylbenzene with PS162 as models for the repeat unit and a polymer chain of unity degree of polymerization shows that there is no pronounced end-group effect that could account for the molar mass dependence of D_T for short chains.

The Soret coefficient of short chains, which can still be regarded as one single more or less rigid unit, increases monotonously with molar mass, as predicted by MD simulations and also observed in case of isotopic substitution. Replacement of the solvent always leads to a constant shift of S_T, independent of M. Whereas the local friction component, as expressed by the solvent viscosity, cancels out in the Soret coefficient, the dependence on the hydrodynamic radius does not. It introduces a solvent-dependent swelling of long polymer chains and determines S_T in the high polymer limit. By generalizing these findings obtained for PS, we come to a very far-reaching conclusion: the same polymer in two different solvents of identical solvent quality has identical Soret coefficients. Of course, this conclusion is based on the data for PS in organic solvents presented in this paper and needs to be tested in further experiments. Preliminary results on poly(*tert*-butyl methacrylate) (tBMA) in cyclohexane, THF, ethyl acetate, and MEK confirm our findings for PS. Recent data on poly(*N*-isopropylacrylamide) (PNIPAM) in organic solvents also support our results, but significant deviations from a constant value of ηD_T are found in case of highly polar and associating solvents such as ethanol and water[31] and, to a lesser extent, chloroform.[32]

Thermal diffusion of a flexible polymer is characterized by the presence of short-range cooperativity and correlation between the monomers. On the other hand, long-range hydrodynamic interactions that dominate Fickian diffusion are absent in thermal diffusion. As a consequence, despite the molar mass independence of D_T, the units relevant for thermal diffusion of a PS chain are correlated segments with a size comparable to the Kuhn segment. Further experiments on flexible and stiff polymers should be conducted in order to test the results reported here for PS. Possibly there are deviations and less clear findings in case of very flexible polymers with short correlation lengths, where the effective segment is still comparable to a solvent molecule.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (SFB481/A8). We thank R. Kita for unpublished data on PNIPAM.

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MA800891P