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On the Molar Mass Dependence of the Thermal Diffusion Coefficient of Polymer Solutions

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The diffusive mass flow in a binary liquid subject to both a concentration and a temperature gradient can be decomposed into two contributions: $\vec{j} = \vec{j}_{\mathrm{D}} + \vec{j}_{\mathrm{T}}$. The Fickian mass diffusion current density $\vec{j}_{\mathrm{D}} = -\rho D \nabla c$ is driven by the concentration and the thermal mass diffusion current density $\vec{j}_{\mathrm{T}} = -\rho D_{\mathrm{T}} c(1 - c)\nabla T$ is driven by the temperature gradient (Soret effect). ρ is the mass density of the mixture and c the weight fraction of component 1.

The collective diffusion coefficient D of dilute polymer solutions shows the well-known molar mass dependence $D \propto M^{-\nu}$ according to the Zimm model with hydrodynamic coupling between the polymer segments. $\nu = 0.5$ for ideal chains in Θ solvents and $\nu \approx 0.6$ for expanded chains in good solvents. D becomes molar mass independent in the semidilute regime above the overlap concentration C^* and follows a scaling law $D \sim C^{0.6\cdots0.7}$,[1] C being the concentration in g/L.

The thermal diffusion coefficient D_{T}, on the other hand, behaves quite differently. As first shown by Giddings and co-workers by means of thermal field flow fractionation on dilute polymer solutions[2−4] for a number of different polymer/solvent combinations, D_{T} is constant for a given system and does not depend on the molar mass of the polymer. The polymer molar masses investigated ranged from approximately 20 to 860 kg/mol. This molar mass independence has later also been found for short polystyrene (PS) oligomers in ethyl acetate and for different alkanes in *n*-hexane at a fixed mole fraction of 0.15.[5] Chan et al. reported a constant thermal diffusion coefficient for aqueous solutions of poly(ethylene glycol) above the trimer.[6] A molar mass independent D_{T} was also observed by Zhang et al.,[7] who investigated solutions of PS in toluene for $M_{\mathrm{w}} \geq 2630$ g/mol up to $c = 0.56$.

A constant D_{T} is equivalent to a constant thermophoretic velocity $\vec{v}_{\mathrm{T}} = D_{\mathrm{T}} \nabla T$. According to Brochard and de Gennes,[8] thermal diffusion is, contrary to collective diffusion, characterized by an absence of long-range interaction between distant monomers. Hence, thermal diffusion corresponds more to a Rouse- than a Zimm-type motion of the polymer, where every monomer experiences both a thermophoretic and a frictional force without hydrodynamic coupling between the monomers. This is similar to the situation encountered in free solution electrophoresis of polyelectrolytes,[9] where the electrophoretic mobility is also molar mass independent.

In a previous publication, we investigated the concentration dependence of D_{T} of PS/toluene over a broad concentration range from dilute (10^{-4} g/cm^3) to concentrated (0.9 g/cm^3).[10] The molar masses ranged from 4.75 to 4060 kg/mol. All samples showed the same D_{T} in the dilute regime and only a slight decay with concentration up to semidilute concentrations of approximately 0.2 g/cm^3. At even higher concentrations, a sharp drop of D_{T} over almost 4 decades was observed, which we attributed to the increasing local friction because of the approach of the glass transition along the concentration axis. Remarkably, also in these experiments, all data fell onto a single universal curve and no molar mass dependence of D_{T} could be observed for $M > 10$ kg/mol. Only for the sample with the lowest molar mass (4.75 kg/mol), there was a slight deviation toward larger values of D_{T} at higher concentrations, which hardly exceeded the experimental error bars. We speculated about the first hint of the molar mass dependence of the glass transition temperature of PS as being responsible for this deviation, but the limited data available for shorter chains did not allow for more detailed discussions.

In this paper, we address the problem of molar mass dependence of the thermal diffusion coefficient in detail. All measurements reported here have been carried out on PS in toluene. While our previous measurements were limited to $M \geq 4.75$ kg/mol,[10,11] the present work focuses on the continuation toward lower molar masses down to short oligomers. In particular, we will identify two conditions where the universal molar mass independence of D_{T} so far assumed in the literature is no longer valid. Both types of deviation are observed for low molar masses, but they occur for different physical reasons. One deviation is already observed in the dilute limit and does not exceed 25%. The other type of molar mass dependence is observed for concentrated solutions. It is huge and can reach three decades or more.

PS of 266, 370, 725, 972, 1110, and 1560 g/mol (Table 1) were obtained from PSS (Mainz). Toluene (p.a.) was purchased from Merck. Samples up to 70% polymer concentration were prepared by adding toluene to the required amount of PS. Higher concentrations of $M >$ 1 kg/mol were prepared by evaporation of toluene from a more dilute sample as described in ref 10. Depending on molar mass and concentration, the solutions were allowed to equilibrate for up to several weeks. The samples were slightly colored with quinizarin for optical absorption. All transport coefficients were measured with a transient holographic grating technique in the same way as in the case of the high molar mass samples in ref 10. A holographic interference grating is used to write a temperature grating into the sample, which then, because of the Soret effect, gives rise to a concentration grating. D, D_{T}, and the Soret coefficient $S_{\mathrm{T}} = D_{\mathrm{T}}/D$ are obtained from the time constant and the amplitude of the diffraction efficiency of the concentration grating in a heterodyne experiment. All measurements were performed at room temperature (295 K). For a quantitative evaluation of the amplitude, the two contrast factors $(\partial n/\partial c)_{p,T}$ and $(\partial n/\partial T)_{p,c}$ are required, which were measured with an Abbe refractometer and an interferometer, respectively.[12] The refractive indices measured as a function of the polymer weight fraction c were fitted with a second-order polynomial to obtain $(\partial n/\partial c)_{p,T}$ as a linear function of c. All contrast factors are summarized together with other polymer parameters in Table 1.

Figure 1 shows the thermal diffusion coefficient D_{T}^0 in the dilute limit ($c \rightarrow 0$). The data for $M \geq$

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Table 1. Data of Polystyrene Samples Investigated

$M_{\rm w}$ kg/mol	$M_{\rm w}/M_{\rm n}$	$(\partial n/\partial c)_{T}p$ 10^{-2}g/g	$(\partial n/\partial T)_{c}p$ 10^{-4} K^{-1}	$T_{\rm g}$ K	$D_{\rm T}^{0}$ 10^{-7} cm^2(sK)$^{-1}$
0.266	1.0	3.52 + 0.35c	−5.64 + 1.49c	-	0.84 ± 0.04
0.370	1.0	5.56 + 0.31c	−5.65 + 1.58c	220[a]	0.92 ± 0.01
0.725	1.09	7.23 + 0.28c	−5.65 + 1.60c	271[b]	0.99 ± 0.04
0.972	1.12	7.56 + 1.17c	−5.64 + 1.80c	291[b]	1.04 ± 0.04
1.11	1.1	7.87 + 1.56c	−5.65 + 1.68c	299[b]	1.02 ± 0.04
1.56	1.06	8.45 + 2.49c	−5.66 + 1.70c	318[b]	1.11 ± 0.02
>10.3	-	-	-	363−373[b]	1.10 ± 0.02

[a] Extrapolated from 23. [b] Interpolated from 23.

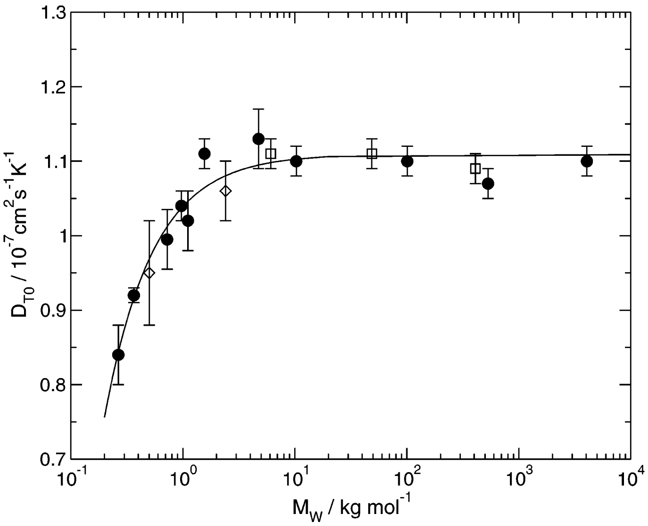

Figure 1. Molar mass dependence of the thermal diffusion coefficient $D_{\rm T}^{0}$ of PS/toluene in the dilute limit $c \rightarrow 0$. Additional data have been taken from refs 13 (□) and 14 (◇). $T = 295$ K. The solid line is a fit of eq 1.

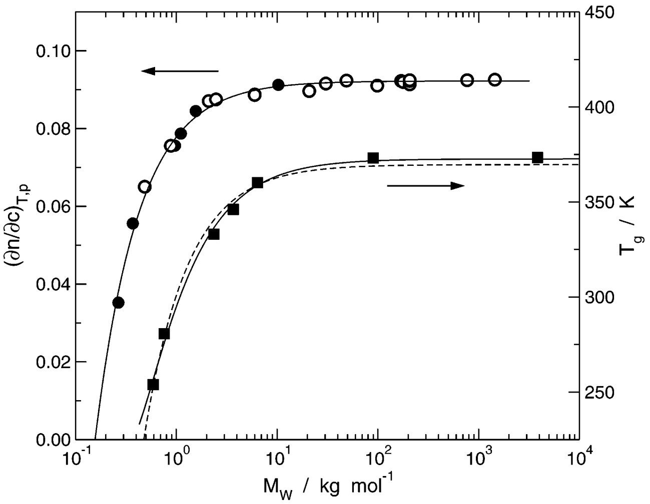

Figure 2. Molar mass dependence of the refractive index increment $(\partial n/\partial c)_{p,T}$ (c is the weight fraction of the polymer) of PS/toluene for $c \rightarrow 0$ ($T = 295$ K, open symbols[24]) and of the glass transition temperature $T_{\rm g}$ of PS.[23] The fit curves are explained in the text.

4.75 kg/mol are from ref 10. Included are also a few results previously obtained in our group.[13,14] Obviously, $D_{\rm T}^{0}$ shows a pronounced molar mass dependence below $M \approx 10$ kg/mol and reaches a constant molar mass independent value of $D_{\rm T}^{0} = 1.11 \times 10^{-7}$ cm^2/(sK) above. For the dimer ($M = 266$ g/mol), it decreases by 25% to $D_{\rm T}^{0} = 0.84 \times 10^{-7}$ cm^2/(sK). This pronounced molar mass dependence of $D_{\rm T}^{0}$, which already sets in at degrees of polymerization $N \approx 20$, is quite different from the molar mass independence of $D_{\rm T}^{0}$ down to short oligomers observed by other authors, as reported in the introductory section.

The molar mass dependence of the thermal diffusion coefficient remarkably parallels the molar mass dependence of the refractive index increment $(\partial n/\partial c)_{p,T}$ for $c \rightarrow 0$, which is plotted in Figure 2. Both quantities y can well be described as a weight average of the respective value for the repeat unit y^{∞}, obtained for infinite chain length, and the value for the end group $y^{\rm e}$:

$$y(M) = \frac{(M - M_{\rm e})\, y^{\infty} + M_{\rm e} y^{\rm e}}{M} \qquad (1)$$

Changes of the partial specific volume of the polymer are neglected in this simple model. The solid lines are fits of eq 1. $M_{\rm e} = 59$ g/mol because the PS chains are terminated on one side by a butyl group and on the other by a hydrogen. For the refractive index increment, we obtain $(\partial n/\partial c)_{p,T}^{\infty} = 0.0922$ and for $(\partial n/\partial c)_{p,T}^{\rm e} = -0.157$ (note that c is the weight fraction of the polymer). The value obtained for the butyl end group is close to the refractive index increment of another alkane, namely n-hexane, in toluene ($(\partial n/\partial c)_{p,T} = -0.159$ at $T = 23$ °C[15]).

The fit of eq 1 to $D_{\rm T}^{0}$ yields $D_{\rm T}^{0,\infty} = 1.11 \times 10^{-7}$ cm^2/(sK) as asymptotic value for the polymer and $D_{\rm T}^{0,\rm e} = -0.10 \times 10^{-7}$ cm^2/(sK) for the end group. The negative thermal diffusion coefficient of the end group indicates thermophilic behavior, which has generally been observed for alkanes (n-hexane[15] and dodecane[16]) in toluene. The interpretation of the absolute value of $D_{\rm T}^{0,\rm e}$ is more complicated. While it has been shown by Schimpf and Giddings that $D_{\rm T}$ of a random copolymer is given by the mass average of the thermal diffusion coefficients of the two homopolymers,[17] it is not clear whether this simple model holds down to the level of the repeat unit and the end group. Contrary to static quantities like the refractive index increment, transport coefficients like $D_{\rm T}$ depend much more on subtle details of the molecules. Already deuteration can change $D_{\rm T}$ significantly,[18] and different alkanes have different $D_{\rm T}$ in the same solvent.[15,16] A microscopic theory of $D_{\rm T}$ is still missing, but a description of the observed molar mass dependence according to eq 1 yields a good parametrization of our data with a reasonable thermal diffusion coefficient of the butyl end group.

Also shown in Figure 2 is the molar mass dependence of the glass transition temperature of the bulk polymer, which also shows a pronounced decay for low M. Different empirical equations have been proposed in the literature. The frequently employed relation $T_{\rm g} = T_{\rm g}^{\infty} - K/M$[19] is formally equivalent to eq 1. It gives an acceptable description of the data (dashed line in Figure 2), but a better fit is obtained with $1/T_{\rm g} = 1/T_{\rm g}^{\infty} - K'/M$ (solid line).[20]

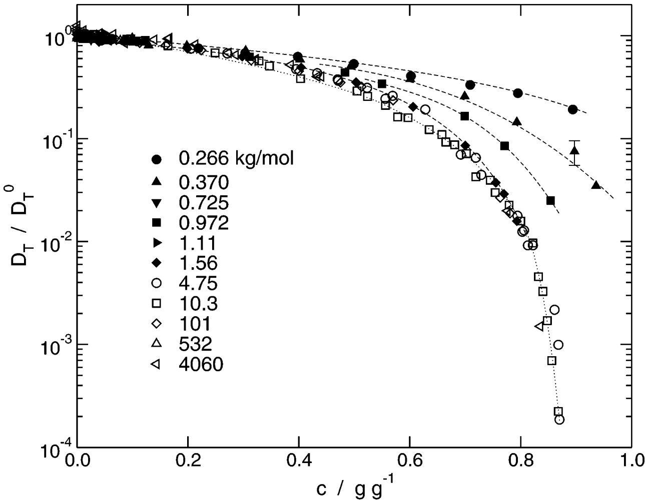

Figure 3. Concentration dependence of normalized thermal diffusion coefficient D_T/D_T^0 of PS/toluene for different molar masses. The open symbols refer to high molar mass data taken from ref 10. $T = 295$ K. The lines are guides to the eye.

Motivated by the insensitivity of the Soret coefficient to the glass transition, we postulated in ref 10 that D_T can be written in the form $D_T = \Delta_T/\eta_{\text{eff}}$. The effective local viscosity η_{eff} is responsible for friction of the monomers, and Δ_T contains all other factors contributing to D_T. Because η_{eff} is identical to the viscosity of the solvent in the dilute limit, irrespective of the molar mass of the polymer, we conclude that the molar mass dependence of D_T^0 is entirely contained in Δ_T.

A dramatic molar mass dependence of D_T can be observed for semidilute and concentrated solutions. Whereas D_T^0 decreases for short chains by approximately 25% as discussed above, D_T shows a strong decrease with increasing molar mass of the polymer by up to 4 orders of magnitude at higher concentrations. In Figure 3, the ratio D_T/D_T^0 is plotted to illustrate this strong effect at higher concentrations.

The weaker concentration dependence of the low molar masses can be attributed to the weaker concentration dependence of their glass transition temperatures. The glass transition temperature T_g of the solution can be estimated from the Fox equation[21] as $1/T_g = c/T_g^p + (1 - c)/T_g^s$, where T_g^p and T_g^s are the glass transition temperatures of polymer and solvent, respectively. The molar mass dependence of T_g^p is shown in Figure 2. The glass transition temperature of pure toluene is $T_g^s = 117$ K.[22] For a concentration of $c = 0.85$ and a polymer molar mass of $M = 10$ kg/mol, the glass transition temperature of the solution is approximately 276 K and, hence, close to the experimental temperature of 295 K. For $M = 370$ g/mol at the same concentration, T_g is only 194 K. Thus, at a given concentration in the concentrated regime approximately characterized by $c > 0.5$, the high molar mass samples are much closer to T_g than their low molar mass counterparts. As a consequence, friction becomes the dominating factor at high polymer concentrations, and the molar mass dependence of D_T is mainly caused by the molar mass dependence of η_{eff}. This is in strong contrast to the dilute and semidilute regime, where η_{eff} is approximately constant and the molar mass dependence is attributed to the friction-independent factor Δ_T. Zhang et al. investigated PS in toluene with a thermal diffusion cell and found, within the scatter of their data, a constant value of D_T^0 in good agreement with the one reported in this paper.[7] However, for their highest concentration ($c = 0.56$), they measured $D_T \approx 0.75 \times 10^{-7}$ cm^2/(sK), which is a factor of 3 larger than our value of $D_T \approx 0.25 \times 10^{-7}$ cm^2/(sK) for high molar masses at the same concentration. Currently, there is no explanation for this observed difference, and additional measurements may be necessary to resolve it. Because of the previously mentioned sensitivity of D_T to molecular parameters, a direct comparison of our results with the work reported by Chan for aqueous solutions of poly(ethylene glycol)[6] and by Wiegand,[5] who observed a molar mass independent D_T for PS in ethyl acetate and a number of alkanes in *n*-hexane, would be highly speculative.

In summary, we have shown that the molar mass independence of the thermal diffusion coefficient, so far regarded in the literature as universal, breaks down under two conditions. In the dilute limit, D_T^0 of PS/toluene is constant only for molar masses above $M \approx 10$ kg/mol and decreases for shorter chains because of an end-group effect. For high concentrations the situation is reversed. Here, local friction is increased by the approach to the glass transition. Consequently, D_T is strongly reduced for high molar masses and less for short chains, which are still farther away from T_g. Interestingly, the molar mass dependence approximately vanishes at an intermediate concentration of $c \approx 0.4$, where the effect of increasing D_T^0 and decreasing D_T due to increased friction almost compensates for all molar masses.

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