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Molar mass dependence of hydrodynamic friction of polystyrene molecules in theta solution in cyclohexane as revealed by photon correlation spectroscopy and sedimentation data

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SUMMARY

The translational diffusion coefficient of polystyrene molecules in dilute theta solution with cyclohexane D_c was studied as a function of the polymer concentration c and the molar mass M by performing photon correlation (PC) measurements and by analyzing data from the literature. The molar mass dependence of the concentration dependent part of D_c was also calculated from the zero concentration extrapolated values with the corresponding effective hydrodynamic radii. For the calculations the Pyun-Fixman theory was applied which regards the polymer coils as soft, interpenetrable spheres with uniform segment density. A similar study has also been presented using data from several sedimentation measurements.

The reliability of the molar mass dependence of the effective hydrodynamic volume depends strongly on the experimental conditions. A comparison of the calculated and measured hydrodynamic interaction parameters on a large sample of experimental data supports the applicability of the Pyun-Fixman theory within the currently accessible accuracy of the measurements.

INTRODUCTION

The purpose of this paper is first to present a systematic study concerning the molar mass and concentration dependence of the diffusion and sedimentation coefficients of quasi monodisperse polystyrene (PS) samples in cyclohexane under theta conditions, and second to interpret the molar mass dependence of these parameters by hydrodynamic theories. Diffusion coefficients obtained by photon correlation (PC) measurements (our experiments and available data from the literature) are analyzed by statistical means. The sedimentation data and their analysis are taken from Kotera and Hamada (1). For the interpretation of the results the hydrodynamic theory given by Pyun and Fixman (2), (3) is applied.

Numerous efforts have been made to involve hydrodynamic interactions in polymer dynamical theories (4-6), however, the goals have not been entirely achieved. Furthermore, frictional properties (diffusion and sedimentation coefficients, viscosity, etc.) play a very important role in polymer characterization (4), (7), (8). A comprehensive analysis of the molar mass dependence of the available data obtained from PC measurements concerning polystyrene in cyclohexane under theta conditions has not yet been published. Such an analysis and a comparison with sedimentation data would further help to improve hydrodynamic theories and to give a more reliable basis for the evaluation of PC measurements for polymer characterization.

The diffusion coefficient of the movement of the center of mass of dissolved polymeric molecules D_c, as well as the sedimentation coefficient s_c and the frictional coefficient f_c are dependent on the polymer concentration. These dependences in dilute polymeric solutions are usually expanded in the following series truncated to include just the linear term (4):

$$D_c = D_0\ (1 + k_D \cdot c + \ldots) \qquad (1)$$
$$s_c = s_0\ (1 + k_s \cdot c + \ldots) \qquad (2)$$
$$f_c = f_0\ (1 + k_s \cdot c + \ldots) \qquad (3)$$

where D_0, s_0 and f_0 are the diffusion, sedimentation and friction coefficients at infinite dilution, respectively. The friction coefficient (the ratio of the sum of the external forces acting on the polymer coils to the average translational velocity of the molecules relative to the solvent) is related through the Einstein relationship with D_0 (see (4)):

$$D_0 = kT/f_0 \qquad (4)$$

where k is the Boltzman factor and T is the absolute temperature. The second virial coefficient of the osmotic pressure in theta systems is zero, i.e. thermodynamic interactions can be neglected. The coefficients in the linear terms in equations (1)-(3) are coupled in this case as follows (4):

$$k_D = -\ (k_s + \bar{v}\ ) \qquad (5)$$

where both k_D and k_s may be expressed as a power function of the molar mass, and $\bar{v}$ is the partial specific volume of the polymer (for PS $\bar{v} = 0.94\ cm^3/g$, (9)). Further on we will define the molar mass dependent coefficient k_s as the hydrodynamic interaction parameter.

As we see later, the hydrodynamic interaction parameter is positive in dilute theta solutions. The corresponding decrease of D_c with increasing concentration is due to the increase of the friction (eq.(3)) which produces a slowing down of the translational self-diffusion of the coil. Hydrodynamic models regard the motion of dissolved polymer molecules in dilute solutions as a compact, rigid body or as an assembly of segments described as compact beds connected with each other. The so described molecules are placed in a fluid undergoing shear flow. The flow pattern will be usually calculated by solving the Navier-Stokes equation with different boundary conditions (see (2-4),(10)) or the dynamics of the chain (long range interactions and short range fluctuations) will be numerically simulated (see e.g. (6)). We apply further the results of the theory of Pyun-Fixman, which regards the polymer molecules as soft, interpenetrable spheres with uniform density and which treats the solvent molecules trapped inside the polymer domains (2), (3).

Strictly monodisperse, synthetic polymers are a priori not available. For the analysis of molar mass dependent properties, only polymer samples with a limited polydispersity index close to 1.0 can be used. This means, that one should consider average material parameters. (Average values are labelled further with a bar over the symbols.) Average molar masses will be substituted in this study with the weight average molar mass $\bar{M}_w$. The influence of this substitution on the results of the PC experiments has been analyzed elsewhere (11).

The diffusion coefficient for a single coil may be related to an effective hydrodynamic sphere, which would show the same frictional properties as the coil. The radius $\bar{R}_h$ of this sphere is defined through the Stokes relation (4), (8):

$$\bar{D} = kT/(6\pi\eta_s\bar{R}_h) \qquad (6)$$

where η_s is the solvent viscosity. The volume of the effective hydrodynamic sphere $\bar{V}_h$ and the corresponding frictional coefficient may be calculated with $\bar{R}_h$ (4):

$$\bar{V}_h = (4/3)\pi\bar{R}_h{}^3 = (4/3)(kT)^3/[\pi^2(6\eta_s\bar{D})^3] \qquad (7)$$

$$\bar{f}_0 = 6\pi\eta\bar{R}_h \qquad (8)$$

where $\bar{R}_h$ may be determined by using samples with known $\bar{M}_w$ and by measuring $\bar{D}_{z,0}$ or $\bar{s}_{w,0}$ (eq. (6), (9)) where $\bar{s}_{w,0}$ is the weight average sedimentation coefficient in the infinite dilution. The sedimentation coefficient $\bar{s}_{w,0}$ is related to $\bar{D}_{z,0}$ through the Svedberg equation:

$$s_{w,0} = \frac{\bar{D}_{z,0}(1 - \rho^* \bar{\nu})\bar{M}_w}{NkT} \qquad (9)$$

where ρ^* is the solvent density and N is the Avogadro number. PC (or sedimentation) measurements on solutions of PS fractions as a function of the polymer concentration result in $\bar{D}_{z,0}$ and $\bar{k}_s$ (or $\bar{s}_{w,0}$ and $\bar{k}_s$). The relationship between $\bar{D}_{z,0}$-$\bar{k}_s$ or $\bar{s}_{w,0}$-$\bar{k}_s$ may be determined by hydrodynamic models.

Using the Pyun-Fixman theory (3), the k_s hydrodynamic interaction parameter may be expressed in the theta point as a function of the effective hydrodynamic volume, V_h and M as follows:

$$k_s = 2.23\, NV_h(1/M) \qquad (10)$$

The above relationship presents the connection between $\bar{D}_{z,0}$ and $\bar{k}_s$ (or $\bar{s}_{w,0}$ and $\bar{k}_s$) through $\bar{V}_h$ (or $\bar{R}_h$).

We note, that the same equivalent sphere cannot be used for calculations of both the frictional coefficient and the viscosity increment. This was shown e.g. by the Kirkwood-Riseman theory (10), where the ratio between $\bar{R}_h$ and $\bar{R}_{h,[\eta]}$ (the latter is the radius of the effective sphere describing the viscosity increment) is:

$$\bar{R}_{h,[\eta]}/\bar{R}_h = 1.32 \qquad (11)$$

EXPERIMENTAL

Photon correlation spectroscopy (PCS) measurements were performed on polystyrene standards with narrow molar mass distribution functions. The $\bar{M}_w$ and the polydispersity index of the samples are shown in Table 1., columns 1-3 in the last two lines. Other details concerning the measurements have been published elsewhere (11)-(14).

The concentration dependent mean decay constant $\bar{\Gamma}_c$ of the autocorrelation function of the scattered light intensity (15) was determined by PCS. The $\bar{D}_{z,c}$ diffusion coefficient was approximated in this study as $\bar{D}_{z,c} \approx \bar{\Gamma}_c/q^2$, where q is the scattering vector. The influence of the neglected part in $\bar{D}_{z,c}$ which contains q^4 (16) has been studied elsewhere (11).

RESULTS, DISCUSSION

We analyzed first the molar mass dependence of the diffusion coefficient $\bar{D}_{z,0}$ and of the hydrodynamic interaction parameter $\bar{k}_s$. For this purpose, several available PCS data were taken from the literature (17)-(20) together with our measurements (12) (see Table 1.).

Table 1.

Results of PCS measurements on dilute polystyrene solutions in cyclohexane near the theta point (35 °C).

$\bar{M}_w \times 10^6$ [dalton]	log $\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{k}_s$ [cm^3/g]	log $\bar{D}_{z,0}$ [log cm^2/sec]	reference
0.021	4.322	<1.06	8	-6.047	(17)
0.11	5.041	<1.06	17	-6.377	
0.2	5.301	<1.06	15	-6.516	
0.67	5.826	<1.15	33	-6.780	
2.7	6.431	1.3	55	-7.076	
1.26	6.100	1.05	58	-6.939	(18)
2.88	6.459	1.09	97	-7.127	
4.48	6.651	1.14	78	-7.215	
5.05	6.703	1.02	89	-7.245	
6.77	6.831	1.14	96	-7.305	
9.35	6.971	1.03	154	-7.388	
0.11	5.041	1.06	19	-6.381	(19)
0.179	5.253	1.07	24	-6.489	
0.67	5.286	1.15	46	-6.749	
4.1	6.613	1.1	98	-7.167	
17.	7.23	-	201	-7.48	(20)
0.7	5.845	<1.08	18	-6.775	(12)
2.38	6.377	<1.07	57	-7.038	

The molar mass dependence of $\bar{D}_{z,0}$ and $\bar{k}_s$ for the values in Table 1. are plotted in Fig. 1. and Fig. 2. These dependences can be well represented by powers of $\bar{M}_w$:

$$\bar{D}_{z,0} = a1 \cdot \bar{M}_w^{-b1} \qquad (12)$$

$$\bar{k}_s = a2 \cdot \bar{M}_w^{b2} \qquad (13)$$

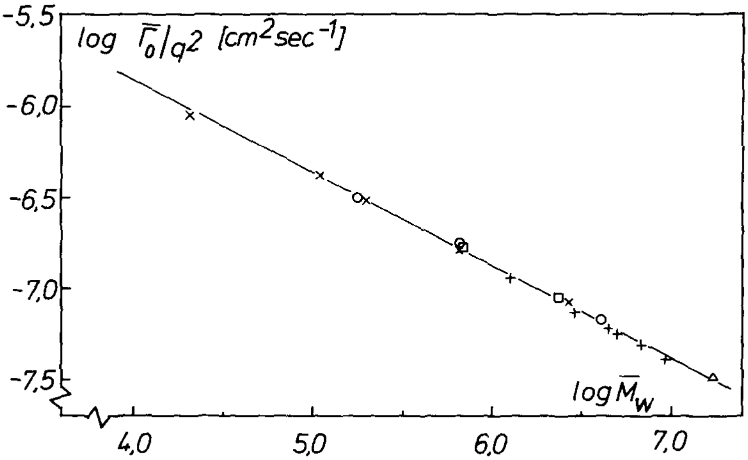

Figure 1.
Dependence of the $\bar{\Gamma}_0/q^2$ diffusion coefficient for polystyrene in theta solution with cyclohexane on the weight average molar mass (solid line - linear fit). (x ▸ (17), + ▸ (18), o ▸ (19), Δ ▸ (20), □ ▸ (12))

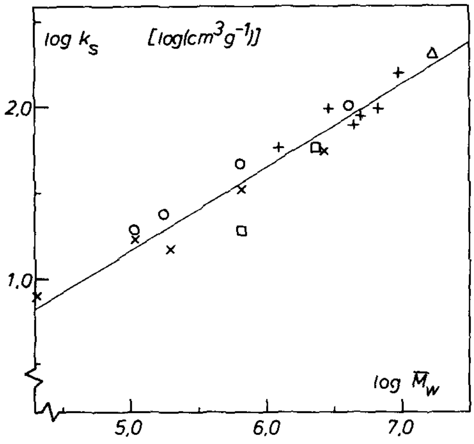

Figure 2.
Dependence of the hydrodynamic interaction parameter for polystyrene in theta solution with cyclohexane on the weight average molar mass (solid line -linear fit).(x ▸ (17), + ▸ (18), o ▸ (19), Δ ▸ (20), □ ▸ (12))

We calculated the constants a1,a2,b1 and b2 in eq. (12) and (13) by applying the least squares method for the linear relationships on the double logarithmic scale. The fitted forms of the equations and the parameters of the least squares fits are summarized in Table 2.

Thermodynamic theories of polymer solutions predict, that in the theta point b1=b2=1/2 (see (4),(7)). The analysis of our fits confirms this well-known result within the standard deviation of the fitted data. According to the fit to the PCS data, eq. (12) has the following numerical form:

$$\bar{D}_{z,0} = 1.49(\pm 0.09)10^{-4}\cdot\bar{M}_w^{-0.507(\pm 0.006)} \ [\mathrm{cm}^2/\mathrm{sec}] \qquad (14)$$

Table 2.
Results of the least squares fits concerning the molar mass dependence of $\bar{D}_{z,0}$ and $\bar{k}_s$ (data from Table 1.).

(*) → σ are the standard deviations which belong to the parameters in the same line

relationship	results of the linear regression	
$\log \bar{D}_{z,0}=\log(a1)-(b1)\log(\bar{M}_w)$	$\log(a1)=-3.826$ (*)	$\sigma=0.035$
	$a1=1.49\times10^{-4}$ [cm^2/sec]	
	$b1=0.507$	$\sigma=5.7\times10^{-3}$
	total root mean square error	$=0.075$
	simple correlation coefficient	$=0.9990$
$\log \bar{k}_s=\log(a2)+(b2)\log(\bar{M}_w)$	$\log(a2)=-1.17$	$\sigma=0.21$
	$a2=6.73\times10^{-2}$ [cm^3/g]	
	$b2=0.47$	$\sigma=0.035$
	total root mean square error	$=0.46$
	simple correlation coefficient	$=0.958$

The numerical values of the constants in eq. (14) may systematicly differ from the true values, since the measurements in the analyzed publications were not corrected concerning q^4 (the contributions from the internal molecular motions were neglected) (16). The statistics and the calculated errors, however, reflect the present experimental situation properly.

The measured and calculated results concerning the molar mass dependence of the hydrodynamic interaction parameter $\bar{k}_s$ are summarized in Table 3. The first column of Table 3. presents the measured molar mass dependence of $\bar{k}_s$. Hydrodynamic volumes, $\bar{V}_h$ shown in the second column of Table 3. are calculated using data extrapolated to zero concentrations by applying the Pyun-Fixman theory (3) (eq. (10),(6),(7),(9)). The third column in Table 1. contains the calculated $\bar{k}_s$ values using the corresponding hydrodynamic volumes from the second column (eq. (10)). Three sets of PC and two sets of sedimentation data are presented in Table 3. The results of the linear regression of this paper concerning PC measurements on PS (Table 3., first line) involve the data of the two other publications ((17), (20), line 2 and line 3 in Table 3.).

The comprehensive analysis of sedimentation coefficients of PS in cyclohexane, under theta conditions by Kotera and Hamada (1) (Table 3., line 4) comprises results of four publications for the direct determination of $\bar{k}_s$ (21) together with their own data. Their evaluation involves 10 data pairs for the $\bar{k}_s$-$\bar{M}_w^{1/2}$ relationship.

We determined the averages of the all analyzed $\bar{k}_s$ and calculated $\bar{k}_s^{calc}$ values of the hydrodynamic interaction parameters in order to compare them on a larger basis. The obtained mean values are:

$$\bar{k}_s(\text{mean})=6.6(\pm1.0)\times10^{-2}\cdot M^{1/2}\ [\text{cm}^3/\text{g}] \tag{15}$$

$$\bar{k}_s^{calc}(\text{mean})=5.8\times10^{-2}\cdot M^{1/2}\ [\text{cm}^3/\text{g}] \tag{16}$$

Table 3.

Results of direct measurements ($\bar{k}_s$) and calculations ($\bar{k}_s^{calc}$) with the hydrodynamic theory of (3) on the basis of the data from the literature concerning polystyrene in cyclohexane, in the theta point.

+ ▸ results of the linear regression of this study
♣ ▸ exponent of the molar mass was not fitted
♥ ▸ part of the regression of this study
♦ ▸ from the measured concentration dependence of $\bar{D}_{z,0}$ and $\bar{s}_{w,c}$

Method, ref.	$\bar{k}_s x10^2 [cm^3/g]$	$\bar{V}_h x10^{26} [cm^3]$	$\bar{k}_s^{calc} x10^2 [cm^3/g]$
PC$^+$	$6.7 \cdot \bar{M}_w^{0.47}$	$3.5 \cdot M^{1.52}$	$4.6 \cdot M^{0.493}$
PC (17)♥	$4.1 \cdot \bar{M}_w^{0.48}$	$5.2 \cdot M^{3/2}$ ♣	$7.0 \cdot M^{1/2}$ ♣
PC (20)♥	---	$4.4 \cdot M^{3/2}$ ♣	$6.0 \cdot M^{1/2}$ ♣
UC (1)	$6.5 \cdot \bar{M}_w^{1/2}$ ♣	$5.1 \cdot M^{3/2}$ ♣	$6.9 \cdot M^{1/2}$ ♣

The comparison of eq.(15) and (16) shows, that the application of the Pyun-Fixman theory for a large set of results gives a molar mass dependence for the hydrodynamic interaction parameter $\bar{k}_s$ which agrees with the experimental results within the statistical error. We note, however, that the theory does not take into account the specific chain structure of macromolecules and the motion of the solvent molecules in the polymer domains. For this reason, the theory is less adequate as a proper polymer model, but still amenable to accurate mathematical treatment.

The estimated total error of $\bar{k}_s$(mean) is about 15 %. The strong scattering of existing experimental data (in the extreme case ±20 %) calls for more accurate and systematic experiments. Only such data would serve as an objective basis for further theoretical developments. The high statistical deviation of the experimental results is caused primarily by improper accuracy of PC measurements (temperature, optical noise and dust problems, etc...) but the unreliability of the sample characteristics (13) and neglected terms in the evaluation of PC measurements (11) may also play an important role. Similar conclusions may be made concerning the results of a very recent PC study of polymethylsiloxane (22).

Finally we note, that it would be theoretically possible to determine the zero concentration extrapolated value of $\bar{D}_{z,0}$ from only one measurement of $\bar{D}_{z,c}$ with a known concentration in the diluted regime so, that the concentration dependence and the extrapolation would be calculated using the hydrodynamic theory. However, the uncertainty of the relationship between $\bar{D}_{z,0}$ - $\bar{k}_s$ and the inaccuracy of the measurements of the present experimental stage do not allow this extrapolation. It is still necessary to perform measurements in 4-5 different concentrations for the reliable determination of $\bar{D}_{z,0}$ and $\bar{k}_s$.

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REFERENCES

1. A. Kotera and T. Hamada, Rept. Progr. Polym. Phys. (Japan) 11, 57 (1968)
2. J.M. Peterson and M. Fixman, J. Chem. Phys. 39, 2516 (1963)
3. I.C.W. Pyun and M. Fixman, J. Chem. Phys. 41, 937 (1964)
4. H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, 1971
5. M. Fixman, Macromolecules 14, 1706 (1981)
6. M. Fixman, Macromolecules 14, 1710 (1981) and F.L. Mc Crackin, C.M. Guttman and A.Z. Ackasu, Macromolecules, 17, 604 (1984)
7. J.P. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, 1971
8. C. Tanford, Physical Chemistry of Macromolecules, John Wiley, New York, 1963
9. Polymer Handbook, ed.by J. Brandrup and E.H. Immergut, Wiley Interscience, New York, 1975
10. J.G.Kirkwood and J. Rieseman, J. Chem. Phys. 16, 565 (1948) and J.G. Kirkwood, R.W. Zwanzig and R.J. Plock, J. Chem. Phys. 23, 213 (1955)
11. I. Tomka and G. Vancso, preprint and to be published
12. I. Tomka and G. Vancso, ACS Polymer Preprints, Nb.2, 1986
13. I. Tomka and G. Vancso, in "Applied Polymer Analysis and Characterization", ed. by J. Mitchell, Jr., Hanser Publishers, in press
14. G. Vancso and I. Tomka, ACS Polymer Preprints, Nb.2, 1986 and to be published
15. B. J. Berne and R. Pecora, Dynamic Light Scattering, Wiley, New York, 1976
16. W. H. Stockmayer and M. Schmidt, Pure appl. Chem. 54, 407 (1982)
17. T.A. King, A. Knox, W.I. Lee and J.D.G. McAdam, Polymer 14, 151 (1973)
18. G. Jones and D. Caroline, Chem. Phys. 37, 187 (1979)
19. C.C. Han and F.L. McCrackin, Polymer 20, 427 (1979)
20. T.A. King, A. Knox and J.D.G.McAdam, J. Pol. Sci. Pol. Symp. 44, 195 (1974)
21. M. Wales and S.J. Rehfeld, J. Pol. Sci., 62, 179 (1962), T. Homma, K. Kawahara, H. Fujita and M. Ueda, Makromol. Chem. 67, 132 (1962), I.H. Billick, J. Phys. Chem., 66, 1941 (1962) and I.H. Billick, ACS Polymer Preprint, 5, 855 (1964)
22. M. Duval and A. Lapp, Makromol. Chem. Rapid Comm. 7, 477 (1986)

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