

Sedimentation Coefficients, Diffusion Coefficients, Partial Specific Volumes, Frictional Ratios, and Second Virial Coefficients of Polymers in Solution^{*,**}

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* Based on a table in the second edition, by P. E. O. Klärner, and H. A. Ende, BASF AG, Ludwigshafen, Germany.

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A. SEDIMENTATION COEFFICIENTS, DIFFUSION COEFFICIENTS, PARTIAL SPECIFIC VOLUMES, AND FRICTIONAL RATIOS OF POLYMERS IN SOLUTION (2, 349–357, 799, 800)

1. Introduction

1.1. Sedimentation Coefficient The sedimentation coefficient s is defined as the sedimentation velocity in a unit force field

$$s = (dr/dt)/(\omega^2 r) \quad (A1)$$

where r is the distance from center of rotation, and ω , the angular velocity. For a given polymer-solvent system, the sedimentation coefficient is dependent on temperature T , pressure p , and polymer concentration C . Experimentally, sedimentation coefficients can be determined only with an ultracentrifuge.

Concentration Dependence

For polymer solutions studied by ultracentrifugation, the following concentration dependence of the sedimentation coefficient holds:

$$1/s = (1/s_0)(1 + k_s C + k_s' C^2 + \dots) \quad (A2)$$

where s_0 is the sedimentation coefficient at zero concentration. In Section B the concentration dependence of s according to Eq. (A2) is listed. In some cases, special extrapolation procedures are used. The tables in Section B also refer to the appropriate reference. For special treatments, see, e.g., Gehaia (358,359).

Sector shaped cells are normally used in an ultracentrifuge. In these cells, the square-dilution rule has to be taken into account (360):

$$C_i/C_0 = (r_0/r_i)^2 \quad (A3)$$

where r_0 and r_i are the distances of the meniscus and of the boundary from the axis of rotation and C_0 and C_i the

$$s_n = M_n \int_0^{\infty} W(M) M^{-1} s(M) dM$$

$$s_w = \int_0^{\infty} W(M) s(M) dM$$

$$s_z = (1/M_w) \int_0^{\infty} W(M) M s(M) dM \quad (A5)$$

where $W(M) = C(M)/\int_0^{\infty} C(M) dM = C(M)/C_0$ is the mass distribution of the polydisperse polymer in the cell and s_n , s_w , and s_z the number average, mass average and z-average of the sedimentation coefficient. In many cases the migration of the maximum of the quantity $\partial C/\partial r$ is determined, which leads to a sedimentation coefficient s_t , that in turn is related, in a complicated manner, to the averages of s in Eq. (A5). Another method of evaluating the sedimentation coefficient is by observing the median, that is the line dividing the gradient curve in two equal areas, yielding a value s_m which is also a rather complicated average. Provided the skewness of the molar mass distribution is not very pronounced, s_w can be calculated by (Ref. 259)

$$s_w = (3s_m - s_t)/2 \quad (A6)$$

Most ultracentrifuges measure the refractive index difference between polymer and solvent, dn , or the refractive index gradient $\partial n/\partial r$ versus r (Schlieren optics). With certain assumptions $\partial n/\partial r$ can be related to the concentration gradient (Ref. 14)

$$\partial n/\partial r = R(\partial C/\partial r) \quad (A7)$$

where R is called the specific refractive index increment. The interference optics measure the deflection of the parallel interference lines in the solution. This deflection is directly proportional to the concentration of the polymer.

The absorption optics measure the optical density of the system as a function of the rotor distance, which, according to the Lambert-Beers law is proportional to the concentration of the polymer. The intensity is measured with a photoelectric scanner.

A multiplexer is used in order to measure several concentrations during one run (869-871).

Sedimentation Coefficient – Molar Mass Relationship

The dependence of s on the molar mass can be given by a power law expression:

$$s = K_s M^{a_s} \quad (\text{A8})$$

where K_s and a_s are empirical constants determined for each polymer-solvent system at given values of temperature and pressure. In Section B, relationship (A8) is listed whenever quoted in the literature, in preference to single s values,

Temperature Dependence, Pressure Dependence

Svedberg and Pedersen (2) and Mosimann and Signer (361) derived expressions for the temperature and pressure dependence of the sedimentation coefficient with restricted validity:

$$s/s^\theta = (\eta_1^\theta/\eta_1)(1 - v_2^\theta \rho_1^\theta)/(1 - v_2 \rho_1) \quad (\text{A9})$$

where s^θ , η_1^θ , v_2^θ and ρ_1^θ denotes the values at the reference temperature and/or pressure. Equation (A9) holds in the case of an incompressible medium and if no changes of size, shape and solvation state of the dissolved molecules in the temperature and pressure region take place. From these assumptions it may be deduced that Eq. (A9) can be applied with sufficient accuracy only on proteins in aqueous solvents.

Due to the high centrifugal fields applied in the ultracentrifuge, pressure gradients with pressures up to 200 bars are encountered in the cell and change appreciably the viscosity and the density of the solvent and the partial specific volume of the polymer. Thus the sedimentation coefficient, s , measured at a pressure p differs from the sedimentation coefficient, s^0 , measured at 0 bar. Application of Eq. (A9) for the calculation of s requires the knowledge of η_1 (362), ρ_1 (given in a number of Handbooks) and v_2 (148). More precise equations for the calculation of the pressure influence on the sedimentation have been worked out by several authors (363,364,365,800). The equation of Oth and Desreux (Ref. 363)

$$s = s^0(1 - \mu p) \quad (\text{A10})$$

has very often been used for the calculation of s^0 (800). The

coefficient μ depends on the polymer-solvent system and varies only slightly with pressure.

In Section B, the intrinsic sedimentation coefficient, $[s^0]$, instead of s^0 , has been occasionally listed. $[s^0]$ is related to Eq. (9): $[s^0] = s^0 \eta_1 / (1 - v_2 \rho_1)$.

1.2. Diffusion Coefficient The translational diffusion coefficient D is defined by Ficks' first law:

$$J = -D \nabla C \quad (\text{A11})$$

where J is the flow of substance (total number of particles transported in unit time across unit surface) and ∇C the concentration gradient. For one dimensional diffusion, Eq. (A11) reduces to

$$(1/A) (\partial n / \partial t) = -D (\partial C / \partial r) \quad (\text{A12})$$

where A denotes the area and n the number of moles. The negative sign in Eqs. (A11) and (A12) indicate that diffusion takes place in the direction of decreasing concentration. For practical reasons, Ficks second law is preferred

$$(\partial C / \partial t) = D \Delta C \quad (\text{A13})$$

where Δ denotes the Laplace operator. Eq. (A13) reduces to

$$(\partial C / \partial t) = D (\partial^2 C / \partial r^2) \quad (\text{A14})$$

for the one dimensional case. Eqs. (A13) and (A14) allow the determination of D when solved with consideration to certain initial and boundary conditions.

Experimentally translational diffusion coefficients can be determined with an ultracentrifuge (see Section 1.3) in special diffusion cells using Eqs. (A11)-(A14) (800) and with dynamic light scattering (DLS). Since 1970, when the dynamic light scattering became available, nearly all diffusion coefficients have been measured by this method. Based on the theory of Pecora (853,854), the experimentally measured autocorrelation function $g_2(t)$ is linked with the diffusion coefficient in polymer solutions (Refs. 730,855):

$$\lim_{c \rightarrow 0} g_2(t) = A + B \left(M_w^{-1} \int_0^\infty MW(M) p(q, M) \exp(-q^2 D(M) t) dM \right)^n \quad (\text{A15})$$

where $n = 1$ for the heterodyne procedure and $n = 2$ for the homodyne one. Eq. (A15) reduces, in the case of a monodisperse polymer solution, to

$$\lim_{c \rightarrow 0} g_2(t) = A + B (p(q, M) \exp(-q^2 D(M) t))^n \quad (\text{A16})$$

A and B are measurable constants. Extrapolation of q against zero yields $P(q, M) = 1$. Note that $g_2(t)$ is the z -average of the function, $\exp(-q_2 D(M)t)$. In this way one obtains the direct measurable quantity D_z from dynamic light scattering on polydisperse polymer solutions.

For polydisperse polymer solutions, Eq. (A16) may be expanded in a series (Ref. 856):

$$\lim_{\substack{C \rightarrow 0 \\ q \rightarrow 0}} g(t) = \exp(-q^2 D_z t) (1 + (\mu_2/2!)t^2 - (\mu_3/3!)t^3 + \dots) \quad (\text{A17})$$

where the moments, μ_i , are related to the molar mass distribution of the polymer (671).

More general methods for the determination of the distribution of the diffusion coefficient and of the molar mass are given elsewhere (857,858).

As has been pointed out, only the translational diffusion coefficient is listed in the tables. For higher modes of the autocorrelation function (e.g. rotation, vibration) see the appropriate literature (853,854).

The entire description of the translational diffusion of a polymer molecule in solution requires the determination of the mutual or cooperative diffusion coefficient, D_m , which characterizes the relaxation of a concentration gradient and the self-diffusion coefficient, D_s , which describes the Brownian or random motions of the polymer molecule (860–863).

$$D_m = (RT/f) (1 - v_2 \rho_1) (1 + 2A_2 MC + 3A_3 MC^2 + \dots) \\ D_s = RT/f$$

At infinite dilution, $D_m = D_s \times D_m$ is normally measured with classical diffusion cells or dynamic light scattering whereas D_s can be studied by measuring the migration of labeled solute molecules (864), by pulsed field gradient NMR (865), and by forced Rayleigh scattering (866). Normally, D_m is given in the tables. In some cases, especially where D_s is extrapolated to zero concentration, $D_s = D_m$ is given in the tables.

Concentration Dependence

The concentration dependence of the diffusion coefficient may be described as

$$D = D_0(1 + k_D C + k'_D C^2 + \dots) \quad (\text{A18})$$

where D_0 is the diffusion coefficient at zero concentration. In Section B a concentration dependence of D according to Eq. (A18) is listed. In some cases, special extrapolation procedures are used. In these cases Section B refers to the appropriate references.

Averages of the Diffusion Coefficient

Similar considerations as made on sedimentation coefficients hold for diffusion coefficients. From measurements

in a diffusion cell, one obtains the various averages of the diffusion coefficient from the distribution of the concentration gradient, $\partial C/\partial r$, in the cell:

$$D_n = M_n \int_0^\infty W(M) M^{-1} D(M) dM \\ D_w = \int_0^\infty W(M) D(M) dM \\ D_z = (1/M_w) \int_0^\infty W(M) M D(M) dM \quad (\text{A19})$$

where $W(M) = C(M)/C_0$.

The diffusion cell may be combined in the same manner as in the case of the ultracentrifuge with Schlieren optics, interference optics, and absorption optics. In most cases, the mass average and the area average of the diffusion coefficient are determined. They can be calculated with the help of Eqs. (A14) and (A19):

$$D_w = \left(\int_0^\infty r^2 (\partial C/\partial r) dr \right) / \left(2t \int_0^\infty (\partial C/\partial r) dr \right) \quad (\text{A20})$$

$$D_A = \int_0^\infty ((\partial C/\partial r) dr)^2 / (4\pi t (\partial C/\partial r)_{\max})^2 \quad (\text{A21})$$

$(\partial C/\partial r)_{\max}$ is the maximum height of $\partial C/\partial r$. The integral in Eq. (A21) is the area of the curve.

As has been pointed out, dynamic light scattering measurements normally yield the z -average of D . Nevertheless it might be possible to determine averages other than D_z with the help of Eqs. (A19) and (A21). In Section B the different averages of D are quoted. In some cases unusual averages are listed. In these cases Section B refers to the appropriate references.

Diffusion Coefficient – Molar Mass Relationship

The diffusion coefficient – molar mass dependence frequently takes the form

$$D = K_D M^{-a_D} \quad (\text{A22})$$

where K_D and a_D are constants for each polymer–solvent system at given values of temperature and pressure. In Section B relationship A(22) is listed whenever quoted in the literature, in preference to single D values.

Temperature Dependence, Pressure Dependence

A similar expression as Eq. (A9) holds under the same restricted conditions for the temperature and pressure dependence of the diffusion coefficient:

$$(D/T)/(D^\theta/T_0) = \eta_1^\theta/\eta_1 \quad (\text{A23})$$

where D^0 and η_1^0 denote the values at the reference temperature T_0 and/or pressure p_0 . As has been pointed out in Eq. (A9), Eq. (A23) can be applied with sufficient accuracy on proteins in aqueous solvents only.

The temperature dependence of the diffusion coefficient is often described by the following exponential function

$$D = D_\infty \exp(-E_D/RT) \quad (\text{A24})$$

where E_D denotes the apparent activation energy of the diffusion and D_∞ the diffusion coefficient at the limit $T = \infty$. In Section B we have listed the temperature and pressure dependence of D whenever quoted in the literature.

1.3. Molar Mass Averages Determined from Sedimentation and Diffusion Coefficients For the experimental determination of the molar mass from sedimentation and diffusion measurements, the Svedberg Eq. (A2) is used:

$$M = (s_0/(1/v_2\rho_1))/(D_0/RT) \quad (\text{A25})$$

Here s_0 and D_0 are the corrected and standardized coefficients for zero polymer concentration. For polydisperse polymers the various averages of the sedimentation and diffusion coefficient s and D are inserted, obtaining certain molar mass averages $M_{\beta,\gamma}$. Thus Eq. (A25) acquires the more general form:

$$M_{\beta,\gamma} = (s_{0,\beta}/(1 - v_2\rho_1))/(D_{0,\gamma}/RT) \quad (\text{A26})$$

For $\beta = n, w, z, \dots$ and $\gamma = n, w, z, \dots$ Eq. (A26) defines several different molar mass averages $M_{n,n}$, $M_{w,n}$, $M_{w,w}$ etc. The averages, $M_{n,n}$, and $M_{w,w}$, are different from M_n and M_w respectively (859). The coefficients with $\beta = n$ and z and $\gamma = n$ are determinable only with large error. Instead, the coefficients with $\beta = t$ and m (see under Section 1.1.) and $\gamma = A$ and w (see under Section 1.2.) are usually evaluated. Thus, rather peculiar averages, e.g. $M_{t,A}$, $M_{m,w}$, and $M_{m,A}$, result. The more straightforward molar mass averages $M_{n,w}$, $M_{w,w}$, $M_{z,w}$, etc., in relation to the familiar averages, M_n , M_w , and M_z , are found elsewhere in the literature (369–371,859).

1.4. Partial Specific Volumes The volume, V^{id} , of an ideal two component system can be expressed in terms of the masses m_1 and m_2 and the specific volumes, v_1^0 and v_2^0 , of the two components by the equation

$$V^{\text{id}} = m_1 v_1^0 + m_2 v_2^0 \quad (\text{A27})$$

Most components do not behave ideally upon mixing; i.e. they react with each other in a way so that the total volume deviates from V^{id} . The total volume can then be written as

$$V = m_1 v_1 + m_2 v_2; \quad v_i = (\partial V / \partial m_i)_{p,T,m_{j \neq i}} \quad (\text{A28})$$

where v_i ($i = 1, 2$) is the partial specific volume of component i . When component 2 is polymer and component 1 solvent, then, for practical reasons it is convenient to introduce the so-called apparent partial specific volume v_2^* which is defined by

$$V = m_1 v_1^0 + m_2 v_2^* \quad (\text{A29})$$

where v_1^0 denotes the specific volume of the solvent. The quantity, v_2^* , now contains the parameter of nonideal mixing of both the solvent and the polymer. In practice, however v_2^* differs not much from v_2 if the polymer concentration is kept low (up to 1%). Dividing Eq. (A29) by the total mass $m_1 + m_2$ leads to

$$v = w_1 v_1^0 + w_2 v_2^* \quad (\text{A30})$$

where v is the specific volume of the solution and $w_i = m_i / \sum m_i$ are the mass fractions of the solvent ($i = 1$) and the polymer ($i = 2$).

With $v = 1/\rho$ and $v_1^0 = 1/\rho_1$, ρ and ρ_1 being the densities of the solution and the solvent, respectively, it is readily found that

$$v_2^* = (1/w_2)(\rho_1 - w_1\rho)/(\rho\rho_1) \quad (\text{A31})$$

Eq. (A31) demonstrates that v_2^* can be determined by measuring ρ_1 and ρ . Numerous methods for determining densities are described in the literature (268,372–379).

In order to determine the partial specific volume from the apparent specific volume, Eq. (A29) yields

$$(\partial(m_2 v_2^*) / \partial m_2)_{m_1} = m_2 (\partial v_2^* / \partial m_2)_{m_1} + v_2^* = (\partial V / \partial m_2)_{m_1} \quad (\text{A32})$$

where $(\partial V / \partial m_2)_{m_1}$ is, according to definition, equal to v_2 . In terms of mass fractions, Eq. (A32) can finally be written as

$$v_2 = v_2^* + w_1 w_2 (\partial v_2^* / \partial w_2) \quad (\text{A33})$$

Most values reported in the literature are v_2^* -values rather than v_2 -values, since extrapolation according to Eq. (A33) is usually omitted. The differences between v_2^* and v_2 are, however, often small.

1.5. Frictional Ratios The molar frictional coefficient, f_{sp} , of an unsolvated spherical molecule may be computed by the formula based on Stokes law:

$$f_{sp} = 6\pi\eta R_H N_A = 6\pi\eta [3N_A M v_2 / (4\pi)]^{1/3} \quad (\text{A34})$$

where η is the viscosity of the solvent and N_A is Avogadro's number. When the shape of a molecule deviates from a sphere, or when it is solvated, then the frictional coefficient, f_0 , of such a molecule is larger than that of the spherical molecule. The frictional ratio, f_0/f_{sp} , thus permits to draw conclusions concerning either solvation or shape of the

molecule. It is possible to calculate the dimensions of the nonspherical molecule, provided a particular model (ellipsoid, cylinder, etc.) for the molecule is adopted and either the degree of solvation is known or assumed to be negligible. The molar frictional coefficient can be determined either from sedimentation velocity data, provided the molar mass is known from independent measurements according to the Svedberg equation

$$f_0 s_0 = M(1 - v_2 \rho_1) \quad (\text{A35})$$

or from diffusion measurements, using the relation

$$f_0 = RT/D_0 \quad (\text{A36})$$

Eqs. (A34)–(A36) are most frequently used for calculating the frictional ratio. f_0/f_{sp} is listed in the tables. Other relationships for the determination of f_0/f_{sp} are quoted in the literature (2). In these cases special reference to the literature is made in the tables.

In few cases, only the molar frictional coefficient f_0 , rather than f_0/f_{sp} , was quoted in the literature. These values are inserted in the same column as the values for the frictional ratio.

1.6. List of Symbols and Abbreviations

Symbols

C	Concentration
C_0	Initial polymer concentration
C_t	Polymer concentration at time t
D	Diffusion coefficient
D_A	Area average of the diffusion coefficient
D_n, D_w, D_z	Number average, mass average, and z-average of the diffusion coefficient
D	Diffusion coefficient at reference temperature and/or pressure
D_0	Diffusion coefficient at zero concentration
η_1	Viscosity of solvent
η_1^θ	Viscosity of solvent at reference temperature and/or pressure
f_{sp}	Molar frictional coefficient of a spherical molecule
f_0	Molar frictional coefficient at zero concentration
k_s, k_s	Concentration coefficients defined by Eq. (A2)
k_D, k_D	Concentration coefficients defined by Eq. (A18)
M	Molar mass of the polymer
M_n, M_w, M_z	Number average, mass average and z-average of the molar mass of the polymer
M	Molar mass determined by Mark–Houwink equation
M_{MW}	Molar mass determined by equations from Mandelkern and Flory, or Wales and Van Holde (see Section 1.7)

$M_{\beta, \gamma}$	Molar mass average determined by Eq. (A26) from $s_{0, \beta}$ and $D_{0, \gamma}$
$M_{s, w}, M_{s, A}, M_{s, D}$	Molar mass average determined from undefined sedimentation coefficient s and D_w, D_A and undefined diffusion coefficient D , respectively
n	Refractive index or number of moles
ω	Angular velocity
r	Distance from center of rotation
r_0	Distance of meniscus from center of rotation
r_t	Distance of boundary from center of rotation at time t
ρ	Density of solution
ρ_1	Density of the solvent
R	Gas constant
s	Sedimentation coefficient
s_n, s_w, s_z	Number average, mass average, and z-average of the sedimentation coefficient
s_θ	Sedimentation coefficient at reference temperature and/or pressure
s^0	Sedimentation coefficient at pressure $p = 0$ bar
s_0	Sedimentation coefficient at zero concentration
$[s_0]$	Intrinsic sedimentation coefficient (see under Section 1.1)
s_m	Sedimentation coefficient determined from migration of gradient curve median
s_t	Sedimentation coefficient determined from migration of gradient curve maximum
T	Temperature
θ	Theta temperature ($A_2 = 0$)
t	Time
v_i	Partial specific volume of component i ($i = 1$, solvent; $i = 2$, solute)
v_1^0	Specific volume of component i
v_2^*	Apparent specific volume of solute

Abbreviations

A	Archibald method
approx.	approximately
CLS	Classical light scattering method
DLS	Dynamic light scattering method
NBS	National Bureau of Standards, USA (now National Institute of Standard and Technology, NIST)
OS	Osmometry
PCC	Pressure Chemical Co., Pittsburg, PA, USA
RT	Room temperature
SE	Sedimentation equilibrium
SRM	Standard reference material
SV	Sedimentation velocity
TS	Toyo Soda Co., Japan
V	Number of single values given in Ref. cited

1.7. Miscellaneous With certain assumptions it is possible to determine the molar mass from a combination of the intrinsic viscosity $[\eta]$ and the limiting sedimentation coefficient s_0 . In this way, Mandelkern and Flory (128) and Wales and Van Holde (134) derived an expression. An

expression similar to the equation between M , $[\eta]$, and s_0 was derived between M , $[\eta]$, and D_0 (128). The molar masses determined from either one of these relationships are referred to as MW.

B. TABLES OF SEDIMENTATION COEFFICIENTS, DIFFUSION COEFFICIENTS, PARTIAL SPECIFIC VOLUMES, AND FRICTIONAL RATIOS OF POLYMERS IN SOLUTION

TABLE 1. POLY(ALKENES)

Polymer	Solvent	T (°C)	$M (\times 10^{-3})$ (g/mol)	$s_0 (\times 10^{13})$ (s)	k_s (cm ³ /g)	$D_0 (\times 10^7)$ (cm ² /s)	k_D (cm ³ /g)	f_0/f_{sp}	v_2 (cm ³ /g)	Remarks	Refs.
Poly(ethylene)	l-Bromonaphthalene	110	4.7	1.42						M_v	38
			14.2	2.03							
			21.8	2.39							
			55.0	3.39							
linear	l-Bromonaphthalene	110	3.5-274	$s_0 = 7.74 \times 10^{-15} M^{0.344}$						M_v	38
		120	69	-4.09						M_{NW}	509
branched		120	136	-5.14						M_{NW}	509
linear	l-Chloronaphthalene	120	88	-5.18						$[\eta] = 51$ cm ³ /g	27
				-1.67						90	
				-2.37						169	
				-3.31							
branched, fractions											
branched per molec.											
1.9				-1.06						$[\eta] = 18$ cm ³ /g	27
2.6				-1.91						33	
3.0				-2.85						56	
2.9				-2.77						60	
4.6				-3.57						66	
5.7				-4.11						74	
6.4				-4.52						88	
13.7				-7.30						118	
16.1				-7.87						129	
26.3				-11.37						139	
	Diphenyl	110							^a		532
		123							^a		
		130	26			9.80				D_A, M_w, D_w given in Ref.	593
			60			6.42					
			79			6.42					
			99			4.73					
			261			3.13					
			493			2.15					
			25.7			0.87					
			503			0.20					
branched	Tetralin	80									
Poly(1-butene)	Ethyl octanoate	22 (T = θ)	800	1.30	55.5					$D_{0,z}; M_w/M_n \approx 3$	619
Poly(isobutene)	Cyclohexane	34 (T = θ)		6.4 ^c	721 $\pm$ 159				1.106 ^b	$D_{0,z}; M_w/M_n \approx 5$ $M_{NW};$ M_v ; Oppanol B 100	409, 410 576
		20	30.9	0.925	54				1.091	M_n	32,621,622
			86.7	1.49	128						
			172	1.94	191						
			672	3.33	510						

TABLE 1. cont'd

Polymer	Solvent	T (°C)	M ($\times 10^{-3}$) (g/mol)	s_0 ($\times 10^{13}$) (s)	k_s (cm ³ /g)	D_0 ($\times 10^7$) (cm ² /s)	k_D (cm ³ /g)	f_0/f_{sp}	v_2 (cm ³ /g)	Remarks	Refs.
Poly(l-hexene)	Acetone	20	46.8	11.5		16.2				s_1 ; D_A ; M_{1A}	53
			222	21.5		6.4					
			571	33.8		3.0			0.793		
Poly(tetrafluoroethylene)	Perfluorotetracosane	20									54
		325	260			3.66	-35.2				1004
			2100			1.21	-130.0				

^a See Ref. for various methods applied and values obtained.
^b Corrected for pressure influence.
^c See Ref. for def. of s .

TABLE 2. POLY(DIENES)

Polymer	Solvent	T (°C)	M ($\times 10^{-3}$) (g/mol)	s_0 ($\times 10^{13}$) (s)	k_s (cm ³ /g)	D_0 ($\times 10^7$) (cm ² /s)	k_D (cm ³ /g)	f_0/f_{sp}	v_2 (cm ³ /g)	Remarks	Refs.
Poly(butadiene)	Diethyl ketone	10.3	60	1.76						M_{MW}	590
			187	2.76							
			350	3.45							
			436	4.28							
			778	4.52							
			1380	5.15							
<i>cis</i> -4	Dodecane	80				23.8					625
<i>cis</i> -4	Hexafluorobenzene	80				16.3					625
95%, 1,4 <i>cis</i>	Diethyl ketone	10.3 ($T = \theta$)		$s_0 = 0.53 \times 10^{-15} M^{0.5}$						$s_{01}, s_{w1}, s_{11}, s_{m,0}$ given in Ref.	574
90%, 1,4 <i>cis</i> (TiI ₄)	Hexane/heptane (1/1)	20	55-1080	$s_0 = 2.80 \times 10^{-15} M^{0.48}$						$M_{s,D}$	323
90%, 1,4 <i>cis</i> (CoCl ₂)	Hexane/heptane (1/1)		34.7-1040	$s_0 = 2.33 \times 10^{-15} M^{0.50}$						$M_{s,D}$	323
<i>cis</i> -4	Hexatriacontan	80									625
Linear	Cyclohexane	25									987
						4.78					
						$D_0 = 1.45 \times 10^{-4} M^{-0.501}$; $11000 \leq M_w \leq 760000$ g/mol					
						$D_0 = 6.34 \times 10^{-5} M^{-0.496}$; $11000 \leq M_w \leq 760000$ g/mol					
						$D_0 = 2.39 \times 10^{-4} M^{-0.670}$; $99000 \leq M_w \leq 1900000$ g/mol					
						$D_0 = 8.87 \times 10^{-5} M^{-0.497}$; $99000 \leq M_w \leq 1900000$ g/mol					
						$D_0 = 1.38 \times 10^{-4} M^{-0.5}$;					
18-armed star	Dioxane	26.5 ($T = \theta$)									
	Cyclohexane	25									
	Dioxane	26.5 ($T = \theta$)									
Poly(butadiene- <i>stat</i> -acrylonitrile)	Methyl ethyl ketone/ cyclohexane (47.5/52.5)	22 ($T = \theta$)	34.8-780	$s_0 = 1.28 \times 10^{-12} M^{0.5}$						D_A ; $M_{s,D}$, k_s given in Ref.	552
	Methyl ethyl ketone/ isopropanol (60/40)	20 ($T = \theta$)	475							D_A ; $M_{s,D}$	552
			205	7.58							
			101	4.65							
				3.43							
Poly(butadiene- <i>co</i> -styrene) branched	Benzene	25	81.9-168	1.21-4.63						See Ref.	406
	Methyl <i>n</i> -propyl ketone	21 ($T = \theta$)	49-514	$s_0 = 1.04 \times 10^{-15} M^{0.5}$							573
21 mass% styrene	Methyl <i>n</i> -propyl ketone	21 ($T = \theta$)	49-514	$s_0 = 0.83 \times 10^{-15} M^{0.5}$						M_n	344
Poly(chloroprene)	Methyl ethyl ketone	25	56-380	$s_0 = 3.1 \times 10^{-15} M^{0.5}$						M_w ; OS; SE	444
									0.995 $\pm$ 0.005		
									0.773		

Poly(isoprene)	Solvent	Conc. (g/100 ml)	Temp. (°C)	S ₀ (S)	D ₀ (cm ² /s)	M _w /M _n	M _w	M _n	[η] (dl/g)	[η] _{sp} /c (dl/g)	f ₀ /f _{sp}	Ref.
Linear	Carbon tetrachloride	5	5	5	$D_0 = 10^{-7.73 \pm 0.08} M^{-0.54 \pm 0.04}$	$M_w/M_n = 1.05-1.11$	626					
	Carbon tetrachloride	50	5	5	$D_0 = 10^{-7.47 \pm 0.05} M^{-0.61 \pm 0.01}$	$M_w/M_n = 1.02-1.07$						
	Carbon tetrachloride	50	21.2-122		$D_0 = 10^{-7.53 \pm 0.15} M^{-0.57 \pm 0.03}$							
	Carbon tetrachloride	50	61.7-630		$D_0 = 10^{-7.22 \pm 0.12} M^{-0.61 \pm 0.03}$							
	Cyclohexane	-	137		2.4							
4-armed star	Carbon tetrachloride	5	173		1.87							
	Carbon tetrachloride	50	380		1.20							
	Carbon tetrachloride	50	795		0.91							
	Carbon tetrachloride	50	1760		0.52							
	Cyclohexane	-	4400		-							
8-armed star	Carbon tetrachloride	5	96		-							
	Carbon tetrachloride	50	810		0.89							
	Carbon tetrachloride	50	3900		0.37							
	Carbon tetrachloride	50	5280		0.305							
	Cyclohexane	-	93		-							
12-armed star	Carbon tetrachloride	5	218		2.4							
	Carbon tetrachloride	50	384		1.88							
	Carbon tetrachloride	50	800		1.06							
	Carbon tetrachloride	50	1480		0.71							
	Cyclohexane	-	3570		0.455							
18-armed star	Carbon tetrachloride	5	270		2.24							
	Carbon tetrachloride	50	485		1.26							
	Carbon tetrachloride	50	930		1.16							
	Carbon tetrachloride	50	125		2.63							
	Cyclohexane	-	275		1.64							
natural rubber, crepe	Carbon tetrachloride	5	330		1.55							
	Carbon tetrachloride	50	450		1.41							
	Carbon tetrachloride	50	760		1.44							
	Carbon tetrachloride	50	1600		0.48							
	Cyclohexane	-	1750		0.46							
natural rubber	Carbon tetrachloride	5	1800		0.41							
	Carbon tetrachloride	50	1600		0.48							
	Carbon tetrachloride	50	270		3							
	Carbon tetrachloride	50	1660		1.01							
	Cyclohexane	-	460-970		$D_0 = 3.98 \times 10^{-2} M^{-0.55}$							
1,4-cis (C ₇ H ₁₅) ₃	Carbon tetrachloride	5	460-970		$s_0 = 5.01 \times 10^{-15} M^{0.45}$							
	Carbon tetrachloride	50	460-970		$s_0 = 7.76 \times 10^{-2} M^{0.42}$							
	Carbon tetrachloride	50	460-970									
	Carbon tetrachloride	50	460-970									
	Cyclohexane	-	460-970									

TABLE 3. ACRYLIC POLYMERS

Polymer	Solvent	T (°C)	M (× 10 ⁻³) (g/mol)	s ₀ (× 10 ¹³) (s)	k _s (cm ³ /g)	D ₀ (× 10 ⁻⁷) (cm ² /s)	k _D (cm ³ /g)	f ₀ /f _{sp}	v ₂ (cm ³ /g)	Remarks	Refs.
Poly(acrylamide)	Water	20	19.4–534	s ₁ = 8.17 × 10 ⁻¹⁵ M ^{0.31}		D _A = 8.46 × 10 ⁻⁴ M ^{-0.69}			0.769	D measured in H ₂ O/KCl (0.2 mol/dm ³); M _{1,A} SV; 15V; M _w /M _n = 1.15–1.4	266, 154
			130–8200	s _w = 1.07 × 10 ⁻¹⁵ M ^{0.48±0.01}		D _{2,0} = 1.24 × 10 ⁻⁴ M ^{-0.53±0.01}			0.708		628
			5000 250, 610						0.693 0.696	C = 0.06, 1.2 g/dm ³ M _w ; M _w /M _n = 1.5; C = 5, 10 g/dm ³	629 630
	Water/NaCl (0.2 mol/dm ³)	20	250, 610						0.687	M _w ; M _w /M _n = 1.5; C = 5, 10 g/dm ³	630
			20								632
			20								633
			25								631
			25								790
H-acrylamide 2,3,3-D ₃ -acrylamide	Water/NaCl Water/NaCl (0.1 mol/dm ³) Water/NaCl (0.1 mol/dm ³)	25	100–8000 8200	s ₀ = 8.17 × 10 ⁻¹⁵ M ^{0.31} s ₀ = 9 × 10 ⁻¹⁵ M ^{0.32} s ₀ = 4.9 × 10 ⁻¹⁵ M ^{0.37}	1570	0.3	88		0.697 0.710	M _w /M _n = 2.5 M _w ; D _{2,0}	634, 635
			25								667
			25								1008
			20								634
			20								634
partially hydrolyzed Pusher 700 (Dow Chemical)	Water/NaCl (1 M) Water/NaCl (2 g/dm ³) Water/NaCl (20 g/dm ³) Water/NaNO ₃ (0.5 mol/dm ³)	25	2330 8000 160 260			0.505 0.630 1.6 0.14 1.29 ± 0.05				M _w ; see Ref. for s ₀ and k _s	636
			26								637
			26								636
			25								636
			25								636
Poly(p-ethoxycarbonyl phenylmethacrylamide)	Water Water/NaCl (0.1 mol/dm ³) Water/NaCl (0.2 mol/dm ³) Acetone	26	460			1.15 ± 0.10 0.280	277			M _w ; D _{2,0} D ₂ ; C = 0.5 g/dm ³	636 637
			479								267
			575 955 1060 1000 740								
			575 955 1060 1000 740								
			575 955 1060 1000 740								
Poly(N-isopropyl- acrylamide)	Dimethylformamide Dimethylformamide/ formamide (90/10) Ethyl acetate Water	15 20 25 27.5 30 32 33 20	260–740 290 1000 1000			0.562 0.383 7.05				D ₂ ; C = 0.5 g/dm ³ ; 4V D ₂ ; C = 0.5 g/dm ³ ; 4V M _w ; D _A	267 267
			290								267
			1000								267
			1000								267
			1000								267
Poly(N-isopropyl methacrylamide)	Water	20	479			1.15 ± 0.10 0.280	277			M _w ; D _{2,0} D ₂ ; C = 0.5 g/dm ³	636 637
			479								267
			575 955 1060 1000 740								
			575 955 1060 1000 740								
			575 955 1060 1000 740								

Poly(<i>N</i> -isopropylmethacrylamide- <i>co</i> -acrylamide)			CLS, DLS	1006
Deionized water				
IPAM-100		3000	0.490	
IPAM-85		3100	0.439	
IPAM-70		4500	0.394	
IPAM-55		3900	0.421	
IPAM-40		2200	0.524	
IPAM		5200	0.335	
Poly(acrylamide- <i>co</i> -sodium-3-acrylamide-3-methylbutanoate- <i>co</i> -(2-(acrylamido)-2-methylpropyl) trimethylammonium chloride)				
AM	NaAMB	AMPTAC		1023
ATABAM 0.5-0.5	Water/NaCl (1 M)	25	0.498	
ATABAM 2.5-2.5		3430	0.313	
ATABAM 5.0-5.0		13900	0.476	
ATABAM 10-10		3450	0.264	
ATABAM 15-15		10800	0.313	
ATABAM 5.0-10		12200	0.361	
ATABAM 10-5.0		11200	0.389	
ATABAM 10-5.0		19400		
Poly(acrylamide- <i>co</i> -3-(2-acrylamido-2-methylpropane dimethylammonio)-1-propane-sulfonate) (AM- <i>co</i> -AMPDAPS)				
DAPSAM-1	Water/1 M NaCl	25	0.505	1010
DAPSAM-5		3200	0.316	
DAPSAM-10-2		12400	0.401	
DAPSAM-10-3		700	0.320	
DAPSAM-25-2		21500	0.397	
DAPSAM-40-2		8200	0.362	
DAPSAM-40-3		15100	0.324	
DAPSAM-60-2		17500	0.360	
DAPSAM-75-2		5400	0.490	
DAPSAM-100		6200	0.628	
Poly(acrylamide- <i>co</i> -NaAMPS- <i>co</i> -AMPTAC)				
ATASAM 0.5-0.5	Water/1 M NaCl	25	0.423	1022
ATASAM 2.5-2.5		6030	0.577	
ATASAM 5-5		2780	0.381	
ATASAM 10-10		5070	0.449	
ATASAM 15-15		5870	0.433	
ATASAM 10-5		6770	0.413	
Poly(NaAMPS- <i>co</i> -AMPTAC)				
ATAS-0	Water/1 M NaCl	25	0.387	1021
ATAS-10-2		6120	0.419	
ATAS-25-2		8220	0.473	
ATAS-40-2		6200	0.385	
ATAS-50-2		7920	0.463	
ATAS-70-2		7680	0.406	
ATAS-100		4980	0.637	
Poly(1,4-benzamide)	Dimethylacetamide/ 3% (g/mol) LiCl	1470		
	96 wt.% H ₂ SO ₄	55	$D_0 = 4.38 \times 10^{-4} M_w^{-0.82}$	1007
Poly(1,4-phenylene terephthalamide)		30	0.072	
		48.3	0.088	
		38.4	0.113	
		22.7	0.159	

[illegible]

TABLE 3. cont'd

Polymer	Solvent	T (°C)	M ($\times 10^{-3}$) (g/mol)	s_0 ($\times 10^{13}$) (s)	k_s (cm^3/g)	D_0 ($\times 10^7$) (cm^2/s)	k_D (cm^3/g)	f_0/f_{sp}	v_2 (cm^3/g)	Remarks	Refs.
	(1.0 mol/dm ³) (0.2 mol/dm ³) (0.012 mol/dm ³) (0.006 mol/dm ³) (0.0012 mol/dm ³) (1.0 mol/dm ³) (0.2 mol/dm ³) (0.012 mol/dm ³) (0.006 mol/dm ³)		420		2.4 4.2 32.0 60.0		0.2 1.0 1.35 $\pm$ 0.05 ^d 27.4 146			M_{SD}	555
	(0.0012 mol/dm ³) (0.2 mol/dm ³) (0.012 mol/dm ³) (0.006 mol/dm ³)		70		0.0 2.75 8.0		22.3 22.3 150 286			M_{SD}	
Poly(ethyl acrylate)	Methyl isobutyl ketone	24.3	34							M_v	148
Poly(ethyl acrylate-co-acrylic acid)	<i>n</i> -Propanol	28	18–155	$s_0 = 1.05 \times 10^{-12} M_n^{0.47}$					0.951	M_{MW}	456
sodium salt	Water/NaCl (0.05 mol/dm ³) (0.1 mol/dm ³) (0.3 mol/dm ³) (0.5 mol/dm ³) (0.7 mol/dm ³) (1.0 mol/dm ³) (1.2 mol/dm ³)		185–1300			$D_{0,z} = 5.76 \times 10^{-4} M^{-0.65}$ $D_{0,z} = 8.55 \times 10^{-4} M^{-0.67}$ $D_{0,z} = 3.73 \times 10^{-4} M^{-0.59}$ $D_{0,z} = 1.54 \times 10^{-4} M^{-0.52}$ $D_{0,z} = 1.41 \times 10^{-4} M^{-0.51}$ $D_{0,z} = 1.24 \times 10^{-4} M^{-0.50}$ $D_{0,z} = 1.10 \times 10^{-4} M^{-0.49}$ $D_{0,z} = 1.35 \times 10^{-4} M^{-0.51}$				$M_w/M_n = 1.8-2.3$	637
Poly(ethyl acrylate-co-methylacrylate)	2-Heptanone										
different comp.	Methyl ethyl ketone	20	77–7440	$s_0 \sim M^{0.43}$						v_2 and M given	506
Poly(ethyl methacrylate)	Acetone	20	34.1–9350	8.95–120		$D_0 \sim M^{-0.57}$ 17.4–0.85		$f_{sp} \sim M^{0.57}$	0.798 0.798 0.7942	M_{LA} $M_{LA}; s_1$; See Ref. extrapolated value	59 18 268
			24.6–7440	7.45–107	23–60	20.0–0.95	0–63			$M_w; s_1; D_A$; See Ref.	52
Poly(isooctyl methacrylate)	Methyl isobutyl ketone (theta-solvent) ^c	22.9 25	410 1036	63.0–67.5					0.863 0.900	M_v A^r	148 427
			875							$C = 2.5 \text{ g/cm}^3; s_w$ (Trautmann)	
									0.789		1053
Poly(phenyl methacrylate)	Toluene	25									
Poly(sulfoalkyl methacrylate)											
alkyl: hexyl	0.1 M NaCl	25	306							$M_w/M_n = 1.5; dn/dc = 0.135 \text{ cm}^3/\text{g}$	100
octyl			494			1.22				$M_w/M_n = 2.0; dn/dc = 0.140 \text{ cm}^3/\text{g}$	
decyl			701			1.02				$M_w/M_n = 1.8; dn/dc = 0.149 \text{ cm}^3/\text{g}$	
ethyl			734			1.00				$M_w/M_n = 2.1; dn/dc = 0.170 \text{ cm}^3/\text{g}$	
Poly(methacrylic acid)	Dimethylsulfoxide	25	34 130 260 429 432 381	0.46 1.02 1.27 1.66 1.85 1.60		0.975				M_{MW}	638