Molecular Weight Dependence of Hydrodynamic and Thermodynamic Properties for Well-Defined Linear Polymers in Solution

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Molecular Weight Dependence of Hydrodynamic and Thermodynamic Properties for Well-Defined Linear Polymers in Solution

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Data on hydrodynamic and thermodynamic properties of several well-defined, linear flexible polymer chains in thermodynamically good solvents and theta solvents are tabulated and critically evaluated. The polymers considered are 1,4-polybutadiene, 1,4-polyisoprene, polyisobutylene, polystyrene, and poly(α-methylstyrene). Extensive data, obtained as a function of molecular weight, are evaluated for the intrinsic viscosity, radius of gyration, hydrodynamic radius, and second virial coefficient. The resulting power law relationships between the measured properties and polymer molecular weight are reported.

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1. Introduction

Properties and processing characteristics of macro-molecules depend not only on polymer type but also frequently exhibit a strong dependence on molecular weight or molecular size. In many instances polymer scientists and engineers also need to be able to predict molecular size or thermodynamic interactions as a function of molecular weight for a given type of macromolecule. The Polymer Handbook[1] provides an exhaustive listing of relationships between molecular weight and parameters such as intrinsic viscosity [η], radius of gyration R_g, hydrodynamic radius R_H, and second virial coefficient A_2. Unfortunately, large differences frequently are seen on comparing results reported by different groups for the same polymer/solvent system. These differences may reflect variations in polydispersity, methods used for molecular weight determination, molecular weight range investigated, tacticity, branching, etc. The Polymer Handbook[1] sometimes makes recommendations on preferred property/molecular weight relationships when discrepancies exist.

In this paper, we compile and critically evaluate data on [η], R_g, R_H, and A_2 for several linear, flexible polymer chains in both "ideal" (theta condition) and thermodynamically good solvents. We restrict our attention to the relatively few polymers where complete data sets ([η], R_g, R_H, and A_2) exist for well-defined, narrow molecular weight distribution materials e.g. polybutadiene (PBD), polyisoprene (PI), polyisobutylene (PIB), and poly(α-methylstyrene) (PαMS). When care is taken to exclude data which appear to be anomalous, it is generally seen that results from various groups can be compiled to generate power law relationships of the form

$$P = CM^v \quad (1)$$

where P is the property being probed as a function of molecular weight M, and C and v are empirically established constants for that system, usually valid over several orders of magnitude in M.

2. Criteria for Data Selection and Evaluation

Four of the polymers covered in this paper (PBD, PI, PS, and PαMS) are materials which can be synthesized in a controlled fashion using anionic polymerization techniques[2].

These methods can lead directly to polymers having extremely narrow polydispersities. Usually the ratio of weight-average molecular weight $\overline{M}_w$ to number-average molecular weight $\overline{M}_n$ for such materials is less than 1.1. While these materials are clearly not monodisperse, their distributions are the most narrow of any synthetic polymers. Furthermore, anionic polymerization using lithium-based initiators in hydrocarbon solvent lead, in the case of the polydienes, to elastomeric materials of consistent microstructure ($\sim$ 92% 1,4 in both cases)[2]. These same initiator systems give atactic (probability of racemic diads (P_r) of about 0.56) polystyrene[3] and poly(α-methylstyrene) ($P_r \approx 0.5$) (4–8).

In the case of PIB, the monomer is not amenable to anionic polymerization but well-defined samples may be readily obtained by fractionating products of cationic polymerization. It should be noted that tacticity is not a consideration with this polymer; also no branching occurs during cationic polymerization of isobutylene.

A great number of studies have appeared on the solution properties of these materials because of their well-defined linear structures, the capacity to produce materials covering a vast range of molecular weights, the solubility of these polymers in many common solvents at room temperature, and because of their commercial importance. This last factor is enhanced because certain block copolymers comprised of these materials function as thermoplastic elastomers. For PBD, PI, PIB, PS, and PαMS "complete" data sets are available, i.e. data for A_2 in thermodynamically good solvents and data for [η], R_g, and R_H in both good and theta solvents have been reported in the literature. Also, in general, results from different groups for a given system are in agreement with one another.

Other important polymers, such as poly(methyl methacrylate), polyethylene, and polypropylene, are excluded from consideration in this work because of the lack of adequately defined samples and/or an overall lack of consistency between values reported by different groups for the same system. Data are also excluded from consideration unless molecular weights were determined by absolute methods (preferably light scattering) and unless adequate details were given on experimental protocol, solvent purity, etc. Data for very low molecular weight samples are not considered because of the departure from linearity of power law relationships at low molecular weights[9–14]. In general, power laws determined under theta conditions are valid above 10,000 in molecular weight. In good solvents the power laws for R_g, R_H, and [η] usually exhibit changes in slope below about 50,000 in molecular weight. The relationship between A_2 and M is usually linear down to about 10,000, depending on polymer type. Data for polymers outside these ranges are not considered. Also, in tabulating the R_g data we took into account the experimental conditions used (most notably the wavelength of the radiation employed) in deciding on the smallest physical sizes which could be reliably measured. R_g values smaller than $R_g/\lambda'' \approx 20$ (λ'' = wavelength of light in the medium) even if they were reported by the original authors, are not considered here. Outliers, determined by considering the typical experimental error associated with the method, are also not considered. The reported power laws were determined by

unweighted linear regression analyses. Because of the narrow polydispersities of these materials, no consideration is given to polydispersity effects[15], which should be quite modest, and power laws are simply reported as a function of molecular weight M. In some cases, good solvent data are reported by different groups at slightly different temperatures, usually 25 and 30 °C. The effect of such small temperature differences on properties of chains in good solvents was observed to be negligible; these data are thus compiled together and a single power law is reported.

3. Data for 1,4-Polybutadiene

Data for 1,4-polybutadiene in the theta solvent dioxane at 26.5 °C are presented in Table 1. In Table 2, data for PBD in cyclohexane at 25 °C (good solvent) are presented.

3.1. Intrinsic Viscosity

The data of Table 1 yield the following Mark-Houwink-Sakurada (MHS) relationship (corr. coeff. = 0.9969):

$$[\eta] = 1.77 \times 10^{-1} M^{0.503} \qquad (2)$$

The exponent of 0.503, based on 12 samples covering about 1.5 orders of magnitude in M, shows that 26.5 °C is very near to the theta temperature for this polymer/solvent pair. Application of the extrapolation method of Burchard[16] and Stockmayer and Fixman[17] (BSF approach), which corrects for slight deviations from theta, yields:

$$[\eta]_\theta = 1.84 \times 10^{-1} M^{1/2} \qquad (3)$$

The good solvent viscosity data of Table 2 result in the MHS equation (corr. coeff. = 0.9998):

$$[\eta] = 3.87 \times 10^{-2} M^{0.697} \qquad (4)$$

This equation is based on 15 polymers covering nearly $2\frac{1}{2}$ orders of magnitude in molecular weight (Fig. 1). Surprisingly this plot is linear all the way down to 11,000 in M. As noted above[9–14], deviations from linearity are expected below a M of about 50,000, but clearly no such curvature is observed in Fig. 1. This effect may be due to the thin and streamlined structure of PBD.

TABLE 2. Polybutadiene in cyclohexane

Ref.	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
24	0.111	25.7		3.14	1.65
	0.236				1.47
	0.393				1.32
	0.394	60.1			1.30
	0.590	80.4		7.93	1.20
	1.14	125	15.2	11.32	1.05
	1.55		18.7		1.00
	1.64	161	19.3		0.98
	1.80		20.3		0.94
	2.56	227	26.1	18.3	0.87
	3.61	287	32.2	22.1	0.80
	7.60		47.9		0.69
26	0.200	39.3			
	0.460	69.2			
	0.710	92.6			
	1.30	142			
	3.55	296			
	5.48	385			
	9.25	567			
	37.4	1450			

3.2. Radius of Gyration

Data on R_g of PBD are much more limited than are those for $[\eta]$ of this material. Based on the available data (Tables 1 and 2) we obtain the following power laws for dioxane (corr. coeff. = 0.9999).

$$R_g = 3.79 \times 10^{-2} M^{0.50} \qquad (5)$$

and for cyclohexane (corr. coeff. = 0.9984)

$$R_g = 1.29 \times 10^{-2} \overline{M}^{0.609} \qquad (6)$$

Both exponents are in reasonable accord with values expected for flexible chains under theta and good solvent conditions.

TABLE 1. Polybutadiene in 1,4-dioxane

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g^a (nm)	R_H (nm)
23	0.108	18.5		
	0.221	27.2		
	0.253	28.4		
	0.527	40.8		
	0.717	47.6		
	0.960	55.0		
	2.32	84.5		
	5.22	129		
	5.71	132		
24	0.111			2.98
	0.393	39.5		
	0.590			6.91
	1.14		12.8	9.50
	1.55		14.9	
	1.64		15.3	
	1.80	83.0	16.0	
	2.56		19.1	14.6
	3.61	122	22.7	16.5

^{a}Calculated from the power law given in Ref. 24.
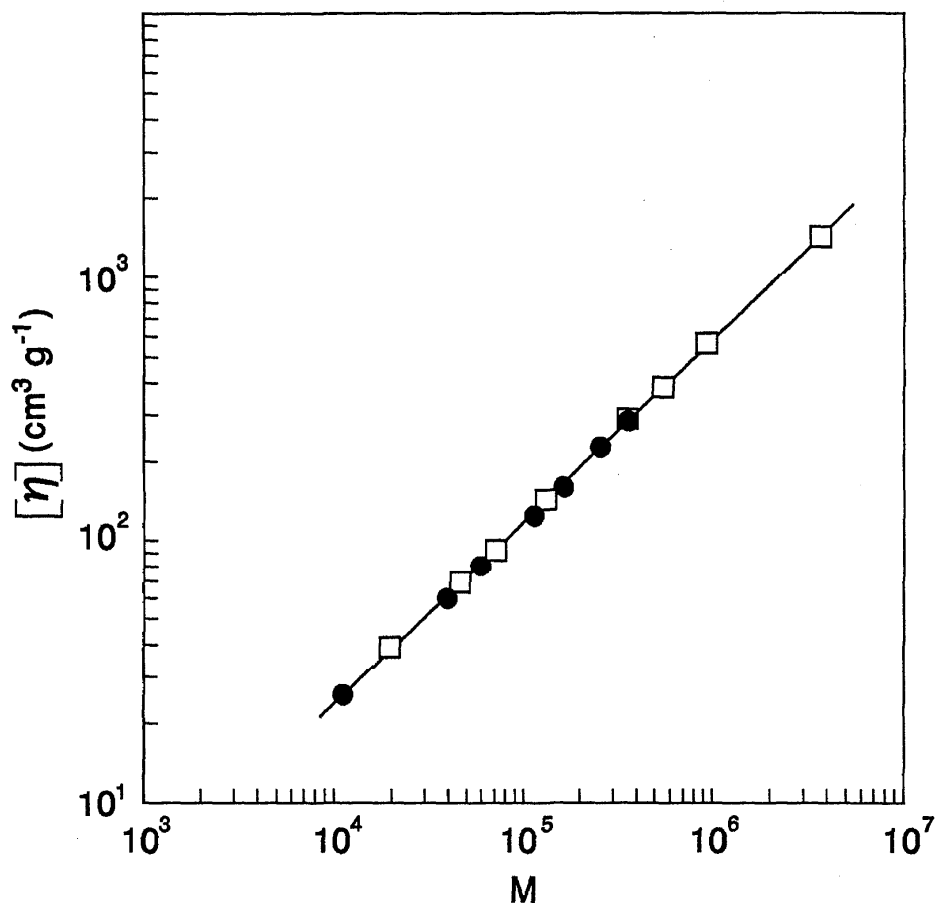
Fig. 1. [η] versus M for 1,4-polybutadiene in the thermodynamically good solvent cyclohexane (● = Ref. 24; □ = Ref. 26).

3.3. Hydrodynamic Radius

Data in dioxane yield the expression (corr. coeff. = 0.9997)

$$R_H = 3.15 \times 10^{-2} M^{0.491} \tag{7}$$

while the data in cyclohexane yield (corr. coeff. = 0.9998)

$$R_H = 1.50 \times 10^{-2} M^{0.570} \tag{8}$$

Application of the procedure of Baumann[18] to the R_H data in dioxane yields the relationship

$$R_H = 2.88 \times 10^{-2} M^{1/2} \tag{9}$$

3.4 Second Virial Coefficient

The data in the thermodynamically good solvent cyclohexane (Table 2) yield the equation (corr. coeff. = 0.998)

$$A_2 = 1.23 \times 10^{-3} M^{-0.212} \tag{10}$$

Generally exponents between about -0.20 and -0.25 are observed in thermodynamically good solvents, in accord with

theoretical expectations[19-22] and experimental findings reported herein.

4. Data for 1,4-polyisoprene

Experimental data for narrow polydispersity, high 1,4-polyisoprenes are collected in Tables 3 (theta solvent, dioxane at 34.5 °C) and 4 (cyclohexane 25 °C).

4.1. Intrinsic Viscosity

Twenty five data points for PI in dioxane at about 34.5 °C covering nearly three orders of magnitude in M yield (corr. coeff. = 0.9998)

$$[\eta] = 1.11 \times 10^{-1} M^{0.513} \tag{11}$$

Application of the BSF procedure (16,17) gives

$$[\eta]_\theta = 1.29 \times 10^{-1} M^{1/2} \tag{12}$$

Based on the analysis of 12 samples in cyclohexane, the power law (corr. coeff. = 0.9996)

$$[\eta] = 1.97 \times 10^{-2} M^{0.733} \tag{13}$$

is determined. The molecular weight range covered is from 6.2×10^4 to 7.24×10^6.

4.2. Radius of Gyration

The dioxane-based R_g data of Table 3 yield (corr. coeff. = 0.996)

$$R_g = 2.75 \times 10^{-2} M^{0.513} \tag{14}$$

Application of the Baumann procedure[18] yields

$$R_g = 3.30 \times 10^{-2} M^{1/2} \tag{15}$$

In cyclohexane (Table 4) twenty five data points lead to (corr. coeff. = 0.993)

$$R_g = 1.26 \times 10^{-2} M^{0.610} \tag{16}$$

TABLE 3. Polyisoprene in 1,4-dioxane

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)
23	0.134	14.2		
	0.195	17.4		
	0.257	19.7		
	0.380	24.9		
	0.401	25.6		
	0.548	30.0		
	0.820	37.0		
	1.15	44.8		
	1.50	49.9		
	1.62	52.2		
	2.28	63.5		
	2.40	63.0		
	3.94	83.5	20.6	
	5.13		23.3	
	5.37	96.4	24.6	
	5.91	102	25.4	
	6.00	103		
	14.1		37.7	
	15.6	166	42.5	
	16.1	170	42.4	
	22.25	197	50.1	
29	3.39	80.9		
30	3.26	75.3	19.1	14.35
	5.68	99.3	25.3	19.27
	5.78	100	25.5	19.53
	24.4	206		41.17
	72.4	355		69.15

4.3. Hydrodynamic Radius

The R_H data obtained in dioxane (Table 3) yield the equation (corr. coeff. = 0.9994)
ya

$$R_H = 2.62 \times 10^{-2} M^{0.498} \tag{17}$$

which upon correction by the Baumann method[18] yields

$$R_H = 2.57 \times 10^{-2} M^{1/2} \tag{18}$$

The cyclohexane R_H data (Table 4) give (corr. coeff. = 0.947)

$$R_H = 1.13 \times 10^{-2} M^{0.592} \tag{19}$$

The correlation coefficient of Eq. 19 is much lower than that typically observed for the other empirical equations reported herein. Nevertheless, the exponent of 0.592 for a good solvent system seems reasonable.

4.4. Second Virial Coefficient

The A_2 data obtained in cyclohexane are plotted in Fig. 2. Clearly large differences are observed between the three data sets, with the multiangle data of Davidson et al.[31] consistently falling below the low-angle laser light scattering (LALLS) data by the same authors[31]. Conversely, the data of Tsunashima and co-workers[30] consistently lie above the other data. By considering only the LALLS data of Davidson et al.[31] we obtain (corr. coeff. = 0.9978)

$$A_2 = 1.32 \times 10^{-2} M^{-0.232} \tag{20}$$

The correlation coefficient for these data is high and the exponent is consistent with those for other linear chains.

5. Data for Polyisobutylene

Data for PIB in the theta solvents benzene and isoamylisovalerate at ca. 25 °C are given in Table 5. In Table 6, data in the good solvent cyclohexane at 25 °C are given.

5.1. Intrinsic Viscosity

Benzene is a commonly used solvent for the measurement of $[\eta]$ for PIB under theta conditions. Unfortunately, it is isorefractive for PIB so it cannot be utilized in light scattering experiments[32]. It has been shown however that $[\eta]$ results obtained in benzene and isoamylisovalerate are virtually identical[32,35]. The combined data for $[\eta]$ in Table 5 yield (corr. coeff. = 0.9990)

$$[\eta] = 1.07 \times 10^{-1} M^{0.504} \tag{21}$$

The BSF approach[16,17] gives

$$[\eta]_\theta = 1.10 \times 10^{-3} M^{1/2} \tag{22}$$

In the good solvent cyclohexane $[\eta]$ data for 33 samples covering the molecular weight range from 4.3×10^4 to 1.41×10^7 lead to (corr. coeff. = 0.9988)

$$[\eta] = 1.21\ 10^{-2} M^{0.751} \tag{23}$$

TABLE 4. Polyisoprene in cyclohexane

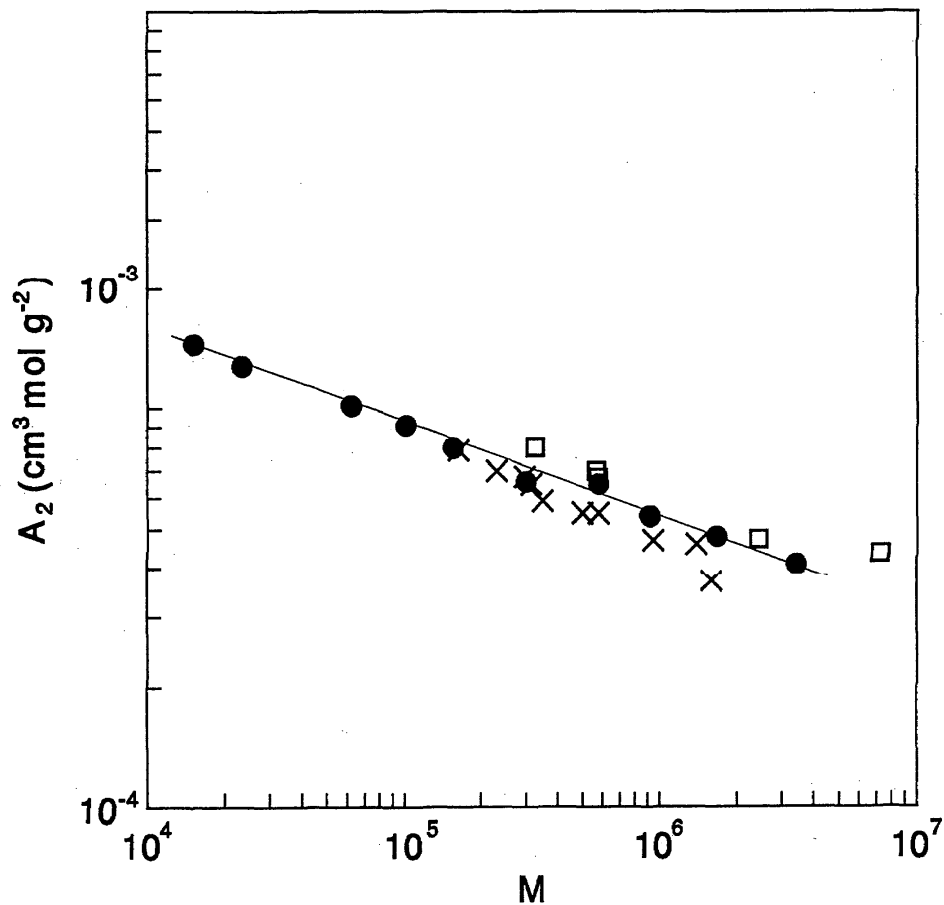| Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
31	0.152			3.49	14.5
	0.234			4.42	12.8
	0.620	63.7		7.72	10.2
	1.01				9.1
	1.56	129		13.3	8.0
	1.64		19.4		7.9[a]
	2.31		24.3		7.0[a]
	2.97		26.2		6.8[a]
	3.02	201			6.6
	3.16		28.0		6.5[a]
	3.50		31.2		5.9[a]
	5.00		37.0		5.5[a]
	5.81	335	41.0	28.6	6.5(5.5[a])
	9.20	466		30.3	5.4
	9.42		48.0		4.7[a]
	13.9		65.0		4.6[a]
	16.0		68.0		3.7[a]
	16.7	702		54.6	4.8
	34.2	1120		83.0	4.1
30	3.26	212	31.6	20.9	8.04
	5.68	333	43.3	29.3	7.03
	5.78	340	43.5	29.4	6.77
	24.4	918	105	70.0	4.74
	72.4	2174	210	140	4.37

[a]Multi-angle light scattering.

FIG. 2. A_2 as a function of M for 1,4-polyisoprene in cyclohexane (● = Ref. 31 via low angle light scattering; x = Ref. 31 via multi-angle light scattering;

TABLE 5. Polyisobutylene in benzene or isoamylisovalerate

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)
32	1.60	45.3		
	2.52	55.3		
	2.81	62.5		
	3.91	70.1	19.1	
	3.95	73.8		
	8.15	102	27.4	
	14.6	136	37.1	
	31.9	206	56.0	
	47.0	246	67.5	
33	0.49	24.1		
	0.86	31.8		
	1.30	39.6		
	4.19	70.9		
	8.54	99.8		
	12.1	117		
	17.9	146		
34	2.81	62.5		
	3.95	73.8		
35	0.64			6.45
	1.33			8.69
	3.30			14.3
	4.48			16.5
	7.44			20.6
	14.8			29.9

5.2. Radius of Gyration

The data for R_g of PIB in the theta solvent isoamylisovalerate are restricted to five polymer samples in the range of 3.91 $\times$ 10^5 to 4.7 $\times$ 10^6. These data result in the power law expression (corr. coeff. = 0.9999)

$$R_g = 2.62 \times 10^{-2} M^{0.511} \tag{24}$$

Application of the Baumann extrapolation procedure[18] to these data gives

$$R_g = 3.00 \times 10^{-2} M^{1/2} \tag{25}$$

R_g data in cyclohexane are more extensive and cover the molecular weight range from 1.6 $\times$ 10^5 to 1.41 $\times$ 10^7. The R_g-M relationship (corr. coeff. = 0.9995) is

$$R_g = 1.37 \times 10^{-2} M^{0.595} \tag{26}$$

5.3. Hydrodynamic Radius

Data on R_H of PIB are limited to those reported by Fetters and co-workers[35]. In isoamylisovalerate (corr. coeff. = 0.9991)

$$R_H = 2.73 \times 10^{-2} M^{0.492} \tag{27}$$

The Baumann correction to these data[18] yields

$$R_H = 2.52 \times 10^{-2} M^{1/2} \tag{28}$$

In cyclohexane (corr. coeff. = 0.9999)

$$R_H = 1.36 \times 10^{-2} M^{0.573} \tag{29}$$

5.4. Second Virial Coefficient

Very extensive A_2 data are available for the PIB/cyclohexane system from several sourcess[32,34-36]. These data were used to generate the following power law relationship (corr. coeff. = 0.957)

$$A_2 = 8.34 \times 10^{-3} M^{-0.213} \tag{30}$$

6. Data for Polystyrene

Data for polystyrene in the theta solvent cyclohexane at 34.5 °C are presented in Table 7. These data constitute the largest data set of this work. This system has been more extensively studied than any other polymer/solvent system because of both the widespread commercial availability of inexpensive, well-defined polystyrene standards and because of a theta temperature which is quite convenient for experimentation. Likewise, extensive data sets are presented for PS in benzene (Table 8), toluene (Table 9), and tetrahydrofuran (Table 11). A complete data set is also available for the PS/ethylbenzene system (Table 10) although fewer data are available here.

6.1. Intrinsic Viscosity

For 92 polymers covering almost four orders of magnitude in molecular weight, the relationship between $[\eta]$ and M for PS in cyclohexane (corr. coeff. = 0.9994) is

$$[\eta]^{CH} = 7.68 \times 10^{-2} M^{0.508} \tag{31}$$

The BSF approach[16,17] yields

$$[\eta]^{CH} = 8.44 \times 10^{-2} M^{1/2} \tag{32}$$

For benzene 27 samples ranging from 9.72 $\times$ 10^4 to 5.68 $\times$ 10^7 in M give (corr. coeff. = 0.9997)

$$[\eta]^{BEN} = 9.87 \times 10^{-3} M^{0.739} \tag{33}$$

In toluene analysis of 38 samples from 4.8 $\times$ 10^4 to 2.36 $\times$ 10^7 yields (corr. coeff. = 0.9989)

$$[\eta]^{TOL} = 9.27 \times 10^{-3} M^{0.734} \tag{34}$$

while ethylbenzene data (22 samples, 5.0 $\times$ 10^4 to 3.88 $\times$ 10^6) yield (corr. coeff. = 0.9994)

$$[\eta]^{EB} = 1.13 \times 10^{-2} M^{0.715} \tag{35}$$

TABLE 6. Polyisobutylene in cyclohexane

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
32	1.60	106			7.36
	2.52	145			6.69
	3.91	203	29.0		6.16
	8.15	342	43.0		4.65
	14.6	552	61.0		4.28
	31.9	989	98.3		3.73
	47.0	1370	124		3.15
36	0.43	37.9			9.55
	0.77	59.2			8.40
	1.81	107	18.7		7.05
	4.88	232	33.4		5.30
	8.78	356	47.6		4.60
	15.8	532	66.8		3.85
	33.9	946	107		3.13
	78.3	1830	177		2.68
	141	2740	252		2.54
34	5.59	277	36.6		4.99
	7.07	329	42.8		5.29
35	1.08	72.2			6.77
	1.26				5.46
	1.27	77.8			
	1.29	81.1			5.50
	1.33	84.7		11.7	6.47
	1.67	102		13.4	5.51
	2.21	116			5.63
	3.25	163			5.30
	3.30	168		19.6	5.22
	4.36	198			5.42
	4.48	207		23.6	5.79
	6.32	254			4.85
	7.45	297		31.2	4.51
	10.1	375			4.26
	14.8	482		46.7	
	15.4				3.73
	16.1	533			3.80

In tetrahydrofuran the data are extensive (63 samples from 5.0 × 10⁴ to 1.81 × 10⁷ in M) and exhibit slightly more scatter than do the data for PS in the other solvents. We believe that much of this scatter may be attributable to failure to consider the need for kinetic energy corrections in many of these experiments. Such corrections are needed frequently when working with THF because of the lower viscosity of this solvent as compared to the common aromatic solvents, e.g. toluene and benzene. To illustrate this point, compare the $[\eta]$ data from Refs. 72 and 73 in Table 11. Two of the samples employed by the two groups were identical (inter-laboratory exchange), yet the $[\eta]$ values found by the latter group were consistently lower by a significant amount. Also, the k_H values found in the latter work were in the range of 0.43 to 0.54. These values are higher than observed in most of the other work in THF (and in other good solvents). When the samples of Ref. 73 were rerun using viscometers having longer flow times, $[\eta]$ values identical to those in Ref. 72 were obtained. We note that we have measured $[\eta]$ values for PS in THF when the THF is rigorously dried and distilled, used as re-

ceived with stabilizer present, and with 1% water intentionally added. The $[\eta]$ values appear to be quite insensitive to these changes in solvent quality. These variations in solvent quality would, however, have a big impact on dn/dc data.

We believe that the $[\eta]$ data reported for PS in THF in Refs. 75–78 may also reflect kinetic energy effects because they are consistently smaller than other $[\eta]$ values. If we exclude these data from consideration and calculate the power law based only on data from Refs. 67, 72, 74, and 80 (34 samples from 5 × 10⁴ to 1.81 × 10⁷ in M; corr. coeff. = 0.9997), we obtain

$$[\eta]^{THF} = 9.96 \times 10^{-3} M^{0.734} . \tag{36}$$

6.2. Radius of Gyration

As was the case with intrinsic viscosity data, many studies of R_g have also appeared for the PS/cyclohexane theta system. Table 7 compiles R_g data from light, neutron, and x-ray scattering experiments performed on solutions. Analyzing data

TABLE 7. Polystyrene in cyclohexane

TABLE 7. Polystyrene in cyclohexane — Continued

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)	Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)
37,38	0.198	11.9			44	3.10	48.7		
	0.440	18.0				4.90	60.3		
	0.505	19.2				12.3	99.2		
	0.550	20.0				24.2	133		
	0.760	24.5				36.3	172		
	0.962	26.6				45.9	186		
	1.25	29.0				55.3	206		
	1.60	34.0				76.2	245		
	1.80	35.4				97.2	275		
	2.47	42.0							
	3.94	54.5	17.5		45	0.37	16.2		
	4.06	55.0				0.50	18.7		
	5.07	60.0				1.11	A27.9		
	6.22	66.0	21.5			2.54	42.4		
	6.26		22.0			3.92	52.3		
	8.62	78.0				9.50	82.3		
	10.5	86.0							
	10.6		27.7		46	0.100	8.90		
	12.0		30.5			0.204	12.3		
	13.3		31.5			0.470	18.4		
	15.6	106	34.8			0.972	26.4		
	40.4		57.1			1.60	34.7		
	44.0		68.1			4.11	55.0		
						13.4	99.0		
39	0.84			6.53		30.8	155		
	1.16	27.9		7.83		48.0	192		
	2.16	38.3				86.7	259		
	2.38			10.4		150	350		
	2.75	41.4				232	435		
	6.75	68.4	22.9	18.5		319	522		
	8.60	77.6	25.5			390	564		
	17.0		37.7	28.2		568	667		
40	2.38	40.9		11.1	47	1.06	28.1		
	4.26	52.8	19.0	14.6		2.94	46.6		
	12.1	92.0	32.2	24.7		4.20	55.7		
	38.5	165	57.5	45.6		6.40	68.7		
	54.7	195	69.2	53.6		9.60	84.2		
41	87.9		87.9		48	0.510	19.0		
	152		116			4.81			
	235		145			0.982	27.0		6.52
	320		167			1.10	29.0		7.28
	380		183			1.83	36.0		8.73
	557		228			3.90	53.0		12.6
						4.11	56.0		13.0
42	2.49	44.0				4.98	61.0		14.3
	3.41	53.1				8.67	74.0		17.9
	7.65	80.0	25.7			18.0	114		26.2
	15.7	116				21.45			26.9
	28.8	153	48.9						
					49	1.09	25.1		
43	0.175	10.78				1.70	33.8		
	0.500	17.63				4.22	51.3		
	1.00	24.79							
	2.33	41.79			50	3.59	51.2		13.0
	6.00	68.77				7.32	73.4		18.7
	18.0	113.9				13.2	98.1		25.1
						35.2	162		

TABLE 7. Polystyrene in cyclohexane — Continued

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)
51	0.205		3.97	
	0.400		5.66	
	0.973		9.10	
52	0.101	9.0		
53	64.8	228	74.1	
	65.5	230	74.6	
54	4.22		18.5	
	7.75		26.0	
	12.6		31.8	
55	0.107		2.76	2.38
	0.146		3.28	4.01
56	12.6			25.5
	28.8			39.3
	44.8			48.1
	50.5			51.5
	67.7			59.2
	93.5			71.7
57	0.21			3.35
	1.10			7.16
	2.00			9.86
	6.70			18.1
	27.0			35.8
58	0.27			3.50
	0.57			5.04
	0.84			6.58
	1.25			7.85
	2.30			10.0
	4.60			14.0
	4.95			14.2

for 37 samples (1.07×10^4 to 5.57×10^7 in M) we derive (corr. coeff. = 0.9995)

$$R_g^{CH} = 2.42 \times 10^{-2} M^{0.512} \qquad (37)$$

If only light scattering data are considered for PS in cyclohexane, we find (M from 3.94×10^5 to 5.57×10^7)

$$R_g = 2.25 \times 10^{-2} M^{0.517} \qquad (38)$$

with a correlation coefficient of 0.9991. Clearly the previous two equations are in close agreement and we give preference to Eq. 37 because of its being based on a larger molecular weight range. Treatment of these data by the method of Baumann[18] yields

$$R_g = 2.79 \times 10^{-2} M^{1/2} \qquad (39)$$

In benzene, analysis of 19 samples over the molecular weight range of 3.42×10^5 to 5.68×10^7 reveals that

$$R_g^{BEN} = 1.21 \times 10^{-2} M^{0.595} \qquad (40)$$

with corr. coeff. = 0.9998. An essentially identical equation is found for PS in toluene (corr. coeff. = 0.9979)

$$R_g^{TOL} = 1.20 \times 10^{-2} M^{0.595} \qquad (41)$$

based on consideration of data for 36 samples covering about the same range of M.

Ethylbenzene appears to be a somewhat less good solvent, in the thermodynamic sense, for PS than is either benzene or toluene. The data here are limited to 10 samples, ranging from 6.0×10^5 to 2.2×10^7 in M, which yield (corr. coeff. = 0.9977)

$$R_g^{EB} = 1.92 \times 10^{-2} M^{0.562} \qquad (42)$$

R_g data for the PS/tetrahydrofuran system (Fig. 3) show considerably greater scatter than for other systems. Based on 21 data points (corr. coeff. = 0.991)

$$R_g^{THF} = 2.45 \times 10^{-2} M^{0.546} \qquad (43)$$

Notice that the four data points at $M \simeq 3.7 \times 10^6$ give R_g values ranging from 91.5 to 105 nm, a range of about 14%. Clearly, the need exists for additional careful studies on this system.

6.3. Hydrodynamic Radius

Extensive high quality data are available for the molecular weight dependence of R_H for PS in cyclohexane. Based on 43 samples (1.07×10^4 to 9.35×10^6; corr. coeff. = 0.9975) we obtain

$$R_H^{CH} = 2.15 \times 10^{-2} M^{0.502} \qquad (44)$$

Application of the Baumann procedure[18] gives

$$R_H^{CH} = 2.18 \times 10^{-2} M^{1/2} . \qquad (45)$$

In contrast to the extensive data for $[\eta]$, R_g, and A_2 for PS in benzene, only one group[59] has reported R_H data for this system. Fortunately, these data cover the broad molecular weight range from 7.75×10^5 to 1.34×10^7 and result in (corr. coeff. = 0.9982)

$$R_H^{BEN} = 1.55 \times 10^{-2} M^{0.552} . \qquad (46)$$

Nevertheless, more studies on R_H of this polymer/solvent pair would appear to be worthwhile.

For PS/toluene, based on 38 samples covering just over two orders of magnitude in M, we compute (corr. coeff. = 0.9974)

$$R_H^{TOL} = 1.06 \times 10^{-2} M^{0.575} \qquad (47)$$

and for PS/ethylbenzene, based on 9 specimens ranging from 9.3×10^4 to 2.2×10^7 in M, we find (corr. coeff. = 0.9982)

TABLE 8. Polystyrene in benzene

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
42	2.46	101			4.46
	3.42	131	24.0		4.12
	7.56	230	37.4		3.34
	15.9	399	57.5		2.91
	28.7	583	82.9		2.25
41	87.6		164		1.82
	150		227		1.66
	232		297		1.44
	319		353		1.28
	390		392		1.22
	568		506		1.09
44	3.10	118			
	4.90	152	30.1		3.72
	12.3	293	50.9		2.86
	24.2	521	79.1		2.33
	36.3	690	98.2		2.21
	45.9	798	112		2.03
	55.3		126		1.89
	76.2		152		1.73
	97.0		173		1.60
	134		211		1.50
46	0.972	47.2			
	1.60	68.8			
	4.11	136			
	13.4	320			
	30.8	600			
	48.0	825			
	87.6	1302			
	150	2004			
	232	2802			
	319	3508			
	390	4007			
	568	5306			
59	7.75			28.0	
	24.2			52.9	
	55.3			77.0	
	97.0			112	
	134			139	
60	0.378				7.7
	1.13	52.4			5.1
	1.77	73.2			4.6
	3.79	127			3.9
	6.19	179			3.25
61	0.364				7.47
	1.17				5.30
	3.79				3.90
	6.19				3.25
	17.5				2.22

$$R_H^{EB} = 1.18 \times 10^{-2} M^{0.564} \tag{48}$$

In contrast to the scatter observed in some other data for the PS/tetrahydrofuran system (see above and below), excellent literature data are available for 27 samples (2.04×10^4 to 2.2×10^7 in M) giving a correlation coefficient of 0.9990. The power law

$$R_H^{THF} = 1.44 \times 10^{-2} M^{0.561} \tag{49}$$

is obtained.

6.4. Second Virial Coefficient

Some of the most extensive and reliable good solvent A_2 results available in the literature are probably those for PS in benzene and toluene. For the former system (corr. coeff. = 0.9949 based on 30 samples)

$$A_2^{BEN} = 1.06 \times 10^{-2} M^{-0.257} \tag{50}$$

whereas for the latter (corr. coeff. = 0.9774 based on 43 samples)

$$A_2^{TOL} = 1.02 \times 10^{-2} M^{-0.258} \tag{51}$$

More than two orders of magnitude in M are covered in both cases, and the data indicate that benzene and toluene are equally good solvents thermodynamically for PS, in agreement with R_g exponents reported above for these systems.

Much less data is available for the PS/ethylbenzene system, but the most extensive and reliable data[68,70] suggest (8 samples; corr. coeff. 0.994)

$$A_2^{EB} = 1.30 \times 10^{-2} M^{-0.285} \tag{53}$$

In tetrahydrofuran 23 data points covering just under three orders of magnitude in M (corr. coeff. = 0.985) yield

$$A_2^{THF} = 9.93 \times 10^{-3} M^{-0.247} \tag{54}$$

7. Data for Poly(α-Methylstyrene)

Data for PαMS in the theta solvent cyclohexane ($\theta \simeq 36\,°C$) and good solvent toluene are presented in Tables 12 and 13, respectively.

7.1. Intrinsic Viscosity

The cyclohexane data for $[\eta]$ of 26 samples over two orders of magnitude in M yield (corr. coeff. = 0.9980)

$$[\eta] = 6.75 \times 10^{-2} M^{0.508} \tag{55}$$

The BSF treatment (16,17) yields

$$[\eta]_\theta = 7.35 \times 10^{-2} M^{1/2} \tag{56}$$

In toluene, 17 samples ranging from 5.9×10^4 to 7.47×10^6 in M yield (corr. coeff. = 0.9989)

$$[\eta] = 6.30 \times 10^{-3} M^{0.748} \tag{57}$$

7.2. Radius of Gyration

The R_g data in cyclohexane give the power law

$$R_g = 2.33 \times 10^{-2} M^{0.513} \tag{58}$$

This result is based on 16 samples from three research groups (corr. coeff. = 0.9979). The Baumann plot gives

$$R_g = 2.77 \times 10^{-2} M^{1/2} \tag{59}$$

This equation is virtually identical to Eq. 39, which relates R_g to M for the similar PS/cyclohexane system.

The R_g data in toluene exhibit considerable scatter (Fig. 4). Linear regression analysis (corr. coeff. = 0.9911) gives

$$R_g = 9.39 \times 10^{-3} M^{0.607} \tag{60}$$

The exponent is slightly larger than expected for a flexible chain/good solvent system[13-15]. More work on this system appears to be needed.

7.3. Hydrodynamic Radius

Excellent and extensive R_H data are available for PαMS in both cyclohexane and toluene. For the former, the data cover almost 3 orders fo magnitude in M and yield (corr. coeff. = 0.9993)

$$R_H = 2.49 \times 10^{-2} M^{0.487} \tag{61}$$

The Baumann procedure[18] yields

$$R_H = 2.17 \times 10^{-2} M^{1/2} \tag{62}$$

In toluene (26 samples; 5.9×10^4 to 7.47×10^6) we find (corr. coeff. = 0.9985)

$$R_H = 1.08 \times 10^{-2} M^{0.569} \tag{63}$$

7.4. Second Virial Coefficient

For PαMS in toluene analysis of 27 samples covering two orders of magnitude in molecular weight result in (corr. coeff. = 0.9964)

$$A_2 = 8.57 \times 10^{-3} M^{-0.271} \tag{64}$$

The magnitude of the exponent is reasonably consistent with theoretical expectations[19-22].

TABLE 9. Polystyrene in toluene

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
39	1.16	47.8		9.21	
	2.16	75.7		13.4	
	2.75	91.8	20.4	15.0	
	6.75	171	32.9	26.1	
	8.60	213	38.5	29.9	
	17.0	361	59.4	44.0	
40	2.38	87		13.4	4.52
	4.26	127	27.8	28.4	4.06
	12.1	260	51.3	33.5	2.74
	31.5	600	99.8	63.0	2.07
	54.7	760	123	78.1	1.91
42	2.52	95.2			4.10
	3.41	118	23.3		3.79
	7.65	216	37.5		3.06
	15.7	371	55.4		2.33
	29.3	545	81.9		2.21
62	0.48	23.9			5.94
	1.17	46.6			4.37
	2.66	83.3			3.59
	3.33	99.2			3.14
	4.99		30.2		
	5.13	135			3.63
	7.01	173			3.22
	7.07		37.4		
	9.80		45.2		
	10.9	236			2.95
	18.6	353	66.3		2.88
	31.5		92.5		
	32.0	541			2.26
	88.0		173		
	91.5	1147			1.93
	232		303		
	236	2245			1.40
63	12.9	280	48.6		2.35
	25.8	478	75.0		1.99
	61.2	922	126		1.64
	111	1429	178		1.34
	159	1997	218		1.21
64	0.99			8.20	6.8
	7.83		38.6	27.0	2.8
	12.8		52.0	36.2	2.7
	28.9		84.4	68.6	2.35
65	6.97		39.2	24.7	
	11.3		50.2	31.6	
	16.5		61.9	39.6	
	29.3		89.2	56.3	
	38.4		104	65.0	
	60.7		137	85.4	
55	0.485			5.36	
	0.97			8.28	
	4.24		28.0	18.5	
58	0.57			5.89	
	0.84			7.16	
	1.25			9.07	
	2.30			12.6	
	4.60			19.4	

TABLE 9. Polystyrene in toluene — Continued

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
66	0.51			5.49	
	0.982			7.44	
	1.10			8.63	
	1.83			11.4	
	3.90			16.1	
	4.70			17.0	
	4.98			19.3	
	8.67			26.0	
	18.0			39.5	
67	3.90	126			
	28.8	525			
	74.0	1050			
	96.0	1250			
	152.0	1700			
	181.0	1900			

TABLE 10. PS in ethylbenzene

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
68	0.93	41.5		7.8	
	3.07			14.7	3.58
	6.20			21.5	3.10
	8.95	206	43.5	26.0	2.48
	18.5	355	62.0	40.1	2.10
	38.8	575	95.0	56.0	1.70
	56.3		118	78.0	1.61
	84.6		161		1.40
69	84.2		161	107	
	220		246	159	
70	37.1		92.5		1.74
43	0.50	26.1			
	1.00	41.7			
71	6.00		34.8		
	18.0		60.8		
72	0.50	26.0			
	1.11	48.3			
	2.07	70.3			
	2.16	70.6			
	2.54	84.6			
	3.92	114			
	6.75	163			
	9.50	225			
	13.5	275			
73	0.944	39.3			
	2.16	69.7			
	4.14	115			
	7.57	178			
	8.67	189			
	13.5	266			
	33.7	519			

8. Conclusions

Values of the hydrodynamic and thermodynamic properties, $[\eta]$, R_g, R_H and A_2, have been collected for five common linear, flexible chains in theta solvents and in good solvents. It is believed that all of the pertinent literature results on studies of narrow polydispersity ($\overline{M}_w/\overline{M}_n \leqslant 1.1$) chains using reliable instrumental methods, where all of the above mentioned parameters are reported, have been examined. Linear power law expressions were observed for all parameters as a function of molecular weight. This work appears to be the first major effort in critically analyzing such data and compiling the corresponding power laws for narrow distribution chains.

Some conclusions are directly obtainable from the data. First, it appears that in some cases the estimated unperturbed dimensions of chains may depend on whether measurements are made on samples in solution or in the bulk[99–101]. Second, it appears that, in most instances, the results from different investigators, in some cases using different methods, are consistent. For example the results from photon correlation spectroscopy and sedimentation velocity provide similar diffusion coefficients and R_H values. Third, in contrast to the claim[102] that the MHS relationship breaks down at very high molecular weights ($M \geqslant 10^6$), the extensive viscosity data presented herein show no such deviations. Finally, the need for additional measurements on certain systems has been noted in the text.
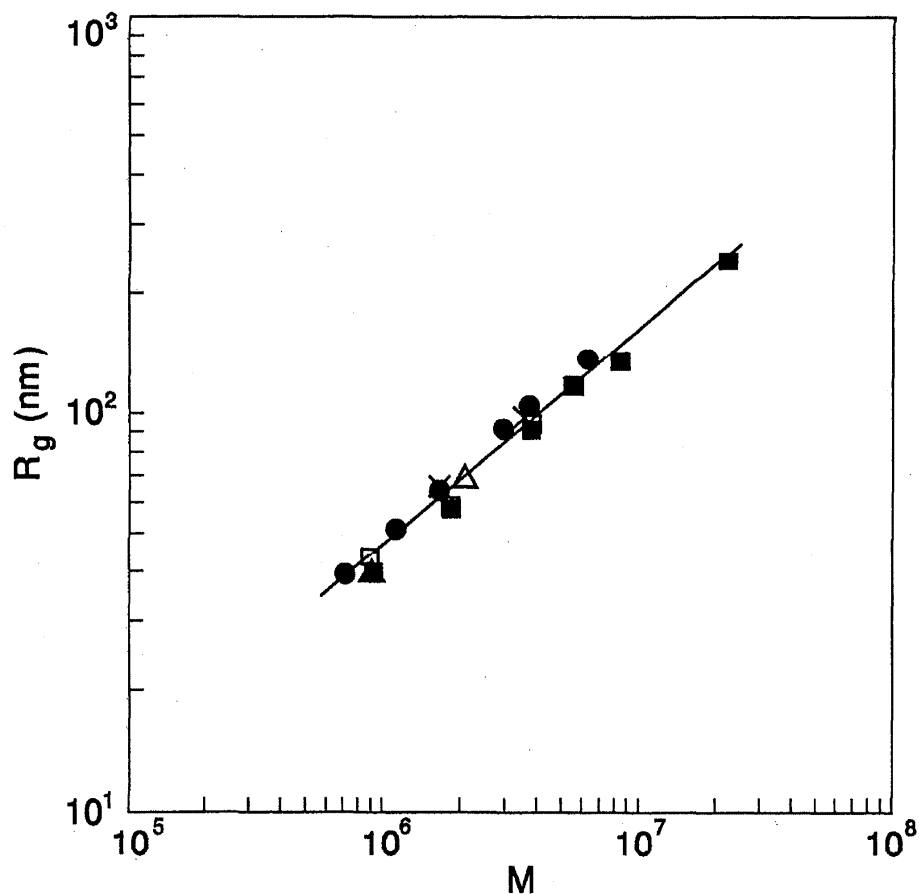
TABLE 11. Polystyrene in tetrahydrofuran

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
72	0.50	28.2			
	1.11	51.1			
	2.07	78.1			
	2.16	79.1			
	2.54	91.8			
	3.92	127			
	4.14	130			
	6.75	186			
	8.67	219			
	8.84	220			
	9.50	250			
	13.5	307			
	33.7	609			
73	0.944	40.5			
	2.16	73.3			
	4.14	122			
	7.57	191			
	8.67	204			
	8.84	205			
	13.5	287			
	17.8	349			
	33.7	556			
74	0.506	29.3			
	0.972	46.4			
	1.59	64.6			
	4.05	132			
	8.29	225			
75	0.68	31.3			
	2.13	81.5			
	2.90	96.7			
	9.34	221			
	22.3	391			
76	2.00	72.6			
	8.67	223			
	21.6	473			

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TABLE 11. Polystyrene in tetrahydrofuran — Continued

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
77	0.51	28.9			
	0.98	46.8			
	1.73	67.2			
	4.11	128			
	8.67	219			
	21.5	380			
78	0.51	28.7			
	0.982	44.0			
	1.73	63.6			
	4.11	128			
	6.70	176			
	26.7	450			
67	0.972	48.7			
	2.00	78.8			
	3.90	134			
	6.70	189			
	12.3	309			
	24.2	498			
	25.3	521			
	45.9	800			
	55.5	895			
	96.0	1350			
	181	2100			
80	0.51	28.0			
	0.972	44.6			
	1.60	65.6			
	3.98	133			
	8.60	222			
81	16.6		66.0		
	35.3		98.3		
82	2.75				4.68
	5.94				4.06
	9.03		39.5		3.41
	20.7		68.5		3.01
65	7.10		39.5	26.3	
	11.2		51.4	33.8	
	16.5		64.3	41.7	
	29.5		91.7	60.2	
	37.1		105	69.5	
	62.7		138	91.1	
68	0.37			5.75	
	0.51			6.31	
	1.10			10.3	
	3.90			20.4	
	4.11			20.2	
	6.00			26.2	
	8.92		43.8		3.96
	18.2		59.0	48.2	2.95
	30.0			62.3	
	38.0		94.5		2.57
	54.8			86.6	
	55.5		118		2.20
	76.0			116	
	84.2		137		2.06

TABLE 11. Polystyrene in tetrahydrofuran — Continued

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
69,83	0.94				5.91
	3.20				4.10
	6.30				3.69
	9.20		40.0		3.09
	18.2				2.56
	18.35		58.0		
	37.7		91.5	69.5	2.19
	54.7		118	89.3	2.01
	83.2		136	109	1.83
	220.0		244	195	1.41
84	0.204			3.7	
	0.510			6.2	
	0.97			8.7	
	1.60			11.9	
	4.11			20.2	
	8.60			29.8	
	18.0			47.1	
85	0.48				6.83
	0.90				5.40
	1.57				5.15
	4.05				3.94
	8.06				3.53

FIG. 3. R_g as a function of M for PS in THF (x – Ref. 81; $\triangle$ – Ref. 82; ● – Ref. 65 □ – Ref. 68; ■ – Refs. 69 and 83).

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TABLE 12. Poly(α-methylstyrene) in cyclohexane

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_g (nm)	R_H (nm)
86	2.04	33.6		
	3.42	42.0		
	4.44	45.5		
	7.68	62.8		
	11.9	81.1		
	18.2	98.5		
	33.0	130		
	74.7	206		
87	0.59	17.6		
	1.18	25.0		
	3.05	40.4		
	6.65	59.1		
	9.03	69.5		
	11.4	76.1		
88	0.49	16.6		
	1.21	25.3		
	1.83	33.0		
	2.68	38.2		
89	0.96	23.3		
	2.20	36.2		
	4.80	52.0	19.1	
	6.60	64.5	22.5	
	8.40	69.5	24.8	
	12.5	90.0	32.8	
	15.4	101	34.6	
	40.0	160	57.5	
91	11.9		32.4	
	18.2		39.6	
	33.0		52.2	
	74.7		78.6	
92	0.246			3.51
	0.71			5.58
	1.09			7.18
	2.93			11.1
	5.84			16.1
	7.26			17.9
	10.1			21.6
	29.0			36.9
93	2.04			9.44
	4.44			13.8
	7.68			18.1
	11.9			20.5
	18.2			27.6
	33.0			37.3
	74.7			56.2
94	0.15			2.76
	0.57			5.09
	0.96			6.84
	2.18			10.1
	4.86			15.1
	8.45			20.0
90	6.65		22.7	
	9.03		26.4	
	11.4		29.6	
	14.0		32.6	
	31.0		48.8	
	34.1		51.3	

TABLE 13. Poly(α-methylstyrene) in toluene

Reference	$M \times 10^{-5}$ (g mol^{-1})	$[\eta]$ (cm g^{-1})	R_g (nm)	R_H (nm)	$A_2 \times 10^4$ (cm^3 mol g^{-2})
86	2.04	62.1			
	3.42	89.5			
	4.44	104			
	7.68	159			
	11.9	242			
	18.2	317			
	33.0	465			
	74.7	940			
95	0.59	24.1		5.33	
	0.76	28.7		6.49	
	1.18	40.3		8.32	
	1.77	52.2		10.1	
	3.05	79.5		14.3	
	3.13	82.1		14.2	
	6.65	139		21.9	
	9.03	170		26.4	
	11.4	198		29.1	
91	2.04				3.24
	3.42		22.3		2.80
	4.44		27.0		2.65
	6.94		34.5		2.20
	11.9		48.0		1.85
	12.4		45.7		1.94
	14.6		55.4		1.82
	18.2		63.0		1.67
	33.0		85.6		1.48
	74.7		137		1.17
96	0.69				4.07
	1.14				3.55
	2.97				2.71
	6.11				2.29
	7.79				2.18
	10.5				2.00
	30.0				1.56
	6.51		29.1		
	10.8		41.4		
	28.0		88.7		
97	5.71		28.1	19.1	2.42
	11.7		41.1	28.1	2.00
	29.6		74.0	50.2	1.48
92	0.71			6.44	4.13
	1.09			8.25	3.78
	2.93			14.2	2.89
	5.84			21.8	2.30
	7.26			24.4	2.23
	10.1			28.9	1.98
	29.0			52.1	1.56
93	2.04			11.9	
	4.44			18.5	
	7.68			25.4	
	11.9			32.0	
	18.2			41.4	
	33.0			57.8	
	74.7			87.5	
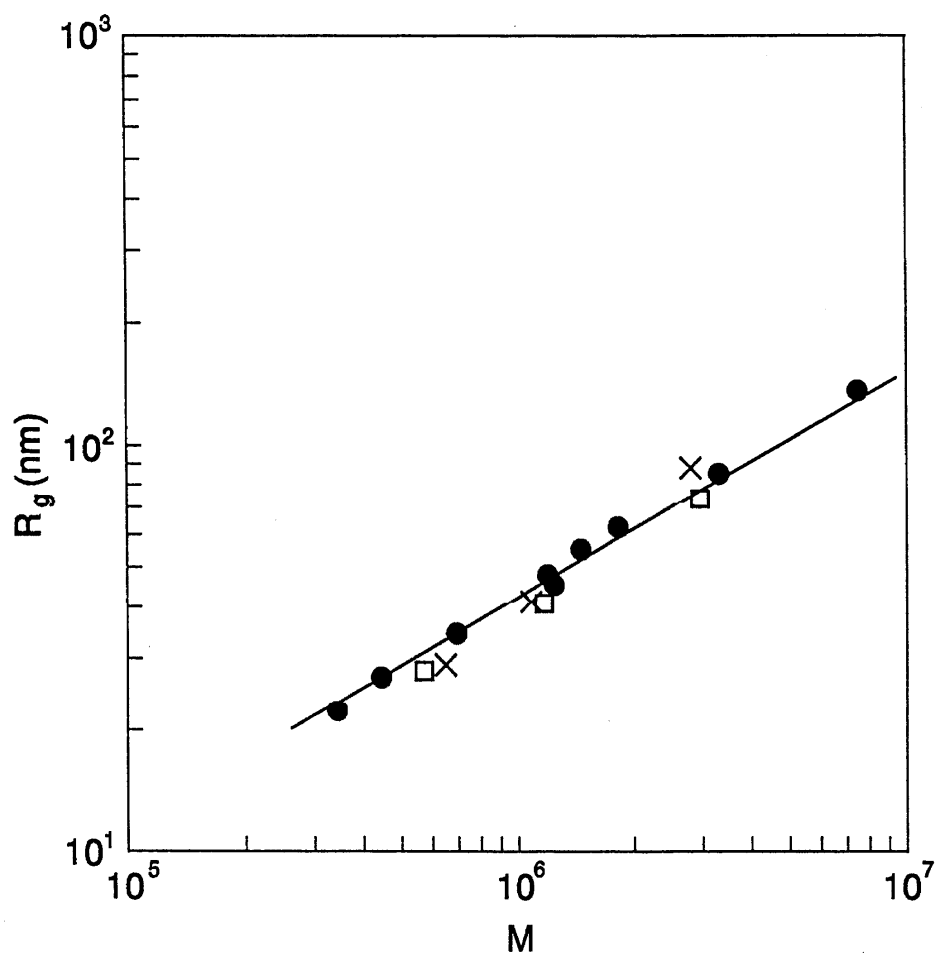
FIG. 4. R_g as a function of M for PαMS in toluene ($\bullet$ - Ref. 91; x - Ref. 96; $\square$ - Ref. 97)

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