

## Relationship between the Hydrodynamic Radius and the Radius of Gyration of a Polymer in Solution

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Recent advances in quasi-elastic laser light scattering techniques have permitted measurements of diffusion coefficients of polymer solutions with a considerable degree of accuracy. From these results, the hydrodynamic radius  $R_H$  can be obtained from the Stokes-Einstein equation. It is our aim in this note to review the relation between  $R_G$  and the radius of gyration,  $R_G$ , calculated according to the Fox-Flory equation. In this wellknown relationship<sup>1)</sup>:

$$R_G^3 = \frac{M[\eta]}{\phi'} \quad (1)$$

where  $M$  is the polymer molecular weight,  $[\eta]$  is the intrinsic viscosity and  $\phi' = 3,1 \cdot 10^{24}$  (with  $[\eta]$  in  $\text{cm}^3/\text{g}$ ). In Eq. (1),  $[\eta]$  is given by the Mark-Houwink equation,

$$[\eta] = K M^a \quad (2)$$

We write:

$$R_H = X R_G \quad R_G = X R_H \quad (3)$$

where  $X$  is a proportionality constant which is assumed to be independent of  $M$  or solvent. Then with the Stokes-Einstein equation:

$$D_0 = k T / (6 \pi \eta_0 R_H) \quad (4)$$

where  $D_0$  is the diffusion coefficient at zero concentration,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $\eta_0$  is the viscosity of the solvent.  $D_0$  can be expressed as

$$D_0 = \frac{k T}{6 \pi \eta_0 X} \left[ \frac{3,1 \cdot 10^{24}}{K M^{1+a}} \right]^{1/3} \quad (5)$$

Eq. (5) can now be used with experimental  $D_0$  values to obtain  $X$ . The results obtained from various cited sources are given in Tab. 1. The physical constants used are summarized in Tab. 2.

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Tab. 1. Ratios of hydrodynamic radius  $R_H$  and radius of gyration  $R_G$  of different polymer-solvent systems from various results of diffusion coefficient ( $D_0$ ) determinations in literature

No.	System	Method <sup>a)</sup>	$10^4 \cdot D_0$ (exptl.) <sup>b)</sup> $\text{cm}^2 \cdot \text{s}^{-1}$	$10^4 \cdot D_0 X$ $\text{cm}^2 \cdot \text{s}^{-1}$ (Eq. (5))	$X = \frac{R_H}{R_G}$	Ref.
1.	Polystyrene (PS)/tetrahydrofuran (THF)	q. e.	$3,45 \cdot M^{-0,564}$	$2,85 \cdot M^{-0,57}$	0,826	2)
2.	PS/ethyl methyl ketone (MEK)	q. e.	$5,5 \cdot M^{-0,561}$	$2,34 \cdot M^{-0,53}$	0,425	3)
3.	PS/MEK	q. e.	$3,1 \cdot M^{-0,53}$	$2,34 \cdot M^{-0,53}$	0,750	4)
4.	PS/toluene	q. e.	$3,9 \cdot M^{-0,577}$	$2,95 \cdot M^{-0,58}$	0,756	5)
5.	PS/THF	q. e.	$3,2 \cdot M^{-0,56}$	$2,85 \cdot M^{-0,57}$	0,891	6)
6.	PS/benzene	q. e.	$2,18 \cdot M^{-0,55}$	$1,60 \cdot M^{-0,55}$	0,734	7)
7.	PS/cyclohexane	q. e.	$1,3 \cdot M^{-0,497}$	$1,01 \cdot M^{-0,50}$	0,777	8)
8.	PS/cyclohexane	q. e.	$1,31 \cdot M^{-0,51}$	$1,01 \cdot M^{-0,50}$	0,771	9)
9.	PS/cyclohexane	q. e.	$1,4 \cdot M^{-0,508}$	$1,01 \cdot M^{-0,50}$	0,721	10)
10.	PS/ <i>trans</i> -decalin	Schlieren patterns	$0,7 \cdot 10^{-3}$ (M.W. = 390 000)	$0,52 \cdot 10^{-3}$	0,743	11)
11.	PS/toluene	Schlieren patterns	$4,25 \cdot 10^{-3}$ (M.W. = 110 000)	$3,38 \cdot 10^{-3}$	0,795	11)
12.	PS/MEK	P. I.	$1,1 \cdot 10^{-3}$ (M.W. = $3,5 \cdot 10^6$ )	$0,84 \cdot 10^{-3}$	0,763	12)
13.	Poly(methyl methacrylate)/chloroform	P. I.	$4,5 \cdot M^{-0,60}$	$3,41 \cdot M^{-0,60}$	0,758	12)
14.	Poly( <i>p-tert</i> -butylphenyl methacrylate)/chloroform	P. I.	$6,0 \cdot M^{-0,60}$	$4,39 \cdot M^{-0,59}$	0,732	12)
15.	Poly( $\alpha$ -methylstyrene)/benzene	q. e.	$5,24 \cdot M^{-0,59}$	$2,64 \cdot M^{-0,57}$	0,504	13)
16.	Poly( $\alpha$ -methylstyrene)/toluene	q. e.	$5,24 \cdot M^{-0,59}$	$3,01 \cdot M^{-0,58}$	0,574	13)

a) q. e. = quasi elastic light scattering. P. I. = polarization interferometry.

b) M.W. = molecular weight.

Tab. 2. Mark-Houwink parameters  $K$  and  $a$ , temperature and solvent viscosity  $\eta_0$  used in calculations for Tab. 1.

Polymer	Solvent	Temp. in °C	$K \cdot 10^3$ cm <sup>3</sup> /g	$a$	Ref.	$\eta_0 \cdot 10^3$ poise <sup>14, 15)a)</sup>
Polystyrene (PS)	tetrahydrofuran	25	14,1	0,70	16)	4,62
PS	ethyl methyl ketone	25	39,0	0,58	17)	4,00
PS	toluene	25	7,5	0,75	18)	5,52
PS	benzene	20	34,0	0,65	19)	6,03
PS	cyclohexane	34,5	85,0	0,50	20)	7,42
PS	<i>trans</i> -decalin	20	81,0	0,50	13)	22,2
Poly(methyl methacrylate)	chloroform	25	5,1	0,79	12)	5,42
Poly( <i>p-tert</i> -butyl- phenyl methacrylate)	chloroform	25	2,4	0,78	12)	5,42
Poly( $\alpha$ -methylstyrene)	benzene	30	10,3	0,72	21)	5,64
Poly( $\alpha$ -methylstyrene)	toluene	25	7,06	0,744	22)	5,52

a) 1 Poise =  $10^{-1} \text{ N} \cdot \text{s} \cdot \text{m}^{-2}$ .

The systems listed in Tab. 1 as entries 2, 15 and 16 give low values of  $X$ . The other 13 polymer-solvent systems appear to be all mutually consistent, however, and have an average value of  $X = 0,77$ , with a standard deviation of 0,05. A higher value for the Flory constant with  $\phi' = 3,7 \cdot 10^{24}$  gives  $X = 0,82$ . (A plurality of values have been suggested for  $\phi'$  and  $\phi$ , which is the constant in terms of end-to-end distance ( $\phi' = 6^{3/2} \phi$ ) and the  $\phi'$  values quoted correspond to  $\phi = 2,1 \cdot 10^{23}$  and  $2,5 \cdot 10^{23}$ , respectively).

The experimental figure of 0,77 is to be contrasted with the predictions of the Kirkwood-Riseman theory<sup>23)</sup> that:

$$R_H = 0,665 R_G \quad (6)$$

and the recent theoretical results of Akcasu and Han<sup>24)</sup> in which

$$R_H = 0,664 R_G \quad (\text{theta-solvents}) \quad (7)$$

and:

$$R_H = 0,537 R_G \quad (\text{good solvents}) \quad (8)$$

We return now to a consideration of the three entries in Tab. 1 which were not included in the averaging to estimate  $X$ . Entries 2 (which was deleted) and 3 (which was included) differ significantly although they refer to the same polymer/solvent combination. Furthermore, the measured virial coefficients  $k_d$  also differ in the equation.

$$D = D_0(1 + k_d c) \quad (9)$$

where  $D$  is the diffusion coefficient at concentration  $c$ . However, McDonnell and Jamieson<sup>25)</sup> have reported that the data of entry 3 are in agreement with their own

results for a polystyrene with molecular weight 160 000. The weight of evidence therefore seems to indicate that the data of entry 2 are aberrant, for reasons which are not clear. We are currently making measurements on this system with the hope of providing further independent data to resolve this disagreement.

The other discordant data (entries 15 and 16) are for atactic poly( $\alpha$ -methylstyrene) samples in toluene and in benzene. The reasons for these discrepancies are also not clear. It is perhaps relevant that the author<sup>13)</sup> analyzed the data of Kato et al.<sup>26)</sup> to obtain the relation:

$$R_G = 1,49 \cdot 10^{-9} M^{0,58} \quad (10)$$

A combination of this result with diffusion coefficients by quasi-elastic light scattering yielded  $R_H/R_G = 0,5$ , which is in good agreement with Eq. (8). However, if Eq. (10) is used in Eq. (1) along with the appropriate Mark Houwink constants from Tab. 2 we obtain a value of  $\phi = 1,45 \cdot 10^{23}$ . This is a very low value for the molecular weight range which was investigated in a good solvent and suggests that the relation in Eq. (10) may not be reliable.

Recently, Caroline and Jones<sup>27)</sup> have compared diffusion results with experimental radii of gyration of polystyrene in a theta solvent and concluded that  $R_H = 0,77 R_G$ . Our summary here is for theta and good solvents and produces the same ratio. It would appear, therefore, that present theoretical treatments may need to be refined to consolidate agreement with experiment.

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