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Polymer excluded volume exponent ν : An experimental verification of the n vector model for $n = 0$

J. P. Cotton

Laboratoire Léon-Brillouin, DPh-G/PSRM, CEN Saclay, B.P. N° 2, 91190 Gif-sur-Yvette, France

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Résumé. — Trois ensembles de mesures (Y. Miyaki *et al.*, *Macromolecules* **11** (1978) 1180 ; M. Fukuda *et al.*, *J. Polym. Sci.* **12** (1974) 871 ; A. Yamamoto *et al.*, *Polymer J.* **2** (1971) 799) de diffusion de lumière par des solutions diluées polystyrène benzène sont analysés ici. Ces mesures, très soignées, donnent les variations des valeurs du rayon de giration $\langle R^2 \rangle^{1/2}$ et du deuxième coefficient du viriel A_2 en fonction de la masse moléculaire du polymère dont la variation couvre trois décades de valeurs.

L'analyse présentée ici consiste à corriger les effets de polydispersité afin d'obtenir la valeur expérimentale de l'exposant de volume exclu ν . La valeur obtenue : $\nu = 0,586 \pm 0,004$ à partir des mesures de $\langle R^2 \rangle^{1/2}$ vérifie mieux la théorie critique ($\nu = 0,588$) que celle de Flory ($\nu = 0,60$). Ceci est confirmé par les mesures de A_2 .

Abstract. — Three light scattering experiments (Y. Miyaki *et al.*, *Macromolecules* **11** (1978) 1180 ; M. Fukuda *et al.*, *J. Polym. Sci.* **12** (1974) 871 ; A. Yamamoto *et al.*, *Polymer J.* **2** (1971) 799) for polystyrene benzene dilute solutions are analysed. These very careful measurements give the variations of the radius of gyration $\langle R^2 \rangle^{1/2}$ and of the second virial coefficient A_2 as a function of the molecular weight ($0.246 \times 10^6 \leq M_w \leq 56 \times 10^6$). These data are corrected here for polydispersity effects and analysed in order to determine the excluded volume exponent ν . The obtained value : $\nu = 0.586 \pm 0.004$ from $\langle R^2 \rangle$ is in better agreement with the critical theory ($\nu = 0.588$) than with the theory of Flory ($\nu = 0.60$). This result is confirmed by the A_2 data.

In dilute polymer solutions the excluded volume interactions between monomers introduce a swelling of the chain characterized [1] by an exponent ν . This exponent, or various combinations of it, are found [2] in the relations which connect the observables of solutions to the practical parameters such as the concentration or the molecular weight M of polymers.

As a particular case, the observables measured by light scattering from dilute solutions are the radius of gyration $\langle R^2 \rangle^{1/2}$ of a chain and the second virial coefficient A_2 which are connected to M using the following relations [1, 3] :

$$\langle R^2 \rangle = KM^{2\nu} \quad (1)$$

$$A_2 = K' M^{3\nu-2} \quad (2)$$

where K and K' are constants.

The first theoretical value of ν , $\nu_F = 0.600$, has been first given by Flory [1] using a controversial [4] mean field theory. More recently de Gennes has shown [5] that ν can be calculated using the n vector

model with $n = 0$. Following this method and using a perturbative expansion of renormalization group functions of field theory in three dimensions, the ν value ($\nu_c = 0.588 \pm 0.001$) has been obtained [6].

The difference between ν_F and ν_c are so small that the experimental ν values found in the literature [7, 8, 9] have so far been not able to differentiate between them. Nevertheless it is of fundamental interest to know if the n vector model and the expansion, mentioned above, are valid for $n = 0$.

The first problem encountered in obtaining ν from eqs. (1) and (2) lies in the difficulty of having a sufficient number of precise data obtained with polymers of the same chemical species in the same solvent and corresponding to a wide range of well characterized molecular weights. This problem is now solved since a set of very careful light scattering experiments for solutions of polystyrene of very high molecular weights have recently completed [9] two others sets of similar data [10, 11]. The data of these sets are summarized in table I. The values of ν

Table I. — *These data are obtained from 3 sets of experiments choosen in the literature for the weak polydispersity of the polymers used. The A set corresponds to experiments of Miyaki et al. [9], B set to these of Fukuda et al. [10] and C set to these of Yamamoto et al. [11]. The values of M_w for the set A are deduced from an average of those measured [9] in benzene and in cyclohexane.*

	$10^{-6} M_w$ Dalton	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	$\langle R^2 \rangle_z^{1/2}$ Å	$\langle R^2 \rangle_c^{1/2}$ Å	A_2 $10^{-4} \text{ cm}^3 \text{ g}^{-2}$	ψ	$\langle R_0^2 \rangle_z^{1/2}$ Å	$\langle R_0^2 \rangle_w^{1/2}$ Å
A	56.3	—	1.10	5 060	4 765	1.09	0.239	2 280	2 170
A	38.5	—	1.05	3 920	3 800	1.22	0.246	1 830	1 785
A	31.9	—	1.06	3 530	3 400	1.28	0.247	1 670	1 620
A	23.4	—	1.05	2 970	2 880	1.44	0.246	1 450	1 420
A	15.1	—	1.06	2 270	2 185	1.66	0.271	1 160	1 130
B	9.70	1.03	—	1 735	1 705	1.60	0.226	—	—
A	8.78	—	1.07	1 640	1 570	1.82	0.270	879	850
B	7.62	1.02	—	1 520	1 500	1.73	0.222	—	—
B	5.53	1.04	—	1 260	1 230	1.89	0.232	—	—
B	4.59	1.05	—	1 120	1 085	2.03	0.250	—	—
B	3.63	1.07	—	982	943	2.21	0.259	—	—
C	2.87	< 1.06	—	829	—	2.25	—	489	—
B	2.42	1.04	—	791	772	2.33	0.221	—	—
C	1.59	< 1.06	—	575	—	2.91	—	—	—
B	1.23	1.02	—	509	503	2.86	0.253	—	—
C	0.756	< 1.06	—	374	—	3.34	—	257	—
C	0.342	< 1.06	—	240	—	4.12	—	168	—
C	0.246	< 1.06	—	195	—	4.42	—	—	—
Solvent :	Benzene A (25 °C) B + C (30 °C)							Cyclohexane A (34.5 °C) C (34.6 °C)	

obtained by these authors from eq. (1) are 0.585 [10], 0.580 [11] and 0.595 [9] following the considered sets of data. Because the polydispersity effects are more important for the higher molecular weights than for the smaller ones, a better accuracy on ν can be obtained from a simultaneous correction of these effects. The treatment of these data is given in the following in order to obtain the exponents of eqs. (1) and (2) respectively.

1. **The radius of gyration.** — The principal difficulty found in obtaining a precise value of ν from eq. (1) is linked with the weight distribution $f(M)$ inherent to the chemical preparation of a polymer. This distribution is generally characterized by the well known [12] different average molecular weight :

$$M_n = \langle M \rangle = \int M f(M) dM \quad (3)$$

$$M_w = \frac{\langle M^2 \rangle}{\langle M \rangle} = \int \frac{M^2}{M_n} f(M) dM = \int M w(M) dM \quad (4)$$

$$M_z = \frac{\langle M^3 \rangle}{\langle M^2 \rangle} = \int \frac{M^3}{M_w M_n} f(M) dM = \int M z(M) dM \quad (5)$$

where $1 = \int f(M) dM$. In a light scattering experiment it is the z average of the radius of gyration $\langle R^2 \rangle_z$

$$\langle R^2 \rangle_z = K \int M^{2\nu} z(M) dM \quad (6)$$

which is obtained [13] while it is the average molecular weight M_w which is measured [12].

In a first step, neglecting the polydispersity of the samples we have fitted the data of table I by a least square method. This treatment leads to

$$\langle R^2 \rangle_z^{1/2} = (0.118 \pm 0.005) M_w^{0.597 \pm 0.003} (\text{Å})$$

in good solvent (benzene). It leads to

$$\langle R_0^2 \rangle_z^{1/2} = (0.27 \pm 0.01) M_w^{0.506 \pm 0.003} (\text{Å})$$

in θ solvent (cyclohexane 34.5 °C) for which it is recognized [1, 3] that the excluded volume effects are compensated and the ν value is 1/2. The exponent value of 0.506 suggests that the polydispersity has a non negligible influence.

In order to take polydispersity into account one has to express $\langle R^2 \rangle_z$ as a function of $M_w^{2\nu}$:

$$\langle R^2 \rangle_z = K \frac{\langle M^{2\nu+2} \rangle}{\langle M^2 \rangle} \frac{M_w^{2\nu}}{M_w^{2\nu}} = K g(\nu) M_w^{2\nu} \quad (7)$$

This equation introduces [13] a corrected value $\langle R^2 \rangle_c$ of the radius of gyration

$$[\langle R^2 \rangle_c = \langle R^2 \rangle_z g^{-1} = K M_w^{2\nu}],$$

which is the $\langle R^2 \rangle$ value for a monodisperse sample with a molecular weight M_w . For the correction the usual [3, 13] Schulz and Zimm distribution [14] is adopted for $f(M)$:

$$f(M) = y^k M^{k-1} e^{-yM} [\Gamma(k)]^{-1}; \quad (8)$$

$$\langle M^\alpha \rangle = \frac{\Gamma(k + \alpha)}{\Gamma(k) y^\alpha}$$

where $\Gamma(k)$ is the gamma function and k and ν are adjustable parameters. A straightforward calculation using eqs. (7) and (8) leads to [13] :

$$g(\nu) = \frac{\Gamma(k + 2\nu + 2)}{\Gamma(k + 2)} (k + 1)^{-2\nu}$$

$$k = \left(\frac{M_w}{M_n} - 1 \right)^{-1} = \left(\frac{M_z}{M_w} - 1 \right)^{-1} - 1. \quad (9)$$

These equations have been used in order to deduce the $\langle R^2 \rangle_c$ values given in table I from the measured ones $\langle R^2 \rangle_z$.

Use of S.Z. distribution [14] corresponds to an approximation which can introduce an error. This error would be of little importance if the parameters of this distribution were evaluated identically from the same type of data, for example from the M_w/M_n ratios. However this uniformity in the treatment cannot be achieved here. The values of k for the set B have to be determined from the M_w/M_n ratios only [11]. But for the set A it is more appropriate to use the M_z/M_w ratios which the authors claimed [9] to be of better accuracy. This procedure is justified, *a fortiori* from the results obtained for θ solvent and from the following test of the S.Z. distribution : For the case of the set A a comparison of the values of k , deduced from M_w/M_n (k_1) and from M_z/M_w (k_2), can be achieved. Following eq. (9) it leads to :

$$4.2 \leq k_1 = 7 \leq 25$$

$$12.5 \leq k_2 = 20 \leq 50,$$

for $M_w = 38.5 \times 10^6$ and similar differences are found for the other values of M_w . The agreement between these values of k is not excellent but it is not so bad [15]. (Let us recall the poor accuracy announced [9] on the M_w/M_n ratios.) Therefore the taken values for k in eq. (9) were deduced from M_z/M_w for the set A and for M_w/M_n for the set B.

This correction (with $\nu = 1/2$) is first tested on the data registered for θ solvent it leads to

$$\langle R_0^2 \rangle_c^{1/2} \equiv \langle R_0^2 \rangle_w^{1/2} = (0.290 \pm 0.007) M_w^{0.500 \pm 0.004} (\text{\AA})$$

for the A set of data. A wider range of M_w values can be obtained by taking the $\langle R_0^2 \rangle_c$ values for the set A and the $\langle R_0^2 \rangle_z$ values for the set C (for which the M_w/M_n values are unfortunately not given). The fit of these inhomogeneously corrected data (denoted $\langle R_0^2 \rangle_{cz}$) leads to :

$$\langle R_0^2 \rangle_{cz}^{1/2} = (0.295 \pm 0.010) M_w^{0.499 \pm 0.003} (\text{\AA}).$$

Comparison between these two relations confirms that the correction is really important for polymers with the highest molecular weights only. On the other hand these results give us confidence in the use of the

S.Z. distribution for the correction since the exponent found is now $1/2$.

For the good solvent, the ν value first adopted for $g(\nu)$ was 0.595 [8, 9] it leads to

$$\langle R^2 \rangle_c^{1/2} = (0.138 \pm 0.008) M_w^{0.585 \pm 0.004} (\text{\AA}).$$

With $\nu = 0.586$, one obtains (see Fig. 1) :

$$\langle R^2 \rangle_c^{1/2} = (0.138 \pm 0.008) M_w^{0.586 \pm 0.004} (\text{\AA})$$

Fig. 1. — Log Log plot of $\langle R^2 \rangle_c^{1/2}$ versus M_w . The straight line corresponds to $0.138 M_w^{0.586}$ (see text). The symbols $\odot$ shows the data of Miyaki *et al.* ($\langle R^2 \rangle_c^{1/2}$); $\times$ for these of Fukuda *et al.* ($\langle R^2 \rangle_c^{1/2}$) and $\oplus$ for these of Yamamoto *et al.* ($\langle R^2 \rangle_z^{1/2}$).

using the corrected data of the 6th column of table I. The ν value found is now consistent with the ν value used in $g(\nu)$. By using these last data and the $\langle R^2 \rangle_z^{1/2}$ values for the C set of which correction has been shown to be very weak for θ solvent one finds :

$$\langle R^2 \rangle_{cz}^{1/2} = (0.133 \pm 0.005) M_w^{0.588 \pm 0.002} (\text{\AA}).$$

These ν values are precise [16] and are in very good agreement [17] with the prediction [5, 6] of 0.588 of the n vector model.

2. The second virial coefficient. — Here the problem is due to the errors for the A_2 values which as well-known [18] are greater than those obtained for the $\langle R^2 \rangle$ values. The polydispersity effects have been shown (see Yamakawa's book [3], p. 220) to be negligible relative to the experimental errors for A_2 i.e. $A_{2w} \simeq A_2$.

The fit of the three sets of A_2 values yields

$$A_2 = (103 \pm 10) \cdot 10^{-4} M_w^{-0.254 \pm 0.007} (\text{cm}^3 \text{g}^{-2})$$

(see Fig. 2) which corresponds to a ν value of 0.582 ± 0.002 . This value is again in better agreement with the critical theory. As a matter of fact these sets of data taken two by two leads to different ν values [0.573 (B + C); 0.587 (A + B) and 0.582 (A + C)]

Fig. 2. — Log Log plot of A_2 versus M_w (low data). The straight line corresponds to $103 M_w^{-0.254}$. The upper curve is semi-log plot of the interpenetration function ψ (see eq. (11)). The symbols used correspond to those of figure 1.

of which dispersion perhaps expresses the systematic errors of each set of experiments.

3. Conclusion. — The importance of polydispersity

on the considered measurement is stressed. Its influence appears clearly on the ν value discussed here. But it is greater on the values of the interpenetration function ψ

$$\psi = K'' A_2 M^2 \langle R^2 \rangle^{-3/2}, \quad K'' = (4 \pi^{3/2} N_a)^{-1} \quad (10)$$

where N_a is the number of Avogadro. A fuller discussion of it has been given elsewhere [3, 19].

Since a power three of the radius of gyration is found here the polydispersity has to be corrected. In figure 2 the following values of ψ are plotted :

$$\psi = K'' A_{2w} M_w^2 \langle R^2 \rangle_c^{-3/2}$$

using the reasonable approximation $A_{2w} \simeq A_2$ already mentioned. Figure 2 shows clearly (see also table I) that ψ is rather a constant for A and B set of data. Its mean value is 0.245 ± 0.005 .

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- [15] The difference between $k_1 = 7$ and $k_2 = 20$ yields a difference of 5% on the value of the coefficient which connects $\langle R^2 \rangle_z^{1/2}$ to $\langle R^2 \rangle_c^{1/2}$.
- [16] It may seem surprising to find an accuracy a little less than 1% while the precision on $\langle R^2 \rangle^{1/2}$ and M_w is of the order of a few percents. But using eqs. (1) and (7) the relative incertitude of ν is given by
$$\frac{\Delta \nu}{\nu} = \frac{\Delta \text{Log} \langle R^2 \rangle_c^{1/2}}{\text{Log} \langle R^2 \rangle_c^{1/2}} + \frac{\Delta \text{Log} M}{\text{Log} M}$$

$$\frac{\Delta \langle R^2 \rangle_c}{\langle R^2 \rangle_c} = \frac{\Delta \langle R^2 \rangle_z}{\langle R^2 \rangle_z} + \frac{\Delta g(\nu, k)}{g(\nu, k)}$$
which leads to a $\Delta \nu$ value of 0.006 for one of the most inaccurate data [9] : $M_w = (23.4 \pm 1) \cdot 10^6$; $\langle R^2 \rangle_z^{1/2} = 2970 \pm 90 \text{ Å}$; $M_z/M_w = 1.05 \pm 0.03$.
- [17] Use of the less accurate value M_w/M_n for the determination of k in set A leads to a smaller central value and a larger inaccuracy of ν . Even then, the obtained results are in better agreement with the n vector model prediction than the earlier 3/5 value.
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