

Excluded volume effect in polyacrylonitrile solutions

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SUMMARY

The paper discusses the validity criteria of the theories on the excluded volume effect for high molecular weight ($M_w = 10^6 - 3 \cdot 10^6$) polyacrylonitrile. The experimental data obtained for both the interpenetration function $\Psi(Z)$ and the hydrodynamic function $\Pi(Z)$ satisfactorily approach the theoretical predictions of the renormalized two-parameter theory for high excluded volume.

INTRODUCTION

In some previously published papers (1,2), high molecular weight polyacrylonitrile samples (PAN, $M_w = 10^6 - 3 \cdot 10^6$) were investigated by light scattering and viscometry, using dimethylformamide (DMF) as solvent. The dependences of the radius of gyration, of the intrinsic viscosity and of the second virial coefficient on the molecular weight were established, and the unperturbed dimensions were discussed. The obtained results were compared to literature data reported for usual length PAN. The relatively large scattering of the experimental data was attributed to the different heterogeneities of the materials, to the different methods of calculation and to the values of the ϕ_0 constants considered.

The present paper is concerned with a comparison of experimental and theoretical data, as given by different theories, on excluded volume effect of high molecular weight PAN.

EXPERIMENTAL

Polyacrylonitrile (PAN) samples with weight-average molecular weights (M_w) ranging from 10^6 to $3 \cdot 10^6$ were obtained by plasma-induced polymerization (3,4).

The viscometric measurements were carried out in dimethylformamide (DMF) in the 15 - 50 °C temperature range (± 0.01 °C), in dimethylacetamide (DMA) and dimethylsulphoxide (DMSO) at 20 °C, and in ethylene carbonate - water (85 : 15 by weight) (ECH) at 44 °C (theta condition (5)), by use of an Ubbelohde suspended-level viscometer. Kinetic energy corrections were found to be negligible, and drainage errors unimportant.

The weight-average molecular weights (M_w), the root-mean-square radii of gyration ($\langle S^2 \rangle^{1/2}$), the second virial coefficients (A_2) and the intrinsic viscosities ($[\eta]$) (as determined by Fedors' method (6)) of the studied samples are given in Table I.

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The $\langle S_0^2 \rangle / M$ values, obtained by different methods of evaluation (our data and literature data) are given in Table II.

Table I.

Weight-average molecular weights (M_w), root-mean-square radii of gyration ($\langle S_z^2 \rangle^{1/2}$ and $\langle S_w^2 \rangle^{1/2}$), second virial coefficients (A_2) and intrinsic viscosities ($[\eta]$) of PAN samples in DMF at 20°C

Sample	$M_w \cdot 10^{-6}$	$\langle S_z^2 \rangle^{1/2} \cdot 10^5$ (cm)	$\langle S_w^2 \rangle^{1/2} \cdot 10^5$ * (cm)	$A_2 \cdot 10^4$ ($\text{cm}^3 \cdot \text{mol} \cdot \text{g}^{-2}$)	$[\eta]$ ($\text{dl} \cdot \text{g}^{-1}$)
1	1.041	0.692	0.595	4.217	-
2	1.132	0.741	0.637	4.064	6.54
3	1.235	0.813	0.699	3.988	6.82
4	1.371	0.998	0.859	3.589	-
5	1.778	0.977	0.841	3.631	-
6	2.367	1.170	1.007	3.456	12.27
7	2.973	1.405	1.209	3.291	14.31
8	3.078	1.429	1.229	3.311	-

* values corrected by use of the Schultz - Zimm distribution, with $M_w / M_n = 1.4$

Table II.

Unperturbed dimensions parameters K_θ and $\langle S_0^2 \rangle / M$ for PAN

Method	$K_\theta \cdot 10^3$ ($\text{dl} \cdot \text{g}^{-1}$)	$\langle S_0^2 \rangle / M \cdot 10^{16}$ (cm^2)
(a) cf. Stockmayer - Fixman eq., DMF, 20°C (2)	2.324	0.1584 (with $\phi_0 = 2.51 \cdot 10^{21}$)
(b) cf. Lenka et al. (7) method, DMF, DMA, DMSO, 20°C (2)	2.006 (with $\phi_0 = 2.51 \cdot 10^{21}$)	0.1435
(c) in theta solvent (ECW, 44°C) (2)	2.977	0.1866 (with $\phi_0 = 2.51 \cdot 10^{21}$)
(d) cf. Kurata - Stockmayer eq., lit. data (8), DMF, 25°C	2.10 ± 0.15	0.1442 (with $\phi_0 = 2.87 \cdot 10^{21}$)
(e) cf. Stockmayer - Fixman eq., lit. data (5), DMF, 25°C	3.60 - 3.10	0.1944 - 0.1734 (with $\phi_0 = 2.87 \cdot 10^{21}$)
(f) cf. Lenka et al. (7) method, lit. data (7)	4.326 (with $\phi_0 = 2.51 \cdot 10^{21}$)	0.2396

RESULTS AND DISCUSSION

1. Excluded volume parameter

The excluded volume effect in dilute polymer solutions is generally discussed in terms of the expansion factor α_s and of the interpenetration function Ψ , defined as the degree of penetration of polymer chains in dilute solution. The interpenetration function, given by

$$\Psi(z) = A_2 M^2 / (4\pi^{3/2} N_A \langle S^2 \rangle^{3/2}) \quad (1)$$

(where N_A is Avogadro's number) is a function of the excluded volume parameters Z .

The expansion factors $\alpha_s^2 = \langle S_w^2 \rangle / \langle S_0^2 \rangle$ and the excluded volume parameters Z (eq. (2)), were calculated from the experimental data (Tables I and II).

$$Z = [1/(4\pi)]^{3/2} (B/A^{3/2}) M^{1/2} \quad (2)$$

In eq. (2), $B = 2.47 \cdot 10^{-27}$ (Table II) (according to (2)), and $A = \langle S_0^2 \rangle / M$.

The values of α_s and Z , obtained with different values for $\langle S_0^2 \rangle / M$ ratios (cf. Table II), are given in Table III.

Table III.

Expansion factors α_s^2 and excluded volume parameters Z for PAN in DMF

Sample	α_s^2 *					Z *		
	(a)	(b)	(c)	(e)	(f)	(a)	(b)	(c)
1	2.1471	2.37	1.82	1.75 - 1.96	1.42	0.90	1.04	0.70
2	2.2626	2.50	1.92	1.84 - 2.07	1.49	0.94	1.09	0.73
3	2.4975	2.76	2.12	2.03 - 2.28	1.65	0.98	1.13	0.76
4	3.3977	3.75	2.88	2.77 - 3.10	2.25	1.03	1.19	0.81
5	2.5115	2.77	2.13	2.05 - 2.29	1.66	1.17	1.36	0.92
6	2.7045	2.98	2.29	2.20 - 2.47	1.79	1.35	1.57	1.06
7	3.1035	3.42	2.63	2.53 - 2.83	2.05	1.52	1.76	1.19
8	3.0978	3.42	2.63	2.52 - 2.83	2.05	1.54	1.79	1.21

* the values for α_s^2 and Z were calculated with the data in Table II for different $\langle S_0^2 \rangle / M$ ratios; for (a) - (f), see Table II

The evaluation of the experimental errors for α_s^2 (according to the different $\langle S_0^2 \rangle / M$ ratios) led to $\pm 25\%$ for all data in Table III and $\pm 13\%$ for our data. These errors are not surprising. Together with the used method, polymer heterogeneity and the selected value of Flory's constant ϕ_0 may modify the results. In this context, the results reported in the present paper for high molecular weight PAN are comparable with those from literature.

The theories of flexible polymers in dilute solutions indicate that the expansion factor α_s and the interpenetration function $\Psi(Z)$ are universal functions of Z .

To test the validity of the theoretical expressions (9) connecting α_s to Z with the experimental data, Figure 1 presents the Z vs. $M_w^{1/2}$ dependence.

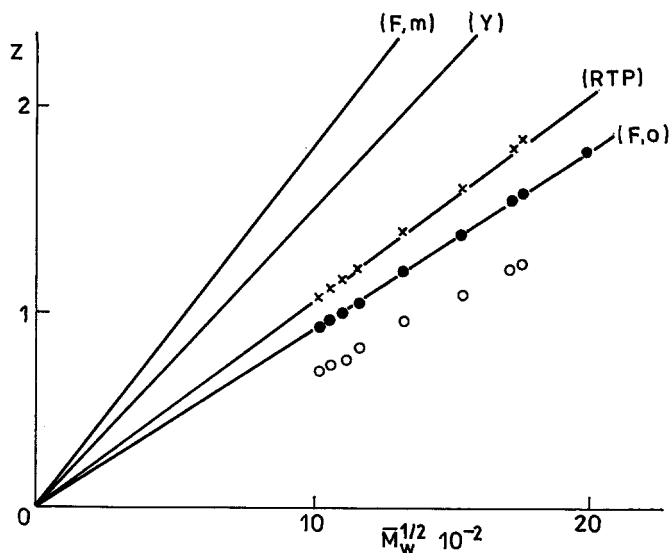


Fig. 1. Test of the linearity between Z and $M_w^{1/2}$ according to different theories (9) for PAN in DMF. F, o - the original Flory theory; F, m - the modified Flory theory; Y - the Yamakawa - Tanaka theory; RTP - the renormalized two - parameter theory of Douglas and Freed. (●) - column (a), (x) - column (b), (o) - column (c) in Table III.

One can see that the experimental data obtained by use of the equation of Lenka et al. (7) for the determination of the unperturbed dimensions are in agreement with the renormalized two - parameter theory (RTP).

2. Interpenetration function

Another criterion of the validity of a given theory states that the values of Z determined from the observed values of α_s and from the observed values of Ψ , using the theoretical expressions for α_s and Ψ , should be consistent. Figure 2 presents the variation of $\Psi(Z)$ as a function of α_s^3 , giving the theoretical curves predicted by the existing models, and the experimental values calculated according to eq. (1).

It follows from nearly all theories that Ψ monotonously increases with α_s^3 up to a constant value. In a theta solvent, the second virial coefficient and hence Ψ are equal to zero, while $\alpha_s = 1$. Both α_s and Ψ increase with increasing solvent quality. If α_s becomes large enough - which is the case for large polymer chains in good solvents - Ψ reaches a constant value $\Psi(\infty)$.

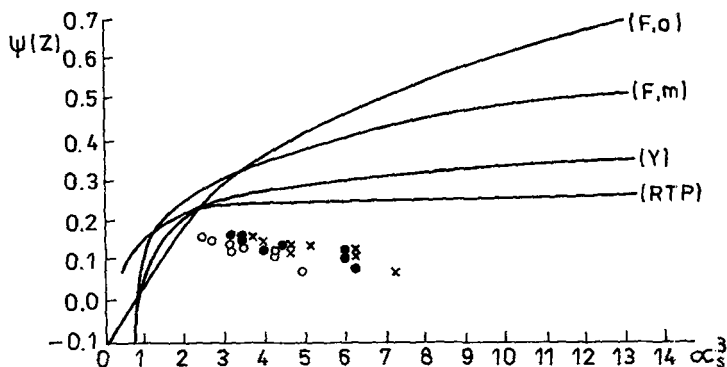


Fig. 2. Plots of $\Psi(Z)$ as a function of α_s^3 for PAN in DMF. α_s^3 was calculated from column (a) - (\bullet), column (b) - (\times), and column (c) - (o) in Table III. For F,o, F,m, Y and RTP - see Fig. 1.

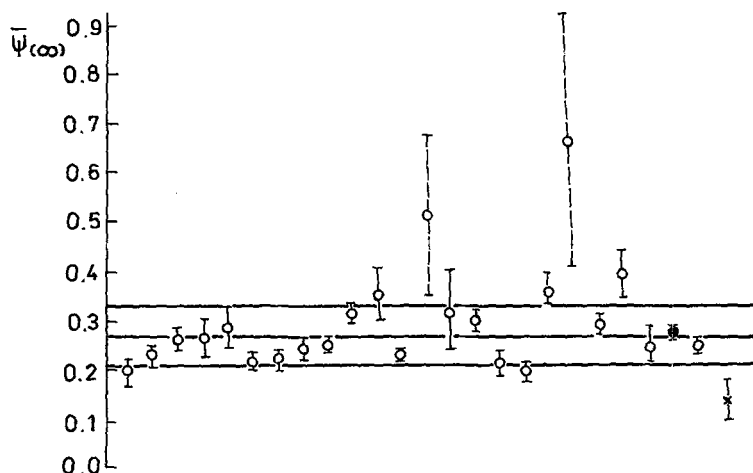


Fig. 3. The average values of $\Psi(\infty)$ for several polymer - solvent systems (10). The hatched bar indicates the weighted average value of $\Psi(\infty)$ and its standard deviation. (\bullet) - poly(butyl methacrylate) in methyl ethyl ketone, at 25°C (our data (11)); (\times) - present data on PAN.

values of Ψ seem to agree with the behaviour predicted by RTP theory, the universality of Ψ should be accepted (10).

The average values of $\Psi(\infty)$ for high excluded volume were compared with the theoretical predictions by Mennen (10). The data are summarized in Figure 3.

From the standard deviation observed considering the RTP theory it is obvious that Ψ is only moderately useful for experimental application, i.e., for the determination of the radius

of gyration from the second virial coefficient or vice versa. Particularly, Ψ can be applied to estimate the order of magnitude.

3. Hydrodynamic penetration function

Similarly to the interpenetration function $\Psi(Z)$, Douglas and Freed (12) define the hydrodynamic penetration function $\Pi(Z)$ as an universal function of Z only in the non-free-draining limit:

$$\Pi(Z) = A_2 M / [\eta] = [2^{1/2} (2 \pi / 6)^{3/2} (N_A / \phi_0)] \Psi \alpha_s^3 / \alpha_\eta^3 \quad (3)$$

which in the RTP theory turns to

$$\Pi(z) = 3.64 (0.207 \lambda_2 + 0.062 \lambda_2^2) (1 - 0.13 \lambda_2)^{3/2} (1 - 0.276 \lambda_2)^{-1} \quad (4)$$

where

$$\lambda_2 = 6.442 Z / (1 + 6.441 Z) \quad (5)$$

The general shape of this function is very similar to that for $\Psi(Z)$, tending to a limit of 1.1 for high excluded volume (Figure 4). By calculating experimentally $\Pi(Z)$, according to eq., (3), with the experimental values of A_2 , M_w and $[\eta]$ (Table I), one observes that the obtained data give an average value of 0.7 ± 0.02 , which is situated under the limit of the theoretical expression of $\Pi(Z)$ given by eq. (4).

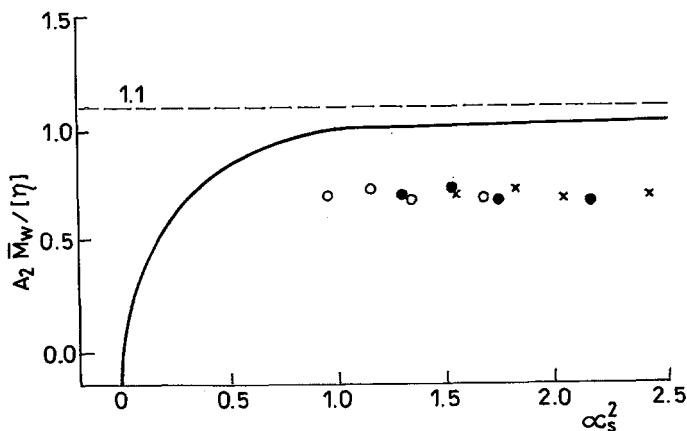


Fig. 4. Plot of $A_2 M_w / [\eta]$ vs. $\alpha_s^2 - 1$ for PAN in DMF. The full curve shows the data obtained according to RTP theory. α_s^2 was calculated from column (a) - (\bullet), column (b) - (\times), and column (c) - (\circ) in Table III.

This behaviour has been extensively tested by experiments performed on several polymers in different solvents. The numerical values of Ψ according to different theories differ and only some of them withstand the experimental test.

The universality of Ψ is difficult to be tested; it depends on three experimental quantities (M_w , A_2 and $\langle S_w^2 \rangle^{1/2}$) which all exhibit a certain error in their determination, and polymer samples are never strictly monodisperse. However, in as much as the experimental

As well as $\Psi(Z)$ function, the hydrodynamic penetration function $\Pi(Z)$, experimentally determined, is affected by the errors in the determination of M_w , A_2 and $[\eta]$. Totalization of the errors leads to differences between experimental and theoretical data.

CONCLUSIONS

Light scattering and viscometric studies on high molecular weight PAN ($M_w = 10^6 - 3 \cdot 10^6$) in DMF, at 20°C, allow the following conclusions:

1) In testing the validity of the theoretical expressions connecting the expansion factor α_s with the excluded volume parameter Z it was observed that experimental data lead to a linear dependence in agreement with the predictions of the RTP theory.

2) The experimental data obtained for $\Psi(Z)$ and $\Pi(Z)$ functions satisfactorily approach those resulting from the RTP theory which predicts asymptotic values of 0.269 and 1.1, respectively, for high excluded volume. For reasons already mentioned, a perfect concordance can not be attained. Thus, in practice, both $\Psi(Z)$ and $\Pi(Z)$ can not be measured with great accuracy.

For high excluded volume, the errors in the determination of the expansion factor α_s do not influence the discussion of the behaviour of $\Psi(Z)$ and $\Pi(Z)$.

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