Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymolecularity Correction Factors for the Thermodynamic Properties of High Molecular Weight Polyacrylonitrile

S. Loan[a]; C. Loan[a]; M. Bercea[a]; B. C. Simionescu[b]
[a] "P. Poni" Institute of Macromolecular Chemistry, Jassy, Romania [b] Department of Macromolecules, "Gh. Asachi" Technical University, Jassy, Romania

To cite this Article Loan, S. , Loan, C. , Bercea, M. and Simionescu, B. C.(1998) 'Polymolecularity Correction Factors for the Thermodynamic Properties of High Molecular Weight Polyacrylonitrile', Journal of Macromolecular Science, Part A, 35: 4, 609 — 620

To link to this Article: DOI: 10.1080/10601329808002000
URL: http://dx.doi.org/10.1080/10601329808002000

J.M.S.—PURE APPL. CHEM., A35(4), pp. 609–620 (1998)

POLYMOLECULARITY CORRECTION FACTORS FOR THE THERMODYNAMIC PROPERTIES OF HIGH MOLECULAR WEIGHT POLYACRYLONITRILE

Silvia Ioan, Catalina Ioan, Maria Bercea
"P. Poni" Institute of Macromolecular Chemistry
6600-Jassy, Romania

Bogdan C. Simionescu*
"Gh. Asachi" Technical University
Department of Macromolecules
6600-Jassy, Romania

Key Words: Polymolecularity Correction Factors, Radius of Gyration, Intrinsic Viscosity, Second Virial Coefficient, Polyacrylonitrile

ABSTRACT

The paper examines the influence of the molecular weight distribution types and the polydispersity index ($M_w/M_n \cong 1.4$) on the values of the root-mean-square radius of gyration, the second virial coefficient and the intrinsic viscosity for high molecular weight polyacrylonitrile (PAN) obtained by plasma-induced polymerization.

INTRODUCTION

The effect of polymers polydispersity on their solution properties has been discussed in innumerable papers and numerical values of polydispersity corrections factors have been tabulated [1-3]. Most of the known polydispersity corrections can be applied for e.g. intrinsic viscosity, mean-square radius of gyration, in order to obtain the correct numerical values of constants K and a in the exponential relationships existing between a molar mass dependent property (P) and the molar mass for a polymer- homologous series of monomolecular polymers (M):

$$P = K \cdot M^{a} \tag{1}$$

The constants K and a depend on the polymer-solvent system and on the temperature.

The effect of polymolecularity on the second virial coefficient was discussed little in the literature and is still controversial [4-7].

It is known that the power law region, where the various macroscopic properties of polymer chains depend on powers of their molecular weights, is the limiting region of very large molecular weights. With increasing the molecular weight in the same thermodynamic conditions, the values of K and a are modified: thus, for high excluded volume, that is ultra-high molecular weight polymers in good solvents, the exponent a tends to asymptotic values [8-10].

In some previously published papers [11-13], high molecular weight polyacrylonitrile samples were investigated by light scattering and viscometry, using dimethylformamide as solvent. The experimental data and the validity criteria of different theories of the excluded volume effect were discussed. The obtained results were compared to literature data reported for usual length PAN with molecular weights of 10^4 order. The relatively large scattering of the experimental data on the unperturbed dimensions was attributed to the different heterogeneities of the materials, to the different methods of calculation and to the values of the Flory constant ϕ_0 considered.

The present paper examines the influence of the polydispersity index M_w/M_n and the molecular weight distribution types on the values of the root-mean-square radius of gyration $<S_Z^2>^{1/2}$, the second virial coefficient (A_2) obtained from light scattering measurements and on the intrinsic viscosity ([η]) for high molecular weight PAN.

EXPERIMENTAL

High molecular weight PAN samples were obtained by plasma-induced polymerization; the synthesis conditions for this process were previously described [14, 15] and yielded relatively low polydispersity samples ($M_w/M_n \cong 1.4$), with weight average molecular weights ranging from 10^6 to $3 \cdot 10^6$.

TABLE 1. M_w, $<S_z^2>^{1/2}$, $<S_w^2>^{1/2}$, A_2 and [η] for PAN samples in DMF at 20°C [11]

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)	$A_2\cdot 10^4$ ($cm^3\cdot mol/g^2$)	[η] (dl/g)
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	-

Light scattering and viscometric measurements studies were performed in dimethylformamide (DMF) at 20°C and between 15 and 50°C (±0.01°C), respectively.

The weight average molecular weights (M_w), the root-mean-square radii of gyration ($<S_z^2>^{1/2}$), the second virial coefficients (A_2) and the intrinsic viscosities [η], as determined by Fedors's method [16], of the studied samples are given in Table 1 [11]. The experimental precision in the determination of these properties was reported as ± 9.0, 5.5, 5.0 and 3.4 %, respectively.

RESULTS AND DISCUSSION

Polymolecularity Correction for the Root-Mean-Square Radii of Gyration

The Table 1 also contains the corrected root-mean-square radii of gyration $<S_w^2>^{1/2}$, considering the polydispersity of the samples $M_w/M_n \cong 1.4$, by using the equation:

$$\langle S_w^2\rangle^{1/2} = F\cdot\langle S_z^2\rangle^{1/2} \tag{2}$$

where $F = (h + 1)/(h + 2 + \beta)$, $h = [M_w/M_n) - 1]^{-1}$ in the Schulz-Zimm distribution, and $\beta = (2\cdot a-1)/3$, a being the exponent in the Mark-Houwink equation which was found to be 0.84 in this study.

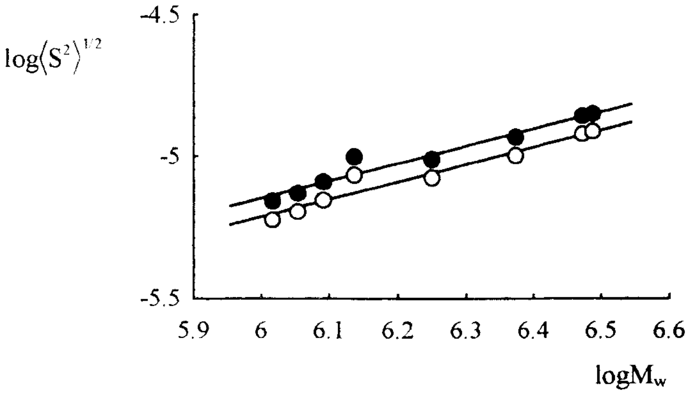

Figure 1. Plot of the logarithm of the root-mean-square radii of gyration $<S_Z^2>^{1/2}$ (o) and $<S_w^2>^{1/2}$ (•) against the logarithm of M_w for PAN samples in DMF at 20°C.

The double logarithmic plot of the root-mean-square radii of gyration in DMF at 20°C vs. M_w are presented in Figure 1. All points fit closely the empirical equations [11].

$$\langle S_z^2\rangle^{1/2} = 0.929 \cdot 10^{-9} \cdot M_w^{0.63} \quad \text{(cm)} \tag{3}$$

$$\langle S_w^2\rangle^{1/2} = 0.799 \cdot 10^{-9} \cdot M_w^{0.63} \quad \text{(cm)} \tag{4}$$

From Equations 3 and 4 it appears that the error introduced by the polydispersity of the samples on ($<S_Z^2>^{1/2}$) is $\cong$ 16.3 %. This is in agreement with the considerations of Bareiss [3] which show that the mean-square radius of gyration is much more affected by the polydispersity as compared to other polymer properties, even in the case of very narrow molecular weight distributions. Thus, for $M_w/M_n = 1.1$, Bareiss reports that the uncorrected values of $<S^2>^{1/2}$ introduce errors greater than 10%.

Polymolecularity Correction for the Intrinsic Viscosity

From the double logarithmic plots of $[\eta]$ vs. M_w at different temperatures, the values given in Table 2 have been established for the Mark-Houwink param-

TABLE 2. Mark-Houwink parameters for PAN in DMF at various temperatures [11]

Temperature (°C)	a	$K \cdot 10^4$
15	0.837	0.513
20	0.839	0.536
25	0.829	0.617
30	0.836	0.512
35	0.836	0.559
40	0.833	0.562
45	0.832	0.562
50	0.830	0.564

eters. Figure 2 illustrates as an example the data on DMF dilute solutions of PAN samples at 20°C.

The polymolecularity correction factors q calculated for the intrinsic viscosity from Equations 5-8 are presented in Table 3.

$$[\eta] = K_v \cdot M_v^a = K_w \cdot M_w^a \tag{5}$$

$$K_w = K_v \cdot q \tag{6}$$

$$q_w^S = \frac{\Gamma(h+a+1)}{(h+1)^a \cdot \Gamma(h+1)} \quad \text{for Schulz - Zimm distribution (S)} \tag{7}$$

$$q_w^{LN} = \left[\frac{M_w}{M_n}\right]^{(a^2-a)/2} \quad \text{for logarithmic normal distribution (LN)} \tag{8}$$

It was observed that the uncorrected values for $[\eta]$ introduce an error of about 1.9% and 2.3% in the Mark-Houwink relation considering the Schulz-Zimm and logarithmic normal distributions, respectively.

Polydispersity Correction for the Second Virial Coefficient

Many theories predict that $0.2 \leq a \leq 0.25$ for the dependence between the second virial coefficient and the molecular weight; this was also confirmed by many experimental tests. This type of dependence is restricted to monodisperse polymer

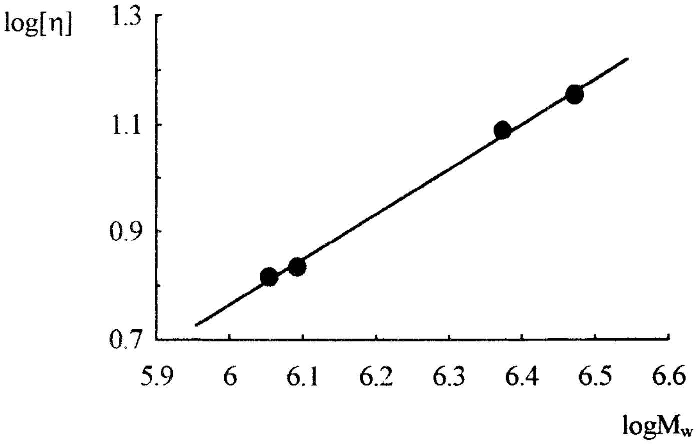

Figure 2. Plot of the logarithm of the intrinsic viscosities against the logarithm of M_W for PAN samples in DMF at 20°C.

TABLE 3. Polymolecularity Correction Factors q_w^S, q_w^{LN} and Mark-Houwink parameters K_W, K_v^{LN}

Temp. (°C)	q_w^S	q_w^{LN}	$K_w \cdot 10^4$	$K_v^S \cdot 10^4$	$K_v^{LN} \cdot 10^4$
15	0.981	0.977	0.513	0.523	0.525
20	0.982	0.978	0.536	0.546	0.548
25	0.981	0.976	0.617	0.629	0.632
30	0.981	0.977	0.512	0.522	0.524
35	0.981	0.977	0.559	0.570	0.572
40	0.981	0.977	0.562	0.573	0.575
45	0.981	0.977	0.562	0.573	0.575
50	0.981	0.977	0.564	0.575	0.578

samples which are seldom obtained experimentally. This is why recent literature has paid more attention to the influence of polydispersity. In order to obtain the correct numerical values of constants K and a , it is necessary to determine the so-called "corresponding averages" [2, 17, 18] $A_{2,av}$ and M_{av} with respect to Equation 9:

$$A_{2,av} = K \cdot M_{av}^a \tag{9}$$

$A_{2,av}$ is the value of the molecular weight which fulfills Equation 9 if K and a are the factor and exponent, respectively, valid for strictly uniform samples.

For a polydisperse polymer sample consisting of molecules with N different lengths, Casassa [6, 19] has proposed the equations:

$$(A_2)_{os} = \sum_{i=1}^{N}\sum_{j=1}^{N} A_{ij} \cdot w_i \cdot w_j \tag{10}$$

$$(A_2)_{ls} = \frac{\sum_{i=1}^{N}\sum_{j=1}^{N} A_{ij} \cdot w_i \cdot w_j \cdot p_i \cdot p_j}{\left[\sum_{i=1}^{N} w_i \cdot p_j\right]^2} \tag{11}$$

where the subscripts "os" and "ls" refer to the osmotic and light scattering virial coefficients, respectively, A_{ij} is the second virial coefficient determined by the interaction between two chains i and j in the sample, w_i and w_j are the weight fractions of polymer chains with molecular weights M_i and M_j respectively. Following Casassa, these sums are approximated by integrals:

$$(A_2)_{os} = \int_0^\infty dp \cdot w(p) \cdot \int_0^\infty dp' \cdot w(p') \cdot A(p,p') \tag{12}$$

$$(A_2)_{ls} = \left(\overline{p_w}\right)^{-2} \cdot \int_0^\infty dp \cdot p \cdot w(p) \cdot \int_0^\infty dp' \cdot p' \cdot w(p') \cdot A(p,p') \tag{13}$$

in which $\overline{p_w}$ stands for the weight average degree of polymerization of the sample, and the second virial coefficients and the weight fractions appear as continuous functions.

Mennen *et al*. [20-22] have found from theoretical and experimental evaluations that the cross coefficient A_{ij} was approximately equal to the second virial coefficient of the lowest molecular weight polymer. They have obtained from Equations 12 and 13 the extensions of the corresponding scaling relation (Equation 1), using different molecular weight distribution functions for poly-disperse polymers:

$$(A_2)_{os} = K \cdot q_{os}^{S}(h,a) \cdot M_n^{-a} \tag{14}$$

$$(A_2)_{ls} = K \cdot q_{ls}^{S}(h,a) \cdot M_w^{-a} \tag{15}$$

for Schulz-Zimm (S) distribution function, and

$$\left(A_2\right)_{os} = K_a \cdot q_{os}^{LS}(h, a) \cdot M_n^{-a} \tag{16}$$

$$\left(A_2\right)_{ls} = K \cdot q_{ls}^{LN}(h, a) \cdot M_w^{-a} \tag{17}$$

for logarithmic normal (LN) distribution function, with:

$$q_w^S(h, a) = (h + 1)^a \cdot \frac{\Gamma(h + 2 - a)}{\Gamma^2(h + 2)} \cdot \sum_{n=0}^{\infty} \frac{\Gamma(2 \cdot h + 4 + n - a)}{\Gamma(h + 3 + n - a)} \cdot 2^{a - 2 \cdot h - 3 - n} \tag{18}$$

and

$$q_w^S(h, a) = q_{os}^S(h + 1, a) \tag{19}$$

for a Schulz-Zimm distribution, and

$$q_w^{IN}(h,a) = 1 + (2 \cdot \pi)^{-1/2} \cdot a \cdot r + \frac{1}{4} \cdot (a^2 - a) \cdot r^2 + \frac{1}{24} \cdot (2 \cdot \pi)^{-1/2} \cdot (5 \cdot a^3 - 6 \cdot a^2) \cdot r^3 + \\ + \frac{1}{32} \cdot (a^2 - a)^2 \cdot r^4 + \ldots.. \tag{20}$$

and

$$q_w^{LN}(h, a) = q_{os}^{LN}(h, a) \tag{21}$$

where $r^2 = 2 \cdot \ln(1 + h^{-1})$, for a logarithmic normal distribution.

Douglas and Freed [23] have determined the polydispersity corrections for a wide variety of polymer properties that have previously been calculated from the two-parameter model, in conjunction with the chain space renormalization group theory. Specific calculations are provided for the properties P, using the Schulz - Zimm distribution when the molecular weight distribution is very narrow, i.e., $M_w/M_n \leq 1.1$.

The dependence of the second virial coefficient A_2 on M_w for PAN samples in DMF at 20°C is shown in Figure 3 and leads to Equation 22.

$$A_2 = 9.44 \cdot 10^{-3} \cdot M_w^{-0.219} \tag{22}$$

Equations 16-21 were used to determine the corrected relations between A_2 and M_w, using the Schulz-Zimm and logarithmic normal distribution functions.

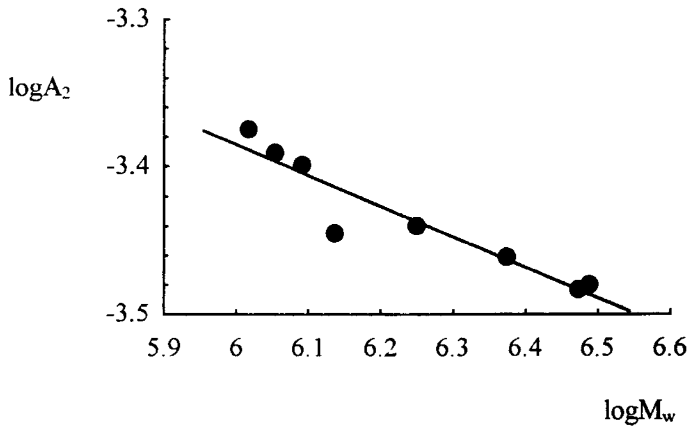

Figure 3. Plot of the logarithm of the uncorrected second virial coefficients against the logarithm of M_w for PAN samples in DMF at 20°C.

Thus, the values of polymolecularity correction factors q calculated for the intrinsic viscosity from Equations 18 and 20 are $q_w^S = 1.037$ and $q_w^{LN} = 1.041$, and yield to the dependences:

$$A_{2,w}^{S} = 9.789\cdot 10^{-3}\cdot M_w^{-0.219} \tag{23}$$

$$A_{2,w}^{LN} = 9.827\cdot 10^{-3}\cdot M_w^{-0.219} \tag{24}$$

which show that the errors introduced by the polydispersity of the samples are 3.558% and 3.952% for a Schulz -Zimm and logarithmic normal distribution, respectively.

Taking into account the experimental errors in the determination of the second virial coefficient (about ± 5 %), one cannot distinguish between the results from Equations 22, 23, and 24, that is between the uncorrected and corrected (for $M_w/M_n \cong 1.4$) results.

Also, previous studies of ultrahigh molecular weight methyl methacrylate - styrene 50:50 random copolymers with $7.3\cdot 10^6 \le M_w \le 66.0\cdot 10^6$ and $M_w/M_n = 1.56$ [24-26] have shown that the uncorrected values for A_2 introduced errors insignificant compared to the experimental errors in the discussion of the excluded volume effect.

Recently, Bareiss and Jung [7] have determined the numerical values of the polymolecularity correction factors by the blob theory for different values of the exponent a and different widths of the molecular weight distributions expressed as M_w/M_n. It appeared that the polymolecularity correction factors were approximately equal to 1.0 for Schulz and logarithmic normal distributions of the molecular weights. Also, they have found that in Equation 9) the weight average molecular weight is a good approximation for M_{av} if A_2 is measured via light scattering, while the number average molecular weight can be inserted for M_{av} if A_2 stems from osmotic pressure measurements.

CONCLUSION

In this work, we discussed the influence of the polymolecularity on the root-mean-square radius of gyration, the intrinsic viscosity and the second virial coefficient for high molecular weight PAN in DMF. Thus, the uncorrected values for $<S_Z^2>^{1/2}$ introduce an error of about 16.3% considering the Schulz-Zimm distribution, which has to be considered in any further evaluations.

In considering the Schulz-Zimm and logarithmic normal distribution functions, the errors introduced by the polymolecularity are 1.9% and 2.3%, respectively, for $[\eta]$ and 3.6% and 3.9%, respectively, for A_2, which are smaller than the experimental ones. The knowledge of the type of distribution (Schulz-Zimm, logarithmic normal, etc.) is important, but its influence is less.

Referring to our previous studies [11, 12], one can conclude that the possible appearance of branches during the polymerization process and the polydispersity of the PAN samples are not responsible for the differences between our data and the literature ones concerning the molecular weight dependences expressed by Equation 1. A close inspection of these variations reveals that there exists a change in the slope of the plots with increasing molecular weight [27]. The observed changes in slopes of log-log relations implies that the behavior in dilute solutions of good polymer-solvent systems cannot be represented by universal exponents. The numerical values of these exponents depend on the molecular weight range over which the analyses of data are performed.

REFERENCES

[1] R. E. Bareiss, *Polymolecularity Correction Factors* in *Polymer Handbook*, J. Brandrup and E. H. Immergut, Eds., 2nd Edition, Wiley-Interscience, New York, 1975, p. IV-115; 3rd ed. with extended tables, 1989.

[2] R. E. Bareiss, *Chemiker Zeitung*, *4*, 97 (1981).

[3] R. E. Bareiss, *Eur. Polym. J.*, *19*, 847 (1983).

[4] R. E. Bareiss, *IUPAC International Symposium "Polymer 91"*, Melbourne, Australia, February 10-14, 1991, Preprints, pp. 522.

[5] W. Burchard, R. Dolega, and W. H. Stockmayer, *Collect. Czech. Chem. Commun.*, *60*, 1653 (1995).

[6] E. F. Casassa, *Polymer*, *3*, 625 (1962).

[7] R. E. Bareiss and B. Jung, *Macromol. Theory Simul.*, *5*, 157 (1996).

[8] H. Fujita, *Macromolecules*, *21*, 179 (1988).

[9] M. K. Kosmos and A. M. Kosmos, *Polymer*, *34*, 3115 (1993).

[10] S. Ioan, M. Bercea, C. I. Simionescu, and B. C. Simionescu, *Ultrahigh Molecular Weight Polymers*, in *Polymeric Materials Encyclopedia*, by J. C. Salamone, Ed., CRC Press, Boca Raton, New York, London, Tokyo, 1996, Vol. 11, p. 8417.

[11] B. C. Simionescu, S. Ioan, M. Bercea, and C. I. Simionescu, *Eur. Polym. J.*, *27*, 553 (1991).

[12] B. C. Simionescu, S. Ioan, M. Bercea, and C. I. Simionescu, *Eur. Polym. J.*, *27*, 589 (1991).

[13] S. Ioan, G. Grigorescu, C. Ioan, and B. C. Simionescu, *Polym. Bull.*, *33*, 119 (1994).

[14] C. I. Simionescu and B. C. Simionescu, *Chem. Zvesti*, *37*, 685 (1983).

[15] C. I. Simionescu and B. C. Simionescu, *Pure Appl. Chem.*, *56*, 427 (1984).

[16] R. F. Fedors, *Polymer*, *20*, 226 (1979).

[17] R. E. Bareiss, O. Chiantore, and M. Guaita, *Makromol. Chem.*, *183*, 951 (1982).

[18] R. E. Bareiss, *Makromol. Chem.*, *184*, 1509 (1983).

[19] E. F. Casassa, *Polymer*, *1*, 169 (1960).

[20] M. G. Mennen, Ph. D. Thesis, Leiden University, The Netherlands September 1989.

[21] M. G. Mennen, J. A. M. Smit, and M. Mandel, *Integration of Fundamental Polymer Science and Technolog -2*, P. J. Lemstra and L. A. Kleintjens, Eds., Elsevier Appl. Sci., London, p. 222, 1988.

[22] M. G. Mennen and J. A. M. Smit, *Polym. Bull*, *23*, 67 (1990).

[23] J. F. Douglas and K. F. Freed, *Macromolecules*, *17*, 1854, 2344 (1984).

[24] C. I. Simionescu, B. C. Simionescu, and S. Ioan, *J. Macromol. Sci.-Chem.* *A22*, 765 (1985).

[25] C. I. Simionescu, S. Ioan, and B. C. Simionescu, *Makromol. Chem. Macromolec. Symp.*, *20/21*, 235 (1988).

[26] C. Ioan, B. C. Simionescu, and C. I. Simionescu, Rev. *Roum. Chim.*, *37*, 11 (1992).

[27] S. Morariu, M. Bercea, C. Ioan, S. Ioan, and B. C. Simionescu, *3eme Colloque Franco-Roumain des Polymeres*, Neptun, Romania, Septembre 3-5,1997.

Received August 10, 1997
Final revision received November 15, 1997