Calculation of the unperturbed dimensions of polymers via an equation derived from the combination of the two-parameters theory with the blob theory

Anastasios Dondos
Department of Chemical Engineering, University of Patras, 26500, Patras, Greece

and Edward F. Casassa
Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA
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A combination of two equations for the viscometric expansion factor, derived from the two-parameters theory and the blob theory, leads to an equation that permits the calculation of the unperturbed dimensions parameter K_θ of a polymer from the values of the parameters K and a of the Mark–Houwink–Sakurada equation. The method is especially useful in the high molecular weight region in which the Stockmayer–Fixman–Burchard equation is not valid.

(Keywords: unperturbed dimensions; two-parameters theory; blob theory)

Comparison of the two equations that give the viscometric expansion factor of a polymer, α_η, which are derived either from the blob theory or the classical two-parameters theory, leads us to propose a new method to obtain the unperturbed dimensions of polymers.

Based on the equation given by Farnoux *et al.*[1], and on the dynamic agreements of Weill and des Cloizeaux[2], the following equation is proposed by Han[3] to directly relate the viscometric expansion factor of a macromolecular chain to the number of blobs N/N_τ:

$$\alpha_\eta^3 = [4(1-\nu)(2-\nu)]/[(2\nu+1)(\nu+1)](N/N_\tau)^{3\nu-1.5} \qquad (1)$$

where ν is the excluded volume index, N is the number of the statistical segments of the chain and N_τ is the number of statistical segments from which one blob is formed.

In a recent article[4] N_τ was replaced by N_c, which is the number of statistical segments of the chain at the onset of excluded volume behaviour. In other words N_c corresponds to the molecular weight M_c in which the exponent a of the Mark–Houwink–Sakurada (MHS) equation becomes greater than 0.5. At this molecular weight the chain consists of one blob. Experimental results[4] have shown the validity of equation (1) after replacement of N_τ by N_c. For a flexible polymer dissolved in an 'ideal' solvent ($a=0.73$ or $\nu=(1+a)/3=0.5766$), in which $N_c=4$ (refs 4, 5), the following experimental relation is obtained with many polymers[4]:

$$\alpha_\eta^3 = 0.765(N/4)^{0.24} \qquad (2)$$

while equation (1), with $\nu=0.5766$, becomes:

$$\alpha_\eta^3 = 0.71(N/4)^{0.23} \qquad (3)$$

or

$$\log \alpha_\eta^3 = \log 0.71 + 0.23 \log(1/4) + 0.23 \log N \qquad (4)$$

Using the relation of the 'classical' polymer solution theory we obtain the following equations for a polymer of molecular weight M, dissolved in an 'ideal' solvent ($a=0.73$):

$$[\eta]/[\eta]_\theta = (K/K_\theta)M^{0.23}$$

or

$$\log \alpha_\eta^3 = \log(K/K_\theta) + 0.23 \log M$$

where K is the constant in the MHS equation and K_θ the unperturbed dimensions parameter. This equation can be transformed as follows

$$\log \alpha_\eta^3 = [\log(K/K_\theta) + 0.23 \log(M/N)] + 0.23 \log N \qquad (5)$$

Comparing equations (4) and (5) we observe that the quantity in brackets in equation (5) is always the same in good solvents, and is equal to $\log 0.71 + 0.23 \log(1/4)$. In equation (5) M/N equals the mass of the statistical segment, m_s, which is obtained from the relation:

$$m_s = AM_L = \left(\frac{K_\theta}{\Phi}\right)^{2/3} M_L^2 \qquad (6)$$

in which A is the Kuhn statistical segment length, M_L is the mass per unit chain length and Φ is Flory's constant ($2.6 \times 10^{23}\ \text{mol}^{-1}$).

Equating the quantity in brackets in equation (5) with the quantity $\log 0.71 + 0.23 \log(1/4)$, and replacing M/N by m_s finally gives the following equation:

$$\log K_\theta = \frac{\log K + 0.46 \log M_L - 3.3}{0.847} \qquad (7)$$

With polystyrene (PS) dissolved in benzene, which is an 'ideal' solvent for this polymer ($a=0.73$), we have obtained a value of $9 \times 10^{-3}\ \text{ml g}^{-1}$ for the constant K, and with $M_L = 42 \times 10^8\ \text{cm}^{-1}$ we obtain $K_\theta = 8.2 \times 10^{-2}\ \text{g}^{-3/2}\ \text{mol}^{1/2}$ from equation (7). This value is generally accepted as the 'best' value for the PS unperturbed dimensions parameter. For poly(methyl methacrylate) (PMMA) in solution in acetone with $K = 5.3 \times 10^{-3}\ \text{ml g}^{-1}$ (ref. 6) and $M_L = 40 \times 10^8\ \text{cm}^{-1}$ we obtain $K_\theta = 5.1 \times 10^{-2}\ \text{ml g}^{-3/2}\ \text{mol}^{1/2}$, which is a generally accepted value for PMMA.

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The characteristic number of segments N_c, or the number of statistical segments from which one blob is formed, is not constant but depends on the quality of the solvent and tends towards infinity when θ conditions are approached. Based on the result that $N_c = N_\tau$ and using equation (1), the following equation was established[7], which gives N_c as a function of the solvent quality expressed by exponent a of the MHS equation:

$$N_c = 0.37a^{-7.7} \tag{8}$$

This equation has been verified by the direct determination of N_c with different polymers dissolved in different solvents[7].

If we now present equations (4) and (5) under their general form, and having $a = 3\nu - 1$, we obtain the following equations:

$$\log \alpha_\eta^3 = \left[\log \frac{4(1-\nu)(2-\nu)}{(2\nu+1)(\nu+1)} + (3\nu - 1.5)\log(1/N_c)\right] + (3\nu - 1.5)\log N \tag{9}$$

$$\log \alpha_\eta^3 = [\log(K/K_\theta) + (3\nu - 1.5)\log(M/N)] + (3\nu - 1.5)\log N \tag{10}$$

Equating the quantities in brackets in equations (9) and (10) and setting $M/N = m_s$ we obtain:

$$\log K_\theta = \frac{\log K + 2B\log M_L - \log C - B\log(1/N_c) - 15.61B}{1-(2/3)B} \tag{11}$$

where $B = 3\nu - 1.5$ and $C = 4(1-\nu)(2-\nu)/(2\nu+1)(\nu+1)$. In equation (11) Φ was set equal to 2.6×10^{23} mol^{-1}.

Equation (11) is valid for any polymer–solvent system when the exponent in the MHS equation presents different values, and it is reduced to equation (7) when the values of a lie near 0.73.

For a number of polymer–solvent systems we have established the MHS laws using viscometric results taken from the literature. Using only the linear part in the presentation $\log[\eta]$ *versus* $\log M$ we obtain, in some cases, values of K and a which are different from the values given in the literature (refs 5 and 8, respectively). With the obtained values of K and a we have calculated values of N_c from equation (8) and values of ν ($3\nu - 1 = a$). From ν we have obtained values for B and C and introducing K, N_c, B and C in equation (11) we have obtained values of K_θ for polymer–solvent systems with $a \neq 0.73$ (*Table 1*). These values can be considered as the 'best' values found in the literature for these polymers. More precisely, the value of K_θ obtained via equation (11) for the PS in ethylcyclohexane is 7.8×10^{-2} ml g$^{-3/2}$ mol$^{1/2}$ while Mays *et al.*[9] obtain $K_\theta = 7.806 \times 10^{-2}$. For atactic polypropylene in benzene a value of $K_\theta = 15.6 \pm 1.5 \times 10^{-2}$ ml g$^{-3/2}$ mol$^{1/2}$ is proposed[10] and in toluene we obtain, using equation (7), $K_\theta = 14 \times 10^{-2}$. For low pressure polyethylene in decalin at 135°C, equation (7) gives $K_\theta = 27.5 \times 10^{-2}$ ml g$^{-3/2}$ mol$^{1/2}$, while the mean value for K_θ of this polymer, obtained from the values given in ref. 11, is 29×10^{-2}. For the system poly(p-trimethylsilylstyrene)–benzene we obtain $K_\theta = 6.7 \times 10^{-2}$ while the equation proposed by Dondos and Benoit[12] gives $K_\theta = 6.6 \times 10^{-2}$. In different poor and marginal solvents Beech and Booth[13] obtain $K_\theta = 17 \times 10^{-2}$ ml g$^{-3/2}$ mol$^{1/2}$ for poly(oxyethylene) and with the viscometric results of Allen *et al.*[14] equation (11) gives $K_\theta = 17.8 \times 10^{-2}$.

The molecular weight per unit length of the polymers, M_L, which is necessary to obtain the K_θ value, is known for most of the polymers and for a new polymer it can be obtained using Flory's method[15].

It should be noted that other relations between K, a

Table 1 Parameters K and a of the MHS equation, the mass per unit chain length M_L, the characteristic number of statistical segments N_C and the calculated value of the unperturbed dimensions parameter K_θ for some polymer–solvent systems

System[a,b]	$K \times 10^3$ (ml g^{-1})	a	$M_L \times 10^{-8}$ (cm^{-1})	N_C	$K_\theta \times 10^2$ (ml g$^{-3/2}$ mol$^{1/2}$)	Ref.
PS–benzene	9.0	0.73	42	4	8.2	5
PS–benzene[c]	7.8	0.75	42	3.5	8.1	22
PS–ethylcyclohexane (75°C)	60.8	0.525	42	53	7.8	9
PS–cyclohexane (50°C)	26	0.61	42	16.5	8.4	23, 24
PS–butanone (MEK)	19	0.645	42	11	8.2	25
PS–1.2-dichloroethane	14.3	0.69	42	6.5	8.0	26
PS–$CHCl_3$	7.1	0.78	42	2.8	8.5	5
PMMA–acetone	5.3	0.73	40	4	5.1	6
PMMA–benzene	5.2	0.76	40	3	5.2	27
PMMA–$CHCl_3$	3.5	0.83	40	1.5	5.2	5, 28
PE–decalin (135°C)	46	0.73	11	4	27.3	29
PP (atactic)–toluene	21.8	0.725	17	4	14	30
PIB–cyclohexane	22.5	0.7	22	5	13	24
POE–benzene	39.7	0.685	11.6	6.7	17.8	14
P(ptmSiS)–benzene	6.0	0.73	70	4	6.7	31
P(2,4 dmS)–toluene	9.3	0.7	53	5.8	7.2	32

[a] PS, polystyrene; PMMA, poly(methyl methacrylate); PE, polyethylene; PP, polypropylene; PIB, polyisobutylene; POE, poly(oxyethylene); P(ptmSiS), poly(p-trimethylsilylstyrene); P(2,4 dmS), poly(2,4 dimethylstyrene)

[b] Where the temperature is not indicated the viscosity measurements were performed at room temperature

[c] Very high molecular weight region (asymptotic value of a)

and K_θ have been proposed[16,17] but they are not based on the combination of the two-parameters theory with the blob theory.

The method proposed here can be considered as a more general method than the Stockmayer–Fixman–Burchard (SFB) method[18,19] because we can use the viscometric results obtained in a very large domain of molecular weights, where the MHS equation is valid, and especially in the region of very high molecular weights. In this region, it is well known that the SFB equation gives erroneous extrapolations and its correction is complicated[20,21]. Moreover the correct values of K_θ obtained with equations (7) and (11) demonstrate that the blob theory and the two-parameters theory do not conflict.

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