Polymer 42 (2001) 897–901

polymer

www.elsevier.nl/locate/polymer

A new relation between the intrinsic viscosity and the molecular mass of polymers derived from the blob model: determination of the statistical segment length of flexible polymers

A. Dondos[a,b,*]

[a]*Department of Chemical Engineering, University of Patras, 26500 Patras, Greece*
[b]*Institute of Chemical Engineering and High Temperature Processes, P.O. Box 1414, 26500 Patras, Greece*

Received 8 June 2000; accepted 29 June 2000

Abstract

Using the relation between the unperturbed dimensions parameter on one hand and the intrinsic viscosity and the statistical segment length of the polymers on the other, as predicted by the two-parameters theory, we have modified Han's equation [Polymer, 20 (1979) 1083], which is derived from the blob theory. According to the proposed equation, plotting $[\eta]/M^{1/2}$ versus $M^{3\nu-1.5}$, where ν is the exclude volume index, we obtain straight lines from the slopes of which we calculate the statistical segment length of flexible polymers. The value of ν is obtained from the value of the exponent of the Mark–Houwink–Sakurada equation. The proposed method is useful in the high molecular mass region in which the Stockmayer–Fixman–Burchard equation is not valid. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer solutions; Viscosity–molecular mass relation; Statistical segment length

1. Introduction

The statistical segment length of flexible polymers is obtained from the unperturbed dimensions parameter, K_θ, of these polymers. The value of K_θ is obtained from the intrinsic viscosity, $[\eta]_\theta$, determined in a theta solvent ($K_\theta = [\eta]_\theta/M^{1/2}$). If a theta solvent is not available the K_θ value is obtained from the values of intrinsic viscosity from measurements performed in a good solvent. In the following paragraphs, we use a graphical method relating the intrinsic viscosity to the molecular mass of this polymer. Among these graphical methods the most widely used is the Stockmayer–Fixman–Burchard (SFB) one [1,2]. Besides Burchard [2], other authors [3–6] have shown that the SFB method is not applicable in the low molecular mass region as well as in the high molecular mass region or in the region of high values of viscometric expansion factor. To deal with the low-molecular mass problem of the SFB equation, we have proposed with Benoît [7] a relation between the intrinsic viscosity and the molecular mass of polymers from which we can obtain the K_θ value from the values of intrinsic viscosity obtained in the region of low molecular masses.

Combining relations derived from the two-parameters theory and the blob theory we have obtained, with Casassa [8], an equation which permits obtaining the K_θ value of polymers even in the region of high molecular masses. This equation contains the parameters K and a of the Mark–Houwink–Sakurada (MHS) equation, which is valid in the high molecular mass region.

In this article we will propose an equation which is derived from the blob model and more precisely from the equation of Han [9]. The equation of Han is transformed in this work using also a relation derived from the two-parameters theory. The resulting new relation, in contrast to the relation obtained with Casassa [8], contains only the parameter a, of the MHS equation, but we need now, in order to obtain the unperturbed dimensions of polymers, to proceed with a graphical representation of intrinsic viscosity as a function of the molecular mass. With the representation proposed here ($[\eta]/M^{1/2}$ versus $M^{3\nu-1.5}$ where ν is the exclude volume index) we obtain good straight lines, even in the high molecular mass region of the polymers, from the slopes of which we obtain directly the statistical segment length of the polymers.

An additional objective of this work is to show that Han's equation is valid when the polymers are dissolved in solvents of different quality and for the entire domain of molecular mass, and not only in the non-free draining limit.

---

[*] Corresponding address: Department of Chemical Engineering, University of Patras, 26500 Patras, Greece. Tel.: +30-61-997-652; fax: +30-61-997-266.

PII: S0032-3861(00)00481-X

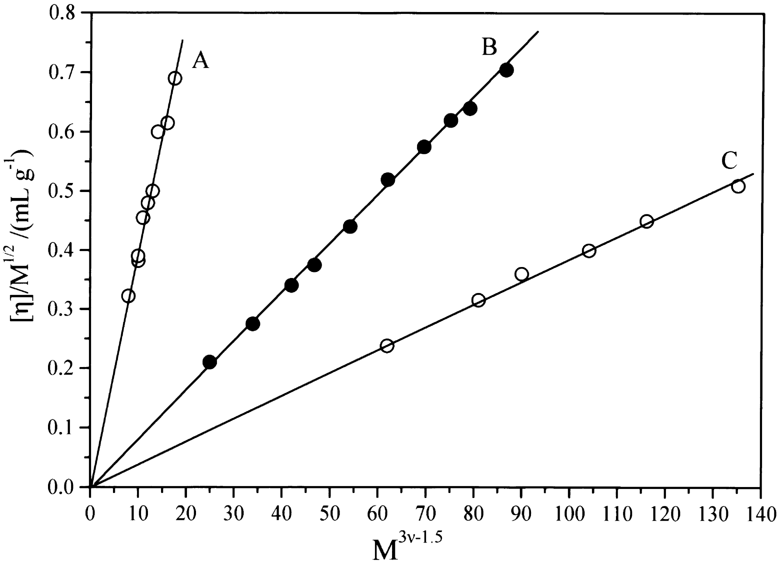

Fig. 1. Variation of $[\eta]/M^{1/2}$ versus $M^{3\nu-1.5}$ (Eq. (4)) for the systems: (A) POE–benzene; (B) PS–benzene; (C) PMMA–$CHCl_3$.

2. Theory and procedure

The following equation proposed by Han [9] is derived from the blob theory [10] and the hydrodynamic considerations of Weill and des Cloizeaux [11]

$$\alpha_\eta^3 = C\left(\frac{N}{N_c}\right)^{3\nu-1.5} \tag{1}$$

This equation relates the viscometric expansion factor of a macromolecular chain, α_η, to the number of blobs of which the chain consists, N/N_c. N is the number of Kuhn statistical segments of the chain and N_c the number of Kuhn statistical segment of which one blob consists. The parameter C is equal to $[4(1-\nu)(2-\nu)]/[(2\nu+1)(\nu+1)]$ where, as we have already mentioned, ν is the excluded volume index. The value of ν is obtained from the exponent a of the MHS equation because we have $3\nu - 1 = a$.

Having $\alpha_\eta^3 = [\eta]/[\eta]_\theta = [\eta]/K_\theta M^{1/2}$ and $N = M/m_s$ (N, as we have already mentioned, is the Kuhn statistical segment number of a fraction of molecular mass M and m_s is the mass of one Kuhn statistical segment), Eq. (1) becomes

$$\frac{[\eta]}{M^{1/2}} = K_\theta C\left(\frac{M}{m_s N_c}\right)^{3\nu-1.5} \tag{2}$$

Between the Kuhn statistical segment length, A, and the unperturbed dimensions parameter, K_θ, from the two-parameters theory, we have the following relation

$$A = \left(\frac{K_\theta}{\Phi}\right)^{2/3} M_L \tag{3}$$

In this relation Φ is the Flory parameter and M_L the molecular mass per unit length of the polymer. From the above relation we have $K_\theta = A^{3/2}\Phi/M_L^{3/2}$ and having $m_s = A\,M_L$, Eq. (2) becomes:

$$\frac{[\eta]}{M^{1/2}} = \frac{A^{3(1-\nu)}\Phi C}{M_L^{3\nu} N_c^{3\nu-1.5}} M^{3\nu-1.5} \tag{4}$$

According to this equation plotting $[\eta]/M^{1/2}$ as a function of $M^{3\nu-1.5}$ we must obtain a straight line which goes through the origin and of which the slope is equal to $A^{3(1-\nu)}\Phi C/M_L^{3\nu}N_c^{3\nu-1.5}$. We must indicate here that Eq. (4) is similar to the equation obtained for the wormlike polymers [12]. The only difference between the two equations is that in the case of wormlike polymers we do not have the term $N_c^{3\nu-1.5}$ because for these polymers we have $N_c = 1$ [13,14].

For the application of Eq. (4) we need the value of ν, or the value of the exponent a of the MHS equation ($3\nu - 1 = a$). The value of the Kuhn statistical segment length, A, is obtained from the slope of the obtained straight line, plotting $[\eta]/M^{1/2}$ as a function of $M^{3\nu-1.5}$, and knowing: (a) the value of M_L of the polymer; (b) the value of $C = [4(1-\nu)(2-\nu)]/[(2\nu+1)(\nu+1)]$; (c) the value of Φ ($\Phi = 2.6 \times 10^{23}$ cgs); and (d) the value of N_c. As we have already mentioned N_c is the number of Kuhn statistical segments of which one blob consists and corresponds to the molecular mass at which the excluded volume behavior appears. According to the thermal blob theory [15], N_c depends on the quality of the solvent and tends to infinity when we approach to the theta solvent. We have proposed an equation relating the value of N_c, for the flexible polymers, with the value of the exponent of the MHS equation [16]. This relation was obtained calculating the N_c value from Eq. (1) and also from a direct determination of the molecular mass at which we observe the appearance of the excluded volume behavior (molecular mass at

Table 1
Exponent of the MHS equation a, excluded volume index ν, parameter of Han's equation C, slopes of the straight lines obtained according to Eq. (4), mass per unit length M_L, number of statistical segments of which one blob consists N_c, Kuhn statistical segment calculated from Eq. (4) A, unperturbed dimensions parameter K_θ and statistical segment length calculated from K_θ, A′, for nine polymer–solvent systems

Systems	a	ν	C	$M_L \times 10^{-8}$ (Da/cm)	Slope × 10^3	N_c	A (Å)	$K_\theta \times 10^2$ (ml/g)	A'(Å)	Refs.
PS–benzene[a]	0.75	0.583	0.69	42	8.18	3.0	19.5	8.2	19.5	[18]
PS–benzene[b]	0.725	0.575	0.71	42	10.5	3.9	20.8	8.2	19.5	Our result, [23]
PS–toluene	0.748	0.583	0.69	42	8.53	3.05	19.8	8.2	19.5	[21,22]
PS–cycloh.(50°)	0.584	0.528	0.89	42	36.0	22.0	21.0	8.2	19.5	[21]
PS–cycloh.(55°)	0.625	0.542	0.83	42	22.0	12.8	20.0	8.2	19.5	Our results
PMMA–$CHCl_3$	0.81	0.603	0.63	40	3.85	1.6	13.3	5	13.3	[19]
POE–benzene	0.686	0.562	0.76	15.5	39.5	6.1	12.7	16.8	12.0	[17]
PE–decalin	0.7	0.567	0.74	11.2	59.0	5.2	12.1	29.5	12.0	[24]
PpmS–toluene	0.74	0.58	0.7	47.6	8.66	3.3	23.0	7.0	19.8	[6]

[a] High molecular mass region.

[b] Low and middle molecular mass region.

which the exponent of the MHS equation becomes higher than 0.5). Having now investigated a great number of polymer–solvent systems, we propose the following relation between N_c and a

$$N_c = 0.3a^{-8} \tag{5}$$

which is slightly different from the relation proposed in our previous work [16]. In the following we use Eq. (5) in order to obtain N_c which is necessary for the determination of statistical segment length, A, as we have already mentioned. For some polymer–solvent systems the obtained value of N_c from Eq. (5), especially when we are not in the high molecular mass region, differs slightly from the value of N_c obtained directly from Eq. (2). Nevertheless, this difference has an insignificant influence on the value of statistical segment length, A, obtained from Eq. (4).

3. Results and discussion

In Fig. 1 we present the variation of $[\eta]/M^{1/2}$ as a function of $M^{3\nu-1.5}$ for three polymer–solvent systems. The viscometric results are taken from the literature (POE–benzene [17], PS–benzene [18] and PMMA-$CHCl_3$ [19]). A good linearity is observed for the three systems, with this representation, indicating the validity of Eq. (4). From the slopes of the straight lines obtained according to the MHS representation for the same systems we have taken the value of a or the value of ν and knowing: C (from the value of ν), M_L (calculated divided the molecular weight of the repeating unit of the polymer by the repeating unit projection length [20] and N_c (calculated from Eq. (5)), and taking $\Phi = 2.6 \times 10^{23}$, we calculate from the slopes of straight lines of Fig. 1, according to Eq. (4), the value of the statistical segment length, A, for these three polymers (Table 1). In order to draw the curves of Fig. 1 the $[\eta]$ values are expressed in

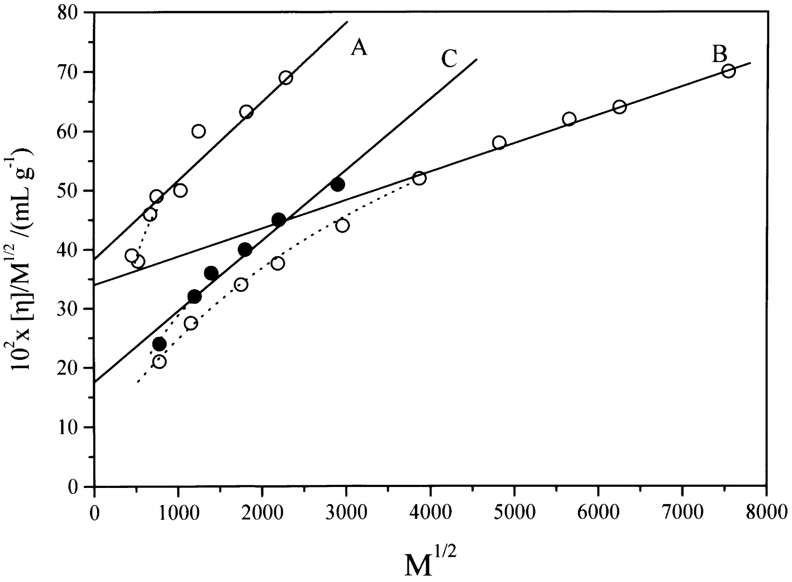

Fig. 2. SFB representation (Eq. (6)) for the systems: (A) POE–benzene; (B) PS–benzene; (C) PMMA–$CHCl_3$.

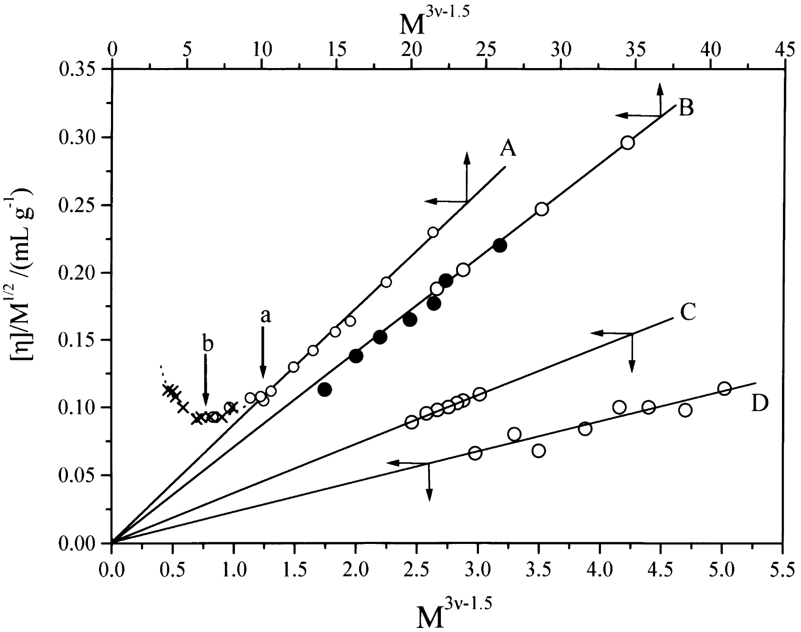

Fig. 3. Variation of $[\eta]/M^{1/2}$ versus $M^{3\nu-1.5}$ (Eq. (4)) for the systems: (A) PS–benzene (○: our results, ×: Ref. [23]); (B) PS–toluene (○: Ref. [22], ●: Ref. [21]); (C) PS–cyclohexane (50°C); (D) PS–cyclohexane (55°C).

ml/g, the M_L is introduced in Da/cm and as we have mentioned the value of Φ is introduced in cgs units. Finally the value of A is obtained in cm and it is given, in the following, in Å in Table 1.

With the same viscometric results with which we have taken the straight lines of Fig. 1 we present now, in Fig. 2, the variation of $[\eta]/M^{1/2}$ as a function of $M^{1/2}$ according to the follow equation (SFB equation [1,2])

$$[\eta]/M^{1/2} = K_\theta + 0.51\, B\Phi M^{1/2} \tag{6}$$

The extrapolation of the linear part of the curves, obtained with viscometric results of Fig. 1, to $M = 0$ must give the unperturbed dimensions parameter, K_θ, of these three polymers. The obtained K_θ values are completely erroneous (K_θ for PS equal to 34×10^{-2} ml/g, K_θ for PMMA equal to 17.5×10^{-2} ml/g, and K_θ for POE equal to 38×10^{-2} ml/g). The best values for K_θ parameter of these polymers are: $K_\theta = 8.2 \times 10^{-2}$ ml/g for PS, 5×10^{-2} ml/g for PMMA and 16.8×10^{-2} ml/g for POE. This result clearly indicates that in the relatively high molecular mass and high molecular mass region we cannot use the SFB representation in order to obtain the unperturbed dimensions of polymers. On the contrary, the proposed here new representation gives correct values for the statistical segment length. These values of A are about the same with the values obtained from the best values of K_θ of these three polymers (Table 1).

The application of Eq. (4) for the systems PS–toluene (curve B), PS–cyclohexane (50°C) (curve C) and PS–cyclohexane (55°C) (curve D) is given in Fig. 3. The viscometric results for the PS–toluene system are taken from two different articles [21,22] in which the exponent of the MHS equation is the same. As we can see in Fig. 3 (curve B), the points coming from the two different works lie on the same straight line from the slope of which we obtain a good value for the statistical segment length of PS (Table 1). The application of Eq. (4) for the PS in cyclohexane at 50°C [21] and 55°C also gives a good value for the Kuhn statistical segment length (Table 1).

In Fig. 3 we also present the application of Eq. (4) for the system PS–benzene (curve A). The viscometric results are obtained by us and by Einaga et al. [23] in the region from the very low to the middle molecular mass. The linearity between $[\eta]/M^{1/2}$ and $M^{3\nu-1.5}$ starts from a molecular mass equal to 24,000 (arrow a in Fig. 3) and in this molecular mass we also have the appearance of power law for the PS–benzene system. This molecular mass is predicted from a previously proposed relation [16]. In the region in which we do not have a power law between $[\eta]$ and M, Eq. (4) is not yet valid (Fig. 3, curve A). We must indicate that in the low and in the middle molecular mass region the PS in benzene presents a lower exponent in the MHS equation ($a = 0.725$) comparing to the exponent obtained in the very high molecular mass region ($a = 0.75$) but the obtained statistical segment length for this polymer in the two molecular mass regions are comparable (Table 1). This result clearly indicates that even we are far from the non-free draining limit (low and middle molecular mass region), Eq. (4) and consequently Eq. (1) present a self-consistency. In curve A of Fig. 3 we also indicate, by the arrow b, the molecular mass of PS at which we have the onset of excluded volume behavior. This

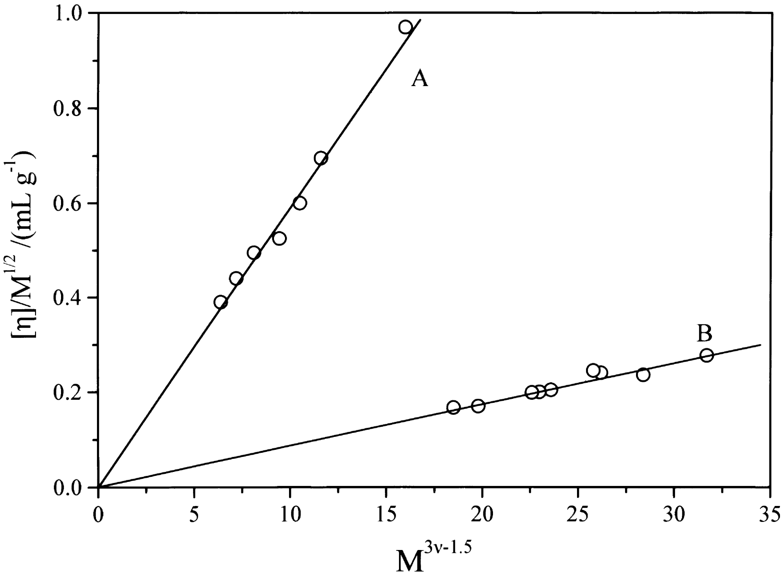

Fig. 4. Variation of $[\eta]/M^{1/2}$ versus $M^{3\nu-1.5}$ (Eq. (4)) for the systems: (A) PE–decalin; (B) PpmS–toluene.

molecular mass corresponds to a number of statistical segments, N_c, given by Eq. (5) ($N_c = 3.9$).

In Fig. 4 we present the application of Eq. (4) for the systems polyethylene–decaline [24] (curve A) and poly(*p*–methyl styrene)–toluene [6] (curve B). The obtained statistical segment lengths for these two polymers lie very close to the values obtained from the K_θ values proposed in the literature, as we can see in Table 1.

4. Conclusions

The method proposed here in order to obtain the Kuhn statistical segment length of flexible polymers must be added to the other existing methods giving the unperturbed dimensions of polymers from viscometric results obtained in good solvents. Comparing this method with the other methods we realize that this one presents the following advantages: (a) we can obtain the unperturbed dimensions of polymers even from the viscometric results measured in the very high molecular mass region, which present a problem for the SFB method; (b) for the graphical representation we need, except from the viscometric results, only the value of the exponent of the MHS equation, which is in general obtained with good precision; and (c) Eq. (4) describes a straight line passing through the origin, thus allowing the determination of parameters values, more precisely the slope of the straight line, with a smaller number of experimental points.

The applicability of Eq. (4), which is derived from Eq. (1), in the entire domain of molecular mass, except below the appearance of the power law, and when the polymers are dissolved in solvents of different quality, clearly indicates that Han's equation (Eq. (1)) is not only valid in the non-free draining limit, $a = 0.8$. Finally, in order to obtain Eq. (4) from Eq. (1), which is derived from the blob theory, we have used Eq. (3), which is taken from the two-parameters theory. The good results obtained using Eq. (4) indicate that these two theories, as we have already shown [8], do not conflict.

References

[1] Stockmayer WH, Fixman M. J Polym Sci 1963;C1:137.
[2] Burchard W. Makromol Chem 1961;50:20.
[3] Cowie JMG. Polymer 1966;7:487.
[4] Dondos A, Benoît H. Polymer 1978;19:523.
[5] Staikos G, Dondos A. Polymer 1980;21:355.
[6] Tanaka G, Imai S, Yamakawa H. J Chem Phys 1970;52:2639.
[7] Dondos A, Benoît H. Polymer 1977;18:1161.
[8] Dondos A, Casassa EF. Polymer 1993;34:3747.
[9] Han CC. Polymer 1979;20:1083.
[10] Farnoux B, Boué F, Cotton JP, Daoud M, Jannink G, Nierlich M, de Gennes PG. J Phys (Fr) 1978;39:77.
[11] Weill G, des Cloizeaux J. J Phys (Fr) 1979;40:99.
[12] Dondos A. Polymer 2000;41:4607.
[13] Yamakawa HH, Stockmayer WH. J Chem Phys 1972;57:2843.
[14] Dondos A. J Chem Phys 1997;107:10 311.
[15] De Gennes PG. Scaling concepts in polymer physics. Ithaca, NY: Cornell University Press, 1979.
[16] Dondos A. Polymer 1992;33:4375.
[17] Allen G, Booth C, Hurst SI, Jones MN, Price C. Polymer 1967;8:391.
[18] Einaga Y, Miyaki Y, Fujita H. J Polym Sci, Polym Phys Ed 1979;17:2103.
[19] Schulz GV, Cantow HJ, Meyerhoff G. J Polym Sci 1953;10:79.
[20] Flory PJ. Statistical mechanics of chain molecules. New York: Interscience, 1969.
[21] Papazian LA. Polymer 1969;10:399.
[22] Yamamoto A, Fujii M, Tanaka G, Yamakawa H. Polym J 1971;2:799.
[23] Einaga Y, Koyama Konishi HT, Yamakawa H. Macromolecules 1989;23:3419.
[24] Chiang R. J Phys Chem 1965;69:1645.