

Crossover effects and molecular mass regions in solutions of worm-like polymers: a new relation for the determination of their statistical segment length, based on the blob model

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Abstract

The study of the viscometric results obtained with a great number of worm-like polymer–solvent systems showed that plotting the variation of the logarithm of the intrinsic viscosity versus the logarithm of the molecular mass of these polymers we observe two crossover points. The first crossover point corresponds to a molecular mass equal to the molecular mass of one Kuhn statistical segment. The second crossover point appears when we reach the complete excluded volume behavior and depends on the quality of the solvent. These two crossover points delimit three molecular mass regions. We indicate the methods to obtain the statistical segment length of worm-like polymers in each of those molecular mass regions. A new method is proposed in order to obtain the statistical segment length of the worm-like polymers based on the Han's equation (Han CC. Polymer 1979; 20:1083) derived from the blob theory. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Worm-like polymers; Statistical segment length; Viscometry

1. Introduction

In the last years, great interest has been manifested in the study of synthetic rigid polymers, due mainly to their mechanical properties. The study of rod-like or worm-like polymers in solution has as main purpose, the determination of their statistical segment length, the value of which determines their rigidity. The determination of the value of the statistical segment length of a worm-like polymer is often based on the relation between the intrinsic viscosity and the molecular mass of a series of fractions of this polymer. A certain number of procedures based on the relation between intrinsic viscosity and molecular mass has been proposed for worm-like polymers. The aim of this work is to explore the domains of molecular mass or of the number of the statistical segments in which we can use these methods. In the case of worm-like polymers, three domains of molecular mass are well delimited because for these polymers we observe two well-determined crossover points in the variation of their solution dimensions as a function of their molecular mass. More precisely, in the Mark–

Houwink–Sakurada (MHS) representation we observe two well-defined crossover points in which we have a variation of the exponent of this equation. Thus we distinguish three regions of molecular mass: region I, below the first crossover point; region II, between the first and the second crossover point and region III, above the second crossover point.

In this article we also propose a new equation relating the intrinsic viscosity to the molecular mass of worm-like polymers, from which we can obtain the Kuhn statistical segment length of these polymers in the region of molecular mass in which we have the appearance of the power law (region III). This equation has been obtained from a combination of relations derived from the blob theory and the two-parameter theory. This combination has been already used in order to obtain a relation that permits the determination of the unperturbed dimensions parameter and in the following statistical segment length of rigid polymers [1]. The relation proposed now is easier to be applied and gives the statistical segment length directly.

In all the relations proposed by us, as well as in the relation which will be proposed here, we use a value for the parameter Φ of Flory, which depends on the quality of the solvent in which the worm-like polymers are dissolved; this value of Φ expresses the draining effect.

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Nomenclature

a	Mark–Houwink–Sakurada exponent
A	Kuhn statistical segment length (given in Å)
B	Exponent of Han's equation ($B = 3\nu - 1.5$)
C	Parameter of Han's equation ($C = 4(1 - \nu)(2 - \nu)/[(2\nu + 1)(\nu + 1)]$)
K	Mark–Houwink–Sakurada constant
K_θ	Unperturbed dimensions parameter (given in ml g ⁻¹)
M'_c	Molecular mass at the onset of power law
M_L	Molecular weight of the chain per unit length
m_s	Molecular mass of Kuhn statistical segment
N	Number of Kuhn statistical segments
N_c	Number of Kuhn statistical segments at the onset of excluded volume behavior
N'_c	Number of Kuhn statistical segments at the onset of power law
<i>Greeks</i>	
α_η	Viscometric expansion factor
Φ	Flory's parameter (given in c.g.s.)
$[\eta]$	Intrinsic viscosity (given in ml g ⁻¹)
ν	Excluded volume index

2. Results and discussion

2.1. Region I (molecular mass below the first crossover point)

In this region a chain of worm-like polymer consists of a relatively low number of monomer units. The number of these units is lower than the number necessary in order to have one Kuhn statistical segment and consequently the chain presents the conformation of a long straight cylinder. In this region, relations between the intrinsic viscosity, $[\eta]$, and the molecular mass are proposed by Kirkwood and Auer

[2], Yamakawa [3] and Doi and Edwards [4]. The statistical segment length in this region can be obtained using the Yamakawa–Fujii method [5]. Other methods, relating the viscosity to the molecular mass, which will be examined in the following, cannot be applied in this region.

As concerns the exponent of the MHS representation, for a rod-like cylinder, the expected value, according to the rigid rod model proposed by Kirkwood and Auer [2] and treated subsequently by Doi and Edwards [4], should lie between 1.6 and 1.7. In Fig. 1 we give the relation between $\log [\eta]$ and $\log M$ for three worm-like polymer–solvent systems and we observe that the slopes of the straight

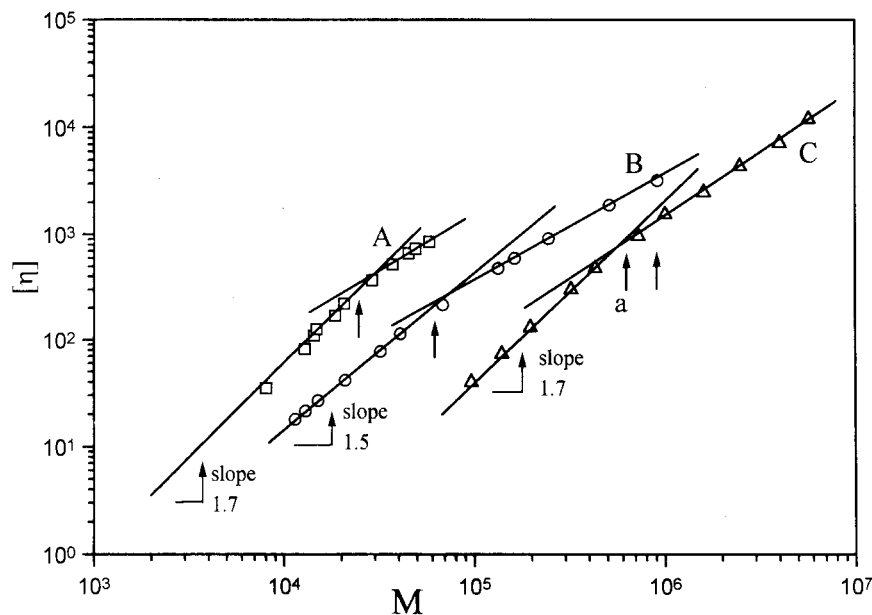


Fig. 1. Log–log plot of $[\eta]$ (in ml g⁻¹) versus M for the systems: (A) PPPhTPhA–H₂SO₄ [8]; (B) PHIC–toluene (25°C) [9]; and (C) Schizophyllane–H₂O [10]. The arrows correspond to the molecular mass of one Kuhn statistical segment. For arrow a see text.

lines, below the crossover point, are in accordance with the rigid rod model. The polymers in Fig. 1 are: (a) poly(*p*-phenylene terephthalamide) (PPPhTPhA) [8]; (b) poly(helyx isocyanate) (PHIC) [9]; (c) native sample of polysaccharide *Schizophyllum commune* (schizophyllan) [10].

2.2. First crossover point

In a recent article [1] we have shown that the chain of a worm-like polymer at the onset of excluded volume behavior consists of one Kuhn statistical segment. This result is obtained using the following equation, proposed by Han [6], which is derived from the blob theory

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

In this equation α_{η} is the viscometric expansion factor, ν the excluded volume index ($3\nu - 1 = \underline{a}$ where \underline{a} is the exponent of the MHS equation), C is equal to $[4(1 - \nu)(2 - \nu)] / [(2\nu + 1)(\nu + 1)]$, N the number of Kuhn statistical segments of the chain and N_c the characteristic number of Kuhn statistical segments contained in a blob or the number of Kuhn statistical segments at the onset of excluded volume behavior. As we have already mentioned, we have obtained that $N_c = 1$ for a great number of worm-like polymers using the viscometric results obtained in the molecular mass domain where we have a complete excluded volume behavior (region III as described in the following). The value of α_{η}^3 is the ratio $[\eta]/K_{\theta}M^{1/2}$ where K_{θ} is the unperturbed dimensions parameter obtained also in the molecular mass region where the complete excluded volume behavior is manifested. This result ($N_c = 1$ at the appearance of excluded volume behavior) is in accordance with the predictions of the Yamakawa and Stockmayer theory [7].

In Fig. 1 we give the MHS representation, as we have already mentioned, for three worm-like polymers and the arrows indicate the molecular mass corresponding to one Kuhn statistical segment of these worm-like polymers. We can observe that the well-defined crossover points lie very close to the molecular masses indicated by the arrows. More precisely, for the system PHIC–Tol. (25°C) we have for the Kuhn statistical segment length, A , a value equal to 740 Å and a molecular mass per unit length, M_L , equal to 74 Da Å⁻¹ consequently we obtain for the statistical segment a molecular mass, m_s , equal to 54 760 which is indicated by the arrow in Fig. 1 (curve B). In other words, the observed first crossover point in the MHS representation corresponds to the transition from a rod-like conformation to a worm-like conformation.

In the case of flexible polymers, on the contrary, the number of Kuhn statistical segments contained in a blob depends on the quality of the solvent and tends to infinity when we approach the theta solvent ($\underline{a} = 0.5$) [11]. The value $N_c = 1$, is observed for the flexible polymers only when these polymers are dissolved in a very good solvent ($\underline{a} \rightarrow 0.8$) [11]. This difference between the two classes of polymers could be understood if we consider that all solvents behave as good solvents for the worm-like polymers, when the chains of these polymers consist of a low number of monomer units or when the molecular mass of these polymers is lower than the molecular mass of one Kuhn statistical segment (below the first crossover point).

Another difference between the worm-like polymers and the flexible polymers is seen in the manner with which we approach the power law in the MHS representation. In the case of worm-like polymers the approach takes place from below, i.e. the $[\eta]$ values in the low molecular mass region are lower than those predicted by the power law or by the

Table 1

Exponent of the MHS equation, \underline{a} , Kuhn statistical segment length, A , mass per unit length M_L , mass at the onset of complete excluded volume behavior M'_c and characteristic number of Kuhn statistical segments at the onset of complete excluded volume behavior (second crossover point) N'_c , for 13 worm-like polymer–solvent systems

Number	System ^a	\underline{a}	A (Å)	M_L (Da/Å)	M'_c	N'_c	References
1	PSi–THF	0.56	75	63	28 000	6	[23]
2	PNIB–H ₂ SO ₄	0.64	156	25	42 000	11	[24]
3	CTDC–NMP	0.66	156	108	195 000	11.5	[22,25]
4	PPDP–EPCH	0.66	38	28.5	16 000	14.5	[21]
5	PPDP– <i>m</i> -cres.	0.675	60	28.5	27 000	16	[21]
6	PMDI–THF	0.68	65	108	100 000	14	[26]
7	PPSQ–benz.	0.7	123	103	215 000	17	[27,28]
8	CTA–DMAc	0.7	140	58	162 000	20	[29]
9	PTDP–TFE	0.73	93	28.5	73 000	27.5	[30]
10	PTDP– <i>m</i> -cres.	0.74	105	28.5	82 000	27	[30]
11	PHIC–hex.	0.77	708	71	2 100 000	42	[31]
12	Polycarbonate–met.Ch	0.78	53	21.7	63 000	55	[32]
13	Nitrocellulose–Ace	0.79	334	57	1 300 000	68	[33,34]

^a The polymers are: (1) poly(methylphenyl silane), (2) poly(naphthoylene imidobenzimidazole), (3) cellulose tris[(3,5-dimethylphenyl)carbamate], (4), (5) poly(phthaloyl-*trans*-2,5-dimethylpiperazine), (6) poly(monodecyl itaconate), (7) poly(phenylsilsesquioxane), (8) cellulose triacetate, (9), (10) poly(terephthaloyl-*trans*-2,5-dimethylpiperazine) and (11) poly(hexyl isocyanate).

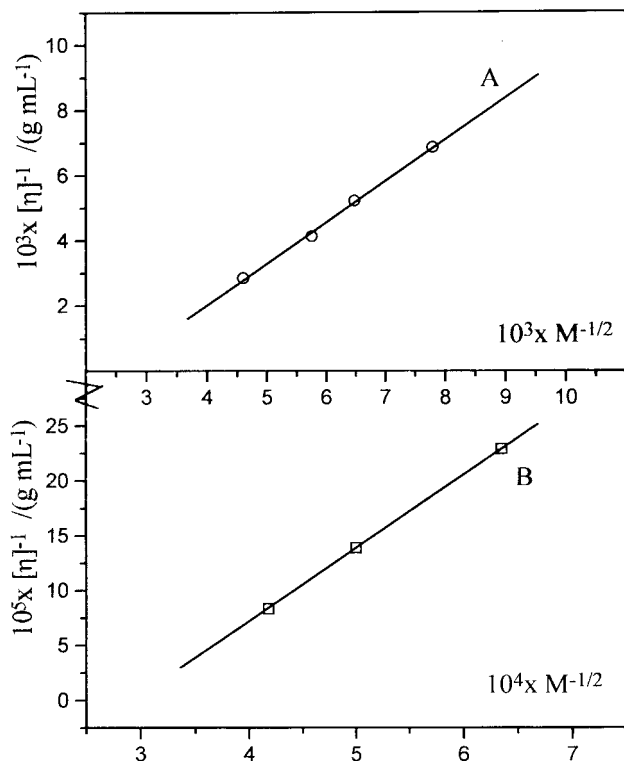


Fig. 2. Variation of $1/[\eta]$ versus $1/M^{1/2}$ (DB) representation, Eq. (2), for the systems: (A) poly(phenylhydroquinone-*co*-terephthalic acid)–mixed solvent [20]; and (B) Schizophyllane–H₂O [10].

MHS representation above the first crossover point (Fig. 1), while in the case of flexible polymers the approach takes place from above [12,13] i.e. the $[\eta]$ values in the low molecular mass region are higher than those predicted by the power law.

2.3. Region II (molecular mass between the first and the second crossover points)

In this region of molecular masses the slope in the representation of $\log[\eta]$ versus $\log M$ becomes lower than 1.6 or 1.7 and in certain cases decreases progressively as we approach the second crossover point or as we approach the beginning of the power law. Nevertheless, in the case of worm-like polymers, contrary of what we observe in the case of flexible polymers, we can obtain a straight line in a relatively large domain of molecular masses in the MHS representation. The values of the exponent of the viscometric laws obtained in the region between the two crossover points lie between 1.2 and 0.8.

The statistical segment length in this region can be determined using the Yamakawa–Fujii method [5] or the representation of viscometric results according to the equation of Bushin et al. [14] and Bohdanecky [15]. A great number of articles have appeared concerning the determination of the statistical segment length of the worm-like polymers using the above two methods.

We have shown [13,16] that in this same region of molecular masses we can use the Dondos–Benoît (DB) equation [17], which originally has been proposed for the determination of the unperturbed dimensions parameter, K_θ , of flexible polymers. The value of K_θ is obtained from the slope of the straight line obtained plotting $[\eta]^{-1}$ as a function of $M^{-1/2}$ according to the following DB equation

$$[\eta]^{-1} = -A_2 + K_\theta^{-1} M^{-1/2} \quad (2)$$

From the value of K_θ we obtain the Kuhn statistical segment

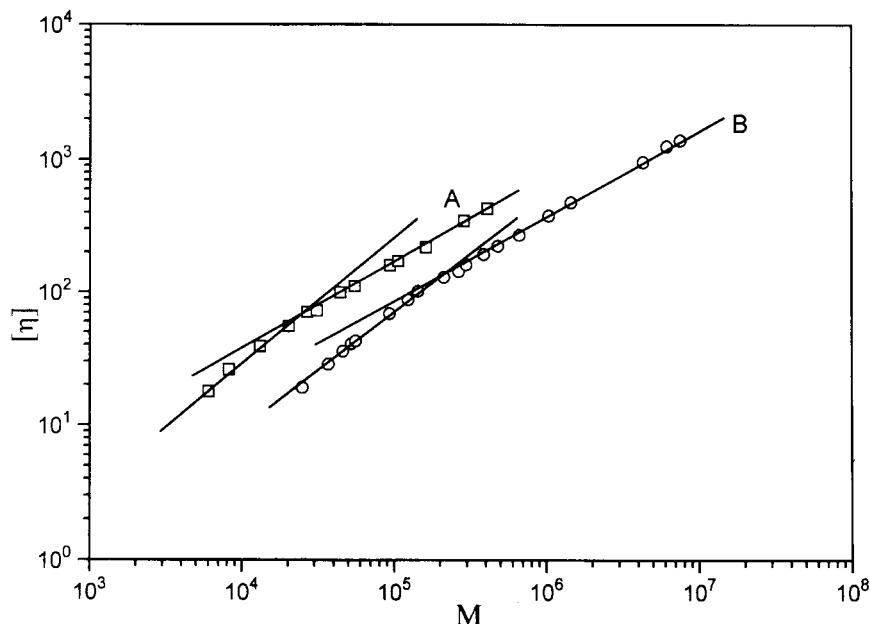


Fig. 3. Log–log plot of $[\eta]$ (in mL g^{-1}) versus M for the systems: (A) PPDP–*m*-cresol [21]; and (B) CTDC–NMP [22].

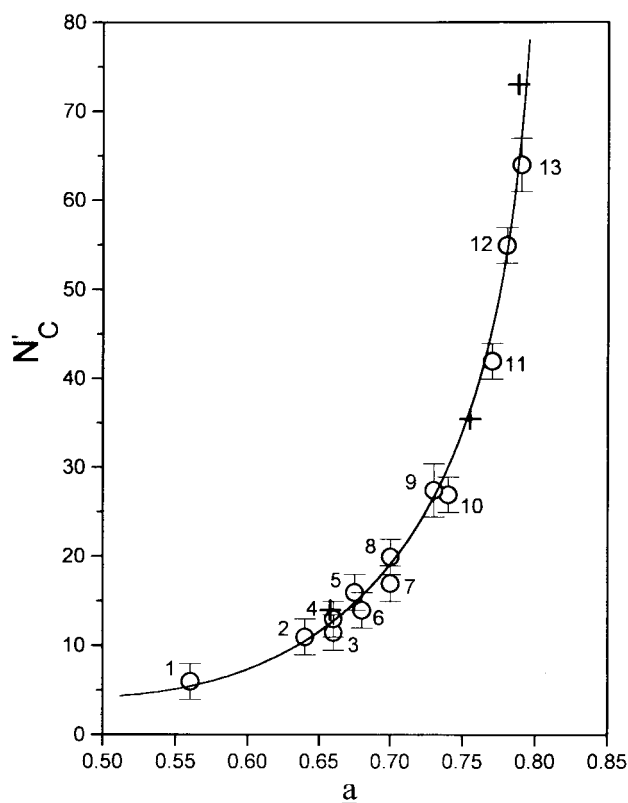


Fig. 4. Relation between the characteristic number N'_c and the exponent \underline{a} of the MHS equation for 13 worm-like polymer-solvent systems. The numbers correspond to the systems given in Table 1.

length, A , from the relation,

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

in which Φ is the Flory's parameter and M_L the mass per unit length.

In the case of worm-like polymers the value of Φ varies with the quality of the solvent, as it is expressed by the exponent of the MHS equation \underline{a} , according to the following relation [13]

$$\Phi = 0.52 \times 10^{23} \underline{a}^{-2.32} \quad (4)$$

The above equation obtained empirically, expresses the influence of the draining effect on the value of the Φ parameter and it is theoretically justified [18,19].

In Fig. 2 we present the application of Eq. (2) to two worm-like polymer-solvent systems which we have not studied in our previous works with this method. The systems are: poly(phenylhydroquinone-*co*-terephthalic acid)-mixed solvent (*o*-dichlorobenzene, *p*-chlorophenol) (curve A) [20] and schizophyllane-H₂O (curve B) [10]. From the slope of curve a we obtain a K_θ value equal to 0.77 ml g⁻¹ and with a value of Φ equal to 0.71×10^{23} (from Eq. (4) with $\underline{a} = 0.87$) and $M_L = 24.53 \text{ Da } \text{\AA}^{-1}$, we obtain from Eq. (3) $A = 120 \text{ \AA}$. The values proposed in the article from which we have

taken the viscometric results [20] are: $A = 120 \text{ \AA}$ (Yamakawa-Fujii method) and $A = 122 \text{ \AA}$ (Bohdanecky method). For the schizophyllane, with the viscometric results obtained for the fractions of higher molecular mass values we obtain $A = 2.900 \text{ \AA}$ (Fig. 2, curve B) while the authors of the work from which the viscometric results are taken [10] give for the Kuhn statistical segment a value of 4.000 \AA using the Yamakawa-Fujii method. The value obtained for the molecular mass of one Kuhn statistical segment m_s , for the schizophyllane, with $A = 4.000 \text{ \AA}$ is equal to 900.000, indicated in Fig. 1 by the arrow (curve C) and this value is higher than the crossover point. With the value of $A = 2.900 \text{ \AA}$ obtained, as we have mentioned above, for the same polymer using the DB equation, we obtain $m_s = 623.000$, and this value is closer to the crossover point observed for this polymer (Fig. 1, curve C, arrow a).

2.4. Second crossover point

In this crossover point we have a transition from a non-complete excluded volume behavior to a complete excluded volume behavior. In the molecular mass region above this point we have a good linearity between $\log[\eta]$ and $\log M$, as in the case of flexible polymers (power law). In Fig. 3 we present the variation of $\log[\eta]$ versus $\log M$ for two worm-like polymer-solvent systems (PPDP-*m*-cresol [21], CTDC-NMP [22]), and we see that the crossover point can be determined with relatively good precision.

We have shown [11] that in the case of flexible polymers, the number of Kuhn statistical segments, N'_c , at this crossover point, for a given polymer, depends on the quality of the solvent and that N'_c of different polymers is the same if the polymers are dissolved in solvents of the same quality. The quality of the solvents is expressed by the exponent \underline{a} of the MHS equation as it is determined in the molecular mass region that lies above this crossover point (region of power law).

Treating the viscometric results of a great number of worm-like polymer-solvent systems, which we found in the literature, we have observed the same behavior for these polymers as for flexible polymers. More precisely, the relation between the characteristic number, N'_c , and \underline{a} is the same for the two classes of polymers. In Fig. 4 we present the variation of N'_c as a function of \underline{a} for 13 worm-like polymer-solvent systems. The determination of the Kuhn statistical number at the crossover point is less precise than the determination of the exponent of the MHS equation and this is indicated by the error bars in Fig. 4. The crosses in the same figure indicate points obtained with three flexible polymer-solvent systems [11]. The curve of Fig. 4 is expressed by the following equation

$$N'_c = 455 \pm (50) \underline{a}^{8.8(\pm 0.5)} \quad (5)$$

and a similar equation was found in the case of flexible polymers [11]. Let us indicate that the number of Kuhn statistical segments at the crossover point N'_c , is obtained

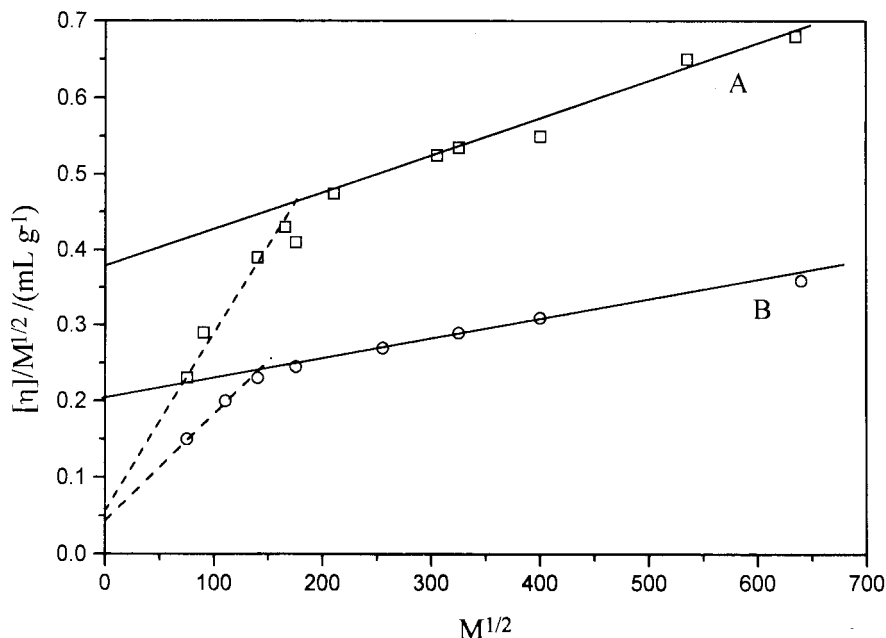


Fig. 5. SFB representation (Eq. (6)) for the systems: (A) PPDP-*m*-cresol [21]; and (B) PPDP-EPCH [21].

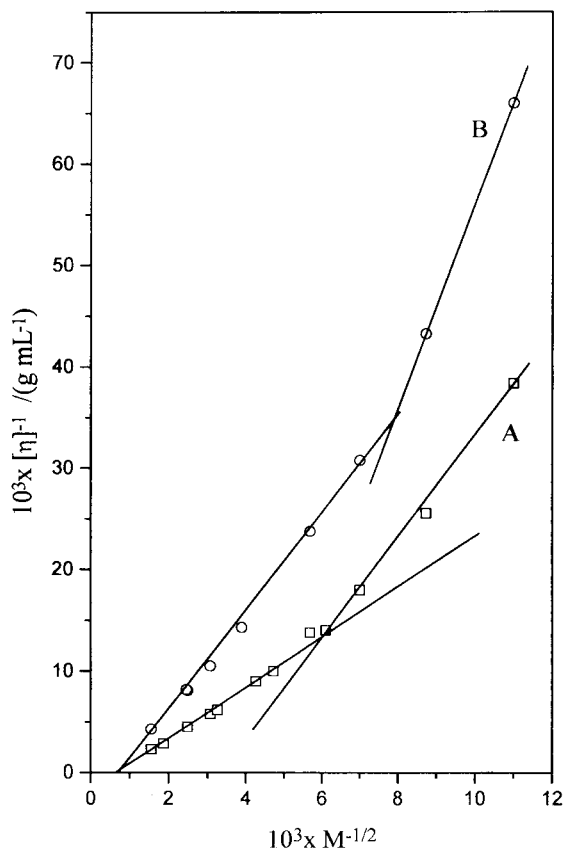


Fig. 6. Variation of $1/[\eta]$ versus $1/M^{1/2}$ (DB representation, (Eq. (2)) for the systems: (A) PPDP-*m*-cresol [21]; and (B) PPDP-EPCH [21].

by dividing the molecular mass corresponding to this point, M'_c , by the molecular mass of the Kuhn statistical segment m_s . It is evident that m_s is obtained by multiplying the statistical segment length A by the molecular mass per unit length M_L . The values of A are determined for all these systems of Fig. 4 from the viscometric results obtained in the molecular mass region above this crossover point, using mainly the DB equation (Table 1) and are very close to the values proposed in the articles from which the viscometric results are taken. The numbers of the systems in Fig. 4 correspond to the systems as given in Table 1. As an example let us indicate that for nitrocellulose, from Eq. (2) we obtain $K_\theta = 1.28 \text{ ml g}^{-1}$, and with $\Phi = 0.9 \times 10^{23}$ (from Eq. (4) with $\underline{a} = 0.79$) Eq. (3) gives $A = 334 \text{ \AA}$; Penzel and Schultz [33,34] give $A = 332 \text{ \AA}$ and Ullman [35] calculates a value for the Kuhn statistical segment of this polymer equal to 310 \AA .

The second crossover point does not have any specific physical meaning but the relation (5) can be used as a guide because it provides for every worm-like polymer-solvent system the number of statistical segments at which we have the onset of power law. Moreover this study clearly shows that flexible and rigid polymers behave similarly, on the contrary to what we observe in the first crossover point, if the chain length is expressed by the number of the statistical segments.

2.5. Region III (molecular mass above the second crossover point or region of power law)

In this region of molecular mass the chains of worm-like polymers consist of more statistical segments than N'_c and we have a complete excluded volume behavior. The

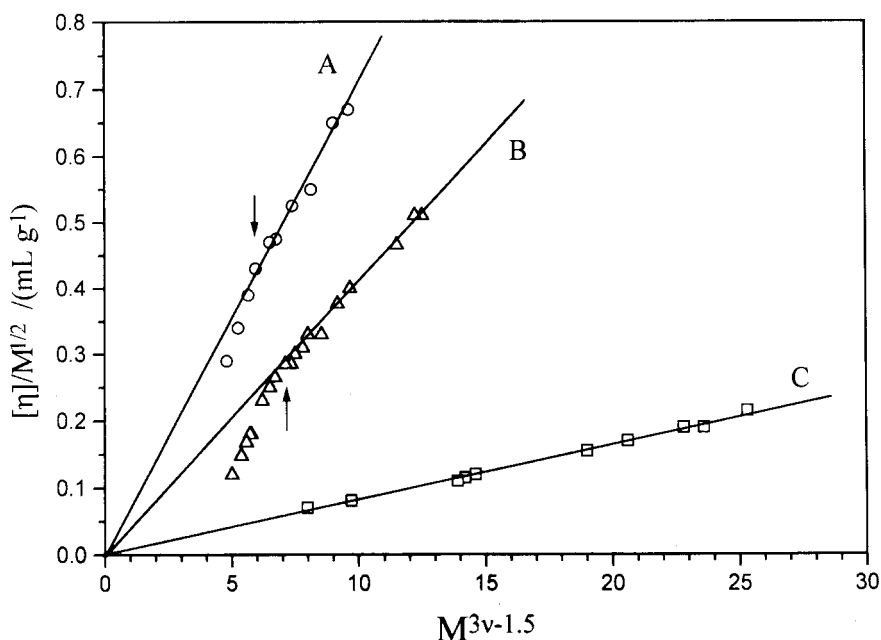


Fig. 7. Variation of $[\eta]/M^{1/2}$ versus $M^{3\nu-1.5}$ (Eq. (8)) for the systems: (A) PPDP-*m*-cresol [21]; (B) CTDC-NMP [22]; and (C) PtBS-cycl. [44]. The arrows indicate the molecular mass corresponding to the characteristic number of statistical segments N'_c (see Table 1).

exponent of the MHS equation, for all the investigated worm-like polymer-solvent systems, is lower than 0.8.

In order to obtain the statistical segment length of worm-like polymers in this region we can use the Yamakawa-Fujii [5], the Bohdanecky [15] and the Dondos-Benoit [17] methods. The values of A obtained with these three methods lie very close to one another and they are very close to the values obtained by optical methods [36].

In our previous works [1,13,16] we have shown that when the fractions of a worm-like polymer consist of a great number of statistical segments ($N > N'_c$) or when we are in the region of the power law (named now region III) we can also apply the Stockmayer-Fixman-Burchard (SFB) equation [37,38],

$$[\eta]/M^{1/2} = K_\theta + 0.51\Phi BM^{1/2} \quad (6)$$

The values of K_θ obtained by plotting $[\eta]/M^{1/2}$ versus $M^{1/2}$ give a value for A from Eq. (3) using Φ from Eq. (4), which is very close to the value obtained from the above mentioned three other methods. Let us consider here the viscometric results obtained from the fractions of poly(phthaloyl-*trans*-2,5-dimethylpiperazine) (PPDP) in solution in *m*-cresol and EPCH [21], according to the SFB and DB equations. In Fig. 5 we present the application of SFB equation and in Fig. 6 we present the DB equation (Eq. (2)). With these two representations we observe a very clear crossover phenomenon for the two PPDP-solvent systems. In the case of *m*-cresol the crossover phenomenon appears at a molecular mass equal to 27 000. At the same molecular mass we observe the crossover point in the MHS representation (Fig. 3, curve A).

Extrapolating the straight lines obtained for $M > M'_c$ (or

$N > N'_c$) in the SFB representation to $M = 0$ and from the slopes of the straight lines obtained also for $M > M'_c$ in the DB representation we obtain about the same values for K_θ . More precisely, from the SFB representation we obtain $K_\theta = 0.38$ in *m*-cresol (Fig. 5, curve A) and $K_\theta = 0.205$ in EPCH (curve B) while from the DB representation we obtain $K_\theta = 0.4$ in *m*-cresol (Fig. 6, curve A) and $K_\theta = 0.21$ in EPCH (curve B).

In the molecular mass region below the second crossover point or in region II, the SFB method is no longer valid. The values of K_θ are very low: about 0.06 in *m*-cresol and 0.04 in EPCH (Fig. 5). On the contrary, the straight lines in the DB representation in the same molecular mass region give values for K_θ in *m*-cresol and EPCH which when introduced in Eq. (3), with the corresponding values of Φ in this molecular mass region, give the same values for A with the values obtained for $M > M'_c$. More precisely, we obtain for $M > M'_c$ in *m*-cresol, as we have already mentioned, $K_\theta = 0.4$ (Fig. 6) and with $\Phi = 1.29 \times 10^{23}$ (exponent \underline{a} of MHS equation equal to 0.675), we finally obtain a value for A equal to 60 Å. For $M < M'_c$ we obtain in the same solvent $K_\theta = 0.2$ (Fig. 6) and with $\Phi = 0.63 \times 10^{23}$ ($\underline{a} = 0.92$) the value of A is equal to 61 Å. These values are comparable to the values of A proposed in the article from which the viscometric results are taken ($A = 64$ Å) [21]. This result indicates the validity of the DB equation in both II and III molecular mass regions.

2.6. A new relation between $[\eta]$ and M for the worm-like polymers

Combining relations derived from the blob theory [39],

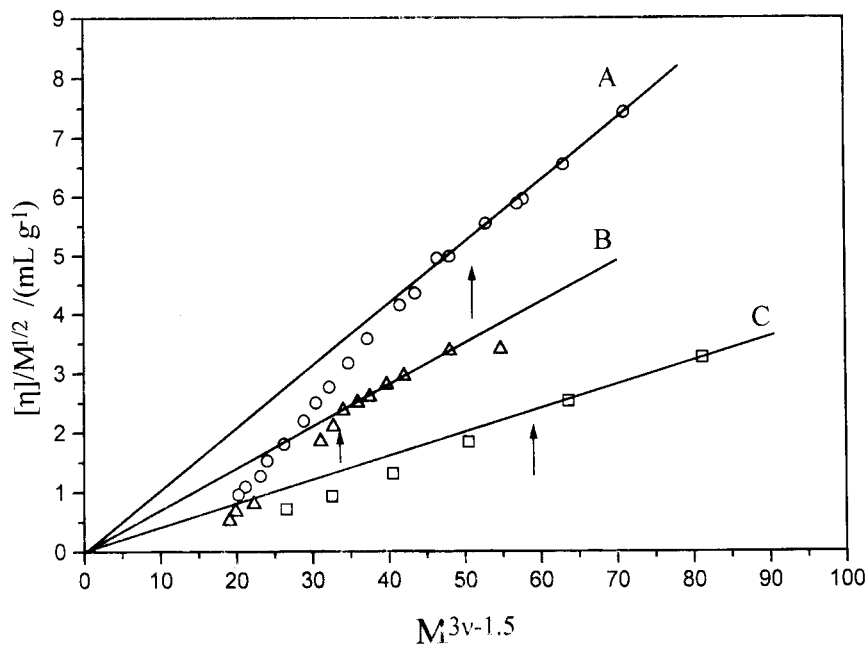


Fig. 8. Variation of $[\eta]/M^{1/2}$ versus $M^{3\nu-1.5}$ (Eq. (8)) for the systems: (A) PHIC-hexane [31]; (B) DNA-H₂O [41–43]; and (C) nitrocellulose (13.9)-acetone [33,34] (the arrows as in Fig. 7).

equation of Han [6, Eq. (1)], and the two parameter theory [40] ($\alpha_\eta^3 = [\eta]/K_\theta M^{1/2}$), we have proposed a relation between $[\eta]$ and M , in the case of flexible polymers, which permits the determination of their unperturbed dimensions especially in the very high molecular mass region in which the SFB equation is no longer valid [45]. Using a similar procedure we have obtained for the worm-like polymers, the following relation from which we obtain their unperturbed dimensions parameter K_θ [1]

$$\log K_\theta = \frac{\log K + 2B \log M_L - \log C - (2/3)B \log \Phi}{1 - (2/3)B} \quad (7)$$

In this equation K is the MHS constant, C is equal to $[4(1-\nu)(2-\nu)]/[(2\nu+1)(\nu+1)]$ and B is equal to $3\nu-1.5$ where ν is the excluded volume index ($3\nu-1 = \underline{a}$, where \underline{a} is the exponent of the MHS equation). In the above equation a term equal to $-B \log(1/N_c)$, is omitted because in the case of worm-like polymers, as we have shown in our previous article [1] and also at the beginning

of this article we have $N_c = 1$. The values of the statistical segment length obtained from the above equation (value of K_θ in Eq. (3)) for a great number of worm-like polymers are in good agreement with the values obtained by other methods [1].

Also, starting now from Han's equation [6, Eq. (1)] and having $\alpha_\eta^3 = [\eta]/K_\theta M^{1/2}$, $N_c = 1$ and $N = M/m_s$ (N is the number of Kuhn statistical segments of the fraction of molecular mass M and m_s the molecular mass of one Kuhn statistical segment) Eq. (1) becomes,

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

From Eq. (3) we have $K_\theta = A^{3/2} \Phi / M_L^{3/2}$ and having $m_s = AM_L$ the above relation becomes

$$\frac{[\eta]}{M^{1/2}} = \frac{A^{3(1-\nu)} C \Phi}{M_L^{3\nu}} M^{3\nu-1.5} \quad (8)$$

Table 2

Excluded volume index ν , Han's equation parameter C , Flory's parameter Φ , mass per unit length M_L , slope of the straight line obtained applying Eq. (8), Kuhn statistical segment length A from Eq. (8) and Kuhn statistical segment length obtained from other methods A' , for six worm-like polymer-solvent systems (PtBS: poly(*p*-tert-butylstyrene))

System	ν	C	$\Phi \cdot 10^{-23}$ (c.g.s.)	M_L (Da \AA^{-1})	Slope (Figs. 7 and 8)	A (\AA)	A' (\AA)	References
PPDP- <i>m</i> -cres.	0.558	0.77	1.29	28.5	0.072	55	58–64	[21]
CTDC-NMP	0.553	0.79	1.36	108	0.0415	162	156	[22,23]
PtBS-cycl.	0.573	0.72	1.1	64	0.008	43	42	[44]
PHIC-cycl.	0.590	0.665	0.95	71	0.104	700	708–840	[31]
DNA-H ₂ O	0.575	0.715	1.095	195	0.070	1148	1130–1150	[41–43]
Nitrocell.-acet.	0.597	0.64	0.898	57	0.042	300	310–332	[33,34]

Plotting $[\eta]/M^{1/2}$ versus $M^{3\nu-1.5}$ we must obtain a straight line that goes through the origin and its slope must be equal to $A^{3(1-\nu)}C\Phi/M_L^{3\nu}$. Knowing from the MHS representation the value of \underline{a} we also know the value of ν , ($3\nu - 1 = \underline{a}$), the value of C and we can also calculate the value of Φ from Eq. (4). So we can calculate, from the slope of the straight line obtained plotting $[\eta]/M^{1/2}$ versus $M^{3\nu-1.5}$, the Kuhn statistical segment length, A , of the worm-like polymers. It is evident that we must know the value of M_L of each polymer.

In Fig. 7 we present the application of Eq. (8) for three worm-like polymer–solvent systems. We can see that we obtain straight lines that go through the origin. The same results are obtained with other three worm-like polymer–solvent systems given in Fig. 8. From the slopes of the straight lines presented in Figs. 7 and 8 we calculated the value of A of the worm-like polymers and the results are given in Table 2. We must note that the value of M_L is introduced in Eq. (8) in Da cm⁻¹ and that the value of A is obtained in cm but in the following is given in Å. In Table 2 we give also the values of A obtained from the authors of the articles from which the viscometric results are obtained as well as the values obtained using the DB equation on these viscometric results. The arrows in Figs. 7 and 8 indicate the molecular mass corresponding to the second crossover point (N'_c Table 1, Fig. 4). For DNA, which is not treated in Table 1 and Fig. 4, the value of N'_c has been calculated now from Eq. (5) ($\underline{a} = 0.725$, $N'_c = 26.8$, $M'_c = 6\,010\,000$, $M_c^{3\nu-1.5}$, $6\,010\,000^{0.225} = 33.5$, arrow in Fig. 8).

As we can see in Table 2 the values of A obtained using Eq. (8) are in good agreement with the results based on other methods. This result clearly indicates the validity of Eq. (8) obtained from the combination of relations that are derived from the blob theory and the two parameter theory. The validity of Eq. (8) also confirms the validity of the two other considerations which we have taken into account in order to obtain this equation, i.e. the dependence of Φ on the quality of the solvent (Eq. (4)) and the value of the number of Kuhn statistical segments at the onset of excluded volume behavior ($N_c = 1$).

We consider that Eq. (8) is preferable to Eq. (7) because (a) it is of a simpler form; (b) it describes a straight line passing through the origin, thus allowing the determination of parameter values with a smaller number of experimental points; and (c) it needs only one parameter of the MHS equation.

3. Conclusions

Treating the viscometric results of a great number of worm-like polymer–solvent systems we have shown that the entire domain of molecular masses can be divided into three regions. These regions are separated by two crossover points that are manifested by plotting the variation of the molecular dimensions of the chains as a function of their

molecular mass. In the molecular mass region below the first crossover point (region I) the chains of the rigid polymers present a conformation of a rod-like cylinder and their length is lower than the length of one Kuhn statistical segment. When the molecular mass becomes equal to the mass of one Kuhn statistical segment we observe the first crossover point, which corresponds to the appearance of excluded volume behavior [1,7]. Between this first crossover point and the second crossover point, which appears when we reach the complete excluded volume behavior, we have a molecular mass region (region II) where we have a non-complete excluded volume behavior. Above the second crossover point the worm-like polymers present a complete excluded volume behavior (region of power law, region III).

The behavior in solution of worm-like polymers is similar to the behavior of flexible polymers, especially in the region III. As we have seen in Fig. 4 the worm-like and the flexible polymers reach this region when their chains contain the same number of statistical segments, if the quality of the solvent is the same for these polymers. Moreover, in region III equations relating the intrinsic viscosity to the molecular mass of flexible polymers are valid for the worm-like polymers as well (equations DB and SFB).

The proposed equation for the determination of the statistical segment length of the worm-like polymers, Eq. (8), derived from relations proposed originally for the flexible polymers indicates also the similarity in the solution behavior between flexible and worm-like polymers. Moreover, the validity of this equation which is derived by combining the equations proposed by the two-parameters theory and the blob theory, indicates that these two theories do not conflict.

The existence of an important draining effect (drastic variation of Φ with the quality of the solvent) in the case of worm-like polymers and the manner with which we approach the power law in the MHS representation are two differences observed between these polymers and the flexible polymers.

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