Colloid Polym Sci 273:626–632 (1995)

ORIGINAL CONTRIBUTION

A. Dondos
G. Staikos

A new approach to the determination of the statistical segment length of wormlike polymers

Received: 15 February 1994
Accepted: 20 January 1995

Prof. Dr. A. Dondos (✉)
G. Staikos
Department of Chemical Engineering
University of Patras
26500 Patras, Greece

Abstract The Stockmayer–Fixman–Burchard (SFB) and the Dondos–Benoit (DB) equations have been applied to determine the unperturbed dimensions parameter K_Θ of wormlike polymers. An empirical relation between the Flory's constant Φ and the Mark–Houwink–Sakurada (MHS) exponent a has been proposed. The Φ values found by this equation are lower than the value 2.5×10^{23} used in the case of flexible polymers and this deviation is attributed to the influence of the draining effect. From the K_Θ value and the so calculated value of Φ, we calculate the Kuhn statistical segment length of wormlike polymers. The obtained – for a great number of wormlike polymers – statistical segment lengths are almost the same as these calculated by the Yamakawa–Fujii and the Bohdanecky methods. The molecular mass regions in which the SFB, the DB, and the MHS equations are valid are explored. A criterion for the distinction between flexible and wormlike polymers is proposed based on the way of approach to the power law.

Key words Wormlike polymers – unperturbed dimensions – Flory's constant Φ – statistical segment length

Introduction

Some years ago, we studied wormlike polymers using relations known from the study of flexible polymers in dilute solutions [1, 2]. More precisely, the statistical segment length was derived from the unperturbed dimensions parameter K_Θ obtained from the Stockmayer–Fixman–Burchard (SFB) representation [3, 4] or the Dondos–Benoit (DB) representation [5]. The obtained statistical segment length values were somewhat lower than the values obtained by the Yamakawa–Fujii (YF) method [6] or by the Bohdanecky method [7].

The principal aim of this work is to make a new approach in the determination of the statistical segment length by introducing an empirical relation between Flory's constant Φ, a parameter necessary to obtain the statistical segment length from the K_Θ value, and the Mark–Houwink–Sakurada (MHS) exponent a. In a recent article [8], one of us proposed two relations which give the molecular mass regions in which the SFB and the DB representations are applicable in the case of flexible polymers. These same relations will be used here even for the wormlike polymers to obtain correct values of K_Θ of these polymers.

We show in this article that there even exists a significant difference between flexible and wormlike polymers, based on the existence of the draining effect in the case of the latter polymers, their behavior in solution presents many similarities if the size of their chains is expressed by the number of their statistical segments and not their molecular masses.

Until now, as a criterion for the distinction between these two classes of polymers, we have used the value of the exponent in the MHS representation. As we will see in the following, this criterion is not sufficient and, for this reason, a new criterion is proposed. In the same direction is also the criterion proposed theoretically in a recent work by Cosmas and Cosmas [9].

Theoretical and procedure

The statistical segment length of the flexible polymers is obtained from the unperturbed dimensions parameter K_Θ obtained mainly from the SFB equation [3, 4].

$$\frac{[\eta]}{M^{1/2}} = K_\Theta + 0.287\,B\Phi M^{1/2} \tag{1}$$

in which $[\eta]$ is the limiting viscosity number, B the long-range interactions parameter, and M the molecular mass of the polymer. In the region of low molecular masses, in which the above equation is not applicable [10, 11], the DB equation [5]

$$\frac{1}{[\eta]} = -A_2 + \frac{A_1}{M^{1/2}} \tag{2}$$

has been used, in which A_2 expresses the long-range interactions and A_1 is the inverse of the K_Θ parameter.

The Kuhn statistical segment, A, is obtained from K_Θ using the equation

$$A = \left(\frac{K_\Theta}{\Phi}\right)^{2/3} M_\mathrm{L} \tag{3}$$

in which M_L is the ratio of the molecular mass to the contour length of the polymer.

As has already been shown [8] the MHS representation reaches its power law only above a characteristic molecular mass M_c'. Below M_c' the slope in this representation decreases continuously until a second characteristic mass M_c is reached. In M_c the slope of this curve takes the value 0.5. According to the blob theory a polymer presenting a mass equal to M_c consists only of one blob. It has also been shown [8] that even the values of M_c and M_c' are different for the different flexible polymers, the numbers of statistical segments corresponding to these molecular masses, N_c and N_c', are the same if the quality of the solvent, as it is expressed by the exponent a of the MHS equation, is the same. More precisely, N_c and N_c' are given by the following equations [8]

$$N_\mathrm{c} = 0.37a^{-7.7} \tag{4}$$

$$N_\mathrm{c}' = 437a^{8.4} \tag{5}$$

As we will see in the following, the above equations, especially Eq. (5), are valid even in the case of the wormlike polymers.

Calculation of the Flory's constant Φ

It is widely accepted that Flory's constant Φ takes the value 2.5×10^{23} mol^{-1} for all the flexible polymers in the non draining limit. On the contrary, in the case of the wormlike polymers, due to the existence of the draining effect, the value of Φ takes values lower than the above value. Introducing now in Eq. (3) the values of K_Θ obtained in our previous work [2] by Eq. (2) for different wormlike polymer-solvent systems, as well as for the system poly(2′,5′-dialkyl-*p*-terphenylene terephthalate)-o-dichlorobenzene recently studied by Kallitsis et al. [12], and introducing also for these same systems the values of the statistical segment length A as they are given in the literature (found by the Yamakawa–Fujii method [6] or by the Bohdanecky method [7]) as well as the corresponding M_L values, different values of Φ have been calculated (Table 1). In the same table the molecular mass region used and the corresponding exponent a of the MHS equation are also given. The so calculated values of Φ have been plotted as a function of the values of a in Fig. 1. The value in the non-draining limit ($a = 0.5$) has also been taken into account. The obtained curve is described by the following equation:

$$\Phi = 0.52 \times 10^{23} a^{-2.32}\,. \tag{6}$$

The above equation, empirically obtained, expresses the influence of the draining effect on the value of the Flory's parameter Φ. It is well known that an increase of the draining effect leads to a decrease of the Φ value. In the case of the wormlike polymers the draining effect increases as the MHS exponent a increases.

Results and discussion

Determination of the statistical segment length

All the viscometric results used in this work obtained with different wormlike polymers have been taken from the literature. Nevertheless, the treatment of these results in this article will be different than the treatment used by the authors in the corresponding articles. We are going to use the already mentioned two graphical methods used almost exclusively until now in the case of flexible polymers, in order to obtain the unperturbed dimensions parameter K_Θ (and then the Kuhn statistical segment length, A) of wormlike polymers.

The first graphical method is based on the well known SFB Eq. (1). This method has been applied in the high molecular weight region and particularly when the number of statistical segments of the wormlike polymers

Table 1 The values of the parameters K_Θ, A, M_L, Φ, a, for seven wormlike polymer-solvent systems at different molecular mass regions.

System	K_Θ (cgs)	A (Å)	M_L (daltons/Å)	$\Phi \times 10^{-23}$ (cgs)	a	Molecular mass region
DNA–0.2 M NaCl	1.6	1130[a])	195	1.15	0.73	$1.5 \times 10^7 – 7 \times 10^7$
	0.92			0.66	1.00	$1.5 \times 10^6 – 1.5 \times 10^7$
PPTP–H_2SO_4 (96%)	1.85	232[b])	20	0.47	0.95	$1.8 \times 10^4 – 6 \times 10^4$
PPSQ–benzene	0.105	148[c])	103	0.61	0.90	$0.6 \times 10^5 – 2.5 \times 10^5$
CTA–dimethylacetamide	0.50	138[b])	58	1.36	0.67	$2.5 \times 10^5 – 6.9 \times 10^5$
	0.32			0.87	0.85	$6.3 \times 10^4 – 2.5 \times 10^5$
CN–acetone	1.2	330[a])	57	0.86	0.88	$8.0 \times 10^4 – 2.5 \times 10^6$
X-500–dimethylsulfoxide	1.4	135[d])	18	0.68	0.80	$1.25 \times 10^4 – 6.5 \times 10^4$
PDTT–dichlorobenzene	0.95	224[e])	27.2	0.40	1.05	$1.0 \times 10^3 – 1.8 \times 10^4$

[a]) Values taken from ref. [6], [b]) Values from ref. [13], [c]) Values from ref. [14], [d]) Values from ref. [15], [e]) Value from ref. [12]. The polymers are: PPTP = poly(*p*-phenylene terepthalamide), PPSQ = poly(phenylsilsesqioxane), CTA = cellulose triacetate, CN = cellulose nitrate, X-500 = poly(terephtholyl-*p*-amino benzhydrazide), PDTT = poly(2′,5′-dialkyl-*p*-terphenylene terephthalate).

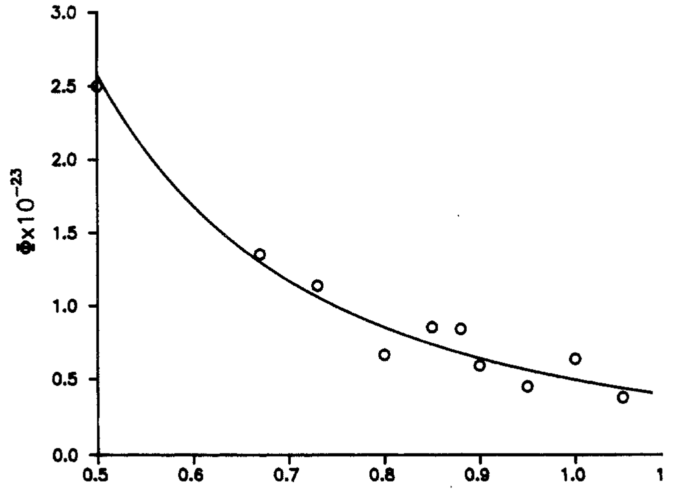

Fig. 1 Variation of the Flory's constant Φ, obtained by Eq. (3) for the systems presented in Table 1, as a function of the MHS exponent a

is higher than that predicted by Eq. (5). More precisely, the SFB equation has been applied for the systems: poly(phenylsilsesqioxane) (PPSQ) – benzene [14, 16, 17], cellulose triacetate (CTA) – dimethylacetamide [18], CTA – tetrachloroethane and poly(hexylisocyanate) (PHIC) – hexane [19]. From the obtained K_Θ values of the above systems and using Eq. (3), we obtain the values of Kuhn statistical segment, A. The Φ values are obtained through Eq. (6) knowing the MHS exponent a of the systems, in the molecular mass region in which the SFB method is applied. M_L is given for each polymer in Table 2 through a calculation based on the geometrical shape of the chain, and it is about the same as values given in the literature.

Figures 2 and 3 show the SFB plots obtained with the above systems. It is obvious that in order to obtain the K_Θ values, given in Table 2, by which the statistical segment length is derived, we have taken into account only the points which lie above a certain, relatively narrow, molecular mass region. We have to observe here that above this region, where the SFB equation is reliably applied, linearity of log $[\eta]$ versus log M is very satisfactory (power law) and the obtained slopes are lower than 0.8 (values of a are indicated in Table 2). On the contrary, below this crossover region the application of SFB equation is not possible because the points obtained present a curvature and an extrapolation of this curve to $M = 0$ gives values for K_Θ unacceptable (very small or even negative values).

The second graphical method is based on the DB equation, Eq. (2). This method has been applied in the low molecular mass as well as in the high molecular mass region of the wormlike polymers. Let us indicate that in the low molecular mass region the wormlike polymers, as the flexible polymers [20], do not obey a power law, but in the case of wormlike polymers the points in the log $[\eta]$ versus log M representation lie on a curve which is assimilated to a straight line with a slope which lies near a value equal to unity.

In Fig. 4 the representation according to Eq. (2) has been applied for the systems: cellulose acetate butyrate (CAB) – chloroform and CAB – nitromethane [21], poly (phenylhydroquinone-co-terephthalic acid) (PPHQTPA)-o-dichlorobenzene/*p*-chlorophenol [22], poly[diisopropyl fumarate) (PDiPF)–benzene [23] and phenyl substituted poly(*p*-benzamide) (PA-2)-dimethylacetamide + 1% LiCl [24]. In Table 2, the K_Θ values of the above systems, obtained as the inverse of the slopes of the curves in Fig. 4, are given. The values of the exponent a of the MHS equation corresponding to the molecular mass regions in which the SFB and the DB equations have been applied and the corresponding values of Φ, according to Eq. (6), are also given in Table 2. Using now Eq. (3) the Kuhn statistical segment, A, for each system has been obtained and is given in Table 2 as well as the value of A proposed

Table 2 The values of the parameters K_Θ, M_L, a, Φ and A, for 11 wormlike polymer-solvent systems

System	K_Θ (cgs)	M_L daltons/Å	a	$\Phi\times10^{-23}$ (cgs)	A (Å)	A/(Å) from literature	ref
PPSQ–benzene	0.21	103	0.70	1.19	150	148	14, 16, 17
CTA–dimethylacetamide	0.47	58	0.67	1.32	135	138	13, 18
CTA–tetrachloroethane	0.20	58	0.64	1.46	72	70	13, 18
PHIC–hexane	2.93	71	0.77	0.95	700	840	19
CAB–chloroform	0.16	58	0.81	0.85	88	–	21
CAB–nitromethane	0.29	58	0.81	0.85	131	–	21
PPHTPA–o-dichlorobenzene/ *p*-chlorophenol	0.79	24.5	0.87	0.72	121	122	22
PDiPF–benzene	0.15	80	0.82	0.82	120	152	23
PA-2–dimethylacetamide + 1% LiCl	1.69	21.2	0.80	0.87	153	246 ± 104	24
PNI–sulfuric acid	1.95	25	0.64	1.46	141	170 ± 30	25
PSi–tetrahydrofuran	0.062	63	1.07	0.44	79	75	26

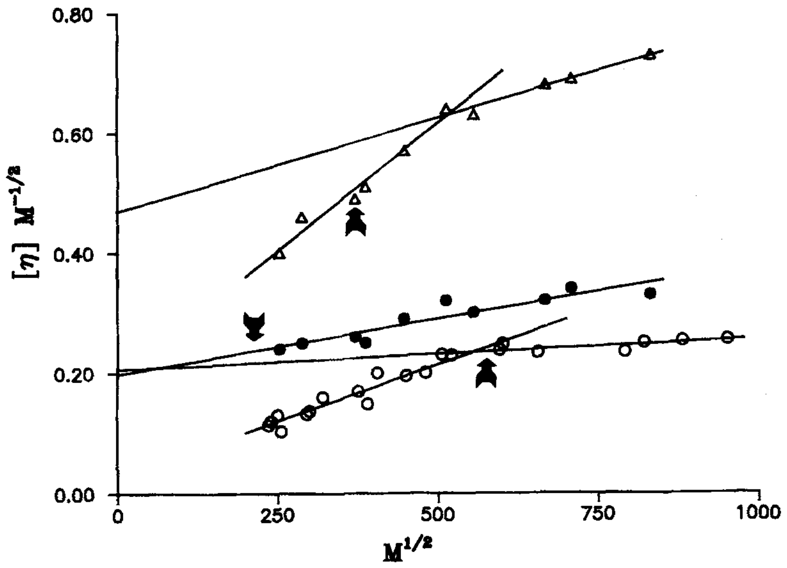

Fig. 2 SFB representation for the systems:
△ CTA–dimethylacetamide,
● CTA–tetrachloroethane,
○ PPSQ–benzene. The arrows indicate the onset of the power law behavior

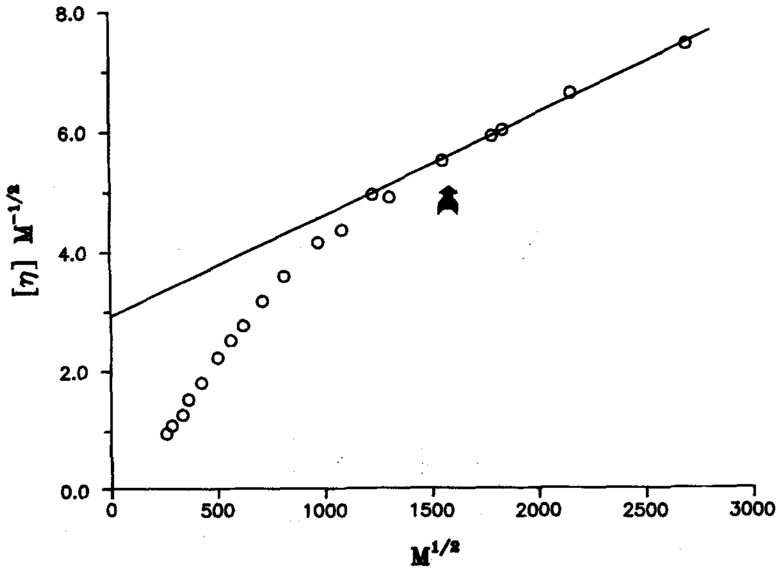

Fig. 3 SFB representation for the system PHIC–hexane. The arrow indicates the onset of the power law behavior

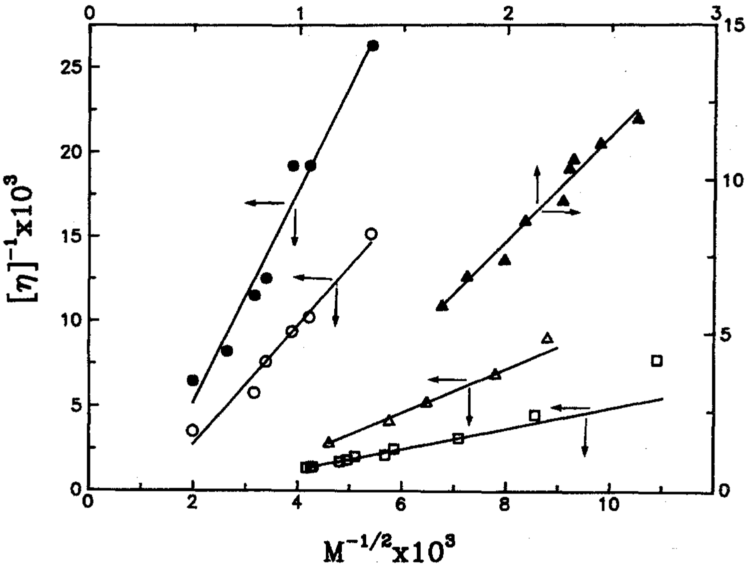

Fig. 4 DB representation for the systems:
● CAB–chloroform,
○ CAB–nitromethane,
▲ PDiPF–benzene,
△ PPHTPA–o-dichlorobenzene/*p*-chlorophenol, □ PA-2–dimethylacetamide + 1% LiCl

by the authors of the works from which the viscometric results have been taken. These authors have used the Yamakawa–Fujii method [6] or the Bohdanecky method [7].

Using the DB equation, we have also calculated the K_Θ value and in the following the A value of the system poly(naphthalene imidobenzimidazole) (PNI) – sulphuric acid [25] from the high molecular mass region and the corresponding values of the system poly(methylphenylsilane) (PSi) – tetrahydrofuran [26], using the viscometric results obtained in the low molecular mass region. The obtained values are also given in Table 2.

Let us indicate that the M_L parameter values given in Table 2 have been calculated as the ratio of the molecular mass to the contour length of the polymer. The exponent a values have been obtained through a $\log[\eta]$ versus $\log M$ representation in the molecular mass region investigated.

An attempt has been made by Leon et al. [27] to obtain the statistical segment length of a wormlike polymer (poly(monodecyl itaconate)) from K_Θ value obtained through SFB equation. If now we use the molecular mass region above a critical molecular mass, we obtain a K_Θ value equal to $7 \pm 1 \times 10^{-2}$ which gives a statistical segment equal to 72.5 ± 7.5 Å comparable to the value of 60 Å calculated by Sharp and Bloomfield [28] through the Bohdanecky method [7].

Domain validity of Eqs. (1) and (2)

It has been shown [20] that the numbers of the Kuhn statistical segments of any flexible polymer at the onset of excluded volume behavior and at the onset of complete excluded volume behavior (onset of the power law between $[\eta]$ and M) are the same if the quality of the solvent, as it is expressed by the MHS exponent, is the same. More precisely, the number of statistical segments at the onset of the excluded volume behavior, N_c, and the number of the statistical segments at the onset of the complete excluded volume behavior N_c' are given by Eqs. (4) and (5) correspondingly. It has been shown that in the case of flexible polymers the SFB equation is valid only in the molecular mass region above N_c', and that in the crossover region delimited by N_c and N_c' only the DB equation is applicable [11].

Using now the MHS exponent values given in Table 2 for the first four polymer-solvent systems, in which the molecular mass region used seems to have reached the power law behavior, we obtain from Eq. (5) the N_c' values corresponding to each polymer-solvent system. Now multiplying N_c' by the corresponding mass of the statistical segment ($A \times M_L$), we obtain the characteristic molecular mass M_c' indicated by the arrows in Figs. 2 and 3. As we can see, these arrows are situated in the molecular mass region above which the validity of the SFB equation starts, except for the system CTA – dimethylacetamide (Fig. 2). This result indicates that we can obtain the characteristic molecular mass M_c' for the flexible and wormlike polymers using the same equation (Eq. (5)). In other words, a flexible and a wormlike polymer, in the onset of the power law, consist of the same number of statistical segments if the quality of the solvent is the same.

We also have to point out that Lavrenko et al. [25] observed a change in the MHS representation of PNI in sulfuric acid at a molecular mass region around 50000.

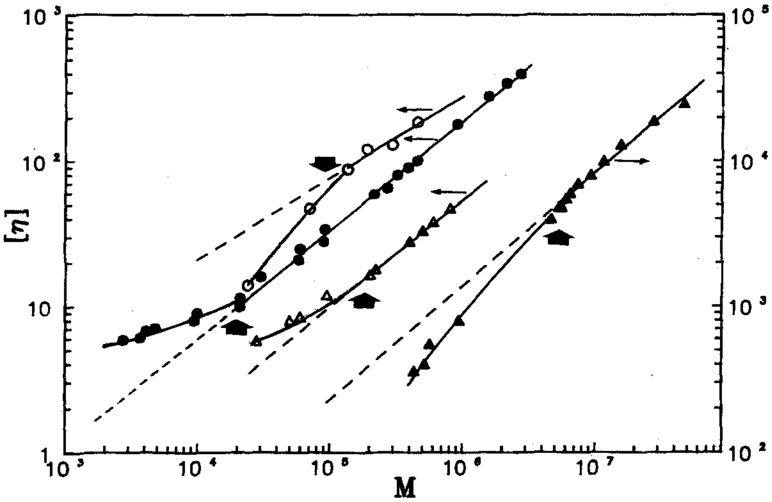

Fig. 5 MHS representation for the systems:
○ APC–dimethylphthalate (data from ref. [31]),
● PMMA–benzene (data from refs. [5, 32]),
△ PTEMA–toluene (data from ref. [33]), ▲ DNA–NaCl 0.2 M (data from refs. [34–36])

Using Eq. (5) and the parameters given for this system in Table 2, we obtain an M_c' value equal to 36 000 which is close to the crossover region observed by these authors.

In the very low molecular mass region or, more precisely, in the region of very low number of statistical segments, the DB equation is not valid. This region is delimited by a statistical segment number given by Eq. (4), and below N_c it is generally accepted that the macromolecular chain does not present any statistical behavior. In the case of the studied wormlike polymers, Fig. 4, the number of the statistical segments was not in general sufficiently low and the DB equation is well applied. Only in the case of the polymer PA-2 does the lowest molecular mass fraction consist of about two statistical segments and it clearly deviates from the straight line obtained with the other fractions.

Distinction between flexible and rigid polymers

A large number of examples from the literature indicates that the approach to the power law behavior (log [η] versus log M) takes place in two different ways: an approach takes place from above, i.e., the [η] values in the low molecular mass region are higher than those predicted by the power law, and the other approach takes place from below, i.e., the [η] values in the low molecular mass region are smaller than those predicted by the power law.

All the polymers studied in this work approach the power law according to the second way (from below) while the flexible polymers approach the power law according to the first way (from above). We believe that the two different ways of approach of the power law establish a criterion in order to separate the polymers into two classes: the rigid and the flexible polymers. This criterion has been predicted theoretically by Kosmas and Kosmas [9]. In Fig. 5 we present relations between log [η] and log M for some polymer solvent systems and we can see that there exists a clear difference in their behavior. According to the proposed criterion DNA and (Acetoxypropyl) cellulose (APC) are wormlike polymers, while poly(methyl methacrylate) (PMMA) and poly[2-(triphenylmethoxy)ethyl methacrylate] (PTEMA) are flexible polymers.

The criterion generally used for the distinction between wormlike and flexible polymers based on the high values of the MHS exponent a ($a > 1$) seems to be not sufficient. In the high molecular mass region the wormlike polymers present values of the exponent a comparable to the values characterizing the flexible polymers (Table 1).

In Fig. 5 the arrows indicate the onset of power law behavior as predicted by Eq. (5). It is noteworthy to point out that even the crossover point for DNA is observed at a very different molecular mass (5×10^6) than for PMMA (2.5×10^4) the corresponding number of statistical segments is about the same ($N_c' = 31$ for DNA and 40 for PMMA) and this occurs because the quality of the solvents, as expressed by the MHS exponent, is about the same.

Conclusion

Using the viscometric results obtained with a great number of wormlike polymers, we have applied equations relating the intrinsic viscosity to the molecular mass as these equations had been proposed for the flexible polymers. Plotting $[\eta]/M^{1/2}$ versus $M^{1/2}$ (SFB equation) in the high molecular mass region and $[\eta]^{-1}$ versus $M^{-1/2}$ (DB equation) in the low molecular mass region as well as in the high molecular mass region, we obtain straight lines.

From the extrapolation to $M = 0$ of the former straight lines and from the inverse of the slope of the latter straight lines the unperturbed dimensions parameter K_Θ of the wormlike polymers was obtained. From the K_Θ value, using a Φ value obtained through an empirical equation proposed in this work, we obtain the Kuhn statistical segment length, A.

The use of relations to obtain the statistical segment length of wormlike polymers, which have been initially proposed for the flexible polymers, indicates that we must accept the existence of excluded volume effect in the wormlike polymers. This effect has been already accepted, even in the case of DNA by some authors [28, 29]. It was also pointed out that even DNA, in the region of high number of statistical segments, reaches a power law with an exponent a lower than unity [30].

The relations obtained in the case of flexible polymers (which give the limits of validity of SFB, DB and MHS equations) have been shown to be valid also in the case of wormlike polymers. Finally, a criterion is proposed to distinguish the class of wormlike polymers from the class of flexible polymers.

References

1. Dondos A, Staikos G (1980) Eur Polym J 16:1215
2. Staikos G, Dondos A (1983) Eur Polym J 19:555
3. Stockmayer WH, Fixman M (1963) J Polym Sci C1:137
4. Burchard W (1961) Makromol Chem 50:20
5. Dondos A, Benoit H (1977) Polymer 18:1161
6. Yamakawa H, Fujii M (1974) Macromolecules 7:128
7. Bohdanecky M (1983) Macromolecules 16:1483
8. Dondos A (1992) Polymer 33:4375
9. Cosmas MK, Cosmas AM (1993) Polymer 34:3115
10. Bohdanecky M, Kovar J, Fortelny I (1979) Polymer 20:813
11. Dondos A (1992) Makromol Chem, Macromol Symp 62:129
12. Kallitsis JK, Gravalos K, Dondos A (1993) Macromolecules 26:5457
13. Dayan S, Maissa P, Vellutini MJ, Sixou P (1982) Polymer 23:800
14. Helminiak TE, Berry G (1978) J Polym Sci Polym Symp 65:107
15. Bianchi E, Ciferri A (1981) J Polym Sci Polym Phys Ed 19:863
16. Helminiak TE, Benner CL, Gibbs WE (1967) Am Chem Soc, Polym Chem Div Preprints 8:284
17. Fang Z, Qin A, Yu T (1986) Makromol Chem, Rapid Commun 7:687
18. Kamide K, Miyazaki Y, Abe T (1979) Polymer J 11:523
19. Murakami H, Norisuye T, Fujita H (1980) Macromolecules 13:345
20. Dondos A (1987) J Phys (Fr) 48:1439
21. Vyas NG, Shashikant S, Patel CK, Patel RD (1979) J Polym Phys Ed 17:2021
22. Krigbaum WR, Tanaka T (1988) Macromolecules 21:743
23. Matsumoto A, Tarui T, Otsu T (1990) Macromolecules 23:5102
24. Krigbaum WR, Tanaka T, Brelsford G, Ciferri A (1991) Macromolecules 24:4142
25. Lavrenko PS, Okatova OV, Vinogradova SY, Rusanov AL, Ponomarev II (1990) Eur Polym J 26:1337
26. Strazielle C, de Malieu AF, Daoust D, Devaux J (1992) Polymer 33:4174
27. Leon A, Gargallo L, Horta A, Radic D (1989) J Polym Sci Polym Phys Ed 27:2337
28. Sharp P, Bloomfield VA (1968) Biopolymers 6:1201
29. Freire JJ, de la Torre JG (1979) Macromolecules 12:971
30. Bloomfield VA, Crothers DM, Tinoco I "Physical Chemistry of Nucleic Acids" Harper and Row NY 1974 (pp 230–234)
31. Laivins GV, Gray DG (1985) Macromolecules 18:1746
32. Cohn-Grinsberg E, Fox TG, Mason HF (1962) Polymer 3:97
33. Dolezalova M, Petrus V, Tuzar Z, Bohdanecky M (1976) Eur Polym J 12:701
34. Rice SA, Doty P (1957) J Am Chem Soc 79:3937
35. Doty P, Marmur J, Eigner J, Shildkraut C (1960) Proc Nat Acad Sci (USA) 46:461
36. Burgi E, Hershey AD (1961) J Mol Biol 3:458