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Viscometric determination of the statistical segment length of wormlike polymers

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A new viscometric method, which consists of plotting the inverse of the intrinsic viscosity *versus* the inverse of the square root of the molecular mass (Dondos and Staikos, *Colloid Polym. Sci.*, 1995, 273, 626) has been applied for the determination of the statistical segment length of a poly(p-phenylene) ribbon-type polymer (Me-LPPP). The same method has also been applied to determine the statistical segment length of other wormlike polymers with viscometric data taken from the literature. The values of the statistical segments obtained using this new method are in close agreement with the values obtained from other methods. © 1998 Elsevier Science Ltd. All rights reserved.

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Introduction

The rigidity of the polymeric chains has attracted a great deal of interest since the earliest efforts in polymer science because it is related to the mechanical properties of polymers. As the more rigid polymers present better mechanical properties, many new wormlike polymers, i.e. polymers presenting a high rigidity, have been prepared during the last few years.

In the case of flexible vinyl polymers, the rigidity has been characterized by the unperturbed dimensions parameter K_Θ obtained viscometrically in an ideal solvent or even in a good solvent using different graphical methods, such as the Stockmayer-Fixman-Burchard (SFB)[1,2] and the Dondos-Benoît (DB)[3,4] method. The DB method has also been used for the determination of the unperturbed dimensions parameter K_Θ of wormlike polymers, as well as the SFB method in some cases (very high molecular mass region)[5,6]. From the K_Θ value, the Kuhn statistical segment length, *A*, is obtained.

In a recent study[7], an improvement in the use of the K_Θ value obtained by the SFB or the DB methods for the determination of *A*, has been proposed. More precisely, the value of the Flory parameter Φ, which is necessary to obtain the statistical segment length from the K_Θ value, is calculated as a function of the Mark–Houwink–Sakurada (MHS) exponent *a* after exploitation of the results obtained in the determination of *A* of different wormlike polymers, by using the Yamakawa–Fujii (YF) method[8]. The use of exponent *a* (instead of the chain contour length and the chain diameter) for the determination of Φ in the draining region has been recently theoretically justified[9,10].

In this article, the rigidity of a ribbon-type wormlike polymer has been viscometrically characterized by the above procedure. In order to check the validity of this procedure the statistical segment lengths of some other wormlike polymers have also been determined using the viscometric results given in the literature. The results obtained show that we now have at our disposal a new

method for the determination of the statistical segment length of wormlike polymers which, compared to the existing methods, is characterized by its simplicity and accuracy.

Theoretical

The statistical segment length of a flexible polymer can be obtained from the unperturbed dimensions parameter K_Θ which, in the case of the low molecular mass region where the excluded volume effect is not important, can be obtained by applying the DB equation[3,4]

$$\frac{1}{[\eta]} = -A_2 + K_\Theta^{-1} M^{-1/2} \qquad (1)$$

in which A_2 expresses the long-range interactions in the case of flexible polymers. As it concerns the wormlike polymers, A_2 should express the draining effect of the chain. This assumption is derived by the results obtained from the application of the relation (1) in a wide molecular mass region of a wormlike polymer[5,6]. According to these results, A_2 approaches zero when equation (1) is applied in the higher molecular mass region where the draining effect becomes very low.

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

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

in which M_L is the mass per unit length. The Flory parameter Φ, which in the case of wormlike polymers depends on the draining effect of the chain, is given by the following empirical equation[7]

$$\Phi = 0.52 \times 10^{23} a^{-2.32} \qquad (3)$$

in which *a* is the exponent of the MHS equation. This equation has been obtained by applying the Yamakawa–Fujii method[8] for the determination of the statistical segment of different wormlike polymers. Lavrenko has recently shown[9,10] that this relation giving the Φ value as a function

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Table 1 Weight average (M_w) and number average (M_n) molecular masses and intrinsic viscosity ([η]) values of five fractions of Me-LPPP in toluene and chloroform at 20°C

$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	[η]/(ml g^{-1})	
		Chloroform	Toluene
5.5 ± 0.5	2.7 ± 0.2	28.1	33.5
8.6 ± 0.7	4.0 ± 0.3	42.1	47.5
10.0 ± 0.8	6.9 ± 0.6	43	49.6
11.2 ± 0.9	7.1 ± 0.6	45.5	55.3
18.0 ± 1.5	10.7 ± 0.9	80	87

Table 2 MHS exponent a and Flory parameter Φ calculated from equation (3), unperturbed dimensions parameter K_Θ calculated through equation (1) and Kuhn statistical segment A determined from equation (2), for the studied systems at 20°C

| System	a	$\Phi \times 10^{-23}$ (mol^{-1})	$K_\Theta \times 10^2$ (ml g$^{-3/2}$ mol$^{-1/2}$)	A (Å)
Me-LPPP/Tol (M_w)	0.78	0.92	10.5	102 ± 10
Me-LPPP/Tol (M_n)	0.58	1.84	19.2	96 ± 10
Me-LPPP/CHCl$_3$ (M_w)	0.84	0.78	8.5	99 ± 10
Me-LPPP/CHCl$_3$ (M_n)	0.61	1.64	15.8	91 ± 10
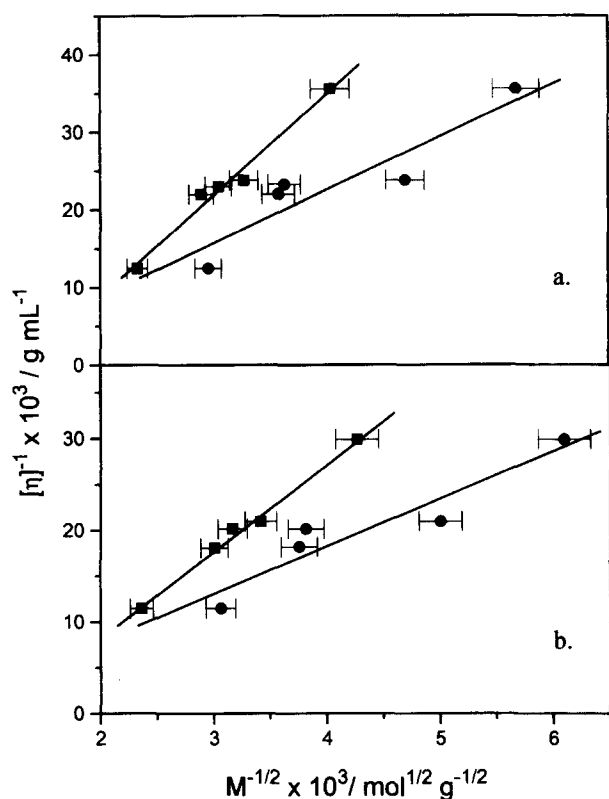
Figure 1 Plot of [η]$^{-1}$ *versus* $M^{-1/2}$ of Me-LPPP (a) in CHCl$_3$ and (b) in toluene at 20°C; squares represent M_w values and circles M_n values

of the MHS exponent a does not need the use of the chain diameter as a second parameter as it happens when Φ is calculated as a function of the chain contour length[8]. As an example, let us indicate that a determination of the Φ parameter from viscometric and light scattering data for the wormlike polymer, cellulose diacetate, in dimethyl-acetamide[11] gives a value equal to 0.79×10^{23} (cgs) for the high molecular mass region, while equation (3) gives

$\Phi = 0.82 \times 10^{23}$ by using the value of the MHS exponent, $a = 0.82$, given in the same study.

Experimental

A poly(*p*-phenylene) ribbon-type polymer Me-LPPP possessing the structure, **g**, given in *Scheme 1* has been synthesized following the method described previously[12,13]. The fractionation of the fully soluble, yellow ladder polymer was done by means of preparative gel permeation chromatography (PS gel; pore width: 10 000 Å; solvent: chloroform).

R: -1.4-C$_6$H$_4$-*n*-C$_{10}$H$_{21}$;   R': -*n*-C$_6$H$_{13}$
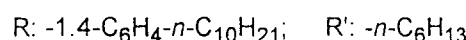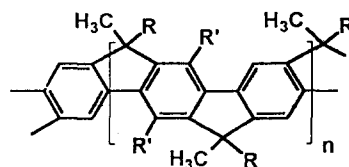
Scheme 1

The M_w and M_n values were determined using GPC calibrated by polystyrene standards. Identical GPC results were obtained using toluene or 1,2-dichlorobenzene as solvents. Direct estimations of M_n by means of vapour pressure osmometry provided only small deviations (*ca.* 10%) when compared to the GPC data.

An automatic viscosity measuring system (Schott Gerate AVS 300) equipped with an Ubbelohde type viscometer has been used to obtain the intrinsic viscosity, [η], values of five fractions of Me-LPPP dissolved in toluene and in chloroform.

Results

The viscometric results have been taken mainly from the literature except for Me-LPPP. The [η], M_w and M_n values obtained for the five fractions of Me-LPPP are given in *Table 1*.

We have to point out that the molecular masses of Me-LPPP have not been determined by a direct method. Nevertheless the comparison of the M_w values obtained by GPC measurements with the M_w values obtained by small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS) in the case of LPPP polymer[14], which only slightly differs from Me-LPPP, indicates that the values of M_w given in *Table 1* are not far from the directly determined values. More precisely, the values of M_w for three fractions of LPPP, obtained by three methods are the following: GPC 25 000, SANS 30 000, SAXS 25 000; GPC 50 000, SAXS 38 000; GPC 99 000, SANS 87 000[14].

The viscosity laws expressing the MHS representation of the results given in *Table 1* are the following:

$$[\eta] = 6.8 \times 10^{-3} M_w^{0.79} \quad \text{(toluene)} \tag{4}$$

$$[\eta] = 9.1 \times 10^{-2} M_n^{0.58} \quad \text{(toluene)} \tag{5}$$

$$[\eta] = 2.8 \times 10^{-3} M_w^{0.85} \quad \text{(chloroform)} \tag{6}$$

$$[\eta] = 5.62 \times 10^{-2} M_n^{0.63Z} \quad \text{(chloroform)} \tag{7}$$

Table 3 MHS exponent a, unperturbed dimensions parameter K_Θ, mass per unit length M_L, and Kuhn statistical segment A for different wormlike polymers obtained by using either M_w or M_n

System	a		K_Θ (ml g$^{-3/2}$ mol$^{-1/2}$)		M_L (g/mol Å)	$A/(Å)$ our method		$A/(Å)$ other methods		Refs.
	(M_w)	(M_n)	(M_w)	(M_n)		(M_w)	(M_n)	(M_w)	(M_n)	
1. Poly(2',5'-dialkyl-p-terphenylene terephthalate)-chloroform, 25°C	0.83	0.91	1.41	1.32	27.2	184	203	144[a]	(288)[a]	[17]
								220[b]		[18]
								380[c]		[19]
2. Substituted p-phenylene-THF, 25°C	0.85	0.88	0.43	0.40	74	235	237	252[a]	(406)[a]	[20]
3. Poly(1,4-phenylene 2,5-di-n-alkoxy-terephthalate)-chloroform, 25°C	1.10	0.91	0.19	0.32	57.1	157	166	130[a]	(216)[a]	[21]
4. Poly(diisopropyl fumarate)-benzene, 30°	0.84	0.91	0.16	0.17	79.4	128	151	152[a]	(170)[a]	[22]
5. (Acetoxypropyl)cellulose-dimethyl phthalate, 25°C	0.89	0.92	0.13	0.11	82	126	119	118[a]	(198)[a]	[23]
6. Aromatic polyamide-hydrazide (x:500)-dimethylsulfoxid, 25°C	0.80		1.22		18.2	106		70[a]		[24]
								98[c]		[24]
7. Poly(3-hexylthiophene)-toluene, 25°C	0.77		0.15		42.6	58		50[a]		[25]
8. Cellulose tris(3,5-dimethylphenyl carbamate)-N-methyl-2-pyrrolidone, 25°C	0.66		0.22		108	149		156[c]		[26]
9. Poly(2-fluoro-p-phenylene-2-fluoroterephthalamide)methanesulf.acid, 25°C	1.08		1.07		21.1	178		160 ± 60[a,c,d]		[27]
10. Poly(hexyl isocyanate)-di chloroethane	0.89		0.88		73	402		420[a,e]		[28]
11. Poly(hexyl isocyanate)-toluene, 10°C	1.20		1.35		73	848		820[a,e]		[28]

[a]Bohdanecky method, [b]magnetic birefrigence, [c]static light scattering, [d]dynamic light scattering, [e]Yamakawa–Fujii method
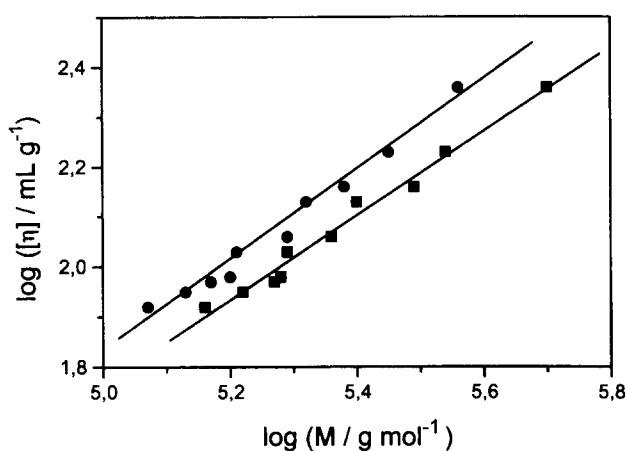
Figure 2 Plot of log $[\eta]$ *versus* log M of poly(di-isopropyl fumarate) in benzene; squares represent M_w values and circles M_n values

The exponent a of the MHS equation obtained for the four systems is also given in *Table 2*, as well as the values of Φ calculated from equation (3).

In *Figure 1*, the viscometric results of *Table 1* are treated according to equation (1). From the slopes of the obtained four straight lines we calculate the K_Θ values of the four systems and these values are given in *Table 2*.

Applying equation (2) with the K_Θ and Φ values of *Table 2* and using an M_L value equal to 93.5 daltons Å^{-1}, as it has been estimated from the repeating unit molecular mass and its projection length, we obtained the Kuhn statistical length, A, of Me-PPPL. The A values of this polymer in the two solvents were almost the same irrespective of whether M_w or M_n was used (*Table 2*).

The Kuhn statistical segment of a polymer differing from the one studied above only in a lateral methyl group (LPPP) has recently been determined using optical methods[14] and the obtained value is 130 Å. The discrepancy observed with the values obtained using the proposed method (*Table 2*) should be attributed to the M_L value used here, determined from the geometrical characteristics of the repeating unit which is lower (93.5 daltons Å^{-1}) compared to that used in Ref. 14.

In the following, the viscometric results obtained from the literature and concerning ten wormlike polymers have been treated according to the method used here. The statistical segment lengths of all these polymers were determined from the unperturbed dimensions parameter value, K_Θ, obtained through equation (1) by using equation (2), where the Φ value was obtained from equation (3). All the A values obtained are given in *Table 3*. In the same table we give the A values proposed by the authors of the articles from which the viscometric results have been taken.

Let us present in more detail the proposed method for the determination of the statistical segment length of the system poly(diisopropyl fumarate)–benzene[22]. In *Figure 2*, the log $[\eta]$ *versus* log M representation is shown for this system. From the curves of this figure we obtained the a value for this system (*Table 3*) and from equation (3) the Φ values are calculated ($\Phi = 0.78 \times 10^{23}$ for M_w, $\Phi = 0.65 \times 10^{23}$ for M_n). The same viscometric data are presented in *Figure 3* according to equation (1). From the slopes of the curves obtained we determined the K_Θ values of this polymer and from equation (2) we finally obtained the A values given in *Table 3*.

From the results presented in *Table 3* it can be seen that: (1) the statistical segment determined by the method used here for different wormlike polymers is in close agreement with the values obtained by other methods[8,15,16] and/or
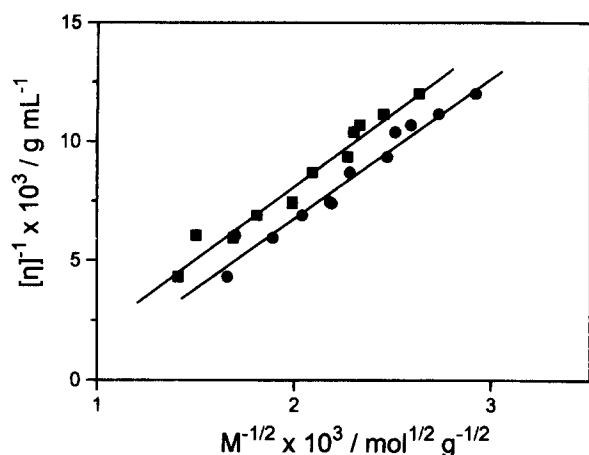
Figure 3 Plot of $[\eta]^{-1}$ *versus* $M^{-1/2}$ of poly(di-isopropyl fumarate) in benzene; squares represent M_w values and circles M_n values

optical methods; (2) by using M_w or M_n values, the method used leads to approximately the same A values; (3) plotting $(M^2/[\eta])^{1/3}$ *versus* $M^{1/2}$ according to the equation proposed in Refs [15,16] and using the analysis given by Bohdanecky[16] the statistical segment lengths of some wormlike polymers have been determined and the values taken are given in parentheses in *Table 3*. In these calculations the number average molecular mass has been used, and as can be seen in *Table 3*, the statistical segment values obtained are substantially overestimated compared to the values obtained by using the weight average molecular mass[17,20-23].

In order to check the reliability of equation (3) we have used the light scattering results obtained with a LPPP fraction in toluene (LPPP-99: $M_w = 87.000$ and $R_g = 1.47 \times 10^{-6}$ cm from Table 1 of Ref. [14]) and the viscometric results obtained with the Me-LPPP studied in this work in the same solvent. Considering that these two polymers present practically the same behaviour in solution, we obtained for the above fraction of LPPP using the MHS law of this study an $[\eta]$ value equal to 48.5 cm^3 g^{-1}. Using these three parameters (M_w, R_g and $[\eta]$) in the well-known Fox–Flory equation, we obtained a Φ value equal to 0.90×10^{23} (cgs) for LPPP-99 while from equation (3) with $a = 0.78$ (*Table 2*) we obtained almost the same value.

In conclusion, the proposed viscometric method[7] for the calculation of the statistical segment length has been used in a new polymer and in some polymers already studied in the literature. The results obtained show that we have a simple and easy to use method to determine the statistical segment length of wormlike polymers.

References

1. Stockmayer, W. H. and Fixman, M., *J. Polym. Sci.*, 1963, C1, 137.
2. Burchard, W., *Makromol. Chem.*, 1961, 50, 20.
3. Dondos, A., *Eur. Polym. J.*, 1977, 13, 829.
4. Dondos, A. and Benoît, H., *Polymer*, 1977, 8, 1161.
5. Dondos, A. and Staikos, G., *Eur. Polym. J.*, 1980, 16, 1215.
6. Staikos, G. and Dondos, A., *Eur. Polym. J.*, 1983, 19, 555.
7. Dondos, A. and Staikos, G., *Colloid Polym. Sci.*, 1995, 273, 626.
8. Yamakawa, H. and Fujii, M., *Macromolecules*, 1974, 7, 128.
9. Lavrenko, P. N., *Colloid Polym. Sci.*, 1996, 274, 640.
10. Lavrenko, P. N., *Polymer Comm.*, 1996, 37, 4409.
11. Kamide, K. and Saito, M., *Polymer J.*, 1982, 14, 517.
12. Scherf, U. and Müllen, K., *Makromol. Chem. Rapid Comm.*, 1991, 12, 489.
13. Scherf, U., Bohnen, A. and Müllen, K., *Makromol. Chem.*, 1992, 193, 1127.
14. Hickl, P., Ballauff, M., Scherf, U., Müllen, K. and Lindner, P., *Macromolecules*, 1997, 30, 27.
15. Bushin, S. V., Tsvetkov, V. N., Lysenko, E. B. and Emel'anov, V. N., *Vysokomol. Soedin.*, 1981, (A)23, 2494.
16. Bohdanecky, M., *Macromolecules*, 1983, 16, 1483.
17. Tiesler, U., Pulina, T., Rehahn, M. and Ballauff, M., *Mol. Cryst. Liq. Cryst.*, 1994, 243, 299.
18. Tiesler, U., Rehahn, M., Ballauff, M., Petekidis, G., Vlassopoulos, D., Maret, G. and Kramer, H., *Macromolecules*, 1996, 29, 6832.
19. Petekidis, G., Vlassopoulos, D., Galda, P., Rehahn, M. and Ballauff, M., *Macromolecules*, 1996, 29, 8948.
20. Vanhee, S., Rulkens, R., Lehmann, U., Rosenauer, C., Schulze, M., Köhler, K. and Wegner, G., *Macromolecules*, 1996, 29, 5136.
21. Galda, P., Kistner, D., Martin, A. and Ballauff, M., *Macromolecules*, 1993, 26, 1595.
22. Matsumoto, A., Tarui, T. and Otsu, T., *Macromolecules*, 1990, 23, 5102.
23. Laivins, G. V. and Gray, D. G., *Macromolecules*, 1985, 18, 1746.
24. Bianchi, E., Ciferri, A., Preston, J. and Krigbaum, W. R., *J. Polym. Sci. Phys. Ed.*, 1981, 19, 863.
25. Bi, X., Ying, Q. and Qian, R., *Makromol. Chem.*, 1992, 193, 2905.
26. Tsuboi, A., Yamasaki, M., Norisuye, T. and Teramoto, A., *Polymer J.*, 1995, 27, 1219.
27. Crob, M. C., Schurtenberger, P. and Suter, U. W., *Macromol. Chem. Phys.*, 1995, 196, 1391.
28. Itou, T., Chikiri, H., Teramoto, A. and Aharoni, S. M., *Polymer J.*, 1988, 20, 143.