Relation between the quality of the solvent and the number of statistical segments of a polymer at the onset of excluded-volume and complete excluded-volume behaviour

Anastasios Dondos
Department of Chemical Engineering, University of Patras, 26110 Patras, Greece
(Received 8 July 1991; revised 15 November 1991; accepted 23 January 1992)

The characteristic numbers of polymers N_c (number of statistical segments at the onset of excluded-volume behaviour) and N'_c (number of statistical segments at the onset of complete excluded-volume behaviour) have been related to the quality of the solvent for many polymer–solvent systems. This relation has been established either by direct experimental determination (crossover points in the $\log[\eta]$ *versus* $\log M$ representation) or using Han's equation. Exponential equations are presented that give the relation between N_c or N'_c and the quality of the solvent as expressed by the Mark–Houwink–Sakurada exponent.

(Keywords: polymer solutions; characteristic numbers; statistical segments; solvent quality; blob theory)

INTRODUCTION

The linearity between $\log[\eta]$ and $\log M$, which is predicted by the Mark–Houwink–Sakurada (MHS) equation for polymers dissolved in good solvents, is apparent only above a given molecular weight (M'_c). Below this molecular weight the points of the $\log[\eta]$ *versus* $\log M$ representation lie on a curve that presents a continuously decreasing slope. At another characteristic molecular weight (M_c) the curve presents a slope equal to 0.5 (Gaussian behaviour). Between these two molecular weights the polymers present a crossover region characterized by a continuous variation of the exponent a in the MHS equation. In other words, this crossover region starts at the onset of excluded-volume behaviour (for $M \geqslant M_c$ we have $a \geqslant 0.5$) and ends at the onset of complete excluded-volume behaviour (for $M \geqslant M'_c$ we have linearity between $\log[\eta]$ and $\log M$).

We have shown[1,2] that the numbers of statistical segments at the limits of the crossover region, N_c and N'_c (N_c corresponds to M_c and N'_c to M'_c), are the same for different polymers if these polymers are dissolved in solvents in which they present the same solubility (same value of the MHS exponent). This same number of statistical segments at the onset of excluded-volume behaviour ($N_c = 4$ for different polymers dissolved in different good solvents for which we have $a \approx 0.73$) permits us to present in a universal manner the variation of the viscometric expansion factor α_η as a function of the number of blobs of the macromolecular chain[2,3]. The number of blobs of a macromolecular chain of molecular weight M or number of statistical segments N is given by the ratios M/M_c or N/N_c, because we consider that at the onset of excluded-volume behaviour, or at the point at which the polymer presents the characteristic number of statistical segments N_c, this chain consists of one blob.

In this article we will study the influence of solvent quality on the characteristic numbers N_c (or M_c) and N'_c (or M'_c), which delimit the crossover region of polymers. In other words we will establish relations between N_c or N'_c and the exponent a of the MHS equation. The determination of the values of N_c will be done either using the equation proposed by Han[4] or by a direct method based on the diagrams obtained for the variation of $\log[\eta]$ *versus* $\log M$. These diagrams will permit us to determine also the value of M'_c and consequently the characteristic number N'_c.

THEORETICAL BACKGROUND

Others have already presented[4,5] the variation of the polymer dimensions (expansion factor) as a function of the parameter N/N_τ, where N is the number of beats, or statistical segments, in the equivalent statistical chain in a given solvent and at a given temperature and N_τ is a temperature-dependent cut-off to separate Gaussian and excluded-volume regimes ($N_\tau = a/\tau^2$ with τ the reduced temperature and a an adjustable parameter). The ratio $N/N_\tau = \tau^2 M_w/anA$ expresses the number of blobs in the chain and depends on the reduced temperature τ, the adjustable parameter anA and the molecular weight of the chain.

If we now consider a series of fractions of a polymer dissolved in a given good solvent at a given temperature, we can replace the ratio N/N_τ by the ratio N/N_c, where N_c is the number of statistical segments of the polymer that corresponds to the molecular weight M_c in which we observe the onset of the excluded volume (N/N_τ is now a non-adjustable parameter).

The expression of the number of blobs in a macromolecular chain by the ratio N/N_c and the relation of the chain dimensions with this ratio is expressed theoretically in the work of Weill and des Cloizeaux[6].

0032-3861/92/204375-04

Using the relation proposed by de Gennes *et al.*[7] and the dynamic agreements of Weill and des Cloizeaux[6] for the intrinsic viscosity, Han[4] proposes the following equation, relating the viscometric expansion factor α_η of a chain with the parameter N/N_c:

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

In fact, the above equation differs from the original equation of Han by the substitution of the adjustable parameter N/N_τ by the non-adjustable parameter N/N_c (refs. 2, 3) where N_c is the number of statistical segments at the cut-off point (onset of excluded-volume behaviour in the plot of $\log[\eta]$ *versus* $\log M$ in a polymer–solvent system, as has already been pointed out). In other words we accept that both ratios N/N_c and N/N_τ give the number of blobs in the chain, but the first ratio is a consequence of the 'distance' of the chain from the equivalent chain presenting the critical molecular weight M_c (N_c statistical segments), while the second ratio is a consequence of the 'distance' of the chain from the θ temperature.

More precisely, in the case of polymer–solvent systems for which we have an exponent in the MHS equation that lies near the value of 0.73, we have shown that the macromolecular chain at the onset of excluded-volume behaviour (M_c) consists of four statistical segments ($N_c=4$)[1,2], and consequently, with $\nu=0.5766$, from equation (1) we obtain:

$$\alpha_\eta^3 = 0.71(N/4)^{0.23} \quad (2)$$

The experimental results for a great number of polymer–solvent systems obey the following equation[2]:

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

Having now confirmed the validity of equation (1), we will use that in this work in order to determine the value of N_c for a given polymer–solvent system, knowing the value of ν of this system and the values of α_η and N of different fractions of the polymer in the given solvent.

TREATMENT OF THE VISCOMETRIC RESULTS

The viscometric results have mostly been taken from the literature or from our previous work. For each polymer–solvent system we have first determined the value of the exponent a in the MHS equation by plotting $\log[\eta]$ *versus* $\log M$. The value of a is obtained from the linear part of the MHS curve. In other words the value of a is obtained by taking into account the molecular-weight region in which we have complete excluded-volume behaviour. Without taking into account the low-molecular-weight region, we obtain for some polymer–solvent systems values for a that are higher than the values given in the corresponding articles. From the value of a we calculate the value of the excluded-volume index ν ($a=3\nu-1$).

Using the same viscometric results from the same polymer–solvent systems and applying the well known Stockmayer–Fixman–Burchard[8,9] equation, we obtain the unperturbed dimensions parameter K_θ of each polymer. In the case of very high values of the viscometric expansion factor α, in order to obtain K_θ, we use a modified Stockmayer–Fixman equation of the form[10]:

$$[\eta]/M^{1/2} = 1/A_1 + (A_2/A_1^2)M^{1/2}(1-DM^{1/2}) \quad (4)$$

In this equation D is related to the exponent a of the MHS equation via $D=12\times10^{-4}\ (a-0.5)$ and $1/A_1$ is equal to K_θ.

Knowing the value of K_θ of a polymer, we calculate the values of $[\eta]_\theta$ of each fraction of this polymer ($[\eta]_\theta=K_\theta M^{1/2}$), and in the following the value of α_η^3 of the fraction ($\alpha_\eta^3=[\eta]/[\eta]_\theta$).

The value of the number of statistical segments N, of which a fraction of a polymer consists, is obtained by dividing the molecular weight of this fraction by the molecular weight m_s of its statistical segment. The value of m_s is obtained from the statistical segment length A and the molecular weight per unit length M_L ($m_s=AM_L$). The value of the Kuhn statistical segment length A is obtained from the value of K_θ and using the following equation:

$$A=(K_\theta/\phi_0)^{2/3}M_L$$

The value of ϕ_0 is obtained as 2.6×10^{23}.

Now, for a given polymer–solvent system, knowing the value of the excluded-volume index ν, the number of statistical segments N of which each fraction of the polymer consists and the viscometric expansion factor α_η^3 of the fractions, we can use equation (1) to obtain the value of the characteristic number N_c of the given polymer in the given solvent. For all polymer–solvent systems the polymer fractions that are taken into account present a molecular weight higher than the molecular weight from which we have the onset of linearity between $\log[\eta]$ and $\log M$.

RESULTS AND DISCUSSION

Using the procedure that we have described above, we have obtained for 19 polymer–solvent systems the values of N_c that we present in *Table 1*. In this same table are given values of a, K_θ, A and m_s. These values permit us to calculate for each fraction of the polymer for the polymer–solvent systems of *Table 1* the values of α_η^3 and N. Introducing α_η^3 N and ν in equation (1) we have calculated the values of N_c. For each polymer–solvent system the value of N_c is a mean value obtained with the different fractions of the polymer.

In *Figure 1* we present the variation of N_c as a function of the exponent a of the MHS equation for the polymer–solvent systems of *Table 1*. For a value of a that tends to 0.5, N_c tends to very high values, as predicted from the scaling theory (the macromolecular chain consists of one blob). In contrast, when the solvent is a very good solvent for the polymer the blobs in the macromolecular chain consist of a low number of statistical segments ($N_c\approx1.8$ for $a=0.83$). For a value of a equal to 0.73 we calculate a value of N_c, which lies near the value of 4; this value was obtained directly by plotting $\log[\eta]$ *versus* $\log M$ (ref. 1).

In the following we have determined directly values of N_c for four polymer–solvent systems by plotting $\log[\eta]$ *versus* $\log M$. As already mentioned[1] the crossover point between Gaussian and excluded-volume behaviour in the $\log[\eta]$ *versus* $\log M$ curve, which gives the value of N_c, is not determined with good accuracy. Nevertheless the experimental values of N_c fit quite well the curve obtained with values of N_c calculated *via* equation (1) (*Figure 1*).

The curve of *Figure 1* is expressed by the equation:

$$N_c=0.37a^{-7.7} \quad (5)$$

Now plotting the variation of $\log[\eta]$ *versus* $\log M$ for

Table 1 Exponent a of the MHS equation, unperturbed dimensions parameter K_θ, statistical segment length A, statistical segment mass m_s and characteristic number N_c for some polymer–solvent systems

System[a]	a	$K_\theta \times 10^2$	A (Å)	m_s	N_c	Ref.
PMMA–$CHCl_3$	0.83	5	13.3	533	1.8	11
PP–decalin (135°C)	0.79	12	10.15	173	2.6	12
PS–$CHCl_3$	0.78	8.2	19.45	817	4	1
PMMA–benzene	0.74	6.5	15.9	635	4	13
PS–toluene	0.735	8.2	19.45	817	4	14
PS–toluene	0.73	9	20.7	869	4.3	15
PS–dioxane	0.71	8.4	19.8	830	3.8	Our work
PS–benzene (10°C)	0.705	12	25.1	1053	5.4	16
PS–1,2-dichloroethane	0.7	9	20.7	869	4.9	15
PBu–cyclohexane (25°C)	0.7	19	10.5	135	6.2	17
POE–benzene (37°C)	0.69	16.5	12.4	193	3.6	18
POE–benzene (25°C)	0.675	22	13.9	215	8.2	19
POE–CCl_4	0.67	18	12	188	6.3	20
POE–acetone	0.66	16.8	11	170	10.5	20
PS–cyclohexane (50°C)	0.64	7.9	19	797	12.8	21
PS–methyl ethyl ketone	0.635	7.9	19	797	13.6	15
PS–*cis*-decalin	0.6	9	20.7	869	17.3	14
PP–3-nonanol	0.56	15.8	12.1	206	40.5	22
PMMA–consolute solvent	0.55	8.5	18.95	758	38	11
PS–$CHCl_3$	0.78				3	1
PS–CCl_4	0.73				3.8	1
PDMS–toluene	0.68		direct determination		6.5	23
POE–H_2O	0.64				9	18
PS–cyclohexane (50°C)	0.58				25	24
PS–cyclohexane (40°C)	0.54				62	24

[a] Polymers are: PMMA, poly(methyl methacrylate); PP, polypropylene; PS, polystyrene; PBu, polybutadiene; POE, polyoxyethylene; PDMS, polydimethylsiloxane

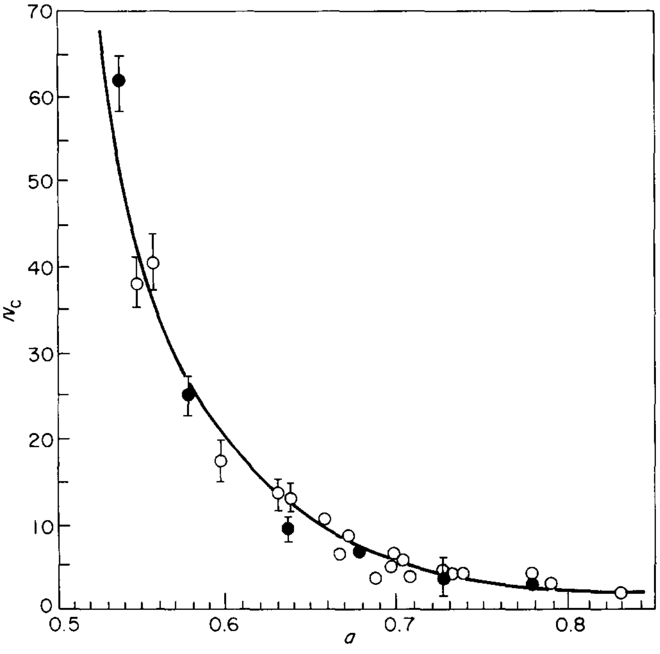

Figure 1 Relation between the characteristic number N_c and the exponent a of the MHS equation. The N_c values that are directly determined are shown as full circles

10 polymer–solvent systems, we have determined the second characteristic number N'_c. This number is the number of statistical segments of the macromolecular chains at the onset of linearity between log[η] and log M. In other words N'_c corresponds to M'_c, at which we have the end of the crossover region, and the chain contains a sufficient number of blobs to exhibit excluded-volume statistics on a macroscopic scale. The accuracy of the determination of N'_c is not very good and for this reason the presentation, in *Figure 2*, of the points for N'_c *versus* the MHS exponent a are given with error bars. The obtained curve is expressed by the equation:

$$N'_c = 437a^{8.5} \tag{6}$$

For a value of a that lies between 0.85 and 0.9, N'_c tends to very high values, and this indicates that for $a > 0.85$ the polymers do not present complete excluded-volume behaviour, even in the region of very high molecular weights.

In the case of the system polyacrylamide–water, which presents an exponent in the MHS equation higher than that of ideal systems, Weill *et al.*[25] find that at the onset of complete excluded-volume behaviour the number of blobs is higher than in ideal systems, and this means that the number of statistical segments N'_c is higher.

CONCLUSIONS

Using an equation derived from the scaling theory as well as a direct method, we have determined the characteristic number N_c (number of statistical segments at the onset of excluded-volume behaviour) and the characteristic number N'_c (number of statistical segments at the onset of complete excluded-volume behaviour). These two numbers depend on the quality of the solvent as expressed by the exponent in the MHS equation.

The two characteristic numbers, N_c and N'_c, which delimit the crossover region in the log[η] *versus* log M plot, change in an opposite manner with the quality of the solvent. When the exponent of the MHS equation presents a value near the value of 0.6, the two numbers tend to coincide and the crossover region becomes a crossover point.

In the case of polymer–solvent systems in which the

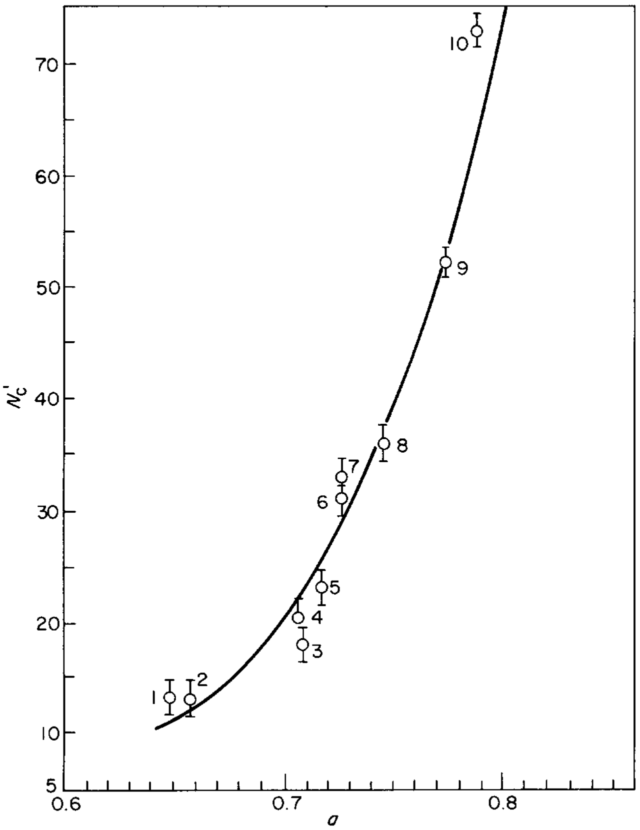

Figure 2 Relation between the characteristic number N'_c and the exponent a of the MHS equation for the following systems: (1) PS-benzene+10% methanol; (2) POE–CCl_4; (3) poly(p-trimethylsilylstyrene)–tetrahydrofuran; (4) poly(α-methylstyrene)–toluene; (5) PS–dioxane; (6) PS–benzene; (7) PS–toluene; (8) poly(p-cyclohexylstyrene)–toluene; (9) PS–$CHCl_3$; (10) PMMA–n-butyl acrylate

solvent is an ideal good solvent for the polymer ($a = 0.73$), the polymers present a value for N_c equal to 4 and a value for N'_c equal to 32. This second number of statistical segments indicates that the MHS equation is valid for a polymer dissolved in an ideal good solvent only when this polymer presents a molecular weight higher than M'_c, which corresponds to 32 statistical segments. It is evident that for a polymer presenting a high rigidity (high value of the statistical segment molecular weight m_s) we need a high molecular weight ($M'_c = 32m_s$) in order for the MHS equation to be valid ($M'_c = 4320$ for PBu and $M'_c = 26000$ for PS (*Table 1*), and $M'_c = 175000$ for poly[2-(triphenylmethoxy)ethyl methacrylate][1]).

REFERENCES

1 Dondos, A. *J. Phys. (Fr.)* 1987, **48**, 1439
2 Dondos, A. *J. Polym. Sci., Polym. Phys. Edn.* 1990, **28**, 2435
3 Dondos, A. *Polym. Commun.* 1987, **28**, 280
4 Han, C. C. *Polymer* 1979, **20**, 1083
5 Akcasu, A. Z. and Han, C. C. *Macromolecules* 1979, **12**, 276
6 Weill, G. and des Cloizeaux, J. *J. Phys. (Fr.)* 1979, **40**, 99
7 Farnoux, B., Boue, F., Cotton, J. P., Daoud, M., Jannink, G., Nierlich, M. and de Gennes, P. G. *J. Phys. (Fr.)* 1978, **39**, 77
8 Stockmayer, W. H. and Fixman, M. *J. Polym. Sci. (C)* 1963, **1**, 137
9 Burchard, W. *Makromol. Chem.* 1961, **50**, 20
10 Dondos, A. and Benoît, H. *Polymer* 1978, **19**, 523
11 Chinai, S. N., Matlack, J. D., Resnick, A. L. and Samuels, R. J. *J. Polym. Sci.* 1955, **17**, 391
12 Yamaguchi, K. *Makromol. Chem.* 1969, **128**, 19
13 Cohn-Ginsberg, E., Fox, T. G. and Masson, H. F. *Polymer* 1962, **3**, 97
14 Kulicke, W. M. and Prescher, M. *Makromol. Chem.* 1984, **185**, 2619
15 Nakata, M. *Makromol. Chem.* 1971, **149**, 99
16 Matsushita, Y., Nakao, Y., Shimizu, K., Noda, I. and Nagasawa, M. *Macromolecules* 1988, **21**, 2790
17 Roovers, J. and Martin, J. E. *J. Polym. Sci., Polym. Phys. Edn.* 1989, **27**, 2513
18 Elias, H. G. *Makromol. Chem.* 1967, **103**, 214
19 Allen, G., Booth, C., Hurst, S. J., Jones, M. N. and Price, C. *Polymer* 1967, **8**, 391
20 Beech, D. R. and Booth, C. *J. Polym. Sci. (A-2)* 1969, **7**, 575
21 Gundert, F. and Wolf, B. A. *Makromol. Chem.* 1986, **187**, 2969
22 Mays, J. W. and Fetters, L. J. *Macromolecules* 1989, **22**, 921
23 Rubio, A. M., Freire, J. J. and de la Tore, J. G. *Macromolecules* 1987, **20**, 1619
24 Tsitsilianis, C. Thesis, University of Patras, 1987
25 François, J., Schwartz, T. and Weill, G. *Macromolecules* 1980, **13**, 564