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Towards a concrete concept of the blob model for polymers in dilute solution

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Plotting the logarithm $R_G/N_c^{1/2}$ as a function of the logarithm of the number of the blobs of the chain, N/N_c, one obtains straight lines according to an equation derived from the blob theory (R_G is the radius of gyration of a polymer containing N statistical segments and N_c is the number of statistical segments of which one blob consists and which depends only on the quality of the solvent). Extrapolating these straight lines, obtained with different linear polymers dissolved in different solvents, to $\log(N/N_c) = 0$ or $N = N_c$ one obtains the expansion of the chains in the interior of the blob $(R_G/N_c^{1/2})_b$. This expansion is found, for a given polymer, to be the same as the expansion of this polymer in Θ conditions $R_{G0}/N^{1/2}$. This result indicates that the chain inside the blob obeys Gaussian statistics. Copyright © 1996 Elsevier Science Ltd.

(Keywords: blob theory; radius of gyration; dimensions of blob)

INTRODUCTION

Over the last few years we have tried to convert the blob theory into a more quantitative theory in order to characterize polymers in solution. We have proposed a relationship which gives the number of statistical segments constituting one blob of the linear polymers[1]. This number depends only on the quality of the solvent and it is independent of the nature of the polymer. Moreover we have determined, with two different methods [2,3], the adjustable parameter $n\alpha$, of the thermal blob theory, relating the number of blobs to the Θ temperature and the molecular mass of the chain. A mean value of $n\alpha$ equal to 10 is obtained using a large number of polymer–solvent systems, for which we know the Θ temperature. Knowing the number of statistical segments of which one blob consists and comparing relationships derived from both the two parameter theory[4] and the blob theory[5], an equation was proposed[6] which gives the unperturbed dimensions parameter, K_Θ, of a polymer and its dependence on the Mark–Houwink–Sakurada equation constants K and a. This combination of equations derived from the blob theory and two parameters theory also leads to the determination of the adjustable parameter [7] relating the number of blobs of a macromolecular chain to its excluded volume parameter z. Knowing this parameter we have proposed an equation which gives the interaction parameter, B, of a polymer in a given solvent as a function of the statistical segment length of the polymer and of the number of statistical segments of which the polymer blob consists in the given solvent[7]. The values of B are tested using the Stockmayer–Fixman representation[8].

The above results have been obtained on the basis of the following assumption. The division of a macromolecular chain of a given polymer, of molecular mass M at a temperature T, into N/N_c or N/N_τ blobs (N is the number of statistical segments of this chain and N_c or N_τ is the number of the statistical segments of which one blob consists) is the consequence of its 'distance' from two points. The first 'distance' is from a molecular mass M_c of the same polymer, which corresponds to the onset of excluded volume behaviour in the same solvent and at the same temperature and which consists of only one blob containing N_c statistical segments (this 'distance' means how much longer is the chain of N statistical segments compared to the chain of N_c and which leads to a division of the former chain into N/N_c 'molecular' blobs). The second 'distance' is from the Θ temperature, at which this same chain of molecular mass M and containing N statistical segments consists of only one blob encompassing the entire number of its statistical segments N (this second 'distance', which leads to a division of the chain into N/N_τ 'thermal' blobs, means how much higher is the temperature in which the chain is found compared to the Θ temperature and it is expressed by the reduced temperature τ). It was shown[1] that $N_c = N_\tau$ for a great number of flexible polymers, in any condition, and consequently we have $N/N_c = N/N_\tau$.

In this present paper, using a great number of viscometric and light scattering results, we demonstrate that the ratio of the radius of gyration of the polymer blob to the square root of the number of its statistical segments, when this polymer is dissolved in a good solvent, is the same as the ratio of the radius of gyration of the entire chain of the polymer to the square root of its statistical segments when this polymer is dissolved in a Θ solvent. This result indicates that inside of the blob the macromolecular chain obeys Gaussian statistics as predicted by the blob theory[5].

THEORY AND PROCEDURE

At the cut-off point separating Gaussian and excluded volume behaviour, the macromolecular chain, according to the blob theory[5], consists of only one blob. In the $\log[\eta]$ *versus* $\log M$ representation (Mark–Houwink–Sakurada (MHS) equation) this point corresponds to the molecular mass where the exponent a of the MHS equation becomes higher than 0.5. Investigating a large number of polymer–solvent systems we have observed that while the molecular mass, M_c at the onset of excluded volume behaviour is different for different polymers, the number of statistical segments of these polymers at this point, n_c, on the contrary, is the same if the polymers are dissolved in solvents of the same quality[9]. This characteristic number of statistical segments, N_c, of which one 'molecular' blob consists, increases, for the same polymer, when the quality of the solvent decreases.

The following equation has been proposed by Han[10] for the viscometric expansion factor of a chain containing N/N_τ 'thermal' blobs that is found in solution in a solvent which presents an excluded volume index $\nu(3\nu - 1 = a)$:

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

Using equation (1) we have calculated for different polymer–solvent systems the characteristic number N_τ of which one 'thermal' blob consists. These calculations have been performed with different values of the excluded volume index ν and it was found[1] that the calculated value of N_τ from equation (1) and the directly determined value[9] of N_c coincide if the quality of the solvent is the same (same value of τ or a of the MHS equation). The dependence of N_τ or N_c on the quality of the solvent, expressed by the exponent a of the MHS equation, is given by the relationship[1]

$$N_c = N_\tau = 0.37a^{-7.7} \qquad (2)$$

Another relationship has been proposed[11,12] between the expansion of a macromolecular coil containing N statistical segments, expressed by the ratio of its radius of gyration to the square root of the number of statistical segments of which one blob consists, $R_G/N_c^{1/2}$, as a function of the number of blobs of the coil N/N_c:

$$\frac{R_G}{N_c^{1/2}} = b\left[\frac{2\nu-1}{2(2\nu+1)}\left(\frac{N}{N_c}\right)^{-1} - \frac{2\nu-1}{3(2\nu+2)}\left(\frac{N}{N_c}\right)^{-2} + \frac{1}{(2\nu+1)(2\nu+2)}\left(\frac{N}{N_c}\right)^{2\nu}\right]^{1/2} \qquad (3)$$

In the present paper we will apply this equation taking into account, from the right-hand side terms, only the term containing the ratio N/N_c. The other two terms containing the ratio N_c/N will be ignored because $N \gg N_c$. The value of N_c will be obtained from equation (2).

Plotting $\log(R_G/N_c^{1/2})$ *versus* $\log(N/N_c)$ we obtain according to equation (3) for different polymer–solvent systems, different straight lines with a slope equal to ν. The extrapolation to $\log(N/N_c) = 0$ must give the expansion of the blob of the chain of a given polymer, because in the limit, $N = N_c$, the chain consists of only one blob. In other words, the ratio $(R_G/N_c^{1/2})_b$ when $N = N_c$ gives the expansion of the chain inside the blob and this expansion must be in the Gaussian state as predicted by the blob theory[5]. For this same polymer in Θ conditions the ratio $R_{G0}/N^{1/2}$, where N is the total number of the statistical segments of the chain and R_{G0} is its radius of gyration in these conditions, which must be the same as the ratio $(R_G/N_c^{1/2})_b$ because in Θ conditions the chain also obeys Gaussian behaviour and consists of only one blob. This equality between these two ratios will be demonstrated in this work.

In order to apply equations (2) and (3) we calculate the necessary parameters as follows. For a given polymer–solvent system we analyse the viscometric results plotting $\log[\eta]$ *versus* $\log M$ in order to obtain the value of the exponent a of the MHS equation or the value of excluded volume index ν $(a = 3\nu - 1)$. The value of the statistical segment N of which one fraction of this polymer consists is obtained by dividing its molecular mass by the molecular mass m_s of a statistical segment. The value of m_s is obtained by multiplying the statistical segment length A by the ratio of the molecular mass to the contour length of the polymer M_L (in this work we use the Kuhn statistical segment expressed in Å). The statistical segment length will be obtained from the following equation:

$$A = \left(\frac{K\theta}{\Phi}\right)^{2/3} M_L \qquad (4)$$

where Φ is Flory's constant and K_Θ the unperturbed dimensions parameter. The parameter K_Θ is obtained by the Stockmayer–Fixman–Burchard (SFB) equation[8,13]:

$$[\eta]/M^{1/2} = K_\Theta + 0.287\Phi BM^{1/2} \qquad (5)$$

or directly if the intrinsic viscosity $[\eta]_\Theta$ of the polymer in Θ conditions is known $(K_\Theta = [\eta]_\Theta/M^{1/2})$. The value of Φ is 2.6×10^{23} (in cgs). The values of M_L are known for most of the polymers investigated or they will be calculated using the Flory method[14]. The viscometric expansion factor a_η of a polymer fraction with a molecular mass equal to M and having an intrinsic viscosity $[\eta]$ will be obtained from the relationship $a_\eta^3 = [\eta]/K_\Theta M^{1/2}$ or by $a_\eta^3 = [\eta]/[\eta]_\Theta$ if the intrinsic viscosities of the fractions of the polymer in a given solvent, $[\eta]$, and in Θ conditions, $[\eta]_\Theta$, are known.

TREATMENT OF THE EXPERIMENTAL RESULTS

The experimental results used in order to apply equation (3) are taken from the literature. In some cases the values of a or K_Θ are slightly different from the values given in the studies from which the viscometric results are obtained. This is due to the fact that we apply the MHS and SFB equations only in the molecular weight regions in which these equations are valid[15]. The values obtained for the number of statistical segments of which one blob consists N_c (from equation (2) and knowing the value of a), the statistical segment length A and the statistical segment mass m_s for eight polymer–solvent systems are given in *Table 1*.

Figure 1 shows $\log(R_G/N_c^{1/2})$ *versus* $\log(N/N_c)$ for

Table 1 Values of the various parameters of the studied polymer–solvent systems

System	a	N_c	$K_\Theta(\times 10^2)^a$	A (Å)	m_s	$R_{G0}/N^{1/2\,b}$	$(R_G/N_c^{1/2})_b$	Reference
PS–toluene	0.725	4.4	8.2	19.4	815	8.2	8.2	16–18
PS–cyclohexane (44.5°C)	0.608	17	8.2	19.4	815	8.2	8.1	16
PP–α-chloronaphthalene (145°C)^c	0.8	2.06	12	10	168	—	8.5	19,20
PαMS–toluene^d	0.72	4.6	7.8	21	992	8.9	8.5	21–23
PpBrS–monochlorobenzene^e	0.69	6.45	5	24.3	1779	10	10	24
PMMA–CHCl_3	0.82	1.7	4.5	12.4	496	10.5	10	25,26
PpmS–toluene^f	0.74	3.75	7.3	20.2	954	9.1	8.9	27
PpmS–MEK	0.65	10.2	7.3	20.2	954	9.1	9.1	27

[a] K_Θ in ml g$^{-3/2}$ mol$^{1/2}$
[b] R_{G0} and R_g in Å
[c] PP, polypropylene
[d] PαMS, poly(α-methylstyrene)
[e] PpBrS, poly(p-bromostyrene)
[f] PpmS, poly(p-methylstyrene)

three systems: polypropylene (PP)–α-chloronaphthalene (curve A), polystyrene (PS)–toluene (curve B) and PS–cyclohexane (45°C) (curve C). For the fractions of PS we have calculated the ratio $R_{G0}/N^{1/2}$, where R_{G0} is their radius of gyration in Θ conditions and N is their statistical segments; the mean value of these ratios is given in *Table 1*. The value of log ($R_{g0}/N^{1/2}$) for the PS is indicated by an arrow in *Figure 1* (all the values of radius of gyration are given in Å). In *Figure 2*, equation (3) is applied for the following systems: poly(methyl methacrylate)–CHCl_3 (curve A), poly(p-bromostyrene)–monochlorobenzene (curve B) and poly(α-methylstyrene)–toluene (curve C). For these three polymers we have also calculated the values of $R_{G0}/N^{1/2}$ and these values are given in *Table 1* and are indicated in *Figure 2* by arrows. In *Figure 3* the variation of log ($R_G/N_c^{1/2}$) as a function of log (N/N_c) is shown for the poly(p-methylstyrene) in solution in toluene (curve A) and MEK (curve B). In this figure the ratio of the radius of gyration of the polymer in Θ conditions to the square root of its statistical segments is also indicated by an arrow.

For most of the systems investigated, the experimental

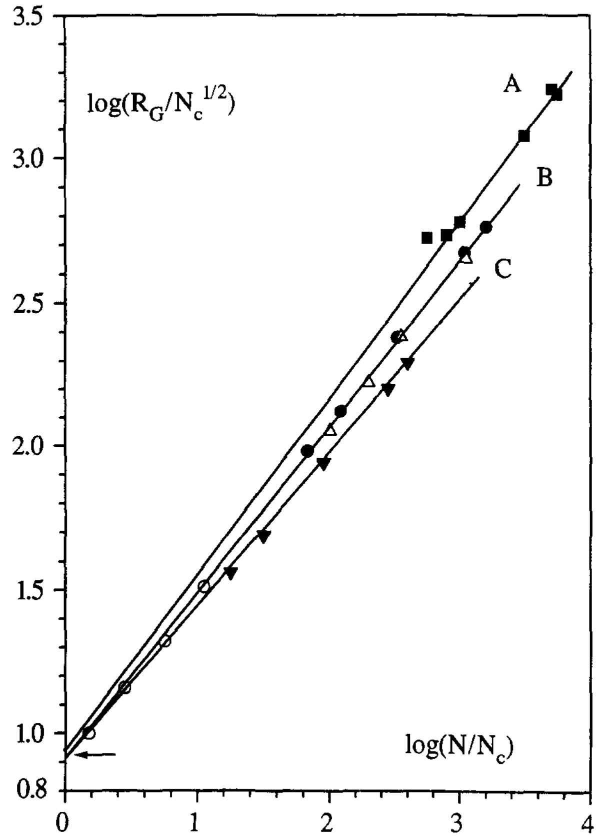

Figure 1 Log($R_G/N_c^{1/2}$) *versus* log (N/N_c) for the systems polypropylene–α-chloronaphthalene (145°C) (curve A), polystyrene–toluene (curve B) and polystyrene–cyclohexane (45.5°C) (curve C). The arrow indicates the log ($R_{G0}/N^{1/2}$) value (Θ conditions) of PS[16]. The values of R for the PS–toluene system are obtained from ref. 16 (●), ref. 17 (△) and ref. 18 (○)

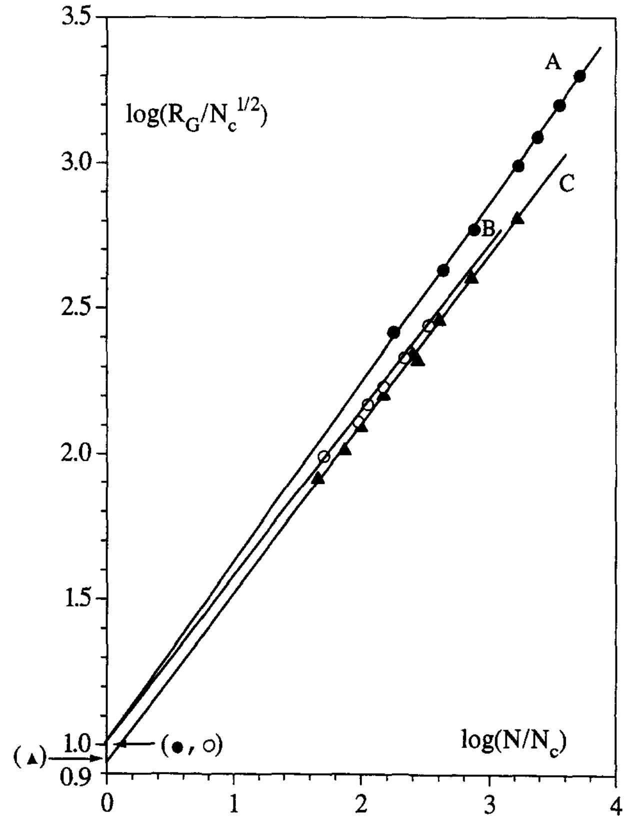

Figure 2 Log($R_G/N_c^{1/2}$) *versus* log (N/N_c) for the systems poly(methyl methacrylate)–CHCl_3[25,26] (curve A), poly(p-bromostyrene)–monochlorobenzene[24] (curve B) and poly(α-methylstyrene)–toluene[21–23] (curve C). The arrows indicate the log ($R_{G0}/N^{1/2}$) value (Θ conditions) of the polymers

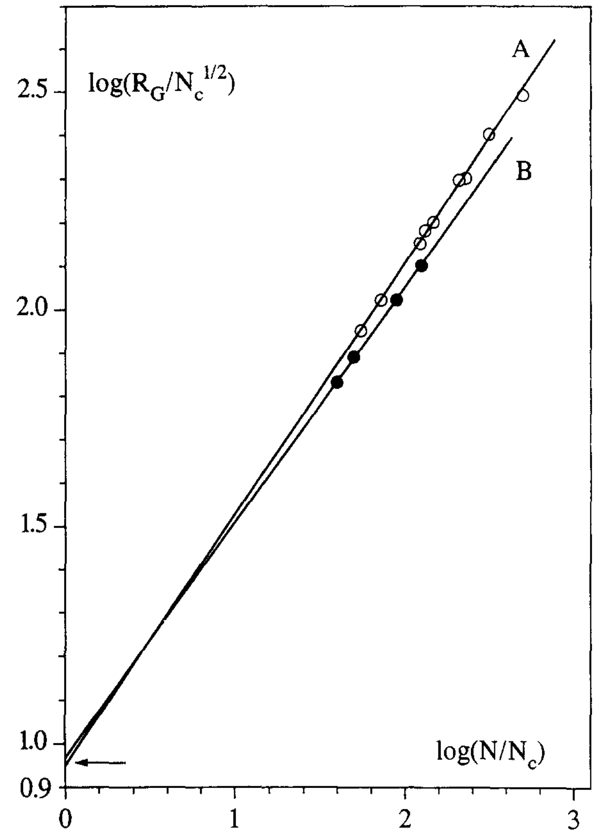

Figure 3 $\text{Log}(R_G/N_c^{1/2})$ *versus* $\log(N/N_c)$ for the systems poly(*p*-methylstyrene)–toluene (curve A)[27] and poly(*p*-methylstyrene)–MEK[27] (curve B). The arrow indicates the $\log(R_{G0}/N^{1/2})$ value (Θ conditions) of the polymer

points used in the construction of the straight lines (*Figures 1–3*) correspond to high molecular masses and therefore lie far from the intercept. In spite of this, the accuracy of the measurements allows for a very accurate extrapolation to the intercept.

We must indicate that in most cases the viscometric results from which the values of a, A and m_s are calculated are obtained not from the same sources from which we have obtained the values of the radius of gyration in good and in Θ solvents. The sources of the viscometric results and the sources from which the values of R_G are obtained are given in *Table 1*.

DISCUSSION AND CONCLUSION

For all the polymer–solvent systems investigated here we obtain straight lines when plotting $\log(R_G/N_c^{1/2})$ *versus* $\log(N/N_c)$ in accordance with equation (3) (*Figures 1–3*). The slopes of these lines are almost identical with the excluded volume index ν as is predicted by equation (3). Let us indicate that for PS in toluene the slope of the straight line of *Figure 1* is 0.58 while for this system the value of ν from the MHS representation is 0.575. For the system PS–cyclohexane (44.5°C) the slope of the straight line in *Figure 1* is 0.533 while ν for this system is 0.536.

The extrapolation of all these straight lines to $\log(N/N_c) = 0$ gives the ratio of radius of gyration to the square root of the number of statistical segments of the blob $(R_G/N_c^{1/2})_b$. As we have already pointed out, for $\log(N/N_c) = 0$ or $N = N_c$ the macromolecular chain of a given polymer consists of only one blob ('molecular' blob) and must show a Gaussian behaviour. If the macromolecular chain of this same polymer containing now N statistical segments ($N \gg N_c$) is found under Θ conditions, it consists also of only one blob and obeys Gaussian statistics. Knowing the radius of gyration of the chain in Θ conditions, R_{G0}, and the number of its statistical segments N one can calculate the ratio $R_{G0}/N^{1/2}$. For all the systems investigated here this ratio is almost the same as the ratio $(R_G/N_c^{1/2})_b$ (*Table 1*) and this result is an argument in the favour of the blob model, which predicts that in the interior of a blob, consisting of N_c statistical segments, the macromolecular chain is found in its unperturbed state[5].

It should also be pointed out that the ratios $(R_G/N_c^{1/2})_b$ and $R_{G0}/N^{1/2}$ are almost the same for all non-polar polymers (the values lie near a mean value of 8.7, *Table 1*). For these same polymers, if one expresses their unperturbed dimensions by the ratio $R_{G0}/M^{1/2}$, then very different values are obtained[28]. This is another example of the universal behaviour of polymers in solution if the macromolecular chain length is expressed by the number of statistical segments instead of the molecular mass[9].

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