Molecular Weight and Temperature Dependence of Polymer Dimensions in Dilute Solution: Use of the Blob Theory in the Region of Effective Excluded Volume Indices

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ABSTRACT: Plotting the logarithm of the viscometric expansion factor α_η or the logarithm of the radius of gyration as a function of the logarithm of the number of blobs of the macromolecular chains, one obtains straight lines in the molecular weight region in which the effective excluded volume indices are observed. The same straight line is obtained with different polymers dissolved in different solvents if the quality of the solvents is the same for all of these polymers. On the contrary, different straight lines are obtained, even with the same polymer, when the quality of the solvents is different (different values of the exponent a in the Mark-Houwink-Sakurada equation or different values of the effective excluded volume indices). The straight lines are described by relations derived from the blob model and this claims in favor of the validity of this model even in the molecular weight region in which the excluded volume indices have not reached their asymptotic values. The adjustable parameter of the blob theory is also obtained in this work.

Introduction

The introduction by de Gennes of the blob concept in the description of macromolecular chains[1] has given a new interest in the study of these chains in both dilute solution and semidilute solution. As a consequence the expansion of the macromolecular chains has been related to the ratio N/N_τ which represents the number of blobs contained in the chain. In this ratio N is the number of statistical segments of the chain and N_τ is the number of statistical segments of which one blob consists. The division of a chain, found in solution at temperature T, into N/N_τ blobs is the consequence of its "distance" from the Θ temperature, as is expressed by the reduced temperature τ, [$\tau = (T - \Theta)/T$]. More precisely, one has $N_\tau = a/\tau^2$ where a is an adjustable parameter.[2]

I have shown[3,4] that one can also express the number of blobs of a polymer coil by the ratio N/N_c. In this ratio N_c is the characteristic number of statistical segments which comprise a chain of the studied polymer at the onset of the excluded volume behavior, at temperature T where this polymer is studied. In other words the division of the chain of molecular weight M containing N statistical segments, in N/N_c blobs, is the consequence of its distance from a chain of molecular weight M_c containing N_c statistical segments. The molecular weight M_c is directly determined[5] (molecular weight in the presentation of Mark-Houwink-Sakurada (MHS) where the exponent a becomes higher than 0.5) and the corresponding N_c is given without an adjustable parameter, in contrast to N_τ.

It was shown that N_c can also be obtained using the equations derived from the thermal blob theory yielding $N_c = N_\tau$.[6] This equality will lead in this article to the determination of the adjustable parameter which is necessary in order to obtain the number of blobs given by the ratio N/N_τ.

The principal aim of this article is to demonstrate that the formulas derived from the thermal blob theory are valid not only with the asymptotic values of both static and dynamic excluded volume indices ($\nu_G = \nu_D = 0.588$ or the exponent in the MHS equation equal to 0.764) but also in the molecular weight region in which the asymptotic values are not reached. In other words I work in the region in which the variation of the dimensions of the macromolecular chains as a function of their molecular weight experimentally obeys power laws (linearity in the MHS representation[7]) but the exponents of these laws are given by the effective and not the asymptotic values of the excluded volume indices. The experimental results will be presented according to the Weill-des Cloizeaux model[7] using static measurements (R_G) or according to the Han model,[8] derived from the previous model, using dynamic measurements ([η]). The dynamic results will be expressed by the viscometric expansion factor α_η^3 ($\alpha_\eta^3 = [\eta]/[\eta]_\Theta$), where $[\eta]_\Theta$ is the intrinsic viscosity in Θ conditions.

All the results presented in this article seem to indicate that the proposed blob model is valid beyond its restrictive assumptions. This has already been demonstrated in the case of the determination of the statistical segments at the onset of the excluded volume behavior, N_c, of different polymers dissolved in different solvents in which the MHS exponent lies between 0.5 and 0.82.[6]

Theoretical Part and Procedure

The theory predicts[9] that an isolated polymer coil in a good solvent is swollen with respect to the random walk configuration when the molecular weight M of this coil is sufficiently great. Below a given value M_c of the molecular weight the coil returns to a configuration which has the essential characteristics of a random walk. In this crossover point (critical molecular weight M_c) the coil changes its configuration and according to the blob theory for $M = M_c$ the coil consists of only one blob.[1]

I have shown that even the critical molecular weight M_c is different for different polymers although the number of statistical segments N_c corresponding to the molecular weight M_c is the same if the polymers are in solution in solvents in which the exponent of the MHS equation is the same.[5,6] This means that the number of statistical segments N_c of which one blob consists is the same for all polymers when they are found in solution in solvents which present the same solubility power for these polymers. The following equation has been proposed relating the number of statistical segments of one blob with the solvent power or the exponent a of the MHS equation[6]

$$N_c = 0.37a^{-7.7} \quad (1)$$

This relation is obtained by application of many visco-

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metric results to the following equation proposed by Han[8]

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

in which the viscometric expansion factor α_η of a given macromolecular chain is related to the excluded volume index ν (or the exponent $\underline{a}$ having $\underline{a} = 3\nu - 1$) and to the number of blobs of this chain given by the ratio N/N_τ, as I have already mentioned. Equation 2 is obtained from the relations proposed by de Gennes et al.[10] and the dynamic agreements of Weill and des Cloizeaux.[7]

Comparing the directly determined value of N_c and the obtained value of N_τ from eq 2, I have shown that these two numbers are the same.[6] Indeed, knowing, for a fraction of polymer, the values of α_η, N, and ν, I obtain, using eq 2, a value of N_τ which coincides with the value of N_c directly determined. N_c corresponds, as I have already mentioned, to the molecular weight M_c where the exponent in the MHS representation becomes higher than 0.5 (appearance of the excluded volume behavior). This direct determination of N_c has already been presented.[5] The result $N_c = N_\tau$ indicates that a polymer coil containing N statistical segments and found in solution in a solvent which, at a temperature T, has an exponent in the MHS equation higher than 0.5 presents a swelling (expressed by α_η) resulting either from its distance from the critical molecular weight M_c (N_c statistical segments) or from its distance from the Θ conditions.

In this article I will present the variation of the viscometric expansion factor α_η of different polymers either as a function of N/N_c ("molecular" blobs) or as a function of $M\tau^2$ ("thermal" blobs) ($M\tau^2$ express the ratio of N/N_τ because $N/N_\tau = M\tau^2/naM_o$, where na is an adjustable parameter and M_o is the molecular weight of the monomer). N_c will be given from eq 1 or it will be directly determined. It is evident that the representation of α_η as a function of $M\tau^2$ is only possible with the polymer–solvent systems in which the reduced temperature τ (or the Θ temperature) is known. By matching the obtained two straight lines using the above procedure and accepting that $N/N_c = N/N_\tau$ I will obtain the adjustable parameter na.

The viscometric expansion factor α_η of a fraction of a given polymer, presenting a molecular weight M, will be obtained by knowing its intrinsic viscosity, $[\eta]$, in the considered solvent and the unperturbed dimensions parameter K_Θ of the polymer in the same solvent ($\alpha_\eta^3 = [\eta]/[\eta]_\Theta = [\eta]/K_\Theta M^{1/2}$). The value of K_Θ (given here in mL g^{-1}) will be obtained using the Stockmayer–Fixman–Burchard (SFB) equation.[11,12] Sometimes the value of K_Θ used in this article is different from the proposed value in the article from which the viscometric results are obtained. This must be attributed to the fact that I apply the SFB equation only in the molecular weight regions in which this equation is valid.[13]

Using the well-known relation

$$A = (K_\Theta/\Phi)^{2/3} M_L \quad (3)$$

in which M_L is the molecular weight of the chain per unit length, I obtain the statistical segment length A (Kuhn segment). The value of Φ is taken equal to 2.6×10^{23}. Multiplying A by M_L I obtain the molecular weight of the statistical segment m_s. Dividing now the molecular weight of each fraction of a polymer by the m_s value of this polymer, I obtain the number N of statistical segments of which the fractions consist.

The macromolecular chain dimensions will also be expressed by the static radius of gyration, R_G, and also they will be presented as a function of the number of blobs N/N_c according to the Weill–des Cloizeaux formula[7]

$$\frac{R_G}{N_c^{1/2}} = \left[\frac{2\nu-1}{2(2\nu+1)}\left(\frac{N}{N_c}\right)^{-1} - \frac{2\nu-1}{3(2\nu+2)}\left(\frac{N}{N_c}\right)^{-2} + \frac{1}{(2\nu+1)(2\nu+2)}\left(\frac{N}{N_c}\right)^{2\nu}\right]^{1/2} \quad (4)$$

in which I take into account only the term containing N/N_c in the ν power.

I must point out that almost all the viscometric results presented in this work concern molecular weights which lie below the molecular weight at which the excluded volume indices reach their asymptotic value ($N/N_c < 3.4 \times 10^3$). In other words the curves presenting the variation of the expansion of the macromolecular chains as a function of the number of blobs are obtained in the region of effective indices.[7]

Treatment of the Experimental Results

The relation between α_η^3 or $R_G/N_c^{1/2}$ versus N/N_c or $M\tau^2$ is presented in this article separately for each polymer–solvent system or for a group of polymer–solvent systems presenting about the same exponent in the MHS equation. This exponent is determined from the molecular weight region in which there is a linear relationship between log $[\eta]$ and log M.

In Figure 1 I display the variation of log α_η^3 versus log (N/N_c) (molecular blobs, curve A) and versus log $M\tau^2$ (thermal blobs, curve B) for the system polystyrene (PS)–benzene which presents an exponent in the MHS equation equal to 0.73. According to eq 2 I must obtain straight lines. The viscometric results have been taken from different articles, as is indicated in the caption of Figure 1. Some viscometric results obtained by me with this system are also compared to the results taken from the literature. The ratio N/N_τ is given from the reduced blob parameter $M\tau^2$, and the value of the reduced temperature is obtained from the Θ temperature of this system (Θ = 113 K[17]). The value of the characteristic number of the statistical segments ($N_c = 4$) is obtained from eq 1, but also it is directly determined for this system.[5] Based on the already mentioned relation,

$$\frac{N}{N_c} = \frac{N}{N_\tau} = \frac{M\tau^2}{naM_o} \quad (5)$$

by matching curve B to curve A, I obtain naM_o equal to 1200 and with $M_o = 104$ for the PS I finally obtain a value for the adjustable parameter na equal to 11.5.

The PS in benzene reaches the power law at a molecular weight equal to 25 000[5,6,15] and at this molecular weight corresponds to 32 statistical segments. With $N_c = 4$ I obtain a number of blobs equal to 8 in the onset of the power law and, as can be seen in Figure 1, this number of blobs starts the linear relation between log α_η^3 and log (N/N_c) (arrow in Figure 1). This critical value of N/N_c is predicted by Weill and des Cloizeaux for the PS–benzene system.[7]

The slopes of the two straight lines of Figure 1 are equal to 0.235, while eq 2 with $\underline{a} = 0.73$ or $\nu = 0.5766$ predicts a value equal to 0.23. For the very high molecular weight fractions ($N/N_c > 3.4 \times 10^3$) it seems that the slopes of the straight lines A and B in Figure 1 become higher than 0.235. This must be attributed to the fact that in this domain of molecular weights even the dynamic index ν_D has reached its asymptotic value[7] and consequently the exponent in the MHS equation must be higher than 0.73. For this reason Einaga et al.[14] find that the exponent in the MHS equation for the system PS–benzene is equal to

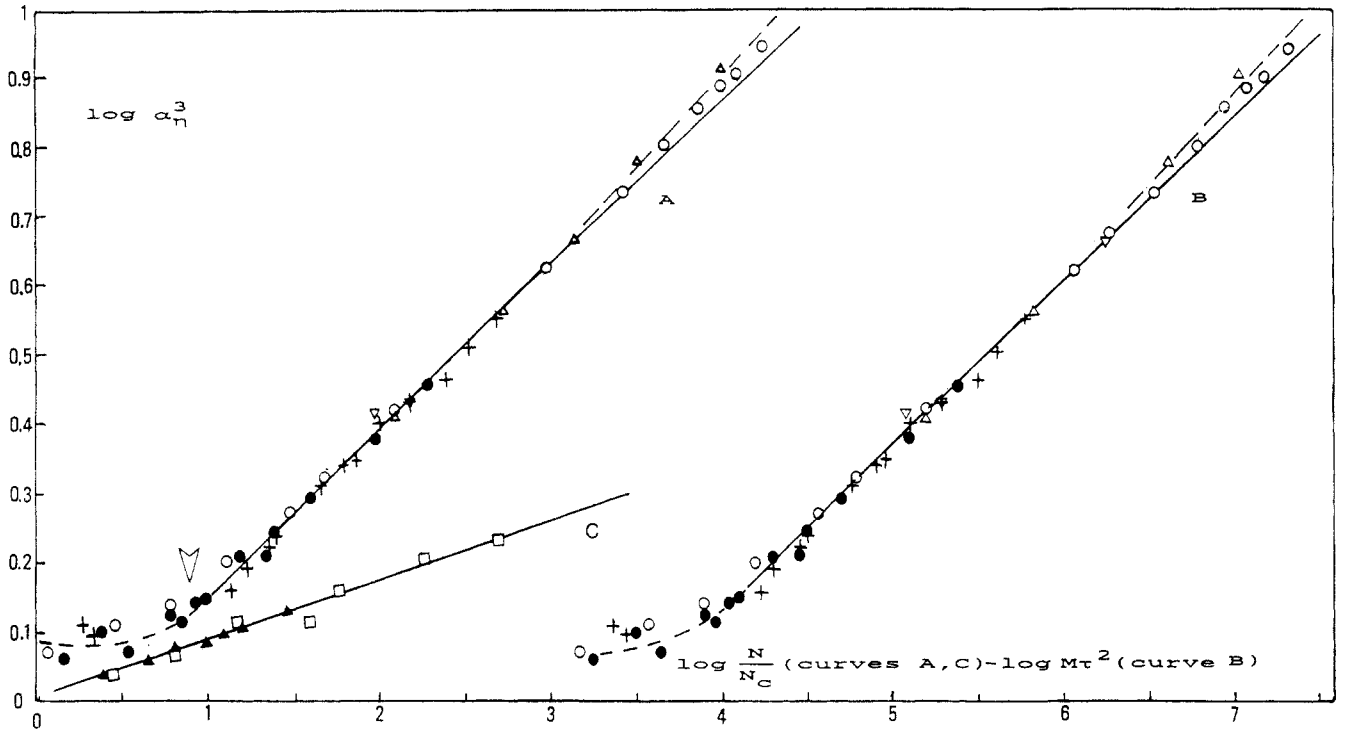

Figure 1. Variation of the viscometric expansion factor α_η as a function of (a, left) the number of "molecular" blobs, N/N_c (curve A and curve C) and (b, right) the number of "thermal" blobs or reduced blob parameter $M\tau^2$ (curve B) for the following systems: (1) PS–benzene at 25 °C [(○) ref 14, (+) ref 15, (▽) ref 16, (△) ref 8, (●) our results], (2) PS–*cis*-decalin [(□) ref 18], (3) PS-cyclohexane 50 °C [(▲) ref 19].

Table I. Exponent of the MHS Equation *a*, Unperturbed Dimensions Parameter K_Θ, Molecular Weight of the Statistical Segment m_s, Characteristic Number of the Statistical Segments N_c, Θ Temperature, and the Adjustable Parameter *na* of the Studied Polymer–Solvent Systems

system	a	10^2K_Θ (mL g^{-1})	m_s	N_c	Θ (K)	*na*
PS–benzene	0.735	8.1	806	4	113	11.5
PS–*cis*-decalin	0.59	8.1	806	21.5		
PS–cyclohexane 50 °C	0.59	8.1	806	21.5		
POE–benzene	0.685	18	180	6		
PmS–CH (30 °C)	0.685	8.5	1046	6	200	9.75
PIB–CH (10 °C)	0.685	13	315	6	126	10
PMMA–(CCl_4 + Meth.)	0.685	7	665	6		

0.75, taking especially into account the fractions of very high molecular weight. The slope of the straight lines for $N/N_c > 3.4 \times 10^3$ is approximately equal to 0.27 (dashed lines in Figure 1), and with the asymptotic value for both indices $\nu = \nu_G = \nu_D = 0.588$,[7] eq 2 predicts a slope equal to 0.264.

The data that are necessary in order to obtain curve A and B of Figure 1 and the parameters obtained from these curves are given in Table I (the K_Θ value is taken as the same for all the viscometric results coming from the different sources).

In order to indicate clearly that eq 2 is valid in solvents of different quality (different values of the MHS exponents) I also present in Figure 1 the variation of log α_η^3 versus log (N/N_c) for the system PS–*cis*-decalin[18] (curve C). Taking into account the linear part in the variation of log $[\eta]$ versus log M, I obtain for this system $\underline{a} = 0.59$ (very poor solvent) or $\nu = 0.53$. From eq 2 I calculate a theoretical slope for the obtained straight line plotting log α_η^3 versus log (N/N_c) equal to 0.09 while the straight line C in Figure 1 presents a slope of 0.085 (the data necessary to obtain curve C are given in Table I).

The system PS–cyclohexane (50 °C) presents an exponent in the MHS equation which lies near the value of 0.59. The points obtained with this system lie in the same curve obtained with the previous system (curve C in Figure 1). This is predicted by eq 2 (same value of ν and same value of N_c). The value of N_c is obtained from eq 1 and it is equal to 21.5 for the two systems, by which I have obtained curve C. In the case of the systems with an exponent of the MHS equation equal to 0.59, the power law starts when the chains contain just more of one blob[6] and for this reason curve C seems to be a straight line till log $(N/N_c) = 0$.

In Figure 2 we display the variation of log α_η^3 versus log (N/N_c) of four polymer–solvent systems: poly(ethylene oxide) (POE)–benzene, poly(*m*-methylstyrene) (PmS)–cyclohexane (30 °C), polyisobutylene (PIB)–cyclohexane (10 °C), and PMMA–(82.5% CCl_4 + 17.5% methanol). All these systems present an exponent in the MHS equation which lies very close to a mean value of 0.685 and from eq 1 I have $N_c = 6$. The obtained straight line with these four systems (curve A in Figure 2) is described by

$$\alpha_\eta^3 = 0.83\left(\frac{N}{6}\right)^{0.19}$$

while with $\underline{a} = 0.685$ or $\nu = 0.56$ eq 2 gives

$$\alpha_\eta^3 = 0.77\left(\frac{N}{6}\right)^{0.185}$$

I must point out that the PMMA in the mixed solvents presents a K_Θ value larger than the conventional one (Table I). This large value of K_Θ in the solvent mixture is expected,[25-27] and only this value permits the points obtained with this system to lie on the same curve obtained with the other three systems (curve A in Figure 2).

The Θ temperature of the systems PmS–cyclohexane and PIB–cyclohexane is known[23,28] (Table I), and I present for these two systems the variation of log α_η^3 as a function of log $M\tau^2$. I obtain two distinct straight lines (B_1 and B_2 in Figure 2), and this must be attributed to the difference in the molecular weight of the monomers of the two

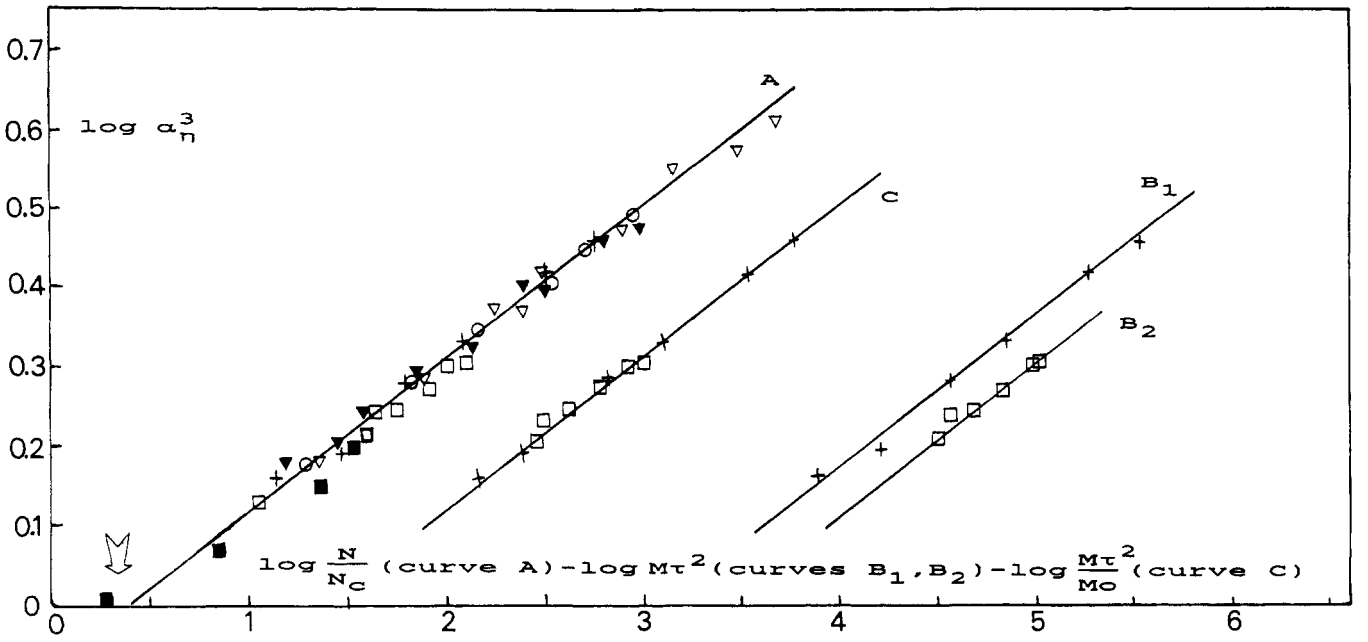

Figure 2. Variation of the viscometric expansion factor α_η as a function of (a, left) the number of "molecular" blobs N/N_c (curve A), (b, right) the number of "thermal" blobs or the reduced blob parameter $M\tau^2$ (curves B_1 and B_2) and (c, middle) the parameter $M\tau^2/M_0$ (curve C) for the following systems: (1) POE–benzene at 25 °C [(■) ref 20 by interpolation, (▽) ref 21, (○) ref 22], (2) PmS–CH at 30 °C [(□) ref 23], (3) PIB–CH at 20 °C [(+) ref 24], (4) PMMA–82.5% CCl_4/17.5% methanol at 25 °C [(▼) our results].

polymers (M_0 = 56 for PIB and M_0 = 118 for PmS). By matching these two curves on curve A, I obtain for PIB naM_0 = 562 and for PmS naM_0 = 1148. With the above two values of M_0 I finally obtain for the adjustable parameter na about the same values (na equal to 10 and 9.75). In order to eliminate the difference in the molecular weight of the monomers I present the variation of log α_η^3 versus log $(M\tau^2/M_0)$ for the above two systems and obtain the common straight line C of Figure 2.

For all the systems of Figure 2 the complete excluded volume behavior must appear when the chain contains twelve statistical segments[6] or two blobs (N_c = 6), and this happens as is indicated by the arrow in Figure 2.

Applying eq 4 to PS in solution in toluene (good solvent) and in *cis*-decaline and cyclohexane (44.5 °C) (marginal solvents), I obtain two different straight lines, as can be seen in Figure 3. The slopes for the system PS–toluene are equal to 0.582 while for the systems PS–*cis*-decalin and PS–cyclohexane (44.5 °C) are equal to 0.55. The given values of the excluded volume index ν in the corresponding articles from which I have taken the values of R_G are respectively 0.58 and 0.54.[18,29] As in Figure 1, when N/N_c becomes higher than 3.4 × 10^3, the points in the curve obtained with the system PS–toluene seem to deviate, leading to a higher slope which is in accordance with the asymptotic values of the excluded volume index (ν_G = 0.588).

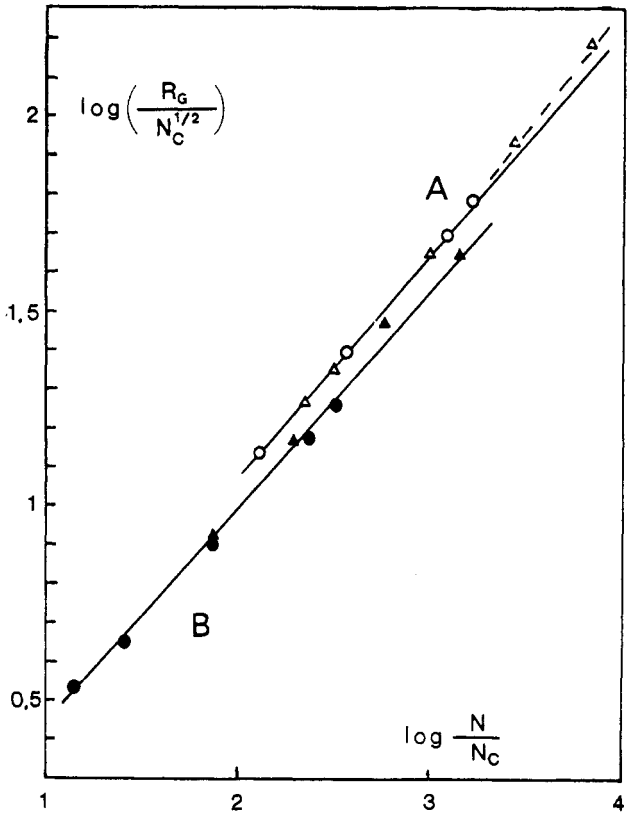

Figure 3. Variation of $R_G/N_c^{1/2}$ as a function of N/N_c according to eq 4, for the following systems: (1) PS–toluene [(△) ref 18], (○) ref 29] (curve A), (2) PS–*cis*-decalin [(▲) ref 18] (curve B), (3) PS–cyclohexane at 44.5 °C [(●) ref 29] (curve B).

Discussion and Conclusions

The results obtained in dilute solutions using dynamic and static measurements and treated in this article according to the blob theory clearly indicate that polymers dissolved in solvents of the same quality (same value of exponent a in the MHS equation) present the same relation between their viscometric expansion factor or their radius of gyration and the number of blobs contained in the polymer coils. On the contrary, the obtained curves with polymers, or the same polymer, dissolved in solvents of different quality are different. We must note that different curves are also obtained, even with the same polymer dissolved in solvents of different quality, when the expansion of the coils was presented as a function of the parameter z,[30,31] which is tightly related to the reduced blob parameter ($N/N_\tau = cz^2$).

In the region of molecular weight where the values of the ratio N/N_c are lower than 3.4 × 10^3 (region of effective indices) there is a good linearity between log α_η^3 or log $(R_G/N_c^{1/2})$ versus log (N/N_c), for all polymer–solvent systems investigated in this work. This linearity is predicted by eq 2 because ν is assumed to be independent

of molecular weight. A curvature in the above representations in the region of effective indices, due to the variation of the dynamic excluded volume index with molecular weight, is difficultly detectable, as predicted by Weill and des Cloizeaux.[7] This result clearly indicates that the blob model is valid beyond its original restricted assumptions. In other words one can use the blob model not only in the asymptotic region but also in the region of effective indices.

In the region of high molecular weight the excluded volume indices (ν_G and ν_D) seem to reach their asymptotic value. More precisely, for $N/N_c > 3.4 \times 10^3$ the curves in Figures 1 and 3 present slopes which are in accordance with the asymptotic value of the excluded volume indices ($\nu_G = \nu_D = 0.588$). Supplementary studies must be undertaken in order to confirm the different behavior of a given polymer–solvent system in the regions of effective and asymptotic values of excluded volume indices.

The adjustable parameter *na*, which is necessary in order to match the number of thermal blobs to the directly determined molecular blobs is found to be about the same with different polymers dissolved in different solvents (mean value of *na* equal to 10). This value has already been found by me,[32] and this has also been proposed by Vidaković and Rondelez.[33] McKrackin, Guttman, and Akcasu,[34] using Monte Carlo calculations, found $na = 7$, and this value is comparable to the value proposed here. Nevertheless I must indicate that the value of *na* proposed in this work has been obtained with polymers dissolved in good and marginal solvents and that lower values have been determined with polymers dissolved in bad solvents.[2,35] The constant value of *na* for the systems investigated in this work indicates that in the case of flexible polymers, in which the number of monomers per statistical segment, n, is low, the parameter a must be high.

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