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Dependence of the Θ Temperature on the Rigidity of the Polymers and the Quality of the Solvents

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Introduction

The knowledge of the Θ temperature of a polymer in a given solvent is necessary when we study this polymer using the two-parameter theory as well as the blob theory. Let us indicate that the second virial coefficient, the χ parameter, the excluded-volume parameter z, and the number of blobs in the chain are tightly related to the Θ temperature.

The determination of the Θ temperature, which for the great majority of the polymer–solvent systems lies fairly below the room temperature, is difficult: very often this temperature is given with an error limit of 50°, and this is due to the uncertainty of the extrapolation methods.

In this paper, using the "best" known values of Θ temperature obtained for different polymer–solvent systems and based on the blob theory, we will derive a relation which gives the value of the reduced temperature of a polymer–solvent system and consequently the Θ temperature, as a function of the rigidity of the polymer and the quality of the solvent. This relation seems to be universal for all the polymer–solvent systems taken into account in this paper.

This work allows for the determination of the adjustable parameter of proportionality which was introduced originally to make the thermal blob picture a quantitative theoretical model.

Theoretical Section

The thermal blob theory is frequently used in order to correlate the expansion of the macromolecular chains with the number of blobs from which they are composed. The number of blobs is given for one chain containing N statistical segments by the ratio N/N_τ where N_τ expresses the number of statistical segments of a single blob. This ratio depends on the "distance" from the cutoff point, which point separates the Gaussian behavior from the excluded-volume behavior. This point is the Θ temperature, and the "distance" from the Θ point, when the chain is found in a temperature equal to T, is expressed by the reduced temperature τ ($\tau = 1 - \Theta/T$). More precisely we have

$$N/N_\tau = M\tau^2/n\alpha M_0 \qquad (1)$$

In this relation the number of blobs, given by the reduced blob parameter N/N_τ, depends not only on the molecular weight of the chain M and the reduced temperature but also on the adjustable parameter $n\alpha M_0$. The numerical value of this parameter, for the PS, is 416 according to Akcasu and Han[1] or equals 1000 ± 50 according to Vidakovic and Rondelez[2] (M_0 is the mass of the monomer).

The ratio N/N_τ has also been expressed, according to Han,[3] by the following equation:

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

In this equation α_η is the viscometric expansion factor and ν is the excluded-volume index.

We have shown that we can also express the number of blobs in a macromolecular chain of molecular weight M and containing N statistical segments by the ratio M/M_c or N/N_c.[4,5] N_c is the number of the statistical segments corresponding to the critical molecular weight M_c in which we have the onset of the excluded-volume behavior in the same temperature. In other words, M_c is the molecular weight in the log $[\eta]$ versus log M representation where the exponent a of the Mark–Houwink–Sakurada equation (MHS) becomes higher than 0.5.[6] For values corresponding to this molecular weight the chain is consisted only of one blob.

In the following we have verified eq 2 by replacing N_τ with N_c.[5] Moreover, we have calculated the values of N_c using eq 2, with different values of ν, or a (because $a = 3\nu - 1$) and we found that the calculated values coincide with the experimental ones.[7] More precisely we have established the following equation relating N_c and a with the calculated and experimentally determined values of N_c.[7]

$$N_c = 0.37a^{-7.7} \qquad (3)$$

Procedure

Having established that the number of blobs in a macromolecular chain is given by either the ratio N/N_τ or N/N_c and having $N/N_c = M/M_c$, we can write

$$\frac{N}{N_\tau} = \frac{N}{N_c} = \frac{M\tau^2}{n\alpha M_0} = \frac{M}{M_c} = \frac{M}{N_c m_s} \qquad (4)$$

where m_s is the molecular weight of the statistical segment. From the above relation we obtain

$$\tau^2 m_s/M_0 = n\alpha/N_c \qquad (5)$$

Taking into account eq 3, we finally obtain

$$\tau^2 m_s/M_0 = (n\alpha/0.37)a^{7.7} \qquad (6)$$

In the following we will establish a relation between $\tau^2 m_s/M_0$ and a using experimental results obtained with some polymer–solvent systems (knowledge of the exponent a and the Θ temperature). For the same systems we will calculate the values of the molecular weight of the statistical segment m_s. For this we will take into account viscometric results obtained with these systems in order to calculate the unperturbed dimensions parameter K_Θ using the different extrapolation methods.[8-10] From the value of K_Θ we can obtain the statistical segment length A using the equation

$$A = (K_\Theta/\Phi_0)^{2/3}M_L \qquad (7)$$

where Φ_0 is Flory's constant and M_L the mass per unit length of the polymer. Multiplying A by M_L, we obtain the molecular mass of the statistical segment m_s.

Results and Discussion

The experimental results (viscometric results and Θ temperature) of the polymer–solvent systems which are taken into account in this work are taken from the literature. Most of the m_s values are already calculated in our previous work.[5,7] The values of Θ temperature are mostly taken from the paper by Fox[11] or some more recent papers.[31] In Table I we give values of m_s, a, and Θ for 15 polymer–solvent systems.

In Figure 1 we display the variation of $\tau^2 m_s/M_0$ as a function of a for the systems of Table I. As we can see in

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Table I
Exponent of the MHS Equation a, Unperturbed Dimension Parameter K_Θ, Molecular Weight of the Statistical Segment m_s, Coefficient of the Steric Hindrance σ, and Θ Temperature of 15 Polymer–Solvent Systems

solvent	a	ref[a]	$K_\Theta \times 10^2$	m_s	σ	Θ (K)	ref[b]
			PS				
benzene	0.735	6, 12, 13	8.1	806	2.2	113	17
toluene	0.725	14–16	8.2	815	2.25	137	18
ethylbenzene	0.68	19	8.0	800	2.2	156	11
dichloroethane	0.67	15	8.2	815	2.25	190	11
dioxane	0.665	20	8.2	815	2.25	198	11
ethyl acetate	0.59	21	8.3	822	2.25	222	11–31
			PMMA				
chloroform	0.83	22–24	5.0	533	1.9	0	11
dichloroethane	0.77	23	4.3	480	1.74	40	11
benzene	0.76	23, 25	4.5	492	1.76	50	11
methyl methacrylate	0.72	23	6.0	600	1.92	110	11
methyl isobenzoate (60 °C)	0.66	11	6.5	632	2.0	220	11
ethyl acetate	0.64	26	5.0	533	1.9	175	11
			PIB				
cyclohexane	0.7	27	13.0	315	1.85	126	11
			Poly(m-methylstyrene)				
benzene (30 °C)	0.76	28	8.2	1020	2.3	106	28
cyclohexane	0.68	28	8.5	1046	2.37	207	28

[a] The references concern the exponent a. [b] The references concern the Θ temperature.

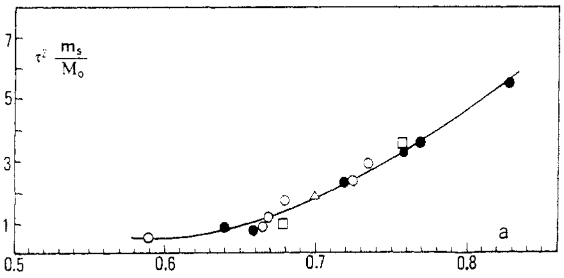

Figure 1. Dependence of the reduced temperature of the polymer–solvent systems of Table I, multiplied by the molecular weight of the polymers' statistical segment, on the exponent of the MHS equation of the systems PS (○), PMMA (●), PIB (△), and PmS (□).

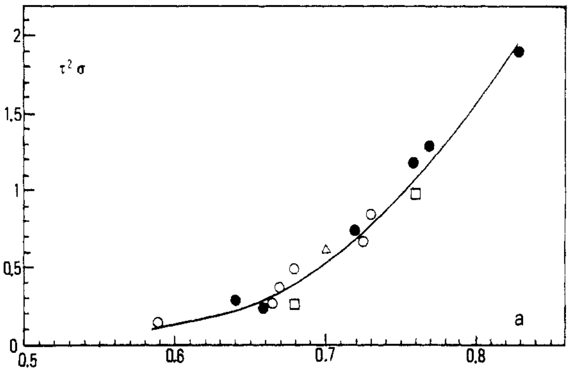

Figure 2. Dependence of the reduced temperature of the polymer–solvent systems of Table I, multiplied by the coefficient of the steric hindrance of the polymers, on the exponent of the MHS equation of the systems (symbols as in Figure 1).

this figure the points obtained with the different systems lie approximately on the same curve which is described by the equation

$$\tau^2 m_s/M_0 = 27.5a^{7.8} \tag{8}$$

The above equation indicates that the relation between the reduced temperature of a polymer–solvent system and the interactions in short and long range of the polymer displays a universal behavior. If two polymers are in solution in two different solvents which present the same value of a, the Θ temperature of the polymer which presents a higher flexibility (lower value of m_s/M_0) will be lower (higher value of τ^2). This is the case for PMMA (mean value of m_s 500) and PS (mean value of m_s 800).

Comparing the relations (6) and (8), we find that they correspond almost to the same value for the exponent a. This indicates the validity of eqs 2 and 3, which is a byproduct of the former. These results are also in accordance with the theory of de Gennes et al.[29] as well as the dynamic agreements of Weill and des Cloizeaux,[30] from which eq 2 is derived.

Comparing again eqs 6 and 8, we obtain $n\alpha = 10.17$ and, with $M_0 = 104$ for PS, we obtain for the adjustable parameter or the coefficient of proportionality $n\alpha M_0$ the value of 1058. This value has been proposed earlier by Vidakovic and Rondelez.[2]

The ratio m_s/M_0 represents the statistical segment length, and this can be directly related, as we have already pointed out, to the rigidity of the chain. The rigidity of a macromolecular chain is also expressed by the ratio $\sigma = (\bar{r}_\Theta^2/\bar{r}_f^2)^{1/2}$ in which $\bar{r}_\Theta^2$ is the mean-square distance between the chain ends in Θ conditions and $\bar{r}_f^2$ is the same distance in the case of free rotation of the monomer units of the same chain. The $\bar{r}_\Theta^2$ is directly related to the parameter K_Θ and *via* 7 to the statistical segment length or m_s. For this reason it seems interesting to present the relation between the reduced temperature and the exponent of the MHS equation using the parameter σ instead of m_s/M_0 and we propose the following relation instead of the relation (6):

$$\tau^2\sigma = Ca^b \tag{9}$$

In order to verify the above relation and determine the numerical constants, we use the values of σ of the polymers which are taken into consideration in this work and which are given in Table I.

Figure 2 shows that we also have a universal relation between $\tau^2\sigma$ and a. The curve obtained is described by the equation

$$\tau^2\sigma = 10.6a^{8.4} \tag{10}$$

This equation is more convenient from the practical point of view as compared with eq 8 because the σ values are more easily accessible.

In conclusion, we propose two relations which allow the calculation of Θ temperature of a polymer–solvent system when we know the exponent of the MHS equation of the system and the unperturbed dimensions of the polymer in the given solvent. Moreover, we have determined the adjustable parameter $n\alpha$ needed for a quantitative comparison of the blob theory and experiment.

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