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An approach to the theta temperature of star polymers based on the blob model

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Using a relation derived from the blob model we obtain an equation giving the Θ temperature of the polymers. This equation predicts for the star shaped polymers a decrease or an increase in their Θ temperature compared with the Θ temperature of the corresponding linear polymers. The value of the Θ temperature of star polymers is tightly related to their degree of branching. The predictions of this model are compared with experimental results. © 1997 Elsevier Science Ltd.

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Introduction

The theta temperature of a branched polymer has been found experimentally to be lower than the theta temperature of the corresponding linear polymer dissolved in the same solvent[1–6]. Candau et al.[7] have proposed a relation which predicts this decrease in the theta temperature of branched polymers. Here we give a relation, based on the blob theory[8], which predicts the theta temperature of star polymers. A decrease in the theta temperature of the relatively low-branched star polymers is predicted, while this relation predicts an increase in the theta temperature for the highly branched star polymers, compared with the corresponding linear polymers. An experiment with a 17-arm star polystyrene gives a theta temperature in cyclohexane for this polymer, higher than the theta temperature of the linear polystyrene.

Theory and procedure

According to the thermal blob theory a macromolecular chain is divided into N/N_τ blobs where N is the number of statistical segments and N_τ is the number of statistical segments of which one blob consists, which corresponds to the temperature-dependent cut-off to separate Gaussian and excluded volume regimes. The following relation correlates the number of blobs to the reduced temperature τ ($\tau = 1 - \Theta/T$) and to the molecular mass M of the chain[9],

$$\frac{N}{N_\tau} = \frac{\tau^2 M}{n\alpha M_0} \tag{1}$$

where M_0 is the molecular mass per monomer and $n\alpha$ is the adjustable parameter needed for quantitative comparison of the theory and experiment. The value of N_τ can be calculated using the following equation proposed by Han[10] and which is based on a relation proposed by Farnoux et al.[11] and on the dynamic agreements of Weill and des Cloizeaux[12]:

$$\alpha_\eta^3 = \frac{4(1-\nu)(2-\nu)}{(2\nu+1)(\nu+1)}\left(\frac{N}{N_\tau}\right)^{3\nu-1.5} \tag{2}$$

In the above equation α_η is the viscometric expansion factor and ν the excluded volume index ($3\nu - 1 = a$), where a is the exponent in the Mark–Houwink–Sakurada (MHS) equation. Knowing the viscometric expansion factor, the number of statistical segments and the excluded volume index of a chain dissolved in a given solvent we can calculate, from equation (2), the characteristic number N_τ.

Knowing the value of N_τ for a polymer solvent system and the Θ temperature of this system from equation (1) we can calculate the adjustable parameter $n\alpha$. We have obtained $n\alpha = 10$ for a great number of polymer–good solvent systems[13]. The same value is proposed by Vidakovic and Rondelez[14].

In this article we use equation (2) in order to obtain the value of N_τ of different star shaped polymers. For an homologous series of a star polymer (same number of branches but of different length) we apply the Stockmayer–Fixman–Burchard (SFB) equation[15,16] and we obtain the unperturbed dimension parameter K_Θ. In the following we obtain the value of α_η ($\alpha_\eta^3 = [\eta]/K_\Theta M^{1/2}$). The value of K_Θ permits us also to calculate the statistical segment length of the polymer A (Kuhn statistical segment) by the relation

$$A = \left(\frac{K_\Theta}{\Phi}\right)^{2/3} M_\mathrm{L} \tag{3}$$

where M_L is the molecular mass per unit length. The value of the molecular mass of the statistical segment m_s is obtained in the following ($m_\mathrm{s} = AM_\mathrm{L}$). Dividing the molecular mass of each fraction by m_s we obtain the number of statistical segments N of which the chains of each fraction consist.

In contrast to what we obtain with the linear polymers, the characteristic number N_τ is not the same for all the fractions of a star polymer; this number increases with increasing molecular mass of the fraction. Equation (2) gives also values for N_τ of a star polymer which are different from those of the corresponding linear polymer dissolved in the same solvent and in which the star and the linear polymer present the same solubility (same value of the index ν).

Having $M = Nm_\mathrm{s}$, from equation (1) we obtain

$$\tau^2 = \frac{n\alpha M_0}{N_\tau m_\mathrm{s}} \tag{4}$$

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This equation allowed us to determine the theta temperature of different linear polymers dissolved in different good solvents, taking $n\alpha$ equal to 10[17].

Using now the above relation for an homologous series of a star polymer and for the corresponding homologous series of a linear polymer, both dissolved in the same solvent at the same temperature and presenting the same solubility in this solvent (same exponent in the MHS equation) and accepting that we have the same adjustable parameter for the two types of polymer, we obtain

$$\frac{\tau_{\mathrm{star}}^2}{\tau_{\mathrm{lin}}^2} = \frac{N_{\tau\mathrm{lin}} m_{\mathrm{slin}}}{N_{\tau\mathrm{star}} m_{\mathrm{sstar}}}$$

Having $\tau = 1 - \Theta/T$ finally we obtain

$$\Theta_{\mathrm{star}} = T - \frac{\sqrt{N_{\tau\mathrm{lin}} m_{\mathrm{slin}}}}{\sqrt{N_{\tau\mathrm{star}} m_{\mathrm{sstar}}}}(T - \Theta_{\mathrm{lin}}) \qquad (5)$$

Let us try to give a physical meaning to the above equation. The product $N_\tau m_s$, that appears in this equation, gives the molecular mass of the blob (N_τ is the number of statistical segments of which one blob consists and m_s is the molecular mass of one statistical segment). If now $N_{\tau\mathrm{star}} m_{\mathrm{sstar}} < N_{\tau\mathrm{lin}} m_{\mathrm{slin}}$ we obtain from equation (5) $\Theta_{\mathrm{star}} < \Theta_{\mathrm{lin}}$. Daoud and Cotton[23] predict that the blob of the branches of star polymers become gradually smaller when we approach the branch point of the molecules. This decrease can explain the above inequality and consequently it can also explain the decrease in the Θ temperature of a star polymer compared with the Θ temperature of the corresponding linear polymer. When we have $N_{\tau\mathrm{star}} m_{\mathrm{sstar}} > N_{\tau\mathrm{lin}} m_{\mathrm{slin}}$, equation (5) gives $\Theta_{\mathrm{star}} > \Theta_{\mathrm{lin}}$. A molecular mass for the blob of the star polymer higher than the mass of the linear polymer can be predicted from the model of Boothroyd and Ball[24]. According to this model, the interior part of a star polymer is an impenetrable sphere that can be considered as one blob. Consequently in the case of highly branched star polymers we can accept that the mean value of the molecular mass of the blobs is higher than the molecular mass of the blobs of the corresponding linear polymers and from equation (5) we obtain $\Theta_{\mathrm{star}} > \Theta_{\mathrm{lin}}$. The choice of one or other model must depend on the number of branches of the star polymer and we expect that the Θ temperature of a star polymer can be higher than the Θ temperature of the corresponding linear polymer only when the former presents a high degree of branching. The same considerations are also valid for Equation (4): a decrease in the molecular mass of the blob, $N_\tau m_s$, leads to an increase in τ^2 or to a decrease in the Θ temperature and vice versa.

Results

Homologous series of linear and of 6-arm star polystyrenes have been studied by Roovers and Bywater[5,18] in cyclohexane at 50°C. Using these viscometric results we obtained the values of m_s and N_τ of different fractions of the linear and star polymers (SFB and MHS representation, applications of equation (3) and equation (2)). In the following, applying equation (5) (with $T = 323$ and $\Theta_{\mathrm{lin}} = 307.5$) we obtain the values of Θ_{star} of different fractions of the star polymer in cyclohexane. The obtained values are presented as open circles in *Figure 1* (the temperature has been converted in to degrees Celsius). The filled circles in the same figure show the experimentally determined theta temperatures of the fractions of the six-branch star polymers[4,5,7]. It is worth noting that the calculated values from equation (5) and the experimentally obtained values lie very close to each other.

Homologous series of 3-arm and 6-arm star PS have been studied in toluene by viscometry[6,5] and we use these results in order to obtain $N_{\tau\mathrm{star}}$ and m_{sstar} and apply in the following equation (5). The parameters of linear PS in this solvent (m_{slin} and $N_{\tau\mathrm{lin}}$) are easily obtained from viscometric results available in our laboratory. The theta temperature of the linear polymer in toluene has been found to be 137 K[19]; equation (4), with $n\alpha = 10$ gives $\Theta = 139$ K[17]. In *Figure 2* we present the theta temperatures of fractions of 3-arm and 6-arm star PS given by equation (5). We observe that the theta temperatures of all the fractions of these branched polymers are lower than the theta temperature of the linear

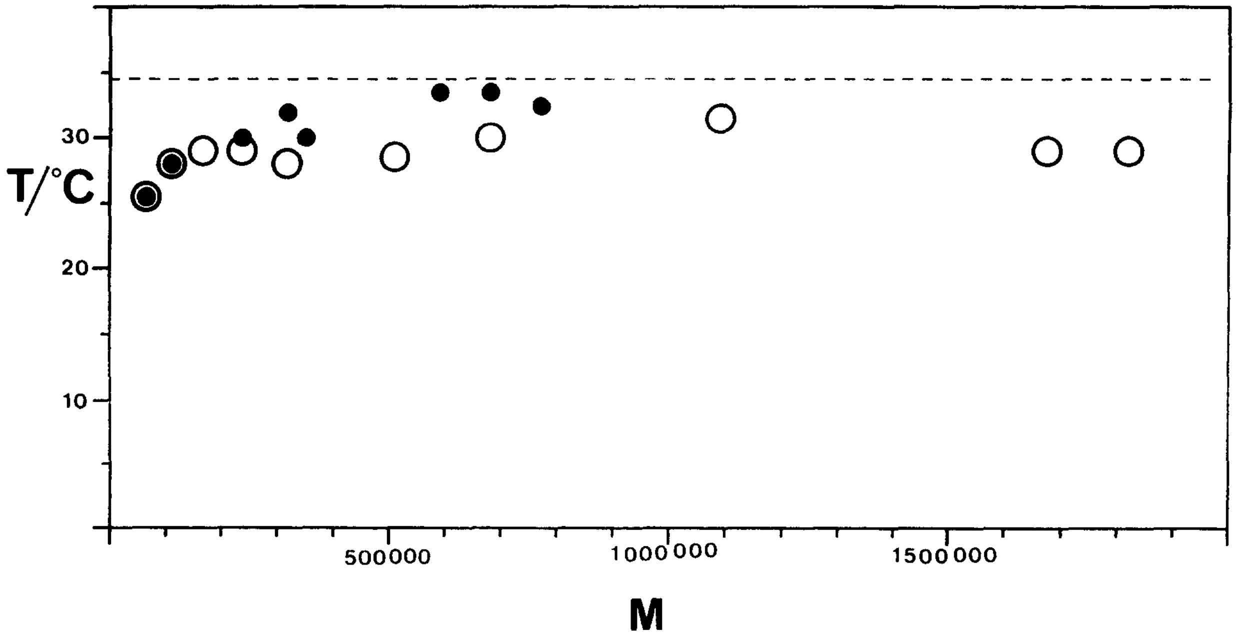

Figure 1 Variation of the theta temperature as a function of the molecular mass of 6-arm star PS in cyclohexane. Open circles present the calculated values from equation (5) and the filled circles present the values obtained experimentally. The dashed line indicates the theta temperature of the linear PS.

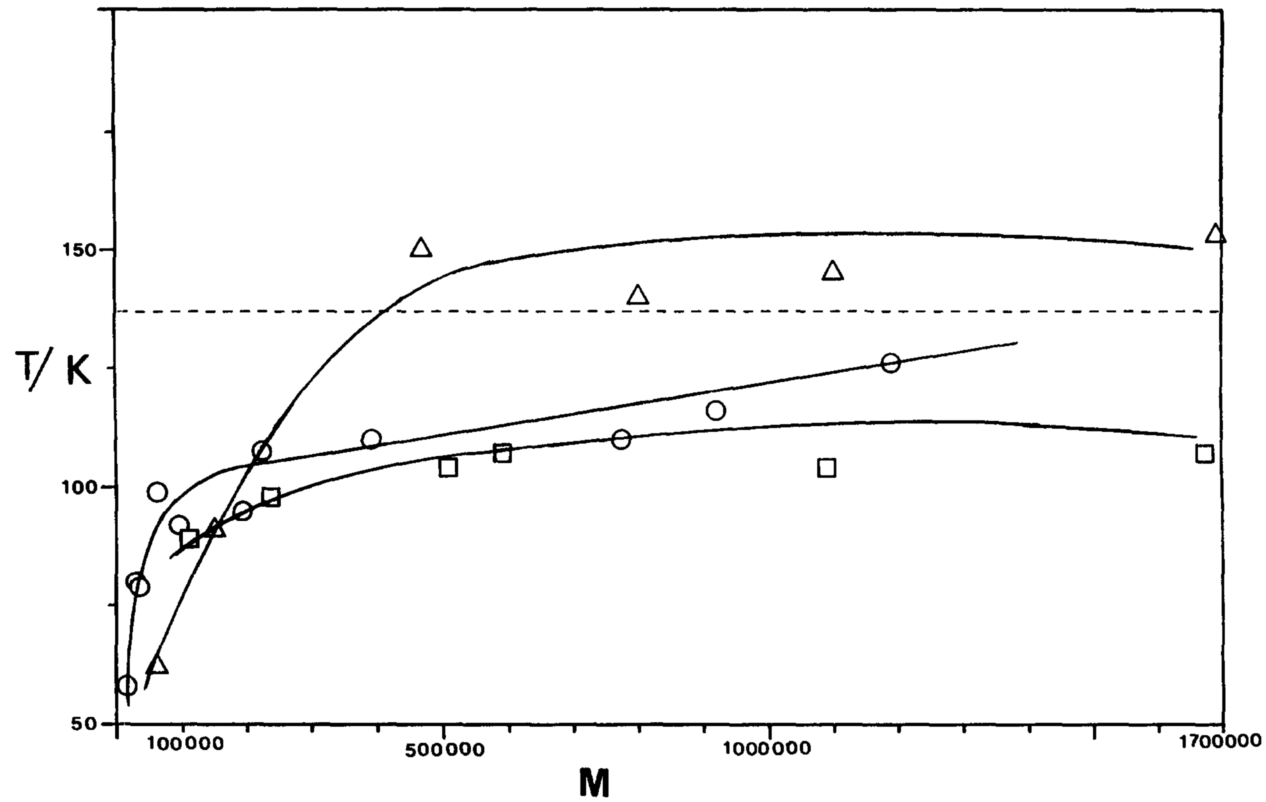

Figure 2 Variation of the theta temperature as a function of molecular mass of 3-arm (○), 6-arm (□) and 12-arm (△) star PS in toluene calculated from equation (5). The dashed line indicates the theta temperature of the linear PS.

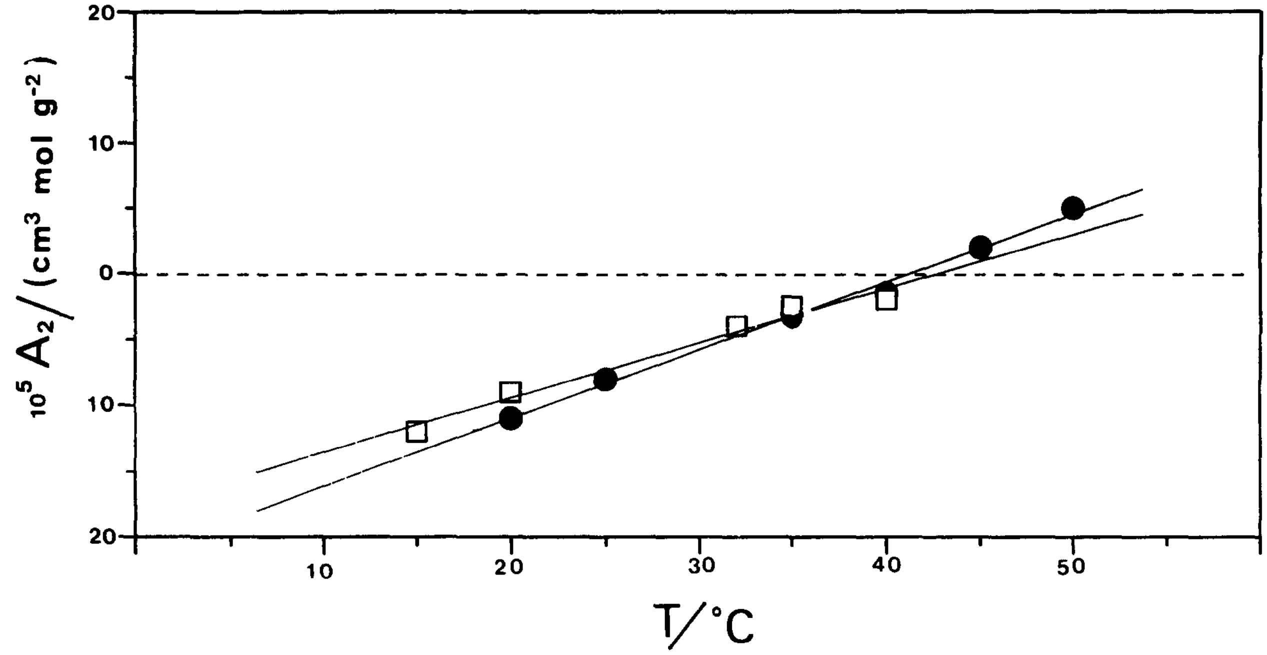

Figure 3 Variation of the second virial coefficient as a function of the temperature of a 17-arm star PS in cyclohexane (the two types of symbols correspond to two independent experiments).

polymer as when cyclohexane was used as solvent (*Figure 1*).

With the viscometric results of a series of 12-arm star PS[6] we have a different behaviour. Although for the low molecular mass fractions the theta temperature is lower than the theta temperature of the corresponding linear polymer, for the high molecular mass fractions equation (5) gives theta temperatures which are slightly higher than the theta temperature of the linear polymers (*Figure 2*). Let us indicate that for the 12-arm star PS, in the case of high molecular mass fractions, no decrease in the Θ temperature compared with the Θ temperature of the linear PS[6] (33°C) is observed. We cannot calculate, using equation (5), the theta temperature of 12-arm star PS in cyclohexane, as we have done in the case of 6-arm star PS, because we do not have viscometric data in this solvent for this star polymer at a temperature higher than the theta temperature.

With a fraction of an 18-arm star PS for which the intrinsic viscosities in toluene and in a theta solvent are given[20], we obtained m_s and N_T. Subsequently we applied equation (5) to calculate a theta temperature equal to 178 K which is higher than the theta temperature of the linear PS ($\Theta_{\text{lin}} = 137$ K). Theta temperatures higher than the theta temperature of the corresponding linear polymers have also been calculated using equation (5) for fractions of multi-arm and 18-arm star polybutadienes dissolved in cyclohexane[21,22]. The higher Θ temperature of these highly branched polymers compared with the Θ temperature of the corresponding linear polymer in cyclohexane is expected because at room temperature the second virial coefficient of these star polymers is lower than the second virial coefficient of the linear polymer[21]. Consequently cyclohexane is a worse solvent at room temperature for the star polymers and we must arrive at their Θ conditions at a temperature higher than the Θ conditions of the linear polymer[19].

In order to verify whether one can obtain experimentally a theta temperature with a branched polymer that is higher than the theta temperature of the corresponding linear polymer we have studied the thermal variation of the second virial coefficient of a 17-arm star PS. The molecular mass of this sample is equal to 270 000. The second virial coefficient was given directly from software controlling the apparatus (spectrogoniometer, model SEM RD, Sematech). As we can see in *Figure 3* the theta temperature of this sample ($A_2 = 0$) lies between 41 and 42°C while the theta temperature of the linear PS is equal to 34.5°C. Let us indicate here that Berry[2] has also obtained experimentally a theta temperature with highly branched PS that was higher than the theta temperature of the linear PS.

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