(19) Edwards, S. F. *J. Phys. A* **1975**, *8*, 1670.
(20) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley: New York, 1987.
(21) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press: New York, 1971.
(22) Hill, T. L. *Statistical Mechanics*; McGraw-Hill: New York, 1956.
(23) Nemirovsky, A. M.; Bawendi, M. G.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 7272. Freed, K. F.; Pesci, A. I. *Ibid.* **1987**, *87*, 7342. Pesci, A. I.; Freed, K. F. *Ibid.* **1989**, *90*, 2003, 2017.
(24) Freed, K. F. *J. Chem. Phys.* **1988**, *88*, 5871.
(25) Dudowitz, J.; Freed, K. F. *Macromolecules*, in press.
(26) Bates, F. S. *Macromolecules* **1987**, *20*, 2221. Ito, H.; Russell, T. P.; Wignall, G. D. *Ibid.* **1987**, 2213. Allen, G.; Chai, Z.; Chong, C. L.; Higgens, J. S.; Tripathi, J. *Polymer* **1984**, *25*, 239.
(27) Anderson, H. C.; Chandler, D. *J. Chem. Phys.* **1970**, *53*, 547; **1971**, *55*, 1918.
(28) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.
(29) Bates, F. S.; Hartney, M. A. *Macromolecules* **1985**, *18*, 2478.
(30) Leibler, L.; Benoit, H. *Polymer* **1981**, *22*, 195.
(31) Dee, G. T.; Walsh, D. J. *Macromolecules* **1988**, *21*, 811.
(32) CRC Handbook of Chemistry and Physics, 66th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985.
(33) Dickman, R.; Hall, C. K. *J. Chem. Phys.* **1986**, *85*, 3023, 4108.
(34) Olvera de la Cruz, M.; Sanchez, I. C. *Macromolecules* **1987**, *20*, 440. Olvera de la Cruz, M., submitted for publication in *J. Chem. Phys.*
(35) McMullen, W. E.; Freed, K. F., work in progress.
(36) Tang, H.; Freed, K. F., unpublished work.

Θ Temperature of Linear and Star Polymers

Fabio Ganazzoli* **and Giuseppe Allegra**

Dipartimento di Chimica, Politecnico di Milano, Piazza L. da Vinci 32, I-20133 Milano, Italy. *Received January 28, 1989; Revised Manuscript Received May 16, 1989*

ABSTRACT: The Θ-temperature dependence on chain length and number of arms f for linear and regular star polymers was determined analytically as the temperature at which balance is reached between the repulsive three-body and the attractive two-body interactions; the latter increase with decreasing temperature, unlike the former, which are essentially constant. From an equivalent bead-and-spring model in the Gaussian approximation, Θ is found to *decrease* with increasing molecular weight for linear and lightly branched chains ($f \leq 4$), whereas it *increases* if $f \geq 5$ to a common asymptotic limit Θ_∞. In fact, for *linear* chains the ratio between the number of the three-body and that of the two-body contacts increases with molecular weight because the minimum chain length for a three-body contact is about twice that for a two-body contact. Therefore, short chains need less temperature lowering to compensate the three-body repulsions than long ones. Conversely, the lower Θ temperature for short *branched* chains with many arms is due to the high density of segments near the star core: this gives rise to a large number of three-body repulsions to be compensated. If the molecular weight is very large, the fraction of segments close to the star core becomes negligible and the same temperature Θ_∞ is attained for any polymer architecture, in agreement with experimental results.

Introduction

It is now accepted that for a given polymer–solvent system the Θ temperature changes in general with polymer architecture and molecular weight, but if the latter is large enough, Θ tends to a common, finite limit.$^{1-4}$ This behavior was clearly shown, for example, by well-characterized regular star polymers, synthesized in recent years by linking monodisperse living polymers (mainly polyisoprene and polystyrene) to a multifunctional reactive center. The Θ temperature of these samples, determined by light scattering as the temperature at which the second virial coefficient A_2 vanishes, follows a general pattern: it is lower the shorter the arms are and the larger their number is. However, for very long arms Θ reaches a constant value Θ_∞ independent of both molecular weight and number of arms. Moreover, Θ_∞ turns out to be equal to the Θ temperature of long linear chains.

This finding rules out the widespread assumption that in the Θ state long-range interactions are merely absent. Rather, it suggests that they compensate in a subtle way: a repulsive component, arising from three-body interactions, is balanced by an attractive component, due to the temperature-dependent two-body interactions. In this paper, we follow this approach to calculate the Θ temperature of linear and star polymers using a simple model. The chain comprises $N + 1$ atoms and f equal arms and therefore N/f atoms per arm if one atom sits on the branch point and will be described by an equivalent bead-and-spring chain with a Gaussian distribution of interatomic distances. Θ is obtained as the temperature at which the overall free energy due to the attractive two-body interactions balances that due to the repulsive three-body interactions.

The larger f is, the higher the density at the star core is, hence the larger the number of three-body contacts is. To compensate this increasingly repulsive contribution, a correspondingly lower temperature is needed to strengthen the attractive contribution, unless N/f is so large that only a negligible fraction of chain atoms is near the core. Therefore, Θ should be lower for stars than for linear polymers, the more so the larger f is and the smaller N/f is, but should tend to the same limit if $N/f \rightarrow \infty$, no matter what the number of arms is. Note that the linear polymer may be viewed as a special case of a star with $f = 1$ or 2.

By this approach, we are implicitly defining the Θ temperature as the temperature at which the mean-square radius of gyration and the mean-square distances are proportional to the molecular weight and to the topological separation along the chain, respectively. Also, in this context Θ is obtained from consideration of isolated chains, whereas the definition based on A_2 would also require us

0024-9297/67/2200-0262$02.50/0

to account for intermolecular interactions. The two definitions are equivalent for linear chains in the large molecular weight limit, but some minor quantitative difference may exist for star polymers.[4]

Theoretical Approach

1. Free Energy Contributions. The equilibrium configuration of a polymer chain may be obtained quite generally by minimization of the free energy. This can be written as[5,6]

$$\mathcal{A} = \frac{A - A_{\text{ph}}}{k_{\text{B}}T} = \mathcal{A}_{\text{el}} + \mathcal{A}_{2\text{S}} + \mathcal{A}_2(T) + \mathcal{A}_3 \qquad (1)$$

where A_{ph} is the free energy of the unperturbed phantom chain devoid of any long-range or medium-range interaction and subjected at most to first-neighbor rotational correlations.

In eq 1, $\mathcal{A}_{\text{el}}$ is the elastic free energy resisting any deformation from the unperturbed phantom chain. $\mathcal{A}_{2\text{S}}$ is a medium-range repulsive contribution due to two-body screened interactions originating from the actual chain thickness;[7] it is assumed to be temperature independent and may be expressed as

$$\mathcal{A}_{2\text{S}} = \frac{K_0}{2}\sum_h\sum_i \langle r^2(h,i)\rangle^{-5/2} \qquad (2)$$

where K_0 is a constant proportional to the mean-square chain thickness and $\langle r^2(h,i)\rangle$ is the mean-square distance between atoms h and i. In the Θ state this term produces a local chain swelling, which tends to a finite limit for distant atoms, so that for linear chains, e.g.

$$\langle r^2(h,i)\rangle_0 = C_\infty l^2|i-h|, \quad |i-h| \gg 1 \qquad (3)$$

where the zero subscript indicates the unperturbed state, l is the bond length, and the asymptotic expansion coefficient has been effectively included in the characteristic ratio C_∞.

$\mathcal{A}_2(T)$ and $\mathcal{A}_3$ are the long-range free-energy contributions due to two-body and three-body contacts, respectively[5]

$$\mathcal{A}_2(T) = {}^1/_2\beta(T)\sum_h\sum_i p_{hi} \qquad (4)$$

$$\mathcal{A}_3 = \frac{1}{3!}\bar{y}\sum_h\sum_i\sum_j p_{hij} \qquad (5)$$

each sum being carried out over all the chain atoms. Here p_{hi} and p_{hij} are the probability densities of two- and three-body contacts, $\bar{y}$ is a positive constant, and $\beta(T)$ is the temperature-dependent binary cluster integral. Following Orofino and Flory,[8] we shall put

$$\beta(T) \propto \frac{T - \Theta_{\text{ph}}}{T}\frac{v_{\text{c}}^2}{v_{\text{s}}} \qquad \bar{y} \propto \frac{v_{\text{c}}^3}{v_{\text{s}}} \qquad (6)$$

where Θ_{ph} is the Θ temperature of the phantom chain, v_{c} is the effective volume per chain atom, and v_{s} is the molecular volume of the solvent. (Θ_{ph} depends only on the monomer–solvent pair and not on polymer architecture or molecular weight.) Therefore the three-body interactions are always repulsive and temperature independent, to a first approximation, whereas the two-body interactions are either repulsive or attractive, depending on whether $T > \Theta_{\text{ph}}$ or $T < \Theta_{\text{ph}}$.

Within the Gaussian approximation, we have[5]

$$p_{hi} = \left[\frac{3}{2\pi\langle r^2(h,i)\rangle}\right]^{3/2} \qquad (7)$$

$$p_{hij} = \left(\frac{3}{2\pi}\right)^3[f(\langle r^2(h,i)\rangle,\langle r^2(i,j)\rangle,\langle r^2(h,j)\rangle)]^{-3/2} \qquad (8)$$

$$f(x,y,z) = {}^1/_2(xy + xz + yz) - {}^1/_4(x^2 + y^2 + z^2) \qquad (8a)$$

Both $\mathcal{A}_2$ and $\mathcal{A}_3$ have a long-range character, therefore determining in the thermodynamic limit the molecular weight dependence of the radius of gyration.

According to the starting assumption, at the Θ temperature the overall long-range interactions effectively cancel. However, Θ cannot coincide with Θ_{ph}, because then $\mathcal{A}_2(\theta_{\text{ph}}) \equiv 0$ and the chain would be in the expansion regime due to the three-body repulsions.[5,9] Therefore, we must have $\Theta < \Theta_{\text{ph}}$ so that the two-body attractions are (slightly) attractive, the more so the larger the three-body interactions are.

To determine Θ, we should then minimize the chain free energy with respect to all the degrees of freedom and require that the attractive two-body and the repulsive three-body interactions balance one another. This procedure was previously carried out by us for linear chains[5] and may be summarized by the single equation

$$\frac{\partial}{\partial\alpha_{\text{s}}^2}[\mathcal{A}_2(\Theta) + \mathcal{A}_3] = 0 \qquad (9)$$

α_{s}^2 being the ratio between the actual mean-square radius of gyration and that of the phantom chain. When dealing with star polymers, this condition leads to an exceedingly complicated equation and therefore we will make here the following, simplifying approximation. In the same paper,[5] we also showed that eq 9 is fully equivalent to

$$\mathcal{A}_2(\Theta) + 2\mathcal{A}_3 = 0 \qquad (9a)$$

We will now extrapolate this result to star polymers and write (see eq 4 and 5)

$$\frac{1}{2}\beta(\Theta)\sum_h\sum_i p_{hi} + \frac{2}{3!}\bar{y}\sum_h\sum_i\sum_j p_{hij} = 0 \qquad (9b)$$

Let us define $\bar{\tau}B$ and K_1 through

$$\bar{\tau}B\left(\frac{2\pi C_\infty l^2}{3}\right)^{3/2} = \beta(T); \qquad K_1\left(\frac{2\pi C_\infty l^2}{3}\right)^3 = \bar{y} \qquad (10)$$

where

$$\bar{\tau} = \frac{T - \Theta_{\text{ph}}}{T} \qquad (10a)$$

We have from eq 7, 8, and 9b

$$\bar{\tau}B\nu_2 + 2K_1\nu_3 = 0 \qquad (T = \Theta) \qquad (11)$$

whence

$$\Theta = \frac{\Theta_{\text{ph}}}{1 + \dfrac{2K_1\nu_3}{B\nu_2}} \qquad (11a)$$

where ν_2 and ν_3 are proportional to the number of two- and three-body contacts, respectively:

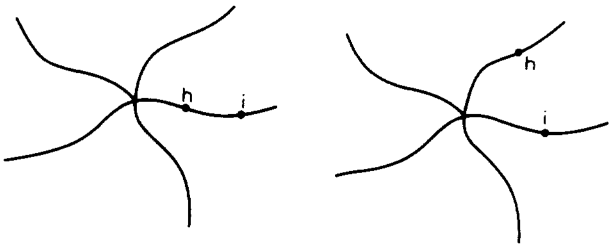
$$\nu_2 = \frac{1}{2}\sum_h\sum_i\left[\frac{C_\infty l^2}{\langle r^2(h,i)\rangle_0}\right]^{3/2} \qquad (12)$$

$$\nu_3 = \frac{1}{3!}\sum_h\sum_i\sum_j\left[f\left(\frac{\langle r^2(h,i)\rangle_0}{C_\infty l^2},\frac{\langle r^2(i,j)\rangle_0}{C_\infty l^2},\frac{\langle r^2(h,j)\rangle_0}{C_\infty l^2}\right)\right]^{-3/2} \qquad (12a)$$

Θ may now be obtained once ν_2 and ν_3 are known.

2. Evaluation of ν_2 and ν_3. In order to calculate the dependence of ν_2 and ν_3 from the molecular weight and

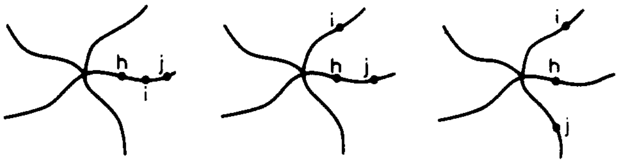
Scheme I



set I multiplicity f

set II multiplicity $f(f-1)/2$

Scheme II



set I multiplicity f

set II multiplicity $f(f-1)/2$

set III multiplicity $f(f-1)(f-2)/3!$

number of arms, let us consider regular star polymers with $N + 1$ atoms and f equal arms, hence N/f atoms per arm.

The two-body interactions may be grouped in two sets with different multiplicities, as shown in Scheme I. Set I comprises the interactions between atoms within the same arm, set II those between atoms on different arms. Both kinds of interactions may be expressed in terms of those of a linear chain of m atoms $\nu_{2,\mathrm{L}}(m)$, m being N/f for set I and $2N/f$ for set II, so that we have

$$\nu_2 = f\nu_{2,\mathrm{L}}\left(\frac{N}{f}\right) + \frac{f(f-1)}{2}\left[\nu_{2,\mathrm{L}}\left(2\frac{N}{f}\right) - 2\nu_{2,\mathrm{L}}\left(\frac{N}{f}\right)\right] \tag{13}$$

In turn, $\nu_{2,\mathrm{L}}(m)$ may be obtained from eq 12a, assuming for simplicity that eq 3 holds for any interatomic separation[10]

$$\nu_{2,\mathrm{L}}(m) = \sum_{h}\sum_{<\, i}(i-h)^{-3/2} = \int_{\bar{k}}^{m}\frac{m-k}{k^{3/2}}\,\mathrm{d}k = 2\bar{k}^{1/2}\left[\left(\frac{m}{\bar{k}}\right)^{1/2} - 1\right]^2 \tag{14}$$

where $k = i - h$ and $\bar{k}$ is a lower cutoff that accounts for the impossibility of contact between atoms separated by $k < \bar{k}$ bonds for stereochemical constraints.[7] By putting $\bar{k} > 0$ we also eliminate the divergence otherwise associated with the lower limit of integration. From eq 13 and 14 we finally get

$$\nu_2 = 2f\bar{k}^{1/2}[\xi + \psi_1(f)\xi^{1/2} - \psi_2(f)] \tag{15}$$

where

$$\xi = N/f\bar{k} \tag{15a}$$

$$\psi_1(f) = f(2 - 2^{1/2}) + 2^{1/2} - 4 \qquad \psi_2(f) = \frac{f-3}{2} \tag{15b}$$

The three-body interactions, on the other hand, may be grouped in three sets, depending on whether the three atoms belong to one, two, or three different arms, as shown in Scheme II. The interactions included in sets I and II may be calculated as before in terms of the three-body interactions of a linear chain with m atoms, $\nu_{3,\mathrm{L}}(m)$. Concerning set III, it has no counterpart in linear chains, where $f = 1$ or 2, and its contribution must be calculated separately; it will be denoted by $\nu_3{}^{\mathrm{III}}$. Accordingly, ν_3 is given by

$$\nu_3 = f\nu_{3,\mathrm{L}}\left(\frac{N}{f}\right) + \frac{f(f-1)}{2}\left[\nu_{3,\mathrm{L}}\left(2\frac{N}{f}\right) - 2\nu_{3,\mathrm{L}}\left(\frac{N}{f}\right)\right] + \frac{f(f-1)(f-2)}{3!}\nu_3{}^{\mathrm{III}} \tag{16}$$

By choosing $h < i < j$, we get from eq 3, 8a, and 12a[10]

$$\nu_{3,\mathrm{L}}(m) = \sum_{h}\sum_{<\, i}\sum_{<\, j}(i-h)^{-3/2}(j-i)^{-3/2} = \int_{\bar{k}}^{m}\mathrm{d}k\int_{\bar{k}}^{m-k}\mathrm{d}k_1\,\frac{m-k-k_1}{k^{3/2}k_1{}^{3/2}} = 4\left\{\frac{m}{\bar{k}} - 2\left(\frac{m}{\bar{k}}\right)^{1/2}\left[1 + \left(1 - \frac{\bar{k}}{m}\right)^{1/2}\right] - \left(\frac{\bar{k}}{m}\right)^{1/2} - 2\arcsin\left(\frac{\bar{k}}{m}\right)^{1/2} + (2+\pi)\right\} \simeq 4\left\{\frac{m}{\bar{k}} - 4\left(\frac{m}{\bar{k}}\right)^{1/2} - 2\left(\frac{\bar{k}}{m}\right)^{1/2} + (2+\pi)\right\} \tag{17}$$

where $k = i - h$ and $k_1 = j - i$; the last approximate equality depends on the assumption $m \gg \bar{k}$, neglecting terms of the order of $(\bar{k}/m)^{3/2}$.

To obtain $\nu_3{}^{\mathrm{III}}$, let us number consecutively the atoms in each arm starting from 1, adjacent to the branch point, to N/f at the free end. The relevant mean-square distances in set III are then given by

$$\langle r^2(h,i)\rangle_0 = C_\infty l^2(h+i) \tag{18}$$

so that we get from eq 8a and 12a

$$\nu_3{}^{\mathrm{III}} = \sum_{h}\sum_{i}\sum_{j}(hi + ij + hj)^{-3/2} = \int\int_{\bar{k}/2}^{N/f}\int\frac{\mathrm{d}h\,\mathrm{d}i\,\mathrm{d}j}{(hi + ij + hj)^{3/2}} \simeq 4\pi\left[1 - \xi^{-1/2}\left(\frac{3}{2} - \frac{1}{2\xi}\right)\right]\ln\left[1 + \left(\frac{2\xi}{33}\right)^{1/2}\right] \tag{19}$$

remembering that $\xi = N/f\bar{k}$. In the above, the first two integrals were evaluated exactly, unlike the last one that can be solved analytically in the limit $\xi \to \infty$ only. Therefore it was calculated numerically for finite ξ's; the approximating result reported in eq 19 is asymptotically correct and reproduces the numerical results to within 1% or less for $\xi \gtrsim 40$.

Upon replacing eq 17 and 19 in eq 16 we eventually get

$$\nu_3 = 4f\left\{\xi + 2\psi_1(f)\xi^{1/2} - (2+\pi)\psi_2(f) + \psi_3(f)\xi^{-1/2} + \psi_4(f)\left[1 - \xi^{-1/2}\left(\frac{3}{2} - \frac{1}{2\xi}\right)\right]\ln\left[1 + \left(\frac{2\xi}{33}\right)^{1/2}\right]\right\} \tag{20}$$

where $\psi_1(f)$ and $\psi_2(f)$ are given in eq 15b and

$$\psi_3(f) = f\left(2 - \frac{1}{2^{1/2}}\right) + \frac{1}{2^{1/2}} - 4$$

$$\psi_4(f) = \frac{\pi}{6}(f-1)(f-2) \tag{20a}$$

Substitution of eq 15 and 20 in eq 11a finally gives

$$\Theta = \frac{\Theta_{\mathrm{ph}}}{1 + \dfrac{4K_1}{B\bar{k}^{1/2}}g(\xi,f)} \simeq \Theta_{\mathrm{ph}} - \Delta\Theta_\infty g(\xi,f) \tag{21}$$

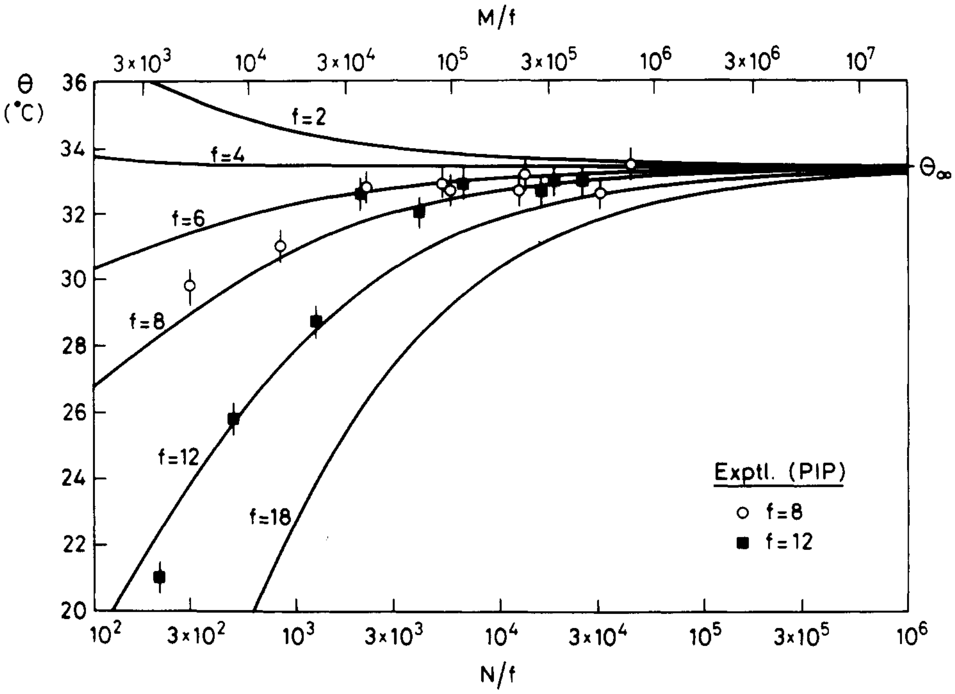


Figure 1. Θ temperature of linear and regular star polymers with f arms plotted as a function of the number of atoms per arm N/f (the linear chain corresponds here to $f = 2$). The curves calculated from eq 21 were fitted to the experimental points[1] from 8- and 12-arm polyisoprene (PIP); the upper abscissa gives the corresponding molecular weight per arm M/f. The asymptotic value Θ_∞ = 33.4 °C common to all the curves is also shown.

where we used the notation

$$\Delta\Theta_\infty = \frac{4K_1\Theta_{\rm ph}}{B\bar{k}^{1/2}} \tag{21a}$$

$$g(\xi,f) = \left\{\xi + 2\psi_1\xi^{1/2} - (2+\pi)\psi_2 + \psi_3\xi^{-1/2} + \psi_4\left[1 - \xi^{-1/2} \times \left(\frac{3}{2} - \frac{1}{2\xi}\right)\right] \ln\left[1 + \left(\frac{2\xi}{33}\right)^{1/2}\right]\right\} / \{\xi + \psi_1\xi^{1/2} - \psi_2\} \tag{21b}$$

Here $\psi_i \equiv \psi_i(f)$ for brevity and the approximate equality in eq 21 derives[5] from $K_1/B \ll 1$, $g(\xi,f)$ being of order unity. For $\xi \gg 1$ we have

$$g(\xi,f) \simeq 1 + \psi_1(f)\xi^{-1/2} \tag{22}$$

so that $g(\xi,f)$ tends asymptotically to 1 independent of f for $\xi \to \infty$. In this case we may write

$$\Theta_{\xi\to\infty} \equiv \Theta_\infty = \Theta_{\rm ph} - \Delta\Theta_\infty \tag{23}$$

and substituting back in eq 21 we can get the molecular weight dependence of Θ with no explicit reference to $\Theta_{\rm ph}$. In particular, for large ξ ($=N/f\bar{k}$) we have

$$\Theta = \Theta_\infty - \Delta\Theta_\infty\psi_1(f)\xi^{-1/2} = \Theta_\infty - \varphi\chi(f)N^{-1/2} \tag{24}$$

where

$$\chi(f) = f^{1/2}\psi_1(f) = f^{1/2}[f(2 - 2^{1/2}) + 2^{1/2} - 4] \tag{24a}$$

and φ is a suitable constant. The Θ temperature tends therefore to Θ_∞ from above or below, depending on the sign of $\psi_1(f)$. More precisely, $\psi_1(f)$ is negative for $f \leqslant 4$ and positive for $f \geqslant 5$, so that Θ decreases with molecular weight in the former case and increases in the latter one.

Discussion

The Θ temperature of linear and regular star polymers calculated from eq 21 is shown in Figure 1 as a function of N/f, i.e., the number of atoms per arm, together with some experimental data from 8- and 12-arm polyisoprene (PIP) in dioxane.[1] (The molecular weight per chain arm for PIP is also reported in the upper abscissa.) Θ_∞ was taken as 33.4 °C and $\Delta\Theta_\infty$ was chosen as 18 °C from a rough fit of the initial slope to the experimental points; $\Theta_{\rm ph}$ is therefore 51.4 °C. Finally, by horizontally adjusting the calculated and the experimental plot we get $\bar{k} = 2$.

The experimental points[1] seem to reach the asymptotic value Θ_∞ rather more abruptly than the calculated curves do, but the overall agreement may be considered as satisfactory in view of the simplifying assumptions made. Moreover, four- and six-branched regular star PIP samples have been reported to have an almost constant Θ temperature,[11] 34 ± 1 °C in dioxane, down to $N/f \simeq 500$, quite in agreement with our predictions. In fact, the calculated curves in Figure 1 show essentially no change at all for $f = 4$ and are only marginally outside experimental error for $f = 6$.

As for the cutoff value $\bar{k} = 2$, obtained from the fit on stars with $f = 8$ and 12, it is certainly too small if viewed as a number of chemical bonds, even taking into account the large flexibility of PIP as suggested by its characteristic ratio[1,12] $C_\infty \simeq 5$: from this value we would expect $\bar{k}$ to be around 20.[7] However, it should be pointed out that for small N/f the two- and three-body contacts between atoms on different arms are quite important. For these contacts, we should not assume the branch point to be monoatomic. Rather, it encompasses a few atoms (ranging from one to seven if $f = 8$ or 12[13]) including some flexible Si atoms, so that two atoms formally separated by $\bar{k}$ bonds *across the branch point* are actually more distant. This also suggests that $\bar{k}$ depends on the chemical structure of the star core. In particular, for linear chains, where the core is not different from the arms, the formal value of $\bar{k}$ should be much larger than 2. This implies that we expect $\Delta\Theta_\infty$ to be smaller than 18 °C; therefore, for linear chains (f = 1 or 2) Θ would be closer to Θ_∞ than is shown in Figure 1, though still decreasing with N. Experimentally, Θ is found to be independent[1,3] of molecular weight for linear chains, although some conflicting data exist that suggest the possibility of a slightly higher value for short chains.[14] We shall come back to this point at the end of this section.

Going now to atactic polystyrene (PS) in cyclohexane, the existing data[2,3] qualitatively support the above trend: the Θ temperature is lower the smaller the molecular weight per arm is and the larger the number of arms is, but Θ_∞ is still the same for linear and star polymers. According to the present approach, $\Delta\Theta_\infty$ should be smaller for PS than for PIP by a factor of about 1.5. In fact, from eq 6 and 10 we have

$$B \propto \frac{v_c^2}{v_s(C_\infty l^2)^{3/2}}; \quad K_1 \propto \frac{v_c^3}{v_s(C_\infty l^2)^3} \tag{25}$$

whence from eq 21a we get

$$\Delta\Theta_\infty \propto \frac{v_c \Theta_{ph}}{\bar{k}^{1/2}(C_\infty l^2)^{3/2}} = \frac{\bar{v}_c \Theta_{ph} M_0}{\bar{k}^{1/2}(C_\infty l^2)^{3/2}} \tag{26}$$

where $\bar{v}_c$ is the apparent partial specific volume in milliliters per gram and M_0 is the molar mass per chain atom.[8,15] For PS the characteristic ratio C_∞ ($\simeq 10$) is twice that of PIP[12] and $\bar{k}$ should change proportionally, whereas l is about the same and Θ_{ph} should be roughly equal (in fact Θ_∞ is 34.5 °C for PS in cyclohexane versus 33.4 °C for PIP in dioxane). As for the other quantities, $\bar{v}_c$ is 1.10 mL/g and $M_0 = 17$ for PIP, while the corresponding values for PS are 0.93 mL/g and 52.[16] We then expect $\Delta\Theta_\infty$ for PS to be close to 12 °C, compared with 18 °C for PIP. It is interesting to note that an independent estimate of $\Delta\Theta_\infty$ for PS in cyclohexane may be directly obtained by eq 21a. In fact, using the values $B = 0.082$ and $K_1 = 1.9 \times 10^{-3}$ proposed by us for this system during the study of single-chain collapse[10] and taking $\bar{k} = 4$ (that is, twice the value for PIP, as suggested before), we get $\Delta\Theta_\infty \simeq 14$ °C, in good agreement with the above figure. Experimentally, the difference $\Theta_\infty - \Theta$ seems to be only marginally smaller for PS in cyclohexane[2] than for PIP in dioxane if $f = 12$ and $N/f = 750$ (about 5 °C versus about 6.5 °C), whereas it is reported to be much larger for four- and six-branched stars.[3] In this case, the observed difference is quite similar to that shown in Figure 1 for the same N/f but for about twice the number of arms. However, it should be pointed out that a few other data do suggest a much smaller difference.[4] In this context, it should also be mentioned that subtle modifications in the chain microstructure and solvent quality (including some possible impurity) may induce a change of the Θ temperature beyond the experimental error.

From a theoretical point of view, the present results may be compared with those obtained through other approaches by Candau et al.[4] (indicated in the following as CRB) and by Kosmas[17] (indicated as K). The CRB theory is based on an extension to branched polymers of the Orofino–Flory theory,[8] which describes the chain as a gas of monomers with inclusion of a segment-density dependence of the interaction free energy. In this way, three-body interactions are effectively introduced in an affine, mean-field approach and Θ is obtained as the temperature where the (affine) expansion coefficient α is unity or the second virial coefficient A_2 vanishes. Kosmas, on the other hand, considers irregularities in the solvent induced by the high density of segments near the star core through an effective pseudopotential between polymer segments and solvent vacancies. Θ is obtained as the temperature at which $A_2 = 0$ via a first-order perturbative approach. Both theories lead to an equation of the general form

$$\Theta = \Theta_\infty - \varphi'\chi'(f)N^{-1/2} \tag{27}$$

where φ' depends only on the given monomer–solvent pair and in CRB theory it depends on whether the $\alpha = 1$ or the $A_2 = 0$ criterion is used, whereas Kosmas gets a still different value. $\chi'(f)$ characterizes the polymer architecture:

$$\chi'_{\mathrm{CRB}}(f) = g^{-3/2} = \left(\frac{f^2}{3f-2}\right)^{3/2} \tag{27a}$$

$$\chi'_{\mathrm{K}}(f) = f(f-3) \tag{27b}$$

Here g is the ratio between the mean-square radius of gyration of the star polymer and that of the linear chain with the same molecular weight. According to Zimm and Stockmayer,[18] for a random-walk phantom chain $g = (3f - 2)/f^2$, whence the last member in eq 27a. Also, Θ_∞ coincides with Θ_{ph} in the CRB theory because it is the temperature at which the binary cluster integral vanishes, unlike in Kosmas' and in our theory. Upon comparison of eq 27 with eq 24, we see that the three approaches predict for Θ the same $N^{-1/2}$ dependence, although this is only valid for quite long arms in our theory. The architecture-dependent prefactor $\chi(f)$ increases in all cases with the number of arms f, but with some qualitative differences. In fact, from eq 27a, $\chi'_{\mathrm{CRB}}(f)$ is positive for any f, so that Θ would always approach Θ_∞ from below, whereas from eq 27b $\chi'_{\mathrm{K}}(f)$ is negative for $f = 1$ or 2 (linear chains), zero for $f = 3$, and positive for $f \geq 4$. On the other hand, we predict $\chi(f)$ to be positive for $f \geq 5$ and negative for $f \leq 4$ (see eq 24a). This point cannot be decided upon with the present experimental data and requires much more accurate determinations of Θ for short chains with three or four arms.

Concerning the molecular weight dependence of Θ for linear chains, we should mention that, considering explicitly the chain connectivity and finiteness, Khokhlov[19] pointed out that the number of three-body interactions is mainly due to those interactions wherein two atoms are close along the chain sequence and the third one is topologically distant. An extension of this argument applies in general to all n-body interactions: due to the chain connectivity, they are predominantly due to interactions involving two groups, one comprising m atoms and the other $n - m$ atoms, each group consisting of topological neighbors. Including these multibody interactions in a renormalized binary cluster integral, Khokhlov showed that the Θ temperature of linear chains approaches the limiting value Θ_∞ from above with $\Theta - \Theta_\infty$ decreasing as $N^{-1/2}$, in keeping with our prediction. Cherayil et al.[20] obtained, inter alia, an analogous result using a combination of perturbation expansion and renormalization group analysis to study linear chains close to the Θ temperature with inclusion of binary and ternary interactions. Interestingly enough, formal divergences could only be eliminated by retaining a cutoff parameter to avoid the physically absent self-interactions. This cutoff was explicitly considered as a phenomenological parameter and is essentially equivalent to our $\bar{k}$. However, it should be stressed that such a cutoff had been previously introduced and estimated by one of us[7] through stereochemical considerations within a detailed chain model. The Θ temperature of linear chains was also studied by Janssens and Bellemans[21] with exact enumerations and Monte Carlo techniques. Using self-avoiding chains on a simple cubic lattice with an attractive intramolecular potential to simulate the Θ state, they obtained the chain-length dependence of the reduced temperature for which $A_2 = 0$. The results fully support the theoretical prediction that for finite linear chains Θ decreases toward Θ_∞ with an $N^{-1/2}$ power law. Unfortunately, analogous Monte Carlo simulations on star polymers[22] are not accurate enough to detect the corresponding difference from Θ_∞.

In conclusion, the decrease of Θ for linear chains to the asymptotic value Θ_∞ appears to be theoretically established provided the chain connectivity is accounted for. The lack of conclusive experimental evidence is possibly to be attributed to the fact that the difference $\Theta - \Theta_\infty$ is too small to be detected, the more so because it requires well-characterized and monodisperse short chains.

Concluding Remarks

The Θ temperature of linear and regular star polymers was determined by assuming that the overall three-body repulsive interactions are balanced by the two-body attractions. This allowed us to calculate the decrease of the actual Θ temperature from the value Θ_{ph} at which the binary cluster integral vanishes. Otherwise said, Θ_{ph} is the Θ temperature of a phantom chain devoid of any long-range interaction and depends only on the monomer–solvent pair.

Θ is found to decrease with increasing molecular weight for linear and lightly branched chains with $f \leqslant 4$ and to increase for $f \geqslant 5$, eventually reaching a common asymptotic limit Θ_∞ ($<\Theta_{ph}$), the difference $|\Theta - \Theta_\infty|$ being in any case proportional to $N^{-1/2}$ through an architecture-dependent coefficient. To understand this contrasting molecular weight dependence of Θ, let us consider the extreme cases of a linear and of a highly branched chain. In the *linear* chain, the number of both the two-body and the three-body interactions (proportional to ν_2 and ν_3, respectively, see eq 12) increases proportionally to $[(N/\bar{k})^{1/2} - c]^2$ for large N (see eq 14 and 17), with c about equal to 1 and 2, respectively. This reflects the requirement that the chain must comprise at least $\bar{k}$ bonds to have a two-body interaction and at least $2\bar{k}$ bonds to have a three-body interaction. Thus, the ratio ν_3/ν_2 increases to an asymptotic limit with increasing N, thereby decreasing Θ (see eq 11a), because in the short chains the relatively more numerous two-body attractions need a smaller temperature lowering to compensate the three-body repulsions. The opposite is true for *highly branched* chains. For a low molecular weight, that is, for short arms, there are a very large number of three-body interactions, in particular those belonging to set II and, even more, to set III in Scheme II. Accordingly, the cutoff effect described above for linear chains is overruled and the ratio ν_3/ν_2 is quite large; hence, Θ must be lower than for linear chains, the more so the larger f is, to strengthen the attractive two-body attractions. With increasing N, the fraction of atoms near the star core becomes smaller and smaller; hence, the only relevant three-body interactions are those belonging to sets I and II wherein at least two out of three atoms are topologically close. Therefore, the ratio ν_3/ν_2 decreases with increasing N toward the value expected for long, linear chain strands, and Θ may increase, thus reflecting the need for comparatively smaller two-body attractions. Eventually, an asymptotic limit Θ_∞ common to all molecular architectures is reached.

The agreement with experiment[1-4] is satisfactory, considering the simplifying assumptions employed in the theory, most notably the use of a bead-and-spring chain in the Gaussian approximation. In particular, we expect some degree of correlation among the atomic positions across the branch point imposed by the constraint of a common end for all the arms; this may be of some relevance when the number of arms is large. From an experimental point of view, we should note that not all the data are as accurate as we may wish, because of the need to have carefully fractionated samples with a well-defined microstructure in high-quality solvents: inaccuracies in the Θ temperatures of 1–2 °C are in fact quite large if one is looking for differences from Θ_∞ of about 5–10 °C at most, and usually smaller.

We finally stress that Θ is currently measured as the temperature at which the second virial coefficient vanishes. On the other hand, we defined Θ as the temperature at which long-range interactions effectively compensate, so that the interatomic mean-square distances are proportional to topological separation, hence the mean-square radius of gyration is proportional to molecular weight. In practice, the two definitions lead to minor differences in the measured Θ values,[4] though these differences may not be completely negligible when the number of arms is large.

Acknowledgment. This work was made possible by a financial contribution from Ministero Pubblica Istruzione, 40% (Italy).

Registry No. PIP, 9003-31-0; PS, 9003-53-6.

References and Notes

(1) Bauer, B. J.; Hadjichristidis, N.; Fetters, L. J.; Roovers, J. E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2410.
(2) Huber, K.; Burchard, W.; Fetters, L. J. *Macromolecules* **1984**, *17*, 541.
(3) Roovers, J. E. L.; Bywater, S. *Macromolecules* **1974**, *7*, 443.
(4) Candau, F.; Rempp, P.; Benoit, H. *Macromolecules* **1972**, *5*, 627.
(5) Allegra, G.; Ganazzoli, F. *J. Chem. Phys.* **1985**, *83*, 397.
(6) Allegra, G.; Ganazzoli, F. *Gazz. Chim. Ital.* **1987**, *117*, 99.
(7) Allegra, G. *Macromolecules* **1983**, *16*, 555.
(8) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957**, *26*, 1067.
(9) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, 1979; Chapter 4.
(10) Allegra, G.; Ganazzoli, F. *Adv. Chem. Phys.* **1989**, *75*, 265.
(11) Hadjichristidis, N.; Roovers, J. E. L. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2521.
(12) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(13) Hadjichristidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* **1978**, *11*, 668.
(14) McIntyre, D.; O'Mara, J. H.; Konouck, B. C. *J. Am. Chem. Soc.* **1959**, *81*, 3498.
(15) Note that in eq 28 of ref 5 we erroneously used v_c, the effective volume per chain atom, instead of $\bar{v}_c$, the apparent partial specific volume.
(16) *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975.
(17) Kosmas, M. K. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 633.
(18) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(19) Khokhlov, A. R. *J. Phys. (Les Ulis, Fr.)* **1977**, *38*, 845.
(20) Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1985**, *83*, 5293.
(21) Janssens, M.; Bellemans, A. *Macromolecules* **1976**, *9*, 303.
(22) Mazur, J.; McCrackin, F. *Macromolecules* **1977**, *10*, 326.