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Notes

Static Properties of Star-Branched Polymers in Dilute Solution

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Introduction

In the past few years, two major experimental investigations into the dilute solution properties of star-branched polymers have been presented. In one,[1] the molecules were relatively low-mass polyethylene stars with 3, 4, 12, and 18 arms, and the mean squared radius of gyration, $\langle S^2 \rangle$, and second virial coefficient, A_2, were determined by small-angle neutron scattering. The other study[2] was made by light scattering. It used a series of polyisoprene molecules with much larger effective Kuhn size and included regular stars with 3, 4, 6, 8, 12, and 18 arms, and as well a number of molecules with up to 56 arms linked by means of a divinylbenzene (DVB) central unit.

For the polyethylene stars, the values of $\langle S^2 \rangle$ and A_2 measured in both Θ and good solvents were found to be in satisfactory agreement with the predictions of what might be regarded as "traditional" mean-field theory. The polyisoprene data were not compared with any particular model but instead were represented by power laws that describe the limiting behavior at large molecular mass and functionality.

Theories that are based on specific microscopic models undoubtedly provide more fundamental insight into a physical system than can be gained from simple scaling laws. It is desirable, therefore, to establish whether the mean field theories that were successful with respect to the polyethylene stars can also be applied to other materials and over a wider range of molecular mass and degree of branching. To this end, the extensive polyisoprene data[2,3] were reanalyzed with the same theoretical expressions as were used in ref 1, and it is the purpose of this Note to present some of the results of this analysis and to discuss the extent to which the theory has been successful.

The theoretical analysis is based upon the smoothed density model, in which the effect of long-range interactions within a polymer chain is calculated from the interactions in a swarm of disconnected segments having the same average distribution in space as the molecule itself. Such a model breaks down when fluctuations in the local segment density become important, as is likely for a chain of very great length. It might be argued, however, that the mean field theory is better suited to branched polymers because the intramolecular segment density is higher and, therefore, more homogeneous.

Results

Dilute Θ Solution. An important feature of traditional two-parameter theories[4] is that at the Θ temperature, defined as the critical precipitation temperature of an infinitely long polymer, A_2 is zero and $\langle S^2 \rangle$ equals the unperturbed, random walk, squared radius of gyration, $\langle S^2 \rangle_0$. However, when the intramolecular segment density is large, as for highly branched molecules, the dilute solution properties are expected to be influenced by effective three-body interactions. Orofino and Flory[5] took into account ternary interactions phenomenologically, by including a concentration-cubed term in the free energy of the mean field theory. This approach has been extended to star polymers, and in the most recent treatment,[1,6] the expansion factor at Θ, $\alpha_{\Theta s} = (\langle S^2 \rangle_\Theta / \langle S^2 \rangle_0)^{1/2}$, of a star with f arms has the form

$$\alpha_{\Theta s}{}^8 - \alpha_{\Theta s}{}^6 = \frac{2}{7}\frac{G}{g^3}A \tag{1}$$

where

$$G = \frac{15f - 14}{(3f - 2)^2}$$

$$g = \frac{3f - 2}{f^2}$$

$$A = \frac{3^{5/2}}{(2\pi)^3}\frac{\bar{v}^3}{2v_0 N_A{}^3}\left(\frac{M}{\langle S^2 \rangle_\Theta}\right)^3_{\text{lin}}({}^1/_3 - \chi_2)$$

Here, $\bar{v}$ is the polymer partial specific volume, v_0 is the volume of a solvent molecule in solution, and ${}^1/_3 - \chi_2$ is Orofino and Flory's third parameter. From eq 1, $\alpha_{\Theta s}$ is seen to be independent of molecular mass, so that, for a given f, the relation $\langle S^2 \rangle_\Theta \sim M$ still applies. Another result is that for large f the expansion factor tends toward a power law, $\alpha_{\Theta s} \sim f^{1/4}$, as has already been predicted from a scaling argument.[7]

Inspection of the polyisoprene results[2,3] in Θ solvent confirms that $\alpha_{\Theta s}$ is independent of M, as predicted, and the observed power law, $\alpha_{\Theta s} \sim f^{0.219}$, is close to the scaling limit given above. A more severe test of eq 1 is made with a plot of $\alpha_{\Theta s}{}^2$ vs $G/(g^3\alpha_{\Theta s}{}^6)$: according to the theory, the data should lie on a straight line passing through the point (0,1). Note, however, that the true $\langle S^2 \rangle_0$ is not measurable by light scattering, and it is the quantity $g\langle S^2 \rangle_{\Theta,\text{lin}}$ that must be used in the calculation of the star expansion factors. Accordingly, the experimental expansion factor is $\alpha_e = \alpha_{\Theta s}/\alpha_{\Theta s,\text{lin}}$, and the plot of $\alpha_e{}^2$ vs $G/(g^3\alpha_e{}^6)$ is a straight line through the point (1,1), with a gradient of $2A/(7\alpha_{\Theta s,\text{lin}}{}^8)$ and an intercept of $1/(\alpha_{\Theta s,\text{lin}}{}^2)$. Figure 1 shows such a plot for the polyisoprene stars, and it is seen that the points are consistent with the theoretical expression (eq 1). This is a gratifying result, for although a similar level of agreement was found with the polyethylene

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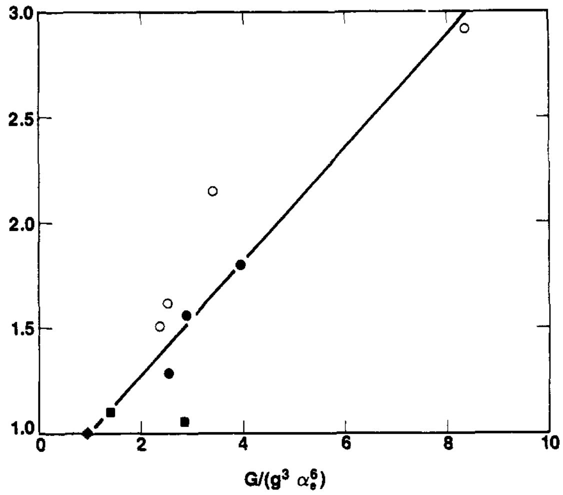

Figure 1. Θ temperature expansions of polyisoprene stars in dioxane plotted according to eq 1. Each point represents one value of *f*: (■) 4- and 6-arm chlorosilane-linked stars;[3] (●) 8-, 12-, and 18-arm chlorosilane-linked stars;[2] (○) DVB-linked stars.[2] The point (◆) at (1,1) is for linear chains. From the gradient and intercept of the straight line, $^1/_3 - \chi_2 = 2.4$.

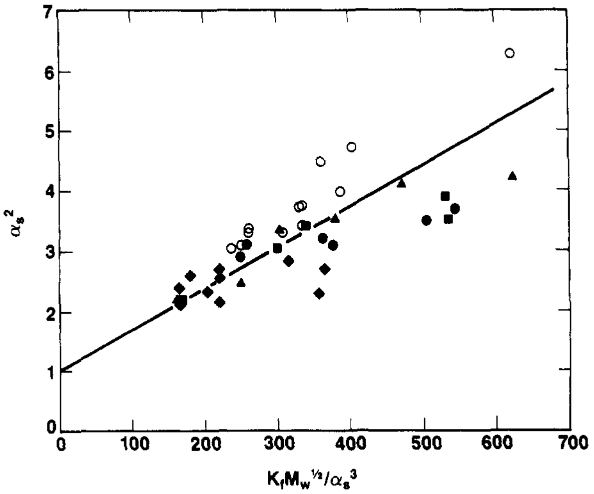

Figure 2. Expansion factors of polyisoprene stars in a good solvent (cyclohexane) plotted according to eq 2. The symbols are (◆) linear molecules, (●) 8-arm stars, (■) 12-arm stars, (▲) 18-arm stars, and (○) DVB-linked stars with various numbers of arms. Within the limitations of the data, the points are consistent with a universal curve. The excluded volume parameter deduced from the gradient of the straight line is $z = 0.0069M^{1/2}$.

molecules, the range of *f* values and molecular masses in the polyisoprene study was much larger. If the physical constants,[3,8] $v_0 = 1.42 \times 10^{-22}$ cm³, $\bar{v} = 1.2$ cm³ g⁻¹, and $(\langle S^2\rangle_\Theta/M)_{\text{lin}} = 1.07 \times 10^{-17}$ cm², are combined with the gradient and intercept of the straight line, then the value of the third parameter is $^1/_3 - \chi_2 = 2.4$ for polyisoprene.

Another prediction of the three-parameter theory[5] is that A_2 is greater than zero at $T = \Theta$ and vanishes at a lower temperature, Θ_{A_2}. According to the theory, the difference $\Theta - \Theta_{A_2}$ increases with *f* and decreases with *M*, and from the observed temperature dependence of A_2, another value of $^1/_3 - \chi_2$ may be calculated. Neutron scattering measurements on a 12-arm polyethylene star[1] yielded a value in good agreement with that deduced from the $\alpha_{\Theta s}$ data. However, the results for the polyisoprene stars are not as encouraging, for although the *f* and *M* dependences are qualitatively correct for large *M*, serious deviations from the theoretical behavior occur for 12- and 18-arm stars with $M \leq 5 \times 10^5$ g mol⁻¹. Moreover, the value of $^1/_3 - \chi_2$ estimated from the Θ_{A_2} results is an order of magnitude smaller than that given above from the Θ expansions, a finding in accord with that given previously[9] for 8- and 12-arm polyisoprenes. Part of the discrepancy might be explained by the swelling due to steric constraints near to the branch point, which has been found to be remarkably large for short-arm star polymers.[10] This effect would tend to reduce $\Theta - \Theta_{A_2}$ from the theoretical prediction, because the segment density is lower than in a Gaussian star, and would be more important for short, many-arm stars. The same effect might also account for the abnormally large value for $^1/_3 - \chi_2$ derived here from the $\alpha_{\Theta s}$ data.

Dilute Solution in Good Solvent. The effect of three-body interactions will be much reduced when polymers are highly swollen in a good solvent, so a two-parameter theory should be sufficient to describe the dilute solution properties. The mean-field theory based on the smoothed density model predicts the expansion factor to take the form

$$\alpha_s^5 - \alpha_s^3 = K_f z \qquad (2)$$

where K_f is a function of *f* only[4] and *z* is the conventional excluded volume parameter, which is proportional to $M^{1/2}$ but independent of molecular architecture. For large *f*, $K_f \sim f^{1/2}$ so that eq 2 predicts the limiting power law $\alpha_s \sim f^{1/10}M^{1/10}$, in agreement once again with the scaling prediction.[7]

In Figure 2, the good solvent polyisoprene data have been plotted to test eq 2. Also included are some earlier results for linear polyisoprene.[11] The large experimental scatter is due to the sensitivity of the plot to α_s, but more importantly, there are no systematic deviations from the straight line for sets of points with different *f* values. This is particularly true for the group of DVB-linked stars, which lie slightly above the rest of the points but close to a single straight line. This represents strong evidence that the single coefficient K_f acts to bring stars of all functionalities onto a universal curve and suggests that the intramolecular excluded volume may be described by a single parameter *z*, independent of branching. From the gradient of the straight line, one can calculate that $z = 0.0069M^{1/2}$.

With the polyethylene stars, further support for the mean-field theory was provided by an analysis of the experimental A_2 values with the Orofino–Flory closed form. Not only did the points lie on a universal curve, but the resultant expression for *z* was in agreement with that obtained from the α_s analysis. However, the values of *z* in that study never exceeded 0.5, and in the small *z* regime, A_2 is not very sensitive to the exact functional form. By contrast, the polyisoprene stars had *z* values up to 10, so representing a more severe test of the theory. In fact, it was not possible to represent the A_2 data on a universal curve, and it must be concluded that a correct intermolecular theory remains to be found.

Discussion

The analysis presented in this Note has shown that so far as molecular dimensions are concerned, the behavior of polyethylene and polyisoprene stars in dilute solution is the same and is well-described by a mean-field theory based on the smoothed density model. The results at the Θ temperature support a three-parameter theory, which includes the effect of ternary interactions, while in good solvents it is sufficient to account only for binary excluded volume. When the same theoretical models are used to calculate A_2, however, less satisfactory agreement is found, especially for large molecular masses.

More detailed conclusions from the present data, and from other measurements on polystyrene and polybutadiene stars, are precluded by the large experimental scatter, which arises from the inclusion of results from many different laboratories, from the general sparcity of measurements and from sample problems such as polydispersity. Further progress will require extensive, careful measurements on a large number of well-characterized molecules, spanning a wide range of molecular mass and functionality.

References and Notes

(1) Boothroyd, A. T.; Squires, G. L.; Fetters, L. J.; Rennie, A. R.; Horton, J. C.; deVallera, A. M. B. G. *Macromolecules* **1989**, *22*, 3130.
(2) Bauer, B. J.; Fetters, L. J.; Graessley, W. W.; Hadjichristidis, N.; Quack, G. F. *Macromolecules* **1989**, *22*, 2337.
(3) Hadjichristidis, N.; Roovers, J. E. L. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2521.
(4) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(5) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957**, *26*, 1067.
(6) Boothroyd, A. T. *Europhys. Lett.* **1989**, *9*, 327.
(7) Daoud, M.; Cotton, J.-P. *J. Phys.* **1982**, *43*, 531.
(8) Hadjichristidis, N.; Xu, Z.; Fetters, L. J.; Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 743.
(9) Bauer, B. J.; Hadjichristidis, N.; Fetters, L. J.; Roovers, J. E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2410.
(10) Horton, J. C.; Squires, G. L.; Boothroyd, A. T.; Fetters, L. J.; Rennie, A. R.; Glinka, C. J.; Robinson, R. A. *Macromolecules* **1989**, *22*, 681.
(11) Davidson, N. S.; Fetters, L. J.; Funk, W. G.; Hadjichristidis, N.; Graessley, W. W. *Macromolecules* **1987**, *20*, 2614.

Registry No. Isoprene (homopolymer), 9003-31-0; ethylene (homopolymer), 9002-88-4.