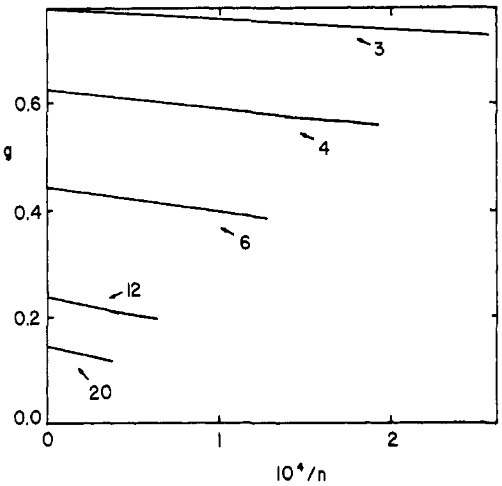

Figure 1. Rotational isomeric state g for unperturbed f-functional polymethylene stars.

of $2n/f$ bonds. The three C_i can be evaluated for the unperturbed chain using matrix methods.[1,12] While we have retained the rotational isomeric state character of the chain, no attention is paid to the actual structure of the branch point itself. The number of bonds in each branch was varied from 20 to 11 520.

Results and Discussion

Figure 1 depicts calculated behavior of g as a function of $1/n$ for unperturbed polymethylene stars in which f is 3, 4, 6, 12, and 20. Asymptotic limits at infinite n are in harmony with predictions obtained using random flight statistics.[11] The value of g for finite stars is somewhat smaller than the random flight limit. Dependence of g on $1/n$ becomes more severe as functionality of the branch point increases. Similar behavior is observed in trifunctional and tetrafunctional polymethylene stars in which detailed attention is given to the structure of the branch point.[5] If n is confined to the range of usual interest, g is well represented as a linear function of $1/n$ for all of the stars considered in Figure 1.

The wormlike chain treatment of stars[9] predicts[10]

$$[\mathrm{d}g/\mathrm{d}(1/L)]_{L\to\infty} = -6a(1 - 2f + f^2 + F)/f^2 \qquad (2)$$

Here a is the persistence length and F is determined by the initial direction of rays as they leave the branch point. The value of F is $-f/2$ if the initial direction of all rays cancel.[9] Since rotational the isomeric state calculations reported here have not included a description of geometry at the branch point, the appropriate value for F is not well defined. We assume $-f/2$ serves as an adequate approximation. The pertinent rotational isomeric state equivalent of eq 2 is then written as

$$[\mathrm{d}g/\mathrm{d}(1/nl)]_{n\to\infty} = -6a(1 - 2.5f + f^2)/f^2 \qquad (3)$$

Rotational isomeric state values for $\mathrm{d}g/\mathrm{d}(1/nl)$ at infinitely large n are obtained from the initial slopes of the lines in Figure 1. They are depicted as a function of $6(1 - 2.5f + f^2)/f^2$ in Figure 2. The points provide a reasonable description of a straight line with negative slope, in harmony with the prediction obtained using wormlike chain statistics.

The slope of the straight line in Figure 2 is −0.34 nm. Consequently, the "shift factor", $2an/L$, is 4.4, which is quite close to the value of 5 used previously by Mansfield and Stockmayer for tri- and tetrafunctional polymethylene stars.[9] The necessary shift factor for starlike polymethylenes does not depend on the functionality of the branch point. However, the shift factor for the branched polymethylenes is smaller by half than that required for linear polymethylene chains.[9,13] We conclude that the wormlike chain treatment, with a single "shift factor", successfully describes the dependence on branch point functionality of g for finite polymethylene stars with any branch point functionality likely to be of interest. Success of the wormlike chain model for stars formed from other types of polymers may not be so impressive, particularly if the corresponding linear chain has a low characteristic ratio.[10]

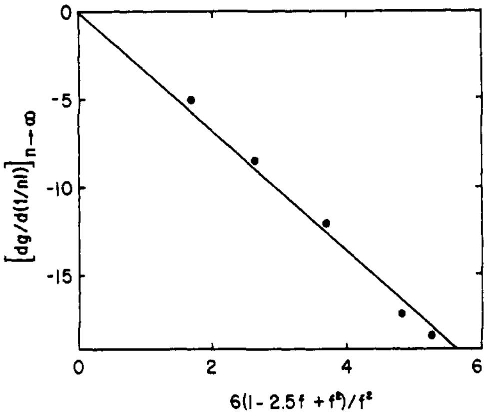

Figure 2. Approach to the asymptotic limit for g by unperturbed polymethylene stars of various functionalities.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A preliminary account of this work was presented at the 184th National Meeting of the American Chemical Society, Sept 12-17, 1982, Kansas City.[14]

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Formula for the Weight-Average Molecular Weight beyond the Gel Point

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The analytic solution of gelation theory for finite systems of f-functional structural units that are reacting in accord with Flory's two assumptions of equal reactivity of unreacted groups and *absence* of intramolecular reaction has recently been obtained by the author.[1] It is evident in the ensemble average, or mean, polymer size distribution, $\bar{m}_k$, $1 \leq k \leq N - M + 1$, derived that, at extents of reaction, α, above the critical extent of reaction, α_c, the gel portion

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Table I
Estimates of the Weight-Average Molecular Weight beyond the Gel Point, α_c, for Finite Systems of Polycondensing, Tetrafunctional Units As Obtained by Simulation, the Extrapolation of These to Infinite System Size, and the Corresponding Values of the Formula Derived in This Note

α	N = 128	N = 256	N = 512	N = 1024	N = 2048	N = 4096	$N \to \infty$ (terms)	eq 2 and 4
0.343 75	0.110 615 5	0.078 037 3	0.056 360 5	0.040 936 1	0.030 318 0	0.023 165 9		0.013 677 8
0.375 00	0.184 121 9	0.158 031 8	0.143 681 6	0.139 520 5	0.141 125 5	0.145 274 8	0.149 424 (2)	0.150 635 0
0.406 25	0.303 671 8	0.300 199 0	0.309 510 8	0.320 362 3	0.324 549 9	0.326 647 8	0.328 876 (4)	0.328 586 2
0.437 50	0.457 465 8	0.473 013 6	0.483 869 3	0.488 263 7	0.489 895 4	0.490 883 4	0.491 415 (4)	0.491 913 1
0.468 75	0.603 410 2	0.617 004 2	0.621 986 6	0.623 716 0	0.624 632 8	0.625 067 4	0.625 369 (4)	0.625 657 5
0.500 00	0.716 847 4	0.724 765 9	0.727 092 7	0.728 300 7	0.728 870 2	0.729 189 5	0.729 532 (4)	0.729 490 2
0.562 50	0.859 899 5	0.863 058 7	0.864 121 7	0.865 105 3	0.865 121 0	0.865 451 7	0.865 533 (3)	0.865 481 2
0.625 00	0.934 836 1	0.935 913 7	0.936 829 9	0.937 194 9	0.937 404 0	0.937 576 0	0.937 692 (3)	0.937 604 5
0.687 50	0.971 856 6	0.972 613 0	0.973 128 3	0.973 469 9	0.973 509 8	0.973 639 7	0.973 713 (3)	0.973 646 1
0.750 00	0.989 235 3	0.989 740 5	0.989 998 6	0.990 207 3	0.990 258 5	0.990 272 2	0.990 332 (3)	0.990 343 3
0.812 50	0.996 521 6	0.996 905 3	0.997 017 8	0.997 124 0	0.997 161 9	0.997 178 4	0.997 191 (3)	0.997 205 3
0.875 00	0.999 185 2	0.999 308 5	0.999 364 3	0.999 439 1	0.999 463 3	0.999 474 0	0.999 488 (3)	0.999 483 3
0.937 50	0.999 879 1	0.999 905 9	0.999 938 8	0.999 958 8	0.999 967 0	0.999 967 5	0.999 977 (3)	0.999 969 0

of almost all systems in the ensemble consists of exactly one molecule. The mean size of the molecule is precisely the weight of the gel as found by Stockmayer[2]

$$NW_g(\alpha) = Nf[(f-1)\alpha - 1]/(f-2), \qquad \alpha_c \le \alpha \le 2/f \tag{1}$$

while the relative fluctuation in the gel size for macroscopic systems is entirely negligible, being of order $N^{-1/3}$, where N is the number of units in the system.

The average contribution of the one gel molecule to the weight-average molecular weight is obviously the single term $[NW_g(\alpha)]^2$. The contribution of the sol and correction due to fluctuations in the gel size in the ensemble are of orders less than N^2, and, as a result, the total limiting weight-average molecular weight is simply

$$\lim_{\substack{N\to\infty \\ \alpha \text{ fixed}}} \frac{1}{N^2} \sum_{k=1}^{N-M+1} k^2 \bar{m}_k = [W_g(\alpha)]^2 \tag{2}$$

with $W_g(\alpha)$ as given by eq 1. (More generally, the contribution of the one gel molecule to the ith moment is $[NW_g(\alpha)]^i$. For $i \ge 2$ this dominates all other contributions in the appropriate infinite limit.) The corresponding expression for extents of reaction below α_c was found by Stockmayer to be

$$\lim_{\substack{N\to\infty \\ \alpha \text{ fixed}}} \frac{1}{N} \sum_{k=1}^{N-M+1} k^2 \bar{m}_k = \frac{1+\alpha}{1-(f-1)\alpha}, \qquad 0 \le \alpha < \alpha_c \tag{3}$$

The discontinuity at α_c in the limiting weight-average molecular weight as given by eq 1–3 is understood as resulting from the change in the dependence on N of $\sum_k k^2 \bar{m}_k$ in the neighborhood of α_c: below α_c this quantity increases as N, above α_c it increases as N^2, and at α_c it increases as $N^{4/3}$. Thus, at α_c, $\sum_k k^2 \bar{m}_k / N$ diverges as $N^{1/3}$ while $\sum_k k^2 \bar{m}_k / N^2$ vanishes as $N^{-2/3}$.

Equation 2 possibly holds for many polymerizing systems beyond α_c, as it follows directly from the likely assumption that the gel consists of one molecule and is independent of the assumption regarding the occurrence of intramolecular reaction. (The form of $W_g(\alpha)$ and the maximum value of α, of course, do depend on the latter assumption. The type of discontinuity at α_c in the limiting weight-average molecular weight described immediately above would, nevertheless, obtain in all cases.)

A solution of f-functional polycondensation that is closely associated with the one discussed so far was earlier put forward by Flory.[3] Stockmayer noted that the two solutions differed above α_c because intramolecular reaction occurred in the gel of Flory's model. Falk and Thomas[4] demonstrated numerically that Flory's formula for the most probable distribution of sol species constitutes the limiting solution for a model for f-functional polycondensation defined by the two assumptions that all unreacted groups are equally reactive and that *all conceivable* intramolecular reactions occur. It will now be shown, in much the same way, that the correct limiting weight-average molecular weight above α_c for the Falk and Thomas model is again given by eq 2, with the weight fraction of gel provided in this case by Flory's formula

$$W_g(\alpha) = 1 - \alpha'(1-\alpha)^2/\alpha(1-\alpha')^2, \qquad \alpha_c \le \alpha \le 1 \tag{4}$$

where α' is on the branch of $\alpha(1-\alpha)^{f-2}$ over $[0, \alpha_c]$.

The Falk and Thomas simulation program for the case where intramolecular reaction occurs was augmented so as to compute the weight-average molecular weight. The program was then run to simulate 10^4 complete tetrafunctional polycondensation reactions for each selected system size, with data collected at selected extents of reaction above $\alpha_c = {}^1/_3$. The averages over the 10^4 reactions of the weight-average molecular weights for each such system size and extent of reaction are given in Table I. Also given at each extent of reaction is the weight-average molecular weight computed from eq 2 and 4. The latter are to be compared with the results of the simulations as extrapolated to infinite system size. The extrapolated value was identified as the constant term in a least-squares fit of the simulation results to a quadratic or cubic polynomial in $1/N$. In the analytic solution of gelation theory as discussed above for the model in which intramolecular reaction is prohibited, the weight-average molecular weight had just such an asymptotic expansion in powers of $1/N$ provided that $N|1-(f-1)\alpha|^3 \gg 1$. Since this condition is satisfied by the entries in Table I neither at the lowest extent of reaction nor at the next two extents of reaction for system sizes less than or equal to the size at which the simulation averages attain their minimum, these data were not used in the extrapolations. The remaining data were fitted to polynomials of the degree specified in Table I to obtain the extrapolated values listed. The close agreement of eq 2 and 4 with these extrapolated values at all extents of reaction at which the extrapolations could be made substantiates the validity of eq 2 in the postgelation regime for this second model of f-functional polycondensation.

Acknowledgment. The author is indebted to Dr. Michael Falk for providing the simulation program used and to Dr. Julian H. Gibbs for support through USPHS Grant No. GM27951-03.

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