Table II
Interplanar *d* Spacings Calculated from the Monoclinic γ-Phase Unit Cell Proposed by Takahashi and Tadokoro

reflection	d,[a] Å	reflection	d,[a] Å
$\underline{1}52$	1.676	$\bar{2}42$	1.595
$\bar{1}52$	1.656	$\underline{4}42$	1.081
242	1.632	$\bar{4}42$	1.059

[a] Calculated from the unit cell a = 4.96 Å, b = 9.58 Å, c = 0.23 Å, and β = 92.9° (ref 6).

lists three pairs of interplanar spacings calculated from the γ-phase unit cell proposed by Takahashi and Tadokoro.[6] For this set, the difference between d_{hkl} and dh_{kl} is within the range of about 0.02–0.04 Å. At the fairly large scattering angles where these reflections occur, two adjacent reflections with d spacings differing by such an amount should be marginally distinguishable. Even if the two reflections were not quite resolvable, the resulting composite reflection would be unusually broad when compared to the width of reflections in which the h or l index was zero (in which case $d_{hkl} = d_{\bar{h}kl}$). We have reexamined our diffraction photographs of the γ phase and have found that none of the reflections listed in Table II (nor any other susceptible reflections) are split or unusually broad. This supports our proposed orthogonal γ-phase unit cell.

One additional piece of evidence exists to support the suggestion that more than one version of the γ phase exists. Lovinger[10,12] has found that annealing the δ phase of PVF_2 can result in transformation to the α, γ, and ϵ phases; the γ phase is by far the major transformation product. The 012 and 032 reflections of the γ phase are visible in the diffraction pattern of such annealed films. In a manner similar to the case of the α phase, the presence of these reflections strongly suggests that the chain packing is nonstatistical. However, the 012 and 032 reflections are systematically absent in structures having C-centered symmetry. The structures for the γ phase proposed both by us[2] and by Takahashi and Tadokoro[6] are C centered. Since the Takahashi samples are obtained under similar annealing conditions to the Lovinger samples, if the 012 and 032 γ-phase reflections are present, the Takahashi structure must be wrong. They appear to be present in their photographs.[9] In the unlikely event that they are due to the presence of α material, three variations of the γ form must be proposed.

To summarize: the recent work of Lovinger[10] strongly suggests the existence of two modifications of the α phase of PVF_2. The monoclinic version results from annealing the orthorhombic modification at high temperatures. Both modifications are crystallographically well defined and are stable for long periods under most conditions; neither version can be claimed as the only "true" α phase of PVF_2. In addition, we feel that a similar situation exists in the case of the γ phase of PVF_2.

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Unperturbed Rotational Isomeric State and Wormlike Polymethylene Stars of High Branch Point Functionality

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Rotational isomeric state theory provides a connection between local covalent structure and the mean unperturbed dimensions of chain molecules.[1] Calculations can rigorously be extended to branched molecules, but complexity of the calculation rapidly increases as branch points increase in number or in functionality, f.[2–4] Polymethylene stars with functionalities of 3 and 4 have been studied using rotational isomeric state calculations which retain a detailed treatment of the geometry and short-range interactions at the branch point.[5–8] Branch point geometries used were those observed in isobutane and neopentane.

Simpler expressions, based on a wormlike chain treatment of the chain statistics,[9] also quite accurately describe unperturbed dimensions of finite polymethylene stars with f = 3 or 4.[9,10] However, the wormlike chain model is not so successful in describing properties of starlike branched molecules obtained from certain other polymers.[10] Here we extend the rotational isomeric state calculations to polymethylene stars with f as large as 20. Detailed geometry at the branch point has been ignored because it becomes somewhat arbitrary for polymethylene stars when f rises above 4. The final approach of g to its asymptotic limit is found to depend on branch point functionality in the manner described by the wormlike chain treatment of stars developed by Mansfield and Stockmayer.[9] Here g is the ratio of unperturbed mean square radii of gyration for branched and linear polymethylenes containing the same number of bonds.[11]

Calculations

The rotational isomeric state model adopted for the unperturbed polymethylene chain is that described by Flory and co-workers.[12] The value of g for an f-functional rotational isomeric state star containing n bonds, or $n_b = n/f$ bonds per branch, was estimated as

$$g = [(f-1)(2n_b+1)^2C_c - (f-2)(n_b+1)^2C_b]/[(n+1)^2C_l] \tag{1}$$

Here C_i denotes the characteristic ratio, $\langle s^2\rangle_i/n_il^2$, where $\langle s^2\rangle_i$ is the mean square radius of gyration and l is the bond length. For C_l we have the linear chain in which n_i is n. By C_c we mean the characteristic ratio for a main chain of $2n/f$ bonds within the branched molecule. Its mean square radius of gyration is calculated using the matrix expression appropriate for a linear chain containing the same number of bonds. The characteristic ratio of one of the branches containing n/f bonds is denoted by C_b. The pertinent mean square radius of gyration is that for a subchain of n/f bonds, located at one end of a main chain

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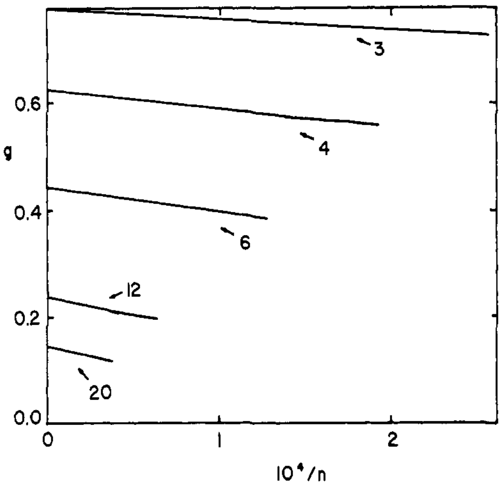

Figure 1. Rotational isomeric state g for unperturbed f-functional polymethylene stars.

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]

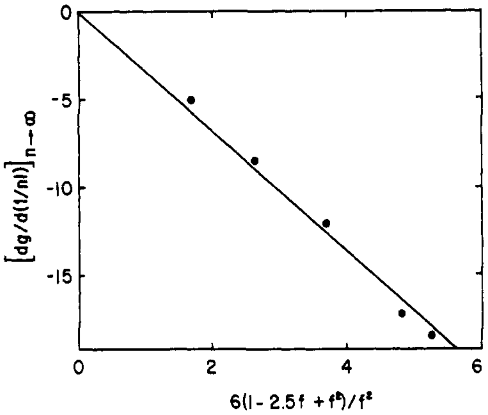

Figure 2. Approach to the asymptotic limit for g by unperturbed polymethylene stars of various functionalities.

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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