On the basis of spectral decomposition alone, our explanation and that of Atalla and VanderHart[5] are equally satisfactory. However, our interpretation is based on cellulose models derived from X-ray fiber diffraction studies. As is typical in most cases of X-ray studies of polymer fibers, the observed X-ray data of cellulose fibers are limited and the computed results are underdetermined. Using the "linked-atom" least-squares methods, crystallographers have been able to carry out meaningful structural refinements and in testing the statistical significance of various models.[19] For instance, they were able to establish that in native cellulose, the "parallel chain" model is preferred over the "antiparallel chain" model by a factor of more than 200 to 1.[11] Nevertheless, due to the underdetermined nature of the system, there is still a residual feeling that the cellulose models may not have been definitively derived. That the line splitting patterns in the solid-state ^{13}C NMR spectra of cellulose 1 and II can now be explained, in a consistent manner, by these X-ray-derived models seems to lend further support to their validity.

Our interpretation of solid-state ^{13}C NMR data gives us the perspective that most native cellulose contain crystallites of varying distribution of two- and eight-chain unit cells. This is in agreement with the view held by Gardner and Blackwell, who, in their X-ray diffraction study,[11] concluded that small, systematic "distortions" in the packing of two-chain unit cells may lead to larger eight-chain unit cells.

Sample Preparations. Emptied *Valonia* vesicles were placed in a British disintegrator for 15 s to help break up the vesicles. They were then boiled in a 1% aqueous sodium hydroxide solution for 3 h. This procedure was repeated once on the same batch of *Valonia* fibers. Subsequently, the fibers were drained and washed with distilled water, followed by a 1-min disintegration. Afterward, a series of solvent exchanges took place: water/acetone (50:50), acetone/methanol (50:50), methanol (100%). This was then filtered in a fritted glass funnel and dried in a vacuum oven.

Delignified ramie was examined in this study without further purification.

Spectroscopic Parameters. Solid-state ^{13}C NMR spectra were obtained on a Varian XL-200 spectrometer operating at 50.3 MHz for ^{13}C. Spectra were obtained with cross-polarization and magic angle spinning, using repetition rates of 2.0 and cross-polarization times of 0.5 ms. The decoupling field strength was 40 kHz, and spin rates ranged from 2.0 to 2.7 kHz. Spectra were referenced externally by assigning the aromatic carbon of hexamethylbenzene to 132.1 ppm. The resolution enhancement composition was carried out by using an increasing exponential weighting with a time constant of 6 ms together with a Gaussian apodization time constant of 18 ms.

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Non-Gaussian Corrections at the Θ Point: Comparison between Theory, Experiment, and Numerical Simulations

The Θ state, as defined by the vanishing of the osmotic second virial coefficient A_2, is frequently identified approximately with an idealized Gaussian state having no polymer–polymer interactions.[1] Experiments on the ratio of the hydrodynamic radius R_H to the radius of gyration R_G at the Θ point, however, exhibit marked deviations[2] from ideal Gaussian chain predictions, perhaps indicating limitations to the naive identification of Gaussian and Θ-point conditions. A number of numerical simulations[3–6] have been performed to estimate the corrections to Gaussian chain predictions arising from residual polymer–polymer interactions as well as from the preaveraging approximation used to calculate R_H. Simulations have been made for the Kirkwood approximation to the hydrodynamic radius[1] R_H(Kirkwood) and substantial deviations are *still* found from Gaussian statistics even for very long chains.[3]

Theoretical calculations, on the other hand, have used a variety of approaches including the three-parameter model[7] with two- and three-body interaction parameters and other models of local chain stiffness[7–11] which employ the Gaussian state as a reference point. Predictions of these calculations are often mutually contradictory[12] and at variance with the results of the lattice chain numerical simulations, leading to the possible interpretation (reinvestigated below) that properties of Θ-state polymers are theoretically nonuniversal, i.e., model dependent.

First, it is clear that large length scale polymer properties, such as A_2, R_H, and R_G, should not be too sensitive to small length scale properties of the true polymer–polymer interactions or those of a model theory, except for a dependence on quantities like the binary and ternary interaction parameters. Hence, it is meaningful to consider these latter properties in a long length scale limit where only a few coarse-grained parameters can possibly appear. It is then sufficient to describe these large-scale observables with models having idealized δ-function type interactions along with even powers of gradients of δ functions. Elementary dimensional analysis shows that the only terms to survive in perturbation expansions in three dimensions are those involving the binary and ternary δ-function interactions. This is the three-parameter model originally formulated by Yamakawa.[7] (The situation in two dimensions is much more complicated as all many body interactions may, in principle, contribute.) Hence, a three-parameter model must summarize all the effects of local chain stiffness and of residual polymer–polymer interactions in the large length scale, high molecular weight limit. Such a three-parameter model has recently been related[13] to the lattice models of Θ chains which involve self-avoiding chains with nearest-neighbor attractive interactions whose magnitude is determined to make A_2 vanish. Hence, it is reasonable to believe that the three-parameter model is sufficient to describe both experimental data and the lattice chain simulations in three dimensions near the Θ point.

Three-parameter model calculations have been performed to first order in the well-known[7,12] binary and ternary interaction parameters z_2^0 and z_3^0, respectively, for A_2, R_H(Kirkwood), $R_G = \langle S^2\rangle^{1/2}$, and the mean square end-to-end distance $\langle R^2\rangle$.[12] The calculations involve a phenomenological cutoff parameter b to remove self-interactions, the chain length N_0, and the Kuhn length l. The calculations are lengthy and will be presented elsewhere.[12] Using the dimensionless parameter $\sigma = (2N_0/\pi b)^{1/2}$ the results are

$$\langle R^2\rangle = N_0 l\{1 + z_2^0[(4/3) - (8/\pi\sigma)] + 4z_3^0[(4/3)\sigma - \pi - (8/\pi)] + ...\} \quad (1)$$

$$\langle S^2\rangle = (N_0 l/6)\{1 + z_2^0[(134/105) - (24/\pi\sigma)] + 4z_3^0[(134/105)\sigma - (117\pi/144) - (8/\pi)] + ...\} \quad (2)$$

$$R_H(\text{Kirkwood}) = [(6\pi N_0 l)^{1/2}/16]\{1 + z_2^0[0.609 - (8/\pi\sigma)] + 4z_3^0[0.609\sigma + 0.965 - (4/\pi)] + ...\} \quad (3)$$

$$A_2 = [(4\pi\langle S^2\rangle_0)^{3/2}(N_A/2M^2)][z_2^0 + 8z_3^0(\sigma/2 - 1)] \quad (4)$$

to first order in z_2^0 and z_3^0, where $\langle S^2\rangle_0 = N_0 l/6$, N_A is Avogadro's number, N_0 is proportional to the molecular weight M, R_H is evaluated in the preaveraging approximation in the nondraining limit,[1] and terms through $(N_0)^0$ have been retained. (Note that z_2^0 is proportional to $N_0^{1/2}$, while z_3^0 is independent of N_0.) The numerical coefficients of z_2^0 in (1)–(4) are well-known,[1,11,14] whereas additional coefficients of z_2^0, containing the dimensionless nonuniversal parameter σ, are new and are retained to maintain all contributions scaling as nonnegative powers of N_0. Previous three-parameter calculations[7-9,15-17] have kept either the numerical[11,12] or the σ-dependent[7,15] portion of the coefficients of z_3^0, producing the inconsistencies mentioned earlier. Bruns'[18] calculations with model potentials apparently include both the nonuniversal and universal contributions to the expansion coefficients.

When $z_2^0 = 0$, then z_3^0 is required to be positive. The further obvious physical constraint that $\langle S^2\rangle \geq \langle S^2\rangle_0$ in (2) implies that $\sigma \geq 4$, a value which makes $\langle R^2\rangle \geq \langle R^2\rangle_0$ and $R_H \geq R_{H,0}$, so for $z_2^0 = 0$ all chain dimensions are expanded due to the repulsive z_3^0. Note also that $\langle R^2\rangle$ is more sensitive to z_2^0 and z_3^0 than are $\langle S^2\rangle$ and R_H, a point considered further below.

The Θ point is *defined* by the vanishing of A_2, and not by the vanishing of z_2^0. Hence, we introduce an effective binary interaction parameter δz_2^0 such that $A_2 = 0$ (at $T = \Theta$) when $\delta z_2^0 = 0$, so z_2^0 and δz_2^0 are related through

$$\delta z_2^0 = z_2^0 + 8z_3^0[(\sigma/2) - 1] \quad (5)$$

Introducing (5) into (1)–(3) expresses these observables in terms of the proper binary interaction parameter δz_2^0 measuring deviations from the *physical* Θ point. This procedure has only been incorporated in the renormalization group calculations of Kholodenko and Freed.[9] Earlier calculations using the polymer–magnet analogy have δz_2^0 measured relative to a nonphysical "tricritical" point.[8,16,19] Equations 5 and 1–3 produce

$$\langle R^2\rangle = N_0 l[1 + (4/3 - 8/\pi\sigma)\delta z_2^0 - 1.900z_3^0 + ...] \quad (6)$$

$$\langle S^2\rangle = (N_0 l/6)[1 + (134/105 - 24/\pi\sigma)\delta z_2^0 + 20.37z_3^0 + ...] \quad (7)$$

$$R_H(\text{Kirkwood}) = [(6\pi N_0 l)^{1/2}/16] \times [1 + (0.6093 - 8/\pi\sigma)\delta z_2^0 + 30.49z_3^0 + ...] \quad (8)$$

as the principal result of this communication. The apparent nonuniversality of (1)–(4), due to the presence of σ, is largely removed by defining the proper Θ point as the reference state where δz_2^0 vanishes along with A_2.

The predicted contraction of $\langle R^2\rangle$ in (6) for large σ is counter to intuition and contrasts with the predicted expansion of $\langle S^2\rangle$ and R_H at $T = \Theta$ in (7) and (8). The contraction may be explained as follows: Equation 5 implies that the binary interaction z_2^0 is negative at $T = \Theta$, where $\delta z_2^0 = 0$. $\langle R^2\rangle$ is more sensitive to z_2^0 than $\langle S^2\rangle$ and R_H since the latter properties give greater weight to short distances along the chain as reflected in the larger cutoff terms in (7) and (8). The large cutoff terms for $\langle R^2\rangle$ at $T = \Theta$ swamp the cutoff independent terms in z_3^0. Hence, caution should be taken in describing polymer dimensions solely on the basis of calculations of $\langle R^2\rangle$, especially for the collapsed polymer state where ternary interactions play a more significant role. Numerical evidence suggests an altogether different scaling behavior between $\langle S^2\rangle$ and $\langle R^2\rangle$ for collapsing chains.[20]

A special Θ point is defined by the vanishing of z_2^0 at a temperature T^*. This T^* is not directly measurable for real polymers, but it may be evaluated for lattice polymers.[13,21] If the physical binary interaction parameter δz_2^0 is taken phenomenologically to be proportional to $[1 - (\Theta/T)]M^{1/2}$, with T the absolute temperature and Θ the Θ temperature,[22] then the difference between the special point and true Θ temperatures has a positive contribution which is proportional to z_3^0 and hence *independent of M*, while another negative contribution is proportional to $z_3^0\sigma^{-1}$, i.e., to $M^{-1/2}$. This agrees well with the simulations of lattice Θ chains by Kremer et al.[21] and by Webman et al.[23] Theory has not previously explained the N_0 independent contributions to the shift, and our result demonstrates the importance of defining the effective binary interaction parameter relative to the physical Θ state and of retaining all contributions scaling with nonnegative powers of N_0 (including the nonuniversal ones containing σ). Our conclusions contrast with previous opinions based on the calculations of Stephen,[8,15] Duplantier,[16] and de Gennes[24] because of neglects of cutoffs in some cases and errors in pursuing the renormalization group analysis in others. The present work appends the important cutoff contributions to ref 17 to provide the correct theory.

Schmidt and Burchard[2] summarize all existing data on polystyrene in Θ solvents for the ratio R_G/R_H. They give the value 1.27 ± 0.06, which departs considerably from the ideal Gaussian chain result of 1.504 in the preaveraging approximation.[25] The difference between the two must arise from a combination of the residual polymer–polymer interactions and the corrections to the preaveraging approximation.

Zimm[4] has performed Monte Carlo simulations of the dynamics of rigid Gaussian chains and estimates an upper bound[6] for the difference between the experimental and

Gaussian values of R_G/R_H, due to corrections for preaveraging. His bound appears to be consistent with the experimental deviation. On the basis of a more realistic description of hydrodynamic interactions, Fixman[6] provides a more conservative estimate of about an 8% change due to corrections for preaveraging, leaving a residual 7% discrepancy with experiment. Fixman's estimate is thus consistent with the Monte Carlo study of Guttman et al.[3] for this ratio, which they find to be $\langle S^2\rangle^{1/2}/R_H$(Kirkwood) = 1.40. Using this latter value in (7) and (8) with $\delta z_2^0 = 0$ leads to the estimate $z_3^0 \approx 0.003$. In addition, a value of z_3^0 can be estimated from the third virial coefficient at the Θ point. A_3 is readily calculated in lowest order to be

$$A_3 = [4\pi\langle S^2\rangle_0]^3 N_A^2 z_3^0/3M^3 \qquad (9)$$

Combining (9) with the data of Flory and Daoust[10,26] yields the rough estimate $z_3^0 \approx 0.006$ for polyisobutylene in benzene. This value is similar to the estimate $z_3^0 \approx 0.005$ of Oyama and Oono[10] for polystyrene in cyclohexane based on an assumed form of a semimicroscopic effective potential and estimates of microscopic parameters associated with this potential. Their self-consistent field study also gives an expression for $\langle S^2\rangle$ in general accord with (7).

The calculations in (6)-(8) can be utilized in a renormalization group analysis[9,12] to provide theoretical expressions that are valid for values of z_3^0 larger than those for which the simple perturbation results of (6)-(8) are meaningful. This renormalization procedure introduces corrections involving[8,9,16,24] logarithms of N. While z_3^0 must be system dependent, the above considerations indicate that it is very likely a rather small parameter. Given the above estimates of z_3^0 and the lack of observation of logarithmic corrections for lattice Monte Carlo chains, these logarithmic corrections are probably too small to be measured[12] and are hardly worth discussion, so the perturbation formulas (6)-(8) provide the first-order renormalization group predictions for the Θ region with the renormalized z_2, z_3 and N replacing the perturbative z_2^0, z_3^0, and N_0.

After submission of this communication, the work of Bruns[27] appeared, which extends the Monte Carlo calculations of Guttman et al. to longer chains. Bruns' long-chain extrapolation at the Θ point ($A_2 = 0$) gives the ratios $\langle S^2\rangle^{1/2}/R_H$(Kirkwood) = 1.464 ± 0.002 and $\langle R^2\rangle/6\langle S^2\rangle$ = 0.990, *both of which* are in good agreement with (6)-(8) for $z_3^0 = 0.001$.

Our three-parameter calculations are in general accord with experiment and Monte Carlo simulations in the sense that our predictions, when used with Θ-chain data, lead to consistent order of magnitude estimates for z_3^0 and that our theory explains the shift from the Gaussian chain Θ point observed in the simulation data. We hope that our calculations stimulate further experimental and numerical simulations of Θ-point polymers to check our predictions.[3] The calculations also underscore the importance of considering expansion factors, the ratio of a quantity to its Θ-state value. Forming ratios like $\langle S^2\rangle/\langle S^2\rangle_\Theta$, $\langle R^2\rangle/\langle R^2\rangle_\Theta$, and $R_H/(R_H)_\Theta$ from (6)-(8) and then using the small estimated values of z_3^0 to expand it from denominators lead to the conclusion[28] that the expansion factors having z_3^0 enter in lowest order as $(z_3^0)^2$ and $z_3^0 z_2^0$. The expansion factors are, hence, less sensitive to the ternary interaction parameter than are the absolute magnitudes of the corresponding properties, a feature contributing to the good agreement of two-parameter renormalization group predictions with experiment.[29] In addition, expansion factors are found to be less sensitive to polydispersity corrections, making them perhaps the most suitable quantities for comparison between experiment and theory.

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Structural Isomerism in Polycondensates. 3. Isomeric Polyureas from Aromatic Carbonates and Nonsymmetric Diamines

Structural isomerism in bipolycondensates from a symmetric (YccY) and a nonsymmetric (XabX) monomer is still a little investigated area. Korshak et al.[1,2] have prepared polyesters with a relatively small prevalence of -accb- enchainments (lowest value of s[3] achieved ca. 0.2) or -acca-/-bccb- enchainments (highest value of s achieved ca. 0.6) from terephthalic acid dichloride and nonsymmetric diols. Regular polyamides containing sequences of the type $(\text{accabccb})_{n/2}$, with $n > 100$ on the average ($s < 0.005$), as well as random polymers ($s \approx 0.5$), and a series of polymers with values of s between these two extremes have already been synthesized.[4]

The degree of regularity depends critically on the ratio of the reaction rates of the two functional groups in the nonsymmetric monomer (i.e., -aX and -bX) with the

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