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Coil–Globule Transition in Polymer Solutions

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ABSTRACT: The major factor contrasting chain collapse at $T < \Theta$ is identified with the pairwise "screened" repulsions arising because the solvent-influenced two-body attractions have their maximum at larger distances than the repulsions due to the covolume (G. Allegra, *Macromolecules*, 16, 555 (1983)). Although the approach is based on separate consideration of all pairwise interactions between the N chain atoms in the Gaussian approximation, the repulsive energy may be translated into mean-field language as $\propto \alpha^{-5}N^{-1/2}$ instead of $\propto \alpha^{-6}$ as for theories considering three-body interactions. Consequently, for a given polymer the coil shrinkage does not exclusively depend on $N^{1/2}(\Theta - T)/T$, and its change vs. this parameter is specifically made smoother by lower N's. Calculations show that in the collapsed state the mean-square distance between far-separated atoms tends to a constant limit, which is indicative of a uniform globule density, in qualitative agreement with the experimental results of Sun, Nishio, Swislow, and Tanaka on atactic polystyrene (*J. Chem. Phys.* 73, 5971 (1980)). However, the theory cannot be applied when N (and/or the globule density) exceeds some appropriate limit, beyond which the multibody interactions should be explicitly considered.

Introduction

Most of the recent theoretical approaches to polymer chain collapse in poor solvents are based on some kind of mean-field criteria. The chain self-attraction is embodied in the pairwise contribution to the free energy (the second virial coefficient), while the repulsive term preventing complete, pointlike collapse is usually represented by the three-body interactions.[1–6]

However, the pairwise interactions themselves appear to be capable of exerting some repulsive effect even below the Θ temperature. In a recent paper one of us showed that, if the attractive potential compensating the covolume chain self-repulsion at the Θ point is assumed to be short-ranged, as seems reasonable in a dilute solution, a net repulsive force is produced between any two chain atoms; if the average interatomic distance is $\langle r \rangle$, its average potential changes as $\langle r \rangle^{-5}$. As a consequence, the mean-square length of a very long chain (N skeletal atoms, $N \gg 1$), although still proportional to N at the Θ point, is larger than that of an ideal phantom chain only subject to local stereochemical constraints and first-neighbor conformational interactions. The corresponding expansion was evaluated as 5%, 22%, and 31% for polyethylene, atactic polystyrene, and isotactic polypropylene, respectively.[7]

It appeared as a natural development to investigate the possibility that pairwise effects alone could interpret the basic features of polymer collapse below the Θ point, considering that the probability of two-atom contacts is largely dominant, at least as long as the density is small in comparison with that of the bulk polymer. The results of the investigation will be reported in this paper; we shall assume the solvent-screened repulsive interactions as the essential factor contrasting chain collapse in the vicinity of the Θ temperature. Although, strictly speaking, this approach is only justified when the density does not exceed some appropriate upper limit, in the present exploratory study it will be extended to a very wide density range. The second characterizing feature of the present investigation consists of considering separately the contraction effect upon the different configurational Fourier modes. This will allow us to obtain the full spectrum of interatomic compression for different distances along the chain, as possibly revealed by the static and/or the dynamic scattering, for example. It should be added that our approach relies on some additional approximations, the most significant of which is the Gaussian distribution for the interatomic distances; their mean-square values are determined from minimization of the chain free energy in a self-consistent type of approach.[8] The results of our calculations will then be compared with some experimental data.[9–12]

The Method

(A) General Equations. The chain free energy will be expressed by the following combination of two expressions already proposed by us in ref 8 (eq 16) and in ref 7 (eq 13):

$$(A - A_0)/k_BT = \sum_{\{q\}}[{}^3\!/_2(\tilde{\alpha}^2(q) - 1) - 3 \ln \tilde{\alpha}(q)] + \beta\left(\frac{3}{2\pi}\right)^{3/2}\sum_{\bar{k}}^{N}(N - k)\langle {r_k}^2\rangle^{-3/2} + K_0\sum_{\bar{k}}^{N}(N - k)\langle {r_k}^2\rangle^{-5/2} \quad (1)$$

where A and A_0 respectively are the free energy of the actual chain and that of the unperturbed, phantom chain,

$$\langle {r_k}^2\rangle = \frac{l^2}{N}\sum_{\{q\}}\tilde{\alpha}^2(q)C(q) \sin^2 (qk/2)/\sin^2 (q/2) \quad (1A)$$

is the mean-square distance between chain atoms separated by k bonds, $\bar{k}$ is the shortest bond separation for two atoms that may come in contact, N and l respectively are the number and length of the chain bonds, $\{q\} = 0, 2\pi/N, 4\pi/N, ..., (N - 1)2\pi/N$ is the Fourier coordinate, $C(q)$ is the generalized characteristic ratio of the q mode, defined as

$$C(q) = \langle \tilde{\mathbf{l}}(q)\cdot\tilde{\mathbf{l}}^*(q)\rangle_0/Nl^2; \quad (1B)$$

$$\tilde{\mathbf{l}}(q) = \sum_{k=1}^{N}\mathbf{l}(k)e^{iqk} \quad (1C)$$

($\mathbf{l}(k)$ is the vector associated with the kth bond, and the subscript zero refers to the unperturbed phantom chain), $\tilde{\alpha}^2(q)$ is the corresponding square-expansion ratio, i.e.

$$\tilde{\alpha}^2(q) = \langle \tilde{\mathbf{l}}(q)\cdot\tilde{\mathbf{l}}^*(q)\rangle/\langle \tilde{\mathbf{l}}(q)\cdot\tilde{\mathbf{l}}^*(q)\rangle_0; \quad (1D)$$

$$\beta = \frac{T - \Theta}{T}v_c \quad (1E)$$

is the excluded-volume parameter where v_c is the effective excluded volume per chain atom,[13] and

$$K_0 = \frac{3}{2}\left(\frac{3}{2\pi}\right)^{3/2}v_c\left[(\langle {r_{si}}^2\rangle - \langle {r_c}^2\rangle) - \frac{T - \Theta}{T}\langle {r_{si}}^2\rangle\right] \quad (1F)$$

is the screened-interaction parameter. Meaning and derivation of 1E and 1F may be given as follows. The space domain of the effective binary-cluster potential $k_BTe(\mathbf{r}) = k_BT[1 - \exp(-w(\mathbf{r})/k_BT)]$ is separated into a solvent-

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influenced, attractive domain where $e_{\mathrm{si}}(\mathbf{r}) < 0$ (si for "screened interactions") and another domain at smaller r's where the covolume replusion prevails ($e_{\mathrm{c}}(\mathbf{r}) > 0$). Then we have[7]

$$e(\mathbf{r}) = 1 - \exp[-w(\mathbf{r})/k_{\mathrm{B}}T] = e_{\mathrm{si}}(\mathbf{r}) + e_{\mathrm{c}}(\mathbf{r}) \quad (1\mathrm{G})$$

$$v_{\mathrm{si}} = \int e_{\mathrm{si}}(\mathbf{r})\,\mathrm{d}^3\mathbf{r}; \qquad v_{\mathrm{c}} = \int e_{\mathrm{c}}(\mathbf{r})\,\mathrm{d}^3\mathbf{r}; \qquad (\beta = v_{\mathrm{c}} + v_{\mathrm{si}}) \quad (1\mathrm{H})$$

$$\langle r_{\mathrm{si}}^2\rangle = v_{\mathrm{si}}^{-1}\int r^2 e_{\mathrm{si}}(\mathbf{r})\,\mathrm{d}^3\mathbf{r}; \qquad \langle r_{\mathrm{c}}^2\rangle = v_{\mathrm{c}}^{-1}\int r^2 e_{\mathrm{c}}(\mathbf{r})\,\mathrm{d}^3\mathbf{r} \quad (1\mathrm{I})$$

Since we may take $w_{\mathrm{c}}(\mathbf{r}) \gg 0$ and $w_{\mathrm{si}}(\mathbf{r}) \leq 0$ and limited, we have $v_{\mathrm{si}} \rightarrow 0$ for large T's so that $\beta \rightarrow v_{\mathrm{c}} \simeq$ constant (see eq 1G and 1H). Consequently, the proportionality constant in the relationship $\beta = Cv_{\mathrm{c}}(T - \Theta)/T^{13}$ may be roughly equated to 1, and we get (1E). As for K_0, the above definition is more general than that given in ref 7 (eq 14) because here T is not necessarily identical with Θ; it may be easily obtained by considering eq 1E together with eq 5–10 of ref 7. However since we shall always assume $|(T - \Theta)/T| \ll 1$, the corresponding term in eq 1F may be neglected, and K_0 will be effectively considered as independent of temperature.

It should be remarked that, in addition to the Gaussian approximation, eq 1 is subject to the assumption that the normal-mode components $\tilde{\mathbf{l}}(q)$ are an orthogonal set; i.e., $\langle\tilde{\mathbf{l}}(q)\cdot\tilde{\mathbf{l}}^*(q')\rangle = 0$ if $q \neq q'$. This implies that the average scalar product $\langle\mathbf{l}(h)\cdot\mathbf{l}(h + k)\rangle$ is independent of the index h and also that the periodic condition $\mathbf{l}(h) = \mathbf{l}(h + N)$ holds. In other words, we are referring to a (suitably averaged) model chain wherein no end effects exist.

Differentiating eq 1 with respect to $\tilde{\alpha}(q)$ and equating to zero, remembering 1A, we get

$$\tilde{\alpha}^2(q) = \left\{1 + \frac{\rho(q)}{\sin^2(q/2)}\int_{\bar{k}}^{N}\left(1 - \frac{k}{N}\right)\left[\frac{\tau B}{I(k)^{5/2}} - \frac{5}{3}\,\frac{K}{I(k)^{7/2}}\right]\sin^2\left(\frac{qk}{2}\right)\mathrm{d}k\right\}^{-1} \quad (2)$$

where the pure numbers τ, $\rho(q)$, B, K, and $I(k)$ are defined as follows:

$$\tau = (\Theta - T)/T; \qquad \rho(q) = C(q)/C(0);$$

$$B = v_{\mathrm{c}}[3/(2\pi C(0))l^2]^{3/2}; \qquad K = K_0/(C(0)l^2)^{5/2};$$

$$I(k) = \langle r_k^2\rangle/(C(0)l^2) = (\text{see (1A)})\frac{1}{2\pi}\int_{-\pi}^{\pi}\rho(q)\tilde{\alpha}^2(q) \times \sin^2(qk/2)/\sin^2(q/2)\,\mathrm{d}q \quad (3)$$

(B) Universal Variables. Let us now search for the parameters, if any, that characterize the universal behavior of the chain in the limit $N \rightarrow \infty$, $q \sim N^{-1}$. We may put in this case $C(q) \equiv C(0)$, $\rho(q) \equiv 1$. It will be useful to solve first the following problem. Given the general function

$$y(q) = f\left[\frac{H}{\sin^2(q/2)}\int_{\bar{k}}^{N}(1 - k/N)(I(k))^{-n}\sin^2(qk/2)\,\mathrm{d}k\right] \quad (4)$$

where f uniquely depends on the quantity inside the square brackets, how should the constant H be modified so that, changing N, q, and $\bar{k}$ into Nh, q/h, and $\bar{k}h$, respectively (h = arbitrary constant), and assuming that $\tilde{\alpha}^2$ does not vary between the corresponding values of q, the argument x of $f(x)$ stays the same. Adopting the new variable $k' = kh$, from the last eq 3 we get $I(k') = hI(k)$ whence, substituting into eq 4, it is easy to check that nothing changes on the right-hand side if H is multiplied by h^{n-3}. In conclusion, under the transformation being considered, $H\cdot N^{3-n}$ is the universal variable for eq 4. Obvious extension of this argument to eq 2 shows that there are two universal variables, corresponding to the two different terms appearing in the square brackets within the integral, to which we must add the ratio $\bar{k}/N$ that specifies its lower limit. The three resulting universal variables are

$$x_1 = \tau BN^{1/2}; \qquad x_2 = K/N^{1/2}; \qquad x_3 = \bar{k}/N \quad (5)$$

(C) Translation into Mean-Field Language. Translation of eq 2 into some appropriate mean-field approximation may be of interest for comparison with current results. Again the simplest and least arbitrary procedure is to consider the limit $q \sim N^{-1} \rightarrow 0$, assuming $\tilde{\alpha}(q \rightarrow 0) \simeq \alpha$(average). If we extend this assumption to any q within the expression producing $I(k)$ (see eq 3), we get $I(k) \equiv \alpha^2 k$; further substitution within the braces of eq 2 gives a term depending on $K\alpha^{-7}(\bar{k})^{-1/2}$, which is the dominant one for $\alpha \rightarrow 0$. Although this result may be acceptable at $T = \Theta$ since in that case the expansion ratio α (slightly larger than unity) is essentially uniform over all the interatomic distances,[7] it is quite a different matter in the present case, in which a long chain under collapse is being considered. In fact, the above term arises from the assumption that *all* the interatomic distances are decreased by the same average factor α, in particular those between atoms separated by $\simeq\bar{k}$ bonds (where $\bar{k}$ is of the order 50; see ref 7). This is obviously contrary to physical expectation, and it is also clearly ruled out by the numerical results obtained by us from eq 2, indicating that a significant shrinkage only sets in for more distant atoms. A reasonable mean-field approximation is to assume $\alpha = 1$, i.e., $I(k) = k$, for $\bar{k} \leq k \leq pN$ and $I(k) = \alpha^2 k$ for $pN < k \leq N$, with a fixed p (<1). Under this assumption, we may also consider for completeness the three-body interactions by adding a term

$$+K_1\sum\sum_{h,\,k=\bar{k}}^{N}(N - h - k)\langle r_h^2\rangle^{-3/2}\langle r_k^2\rangle^{-3/2} \qquad (>0)$$

to the free energy of eq 1, then differentiating with respect to α, and finally integrating over h and k. The result is the "generalized" Flory equation[14]

$$\alpha^5 - \alpha^3 = -C_1\tau BN^{1/2} + C_2K/(\alpha^2N^{1/2}) + C_3K_1/\alpha^3 \quad (6)$$

where C_1, C_2, and C_3 are positive constants respectively referring to the attractive effect, to the repulsive two-body ("screened") interactions, and to the repulsive three-body interactions. It should be stressed that the first term derives from the two-body contribution plus that of the three-body contacts wherein two out of the three atoms are close to each other. By generalization of this concept, according to the approach of Khokhlov[15] we will consider henceforth the effective, or renormalized, pairwise parameter τB (eq 3) as due to the superposition of all the appropriate n-body interactions that are separable into two groups each involving adjacent atoms only. Furthermore, according to ref 7 and 8 we shall consider henceforth $C_1 \approx 1$. (At $T = \Theta$, τ is zero, and for the reasons stated at the beginning of this section, the C_2 term may be replaced by $C_2'K/(\alpha^2\bar{k}^{1/2})$ if $N \rightarrow \infty$; see ref 7, eq 17.) It is clear from eq 6 that the screened-interaction term differs from the classical three-body effect both because of the α^{-2} instead of α^{-3} dependence and because it decreases with molecular weight. In other words, unlike the quoted theories,[1-4] in our case tendency toward collapse is progressively more difficult for shorter chains, even considering the reduced variable $x_1 = \tau B N^{1/2}$. As for the asymptotic behavior of α at large x_1, setting $C_3 = 0$, eq 6 gives

$$\alpha \propto (\tau N)^{-1/2} \qquad (7)$$

to be compared with $\tau^{-1/3}N^{-1/6}$ if $C_2 = 0$.[1-4] Consequently, neglecting the three-body term, the density ($\propto N/(\alpha N^{1/2})^3$) goes as $N\tau^{3/2}$, suggesting that the asymptotic size of the globule is independent of N for a given τ.

(D) Chain Compression for Different Interatomic Separations. We may now get more insight into the problem if we set aside the mean-field approximation and neglect the three-body interactions, solving eq 2 for small q after suitably guessing the asymptotic limit of $I(k)$. Let us assume that I is a finite, constant value in

$$I = \lim_{k\to\infty} I(k) = \lim_{k\to\infty} \langle r_k^2\rangle/(C(0)l^2) \qquad (8)$$

and let us show that it satisfies eq 2 for $q \to 0$. Accepting eq 8 for all k's as a first approximation and remembering (3), eq 2 reduces to ($\rho(q) \simeq 1$, $\sin(q/2) \simeq q/2$)

$$\tilde{\alpha}^2(q) = \left\{1 + \frac{N}{q^2}\left[\frac{\tau B}{I^{5/2}} - \frac{5}{3}\,\frac{K}{I^{7/2}}\right]\right\}^{-1} \qquad (9)$$

Since in the collapsed region $\tilde{\alpha}^2(q) \ll 1$, the quantity in square brackets is positive and we may define

$$H^{-2} = N\left[\frac{\tau B}{I^{5/2}} - \frac{5}{3}\,\frac{K}{I^{7/2}}\right] \qquad (10)$$

so that (9) reduces to

$$\tilde{\alpha}^2(q) = H^2q^2/(1 + H^2q^2) \qquad (11)$$

Deriving now $\langle r_k^2\rangle$ from the last eq 3, we get ($k \gg H$, $\sin(q/2) \simeq q/2$)

$$\langle r_k^2\rangle = \frac{C(0)l^2H^2}{\pi}\int_{-\pi}^{\pi}\frac{1-\cos(qk)}{1+H^2q^2}\,\mathrm{d}q \qquad (12)$$

Since the significant contribution to the integral derives from $qH \ll 1$, the integration limits may be replaced by $\pm\infty$. Using Cauchy's theorem, we get

$$\langle r_k^2\rangle = HC(0)l^2[1 - \exp(-k/H)] \qquad (13)$$

and if we recycle this result into eq 2, we get a negligible change for eq 11. In conclusion, the starting assumption (i.e., eq 8) is proven to be valid, and the constant H coincides with I. As for the assumption $H \gg 1$, it appears to be adequate so long as it requires that the asymptotic interatomic distance should be much larger than that between neighboring atoms in the unperturbed chain. Substituting now $H = I$ in eq 10, we get the following (approximate) equation producing I as a function of N, τB, and K:

$$I^{3/2}/N = I\tau B - \tfrac{5}{3}K \qquad (14)$$

whence for $N \to \infty$ the asymptotic mean-square distance reaches its minimum value (see also (1F) and (3))

$$\langle r_k^2\rangle_{N\to\infty} = \frac{5}{2}\,\frac{\langle r_{si}^2\rangle - \langle r_c^2\rangle}{\tau} \qquad (15)$$

It should be noted that this result agrees with the mean-field prediction given by eq 7.

The above-discussed behavior is essentially confirmed by our numerical results (see following). The existence of an asymptotic distance between topologically remote atoms agrees with the model of the chain being confined within a fixed volume, or globule, wherein the density is uniform. For a given τ (or temperature), the mean-square diameter of the globule decreases with increasing N, reaching a constant asymptotic limit proportional to the value given by eq 15, while for large, fixed N it varies as τ^{-1}. The dependence of I, i.e., $\langle r_k^2\rangle$, from both $\tau BN^{1/2}$ and $K/N^{1/2}$ should be stressed; it is the counterpart of the apparent molecular-weight dependence of the collapsed branch (see the curves reported in Figures 1 and 2, where the commonly used variable $\tau M^{1/2}$ is reported on the abscissa instead of $\tau BN^{1/2}$), unlike the upper branch, which approximately appears to be a function of $\tau BN^{1/2}$ only.

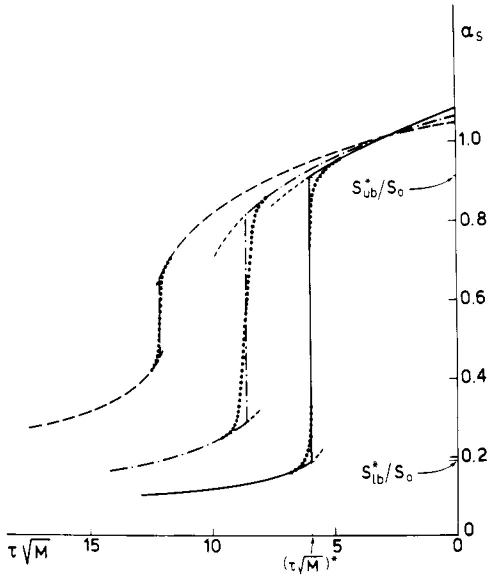

Figure 1. Expansion factor of the radius of gyration $\alpha_S = S/S_0$ plotted vs. $\tau M^{1/2}$ for the model polymer (see Table I). The reference state (with a zero subscript) is the unperturbed phantom chain. Continuous line, $N = 10^5$; dash–dot line, $N = 10^4$; dashed line, $N = 10^3$ skeletal bonds/chain. The molecular mass per chain atom m is 21. The short-dashed lines indicate metastable states throughout. The vertical lines show the transition coordinates $(\tau M^{1/2})^*$ where a crossover of the single-chain free energy from the upper curve (with radius of gyration S^*_{ub}) to the lower curve (with radius of gyration S^*_{lb}) occurs. The smoothing of the transition due to the Boltzmann distribution between the two states is shown by the dotted lines (see text).

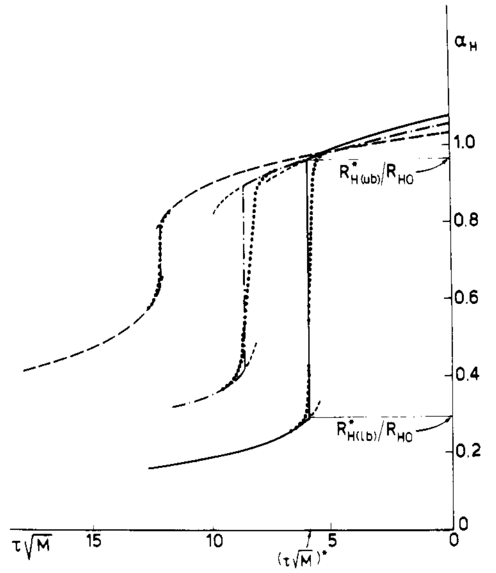

Figure 2. Expansion factor of the hydrodynamic radius $\alpha_H = R_H/R_{H0}$ (see Figure 1).

Numerical Results and Discussion

As done in previous similar studies,[7,8] the integral equation (2) was solved by us numerically through an

Table I[a]
Parameters Characterizing the Configurational Properties of the Polymers Investigated in the Present Study

	a	b	c	$C(0)$	$\bar{k}$	v_c, Å^3	d, Å	K	B
(A) model polymer	0.0910	0.9840	0.489	6.18	45	37.0	5.7	0.36	0.22
(B) atactic polystyrene	0.0887	0.9883	0.418	8.00	50	76.9	7.33	0.65	0.31

[a] $C(q) = a/(1 - b\cos(q)) + c$; l (C-C bond length) = 1.54 Å; $\bar{k}$ = minimum number of chain bonds for an intramolecular contact; v_c = volume pervaded by the chain per skeletal atom; d = distance between contacting chains; $\langle r_{si}^2\rangle \cong d^2 \cong 2\langle r_c^2\rangle$; $K = (3/2)(3/2\pi)^{2/3}v_c(\langle r^2{}_{si}\rangle - \langle r_c^2\rangle)/(C(0)l^2)^{5/2}$; $B = v_c[3/(2\pi C(0)l^2)]^{3/2}$.

iterative procedure; i.e., choosing some approximate function $\tilde{\alpha}^2(q)_0$, first $I(k)$ was derived from (3), then $\tilde{\alpha}^2(q)_1$ from (2), and a new cycle was started. However, at values of τ close to the collapse or larger, this procedure may not converge properly, and we used as a starting function for the new cycle a suitably weighted average produced by the two previous cycles (the weights being 2 for the next-to-last cycle and 1 for the last cycle). No constraint on bond lengths was imposed,[7] in view of the small error implied throughout the range of our calculations. An average of about 10 iterations was required to reach satisfactory convergence, except in the vicinity of the transition, where this number could reach as high as 30–40; the degree of relative stability of the final results was about 10^{-4} in terms of $\tilde{\alpha}(q)$ and 10^{-7} in terms of free energy. The convergence proved to be most rapid if the first-approximation function $\tilde{\alpha}^2(q)_0$ was identical with the final result for the previous τ, and the τ itself was changed monotonically from one calculation to the next.

To obtain results with a general meaning, we performed a first set of calculations on a model polymer with different molecular weights, the parameters of which are somehow intermediate between those of polyethylene and of isotactic polypropylene[7] and are roughly similar to those of syndiotactic polypropylene.[16] Then we also carried out a more limited amount of calculations on a polymer with approximately the parameters of atactic polystyrene,[7] with the main purpose of comparing our results with some experimental data.[9-12]

(A) Model Polymer. The parameters required to evaluate the quantities listed in eq 3 are reported in Table I. Figures 1 and 2 respectively show the calculated ratios $\alpha_S = S/S_0$ and $\alpha_H = R_H/(R_H)_0$ between the radius of gyration S, the hydrodynamic radius R_H, and their unperturbed, phantom chain values vs. $\tau M^{1/2}$ ($M = Nm$, where m is the molar mass per chain atom). The radii are defined as

$$S^2 = \frac{1}{2(N+1)^2}\sum_{i,j=1}^{N+1}\sum\langle r^2{}_{|j-i|}\rangle$$
$$R_H^{-1} = \frac{1}{(N+1)^2}\sum_{i,j=1}^{N+1}\sum{}'\left\langle\frac{1}{r_{|j-i|}}\right\rangle \tag{16}$$

where the apex in the second double sum is meant to exclude the terms with $i = j$, while $\langle 1/r_k\rangle = (6/\pi\langle r_k^2\rangle)^{1/2}$ in the Gaussian approximation. Three molecular weights are taken into consideration, separated by a factor 10 from one another. The vertical bars connecting the collapsed, lower branch with the upper one indicate the "transition" coordinate $(\tau M^{1/2})^*$ corresponding to identical free-energy values for the two branches, as shown in Figure 3; the short-dashed lines indicate "metastable" states. It should be pointed out, however, that the present language applies strictly to the thermodynamic limit $N \rightarrow \infty$ only. In fact, *for given values of* x_1, x_2, and x_3, *it is easy to show that the free energy is proportional to* N (see eq 1). This implies that for finite N's the Boltzmann distribution between the two states makes the transition somehow smooth (see dotted lines in Figures 1 and 2, respectively obtained after averaging over α_S^2 and α_H^{-1} from eq 16); in this respect the chain length itself should be regarded as an additional variable. In terms of the universal variables x_1 and x_2 (see eq 5; x_3 has little importance), Figure 4 shows the plots of $x_1^* = (\tau BN^{1/2})^*$ and of $r_S = S$(upper branch)$^*/S$(lower branch)* vs. $x_2 = K/N^{1/2}$.

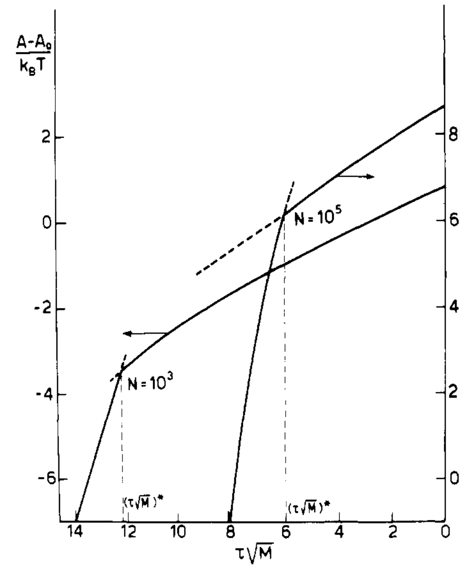

Figure 3. Free-energy excess over the unperturbed phantom chain in k_BT units plotted vs. $\tau M^{1/2}$ for the two extreme molecular weights of the model polymer. The number of chain atoms N is shown on the curves (see Figure 1). $(\tau M^{1/2})^*$ shows the same transition coordinate from upper to lower curves as in Figures 1 and 2.

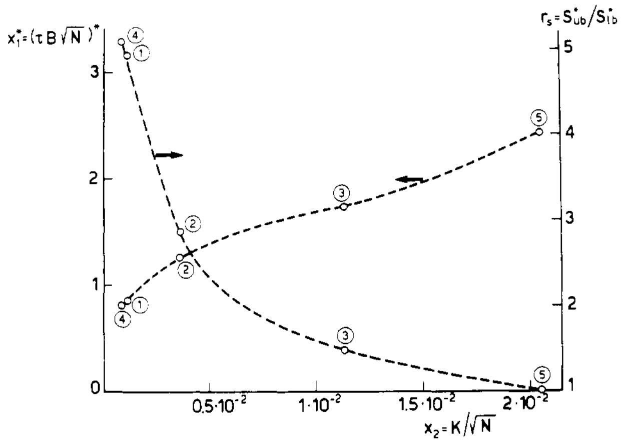

Figure 4. Transition coordinates $x_1^* = (\tau BN^{1/2})^*$ and $r_S = S^*{}_{ub}/S^*{}_{lb}$ plotted vs. $x_2 = K/N^{1/2}$ showing the universal behavior of the model polymer and of atactic polystyrene. The numbers on the curves refer to (cf. Table I) (1) model polymer, $N = 10^5$; (2) model polymer, $N = 10^4$; (3) model polymer, $N = 10^3$; (4) atactic polystyrene, $N = 5 \times 10^5$; and (5) atactic polystyrene, $N = 10^3$.

Figure 5 shows the equilibrium scattered intensity vs. $Q = 4\pi\sin(\theta/2)/\lambda$ for both the longest and the shortest chain considered in Figures 1 and 2; results are given for

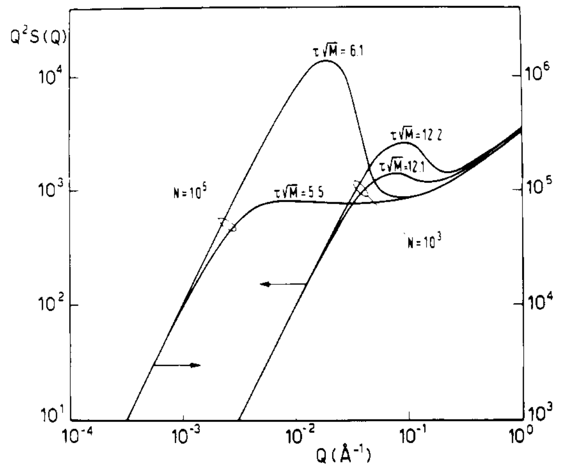

Figure 5. Static scattering factor plotted as $Q^2S(Q)$ vs. Q for the extreme molecular weights of the model polymer (Table I, eq 17). The N and $\tau M^{1/2}$ values are reported on the curves. For each chain two plots are shown, corresponding to states just preceding and following the collapse transition.

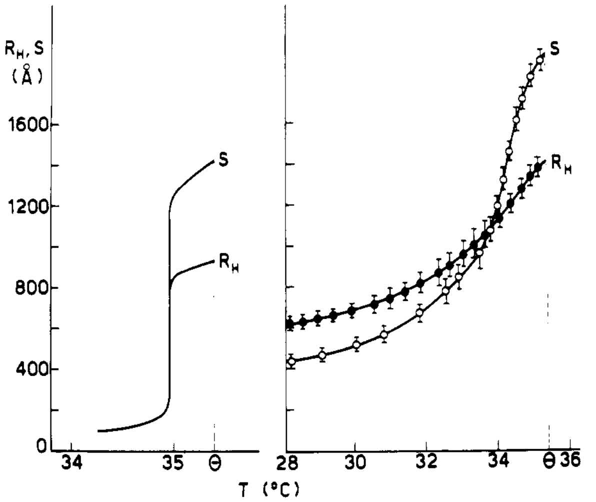

Figure 6. Calculated (left) and measured (right, from ref 10) radius of gyration S and hydrodynamic radius R_H vs. T for a polystyrene chain with a molecular weight 2.6×10^7 ($N = 5 \times 10^5$). Note the different scales on the abscissa. Both curves terminate at the Θ temperature, i.e., 35.4 °C for atactic polystyrene in cyclohexane.

both a noncollapsed and a collapsed state of the same chain in the vicinity of the transition. The following expression was adopted within the Gaussian approximation

$$S(Q) = \sum_{i,j=1}^{N+1} \sum \exp(-\tfrac{1}{6}Q^2\langle r_{|j-i|}^2\rangle) \qquad (17)$$

(B) Atactic Polystyrene. In Figure 6 calculated plots of S and R_H vs. T for an atactic polystyrene chain with 5×10^5 skeletal atoms are reported (see parameters in Table I), together with the corresponding experimental results of Sun, Nishio, Swislow, and Tanaka.[10] The critical data calculated for this as well as for a shorter chain ($N = 1000$) with the same parameters are reported in Figure 4 together with those of the previous model polymer.

Figure 4 illustrates rather well the influence of the universal parameter $x_2 = K/N^{1/2}$ on the collapse transition. Essentially, while the critical normalized undercooling $x_1^* = (\tau B N^{1/2})^*$ changes rather little over a wide range of x_2, a substantial variation may be observed in the sharpness of the transition as expressed by the ratio $r_S = S^*$(upper branch)/S^*(lower branch), which increases with increasing N. As for the lower values of the ratio $r_H = R_H^*$(upper branch)/R_H^*(lower branch) compared with r_S (compare Figures 1 and 2 and see Figure 6), they are clearly explained by the virtual invariance of the short-range interatomic distances upon collapse, together with their stronger influence on R_H rather than on S (see eq 16); a similar interpretation was offered by Weill and des Cloizeaux.[17] In turn, the short-range invariance is reflected by the approximate analytical form of $\tilde{\alpha}^2(q)$ given in eq 11, showing that $\tilde{\alpha}^2(q) \rightarrow 1$ for large q, i.e., for localized configurational modes. It should also be stressed that this effect is fully consistent with de Gennes' "blob" model.[18] The experimental results of Sun et al.[10] (see Figure 6) provide a clear confirmation of the different behavior of R_H and S upon collapse. It must be remarked, though, that the calculated ratios of r_S and r_H (6.3 and 4.0, respectively) appear to be larger than the corresponding ratios estimated from the experimental data (~3.5 and ~2.3 respectively) and, especially, that the calculated values of both R_H and S in the collapsed region are too small compared with experiment. Even discounting an apparently larger experimental size of the unperturbed chain than considered in our calculations,[7] which might be reconciled by taking a value of $C(0)$ about 50% larger than assumed by us, the calculated size after collapse is between 2 and 3 times less than observed. Another inconsistency appears to exist between $\Delta T^* = \Theta - T^*$ as calculated by us (0.4 °C) and the observed value (~1.3 °C, identifying T^* with the temperature at which the inflection points for both R_H and S are observed in Figure 6). While this might be partly ascribed to the experimental molecular-weight dispersion ($M_w/M_n = 1.3$), producing some broadening in the transition, as well as to a possible hysteresis effect in the process (see, e.g., the short-dashed lines in Figure 1, especially those associated with the largest molecular weight), the excessive contraction calculated upon collapse could be due to an underestimate of the mean-square distance between the axes of contacting chains $\langle r_{si}^2\rangle$,[7] thus entailing an underestimate of the screening constant K (see Table I). However, it should be clearly remarked that within the collapsed region the average globule density calculated for our model approaches in this case the bulk polymer's (~1 g/cm^3), suggesting that the molecular weight under consideration is at least close to the upper limit of the present theory. Otherwise said, the three-body interactions should probably give a significant contribution. In spite of these remarks, comparison between our results and experiment (Figure 6) may be considered as roughly satisfactory. As for other authors' experimental data on lower molecular-weight polystyrene fractions the situation is not completely clear.[9,11] As a general statement, it may be said that no size reduction with temperature even roughly comparable with that reported by Sun et al.[10] has been observed as yet. However, this may be accounted for, at least in part, within the present approach as a molecular-weight effect. Namely, for M between 10^4 and 10^6,[9,11] the parameter $K/N^{1/2}$ is between ~5×10^{-2} and ~0.5×10^{-2} (see Table I), and the expected transition sharpness r_S (see Figure 4) is much smaller, if anything, than for $K/N^{1/2} = 0.09 \times 10^{-2}$, corresponding to the results of Sun et al.[10] (Of course, r_S would be further reduced if the actual K were larger than the figure assumed by us, as already hypothesized in discussion of Figure 6.) Although the presently available data do not appear to be sufficient for a thorough revision of our parameters, we may further comment that the relatively sharp coil contraction observed for $\tau M^{1/2}$ in the interval between 12 and 16 for $M = 2.9 \times 10^4$ [9] and 4.1×10^5 [11] may be taken as indicative of a collapse (quasi-) transition and that the corresponding transition coordinates predicted by us ($(\tau M^{1/2})^* > 19$ and $(\tau M^{1/2})^* \simeq 13$, respectively, from Figure 4) are close to the above range.

To our knowledge no diffraction data have been reported in the literature hitherto, which might offer a comparison with the computed spectra reported in Figure 5. Needless to say, the characteristic maximum associated with the collapsed chains is yet another manifestation of the long-range intramolecular clustering while the essential invariance of the spectra at higher Q's is related with the short-range configurations being unaltered by the collapse.

Concluding Remarks

We have shown that an interaction scheme formally based on two-atom contacts is capable of roughly describing some of the basic features of polymer collapse in dilute solution observed hitherto. We adopted for polystyrene the same steric parameters previously derived from theoretical considerations and crystallographic data;[7] any adjustment should only be made after additional experimental data become available. It seems important to stress that, although the pairwise screened interactions should be considered in conjunction with the three-body repulsions for high molecular weights, the former effect should prevail in the case of short chains. Specifically, if we consider a given value of $\tau B N^{1/2} = x_1$, the screened and the three-body terms would have equal values for (assuming $\alpha^5 - \alpha^3 \approx 0$, $C_1 \simeq 1$,[7,8] and $C_3 K_1 = y$, according to current symbolism;[1,2] see eq 6)

$$N = \bar{N} = \frac{2^{2/3}(C_2K)^2}{y^{4/3}x_1^{2/3}} \propto K^2 y^{-4/3} x_1^{-2/3} \qquad (18)$$

For $N < \bar{N}$ the pairwise interactions should prevail and vice versa. In particular, taking for polystyrene $x_1^* \simeq 0.8$ with $N = 5 \times 10^5$ (i.e., the chains considered in Figure 6), α^*(lower curve) is ~0.15 from our calculations, and eq 6 gives $C_2K \simeq 12$, if y $(=C_3K_1) = 0$. From the experimental S plot of Figure 6, we have $\alpha^*_{\mathrm{exp}} \approx {}^1/_3$, whence $y \approx 0.025$ if eq 6 is to be fulfilled with the same C_2K as above. These data give (eq 18, $x_1 = x_1^* \approx 1$) $\bar{N} \approx 2 \times 10^4$; i.e., $\bar{M} = \bar{N}m \approx 10^6$. In other words, if we accept the parameters' estimates of Table I, for molecular weights *roughly* smaller than this limit the pairwise screened interactions should represent the prevailing factor contrasting chain collapse, while for larger M's the three-body effects should dominate in their turn. This is illustrated in Figure 7, where we report α vs. T plots obtained from eq 6 with the above parameters for two different molecular weights of polystyrene, the larger of which coincides with that considered in Figure 6.

In the same connection, the excellent interpretation of the collapse transition of high-molecular-weight polystyrene (>10^6) obtainable from the theory of Sanchez[10] should be pointed out; it is also noteworthy that it is based in principle on the consideration of all possible multiple-body interactions, although within a mean-field approach.[5] As a specific merit to be ascribed to the present approach, let us point out that it also gives information on the chain contraction through the whole range of interatomic separation, thus enabling inter alia evaluation of both S and R_{H} (see Figure 1 and 2), unlike the mean-field approaches. On the other hand, from a conceptual viewpoint one should recall that a substantial share of the three-body and higher order interactions are already included in the *effective* or renormalized, pairwise terms, as shown by Khokhlov.[15]

It is interesting to remark that Webman, Lebowitz, and Kalos[19] carried out Monte Carlo simulations on chain collapse by considering a Lennard-Jones type interatomic potential with an attractive contribution, in some analogy with the present approach. They find, in essential agreement with our conclusions, that the transition is somewhat more pronounced with increasing N than a universal relationship $\alpha = f(\tau B N^{1/2}, y)$ would imply. Also, for a given N and large τ they find $\alpha \propto \tau^{-a}$, where the exponent a is around ${}^1/_2$ or more (see Figure 3 of ref 18). This result should be compared both with the figure ${}^1/_3$ predicted by the mean-field theories based on three-body effects and with the limiting value $a = {}^1/_2$ given by our eq 7. Again in qualitative agreement with our conclusions, the above Monte Carlo result may be attributed to the pairwise repulsions prevailing over the three-body interactions, as it is also suggested by the relatively small molecular weight considered by the quoted authors (their largest value is roughly $M \approx 10^5$ in terms of polystyrene chains).[19]

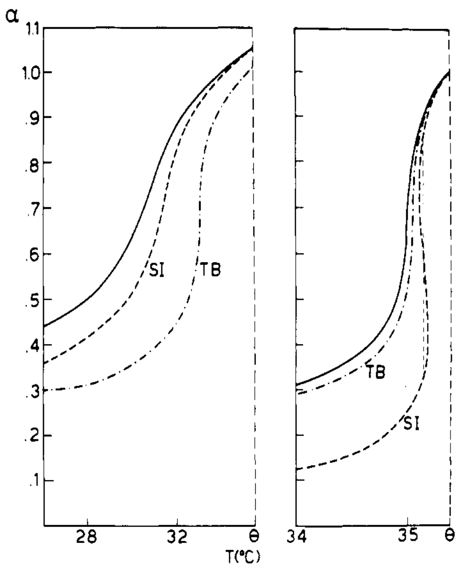

Figure 7. α ratio calculated vs. T in the mean-field approximation from eq 6 for polystyrene in cyclohexane with $M = 0.52 \times 10^6$ (i.e., $N = 10^4$, at left) and $M = 26 \times 10^6$ (i.e., $N = 5 \times 10^5$, at right). The solid-line curves are obtained with $C_1 = 1$, $C_2K = 12$, and $C_3K_1 = 0.025$, while those labeled SI (screened interactions) and TB (three body) correspond to suppression of C_3 and of C_2, respectively. The vertical dashed line on the right-hand side (SI) indicates the equilibrium transition.

As a final comment, the free-energy dependence on temperature in the vicinity of the collapse (see Figure 3) suggests a first-order transition in the thermodynamic limit $N \rightarrow \infty$. Although this conclusion is only valid from a formal viewpoint, since it implies neglecting higher order interactions which are certainly relevant in the above limit, it may be interesting to remark that the same conclusion is true of the mean-field approaches of Ptitsyn, Kron, and Eizner[1] and de Gennes[2] (for small y), although being in contrast with other models, such as Sanchez's,[5] predicting a second-order transition. However, it should be pointed out that, even for relatively small N's, the existence of two distinct free-energy minima with probably strong entropic barriers, as required by such highly concerted configurational rearrangements, may mask the real thermodynamic nature of the transition. Also, it seems worth stressing that even for finite N's the present description is strictly biphasic, i.e., a given chain may only be observed in the collapsed or in the more expanded state, at a given time.

Note Added in Proof. After submission of this paper for publication, Stěpánek, Koňák, and Sedláček published results concerning polystyrene solutions with $M_{\mathrm{w}} = 2 \times 10^6$ (*Macromolecules*, **15**, 1214 (1982)). Compared with the results of Figure 6, they show a larger disagreement with our calculations in terms of T and a better agreement in terms of S and R_{H}.

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Conformational Characteristics of Polyisobutylene

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ABSTRACT: The intramolecular energy of segments in a poly(1,1-dimethylethylene) chain (PIB) has been estimated by calculations on structures $CH_3-[C(CH_3)_2CH_2]_x-H$, with $x = 2$ (dimer), 3 (trimer), and 4 (tetramer), and on a hexad of structure $CCH_2-[C(CH_3)_2CH_2]_6-C$. PIB chains are subject to large steric repulsions that computations on analogues of low molecular weight do not properly take into account since the steric strain is relieved at the chain ends. We introduce an *iterative scheme* that eliminates end effects and correctly estimates the effects of steric strain on the configuration of the long-chain PIB molecule. Strain energy estimations for 2,2,4,4-tetramethylpentane, as well as for a diad in a long PIB chain, agree well with experimental values. The two-bond repeat regular conformation of lowest computed energy is an 8_3 helix, with helix parameters in excellent agreement with the conformation in crystalline PIB according to X-ray crystallographic results. The detailed analysis of all diad, triad, and tetrad conformations and of more than 100 conformations for the hexad is complex; the steric stress in PIB chains is manifested in interactions that are transmitted beyond nearest neighbors. In good approximation, however, the significant conformations of PIB can be represented by a four-state rotational isomeric scheme, with only one adjustable statistical weight parameter. Rotational isomeric states are located at +15° (t_+), −15° (t_-), +130° (g_+^+), and −130° (g_-^+). Skeletal ∠CCC bond angles are 123° at the methylene groups and 109° at the quaternary carbon atoms. Conformations divide into a "+ class" and a "− class". Bond conformations tend to be followed by those from the same class, changes from one to the other being rare. The characteristic ratio and its temperature coefficient, computed with the four-state scheme, agree well with experimental values.

Introduction

Poly(1,1-dimethylethylene), or polyisobutylene (PIB), is a prominent example of symmetrically substituted vinylidene chains. Its constitution, represented by

$$CH_3-[C(CH_3)_2CH_2]_x-H$$

is simple, and reliable experimental results on the molecular conformation in the crystalline state and in solution are available. Nevertheless, no satisfactory theoretical model for the conformational characteristics of this polymer has been presented heretofore.

The crystal structure of PIB has been studied by several investigators using X-ray fiber diagrams.[1-6] At present, there is general agreement that PIB assumes an 8_3 helix in the crystalline state,[4-7] distorted somewhat to allow for denser packing into an orthorombic unit cell.[6,7] The average skeletal bond angles are quoted[6,7] as $\angle C-CH_2-C \approx 128°$ and $\angle CH_2-C-CH_2 \approx 110°$ and the average torsion angles as ca. 125° and 15° (relative to the trans conformation).

Principal results on the spatial configuration of the PIB chain consist of the unperturbed chain dimensions and their temperature coefficient. Measurement of the intrinsic viscosities of samples spanning a wide range of molecular weights carried out in two considerably different Θ-solvents, benzene[8,9] and isoamyl valerate,[10] yielded characteristic ratios C_∞ in the range $6.6 \leq C_\infty \leq 6.9$ at ca. 300 K. The temperature coefficient $d \ln C_\infty/dT$ has been determined from stress–temperature measurements at constant pressure[11] as well as at constant volume[12] on samples of cross-linked PIB (butyl rubber) and from the temperature dependence of the intrinsic viscosity in *n*-hexadecane.[13] Between 291 and 368 K the temperature coefficient assumes a small negative value of ca. −0.2 (±0.2) $\times 10^{-3}$ K^{-1}. Experimental results on C_∞ and $d \ln C_\infty/dT$ are listed in Table I.

Several theoretical studies of the conformational characteristics of randomly coiled PIB chains have been reported.[5,14-21] Early attempts[14-16] were carried out under the assumptions that the bonds within a diad are restricted to torsion angles similar to the ones believed at the time to occur in the helical conformations of crystalline PIB and that neighboring diads are essentially uncorrelated. Subsequent examination[5,17] indicated these models to be oversimplified and that additional rotational states should

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