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Variation of the Hydrodynamic Radius of Model Chains with Intermolecular Separation and Concentration†

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ABSTRACT: The reciprocal hydrodynamic radius r_h^{-1} of a single chain within an isolated chain pair has been calculated as a function of chain separation R within the pair by using a Monte Carlo technique for the construction of the ensembles of five-way cubic lattice model chains, for which the calculations were carried out. It is observed that r_h shows qualitatively the same variations with R as the squared radius of gyration s^2; their relative extent, however, is much less than would be trivially expected (i.e., half of the relative variations of s^2). As a consequence, the coefficients describing the concentration dependence of r_h^{-1} and s^2, which may be obtained by integrating the relative deviations—weighted with the pair distribution function $G(R)$—over the space, k_{1/r_h} and k_{s^2}, are linked by a factor $-C$, C being as small as ≈ 0.3 only, fairly independent of thermodynamic conditions (athermal or Θ). On the other hand, the concentration dependence of any average reciprocal distance between two segments i and j of the chain (except $j - i = 1$), $k_{1/r_{ij}}$, is linked to that of the average squared distance, $k_{r_{ij}^2}$, by a factor of $-C_{ij}$, C_{ij} being ≈ 0.65 for athermal and ≈ 0.7 for Θ systems. It is shown that the deviation of these latter values from the trivially expected ones of 0.5 is due to the distortion of the r_{ij} distribution by intermolecular interaction while the low value of C (in spite of the high values of C_{ij}) arises from the fact that intermolecular interaction does not lead to a uniform change of intrachain distances but affects larger (average) intramolecular separations much more strongly than smaller ones, even on a relative scale.

Introduction

There are three quantities that are widely in use to characterize the dimensions of randomly coiled polymer molecules: (1) the squared end-to-end distance r_{0n}^2, which is the easiest one to be obtained theoretically but lacks a straightforward method of experimental determination; (2) the squared radius of gyration s^2, which is readily determined from light scattering experiments; and (3) the hydrodynamic radius r_h, which reflects the effect of coil size on polymer transport properties. Interestingly enough, s^2 and r_h may be obtained from the same basic set of individual data within a chain, i.e., the (double) sum of all distances r_{ij} between two individual points i and j of the chain

$$s^2 = \frac{1}{(n+1)^2} \sum_{0 \le i < j \le n} r_{ij}^2 \tag{1}$$

$$r_h^{-1} = \frac{2}{n(n+1)} \sum_{0 \le i < j \le n} r_{ij}^{-1} \tag{2}$$

n being the number of bond vectors successively connecting the $n + 1$ skeleton points forming the chain.

Recently, a lot of interest has been directed toward the dependence of chain dimensions on intermolecular separation and on concentration on the one hand and toward the implications that these dependences have on the diffusion coefficient on the other. In our first contribution[1] to this field, we have evaluated the variation of s^2 and r_{0n}^2 with intermolecular separation R for four-way and five-way cubic lattice chains with $n = 49$ for athermal as well as for Θ conditions. These data may be easily converted into a quantity k_X characterizing the (relative) change of the quantity X (here $X = r_{0n}^2$ and s^2) with polymer volume fraction φ, defined as the fraction of occupied lattice sites, in the low-concentration limit ($\Delta X_\varphi / X_{\varphi=0} = k_X \varphi$)

$$k_X = \frac{4\pi}{n+1} \int_0^\infty \frac{X(R) - \langle X \rangle_0}{\langle X \rangle_0} G(R) R^2 \, \mathrm{d}R \tag{3}$$

where $\langle X \rangle_0$ is the ensemble average of quantity X for isolated chains (i.e., $R = \infty$) and $X(R)$ is the value of X at separation R. Thus this method, at least if the pair distribution function $G(R)$ is known, in principle also provides an access to the concentration dependence of polymer dimensions in these systems. The outstanding result has been that while k_X had the expected negative value for athermal systems in all cases, there was a positive concentration effect in the Θ systems.[1] Furthermore, in this context some information was obtained on the variation of the average shape of the model chains with separation R. Although there was no specific information on r_h contained in our paper, our results have been incorporated qualitatively by Akcasu et al.[2,3] into their discussion of the temperature effect on the concentration dependence of the diffusion constant of polymers. In a further ingenious effort, which deserves full general acknowledgment, Akcasu and Hammouda[4] used some of our data on five-way cubic lattice chains ($n = 49$) to estimate the effect of (intramolecular) chain deformation by intermolecular encounters and also tried to provide estimates for the concentration dependence of the hydrodynamic radius r_h by introducing the assumption that on interaction all individual distances within the chains suffer the same relative changes as s^2 and its components parallel and perpendicular to $\mathbf{R}$. Their conclusion was that (a) the concentration correction is rather small and is limited to a few percent at most, even at the upper end of the concentration regime for which the validity of a first-order correction can be assumed, and (b) that the coefficients relating the concentration dependence of r_h^{-1} and s^2 are in a ratio of ca. -0.65 for athermal and ca. -0.41 for Θ conditions.

In a recent paper[5] we were able to show that the binary encounters between polymer molecules have to be characterized not only through the variation in average shape and size of the individual molecules but also through the relative orientation that the usually ellipsoidal molecules assume relative to each other at any separation.

In order to obtain a deeper insight into the conformational and dimensional changes that occur in the interior of a chain when undergoing a binary encounter, we have extended our method of evaluating the concentration dependence of model chain dimensions developed in ref 1 to other characteristic distances within the chain such as the distance between center of mass and chain ends or

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† Dedicated to Prof. Dr. J. Schurz, Institute of Physical Chemistry, University of Graz, Styria, Austria, with our best wishes on occasion of his 60th birthday.

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between center of mass and middle segment etc. and also started to apply our method to the hydrodynamic radius r_h itself. Whereas the concentration dependence of the former quantities was well within the frame of expectance, the first preliminary results concerning the variation of r_h^{-1} with concentration and separation already showed that the effects amounted to little more than one-quarter of those observed for s^2 only![5]

In the following we want to report in more detail on these results and to extend our investigation to the components of r_h and s^2, i.e., the total set of separations between all segments r_{ij}. Due to the fact that according to Stokes's law the friction coefficient, which enters into the *denominator* of the expression for the diffusion coefficient D, is proportional to r_h, the reciprocal of the hydrodynamic radius, r_h^{-1}, may be taken as a measure of D. Furthermore, the quantity that is defined primarily is r_h^{-1} (eq 2). For these reasons and in order to facilitate application of our findings to the quantity of real interest, namely D, we have preferred to represent all our data in terms of r_h^{-1} (and not in terms of r_h itself). As the primary objective of this study is single-chain properties subject to intermolecular interaction, the concentration dependence of r_h^{-1} may be considered to be characteristic of the concentration dependence of D_0, the short-time limit of the coefficient of self-diffusion.[2,4] It should be noted, however, that quite generally k_X is always very close to $-k_{1/X}$, so that within the limits of accuracy k_{r_h} may be replaced by $-k_{1/r_h}$.

Procedure

Essentially the same techniques were adopted as outlined in previous publications:[1,5-7] First, ensembles consisting of 1500 (athermal conditions) or 900 (Θ conditions) individual self-avoiding five-way cubic lattice chains (n = 24, 49, 99, and 199) characteristic of the desired thermodynamic conditions (athermal or Θ) were prepared according to a Monte Carlo (Metropolis–Rosenbluth) process. In order to ensure negligible correlation between the indivdual chains within the ensemble, a high number of intercalated steps was predecided between any two successive chains included in the ensemble. Furthermore, the generation process was restarted with a new (equilibrated) parent chain after about 10 chains had been produced in the manner described. Each pair that could be formed from the ensemble (404 550 pairs in all for Θ conditions and 1 124 250 for athermal conditions) was then checked for its Boltzmann factor f of intermolecular interaction at any (integer) separation R along the lattice axes between the rounded coordinates of the two centers of gravity of the two chains, f being zero in case of double occupancy (incompatible pairs) and $\exp(-n_{IJ}\phi)$ for compatible pair configurations, n_{IJ} being the number of intermolecular contacts between two chains I and J (occupancy of adjacent lattice sites) and ϕ the parameter characterizing the thermodynamic conditions ($\phi = 0$ for athermal systems, $\phi = -0.255$, which is the value making the second osmotic virial coefficient vanish, for Θ systems[8]). Any averaged properties $X(R)$ of the chains in contact (i.e., forming pairs at separation R) then were evaluated according to

$$X(R) = \sum_{I>J} f_{I,J} X_{I,J} / \sum_{I>J} f_{I,J} \qquad \text{(all pairs)} \qquad (4)$$

$X_{I,J}$ being the mean of the property X of the two members I and J of the pair under consideration. Naturally, as $f_{I,J}$ can take values of 1 (compatible pairs) or 0 (incompatible pairs) only for athermal systems, eq 4 reduces to

$$X(R) = \sum_{I>J} X_{I,J} / N_{\text{compatible pairs}} \qquad (5)$$

with the summations carried out for compatible pairs only.

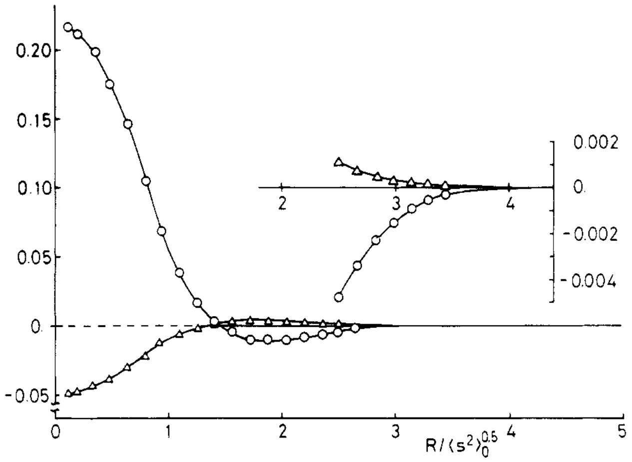

Figure 1. Deviation of the squared radius of gyration and of the reciprocal hydrodynamic radius from and relative to their values at infinite separation ($\langle s^2\rangle_0$ or $\langle r_h^{-1}\rangle_0$, respectively) as a function of (reduced) intermolecular separation, $R/\langle s^2\rangle_0^{1/2}$, for isolated pairs of five-way cubic lattice chains (n = 99) under athermal conditions: (○) $(s^2(R) - \langle s^2\rangle_0)/\langle s^2\rangle_0$ ($\langle s^2\rangle_0 = 40.8$); $(r_h^{-1}(R) - \langle r_h^{-1}\rangle_0)/\langle r_h^{-1}\rangle_0$ ($\langle r_h^{-1}\rangle_0 = 0.202$).

As no significant variation of data could be detected if R occasionally was chosen along other than the main axes of the lattice (e.g., along the square or room diagonals of the lattice etc.) spherical symmetry of interaction between chains was assumed. Data of $X(R)$ obtained by the procedure outlined above therefore were considered to be characteristic of the quantity X not only for values of R in the direction of the main axes of the lattice but also of any separation R in space, which is, of course, an absolute prerequisite for the applicability of eq 3. Integral quantities k_X characterizing the low-density limit of the concentration dependence of X accordingly were calculated from eq 3, the integration being replaced by a suitable summation procedure. The pair distribution function $G(R)$, which enters into this equation, was evaluated as the average value of the Boltzmann factor of intermolecular interaction $f_{I,J}$ over all pairs

$$G(R) = \sum_{I>J} f_{I,J}(R) / N_{\text{all pairs}} \qquad (6)$$

Results

(a) Hydrodynamic Radius. The dependence of r_h^{-1} on separation R for athermal and Θ chains covering 100 lattice points each (n = 99) is shown in Figures 1 and 2 for athermal and Θ conditions, respectively. For comparison, the variation of s^2 is also included in these diagrams. It may be well recognized from Figures 1 and 2 that the hydrodynamic radius (or here rather its reciprocal) reflects the influence of intermolecular interaction in the same typical qualitative way as does the radius of gyration or the end-to-end distance.[1] In fact, $r_h(R)$ shows the same number of zeroes as $s^2(R)$ at almost the same positions. Defining generically the relative deviation of a quantity X from its ensemble average at infinite separation as

$$(\Delta X)_{\text{rel}} \equiv (X(R) - \langle X\rangle_0)/\langle X\rangle_0 \qquad (7)$$

in accordance with our preliminary observation[5] $(\Delta r_h^{-1})_{\text{rel}}$ always is much smaller than $(\Delta s^2)_{\text{rel}}$. Except for separations in the closest proximity of the zeroes of the two curves where there may be some irregularities, the ratio $-(\Delta r_h^{-1})_{\text{rel}}/(\Delta s^2)_{\text{rel}}$ amounts to only ≈ 0.3 at $R = 0$ and becomes even smaller on increasing separation, in athermal as well as in Θ systems.

As a consequence the (absolute value of the) coefficient k_{1/r_h} characterizing the concentration dependence of r_h^{-1},

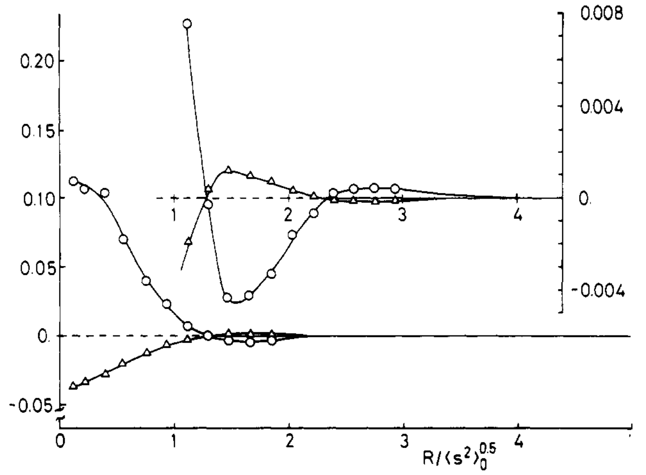

Figure 2. Deviation of the squared radius of gyration and of the reciprocal hydrodynamic radius from and relative to their values at infinite separation ($\langle s^2\rangle_0$ or $\langle r_h^{-1}\rangle_0$, respectively) as a function of (reduced) intermolecular separation, $R/\langle s^2\rangle_0^{1/2}$, for isolated pairs of five-way cubic lattice chains ($n = 99$) under Θ conditions: (○) $(s^2(R) - \langle s^2\rangle_0)/\langle s^2\rangle_0$ ($\langle s^2\rangle_0 = 29.4$); (△) $(r_h^{-1}(R) - \langle r_h^{-1}\rangle_0)/\langle r_h^{-1}\rangle_0$ ($\langle r_h^{-1}\rangle_0 = 0.231$).

evaluated with eq 3, is much smaller than the corresponding coefficient k_{s^2}, describing the concentration dependence of s^2. If we assume the two coefficients to be related by an equation of the type

$$k_{1/r_h} = -Ck_{s^2} \tag{8}$$

C would have a value of ≈0.3, nearly independent of thermodynamic conditions. Similar conclusions have been reached also for the other chain lengths examined ($n = 24$, $n = 49$, and $n = 199$), the basic data being listed in Table III.

(b) Individual Components r_{ij}^2 and $1/r_{ij}$. In order to reduce the abundance of data, first the data of individual components were collected in classes of constant $j - i$, i.e., groups comprising the averaged data of all segment pairs i and j separated by an equal number of bonds $d \equiv j - i$. When the dependences of $(\Delta r_d^{-1})_{\rm rel}$ and $(\Delta r_d^2)_{\rm rel}$ on intermolecular separation R are compared, a somewhat different impression is obtained than for the comparison of Δr_h^{-1} and Δs^2 described earlier: While the zeroes of the two curves in this case also coincide fairly well, the variation of the reciprocal quantities $(r_d^{-1})_{\rm rel}$ with R relative to that of $(r_d^2)_{\rm rel}$ is much more pronounced than it has been observed for the variation of $(r_h^{-1})_{\rm rel}$ compared to that of $(s^2)_{\rm rel}$. As an example, the dependence of $(\Delta r_d^{-1})_{\rm rel}$ and $(\Delta r_d^2)_{\rm rel}$ on R is shown in Figures 3 and 4 for athermal and Θ conditions, respectively, for $d = 24$ and $d = 99$ ($n = 99$).

Accordingly, the coefficients C_d connecting the concentration dependence of the two quantities r_d^{-1} and r_d^2, k_{1/r_d} and $k_{r_d^2}$

$$k_{1/r_d} = -C_d k_{r_d^2} \tag{9}$$

will have much higher numerical values than have been observed for C (eq 8). Actually, there is a slight dependence of C_d on thermodynamic conditions, C_d being somewhat larger for Θ systems than for athermal ones

$$k_{1/r_d} \approx -0.6_5 k_{r_d^2} \quad \text{(athermal systems)} \tag{10}$$

$$k_{1/r_d} \approx -0.7 k_{r_d^2} \quad \text{(Θ systems)} \tag{10a}$$

Of course, there is a strong variation of the absolute values of k_{1/r_d} and $k_{r_d^2}$ with the separation of the two segments i and j within the chain. Figure 5 illustrates the dependence of k_{1/r_d} (and $k_{r_d^2}$) on the number of segments separating segments j and i, $d \equiv j - i$, for athermal and Θ conditions ($n = 49$). The dependence of both k_{1/r_d} and $k_{r_d^2}$ on d, however, is nearly the same, especially for the athermal case, so that, at least as a crude approximation, eq 10 and 10a are valid irrespective of the actual value of d.

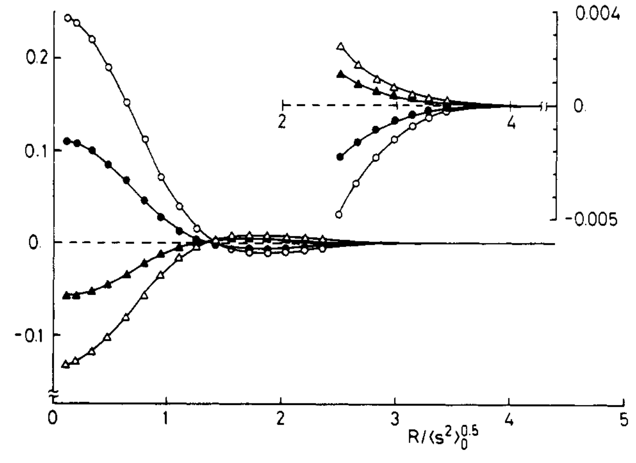

Figure 3. Deviation of the averaged squared and reciprocal distances between all segments i and j separated by 49 and 24 bonds, respectively, from and relative to their values at infinite separation ($\langle r_d^2\rangle_0$ or $\langle r_d^{-1}\rangle_0$, respectively) as a function of (reduced) intermolecular separation, $R/\langle s^2\rangle_0^{1/2}$, for isolated pairs of five-way cubic lattice chains ($n = 99$) under athermal conditions: (○) $(r_d^2(R) - \langle r_d^2\rangle_0)/\langle r_d^2\rangle_0$, ($d \equiv j - i = 49$, $\langle r_d^2\rangle_0 = 123.2$); (●) $(r_d^2(R) - \langle r_d^2\rangle_0)/\langle r_d^2\rangle_0$, ($d \equiv j - i = 24$, $\langle r_d^2\rangle_0 = 54.3$); (△) $(r_d^{-1}(R) - \langle r_d^{-1}\rangle_0)/\langle r_d^{-1}\rangle_0$ ($d \equiv j - i = 49$, $\langle r_d^{-1}\rangle_0 = 0.110$); (▲) $(r_d^{-1}(R) - \langle r_d^{-1}\rangle_0)/\langle r_d^{-1}\rangle_0$ ($d \equiv j - i = 24$, $\langle r_d^{-1}\rangle_0 = 0.163$).

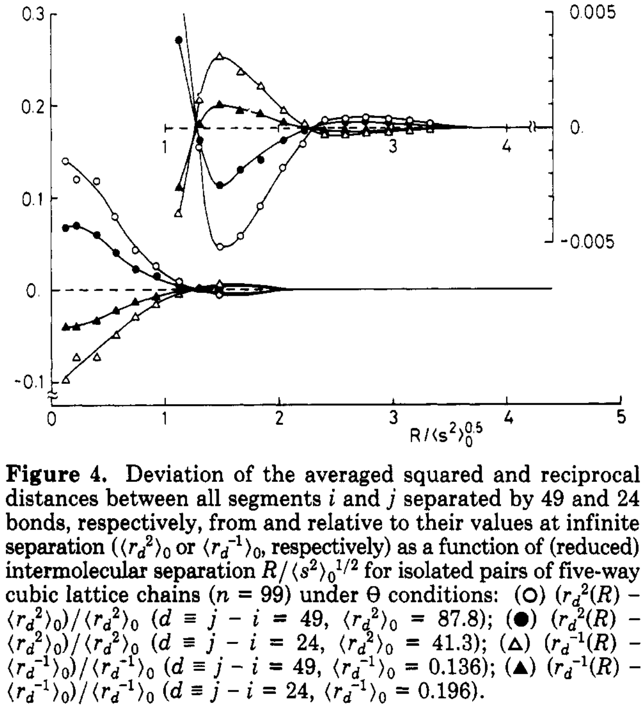

Figure 4. Deviation of the averaged squared and reciprocal distances between all segments i and j separated by 49 and 24 bonds, respectively, from and relative to their values at infinite separation ($\langle r_d^2\rangle_0$ or $\langle r_d^{-1}\rangle_0$, respectively) as a function of (reduced) intermolecular separation $R/\langle s^2\rangle_0^{1/2}$ for isolated pairs of five-way cubic lattice chains ($n = 99$) under Θ conditions: (○) $(r_d^2(R) - \langle r_d^2\rangle_0)/\langle r_d^2\rangle_0$ ($d \equiv j - i = 49$, $\langle r_d^2\rangle_0 = 87.8$); (●) $(r_d^2(R) - \langle r_d^2\rangle_0)/\langle r_d^2\rangle_0$ ($d \equiv j - i = 24$, $\langle r_d^2\rangle_0 = 41.3$); (△) $(r_d^{-1}(R) - \langle r_d^{-1}\rangle_0)/\langle r_d^{-1}\rangle_0$ ($d \equiv j - i = 49$, $\langle r_d^{-1}\rangle_0 = 0.136$); (▲) $(r_d^{-1}(R) - \langle r_d^{-1}\rangle_0)/\langle r_d^{-1}\rangle_0$ ($d \equiv j - i = 24$, $\langle r_d^{-1}\rangle_0 = 0.196$).

As a next step, the influence of the position of the subchain of length d within the chain was examined. While the ensemble averages $\langle r_{ij}^{-1}\rangle_0$ and $\langle r_{ij}^2\rangle_0$ show only a slight (but significant) trend when i (together with j) is varied[9] at constant $(j - i)$, there are marked changes as well for ΔX as for k_X values, which are presented in Table I. In all cases, both for athermal and for Θ conditions, much larger effects are recognized for those quantities referring to bonds near the middle of the chain than for those closer to the chain ends. An illustration of this behavior is given in Figure 6 for athermal and Θ conditions, where the relative deviations of the distances between segments separated by 49 bonds in a chain comprising $n = 99$ bonds,

Table I
Dimensions of Chain Elements ($j - i = 12$) and Their Concentration Dependence as a Function of the Position (i) of the Chain Element within a Chain Consisting of $n = 49$ Bond Vectors

thermodyn cond	i	$\langle r_{ij}^2\rangle_0$	$(\Delta r_{ij}^2)_{\rm rel}$ at $R = 0$	$k_{r_{ij}^2}$	$\langle r_{ij}^{-1}\rangle_0$	$(\Delta r_{ij}^{-1})_{\rm rel}$ at $R = 0$	$k_{1/r_{ij}}$
ath	1	22.20	0.019	−0.19	0.253	−0.011	+0.14
ath	7	23.21	0.062	−0.32	0.244	−0.037	+0.20
ath	13	23.22	0.13	−0.30	0.243	−0.077	+0.19
ath	19	23.73	0.17	−0.35	0.237	−0.093	+0.21
Θ	1	19.20	0.014	+0.047	0.282	−0.011	−0.038
Θ	7	19.38	0.048	+0.073	0.275	−0.025	−0.049
Θ	13	19.62	0.11	+0.086	0.273	−0.057	−0.064
Θ	19	19.67	0.13	+0.10	0.274	−0.076	−0.068

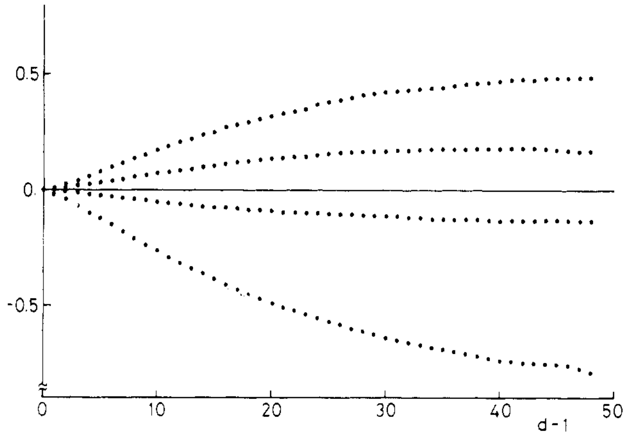

Figure 5. Coefficients k_X describing the concentration dependence of X ($X \equiv r_d^2$ and $X \equiv r_d^{-1}$, the averaged squared and reciprocal distances, respectively, between all segments i and j separated by an equal number of bonds $d \equiv j - i$) as a function of d for five-way cubic lattice chains ($n = 49$). From top to bottom: k_{1/r_d} (athermal conditions); $k_{r_d^2}$ (Θ conditions); k_{1/r_d} (Θ conditions); $k_{r_d^2}$ (athermal conditions).

which are observed for $R = 0$, are plotted as a function of their position within the chain.

The influence of position on $k_{1/r_{ij}}$ and $k_{r_{ij}^2}$ (at $j - i$ = constant) again is fairly the same in both cases. However, while there is a slight tendency for $C_{ij} \equiv (-k_{1/r_{ij}}/k_{r_{ij}^2})$ to increase on moving segments j and i progressively into the interior of the chain for athermal systems, the opposite trend is observed for Θ systems.

Discussion

At first sight, as $(\Delta s^2)_{\rm rel}$ and k_{s^2} refer to a quadratic dimension while $(\Delta r_{\rm h}^{-1})_{\rm rel}$ and $k_{1/r_{\rm h}}$ are characteristic of an inverse linear dimension, it should be expected that $(\Delta s^2)_{\rm rel}$ and $(\Delta r_{\rm h}^{-1})_{\rm rel}$, and also k_{s^2} and $k_{1/r_{\rm h}}$, are linked by a coefficient of −0.5; i.e., the proportionality constant C in eq 8 should have a value of 0.5 (the minus sign accounting for the fact only that $r_{\rm h}^{-1}$ represents an *inverse* linear quantity). Analogous considerations, of course, should be valid when $(\Delta r_d^2)_{\rm rel}$ and $(\Delta r_d^{-1})_{\rm rel}$ (plus $k_{r_d^2}$ and k_{1/r_d}), and even more generally $(\Delta r_{ij}^2)_{\rm rel}$ and $(\Delta r_{ij}^{-1})_{\rm rel}$ (plus $k_{r_{ij}^2}$ and $k_{1/r_{ij}}$) are compared, i.e., also for the quantities C_d and C_{ij}.

The results presented in the preceding section show clearly that neither Δs^2 and $\Delta r_{\rm h}^{-1}$ nor any Δr_{ij}^2 and Δr_{ij}^{-1} follow this simple rule. What makes things even more complicated is the fact that while C_d and most of the C_{ij} for the individual distances r_{ij} markedly exceed the value of 0.5, C itself (for the quantities of primary interest s^2 and $r_{\rm h}^{-1}$ representing the combined action of *all* individual distances between segments) is about only half that value. The following discussion therefore will try to account for both the low C values of $r_{\rm h}^{-1}$ and the high C_{ij} values of r_{ij}^{-1} and r_d^{-1}, respectively, and will also look for some explanation for the slight differences in behavior of athermal and Θ systems.

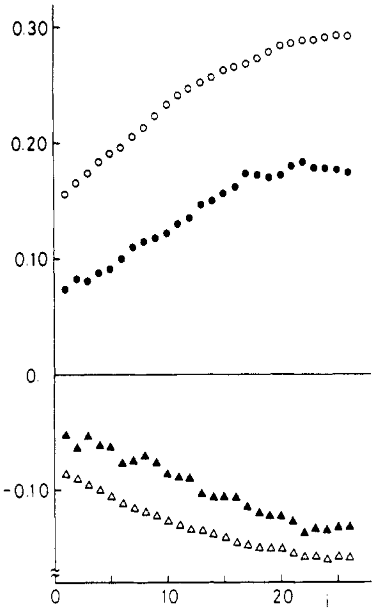

Figure 6. Dependence of the relative deviations of the squared (○, ●) and reciprocal (△, ▲) distances between segments j and i separated by $j - i = 49$ bonds in a chain comprising 99 bonds on their position i within the chain observed for $R = 0$ for athermal (open symbols) and Θ conditions (full symbols).

To a certain extent, apart from a factor of 2, the squared radius of gyration, s^2, and the hydrodynamic radius, $r_{\rm h}$, may be considered to be different averages of the same quantities (the individual distances between segments). So s^2 constitutes some kind of a (reduced) second moment of the r_{ij}'s while $r_{\rm h}^{-1}$ formally plays the role of a (reduced) moment of order −1. Quite generally, the behavior of higher (more positive) order moments is dominated by the behavior of its larger constituents while, in comparison with the former ones, the reverse is true for the moments of lower order. This principle is easily recovered when the values of $(s^2)^{1/2}$ and $r_{\rm h}$ are compared with each other. Analogous considerations apply to the relative changes of s^2 and $r_{\rm h}$ on intermolecular interaction, which may be written (all sums for $i < j$)

$$(\Delta s^2)_{\rm rel} = \frac{1}{\langle s^2\rangle_0}\,\frac{1}{(n+1)^2}\sum(\Delta r_{ij}^2)_{\rm rel}\langle r_{ij}^2\rangle_0 = \frac{\sum(\Delta r_{ij}^2)_{\rm rel}\langle r_{ij}^2\rangle_0}{\sum\langle r_{ij}^2\rangle_0}$$

$$(\Delta r_{\rm h}^{-1})_{\rm rel} = \frac{1}{\langle r_{\rm h}^{-1}\rangle}\,\frac{2}{n(n+1)}\sum(\Delta r_{ij}^{-1})_{\rm rel}\langle r_{ij}^{-1}\rangle_0 = \frac{\sum(\Delta r_{ij}^{-1})_{\rm rel}\langle r_{ij}^{-1}\rangle_0}{\sum\langle r_{ij}^{-1}\rangle_0}$$

and also to the integral quantities characterizing the concentration dependence of s^2 and $r_{\rm h}^{-1}$

$$k_{s^2} = \left(\sum k_{r_{ij}^2}\langle r_{ij}^2\rangle_0\right) / \sum \langle r_{ij}^2\rangle_0$$

$$k_{1/r_\mathrm{h}} = \left(\sum k_{1/r_{ij}}\langle r_{ij}^{-1}\rangle_0\right) / \sum \langle r_{ij}^{-1}\rangle_0$$

This might give the key for understanding, at least partially, the quantitative relation between $(\Delta s^2)_\mathrm{rel}$ and $(\Delta r_\mathrm{h}^{-1})_\mathrm{rel}$ values and between k_{s^2} and k_{1/r_h}, provided that the quantities $(\Delta r_{ij}^2)_\mathrm{rel}$, $(\Delta r_{ij}^{-1})_\mathrm{rel}$, k_{s^2}, and k_{1/r_h} vary with $\langle r_{ij}^2\rangle_0$ or with $\langle r_{ij}^{-1}\rangle_0$. As may be easily deduced from Figure 5, this is in fact the case, Δr_{ij}^2 clearly being an increasing and Δr_{ij}^{-1} a decreasing function of $j - i$. As it is too difficult to give an exact treatment for the ratio $(\Delta r_\mathrm{h}^{-1})_\mathrm{rel}/(\Delta s^2)_\mathrm{rel}$ or, as a further consequence, for the ratio $k_{1/r_\mathrm{h}}/k_{s^2}$, we shall be content with making a crude assessment only on the following basis: We start with a certain ratio $-k_{1/r_{ij}}/k_{r_{ij}^2} \equiv C_{ij}$ and (a) assume, as a zeroth approximation, relationships of the form

$$k_{r_{ij}^2} \sim (j - i) \qquad r_{ij}^2 \sim (j - i)^{1+\epsilon} \qquad r_{ij}^{-1} \sim (j - i)^{-0.5(1+\epsilon)}$$

with $\epsilon = 0$ for Θ chains and $\epsilon = 0.2$ for athermal chains, and (b) replace summations by integration in the long-chain limit. Under these conditions we obtain ($x = i/n$ being the reduced position of segment i along the chain)

$$-k_{1/r_\mathrm{h}}/k_{s^2} = \frac{C_{ij}\int_0^1 (x^{0.5(1-\epsilon)} - x^{0.5(3-\epsilon)})\,\mathrm{d}x}{8\int_0^1 (x^{2+\epsilon} - x^{3+\epsilon})\,\mathrm{d}x} = \frac{1}{2}C_{ij}\frac{(3+\epsilon)(4+\epsilon)}{(3-\epsilon)(5-\epsilon)} \quad (11)$$

This means that the ratio $-k_{1/r_\mathrm{h}}/k_{s^2}$ takes a value of $(2/5)C_{ij}$ for Θ conditions and $(1/2)C_{ij}$ for athermal conditions. Clearly, this is an oversimplification of the delicate situation, which we have to deal with, but nevertheless, this assessment predicts fairly well the extent to which C is lower than C_{ij}.

In order to contribute to the understanding of the second important finding, i.e., $C_d > 0.5$, it should be recalled that all r_{ij}^2 and all r_{ij}^{-1} are ensemble averages, showing a certain distribution (for convenience, in most cases a Gaussian distribution is assumed for all r_{ij}^2). Now, all effects, which occur on intermolecular interaction, stem from the fact that certain pair configurations are eliminated due to incompatibility (in addition in Θ systems others may be given an increased weight due to a higher Boltzmann factor). Naturally, this "mechanism of selection" may also extend to the distributions of r_{ij} in such a way that not only the averages are shifted but also the type and the dispersion of the distribution are altered. It is immediately clear how such an effect will work. As we may define

$$\langle r_{ij}^2\rangle = \sum f_{r_{ij}} r_{ij}^2 \qquad \langle r_{ij}^{-1}\rangle = \sum f_{r_{ij}} r_{ij}^{-1}$$

where $f_{r_{ij}}$ is the normalized distribution function, any change in type of $f_{r_{ij}}$ will influence the ratio $\langle r_{ij}^2\rangle/\langle r_{ij}^{-1}\rangle^{-2}$ and accordingly lead to C_{ij} values deviating from 0.5. Actually, the ratio

$$q \equiv \langle r_{ij}^2\rangle^{1/2}/\langle r_{ij}^{-1}\rangle^{-1}$$

may be taken as that very measure of the dispersion of the distribution, which is the most characteristic one for the problem under consideration. As a matter of fact q varies sensibly with R on intermolecular interaction, an example being given in Figures 7 and 8 for the end-to-end distances in chains of $n = 49$ for athermal and Θ conditions, respectively. Although $q(R)$ never deviates by more than 6% from its value for isolated chains, this variation is by no means negligible and turns out to be in fact responsible for $C_{ij} > 0.5$.

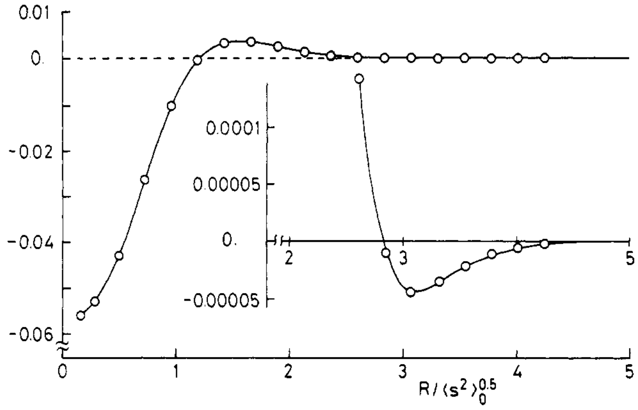

Figure 7. Dependence of the ratio $q = \langle r_{0n}^2\rangle^{1/2}/\langle r_{0n}^{-1}\rangle^{-1}$ (r_{0n}^2 and r_{0n}^{-1} being the squared and reciprocal end-to-end distance) from and relative to its value for isolated chains $q_0 = 1.26$ as a function of (reduced) intermolecular separation $R/\langle s^2\rangle_0^{1/2}$ for isolated pairs of five-way cubic lattice chains ($n = 49$) under athermal conditions.

A quantitative evaluation of the influence the distortion of the distribution of r_{ij} takes on C_{ij} can be done in the following way (for simplicity the index ij to r is dropped in this section):

Let $q(R) = \langle r^2\rangle^{1/2}/\langle r^{-1}\rangle^{-1}$ as before be a measure of characterizing the dispersion of the r_{ij} distribution in interacting chains and $q_0 = \langle r^2\rangle_0^{1/2}/\langle r^{-1}\rangle_0^{-1}$ be its value for isolated chains ($R = \infty$). Defining

$$\langle r^2\rangle_\mathrm{rel} \equiv \langle r^2\rangle/\langle r^2\rangle_0$$

$$\langle r^{-1}\rangle_\mathrm{rel} \equiv \langle r^{-1}\rangle/\langle r^{-1}\rangle_0$$

then

$$\langle r^{-1}\rangle_\mathrm{rel} \equiv (q/q_0)\langle r^2\rangle_\mathrm{rel}^{-1/2}$$

Now we may write (with $\mathbf{dR}$ instead of $4\pi R^2\,\mathrm{d}R$ for abbreviation)

$$(n+1)k_{r^2} = \int_0^\infty (\langle r^2\rangle_\mathrm{rel} - 1)G(R)\,\mathbf{dR} = \int_0^\infty \langle \Delta r^2\rangle_\mathrm{rel} G(R)\,\mathbf{dR}$$

and

$$(n+1)k_{1/r} = \int_0^\infty (\langle r^{-1}\rangle_\mathrm{rel} - 1)G(R)\,\mathbf{dR} = \int_0^\infty \langle \Delta r^{-1}\rangle_\mathrm{rel} G(R)\,\mathbf{dR}$$

substituting for $\langle r^{-1}\rangle_\mathrm{rel}$ gives

$$(n+1)k_{1/r} = \int_0^\infty [(q/q_0)\langle r^2\rangle_\mathrm{rel}^{-1/2} - 1]G(R)\,\mathbf{dR} \quad (12)$$

Expanding $\langle r^2\rangle_\mathrm{rel}^{-1/2} \equiv (1 + \langle \Delta r^2\rangle_\mathrm{rel})^{-1/2}$ and rejecting higher terms yields

$$k_{1/r} \approx (n+1)^{-1}\int_0^\infty [(q/q_0)(1 - 0.5\langle \Delta r^2\rangle_\mathrm{rel}) - 1] \times G(R)\,\mathbf{dR} = -0.5(n+1)^{-1}\int_0^\infty (q/q_0)\langle \Delta r^2\rangle_\mathrm{rel} G(R)\,\mathbf{dR} + (n+1)^{-1}\int_0^\infty [(q/q_0) - 1]G(R)\,\mathbf{dR} \equiv 0.5I_1 + I_2 \quad (13)$$

For $q/q_0 = 1$ (no selection) the second term would vanish and the first one reduce to $-0.5k_{r^2}$.

Actually, due to the small deviation of q/q_0 from unity plus some compensating effects from positive or negative changes, the first term does not differ very much from

Table II

Compilation of Data Characterizing the Connection between the Distortion of the Distribution of Intrachain Distances Caused by Intermolecular Interaction and the Deviation of the Ratio C_d from Its Trivial Value of 0.5 for Chain Elements Separated by d Bond Vectors within a Chain Comprising a Total of n = 49 Bonds

thermodyn cond	d	$k_{r_d^2}$	k_{1/r_d}	C_d[a]	I_1[b]	I_2[b]	$-I_1/k_{r_d^2}$	$-I_2/k_{r_d^2}$	C_d[c]
ath	12	−0.292	0.189	0.65	0.292	0.0413	1.000	0.14	0.64
ath	24	−0.539	0.355	0.66	0.542	0.0744	1.006	0.14	0.64
ath	36	−0.688	0.442	0.64	0.695	0.0775	1.010	0.11	0.62
Θ	12	0.0790	−0.0546	0.69	−0.0787	−0.0170	0.996	0.22	0.71
Θ	24	0.147	−0.100	0.68	−0.145	−0.0353	0.986	0.24	0.73
Θ	36	0.176	−0.128	0.73	−0.170	−0.0527	0.966	0.30	0.78

[a] Directly evaluated from $k_{r_d^2}$ and k_{1/r_d}; values are identical with those calculated with the exact relationship given by eq 12. [b] For definition see text (eq 13). [c] Calculated according to the approximate relationship $C_d = -(0.5I_1 + I_2)/k_{r_d^2}$ (eq 13).

Table III

Compilation of the Most Important Data Characterizing the Concentration Dependence of Chain Dimensions, with Special Reference to the Quantity $(k_{1/r_h})_{Akc}$ As Calculated according to Akcasu and Hammouda[4]

thermodyn cond	n	$\langle s^2\rangle_0$	$\langle r_h^{-1}\rangle_0$	k_{s^2}	k_{1/r_h}	C	k_{r_h}	$(k_{1/r_h})_{Akc}$	$k_{1/\langle s^2\rangle^{1/2}}$
ath	24	7.39	0.401	−0.30	0.081	0.27	−0.080	0.19	0.16
ath	49	17.98	0.286	−0.53	0.15	0.29	−0.15	0.34	0.28
ath	99	40.80	0.202	−0.94	0.27	0.29	−0.27	0.58	0.49
ath	199	97.28	0.140	−1.34	0.41	0.30	−0.40	0.84	0.71
Θ	24	6.40	0.424	0.092	−0.029	0.31	0.030	−0.031	−0.040
Θ	49	13.96	0.314	0.14	−0.046	0.34	0.048	−0.056	−0.062
Θ	99	29.39	0.231	0.17	−0.057	0.33	0.058	−0.074	−0.080
Θ	199	61.15	0.168	0.23	−0.077	0.34	0.079	−0.097	−0.100

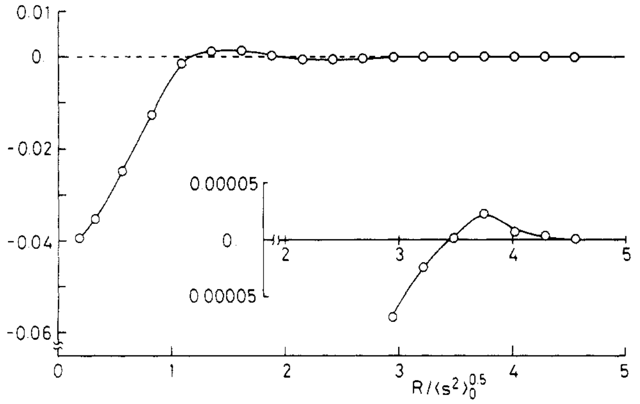

Figure 8. Dependence of the ratio $q = \langle r_{0n}^2\rangle^{1/2}/\langle r_{0n}^{-1}\rangle^{-1}$ (r_{0n}^2 and r_{0n}^{-1} being the squared and reciprocal end-to-end distance) from and relative to its value for isolated chains q_0 = 1.31 as a function of (reduced) intermolecular separation $R/\langle s^2\rangle_0^{1/2}$ for isolated pairs of five-way cubic lattice chains (n = 49) under Θ conditions.

$-0.5k_{r^2}$ for athermal as well as for Θ systems. The second term, however, which can be understood as a coefficient describing the concentration dependence of the dispersion of the distribution of r_{ij}, is negative for athermal and positive for Θ systems. As k_{r^2} is negative for athermal and positive for Θ chains, this leads to the effect that both terms always have the same sign, thus increasing the formal constant C_{ij} in the relation $k_{1/r_{ij}} = -C_{ij}k_{r_{ij}^2}$ beyond the value of 0.5.

A selection of data for athermal and Θ chains (n = 49) is given in Table II. From these data it can be depicted that the higher C_d values of Θ chains (compared to athermal ones) arise from the fact that while the absolute value of I_1 is much smaller for Θ chains (approximately by a factor of 4), the correction terms I_2 are separated by a factor of 2 only. Thus, although the distortion of the distribution of r_{ij} is smaller for Θ systems, it makes the relatively more important contribution to k_{1/r_h} compared to athermal systems. It is this effectively higher sensitivity of the $k_{1/r_{ij}}$ values of Θ systems toward the distortion of r_{ij} distribution that fairly compensates for the lower factor of $^2/_5$ (compared to $^1/_2$ for athermal chains) as it has been evaluated above as a zeroth approximation of the transformation of C_{ij} values into C. As the result of this compensating effect, roughly the same C values (≈0.3) are obtained for athermal as well as Θ systems.

It remains to compare the data obtained within this paper to those that would result from application of Akcasu's and Hammouda's method (eq 18–21, ref 4) using the same ensembles of chains in both cases, however, retaining *our* definition of volume fraction. As already mentioned shortly in the Introduction, Akcasu and Hammouda[4] in their derivation (a) used separate Gaussian distributions for the characterization of the segment distribution in the direction perpendicular and parallel to **R** and (b) assumed all subchains to expand (or contract) in a uniform manner on the same relative scale in these two directions as the two radii of gyration, $\langle s_\perp^2\rangle^{0.5}$ and $\langle s_\parallel^2\rangle^{0.5}$. The relevant data that are necessary for carrying out such a comparison are compiled in Table III. The fifth and the sixth column refer to k_{s^2} and k_{1/r_h}, respectively, as they have been evaluated according to the methods outlined in this paper.[10] In addition, the coefficient describing the concentration dependence of r_h itself, k_{r_h}, which not unexpectedly is very close to $-k_{1/r_h}$, is also listed in column 8 of this table. Naturally, therefore, all these values fully reflect the influence of all changes in size, shape, and relative orientation of the chains within an isolated pair, which are caused by intermolecular interaction. Column 9 then represents the results that are obtained for the concentration dependence of r_h^{-1}, $(k_{1/r_h})_{Akc}$, by applying Akcasu's method. In order to separate the effect originating from the consideration of the variation of (average) shape caused by intermolecular interaction (assumption a of Akcasu's theory) from the eventual shortcomings introduced by the assumption of a "uniform expansion and contraction" of all subchains by intermolecular interaction (assumption b of Akcasu's theory), a quantity "$k_{1/\langle s^2\rangle^{1/2}}$" is given in column 10 which we have calculated without taking into account the shape variations (this means abandoning the separation into the dimensions parallel and perpendicular to **R** according to assumption a), however, retaining the general principle (argument b) introduced by Akcasu of subjecting all intramolecular distances r_{ij} to a single direction-independent "expansion (or contraction) factor" for all values of $j - i$, in this case $s^2(R)/\langle s^2\rangle_0 = (s_{\parallel}^2(R) + 2s_{\perp}^2(R))/\langle s^2\rangle_0$. It turns out that these values, within the limits of accuracy, equal $-0.5k_{s^2}$. This result could have been easily derived in closed form under the assumption of Gaussian statistics and of a single expansion factor for all r_{ij}. Thus, the difference between columns 9 and 10 actually should represent the contribution of shape variation to the concentration dependence of r_h. Although these differences are by no means negligible, taking into account the variation of shape, in the way done by Akcasu, actually does not lead to an unanimous improvement: while there is a slight reduction of the difference between the data of columns 6 and 9 (over that between the data of columns 6 and 10) for Θ chains, the reverse is true for athermal systems. The *real* basic reason for the (partial) failure of Akcasu's treatment, however, appears to lie in the introduction of the assumption b of a d-independent (in the sense outlined above) "chain expansion" or "chain compression" caused by intermolecular interaction, which would lead to d-independent k_d values. Replacement of this "uniform expansion or contraction assumption" for all subchains by a more realistic one, therefore, invariably should lead to a substantial improvement of the Akcasu–Hammouda treatment. The inadequacy of this assumption which, for instance, may be easily extracted from our Figures 3 and 4, Figure 5, or Table II, apart from the distortions of the r_{ij} distributions on intermolecular interactions appears to be another example of the non-Gaussian character of intermolecular interaction effects between chain molecules regardless of thermodynamic conditions.

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(8) Admittedly, the value of ϕ that is necessary to make the excluded volume vanish is slightly dependent on n. Actually, the value chosen ($\phi = -0.255$), within statistical scatter, leads to a zero excluded volume for $n = 24$ and $n = 49$. Accordingly, there is a slightly positive excluded volume for $n = 99$ and $n = 199$, which, however, amounts to a few percent of that observed for athermal conditions only (3.5% and 6.5%, respectively).
(9) This is in qualitative accordance with the results of the first-order perturbation theory for r_{ij}^2 (Kurata, M.; Yamakawa, H.; Teramoto, E. *J. Chem. Phys.* **1958**, *28*, 785) and r_{ij}^{-1} (Barrett, A. J. *J. Phys. A: Math. Gen.* **1983**, *16*, 2321), respectively.
(10) A detailed discussion of the chain length dependence of these quantities will be given together with a theoretical approach to the problem (Olaj, O. F.; Zifferer, G.; Mann, E., to be published).

Complexation of Stereoregular Poly(methyl methacrylates). 7. Theoretical Aspects

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ABSTRACT: In a suitable solvent isotactic (it) and syndiotactic (st) poly(methyl methacrylates) associate into a stereocomplex with an it/st = $^1/_2$ composition. A simple model, introduced by Khodakov et al., for the complexation of a long macromolecule (matrix) and much shorter macromolecules (oligomers) is adapted to this particular stoichiometry. It is shown that the heat of complexation per complex unit is determined experimentally by taking an excess of matrix rather than an excess of oligomers. The ratio of the amount of oligomer and the amount of matrix for which the maximum possible heat of complexation per gram of macromolecules occurs is shown to depend strongly on the chain length of the oligomers and on the stoichiometry of complexation. The influence of the polydispersity of the oligomers on the behavior of the heat of complexation as a function of the matrix/oligomer ratio is discussed. A simple relation for the critical chain length, defined as the chain length of the oligomers, below which no appreciable complexation takes place, is derived and is shown to be independent of the complexation stoichiometry.

Introduction

In certain solvents, the isotactic and syndiotactic sequences of it- and st-PMMA associate, leading to the formation of a stereocomplex, a concept first introduced by Liquori et al.[3] The composition of the stereocomplex has long been a point of controversy and only recently[4] was it shown unambiguously that both components are present in a ratio it/st = $^1/_2$. The structure of the stereocomplex is still not completely clear. Kusanagi et al.[5] suggested that it should be closely related to the double-stranded helix of it-PMMA. Then Bosscher et al.[6] concluded that the X-ray diffraction data and conformational energy calculations point to a double-stranded helix consisting of an isotactic 30/4 helix surrounded by a syndiotactic 60/4 helix, with an identity period of 73.6 Å.

Another remarkable observation is that the stereocomplex can be formed in situ by free-radical polymerization of methyl methacrylate to predominantly syndiotactic PMMA due to the presence of it-PMMA as a template.[7,8] Moreover, the presence of a template matrix leads to a rate enhancement, due to a delayed termination reaction of those growing chains which are bound to the matrix.[9]

Double-stranded helical structures are well-known for various synthetic polynucleotides as well as for natural DNA, and several models, e.g., the perfect-matching, the imperfect-matching, and the hairpin models, have been

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