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The Ideal and the Pseudoideal State of Macromolecules: A Comparison

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ABSTRACT: By means of Monte Carlo calculations on lattice walks it could be shown that (a) the two definitions of the Θ-temperature (the second osmotic virial coefficient equals zero; the mean square end-to-end distance is proportional to the number of bonds) are equivalent in the asymptotic limit, (b) none of the existing theories based on models with short-range interferences gives correct results for the configurational properties of a Θ-chain, and (c) there is some evidence that the distribution functions, which are valid for random-flight chains, do not describe exactly the behavior of Θ-chains.

Introduction

The Θ-point of a polymer solution can be viewed as that state of the system at which the repulsive energies between the segments of the dissolved polymer are balanced by attractive energies. A polymer chain in a solution at the Θ-point is therefore called "pseudoideal", comparable to a real gas at the Boyle temperature. The architecture of polymer chains in the Θ-state is generally believed to be identical with that of ideal chains, i.e., chains without long-range interferences, and the huge arsenal of formalism developed for this case can then be used to describe the chain configuration. That is the reason why the Θ-state is paid particular attention by polymer chemists.

Ideal chains are chains with only short-range interferences. In the past the statistical examination of the geometry of model chains has been developed gradually by extending the number of structural units which are considered to interact. The sequence of the models is as follows: (a) interactions between first neighbors: a freely jointed chain;[1] (b) interactions between first and second neighbors: a chain with fixed valence angles;[2] (c) interactions between first, second, and third neighbors: a chain with fixed valence angles and restricted rotation;[3] and (d) interactions between first, second, third, and fourth neighbors: a chain in which interdependent rotation is taken into account.[4] These models can be represented by Markoff processes. They have, therefore, among others the following properties (in the asymptotic limit): (1) the mean square end-to-end distance $\langle h^2 \rangle$ and the mean square radius of gyration $\langle r^2 \rangle$ are proportional to the number of bonds n comprising the chain; (2) the end-to-end distance obeys Gaussian statistics.

Now the question arises whether a dissolved polymer chain in the Θ-state is really equivalent to any of the Markoff chains described above. This question is justified, because long-range interferences are not considered for ideal chains, whereas they do exist for pseudoideal chains even if they are balanced.

In this connection there is a further problem: The Θ-point has two definitions: (1) the point at which an isolated polymer molecule behaves as a random coil (i.e., $\langle h^2 \rangle \sim n$), and (2) the point at which the second osmotic virial coefficient of the polymer solution, A_2, vanishes. These two definitions are not necessarily consistent. The possibility that they may not be is suggested by a comparison of the results of Janssens and Bellemanns[5] with those of McCrackin et al.[6] Both teams determined the Θ-temperature of chains on a 5-choice cubic lattice by Monte Carlo methods. Janssens and Bellemanns using the condition $A_2 = 0$ found the reduced interaction potential $\Phi_\Theta = (w/kT)_{T=\Theta} = 0.2693$ as $n \to \infty$, whereas McCrackin et al. using the condition $\langle h^2 \rangle \sim n$ reported $\Phi_\Theta = 0.275$.

In this work we investigate the two problems described above by means of Monte Carlo calculations.

Model and Basic Equations

The polymer chains are simulated by nonintersecting walks on a 5-choice cubic lattice. We chose this model since its Θ-point behavior has already been studied by other authors,[5-8] and a comparision of their results with ours is thus facilitated. A chain consists of n steps (bonds) of length l (lattice spacing) each. Empty sites are considered as occupied by solvent molecules. An interaction energy $-w$ is attached if two nonbonded segments of the chain form a contact; i.e., they are separated by a lattice spacing. The energy of a single chain with configuration j can then be calculated by

$$W_1(j) = \sum_{l=3}^{n} \sum_{k=0}^{l-3} w_{kl}^{(j)} = -n_j w \qquad (1)$$

$w_{kl}^{(j)}$ means the interaction energy between the segments k and l, and n_j is the number of contacts in configuration j. (It has to be pointed out that these "energies" are potentials of mean forces in reality. They depend on the temperature and on the activity of the solvent).

Now w (or more generally Φ) has to be determined so that the chains assume pseudoideal behavior. The relations used in Monte Carlo calculations so far are as follows:

(1)[7] $\langle h^2 \rangle = nl^2$. Here the pseudoideal chain is presumed to behave like the ideal model a. This is surely not admissible.

(2)[8] $\langle h^2 \rangle \sim n$. This proportion is only valid in the asymptotic limit in most cases. Since the chains that can be treated by Monte Carlo methods are short ($n \lesssim 1000$), the value obtained for Φ_Θ may be too large.

(3)[9] The binary cluster integral β_2 equals zero. This condition is deduced from the perturbation expansion where it nullifies all binary contact terms. The numerical value of β_2 can only be estimated roughly, because β_2 is introduced by the factorization

$$\int f(\vec{r})\{1 - \exp[\Phi(\vec{r})]\}\, \mathrm{d}\vec{r} \to f(\vec{0}) \int \{1 - \exp[\Phi(\vec{r})]\}\, \mathrm{d}\vec{r} = \beta_2 f(\vec{0}) \qquad (2)$$

which is only exact for δ-function potentials or for very long chains.[11] Both requirements are, however, not met here. Moreover, triple-contact terms have to be considered. The temperature at which these terms vanish generally differs from the corresponding temperature of binary contact terms.

Because of the shortcomings of these relations the condition $A_2 = 0$ is used in this work. It can be applied to chains of any length and is a well-suited quantity to study the behavior of a dilute solution from a thermodynamical

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viewpoint. To our knowledge only two investigations of the Θ-state have been published so far which are based on the condition $A_2 = 0$. Kirste[12] reports on the radius of gyration of stiff model chains serving as a prototype of cellulose trinitrate. Olaj et al.[13] worked on the dimensions and shapes of chains as a function of their spatial separation. They did, however, not use the rigorous expression for A_2 but only an approximation, in which intramolecular interaction terms are neglected.

The starting point of our calculations is the viral expansion of the osmotic pressure

$$\Pi/(kT) = \rho + B_2\rho^2 + ... \tag{3}$$

in terms of the number density ρ of the solute. Virial coefficients of higher order need not be considered, because their influence is negligible for small concentrations. The second virial coefficient B_2 is proportional to A_2 and according to the McMillan–Mayer theory[14,15] given by

$$\begin{aligned}B_2 = -\frac{1}{2V}\int[F_2(1,2) - F_1(1)F_1(2)]\ \mathrm{d}(1,2) = \\ (1/2)\left\{\int \exp\{-\beta[W_1(1) + W_1(2)]\}\ \mathrm{d}(1 - \right. \\ \vec{s}_1)\ \mathrm{d}(2 - \vec{s}_2)\int\{1 - \exp[-\beta W_{12}(1,2)]\} \\ \left.\mathrm{d}\vec{s}_{12}\right\}\Big/\left\{\int \exp\{-\beta[W_1(1) + W_1(2)]\}\ \mathrm{d}(1 - \vec{s}_1)\ \mathrm{d}(2 - \vec{s}_2)\right\}\end{aligned} \tag{4}$$

with $\beta = 1/(kT)$ and $W_{12}(1,2)$ the intermolecular potential of mean force between the two polymer molecules 1 and 2. $\int \mathrm{d}(1 - \vec{s}_1)\ \mathrm{d}(2 - \vec{s}_2)$ is an integration over all coordinates of the segments of the molecules 1 and 2 except the coordinates of the centers of mass. $\int \mathrm{d}\vec{s}_{12}$ is an integration over the relative positions of the centers of mass.

To apply eq 3 and 4 to lattice models the number density ρ is converted to the colume fraction $\phi = (n + 1)v\rho$ (v = volume of a lattice site), and the integrations are replaced by summations.

One obtains

$$\Pi v/(kT) = \phi/(n + 1) + B_2{}^*\phi^2 + ... \tag{5}$$

with

$$\begin{aligned}B_2{}^* = \frac{1}{2(n + 1)^2}\ [\sum_i\sum_j \exp\{-\beta[W_1(i) + W_1(j)]\}\sum_p\{1 - \\ \exp[-\beta W_{12}(ijp)]\}]/[\sum_i\sum_j \exp\{-\beta[W_1(i) + W_1(j)]\}]\end{aligned} \tag{6}$$

The summations over i and j extend over all possible configurations of two chains. Because of the huge number of terms we did not sum over the whole population of configurations but only over the relatively small sample of 50 000 pairs of configurations generated by a Monte Carlo method. The p summation over all possible relative positions of the two chains which contribute to the sum (intersections and nearest-neighbor contacts) was performed exactly. The method used was similar to that of Janssens and Bellemanns.[5]

$B_2{}^*$ was calculated for several values of n (up to 64) and Φ. The quantities Φ_Θ which nullify $B_2{}^*$ were found by interpolation and are shown in Table I. The agreement between our values and those of Janssens and Bellemanns,[5] whose calculations extend up to $n = 40$, is almost perfect. These authors have shown that the plot $\exp(\Phi_\Theta)$ vs. $n^{-1/2}$ is linear. We found a strict linearity (correlation coefficient = 0.9996) for $n > 15$ so that reliable values of Φ_Θ for long chains could be obtained by linear extrapolation.

Mean square end-to-end distances, radii of gyration, and quasi radii of gyration as well as some of their reduced moments, δ, were now determined for those bond numbers (i.e., up to $n = 1024$) and reduced temperatures given in Table I. For this purpose samples of 100 000 chains were generated in each case by a Monte Carlo technique of inversely restricted sampling.[16] The quantities mentioned above were calculated by using the relations

Table I

n Dependence of the Reciprocal Reduced Temperature for Which $A_2 = 0$[a]

n	Φ_Θ	n	Φ_Θ
8	0.2363	64	0.2574
10	0.2392	128	0.2608 (e)
12	0.2417	256	0.2634 (e)
16	0.2452	512	0.2649 (e)
24	0.2494	1024	0.2662 (e)
36	0.2532	∞	0.2693 (e)

[a] The values marked by (e) were obtained by extrapolation. The standard deviation of the calculated values is <0.0001 and that of the extrapolated ones about 0.0005.

$$\delta_{p,q}{}^x = \frac{\langle x^p\rangle}{\langle x^q\rangle^{p/q}} \qquad \text{with } x \in \{h, r, s\} \tag{7}$$

$$\langle h^{2k}\rangle = Q^{-1}\sum_j(\vec{r}_n{}^{(j)} - \vec{r}_0{}^{(j)})^{2k}\ \exp[-\beta W_1(j)] \tag{8}$$

$$\langle r^{2k}\rangle = Q^{-1}(n + 1)^{-k}\sum_j(\sum_{i=0}^{n} s_i{}^{(j)2})^k\ \exp[-\beta W_1(j)] \tag{9}$$

$$\langle s^{2k}\rangle = Q^{-1}(n + 1)^{-1}\sum_j\ \sum_{i=0}^{n} s_i{}^{(j)2k}\ \exp[-\beta W_1(j)] \tag{10}$$

$$Q = \sum_j \exp[-\beta W_1(j)] \tag{11}$$

$\vec{r}_i{}^{(j)}$ is the position of segment i and $s_i{}^{(j)2}$ its squared distance from the center of mass, both taken from configuration j. The relative standard deviations for $\langle h^2\rangle$ and $\langle r^2\rangle$ were always about 0.25% and 0.16%, respectively.

A further quantity of interest is the mean reciprocal hydrodynamic radius, the major part of which is defined by

$$\langle 1/r_{\mathrm{H}}\rangle = Q^{-1}(n + 1)^{-2}\sum_j\ \sum_{\substack{k=0\\ k\neq l}}^{n}\ \sum_{l=0}^{n} \exp[-\beta W_1(j)]/r_{kl}{}^{(j)} \tag{12}$$

$r_{kl}{}^{(j)}$ is the distance between the segments k and l in configuration j.

Results and Discussion

The dependence of $\langle h^2\rangle/(nl^2)$ and $\langle r^2\rangle/\langle r^2\rangle_0$ with $\langle r^2\rangle_0 = n(n + 2)l^2/(6(n + 1))$ on the number of bonds for $A_2 = 0$ is given in parts a and b, respectively, of Figure 1. The corresponding curves for a random walk chain (model a), for a chain without immediate reversals (model b), and for a chain with interdependent rotation (four-bond rings are forbidden and contact energies between a segment and its third neighbor are taken into account; model d) are also shown for comparison. These figures make evident that none of the theories for chains with short-range interferences is able to describe the architecture of a pseudoideal chain. An adjustment to Θ-behavior can possibly be achieved for model d if Φ is treated as an adjustable parameter. That would be, however, a very unsatisfactory solution of the problem. Remarkable is the slow convergence, if any, of the curves with $A_2 = 0$ in contrast to the other curves.

Now we try to find out the reason for the difference between our value of Φ_Θ as $n \to \infty$ and that reported by McCrackin et al.[6] This can be done by inspection of Figure 2 where $\langle h^2\rangle/(nl^2)$ and $\langle r^2\rangle/\langle r^2\rangle_0$ have been plotted as a

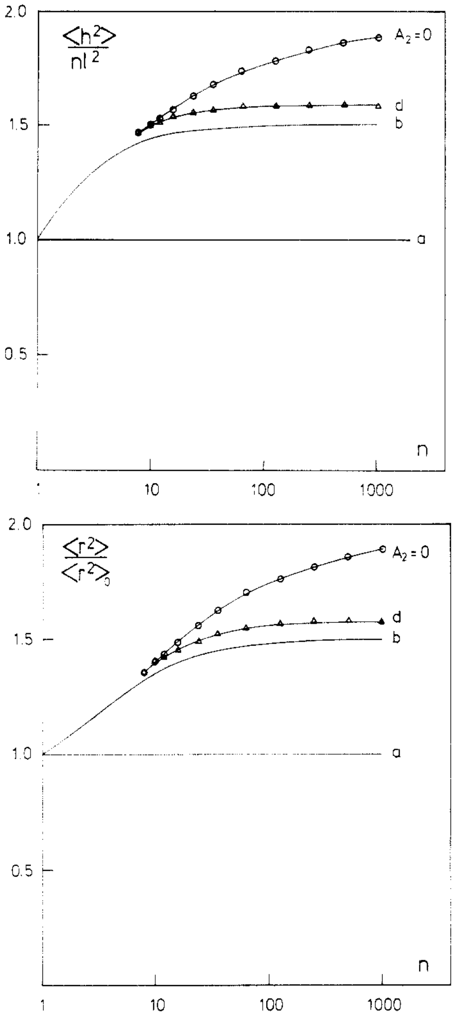

Figure 1. Dependence of the reduced mean square (a, top) end-to-end distance and (b, bottom) radius of gyration on the number of bonds for some random-flight chain models and the Θ-chain ($A_2 = 0$). The kind of the respective model is marked with small letters.

function of Φ for some values of n. This kind of plot is more sensitive than that of McCrackin et al.,[6] who plotted ln $\langle h^2\rangle$ vs. ln n for some values of Φ. If $\langle h^2\rangle$ is proportional to n at some value of Φ, the curves belonging to various n will intersect in one point. The same is valid for $\langle r^2\rangle$.

The figures show some of these curves. Each of them fits three data points calculated for $\Phi = 0.285$, $\Phi = 0.275$, and Φ_θ. The first and the third points are marked by symbols characterizing n, while the second point is not plotted to avoid cluttering. It can be seen that the curves are nearly linear within the range considered. For n not too short they intersect in the vicinity of $\Phi = 0.275$, but they do not intersect in one point. On the contrary, Φ of the intersecting points decreases with increasing n, and it is an obvious conclusion that Φ approaches 0.2693 (dashed line) as $n \rightarrow \infty$, i.e., the value for which $A_2 = 0$ in the asymptotic limit.

A further insight into the asymptotic behavior can be gained from Figure 2 by directing the attention to the left of the dashed line where the points belonging to $A_2 = 0$ are plotted. For $n > 100$ they can be connected by a straight line. A linear extrapolation to $\Phi = 0.2693$ seems, therefore, to be reasonable and leads to the asymptotic relations $\langle h^2\rangle = 1.93nl^2$ and $\langle r^2\rangle = 1.95nl^2/6$. Since the coefficients are nearly equal, the two equations confirm the relation $\langle h^2\rangle = 6\langle r^2\rangle$, which has always been accepted for Θ-systems. The coefficients 1.93 (1.95) differ considerably from those given by McCrackin et al.[6] (1.69). As discussed above the reason for this difference is due to the fact that the asymptotic behavior has not yet been attained in the range of n (120–2000) considered by the authors.

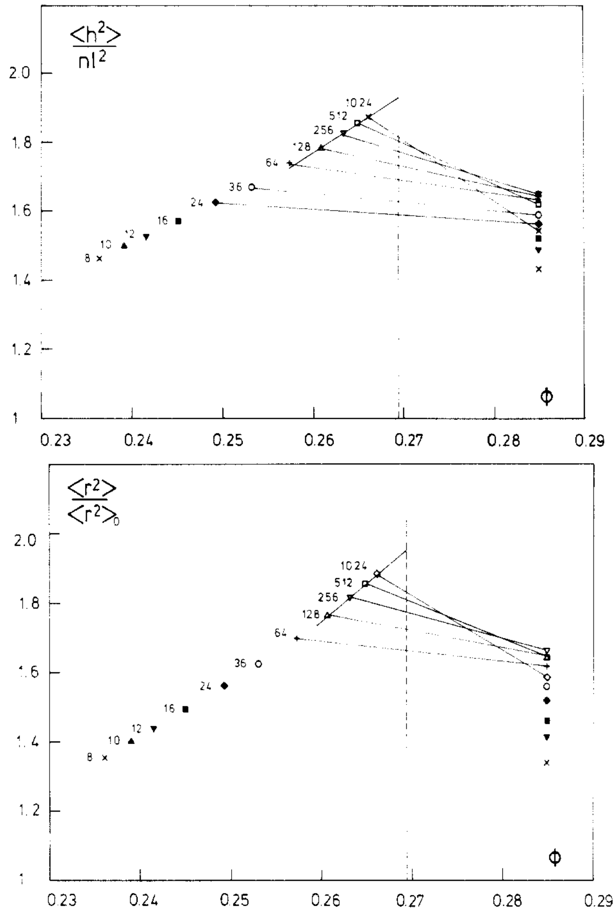

Figure 2. Dependence of the reduced mean square (a, top) end-to-end distance and (b, bottom) radius of gyration on the interaction energy. The bond numbers are used as a parameter.

The increasing steepness of descent with increasing n in the figures indicates a collapse transition in the Θ-region. Since this phenomenon has often been discussed in literature,[6,9,10,16-19] we do not go into details here. Inspection of Figure 2 suggests that the transition should occur at $\Phi = 0.2693$ in the asymptotic limit. The corresponding curve should follow the dashed line.

For very long random flight chains the distribution functions of the quantities h, r, and $\bar{s}$ do not depend on the local features of the model concerned. Since they can be derived analytically, they can be compared with those of Θ-chains. For that purpose some reduced moments of the distribution functions of the Θ-chains were calculated by Monte Carlo methods. In Figure 3 they were plotted against $1/n$. To test the reliability of an extrapolation to

Table II
Reduced Moments for Random-Flight and Θ-Chains in the Asymptotic Limit

	$\delta_{p,2}{}^h$		$\delta_{p,2}{}^r$		$\delta_{p,2}{}^s$	
p	Θ	random flight	Θ	random flight	Θ	random flight
4	1.65 ± 0.01	1.667	1.254 ± 0.009	1.267	1.968 ± 0.008	2.000
6	3.80 ± 0.07	3.889	1.96 ± 0.02	2.003	6.23 ± 0.06	6.444
8	11.4 ± 0.2	11.667	3.71 ± 0.06	3.870	27.8 ± 0.7	29.333

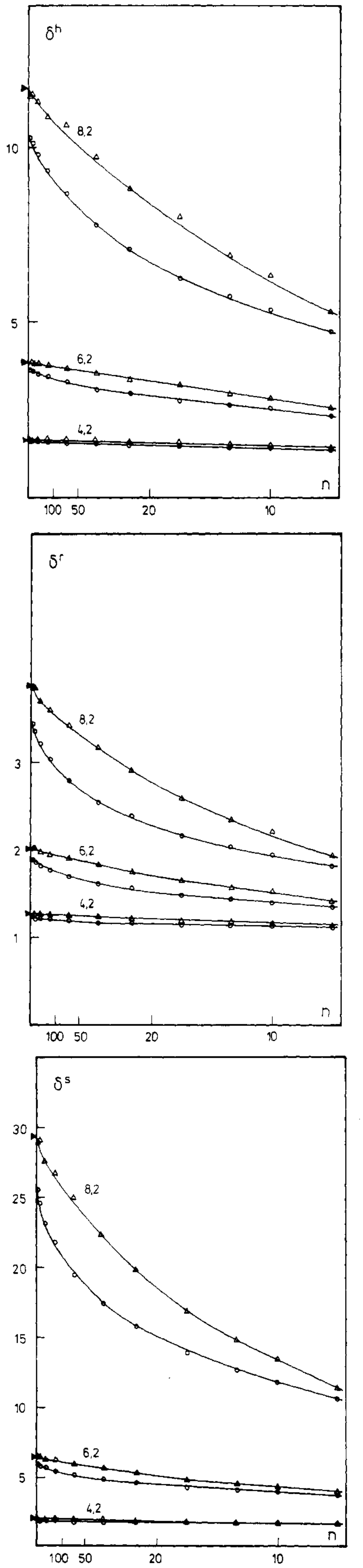

Figure 3. Reduced moments $\delta_{4,2}$, $\delta_{6,2}$, and $\delta_{8,2}$ of the distribution function of the (a, top) end-to-end distance, (b, center) radius of gyration, and (c, bottom) quasi radius of gyration plotted vs. the reciprocal bond number for model b (△) and the Θ-chain (○).

$1/n \rightarrow 0$ the same procedure has been performed for Monte Carlo data of model b. Each of the data sets was fitted to a kth-order polynomial by the method of least squares. The F test was used to find out the proper value of k. As can be seen this method works very well for the random flight model, because the extrapolated values differ only by a small amount (1.3% at the most) from the theoretical ones which are marked on the δ axes. The values found by extrapolation of the Θ-chain curves are always smaller than the random-flight values, and their

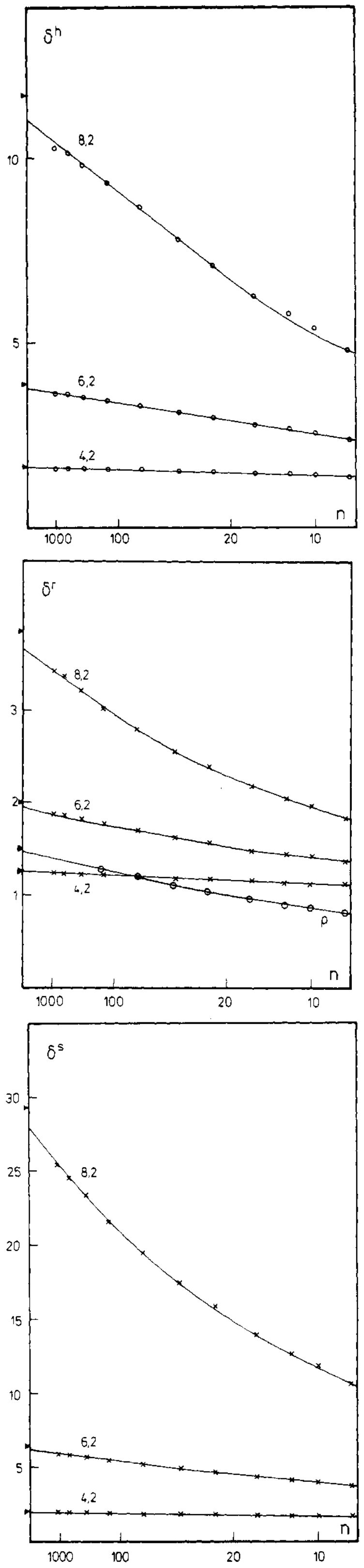

Figure 4. Reduced moments $\delta_{4,2}$, $\delta_{6,2}$, and $\delta_{8,2}$ of the distribution function of the (a, top) end-to-end distance, (b, center) radius of gyration, and (c, bottom) quasi radius of gyration plotted vs. the reciprocal square root of the bond number.

difference increases with increasing order of the reduced moments.

Since the lines of the Θ-chains are strongly curved in the range of small $1/n$ and an extrapolation may, therefore, give unreliable results, the data sets were fitted again, but this time to polynomials in $n^{-1/2}$ (Figure 4). The curves are more linear compared to those of Figure 3, but the result is similar for both fittings. The curve for $\rho = \langle r^2\rangle^{1/2}\langle 1/r_H\rangle$ is also included in Figure 4b. The infinite n limit of this curve is 1.464 ± 0.002 and thereupon less than 1.5045 found for random-flight chains but greater than the Monte Carlo value of Guttman et al.[8] (1.40). The reason for the difference between our value and that of Guttman et al. is that the latter has been calculated with $\Phi_\theta = 0.275$, which is not correct for infinitely long chains.

The asymptotic values of the reduced moments together with their standard deviations are listed in Table II. We see that a part of the random flight values is beyond the 95% confidence interval of the Θ-chain values and that the latter are always smaller than the former. These deviations seem, therefore, to be systematic rather than due to chance and suggest the conclusion that the distribution functions of random-flight chains do not describe the behavior of Θ-chains. However, in view of the fact that this result is based on extrapolations, we cannot state it with certainty.

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Solid-State Photochemistry of Poly(ethylene-*co*-carbon monoxide). Model Studies of Polyethylene Photochemistry

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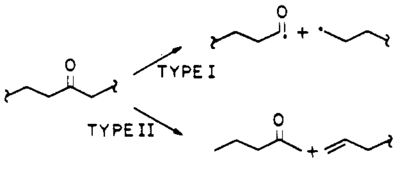
ABSTRACT: The solid-state photolysis of an ethylene–carbon monoxide (E/CO) copolymer was studied at wavelengths above 285 nm under both argon and oxygen atmospheres. Degradation was monitored and characterized by ultraviolet and infrared spectroscopy, gel permeation chromatography, gas evolution and uptake measurements, and quantum yield determinations. The microstructure of the copolymer, as determined by carbon-13 NMR spectroscopy, was found to be very similar to that of branched polyethylene, with nearly all of the oxygen accounted for as backbone ketonic carbonyl groups. Microstructural changes were also probed by this method. The changes in functional groups and the quantum yields were consistent with a dominant Norrish type II chain scission process. Acetyl group concentration, determined by NMR, reached a maximum during earlier exposure times. Reductions were observed at longer exposure times in the rate of gas evolution, the rate of chain scission, the rate of loss of carbonyl, and the rate of accumulation of vinyl groups. These rate decreases were attributed to a depletion of ketonic carbonyls that was more rapid in the amorphous regions than in the crystalline regions of the copolymer. In accord with earlier proposals, backbone ketonic carbonyl groups were found to be poor initiators in polyolefin photooxidation.

Introduction

The initiation of degradation and loss of physical properties of solid polyolefins during exposure to sunlight and air have been attributed to low concentrations of adventitious chromophores, since "pure" saturated hydrocarbons are not expected to adsorb light at wavelengths longer than 290 nm.[1,2] Many studies have attempted to identify the chromophores and to determine their importance in initiating and propagating degradation of the polymers.[3-5] Chromophores, including peroxides, ketonic carbonyls, and unsaturation, have been identified and their photochemistry has been examined.[6-8]

The embrittlement of polyethylene during photooxidation results from a combination of chain cross-linking and scission processes. Some of the scissions have been attributed to the following Norrish reactions of ketone groups located in the molecular chain.[9]



Guillet and co-workers have extensively studied the photochemistry of ketone-containing polymers under a wide range of experimental conditions.[10,11] They examined the effects of structure, viscosity, temperature, and wavelength on the photochemical and photophysical processes of these plastics, which they propose for use as environmentally favorable, photodegradable packaging

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