Rotational Isomeric State Calculations of the Dynamic Structure Factor and Related Properties of Some Linear Chains. 1. The $\rho = \langle S^2 \rangle^{1/2} \langle R_H^{-1} \rangle$ Parameter

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ABSTRACT: Monte Carlo simulations were applied to estimate the characteristic ratios and ρ parameters from the rotational isomeric state models for poly(methylene), poly(oxymethylene), polybutadiene, and polyisoprene. Here the ρ parameter is defined as the ratio of the radius of gyration to the hydrodynamic radius. The ρ parameters of these real chains in the unperturbed state show only a slight dependence on the microconformation in the limit of large molecular weights and were found close to 1.504, which is the value of an idealized Gaussian chain. The estimated ρ parameters of the real chains appear to be correlated to the chain stiffness and increase with the characteristic ratios.

Introduction

Since the early work by Kuhn[1] the concept of Gaussian chain behavior has proved a most useful approximation for long polymeric chains. Over the years, new development in instrumentation has provided us with results of high precision and also with new measurable quantities. The high quality of experimental data has made necessary an improvement of statistical techniques for the calculation of these chain properties taking into account the special microconformations of the individual chains. Most successful has been the concept of the rotational isomeric state (RIS) model, which was developed into a very powerful technique mainly by Flory.[2]

Up to now Flory's technique has been applied to the calculation of the static or equilibrium properties. Here we now make an attempt to derive also dynamic quantities such as, for instance, the translational diffusion coefficient D and the angular dependence of the first cumulant of the dynamic structure factor, which can be measured, at least to some extent, by dynamic light or dynamic neutron scattering. Again the corresponding quantities have been calculated first on the basis of the simple Gaussian chain model, and it appears of interest to know how much influence the actual conformation has on these quantities.

The dynamic structure factor

$$S(q,t) = \langle \rho^*(0)\rho(t) \rangle_{\text{ensemble}} \tag{1}$$

with

$$\rho(t) = \sum_j \exp(i\mathbf{q}\cdot\mathbf{r}_j(t)) \tag{2}$$

is a time-dependent quantity which can be directly observed by the photon correlation technique. It provides a new way of characterizing polymer chains in solution.[3] Here $\mathbf{r}_j(t)$ denotes the position of the jth scattering element at time t and the scattering vector $\mathbf{q}$, whose magnitude is given by

$$q = (4\pi/\lambda) \sin(\theta/2) \tag{3}$$

Akcasu and Gurol[4] have recently further developed Kirkwood's theory,[5] and they showed that the first cumulant Γ of the dynamic structure factor

$$\Gamma \equiv -[\mathrm{d} \ln S(q,t)/\mathrm{d}t]_{t=0} \tag{4}$$

is related to the equilibrium average of the system as

$$\Gamma = \sum_j \sum_k \langle (\mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}) \exp(i\mathbf{q}\cdot\mathbf{r}_{jk}) \rangle_{\text{eq}} \sum_j \sum_k \langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk}) \rangle_{\text{eq}} \tag{5}$$

with $\mathbf{D}_{jk}$ being an element of the diffusion tensor which includes the hydrodynamic interaction between the chain element j and k according to the Oseen approximation. It is given by

$$\mathbf{D}_{jk}/k_B T = \delta_{jk}\zeta_j^{-1}\mathbf{1} + (1 - \delta_{jk})(8\pi\eta_0 \mathbf{r}_{jk})^{-1}(1 + \mathbf{r}_{jk}\mathbf{r}_{jk}/r_{jk}^2) \tag{6}$$

Here, $\mathbf{r}_{jk}$ represents the vector from the jth element to the kth element, η_0 the solvent viscosity, and ζ_j the frictional coefficient of the jth element. The denominator of eq 5 is identified as the static structure factor $N^2P(q)$. The translational diffusion coefficient is obtained from the initial slope of Γ/q^2; i.e.

$$D = \lim_{q\to\infty} (\Gamma/q^2) \tag{7}$$

which reduces to Kirkwood's equation[5] for the zero-time diffusion coefficient

$$D = (k_B T/N\zeta) + (k_B T/6\pi\eta_0 N^2) \sum_{j\neq k} \langle r_{jk}^{-1} \rangle \tag{8}$$

For a further characterization of chains a dimensionless quantity, ρ, is introduced,[6,7] which is defined as the ratio of the radius of gyration $\langle S^2 \rangle^{1/2}$ to the hydrodynamic radius R_H

$$\rho = \langle S^2 \rangle^{1/2}/R_H \tag{9}$$

Here the hydrodynamic radius is expressed in terms of the translational diffusion coefficient D via the Stokes–Einstein relationship

$$R_H = k_B T/6\pi\eta_0 D \tag{10}$$

where k_B denotes Boltzmann's constant. The ρ parameter has been calculated for Gaussian chain polymers of various architectures of high molecular weight where the free draining, i.e., the first term in eq 8, can be neglected.[6] By definition the ρ parameter involves no molecular parameters such as the segment length and thus provides a criterion to distinguish the molecular architecture without any further data processing.

The translational diffusion coefficient is obtained from eq 8 with high accuracy due to the recent development of photon correlation spectroscopy, which allows measurement of the first cumulant of a time correlation function. Using Kirkwood's equation (8), one calculates ρ to be 1.504 in the limit of nondraining for monodisperse linear polymers which obey the Gaussian distribution. ρ values

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around 15% lower than quoted above were found by reexamining data in the literature for polystyrene in a Θ solvent (i.e., $\rho = 1.27 \pm 0.06$[8]). A similar ρ value has also been reported for poly(methyl methacrylate) in a Θ solvent (i.e., $\rho = 1.16$[9]) and for poly(dimethylsiloxane) ($\rho = 1.1$).[10] The reason for this discrepancy is attributed to the Oseen tensor approach, which only takes into account the pairwise hydrodynamic interactions.[7] All theories[11-13] proposed to improve Oseen's first-order approximation fail in this respect in explaining the larger effective hydrodynamic radius found experimentally. Several Monte Carlo calculations[14,17] are available for the hydrodynamic behavior of chain molecules in solution where the approximations introduced by Kirkwood and Riseman[5,18] are avoided though the hydrodynamic interactions are considered again in terms of Oseen's tensor. Most of those calculations confirm the results presented by Kirkwood and Riseman.

In this first part of our report, we examine the conformational dependence of ρ for various real chain molecules which are represented by the rotational isomeric state model and we compare this result with that for an ideal Gaussian chain. The conclusion drawn here is that the conformational dependence of ρ is small but apparently significant, and ρ is close to 1.50 estimated for the Gaussian chain molecule within Oseen's first-order approximation for the hydrodynamic interaction.

The second part of our report deals with the first cumulants calculated for polymer chains represented by the rotational isomeric state model by the use of the Monte Carlo procedure over a wide range of q. Here the preaverage approximation is avoided throughout, and the local chain structure is considered to be specifically represented in order to model real chains. The first cumulant thus estimated is expected to hold even at high values of the scattering vector.

Simulation Model

We adapt a rotational isomeric state model[2] for poly(methylene), poly(oxymethylene), *cis*-1,4-polybutadiene, *cis*-1,4-polyisoprene, *trans*-1,4-polybutadiene, and *trans*-1,4-polyisoprene. A chain consists of N skeletal atoms connected by $N - 1$ bonds respectively in one of corresponding rotational isomeric states. The chain configurations are generated by the Monte Carlo procedure[19] according to the conditional bond conformation probabilities.[2] The latter were calculated from the statistical weight parameters corresponding to each rotational isomeric state. Then the jth skeletal coordinate vector, $\mathbf{r}_j$, relative to the chain coordinate system is given by[20]

$$\mathbf{r}_j = \mathbf{r}^0{}_j + \sum_{m=1}^{i} \{\prod_{l=1}^{m} \mathbf{T}_{\chi_l} (\mathbf{r}^0{}_m - \mathbf{r}^0{}_{m-1})\} \tag{11}$$

with

$$\mathbf{T}_{\chi_l} = \begin{pmatrix} [\cos^2 \alpha_l + \cos \chi_l \sin^2 \alpha_l] & [\cos \alpha_l \sin \alpha_l \times (1 - \cos \chi_l)] & [-\sin \alpha_l \sin \chi_l] \\ [\cos \alpha_l \sin \alpha_l \times (1 - \cos \chi_l)] & [\sin^2 \alpha_l + \cos^2 \alpha_l \cos \chi_l] & [\cos \alpha_l \sin \chi_l] \\ [\sin \chi_l \sin \alpha_l] & [-\sin \chi_l \cos \alpha_l] & [\cos \chi_l] \end{pmatrix} \tag{12}$$

Here, χ_l denotes the lth rotational isomeric state with respect to the trans state where $\chi_l = 0$, and $\mathbf{r}^0{}_j$ gives the position of the jth skeletal atom in the standard chain conformation on the XY plane where the x coordinate of each atom should be positive and increases with its label number. The angle α_l is defined as

$$\alpha_l = \tan^{-1} [(y^0{}_l - y^0{}_{l-1})/(x^0{}_l - x^0{}_{l-1})] \tag{13}$$

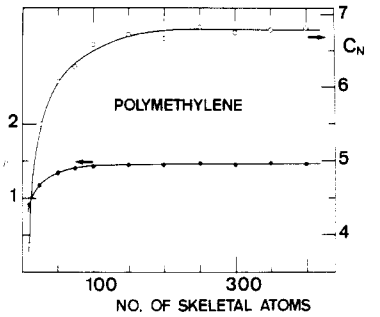

Figure 1. Parameter $\rho = \langle S^2 \rangle^{1/2}/R_H$ and characteristic ratio C_N of poly(methylene).

where the $x^0{}_j$'s and $y^0{}_j$'s are the x and y components of $\mathbf{r}^0{}_j$, respectively. The radius of gyration, $\langle S^2 \rangle$, and the hydrodynamic radius, R_H, are calculated for each generated chain as

$$\langle S^2 \rangle^{(i)} = (1/N^2) \sum_{j>k} r_{jk}{}^{(i)2} \tag{14}$$

and

$$R_H{}^{(i)} = N^2/(\sum_{j>k} (1/r_{jk}{}^{(i)})) \tag{15}$$

The adequacy of the Monte Carlo sampling is checked by comparing the characteristic ratios estimated here with the values obtained by statistical mechanical averaging.[2] The ρ parameter is calculated through eq 9 from the values of $\langle S^2 \rangle$ and $R_H{}^{-1}$ which are obtained by the present RIS method.

Results and Discussion

The simulations were performed with a FACOM M160AD computer at the Institute for Chemical Research, Kyoto University, with 1000–10 000 samplings being made for each simulation.

Poly(methylene). Three rotational isomeric states are allowed to describe a poly(methylene) chain where these three RIS, trans, gauche$^+$, and gauche$^-$, correspond to the rotational angles $\chi = 0$, +120°, and −120°, respectively. The carbon–carbon bond angle was taken to be 112° and the carbon–carbon bond length 1.53 Å. The conditional bond conformation probabilities are given[2] as

$$\mathbf{P} = \begin{bmatrix} 0.321 & 0.138 & 0.138 \\ 0.138 & 0.059 & 0.0052 \\ 0.138 & 0.0052 & 0.059 \end{bmatrix} \tag{16}$$

which correspond to $E_\sigma = 500$ cal/mol and $E_\omega = 2000$ cal/mol, with E_σ being the energy of a gauche state relative to trans and E_ω for a g^+g^- pair in excess of the energy $2E_\sigma$. The values chosen for the parameters are appropriate for a poly(methylene) chain at 140 °C. The characteristic ratio, C_N, has been calculated for poly(methylene) chains by the described Monte Carlo simulations, and this result is compared with the value of $C_\infty = 6.87$, which has been derived by Flory's statistical mechanical average technique.[2] The present Monte Carlo result is consistent with that given by the statistical mechanical averaging. See Figure 1. The ρ value increases with N (the number of skeletal atoms) and becomes constant at larger N's. In the limit of large N we find $\rho_\infty = 1.48$, which is close to 1.504 obtained for Gaussian chains.[21]

Poly(oxymethylene). The repeating unit of a poly(oxymethylene) chain consists of the C–O bond where the length of the C–O bond is 1.43 Å. The bond angles at methylene and oxygen are nearly identical and were ap-

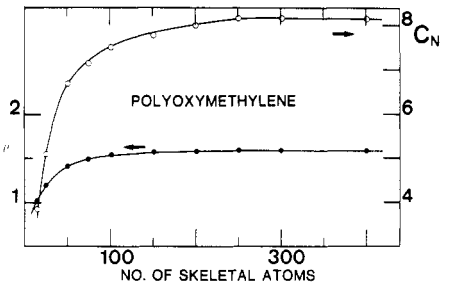

Figure 2. Parameter ρ and characteristic ratio C_N of poly(oxymethylene).

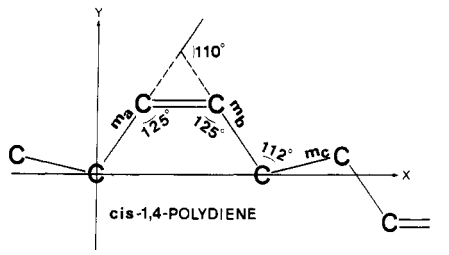

Figure 3. Initial conformation of skeletal bonds of *cis*-1,4-polydienes.

proximated by 110°. Three RIS are allocated to each bond where the rotational angles are 0° and ±120°, corresponding to trans and gauche, respectively. The statistical weight matrices[16] are written in the form

$$U_a = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (17)$$

$$U_b = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} \quad (18)$$

where the subscripts a and b specify the pair of bonds C–O and O–C and the pair of bonds O–C and C–O, respectively. $\sigma = 12$ and $\omega = 0.05$ are assigned[2,22] to be consistent with experimental results, i.e., the energy for gauche relative to trans is ca. −1.5 kcal/mol. The conditional bond conformation probabilities are thus calculated as

$$P_a = \begin{bmatrix} 0.0089 & 0.0567 & 0.0567 \\ 0.0567 & 0.3636 & 0.0182 \\ 0.0567 & 0.0182 & 0.3636 \end{bmatrix} \quad (19)$$

$$P_b = \begin{bmatrix} 0.0087 & 0.0568 & 0.0568 \\ 0.0568 & 0.3820 & 0 \\ 0.0568 & 0 & 0.3820 \end{bmatrix} \quad (20)$$

The results for ρ and C_N are given in Figure 2. In the limit of large N the characteristic ratio is $C_\infty = 8.16$; the ρ parameter $\rho_\infty = 1.60$ is larger than the value 1.504 for Gaussian chains. It reflects some change in the local chain architecture because of chain stiffness (large C_∞).

***cis*-1,4-Polybutadiene and *cis*-1,4-Polyisoprene.** The repeating unit $-(CH_2CH{=}CHCH_2)-$ or $-(CH_2C(CH_3){=}CHCH_2)-$ of either *cis*-1,4-polybutadiene or *cis*-1,4-polyisoprene consists of three C–C bonds and one C=C bond, where the length of the C–C bond is 1.53 Å, and the C=C and C–C bonds are joined at a bond angle supplement of 110° (Figure 3). The RIS of each skeletal bond in *cis*-1,4-polybutadiene is represented in terms of a 6 × 6 statistical weight matrix having rows associated with states of the preceding bond and columns with states of the present bond. Both row and column indices refer to the rotational angles 0°, 60°, 120°, 180°, −120°, and −60° in this specified order. The weight matrices for each bond are thus given by[23]

$$U_a = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (21)$$

$$U_b = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & \gamma & 0 & 0 & 0 & \gamma \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & \gamma & 0 & 0 & 0 & \gamma \end{bmatrix} \quad (22)$$

$$U_c = \begin{bmatrix} 1 & 0 & \sigma & 0 & \sigma & 0 \\ 1 & 0 & \sigma & 0 & \sigma & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \sigma & 0 & \sigma & 0 \end{bmatrix} \quad (23)$$

where $\gamma = 10$ and $\sigma = 1.4$ for *cis*-1,4-polybutadiene and $\gamma = 10$ and $\sigma = 0.543$ for *cis*-1,4-polyisoprene.[23,24] The corresponding bond conformation probabilities are then given as follows:

***cis*-1,4-Polybutadiene**

$$P_a = \begin{bmatrix} 0.012 & 0.126 & 0 & 0 & 0 & 0.126 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.017 & 0.176 & 0 & 0 & 0 & 0.176 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.017 & 0.176 & 0 & 0 & 0 & 0.176 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (24)$$

$$P_b = \begin{bmatrix} 0 & 0.023 & 0 & 0 & 0 & 0.023 \\ 0.023 & 0.227 & 0 & 0 & 0 & 0.227 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.023 & 0.227 & 0 & 0 & 0 & 0.227 \end{bmatrix} \quad (25)$$

$$P_c = \begin{bmatrix} 0.012 & 0 & 0.017 & 0 & 0.017 & 0 \\ 0.125 & 0 & 0.176 & 0 & 0.176 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.125 & 0 & 0.176 & 0 & 0.176 & 0 \end{bmatrix} \quad (26)$$

***cis*-1,4-Polyisoprene**

$$P_c = \begin{bmatrix} 0.022 & 0 & 0.012 & 0 & 0.012 & 0 \\ 0.229 & 0 & 0.124 & 0 & 0.124 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.229 & 0 & 0.124 & 0 & 0.124 & 0 \end{bmatrix} \quad (27)$$

$$P_a = \begin{bmatrix} 0.022 & 0.229 & 0 & 0 & 0 & 0.229 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.012 & 0.124 & 0 & 0 & 0 & 0.124 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.012 & 0.124 & 0 & 0 & 0 & 0.124 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (28)$$

$$P_b = \begin{bmatrix} 0 & 0.023 & 0 & 0 & 0 & 0.023 \\ 0.023 & 0.227 & 0 & 0 & 0 & 0.227 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.023 & 0.227 & 0 & 0 & 0 & 0.227 \end{bmatrix} \quad (29)$$

The results of the Monte Carlo calculations are shown in Figures 4 and 5. The characteristic ratios were estimated as 3.76 and 3.95, respectively, for *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene, which are approximately 30% lower than the corresponding experimentally observed values.[23] The ρ_∞ parameters 1.45 and 1.44 are close to that of a Gaussian chain.

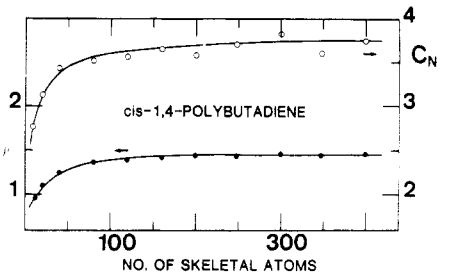

Figure 4. ρ parameter and characteristic ratio C_N of *cis*-1,4-polybutadiene.

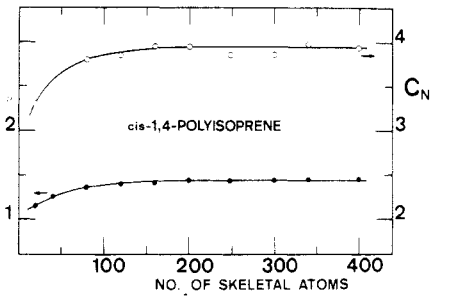

Figure 5. ρ parameter and characteristic ratio of *cis*-1,4-polyisoprene.

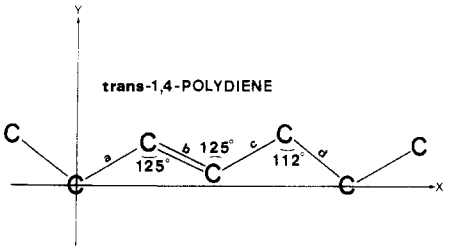

Figure 6. Initial conformation of skeletal bonds of *trans*-1,4-polydienes.

***trans*-1,4-Polybutadiene and *trans*-1,4-Polyisoprene.** The skeletal bonds of the repeat units are illustrated in Figure 6. The bond lengths and the bond angles are the same as given in the preceding section for the cis polymers. The RIS of each skeletal bond (a, b, c and d as shown in Figure 6) is again represented in terms of a 6 × 6 statistical weight matrix, which is given for each bond as

$$U_a = \begin{bmatrix} 0 & 1 & 0 & \alpha & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & \beta\alpha & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & \beta\alpha & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (30)$$

$$U_b = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (31)$$

$$U_c = \begin{bmatrix} 0 & 1 & 0 & \alpha & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (32)$$

$$U_d = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \sigma & 0 & \sigma & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \beta\sigma & 0 & \beta\sigma & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \sigma & 0 & \sigma & 0 \end{bmatrix} \quad (33)$$

with $\alpha = 0.96$, $\beta = 0.24$, and $\sigma = 1$ for *trans*-1,4-polybutadiene and $\alpha = 0.96$, $\beta = 0.124$, and $\sigma = 0.543$ for *trans*-1,4-polyisoprene. The two $\beta\sigma$ elements in U_d have to be replaced by 0 for *trans*-1,4-polyisoprene. The corresponding bond conformation probabilities are then calculated as follows:

***trans*-1,4-Polybutadiene**

$$P_a = \begin{bmatrix} 0 & 0.158 & 0 & 0.152 & 0 & 0.158 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.119 & 0 & 0.027 & 0 & 0.119 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.119 & 0 & 0.027 & 0 & 0.119 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (34)$$

$$P_b = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0.397 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.207 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.397 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (35)$$

$$P_c = \begin{bmatrix} 0 & 0.397 & 0 & 0.207 & 0 & 0.397 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (36)$$

$$P_d = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0.158 & 0 & 0.119 & 0 & 0.119 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.152 & 0 & 0.027 & 0 & 0.027 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.158 & 0 & 0.119 & 0 & 0.119 & 0 \end{bmatrix} \quad (37)$$

***trans*-1,4-Polyisoprene**

$$P_a = \begin{bmatrix} 0 & 0.187 & 0 & 0.179 & 0 & 0.187 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.101 & 0 & 0.021 & 0 & 0.101 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.101 & 0 & 0.021 & 0 & 0.101 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (38)$$

$$P_b = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0.389 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.221 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.389 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (39)$$

$$P_c = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0.500 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.500 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (40)$$

$$P_d = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0.276 & 0 & 0.112 & 0 & 0.112 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0.276 & 0 & 0.112 & 0 & 0.112 & 0 \end{bmatrix} \quad (41)$$

The results of the Monte Carlo calculations are shown in Figures 7 and 8. The characteristic ratios estimated here are 5.80 and 7.26, respectively, for *trans*-1,4-polybutadiene and *trans*-1,4-polyisoprene and are consistent with those found experimentall.[24] The ρ parameters were estimated as 1.46 and 1.49, respectively.

The results from all simulations are summarized in Table I of the succeeding paper, part 2. The ρ values evidently depend slightly on the characteristic ratio; i.e., they increase with chain stiffness. See Figure 9. The experimentally observed ρ values seem to show the same

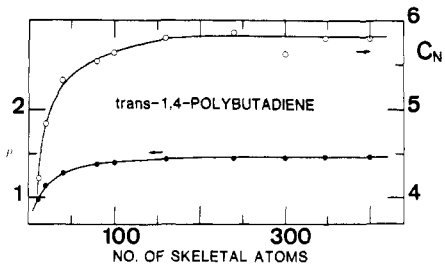

Figure 7. ρ parameters and characteristic ratio C_N of *trans*-1,4-polybutadiene.

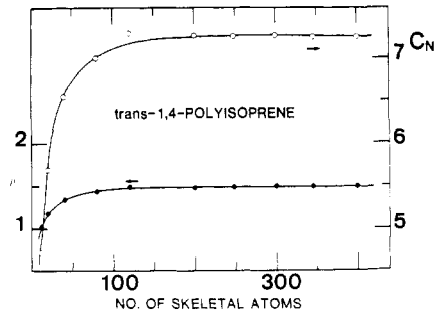

Figure 8. ρ parameter and characteristic ratio C_N of *trans*-1,4-polyisoprene.

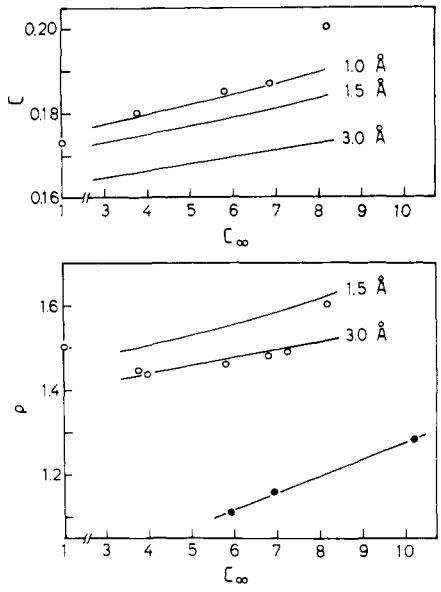

Figure 9. Dependence of the ρ parameter on the characteristic ratio C_∞: open circles, this simulation; filled circles, experimental results for PDMS,[28] PMMA,[28] and PS[28]; curves indicated by 1.5 and 3 Å correspond to the hybrid theory where the numbers indicate the chain diameters.

trend though the values are consistently somewhat lower.[8,10]

Figure 9 also shows for comparison a result from the hybrid theory by Schmidt and Stockmayer.[25] Although a qualitative agreement is observed, it appears necessary to add some remarks in order to draw attention to the fundamental difference in the present simulation to the hybrid theory.[26]

The hybrid theory employs a continuous thread following the chain distance distribution given by Koyama[26] to represent a semiflexible chain molecule. Here the sums in Kirkwood's equation (8) are replaced by integrals with an arbitrary nonzero positive value allocated to the lower limit to avoid the familiar singularity. This lower limit is interpreted as an effective hydrodynamic diameter of the chain which represents the lowest limit of hydrodynamic interaction.[25] The ρ values calculated from this theory depend sensitively on this arbitrary value. A good description of ρ values is obtained with 3 Å, with the exception of poly(oxymethylene), where a diameter of 1.5 Å has to be chosen. The calculated ρ values also depend on the contour length when the chain stiffness parameter, i.e., the Kuhn length, is fixed. For the rotational isomeric state model we have observed no molecular weight dependence of ρ when N is sufficiently large in the present simulation, which stands in contrast to the predicted N dependence in the hybrid theory. Available experimental data confirm the constancy of the ρ values specific to the polymer species in the Θ solvent.[27]

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