

Chapter 2

Models for Polymer Chains

In this chapter a brief description is given of several fundamental models for polymer chains, both discrete and continuous, the latter being obtained as a continuous limit of the former under certain conditions. The *unperturbed* chains without excluded volume are considered throughout the chapter but all basic equations are valid for both unperturbed and *perturbed* chains unless otherwise noted. Thus the symbol $\langle \cdots \rangle$ is used without the subscript 0 to denote an conformational average even in the unperturbed state, for simplicity.

2.1 Discrete Models

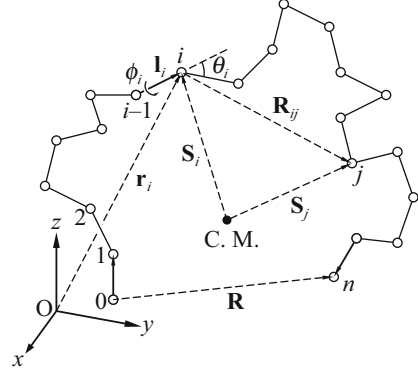
2.1.1 Average Chain Dimensions

Consider a single chain composed of $n + 1$ identical main chain atoms, say carbon atoms, which are joined successively by single bonds and which are numbered 0, 1, 2, $\cdots$, n from one end to the other. Let $\mathbf{r}_i$ be the vector position of the i th carbon atom ($i = 0, 1, \cdots, n$) in the instantaneous configuration of the chain, as depicted in Fig. 2.1. The vector $\mathbf{l}_i$ defined by

$$\mathbf{l}_i = \mathbf{r}_i - \mathbf{r}_{i-1} \quad (i = 1, 2, \cdots, n) \quad (2.1)$$

is called the i th bond vector, whose magnitude l_i is the bond length. The angle θ_i ($i = 1, 2, \cdots, n - 1$) between the vectors $\mathbf{l}_i$ and $\mathbf{l}_{i+1}$ is the supplement of the i th bond angle. The angle between the two planes containing $\mathbf{l}_{i-1}$ and $\mathbf{l}_i$, and $\mathbf{l}_i$ and $\mathbf{l}_{i+1}$, respectively, defines the internal rotation angle ϕ_i ($i = 2, \cdots, n - 1$) about the i th bond, which is chosen to be zero when $\mathbf{l}_{i-1}$ and $\mathbf{l}_{i+1}$ are situated in the *trans* position with respect to each other. For the present purpose, both l_i and θ_i may be fixed at constant values (except for hypothetical cases), ignoring atomic vibrations. This is

Fig. 2.1 Instantaneous configurations of a discrete chain and its various configurational quantities



the *discrete model*. In what follows, we assume that $l_i = l$ and $\theta_i = \theta$ for all i , for simplicity.

Now the end-to-end vector $\mathbf{R} = \mathbf{r}_n - \mathbf{r}_0$ of the chain is the resultant of n bond vectors, that is,

$$\mathbf{R} = \sum_{i=1}^n \mathbf{l}_i, \quad (2.2)$$

so that the *mean-square end-to-end distance* $\langle R^2 \rangle$ as a measure of the average chain dimension is given by

$$\begin{aligned} \langle R^2 \rangle &= \sum_{i=1}^n \sum_{j=1}^n \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= nl^2 + 2 \sum_{1 \leq i < j \leq n} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle. \end{aligned} \quad (2.3)$$

Further, if $\mathbf{S}_i$ is the vector distance of the i th carbon atom from the center of mass (C.M.) of the chain, the *radius of gyration* S is defined by

$$S^2 = \frac{1}{n+1} \sum_{i=0}^n S_i^2. \quad (2.4)$$

Assume that an equal mass is centered at each carbon atom, and by definition, we have

$$\sum_{i=0}^n \mathbf{S}_i = \mathbf{0}. \quad (2.5)$$

If $\mathbf{R}_{ij} = \mathbf{S}_j - \mathbf{S}_i$ is the vector distance between the i th and j th carbon atoms, then we obtain the well-known formula for the *mean-square radius of gyration* $\langle S^2 \rangle$, which is another measure of the average chain dimension,

$$\langle S^2 \rangle = \frac{1}{(n+1)^2} \sum_{0 \leq i < j \leq n} \langle R_{ij}^2 \rangle. \quad (2.6)$$

The simple derivation of Eq. (2.6) is given in the earlier book (MTPS) [1].

Note that Eqs. (2.3) and (2.6) are valid for both unperturbed and perturbed chains.

2.1.2 Random-Flight Chains: The Gaussian Chain

The simplest hypothetical discrete model is obtained by setting $\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle = 0$ for $i \neq j$ in Eqs. (2.3); thus it has no correlations between any two bonds even with the uniform distribution of θ in its possible range from 0 to π , so that

$$\langle R^2 \rangle = nl^2. \quad (2.7)$$

This is the *random-flight chain* or the *freely jointed chain*; it is also called the *random-coil model* [2]. For this chain $\langle R^2 \rangle$ is proportional to n .

Now suppose that the initial (0th) carbon atom is fixed at the origin of a Cartesian coordinate system and let $P(\mathbf{R})d\mathbf{R}$ then be the probability of finding the terminal (n th) carbon atom in the volume element $d\mathbf{R} = dxdydz$ at $\mathbf{R}(x, y, z)$. In the asymptotic limit of large n the distribution function $P(\mathbf{R})$ of $\mathbf{R}$ for this chain is found to be [1, 3, 4]

$$P(\mathbf{R}) = \left(\frac{3}{2\pi nl^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2nl^2} \right). \quad (2.8)$$

That is, in this limit the random-flight chain becomes the *Gaussian chain*. As is readily seen from Eq. (2.8), the latter chain has the same second moment $\langle R^2 \rangle = nl^2$ as the former for arbitrary n . For the Gaussian chain we also have the well-known relation [1, 5]

$$\langle S^2 \rangle = \frac{1}{6} \langle R^2 \rangle. \quad (2.9)$$

2.1.3 Freely Rotating Chains

Next we consider a model in which both l and θ are fixed but in which the distribution of ϕ_i is uniform in its range from $-\pi$ to π . This model is called the

freely rotating chain. In this case it is easy to show that $\langle \mathbf{l}_i \cdot \mathbf{l}_{i+1} \rangle = l^2 \cos \theta$ ($i = 1, \dots, n-1$) and in general $\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle = l^2 \cos^{j-i} \theta$ ($i < j$). On performing the summations in the second line of Eqs. (2.3) after substitution of this result, we obtain [6–8]

$$\langle R^2 \rangle = nl^2 \frac{1 + \cos \theta}{1 - \cos \theta} - 2l^2 \cos \theta \frac{1 - \cos^n \theta}{(1 - \cos \theta)^2}. \quad (2.10)$$

For this case, if $0 < \theta < \pi/2$, $\langle R^2 \rangle/n$ increases monotonically with increasing n and approaches the constant $l^2(1 + \cos \theta)/(1 - \cos \theta)$; that is [2],

$$\langle R^2 \rangle = nl^2 \frac{1 + \cos \theta}{1 - \cos \theta} \quad \text{for } n \gg 1. \quad (2.11)$$

From Eq. (2.6) with Eq. (2.10), we also obtain [9, 10]

$$\begin{aligned} \langle S^2 \rangle &= \frac{l^2}{6} \frac{1 + \cos \theta}{1 - \cos \theta} n + \frac{l^2}{6} \frac{1 - 6 \cos \theta - \cos^2 \theta}{(1 - \cos \theta)^2} \\ &+ \frac{l^2}{6} \frac{-1 + 7 \cos \theta + 7 \cos^2 \theta - \cos^3 \theta}{(1 - \cos \theta)^3} \frac{1}{n+1} \\ &- \frac{2l^2 \cos^2 \theta}{(1 - \cos \theta)^4} \frac{1 - \cos^{n+1} \theta}{(n+1)^2}. \end{aligned} \quad (2.12)$$

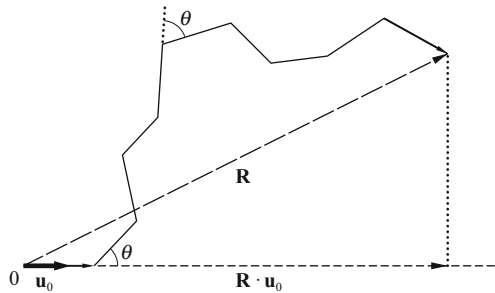
Similarly, we can calculate the average $\langle \mathbf{R} \cdot \mathbf{u}_0 \rangle$ with $\mathbf{u}_0 = \mathbf{l}_1/l$ being the unit vector in the direction of the first bond $\mathbf{l}_1$ as follows,

$$\langle \mathbf{R} \cdot \mathbf{u}_0 \rangle = l^{-1} \sum_{i=1}^n \langle \mathbf{l}_1 \cdot \mathbf{l}_i \rangle = l \frac{1 - \cos^n \theta}{1 - \cos \theta}. \quad (2.13)$$

The scalar product $\mathbf{R} \cdot \mathbf{u}_0$ is the projection of $\mathbf{R}$ in the direction of $\mathbf{l}_1$, as depicted in Fig. 2.2. If we assume again that $0 < \theta < \pi/2$, we have

$$\lim_{n \rightarrow \infty} \langle \mathbf{R} \cdot \mathbf{u}_0 \rangle = \frac{l}{1 - \cos \theta}. \quad (2.14)$$

Fig. 2.2 Persistence of the component of $\mathbf{l}_i$ in the direction $\mathbf{u}_0 = \mathbf{l}_1/l$ of the first bond in a freely rotating chain



The quantity on the left-hand side of Eq. (2.14) is called the *persistence length* [11, 12], and we denote it by q . The origin of this term is that the situation is similar to that encountered in the kinetic theory of gases, in which the component of the velocity $\mathbf{u}$ of a particle in its initial direction $\mathbf{u}_0$ persists after collisions. We have $q > l$ for the freely rotating chain and $q = l$ for the random-flight chain. Thus q is often used as a measure of *chain stiffness* but this is not always correct [13, 14] (see also below).

2.1.4 Chains with Coupled Rotations: The Rotational Isomeric State Model

In the real chain with fixed bond lengths and bond angles there are hindrances to internal rotations and ϕ_i is not uniformly distributed. In this case the chain has a potential energy $E(\{\phi_{n-2}\})$ as a function of all $(n - 2)$ internal rotation angles $\{\phi_{n-2}\} = \phi_2, \dots, \phi_{n-1}$, so that the average $\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle$ in Eqs. (2.3) must be calculated statistical-mechanically with the Boltzmann factor or the chain conformational partition function Z ,

$$Z = \int \exp[-E(\{\phi_{n-2}\})/k_B T] d\{\phi_{n-2}\}, \quad (2.15)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and $d\{\phi_{n-2}\} = d\phi_2 \cdots d\phi_{n-1}$.

For illustration, we consider the simplest of such *chains with coupled rotations*, that is, the one only with the rotational potential E_1 about each bond and the correlation E_2 between rotations about two successive bonds. In fact, higher-order neighbor interactions of this kind may be neglected in many cases. The total rotational potential E may then be written in the form

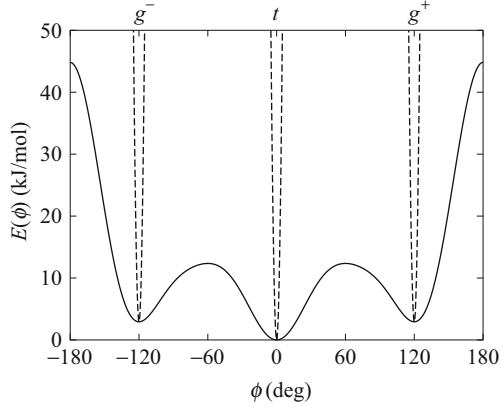
$$E(\{\phi_{n-2}\}) = \sum_{i=2}^{n-1} E_i(\phi_{i-1}, \phi_i), \quad (2.16)$$

where

$$E_i(\phi_{i-1}, \phi_i) = E_{1i}(\phi_i) + E_{2i}(\phi_{i-1}, \phi_i) \quad (2.17)$$

with $E_{22} = 0$. In particular, a hypothetical chain with $E_i = E_{1i}$ is called the *chain with independent rotations*. The potential E_{1i} may be regarded as close to the potential $E(\phi)$ about the central C–C bond in n -butane, which has three minima corresponding to the three stable conformations or rotational isomers: *trans* (t) ($\phi \simeq 0^\circ$), *gauche*⁺ (g^+) ($\phi \simeq 120^\circ$), and *gauche*[−] (g^-) ($\phi \simeq -120^\circ$), as illustratively shown in Fig. 2.3. On the other hand, E_{2i} becomes very large for the

Fig. 2.3 Internal-rotational potential of n -butane. The dashed lines represent the RIS approximation



conformation $(\phi_{i-1}, \phi_i) = (g^+, g^-)$ or (g^-, g^+) . This is the so-called *pentane effect* [15, 16].

With such potentials, however, the mathematical treatments become very difficult. It is therefore convenient to introduce an assumption such that ϕ_i takes only the three or more discrete values corresponding to the potential minima, t , g^+ , g^- , and so on, thus approximating E_{li} by a finite set of discrete levels or sharp square-well potentials at those ϕ_i , as shown in the dashed lines in Fig. 2.3 [17, 18]. This is the *rotational isomeric state (RIS) model*. Equation (2.15) with Eq. (2.16) may then be reduced to

$$Z = \sum_{\{\phi_{n-2}\}} \prod_{i=2}^{n-1} u_{\mu\nu,i}, \quad (2.18)$$

where

$$u_{\mu\nu,i} = \exp[-E_i(\mu, \nu)/k_B T] \quad (2.19)$$

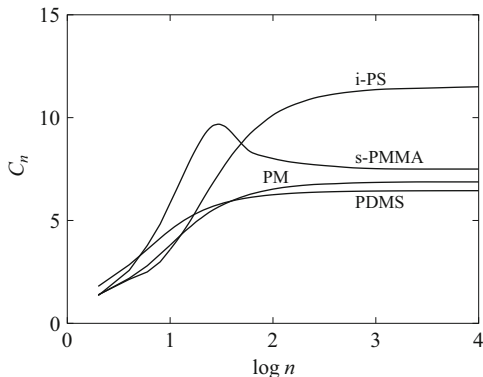
with $\mu, \nu = t, g^+, g^-, \dots$. Thus the problem becomes equivalent to that of the one-dimensional Ising model [19–23].

The results for $\langle R^2 \rangle$ are often given for the *characteristic ratio* C_n defined by [23]

$$C_n = \langle R^2 \rangle / nl^2. \quad (2.20)$$

In Fig. 2.4 values of C_n so calculated are plotted against $\log n$ for polymethylene (PM), poly(dimethylsiloxane) (PDMS), isotactic polystyrene (i-PS), and syndiotactic poly(methyl methacrylate) (s-PMMA), for illustration.

Fig. 2.4 Characteristic ratio C_n for typical flexible polymers



2.2 Continuous Models

For a discrete chain of n bonds, each of length l , we define the total *contour length* L and the contour distance s ($0 \leq s \leq L$) of the i th carbon atom from the initial (0th) one along the chain by the equations

$$L = nl, \quad s = li, \quad (2.21)$$

respectively. We let $n \rightarrow \infty$ and $l \rightarrow 0$ at constant L (and $i \rightarrow \infty$ at constant s) in such a way that the discrete chain contour becomes a continuous and differentiable space curve. This is the *continuous model* which is mainly considered in this book. It is specified by certain additional conditions imposed in the limiting process [11, 13, 14, 24].

In any case we can define the unit vector $\mathbf{u}(s)$ tangent to the curve at the contour point s , that is,

$$\mathbf{u}(s) = \frac{d\mathbf{r}(s)}{ds} \quad (2.22)$$

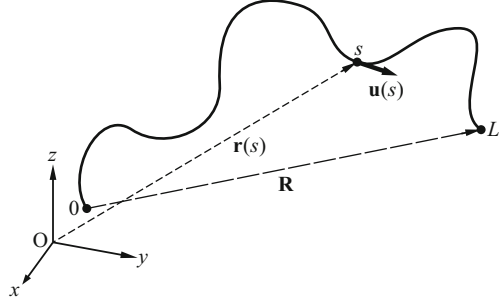
with $\mathbf{r}_i = \mathbf{r}(s)$ being the radius vector, as depicted in Fig. 2.5. Equation (2.22) is the continuous limit of $\mathbf{l}_i/l$ with $\mathbf{l}_i$ being given by Eq. (2.1). The end-to-end vector $\mathbf{R}$ may then be expressed in terms of $\mathbf{u}$ as

$$\mathbf{R} = \mathbf{r}(L) - \mathbf{r}(0) = \int_0^L \mathbf{u}(s) ds \quad (2.23)$$

as the continuous limit of Eq. (2.2), so that we have

$$\langle R^2 \rangle = \int_0^L \int_0^L \langle \mathbf{u}(s_1) \cdot \mathbf{u}(s_2) \rangle ds_1 ds_2 \quad (2.24)$$

Fig. 2.5 Instantaneous configurations of a continuous chain and its configurational quantities



as the continuous limit of Eqs. (2.3). If $\mathbf{R}(s_1, s_2)$ is the vector distance between the contour points s_1 and s_2 ($s_1 \leq s_2$), Eq. (2.6) becomes

$$\langle S^2 \rangle = \frac{1}{L^2} \int_0^L ds_1 \int_{s_1}^L ds_2 \langle R^2(s_1, s_2) \rangle. \quad (2.25)$$

For the unperturbed chain there holds the relation $\langle R^2(s_1, s_2) \rangle = \langle R^2(s) \rangle$ with $s = s_2 - s_1$ [1], and therefore Eq. (2.25) reduces to

$$\langle S^2 \rangle = \frac{1}{L^2} \int_0^L (L-s) \langle R^2(s) \rangle ds. \quad (2.26)$$

Necessarily, we have, for the continuous chain above,

$$\mathbf{u}^2(s) = 1 \quad \text{for } 0 \leq s \leq L. \quad (2.27)$$

Indeed, this relation is satisfied by the *Kratky–Porod (KP) wormlike chain* [11] and also the *helical wormlike (HW) chain* [13, 14] treated in this book. In anticipation of the results we here note only that the former is obtained as a continuous limit of the freely rotating chain, while the latter is obtained from a discrete chain with coupled rotations by some coarse-graining, followed by the continuous-limiting process. However, in order to make the model more tractable, the constraint of Eq. (2.27) is often relaxed, thereby leading to various modifications [13, 25, 26] of the former. Further, we note that for the continuous chain the *Kuhn segment length* A_K and the *persistence length* q are defined by

$$A_K = \lim_{L \rightarrow \infty} (\langle R^2 \rangle / L), \quad (2.28)$$

$$q = \lim_{L \rightarrow \infty} \langle \mathbf{R} \cdot \mathbf{u}_0 \rangle \quad (2.29)$$

with $\mathbf{u}_0 = \mathbf{u}(0)$, which in general satisfy the relation

$$A_K = 2q, \quad (2.30)$$

but that neither A_K nor q is a measure of chain stiffness except for the KP chain [13, 14].

Finally, we consider a *continuous* Gaussian chain and give some fundamentals related to it. Its $\langle R^2 \rangle$ must be given by

$$\langle R^2 \rangle = lL. \quad (2.31)$$

This is rather the defining equation for the “bond length” l for the chain of total contour length L . It is evident that the above-mentioned continuous limit of the random-flight chain cannot be taken to obtain this continuous chain when $\langle R^2 \rangle$ and L are given. Its rigorous treatment requires an elaborate maneuver [25, 27]. Thus we follow instead a simple fashion to regard L merely as a continuous variable for very large n in the discrete random-flight chain, as usually done [1, 4, 28]. This suffices for the present purpose (see also Appendix 1 in Chap. 3). It is then convenient to rewrite Eq. (2.8) as

$$P(\mathbf{R}; L) = \left(\frac{3}{2\pi lL} \right)^{3/2} \exp\left(-\frac{3R^2}{2lL} \right). \quad (2.32)$$

This $P(\mathbf{R}; L)$ is the solution of the differential equation

$$\left(\frac{\partial}{\partial L} - \frac{l}{6} \nabla_R^2 \right) P(\mathbf{R}; L) = 0 \quad (2.33)$$

subject to the boundary condition

$$P(\mathbf{R}; 0) = \delta(\mathbf{R}), \quad (2.34)$$

where ∇_R^2 is the Laplacian operator with respect to $\mathbf{R}$ and $\delta(\mathbf{R})$ is a three-dimensional Dirac delta function.

Now we introduce the *Green function* $G(\mathbf{R}; L)$ defined by

$$\begin{aligned} G(\mathbf{R}; L) &= P(\mathbf{R}; L) & \text{for } L > 0 \\ &= 0 & \text{for } L < 0, \end{aligned} \quad (2.35)$$

where $P(\mathbf{R}; L)$ is given by Eq. (2.32). Equation (2.33) with Eq. (2.34) may then be reduced to

$$\left(\frac{\partial}{\partial L} - \frac{l}{6} \nabla_R^2 \right) G(\mathbf{R}; L) = \delta(L) \delta(\mathbf{R}). \quad (2.36)$$

If we integrate both sides of Eq. (2.36) over L from $-\epsilon$ to ϵ with ϵ being positive and small, then the left-hand side becomes

$$\int_{-\epsilon}^{\epsilon} \frac{\partial G(\mathbf{R}; L)}{\partial L} dL = G(\mathbf{R}; \epsilon), \quad (2.37)$$

and the right-hand side becomes $\delta(\mathbf{R})$, so that we have

$$\lim_{L \rightarrow +0} G(\mathbf{R}; L) = \delta(\mathbf{R}). \quad (2.38)$$

Thus the solution of Eq. (2.36) is indeed that of Eq. (2.33) subject to the boundary condition of Eq. (2.34). If L is regarded as “time,” Eq. (2.33) or (2.36) is just the diffusion equation associated with the random process (position) $\mathbf{r}(s)$ of a Brownian particle with diffusion coefficient $l/6$ at a long time.

Note that for this chain the *bond correlation function* $\langle \mathbf{u}(s_1) \cdot \mathbf{u}(s_2) \rangle$ is *formally* given by

$$\langle \mathbf{u}(s_1) \cdot \mathbf{u}(s_2) \rangle = l\delta(s_1 - s_2), \quad (2.39)$$

because substitution of this equation into Eq. (2.24) recovers Eq. (2.31).

References

1. H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper & Row, New York, 1971). Its electronic edition is available on-line at the URL: <http://hdl.handle.net/2433/50527>
2. W. Kuhn, *Kolloid Z.* **68**, 2 (1934)
3. Lord Rayleigh, *Philos. Mag.* **37**, 321 (1919)
4. S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943)
5. P. Debye, *J. Chem. Phys.* **14**, 636 (1946)
6. H. Eyring, *Phys. Rev.* **39**, 746 (1932)
7. R.M. Fuoss, J.G. Kirkwood, *J. Am. Chem. Soc.* **63**, 385 (1941)
8. F.T. Wall, *J. Chem. Phys.* **11**, 67 (1943)
9. R.A. Sack, *Nature* **171**, 310 (1953)
10. H. Benoit, P. Doty, *J. Phys. Chem.* **57**, 958 (1953)
11. O. Kratky, G. Porod, *Recl. Trav. Chim.* **68**, 1106 (1949)
12. See also S.E. Bresler, Ya.I. Frenkel, *Acta Phys.-Chim. USSR* **11**, 485 (1939)
13. H. Yamakawa, *Annu. Rev. Phys. Chem.* **35**, 23 (1984)
14. H. Yamakawa, in *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*, ed. by M. Nagasawa (Elsevier, Amsterdam, 1988), p. 21
15. K.S. Pitzer, *J. Chem. Phys.* **8**, 711 (1940)
16. W.J. Taylor, *J. Chem. Phys.* **16**, 257 (1948)
17. M.V. Volkenstein, *Dokl. Akad. Nauk SSSR* **78**, 879 (1951); *Configurational Statistics of Polymeric Chains* (Interscience, New York, 1963)
18. See also R. Kubo, *J. Phys. Soc. Jpn.* **4**, 319 (1949)
19. S. Lifson, *J. Chem. Phys.* **30**, 964 (1959)
20. K. Nagai, *J. Chem. Phys.* **31**, 1169 (1959); **37**, 490 (1962)

21. T.M. Birshtein, O.B. Ptitsyn, Zh. Tekh. Fiz. **29**, 1048 (1959); T.M. Birshtein, Vysokomol. Soedin. **1**, 798 (1959); T.M. Birshtein, E.A. Sokolova, Vysokomol. Soedin. **1**, 1086 (1959)
22. C.A.J. Hoeve, J. Chem. Phys. **32**, 888 (1960)
23. P.J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969)
24. A. Miyake, Y. Hoshino, J. Phys. Soc. Jpn. **46**, 1324 (1979)
25. K.F. Freed, Adv. Chem. Phys. **22**, 1 (1972)
26. H. Yamakawa, Annu. Rev. Phys. Chem. **25**, 179 (1974); Pure Appl. Chem. **46**, 135 (1976)
27. K.F. Freed, *Renormalization Group Theory of Macromolecules* (Wiley, New York, 1987)
28. M. Doi, S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986)

Helical Wormlike Chains in Polymer Solutions

Yamakawa, H.; Yoshizaki, T.

2016, XIV, 511 p. 183 illus., Hardcover

ISBN: 978-3-662-48714-3