ciety, and by the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) J. D. Ferry, "Viscoelastic Properties of Polymers", Wiley, New York, N.Y., 1970.
(2) D. W. McCall, *Acc. Chem. Res.*, **4**, 223 (1971).
(3) T. M. Connor, *J. Polym. Sci., Part A-2*, **8**, 191 (1970).
(4) E. Jenckel and R. Heusch, *Kolloid-Z.*, **130**, 89 (1953).
(5) Plasticization and Plasticizer Processes, American Chemical Society, Washington, D.C., 1965.
(6) P. R. Saunders, D. M. Stern, S. F. Kurath, C. Sakoonkim, and J. D. Ferry, *J. Colloid Sci.*, **14**, 222 (1959).
(7) Z. Veksli and W. G. Miller, *Macromolecules*, **8**, 248 (1975).
(8) W. G. Miller and Z. Veksli, *Rubber Chem. Technol.*, **48**, 1078 (1975).
(9) Z. Veksli, W. G. Miller, and E. L. Thomas, *J. Polym. Sci., Polym. Symp.*, **No. 54**, 299 (1976).
(10) R. Baltzly, I. M. Berger, and A. A. Rothstein, *J. Am. Chem. Soc.*, **72**, 4149 (1950).
(11) D. Kivelson, *J. Chem. Phys.*, **33**, 1094 (1960).
(12) S. A. Goldman, G. V. Bruno, C. F. Polnaszek, and J. H. Freed, *J. Chem. Phys.*, **56**, 716 (1972).
(13) J. H. Freed, G. V. Bruno, and C. Polnaszek, *J. Phys. Chem.*, **75**, 3385 (1971).
(14) S. A. Goldman, G. V. Bruno, and J. H. Freed, *J. Phys. Chem.*, **76**, 1858 (1972).
(15) R. P. Mason, C. F. Polnazek, and J. H. Freed, *J. Phys. Chem.*, **78**, 1324 (1974).
(16) D. W. McCall, *Natl. Bur. Stand. (U.S.), Spec. Publ.*, **No. 301**, 475 (1969); *Acc. Chem. Res.*, **4**, 223 (1971).
(17) R. J. Kurland and E. B. Wilson, Jr., *J. Chem. Phys.*, **27**, 585 (1957).
(18) A. L. Buchachenko, A. L. Kovarskii, and A. M. Wassermann, *Usp. Khim. Fiz. Polim.*, 31 (1973); Z. A. Rogovin, Ed., "Advances in Polymer Science," Halsted Press, New York, N.Y., 1976, p 26.
(19) A. M. Wasserman, A. L. Buchachenko, A. L. Kovarskii, and M. B. Neiman, *Vysokomol. Soedin., Ser. A*, **10**, 1930 (1968).
(20) D. R. Hersbach, "Bibliography for Hindered Internal Rotation and Microwave Spectroscopy", Lawrence Radiation Laboratory, University of California, Berkeley, Calif., 1962.
(21) A. N. Bhat, R. C. Fay, D. F. Lewis, A. F. Lindmark, and S. H. Strauss, *Inorg. Chem.*, **13**, 886 (1974).
(22) P. R. Sundararsjan and P. J. Flory, *J. Am. Chem. Soc.*, **96**, 5025 (1974).
(23) J. H. Freed, *Annu. Rev. Phys. Chem.*, **23**, 265 (1972).
(24) J. Fujita and A. Kishimoto, *J. Chem. Phys.*, **34**, 393 (1961).
(25) R. S. Moore and J. D. Ferry, *J. Phys. Chem.*, **66**, 2699 (1962).
(26) C. P. Wong, J. L. Schrag, and J. D. Ferry, *J. Polym. Sci., Part A-2*, **8**, 991 (1970).
(27) E. L. Wee and W. G. Miller, *J. Phys. Chem.*, **77**, 182 (1973).
(28) K. Ueberreiter and G. Kanig, *J. Chem. Phys.*, **18**, 399 (1950).
(29) S. L. Regen, *J. Am. Chem. Soc.*, **96**, 5275 (1974).
(30) F. Heatley and A. Begum, *Polymer*, **17**, 399 (1976).
(31) K. Sato and A. Nishioka, *J. Polym. Sci., Part A-2*, **10**, 489 (1972).
(32) E. Helfand, *J. Chem. Phys.*, **54**, 4651 (1971).
(33) T. F. Schatzki, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **6**, 646 (1965).
(34) P. H. Verdier and W. H. Stockmayer, *J. Chem. Phys.*, **36**, 227 (1962).
(35) L. Monnerie and F. Geny, *J. Chim. Phys. Phys.-Chim. Biol.*, **66**, 1691 (1969).
(36) Y. Y. Gotlib, *J. Polym. Sci., Part C*, **16**, 3365 (1968).
(37) J. E. Anderson and K. J. Liu, *J. Chem. Phys.*, **49**, 2850 (1968).
(38) V. W. Graessley, *Forschr. Hochopolym.-Forsch.*, **16**, 1 (1974).
(39) P. J. Hains and G. Williams, *Polymer*, **16**, 725 (1976).
(40) R. G. Kirste, W. A. Kruse, and J. Schelten, *J. Macromol. Chem.*, **162**, 299 (1972).
(41) R. G. Kirste, W. A. Kruse, and K. Ibel, *Polymer*, **16**, 120 (1975).
(42) D. Y. Yoon and P. J. Flory, *Polymer*, **16**, 645 (1975).
(43) D. Y. Yoon, P. R. Sundararajan, and P. J. Flory, *Macromolecules*, **8**, 776 (1975).
(44) On leave of absence from the Institute Ruder Bošković, Zagreb, Yugoslavia.

A Hypothesis on Polymer Chain Configurations. Helical Wormlike Chains

Hiromi Yamakawa

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.
Received December 7, 1976

ABSTRACT: The following hypothesis on polymer chain configurations is presented: "On the bond length or somewhat longer scales, any real chain may be represented by the continuous helical wormlike chain, i.e., a hybrid of the three extreme forms of rod, coil, and helix." Various salient aspects of the new model itself are deduced from this hypothesis. The basic model parameters are the curvature λ^{-1} of the elastic potential curve multiplied by $2/kT$ at its minimum, the radius ρ and pitch h of the characteristic helix corresponding to minimum energy, and the shift factor M_L, defined as the molecular weight per unit contour length. In particular, it is concluded that M_L is closely related to the length scales to be adopted for a given chain and that the parameter λ^{-1} may be used as an absolute measure of chain stiffness for all types of real chains.

Since the beginning of the theoretical or statistical-mechanical investigations of the properties of polymeric systems, Kuhn random flight or Gaussian chains[1-3] have long retained an important place as standard molecular models for randomly coiled, flexible macromolecules. The details of the chemical structure of real chains are smeared out in such models, but this suffices to permit understanding of the majority of basic physical processes such as excluded volume effects and steady-state transport and dynamical phenomena.[2,3] As is well known, the random-flight model may be characterized by the so-called Markov nature such that the mean-square end-to-end distance is proportional to the number of bonds in the chain in its unperturbed state without excluded volume. However, the Markov nature breaks down for real short chains and is valid only asymptotically for long enough chains, particularly for semiflexible or stiff chains. This non-Markov nature arises from a sort of stiffness or static rigidity, as introduced by the constraints on the internal degrees of freedom such as fixed bond lengths, fixed bond angles, and hindered internal rotations. Necessarily, the study of such effects and also various configuration-dependent properties requires molecular models on the atomic level. There is little doubt that among these, rotational isomeric state models[4-7] are best established and most widely accepted at the present time.

However, the rotational isomeric state model is not always convenient in use, especially in the study of the properties usually covered by the random-flight model. The difficulty may often be overcome by adopting continuous models such as the Kratky-Porod (KP) wormlike chain[3,8,9] and its modifications.[10] Such models, smearing the detailed chemical structure, are therefore similar to the random-flight model in spirit but can interpolate from the two extremes of random coil and rod to preserve the non-Markov nature. In recent

years, indeed, there has been a renewal in studying the conformational and transport properties of stiff chain macromolecules.[9,10] DNA is one of the typical examples for which the KP model is valid. In principle, the continuous model may be considered a good approximation as far as the molecular information on the bond length or somewhat longer scales is concerned. Even under such circumstances, however, most of the real chains other than those of high axial symmetry such as DNA cannot be strictly represented by the KP chain, since it takes account of the correlation between the tangents to the chain but not of the correlation between the curvatures leading to a sort of chain skewness or spiral.

Thus, we have very recently proposed a very general continuous model, called the helical wormlike chain, which may be regarded as a hybrid of the three extreme forms of rod, random coil, and regular helix, and developed its statistical-mechanical theory in a series of papers entitled "Statistical Mechanics of Helical Wormlike Chains" (SMHWC).[11-14] We are now inclined to believe that the assumption of this model is valid as a working hypothesis for all real chains. At this stage before proceeding to make further developments, it may therefore be regarded as pertinent to deduce various salient aspects of the new model itself, some of which have already been discussed, starting from the hypothesis above.

Hypothesis and Model

Our working hypothesis may be stated as follows: "On the bond length or somewhat longer scales, any real chain may be represented by the continuous helical wormlike chain, i.e., a hybrid of the three extreme forms of rod, coil, and regular helix", as schematically depicted in Figure 1. The model may also be regarded as a wormlike chain randomly possessing complete or incomplete helical conformations or spiral configurations. However, the term "helix" requires some comments. By it, we do not necessarily mean the helix in α-helices, DNA, and the like. The helix axis may rather be chosen as the chain contour of our model in its application to such cases without interrupted helical parts, while we take the contour along the actual main chain in its application to the helix–coil transition in polypeptide chains. Thus, the length scales to be adopted depend, to some extent, on a given real chain and also on what property or behavior is considered.

For the statistical-mechanical development, the helical wormlike chain as well as the KP chain may be treated as a space curve. The form of any space curve may be determined by the curvature $\kappa(s)$ and torsion $\tau(s)$, defined in differential geometry,[15] as functions of the contour distance s from one end, where s is assumed to range from 0 to t for the chain of total contour length t. Now, if the chain is regarded as an elastic thin wire, its configurational energy U per unit contour length at s is given by

$$U = \tfrac{1}{2}\alpha[\kappa(s) - \kappa_0(s)]^2 + \tfrac{1}{2}\beta[\tau(s) - \tau_0(s)]^2 \qquad (1)$$

as derived by Bugl and Fujita,[16] where α and β are the bending and torsional force constants, respectively. The total configurational energy of the chain is obtained by integration of U over s from 0 to t. It has the minimum value of zero when $\kappa(s) = \kappa_0(s)$ and $\tau(s) = \tau_0(s)$. The helical wormlike chain may be obtained by taking $\kappa_0(s)$ and $\tau_0(s)$ as constants independent of s,

$$\kappa_0(s) = \kappa_0$$
$$\tau_0(s) = \tau_0 \qquad (2)$$

In other words, the configurational energy of the helical wormlike chain becomes a minimum when it takes a helical form. This regular helix specified by κ_0 and τ_0 is referred to as the *characteristic* helix, whose radius ρ and pitch h are given by

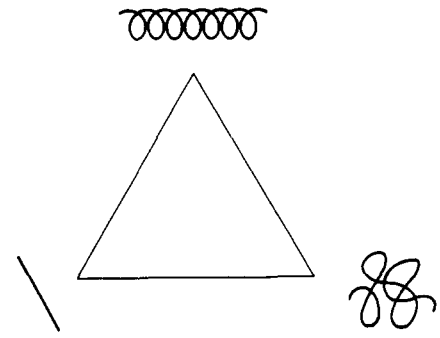

Figure 1. Hypothesis on polymer chain configurations.

$$\rho = \kappa_0/(\kappa_0^2 + \tau_0^2)$$
$$h = 2\pi\tau_0/(\kappa_0^2 + \tau_0^2) \qquad (3)$$

Equations 1 and 2 provide the statistical-mechanical basis of the helical wormlike chain. The KP chain may now be redefined as a special case of the former with $\kappa_0 = 0$ irrespective of the values of β and τ_0, so that its energy becomes a minimum when it takes the rod (straight line) form. It must however be noted that in the use of eq 1 our picture of a polymer chain, as depicted in Figure 1, is quite different from that of Bugl and Fujita, i.e., a Rouse-like chain with coil springs. This is one of the reasons why we dare to call our model the helical wormlike chain.

Equations 1–3 require some further comments. In the derivation of the differential equation for the distribution function,[11] κ is taken to be always nonnegative, for convenience, and τ is either positive or negative, so that κ_0 (or ρ) ≥ 0 and τ_0 (or h) $\neq 0$, the characteristic helix being right handed for $\tau_0 > 0$ and left handed for $\tau_0 < 0$. (Note that in SMHWC-I,[11] h was defined to be positive with $|\tau_0|$.) On this assumption, the characteristic space curve corresponding to minimum energy is not permitted to take, for instance, a two-dimensional wave form, for which $\kappa_0(s)$ changes sign with s and $\tau_0(s)$ is always zero. This is a direct consequence of the hypothesis. However, such cases, for which the characteristic curve is two dimensional, will probably not occur for real polymer chains. For example, if the energy of a simple real chain becomes a minimum for the all-trans conformation (a wave form microscopically but a straight line macroscopically), it may rather be represented by the KP chain with $\kappa_0 = 0$ on the proper length scales.

It is convenient to introduce instead of α and β the parameters,

$$\lambda^{-1} = 2\alpha/kT \qquad (4)$$
$$\sigma = \alpha/\beta - 1 \qquad (5)$$

where kT has the usual meaning. The parameter λ^{-1} is equal to the Kuhn length of the KP chain, and σ is Poisson's ratio ranging from 0 to 0.5.[17] The moments for the helical wormlike chain are known to be insensitive to the change in σ,[11] and therefore it is not an important parameter and may be set equal to zero for most cases, for simplicity. The force constants α and β are the curvatures of the potential curves at their minima of zero, so that λ^{-1} may be regarded as a stiffness parameter for the helical wormlike chain as well as the KP chain. Thus, until the number of bonds in the real chain or its molecular weight is explicitly introduced, the basic model parameters are λ^{-1}, κ_0, and τ_0 (or λ^{-1}, ρ, and h), all of which should be regarded as possibly dependent on both temperature and solvent.

For convenience, all lengths are measured in units of λ^{-1} throughout the remainder of this section. Then, the mean-

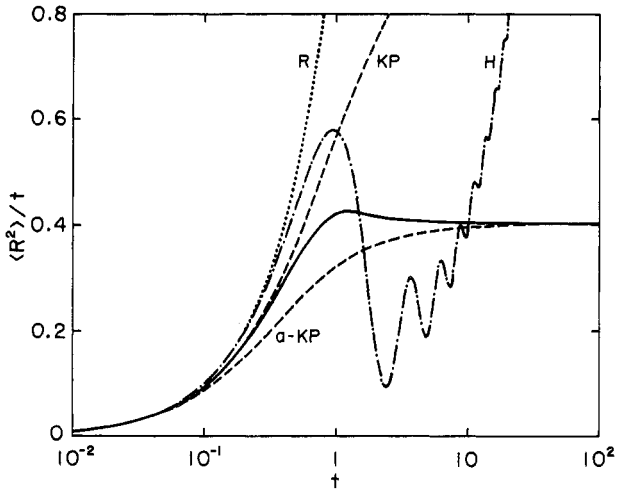

Figure 2. The ratio $\langle R^2\rangle/t$ plotted against the logarithm of the contour length t for $\kappa_0 = 2.5$, $\tau_0 = 0.5$, and $\sigma = 0$, all lengths being reduced by λ. The dotted curve R represents the values for the rod, the broken curve KP represents the unassociated KP chain with $\kappa_0 = 0$, and the chain curve H and broken curve a-KP represent the characteristic helix and associated KP chain with the same model parameters as those of the helical wormlike chain, respectively.

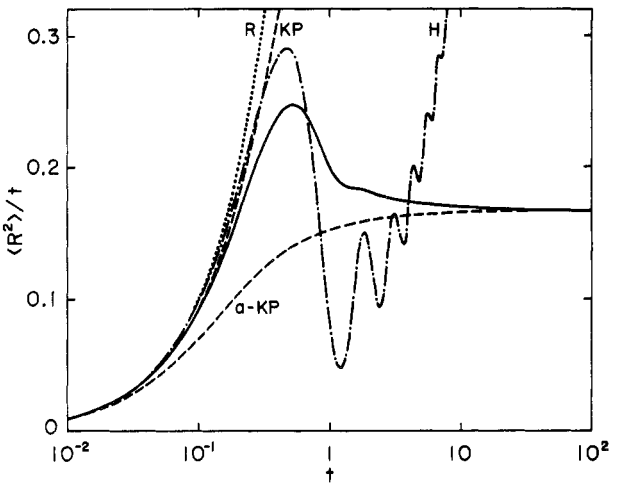

Figure 3. The ratio $\langle R^2\rangle/t$ plotted against the logarithm of the contour length t for $\kappa_0 = 5$, $\tau_0 = 1$, and $\sigma = 0$; see legend to Figure 2.

square end-to-end distance $\langle R^2\rangle$ for the present model is given by

$$\langle R^2\rangle = c_\infty t + c_0 + \sum_{i=1}^{3} c_i e^{-z_i t} \tag{6}$$

with

$$c_\infty = \frac{2[(2+\sigma)^2 + \tau_0^2]}{f(0)} \tag{7}$$

$$c_0 = -\tfrac{1}{2}c_\infty^2 + \frac{2\kappa_0^2[(2+\sigma)^2 - \tau_0^2]}{[f(0)]^2} \tag{8}$$

$$c_i = \frac{2[(2+\sigma-z_i)^2 + \tau_o^2]}{z_i^2(z_i - z_j)(z_i - z_k)} \tag{9}$$

$$(i \neq j \neq k; i, j, k = 1, 2, 3)$$

where $-z_i$ ($i = 1, 2, 3$) are the three simple roots of the cubic equation,

$$f(p) \equiv (p+2)[(p+2+\sigma)^2 + \tau_0^2] + \kappa_0^2(p+2+\sigma) = 0 \tag{10}$$

and we have omitted the rare case of multiple roots and combined eq 40 and 54 of SMHWC-I into eq 6.

Irrespective of the kind of roots, $\langle R^2\rangle$ has the three limiting forms corresponding to the rod, coil, and characteristic helix in Figure 1,

$$\lim_{\substack{t\to 0 \\ (\text{const }\lambda)}} \langle R^2\rangle = t^2 \qquad \text{(rod)} \tag{11}$$

$$\lim_{\substack{t\to \infty \\ (\text{const }\lambda)}} \langle R^2\rangle = c_\infty t \qquad \text{(coil)} \tag{12}$$

$$\lim_{\lambda\to 0} \langle R^2\rangle \equiv R_H^2 = \frac{\tau_0^2 t^2}{\kappa_0^2 + \tau_0^2} + \frac{4\kappa_0^2}{(\kappa_0^2 + \tau_0^2)^2}\sin^2[\tfrac{1}{2}(\kappa_0^2 + \tau_0^2)^{1/2}t] \qquad \text{(helix)} \tag{13}$$

where the symbol lim indicates that the asymptotic form is taken. R_H is the end-to-end distance of the characteristic helix, and eq 13 for R_H^2 should be considered to be re-reduced by the original λ, though it does not apparently depend on whether it is reduced or unreduced. Also note that we have taken the limits above by varying the unreduced t and λ separately, though we had done the limits without this separation previously;[11] the present procedure is clearer. Thus, in the limit of unreduced $t \to \infty$, R_H becomes equal to that of the infinitely long helix given by the leading term on the right-hand side of eq 13 or 61 or SMHWC-I.

It is also convenient to consider the KP chain such that its Kuhn length is c_∞ (in units of λ^{-1}) and it is referred to as the *associated* KP chain; its mean-square end-to-end distance $\langle R^2\rangle_{\text{a-KP}}$ is given by

$$\langle R^2\rangle_{\text{a-KP}} = c_\infty t - \tfrac{1}{2}c_\infty^2[1 - \exp(-2t/c_\infty)] \tag{14}$$

The average configuration of this chain may be considered to change with t (at constant λ) on the base of the triangle in Figure 1. Note that $c_\infty \leq 1$ and that $c_\infty = 1$ for the unassociated KP chain with $\kappa_0 = 0$ in c_∞.

For $t \ll 1$ (at constant λ), $\langle R^2\rangle$ may be expanded as

$$\langle R^2\rangle = t^2[1 - \tfrac{2}{3}t + \tfrac{1}{12}(4 - \kappa_0^2)t^2 - \ldots] \qquad (t \ll 1) \tag{15}$$

$$\langle R^2\rangle_{\text{a-KP}} = t^2\left(1 - \frac{2}{3c_\infty}t + \frac{1}{3c_\infty^2}t^2 - \ldots\right) \qquad (t \ll 1) \tag{16}$$

$$R_H^2 = t^2(1 - \tfrac{1}{12}\kappa_0^2 t^2 + \ldots) \qquad (t \ll 1) \tag{17}$$

It is seen that as t is decreased to zero (at constant λ) the helical wormlike chain as well as the KP chain, unassociated or associated, become the rod through the WKB rod[18] whose mean-square end-to-end distance is given by the first two terms on the right-hand side of eq 15 or 16, and also R_H approaches the rod limiting value, though not through the WKB rod.

In SMHWC-I and -II,[11,12] we already presented numerical results for $\langle R^2\rangle$ and also $\langle R^{2m}\rangle$ for various values of the model parameters. Among these, the two typical cases of $\kappa_0 = 2.5$, $\tau_0 = 0.5$, and $\sigma = 0$ and of $\kappa_0 = 5$, $\tau_0 = 1$, and $\sigma = 0$ are reproduced in Figures 2 and 3, respectively, where the values (full curves) of $\langle R^2\rangle/t$ instead of $\langle R^2\rangle/c_\infty t$ as before are plotted against the logarithm of t. The dotted curves R represent the values of $\langle R^2\rangle/t = t$ for the rod, and the broken curves KP the corresponding values for the unassociated KP chain given by eq 14 with $c_\infty = 1$. In the figures are also shown the values of R_H^2/t for the characteristic helix and of $\langle R^2\rangle_{\text{a-KP}}/t$ for the associated KP chain, each with the same model parameters as those of the corresponding helical wormlike chain, by the chain curves H and broken curves a-KP, respectively.

It is seen that as t is increased from zero to infinity, the ratio $\langle R^2\rangle/t$ for the helical wormlike chain first increases along the dotted curve R, then exhibits helical behavior, and finally levels off to the coil limiting value c_∞. The value of λ in Figure 3 may be considered to be just one-half of that in Figure 2, and

Table I
Values of the Model Parameters for Various Polymer Chains

Polymer	C_∞	A_K, Å	λ^{-1}, Å	ρ, Å	h, Å	M_L, Å^{-1}	M_L^*, Å^{-1}	M_L', Å^{-1}
PM	6.87[a]	15.0	15.2	0.47	23.4	10.1	11.0	9.15
PDMS	6.43[b]	13.6	15.8	19.7	7.7	19.6	25.5	22.6
POM	8.5[c]	16.8	17.5	0.10	3.0	18.7	12.8	10.5
i-PP	4.2[d]	9.44	14.2	1.53	−12.4	13.8	16.5	13.7
s-PP	11.0[d]	24.7	26.2	0.21	5.2	15.6	16.5	13.7
i-PS	11.9[e]	20.2	33.5	0.99	−7.6	41.2	40.8	34.0
s-PS	18.2[e]	35.3	38.2	0.23	5.0	38.9	40.8	34.0
i-PMMA	10.3[f]	16.7	21.9	10.7	53.7	34.6	38.6	32.7
a-PMMA	9.4[f]	16.3	44.6	15.5	21.2	37.2	38.6	32.7
s-PMMA	7.6[f]	12.9	60.0	14.4	15.6	36.5	38.6	32.7

[a] See ref 28. [b] See ref 29. [c] See ref 27 and 30. [d] See ref 31. [e] See ref 32 and 33. [f] See ref 23.

indeed, the helical behavior of the model is more remarkable in the former than in the latter. (Note that the unreduced κ_0 and τ_0 have the dimension of reciprocal length.) Further, the values of $\langle R^2 \rangle$ for the helical wormlike chain are naturally always smaller than those for the rod and even those for the unassociated KP chain. Unless both κ_0 and τ_0 are very large, or λ is very small, the values of $\langle R^2 \rangle$ for the helical wormlike chain are greater than those for the associated KP chain, as displayed in the figures. If λ is very small, the chain is close to the characteristic helix (and then the full curve will cross the broken curve a-KP). The chain contour of the model should then be readjusted, as mentioned earlier, so that the case of very small λ may not actually occur in the natural state except for the helix–coil transition. Thus, we may conclude that the values of $\langle R^2 \rangle$ for the helical wormlike chain, when applied to real chains in their natural state, are always greater than those for the associated KP chain. These are also direct consequences of the hypothesis.

For very typical cases, the ratio $\langle R^2 \rangle / t$ as a function of t exhibits a maximum, as shown in Figures 2 and 3. However, we note that even in the case for which $\langle R^2 \rangle / t$ increases monotonically with increasing t, the helical nature of the model is revealed markedly by the persistence vector **A**, as defined as the mean end-to-end vector with the initial tangent and curvature vectors fixed, as well as that of the rotational isomeric state model,[19,20] as shown in SMHWC-IV (persistence vectors).[14]

Model Parameters

In order to apply the continuous model to a real chain, we must convert the contour length t of the former to the number of bonds in the latter or the molecular weight. For convenience, this is done by introducing the so-called shift factor M_L, as defined as the molecular weight per unit contour length of the continuous model. It should be considered a model parameter to be determined[21,22] together with λ^{-1}, κ_0, τ_0 (or ρ, h), and σ from a comparison with real chains. Indeed, we determined these parameters for various chains, assuming $\sigma = 0$ for simplicity, from a comparison with rotational isomeric state models with respect to either the characteristic ratio C_n or the persistence vector **A**, using their values computed by Flory and co-workers. The criteria for the determination were discussed in detail[11,14] and are not repeated here. In this section, all lengths are unreduced.

In Table I are reproduced the results obtained in SMHWC-I and -III (scattering functions)[13] for isotactic, atactic, and syndiotactic poly(methyl methacrylate) (i-, a-, and s-PMMA) chains[23] from C_n (the fraction of meso dyads in a-PMMA being 0.2), and in SMHWC-IV for polymethylene (PM),[24] poly(dimethylsiloxane) (PDMS),[25] and isotactic and syndiotactic polystyrene (i- and s-PS)[26] chains from **A**. The table also includes the values determined here for polyoxymethylene (POM)[27] and isotactic and syndiotactic polypropylene (i- and s-PP)[26] chains from **A**. All of them may well be represented by the helical wormlike chains with κ_0 (or ρ) $\neq 0$. In the second and third columns of the table are given the values of the characteristic ratio C_∞[23,27–33] and the Kuhn length A_K, respectively, the latter being defined by

$$A_K = c_\infty \lambda^{-1} \tag{18}$$

with the reduced κ_0 and τ_0 in c_∞. Note that the $A_K = \lambda^{-1}$ for the KP chain with $\kappa_0 = 0$ and $c_\infty = 1$. In the eighth column are given the values M_L^* of M_L computed by taking the contour length t as the length of the rotational isomeric state model chain fully extended to the all-trans conformation, or as the average of two lengths at full extension, one with all θ_1 and the other with all θ_2 angles, in the case of chains with the two different bond angles θ_1 and θ_2, and also in the ninth column the values M_L' computed by taking t as the total sum of bond lengths. We note that the shift factor f of Maeda, Saito, and Stockmayer[21] is defined as the number of bonds in the real chain per unit *reduced* contour length of the continuous chain, so that for chains with identical bond lengths and angles θ, $f'/f^* = \sin^2(\theta/2)$, while $M_L'/M_L^* = \sin(\theta/2)$. We prefer our definition of M_L, since M_L^* and M_L' can be expressed in terms of only the structural parameters of the chain.

It is seen that M_L is close to M_L^* in most cases and is intermediate between M_L^* and M_L' in some other cases. PDMS, POM, and i-PP require some comments. For PDMS, M_L is rather close to M_L', and the same result is obtained if we make an analysis of C_n assuming the KP chain. The reason for this probably is that one of the two greatly different supplementary bond angles is unusually small (37°), so that the chain contour may be taken along the actual main chain. For i-PP, the chain contour is taken closely along the actual helical sequence, so that its M_L is also close to M_L'. For POM, on the other hand, the chain contour is taken along the helix axis rather than along the actual helical sequence, so that M_L is considerably greater than even M_L^*. (Maeda et al.[21] have reported that f of POM determined from C_n is close to f^* if the KP chain is assumed.) The z component of the persistence vector of the POM chain vanishes because of the equal probabilities of occurrence of right- and left-handed helices,[27,30] and it may be represented approximately by the helical wormlike chain with ρ nearly equal to zero. Thus, it should be emphasized that the parameter M_L in general is closely related to the length scales to be adopted for a given chain. This parameter and also λ^{-1}, ρ, and h together provide important information that serves to picture the average configuration of a real chain on the proper length scales of interest to us. As for ρ and h, we only note that the characteristic helix specified by them does not necessarily correspond to the conformation of minimum energy in the rotational isomeric state model.

As noted earlier, for the KP chain with $\kappa_0 = \rho = 0$, the parameter λ^{-1} is equal to the Kuhn length A_K. (This condition is satisfied approximately by PM and POM chains.) In this case, λ^{-1} is just twice the persistence length of the KP type.[8] For the helical wormlike chain, the component of the persistence vector in the direction of the initial unit tangent vector $\mathbf{u}_0$ in the limit $t \to \infty$ is equal to one-half of A_K (not of λ^{-1}) and has the meaning of the persistence length, but it also has the nonvanishing components in the directions perpendicular to $\mathbf{u}_0$.[14] Thus, we recommend to use the Kuhn length rather than the persistence length. For the same kind of chains, e.g., PMMA chains, differing in tacticity, A_K is theoretically proportional to C_∞, but is not necessarily proportional to λ^{-1}. The fact that the former proportionality does not strictly hold in Table I arises from the slight differences in the determined M_L. The breakdown of the latter proportionality indicates that although the Kuhn length or the persistence length is a measure of chain stiffness for the KP chain, this criterion is in general not appropriate. Thus, we propose that the parameter λ^{-1} should be adopted as an absolute measure of chain stiffness for all types of real chains, considering its physical meaning. Then, for example, s-PMMA chains may be regarded as more stiff than i-PMMA and also PS chains, though A_K (or C_∞) of the former is smaller than those of the latter. This is also a consequence of the hypothesis.

Concluding Remarks

From the practical point of view in part, we initiated the study of the helical wormlike chain that can mimic the conformational behavior of real chains or rotational isomeric state models. From the analysis made so far, it is however clear that our model can provide interesting information about chain configurations on the bond length or somewhat longer scales, which is therefore different in quality from that obtained from the rotational isomeric state model alone. We believe that the former has significance more than a convenient replacement of the latter. Although the model parameters have been determined so far from a comparison with rotational isomeric state models with respect to the computed moments, this must also be done from an analysis of experimental data on, for instance, steady-state transport coefficients. Evaluation of them will be carried out in another series of papers. The statistical-mechanical problems, which remain, will be studied in the SMHWC series. The dynamical problems are also interesting in relation to the kinetic rigidity of the chain, but it can be shown that adoption of the helical wormlike chain, as it is, leads to a nonlinear equation of motion, as in the case of the KP chain of fixed length.[34,35] For the study of such problems, some device will therefore be necessary.

References and Notes

(1) W. Kuhn, *Kolloid-Z.*, **68**, 2 (1934); **76**, 258 (1936); **87**, 3 (1939).
(2) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(3) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971.
(4) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains", Interscience, New York, N.Y., 1963.
(5) P. J. Flory "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969.
(6) P. J. Flory, *Macromolecules*, **7**, 381 (1974).
(7) K. Nagai, "Conformational Statistics of Polymeric Chains: Selected Papers of Kazuo Nagai", 1974.
(8) O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas*, **68**, 1106 (1949).
(9) H. Yamakawa, *Annu. Rev. Phys. Chem.*, **25**, 179 (1974).
(10) H. Yamakawa, *Pure Appl. Chem.*, **46**, 135 (1976).
(11) H. Yamakawa and M. Fujii, *J. Chem. Phys.*, **64**, 5222 (1976).
(12) H. Yamakawa, M. Fujii, and J. Shimada, *J. Chem. Phys.*, **65**, 2371 (1976).
(13) M. Fujii and H. Yamakawa, *J. Chem. Phys.*, **66**, 2578 (1977).
(14) H. Yamakawa and M. Fujii, *J. Chem. Phys*, **66**, 2584 (1977).
(15) D. J. Struik, "Differential Geometry", Addison-Wesley, Reading, Mass., 1950, Chapter 1.
(16) P. Bugl and S. Fujita, *J. Chem. Phys.*, **50**, 3137 (1969).
(17) L. D. Landau and E. M. Lifshitz, "Theory of Elasticity", Addison-Wesley, Reading, Mass., 1959, p 14.
(18) H. Yamakawa and M. Fujii, *J. Chem. Phys.*, **59**, 6641 (1973).
(19) P. J. Flory, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 1819 (1973).
(20) P. J. Flory and D. Y. Yoon, *J. Chem. Phys.*, **61**, 5358 (1974).
(21) H. Maeda, N. Saito, and W. H. Stockmayer, *Polym. J.*, **2**, 94 (1971).
(22) H. Yamakawa and M. Fujii, *Macromolecules*, **7**, 128 (1974).
(23) D. Y. Yoon and P. J. Flory, *Polymer*, **16**, 645 (1975).
(24) D. Y. Yoon and P. J. Flory, *J. Chem. Phys.*, **61**, 5366 (1974).
(25) P. J. Flory and V. W. C. Chang, *Macromolecules*, **9**, 33 (1976).
(26) D. Y. Yoon and P. J. Flory, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1425 (1976).
(27) A. Abe, J. W. Kennedy, and P. J. Flory, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1337 (1976).
(28) R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, **50**, 4165 (1969); **50**, 4178 (1969); see also ref 5, p 144.
(29) P. J. Flory and J. A. Semlyen, *J. Am. Chem. Soc.*, **88**, 3209 (1966); see also ref 5, p 174.
(30) P. J. Flory and J. E. Mark, *Makromol. Chem.*, **75**, 11 (1964); see also ref 5, p 159.
(31) U. W. Suter and P. J. Flory, *Macromolecules*, **8**, 765 (1975).
(32) D. Y. Yoon and P. J. Flory, *Macromolecules*, **9**, 294 (1976).
(33) D. Y. Yoon, P. R. Sundararajan, and P. J. Flory, *Macromolecules*, **8**, 776 (1975).
(34) R. A. Harris and J. E. Hearst, *J. Chem. Phys.*, **44**, 2595 (1966).
(35) K. Soda, *J. Phys. Soc. Jpn.*, **35**, 866 (1973).

Scattered Intensity from a Chain in a Rubber Network

Dale S. Pearson

Materials Science and Engineering Department, Northwestern University, Evanston, Illinois 60201.
 Received February 16, 1977

ABSTRACT: A scattering law, $S(\mathbf{q})$, is derived for a chain in a rubber network in which the chains interact only at the cross-links, i.e., a "phantom" rubber network. The result is compared to a scattering law previously derived by Jannink and co-workers for a network chain whose units move affinely with the applied strain. The scattered intensity for the two cases has a significantly different dependence on $|\mathbf{q}|$ where $\mathbf{q}$ is the scattering vector defined as the difference between the incident and scattered wave vectors. For example, the new expression for $S(\mathbf{q})$ indicates that the radius of gyration of a chain in a phantom rubber network changes less rapidly with the applied strain than an affinely deformed chain. This prediction is consistent with recent neutron scattering results on rubber networks.

Neutron scattering has proven to be a useful method for investigating the static and dynamic properties of polymers. One of the important applications has been the determination of the shape of polymer molecules in concentrated systems by measuring the scattering from labeled chains. This method, of course, could be used to study rubber networks. Recently, Jannink et al.[1] derived the scattering law $S(\mathbf{q})$ for a polymer chain in a stretched network. In their analysis it was assumed