18–15–18 BSB at 200 °C is not in accord with their observation of Newtonian behavior at 130 °C. Arnold and Meier[18] find that a 10–50–10 SBS is non-Newtonian at 200 °C, which concurs with our prediction of a transition at 213 °C. One would like to see more studies as detailed as Gouinlock and Porter's.

Finally, a few words should be said about the validity of the narrow interphase approximation. We see in Table II that the radii of typical spherical domains range upward from 8 nm. One calculates[6] using the same parameters an interfacial thickness of 1.7 nm between PS and PB, and 1.8 nm between PS and PI (at 20 °C, if equilibrium is achieved, this would be 1.4 and 1.5 nm, respectively). For comparison with spherical domain radii these thicknesses should be halved, i.e., divided between the two domains. An interphase of 2.0 nm has been reported for PS–PI by Hashimoto et al.[19] for lamellar domains. A slightly larger value, reported for spherical domains,[14] may be due to the fact that the X-ray technique does not distinguish between interfacial density distribution and domain size fluctuation. In all, it would seem that the narrow interphase approximation is quite useful, especially in view of the magnitude of other uncertainties. In ref 3 we have presented a comparison of the density profiles and free energies calculated with and without the narrow interphase approximation. Again one concludes that even at this level of detail the approximation is generally good. Near the instability discussed in the paragraphs above the approximation is beginning to break down. The full solution shows fairly large domain interpenetration and does not clearly manifest the first-order transition. Thus the stability limits calculated above must be regarded as surrounded with some ambiguity, as mentioned.

Our next project is an application of the theory to cylindrical geometry, so that the boundaries of stability of the various geometric forms can be mapped as a function of block size.

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Wormlike Chains Near the Rod Limit: Moments and Particle Scattering Function

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ABSTRACT: Nagai's modification of the Hermans–Ullman recurrence formula was applied to calculate moments $\langle \mathbf{R}^{2m}(\mathbf{R}\cdot\mathbf{u}_0)^n \rangle$ ($m, n = 0, 1, 2, ...$), $\langle 1/R \rangle$, and the distribution function $G(\mathbf{R};t)$ of the Kratky–Porod wormlike chain up to the fifth-order corrections to the rod limit. Here $\mathbf{R}$ is the end-to-end vector, t is the contour length, and $\mathbf{u}_0$ is the unit tangent vector at one end of the chain. An analytical expression for the particle scattering function $P(\theta)$ of the chain was derived by use of the Fourier transform of the $G(\mathbf{R};t)$. The $P(\theta)$ obtained is useful for analysis of scattered intensities from rodlike macromolecules with a contour length shorter than or comparable to the Kuhn statistical segment length.

The Kratky–Porod (K–P) wormlike chain[1] has long been appreciated as a relevant model for stiff or semiflexible macromolecules. Although much work[2-4] has been on its statistical properties, there still remain quite a few problems to be solved. The present paper is concerned with a theoretical calculation of some properties of the K–P chain near the rod limit.

Daniels[5] was the first to calculate the deviation of the distribution function $G(\mathbf{R},\mathbf{u}_0;t)$ of the K–P chain from the Gaussian distribution correct to the first power in t^{-1}. Here $\mathbf{R}$ is the end-to-end vector of the chain, $\mathbf{u}_0$ is the unit tangent vector at its one end, and t is its reduced contour length. Later, Gobush et al.[6] derived the deviation of the conditional distribution function $G(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t)$ from the Gauss limit to the second power in t^{-1}, where $\mathbf{u}$ is the unit tangent vector at the other end of the chain. At about the same time Nagai[7] obtained the distribution function $G(\mathbf{R};t)$ in the same approximation. All these calculations took the Gaussian chain as the zeroth approximation and introduced successively the stiffness characteristic of the K–P chain into it. However, we may start with a completely rigid rod as the zeroth approximation and correct it for chain flexibility in order to explore the behavior of the K–P chain. In fact, this type of approach was first taken by Yamakawa and Fujii,[8] who, using the WKB method, calculated the deviation of $G(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t)$ from the rod limit up to the first order of t. However, they remarked that the distribution function obtained cannot be integrated analytically with respect to $\mathbf{u}$ and $\mathbf{u}_0$. Thus the Yamakawa–Fujii approach does not seem inviting for the

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purpose of determining $G(\mathbf{R},\mathbf{u};t)$ or $G(\mathbf{R},\mathbf{u}_0;t)$ up to a higher power in t. In principle, $G(\mathbf{R},\mathbf{u}_0;t)$ can be obtained if we evaluate the moments $\langle \mathbf{R}^{2m}(\mathbf{R}\cdot\mathbf{u}_0)^n\rangle$ for all nonnegative integers m and n. The availability of these moments is useful also for calculation of the statistical averages of quantities which depend not only on $\mathbf{R}$ but also on $\mathbf{u}_0$. In particular, it is possible with $\langle \mathbf{R}^{2m}\rangle$ to determine the distribution function $G(\mathbf{R};t)$ and the particle scattering function $P(\theta)$. The present paper purports to investigate the K–P chain near the rod limit by calculating $\langle \mathbf{R}^{2m}\cdot(\mathbf{R}\cdot\mathbf{u}_0)^n\rangle$ in powers of t. The calculation is performed up to the fifth power of t.

Moments

For our purpose, it is convenient to use Nagai's modification[7] of the Hermans–Ullman recurrence formula.[9] This allows us to write $\langle \mathbf{R}^{2i}(\mathbf{R}\cdot\mathbf{u}_0)^{m-i}\rangle$ ($i, m = 0, 1, 2, ..., m \geq i$) in powers of t as

$$\langle \mathbf{R}^{2i}(\mathbf{R}\cdot\mathbf{u}_0)^{m-i}\rangle = (m+i)!t^{m+i}\sum_{n=0}^{\infty}(-1)^n\frac{[m(m+1)]^n}{(m+i+n)!}f_{m,m-i,n}t^n \quad (1)$$

where the coefficients $f_{m,m-i,n}$ can be determined by the recurrence relation

$$f_{m,m-i,n} = \frac{(m-i)(m-i+1)}{m(m+1)}f_{m,m-i,n-1} + \frac{2i}{m+i}f_{m,m-i+1,n} + \frac{m-i}{m+i}\left(\frac{m-1}{m+1}\right)^n f_{m-1,m-i-1,n} - \frac{(m-i)(m-i-1)}{m(m-1)}\left(\frac{m-1}{m+1}\right)^n f_{m-1,m-i-2,n-1} \quad (2)$$

with

$$f_{m,m-i,0} = 1 \quad (3)$$

In eq 1, both $\mathbf{R}$ and t are measured in units of the Kuhn statistical segment length $2q$ (q is equal to the persistence length). If eq 3 is introduced into eq 2 with $i = 0$ and $n = 1$, we have

$$f_{m,m,1} = \frac{2}{m+1} + \frac{m-1}{m+1}f_{m-1,m-1,1} \quad (4)$$

Solution to this recurrence equation gives

$$f_{m,m,1} = 1 \quad (5)$$

Next, we introduce eq 3 and 5 together with $i = 1$ and $n = 1$ into eq 2, then

$$f_{m,m-1,1} = \frac{2(2m-1)}{m(m+1)} + \left(\frac{m-1}{m+1}\right)^2 f_{m-1,m-2,1} \quad (6)$$

which may be solved to give

$$f_{m,m-1,1} = \frac{(3m-1)(m+2)}{3m(m+1)} \quad (7)$$

In a similar way, we find that

$$f_{m,m-2,1} = \frac{(3m-2)(m+3)}{3m(m+1)} \quad (8)$$

$$\vdots$$

$$f_{m,m-i,1} = \frac{(3m-i)(m+i+1)}{3m(m+1)} \quad (9)$$

Equation 9 can be proved by mathematical induction. Substitution of this equation into eq 2 gives $\langle \mathbf{R}^{2i}(\mathbf{R}\cdot\mathbf{u}_0)^{m-i}\rangle$ correct to the first power in t.

Once $f_{m,m-i,1}$ is obtained, the expression for the second-order coefficient $f_{m,m-i,2}$ can be derived in the same way as for $f_{m,m-i,1}$. The $f_{m,m-i,2}$ obtained is then used to derive the third-order coefficient $f_{m,m-i,3}$. In this way, we have calculated $f_{m,m-i,n}$ up to $n = 5$. The results are given in the Appendix.

Substitution of eq 3, 9, and A1 through A4 in the Appendix into eq 1 leads to the desired moments $\langle \mathbf{R}^{2i}(\mathbf{R}\cdot\mathbf{u}_0)^{m-i}\rangle$. In particular, $\langle \mathbf{R}^{2m}\rangle$ and $\langle(\mathbf{R}\cdot\mathbf{u}_0)^m\rangle$ are given by

$$\langle \mathbf{R}^{2m}\rangle = t^{2m}\Big[1 - \tfrac{2}{3}mt + \frac{m(14m+1)}{45}t^2 - \frac{2m}{945}(62m^2+3m-2)t^3 + \frac{m}{9450}(508m^3 - 84m^2 - 19m + 15)t^4 - \frac{m}{467775}(10220m^4 - 6236m^3 + 1597m^2 + 731m - 372)t^5 + ...\Big] \quad (10)$$

$$\langle(\mathbf{R}\cdot\mathbf{u}_0)^m\rangle = t^m\Big[1 - mt + \frac{m}{6}(5m-1)t^2 - \frac{m}{90}(61m^2 - 51m + 20)t^3 + \frac{m}{2520}(1385m^3 - 2718m^2 + 2659m - 990)t^4 - \frac{m}{113400}(50521m^4 - 181250m^3 + 323975m^2 - 291070m + 102864)t^5 + ...\Big] \quad (11)$$

The terms outside the brackets in these expressions represent the values for straight rods. The first-order correction terms inside the brackets, i.e., the terms of order t, agree with those derived by Yamakawa and Fujii[8] from their $G(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t)$, and the remaining higher-order corrections are new. It may be noted that eq 10 and 11 with $m = 1$ agree with the t expansions of the exact moments[2]

$$\langle \mathbf{R}^2\rangle = t - \tfrac{1}{2}(1 - e^{-2t}) \quad (12)$$

$$\langle \mathbf{R}\cdot\mathbf{u}_0\rangle = \tfrac{1}{2}(1 - e^{-2t}) \quad (13)$$

Distribution Function

The Fourier transform $I(\mathbf{s};t)$ of $G(\mathbf{R};t)$, i.e.,

$$I(\mathbf{s};t) = \int G(\mathbf{R};t)e^{i\mathbf{s}\cdot\mathbf{R}}\,d\mathbf{R} \quad (14)$$

may be expressed in terms of $\langle \mathbf{R}^{2m}\rangle$ as

$$I(\mathbf{s};t) = \sum_{m=0}^{\infty}(-1)^m\frac{\mathbf{s}^{2m}\langle \mathbf{R}^{2m}\rangle}{(2m+1)!} \quad (15)$$

Substitution of eq 10 into eq 15, followed by summation, gives

$$I(\mathbf{s};t) = j_0(z) + \frac{z}{3}j_1(z)t + \frac{z}{90}[6j_1(z) - 7zj_0(z)]t^2 + \frac{z}{1890}[(24 - 31z^2)j_1(z) + 34zj_0(z)]t^3 + \frac{z}{37800}[(212z^2 + 120)j_1(z) + z(127z^2 - 320)j_0(z)]t^4 + \frac{z}{3742200}[(2555z^4 - 8136z^2 + 4320)j_1(z) - 4z(3053z^2 - 1620)j_0(z)]t^5 + ... \quad (16)$$

with

$$z = st \quad (17)$$

where j_0 and j_1 denote the spherical Bessel functions of zeroth and first order, respectively. The Fourier inversion of eq 16 yields

$$G(\mathbf{R};t) = \frac{1}{4\pi t^2} f_0(t)\delta(\xi) + \frac{f_1(t)}{4\pi R}\frac{d\delta(\xi)}{d\xi} + \frac{f_2(t)}{4\pi R}\frac{d^2\delta(\xi)}{d\xi^2} + \frac{f_3(t)}{4\pi R}\frac{d^3\delta(\xi)}{d\xi^3} + \frac{f_4(t)}{4\pi R}\frac{d^4\delta(\xi)}{d\xi^4} + \frac{f_5(t)}{4\pi R}\frac{d^5\delta(\xi)}{d\xi^5} + \ldots \quad (18)$$

where

$$\xi = R - t \quad (19)$$

and

$$f_0(t) = 1 + \frac{t}{3} + \frac{t^2}{15} + \frac{4t^3}{315} + \frac{t^4}{315} + \frac{4t^5}{3465} + \ldots$$

$$f_1(t) = f_0(t) - 1$$

$$f_2(t) = t^3\left(\frac{7}{90} - \frac{t}{630} + \frac{t^2}{350} + \frac{23t^3}{51975} + \ldots\right)$$

$$f_3(t) = t^5\left(\frac{31}{1890} - \frac{53t}{9450} + \frac{113t^2}{51975} + \ldots\right)$$

$$f_4(t) = t^7\left(\frac{127}{37800} - \frac{1073t}{415800} + \ldots\right)$$

$$f_5(t) = \frac{73t^9}{106920} + \ldots \quad (20)$$

The notation δ denotes the Dirac δ function, and its derivatives should be understood in the sense of Schwartz's distribution. In the limit of $t = 0$, eq 18 reduces to

$$G(\mathbf{R};t) = \frac{1}{4\pi t^2}\delta(R - t) \quad (21)$$

which represents the distribution function of $\mathbf{R}$ for the rigid rod of length t.

The mean reciprocal distance $\langle 1/R \rangle$ can be evaluated by use of eq 18, yielding

$$\langle 1/R \rangle = \frac{1}{t}\left(1 + \frac{t}{3} + \frac{t^2}{15} + \frac{4t^3}{315} + \frac{t^4}{315} + \frac{4t^5}{3465} + \ldots\right) \quad (22)$$

The coefficient $^1/_3$ of the term of order t agrees with the value obtained by different approaches.[8,10] We note that eq 22 is derived from eq 10 by putting $m = -^1/_2$, although eq 10 has been obtained for nonnegative integers m.

Particle Scattering Function

The particle scattering function $P(\theta)$ may be calculated from[4]

$$P(\theta) = \frac{2}{L^2}\int_0^L (L - t)I(\mathbf{k};t)\,dt \quad (23)$$

where L is the reduced contour length (measured in units of $2q$) of the K-P chain and k is the magnitude of the reduced scattering vector defined by

$$k = \frac{8\pi q}{\lambda}\sin(\theta/2) \quad (24)$$

with θ the scattering angle and λ the wavelength of the incident beam in solution. Introduction of eq 16 with s replaced by k into eq 23, followed by integration, gives

$$P(\theta) = P_0 + P_1L + P_2L^2 + P_3L^3 + P_4L^4 + P_5L^5 + \ldots \quad (25)$$

where

$$P_0 = \frac{2}{x^2}(xSi(x) + \cos x - 1)$$

$$P_1 = \frac{2}{3x^3}(2x - 3\sin x + x\cos x)$$

$$P_2 = \frac{1}{45x^4}[216 - (156x - 7x^3)\sin x - (216 - 48x^2)\cos x]$$

$$P_3 = \frac{1}{63x^5}\left[-256 + \left(1512 - 500x^2 + \frac{307}{15}x^4\right)\times \sin x - \left(1256x - 124x^3 + \frac{31}{15}x^5\right)\cos x\right]$$

$$P_4 = \frac{1}{21x^6}\left[-4608 + \left(4048x - 488x^3 + \frac{2261}{150}x^5 - \frac{127}{900}x^7\right)\times \sin x + \left(4608 - 1744x^2 + \frac{296}{3}x^4 - \frac{87}{50}x^6\right)\cos x\right]$$

$$P_5 = \frac{1}{x^7}\left[\frac{10240x}{33} - \left(3264 - \frac{43616}{33}x^2 + \frac{8344}{99}x^4 - \frac{101224}{51975}x^6 + \frac{367}{18900}x^8\right)\sin x + \left(\frac{97472}{33}x - \frac{12832}{33}x^3 + \frac{7064}{495}x^5 - \frac{1024}{4725}x^7 + \frac{73}{53460}x^9\right)\cos x\right] \quad (26)$$

$$x = kL \quad (27)$$

and

$$Si(x) = \int_0^x \frac{\sin \eta}{\eta}\,d\eta \quad (28)$$

In the limit of $L = 0$, eq 25 reduces to

$$P(\theta) = \frac{2}{x^2}(xSi(x) + \cos x - 1)$$

which is the well-known expression for rigid rods.[11] For small values of x, eq 25 is expanded in powers of k^2 to give

$$P(\theta) = 1 - \frac{k^2}{3}\langle S^2 \rangle + 0(k^4) \quad (29)$$

with

$$\langle S^2 \rangle = \frac{L^2}{12}\left(1 - \frac{2L}{5} + \frac{2L^2}{15} - \frac{4L^3}{105} + \frac{L^4}{105} - \frac{2L^5}{945} + \ldots\right) \quad (30)$$

Equation 30 agrees with the L expansion of the exact (reduced) mean-square radius of gyration[12]

$$\langle S^2 \rangle = \frac{L}{6} - \frac{1}{4} + \frac{1}{4L} - \frac{1}{8L^2}(1 - e^{-2L}) \quad (31)$$

The numerical values of $\langle S^2 \rangle$ computed from eq 30 approximate the exact values within 7×10^{-4}% for $L = 0.5$, 0.05% for $L = 1$, and 0.6% for $L = 1.5$. Thus it may be expected that eq 25 gives a close approximation to the initial slope of $P(\theta)$, i.e., $(dP(\theta)/dk^2)_{k=0}$, provided $L \leq 1.5$. However, unless $L \ll 1$, this equation should fail to predict the behavior of $P(\theta)$ at large x, because P_4 and P_5 diverge at such x values.

Koyama[13] has derived approximate expressions for $P(\theta)$ at very large and small x. His expression for very large x is written in our notation as

$$P(\theta) = P_0 + P_1L$$

which conforms to eq 25 with only the first two terms

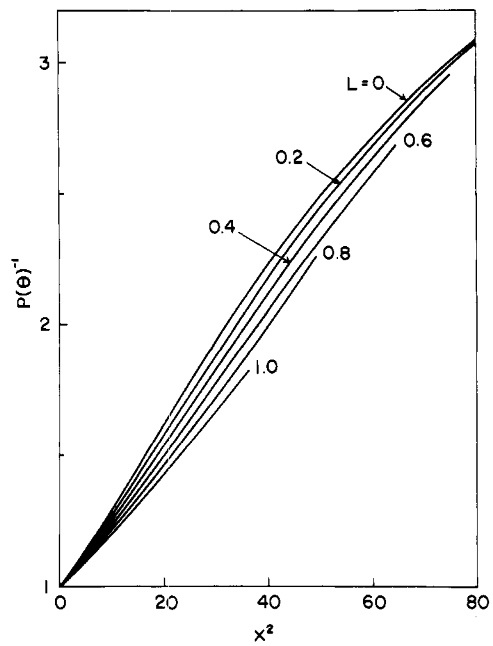

Figure 1. Values of $P(\theta)^{-1}$ calculated from eq 32 for the indicated values of the reduced contour length L.

retained. Thus we see that Koyama's asymptotic expression for large x should be valid only for small L.

Equation 25 may be rewritten

$$P(\theta)^{-1} = P_0^{-1}(1 + P_1^*L + P_2^*L^2 + P_3^*L^3 + P_4^*L^4 + P_5^*L^5 + \ldots) \quad (32)$$

with

$$P_1^* = -P_1/P_0$$

$$P_2^* = -P_2/P_0 + (P_1/P_0)^2$$

$$P_3^* = -P_3/P_0 + 2P_1P_2/P_0^2 - (P_1/P_0)^3$$

$$P_4^* = -P_4/P_0 + (P_2^2 + 2P_1P_3)/P_0^2 - 3P_1^2P_2/P_0^3 + (P_1/P_0)^4$$

$$P_5^* = -P_5/P_0 + 2(P_1P_4 + P_2P_3)/P_0^2 - 3P_1(P_2^2 + P_1P_3)/P_0^3 + 4P_1^3P_2/P_0^4 - (P_1/P_0)^5 \quad (33)$$

Numerical computations with various sets of x and L indicated that eq 32 converges more rapidly than the reciprocal of eq 25. We therefore use eq 32 in the following discussion.

Figure 1 illustrates the curves of $P(\theta)^{-1}$ against x^2 for the indicated values of L. The computations for $L \geq 0.4$ have been truncated at x^2 values beyond which the convergence became badly poor. We note that, in the range of $0 < k^2 \leq 11$ where the numerical values of $P(\theta)$ are available in the table of Yamakawa and Fujii,[14] our $P(\theta)^{-1}$ values for $L = 0.5$ and $L = 1$ agree closely with those of these authors.

The $P(\theta)$ curve for $L = 0$ (rigid rods) in Figure 1 appears to be quite linear over the range of x^2 from zero to 40. If this linear portion is taken as the initial tangent to the $P(\theta)^{-1}$ vs. x^2 curve, the mean-square radius of gyration is overestimated by about 10%. In fact, close examination reveals that the curve for $L = 0$ deviates significantly from the initial tangent for x^2 larger than 5. If, according to Berry,[15] $P(\theta)^{-1/2}$ is plotted against x^2, this limiting value of x^2 is extended to 15. Similar arguments can be applied to the curves for nonzero L. For example, when $L = 0.4$, the limiting x^2 is about 5 on the conventional $P(\theta)^{-1}$ vs. x^2 plot, whereas it is about 25 on the Berry square root plot. Therefore, even for very stiff chains Berry's method of analysis of light-scattering data is advantageous for the determination of $\langle S^2 \rangle$, provided that the molecular weight distribution of the sample is narrow.

In conclusion, our analytical expression for $P(\theta)$, eq 32, is useful for the K–P chain with a contour length shorter than or equal to the Kuhn statistical segment length, i.e., $L \leq 1$. On the other hand, the numerical table of Yamakawa and Fujii[14] and the asymptotic expression of Sharp and Bloomfield[16] for $P(\theta)$ are appropriate for $10 \geq L > 1$ and $L \geq 10$, respectively. These three contributions, when properly combined, afford us with theoretical information about the $P(\theta)$ function of the K–P chain over the entire range of L.

Appendix

The results for $f_{m,m-i,n}$ (n = 2, 3, 4, and 5) are

$$f_{m,m-i,2} = \frac{(m+i+2)(m+i+1)}{90[m(m+1)]^2}[75(m-i) \times (m-i-1) + 12(7i+5)(m-i) + 2i(14i+1)] \quad (A1)$$

$$f_{m,m-i,3} = \frac{(m+i+3)!}{90[m(m+1)]^3(m+i)!}\left[61\frac{(m-i)!}{(m-i-3)!} + \frac{2}{7}(323i+462)(m-i)(m-i-1) + \frac{6}{7}(62i^2+85i+35)(m-i) + \frac{4i}{21}(62i^2+3i-2)\right] \quad (A2)$$

$$f_{m,m-i,4} = \frac{(m+i+4)!}{90[m(m+1)]^4(m+i)!}\left[\frac{1385}{28}\frac{(m-i)!}{(m-i-4)!} + \frac{2}{63}(2951i+6291)\frac{(m-i)!}{(m-i-3)!} + \frac{1}{105}(7762i^2+20903i+15750)(m-i)(m-i-1) + \frac{4}{35}(254i^3+473i^2+368i+105)(m-i) + \frac{i}{105}(508i^3-84i^2-19i+15)\right] \quad (A3)$$

$$f_{m,m-i,5} = \frac{(m+i+5)!}{90[m(m+1)]^5(m+i)!}\left[\frac{50521}{1260}\frac{(m-i)!}{(m-i-5)!} + \frac{1}{9}\left(\frac{631621i}{770}+2314\right)\frac{(m-i)!}{(m-i-4)!} + \frac{1}{189}\left(\frac{940402}{55}i^2 + \frac{755119}{11}i + 74925\right)\frac{(m-i)!}{(m-i-3)!} + \frac{2}{7}\left(\frac{85234}{495}i^3 + \frac{7077}{11}i^2 + \frac{453806}{495}i + 472\right) \times (m-i)(m-i-1) + 2\left(\frac{730}{99}i^4 + \frac{54622}{3465}i^3 + \frac{2183}{126}i^2 + \frac{65101}{6930}i + 2\right)(m-i) + \frac{2i}{10395}(10220i^4 - 6236i^3 + 1597i^2 + 731i - 372)\right] \quad (A4)$$

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Electronic Structures and Conformations of Polyoxymethylene and Polyoxyethylene

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ABSTRACT: The CNDO/2 method using the tight-binding approximation for polymers was applied to hexagonal (HPOM), orthorhombic (OPOM), and trans zigzag (ZPOM) polyoxymethylenes and to helical (HPOE) and trans zigzag (ZPOE) polyoxyethylenes. The CNDO/2 calculations were also carried out for a model molecule of POE, $CH_3OCH_2CH_2OCH_3$. One of the main factors to stabilize HPOE was demonstrated clearly by the examinations of the model molecule. The relative stabilities among HPOM, OPOM, and ZPOM, and between HPOE and ZPOE, were reasonably reproduced by the present calculations. Contribution of the intrasegment and intersegment energies to the total energy were discussed in connection with the relative stabilities of the various conformations. The O···O electrostatic repulsions in the treated molecules were also discussed in terms of the electronic structures of the molecules. The band structures of POM and POE were proposed.

Normal form polyoxymethylene, hexagonal (HPOM),[2] is obtained under the γ-ray irradiation polymerization of trioxane or tetraoxane in the solid phase.[3] On the other hand under special conditions, the polymer appears in the orthorhombic form (OPOM).[4] Both in HPOM and OPOM each molecule stays in the G conformation about a C–O or O–C bond. The planar zigzag form (ZPOM) can also be accepted for consideration. Among these three forms, the relative stability can be considered in the order, HPOM > OPOM > ZPOM. Polyoxyethylene (POE) forms crystalline complexes for example with urea[5] and $HgCl_2$[6,7] in which a POE molecule has various conformations. The planar zigzag conformer (ZPOE) is stable under tension.[8b] Under the ordinary condition, the helical conformer (HPOE), in which the conformation around the bonds O–C–C–O is TGT, is the stable form.[8] Therefore, the stability between HPOE and ZPOE is considered to be in the order, HPOE > ZPOE.

With the model molecules such as $CH_3OCH_2OCH_3$ and/or $CH_3OCH_2OCH_2OCH_3$ for POM, dipole moment,[9] electron diffraction,[10] and semiempirical MO[11] studies have been reported previously. Vibrational analyses of a model molecule for POE $CH_3OCH_2CH_2OCH_3$ have been extensively investigated,[12] and CNDO/2 calculations[13] have also been carried out. Furthermore, the results of statistical mechanical treatments on polyethylene (PE), POM, and POE have been adequately reviewed by Flory.[14]

POM can be considered to have a similar chemical unit to PE substituted by oxygen instead of one methylene group, while POE has a unit in which an O atom combines to a PE residue. Accordingly, it is worth mentioning that there seems to be intimate relations between the electronic structures for PE, POM, and POE.

The electronic structures of polymers have been extensively examined by Imamura and his co-workers.[15–17] Their methods were applied to PE,[15,16] polyglycine,[16,17] poly-L-alanine,[17] $(SN)_x$ and $(SCH)_x$,[18] and later to poly-L-proline I and II.[19]

In the present study, we have investigated the electronic structures of POM and POE with the aid of the CNDO/2 method[20] in terms of the tight-binding approximation.[21] Actual numerical calculations were carried out on the basis of the method reported by Imamura and Fujita.[17] The CNDO/2 calculations were also carried out for a model molecule of POE, $CH_3OCH_2CH_2OCH_3$.

I. Method of Calculations

The total energy of a polymer can be expressed as follows:[17]

$$E_{\text{total}} = \sum_{A} E_A + \sum_{A}\sum_{A<B} E_{A,B}^{(0,0)} + \sum_{j}\sum_{A}\sum_{B} E_{A,B}^{(0,j)} \quad (1)$$

One-center term:

$$E_A = \sum_{t}^{\text{on A}} P_{tt}[-\tfrac{1}{2}(I_t + A_t) - (Z_A - \tfrac{1}{2})\gamma_{A,A}^{(0,0)}] + \tfrac{1}{2}\sum_{t}^{\text{on A}}\sum_{t_1}^{\text{on A}} [P_{tt}P_{t_1t_1} - \tfrac{1}{2}(P_{tt_1})^2]\gamma_{A,A}^{(0,0)} \quad (2)$$

Intrasegment two-center term:

$$E_{A,B}^{(0,0)} = 2\beta_{AB}^{0}\sum_{t}^{\text{on A}}\sum_{t_1}^{\text{on B}} P_{tt_1}S_{tt_1}^{(0,0)} - \tfrac{1}{2}\sum_{t}^{\text{on A}}\sum_{t_1}^{\text{on B}} (P_{tt_1})^2\gamma_{A,B}^{(0,0)} + [P_{AA}P_{BB}\gamma_{A,B}^{(0,0)} - P_{AA}Z_B\gamma_{A,B}^{(0,0)} - P_{BB}Z_A\gamma_{A,B}^{(0,0)} + (Z_AZ_Be^2/R_{AB})] \quad (3)$$

Intersegment two-center term:

$$E_{A,B}^{(0,j)} = \beta_{AB}^{0}\sum_{t}^{\text{on A}}\sum_{t_1}^{\text{on B}} P_{t_1t}^{+j}S_{tt_1}^{(0,j)} - \tfrac{1}{4}\sum_{t}^{\text{on A}}\sum_{t_1}^{\text{on B}} P_{t_1t}^{+j}P_{tt_1}^{-j}\gamma_{A,B}^{(0,j)} + \tfrac{1}{2}[P_{AA}P_{BB}\gamma_{A,B}^{(0,j)} - P_{AA}Z_B\gamma_{A,B}^{(0,j)} - P_{BB}Z_A\gamma_{A,B}^{(0,j)} + (Z_AZ_Be^2/R_{AB})] \quad (4)$$

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