Recently, Rosser et al.[8] reported on a polystyrene prepared by emulsion polymerization with $M_w = 18 \times 10^6$, with a fairly narrow molecular weight distribution, and with $[\eta] = 3150$ for toluene at 20 °C. This would mean the same type of deviation from the linear log–log relation as that claimed by McIntyre.[7]

Any deviation from the linear plot would have to originate from a change in the radius of gyration. Different methods of investigation pertaining to the radius of gyration, such as light scattering ($R^2 \alpha M^{1+\epsilon}$), diffusion ($D \alpha M^{-b}$), and sedimentation ($S \alpha M^{1-b}$) on the same polystyrene samples of Table I, resulted in typical straight line double logarithmic plots[9] as can be expected for a thread-like coiling polymer. Considering all of the presented data, it is throught that the results of this work are more reliable than the three viscosity numbers for high molecular weight polystyrene in a good solvent reported elsewhere.[7,8]

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A Generalized Bead and Spring Model for the Dynamics of DNA in Solution. Application to the Intrinsic Viscosity

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ABSTRACT: A generalized version of the Rouse–Zimm model is applied to the calculation of the intrinsic viscosity of DNA. Some approximations of the model are examined, and some corrections are introduced in the evaluation of the eigenvalues from which the intrinsic viscosity is calculated. The theoretical results are compared with experimental data to obtain the molecular parameters of the model. The statistical segment length so obtained is analyzed together with that extracted from the wormlike chain model and also from experimental data of other macroscopic properties. A first estimation of the excluded volume effects is also discussed.

In the study of chain macromolecules in solution, two different models can be used: the continuous Kratky–Porod[1] wormlike chain and the discrete Rouse–Zimm bead-and-spring model.[2,3] The former has the great advantage of representing chain stiffness between the limiting cases of flexible coil and rigid rod, while the latter, in its original formulation,[3] is only valid for flexible chains. However, the Rouse–Zimm model is, by far, superior to the wormlike chain in the simplicity of the physical concepts and mathematical details embodied in the evaluation of dynamical properties, and, consequently, it is currently considered the most adequate description of the low-frequency dynamics of flexible polymers in solution. In the model, intramolecular motions are represented by a set of relaxation times or equivalent eigenvalues, from which many dynamical properties (intrinsic viscosity,[3] quasielastic light scattering,[4] flow linear dichroism,[5] etc.) are easily derived.

The above considerations illustrate the potential usefulness of extending the applicability of the Rouse–Zimm model to stiff chains such as DNA, specially if the model parameters can have some molecular interpretations as has been recently suggested by Lin and Schurr.[6] A first attempt in this direction was made by Simon,[7] who proposed a generalized version of the model in which chain stiffness is taken into account as a first perturbation by introducing springs connecting second-neighboring beads. Comparison of this model with experimental data of total-intensity light scattering and sedimentation coefficients of high-molecular-weight DNA has been made[8] and shows that the statistical length predicted by the model is similar to that obtained for a wormlike chain. For these properties, however, explicit introduction of the relaxation times corresponding to the realistic nondraining limit of hydrodynamic interactions is not needed, and, therefore, the theory has also to be tested with other properties more directly related to the relaxation times.

In the present work, we performed a comparison of the Simon model with existing[9] experimental data of the intrinsic viscosity of high-molecular-weight DNA. These data (along with others for DNA fragments of lower molecular weight[10,11]) have been previously interpreted[12,13] by means of the Yamakawa–Fujii theory[12,14] that describes the hydrodynamic behavior of a wormlike chain, and, consequently, they seem very adequate to check the theoretical expressions for the eigenvalues derived from the Simon model.

In our revision of the calculations for these eigenvalues, we have arrived at an approximate expression significantly different from that of Simon. We have verified the validity of our new expression by comparing numerical eigenvalues calculated from it with those obtained by exact diagonalization.

The comparison between the revised theory and the experimental data yields values for the two parameters of the model that do not completely agree with those obtained with other properties. This fact is discussed in terms of excluded volume effects, which are larger for the intrinsic viscosity. We have made an estimation of these effects that give a statistical length of DNA close to the one corresponding to an excluded volume wormlike model.[15–17]

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Our main conclusion is that the revised Simon theory essentially reproduces the results of the rigorous Yamakawa and Fujii treatment for the intrinsic viscosity and, therefore, the expressions for the eigenvalues presented here can be applied to theoretical calculations corresponding to other dynamic properties for which the mathematically complicated wormlike model would be impractical.

Revision of Theoretical Expressions

(A) Reciprocal Distance Averages. Considering a linear chain composed of $N + 1$ beads joined by N first-neighbor springs and $N - 1$ second-neighbor springs, it is shown[7] that the eigenvalues for the model matricial equation in the absence of hydrodynamic interactions (free-draining limit of the Rouse model[1]) are given by the exact expression

$$\lambda_k = 4\left[\sin^2\frac{\pi k}{2(N+1)} + \beta\sin^2\frac{\pi k}{(N+1)}\right] \qquad k = 1, ..., \mathrm{N} \quad (1)$$

where β is the stiffness parameter of the chain.[7]

However, we should consider the nondraining limit where hydrodynamic interactions between beads are strong. In this other limit, the eigenvalues depend on $\langle R_{ij}^{-1}\rangle$, the reciprocal average between every two different beads along the chain.

$\langle R_{ij}^{-1}\rangle$ is obtained for flexible chains by

$$\langle R_{ij}^{-1}\rangle = (6/\pi)^{1/2}\langle R_{ij}^{2}\rangle \quad (2)$$

where $\langle R_{ij}^{2}\rangle$ is the corresponding quadratic average. It is assumed that eq 2 is also valid for not too large rigidities. $\langle R_{ij}^{2}\rangle$ is evaluated from[7]

$$\langle R_{ij}^{2}\rangle = b^2\sum_{k=1}^{N}(Q_{ik} - Q_{jk})^2\lambda_k^{-1} \quad (3)$$

with

$$Q_{ik}Q_{jk} = \frac{1}{(N+1)}\{\cos\,[\pi k(i-j)/(N+1)] + \cos\,[\pi k(i+j)/(N+1)]\} \quad (4)$$

b is the statistical distance between adjacent beads and Q_{ij} is an element of the matrix of eigenvectors in the Rouse model.

We use eq 1, 3, and 4 to obtain an analytical expression for $\langle R_{ij}^{2}\rangle$. First we transform the sum in eq 3 to an integral and substitute $N + 1$ by N. These approximations are valid for large N. Then, in order to calculate $\langle R_{ij}^{2}\rangle$, integrals of the type

$$I(n) = \int_1^N \frac{\cos\,(n\pi k/N)\,\mathrm{d}k}{\sin^2\,(\pi k/2N) + \beta\sin^2\,(\pi k/N)} \quad (5)$$

have to be handled.

We have evaluated these integrals by changing the integration variable from k to $z = e^{i\pi k/N}$. Assuming π/N is very close to zero, every $I(n)$ turns out to be half the value of the new complex integral extended to the $|z| = 1$ circumference. The calculus of residues allows us to obtain analytical expressions for $I(n)$ from which $\langle R_{ij}^{2}\rangle$ is calculated. Four poles are involved in the problem. Two of them, $z_1 = z_2 = 1$, are on the contour of integration, while $z_3 = -1 - (1 - (1 + 4\beta)^{1/2})/2\beta$ must also be considered. $z_4 = -1 + (1 - (1 + 4\beta)^{1/2})/2\beta$ is outside the unit circle for any realistic β (it was reported[8] earlier that β should be between the values of 0 and -0.25). Neglecting terminal effects, i.e., considering the dependence of $\langle R_{ij}^{2}\rangle$ on i and j being exerted through the single variable $|i - j|$, the result obtained is

$$\langle R_{ij}^{2}\rangle = b^2(1 + 4\beta)^{-1}[|i - j| + 2\beta/(1 + 4\beta)^{1/2}] \quad (6)$$

Table I: b<R_{ij}^{-1}> Calculated by Several Methods

β	$\vert i - j\vert$	eq 2 and 6	eq 7	eq 8
0.1	2	0.803	0.801	0.781
0.1	5	0.520	0.520	0.515
-0.1^{a}	2	0.587	0.583	0.584
-0.1	5	0.356	0.355	0.356
-0.2	2	0.425	0.387	0.358
-0.2	5	0.221	0.218	0.210

[a] For $\beta = -0.109$, eq 7 and 8 become identical. This explains the good agreement between both equations at $\beta = -0.1$.

We have verified that eq 6 reproduces the exact numerical results from direct application of eq 1, 3, and 4 within a very small error range for $N \geq 100$, even for small $|i - j|$ and large $|\beta|$.

From eq 2 and 6 a simple expression for $\langle R_{ij}^{-1}\rangle$ is achieved

$$\langle R_{ij}^{-1}\rangle = (6/\pi)^{1/2}b^{-1}(1 + 4\beta)^{1/2}|i - j|^{-1/2} \times \{1 - [\beta/(1 + 4\beta)^{1/2}]|i - j|^{-1}\} \quad (7)$$

(In order to obtain eq 7 we have performed a first-order power expansion on the variable $|i - j|^{-1}$.)

Equation 7 should be compared with the similar one given by Simon[7]

$$\langle R_{ij}^{-1}\rangle = (6/\pi)^{1/2}b^{-1}(1 + 4\beta)^{1/2}|i - j|^{-1/2} \times [1 - (4\beta/3)|i - j|^{-1}] \quad (8)$$

Equation 8 was derived by previous substitution of eq 1 by an uncompleted second-order power expansion of the eigenvalues on the variable k followed by a further first-order β-power expansion of $\langle R_{ij}^{2}\rangle$. Terminal effects were also eliminated from the procedure.

Comparison of numerical results for $\langle R_{ij}^{-1}\rangle$ from eq 7 and 8 with results from a direct evaluation of $\langle R_{ij}^{-1}\rangle$ utilizing eq 2 and 6 reveals that our eq 7 is a more accurate approximation of the last results (Table I). However, differences between the three sets of numbers are small in all interesting cases, and, consequently, the influence of these differences in the final eigenvalues should be small.

(B) Eigenvalues. Equation 7 can be directly applied to the calculation of eigenvalues in the nondraining limit. The procedure is essentially that followed by Simon[7] and Kumbar[18] though we make some corrections which noticeably change the numerical results.

The matricial equation in the Simon model is

$$\mathbf{H}\mathbf{G}\alpha = \lambda\alpha \quad (9)$$

$\mathbf{H}$ is the same hydrodynamic interaction matrix defined by Zimm[3] whose elements are related to reciprocal averages. $\mathbf{G}$ is

$$\mathbf{G} = \mathbf{A} + \beta\mathbf{B} \quad (10)$$

where $\mathbf{A}$, Zimm's coordinate matrix,[3] represents the first nearest-neighbor springs forces while $\mathbf{B}$ is another matrix defined by Simon[7] which takes care of the second nearest-neighbor spring forces. Simon gives an integral operator representation to $\mathbf{G}$ identical with $\mathcal{A}$ (integral representation of $\mathbf{A}$ in the Zimm theory). In our analysis, however, the correct G (integral representation of $\mathbf{G}$) turns out to be

$$G = (1 + 4\beta)\mathcal{A} \quad (11)$$

Therefore, the correct G differs in a $(1 + 4\beta)$ factor from the one utilized in the Simon theory. This factor propagates through the mathematical procedure to the final results for the eigenvalues.

As $\mathbf{G}$ has more off-diagonal elements than $\mathbf{A}$, its integral

Table II: Eigenvalues for the Simon Model ($N = 50$)

β	λ_1			$\sum_{i=1}^{N} \lambda_i^{-1}$		
	a	eq 16	*b*	*a*	eq 16	*b*
0	1.09×10^{-2}	1.12×10^{-2}	1.12×10^{-2}	203	191	191
−0.05	8.33×10^{-3}	8.23×10^{-3}	1.01×10^{-2}	256	245	209
−0.1	5.90×10^{-3}	5.50×10^{-3}	8.82×10^{-3}	345	349	236
−0.15	3.65×10^{-3}	3.11×10^{-3}	7.24×10^{-3}	527	584	284
−0.20	1.63×10^{-3}	1.19×10^{-3}	5.15×10^{-3}	1092	1442	394

[a] Exact diagonalization. [b] From Simon's expressions.

representation should be less accuate for small chains (matrices **A**, **G**, and **H** are $(N + 1)$ dimensioned). Thus, approximate eigenvalues from an integral equation equivalent to eq 9 are only adequate for large N or small $|\beta|$.

From eq 7, 10, and 11, together with the integral operator representations for **A** and **H** derived by Zimm,[3] we arrive at the following integral equation

$$(1 + 4\beta)\frac{\mathrm{d}^2}{\mathrm{d}r^2}\,\alpha(r) + (1 + 4\beta)^{3/2}h\left[\int_{-1}^{-1/N} f(r,s)\,\mathrm{d}s + \int_{1/N}^{1} f(r,s)\,\mathrm{d}s\right] = (-N^2/4)\lambda\alpha(r) \quad (12)$$

where h is the hydrodynamic interaction parameter[3] and

$$f(r,s) = \alpha''(s)|r - s|^{-1/2}\left[1 - \frac{2\beta}{(1 + 4\beta)^{1/2}}|r - s|^{-1}\right] \quad (13)$$

At this point, Simon has approximated the integral limits $1/N$ to zero while ignoring the $\alpha''(r)$-depending term in eq 12. Later, Osaki[19] investigated the validity of these approximations in the treatment of a similar integral equation within the Zimm theory.[20] He concludes that they are equivalent to assuming the value 0.25 for the reduced hydrodynamic interaction parameter, $h^* = hN^{-1/2}$. We handle eq 12 by following Osaki's procedure[19] and we get

$$(1 + 4\beta)h\left\{\int_{-1}^{1}\alpha''(s) \times |r - s|^{-1/2}(1 + 4\beta)^{1/2}\,\mathrm{d}s - 2\beta h\left[\int_{-1}^{r-\epsilon}\alpha''(s) \times |r - s|^{-3/2}\,\mathrm{d}s + \int_{r+\epsilon}^{1}\alpha''(s)|r - s|^{-3/2}\,\mathrm{d}s\right]\right\} = -\left(\frac{N^2}{4}\right)\lambda\alpha(r) \quad (14)$$

where

$$\epsilon = N\left\{N + \frac{(1 + 4\beta)^{1/2}}{2\beta}\left[1 - \frac{1}{(1 + 4\beta)^{1/2}4h^*}\right]\right\}^{-2} \quad (15)$$

h^* seems to be close to 0.25 for most flexible polymers[19] in solution and even for shorter chain molecules.[21] Consequently, we also have introduced the value 0.25 for h^* in the calculation of ϵ from eq 15.

Eigenvalues are obtained from eq 14 without any further modification of the scheme followed by Simon[7] and Kumbar.[18] The result is

$$\lambda_k = (4/N^2)h(1 + 4\beta)^{3/2}\pi k^{1/2}\left[F_k(\tfrac{1}{2},0) - \frac{\pi k\beta}{N(1 + 4\beta)^{1/2}}F_k(\tfrac{3}{2},\epsilon)\right] \quad (16)$$

where

$$F_k(n,x) = \pi k A_k(n,x) - nB_k(n,x) \quad (17)$$

and

$$A_k(n,x) = (2\pi)^{-1/2}\int_{2x}^{\pi k} t^{-n}\cos t\,\mathrm{d}t \quad (18a)$$

$$B_k(n,x) = (2\pi)^{-1/2}\int_{2x}^{\pi k} t^{-n}\sin t\,\mathrm{d}t \quad (18b)$$

$A_k(^1/_2,0)$ and $B_k(^1/_2,0)$ are the Fresnel integrals $C_{1/2}(\pi k)$ and $S_{1/2}(\pi k)$. $A_k(^3/_2,\epsilon)$ and $B_k(^3/_2,\epsilon)$ can be calculated from them.[7,18]

We have performed the exact diagonalization of **H**·**G** for $N = 50$ in order to verify the validity of eq 16 to 18. In the calculations, **H** has been built from the values of the reciprocal averages defined by eq 1 to 4 while h^* has been set to be 0.25. Results obtained from eq 16 and from exact diagonalization are shown in Table II where they are also compared with those evaluated by us from the expression for λ_k given by Simon.[7] From this comparison, the values from eq 16 appear to agree much better with the exact ones than the values from Simon's expression. Therefore, eq 16 is proved to be a more suitable approximation. We have verified that this is largely caused by the additional $(1 + 4\beta)$ factor described above, and, consequently, the other modifications introduced in this section turn out to be only minor improvements of the theory. It should also be noticed that eq 16 becomes a poor approximation for large $|\beta|$. Fortunately, an increase of N produces better approximate results for the same β as was previously discussed. For further calculations described in the next sections N will be larger than 50.

The Intrinsic Viscosity

As in the Rouse–Zimm theory,[3] the steady-flow intrinsic viscosity, $[\eta]$, of a polymer is evaluated from the Simon model, using the expression

$$[\eta] = \frac{(\pi^3/3)^{1/2}N_\mathrm{A}}{4M_\mathrm{L}}b^2N^{1/2}\sum_{k=1}^{N}(\lambda_k')^{-1} \quad (19)$$

where N_A is Avogadro's number, M_L is the polymer mass per unit length, related to the polymer molecular weight, M, by

$$M = NbM_\mathrm{L} \quad (20)$$

and

$$\lambda_k' = (N^2/4)h^{-1}\lambda_k \quad (21)$$

Equations 16 to 21 allow us to study the molecular weight dependence of $[\eta]$ as a function of the model parameters,[8] i.e., the statistical segment length, $b/(1 + 4\beta)$, and the stiffness parameter β.

We have made this study for DNA by setting $M_\mathrm{L} = 1950$ daltons/nm. We also have compared our results with experimental data by Hearst et al.[9] by means of a least-squares method. The comparison yields values for the two stiffness parameters. We have obtained $b/(1 + 4\beta) = 105$ nm and $\beta = -0.20$ to -0.24. The theoretical results for $[\eta]$

are found to be strongly dependent on $b/(1 + 4\beta)$ but weakly dependent on β. This fact together with significant scattering in the experimental data explains the uncertainty in β. Yamakawa and Fujii[12] have shown that the wormlike chain best fits the intrinsic viscosity of DNA for a statistical length of 110 nm. Therefore, the corrected Simon model and the wormlike chain give similar results when compared with intrinsic viscosity data of DNA.

Discussion

The wormlike chain is considered to be the physically most adequate model to describe the DNA molecule. Yamakawa and Fujii[14] have derived the intrinsic viscosity formalism for this model and compared their theoretical results with experimental data. They have obtained 110 nm for the statistical length and $d = 2.4$ nm for the molecular diameter. Godfrey and Eisenberg[13] have performed a similar comparison in which recent accurate data of low molecular weight fractions[10,11] were included. The best fit was found for a statistical length of 117.5 nm and $d = 1.2$ nm. However, by setting $d = 2.0$ nm (a quite more realistic value), the best fit corresponds to a statistical length of 100 nm. This indicates that ±10% derivations in the statistical length can be expected,[13] in the analysis of a given property, owing to different choices of experimental data and the simultaneous fit of the second parameter (d, or β in our case).

On the other hand, our comparison of the Simon model with intrinsic viscosity data has been made with the main purpose of verifying the usefulness of the analytical expressions given in the Revision of Theoretical Expressions section in their application to theoretical prediction of physical properties. In consequence, the comparison has been restricted to a range of high molecular weights in order to assure a large value of N, so that those expressions are mathematically justified.

In the previous wormlike model analysis,[14,15] a wide range of molecular weights has been used, and, therefore, excluded volume effects are not equally represented in all the experimental data. Fortunately, the wormlike model describes very well the experimental variation of the slope $d[\eta]/d \log M$, and then excluded volume, although surely important at high M, does not have to be taken into account. Our results, however, fail in this regard so that an explicit introduction of excluded volume effects is necessary, at least as a first-order correction. The only way to avoid these effects would be considering only short DNA molecules,[10,11] but the restriction of high N in our formulation makes it impossible.

The molecular parameters of the model obtained from intrinsic viscosity data do not coincide with the values obtained from other properties of DNA in solution. Namely, $b/(1 + 4\beta) = 130$ nm has been found by comparison with sedimentation coefficient and light-scattering data.[8] Yamakawa and Fujii have also found a similar discrepancy in their analysis of the sedimentation coefficient and $[\eta]$ with the wormlike chain.[12,14]

The intrinsic viscosity is a property that depends strongly on excluded volume effects. Hence, a satisfactory fit of theory and experiment cannot be obtained unless excluded volume is somehow introduced in the theory. This fact is more clearly observed in Figure 1 where intrinsic viscosity values against molecular weight are represented. Figure 1 shows that the two adjusted parameters cannot completely describe the experimental dependence of $[\eta]$ on M. In fact, there is no pair of parameters able to predict the value 0.68 for the slope followed by experimental points in Figure 1. We have verified that theoretical curves cover just the range of values 0.55–0.60, and, therefore, it seems that only excluded volume can raise the theoretical slopes close to the experimental one. The excluded volume can be introduced in the intrinsic viscosity theory by use of an expansion parameter for the end-to-end distance.[22] In our case the parameter is defined by

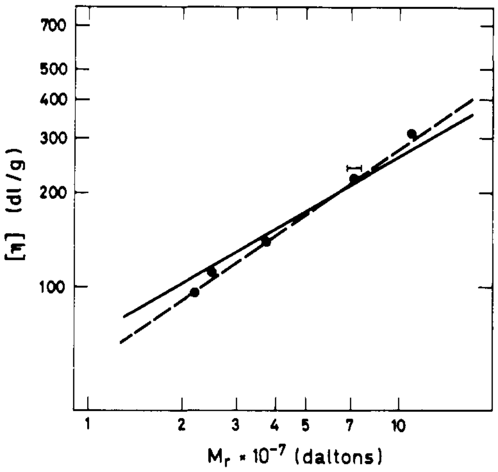

Figure 1. Intrinsic viscosity of DNA vs. molecular weight. Dots indicate experimental points from ref 9. The full curve represents theoretical values from eq 19 for $b/(1 + 4\beta) = 100$ nm and $\beta = -0.21$. The broken curve represents theoretical values from eq 24 (i.e., with excluded volume) for $b/(1 + 4\beta) = 50$ nm, $\beta = -0.22$, and $\epsilon' = 0.11$. (See text for discussion.)

$$\alpha_R^2 = \frac{N^{1+\epsilon'} + 2\beta/(1 + 4\beta)^{1/2}}{N + 2\beta/(1 + 4\beta)^{1/2}} \qquad (22)$$

where ϵ' is the excluded volume parameter, so that

$$\langle R_{ij}^2 \rangle = b^2(1 + 4\beta)^{-1}[|i - j|^{1+\epsilon'} + 2\beta/(1 + 4\beta)^{1/2}] \qquad (23)$$

It is possible to calculate $[\eta]$ from eq 23 if one follows the treatment first proposed by Bloomfield and Zimm[23] for the Rouse–Zimm theory and extended by Kumbar[18] for the Simon model. However, in order to make a first estimation of the excluded volume effect on $[\eta]$ in a simple way, we consider this effect restricted to a uniform expansion of the chain so that it can be appropriately described by substituting b by $\alpha_R b$ in eq 19. Thus

$$[\eta] = \frac{(\pi^3/3)^{1/2} N_A b^2}{4M_L} \alpha_R^2 N^{1/2} \sum_{k=1}^{N} (\lambda_k')^{-1} \qquad (24)$$

Comparisons between theoretical results from eq 22 and 24 and the experimental data[9] for DNA have been made by setting $\epsilon' = 0.11$[15,23] in eq 22. We obtain $b/(1 + 4\beta) = 50$ nm and $\beta = -0.22$. With these parameters, a satisfactory fitting between theoretical and experimental curves is achieved as is shown in Figure 1.

The new value for the statistical length is noticeably smaller than the one obtained in the previous section (without excluded volume). However, it closely agrees with the value of 54.2 nm found by Sharp and Bloomfield[16] for an excluded volume wormlike chain. A decrease of the statistical length caused by introduction of excluded volume is also observed in the study of the wormlike chain with experimental data of other properties.[15,17]

Noda[24] has also calculated the statistical length of the wormlike chain with small excluded volume interactions from intrinsic viscosity data of DNA. As he employs a perturbation method essentially different from that described here, his result cannot be equivalent to ours. In any case, he obtains the value 130 nm in strong disagreement with the rest of the convergent results from excluded volume theories discussed in the section.

The parameter β does not seem to be highly affected by excluded volume. However, our result does not correspond to the value of -0.14 reported earlier[8] from the sedimentation coefficient and light-scattering data. The high sensitivity of β to experimental error in $[\eta]$ was pointed out in the previous section. Something similar also happens to the other properties[8] and, therefore, we conclude that the discrepancies in β are at least consistent within the range of error for the experimental data.

It was shown in the Revision of Theoretical Expressions section how the approximate eigenvalues lose their accuracy as $|\beta|$ increases. In our calculations for $N = 50$, this effect becomes significant for $\beta \leq -0.10$. The values of N employed in the intrinsic viscosity calculations in the two previous sections are in all interesting cases much larger than 50, and, thus, exact diagonalization results are impractical. Fortunately, the accuracy of the approximate eigenvalues increases with N, and, therefore, they should be appropriate even for the region $\beta \leq -0.10$ where our final results are located. Nevertheless, slight errors in the approximate eigenvalues may contribute somewhat to uncertainty in the final value of the very sensitive parameter β.

In conclusion, the statistical length obtained in this work is very close to that extracted from the more realistic Yamakawa–Fujii theory. This fact indicates that the results given for the wormlike chain formalism can be reproduced by the Simon model in the high molecular weight range (extension of the Simon model to shorter chains can be done by exact diagonalization of eq 9). It seems, therefore, that this simple model can be usefully applied to other dynamical properties for which the wormlike coil treatment became difficult.

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Static and Dynamic Studies on the End-to-End Intrachain Energy Transfer on a Polysarcosine Chain[1]

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ABSTRACT: Polysarcosines having a terminal β-naphthylamide group and a terminal (dimethylamino)naphthalenesulfonyl (dansyl) group were synthesized by the NCA polymerization method, and the intramolecular energy transfer from the naphthylamide group to the dansyl was studied in ethanol solution. The efficiency of the energy transfer at the photostationary state was over 0.9 for short chains having the number average degree of polymerization $\bar{n}$ smaller than 7. The efficiency decreased with an increase in the chain length, but it was still as large as 0.33 at $\bar{n} = 60$. To explain these results, two different mechanisms were considered, i.e., static and dynamic transfer. The former occurs between an energy donor and an acceptor which are closer than a critical distance r_0 at the time of excitation. The latter occurs between a donor–acceptor pair which is well separated at the time of excitation and eventually becomes closer than r_0 by the chain motion during the lifetime of the donor-excited state. The efficiencies observed for long chains were much higher than those expected for the static transfer which were evaluated from a Monte-Carlo conformational calculation. The efficiency for the dynamic transfer was separately evaluated from the fluorescence decay rate of the terminal naphthylamide group. The sum of the efficiencies observed for dynamic transfer and calculated for static transfer was in good agreement with the total efficiency observed in the photostationary state.

Recently, much attention has been focused on the use of the fluorescence probe method for the study of the conformations of a polymer chain in solution.[2] The method may not only clarify general conformational properties of polymer chains but also become a powerful approach to the study of functions of biopolymers.[3,4] There are several advantages in the fluorescence method. (1) The high sensitivity enables measurement at high dilution, which is needed for the study of intramolecular interactions. (2) Most of the fluorescence probes do not interact with each other in their ground states and hence do not disturb the conformational equilibrium of polymer chains in solution, making it possible to observe their "native" properties. (3) The fluorescence quenching or the excimer (exciplex) formation is a typical diffusion-controlled process,[5,6] and study of these phenomena on a polymer chain provides information on the chain dynamics. The last point is in contrast to the study of chemical reactions or charge-transfer interactions on a polymer chain which provides equilibrium or a static property of the chain.

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