been observed previously by others.[30,31] Goodman and Rosen[30] found that cooligomers of γ-ethyl L-glutamate (ELG) and glycine exhibited no secondary structure ($b_0 = 0$) in trifluoroethanol, whereas the oligomers of ELG of comparable size showed considerable helix content ($b_0 = -165$ for a $\overline{DP}$ of 8). They attributed the effect of glycine to the ease of solvation of amide groups. Fraser, *et al.*,[31] noticed that the incorporation of glycine in a regular-sequence copolymer with ELG reduced the stability of the ELG helix, as detected by its effect on the solvent-induced helix–coil transition in a mixture of ethylene dichloride (EDC) and dichloroacetic acid (DCA). Block and Kay,[32] who studied block copolymers of glycine and γ-benzyl L-glutamate in the same solvent mixture, found that glycine residues at the ends of the block copolymer did not adopt the helical structure formed by the glutamate residues in the middle of the copolymer. This is in agreement with the low values of s found here for glycine. They[32] also studied random copolymers of these two monomers and observed a much higher helix content than they expected for a truly random copolymer; from this they concluded that their copolymers were not random, since they expected every glycine residue (including isolated ones) to be nonhelical. However, as shown here, in a *random* copolymer, isolated glycine residues (imbedded among strong helix-forming ones) can be forced to adopt a helical conformation (see Figure 10).

(D) Helix–Coil Transition in Organic Solvents. The random copolymers P(BzG:Gly) (samples II–VII) are soluble in mixtures of DCA and EDC. Hence, their thermal transitions in a 70/30 (w/w) DCA–EDC mixture (which are inverted ones[33] in this case) were examined, and will be reported in greater detail in a subsequent paper.[34] It was observed[34] that the thermal transition curves of these random copolymers are shifted to higher temperature with increasing glycine content, indicating that glycine is a helix breaker in this mixed solvent. An analysis for the σ and s values of polyglycine in this organic solvent,[34] and a comparison with the values of Table IV for water, should provide information about the influence of solvent on σ and s.

IV. Conclusion

In summary, we have synthesized water-soluble random copolymers containing glycine and hydroxybutylglutamine and studied their melting behavior in water. By applying the "host–guest technique"[3,4] for obtaining parameters for the "guest" amino acid (glycine), we have determined the Zimm–Bragg parameters s and σ for the coil-to-helix transition for polyglycine in water. The relatively low values of s and its temperature dependence have been found to agree with those predicted by Gō, *et al.*,[28] on the basis of conformational energy calculations. They also provide an explanation for the nonoccurrence of the α-helical form of polyglycine in water at normal temperatures. The implications of the finding that glycine acts as a strong helix breaker in water are discussed in connection with the analysis of protein conformation.

Acknowledgments. We are indebted to Mr. Hua Tjan for carrying out the nitrogen and amino acid analyses, to Mrs. Patricia von Dreele for helpful discussions, and to Mr. Peter Lewis for making available the computer program used to obtain the data of Figure 10.

(30) M. Goodman and I. G. Rosen, *Biopolymers*, **2**, 537 (1964).
(31) R. D. B. Fraser, B. S. Harrap, T. P. Macrae, F. H. C. Stewart, and F. Suzuki, *ibid.*, **5**, 251 (1967).
(32) H. Block and J. A. Kay, *ibid.*, **5**, 243 (1967).
(33) P. Doty and J. T. Yang, *J. Amer. Chem. Soc.*, **78**, 498 (1956).
(34) V. S. Ananthanarayanan, E. Leroy, R. H. Andreatta, and H. A. Scheraga, manuscript in preparation.

A Theory of the Rate of Conformational Change of Isotactic Poly(α-olefin) Molecules in Solution

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ABSTRACT: A theory of the effect of hydrodynamic interaction on the uncoiling of isotactic poly(α-olefins) in solution is given. The quantity calculated is the optical rotation in a temperature-jump experiment. The model uses Kramers' theory for the escape of particles over potential barriers and neglects cooperative interactions. As an example, the optical activity change of poly((*S*)-4-methyl-1-hexene) resulting from a temperature jump is predicted.

The rate of conformational change in molecules is a subject of considerable interest. For small molecules these rates depend on properties of neighboring atomic groups and bonds and on solute–solvent interactions. In macromolecules, they may depend, in addition, on the degree of polymerization.

A case of particular interest is the rate of unwinding of spiraled macromolecules. For example, a number of authors have considered, theoretically, the rate of unwinding of the double helix of DNA. In this paper we wish to consider a somewhat simpler case, that of isotactic poly(α-olefins). These molecules exist in solution primarily as helices because of steric factors. They were chosen for study because they are, at least in first approximation, free of complicating long-range cooperative interactions, and because their conformational changes are amenable to convenient experimental study, in many cases, through monitoring their optical activity.

The paper is organized as follows. Section I discusses the model and solves the problem formally. Section II concerns the rotatory friction coefficients which enter the solution. Section III presents the final results and Section IV is a discussion.

Simply stated, the problem is: do short molecules unwind more rapidly than large ones? Do the centers of molecules unwind more slowly than the ends? This paper considers the effects of hydrodynamic interactions on the answers to these questions.

I. The Model

Equilibrium studies have shown that the minimum energy conformation for isotactic polymers is helical.[1] In solution[2] the backbone of the molecule is supposed to consist of alternating segments of left and right chirality, with side groups assuming conformations consonant with the main-chain spiral sense. If there is an asymmetric center in the side group, then a different set of conformations will be favored when the main chain is in a left-handed spiral than when it is in a right-handed one.[3,4] The preference for a given conformation can be described in terms of a free energy difference, ΔE, between the favored and unfavored spiral sense of a given monomer. If p_+ and p_- are the probabilities of occurrence of a favored or unfavored monomer conformation, respectively, then

$$\Delta E = kT \ln (p_+/p_-) \tag{1}$$

where

$$P_\pm = \frac{\sum_{\{n_\pm\}} \exp(-E_{n_\pm}/kT)}{\sum_{\{n_+\}} \exp(-E_{n_+}/kT) + \sum_{\{n_-\}} \exp(-E_{n_-}/kT)} \tag{2}$$

E_{n_+} and E_{n_-} are the energies of a side group in conformations n_+ and n_-, respectively, and the sums indicated are over all conformations possible when the main chain is in the favored (+) or unfavored (−) spiral sense. If the side group has no asymmetries, then E_{n_+} and E_{n_-} would be equal and there would be no favored chirality for the molecule. Let us note that E is really a free energy and is largely entropic in origin.

In general, it is difficult to estimate the conformation energies. However, Luisi and Pino[4] have found suitable values of ΔE for the particular molecule poly((*S*)-4-methyl-1-hexene). A more complete discussion may be found in their paper.

At the intersection of segments with opposing chirality, the normal conformations are changed and there is a resulting junction energy, ΔU, defined as

$$2\Delta U = (E_{+-} + E_{-+}) - (E_{++} + E_{--}) \tag{3}$$

where E_{++} and E_{--} are the energies of monomer pairs with favored and unfavored chirality, while E_{+-} and E_{-+} are the energies of junction pairs. Although E_{+-} and E_{-+} need not be equal, use of the average value for ΔU is proper since on the average there must be an equal number of (+−) and (−+) junctions. Since ΔU is due to close-in interactions, it is relatively independent of a particular molecule. Values of ΔU are given by Luisi and Pino.[4]

One should note that Luisi and Pino[4] have alternatively defined ΔE in terms of the pair energies.

$$2\Delta E = (E_{++} - E_{--}) \tag{4}$$

(1) G. Natta and F. Danusso, "Stereoregular Polymers and Stereospecific Polymerizations," Pergamon Press, Oxford, 1967; T. M. Birshtein and O. B. Ptitsyn, "Conformations of Macromolecules," Interscience, New York, N. Y., 1966.

(2) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Montagnoli, *Makromol. Chem.*, **61**, 207 (1963).

(3) P. Pino and P. L. Luisi, *J. Chim. Phys. Physicochim. Biol.*, **65**, 130 (1968).

(4) P. L. Luisi and P. Pino, *J. Phys. Chem.*, **72**, 2400 (1968).

TABLE I
PROPERTIES

	++	−−	+−, −+
Index, γ	1	2	3
Relative energy, E_γ	0	$2\Delta E$	$\Delta E + \Delta U$
Optical activity, M_γ	$2M_+$	$2M_-$	$M_+ + M_-$
Equilibrium probability, a_γ	Z^{-1}	$Z^{-1} \exp(-2\Delta E/kT)$	$2Z^{-1}[-(\Delta U + \Delta E)/kT]$

They have also been able to account for the optical activity of the isotactic poly(α-olefins) by associating monomeric optical activities M_+ and M_- with the favored and unfavored conformations using Brewster's rules.[5]

$$\langle M \rangle = M_+ p_+ + M_- p_- \tag{5}$$

The monomeric optical activities depend, of course, upon the particular molecule in question. Values of M_+ and M_- have been given[4] for poly((*S*)-4-methyl-1-hexene).

The present work describes a model for the rate of change of polymeric configurations suggested by the above-mentioned equilibrium studies.[1-4] The conformational change is caused by perturbation from equilibrium—a temperature jump—and can be monitored, but not affected, by measurements of the optical activity as the system advances toward its new equilibrium state.

Consider the three conformations which a pair of monomers may exhibit: (1) both of favored chirality, ++; (2) both of unfavored chirality, −−; (3) each of a different chirality, +− or −+. Relative energies E_γ and optical activities M_γ may be associated with each of these pairs, and equilibrium probabilities a_γ may be computed. The results are displayed in Table I. In Table I, Z_T is the partition function

$$Z_T = 1 + \exp(-2\Delta E/kT) + 2\exp(-[\Delta U + \Delta E]/kT) \tag{6}$$

The factor 2 in a_3 is the statistical weight due to the possibility of +− and −+ pairs. Although the assignment of M_+ or M_- to M_3 may not be exact, since the conformations occupied by the side groups in a junction pair are not necessarily those in a nonjunction pair, it will be used as a reasonable approximation. Both a_3 and M_3 are much smaller than the other values of a_γ and M_γ, and the error introduced by this procedure is small. Possible end effects on the chain conformation are also neglected.

Let $a_\gamma(N, l, t)$ be the probability that pair l of a polymer with N monomers is in form γ at time t. Then

$$\sum_\gamma a_\gamma(N, l, t) = 1 \tag{7}$$

and the optical activity per monomer at time t is

$$\langle M(t) \rangle = \frac{1}{2(N-1)} \sum_{l=1}^{N-1} \sum_\gamma a_\gamma(N, l, t) M_\gamma \tag{8}$$

If the probability of transition of pair l on an N-length polymer from form γ to form κ is $P_{\gamma\kappa}(N, l)$, then the rate of change in $a_\gamma(N, l, t)$ is

$$\dot{a}_\gamma(N, l, t) = \sum_{\kappa \pm \gamma} [-a_\gamma(N, l, t) P_{\gamma\kappa}(N, l) + a_\kappa(N, l, t) P_{\kappa\gamma}(N, l)] \tag{9}$$

This is the usual gain-loss equation, or master equation, and is based on the assumption that each pair is independent.

(5) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).

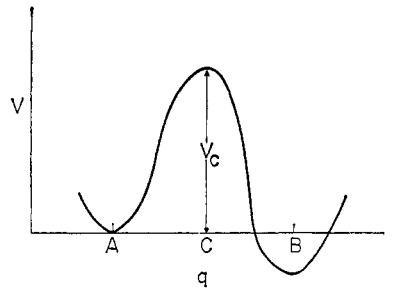

Figure 1. Potential energy curve, schematic.

Since a direct transition between pairs ++ and −− is impossible, $P_{21}(N, l) = P_{12}(N, l) = 0$ and eq 7 and 9 may be combined to give

$$\dot{\mathbf{a}}(N, l, t) \equiv \begin{pmatrix} \dot{a}_1 \\ \dot{a}_2 \end{pmatrix} = \begin{pmatrix} P_{31} \\ P_{32} \end{pmatrix} - \mathbf{C}_{N,l} \cdot \mathbf{a}(N, l, t) \quad (10)$$

where

$$\mathbf{C}_{N,l} = \begin{pmatrix} 2P_{13}(N, l) + P_{31}(N, l) & P_{31}(N, l) \\ P_{32}(N, l) & 2P_{23}(N, l) + P_{32}(N, l) \end{pmatrix} \quad (11)$$

The solution to eq 10 is

$$\mathbf{a}(N, l, t) = \mathbf{a}(N, l, \infty) + e^{-\mathbf{C}_{N,l}t}[\mathbf{a}(N, l, 0) - \mathbf{a}(N, l, \infty)] \quad (12)$$

Combining eq 8 and 12 gives

$$\langle M(t) \rangle = {}^1/_2(M_+ + M_-) + {}^1/_2(M_+ - M_-)b(t) \quad (13)$$

with

$$b(t) = \frac{1}{N-1} \sum_{l=1}^{N-1} [a_1(N, l, t) - a_2(N, l, t)] \quad (14)$$

Thus if the transition probabilities $P_{\gamma\kappa}(N, l)$ were known, then the behavior of the optical activity could be calculated.

II. Transition Probabilities and the Rotatory Friction Coefficient

The various transition probabilities are related at equilibrium by

$$P_{13}(N, l) = \frac{a_3}{a_1} P_{31}(N, l) = \exp(-(\Delta U + \Delta E)/kT) P_{31}(N, l) \quad (15a)$$

$$P_{23}(N, l) = \frac{a_3}{a_2} P_{32}(N, l) = \exp(-(\Delta U - \Delta E)/kT) P_{32}(N, l) \quad (15b)$$

assuming that, at equilibrium, the probability of occupation of a given form is independent of the chain length or bond position.

We shall apply Kramers' theory[6] for the escape of a particle over a potential barrier to these transitions. Under the conditions of sufficiently high barriers and long enough times, Kramers' theory gives

$$P_{\gamma\kappa}(N, l) = \frac{\omega_A \omega_C}{2\pi\rho(N, l)} \exp(-V_C/kT) \quad (16)$$

(6) H. A. Kramers, *Physica*, 7, 284 (1940). Kramers' theory has been previously applied to a polymer conformational problem in a different context (dielectric relaxation in molten polymers) by Y. Y. Gotlib, *J. Polym. Sci., Part C*, No. 16, 3365 (1968), and by E. Helfand, private communication.

where $\rho(N, l)$ is the friction coefficient for the transition involved and the factor $(2\pi)^{-1}\omega_A\omega_C \exp(-V_C/kT)$ is an energy term due to a potential which may be written as $V(q) \approx ({}^1/_2)\omega_A q^2$ near the initial minimum at A and as $V(q) \approx V_C - ({}^1/_2)\omega_C(q - q_C)^2$ near the barrier at C shown in Figure 1.

Since accurate potential energy surfaces are not available, it is necessary to estimate the values of the energy barrier for the particular molecule in question. The barrier should, however, be independent of chain length and bond position and only weakly dependent on the side group involved. Further, for isotactic poly(α-olefins), the transitions from form 3 to forms 1 or 2 are very similar. Assuming the energy factors equal gives

$$P_{31}(N, l) = P_{32}(N, l) = P'/\rho(N, l) \quad (17)$$

where

$$P' = \frac{\omega_A\omega_C}{2\pi} \exp(-V_C/kT) \quad (18)$$

The friction coefficient $\rho(N, l)$ can be treated at different levels of approximation. We consider here several cases. In case a, $\rho(N, l) = \rho_{0a}$. The friction coefficient is constant. Although unphysical, this model has mathematical simplicity. For case b, $\rho(N, l) = \rho_{0b}g_b(N)$. The friction coefficient is proportional to some function of the chain length $g_b(N)$. This is the form taken by the free draining model. Internal hydrodynamic interactions are neglected and $\rho(N, l)$ is independent of bond position l. In case c, $\rho(N, l) = \rho_{0c}h(N, l)$. The friction coefficient is proportional to some function of both chain length and bond position. This is a physically realistic but mathematically more complex form.

Let us consider case c in more detail. An approximation to $\rho(N, l)$ can be obtained through an observation by Riseman and Kirkwood:[7] according to molecular theories, the rotatory friction coefficient ρ is related to the intrinsic viscosity $[\eta]$ by the equation

$$\rho = 100\gamma(M/L_0)\eta_0[\eta] \quad (19)$$

where M is the molecular weight of the polymer, L_0 is Avogadro's number, η_0 is the solvent viscosity, and γ is a constant dependent on molecular geometry which has the values 2, 2.4, and 4 for rigid rods,[7] spheres,[7] and flexible[8] molecules, respectively. Using $[\eta] = KM^{1/2}$ to relate the intrinsic viscosity to the chain size (or $[\eta] = \alpha^3 K M_0^{1/2}\eta^{1/2}$ in a non-θ solvent, where α is a measure of the deviation from ideality of the root-mean-square chain length, $\alpha = \langle r^2 \rangle^{1/2}/\langle r_0^2 \rangle^{1/2}$, and $M = nM_0$, where M_0 is the molecular weight of a monomer unit and n is the number of monomers in the particle), eq 19 becomes

$$\rho_n = (\alpha^3)100\gamma(M_0^{3/2}/L_0)\eta_0 K n^{3/2} \quad (20)$$

for the rotatory friction coefficient of a particle of length n.

To evaluate $\rho(N, l)$, the rotatory friction coefficient for motion about bond l of an N-length polymer, a simple model was used. Since no external torques are involved, the mean center of mass rotation is zero. Hence

$$\omega_l I_l - \omega_{N-l} I_{N-l} = 0 \quad (21)$$

where ω_l and I_l are the angular velocity and moment of inertia of the chain segment with length l. The quantity of interest is the relative velocity $\omega = \omega_l - \omega_{N-l}$ which is proportional to the total torque exerted on the fluid

(7) J. Riseman and J. G. Kirkwood, *J. Chem. Phys.*, **18**, 512 (1950).
(8) J. Riseman and J. G. Kirkwood, *ibid.*, **17**, 442 (1949).

$$T = \rho(N, l)\omega = \rho_l|\omega_l| + \rho_{N-l}|\omega_{N-l}| \quad (22)$$

Combining eq 21 and 22 gives

$$T = \left(\frac{\rho_l I_{N-l} + \rho_{N-l} I_l}{I_{N-l} + I_l}\right)\omega = \rho(N, l)\omega \quad (23)$$

The moment of inertia of a flexible polymer is proportional to the square root of its length. Thus, taking $I_l = \beta l^{1/2}$ and ρ_l defined by eq 20 gives

$$\rho(N, l) = 100\alpha^3\gamma\frac{M_0^{3/2}}{L_0}\eta_0 K N^{3/2}\left[\left(\frac{l}{N}\right)\left(1 - \frac{l}{N}\right)\right]^{1/2} \quad (24)$$

which has the form

$$\rho(N, l) = \rho_{0\infty}g_{0\infty}(N)h_{0\infty}(l/N) \quad (25)$$

Equation 25 is the approximation for the friction coefficient in case c which we shall use. Most of the hydrodynamic interaction has been accounted for semiempirically through the use of eq 19, although the interactions between the two parts of the model in relative rotation have been neglected.

III. Results

Using eq 15 the matrix $\mathbf{C}_{N,l}$ becomes

$$\mathbf{C}_{N,l} = \frac{P'}{\rho(N, l)} \times \begin{pmatrix} 1 + 2\exp(-(\Delta U + \Delta E)/kT) & 1 \\ 1 & 1 + 2\exp(-\Delta U - \Delta E)/kT) \end{pmatrix} \quad (26)$$

which may be used in eq 12 to give

$$b(t) = A_0 + A_1\left[\frac{1}{N-1}\sum_{l=1}^{N-1} e^{-\lambda_{+Nl}t}\right] + A_2\left[\frac{1}{N-1}\sum_{l=1}^{N-1} e^{-\lambda_{-Nl}t}\right] \quad (27)$$

where

$$A_0 = a_1 - a_2 \quad (28a)$$

$$A_1 = (\Delta a_1 + \mu\Delta a_2)\left(\frac{1-\mu}{1+\mu^2}\right) \quad (28b)$$

$$A_2 = (\mu\Delta a_1 - \Delta a_2)\left(\frac{1+\mu}{1+\mu^2}\right) \quad (28c)$$

$$\Delta a_\gamma = a_\gamma(T_0) - a_\gamma(T) \quad (29)$$

$$\mu = (e^{-(\Delta U-\Delta E)/kT} - e^{-(\Delta U+\Delta E)/kT}) + \{1 + (e^{-(\Delta U-\Delta E)/kT} - e^{-(\Delta U+\Delta E)/kT})^2\}^{1/2} \quad (30)$$

and $\lambda_{\pm Nl}$ are the eigenvalues of $\mathbf{C}_{N,l}$

$$\lambda_{\pm Nl} = \frac{P'}{\rho(N,l)}[1 + e^{-(\Delta U-\Delta E)/kT} + e^{-(\Delta U-\Delta E)/kT} \pm \{1 + (e^{-(\Delta U-\Delta E)/kT} - e^{-(\Delta U+\Delta E)/kT})^2\}^{1/2}] \quad (31)$$

Equation 12 could also have been solved if the approximation in eq 15 were not used, that is, for a nonsymmetric $\mathbf{C}_{N,l}$.

The results obtained may be most easily compared to experiment by casting eq 13 into the form

$$\frac{\langle M(t)\rangle - \langle M(\infty)\rangle}{\langle M(0)\rangle - \langle M(\infty)\rangle} = \frac{A_1}{A_1 + A_2}\left[\frac{1}{N-1}\sum_{l=1}^{N-1} e^{-\lambda_{+Nl}t}\right] + \frac{A_2}{A_1 + A_2}\left[\frac{1}{N-1}\sum_{l=1}^{N-1} e^{-\lambda_{-Nl}t}\right] \quad (32)$$

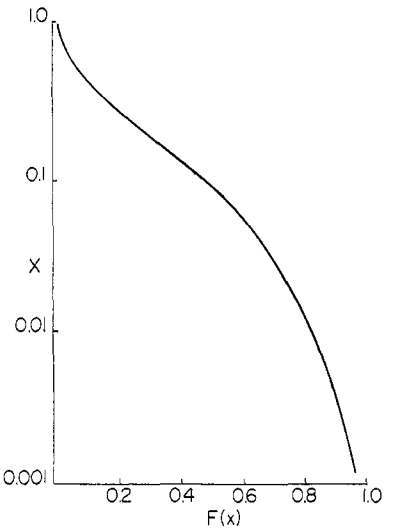

Figure 2. $F(x)$ as a function of x.

The left-hand side of eq 32 consists of measurable experimental quantities, while the right-hand side is the corresponding theoretical expression derived above for the normalized time-dependent behavior of the optical activity.

The frictional coefficients occur only in the λ factors in the exponents. Therefore, the time dependence of the optical activity ought to be a fairly sensitive test of the approximation used for $\rho(N, l)$. In particular, for cases a and b above, there is no l dependence of λ, and one merely has a sum of two exponentials. We shall concentrate on case c.

In case c we can write

$$\frac{\langle M(t)\rangle - \langle M(\infty)\rangle}{\langle M(0)\rangle - \langle M(\infty)\rangle} = \frac{A_1}{A_1 + A_2}F(\sigma_+ Rt) + \frac{A_1}{A_1 + A_2}F(\sigma_- Rt) \quad (33)$$

where

$$\sigma_\pm = \lambda_{\pm Nl}/P(N, l) \quad (34)$$

which, by (25) and (31), is independent of l. The function $F(x)$ is given by

$$F(x) = \frac{1}{N-1}\sum_{l=1}^{N-1}\exp(-x/h(l/N)) \quad (35)$$

and R is given by $P'\rho_{0\infty}g_{0\infty}$ (see eq 25).

We have computed the function $F(x)$ for various values of N and x by direct summation. It was found to approach its asymptotic form quickly, as N increases. Its limiting values are 1 and 0 as x goes from 0 to ∞, and in the physically interesting region where $F(x)$ changes rapidly, the values for $N = 25$ are within 5% of those for $N = 1000$. By $N = 100$, the difference is within 1%. Since it is necessary to choose $N \geq 30$ for the average optical activity per monomer to be independent of the chain length, the asymptotic values may be used. $F(x)$ for $N = 1000$ is given in Table II and Figure 2.

The results in eq 33 and 34 are given in terms of the scaling parameters $\sigma_\pm$ and R. The difficulties in choosing accurate values for P' and ρ can thereby be circumvented by initializing the values experimentally with a given molecular weight sample and then comparing results for samples of different molecular weights. Thus if eq 25 were a good approximation for $\rho(N, l)$, then results for samples of different molecular weights should all fit on the same curve if the time scale were adjusted by the factor $(N/N_0)^{3/2}$.

TABLE II
THE FUNCTION $F(x)$

x	$F(10^{-3}x)$	$F(10^{-2}x)$	$F(10^{-1}x)$
1	0.962	0.839	0.464
2	0.940	0.761	0.293
3	0.922	0.702	0.196
4	0.907	0.654	0.134
5	0.893	0.613	0.094
6	0.881	0.577	0.066
7	0.869	0.544	0.047
8	0.858	0.515	0.034
9	0.848	0.488	0.024

To illustrate the predicted behavior, the necessary parameters were estimated for the molecule poly((*S*)-4-methyl-1-hexene) undergoing a 10° temperature jump from 290 to 300°K. The results are shown in Figure 3. Case b is characterized by linear behavior, while case c gives a convex curve in the semilogarithmic plot chosen. In both cases a value of $R = 10^{-2}$ sec^{-1} was used, being a result of typical choices of the parameters $\alpha \sim 1$–2, $\gamma \sim 2$–4, $K \sim 0.001$–0.002 dl g^{-1} (g mol wt)$^{-1/2}$ for similar isotactic molecules,[9] and $\eta_0 \sim 0.5$–2 cP with a chain length $N = 100$ and a guessed value of 10^{-24} kcal for P'.

IV. Discussion

The results presented in section III can be compared with experimental measurements to indicate the dependence of the friction coefficient upon chain length and bond position. Hydrodynamic interactions between different chain elements are included, but cooperative phenomena are not. Thus a zipper-type of motion might be partially treated using this model, whereas motion involving compensatory counter-rotations which propagate a change down the chain would not.

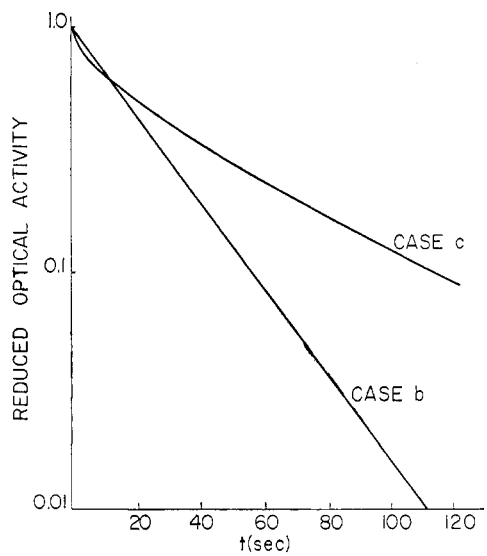

Figure 3. Reduced optical activity $[\langle M(t)\rangle - \langle M(0)\rangle]/[\langle M(\infty)\rangle - \langle M(0)\rangle]$ as a function of time for $R = 10^{-2}$ sec^{-1}.

(9) P. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.

The approach used to describe the optical activity behavior is essentially an independent-pair approximation for the Ising model. Time-dependent models displaying the effect of cooperative interactions between chain elements on conformational changes in polymers have been treated by a number of authors.[10] These papers neglect the effect of hydrodynamic interactions. Our work, on the other hand, drastically oversimplifies the cooperative character of the chain, but treats hydrodynamic interaction at least approximately. It would certainly be desirable to have a unified treatment of these two effects, but, to our knowledge, such a treatment has not yet been developed.

Although poly((*S*)-4-methyl-1-hexene) is used in section III as a convenient illustration of the behavior discussed, eq 32 is applicable without change to any optically active poly(α-olefin) for which ΔU and ΔE are known. ΔU is assumed to be equal for all of the polymers in question[4] and ΔE may be approximated by

$$\Delta E = kT \ln (\nu_+/\nu_-) \tag{36}$$

where ν_+ and ν_- are the number of conformations available to the side groups when the main chain is in the + or − spiral sense. Although this approximation is not good over a large temperature range,[4] it may prove useful here. Values of ν_+ and ν_- are given in ref 3 for several optically active poly(α-olefins). Behavior of other optically active polymers might be described by adjusting the value of ΔU.

The use of the scaling factor R permits the data to be unified. It also obviates the necessity of knowing accurate values for the various constants involved. Should case b prove applicable, which is unlikely, then the function $g_b(N)$ can be fit by adjustment of the time scales for different choices of N. This would indicate the relative friction coefficient of long and short chains. Any nonlinear behavior of the experimental values for eq 32 would indicate that the N and l dependences are both significant. The specific form used in eq 34 is one possible approximation to this function. Since, in particular, $\rho(N, l)$ is smaller for l/N near 0 and 1 than for l/N near $1/2$, the ends of the chain, in this model, may be said to move more freely than the centers, as one would expect physically.

Should our prediction turn out not to agree with experiment, one might suspect either our neglect of cooperative effects or our approximation to the rotatory friction constant to be at fault. In this event, we should suspect the neglect of cooperative rotations to be the major culprit, and suggest that this is the direction in which an attempt at major refinement of the theory should turn.

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