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Optical Rotatory Properties of Vinyl Polymers[1]

Akihiro Abe

Contribution from the Central Research Laboratory, Showa Denko Company, Tamagawa, Ohta-ku, Tokyo, Japan. *Received September 25, 1967*

Abstract: The conformational analysis of optically active poly-α-olefins such as poly-(*S*)-3-methyl-1-pentene, poly-(*R*)-3,7-dimethyl-1-octene, poly-(*S*)-4-methyl-1-hexene, poly-(*S*)-5-methyl-1-heptene, and poly-(*S*)-6-methyl-1-octene is presented. Polymer chains of various tacticities are treated in the rotational isomeric state approximation, in consideration of the steric interactions between nonbonded groups separated by three and by four C–C bonds. Proper account of the side-chain conformations is shown to be essential in each instance. Optical activities of these polymers are evaluated within the framework of the revised version of the Whiffen–Brewster empirical rule. It is shown that the optical rotatory power of a polymer having asymmetric sites in the α or β position with respect to the main chain is large and nearly insensitive to the stereochemical arrangements of the chain units. When the asymmetric center in the side chain is situated at the γ or a farther position, however, we anticipate quite a remarkable dependence of the rotatory power on stereoregularity. Comparison with the experimental observations suggests that the stereoregularity of the allegedly isotactic samples used in the experiments may have been somewhat less than perfectly isotactic. Within the reasonable range of conformational energies, the calculated temperature coefficients of the optical rotations show satisfactory agreement with observations. Asymptotic behavior of the optical rotation with degree of polymerization is also discussed.

The optically active poly-α-olefins were prepared and studied independently by Bailey and Yates,[2] Pino and coworkers,[3-5] Murahashi, Nozakura, and coworkers,[6] and Goodman, *et al.*[7] Various features characteristic of these polymer systems were recently reviewed by Schulz and Kaiser,[8] Pino,[9] and Goodman, Abe, and Fan.[10] The observed optical rotatory powers of poly-α-olefins having asymmetric sites located at the α or β portion with respect to the main chain were much greater than those of low molecular weight model compounds. Polymers with optically active centers at the γ or δ position were prepared by Pino, *et al.*[3-5] They found in a series of investigations that the optical activity enhancement of the polymer decreases rapidly as the number of carbon atoms between the asymmetric center and the polymer backbone chain exceeds two. Optical rotatory dispersions of these polymers in various organic solvents were all found to fit the simple one-term Drude plot.[5-7] Studies of the effect of temperature upon optical rotation[4-7] showed that the temperature coefficients of molar optical rotation $\Delta[\mathrm{M}]/\Delta T$ of the stereoregular polymers are negative and their magnitudes are much larger than those of low molecular weight analogs. Here [M] is defined for a polymer as the optical activity per monomeric residue. However, no temperature effect has been observed on the absorption maximum of the chromophore as estimated graphically from the Drude's relation.[7] It has been also noted that while the ratio $\Delta[\mathrm{M}]/\Delta T$ increases

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[1] Presented at the Symposium on Macromolecular Chemistry, Tokyo, 1966.

[2] W. J. Bailey and E. T. Yates, *J. Org. Chem.*, **25**, 1800 (1960).

[3] P. Pino, G. P. Lorenzi, and L. Lardicci, *Chim. Ind.* (Milan), **42**, 712 (1960).

[4] P. Pino and G. P. Lorenzi, *J. Am. Chem. Soc.*, **82**, 4745 (1960); P. Pino, G. P. Lorenzi, L. Lardicci, and F. Ciardelli, *Vysokomolekul. Soedin.*, **3**, 1597 (1961).

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

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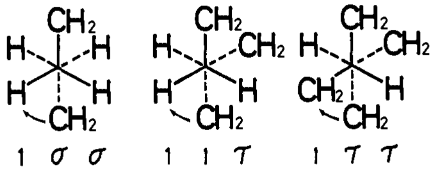
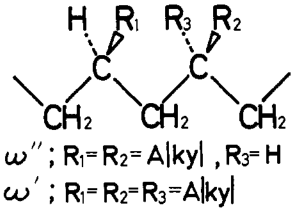
[8] R. C. Schulz and E. Kaiser, *Fortschr. Hochpolymer-Forsch.*, **4**, 236 (1965).

[9] P. Pino, *ibid.*, **4**, 393 (1965).

[10] M. Goodman, A. Abe, and Y.-L. Fan, "Macromolecular Reviews," Vol. I, A. Peterlin, *et al.*, Ed., Interscience Publishers, Inc., New York, N. Y., 1966.



(a) Three Bond Interaction



(b) Four Bond Interaction

Figure 1. Conformational statistical weight factors in consideration of nonbonded interactions.

by decreasing the wavelength, the ratio $(1/[M])(\Delta[M]/\Delta T)$ remains almost constant over a wide range of wavelength.[7] Essentially the same behavior has been reported in the study of the optically active poly(vinyl ethers)[11] and polyaldehydes.[12]

On the basis of these observations, the present author and Goodman[12] have previously suggested that the large optical rotatory enhancement of these polymers arises from the conformational rigidity around the asymmetric centers. The secondary optical rotatory contribution due to the asymmetry of the isotactic helical section of the polymer backbone cannot be very important. In fact, when Brewster's empirical rule,[13] which has proved to be quite useful for the low molecular weight paraffinic hydrocarbons, is applied,[5] the calculated optical activities corresponding to the most probable conformations of an isotactic poly-α-olefin agree with the experimental values in the case of poly-(*S*)-3-methyl-1-pentene, poly-(*R*)-3,7-dimethyl-1-octene, and poly-(*S*)-4-methyl-1-hexene. The agreement is rather poor, however, for such polymers as poly-(*S*)-5-methyl-1-heptene and poly-(*S*)-6-methyl-1-octene.

On the other hand, recent developments in theory[14,15] permit theoretical treatments of polymer chain conformations in the rotational isomeric state approximation.[16] Especially an advanced technique developed by Flory and Jernigan[15] beautifully avoids the limitations inherent to the previous eigenvalue method. Above all, the former is valuable in its applicability to polymer chains having any specified stereosequence. Application of these methods to the real polymer systems has been successful in correlating various observations to theory.[17,18] Lately Birshtein and Luizi[19] and Allegra, Corradini, and Ganis[20] independently discussed the conformational asymmetry characteristic of polymers with asymmetric centers in the side chains. The observed optical activity enhancement of isotactic polymers[2-7] was attributed to the existence of one sense of helix in preference to the other.

The purpose of this paper is to present a more detailed conformational analysis of optically active poly-α-olefins. Polymers such as those mentioned above are treated with proper account of the main-chain and side-chain conformations. Since the pendant groups in these polymer systems are so bulky that they confer rigidity on the main chain,[18] the statistical average must be taken over all conformations of both the backbone and the side chain.

General Treatment of Vinyl-Chain Conformations

Conformational Statistical Weight Factors. Throughout the present paper, we adhere to the three rotational isomeric state scheme. The three states t, g^+, and g^- are considered to occur at the rotation angles of 0, $2\pi/3$, and $4\pi/3$, respectively. The relative stability among these states largely depends on the extent of steric restraints inflicted by nearby groups. The spatial interactions here considered are the three-bond and four-bond interactions as defined in our previous paper.[21] While the former depends on the rotation about a single C–C bond, the latter involves interactions dependent upon two consecutive bond rotations.

As examination of models indicates, the stereochemical arrangements shown in Figure 1 can be taken as the elemental structural units for the hydrocarbon polymer systems where our interests in the foregoing treatments are focused. The three-bond interactions shown in Figure 1a are all considered to be in the *trans* state. The clockwise rotation about the rear carbon as indicated by the arrow successively yields the g^+ and g^- rotational states. The associated statistical weight factors, normalized to a weight of unity for the lowest energy state, are given in the order t, g^+, and g^- under each diagram. The experimental value of *ca.* 500 cal mole^{-1} for the energy difference between the *trans* and *gauche* states of lower *n*-alkanes[22-24] has been widely accepted.[21,25] Thus, $-RT \ln \sigma \cong 500$ cal mole^{-1}.

Conformations of 2-methylbutane and 2,3-dimethylbutane have been studied by spectroscopic[26] and thermodynamic methods.[27] Both measurements are in agree-

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(18) P. J. Flory, J. E. Mark, and A. Abe, *J. Am. Chem. Soc.*, **88**, 639 (1966).

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(23) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); W. B. Person and G. C. Pimentel, *J. Am. Chem. Soc.*, **75**, 532 (1953).

(24) The free-energy difference for the gaseous *n*-alkanes is estimated to be *ca.* 600 cal mole^{-1} by K. Kuchitsu, *J. Chem. Soc. Japan*, **32**, 748 (1959), and by L. S. Bartell and D. A. Kohl, *J. Chem. Phys.*, **39**, 3097 (1963).

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(26) J. K. Brown and N. Sheppard, *J. Chem. Phys.*, **19**, 976 (1951).

(27) D. W. Scott, J. P. McCullough, K. D. Williamson, and G. Waddington, *J. Am. Chem. Soc.*, **73**, 1707 (1951).

ment for 2,3-dimethylbutane. A very small, approximately zero energy difference was observed between the rotational isomers, suggesting the statistical weight parameter $\tau \cong 1$ for this compound. The energy difference between the two conformers of 2-methylbutane, however, has not been clearly understood. Scott, *et al.*,[27] suggested that the difference would possibly amount to several kilocalories per mole from thermodynamic measurements. Brown and Sheppard,[26] on the other hand, stated that the observed simplification of the Raman spectrum on solidification does not rule out the possibility of two coexisting isomers in the liquid state. Calculations of conformational energies[18,21] in consideration of the torsional potentials intrinsic to C–C bonds and the short-range interactions between nonbonded groups indicate the corresponding energy difference to be of the order of 1 kcal mole^{-1}. In view of these divergent results among different methods, we may only assume $0 < \tau < \sigma$ for 2-methylbutane at variance with the τ deduced for 2,3-dimethylbutane. As the succeeding developments will show, however, it is inconsequential to distinguish between these two τ's. Confining attention to the polymer systems under consideration, only the 2-methylbutane-like τ becomes important.

Four-bond interactions depicted in Figure 1b manifest high steric conflicts between R_1 and R_2 groups. The statistical weight factors ω' and ω'' were previously[28] introduced in those cases where the repulsive four-bond interactions are alleviated by adjustment of one and both rotation angles, respectively, about the pair of consecutive bonds. Consequently the positions of the potential energy minima should be largely displaced from those of the threefold symmetry.[18,21] The energy of *ca.* 2 kcal mole^{-1} for $E_{\omega''} = -RT \ln \omega''$ has been derived[21] from the conformational calculations and also from the analysis of the observed data on the unperturbed end-to-end distance of polyethylene chain. The conformation designated with ω' should involve much higher interaction energy. Proper bond rotation about CHR_1–CH_2 of Figure 1b may bring R_1 away from the highly repelling R_2. However, the three-bond interaction between the CH, which carries R_1, and R_3 becomes quite repulsive when R_3 is larger than H, and this therefore compensates the effect of mitigation of the four-bond interaction between R_1 and R_2.

Configurational Partition Function in Consideration of Side-Chain Conformations. Vinyl polymer systems such as shown in Figure 2 have been treated previously.[18] Statistical weight matrices U' and U'' were introduced to represent the polymer main-chain conformations about bonds like i and $i + 1$, respectively. The stereochemistry of the asymmetric –CHR– groups in the polymer backbone requires distinction between U_d' and U_l' for bond i, and that between U_{dd}'', U_{ld}'', U_{dl}'', and U_{ll}'' for bond $i + 1$. Here the subscripts d and l are used to specify the spatial arrangements of substituents on the participating tertiary carbon atoms. Each of these U'' matrices includes the effect of stereochemical arrangements of two neighboring asymmetric centers and is endowed with double subscripts. According to the previous definition,[18] a portion of a vinyl chain shown in Figure 2, for example, should be read as -*ddld*- when viewed from left to right.

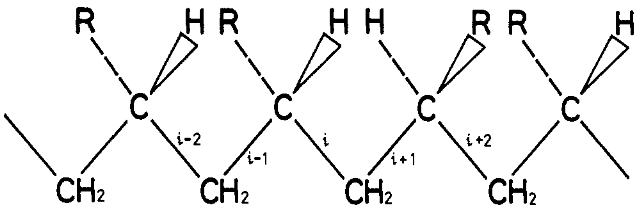

Figure 2. Schematic view of a vinyl chain in its planar *trans* conformation.

Since we assume pairwise dependent potentials for the bond rotation, the conformational statistical weights associated with a given bond may be arranged in a 3 × 3 square matrix scheme. The statistical weight matrices previously formulated for polypropylene and the related polymer chains[29] are reproduced in eq 1 and 2, where

$$U_d' = \begin{bmatrix} 1 & 1 & \tau \\ 1 & 1 & 0 \\ 1 & \omega'' & \tau \end{bmatrix} \qquad U_l' = \begin{bmatrix} 1 & \tau & 1 \\ 1 & \tau & \omega'' \\ 1 & 0 & 1 \end{bmatrix} \tag{1}$$

$$U_{dd}'' = \begin{bmatrix} \omega'' & \tau\omega' & 1 \\ 1 & \tau\omega' & \omega'' \\ \omega' & 0 & \omega' \end{bmatrix} \qquad U_{ll}'' = \begin{bmatrix} \omega'' & 1 & \tau\omega' \\ \omega' & \omega' & 0 \\ 1 & \omega'' & \tau\omega' \end{bmatrix}$$

$$U_{dl}'' = \begin{bmatrix} 1 & \omega'' & \tau\omega' \\ \omega'' & 1 & \tau\omega' \\ \omega' & \omega' & 0 \end{bmatrix} \qquad U_{ld}'' = \begin{bmatrix} 1 & \tau\omega' & \omega'' \\ \omega' & 0 & \omega' \\ \omega'' & \tau\omega' & 1 \end{bmatrix} \tag{2}$$

the rows of these matrices are indexed to rotational states in the order t, g^+, and g^- for the preceding bond and the columns to those for the bond under consideration. The pseudo-asymmetric character of the d and l configuration defined for a vinyl chain can be realized in this matrix representation. Interchange of the second row (g^+) with the third one (g^-), followed by a similar replacement between the second (g^+) and the third column (g^-) achieves the inversion of asymmetric centers from d to l or *vice versa.*[30] Choosing an appropriate pair of U_i' and U_{i+1}'', we obtain the configurational partition function for a given polymer chain by[18]

$$Z = J^{\mathrm{T}}\left[\prod_{i/2=1}^{(n/2)-1} (U_i'U_{i+1}'')\right]J \tag{3}$$

where J is the 3 × 1 column matrix with all elements equal to unity, and J^{T} is the transpose of J. The matrix U_2' defined for the second bond of the chain, for which no preceding bond rotational states are specified, is expressed in diagonal form.

These treatments developed for the polypropylene-like structure can be easily extended to our present vinyl-chain systems where the exact account of side-chain conformations is required. For this purpose, each element in the U' matrices given in eq 1 should be multiplied by a factor representing the statistical weights for all the possible side-chain conformations when the adjoining skeletal bonds are in the specified rotational isomeric states. Let the skeletal bonds $i - 1$ and i shown in Figure 2 be in the rotational states of ζ and η, respectively. For an n-alkyl or a methyl-branched side chain (*e.g.*, poly-1-pentene, poly-3-methyl-1-pentene, etc.), the

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(28) See footnote 10 of ref 18.

(29) See eq 7–10 of ref 18.

(30) P. J. Flory, *J. Am. Chem. Soc.*, **89**, 1798 (1967).

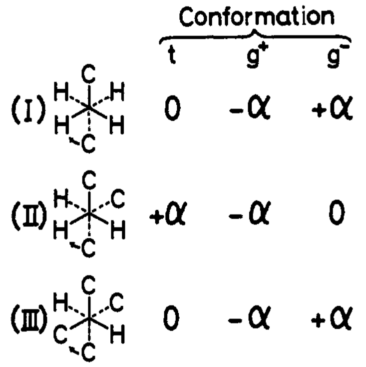

Figure 3. Optical rotatory parameters characteristic of the bond conformations deduced from the Brewster rule.

statistical weight factor attributable to the side chain is simply given by

$$\beta(\zeta,\eta) = J^{\mathrm{T}}\left[\prod_{j=1}^{m-1} S_j\right]J \qquad (4)$$

where S_j represents the statistical weight matrix for bond j in the side chain, and m is the number of C–C bonds from the branch point to the terminal carbon of the side chain. Here we define the rotational isomeric states t, g^+, g^- for the first articulated bond ($j = 1$) by the relative position of the following bond ($j = 2$) in reference to the preceding bond $i - 1$ of the main chain. Then S_1 takes a diagonal form because it involves only the interaction dependent upon rotation about a single bond. Since we only consider the spatial interactions between groups separated by less than four C–C bonds, S_2 is independent of the main chain conformation, but depends only on the configuration (*i.e.*, d or l) of the tertiary carbon at the main chain–side chain juncture. The statistical weight matrices for the third and the higher bonds are determined solely by the side-chain configuration.[31] Multiplying the corresponding (ζ,η) element of the appropriate U' matrix in eq 1 by the factor $\beta(\zeta,\eta)$ thus derived, we obtain new matrices U_d' and U_l' as expressed in their generalized form.

Since we confine our attention only to the three- and four-bond interactions, the matrices U'' given in eq 2 should not be affected by the side-chain conformation and are therefore applicable to the present polymer systems without alteration.

Procedures for Evaluation of Optical Rotatory Power. According to the Whiffen[32]–Brewster[13] empirical rule, the molar optical rotation of a chain molecule is given as a sum of the specific contributions ascribable to the individual constituent bonds. Considering the fact that this simple additivity rule, though without rigorous theoretical justification, has been shown to be valid for a variety of hydrocarbons, we also take advantage of this empirical method in studying the optical rotatory behavior of poly-α-olefins. Values of optical rotation deduced from the Brewster rule for various paraffinic C–C bonds are summarized in Figure 3, where α is taken to be about 60°, regardless of the chemical structure of the terminal carbons. The *trans* conformation shown on the left of each row yields *gauche*$^+$ and *gauche*$^-$ arrangements by the clockwise rotation of the rear carbon by $2\pi/3$ and $4\pi/3$, respectively. The incorporation of this scheme into our rotational isomeric state treatment[33] facilitates evaluation of a statistical average of optical rotation over various conformations of an entire molecule.

Let us first treat an n-paraffin chain for simplicity. The configurational partition function Z is given by[21]

$$Z = J^{\mathrm{T}}\left[\prod_{i=2}^{n-1} U_i\right]J \qquad (5)$$

where $U_2 = \mathrm{diag}(1, \sigma, \sigma)$ and

$$U_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega'' \\ 1 & \sigma\omega'' & \sigma \end{bmatrix} \qquad (6)$$

for $3 \leqq i \leqq n - 1$. The molar optical rotation may be obtained by

$$[\mathrm{M}] = Z^{-1}J^{\mathrm{T}}\left[\sum_{i=2}^{n-1} U_2 \cdots U_{i-1}(U_iA_i)U_{i+1} \cdots U_{n-1}\right]J \qquad (7)$$

Here A_i is a diagonal matrix representing the optical rotatory contribution of bond i

$$A_i = \mathrm{diag}(\alpha_t, \alpha_{g^+}, \alpha_{g^-}) \qquad (8)$$

where α_s ($s = t$, g^+, or g^-) is the optical rotation ascribable to bond i when it is in the rotational state s. Thus, with reference to Figure 3, we obtain

$$A_i = \mathrm{diag}(0, -\alpha, \alpha) \qquad (8')$$

for a bond $2 \leqq i \leqq n - 1$ of an n-paraffin chain. The summation in eq 7 can be replaced by a series of multi-

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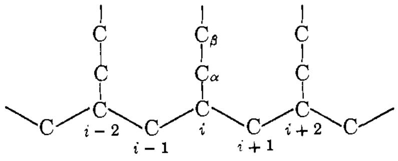
(31) It is convenient, in practice, to formulate these statistical weight matrices in two steps.[18] First consider only the three-bond interactions dependent upon a single rotation about bond j. The statistical weights associated with the rotational states t, g^+, and g^- are placed in a diagonal matrix (say D_j). The four-bond interactions, which arise when the rotational states of the preceding bond $j - 1$ are additionally considered, are separately incorporated in a 3 × 3 matrix (say V_j). Here the rows are indexed to the rotational states of bond $j - 1$, the columns to those of bond j. Then S_j can be given by

$$S_j = V_jD_j$$

It should be noted here that the matrix V_1 involves the special complexity inherent to the first articulated bond. The four-bond inter-



actions to be treated here are those arising from the steric conflicts between the C_β group in the side chain and the C_{i-2} or the C_{i+2} group in the backbone chain as illustrated in the diagram. Accordingly, the matrix V_1 should be defined for each pair of rotational states (*i.e.*, ζ and η, respectively) of the adjoining skeletal bonds, and is expressed in diagonal form. In like manner, it is easily shown that the matrices D_1 and V_2 depend on the configuration, but not on the conformation, of the main chain.

(32) D. H. Whiffen, *Chem. Ind.* (London), 964 (1956).

(33) According to the Brewster original selection rule, the high-energy conformations such as those designated with the statistical weights of τ, ω', or ω'' in Figure 1 are entirely prohibited. In addition, the occurrence of the *gauche* conformations in n-alkanes is assumed to be energetically equally probable to that of the *trans* state. These assumptions are tantamount to putting $\omega' = \omega'' = \tau = 0$ and $\sigma = 1$ in our present rotational isomeric state scheme. Here suppositions for the three-bond interactions are obviously unrealistic. As Brewster[13] suggested, his selection rule may work because there is some compensation of errors in the method. In fact, reexamination of the empirical calculations of the optical activities was attempted for the same paraffinic hydrocarbon systems as those studied by Brewster. The relaxation of Brewster's aforementioned condition did not appreciably improve the agreement between the calculated and observed values of optical rotation over the range of $\sigma = 1.0\sim0.5$ and $\tau = 0.5\sim0.1$.

plications of the matrix H_i defined for bond i as

$$H_i = \begin{bmatrix} U_i & \bigcirc \\ U_i A_i & U_i \end{bmatrix} \tag{9}$$

where $\bigcirc$ is a 3 × 3 zero matrix. Then we have

$$[\mathrm{M}] = Z^{-1}\left\{[0\ 0\ 0\ J^{\mathrm{T}}]\left[\prod_{i=2}^{n-1} H_i\right]\begin{bmatrix} J \\ 0 \\ 0 \\ 0 \end{bmatrix}\right\} \tag{10}$$

and

$$Z = [J^{\mathrm{T}}\ 0\ 0\ 0]\left[\prod_{i=2}^{n-1} H_i\right]\begin{bmatrix} J \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{11}$$

By inspecting the character of eq 6 and 8′, however, it may be easily illustrated without practice that the optical rotatory contributions from the g^+ and g^- conformations just cancel each other, and, in accord with our experience, no optical activity can be expected from n-paraffins in the free state.

In a vinyl polymer system where conformations of the skeletal bonds are largely affected by the spatial interactions of side chains, optical rotatory contributions of side chains are equally important. We introduce matrices W' and W'' to represent the optical rotatory contributions of such groups as treated in the statistical weight matrices U' and U'', respectively. For an isotactic d chain, we define

$$W_d' = U_d' A_d' + R_d \tag{12}$$

$$W_{dd}'' = U_{dd}'' A_d'' \tag{13}$$

where A_d' and A_d'' are diagonal matrices representing the optical rotatory contributions from bonds like i and $i + 1$ depicted in Figure 2, respectively. With the information furnished in Figure 3

$$A_d' = \mathrm{diag}(\alpha,\ -\alpha,\ 0) \tag{14}$$

$$A_d'' = \mathrm{diag}(-\alpha,\ 0,\ \alpha) \tag{15}$$

The term R_d in eq 12 is responsible for the side-chain contribution and is given by eq 16. When the adjoining

$$R_d = \begin{bmatrix} \gamma(t,t) & \gamma(t,g^+) & \tau\gamma(t,g^-) \\ \gamma(g^+,t) & \gamma(g^+,g^+) & 0 \\ \gamma(g^-,t) & \omega''\gamma(g^-,g^+) & \tau\gamma(g^-,g^-) \end{bmatrix} \tag{16}$$

skeletal bonds on both sides of the side chain are in the rotational states of ζ and η, respectively, we define $\gamma(\zeta,\eta)$, in analogy to $\beta(\zeta,\eta)$ given in eq 4, as

$$\gamma(\zeta,\eta) = J^{\mathrm{T}}\left[\sum_{j=1}^{m-1} S_1 \cdots S_{j-1}(S_j A_j)S_{j+1} \cdots S_{m-1}\right]J \tag{17}$$

where A_j represents the optical rotatory contribution ascribable to bond j of the side chain. In a polypropylene-like system, where no rotatory isomeric states can be defined for the side chain (*i.e.*, $m = 1$ in eq 17), the term R_d vanishes from eq 12. The statistical weight factors given in the R_{d} matrix (eq 16) indicate the relative importance of spatial interactions between the backbone and the pendant group. These have been previously deduced for polypropylene in eq 1.

The corresponding matrices for the isotactic l sequence are given by

$$W_l' = U_l' A_l' + R_l \tag{18}$$

$$W_{ll}'' = U_{ll}'' A_l'' \tag{19}$$

where $A_l' = A_d''$ and $A_l'' = A_d'$ from the symmetry considerations. The matrix R_l accommodates the side-chain contribution in a similar manner as R_d in eq 16. In case of a stereoirregular vinyl chain, we must additionally define W_{dl}'' and W_{ld}'' for syndiotactic placements.

$$W_{dl}'' = U_{dl}'' A_l'' \tag{20}$$

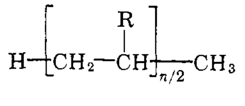
$$W_{ld}'' = U_{ld}'' A_d'' \tag{21}$$

For further calculations of the molar optical rotation, the method developed from eq 5–11 is applicable with some simple modifications to the present system. Details will be given in a later section.

Analysis of Asymmetric Poly-α-olefin Systems

As shown previously[18] in the treatment of vinyl chain dimensions, the contribution from the high-energy conformation given the statistical weight of ω' in Figure 1 may be quite negligible. It follows from this that the conformational statistical weight matrices U' and U'' for a vinyl chain can be expressed in the 2 × 2 matrix scheme for the *trans–gauche* three rotational state model.[18] In the first approximation, we further assume $\omega'' = 0$. This condition will be relaxed later, however, when the temperature dependence of optical rotation is discussed.

Conformational analyses are carried out for the vinyl polymer system such as



$$\mathrm{H{-}[CH_2{-}CH(R)]_{n/2}{-}CH_3}$$

where the pendant group **R** bears one asymmetric center. In practice, a series of poly-α-olefins having an asymmetric site at α, β, γ, or δ with respect to the skeletal carbon is treated. The statistical weight matrices U' for such a vinyl polymer may be given in their 2 × 2 forms as

$$U_d' = \begin{bmatrix} \beta(t,t) & \beta(t,g^+) \\ \beta(g^-,t) & 0 \end{bmatrix} \qquad U_l' = (U_d')^{\mathrm{T}} \tag{22}$$

Here $(U_d')^{\mathrm{T}}$ is the transpose of U_d'. It should be noted here that these U' matrices do not become symmetric, *i.e.*, $\beta(t,g^+) \neq \beta(g^-,t)$, because of the asymmetric nature of the side chain. The statistical weight matrices U'' given in eq 2, on the other hand, become symmetric when reduced to 2 × 2 order (eq 23).

$$\begin{aligned} U_{dd}'' = U_{ll}'' &= \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ U_{dl}'' = U_{ld}'' &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \end{aligned} \tag{23}$$

The matrices U_d' obtained for the individual polymers are summarized in eq 24–28,[34] where C* indicates the

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(34) In the first two cases, where the asymmetric site is located on the vicinal carbon to the main chain, the D_1 matrix comprises the 2,3-dimethylbutane-like three-bond interactions. Thus we have for a d-

$R = -C^*H(CH_3)CH_2CH_3\ (S)$

$$U_d' = \begin{bmatrix} 0 & 1 \\ 2 & 0 \end{bmatrix} \tag{24}$$

$R = -C^*H(CH_3)(CH_2)_3CH(CH_3)CH_3\ (R)$

$$U_d' = \begin{bmatrix} 0 & 4 + 8\sigma + 2\tau + 2\sigma^2 + 2\sigma\tau \\ 2 + 4\sigma + \tau + \sigma^2 + \sigma\tau & 0 \end{bmatrix} \tag{25}$$

$R = -CH_2C^*H(CH_3)CH_2CH_3\ (S)$

$$U_d' = \begin{bmatrix} 0 & 1 + \tau \\ 2 + \tau & 0 \end{bmatrix} \tag{26}$$

$$U_{d;2}' = \begin{bmatrix} 2 + \tau & 0 \\ 0 & 3 + 2\tau \end{bmatrix} \tag{26$'$}$$

$$U_{d;n}' = \begin{bmatrix} 1 + \tau & 0 \\ 0 & 3 + 2\tau \end{bmatrix} \tag{26$''$}$$

$R = -(CH_2)_2C^*H(CH_3)CH_2CH_3\ (S)$

$$U_d' = \begin{bmatrix} 3\tau + 4\tau^2 & 3 + \sigma + 7\tau + \sigma\tau + 4\tau^2 \\ 3 + 2\sigma + 7\tau + \sigma\tau + 4\tau^2 & 0 \end{bmatrix} \tag{27}$$

$$U_{d;2}' = \begin{bmatrix} 3 + 2\sigma + 7\tau + \sigma\tau + 4\tau^2 & 0 \\ 0 & 6 + 3\sigma + 11\tau + 2\sigma\tau + 4\tau^2 \end{bmatrix} \tag{27$'$}$$

$$U_{d;n}' = \begin{bmatrix} 3 + \sigma + 7\tau + \sigma\tau + 4\tau^2 & 0 \\ 0 & 6 + 3\sigma + 11\tau + 2\sigma\tau + 4\tau^2 \end{bmatrix} \tag{27$''$}$$

$R = -(CH_2)_3C^*H(CH_3)CH_2CH_3\ (S)$

$$U_d' = \begin{bmatrix} 3\tau + 3\sigma\tau + 4\tau^2 + 2\sigma\tau^2 & 3 + 6\sigma + 7\tau + \sigma^2 + 9\sigma\tau + 4\tau^2 + \sigma^2\tau + 2\sigma\tau^2 \\ 3 + 6\sigma + 7\tau + 2\sigma^2 + 9\sigma\tau + 4\tau^2 + \sigma^2\tau + 2\sigma\tau^2 & 0 \end{bmatrix} \tag{28}$$

asymmetrically substituted carbon, and (*R*) and (*S*) denote the configuration about C* expressed in the absolute notation.

When the polymer chain is finite, we should additionally define U_2' and U_n' for the chain terminals. Both matrices may be expressed in diagonal form, because of the absence of the preceding or the following bond rotational states, respectively. In the above prescription, these matrices are also included in two representative polymer systems, chosen for a later purpose. Here the relations $U_{l;2}' = U_{d;n}'$ and $U_{l;n}' = U_{d;2}'$ are operative for the *l* configuration.

In the case of polymers such as poly-(*S*)-3-methyl-1-pentene, poly-(*R*)-3,7-dimethyl-1-octene, and poly-(*S*)-4-methyl-1-hexene, as investigation of the model reveals, the transition statistical weight between the two stable main-chain conformations is negligibly small. This corresponds to suppression of the (1,1) and (2,2) elements of U_d' and U_l'. The preferred conformations for the left-handed helix consist of sequences of either g^-t or tg^- pairs of consecutive bonds flanking the tertiary carbon in the skeleton. Interchange between these two conformations occurs whenever a syndiotactic placement *dl* or *ld* is involved, but the left-handed form persists irrespective of the stereochemical sequence. The right-handed helix comprises the conformations tg^+ or g^+t correspondingly. Hence, with a stereochemical chain sequence of . . . *ddld* . . . , for example, the following conformations are the ones of lowest energy.[35]

$$\cdots\overset{d}{(g^-t)}\overset{d}{(g^-t)}\overset{l}{(tg^-)}\overset{d}{(g^-t)}\cdots$$

i

$$\cdots(tg^+)(tg^+)(g^+t)(tg^+)\cdots$$

ii

Here the possibility of transforming the sense of helix from left (i) to right (ii) or *vice versa* is prohibitively low. The relative importance of the conformations i and ii is not equal, however, in a polymer system with asymmetric side chains. If we neglect some trivial end effects for a high polymer, the proportions of left-handed helical forms to right-handed ones are found to be 2^x for poly-(*S*)-3-methyl-1-pentene, $(^1/_2)^x$ for poly-(*R*)-3,7-dimethyl-1-octene, and $[(2 + \tau)/(1 + \tau)]^x$ for poly-(*S*)-4-methyl-1-hexene, respectively. Here x is the number of monomeric units in a polymeric chain. Within our present approximations, the relations in eq 29 and 30 and similarly 29′ and 30′ exist in general for these polymer systems. It is implied here that the helix con-

$$\overset{d}{U_d'}(\overset{l}{U_{dl}''U_l'}\overset{d}{U_{ld}''})U_d' = \overset{d}{U_d'}(\overset{d}{U_{dd}''U_d'}\overset{d}{U_{dd}''})U_d' \tag{29}$$

$$\overset{d}{U_d'}(\overset{l}{U_{dl}''U_l'}\overset{l}{U_{ll}''})U_l' = \overset{d}{U_d'}(\overset{d}{U_{dd}''U_d'}\overset{l}{U_{dl}''})U_l' \tag{30}$$

$$\overset{l}{U_l'}(\overset{d}{U_{ld}''U_d'}\overset{l}{U_{dl}''})U_l' = \overset{l}{U_l'}(\overset{l}{U_{ll}''U_l'}\overset{l}{U_{ll}''})U_l' \tag{29$'$}$$

$$\overset{l}{U_l'}(\overset{d}{U_{ld}''U_d'}\overset{d}{U_{dd}''})U_d' = \overset{l}{U_l'}(\overset{l}{U_{ll}''U_l'}\overset{d}{U_{ld}''})U_d' \tag{30$'$}$$

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chain of poly-(*S*)-3-methyl-1-pentene, D_1 = diag(1, τ, τ). Within the present approximations for four-bond interactions (*i.e.*, $\omega' = \omega'' = 0$), on the other hand, the matrices V_1, defined for each pair of rotational states ζ and η of the adjoining skeletal bonds $i - 1$ and i, respectively, are given by

ζ, η	V_1
t, t	diag(0, 0, 0)
t, g^+	diag(0, 1, 0)
g^-, t	diag(0, 0, 1)
g^-, g^+	diag(1, 1, 1)

where the last conformation (g^-, g^+) is unstable, however, because of the four-bond steric conflicts between methine groups associated with bonds $i - 2$ and $i + 1$ of the main chain. Combining these with the aforementioned D_1 matrix, we have S_1 = diag(0, τ, 0) for (t,g^+) and S_1 = diag(0, 0, τ) for (g^-,t). The two remaining rotational states here may be considered to be energetically equivalent. Thus the 2,3-dimethylbutane-like τ characterizing these states may cancel each other. The same conclusion can be reached with respect to the *l* configuration. Consequently all of the τ factors in the U' matrices given here represent the statistical weight characteristic of the 2-methylbutane-like system.

(35) The dyad pair expressed in this scheme departs from that used previously.[18] The expression i, for example, would be read in the previous convention as

$$\cdots g^-)^d(tg^-)^d(tt)^l(g^-g^-)^d(t\cdots$$

Revision was made in order to facilitate further discussion by improving correspondence to the U' matrix, which relates to the rotational states of a pair of bonds like $i - 1$ and i as depicted in Figure 2.

tent in terms of *gauche*$^+$ or *gauche*$^-$ does not vary with stereoregularity of the polymer sequence, though the chain configuration in a geometrical sense is variable. We thus reach the conclusion that, irrespective of the stereochemical chain sequence, one sense of helical conformation prevails overwhelmingly in solution over the other.

When the asymmetric site in the side chain is separated by more than two carbon atoms from the skeletal carbon, we can no longer postulate $U_d'(t,t) = U_l'(t,t) \cong 0$. Transitions between the two preferred helical conformations through *tt* may not require as high an energy as those presumed for the aforementioned 3- or 4-substituted α-olefin polymers. Introduction of a factor larger than zero into the (1,1) element of U_d' and U_l' endows some conformational flexibility to the chain.[36] However, configurational aspects characteristic of vinyl chain systems[18] still govern the type of transitions which occur. They may be summarized as shown in Table I.

Table I. Transitions between the Two Stable Screw Conformations *via* the (t,t) Element of U'

Configuration	Transition
$\cdots ddd \cdots$	$\cdots(tg^+)(tt)(g^-t)\cdots$
$\cdots ldd \cdots$	$\cdots(g^+t)(tt)(g^-t)\cdots$
$\cdots ldl \cdots$	$\cdots(g^+t)(tt)(tg^-)\cdots$
$\cdots lll \cdots$	$\cdots(tg^-)(tt)(g^+t)\cdots$
$\cdots dll \cdots$	$\cdots(g^-t)(tt)(g^+t)\cdots$
$\cdots dld \cdots$	$\cdots(g^-t)(tt)(tg^+)\cdots$

The fraction of left-handed (g^-) or right-handed (g^+) conformations for polymer chains under consideration may be calculated by an ordinary procedure. Let us introduce an arbitrary parameter p in the (g^-t) and (tg^-) element of U_d' and U_l', respectively, for a labeling purpose. We have

$$U_d' = \begin{bmatrix} \beta(t,t) & \beta(t,g^+) \\ p\beta(g^-,t) & 0 \end{bmatrix} \qquad U_l' = (U_d')^{\mathrm{T}} \qquad (31)$$

Then the fraction of g^- conformation, for example, should be given by

$$f_{g^-} = (\partial \ln Z/\partial \ln p)_{p=1} \qquad (32)$$

where Z is the configurational partition function defined similarly to eq 3. The fraction of the g^+ conformation can be evaluated in like manner. The results obtained for poly-(*S*)-5-methyl-1-heptene are shown in Table II. Here calculations are carried out for Monte Carlo chains with 100 monomeric units. In keeping with the previous usage,[18] p_r represents the probability that the stereochemical configuration of any given unit is identical with that of its predecessor in the chain. The chain configurations are determined by a series of random numbers generated in the range 0–1. Each random number larger than p_r implies a configurational switch-over between *d* and *l*. The replication probability p_r defined in this manner may be also regarded as the probability of an isotactic dyad placement. The ratios of the left-handed conformations over the right-handed ones are given in the fourth and seventh rows of Table II for two sets of statistical weight parameters. The ratio decreases rapidly as the stereoregularity of the polymer departs from an isotactic order ($p_r = 1.0$). The values of the ratio are almost invariant, however, in the range from $p_r = 0.9$ to 0.0. It is indicated in the table that the helix content at a given value of p_r varies sensibly with the statistical weight factor τ. This may be reasonably well understood by considering that the transition elements $U_d'(t,t)$ and $U_l'(t,t)$, as given in eq 27, are determined merely as a function of τ. The importance of the transitions through such conformations as those shown in Table I should be realized here.

Table II. Variation of Helix Content (%) with Replication Probability, p_r, Calculated for Poly-(*S*)-5-methyl-1-heptene of 100 Monomer Units

	Sense	p_r				
Parameter	of helix	0.0 (syndio)	0.1	0.4	0.9	1.0 (iso)
$\sigma = 0.50$	Left	66.2	64.3	67.2	68.5	88.5
$\tau = 0.25$	Right	24.6	26.3	23.9	25.3	8.7
$\omega'' = 0$	Ratio	2.7	2.4	2.8	2.7	10.2
$\sigma = 0.50$	Left	51.3	50.3	53.0	57.1	82.7
$\tau = 0.50$	Right	32.8	34.0	32.6	34.6	14.5
$\omega'' = 0$	Ratio	1.6	1.5	1.6	1.7	5.7

One would expect an analogous behavior for poly-(*S*)-6-methyl-1-octene to that of poly-(*S*)-5-methyl-1-heptene. The ratios of the helix content should be much closer to unity in this system, however.

Optical Rotatory Properties of Stereoregular Isotactic and Syndiotactic Polymers

According to the previous prescription given in eq 12, 14, and 16–18, the matrices such as W_d' and W_l' were derived for the individual polymer systems as shown in eq 33–42. Here the matrices W_d' and W_l are, in

R = -C*H(CH$_3$)CH$_2$CH$_3$ (*S*)

$$W_d' = \begin{bmatrix} 0 & -3 \\ 4 & 0 \end{bmatrix}\alpha \qquad (33)$$

$$W_l' = \begin{bmatrix} 0 & 4 \\ -3 & 0 \end{bmatrix}\alpha \qquad (34)$$

R = -C*H(CH$_3$)(CH$_2$)$_3$CH(CH$_3$)CH$_3$ (*R*)

$$W_d' = \begin{bmatrix} 0 & -8 - 16\sigma - 4\tau - 4\sigma^2 - 4\sigma\tau \\ 6 + 14\sigma + 3\tau + 6\sigma^2 + 4\sigma\tau & 0 \end{bmatrix}\alpha \qquad (35)$$

$$W_l' = \begin{bmatrix} 0 & 6 + 14\sigma + 3\tau + 6\sigma^2 + 4\sigma\tau \\ -8 - 16\sigma - 4\tau - 4\sigma^2 - 4\sigma\tau & 0 \end{bmatrix}\alpha \qquad (36)$$

R = -CH$_2$C*H(CH$_3$)CH$_2$CH$_3$ (*S*)

$$W_d' = \begin{bmatrix} 0 & -4 - 3\tau \\ 6 + 3\tau & 0 \end{bmatrix}\alpha \qquad (37)$$

---

(36) In the previous treatment of the polymer end-to-end dimension,[18] where no rigorous analyses of the side-chain conformations are required, a factor τ^* was used to represent the relative importance of the *tt* state over the $tg^{\pm}$ or $g^{\mp}t$ conformations. When the pendant group is methyl, obviously $\tau^* \cong 1$. For polymers with longer alkyl side chains such as poly-1-butene or poly-1-pentene, we may put $\tau^* \cong \tau$.

principle, untransferable into each other by any simple transposition of the elements. An apparent relation $W_d' = (W_l')^{\mathrm{T}}$ found in the first three systems is not operative when the higher energy conformations such as those designated with ω'' are additionally taken into consideration. In cases of poly-(*S*)-4-methyl-1-hexene and poly-(*S*)-5-methyl-1-heptene, also included for later use, are the matrices $W_{d;2}'$, $W_{d;n}'$, $W_{l;2}'$, and $W_{l;n}'$, each representing the optical rotatory contribution of a terminal group for a finite chain.

$$W_{d;2}' = \begin{bmatrix} 6 + 3\tau & 0 \\ 0 & -2 - 2\tau \end{bmatrix}\alpha \tag{37$'$}$$

$$W_{d;n}' = \begin{bmatrix} -3 - 2\tau & 0 \\ 0 & 1 \end{bmatrix}\alpha \tag{37$''$}$$

$$W_l' = \begin{bmatrix} 0 & 6 + 3\tau \\ -4 - 3\tau & 0 \end{bmatrix}\alpha \tag{38}$$

$$W_{l;2}' = \begin{bmatrix} -4 - 3\tau & 0 \\ 0 & 4 + 2\tau \end{bmatrix}\alpha \tag{38$'$}$$

$$W_{l;n}' = \begin{bmatrix} 4 + 2\tau & 0 \\ 0 & 1 \end{bmatrix}\alpha \tag{38$''$}$$

R = $-(\mathrm{CH_2})_2\mathrm{C^*H(CH_3)CH_2CH_3}$ (*S*)

$$W_d' = \begin{bmatrix} 3\tau + 4\tau^2 & -6 - 5\sigma - 11\tau - 4\sigma\tau - 4\tau^2 \\ 6 + 8\sigma + 11\tau + 4\sigma\tau + 4\tau^2 & 0 \end{bmatrix}\alpha \tag{39}$$

$$W_{d;2}' = \begin{bmatrix} 6 + 8\sigma + 11\tau + 4\sigma\tau + 4\tau^2 & 0 \\ 0 & -6 - \sigma - 11\tau - 2\sigma\tau - 4\tau^2 \end{bmatrix}\alpha \tag{39$'$}$$

$$W_{d;n}' = \begin{bmatrix} -3 - 4\sigma - 4\tau - 3\sigma\tau & 0 \\ 0 & 2\sigma \end{bmatrix}\alpha \tag{39$''$}$$

$$W_l' = \begin{bmatrix} -3\tau - 4\tau^2 & 6 + 8\sigma + 11\tau + 4\sigma\tau + 4\tau^2 \\ -6 - 5\sigma - 11\tau - 4\sigma\tau - 4\tau^2 & 0 \end{bmatrix}\alpha \tag{40}$$

$$W_{l;2}' = \begin{bmatrix} -6 - 5\sigma - 11\tau - 4\sigma\tau - 4\tau^2 & 0 \\ 0 & 6 + 5\sigma + 11\tau + 2\sigma\tau + 4\tau^2 \end{bmatrix}\alpha \tag{40$'$}$$

$$W_{l;n}' = \begin{bmatrix} 3 + 6\sigma + 4\tau + 3\sigma\tau & 0 \\ 0 & 2\sigma \end{bmatrix}\alpha \tag{40$''$}$$

The associated matrices W'', which are applicable to bonds connecting $\mathrm{CH_2}$ with CHR, can be approximated in the 2 × 2 matrix scheme by eq 43. Hereafter we adopt the Brewster value, $\alpha = 60°$, for optical rotations with the sodium D-line.

$$W_{dd}'' = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}\alpha \qquad W_{ll}'' = -W_{dd}''$$
$$W_{dl}'' = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\alpha \qquad W_{ld}'' = -W_{dl}'' \tag{43}$$

In accordance with the common usage, we define [M] for a polymer system as the optical rotatory power per monomer residue. Then, for a chain of the type depicted in the preceding section, we have eq 44, where H'

$$[\mathrm{M}] = (2/nZ)[0\;0\;J^{\mathrm{T}}]\left[\prod_{i/2=1}^{(n/2)-1}(H_i'H_{i+1}'')H_n'\right]\begin{bmatrix} J \\ 0 \\ 0 \end{bmatrix} \tag{44}$$

and H'' correspond to H defined in eq 9. With a proper choice of a set of U' and W' or of U'' and W'' for the *k*th bond, the H_k's are defined by

$$H_k = \begin{bmatrix} U_k & 0 \\ W_k & U_k \end{bmatrix} \tag{45}$$

Accordingly, J is also reduced to the 2 × 1 column array.

For the limit $n = \infty$, values of [M] may be calculated by the eigenvalue method. Thus

$$[\mathrm{M}] = \lambda^{-1}X^*(W_i'U_{i+1}'' + U_i'W_{i+1}'')X \tag{46}$$

where X^* is the eigenrow corresponding to the maximum eigenvalue λ of $(U_i'U_{i+1}'')$, and X is the eigencolumn for the same eigenvalue.

Variation of the optical rotatory power with the degree of polymerization is first studied. The results of calculations are shown in Figures 4 and 5, respectively, for polymers of (*S*)-4-methyl-1-hexene and of (*S*)-5-methyl-1-heptene. In the low molecular weight region where the end effect is important, we may distinguish three kinds of molecular asymmetry for syndiotactic chain sequences: (a) a chain having the same configuration (either *d* or *l*) at both ends, (b) that having the *d* configuration on one end and the *l* on the opposite chain

R = $-(\mathrm{CH_2})_3\mathrm{C^*H(CH_3)CH_2CH_3}$ (*S*)

$$W_d' = \begin{bmatrix} 3\tau + 4\sigma\tau + 4\tau^2 + 2\sigma\tau^2 & -6 - 14\sigma - 11\tau - 6\sigma^2 - 18\sigma\tau - 4\tau^2 - 5\sigma^2\tau - 2\sigma\tau^2 \\ 6 + 16\sigma + 11\tau + 10\sigma^2 + 20\sigma\tau + 4\tau^2 + 5\sigma^2\tau + 2\sigma\tau^2 & 0 \end{bmatrix}\alpha \tag{41}$$

$$W_l' = \begin{bmatrix} -3\tau - 2\sigma\tau - 4\tau^2 - 2\sigma\tau^2 & 6 + 16\sigma + 11\tau + 10\sigma^2 + 20\sigma\tau + 4\tau^2 + 5\sigma^2\tau + 2\sigma\tau^2 \\ -6 - 14\sigma - 11\tau - 6\sigma^2 - 18\sigma\tau - 4\tau^2 - 5\sigma^2\tau - 2\sigma\tau^2 & 0 \end{bmatrix}\alpha \tag{42}$$

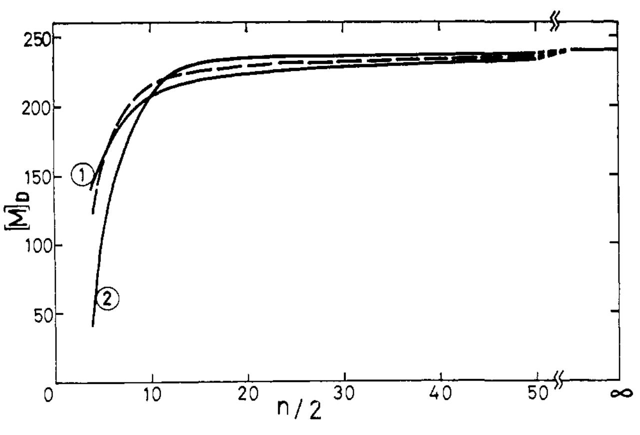

Figure 4. Variation of the mean residue optical rotation with the degree of polymerization. Calculated for the stereoregular isotactic and syndiotactic chains of poly-(*S*)-4-methyl-1-hexene with $\tau = 0.25$ and $\omega'' = 0$. The solid curves ① and ② correspond to syndiotactic sequences of $(ld)_{n/4}$ and $(dl)_{n/4}$, respectively. A syndiotactic chain comprising an odd number of monomeric units, *i.e.*, $d(ld)_{n/4}$ or $l(ld)_{n/4}$, and an isotactic sequence are all represented by the dotted curve.

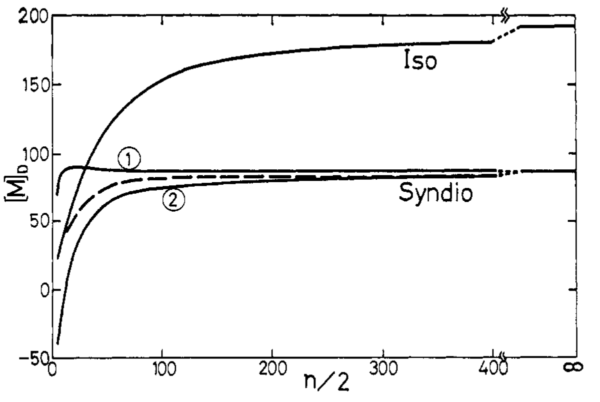

Figure 5. The mean residue optical rotation calculated as a function of the degree of polymerization for the stereoregular isotactic and syndiotactic poly-(*S*)-5-methyl-1-heptene chains, using the following statistical weight parameters: $\sigma = 0.50$, $\tau = 0.25$, and $\omega'' = 0$. The solid curves ① and ② refer to the chain sequences comprising an even number of syndiotactic units, $(ld)_{n/4}$ and $(dl)_{n/4}$, respectively. The dotted curve corresponds to that composed of an odd number of syndiotactic units.

terminal, and (c) that in the reversed order to (b). While the first chain consists of an odd number of monomeric units, each of the latter two chains comprises an even number of monomer units. A syndiotactic polymer with an even number of monomeric units is racemic in nature. Hence the secondary contribution from the molecular asymmetry of this type to the optical activity is eliminated in this system. The difference between the curves 1 and 2 in Figures 4 and 5 diminishes as the end-group contribution becomes negligible in the high molecular weight region. No such complexities can be expected for an isotactic chain.

As shown in Figure 4, an isotactic poly-(*S*)-4-methyl-1-hexene behaves exactly in the same manner as does a syndiotactic chain with an odd number of monomeric units over the entire molecular weight range. This may be foreseen from the relationships given in eq 29 and 29′ as combined with the equalities in eq 47 and 47′. In

$$\begin{aligned}\overset{d}{U_d'}(U_{dl}''\overset{l}{W_l'}U_{ld}'')\overset{d}{U_d'} &= \overset{d}{U_d'}(U_{dd}''\overset{d}{W_d'}U_{dd}'')\overset{d}{U_d'}\\ U_d'(U_{dl}''U_l'W_{ld}'')U_d' &= U_d'(U_{dd}''U_d'W_{dd}'')U_d'\end{aligned} \tag{47}$$

$$\begin{aligned}\overset{l}{U_l'}(U_{ld}''\overset{d}{W_d'}U_{dl}'')\overset{l}{U_l'} &= \overset{l}{U_l'}(U_{ll}''\overset{l}{W_l'}U_{ll}'')\overset{l}{U_l'}\\ U_l'(U_{ld}''U_d'W_{dl}'')U_l' &= U_l'(U_{ll}''U_l'W_{ll}'')U_l'\end{aligned} \tag{47′}$$

the case of poly-(*S*)-5-methyl-1-heptene as indicated in Figure 5, on the other hand, the values of $[M]_D$ for an isotactic chain exceed those of a syndiotactic one. The discrepancy becomes larger as the degree of polymerization increases. Comparison of Figures 4 and 5 shows that the residual optical rotation $[M]_D$ reaches an asymptotic value far more rapidly in the poly-(*S*)-4-methyl-1-hexene than in the poly-(*S*)-5-methyl-1-heptene system. This may be again taken to be the reflection of the difference in the conformational rigidity of these polymer backbone chains.

It may be suggested by inspecting the constitution of the *U* and *W* matrices given in eq 24–28 and 33–42, respectively, that while a polymer of either 3- or 4-methyl-substituted α-olefin should show quite an analogous behavior to that of poly-(*S*)-4-methyl-1-hexene, a polymer derived from an α-olefin having a methyl substituent on 5 or higher positions possesses the characteristics peculiar to the poly-(*S*)-5-methyl-1-heptene system.

Calculated values of $[M]_D$ for various poly-α-olefin chains with $n = \infty$ are shown in the third and fourth columns of Table III. Values listed in the second column are those experimentally observed for highly isotactic polymers. In the first three polymer systems, where the calculated optical rotations are independent of the type of stereochemical sequences, the agreement with observations is quite reasonable. For the last two polymers, however, the observed values are rather close to those calculated for syndiotactic chains. Nevertheless, this does not necessarily imply that the stereoregularities of the polymer samples used in the last two cases are very low.

Table III. Comparison of the Highest Observed Mean Residue Rotations and Those Calculated for Stereoregular Chains

Polymer	$[M]_D$ (obsd), deg	$[M]_D$ (calcd), deg[a] Isotactic	$[M]_D$ (calcd), deg[a] Syndiotactic
Poly-(*S*)-3-methyl-	+161[b]		
1-pentene	+214[c]	+180	+180
Poly-(*R*)-3,7-di-	−154[b,e]		
methyl-1-octene	−110[d,e]	−180	−180
Poly-(*S*)-4-methyl-	+288[b]		
1-hexene	+263[c]	+240	+240
Poly-(*S*)-5-methyl-	+68.1[b]	+192	+86.7
1-heptene		(+180)	(+55.4)
Poly-(*S*)-6-methyl-	+20.4[b]	+198	+38.2
1-octene		(+187)	(+17.3)

[a] Calculated for $\sigma = 0.50$, $\tau = 0.25$, and $\omega' = \omega'' = 0$. Bracketed values were obtained by using $\tau = 0.50$. [b] See ref 5. [c] See ref 6. [d] See ref 7. [e] Optical purity of the starting monomer is about 75%.

Stereoirregular Polymers

The mean optical rotatory power of the stereoirregular polymers can be evaluated by applying the procedure

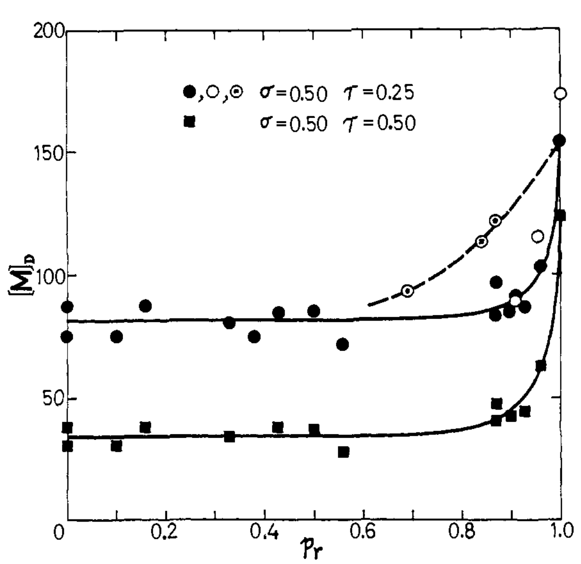

Figure 6. Variation of the mean residue optical rotation with the replication probability p_r, calculated for poly-(*S*)-5-methyl-1-heptene of 100 monomer units using the statistical weight parameters as indicated. The results obtained for 200 monomer units are also included and shown by open circles. The points marked with ⊙ represent calculations carried out for the chain sequence in which the stereoirregular units of *dld* or *ldl* disperse randomly among *d* or *l* chains, respectively. In this case, the abscissa is defined to indicate the isotactic dyad content.

represented by eq 44 and 45, but with *U* and *W* matrices properly chosen for the chain sequence.

Within the limit of the present approximations, we have the relations shown in eq 48 and 48′ between the conformation *dll* and *ddl*, and between *ldd* and *lld* in the poly-(*S*)-4-methyl-1-hexene and the related polymer systems. Similar equalities between the conformation

$$\begin{array}{lcl} d \qquad l \qquad l & & d \qquad d \qquad l \\ U_d'(U_{dl}''W_l'U_{ll}'')U_l' &=& U_d'(U_{dd}''W_d'U_{dl}'')U_l' \\ U_d'(U_{dl}''U_l'W_{ll}'')U_l' &=& U_d'(U_{dd}''U_d'W_{dl}'')U_l' \end{array} \qquad (48)$$

$$\begin{array}{lcl} l \qquad d \qquad d & & l \qquad l \qquad d \\ U_l'(U_{ld}''W_d'U_{dd}'')U_d' &=& U_l'(U_{ll}''W_l'U_{ld}'')U_d' \\ U_l'(U_{ld}''U_d'W_{dd}'')U_d' &=& U_l'(U_{ll}''U_l'W_{ld}'')U_d' \end{array} \qquad (48')$$

dld and *ddd* and between *ldl* and *lll* for the same polymer systems have been mentioned in the preceding section (eq 47 and 47′). Equation 48 and 48′ may be combined with eq 30 and 30′, respectively, to show that the optical rotatory powers of these polymers are, except for some trivial end effects, independent of the stereoregularity of the chain. It is then easily shown, without any practical calculations, that the values of [M]D for $n = \infty$ should be invariable from those given in Table III, with any stereochemical sequence from the isotactic to the syndiotactic.

For polymers of (*S*)-5-methyl-1-heptene or (*S*)-6-methyl-1-octene, as apparent from Table III, quite a large stereoregularity dependence can be anticipated. Calculations were carried out for Monte Carlo chains of poly-(*S*)-5-methyl-1-heptene with 100 monomer units. The optical rotation [M]D is plotted against the replication probability p_r for two sets of statistical weight parameters in Figure 6. The large optical rotation obtained for a perfectly isotactic polymer decreases very sharply with the presence of several per cent of syndiotactic placements. Over the rest of the range, values of [M]D are quite insensitive to p_r. Such optical rotatory behaviors are evidently related to the variation of helix content with tacticity, which has been shown in Table II.

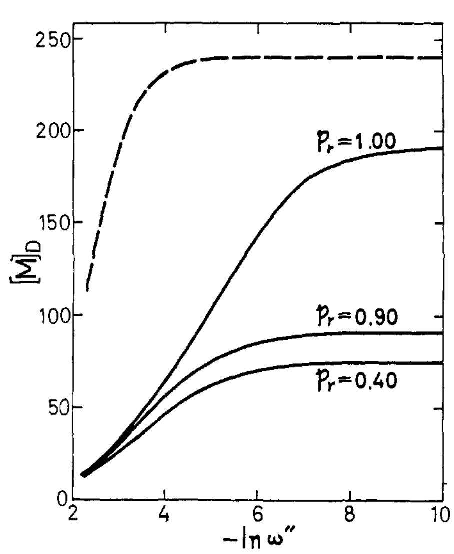

Figure 7. Influence of the pentane effect on the mean residue optical rotation for $\omega'' > 0$. The other parameters used are $\sigma = 0.50$ and $\tau = 0.25$, respectively. The results obtained for an isotactic poly-(*S*)-4-methyl-1-hexene of infinite chain length are shown by the dotted curve. The uppermost solid curve is calculated for an isotactic poly-(*S*)-5-methyl-1-heptene with an infinite chain length. The other two solid curves are computed for poly-(*S*)-5-methyl-1-heptene of 100 monomer units with tacticities as indicated.

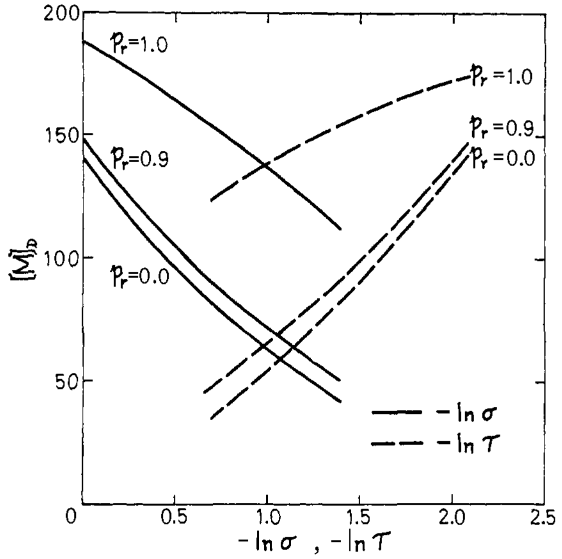

Figure 8. The mean residue optical rotation calculated as a function of $-\ln \sigma = E_\sigma/RT$ and $-\ln \tau = E_\tau/RT$. Calculations were carried out for an isotactic, a moderately isotactic, and a syndiotactic poly-(*S*)-5-methyl-1-heptene chain of 100 monomer units. The solid curves were derived for $-\ln \sigma$ with $\tau = 0.25$ and $\omega'' = 0$, and the dotted curves for $-\ln \tau$ with $\sigma = 0.50$ and $\omega'' = 0$.

Calculations were also carried out for another possibility of the chain sequence. That is, if the stereochemistry of monomer addition to the growing polymer chain end is controlled by the asymmetric site located innately on the heterogeneous catalyst surface as suggested by Cossee and Arlman,[37] and others,[38] the occasional interruptions of isotactic sequences may occur predominantly by insertion of an opposite configurational unit. Such a scheme will yield a polymer with stereoirregular placements of the type *dld* dispersed randomly among *d* chain sequences, or alternatively *ldl* among *l* sequences. Generation of a polymer sequence of this sort can be accomplished with the aid of a series of random numbers. The dotted curve in Figure 6 shows the variation of the mean optical rotation with tacticity (in terms of the isotactic dyad content). The general trend is unchanged by such modifications, although the optical rotatory power decreases more slowly with decrease in isotacticity in this polymer sequential scheme.

With these results we reach the conclusion that the stereoregularities of the samples used in the experiments[3–7] cited above may have been somewhat less than perfectly isotactic. The assumption of approximately 10% of heterotacticity ($p_r = 0.9$) in the case of poly-(*S*)-5-methyl-1-heptene and poly-(*S*)-6-methyl-1-octene brings the calculated optical rotations in the range of those observed. For polymers such as poly-(*S*)-3-methyl-1-pentene, poly-(*R*)-3,7-dimethyl-1-octene, and poly-(*S*)-4-methyl-1-hexene, as pointed out previously, the agreement between the observed and the calculated is unaffected by such an assumption. The isotacticity of these polymer samples could be probably as low as those of the former group.

Temperature Dependence of Optical Rotatory Power

Variation of the optical rotation [M]D with temperature is given by eq 49. Thus, the temperature coefficient

$$\mathrm{d}\ln[\mathrm{M}]_\mathrm{D}/\mathrm{d}T = -(1/T)[\ln\sigma\,(\partial\ln[\mathrm{M}]_\mathrm{D}/\partial\ln\sigma) + \ln\tau\,(\partial\ln[\mathrm{M}]_\mathrm{D}/\partial\ln\tau) + \ln\omega''\,(\partial\ln[\mathrm{M}]_\mathrm{D}/\partial\ln\omega'')] \qquad (49)$$

about given values of σ, τ, and ω'' may be estimated from the theoretical curves presented in Figures 7 and 8.

In the poly-(*S*)-3-methyl-1-pentene, poly-(*R*)-3,7-dimethyl-1-octene, and poly-(*S*)-4-methyl-1-hexene systems, the coefficients (∂ ln [M]D/∂ ln σ) and (∂ ln [M]D/∂ ln τ) may be readily shown to be zero, except for trivial end-group contributions, if four-bond interactions are suppressed by taking $\omega'' = 0$. The observed temperature dependence of [M]D for these polymers[4–7] must be attributed therefore to nonzero coefficients (∂ ln [M]D/∂ ln ω''). The *U* and *W* matrices for the case $\omega'' > 0$ are given in eq 50–54 for poly-(*S*)-4-methyl-1-hexene.

$$U_d' = (U_l')^\mathrm{T} = \begin{bmatrix} 3\omega'' + 2\tau\omega'' & 1 + \tau + 5\omega'' + 2\tau\omega'' \\ 2 + \tau + 2\omega'' + 2\tau\omega'' & 3\omega'' + 2\tau\omega'' \end{bmatrix} \qquad (50)$$

$$U_{dd}'' = U_{ll}'' = \begin{bmatrix} \omega'' & 1 \\ 1 & \omega'' \end{bmatrix} \qquad U_{dl}'' = U_{ld}'' = \begin{bmatrix} 1 & \omega'' \\ \omega'' & 1 \end{bmatrix} \qquad (51)$$

$$W_d' = \begin{bmatrix} 4\omega'' + 2\tau\omega'' & -4 - 3\tau - 2\omega'' \\ 6 + 3\tau - 2\omega'' & -2\omega'' - 2\tau\omega'' \end{bmatrix}\alpha \qquad (52)$$

$$W_l' = \begin{bmatrix} -2\omega'' - 2\tau\omega'' & 6 + 3\tau - 2\omega'' \\ -4 - 3\tau - 2\omega'' & 4\omega'' + 2\tau\omega'' \end{bmatrix}\alpha \qquad (53)$$

$$W_{dd}'' = -W_{ll}'' = \begin{bmatrix} -\omega'' & 1 \\ -1 & \omega'' \end{bmatrix}\alpha \qquad W_{dl}'' = -W_{ld}'' = \begin{bmatrix} 1 & -\omega'' \\ \omega'' & -1 \end{bmatrix}\alpha \qquad (54)$$

With the assumption $\omega'' = 0$, these matrices are necessarily reduced to the simpler forms given in the previous sections. The equalities described in eq 29, 29′, 30, 30′, 47, 47′, 48, and 48′ are still valid. For a high polymer, therefore, the coefficient (∂ ln [M]D/∂ ln ω'') should be independent of the stereochemical arrangement of the chain units. The dotted curve in Figure 7 shows a plot of [M]D against $-\ln\omega'' = E_{\omega''}/RT$, where values of optical rotation were calculated by the eigenvalue method for chains with $n = \infty$. The range of the conformational energy $E_{\omega''}$ affording agreement with the experimentally observed temperature coefficient, d ln [M]D/d$T = -4 \times 10^{-3}$ deg^{-1}, is *ca.* 2–3 kcal mole^{-1}, being in good accordance with the previous estimation.[21]

In Figure 8, [M]D is plotted against $-\ln\sigma$ and $-\ln\tau$ for the poly-(*S*)-5-methyl-1-heptene system. It may be interesting to note here that the signs of the coefficients (∂ ln [M]D/∂ ln σ and ∂ ln [M]D/∂ ln τ) are opposite to each other. Numerical results obtained for a set of parameters $\sigma = 0.5$ and 0.25 are tabulated in Table IV for several representative stereochemical sequences. The magnitude of the temperature coefficient of the optical rotation increases sharply with replication probability between 1.0 and 0.9. The value calculated for a chain with $p_r = 0.9$ is approximately in the range of that observed,[5] d ln [M]D/d$T = -5 \times 10^{-3}$ deg^{-1}.

Table IV. Partial Derivatives of [M]D with Respect to σ and τ, and Temperature Coefficients Calculated Therefrom

p_r	∂ ln [M]D/∂ ln σ[a]	∂ ln [M]D/∂ ln τ[b]	d ln [M]D/dT[c] × 10^3, deg^{-1}
1.0	0.351	−0.238	−0.29
0.9	0.729	−0.795	−2.00
0.0	0.843	−0.930	−2.36

[a] Obtained for $\tau = 0.25$ and $\omega'' = 0$. [b] Obtained for $\sigma = 0.50$ and $\omega'' = 0$. [c] Values estimated at $T = 298$°K.

Variation of the optical rotations with ω'' was examined as well for the last polymer system. Calculations were performed with the matrices shown in eq 55–57″. As for the matrices U'' and W'', those given previously in eq 51 and 54 are equally applicable here. The results obtained for chains with various tacticities are shown by the solid curves in Figure 7, where the uppermost solid curve ($p_r = 1.0$) was derived for a polymer with an infinite chain length, while the others were computed for Monte Carlo chains with 100 monomer units. Within the aforementioned range of $E_{\omega''}$ (2 to 3 kcal mole^{-1}) the calculated temperature coefficients d ln [M]D/dT are *ca.* -7×10^{-3}, -4×10^{-3}, and -4×10^{-3} deg^{-1} for $p_r = 1.0$, 0.9, and 0.0, respectively. For the isotactic chain sequence, a fairly large energy $E_{\omega''} = -RT$ ln

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[37] P. Cossee, *J. Catalysis*, 3, 80 (1964); E. J. Arlman, *ibid.*, 3, 89 (1964); E. J. Arlman and P. Cossee, *ibid.*, 3, 99 (1964); E. J. Arlman, *ibid.*, **5**, 178 (1966).

[38] See L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Interscience Publishers Inc., New York, N. Y., 1966.

$$U_d' = (U_l')^{\mathrm{T}} = \begin{bmatrix} 3\tau + 4\tau^2 + 6\omega'' + 3\sigma\omega'' + 9\tau\omega'' + 2\sigma\tau\omega'' & 3 + \sigma + 7\tau + \sigma\tau + 4\tau^2 + 4\omega'' + 7\sigma\omega'' + 5\tau\omega'' + 3\sigma\tau\omega'' \\ 3 + 2\sigma + 7\tau + \sigma\tau + 4\tau^2 + 4\omega'' + 3\sigma\omega'' + 5\tau\omega'' + 3\sigma\tau\omega'' & 6\omega'' + 3\sigma\omega'' + 11\tau\omega'' + 2\sigma\tau\omega'' + 4\tau^2\omega'' \end{bmatrix} \tag{55}$$

$$U_{d;2}' = U_{l;n}' = \begin{bmatrix} 3 + 2\sigma + 7\tau + \sigma\tau + 4\tau^2 + 4\omega'' + 3\sigma\omega'' + 5\tau\omega'' + 3\sigma\tau\omega'' & 0 \\ 0 & 6 + 3\sigma + 11\tau + 2\sigma\tau + 4\tau^2 + 2\omega'' + 7\sigma\omega'' + \tau\omega'' + 4\sigma\tau\omega'' \end{bmatrix} \tag{55'}$$

$$U_{d;n}' = U_{l;2}' = \begin{bmatrix} 3 + \sigma + 7\tau + \sigma\tau + 4\tau^2 + 4\omega'' + 7\sigma\omega'' + 5\tau\omega'' + 3\sigma\tau\omega'' & 0 \\ 0 & 6 + 3\sigma + 11\tau + 2\sigma\tau + 4\tau^2 + 2\omega'' + 7\sigma\omega'' + \tau\omega'' + 4\sigma\tau\omega'' \end{bmatrix} \tag{55''}$$

$$W_d' = \begin{bmatrix} 3\tau + 4\tau^2 + 6\omega'' + 5\sigma\omega'' + 9\tau\omega'' + 2\sigma\tau\omega'' & -6 - 5\sigma - 11\tau - 4\sigma\tau - 4\tau^2 - 2\omega'' - 3\sigma\omega'' - \tau\omega'' \\ 6 + 8\sigma + 11\tau + 4\sigma\tau + 4\tau^2 + 2\omega'' - 3\sigma\omega'' + \tau\omega'' & -6\omega'' - \sigma\omega'' - 11\tau\omega'' - 2\sigma\tau\omega'' - 4\tau^2\omega'' \end{bmatrix}\alpha \tag{56}$$

$$W_{d;2}' = \begin{bmatrix} 6 + 8\sigma + 11\tau + 4\sigma\tau + 4\tau^2 + 2\omega'' - 3\sigma\omega'' + \tau\omega'' & 0 \\ 0 & -6 - \sigma - 11\tau - 2\sigma\tau - 4\tau^2 - 2\omega'' - 11\sigma\omega'' - \tau\omega'' - 4\sigma\tau\omega'' \end{bmatrix}\alpha \tag{56'}$$

$$W_{d;n}' = \begin{bmatrix} -3 - 4\sigma - 4\tau - 3\sigma\tau + 2\omega'' + 4\sigma\omega'' + 4\tau\omega'' + 3\sigma\tau\omega'' & 0 \\ 0 & 2\sigma - 4\sigma\omega'' \end{bmatrix}\alpha \tag{56''}$$

$$W_l' = \begin{bmatrix} -3\tau - 4\tau^2 - 6\omega'' - \sigma\omega'' - 9\tau\omega'' - 2\sigma\tau\omega'' & 6 + 8\sigma + 11\tau + 4\sigma\tau + 4\tau^2 + 2\omega'' - 3\sigma\omega'' + \tau\omega'' \\ -6 - 5\sigma - 11\tau - 4\sigma\tau - 4\tau^2 - 2\omega'' - 3\sigma\omega'' - \tau\omega'' & 6\omega'' + 5\sigma\omega'' + 11\tau\omega'' + 2\sigma\tau\omega'' + 4\tau^2\omega'' \end{bmatrix}\alpha \tag{57}$$

$$W_{l;2}' = \begin{bmatrix} -6 - 5\sigma - 11\tau - 4\sigma\tau - 4\tau^2 - 2\omega'' - 3\sigma\omega'' - \tau\omega'' & 0 \\ 0 & 6 + 5\sigma + 11\tau + 2\sigma\tau + 4\tau^2 + 2\omega'' + 3\sigma\omega'' + \tau\omega'' + 4\sigma\tau\omega'' \end{bmatrix}\alpha \tag{57'}$$

$$W_{l;n}' = \begin{bmatrix} 3 + 6\sigma + 4\tau + 3\sigma\tau - 2\omega'' - 6\sigma\omega'' - 4\tau\omega'' - 3\sigma\tau\omega'' & 0 \\ 0 & 2\sigma - 4\sigma\omega'' \end{bmatrix}\alpha \tag{57''}$$

ω'' is required in order to attain the experimentally observed temperature coefficient. The values for lower isotacticities are consistent with the experimental observations. Hence the investigations developed here on the temperature dependence support the conclusion drawn in the preceding section.

The variation of the optical rotation with temperature in the other polymer systems can be interpreted likewise. While polymers of (*S*)-3-methyl-1-pentene and (*R*)-3,7-dimethyl-1-octene behave in a similar manner as poly-(*S*)-4-methyl-1-hexene, poly-(*S*)-6-methyl-1-octene possesses characteristics comparable to those of poly-(*S*)-5-methyl-1-heptene.

Concluding Remarks

Because of the cooperative nature of the spatial interactions between neighboring groups, conformational rigidity about the polymer main chain depends on the stereochemical arrangements along the backbone chain. The highest cooperativity in the vinyl polymer system is realized for the isotactic structure. Introduction of a small portion of heterotactic units largely alleviates the stiffness characteristic of the isotactic chain.[18]

Conformational rigidity of the chain skeleton is also affected by the bulkiness of the pendant groups. For a vinyl polymer with side groups R = CH_3, as discussed in the previous paper,[18] the (t,t) element of U_d' and U_l' may be assigned a statistical weight of unity, being comparable with those of the $(t,g^{\pm})$ and $(g^{\mp},t)$ elements in the corresponding matrices. When the polymer system involves R = CH_2CH_3 or longer alkyl side chains, we have assumed $U_d'(t,t) = U_l'(t,t) \cong \tau$. These elements are further reduced to the order of ω'' for polymers of 3- or 4-substituted α-olefins. Accordingly, the number of allowed main-chain conformations drastically diminishes in this order. Particularly in the last polymer system mentioned above, the stiffness of the chain in terms of the number of low-energy conformations no longer alters with the stereochemical configuration of the chain, while the geometrical properties such as polymer end-to-end dimensions largely depend on the stereochemical arrangements of the chain units.

Optical rotatory properties of copolymers prepared from the monomer mixture comprising (*R*) and (*S*) antipodes were recently studied by Pino, Ciardelli, Montagnoli, and Pieroni.[39] When the asymmetric tertiary

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(39) P. Pino, F. Ciardelli, G. Montagnoli, and O. Pieroni, *J. Polymer Sci.*, B5, 307 (1967).

carbons are located at the α or β position with respect to the polymer main chain, the observed relations between the mean residue optical rotation $[M]_D$ and the optical purity of the polymerization system were nonlinear. Our preliminary studies on the basis of the conformational analyses presented in this paper seems to be quite consistent with these observations. The general conclusions reached in the present treatment regarding the stereochemistry of poly-α-olefins are thus given further support. Full details will be published elsewhere.

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The Poisoning of Ion-Exchange Resins. Inhibition of Cation Exchange by Cationic Surface-Active Agents

Hamish Small

Contribution from the Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640. *Received November 9, 1967*

Abstract: It has been observed that low concentrations of amphiphilic cations, *e.g.*, the cetyldimethylbenzylammonium cation, can markedly reduce the rate of Na^+–Na^+ exchange between the Na^+ form of a styrene-based sulfonic acid type cation exchanger and an aqueous solution of a sodium salt. It is proposed that the amphiphilic ion exerts its effect by forming a lipid-like layer around the resin particle which impedes ion transfer between the aqueous and resin phases. The model bears a resemblance to present-day concepts of the biological membrane and is pertinent to the fouling of ion-exchange resins.

Under appropriate conditions the exchange of small inorganic ions between synthetic ion-exchange resins and aqueous solutions takes place rapidly.[1–3] The exchange reactions which are diffusion controlled can typically have half-times on the order of 1 min. It has been discovered that certain amphiphilic ions, *e.g.*, cationic and anionic surfactants, can intervene in these fast reactions to produce marked inhibitory effects. It is believed that this inhibition is a result of the formation of a lipid-like layer at the resin–solution interface which impedes ion transfer between the aqueous and resin phases. There are aspects of such a model which have qualitative parallels in the Davson and Danielli concept of the biological cell membrane.[4]

Experimental Section

Preparation of Resins. A sample of very uniformly sized resin particles was obtained by screening a quantity of commercial cation-exchange resin, Dowex[5] 50W X8 (20–50 mesh) Na^+ form, and harvesting those beads which stuck in a 30-mesh (U. S.) screen. The uniformly sized resin was labeled with radiosodium by contacting it for 2 hr with an aqueous solution of sodium hydroxide which contained the ^{22}Na radioisotope.

Measurement of Ion-Exchange Rates. A small quantity (about 0.2 g) of the radioactively labeled resin was introduced into a U-shaped tube provided on one arm with a plug of crumpled platinum wire which acted as a retainer for resin when solutions were pumped through the U tube. The tube containing the labeled resin was in turn placed in the well of a γ-scintillation detector which was associated with a rate meter–recorder combination (Figure 1). In this way, an instantaneous record of the resin activity was provided throughout the course of a kinetic experiment. The ion-exchange reaction was effected by pumping through the U tube an appropriate aqueous electrolyte (unlabeled) at such a rate (12 ml/min) that the amount of the exchanging ion supplied to the resin was well in excess of the resin demand. The method thus satisfied the criteria of the "infinite bath technique" of Boyd, *et al.*[1] The rate of removal of sodium ion from the resin, *i.e.*, the rate of exchange, was obtained from the record of the decline of activity of the resin as expressed on the recorder trace. The history of the exchange is expressed graphically as a plot of F *vs.* time (t), where F is the fraction of sodium removed by the aqueous electrolyte.

Surface-Active Agents. The surface-active agents used were obtained as commercial preparations which in some cases contained, in addition to the major component, appreciable quantities of closely related species. The surface-active cationic species studied were cetyldimethylbenzylammonium ($CDMBA^+$),[6a] lauryldimethylbenzylammonium ($LDMBA^+$),[6b] cetylpyridinium (CPy^+),[6c] cetyltrimethylammonium ($CTMA^+$),[6c] and laurylisoquinolinium (LIQ^+).[6d]

Experimental Results and Discussion

Rate of Uninhibited Na^+–Na^+ Exchange. Since it will be a major aim in this paper to demonstrate the inhibitory effect of certain amphiphilic ions on fast exchange reactions, it is instructive to first examine a typical uninhibited reaction. The self-exchange of sodium ions between a resin and solution phase is a typically fast reaction whose mechanism is well understood.[1] Moreover, the reaction is particularly amenable to examination by the radiochemical technique. The sodium form of Dowex 50W X8 (30 mesh) was flushed with 0.1 *M* NaCl and the fractional exchange determined as a function of time. The results are illustrated in Figure 2. Exchange is essentially complete within a few minutes and the rate may be conveniently expressed as a half-time, *i.e.*, the time taken to attain half-

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(1) G. E. Boyd, A. W. Adamson, and L. S. Myers, *J. Am. Chem. Soc.*, **69**, 2836 (1947).

(2) D. Reichenberg, *ibid.*, **75**, 589 (1953).

(3) F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 250 ff.

(4) H. Davson and J. F. Danielli, "Permeability of Natural Membranes," 2nd ed, Cambridge University Press, London, 1952.

(5) Dowex is a registered trademark of The Dow Chemical Co.

(6) (a) "Cetol," Fine Organics, Inc.; (b) "Culversan 60LC," Culver Chemical Co.; (c) Fine Organics, Inc.; (d) "Isothan Q-15" Onyx Chemicals.