

$2^3\Sigma_g^-$ emission was observed in solutions of perylene, 9,10-diphenylanthracene, anthracene, and rhodamine B. The data of Table VIII agree with these results.

The two-step energy transfer mechanism involving singlet oxygen monomers and the fluorescer triplet as an intermediate has thus been shown to be more significant than the singlet oxygen collisional-pair mechanism. However, the data do not rule out the presence of the collisional pair transfer. Indeed, the $(^1\Delta_g)_2$ state was shown to be produced in the systems studied.

Transfer from collisional pair states would be expected to occur to those acceptors with absorption having a high degree of overlap with the collisional pair emission.

Acknowledgments. This work was supported through funds provided by the United States Atomic Energy Commission under Contract No. AT(30-1)-905. We wish to thank A. F. Vaudo for discussions on energy transfer theory.

Optical Rotatory Properties of Vinyl Copolymers¹

Akihiro Abe

Contribution from the Central Research Laboratory, Showa Denko Company, Tamagawa, Ohta-ku, Tokyo, Japan. Received August 30, 1969

Abstract: Variation of optical rotatory properties with copolymer composition was studied for some poly- α -olefin systems comprising two optical antipodes, and for those composed of an optically active monomer and inactive comonomer with isomeric structure. Optical activities of these polymers were evaluated within the framework of the revised version of the Whiffen-Brewster empirical rule. For a copolymer chain with moderately blocked structure, poly-(*R*)(*S*)-4-methylhex-1-ene exhibits sizable deviation from linearity in the optical rotation vs. copolymer composition plot, while poly-(*R*)(*S*)-5-methylhept-1-ene gives a nearly linear relation. The agreement with experimental observation is satisfactory in both cases. Extension of the treatment to the copolymer system derived from (*S*)-4-methylhex-1-ene and 4-methylpent-1-ene or 5-methylhex-1-ene again predicts some departure from linearity. The results compare favorably with experimental data for the former system. The conformational asymmetry characteristic of a copolymer system containing a comonomer having a branched structure at the position γ (or further) to the vinyl group is also discussed.

Theoretical interpretation of optical rotatory properties of poly- α -olefins such as poly-(*S*)-3-methylpent-1-ene, poly-(*R*)-3,7-dimethyloct-1-ene, poly-(*S*)-4-methylhex-1-ene, poly-(*S*)-5-methylhept-1-ene, and poly-(*S*)-6-methyloct-1-ene has been presented in the preceding paper.² Conformational analysis based on the rotational isomeric state approximation revealed that the rigidity of the backbone chain is largely influenced by the side chain configuration. When the asymmetric site is located at the α or β position with respect to the main chain tertiary carbon, the number of conformations permitted to the skeletal chain is severely restricted, due to the high energy four-bond steric interactions. Such considerations, combined with the Whiffen³-Brewster⁴ empirical rule, lead to the prediction of a large optical rotatory power of these polymer systems, regardless of the tacticity of the chain. When the distance between the asymmetric site and the backbone chain is further apart, the chain becomes less stiff. It was shown as a consequence that configuration along the chain may be an important factor determining the optical rotatory properties of polymers such as poly-(*S*)-5-methylhept-1-ene. Conformational analysis of isotactic poly-(*S*)-4-methylhex-1-ene has been also reported independently by Luisi and Pino.⁵

Recently optical rotatory properties of copolymers prepared from the monomer mixture comprising (*R*) and (*S*) optical antipodes were studied by Pino, Ciardelli, Montagnoli, and Pieroni.⁶ When the optical activity of the polymer was plotted against the optical purity of the starting monomer, sizable deviation from linearity was observed for poly-(*R*)(*S*)-3,7-dimethyloct-1-ene and poly-(*R*)(*S*)-4-methylhex-1-ene. In the case of poly-(*R*)(*S*)-5-methylhept-1-ene, however, the relation was nearly linear.

Extension of our previous treatment to such copolymer systems⁷ is straightforward. Copolymers of optically active monomers like (*S*)-4-methylhex-1-ene with inactive symmetric comonomers are also examined. The results of calculations are compared with experimental data reported by Carlini, Ciardelli, and Pino.⁸

Stereochemistry of the Polymer System

Steric interactions here considered are those between the groups separated by three and by four C-C bonds. In keeping with the previous usage,^{2,9} this paper intro-

(6) P. Pino, F. Ciardelli, G. Montagnoli, and O. Pieroni, *J. Polym. Sci., Part B*, **5**, 307 (1967).

(7) Procedures for taking statistical mechanical averages for such stereoirregular copolymer systems were first developed by P. J. Flory, *Proc. Nat. Acad. Sci. U. S.*, **51**, 1060 (1964), and by P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965). See also P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience Publishers, New York, N. Y., 1969.

(8) C. Carlini, F. Ciardelli, and P. Pino, *Makromol. Chem.*, **119**, 244 (1968).

(9) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966); P. J. Flory, J. E. Mark, and A. Abe, *ibid.*, **88**, 639 (1966).

(1) Presented at the 22nd Annual Meeting of Chemical Society of Japan, Tokyo, 1969.

(2) A. Abe, *J. Amer. Chem. Soc.*, **90**, 2205 (1968).

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

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

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

duces statistical weight parameters σ for three-bond interactions such as those encountered in *n*-butane, τ for the ones in 2-methylbutane, ω'' for four-bond interactions in *n*-pentane, respectively. Values of such statistical weight parameters are estimated from various sources^{2,9,10} as $\sigma \cong 0.5 \tau$, $\cong 0.1-0.25$ and $\omega'' \cong 0.01$. Contributions from conformations subject to the highly repulsive interactions designated previously by ω' and ω may be negligibly small.

$$U_d' = U_l' = \begin{bmatrix} 2\tau + \tau^2 + 4\omega'' + 2\sigma\omega'' + 2\tau\omega'' & 2 + \sigma + 3\tau + \tau^2 + 2\omega'' + 3\sigma\omega'' + \tau\omega'' \\ 2 + \sigma + 3\tau + \tau^2 + 2\omega'' + 3\sigma\omega'' + \tau\omega'' & 4\omega'' + 2\sigma\omega'' + 4\tau\omega'' + \tau^2\omega'' \end{bmatrix} \quad (5)$$

$$U_{d;2}' = U_{l;2}' = U_{d;n}' = U_{l;n}' = \begin{bmatrix} 2 + \sigma + 3\tau + \tau^2 + 2\omega'' + 3\sigma\omega'' + \tau\omega'' & 0 \\ 0 & 4 + 2\sigma + 4\tau + \tau^2 + 4\sigma\omega'' \end{bmatrix} \quad (5')$$

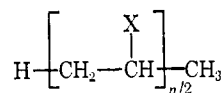
Statistical weight matrices U_d' for the polymer system derived from (*S*)-4-methylhex-1-ene and (*S*)-5-methylhept-1-ene are given by eq 50 and 55 of the preceding paper.² The other statistical weight matrices required for the present calculations may be obtained by simple transformation of these equations

$$U_{d;R}' = U_{l;S}' = (U_{d;S}')^T \quad (1)$$

and

$$U_{l;R}' = U_{d;S}' \quad (2)$$

where $(U_{d;S}')^T$ is the transpose of $U_{d;S}'$. The subscripts *d* and *l* define the configuration about the pseudo-asymmetric tertiary carbon in the main chain, and *R* and *S* represent the asymmetry of the side chain. Special attention should be paid to the terminals of the chain molecules. The matrices U_2' and U_n' have been defined² for the second and the last bond, respectively, of the vinyl polymer system represented generally by



When $\text{X} = -\text{CH}_2\text{C}^*\text{H}(\text{CH}_3)\text{CH}_2\text{CH}_3$ (*S*), then

$$U_{d;2;S}' = U_{l;n;S}' = \begin{bmatrix} 2 + \tau + 2\omega'' + 2\tau\omega'' & 0 \\ 0 & 3 + 2\tau + 4\omega'' + 2\tau\omega'' \end{bmatrix} \quad (3)$$

$$U_{d;n;S}' = U_{l;2;S}' = \begin{bmatrix} 1 + \tau + 5\omega'' + 2\tau\omega'' & 0 \\ 0 & 3 + 2\tau + 4\omega'' + 2\tau\omega'' \end{bmatrix}$$

The corresponding matrices for the system with $\text{X} = -(\text{CH}_2)_2\text{C}^*\text{H}(\text{CH}_3)\text{CH}_2\text{CH}_3$ (*S*) have been given by eq 55' and 55'' of the preceding paper.² Finally, those associated with the (*R*) configuration can be deduced from the relation prescribed by eq 1 and 2.

A later section will treat copolymers of (*S*)-4-methylhex-1-ene with an optically inactive comonomer like 4-methylpent-1-ene or 5-methylhex-1-ene. In reflection of the molecular structure, the statistical weight matrices shown in eq 4 ($\text{X} = -\text{CH}_2\text{CH}(\text{CH}_3)_2$) and 5 (X

$= -(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$) for the latter monomers are symmetric.

$$U_d' = U_l' = \begin{bmatrix} 2\omega'' & 1 + 2\omega'' \\ 1 + 2\omega'' & 2\omega'' \end{bmatrix} \quad (4)$$

$$U_{d;2}' = U_{l;2}' = U_{d;n}' = U_{l;n}' = \begin{bmatrix} 1 + 2\omega'' & 0 \\ 0 & 2 + 2\omega'' \end{bmatrix} \quad (4')$$

On the other hand, the U'' matrices include the effect of stereochemical arrangements of substituents on two neighboring tertiary carbons in the skeletal chain, but may be defined independently of the side chain configuration. Therefore, eq 51 of the preceding paper² is commonly applicable to any poly- α -olefins under present consideration.

Evaluation of Optical Rotatory Power

Statistical mechanical average of the optical rotatory contribution from the individual structural units is evaluated by the method prescribed in the preceding paper.² Then the mean optical rotatory power attributable to a monomer residue is given by

$$[\text{M}] = (2/nZ)[0 \ 0 \ J^T] \left[\prod_{(i/2)=1}^{(n/2)-1} (H_i' H_{i+1}') \right] H_n' \begin{bmatrix} J \\ 0 \\ 0 \end{bmatrix} \quad (6)$$

where

$$Z = J^T \left[\prod_{(i/2)=1}^{(n/2)-1} (U_i' U_{i+1}') \right] U_n' J \quad (7)$$

and

$$J = \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

J^T is the transpose of J . The matrices W' and W'' have been introduced previously for the purpose of representing the optical rotatory contribution ascribable to a skeletal bond when the preceding bond is in the specified rotational states. The side chain contribution is taken into consideration in the W' matrices, as in the case of the corresponding statistical weight matrices U' . With a proper choice of a set of U' and W' or of U'' and W'' for a given bond, the H 's in eq 6 are defined by

$$H = \begin{bmatrix} U & \circ \\ W & U \end{bmatrix} \quad (8)$$

where \circ is a 2×2 zero matrix. For polymers of (*S*)-4-methylhex-1-ene and (*S*)-5-methylhept-1-ene, the W' matrices are given in eq 52 and 53 and 56 and 57, respectively, of the preceding paper.² From the symmetry consideration, the corresponding matrices for the optical antipodes having the (*R*) configuration

(10) Estimated from studies on the unperturbed end-to-end distance for various poly- α -olefin systems: A. Abe, to be published.

may be obtained using the relation given in eq 9.

$$\begin{aligned} W_{d;R}' &= -W_{l;S}' \\ W_{l;R}' &= -W_{d;S}' \end{aligned} \quad (9)$$

When $X = -CH_2C^*H(CH_3)CH_2CH_3$, the following equations apply for the chain terminals.

$$\begin{aligned} W_{d;2;R}' &= -W_{l;2;S}' = \\ \left[\begin{array}{cc} 4 + 3\tau + 2\omega'' & 0 \\ 0 & -4 - 2\tau - 2\omega'' - 2\tau\omega'' \end{array} \right] \alpha \end{aligned} \quad (10)$$

$$\begin{aligned} W_{l;2;R}' &= -W_{d;2;S}' = \\ \left[\begin{array}{cc} -6 - 3\tau + 2\omega'' & 0 \\ 0 & 2 + 2\tau + 6\omega'' + 2\tau\omega'' \end{array} \right] \alpha \end{aligned}$$

and

$$\begin{aligned} W_{d;n;R}' &= -W_{l;n;S}' = \\ \left[\begin{array}{cc} -4 - 2\tau + 4\omega'' + 2\tau\omega'' & 0 \\ 0 & -1 + 2\omega'' \end{array} \right] \alpha \end{aligned} \quad (10')$$

$$\begin{aligned} W_{l;n;R}' &= -W_{d;n;S}' = \\ \left[\begin{array}{cc} 3 + 2\tau - 3\omega'' - 2\tau\omega'' & 0 \\ 0 & -1 + 2\omega'' \end{array} \right] \alpha \end{aligned}$$

α represents the magnitude of the optical rotatory contribution attributable to a C-C bond when associated with a skew conformation.¹¹ In the succeeding treatment, unless otherwise noted, Brewster value,⁴ $\alpha = 60^\circ$, is assumed. Similar matrices for poly-(S)-5-methylhept-1-ene have been derived in eq 56', 56'', 57', and 57'' of the preceding paper.² Those for the (R) configuration may be obtained from the relation given by eq 9.

The W' matrices for the system, which will be identified later as a comonomer, are summarized in eq 11 ($X = -CH_2CH(CH_3)_2$) and in eq 12 ($X = -(CH_2)_2CH(CH_3)_2$).

$$W_a' = -W_l' = \left[\begin{array}{cc} 2\omega'' & -3 \\ 3 & -2\omega'' \end{array} \right] \alpha \quad (11)$$

$$W_{d;2}' = -W_{l;2}' = \left[\begin{array}{cc} 3 & 0 \\ 0 & -2 - 2\omega'' \end{array} \right] \alpha \quad (11')$$

$$W_{d;n}' = -W_{l;n}' = \left[\begin{array}{cc} -2 + 2\omega'' & 0 \\ 0 & 0 \end{array} \right] \alpha \quad (11'')$$

Finally, the W'' matrices are independent, by their definition, of the side chain asymmetry; accordingly, those given in eq 54 of the preceding paper² are valid without modification.

Calculations of the optical rotation were carried out for polymer chains of various tacticities comprising 100 monomer units ($n = 200$). Stereoirregular chains are generated using a series of random numbers ranging from 0 to 1 for a given value of replication probability p_r of the identical unit.^{2,9} The parameter p_r defined in this manner may be also regarded as the probability of an isotactic dyad placement.¹² The arrangement of

(11) See Figure 3 of ref 2.

(12) The polymerization mechanism proposed by P. Cossee, *J. Catal.*, **3**, 80 (1964), E. J. Arlman, *ibid.*, **3**, 89 (1964), E. J. Arlman and P. Cossee, *ibid.*, **3**, 99 (1964), and E. J. Arlman, *ibid.*, **5**, 178 (1966), suggests that the stereoirregularity introduced in the α -olefin polymers may be predomi-

(R) and (S) monomer residues along a polymer chain is another factor to be considered. Three typical examples of copolymer chains were examined such as (a) blocked, (b) moderately blocked, and (c) random structures. While the first sequence (a) is simply expressed by the general formula ($S_{n-m/2}$) ($R_{m/2}$), where $n \geq m \geq 0$, the last one (c) is generated from a table of random numbers. The chain sequence (b) possesses characteristics between these two extremes.¹³

Results of Calculation

Variation of the optical rotatory power with the composition of the copolymer is shown in Figure 1 for poly-(R)(S)-4-methylhex-1-ene. In this particular polymer system, as pointed out previously,² optical rotatory properties do not much depend on the tacticity along the polymer chain, and therefore computation carried out for a given tacticity suffices to represent the behavior of polymers with any chain configuration from the isotactic to the syndiotactic. Suppression of the transition between the two stable helical conformations by choosing $\omega'' = 0$ forces the polymer chain to be in one of the two anticlined stereochemical arrangements. Under this condition, slight excess of either (R) or (S) monomer residue over the other causes a large free energy difference between these two conformations, irrespective of the arrangement of (R) and (S) units along the chain. Except in the vicinity of $f_s = 0.5$, where a sharp drop in the molar optical rotation is expected, the calculated values of the mean residue rotation are very large over a wide range of composition as indicated by curves 1 in Figure 1. As the statistical weight parameter ω'' increases, the chain becomes more flexible. Consequently, the optical rotatory power tends to decrease gradually with f_s . Examples are shown by curves 2, 3, and 4 in Figure 1 for $\omega'' = 0.003$, 0.01, and 0.03, respectively. It is important to note here that the optical rotatory behavior of such copolymer systems is quite sensitive, in the range of ω'' studied, to the arrangement of (R) and (S) monomer residues along the chain. The dependence of the optical rotation on polymer composition is nearly linear for polymers with blocked structures (*cf.* Figure 1a). As the sequential distribution of the units becomes more random, the curve tends to be more convex (Figures 1b and 1c). If we let $\omega'' = 1$ as an extreme case for the independent potential for the bond rotation, a linear relation should be observed without regard to the arrangement of the units. In such a case, however, values of optical rotation are necessarily low.

Insertion of another methylene unit between the main chain tertiary carbon and the asymmetric center

nantly of the type $\dots dld \dots$ or $\dots ld \dots$. Calculations for such polymer sequences were also included in the preceding paper,² where the optical rotatory behavior of homopolymers were studied in relation to the stereoregularity of the system. Variation arising from such modification should not be essential here since this treatment will include chain of various tacticities ranging from the isotactic to the syndiotactic.

(13) Such a chain sequence was formulated on the assumption that the asymmetric selection of the monomer occurs either at the growing polymer chain end or at the catalyst site at a constant rate throughout the course of the polymerization. A value of 0.9 was arbitrarily chosen for the preference of the monomer with the identical configuration. It should be noted however that the method of formulation is unimportant as long as chains of various monomer compositions are generated in a consistent manner.

$$W_a' = -W_l' = \begin{bmatrix} 2\tau + \tau^2 + 4\omega'' + 2\sigma\omega'' + 2\tau\omega'' & -4 - 4\sigma - 4\tau - \tau^2 \\ 4 + 4\sigma + 4\tau + \tau^2 & -4\omega'' - 2\sigma\omega'' - 4\tau\omega'' - \tau^2\omega'' \end{bmatrix} \alpha \quad (12)$$

$$W_{d,2}' = -W_{l,2}' = \begin{bmatrix} 4 + 4\sigma + 4\tau + \tau^2 & 0 \\ 0 & -4 - 2\sigma - 4\tau - \tau^2 - 4\sigma\omega'' \end{bmatrix} \alpha \quad (12')$$

$$W_{d,n}' = -W_{l,n}' = \begin{bmatrix} -2 - 3\sigma - \tau + 2\omega'' + 3\sigma\omega'' + \tau\omega'' & 0 \\ 0 & 0 \end{bmatrix} \alpha \quad (12'')$$

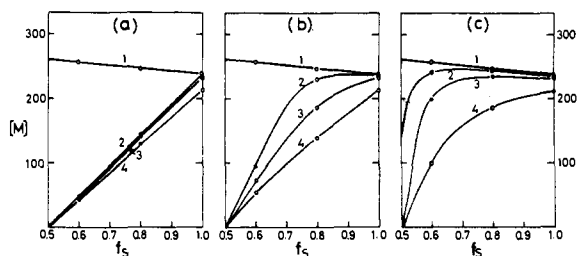


Figure 1. Variation of the mean residue optical rotation with the copolymer composition, calculated for poly-(*R*)(*S*)-4-methylhex-1-ene ($n = 200$) with (a) blocked, (b) moderately blocked, and (c) random arrangements of the two optical antipodes. The curves were derived for (1) $\omega'' = 0$, (2) $\omega'' = 0.003$, (3) $\omega'' = 0.01$, and (4) $\omega'' = 0.03$, respectively, another parameter τ being kept constant at 0.25 throughout.

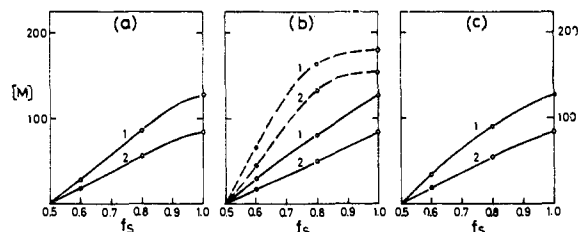


Figure 2. The mean residue optical rotation vs. the copolymer composition for an isotactic poly-(*R*)(*S*)-5-methylhept-1-ene ($n = 200$) with (a) blocked, (b) moderately blocked, and (c) random arrangements of the constituent monomer units. The solid curves indicate the results calculated for $\omega'' = 0.01$, and the dotted ones shown in b are those for $\omega'' = 0$. The difference between curves 1 ($\tau = 0.1$) and 2 ($\tau = 0.25$) indicates the effect of τ in each category. In all the cases, the parameter σ is taken to be 0.5.

in the side chain greatly reduces the stiffness of the backbone chain. In such a polymer system, as pointed out in the preceding paper,² the values of optical rotation should depend intrinsically on the chain configuration. Calculations carried out for the isotactic, the moderately isotactic, and the syndiotactic configuration are shown in Figures 2, 3, and 4, respectively. It should be worth noticing here that the stereochemical configuration characteristic to the vinyl polymer system is no longer pseudoasymmetric. For simplicity, consider two isomeric block copolymers in perfectly isotactic *d* and *l* configurations, respectively. Examples are shown in Table I, where *R* and *S* denote the asymmetry of the side chain. Stable conformations deduced from eq 1 and 2 for each part of the isotactic configurations

Table I. Transition between the Two Stable Screw Conformations

Configuration	Probable conformation
$\cdots S_l S_l R_l R_l \cdots$	$\cdots (tg^-)(tt)(g^+t)(g^+t) \cdots$
$\cdots S_d S_d R_d R_d \cdots$	$\cdots (g^-t)(g^-g^+)(tg^+)(tg^+) \cdots$

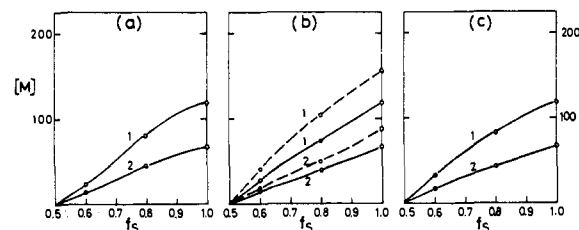


Figure 3. The mean residue optical rotation vs. the copolymer composition for a moderately isotactic poly-(*R*)(*S*)-5-methylhept-1-ene ($p_r = 0.9$) with (a) blocked, (b) moderately blocked, and (c) random copolymer structures. For the statistical weight parameters used in calculations, see the legend to Figure 2.

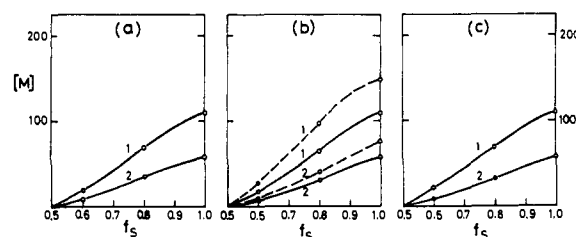


Figure 4. The mean residue optical rotation vs. the copolymer composition for a syndiotactic poly-(*R*)(*S*)-5-methylhept-1-ene with (a) blocked, (b) moderately blocked, and (c) random copolymer structures. For the statistical weight parameters used in calculations, see the legend to Figure 2.

are linked together by a probable transition element as indicated by the underline. In the first configuration, transition between the two stable helical conformations is permitted through the low energy arrangement associated with $U_l'(t,t)$, whereas a similar transition in the latter configuration occurs inevitably through the high energy conformation such as $U_d''(g^-,g^+)$. In such a case, if ω'' is sufficiently small, succession of the preceding conformation (g^-t) beyond the junction between the *S* and *R* sequences may become a preferable form of the system. It follows from this that the conformational free energy is not the same for these two isomeric configurations. In practice, the conformational partition function Z as defined by eq 7 was evaluated for copolymer chains such as $S_{80}R_{20}$ in the isotactic *d* and *l* configurations, respectively. The difference arising from the chain configuration as expressed in terms of $\ln(Z_l/Z_d)$ is given in the third column of Table II,

Table II. Correlation between the Sequential Distribution of Optical Antipodes and the Chain Configurations

Parameter		$\ln(Z_l/Z_d)$	[M]	
τ	ω''		<i>l</i> chain	<i>d</i> chain
0.1	0	0.946	117.7	177.5
0.1	0.01	0.344	82.6	85.6
0.25	0	0.860	105.1	151.9
0.25	0.01	0.265	55.0	55.9

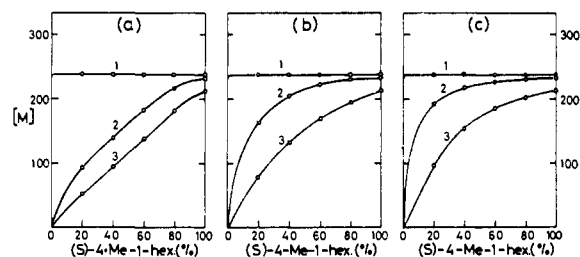


Figure 5. Optical rotatory properties of copolymers derived from (*S*)-4-methylhex-1-ene and 4-methylpent-1-ene ($n = 200$): (a) blocked, (b) moderately blocked, and (c) random. The mean residue optical rotation is plotted against the content of optically active species. The statistical weight parameters used in calculations are (1) $\omega'' = 0$, (2) $\omega'' = 0.01$, and (3) $\omega'' = 0.03$, respectively, τ being kept at 0.25.

where the subscripts d and l denote the configuration of the isotactic chain. The effect of such asymmetry diminishes of course as ω'' increases, but not to zero even at $\omega'' = 0.01$. These results may suggest that the chain configuration as expressed customarily by d and l is not fully independent of the sequential distribution of (*R*) and (*S*) monomer units.¹⁴ The effect on the optical rotatory properties was examined on the same chain sequence, as shown in Table II. When $\omega'' = 0$, the calculated values of molar optical rotation depend largely on the chain configuration. As may be expected from the conformational aspects described above, the lower value obtained for the isotactic l chain is close to that deduced by the linear interpolation for the copoly-

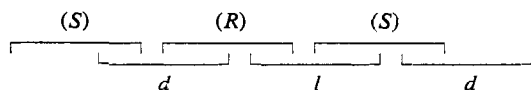
(14) When the transformation from the *S* to the *R* sequence accompanies simultaneous reversal of the configuration, e.g., $\dots S_l S_l R_d R_d \dots$ or $\dots S_d S_d R_l R_l \dots$, the transition between the stable conformations may take place effectively through $U'(t, t)$. Hence the total number of conformations calculated for chains of $S_{80}R_{20}$ is approximately equal to that for the isotactic l chain. These considerations may be summarized in a simplified scheme such as shown below

	from \ to	$R_d(tg^+)$	$R_l(tg^+)$
$S_d(tg^-)$		ω''	τ
$S_l(tg^-)$		τ	τ

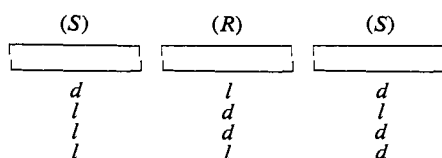
and similarly

	from \ to	$S_d(tg^-)$	$S_l(tg^-)$
$R_d(tg^+)$		τ	τ
$R_l(tg^+)$		τ	ω''

where the most stable conformations are indicated in parentheses for the individual configurations. Each element in the scheme represents the approximate order of the statistical weight required for the specified transition. By this simplification, one may easily evaluate the conformational rigidity of a given copolymer system. The flexibility of the chain should be lowest, and in many cases, the optical rotatory power is highest, in a system where unfavorable combinations such as $\dots S_d R_d \dots$ and $\dots R_l S_l \dots$ are concentrated. Schematically



On the other extreme, the highest flexibility is found in the following chain systems



The conformational asymmetry of this sort tends to be less important when the sequential distribution of (*R*) and (*S*) monomer units becomes more random, or when the configuration of the chain is in the range of the atactic or the syndiotactic.

mer composition. Such discrepancy between the two chain configurations nearly disappears when a more realistic value of ω'' is used. In practice, calculations were carried out for a moderately blocked copolymer with an isotactic d configuration, as illustrated in Figure 2b. Here the large deviation from the linearity for $\omega'' = 0$, as indicated by the dotted curves, vanishes when ω'' increases to 0.01. The conclusion is thus reached that the correlation between the sequential distribution of optical antipodes and the chain configuration may be practically negligible as far as the optical rotatory properties are concerned. In the present treatment, these two factors are assumed to be independent of each other. It is a direct consequence that the optical rotatory properties of a moderately blocked copolymer treated in Figure 3b exhibit a linear dependence on the composition even when $\omega'' = 0$.

The results obtained for $\omega'' = 0.01$ are shown by the solid curves in Figures 2, 3, and 4, respectively, where the difference between curves 1 and 2 indicates the effect of τ in a given chain system. The parameter σ is kept constant throughout. Variation of the optical rotatory power with the composition was found to be nearly linear in every case examined. The magnitude of optical rotation varies somewhat with the chain configuration. Comparison between the optical rotatory behaviors of poly-(*R*)(*S*)-4-methylhex-1-ene and poly-(*R*)(*S*)-5-methylhept-1-ene reveals the importance of the (t, t) element in the U' matrices. It largely determines the chain characteristics of these poly- α -olefins.

Calculations are further extended to the copolymer system derived from (*S*)-4-methylhex-1-ene with an optically inactive comonomer such as 4-methylpent-1-ene or 5-methylhex-1-ene. For copolymers with 4-methylpent-1-ene, as in the case of poly-(*R*)(*S*)-4-methylhex-1-ene, the optical rotatory power is independent of the chain configuration. Thus, computations were carried out for an arbitrarily chosen polymer configuration ($p_r = 0.9$). The results are illustrated in Figure 5. Deviation from the linearity in the plot indicates that the optically inactive component with a symmetric side chain is undoubtedly incorporated in one of the helical conformations in excess over the other. Except in the case when $\omega'' = 0$, the degree of such conformational asymmetry depends largely on the arrangement of the constituent monomer units along the chain. Vicinal interactions between the two components are most frequent in the random copolymer system. Correspondingly the curves are most convex in Figure 5c.

When 5-methylhex-1-ene having a branched structure at the γ position with respect to the vinyl group is chosen as a comonomer, the chain becomes more flexible. Here, even when $\omega'' = 0$, reversal of helix screw sense through the low energy conformation associated with $U'(t, t)$ is permitted. The extent of such transition should however depend on the configuration and also on the arrangement of the monomer units along the chain. According to some tentative calculations for a model chain represented by $A_{80}B_{20}$, where A denotes the (*S*)-4-methylhex-1-ene and B the 5-methylhex-1-ene residue, values of $[M]$ found for $\sigma = 0.5$, $\tau = 0.25$, and $\omega'' = 0$ are $+228^\circ$ and $+195^\circ$ for the perfectly isotactic d and l configuration, respectively. When $\omega'' = 0.01$, the other parameters being kept constant, these values decrease to $+203^\circ$ and $+190^\circ$, respectively.

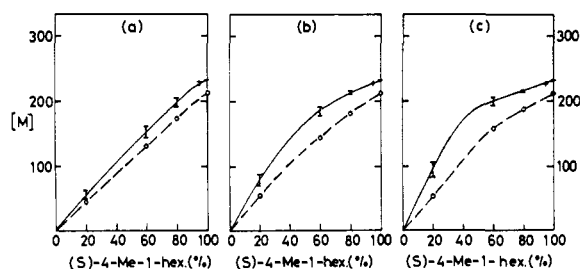


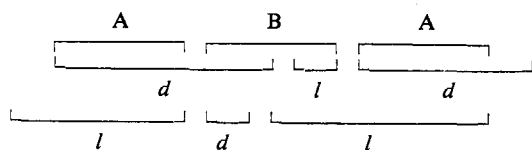
Figure 6. Optical rotatory properties of copolymers prepared from (*S*)-4-methylhex-1-ene and 5-methylhex-1-ene ($n = 200$): (a) blocked, (b) moderately blocked, and (c) random. The mean residue optical rotation calculated for $\sigma = 0.5$, $\tau = 0.25$, and $\omega'' = 0.01$ varies with the chain configuration within the range specified by the error bars. The dotted curves indicate the results obtained for $\omega'' = 0.03$.

The conformational asymmetry responsible for such difference is the same kind as that stated in detail in the case of poly-(*R*)(*S*)-5-methylhept-1-ene. This may again suggest some possible complexity in the copolymerization mechanism.¹⁵ Within the reasonable range of the conformational energy, however, the effect arising from such asymmetry on the optical rotatory properties of the copolymer may be subsidiary. Calculations carried out for copolymer chains with blocked, moderately blocked, and random structures, respectively, are shown in Figure 6. Within the range indicated by the error bars, the mean residue optical rotation varies with the chain configuration. The statistical weight parameters used in the calculations are $\sigma = 0.5$, $\tau = 0.25$, and $\omega'' = 0.01$, respectively. As shown in footnote 15, the isotactic configuration does not necessarily exhibit the highest optical rotation. As the neighboring contacts between the two constituent monomers increase by going toward the random structures (*i.e.*, from a to c in Figure 6), the curves depart more from the linearity. To have a linear relation for a random copolymer, it must be assumed that $\omega'' > 0.03$, as may be inferred from the dotted curves in Figure 6. Therefore, some deviation from the linear relation between the optical activity and the composition is again expected, if these two monomers are copolymerized in an appropriate manner.

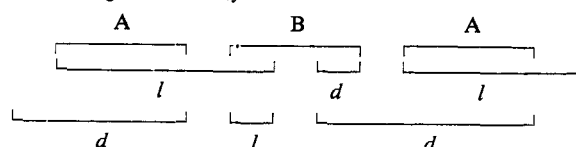
Comparison with Experimental Results

Experimental results are available for some of the copolymer systems treated in the preceding section.

(15) For a moderately blocked copolymer, conformational free energy of the chain can be maximum or minimum when the associated configuration is properly selected. Following the schematic representation used previously in footnote 14, the lowest flexibility is expected for such chains as



and for the highest flexibility



where A represents the (*S*)-4-methylhex-1-ene and B the 5-methylhex-1-ene residue, respectively.

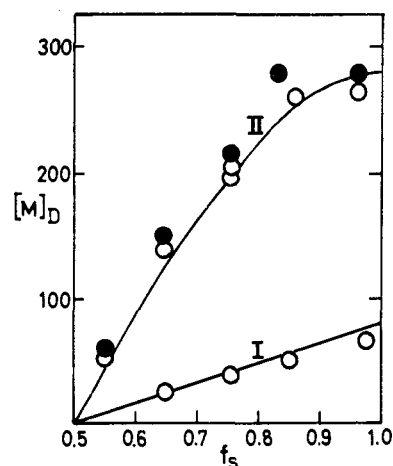


Figure 7. Comparison with experimental results for poly-(*R*)(*S*)-5-methylhept-1-ene (I) and poly-(*R*)(*S*)-4-methylhex-1-ene (II). The solid curves were calculated for moderately blocked structures with $\sigma = 0.5$, $\tau = 0.25$, $\omega'' = 0.01$, and $\alpha = 72^\circ$. Experimental points were those observed⁶ on unfractionated (○) and on cyclohexane soluble fractions (●).

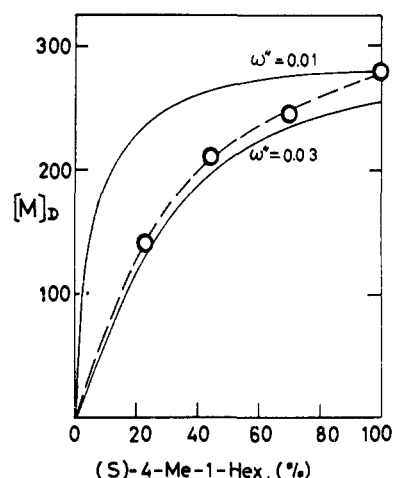


Figure 8. Comparison with experimental results for copolymers prepared from (*S*)-4-methylhex-1-ene and 4-methylpent-1-ene. The solid curves are duplicated from the curves 2 and 3 in Figure 5c, derived for a random copolymer structure, but with $\alpha = 72^\circ$. Experimental points indicated by ○ were observed⁸ on cyclohexane soluble fractions.

Optical rotatory properties of poly-(*R*)(*S*)-4-methylhex-1-ene and poly-(*R*)(*S*)-5-methylhept-1-ene studied by Pino, *et al.*,⁶ are reproduced in Figure 7, where the abscissa for the experimental points indicates the optical purity of the monomer mixture prior to the polymerization. According to the authors, the optical purity of the recovered monomer was found to be slightly lower than that of the initial value. Theoretical curves I and II are duplicated from curve 2 in Figure 3b and curve 3 in Figure 1b, respectively. Here, however, Brewster's α value is taken to be 72° instead of 60° so as to get the best agreement for the homopolymers ($f_s = 1.0$). Over the entire range of the composition, experimental results are well reproduced by the theoretical curves which were derived for copolymers having moderately blocked structures and a moderately isotactic configuration ($p_r = 0.9$).

Copolymerization of (*S*)-4-methylhex-1-ene with 4-methylpent-1-ene has been examined by Carlini, *et al.*⁸ In Figure 8, the observed optical activity is plotted

against the copolymer composition which was determined by infrared spectroscopy. Calculations corresponding to such copolymer systems have been given in Figure 5. For comparison purposes, curves 2 and 3 in Figure 5c are reproduced in Figure 8. Here $\alpha = 72^\circ$ is adopted in keeping with the previous treatment. Although not much is known for the copolymer structure, one may expect *a priori* a random or at most a moderately blocked arrangement, in consideration of the similarity in the molecular structure between the two components. When $\omega'' = 0.03$ is chosen for such a copolymer sequence, the agreement between theory and experiments may be satisfactory. A value of 0.03 for ω'' , however, seems to be slightly high in comparison with that previously estimated from the study on poly-(R)(S)-4-methylhex-1-ene.

Concluding Remarks

Conformational rigidity of the vinyl polymer chain is largely determined by the bulkiness of the pendant groups. All the monomers treated in this paper have a methyl branch either at the β or at the γ position with respect to the vinyl group. Difference between these two series of monomers, when polymerized, may be found in the (t,t) element of the U' matrices. With the former structure, $U'(t,t) \cong \omega''$, suggesting that the transition between the two anticlined skeletal conformations through (tt) is as hard as those through (g^+g^-) or (g^-g^+) . Stereochemistry of the side chain derived from the latter monomer permits such transition with the statistical weight of $U'(t,t) \cong \tau$. The optical rotatory properties of the binary copolymers chosen from these monomers apparently reflect characteristics of the structural feature for a given combination, and may provide some important information concerning the polymerization mechanism.

Within the reasonable range of conformational energies, optical rotatory behaviors of the copolymer derived from (R)- and (S)-4-methylhex-1-ene, or from (R)- and (S)-5-methylhept-1-ene were shown to be consistent with those expected from a moderately blocked structure, which may be the most probable one in consideration of the asymmetric nature of polymerization.¹⁶ Experimental observations on the copolymers of (S)-4-methylhex-1-ene with 4-methylpent-1-ene may be interpretable based on a chain model with a moderately blocked or a random arrangement of the two monomer units.

According to Nozakura, *et al.*,¹⁷ who polymerized a monomer mixture comprising (S)-4-methylhex-1-ene and its isomer 5-methylhex-1-ene (optical purity *ca.* 19%), the observed optical rotation of this copolymer was found to be *ca.* 20% of that for the polymer bearing the maximum optical purity. Calculations for such a copolymer system have been presented in Figure 6. If the copolymer is composed of a binary random array of the two components, some deviation from linearity is expected. The relation may be linear only when the polymerizate is a mixture of two homopolymers or a highly blocked copolymer. This is not likely to be the case, as Nozakura, *et al.*,¹⁷ pointed out. Determination of the copolymer composition should clarify this point.

Acknowledgment. The author wishes especially to thank Professor P. J. Flory of Stanford University for his unflinching encouragement and critical reading of the manuscript.

(16) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Natta, *J. Amer. Chem. Soc.*, **84**, 1487 (1962); P. Pino, F. Ciardelli, and G. P. Lorenzi, *ibid.*, **85**, 3890 (1963).

(17) S. Nozakura, S. Takeuchi, H. Yuki, and S. Murahashi, *Bull. Chem. Soc. Jap.*, **34**, 1673 (1961).

The Lithium Bond^{1a}

Peter A. Kollman,^{1b} Joel F. Liebman,^{1c} and Leland C. Allen

Contribution from the Department of Chemistry,

Princeton University, Princeton, New Jersey 08540. Received August 7, 1969

Abstract: Examples of lithium bonding analogous to hydrogen bonding are investigated. Systems studied and compared with available experimental data comprise H-F...Li-F, H-F...H-F, Li-F...H-F, LiF...Li-Li, Li-F...H-H, and Li-F...Li-F. In addition, calculations for ir frequency shifts and intensity enhancements reveal interesting characteristics of hydrogen and lithium bonding. A large difference in energy of complex formation and charge redistribution is shown to exist between the two dimers Li-F...Li-Li and Li-F...H-H. Cyclic *vs.* linear configurations were considered for the systems (LiF)₂, (HF)₂, and LiFHF. The known cyclic structure of (LiF)₂ is correctly predicted with an energy of formation close to the experimental value. Molecular orbital energy changes as the characterizing feature of donor-acceptor complex formation are discussed.

There has been considerable theoretical and experimental interest in hydrogen bonding.² Hydrogen has been implicitly assumed to be unique with regard to

intermolecular interactions, but since lithium is a congener of hydrogen, it is a logical isomorphic replacement to substitute the hydrogen with lithium in normal hy-

(1) (a) Research support in part by the Chemistry Section of the National Science Foundation, Grant No. NSF-8907; (b) National Science Foundation Predoctoral Fellow, 1966-1970; (c) National Science Foundation Predoctoral Fellow, 1968-1970.

(2) See P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969), for general references.