The Epimerization of 2,4,6,8-Tetramethylnonane and 2,4,6,8,10-Pentamethylundecane, Low Molecular Weight Model Compounds of Polypropylene

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Abstract: The epimerization equilibria for the diastereomers of 2,4,6,8-tetramethylnonane (I) and 2,4,6,8,10-pentamethylundecane (II) were determined between 200 and 300° using palladium on charcoal as catalyst. The equilibrium for the diastereomers of I was also determined at −75°C in the presence of chlorosulfonic acid. The results are interpreted in terms of a rotational isomeric state model and the corresponding conformational parameters were calculated ($E_\eta = 70 \pm 10$ cal mol^{-1}, $E_\omega = 1900 \pm 100$ cal mol^{-1}, $E_\tau = 900 \pm 400$ cal mol^{-1}). The above values yield correct values for the optical activity of both (4*R*,6*R*)-(I) and (4*S*,8*S*)-(II) and are consistent with conformational energies calculated from experimental values of the unperturbed dimensions of polypropylene.

Though the epimerization of cyclic hydrocarbons has been extensively investigated in both liquid[1-13] and gas phase,[14-17] the present knowledge about the epimerization of acyclic hydrocarbons seems to be limited to that obtained from the investigation of 2,4-diphenylpentane and 2,4,6-triphenylheptane.[18,19] The epimerization of suitable low molecular weight compounds is of interest because the composition of the equilibrium mixture can be used, adopting appropriate models,[18-22] to attempt the evaluation of conformational parameters which are applicable to the investigation of conformational equilibria in high molecular weight compounds.

In order to obtain conformational parameters which can be used for the conformational analysis of poly-α-olefins we have investigated the relative stabilities of the diastereomers of 2,4,6,8-tetramethylnonane (I) and 2,4,6,8,10-pentamethylundecane (II), which can be considered tetramers and pentamers of polypropylene having a hydrogen atom and a methyl group as terminal groups. Diastereomeric mixtures and pure diastereomers of I and II were previously prepared and investigated by our group.[23-26] The present paper deals with the quantitative determination of the relative stabilities of the diastereomers at different temperatures in liquid phase. The conformational parameters, evaluated according to the method of Flory[20,22] from the equilibrium compositions, have been successfully used in the calculation of the optical activity of (4*R*,6*R*)-(I) and of (4*S*,8*S*)-(II) and of the temperature coefficient of the optical activity of the latter compound.

Results

According to Allinger, *et al.*,[6-12] the epimerization of cyclic saturated hydrocarbons readily occurs around 300° using palladium on charcoal as catalyst. Preliminary experiments using 2,4,6-trimethylheptane[27] had shown that practically no isomerization occurs between 250 and 300°. Under the same conditions I and II epimerize and equilibrium mixtures of the diastereomers can be obtained, secondary products being less than 1% even after 3 months at 290°.

The epimerization of I occurs more rapidly neat than with *n*-octane as solvent[28] (Figure 1). Below 240° the reaction becomes too slow to evaluate equilibrium compositions with sufficient accuracy; consequently an attempt was made to accelerate the reaction by operating under high hydrogen pressure.[29] As expected,[30] the reaction proceeded much more rapidly under 200 atm of hydrogen and the equilibrium composition could be estimated with sufficient accuracy after a much shorter reaction time (Table I).

Equilibrium conditions for I were approached starting with mixtures containing a large excess of meso ("isotactic") or the racemic ("syndiotactic") diastereomer. For II mixtures were used that contained different amounts of the three possible diastereomers (two meso forms {"isotactic" and "syndiotactic"} and one racemic form {"heterotactic"}), so that the equilibrium was reached from both sides for every diastereomer. Table II shows the equilibrium compositions as determined by gas chromatography of the reaction products.

The equilibrium in I is described by two equilibrium constants

$$\begin{tikzcd} & (+)\text{ form} \\ \text{meso form} \arrow[ur, shift left, "K_{x(+)}"] \arrow[dr, shift left] & \\ & (-)\text{ form} \arrow[ul, shift left, "K_{x(-)}"] \end{tikzcd}$$

and $K_x^{(+)} = K_x^{(-)} = K_x$ in a symmetric milieu.[31] The standard enthalpy of reaction was obtained from a linear first-order regression between $R \ln (K_x)$ and $1/T$. In the temperature range 200 to 290° the values of $R \ln (K_x)$ *vs.* $1/T$ lie convincingly on a straight line, $\Delta H°$ being −210 cal mol^{-1} (estimated standard deviation = 25 cal mol^{-1}). The standard entropy of reaction was calculated using $\Delta S_T° = R \ln (K_x) + \Delta H°/T$ and gave a constant value of +1.11 cal mol^{-1} deg^{-1} between 200 and 290° (maximum deviation = 0.01 cal mol^{-1} deg^{-1}).

Many attempts were made to extend the temperature range in which equilibrium compositions could be measured. Catalyst and reaction conditions described in the literature were carefully reproduced and successfully tested using the compounds reported by different authors.[1-4,32-42] However, overwhelming formation of secondary products from I has been observed with sulfuric acid 96% at 60°,[32-34] 99.0 and 99.5% at 0 and 25°,[3,4] a 10 to 1 mixture of sulfuric acid 96% and chlorosulfonic acid,[35] aluminum bromide at 0°,[36] aluminum chloride above 0°,[1,2,37,38] and a silica-alumina-rhenium oxide catalyst at 80 to 120°.[39] No epimerization or isomerization was found using sulfuric acid 96% at 0°, acidic cracking catalysts at 60 to 100°,[40,41] potassium tetrachloroplatinate(II) or tetrachloropalladate(II) containing catalytic systems at 120°,[42] or, finally, aluminum chloride below 0°.

The only successful result was obtained with chlorosulfonic acid at −75°.[34,35,43] In this case the formation of secondary products occurred very slowly (Figure 2) and the

Table I. Epimerization of I (Initial Meso Form Content 62%) in the Presence and in the Absence of Hydrogen[a]

p_{H_2}, atm	Time required to reach equilibrium, days	Equilibrium composition, % meso form
[b]	90	48.5
200	7	48.5

[a] 1 *M* solutions in *n*-octane at 270°. [b] No hydrogen was introduced at the start of the experiment.

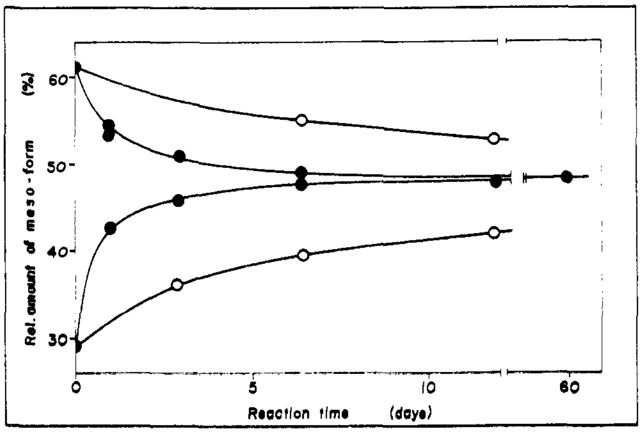

Figure 1. Epimerization of I at 240° with palladium on charcoal. Filled circles represent experiments with neat I; circles represent experiments with 1 *M* solutions of I in *n*-octane.

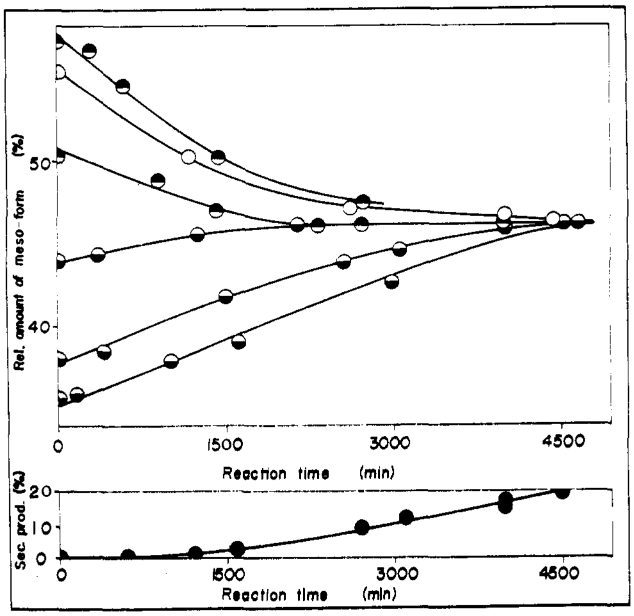

Figure 2. Epimerization of I at −75° with concentrated chlorosulfonic acid. The ◓ represent experiments with initial prevalence of the meso diastereomer; the ◒ represent experiments with initial prevalence of the racemic pair, both with 1 *M* solutions of I in *n*-pentane. ○ show experiments with 2 *M* solutions of I in *n*-pentane. ● represent the amount of side products formed during the reaction.

equilibrium composition of the diastereomers of I, *45.9 ± 0.2% meso form at −75°* (12 replications), could be evaluated. The corresponding value, extrapolated to −75° from the thermodynamic data in the temperature interval 200 to 290°, is 40% meso form, indicating that R ln (K_x) *vs.* $1/T$ cannot be treated as a straight line over the temperature interval −75 to 290°.[44]

Experimental Section

Materials. Mixtures of the diastereomers of 2,4,6,8-tetramethylnonane and 2,4,6,8,10-pentamethylundecane were prepared and the diastereomers separated as previously described.[23,25]

(+)-(4*S*,8*S*)-2,4,6,8,10-Pentamethylundecane. (−)-(4*S*)-2,4,-8,10-Tetramethylundecan-6-one[46] (11.3 g, 0.050 mol) (optical purity 62.8%) in anhydrous ether was slowly added to a stirred solution of 0.054 mol of methylmagnesium bromide in ether. After 1 hr at 40° the mixture was hydrolyzed with dilute sulfuric acid and ice and extracted with ether. (−)-(4*S*)-2,4,6,8,10-Pentamethylundecan-6-ol (7.9 g, 0.033 mol, 66%) was obtained after rectification (bp 84–85° (0.5 mm), $n\text{D}^{25}$ 1.4423, $d^{25}{}_4$ 0.8265, $[\alpha]^{25}\text{D}$ −3.93 deg ml/(g dm)).

Anal. Calcd: C, 79.26; H, 14.14. Found: C, 79.53; H, 14.09.

(−)-(4*S*)-2,4,6,8,10-Pentamethylundecan-6-ol (20.7 g, 0.085 mol) was distilled rapidly in the presence of iodine and the resulting mixture was hydrogenated in diethyl ether over Raney nickel at 120° under 130 atm of hydrogen. Distillation over sodium yielded 15.0 g (0.066 mol, 77%) of a mixture of *meso*- and (+)-(4*S*,-8*S*)-2,4,6,8,10-pentamethylundecane (bp 117° (15 mm), $n^{25}\text{D}$ 1.4284, $\alpha^{25}\text{D}$ (l = 1 dm) = +3.10°).

Anal. Calcd: C, 84.86; H, 15.14. Found: C, 84.92; H, 14.97.

Equilibration with Palladium. Microscale Version. This version is essentially the one proposed by Allinger and Coke.[7] Alkane or alkane solution (0.1 ml) was placed in a Pyrex tube (diameter 3 mm inside, 6 mm outside) with 20 mg of palladium on charcoal 10%, and the tube was sealed, keeping the substance at liquid nitrogen temperature and under vacuum. Care was taken to seal the tube so that the formed ampoules would be more than 90% filled with the solid-liquid mixture at the reaction temperature. The remaining end of the ampoules was used to hang them in a thermostated bath of liquid salts (potassium nitrite:sodium nitrate = 100:85) for the required amount of time (from 10 days at 290° to 60 days at 240° with neat 2,4,6,8-tetramethylnonane). After the reaction time was over, the ampoules were immersed in an ice bath and immediately afterwards in liquid nitrogen (total cooling time less than 30 sec). After the contents of the tube had melted again, they were centrifuged, cooled with liquid nitrogen, and opened; finally, the liquid was pipeted away and analyzed.

Experiments under Hydrogen Pressure. A 5-ml glass ampoule was fitted around the thermoelement finger of a 70-ml steel vessel. About 1.5 ml of the alkane or alkane solution together with 1.5 g of palladium on charcoal 10% were placed in the ampoule and the ampoule was set in the steel bomb. The air was carefully replaced by nitrogen and the nitrogen in turn by hydrogen (50 atm); the bomb was placed in an electric oven, thermostated at the desired temperature, and the hydrogen pressure (200 atm) was established. After the required amount of time (7 days at 240° to 30 days at 200° with a 2 *M* solution of 2,4,6,8-tetramethylnonane in *n*-octane), the bomb was immersed in an ice bath, the hydrogen pressure was released, the bomb was opened, and the liquid was analyzed.

Table II. Equilibrium Compositions of the Diastereomeric Mixtures of I and II, Obtained with Palladium on Charcoal as Catalyst

Compd	Temp, °C	No. of experiments	Equilibrium composition[a] % "isot"	% "synd"	% "heter"
I	200	4	47.9 ± 0.2	52.1 ± 0.2	
I	240	4	48.2 ± 0.05	51.8 ± 0.05	
I	250	12	48.3 ± 0.2	51.7 ± 0.2	
I	270	11	48.5 ± 0.2	51.5 ± 0.2	
I	290	8	48.8 ± 0.1	51.2 ± 0.1	
II	270	8	23.7 ± 0.2	26.3 ± 0.2	50.0 ± 0.2

[a] The limits indicated are standard deviations calculated from repetitive runs.

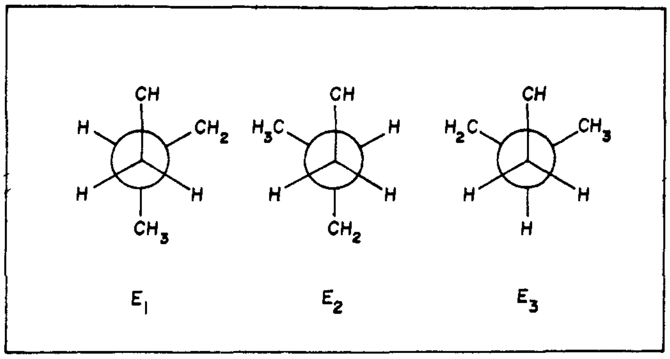

Figure 3. Newman projections of the rotational isomeric states around a main chain polypropylene bond.

Equilibration with Chlorosulfonic Acid. Apparatus. The reaction vessel was a round-bottom glass tube (22 mm inside diameter) fitted into a thermostated glass jacket with a ground glass joint. A series of three identical reaction devices containing magnetic stirrers was used, connected so that the cooling liquid ran through all three. The middle one was used for the equilibration reaction and closed with an elastic rubber stopper that permitted leakfree insertion of a hypodermic needle. The other two were used to monitor the temperature and their reaction tubes were filled with methylcyclohexane.

Procedure. Chlorosulfonic acid (0.5 to 2 ml) was placed in the reaction vessel, and the vessel was closed and cooled to reaction temperature. The same volume of alkane or alkane solution was introduced with a syringe and the reaction was started by vigorous stirring. After the required time (1 to 3 days at −75°), stirring was stopped, the emulsion was allowed to break (3 to 5 min), the organic layer was transferred into a glass ampoule containing frozen sodium hydroxide solution (10%), and the ampoule was sealed. The ampoule was thawed, shaken to destroy traces of acid, and reopened, and the organic layer was analyzed.

Analysis. The samples were analyzed by vpc on a Perkin-Elmer F11 gas chromatograph with a flame ionization detector and a parametric amplifier. Complete separation for all compounds of interest was obtained on a 50 m Apiezon-L capillary column (0.1-in. diameter) with a carrier gas flow of 1 ml/min (nitrogen) at 100 to 110°. The signal on the integrator plug of the amplifier was measured with a Solartron LM1420.2 integrating digital volt meter and punched on paper tape with a system consisting of a Solartron 1461 Clock and Scanner, a Solartron LU1972 Serialieser, and a Facit Punch. Because peak widths were in the order of 2 to 3 min, a punch frequency of 3 $\sec^{-1}$ was sufficient.

The paper tapes were processed by a CDC 6400/6500 computer with a Fortran program specially designed for this purpose. The program, working on a circular buffer of 100 places, detected, separated, identified, and integrated the vpc peaks and showed the relative amount of the diastereomers of interest. A representative test run with 2,4,6,8-tetramethylnonane with four repetitions gave a relative amount of the meso form of 27.37% with an estimated standard deviation of 0.04%.

Discussion

For all observed temperatures the meso form of I is more stable than an enantiomeric species. Since the predominance is small, the entropy of mixing is large enough to make the racemic form (taking the mixture of enantiomers as standard state) more stable than the meso form for all observed temperatures. In II, the "isotactic" meso form is less stable than the "syndiotactic" one, one enantiomer of the "heterotactic" form having an intermediate stability at 270°. Again, taking the racemic mixture of the two "heterotactic" enantiomers as standard state, the entropy of mixing is sufficient to make the racemic "heterotactic" form more stable with respect to each meso form.

These results agree with almost all experimental values for equilibria in similar compounds reported in the literature.[18,19,21,47,48]

An equitable comparison between the stability of dimers and trimers with that of isotactic and syndiotactic diads and triads and heterotactic triads in the corresponding polymers cannot be made, as the stability of the low molecular weight models is substantially influenced by the fact that two of the units are located at the end of the chain. For our tetramer and pentamer models one would hope that the observed diads and triads reflect better the behavior of diads and triads in a polypropylene chain.

In order to get a more quantitative approach to the conformational equilibrium of the diastereomers of I and II a method proposed by Flory[20,22] was applied. His approach gives the following equation for the composition of the equilibrium mixture of I

$$f_{\mathrm{iso,\ TMN}} = \frac{Z_{\mathrm{iso,\ TMN}}}{Z_{\mathrm{iso,\ TMN}} + Z_{\mathrm{synd,\ TMN}}} = f(T, E_\eta, E_\omega, E_\tau) \tag{1}$$

where the Z_k are the conformational partition functions for the two disastereomers. These conformational partition functions depend only on the statistical weights u_j, and the u_j in turn are calculated from the conformational "energies" E_j by $u_j = \exp(-E_j/RT)$. For a model with three rotational isomeric states around one bond,[22,49,50] the E_j are defined as (Figure 3): $E_\eta = E_2 - E_1$ (a 1-4 interaction, dependent on the chain conformation around one bond), $E_\tau = E_3 - E_1$ (a 1-4 interaction, dependent on the chain conformation around one bond), E_ω the additional energy associated with certain combinations of rotation angles, as in g^+g^- conformations in *n*-pentane (a 1-5 interaction, dependent on the chain conformation around two consecutive bonds). The corresponding statistical weights are η, τ, and ω. The conformation with energy E_1 (Figure 3) has a statistical weight of 1.

The conformational partition functions are given by

$$Z_{\mathrm{iso,\ TMN}} = \mathbf{J}^*\mathbf{U}_1{}^{(2)}\mathbf{U}_m{}^{(2)}\mathbf{U}_{x-1}{}^{(2)}\mathbf{J}$$

and

$$Z_{\mathrm{synd,\ TMN}} = \mathbf{J}^*\mathbf{U}_1{}^{(2)}\mathbf{U}_r{}^{(2)}\mathbf{U}_{x-1}{}^{(2)}\mathbf{J}$$

where $\mathbf{J}^* = [1\ 0\ 0]$ and $\mathbf{J} = [1\ 1\ 1]^T$ for a model with three rotational isomeric states around one bond. $\mathbf{U}_m{}^{(2)} = \mathbf{U}'\mathbf{U}_m''$ and $\mathbf{U}_r{}^{(2)} = \mathbf{U}'\mathbf{U}_r''$ are the diad matrices given by Flory.[22] $\mathbf{U}_1{}^{(2)}$ and $\mathbf{U}_{x-1}{}^{(2)}$ are the diad matrices for the terminal diads. $\mathbf{U}_1{}^{(2)}$ is derived from $\mathbf{U}_m{}^{(2)}$ or $\mathbf{U}_r{}^{(2)}$ by replacing the statistical weight 1 (for the conformation with energy E_1 in Figure 3) with η for the second C–C bond in the chain, since the CH_2 group is replaced by the CH_3 group for conformations around C–C bond 2 ($\mathbf{U}_m{}^{(2)}$ and $\mathbf{U}_r{}^{(2)}$ give the same result because the conformations with energy E_1 and E_2 in Figure 3 have identical energy for the second bond in the chain). A similar treatment of the conformations around the penultimate C–C bond of the chain yields $\mathbf{U}_{x-1}{}^{(2)}$.

Equation 1 yields a theoretical value for $f_{\mathrm{iso,TMN}}$ (the fraction of tetramer molecules that are in meso configuration at equilibrium) when a set of conformational energies is used to calculate u_j's, the statistical weight matrices U_i[51] and the Z_k's. Choosing T as the independent variable and $f_{\mathrm{iso,TMN}}$ as the dependent variable, eq 1 defines a function with three unknown parameters, the "conformational energies," that can be chosen so that eq 1 optimally reproduces our experimental results for I (Table II, and the single value at −75°). Assuming the model to be correct, those "best" parameters can then be regarded as conformational energies, if no systematic error in the experiment biased the results.

To find the "best" parameters, we applied Marquart's strategy[52] to the problem, using his slightly modified com-

Table III. Relative Concentration of the "Allowed" Conformers of I at Different Temperatures, Assuming $E_\eta = 70$ cal/mol, $E_\omega = 1900$ cal/mol, and $E_\tau = 900$ cal/mol

	−75°	25°	300°
Isotactic Form, "All Trans" Being 			
g^+ t g^+ t g^+ t	26.1	20.8	7.6
g^+ t g^+ t t g^-	21.8	18.5	7.2
g^+ t t g^- t g^-	21.8	18.5	7.2
t g^- t g^- t g^-	26.1	20.8	7.6
Total	95.8	78.6	29.6
Syndiotactic Form, "All Trans" Being 			
t t t t g^+ g^+	18.5	16.0	6.8
g^+ g^+ t t g^+ g^+	22.1	18.0	7.2
t t t t t t	15.5	14.2	6.4
g^+ g^+ t t t t	18.5	16.0	6.8
t t g^- g^- t t	22.1	18.0	7.2
Total	96.7	82.2	34.4

Table IV. Calculated and Experimentally Found Equilibrium Compositions for the Diastereomers of II at 270°[a]

Diastereomer	Concentration, % Calcd[b]	Concentration, % Exptl[c]
Isotactic meso form (4*R*, 6*s*, 8*S*)	23.4 ± 0.2	23.7 ± 0.2
Heterotactic racemic form (4*R*, 8*R*) + (4*S*, 8*S*)	50.2 ± 0.1	50.0 ± 0.2
Syndiotactic meso form (4*R*, 6*r*, 8*S*)	26.4 ± 0.2	26.3 ± 0.2

[a] $E_\eta = 70 \pm 10$ cal/mol, $E_\omega = 1900 \pm 100$ cal/mol, and $E_\tau = 900 \pm 500$ cal/mol. [b] The indicated limits are the maximum variations obtained by varying the energy parameters in their 95% confidence limits. [c] The indicated limits are the standard deviations guessed from eight replications.

puter program[53] to minimize the sum over the squares of the differences between experimental and theoretical values at all experimental temperatures, and obtained

$$E_\eta = 70 \pm 10 \text{ cal mol}^{-1}$$

$$E_\omega = 1900 \pm 100 \text{ cal mol}^{-1}$$

$$E_\tau = 900 \pm 400 \text{ cal mol}^{-1}$$

where the indicated limits are the nonlinear confidence limits for a probability of about 95%.[54] Of course, these values make sense only within the applied model, and are therefore limited by the approximations of the approach.[55,56]

From the above energies, the concentrations of the most preferred conformations at different temperatures have been calculated (Table III) for the tetramer I. From Table III and within the limits of the approximations included in Flory's approach, it appears that at low temperatures a simplified conformational analysis, excluding as "not allowed" all conformations containing a 1-5 interaction (E_ω), could be justified for open chain paraffins, because the sum of the molar fractions of the "allowed" conformers in all cases is over 0.95. To assume that all "allowed" conformations have the same energy ($E_\eta = 0$), however, would result in a slight error, as can be seen from the partition of the molar fractions of the different conformers. On the other hand, it is obvious that at high temperatures many "not allowed" conformations have significant populations too, since the sum of the molar fractions of the "allowed" conformations in all cases is less than 0.35.

With a formula similar to eq 1 the equilibrium composition of the mixture of diastereomers of II was calculated from the values for the conformational energies mentioned above. The good agreement between experiment and calculation is shown in Table IV.

The deviations from the Bernoullian sequence distribution as predicted by Flory[22] are too small to be observed ($f_{\text{iso, II}} = 0.487$ and so $f^2_{\text{iso, II}} = 0.237$, $\{1 - f_{\text{iso, II}}\}^2 = 0.263$ and $2f_{\text{iso, II}}\{1 - f_{\text{iso, II}}\} = 0.500$, which are equal to the values in Table IV). Calculations of the contents of isotactic diads in chains of variable length[59] did not show experimentally detectable variations with the chain length, and the experimentally determined content of isotactic diads in the tetramer model I ($f_{\text{iso, I}} = 0.485$) and the pentamer model II ($f_{\text{iso, II}} = 0.487$) are certainly equal within experimental error.

A completely independent check of the substantial soundness of the conformational scheme proposed by Flory[22] is given by the calculation of the optical activity of (4*R*,6*R*)-(I) as well as of the optical activity and its temperature coefficient of (4*S*,8*S*)-(II) with the conformational parameters calculated from the equilibrium compositions of I using the Brewster method[60] (see Appendix). In addition to all the assumptions that are inherent in Flory's treatment of the equilibrium data, we further assumed that bond angles are tetrahedral and the conformations are exactly staggered.[61]

As shown in Table V, not only the agreement between calculated and experimental values of the optical rotation at room temperature is excellent, but also a good agreement between calculated and observed values for the temperature coefficient of the optical rotation of a *n*-heptane solution of (4*S*,8*S*)-(II) has been found.

Conclusions

The present research has shown that in compounds I and II the "syndiotactic" diastereomer appears in a higher concentration in the equilibrium mixture than the "isotactic" one (taking for "syndiotactic" I, the racemic mixture as standard state), the difference increasing, at least in the case of I, with decreasing temperature.

The attempt to evaluate the conformational energy parameters E_η, E_τ, and E_ω according to Flory's method has led to results which are valid for both model compounds I and II, and not only are consistent with earlier data measured on open chain and cyclic compounds,[9,22,62] but also allow the calculation of the optical activity and its tempera-

Table V. Calculated and Experimentally Determined Optical Activity of (4*R*,6*R*)-(I) and (4*S*,8*S*)-(II)[a]

Compd	Temp, °C	$[M]_{589\text{ nm}}^T$ Calcd	$[M]_{589\text{ nm}}^T$ Exptl	$-\Delta[M]_{589\text{ nm}}/\Delta T$ Calcd	$-\Delta[M]_{589\text{ nm}}/\Delta T$ Exptl	$[M]_{436\text{ nm}}^T$ Calcd	$[M]_{436\text{ nm}}^T$ Exptl	$-\Delta[M]_{436\text{ nm}}/\Delta T$ Calcd	$-\Delta[M]_{436\text{ nm}}/\Delta T$ Exptl
(4*R*,6*R*)-(I)	17	−22.5 ± 1	−23.0 ± 0.3						
(neat liquid)			*b*						
(4*S*,8*S*)-(II)	25	29.6 ± 1.5	31.8			56.2 ± 3	62.6		
(in *n*-heptane)[c]	0–90			−0.13	−0.11			−0.24	−0.21

[a] The indicated limits are the maximum variations obtained by varying the energy parameters in their 95% confidence limits. [b] Pino, Pucci, Benedetti, and Bucci, ref 23. [c] 63.54 mg/ml (25°) of a sample with optical purity 62.8% and diastereomeric purity 58.0%, extrapolated to 100% optical and diastereomeric purity.

ture coefficient for the optically active diastereomers of I and II. The calculated values are in surprisingly good agreement with the experimental ones. Although the conformational energy parameters found in this work are not necessarily applicable for calculation of the conformational equilibria of polypropylene of different tacticities, they are in extremely good agreement with the ones recently calculated by Biskup and Cantow,[63] starting with the experimental values of characteristic ratios of polypropylene of various tacticities in "Θ" conditions around 130° and using the same model for the calculations.

Therefore, it seems that by using values of the conformational energies obtained investigating the epimerization of low molecular weight model compounds of polypropylene and by using the same type of conformational model for the conformational equilibria of polypropylene itself, it is possible to obtain values for the characteristic ratio in "Θ" conditions which are consistent with the experimental ones.

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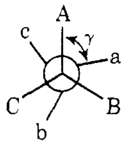
Appendix

Brewster's "uniform conductor model"[60] for the optical activity in the transparent wavelength region has been used to calculate the contributions of a segment of three bonds to the optical rotation of the whole conformer, and hence the optical rotation of a conformer, without making any assumptions about the conformational equilibrium. Therefore, we would expect it to be compatible with our type of conformational analysis.

With Brewster's equations one can formulate the contribution of the conformation of one chain element containing one bond to the optical rotation of the whole conformer as



$$[\Delta M]_\lambda / f(n) = \sin\gamma(C_{Aa} + C_{Bb} + C_{Cc}) - \sin(120° - \gamma)(C_{aB} + C_{bC} + C_{cA}) + \sin(120° + \gamma)(C_{Ab} + C_{Bc} + C_{Ca})$$

where $f(n) = [(3n + 2)/3][(3n + 2)/3n]$ with n being the average refractive index of the solution and the C_{ij} being constants, dependent only on the group or atom refractivities of i and j, bond lengths, bond angles, and the wavelength. The following matrix method is similar to the one applied by Abe.[64]

With the "matrix of the optical activities of bond i," $\mathbf{A}_{i,\lambda}$

$$\mathbf{A}_{i,\lambda} = \mathrm{diag}\,[[\Delta M]_{\lambda,t}, [\Delta M]_{\lambda,g^+}, [\Delta M]_{\lambda,g^-}]_i$$

we construct[22,64]

$$\mathbf{H}_{i,\lambda} = \begin{bmatrix} \mathbf{U}_i & \mathbf{U}_i\mathbf{A}_{i,\lambda} \\ 0 & \mathbf{U}_i \end{bmatrix}$$

and obtain the optical rotation of the mixture of the conformers with

$$\langle [M]_\lambda \rangle = Z^{-1}[\mathbf{J}^*0]\left\{\prod_{i=2}^{n-1} \mathbf{H}_{i,\lambda}\right\}\begin{bmatrix} 0 \\ \mathbf{J} \end{bmatrix}$$

Admitting that the optical activity of each conformer does not vary with temperature, the change of optical rotation with temperature must be related only to the changes in conformational equilibrium compositions. Therefore it is possible to calculate the optical activity from the conformational parameters for every temperature.

References and Notes

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(56) Recently, more sophisticated models have been used to investigate the conformational equilibria in polypropylene.[57,58] In the model proposed by Boyd and Breitling,[57] three conformational energies, E_g, E_{SK}, and E_ω are used. E_{SK} corresponds approximately to E_τ, E_g to $(E_\tau - E_\eta)$. E_ω has the same meaning as in this paper. According to this model, chain dimensions in agreement with experimental values have been found using the following values for the conformational energies deduced from potential energy calculations on an isolated 2,4,6-trimethylheptane molecule: E_g = 400 cal mol^{-1}, E_{SK} = 600 cal mol^{-1}, and E_ω = 1300 cal mol^{-1}. Using the Boyd–Breitling model to fit the epimerization data, however, the relatively high values E_g = 1100 ± 500 cal mol^{-1}, E_{SK} = 1200 ± 500 cal mol^{-1}, and E_ω = 2100 ± 100 cal mol^{-1} have been found.

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$$f_{\mathrm{iso},x} = (x-3)^{-1}\frac{[\mathbf{J}^*0]\hat{\mathbf{U}}_1\hat{\mathbf{U}}^{x-3}\hat{\mathbf{U}}_{x-1}\begin{bmatrix}0\\ \mathbf{J}\end{bmatrix}}{\mathbf{J}^*\mathbf{U}_1\mathbf{U}^{x-3}\mathbf{U}_{x-1}\mathbf{J}}$$

with

$$\mathbf{U}_1 = \begin{bmatrix}\mathbf{U}_1 & 0\\ 0 & \mathbf{U}_1\end{bmatrix} \text{ and } \hat{\mathbf{U}}_{x-1} = \begin{bmatrix}\mathbf{U}_{x-1} & 0\\ 0 & \hat{\mathbf{U}}_{x-1}\end{bmatrix}$$

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A ^{1}H Nuclear Magnetic Resonance Determination of the Conformations of the Polyene Chain Portions of 9-*cis*- and 13-*cis*-Retinal in Solution

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Abstract: The conformations of the polyene chain portions of 9-*cis*- and 13-*cis*-retinal have been investigated by ^{1}H nmr spectroscopy, including the measurement of long-range nuclear spin–spin coupling constants, chemical shifts, spin–lattice relaxation times, and nuclear Overhauser enhancements. Each isomer is found to exist in solution with a planar s-trans conformation from 7C to 15C. The T_1 data indicate that there is enhanced flexibility about the 14–15 single bond, although the average conformation is planar. ^{1}H nmr spectral parameters for the model compound β-ionone are also presented.

I. Introduction

9-*cis*-Retinal will combine with opsin to form an analogous visual pigment, isorhodopsin.[1] 13-*cis*-Retinal has recently been shown to be the natural chromophore of the bacterial pigment bacteriorhodopsin.[2] Although bacteriorhodopsin, which serves the function of a proton pump,[3] and the bacterial membrane in which it is found, bear little resemblance to rhodopsin and rod disk membranes in their chemical compositions, it is of great interest that bacteriorhodopsin undergoes a bleaching sequence with intermediates analogous to those of rhodopsin.[4] It is thus important to ascertain the solution conformations of the polyene chain portions of these two chromophores. This effort is undertaken in the present paper, using the same ^{1}H nuclear magnetic resonance techniques which were used in earlier work to study *all-trans*- and 11-*cis*-retinal.[5] These include the observation of long-range nuclear spin–spin coupling constants, chemical shifts, spin–lattice relaxation times (T_1's), and nuclear Overhauser enhancements (NOE's). In addition, the ^{1}H nmr spectral parameters for the model compound β-ionone are presented.

II. Methods

9-*cis*-Retinal was obtained from Sigma Chemical Co.; β-ionone and 13-*cis*-retinal were brought from Eastman Organic Chemicals Co. All three compounds were used as obtained without purification. Acetone-d_6 was purchased from Stohler Isotope Chemicals Co. Samples were prepared in acetone-d_6 solution and degassed using at least five freeze–pump–thaw cycles. The approximate concentrations of the samples were: β-ionone, 0.5 *M;* 9-*cis*-retinal 0.3 *M;* and 13-*cis*-retinal, 0.5 *M*. Hexamethyldisiloxane (HMDS), 1–5% (v/v), was used in each case as the internal reference signal. ^{1}H nmr measurements were made as previously described[5] using an XL-100 nmr spectrometer operating in the Fourier transform mode at 100.1 MHz. For the NOE measurements, the peak intensities were obtained by manual planimetry if the decoupling was continuous, or the peak heights were used if the decoupler was gated off during the acquisition of the free induction decay. For the T_1 measurements, the peak intensities were taken as the peak heights.

For the analysis of the olefinic region of the spectrum of each isomer, the program LAOCN3[6] was used. For each isomer, the two spin sets 7H, 8H and 10H, 11H, 12H, 14H, and 15H were used to fit the olefinic and aldehyde chemical shifts and vicinal coupling constants. The long-range couplings reported for 13-*cis*-retinal were estimated with the aid of the interactive spectral simulation program SIMEQ.[7] Nuclear Overhauser enhancements and spin–lattice relaxation times were calculated using the program GENOE.[8] This program calculates NOE's using the formula of Noggle and Schirmer,[9] assuming predominantly intramolecular dipole–dipole relaxation. T_1's were calculated assuming 100% intramolecular dipole–dipole relaxation. For these calculations the olefinic and methyl protons from 8H to the end of the chain were included. The interproton distance input for GENOE was computed using the program ROCOR.[8] For both isomers, the geometry assumed for the polyene chain