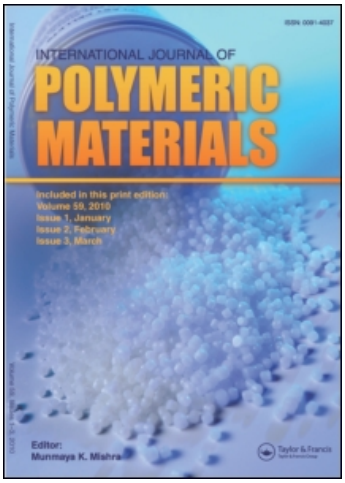

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Conformational Properties of Optically Active Stereoregular Polymers

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Conformational Properties of Optically Active Stereoregular Polymers†

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The relationship between configuration and conformation of stereoregular polymers is reviewed. The reason for the frequent occurrence of helical conformations in the solid state is discussed, as well as the difficulties encountered in the experimental investigation of the conformational equilibrium of macromolecules in solution. As far as the local conformation of the repeat units of polymers in solution is concerned, satisfactory information is available only in the case of isotactic poly(α-olefins). This is mostly due to the successful combination of statistical mechanical calculations and experimental measurements of optical activity in isotactic poly(α-olefins) containing asymmetric carbon atoms in the lateral chain. In this case optical activity measurements provide a demonstration of the existence of the short range helical order in solution. It is further shown that a series of independent experiments (including some recent end-to-end distance measurements) confirm the detailed picture of the macromolecule in solution which was obtained through conformational analysis and statistical calculations. The influence of the asymmetry of the repeat unit on the main chain conformation is discussed, with reference to the analogous situation in biopolymers. The problem of conformational transitions is also considered and the difference in behaviour between stereoregular synthetic polymers and biopolymers is discussed. Conformational transitions are related to the existence of conformational rigidity in macromolecules, and the thermodynamic and kinetic bases of this latter phenomenon are discussed. Further analogies and differences between the conformational properties of stereoregular synthetic polymers and biopolymers are considered. Finally, it is shown how the data obtained for isotactic poly(α-olefins) can be generalized for understanding some of the basic features which characterize the conformation of macromolecules in solution.

1 INTRODUCTION: HELICAL CONFORMATION OF STEREOREGULAR POLYMERS IN THE CRYSTALLINE STATE

In this paper, I will discuss the relationships between configurational and conformational properties of macromolecules, with particular emphasis on

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the optically active ones. I will limit myself to linear stereoregular polymers, as they present the greatest interest and the lowest degree of formal complexity.

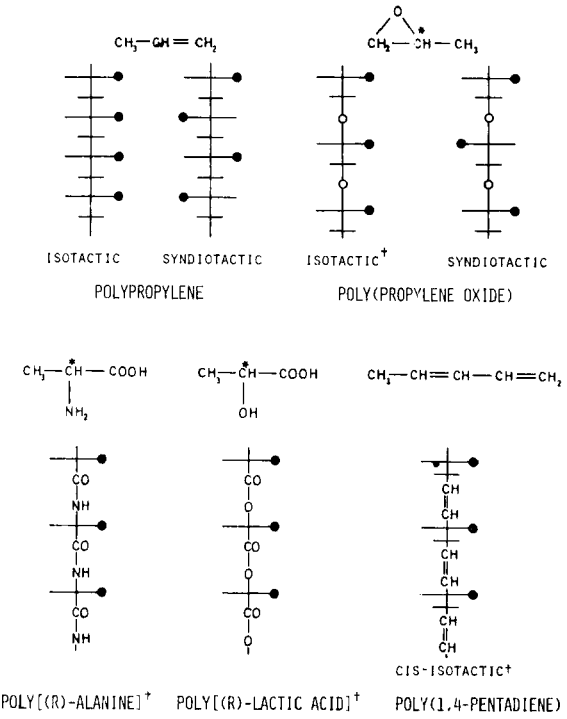


FIGURE 1 Fisher projections of some typical stereoregular linear polymers. Chiral macromolecules denoted by dagger, (●—) represent CH_3 group.

Some of the basic stereochemical properties of macromolecules can be visualized with the help of Fisher projections as shown in Figure 1. In the case of isotactic and syndiotactic polypropylene, we have tertiary carbon atoms which are formally asymmetric; the chains are, however, superimposable with their mirror images and they are not chiral (we consider the chain with equal endings). Quite different is the case of isotactic poly(propylene oxide), as in this case the two mirror-image chains are not superimposable and the chain is a truly asymmetric compound. Note, however, that in the syndiotactic form of the same polymer there is no chirality: this chain and its mirror image are the same compounds. The case of isotactic poly(propylene oxide) can be generalized: each time that an isotactic chain contains a tertiary C atom surrounded by two chemically different groups, we have a chiral macromolecule. The case of polypentadiene is interesting as the monomer is a

non-dissymmetric compound. Asymmetric C atoms are formed in the chain, and, by using asymmetric catalysts, it is possible to obtain optically active polymers.[1] For a more detailed discussion of the stereochemistry of macromolecules, with emphasis on their chiro-optical properties, the reader is referred to the reviews by Farina and Bressan,[2] Schulz and Kaiser,[3] Pino,[4] Luisi and Ciardelli,[5] Goodman, Abe and Fan,[6] Pino, Ciardelli and Zandomeneghi.[7] Here I prefer to consider directly the problem of the influence of asymmetric carbon atoms on chain conformation. Furthermore, since biopolymers are also stereoregular asymmetric and linear macromolecules, it may be interesting to point out the possible similarities and differences between them and synthetic non-biological polymers.

In order to introduce the problem of the conformational equilibria in macromolecules, let us first consider the case of isotactic polypropylene and other isotactic non-dissymmetric vinyl polymers.

Isotactic poly(α-olefins) assume helical conformations in the crystalline state. This has been found experimentally by X-rays, and it can be also qualitatively guessed on the basis of considerations of energy interactions, by using simple molecular models. In the zigzag planar conformation of isotactic polypropylene, the hydrogens of the vicinal methyl groups give rise to prohibitive 1–4 C–C bond energy interactions (see Figure 2). In order to avoid these high

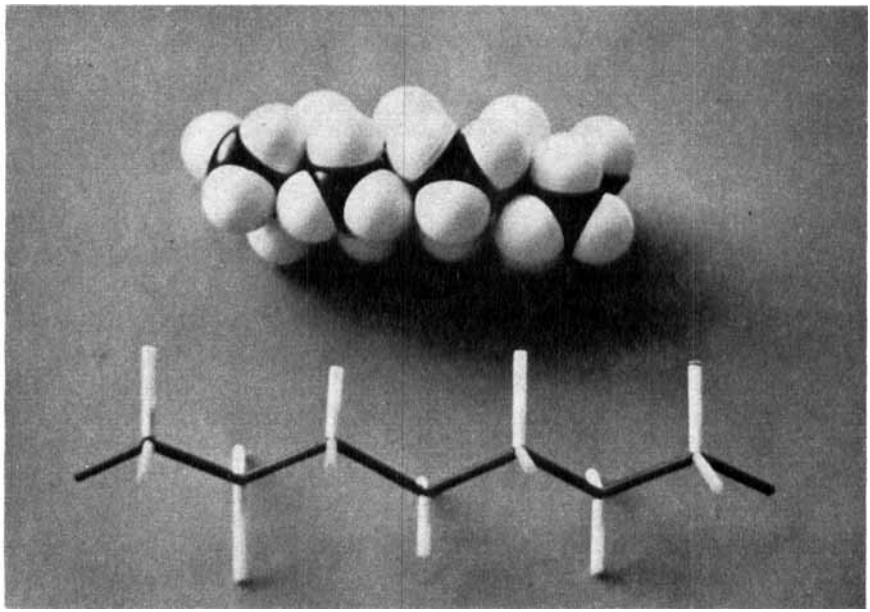


FIGURE 2 A section of isotactic polypropylene chain in the zigzag planar conformation. Note that the main chain in the space-filling model is slightly distorted, due to the steric hindrance between vicinal methyl groups.

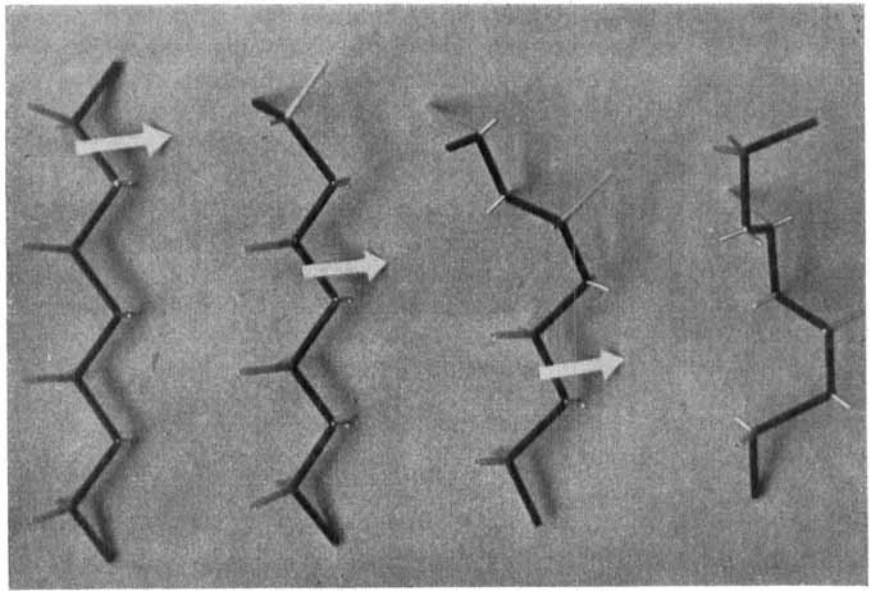


FIGURE 3 A diagram showing the spatial requirements to build a 3_1 helix in isotactic vinyl polymers, starting from the zigzag planar conformation. The arrow indicates each time the bond around which a clockwise rotation of 120° should be performed. The final figure shows four units in a right-handed helical section (the observer goes from one substituent to the other in a clockwise sense). Note that the "fourth" substituent is exactly in the same position as the "first" one.

energy interactions, and at the same time to maintain all bonds in the staggered conformations, one can rotate each main chain bond, in such a way that only methyl groups and H atoms are in the 1–4 bond interaction conformation. By doing so along the entire chain, a 3_1 helix arises, as shown in Figure 3 (3_1 means that each helical turn contains 3 repeat units). Two internal rotation angles characterize completely a helical structure of this type. This is illustrated in Figure 4, which shows the Newman projections of the two enantiomeric left-handed and right-handed helices.

Many stereoregular vinyl polymers assume this type of helical conformation in the crystalline state.[8] The fact that the chemical nature and the size of the lateral chain does not influence the helical conformation (for instance isotactic polypropylene, polystyrene and poly(5-methyl-l-heptene) assume the same 3_1 helix) is taken as an indication that the chain conformation depends only on intramolecular interactions; specifically the chain-to-chain interactions of the crystal lattice would not play an important role in this regard.[8]

Biopolymers also tend to exist in helical conformations: the α helix of Pauling and Corey in polypeptides, the double helix in nucleic acids, the helical structure of amylose, are well known examples. The reason for the

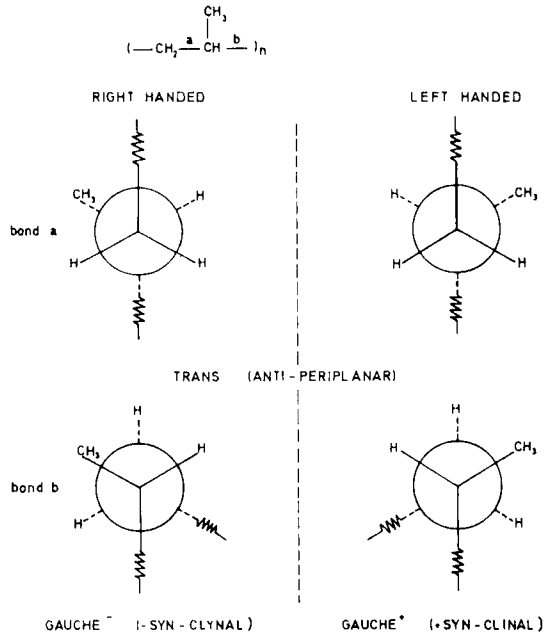


FIGURE 4 Newman projections of the two repeat unit main chain bonds in the right-handed $[(tg^-)_n]$ and left-handed $[(tg^+)_n]$ 3_1 helix. For the notation $\pm$ syn-clinal and anti-periplanar, see Ref. 15.

common occurrence of helical conformations in macromolecular systems lies in the fact that a configurational linear order must correspond, at least in the solid state, to an ordered spatial repetition of the repeat unit conformation. Only zigzag planar chains or helical conformations meet this so-called postulate of equivalence,[8] according to which all repeat units have to be in the same stereochemical, and therefore energetic, environment. In the case of chains having side groups which give prohibitive interactions in the zigzag planar conformation, the helix is the only structure which the macromolecule can assume.

2 PROBLEMS OF THE CHAIN CONFORMATION IN SOLUTION

What happens to this regular helical conformation upon going from the solid state to the solution? Is the helical order maintained, or is it destroyed, because of the thermal motions which characterize the solution state?

One characteristic of paraffins in liquid state and in solution is the large velocity of rotation around C–C bonds from one energy minimum to another.

The energy barriers among the staggered conformations of bonds are of the order of 3-6 kcal/mol per bond, and correspondingly we have an extremely high frequency of these conformational transitions. The order of magnitude of the corresponding rate constant is around 10^9 s^{-1} at room temperature. It can be experimentally proved, that in vinyl polymers in solution we have similar values for the frequency of bond rotation.[9] The solid state helical order is clearly incompatible with this fast movement of all C–C bonds. On the other hand, the lowest energy state for a repeat unit is obtained when this is inserted in a helical section. We are therefore looking for a compromise between the maintenance of the helical order, and the fast rotation of C–C bonds. The corresponding model accepted nowadays for the macromolecule in solution is the following:[10] The macromolecule is seen as a mixture of an enormous number of conformers in very rapid equilibrium, with helical sections of opposite screw sense coexisting in the same macromolecule. The macromolecule can be considered as a classical "random coil", in which however the segments are spiraled. The conformational reversals, which interconnect helical sections of opposite screw sense, correspond to local deviations from the helical order, and therefore they produce an increase of conformational energy. However, this apparent loss of stability is compensated for by entropic stabilization due to the large multiplicity of chain rotamers. As only helical conformations are allowed for the various chain segments, the fast rotation of bonds is not inconsistent with a high percentage of helical order in solution.

Clearly, we can seek only statistical information about the conformational equilibria of these macromolecules in solution. Some typical conformational properties in solution are the average length of the spiraled sections, the probability of a conformational reversal, and the end-to-end distance.

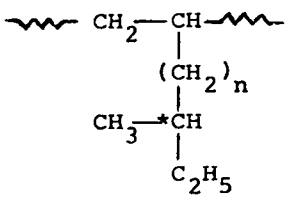
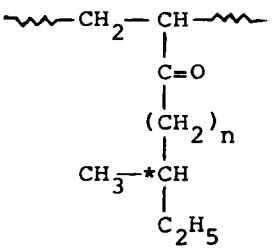
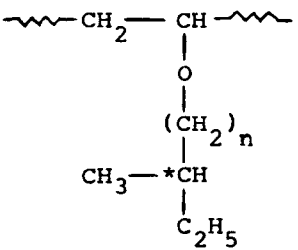
3 OPTICALLY ACTIVE POLYMERS

There are no direct methods which give unequivocal information about conformational properties such as the average length of spiraled sections of the chains in solution. Particularly in the case of polyhydrocarbons, which lack suitable chromophoric groups, the problem of checking experimentally the spiralization properties and of determining the percentage of conformational reversals in solution, seemed quite a hopeless one. We needed some way to introduce into these structures a chemical signal sensitive to the conformational equilibrium. From this consideration came the idea[11] to synthetize and investigate optically active poly(α-olefins), having the structure reported in Table I.

Since optical activity is sensitive to conformational equilibria, one could

TABLE I

Some of the investigated optically active polymers. For a review see Ref. 4

		
n = 0,1,2,3	n = 0,1,2	n = 0,1
Isotactic poly(α-olefins)	Polyvinylketones	Polyvinylethers

imagine correlating the optical activity—which is easily and directly measureable—of these polymers in solution with their conformational properties, as has been done for polypeptides. We cannot expect, however, that the conformational equilibrium in these polymers is just the same as in the optically inactive ones. As shown in Figure 5, the left- and right-handed chains of polypropylene are enantiomers, whereas the left-handed and right-handed chains of isotactic optically active poly(α-olefins) are diastereoisomers. Therefore the stability of left- and right-handed helical conformations may be somewhat different in asymmetric poly(α-olefins). Then, if the repeat units are spiraled in solution, one might expect a prevalence of one sense of spiralization over the other; and also that left-handed and right-

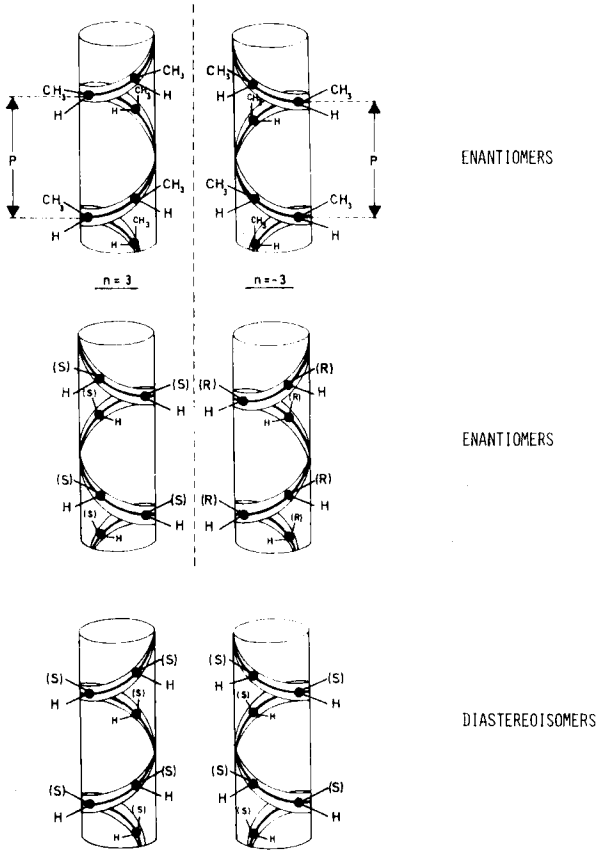


FIGURE 5 A simplified diagram showing the enantiomeric and diastereoisomeric relationship of vinyl-polymer helices. *n* is the number of repeat units per turn, *P* is the helix pitch. (S) and (R) represent chemical groups containing asymmetric carbon atoms of opposite chirality.

handed sequences may have different average lengths. We can directly demonstrate this difference of conformational properties of left-handed and right-handed repeat units, with the classical conformational analysis usually employed for paraffins. One can show in fact that in the case of poly-[(3*S*-methyl-l-pentene], the repeat unit† can exist either in two zero energy conformations (conformations without high energy interactions) when inserted in the left-handed screw sense of the main chain, or only in one zero energy conformation in the opposite screw sense.[11] This is shown in Figure 6.

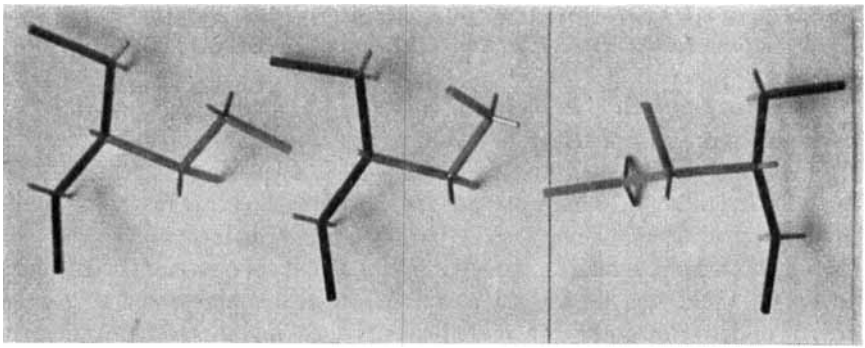


FIGURE 6 Simplified molecular models of the repeat unit of poly[(3*S*)-methyl-1-pentene] inserted in a left-handed and right-handed 3_1 helix. Darker shade—main chain; lighter shade—side chain. At 300 °K the energy difference is ΔE = 360–390 cal/mol of repeat units (calculated from the partition functions given in Table III*b* with $\Delta E\omega$ = 2 – 2.5 kcal/mol of repeat units).

On the basis of the corresponding partition functions, one can calculate that the energy difference between left-handed and right-handed regularly spiraled sections is around 400 cal/mol at room temperature (*cf.* Figure 6).[12,13]

In this way, we can see a first important consequence of the asymmetry as far as the chain conformation is concerned, namely that a particular configuration of the repeat unit carbon atoms brings about the prevalence of one screw sense of the main chain. Also the helices of natural biopolymers are generally found in only one screw sense: The α helix, as postulated originally by Pauling and Corey, is right-handed, the double helices of DNA molecule are also right-handed; most of the helices of polysaccharides are left-handed. The reason why only one screw sense is allowed, is exactly the reason outlined for optically active poly(α-olefins), namely, the two opposite screw senses are diastereoisomers, due to the presence of asymmetric centers in each repeat unit. The fact that in poly(α-olefins), the asymmetric carbon atoms are in the

†In agreement with recent IUPAC recommendation, we use "repeat unit" (instead of "monomeric unit", used in our previous papers). For the same reason we write differently chiral compounds, *e.g.* poly[(3*S*)-methyl-l-pentene] instead of poly-(*S*)-3-methyl-l-pentene.

lateral chain and that in all the biopolymers the asymmetric carbon atoms are in the main chain, does not alter the argument.

This relation between repeat unit configuration and sense of spiralization of the main chain can be visualized in Figure 7 for the examples of poly(α-amino acids) and poly(α-olefins). In the first case, an (*S*) absolute configuration brings about a right-handed helix; in the second case, an (*S*) absolute configuration brings about a left-handed helix.

4 STATISTICAL THERMODYNAMICS OF ISOTACTIC OPTICALLY ACTIVE POLY(α-OLEFINS) IN SOLUTION

In collaboration with Volkenstein's group we investigated the thermodynamics of optically active poly(α-olefins) in solution.

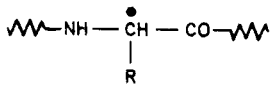
The statistical treatment, based on the well known Ising model, expresses analytically the conformational properties of these chiral macromolecules in solution in terms of two energy parameters[10,14] defined in Table II and Table III. One of the main advantages of this statistical treatment is that these energy parameters have a physical meaning. In fact, ΔU represents the "average energy of despiralization", or, more properly speaking, the average difference of energy, per mol of repeat units, between a regularly spiraled couple of repeat units and a couple of repeat units containing a conformational reversal;

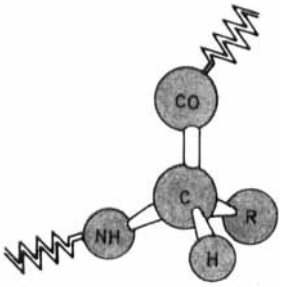
TABLE II

Statistical parameters of the rotational-isomer model. See Ref. 10 for details[a]

Conformation of the kth repeat unit	Ω_k
Probability that the kth and k-1)th units have conformations as specified	$g(\Omega_{k-1},\Omega_k)$
Main assumptions for the chain partition function Z: rotational-isomeric state approximation; no external forces; only nearest neighbour interactions	$Z = \sum_{\Omega_1}\sum_{\Omega_2}\ldots\sum_{\Omega_n}\prod_{k=1}^{n} g(\Omega_{k-1},\Omega_k)$
If the repeat unit can assume only two conformations (in the main chain), the terms $g(\Omega_{k-1},\Omega_k)$ may be regarded as the elements of a 2 × 2 matrix **G** with eigenvalues λ	$\mathbf{G} \equiv \begin{pmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{pmatrix}$
	$\lambda_{1,2} = \frac{1}{2}(g_{11} + g_{22}) \pm [\frac{1}{4}(g_{11} - g_{22})^2 + g_{12}g_{21}]^{\frac{1}{2}}$
Some conformational properties:	
First order distribution functions	$w(\Omega^{(1)}) = (\lambda_1 - g_{22})/(\lambda_1 - \lambda_2)$, etc.
Second order distribution functions	$w(\Omega^{(1)}\Omega^{(1)}) = g_{11}(\lambda_1 - g_{22})/[\lambda_1(\lambda_1 - \lambda_2)]$, etc.
Conditional transition probabilities	$w(\Omega^{(1)}\rightarrow\Omega^{(2)}) = (\lambda_1 - g_{11})/\lambda_1$, etc.
Mean lengths of regular sequences	$\nu(\Omega^{(1)}) = \lambda_1/(\lambda_1 - g_{11})$, etc.

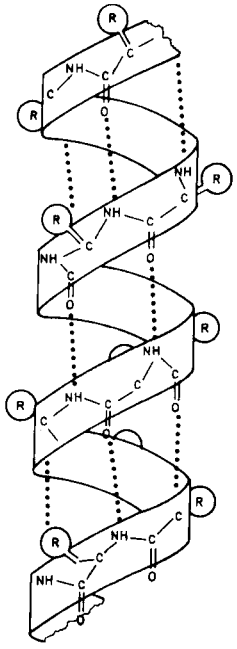
[a] See footnote [a] of Table III*a*.

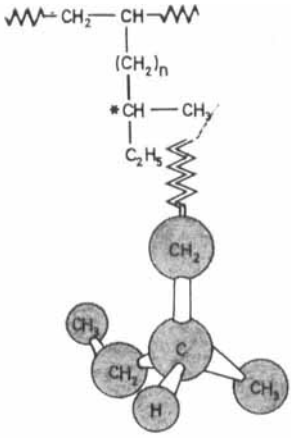




(S) ABSOLUTE CONFIGURATION

RIGHT HANDED
α-HELIX





(R) ABSOLUTE CONFIGURATION

RIGHT HANDED
3_1—HELIX

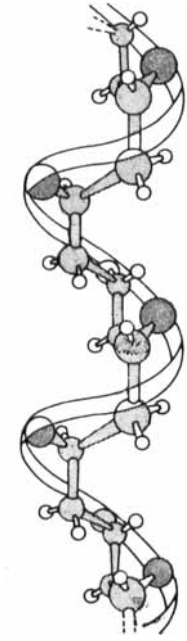


FIGURE 7 The relationship between the main chain conformation and the absolute configuration of the asymmetric carbon atom of the repeat unit in poly(α-amino acids) and isotactic optically active poly(α-olefins). In this last case, the lateral chain for simplicity is shown as a single R group.

ΔE measures the energy difference, per mol of repeat units, between the left-handed and right-handed regularly spiraled sections.

A discussion of the mathematical treatment will not be given in this paper. Bear in mind however, that in this treatment only nearest-neighbor interactions are taken into account, and therefore the macromolecule is seen as a unidimensional system in which the degree of cooperativity (namely the degree of mutual influence of the repeat units with each other) is limited to two; in other words, we consider interactions up to 4 C–C bonds. Note also that if the vinyl macromolecules do not contain asymmetric C atoms, then $\Delta E = 0$ and the conformational properties are characterized by only one energy parameter, ΔU.[10,14]

It has also been possible to obtain numerical values for ΔE and ΔU for various optically active poly(α-olefins). This has been done by expressing ΔE and ΔU in terms of the conformational partition functions of couples of contiguous repeat units [12] as shown in Tables III*a* and III*b*. This is actually one of the main advantages of working with paraffins, namely that the number of allowed conformations and the energy difference between the various conformations can be semiquantitatively established with some confidence.

TABLE III*a*

Relation between the rotational-isomer model and the conformational partition function of the repeat unit for ideally isotactic macromolecules[a]

Energy difference between left-hand and right-hand spiraled conformations of the main chain (per mol of repeat units)	$\Delta E = U(\Omega^{(2)},\Omega^{(2)}) - U(\Omega^{(1)},\Omega^{(1)}) = \mathbf{R}T \ln(g_{11}/g_{22}) \approx \mathbf{R}T \ln(Q_l/Q_d)$ where, *e.g.*, Q_l is the conformational partition function of the repeat unit in a regularly left-hand spiraled sequence
Average energy excess due to a conformational reversal (per mol of repeat units)	$\Delta U = \frac{1}{2}[U(\Omega^{(1)},\Omega^{(2)}) + U(\Omega^{(2)},\Omega^{(1)}) - U(\Omega^{(2)},\Omega^{(2)}) - U(\Omega^{(1)},\Omega^{(1)})] = \frac{1}{2}\mathbf{R}T \ln\left(\frac{g_{11}g_{22}}{g_{12}g_{21}}\right) \approx \frac{1}{2}\mathbf{R}T \ln\left(\frac{Q_l\, Q_d}{Q_{ld}Q_{dl}}\right)$ where, *e.g.*, Q_{dl} is the conformational partition function of the left-hand spiraled repeat unit preceded by a right-hand spiraled one. ($Q_l \neq Q_{dl}$!)

[a] The right-hand and left-hand spiraled conformations of the repeat unit are assigned indices 1 and 2, respectively.

The actual calculations procedure is rather cumbersome, and I will skip it, limiting myself to the results. For instance, for poly[(4*S*-methyl-l-hexene] (PS4MH), the energy difference between right-handed and left-handed repeat unit, ΔE, is 330 cal/mol, whereas the excess energy due to a conformational reversal, ΔU, is 1100 cal/mol (*cf.* Table IV). As a consequence of these energy

TABLE III*b*

Conformational partition functions of some isotactic optically active poly(α-olefins)[a]

Polymer	Q_l	Q_d	Q_{ld}	Q_{dl}
Poly[(3*S*)-methyl-1-pentene]	$2+2\omega$	$1+4\omega$	$3\omega^2+7\omega^2\tau$	8ω
Poly[(4*S*)-methyl-1-hexene]	$2+\tau+2\omega$	$1+\tau+5\omega$	$\omega Q_l Q_d+\omega\tau(Q_l+Q_d{}^2)$	$\tau\omega(Q_l+Q_d)^2+Q_lQ_d(\omega+2\tau\omega)$
Poly[(5*S*)-methyl-1-heptene]	$3+\sigma(2+\tau)+7\tau$	$3+\sigma(1+\tau)+7\tau$	$\omega Q_l Q_d+\tau\omega(Q_l+Q_d{}^2)$	$\tau(3+4\tau)(Q_l+Q_d)+\omega Q_lQ_d+\omega\tau Q_l[Q_d+2+4\tau+\sigma(1+\tau)]$
Poly[(3*S*),4-dimethyl-1-pentene]	$1+3\omega$	4ω	$\omega^2+3\tau\omega^2$	$7\omega^2$
Poly[(3*S*)-ethyl-5-methyl-1-hexene]	$1+4\omega$	$1+2\omega$	$4\tau\omega^2+6\omega^3$	$\tau\omega^2+7\omega^2$

[a]For the definition of σ,τ,ω see Figure 8. See also Refs. 12 and 14.

parameters, the macromolecules of PS4MH consist of alternating left-handed and right-handed sequences containing 35 and 2 repeat units respectively; the macromolecule has *ca.* 95% repeat units which are left-hand spiraled, while only *ca.* 5% are right-hand spiraled.[12] However, the most interesting result is that with a very small ΔE value (of the order of 300–400 cal/mol), the degree of left-hand spiralization is larger than 90%. This is a clear example of the effect of cooperativity in linear macromolecules. The thermodynamics—and therefore the conformational equilibria—of these asymmetric macromolecules in solution can be interpreted only on the basis of the interplay of the cooperativity parameter with the local energy parameter. The same feature holds for polypeptides.[16–19]

It is also interesting to compare the calculated conformational properties of PS4MH with those of non-asymmetric polymers having analogous structures. Poly(4-methyl-l-pentene) (P4MP) has $\nu = 15$, although it has about the same ΔU value. Also notice that the end-to-end distance is much enhanced in the asymmetric structure. This enhancement of the average dimensions is another striking effect of the influence of the asymmetry of the lateral chain on the overall macromolecular structure.

All these calculations are based on the values of conformational energy differences known in paraffins. Only three of these energy parameters are relevant, and their significance is shown in Figure 8. All of the conformational

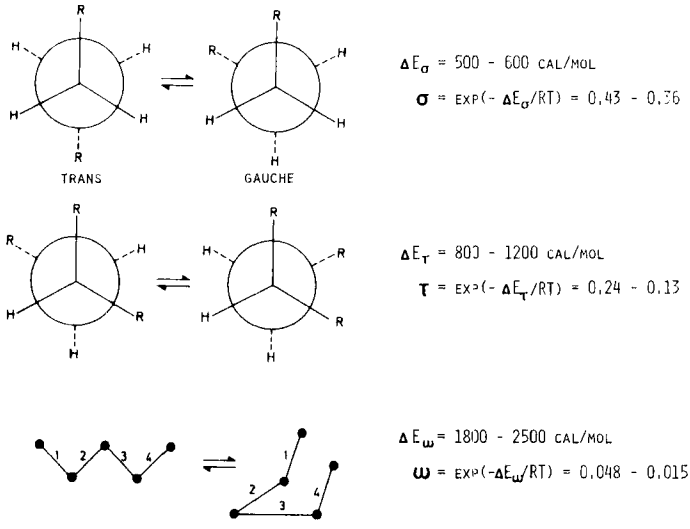
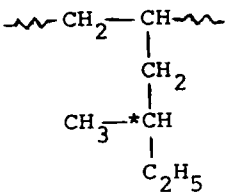
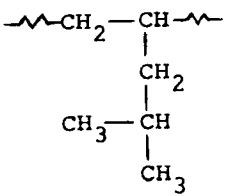


FIGURE 8 The three energy parameters which determine the conformation equilibria in paraffins. Parameters σ and τ relate to three-bonds interactions, ω to four-bonds interaction (includes only 1–4 contribution). Their numerical values correspond to the temperature $T = 300$ °K.

TABLE IV

Conformational properties of some poly(α-olefins)[a]

Formula	Name	ΔE cal/mol of repeat units	ΔU cal/mol of repeat units	w_l[b]	v_l[c]	v_d[e]	h^2/nl^2
	Poly[(4*S*)-methyl-1-hexene]	330	1100	0.93	31	2.2	48
	Poly(4-methyl-1-pentene)	0	1400	0.50	12	12	15

[a] Calculation carried out for $T = 300°K$ with $\Delta E_\sigma = 500$ cal/mol (*gauche-trans*), $\Delta E_\tau = 900$ cal/mol (double vicinal *gauche*), $\Delta E_\omega = 2500$ cal/mol (pentane interaction).

[b] Mole fraction of left-hand spiraled repeat units.

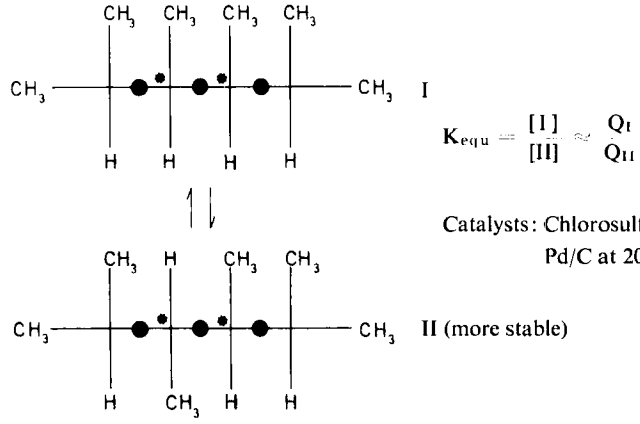
[c] Average number of repeat units in a left-hand spiraled sequence.

[e] Average number of repeat units in a right-hand spiraled sequence.

partition functions of stereoregular poly(α-olefins) in solution are finally a function of E_σ, E_τ, E_ω. Clearly, the precision of these values is reflected in the reliability of the calculated values of the conformational properties of polymers. This point has been considered in detail by Flory and his group.[20,21] Independent values of these energy parameters have been obtained by Suter and Pino:[22] Their method and results are illustrated in Table V. One tries to

TABLE V

Epimerization scheme for 2,4,6,8-tetramethylnonan, a low-molecular weight model for polypropylene.[22] Dots indicate the CH_2 groups, Q_I and Q_{II} the conformational partition functions of I and II, respectively.



find conditions of epimerization of paraffinic model compounds of polypropylene till a true thermodynamical equilibrium is reached between the diastereoisomers. Since for these compounds the difference in energy is due only to conformational effects, the equilibrium constant can be expressed in terms of the conformational partition functions of the two diastereoisomers, *i.e.*, in terms of E_σ, E_τ, E_ω. By the experimental determination of the equilibrium constant at various temperatures, one can determine in a rather accurate way the energy parameters E_σ, E_τ, E_ω. Of course, the reliability of this method depends on the basic approximations of our conformational analysis scheme. Those are primarily the isomeric state approximation,[23] according to which only staggered conformations of bonds are taken into account; and the approximation that E_σ, E_τ, E_ω do not change with temperature. Furthermore, as far as the reliability of the calculated values of the conformational properties of polymers is concerned, one should consider the series of approximations made in going from low molecular weight compounds to polymeric chains; that the chains are perfectly isotactic and of infinite length; that only rotations

of bonds (and for instance no oscillations around the energy minima[10]) are responsible for the chain flexibility, etc. With this in mind we do not take too literally the results of our calculations. However, we believe in the soundness of the overall picture, as shown in Table IV, from a qualitative viewpoint. By and large all the experimental data confirm this model, as discussed in the next section.

5 EXPERIMENTAL INVESTIGATION OF THE CONFORMATIONAL PROPERTIES OF OPTICALLY ACTIVE POLYMERS IN SOLUTION

Some of these experimental investigations have been with us for several years: for instance, the study of the optical activity of polymers in solution, and the comparison of the experimental molar rotation with that calculated on the basis of semi-empirical methods.[11] Table VI gives an example of this procedure. In these cases in which 90–95% spiralization in the more favorable screw sense is predicted, one finds, as expected, that $[\Phi]_D$ corresponds to that calculated for the left-hand helix; on the contrary, for those polymers characterized by a small ΔE (and therefore by a w_l close to w_d), we find, as expected, that the experimental $[\Phi]_D$ is close to the arithmetic average of the contributions of the two helices.[4,11,12]

The high value of the molar rotation is worth more consideration. $[\Phi]_D$ refers to one mole of repeat unit and is independent of molecular weight.[24]

TABLE VI

Relationship between optical activity and percentage of main chain left-handed spiralization in optically active isotactic poly(α-olefins)

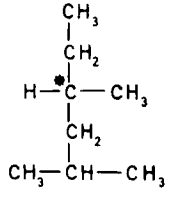
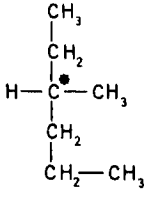
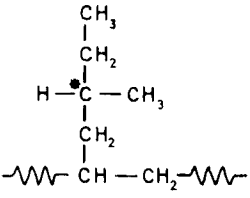
Polymer	n^a	w_l^b	$[\Phi]_{D,\text{calc}}{}^c$			$[\Phi]_{D,\text{exp}}{}^d$
			e	f	g	
Poly[(3*S*)-methyl-1-pentene]	0	0.99	+180	−240	+40	+161
Poly[(4*S*)-methyl-1-hexene]	1	0.95	+240	−300	+60	+288
Poly[(5*S*)-methyl-1-heptene]	2	0.60	+228	−225	+22	+68

[a] Number of CH_2 groups in the side chain (see Table I).
[b] Calculated mole fraction of left-hand spiraled repeat units at 300 °K.[12]
[c] Calculated according to Brewster.[31]
[d] In aromatic hydrocarbon solution at 300 °K, referred to one repeat unit[11].
[e] Average of the values calculated for the allowed conformations inserted in a *left-handed* helical sequence.
[f] Average of the values calculated for the allowed conformations inserted in a *right-handed* helical sequence.
[g] Average for *all* the allowed conformations.

Therefore we can compare it directly with the molar rotation of low-molecular weight compounds having a structure similar to the polymer repeat unit. Generally the molar rotation of optically active low molecular weight paraffins is much lower (*cf.* Table VII) as is the temperature coefficient of molar rotation.[11] This large enhancement of optical activity in polymers is due to the displacement of the conformational equilibrium towards repeat unit conformations which are consistent with the left-handed screw sense of the main chain.

TABLE VII

Optical activity properties of poly[(4*S*)-methyl-1-hexene] and its low molecular weight model compounds

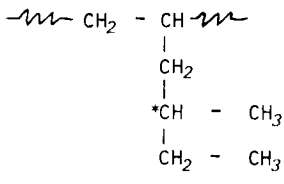
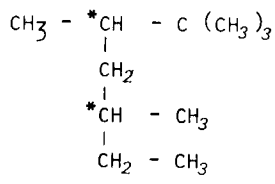
			
$[\Phi]^{25}_D$	+ 21.4	+ 9.9	+ 290
$\frac{\Delta[\Phi]_D}{\Delta T}$	—	− 0.009	− 0.68

These conformations happen to have a very large and positive rotation,[11] as calculated by Brewster's method (*cf.* Table VI). On the contrary, in low molecular weight model compounds, conformations having positive and negative rotation are present in equilibrium with comparable statistical weight and therefore the average optical activity is generally a small number. The same argument explains the difference in the temperature coefficient of $[\Phi]_D$: by increasing the temperature the statistical weight of the less stable conformations increases. For the polymer, this means that the percentage of right-handed repeat units increases, and since the corresponding conformations have a large and negative molar rotation,[11] the net polymer molar rotation decreases. In the low molecular weight compounds, the increase of temperature corresponds to a non specific increase of the population of conformations with both positive and negative rotation, and the net effect is small. Also, the relation between optical activity and conformation depends on the structure of the repeat unit; in particular, on the distance of the asymmetric carbon atom from the main chain. This point is discussed at length in other papers of the group of Pino.[11,12,25-27] Here, I would like to mention one point, which is relevant as far as the comparison of poly(α-olefins) with

biopolymers is concerned. According to our explanation, the enhancement of the optical activity is due to a particular position of the conformational equilibrium of the repeat unit. The question can be raised, whether such an enhancement could not be ascribed, instead, to a new optically active chromophor originated by the helix itself. It is known in fact that this is the case in helical polypeptides, where the interaction of the consecutive peptide chromophores in the ordered helical conformation gives rise to a new electronic transition.[28] There are two lines of reasoning to demonstrate that this is not the case for optically active poly(α-olefins). On the one hand, the electronic transition takes place in these polymers at the same wavelength as in low molecular weight model compounds.[25,26] On the other hand, it has been possible to demonstrate directly that, in open chain paraffins, a particular position of the conformational equilibrium can cause very large molar rotations.[29,30] One example of this is shown in Table VIII: the model compound, according to classical conformational analysis, exists in only two "allowed" conformations which, as calculated by the method of Brewster,[31] have a large and positive molar rotation.

TABLE VIII

Conformational partition function and optical activity of poly[(4*S*)-methyl-1-hexene] and of a conformationally rigid model compound

	 Poly[(4*S*)-methyl-1-hexene] (5 bonds contribute to $[\Phi]$)[b]	 (3*R*,5*S*),2,2-tetramethylheptane[a] (only 3 bonds contribute to $[\Phi]$)[b]
Q	$2 + \tau + 2\omega$ (left-handed repeat unit)	$2 + \tau + 4\omega$
$[\Phi]_{D,calc}$[b]	+ 240 (left-handed repeat unit)	+ 120
$[\Phi]_{D,exp}^{25}$	+ 288[c]	+ 137.8

[a] Model compound for the right-handed repeat unit of the polymer (only one "allowed" conformation). For this and other "conformationally rigid" low molecular weight paraffins, see Refs. 29, 30 and 36.

[b] According to Brewster.[31]

[c] In aromatic solvent.

We can see from Table VIII that the experimental value is very close to the calculated value both in the polymer and in the low molecular weight compound, *i.e.*, the optical activity predicted on the basis of conformational factors alone explains completely the high optical activity found experimentally.

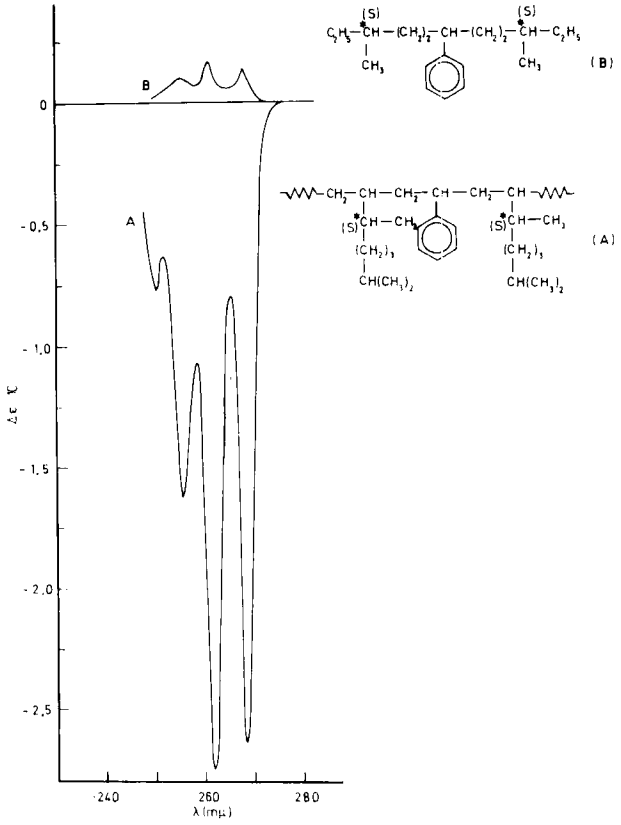


FIGURE 9 CD spectra of a styrene/(3*R*),7-dimethyl-l-octene copolymer (*A*) and its low molecular weight model compound (3*S*,9*S*)-dimethyl-6-phenyl-undecane (*B*) in $CHCl_3$ at 25 °C. The quantity $\Delta\epsilon$ is referred to a styrene repeat unit. See Ref. 32.

Other investigations are more recent, as CD studies of the kind shown in Figure 9: A copolymer obtained from a monomer mixture of optically active (3*R*),7-dimethyl-l-octene with styrene shows a negative Cotton effect at about 260 nm due to the phenyl group.[32] This demonstrates that styrene units become dissymmetric in the copolymer chains, which is easily explained on the basis of the preferential right-handed screw sense of spiralization of sections of (3*R*),7-dimethyl-l-octene units. This is a clear example of an asymmetry induced by conformational effects.

Recently, Neuenschwander and Pino[33] have been able to demonstrate experimentally another important property of optically active poly(α-olefins) in solution: the enhancement of the end-to-end distance with respect to optically inactive polymers of analogous structure. One way to rationalize this enhancement is to consider that the asymmetric macromolecules of poly[(4*S*)-methyl-l-hexene] or poly[(3*S*)-methyl-l-pentene] have a much smaller number of chain conformational reversals than the optically inactive analogs. The persistence length of regularly spiraled sections is then much higher, and therefore the macromolecule is more extended in solution (*cf.* Table IV). In Figure 10 the comparison of the unperturbed end-to-end distance of isotactic

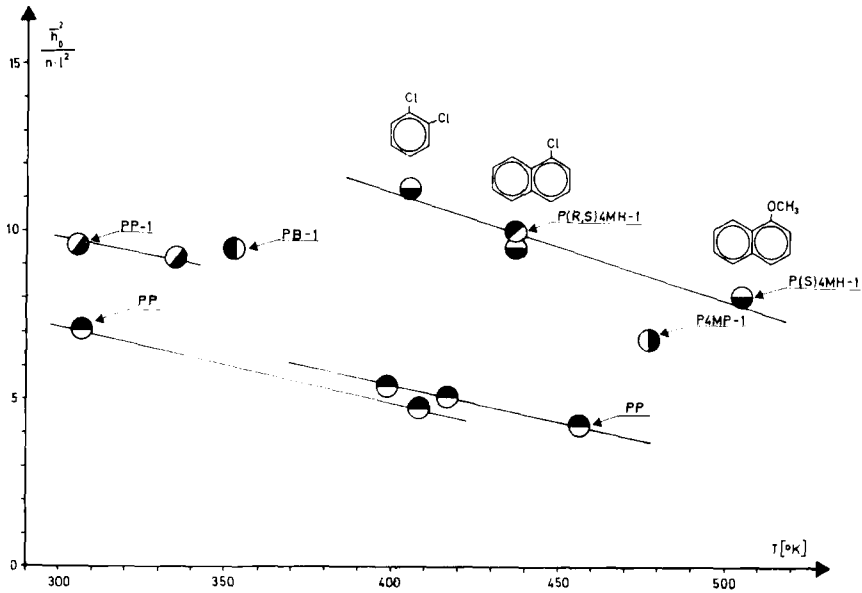


FIGURE 10 Unperturbed end-to-end dimensions of isotactic fractions of poly(α-olefins) (see Ref. 33). The experiments on poly[(4*S*)-methyl-1-hexene] [P(S)4MH-1], poly[(4*R*,*S*)-methyl-1-hexene] [P(R,S)4MH-l] and poly(4-methyl-1-pentene) (P4MP-1) have been carried out in our laboratory by P. Neuenschwander. The data for poly(1-butene) (PB-1), poly(1-pentene) (PP-1) and polypropylene (PP) have been recalculated from literature[47–51] using $\Phi = 2.86 \times 10^{21}$.

fractions of poly[(4*S*)-methyl-l-hexene] and poly(4-methyl-l-pentene) is reported.[33] It is evident that the enhancement of the average dimensions of the optically active polymer, as well as of the temperature coefficient of the end-to-end distance, are appreciably larger than those of the optically inactive one. It is unfortunate that we are not able to make these measurements in the

lower temperature region, where the effect should be even larger, and where a deviation from linearity is expected[27] in the case of an optically active polymer. But for these high melting polymers the θ conditions cannot be found at lower temperature and furthermore, their poor solubility prevents light scattering studies in good solvents.

6 OPTICALLY ACTIVE POLYMERS OTHER THAN POLY-(α-OLEFINS)

Many optically active stereoregular polymers other than poly(α-olefins) have been prepared and investigated to date to clarify the relation between optical activity and stereoregularity and/or optical activity and conformation.

Optical active polymers can be formally divided into two families: polymers in which the asymmetric centers are in the main chain; and polymers in which the asymmetric centers are in the lateral chains. Among the latter are poly(α-olefins) and other vinyl polymers shown in Table I. Other examples of both classes of compounds are shown in Table IX. For more examples, the reader is referred to the latest reviews.[4,5,7] Some of the problems of the synthesis and characterization of optically active polymers are reviewed by Pino.[4] The relation between asymmetry of the macromolecule and asymmetry of the monomer has also been extensively discussed[2,4,5] as well as the use of optically active monomers to get information about the polymerization mechanism.[3,4]

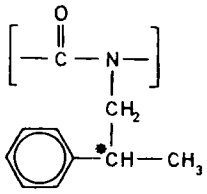
The study of the optical activity of polymers is based on the comparison with monomers or low molecular weight model compounds. There are two main questions to be asked in this regard: (a) whether the electronic transitions are the same in polymers and in low molecular weight models, and (b) whether there is a substantial difference in the rotational strength.

The presence of a new (or perturbed) electronic transition in the polymers is usually taken as an indication of the existence of an interaction between vicinal chromophoric groups, which in turn may indicate that a conformatio nal order is established in the macromolecular structure. Typical is the case of some polypeptides, in which the rigid α-helical structure is considered to be the cause of the new characteristic UV band. The existence of helical conformations in solution has been proposed on the basis of the analysis of ORD curves and of the corresponding location of the electronic transitions, in the case of poly(2-ethyl-aziridine) (*cf.* Table IX) and its *N*-benzoylated derivative.[38] In other cases, optical activity data are useful to rule out the existence of ordered helical conformations, as in the case of poly[(*S*)-lactic acid],[39] poly(L-α-hydroxyisovalerate),[40] and for polyamides obtained from β-,γ- and δ-methyl-ω-caprolactam[41] (Table IX).

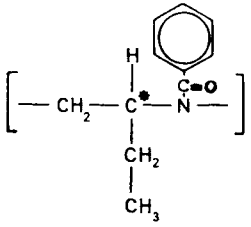
When the electronic transitions in polymers and model compounds are the

TABLE IX

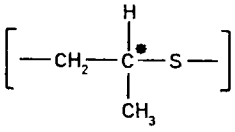
Some typical optically active polymers



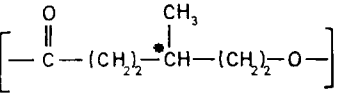
Poly(d-β-phenylpropyl isocyanate)[a]
Goodman and Chen[34]



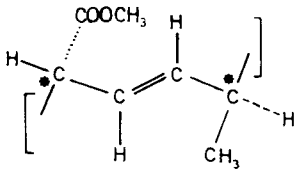
Poly(*N*-benzoyl-2-ethylaziridine)[a]
Tsuboyama and Yanagita[38]



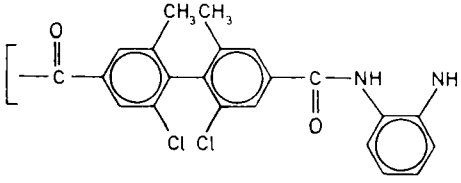
Poly(propylene sulfide)
Spassky and Sigwalt[35]



Poly(*R*)-γ-methyl-ε-caprolactone]
Overberger and Kaye[37]



Poly(methyl sorbate)
(erythro diisotranstactic)
Natta *et al.*[1]



An example of atropoisomerism in macromolecules
Overberger and Yoshimura[13]

ordered conformation in solution has been suggested on the basis of CD and ORD techniques.

same, the simple comparison of the rotational strength can be of some utility. For instance, an enhancement of the molar rotation in polymers can be taken as an indication of a displacement of the conformational equilibrium of the repeat units towards those conformations which are consistent with the restrictions imposed by the macromolecular structure; and this in turn may be taken as an indication of cooperative interactions which induce a conformational order along the chain. Optically active poly(α-olefins) are the best known example of this kind; polyvinylethers and polyvinylketones (*cf.* Table I) as well as polyisocyanates[34] belong to the same category. A much larger number of examples and a deeper discussion of the chiral-optical properties of polymers can be found in the reviews mentioned above.[2-7] However even from this brief consideration it is apparent that although optical activity in some instances can be useful to obtain information about the conformation of polymers in solution, the information gained in this way is only qualitative. We would like to know something more detailed and quantitative about the chain in solution. For instance, what is the average length of chain sections in a given conformation, and/or the percentage of repeat units in the various possible conformations? In other words, we would like to have the kind of information summarized in Table IV for poly[(4*S*)-methyl-l-hexene].

In this regard, our knowledge of most of these polymers is still poor or completely lacking. In order to understand why it is so, it is useful to summarize how the problem has been brought to a satisfactory solution for optically active poly(α-olefins). In this case, the strategy has been based on three well established points: (a) reliable knowledge of the conformational equilibria of low molecular weight models (paraffins), and of the corresponding energy difference among the various conformers; (b) a semiempirical method to calculate the optical activity as a function of the conformational equilibrium; (c) a detailed statistical mechanical treatment, which allows the prediction of conformational properties such as the end-to-end distance.

It has been therefore possible to guess the most probable conformations of the repeat unit, to calculate the corresponding optical activity, and to compare it with the experimental data. The good agreement between calculated and experimental $[\Phi]_D$ values was indicative of the soundness of the hypothesized conformational equilibria. Later on, on the basis of this conformational equilibrium, numerical values have been obtained of ΔE and ΔU (and therefore of all the conformational properties as well). The experimental check of some of these calculations (enhancement of $< h^2 >$ and of its temperature coefficient) have been taken as an independent demonstration of the substantial validity of the model illustrated in Tables IV and VI.

For most of the polymeric systems other than poly(α-olefins), we do not have any detailed information about the conformational equilibria of model compounds. Quite often, we do not even know if the most stable bond con-

formation is in the eclipsed or in the staggered form. Therefore, we do not have any idea of the conformational energy differences among the rotamers. Statistical mechanical treatments are not available or lead to final equations which are in terms of unknown energy parameters. Also, no successful semi-empirical way to predict the optical activity as a function of the conformational equilibrium is known for compounds other than paraffins. In many instances we do not have information about the energy barriers hindering bond rotation, so we do not know if the chain exists in a random coil or as a rigid rod.

In some cases, an idea of the preferred conformation of the repeat unit can be inferred from the polymer conformation in the solid state. However this alone is not enough, particularly if the polymer contains polar groups which may interact with the solvent. The problem of the influence of the solvent-solute interactions on the chain conformation is actually a very difficult one. The reason why conformational problems for poly(α-olefins) in solution are in a more advanced stage than for other polymers lies also in the fact, that for these apolar hydrocarbon chains the solvent does not influence the conformational energy difference between rotamers, and therefore can be disregarded.

In conclusion, one can say that the whole picture of studying the conformation of polymers in solution does not seem so encouraging. The only way to avoid this impasse is to obtain detailed information on the conformational properties of low molecular weight compounds. This probably can be achieved on the basis of theoretical calculations of energy minima, which recently are much more precise and reliable. The problem is however, how to take into account the influence of the solvent on the conformation. It is clear, in fact, that knowledge of the conformational properties of the isolated molecule is not enough for our purpose.

The next necessary step would be the study of the relation between optical activity and conformation in low molecular weight compounds which have previously been well defined conformationally. Here, the use of "conformationally rigid"[29,30] compounds—namely compounds having only a very small number of stable conformations—should be advantageous. The satisfactory understanding of conformational equilibria in polymers will progress only to the extent by which this preliminary background will be covered.

Some qualitative and quite general considerations on the conformation of polymers in solution are, however, possible by extrapolating our knowledge acquired with poly(α-olefins). We can say in fact that in these cases in which the helical conformation is present in the solid state, and the chain exists as a random coil, the solution state will be characterized by a short range helical order, with fast interconversion of the two screw senses and fast changes in the length of the spiraled sections. Also, we should have a prevalence of one

sense of spiralization over the other, whenever the repeat unit contains chirality centers. The extent of these effects depends, however, on the energy parameters. If, for instance, the despiralization energy is very low [ΔU in the case of poly(α-olefins)] and if the energy difference between the possible monomeric unit conformations is also small, the length of the spiraled sections will be so short, that complete disorder will be achieved in solution. On the contrary, if the energy parameters characterizing the conformational equilibrium are large enough, we can have a helical order in solution even higher than that found in isotactic poly(α-olefins). Possibly, we could reach in solution an order close to that characterizing the solid state.

7 CONFORMATIONAL TRANSITIONS IN STEREOREGULAR POLYMERS

Conformational transitions of the helix-coil type have been often found in poly(α-amino acids) and other biopolymers in solution.[16,17,42] This phenomenon has never been reported in the case of poly(α-olefins) despite their inferred high helix content. The reason for this difference may be seen in the fact that the chain of vinyl polymers is already a random coil in which the spiraled sections possess a large mobility. On the contrary, the helix of polypeptides is a rigid structure, which may collapse abruptly when a certain solvent composition or temperature is reached.

It is, however, worth while to consider more closely the differences and possible similarities of biopolymers and stereoregular synthetic optically active polymers as far as conformational transitions are concerned. For this, let us consider first the thermodynamic parameters that, in the two cases, describe the conformational properties. Reference is made again to poly(α-olefins), as they are conformationally well characterized. As it is well known, the thermodynamics of helix-coil transition in biopolymers is described in terms of two energy parameters, s and σ, in line with the classical statistical treatment of Zimm and Bragg.[17] The parameter σ is the initiation parameter, which accounts for the difficulty of initiating an helical region. As such, it is a cooperativity parameter, namely it has to do with the interaction energy between contiguous repeat units. The parameter s is related to the energy difference between conformational states of the repeat unit. It appears that the physical meaning of s and σ is very close to that of ΔE and ΔU of poly(α-olefins) (*cf.* Tables II and III). From this, one can infer that the conformational properties of optically active stereoregular polymers are governed by the same basic thermodynamics as those of biopolymers.

As an objection to this formal analogy, the point could be made, that in biopolymers, contrary to poly(α-olefins), two kinds of effects are present which

seem to be important for conformation: interactions other than near-neighbor interactions (for instance hydrogen bonding) and interactions with the solvent.

As far as the hydrogen bonding and other stabilizing intramolecular forces are concerned, the recent research has shown that they are not essential for the establishment of the ordered conformation. We have in fact, helical polypeptides—the polyproline is an example[18]—in which H-bonds are not present.

Furthermore, the conformation of some peptide sequences can be calculated with satisfactory precision taking into account only nearest-neighbour interactions.[19] It seems therefore that, at least in some instances, the main factors which govern the stability of the helix conformation are the same in poly(α-olefins) and polypeptides—namely short range interactions between vicinal repeat units.

Interactions with solvent, particularly those due to charged groups in polymers and solvent molecules, is a characteristic of biopolymers which does not find any correspondence in poly(α-olefins), and certainly the large enthalpy and entropy effects associated with solvation influence to a large extent the chain conformation in solution. The parallelism between the statistical treatment of polypeptides and poly(α-olefins) can then be maintained, once solvent effects are considered in the actual value of the energy parameters s for each set of conditions.

It seems therefore that the difference between optically active poly(α-olefins) and polypeptides may lie only in the numerical value of the two thermodynamic parameters. In other words, in order to have in optically active poly(α-olefins) (and in synthetic polymers in general) sharp conformational transitions as those found in biopolymers, one should look for conditions at which $\exp(-\Delta E/\mathbf{R}T)$ and $\exp(-\Delta U/\mathbf{R}T)$ are close to s and σ, respectively. From Tables IV, VI and VII it is apparent that this is not easy, as σ and s found in polypeptides are much smaller than the corresponding parameters in poly(α-olefins). The only way to obtain high values of ΔE and ΔU seems to lie in new structures which are characterized by a large conformational rigidity. We have been looking for some of these structures, and one example is given in Figure 11. Poly[(3*S*),4-dimethyl-l-pentene], according to our conformational analysis and calculations,[12] is characterized by an exceptionally high ΔE value, so that even at room temperature the polymer should be left-hand spiraled by more than 99%, and the regularly spiraled sections should consist of several hundred repeat units. We have prepared this polymer,[43] and the study of its physicochemical properties has just begun. We are very curious to see, for instance, if sharp conformational transitions occur. One difficulty here lies in the poor solubility of this compound. This poor solubility we can partially rationalize on the basis of conformational effects. In the case of the apolar poly(α-olefins), in fact, most of the driving forces for the solubilization are entropic, *i.e.*, due

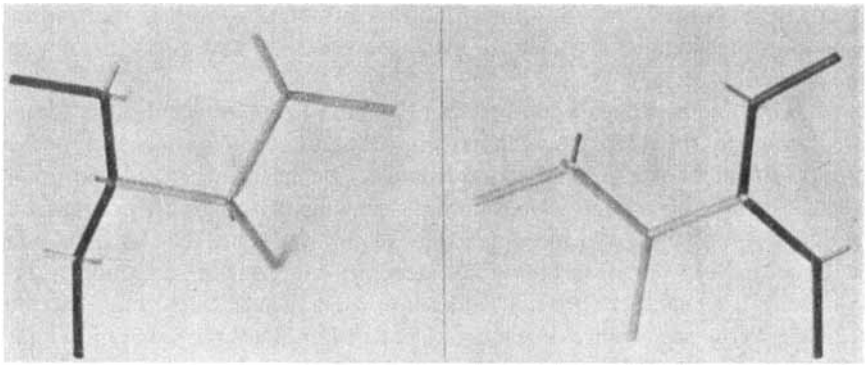


FIGURE 11 Simplified molecular models of the repeat unit of poly[(3*S*), 4-dimethyl-1-pentene] inserted in a left-handed and right-handed 3_1 helix. Darker shade—main chain; lighter shade—side chain. At 300 °K the energy difference is $\Delta E \simeq$ 1200–1700 cal/mol of repeat units (calculated from the partition functions listed in Table III*b* with $\Delta E_\omega \simeq$ 2000–2500 cal/mol of repeat units).

to the multiplicity of chain rotamers which are established in solution. It is then conceivable that for a polyhydrocarbon for which such a random coil state cannot be easily achieved, the solubility tends to be smaller. This point indicates another important difference between poly(α-olefins) and biopolymers which contain charged or ionizable groups. These groups, being able to interact with the solvent, may give rise to driving forces for solubilization. The solubility of a biopolymer (or of any polyelectrolyte) is therefore not inconsistent with conformational rigidity of the chain.

8 CONFORMATIONAL RIGIDITY IN MACROMOLECULES

In the previous section we have used the term "conformational rigidity." I would like now to consider briefly its meaning. With conformational rigidity we mean, quite loosely, that the conformational equilibrium in solution is overwhelmingly displaced towards one (or very few) conformation(s), among the very many that would in principle be allowed on the basis of the rotation of all bonds.[29,30] As far as polymers are concerned, several polypeptides investigated up to date seem to possess this feature, *i.e.*, the macromolecules are able to maintain in solution a unique, well defined conformation. Proteins and enzymes in their native state, as well as nucleic acids, are also supposed to be conformationally rigid. In all these cases, oscillations of the bonds around the energy minima are not denied, but the rapid and continuous jumping of bonds from one energy minimum to another does not supposedly take place. It is also generally assumed that for these rigid biopolymers the conformations

in solution and solid state are the same, another indication that the conformation chosen by a given polypeptide chain is the only one allowed under normal conditions.

There is a well known teleological rationalization for the phenomenon of conformational rigidity in biopolymers: namely that conformational rigidity is the prerequisite for biological function. For instance, for enzymatic catalysis to occur it is necessary that in the enzyme-substrate complex very precise and fixed geometrical coordinates are respected. This high efficiency of the enzymatic catalysis would be inconsistent with a complete and disordered rotation of all the main chain bonds. On the basis of the argument, that conformational rigidity is essential for the biological activity, one could even say that conformational rigidity is the result of natural selection: namely that the mobile protein structures might have been discarded in the course of evolution.[44]

At least in the simple case of homopolymers, can we understand their conformational rigidity on the basis of thermodynamics? A question in this regard is whether the conformational rigidity is caused by thermodynamic or kinetic factors. The meaning of this question can be discussed on the basis of Figure 12(I) which represents a molecule that exists in two conformations, A

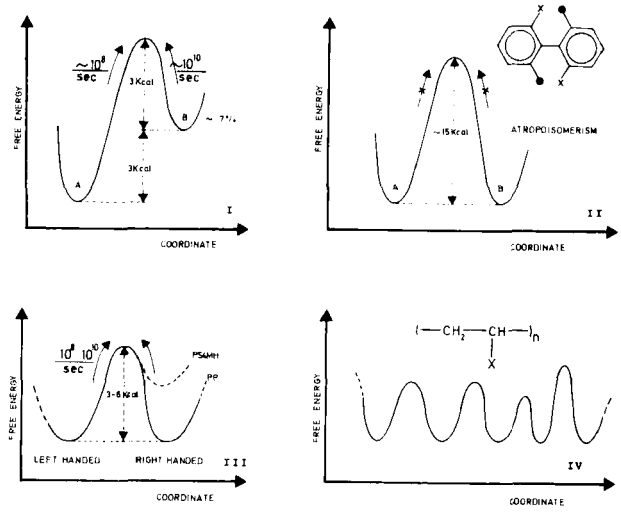


FIGURE 12 Schematic diagrams to illustrate the thermodynamic and kinetic conformational rigidity. (I) Thermodynamic conformational rigidity in a simple molecule existing in two conformers, A and B. (II) Kinetic conformational rigidity due to the excessively high energy barrier between the possible conformers. (III) Thermodynamic conformational rigidity in the repeat unit of isotactic poly(α-olefins). (IV) Free energy profile for the macromolecule of isotactic poly(α-olefins). There is an extremely large number of allowed *chain* conformations, although only two conformations are allowed to each repeat unit. For instance, for $n = 100$ and 10 conformational reversals, *ca.* 10^{20} possible chain conformations are possible.

and B, which differ by 3kcal/mol. There are energy barriers of 3 and 6 kcal/mol separating the two conformers. As you can see from these rough calculations, with an energy difference of 3 kcal/mol less than 1% of **B** is present at equilibrium. This situation can be described in terms of a thermodynamic conformational rigidity, namely the conformational equilibrium is displaced overwhelmingly towards one particular conformation. However, the transformation between the two states A and B is quite fast at room temperature, faster than $\simeq 10^8\ s^{-1}$. In the case of the kinetic conformational rigidity, on the contrary, the potential energy barrier $\Delta U^{\neq}$ is so high that it cannot be overcome under operational conditions. An example is given in Figure 12(II): although the two conformers have the same energy, there is no equilibrium as the rate of transformation with $\Delta U^{\neq} = 15$ kcal/mol is practically zero at room temperature. It is interesting that, if the experimental method that we use to study the equilibrium is not sensitive to 1% of **B**, one could say that in both cases [Figures 12(I) and 12(II)] the molecule never moves from the state A.

Let us now consider the macromolecules. Figure 12(III) represents the case of the repeat unit of polypropylene, in which *l* and *d* repeat units have the same energy and are separated by a relatively small energy barrier. Poly[(4*S*)-methyl-l-hexene] units are characterized by a similar energy profile, with the difference that the state *d* is destabilized. The energy profile of the two macromolecules can be represented by the Figure 12(IV) which shows that even though the repeat unit has only two allowed conformations, the chain has an almost infinite number of chain isomers of equal or very similar energy. On the basis of this consideration, it is apparent that for a macromolecule it is really a dramatic feature to exist in only one conformation.

On the basis of the above discussion we can now see the relevance of the question: what is the origin of conformational rigidity in macromolecules? This question actually marks the point at which the height of the energy barriers (kinetics) and the energy differences between the conformational energy minima (thermodynamics) have to be considered together. This question also points to a problem that in macromolecular chemistry is not yet sufficiently investigated and understood—the conformational dynamics of the chain in solution. Recently, some aspects of this problem have been considered by Poul and Mazo[45] and Morawetz.[46]

In the case of poly(α-olefins), it seems that the thermodynamic conformational rigidity is the only one we can achieve. There is no reason in fact to believe that the potential energy barriers are much higher in polymers with respect to low molecular weight paraffins. On the basis of the discussion outlined in terms of Figure 12(III) (example of polypropylene) we can also see the necessary condition for conformational rigidity in the chain. This is, that only one conformation must be allowed to the repeat unit. It follows from this statement that only optically active polymers can yield conformationally

rigid polymers. The asymmetry is in fact the only means to exclude one of the two screw senses from the conformational equilibrium.

The origin of conformational rigidity in poly(amino acids), proteins and biopolymers in general is not so clear.[44] Actually the problem of the conformational dynamics is far from being understood even in simple peptides and other low molecular weight models of biopolymers. This problem is, however, important. Should we find, for instance, that the energy barriers in proteins are as small as those in poly(α-olefins), we would in fact conclude that biopolymers are characterized in solution by a fast equilibrium among very many chain conformers, although one particular chain conformation is by far the most stable one.

9 CONCLUSION

The main concepts that I have covered in this paper, *i.e.*, configurational order, asymmetry, helical conformations of the main chain, conformational rigidity, and conformational transitions, are all interrelated properties. In particular, a linear macromolecule with a regular configuration order will generally assume a regular chain conformation. This main chain regular conformation is often a helix, which is the structure that respects at the same time the postulate of the steric equivalence of the repeat units, and the minimum of chain conformational energy. Nearest-neighbour interactions are generally sufficient to stabilize the helical structure and to determine most of the conformational properties in solution.

The presence of asymmetric carbon atoms in the repeat unit brings about the prevalence of one sense of spiralization. There is a direct relationship between the configuration of the asymmetric atoms in the repeat unit and the prevailing screw sense. In turn, this phenomenon of prevalence of one screw sense may take the extreme form of a conformational rigidity and/or atropoisomerism. In some biopolymers, this rigidity seems to be the prerequisite for the precise stereochemistry interactions accompanying the biochemistry. All these conformational features are not characteristic of a unique class of macromolecules, but may be shared by all asymmetric stereoregular linear macromolecules, depending only upon the conformational energy parameters which characterize the thermodynamics of the chain in solution. Synthetic isotactic poly(α-olefins) with an asymmetric C atom inserted in the lateral chain, due to their structural simplicity, due to the absence of intramolecular interactions, and of strong solvent effects, may be useful models for investigating the conformational properties of macromolecules in solution.

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DISCUSSION

Prof. H.-G. Elias (*Midland Macromolecular Institute, Midland, Michigan*): Can the dramatic increase of optical activity of the optically active poly(α-olefins) over that of their low molecular weight analogs be in part due to intermolecular association? Crystalline syndiotactic polypropylene exhibits in the IR spectrum a so-called "crystalline band" at 868 cm^{-1} which disappears on melting.[1] The proper position for this band can be calculated for helical PP in the *ttgg* conformation.[2,3] It was thus concluded that conformation alone is responsible for the crystalline band whereas packaging effects can be neglected.[4] The crystalline band is not present in 4% carbontetrachloride solutions, but it appears at room temperature in benzene solutions.[5] One would thus conclude that syndiotactic polypropylene consists of long helical sequences in benzene solutions, whereas helical segments seem too few and/or too short in CCl_4. However, the band intensity decreases over the same temperature range as does the tendency towards intermolecular association.[5] Syndiotactic polypropylene is not associated in CCl_4 solutions. Association tendency and the appearance of a crystalline band thus go hand in hand, implying an effect of packaging on spectroscopic properties.

Prof. P. L. Luisi: We can exclude rather clearly that association influences the

optical rotation in our poly(α-olefins). The molar rotation is in fact independent of concentration of the polymer solution, is independent of the polymer molecular weight (above a polymerization degree of *ca.* 10), and is independent of the solvent. With this, I do not deny the possible existence of association phenomena in our polymer solutions. Actually, Neuenschwander in our group found that a few solvents show Zimm plots which are typical of association. The polymer optical activity is however not affected, which reflects the fact that $[\Phi]_D$ is only a function of the local conformational equilibrium of the repeat units. As a further proof that interactions among the macromolecules do not affect $[\Phi]_D$, one could mention that for poly[(3*S*)-methyl-l-pentene] the optical activity in solution is very close to that found in the solid state. Furthermore, the fact that values of $[\Phi]_D$ as high as those found in polymers, can be also found in particular low molecular weight model compounds, is another independent proof that conformational factors alone are responsible for the enhancement of optical activity.

Prof. G. Challa (*State University of Groningen, Groningen*): You showed that the optical activity per segment of isotactic polymers may be about 20 times higher than that of monomeric model compounds. In this case the asymmetric center was situated in the side groups of the chains, so the atactic polymer would also show optical activity. Is the ratio of optical activity with respect to the model compounds much lower than 20 in the case of the atactic polymer?

Prof. P. L. Luisi: In the optically active isotactic poly(α-olefins) investigated thus far, the optical activity is proportional to the stereoregularity: the higher the stereoregularity, the higher the optical activity. For the least stereoregular fraction of poly[(3*S*)-methyl-l-pentene] (soluble in diethyl ether), $[\Phi]_D^{25}$ is 127, and for poly[(4*S*)-methyl-l-hexene] it is about 180 (compared with 160 and 290, respectively, for the most stereoregular fractions). These "least stereoregular" fractions still possess a relatively high crystallinity and melting point, and they are certainly far from the "pure atactic" state. It is therefore difficult to give a $[\Phi]_D$ value for the atactic polymers, although it should be remarkably lower than that of our least stereoregular fraction.

Discussion References

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