posite of low-density polyethylene a large and steadily increasing degree of orientation is produced when the degree of stretching is increased. A smaller but still increasing degree of orientation can be observed in the plasticized PVC and elastomer-modified PP. In the composite of PP without elastomer the elongation was not uniform; thus, the degree or ordering cannot be given as a function of the stretching degree.

The r_z/r_y parameters for the Mn^{2+} ion and for the defect centers are plotted against the stretching degree in Figures 8 and 9. If the samples are compression molded without stretching, the degree of orientation varies in the order of PVC > PE > PP $\approx$ PS. It can be seen—most clearly for the PE composites—that the orientation due to compression molding is partially deteriorated by the subsequent stretching, and a new type of orientation is built up perpendicular to the stretching direction, which yields to the increase of r_y/r_x.

By a few randomly selected examples we have demonstrated that EPR spectroscopy is a useful technique for studying the orientation of fillers for a wide variety of composites. The ordering of polymer composites in the course of mechanical deformations is, however, a rather complex process. It depends on the morphology of the filler and the polymer, the structure of the polymer chain, the temperature and other conditions of the processing and the presence of different additives such as elastomers, plasticizers, etc. Only a systematic study of these factors can elucidate the mechanism of ordering, which can make a valuable contribution to our understanding of the role which the different additives play in the mechanical properties of polymer composites.

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Hemitactic Polymers

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ABSTRACT: Hemitactic polymers constitute a new class of macromolecular stereoisomers in which only one tertiary carbon atom in every two has a definite configuration. The selection rules governing the distribution of stereosequences in such polymers, in particular in hemiisotactic polymers, are discussed together with a probabilistic approach which makes it possible to determine their relative frequencies. The structural features distinguishing hemitactic polymers from conventional atactic polymers and their possible uses are discussed.

After the structure of isotactic and syndiotactic polymers had been brought to light in the mid-1950s, no new form of stereoisomerism in vinyl polymers was observed for a quarter of a century. Since that time, the study of macromolecular stereochemistry has moved ahead in three main directions: synthesis of polymers having complex tacticity (ditactic, tritactic, etc.) from non-vinyl monomers; synthesis of chiral polymers; and a quantitative study, in both theoretical and experimental terms, of microtacticity and of its relationship with the mechanism of polymerization.

By an odd coincidence two contributions appeared in a single issue of this journal (September–October, 1982), both proving the existence of vinyl polymers with hitherto unobserved structures. These were the chiral copolymers having structure ...mrrmrrmrr... obtained by Wulff and Hohn[1] and the hemitactic polypropylene prepared by our own group.[2]

The aim of this paper is to illustrate the structural characteristics of hemitactic polymers and to outline the differences between these and conventional atactic polymers. A second article, published in this same issue,[3] illustrates an example of a hemitactic polymer—hemiisotactic polypropylene—and its usefulness in deepening our understanding of the ^{13}C NMR spectrum of polypropylene.

Hemitacticity and Hemiisotacticity

Following the definition given in the preceding article,[2] hemitactic polymers contain two distinct series of tertiary carbon atoms which alternate with each other: in the odd series the arrangement of the substituents is exactly defined, while in the even series their arrangement is random. In other words, only one tertiary carbon atom out of two is under the influence of an ordering rule. It was for this reason that we proposed the term *hemitactic* polymer to denote a sample of polypropylene having such a structure (hemi from the Greek: half).

A further step toward a structural characterization is to define the type of arrangement existing in the odd series. For example, the substituents bonded to carbons 1, 3, 5,

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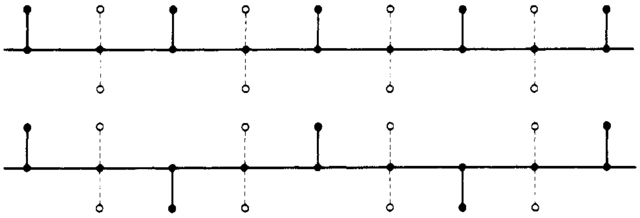

Figure 1. Schematic representation of hemiisotactic and hemisyndiotactic polymers.

Table I
Number of Stereosequences in Atactic, Hemiisotactic, and Hemisyndiotactic Polymers

sequence	atactic	hemiisotactic	hemisyndiotactic
dyads	2	2	2
triads	3	3	3
tetrads	6	4	4
pentads	10	7	6
hexads	20	8	8
heptads	36	14	13
octads	72	16	16
nonads	136	28	25
decads	272	32	32
undecads	528	54	51

etc., may be related to one another (the polymer chain being represented in a planar zigzag conformation or in a Fischer projection) by a simple translation axis or by a mirror glide plane. In the former case we may speak of a *hemiisotactic* polymer, in the latter of a *hemisyndiotactic* polymer (Figure 1).

In terms of microtacticity, the term hemiisotactic is applied to a polymer consisting of a statistical succession of mm and rr triads, or even to a polymer in which any closed odd sequence of homosteric dyads is prohibited (for instance: mrm, rmmmr, etc.). In its turn, a hemisyndiotactic polymer consists of statistical successions of nonoverlapping mr and rm triads. The selection rules in this case are the absence of homosteric tetrads (such as mmm and rrr) and the absence of consecutive, even though not adjacent, equal homosteric triads (as mmrmm or rrmrmrr).

The severity of the selection rules given here is brought to light by the drastic reduction in the number of permitted sequences which comes about as the length of the observed sequences increases. The number of sequences for hemiisotactic and hemisyndiotactic polymers, compared with that for a generic atactic polymer, is given in Table I.

The generation of permitted sequences in hemiisotactic polymers is outlined in Figures 2 and 3 for even and odd sequences. The former is particularly simple because duplication of the number of sequences takes place at each stage and for each type of sequence, while in the latter the number of new branches of the tree varies depending on the selection rules and on the symmetry of the sequences (sequences which differ from one another only in the sense of observation are considered only once). It may be pointed out that, with the sole exception of homosteric sequences, the ability of the odd sequences to split into three or four sequences of higher order is not homogeneous along a given branch, but appears once every two generations: for example, the triad mr gives rise to a single pentad (mmrr), which splits into four heptads; in turn, each of the heptads gives rise to a single nonad which splits into four undecads, and so on.

A Probabilistic Approach

This section aims to translate the earlier discussion into more general and quantitative terms. If we first consider a hemiisotactic polymer, taking α as the probability of finding an mm triad centered on a disordered carbon, the probability of finding an rr triad will be $1 - \alpha$, bearing in mind that the probabilities of mr and rm triads centered on the disordered carbon are nil. If we shift the point of observation to an ordered carbon, the probability of finding an mm triad will be α^2, since two independent events must have taken place, each having probability α. The probability of finding any given triad along the chain will be half the sum of the probabilities of finding the same triad centered on the ordered and disordered carbon atoms. The same sort of reasoning may be applied to odd sequences of any length (Table II).

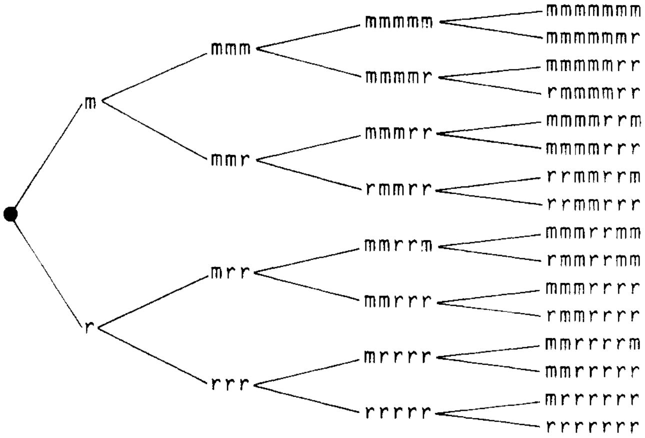

Figure 2. Generation of permitted even sequences in hemiisotactic polymers.

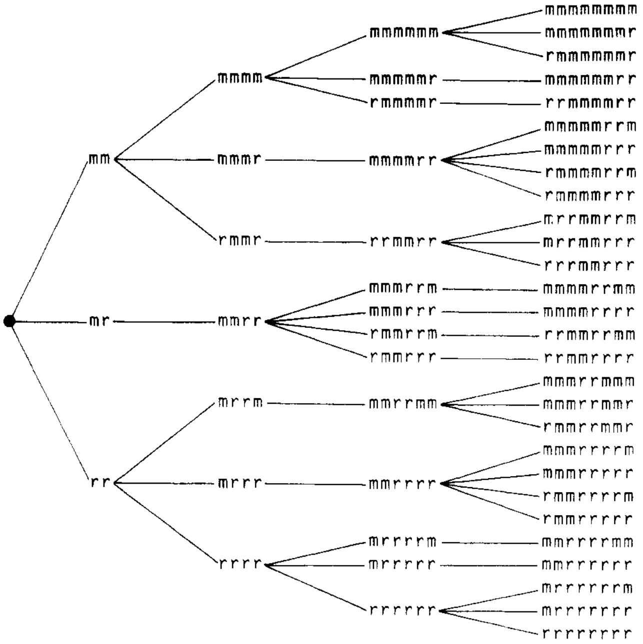

Figure 3. Generation of permitted odd sequences in hemiisotactic polymers.

The probability of existence of dyads, tetrads, and all even sequences is also half the sum of the probabilities relative to the sequences centered on the two different methylene groups, those respectively to the left and right of a given tertiary carbon (of the ordered or disordered series). The global probability follows a binomial expression in α and $1 - \alpha$ with a power equal to half the length of the sequence considered (1 for dyads, 2 for tetrads, etc.). Formulas for permitted sequences are found in Table II.

Triads, pentads, and higher odd sequences may be divided into three classes: some are centered solely on ordered carbons, others on disordered carbons, while only

Table II
Stereosequence Probabilities in Hemiisotactic Polymers

sequence	probability
	Dyads
m	α
r	$1 - \alpha$
	Triads
mm	$^{1}/_{2}(\alpha + \alpha^2)$
mr	$\alpha(1 - \alpha)$
rr	$^{1}/_{2}((1 - \alpha) + (1 - \alpha)^2)$
	Tetrads
mmm	α^2
mmr	$\alpha(1 - \alpha)$
mrr	$\alpha(1 - \alpha)$
rrr	$(1 - \alpha)^2$
	Pentads
mmmm	$^{1}/_{2}(\alpha^2 + \alpha^3)$
mmmr	$\alpha^2(1 - \alpha)$
rmmr	$^{1}/_{2}\alpha(1 - \alpha)^2$
mmrr	$\alpha(1 - \alpha)$
mrrm	$^{1}/_{2}\alpha^2(1 - \alpha)$
mrrr	$\alpha(1 - \alpha)^2$
rrrr	$^{1}/_{2}((1 - \alpha)^2 + (1 - \alpha)^3)$
	Hexads
mmmmm	α^3
mmmmr	$\alpha^2(1 - \alpha)$
mmmrr	$\alpha^2(1 - \alpha)$
rmmrr	$\alpha(1 - \alpha)^2$
mmrrm	$\alpha^2(1 - \alpha)$
mmrrr	$\alpha(1 - \alpha)^2$
mrrrr	$\alpha(1 - \alpha)^2$
rrrrr	$(1 - \alpha)^3$
	Heptads
mmmmmm	$^{1}/_{2}(\alpha^3 + \alpha^4)$
mmmmmr	$\alpha^3(1 - \alpha)$
rmmmmr	$^{1}/_{2}\alpha^2(1 - \alpha)^2$
mmmmrr	$\alpha^2(1 - \alpha)$
rrmmrr	$^{1}/_{2}\alpha(1 - \alpha)^2$
mmmrrm	$\alpha^3(1 - \alpha)$
mmmrrr	$\alpha^2(1 - \alpha)^2$
rmmrrm	$\alpha^2(1 - \alpha)^2$
rmmrrr	$\alpha(1 - \alpha)^3$
mmrrmm	$^{1}/_{2}\alpha^2(1 - \alpha)$
mmrrrr	$\alpha(1 - \alpha)^2$
mrrrrm	$^{1}/_{2}\alpha^2(1 - \alpha)^2$
mrrrrr	$\alpha(1 - \alpha)^3$
rrrrrr	$^{1}/_{2}((1 - \alpha)^3 + (1 - \alpha)^4)$
	Octads
mmmmmmm	α^4
mmmmmmr	$\alpha^3(1 - \alpha)$
mmmmmrr	$\alpha^3(1 - \alpha)$
rmmmmrr	$\alpha^2(1 - \alpha)^2$
mmmmrrm	$\alpha^3(1 - \alpha)$
mmmmrrr	$\alpha^2(1 - \alpha)^2$
rrmmrrm	$\alpha^2(1 - \alpha)^2$
rrmmrrr	$\alpha(1 - \alpha)^3$
mmmrrmm	$\alpha^3(1 - \alpha)$
rmmrrmm	$\alpha^2(1 - \alpha)^2$
mmmrrrr	$\alpha^2(1 - \alpha)^2$
rmmrrrr	$\alpha(1 - \alpha)^3$
mmrrrrm	$\alpha^2(1 - \alpha)^2$
mmrrrrr	$\alpha(1 - \alpha)^3$
mrrrrrr	$\alpha(1 - \alpha)^3$
rrrrrrr	$(1 - \alpha)^4$
	Nonads
mmmmmmmm	$^{1}/_{2}(\alpha^4 + \alpha^5)$
mmmmmmmr	$\alpha^4(1 - \alpha)$
rmmmmmmr	$^{1}/_{2}\alpha^3(1 - \alpha)^2$
mmmmmmrr	$\alpha^3(1 - \alpha)$
rrmmmmrr	$^{1}/_{2}\alpha^2(1 - \alpha)^2$
mmmmmrrm	$\alpha^4(1 - \alpha)$
mmmmmrrr	$\alpha^3(1 - \alpha)^2$
rmmmmrrm	$\alpha^3(1 - \alpha)^2$
rmmmmrrr	$\alpha^2(1 - \alpha)^3$
mrrmmrrm	$^{1}/_{2}\alpha^3(1 - \alpha)^2$
mrrmmrrr	$\alpha^2(1 - \alpha)^3$
rrrmmrrr	$^{1}/_{2}\alpha(1 - \alpha)^4$
mmmmrrmm	$\alpha^3(1 - \alpha)$
mmmmrrrr	$\alpha^2(1 - \alpha)^2$
rrmmrrmm	$\alpha^2(1 - \alpha)^2$
rrmmrrrr	$\alpha(1 - \alpha)^3$
mmmrrmmm	$^{1}/_{2}\alpha^4(1 - \alpha)$
mmmrrmmr	$\alpha^3(1 - \alpha)^2$
rmmrrmmr	$^{1}/_{2}\alpha^2(1 - \alpha)^3$
mmmrrrrm	$\alpha^3(1 - \alpha)^2$
mmmrrrrr	$\alpha^2(1 - \alpha)^3$
rmmrrrrm	$\alpha^2(1 - \alpha)^3$
rmmrrrrr	$\alpha(1 - \alpha)^4$
mmrrrrmm	$^{1}/_{2}\alpha^2(1 - \alpha)^2$
mmrrrrrr	$\alpha(1 - \alpha)^3$
mrrrrrrm	$^{1}/_{2}\alpha^2(1 - \alpha)^3$
mrrrrrrr	$\alpha(1 - \alpha)^4$
rrrrrrrr	$^{1}/_{2}((1 - \alpha)^4 + (1 - \alpha)^5)$

the homosteric sequences $(m)_{2n+1}$ and $(r)_{2n+1}$ have non-nil contributions from the two statistics. This finding might be employed, using suitable labels, to enhance or depress part of the NMR signals and facilitate assignment. Such a procedure cannot be applied to dyads and other even sequences since all derive to the same degree from the two partial statistics.

The ideal hemiisotactic polymer is defined as the one for which $\alpha = 0.5$. The relative frequencies of the sequences in this case are given in Table III. Nonideal hemiisotactic polymers may nonetheless be found for values of α between 0 and 1. Extreme cases and those close to the extremes are outside our consideration since at $\alpha = 1$ the polymer is completely isotactic and at $\alpha = 0$ it is completely syndiotactic and no longer hemitactic. Small variations of α around 0.5 lead to noteworthy variations in the probability of existence of the various sequences. This fact permits a highly accurate determination of the value of α.

The probabilistic approach may be extended to the case in which the stereoregularity of the ordered series of tertiary carbon atoms is not complete. Assuming a mechanism in which the stereochemistry of the two series of tertiary carbon atoms is fixed in two subsequent steps,[3] we take β to be the probability of finding two methyls of the ordered series in the isotactic position and suppose there to be no correlation between successive events of this type. Again α is the probability, conditional to β, that the methyl of the disordered series is at the center of an mm triad and α' the probability, conditional to $1 - \beta$, that the disordered methyl is at the center of an mr triad (Figure 4). The frequencies of mm, rr, mr, and rm triads centered on a carbon atom of the disordered series are respectively equal to $\alpha\beta$, $(1 - \alpha)\beta$, $\alpha'(1 - \beta)$, and $(1 - \alpha')(1 - \beta)$. The development of the statistical formulas for even sequences up to hexads and for odd sequences up to heptads is given in the Appendix; the results are reported in Table III.

The case of $\beta = 1$ has already been discussed above, with reference to the hemiisotactic polymer. For values of β close to 1, the polymer may still be considered to be prevalently hemiisotactic, though the probabilities of the various sequences differ from the ideal values. The con-

Table III
Stereosequence Distribution in Hemiisotactic, Atactic, and Hemisyndiotactic Polymers

		numerical examples[c,d]				
		hemiisotactic		atactic	hemisyndiotactic	
sequences	statistical expression[a,b]	$\beta = 1$	$\beta = 0.95$	$\beta = 0.5$	$\beta = 0.05$	$\beta = 0$
	Dyads					
1 m	$^1/_2(A + B)$	1	1	1	1	1
2 r	$^1/_2(C + D)$	1	1	1	1	1
	Triads					
1 mm	$^1/_2(M + AB)$	3	2.9	2	1.1	1
2 mr	$H + K + AD + CB$	2	2.2	4	5.8	6
3 rr	$^1/_2(R + CD)$	3	2.9	2	1.1	1
	Tetrads					
1 mmm	$^1/_2(AM + MB)$	1	0.95	0.5	0.05	0
2 mmr	$AH + CM + MD + KB$	1	1	1	1	1
3 rmr	$^1/_2(CH + KD)$	0	0.05	0.5	0.95	1
4 mrm	$^1/_2(AK + HB)$	0	0.05	0.5	0.95	1
5 mrr	$AR + CK + HD + RB$	1	1	1	1	1
6 rrr	$^1/_2(CR + RD)$	1	0.95	0.5	0.05	0
	Pentads					
1 mmmm	$^1/_2(AMB + MM)$	3	2.755	1	0.055	0
2 mmmr	$AMD + CMB + MH + KM$	2	2.090	2	0.290	0
3 rmmr	$^1/_2(CMD + KH)$	1	0.955	1	1.855	2
4 mmrm	$AHB + AKB + MK + HM$	0	0.290	2	2.090	2
5 mmrr	$AHD + CKB + MR + RM$	4	3.710	2	1.910	2
6 rmrm	$AKD + CHB + HH + KK$	0	0.110	2	5.510	6
7 rmrr	$CHD + CKD + KR + RH$	0	0.290	2	2.090	2
8 mrrm	$^1/_2(ARB + HK)$	1	0.955	1	1.855	2
9 mrrr	$ARD + CRB + HR + RK$	2	2.090	2	0.290	0
10 rrrr	$^1/_2(CRD + RR)$	3	2.755	1	0.055	0
	Hexads					
1 mmmmm	$^1/_2(AMM + MMB)$	1	0.903	0.25	0.003	0
2 mmmmr	$AMH + CMM + MMD + KMB$	1	0.950	0.50	0.050	0
3 rmmmr	$^1/_2(CMH + KMH)$	0	0.047	0.25	0.047	0
4 mmmrm	$AMK + AKM + MHB + HMB$	0	0.095	0.50	0.095	0
5 mmmrr	$AMR + CKM + MHD + RMB$	1	0.950	0.50	0.050	0
6 rmmrm	$CMK + AKH + KHB + HMD$	0	0.050	0.50	0.950	1
7 rmmrr	$CMR + CKH + KHD + RMD$	1	0.905	0.50	0.905	1
8 mrmrm	$^1/_2(AKK + HHB)$	0	0.003	0.25	0.903	1
9 mrmrr	$AKR + CKK + HHD + RHB$	0	0.050	0.50	0.950	1
10 rrmrr	$^1/_2(CKR + RHD)$	0	0.047	0.25	0.047	0
11 mmrmm	$^1/_2(AHM + MKB)$	0	0.047	0.25	0.047	0
12 mmrmr	$AHH + CHM + MKD + KKB$	0	0.050	0.50	0.950	1
13 rmrmr	$^1/_2(CHH + KKD)$	0	0.003	0.25	0.903	1
14 mmrrm	$AHK + ARM + MRB + HKB$	1	0.905	0.50	0.905	1
15 mmrrr	$AHR + CRM + MRD + RKB$	1	0.950	0.50	0.050	0
16 rmrrm	$CHK + ARH + KRB + HKD$	0	0.050	0.50	0.950	1
17 rmrrr	$CHR + CRH + KRD + RKD$	0	0.095	0.50	0.095	0
18 mrrrm	$^1/_2(ARK + HRB)$	0	0.047	0.25	0.047	0
19 mrrrr	$ARR + CRK + HRD + RRB$	1	0.950	0.50	0.050	0
20 rrrrr	$^1/_2(CRR + RRD)$	1	0.903	0.25	0.003	0
	Heptads					
1 mmmmmm	$^1/_2(MMM + AMMB)$	3	2.617	0.5	0.003	0
2 mmmmmr	$MMH + KMM + AMMD + CMMB$	2	1.985	1	0.015	0
3 rmmmmr	$^1/_2(KMH + CMMD)$	1	0.907	0.5	0.093	0
4 mmmmrm	$MMK + HMM + AMHB + AKMB$	0	0.276	1	0.104	0
5 mmmmrr	$MMR + RMM + AMHD + CKMB$	4	3.524	1	0.096	0
6 rmmmrm	$KMK + HMH + CMHB + AKMD$	0	0.104	1	0.276	0
7 rmmmrr	$KMR + RMH + CMHD + CKMD$	0	0.276	1	0.104	0
8 mrmmrm	$^1/_2(HMK + AKHB)$	0	0.007	0.5	0.993	1
9 mrmmrr	$HMR + RMK + AKHD + CKHB$	0	0.185	1	1.815	2
10 rrmmrr	$^1/_2(RMR + CKHD)$	2	1.717	0.5	0.903	1
11 mmmrmm	$MHM + MKM + AMKB + AHMB$	0	0.276	1	0.104	0
12 mmmrmr	$MHH + KKM + AMKD + CHMB$	0	0.104	1	0.276	0
13 rmmrmm	$KHM + MKH + CMKB + AHMD$	0	0.104	1	0.276	0
14 rmmrmr	$KHH + KKH + CMKD + CHMD$	0	0.096	1	3.524	4
15 mmmrrm	$MHK + HKM + AMRB + ARMB$	2	1.814	1	0.186	0
16 mmmrrr	$MHR + RKM + AMRD + CRMB$	2	1.985	1	0.015	0
17 rmmrrm	$KHK + HKH + CMRB + ARMD$	2	1.806	1	3.524	4
18 rmmrrr	$KHR + RKH + CMRD + CRMD$	2	1.814	1	0.186	0
19 mrmrmm	$HHM + MKK + AKKB + AHHB$	0	0.015	1	1.985	2
20 mrmrmr	$HHH + KKK + AKKD + CHHB$	0	0.006	1	5.234	6
21 rrmrmm	$RHM + MKR + CKKB + AHHD$	0	0.186	1	1.814	2
22 rrmrmr	$RHH + KKR + CKKD + CHHD$	0	0.015	1	1.985	2

Table III (Continued)

		numerical examples[c,d]				
		hemiisotactic		atactic	hemisyndiotactic	
sequences	statistical expression[a,b]	$\beta = 1$	$\beta = 0.95$	$\beta = 0.5$	$\beta = 0.05$	$\beta = 0$
23 mrmrrm	*HHK + HKK + AKRB + ARHB*	0	0.096	1	3.524	4
24 mrmrrr	*HHR + RKK + AKRD + CRHB*	0	0.104	1	0.276	0
25 rrmrrm	*RHK + HKR + CKRB + ARHD*	0	0.104	1	0.276	0
26 rrmrrr	*RHR + RKR + CKRD + CRHD*	0	0.276	1	0.104	0
27 mmrrmm	$^1/_2$(*MRM + AHKB*)	2	1.717	0.5	0.903	1
28 mmrrmr	*MRH + KRM + AHKD + CHKB*	0	0.186	1	1.814	2
29 rmrrmr	$^1/_2$(*KRH + CHKD*)	0	0.007	0.5	0.993	1
30 mmrrrm	*MRK + HRM + AHRB + ARKB*	0	0.276	1	0.104	0
31 mmrrrr	*MRR + RRM + AHRD + CRKB*	4	3.524	1	0.096	0
32 rmrrrm	*KRK + HRH + CHRB + ARKD*	0	0.104	1	0.276	0
33 rmrrrr	*KRR + RRH + CHRD + CRKD*	0	0.276	1	0.104	0
34 mrrrrm	$^1/_2$(*HRK + ARRB*)	1	0.907	0.5	0.093	0
35 mrrrrr	*HRR + RRK + ARRD + CRRB*	2	1.985	1	0.015	0
36 rrrrrr	$^1/_2$(*RRR + CRRD*)	3	2.617	0.5	0.003	0

[a] For explanation of symbols, see the Appendix. [b] The expressions for triads, pentads, and heptads are divided into two parts: the former refers to sequences centered on ordered, the latter on disordered carbons. [c] Values calculated taking $\alpha = \alpha' = 0.5$. [d] In order to obtain whole numbers for hemiisotactic and hemisyndiotactic polymers, the probability values were multiplied by the following factors: dyads = 2; tetrads = 4; hexads = 8; triads = 8; pentads = 16; heptads = 32.

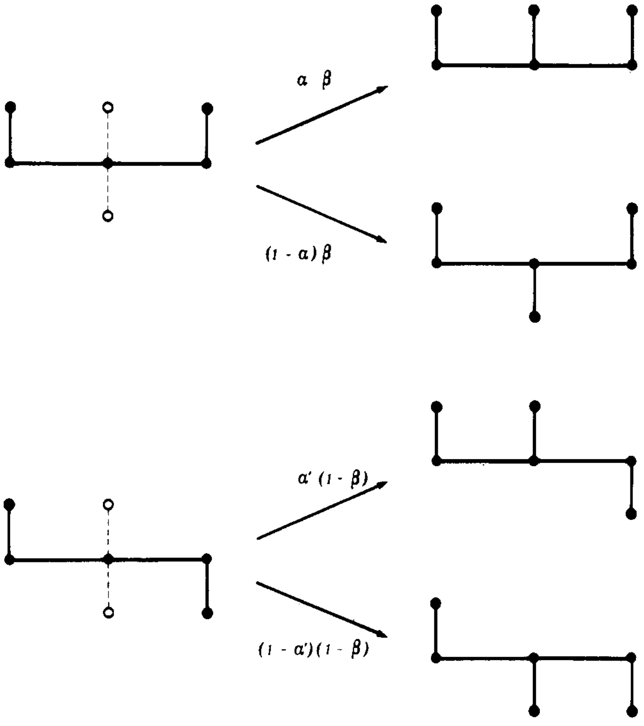

Figure 4. Probabilities of triads centered on disordered carbons.

centration of some sequences, prohibited for $\beta = 1$, increases rapidly by decreasing β (see in particular heptads 4, 7, 11, 26, 30, and 33 of Table III). At the same time, a remarkable variation of the ratio between allowed sequences is observed: as a matter of fact, the ratio mrrrrr/rrrrrr increases by more than 13% for a variation of β from 1 to 0.95 (see Table III). From the experimental values of sequence concentration we can thus determine the value of β.

With $\beta = 0$ and $\alpha' = 0.5$ we have an ideal hemisyndiotactic polymer in which the ratio between the mm:mr:rr triads is 1:6:1. It is interesting to observe that taking either $\alpha' = 0$ or $\alpha' = 1$, the polymer would no longer be hemitactic but would have a rigorously heterotactic (...mrmrmr...) structure.

When $0 < \beta < 1$, $0 < \alpha < 1$, and $0 < \alpha' < 1$, the polymer will be sterically disordered but with a different degree of disorder for the even and odd tertiary carbons. The ideal atactic polymer would have $\beta = \alpha = \alpha' = 0.5$.

The numerical values of sequence probabilities in some cases of singular interest are listed in Table III.

Discussion

From the above, and in particular from the findings presented in Table III, there emerge certain structural features which are typical of hemiisotactic polymers. More precisely a hemiisotactic polymer may be considered as a polymer having a Bernoulli distribution of mm and rr triads. The average length of the homosteric sequences, expressed in terms of m and r dyads, is twice that predicted for a true atactic polymer (i.e., its structure is shifted toward that of a stereoblock polymer).

At the hexad and heptad level (and this is even truer if we extend our examination to longer sequences) the atactic polymer shows a highly dispersed microstructure: all sequences have very small and almost uniform statistical weights, while only a few sequences are permitted in the hemiisotactic polymer, and these have a relatively high frequency. This directly influences certain properties, first and foremost the general aspect of the ^{13}C NMR spectrum, where relatively few but sharp and intense peaks are to be found. This is highly useful in the interpretation of the spectra of conventional disordered polymers.

If we take into consideration the distribution of the substituents (or the relative configuration of the tertiary carbon atoms along the chain) instead of that of the steric dyads, each hemiisotactic macromolecule is highly unbalanced in favor of one of the possible situations—for $\alpha = 0.5$ the unbalance amounts to three to one. No forecast can however be made as to the possibility of crystallization of hemiisotactic polymers. This possibility depends on the nature of the substituents and on the ability of the crystal structure to tolerate a considerable number of defects. The situation might be improved by increasing the value of α: at $\alpha = 0.8$ the length of the ...mm... blocks rises considerably and the number of configurational defects (expressed as the fraction of substituents in the wrong place compared with a perfectly isotactic polymer) drops to 10%. Similarly a value of $\alpha < 0.5$ would move the structure toward that of a syndiotactic polymer.

Hemisyndiotactic polymers can be considered along similar lines: for brevity's sake and because of the lack of practical examples for consideration, we will treat them very briefly. One point must be underlined here in order to show their potential usefulness in the field of structural analysis. If we apply the selection rules or use the computation scheme given in the Appendix and in Table III, it may be seen that the structural information contained in such polymers is almost precisely complementary to that contained in hemiisotactic polymers. Only three heptads are in fact common to the two polymers: rrmmrr, rmmrrm, and mmrrmm. The remaining 10 are mainly grouped amid the sequences centered on the mr triad, where the information content of the hemiisotactic polymer is very limited. The combined use of the two hemitactic polymers would make it possible to achieve the assignment of 24 out of the 36 heptad signals and of 14 of the 20 hexads.

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Appendix

The probabilities of triads that center on a disordered carbon (see Figure 4) are

$$\mathrm{mm} = \alpha\beta = M$$

$$\mathrm{rr} = (1-\alpha)\beta = R$$

$$\mathrm{mr} = \alpha'(1-\beta) = H$$

$$\mathrm{rm} = (1-\alpha')(1-\beta) = K$$

The probability of each dyad placed in a defined position inside the above triads is the sum of the probability of existence of the related triads:

$$(\mathrm{m/r})\mathrm{m} = M + K = A$$

$$\mathrm{m}(\mathrm{m/r}) = M + H = B$$

$$(\mathrm{m/r})\mathrm{r} = R + H = C$$

$$\mathrm{r}(\mathrm{m/r}) = R + K = D$$

where (m/r) means that the second dyad has an undetermined structure.

The probabilities of triads that center on an ordered carbon is the product of the probabilities of the two related dyads. The probability of a general triad is half of the sum of the probabilities of both series of triads (centered on ordered or disordered carbons). For the non-symmetric triad mr, both directions of observation of the chain are to be considered.

The probability of a longer sequence is half of the sum of products of the probabilities of the single blocks, taking into account all the possible ways of formation of that sequence.

This treatment resembles in many respects those proposed by Frisch, Mallows, and Bovey[4] and by Chujo, Kamei, and Nishioka[5] for polymers derived from CHA = CHB monomers, but differs in the choice of the independent probability parameters, which are related to a different way of sequence generation.

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Resolution of the Carbon-13 Nuclear Magnetic Resonance Spectrum of Hemiisotactic Polypropylene at the Decad and Undecad Level

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ABSTRACT: Hemiisotactic polypropylene was obtained by a two-stage process from *trans*-2-methylpentadiene and its structure determined from its 50.3-MHz ^{13}C NMR spectrum. The particular distribution of the steric sequences and the choice of suitable experimental conditions made it possible to obtain a spectrum with an unprecedented degree of resolution. Out of 17 well-resolved peaks on the methyl spectrum, 5 are attributed to single nonads and 5 to the following undecads: mmmmmmmmrr, rrmmmmmmrr, rrmmrrmmrr, mmmmrrmmrr, and mmmmrrmmmm. Two signals in the methylene spectrum should be assigned to single decads. The degree of hemiisotacticity of polypropylene (α = 0.5, β = 0.96) and the degree of isotacticity of the starting poly(2-methylpentadiene), obtained by inclusion polymerization in perhydrotriphenylene (96% isotactic dyads), were determined by intensity measurements.

In 1982 we announced the synthesis of a new stereoisomer of polypropylene, for which we proposed the name of hemitactic polypropylene.[1] The distinguishing feature of this polymer is the presence of two different series of tertiary carbon atoms which are constitutionally equivalent and alternate with each other: in the odd series the arrangement of the substituents is precisely defined, while in the even series the arrangement is random. A detailed study of the structure of hemitactic polymers is provided in the article immediately preceding this one,[2] hereafter referred to as part 2, part 1 being ref 1.

In the light of the discussion reported in part 2 we now propose the adoption of a more precise name for the new polymer, so as to specify that an isotactic succession exists between the tertiary carbons of the odd (ordered) series. Henceforth, the term *hemiisotactic* will be used for this polymer instead of the more general term hemitactic. Hemiisotactic polypropylene (hit-PP) differs from the other partially ordered polypropylenes as yet known. These have a low degree of stereoregularity, while in the hemiisotactic polypropylene we find the ordered superimposition of an almost perfect stereoregularity on a com-

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