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Micro- and Macroconformation of Macromolecules

6. Configurational and Conformational Influences on the ^{13}C-NMR Spectra of Inverted Polypropylenes

M. Möller, W. Ritter* and H.-J. Cantow

Institut für Makromolekulare Chemie der Universität Freiburg, Stefan-Meier-Straße 31,
7800 Freiburg i.Br., Federal Republic of Germany

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SUMMARY

From the temperature dependence of ^{13}C-NMR chemical shift measurements under fast exchange conditions, using the methyl carbon atom as indicator, it was concluded that for erythrodiisotactic head-to-head tail-to-tail polypropylenes the temperature dependence of the conformers around the methine-methine bond may be analyzed quantitatively. In the present paper the ^{13}C-NMR analysis has been expanded to inverted polypropylenes of arbitrary ditacticity. Methyl, methylene as well as methine resonances have been taken into account for assignements. Conformational influences on the ^{13}C-NMR spectrum are discussed as well as the relevance of low molecular weight models for diads.

INTRODUCTION

The structure normally built up by addition polymerization is head-to-tail. Depending on the type of the asymmetric monomer, however, head-to-head diads and, consequently, tail-to-tail diads are placed in the macromolecules in a non-neglegible proportion. Polyvinylfluoride and polypropylene, typically, exhibit relatively high concentration of inversions depending on the type of polyreaction. Such irregularities within the chain have significant influences on the applicational properties, although fundamental research on structure-properties relationships is still in the beginning. Inverted sequences are also present in copolymers of the ethylene-propylene type, especially when polymerized with catalysts which favour atactic arrangement.

Macromolecules containing inverted diads exclusively have to be synthesized non-conventionally. INOUE et al. (INOUE, HELBIG and VOGL, 1977) have obtained head-to-head polystyrene by selective reduction of 1,4-poly(2,3-diphenylbutadiene-1,3). ARICHI et al. (ARICHI, PEDRAM and COWIE, 1979) have synthesized head-to-head polypropylenes by hydrogenation of 1,4-poly(hexadiene-2,4)and of 1,4-poly(2,3-dimethylbutadiene-1,3), respectively. They investigated dynamic mechanical damping spectra as well as dilute solution properties. DOI (DOI et al., 1977, DOI, 1979) first started ^{13}C-NMR analysis of inversions within polypropylene macromolecules.

Generally inverted asymmetrically substituted polyolefines show a different type of the NMR spectra when compared with head-to-tail macromolecules, because of their different symmetry. Shift influences may be analyzed with respect to direction and to distance. From ^{13}C chemical shift under fast exchange conditions it was concluded that meso-4,5-dimethyloctane is the low molecular weight model representative for erythrodiisotactic inverted polypropylene. Both exhibit identical temperature dependence of the chemical shift of the methyl carbon and, consequently, of the populations of the conformers of the head-to-head diad and identical energy differences between

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* Permanent address: Henkel KGaA, 4000 Düsseldorf, Federal Republic of Germany

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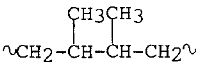
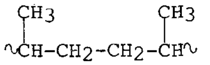
the competing anti and gauche conformers (RITTER, MÖLLER and CANTOW, 1980, MÖLLER, RITTER and CANTOW, 1980, MÖLLER and CANTOW, 1980). This fact seems to be remarkable because the macromolecule has to move in a cooperative manner at a segmental level, whereas the low molecular weight models may move freely in an isotropic manner. As a further consequence of the experimental findings it has been found that all erythro-type inverted polypropylenes may be represented by the low molecular weight head-to-head models, the configuration of the erythro groups relative to each other being of no influence on the methyl carbon chemical shift. Consequences of the microconformation around the head-to-head bond on the unperturbed macroconformation of the macromolecules have been discussed in this context.

In this paper the investigations are expanded towards head-to-head- tail-to-tail polypropylenes, which include virtually all ditactic sequences being realizable. Besides the methyl carbon methine and methylene carbons are used as indicators for configurational as well as of conformational arrangements. One of the crucial questions was how informations concerning the influence of the relative position of erythro and threo groups relative to each other on the segmental conformation may be detectable from ^{13}C-NMR fast exchange data at room temperature.

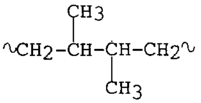
Some remarks may be made concerning the denomination of the sequences which build up the macromolecules. A diad within the inverted polypropylene chain is consisting on two monomeric units. It may exist in four isomeric forms:


$\sim CH_2-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_2\sim$

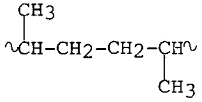
m_o


$\sim\overset{CH_3}{CH}-CH_2-CH_2-\overset{CH_3}{CH}\sim$

m_2

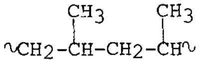

$\sim CH_2-\overset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2\sim$

r_o

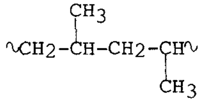

$\sim\overset{CH_3}{CH}-CH_2-CH_2-\underset{CH_3}{CH}\sim$

r_2

Thus the different diads are denominated simply by their relative configuration, m or r, the index, $_o$ or $_2$, indicating the number of C's situated between the asymmetric carbons. When including head-to-tail polypropylene sequences two additional diads occur:


$\sim CH_2-\overset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}\sim$

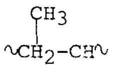
m_1

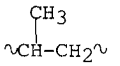

$\sim CH_2-\overset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}\sim$

r_1

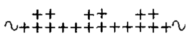
Additional diads, arising from ethylene sequences, appear in ethylene-propylene copolymers. Wether the sequences obey Bernoulli-type statistics or not will be determined by the type of polymerization mechanism. Highly ordered sequences build up tactic polymers, which are crystallizable dominantly.

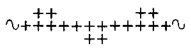
The inverted type polypropylene macromolecules, consequently, are alternating copolymers consisting of two types of subunits differing in direction:

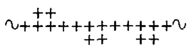

$\sim CH_2-\overset{CH_3}{CH}\sim$

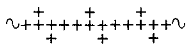

$\sim\overset{CH_3}{CH}-CH_2\sim$

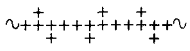
We may apply now the nomenclature proposed by NATTA (NATTA, 1962) for alternating copolymers. Taking into consideration now five diads six stereoregular forms of inverted polypropylenes may exist, besides the atactic one. They are given in the following, applying simplified signs:

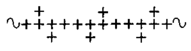

erythrodiisotactic
$m_om2m_om2m_o$


erythrodisyndiotactic
$m_or2m_or2m_o$


erythrodiatactic
$m_or2m_om2m_o$


threodiisotactic
$r_or2r_or2r_o$

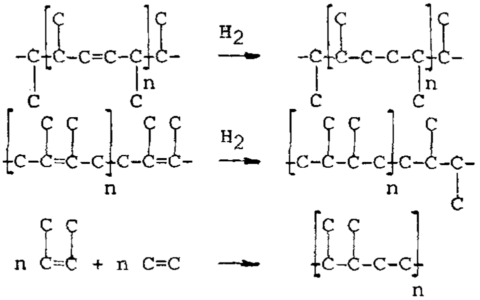

threodisyndiotactic
$r_om2r_om2r_o$


threodiatactic
$r_om2r_or2r_o$

SYNTHESES

The isomeric head-to-head- tail-to-tail polypropylenes - 1,2-dimethyltetramethylens - can be synthesized on three different routes:

1. via hydrogenation of 2,5-poly(hexadiene-2,4)
2. via hydrogenation of 1,4-poly(2,3-dimethylbutadiene-1,3)
3. via copolymerization ethylene-cis-butene-1



3 yields erythrodiisotactic macromolecules. Polymerizing hexadiene-2,4 or 2,3-dimethylbutadiene-1,3, respectively, the type of stereoregularity of the polymers built up depends on the type of polyreaction, anionic, cationic, radical or coordination type. The consequences of hydrogenation, finally, are different for both types of polydienes, 2,5-poly(hexadiene-2,4) and 1,4-poly(2,3-dimethylbutadiene-1,3), because of the situation of the double bond: in the first case the relative configuration of the tertiary carbon atoms is not influenced, in the second the assymmetric carbon atoms are formed by hydrogenation. Syn-hydrogenation of the cis double bond yields the meso h-h-diad, whereas the racemic h-h-diad results from the trans double bond.

Thus, five types of poly(1,2-dimethyltetramethylene)s with different ditacticity could be synthesized: erythrodiisotactic, erythrodiatactic, threodiisotactic, threodiatactic and entirely atactic. Erythro- and threodisyndiotactic inverted polypropylenes have not been realized.

The detailed synthesis routes, as described in the literature, will be reported and cited in a more extended paper being under preparation.

The simplest low molecular weight molecule, which exhibits analogous structure like the h-h-diad within h-h-t-t-polypropylenes, the 3,4-dimethylhexane, has been synthesized in its pure meso form. Starting with cis-1,2,3,6-tetrahydrophthalic acic anhydride reduction of the acid functions yields cis-1,2-dimethylcyclohexene-4. By oxidative ring scission meso-3,4-dimethyl adipinic acid is formed, which has been reduced to meso-3,4-dimethylhexane, finally. The diastereomer mixture as well as the d-form of 3,6-dimethyloctane serve as simplest low molecular weight models for the tt-diad within the macromolecules. The latter has been synthesized by transforming optically active S(-)-2-methylbutanol to (S)2-methylbutylbromide, which yields (S,S)2,6-dimethyloctane via WURTZ-FITTIG synthesis.

NUCLEAR MAGNETIC RESONANCE INVESTIGATIONS AND DISCUSSION

Figure 1 presents the ^{13}C-NMR spectrum of an atactic poly(1,2-dimethyltetramethylene). It shows up fine structure within all resonance regions. It is evident that each of the signal groups clearly is split up into two subgroups. In Figure 1 corresponding spectra are given too for the diastereomer mixture meso-dl- 3,4-dimethylhexane and pure meso-3,4-dimethylhexane. Comparing with the spectrum of the polymer it turns out that the shift differences caused by the configuration are quite identical for both macromolecule and low molecular weight compound meso-dl mixture. Consequently, the splitting of the polymer signals in two subgroups for each carbon is caused by the

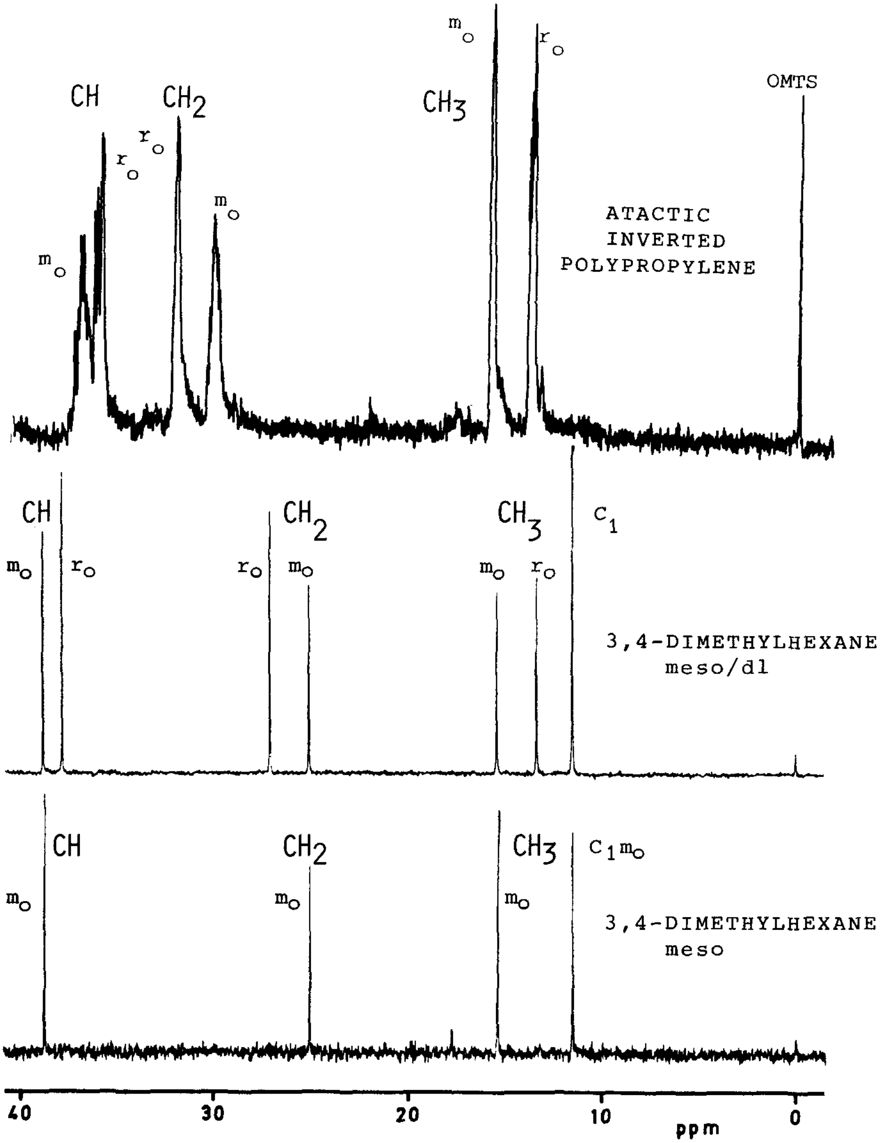


Figure 1: ^{13}C-NMR spectra in $CDCl_3$, 303 K, ^{1}H broad band decoupled, 22.625 MHz

Table I: ^{13}C-NMR chemical shifts, δ, and shift differences, Δδ, of 3,4-dimethylhexanes and of erythro- and threo-diisotactic inverted polypropylenes

C-atom	3,4-dimethylhexane			erythrodiis.	threodiis.	h-h-PP
	meso (m_o) δ	dl (r_o) δ	Δδ	$m_2\dot{m}_o m_2 m_o$ δ	$\dot{r}_o r_2 r_o$ δ	Δδ
CH	38.64	37.67	0.96	$37,21_7$	36.43_9	0.78
CH_2	24.95	26.90	-1.95	30.36_3	32.32_4	-1.96
CH_3+	15.36	13.72	2.03	15.99_2	13.83_0	2.16

+methyl in 3-position ˙carbon position under resonance relative configurations of the head-to-head diad within which the observed ^{13}C nucleus is situated. Meso-3,4-dimethylhexane gives the assignments. Table I presents the chemical shifts for the low molecular weight isomers as well as for erythrodiisotactic and for threodiisotactic h-h-t-t polypropylene. Table II shows the chemical shifts of erythro- and of threodiatactic poly(1,2-dimethyltetramethylene).For the threodiatactic macromolecules one observes onefold splitting of the signals, whereas for the erythrodiatactic ones twofold spliiting is observed. This means: The chemical shift is influenced by the relative configurations of one of the tt-diads which is adjacent to the C-atom under resonance in the threodiatactic case, whereas the erythrodiatactic macromolecule distinguishes the relative configurations of both the tt-diads adjacent to the nucleus observed. Although the differences in the molecular structure are analogous completely this effect is evident, and it has to be connected with the conformational situation of the respective groups.

Table II: ^{13}C-NMR chemical shifts, δ, and shift differences,$\Delta\delta$, of erythrodiatactic and of threodiatactic poly(1,2-dimethyltetramethylene) in $CDCl_3$

C-atom	erythrodiatactic polymer sequence	δ	$\Delta\delta$	threodiatactic polymer sequence	δ	$\Delta\delta$
CH	$m_2\dot{m}_om_2m_o$	37.65_4 37.36_3 37.21_4 36.81_2	0.33 0.11 0.40	$\dot{r}_or_2r_o$ $\dot{r}_om_2r_o$	36.43_8 36.22_8	0.21
CH_2	$m_2m_{\dot{o}}m_2m_o$	30.63_9 $30,36_2$ 29.99_0	0.28 o.37	$r_{\dot{o}}r_2r_o$ $r_{\dot{o}}m_2r_o$	32.32_4	
CH_3	$m_2\dot{m}_om_2m_o$	15.99_2 15.87_8 15.78_2	0.11 0.10	$\dot{r}_or_2r_o$ $\dot{r}_om_2r_o$	13.83_1 13.74_0	0.09

Figure 2 presents the ^{13}C-NMR spectra of the methine, the methylene and of the methyl carbons of poly(1,2-dimethyltetramethylene)s,with different configurational sequence structure. At the top one finds the completely erytrodiisotactic sample, at the bottom the threodiisotactic one. Downwards and upwards, respectively, the NMR traces are given for polymers with decreasing stereoregularity. In the middle of the figure the spectrum of the completely atactic inverted polypropylene is presented. Assignments are marked when they could verified with the aid of comparison of spectra.

An additional attempt has been made to assign the remaining sequences within threo- and erythrodiatactic h-h-t-t inverted polypropylenes with the aid of a low molecular weight model compound. 3,6-dimethyloctane exhibits a structure analogous to the tt-triad within inverted polypropylene. Figure 3 gives the spectrum of a 3,6-dimethyloctane sample, where the mixture of dl-isomers has been enriched by the pure SS-isomer. The signals of the dl-molecules have been signed with r_2, those of the meso-molecules with m_2. Table III presents the measured chemical shifts.

Comparing the configurative splittings with those determined for the polymers (Tables II-III) one finds that wether the absolute values nor the relative situation agrees. Apparently 3,6-dimethyloctane is not a model representative for the respective macromolecules. It does not describe the fine structure of the h-h-t-t polypropylene spectra. Figure 4 compares the NMR patterns.

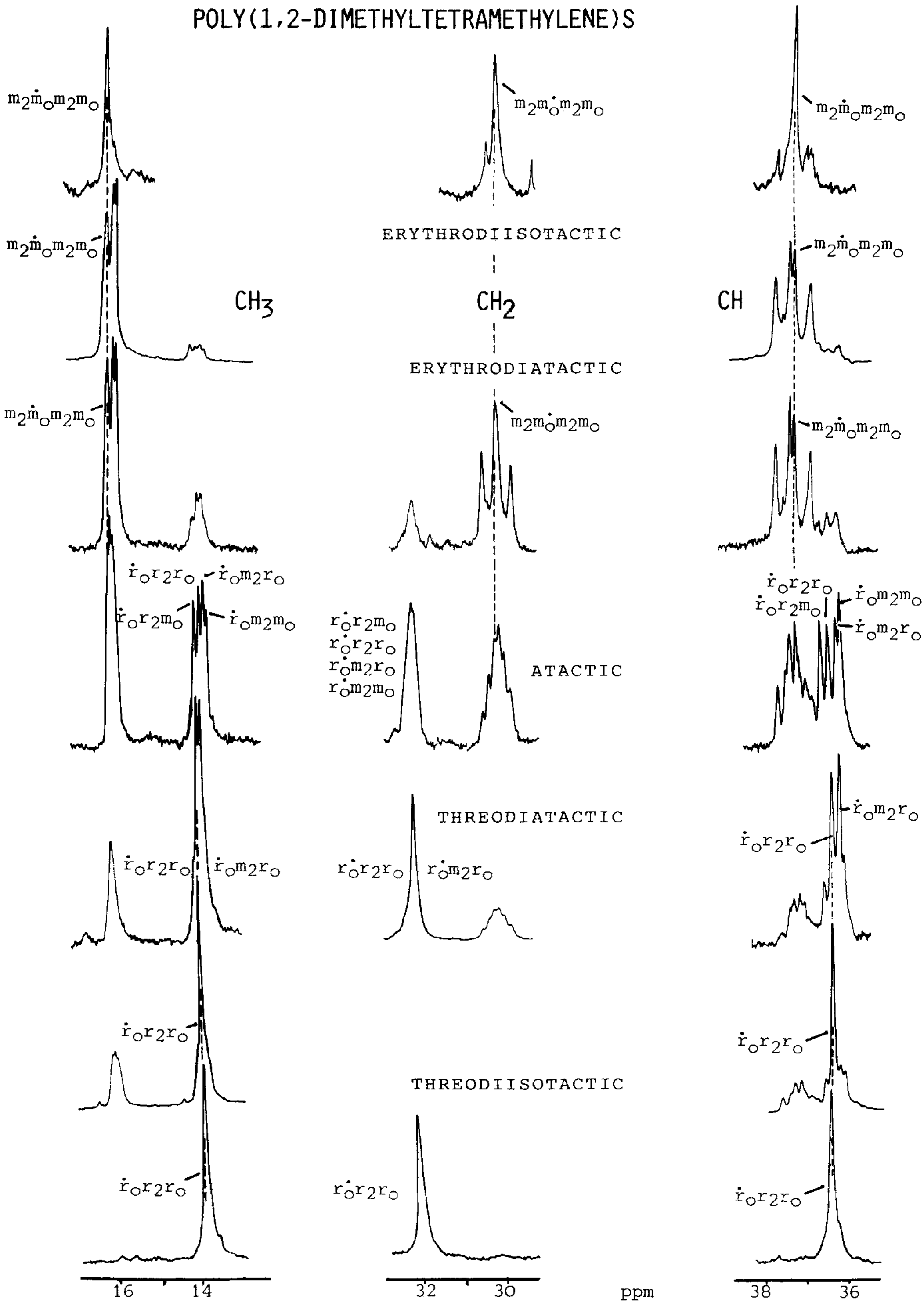

POLY(1,2-DIMETHYLTETRAMETHYLENE)S
$m_2\dot{m}_o m_2 m_o$
$m_2 m_{\dot{o}} m_2 m_o$
$m_2\dot{m}_o m_2 m_o$
ERYTHRODIISOTACTIC
$m_2\dot{m}_o m_2 m_o$
$m_2\dot{m}_o m_2 m_o$
CH$_3$
CH$_2$
CH
ERYTHRODIATACTIC
$m_2\dot{m}_o m_2 m_o$
$m_2 m_{\dot{o}} m_2 m_o$
$m_2\dot{m}_o m_2 m_o$
$\dot{r}_o r_2 r_o$
$\dot{r}_o m_2 r_o$
$\dot{r}_o r_2 m_o$
$\dot{r}_o m_2 m_o$
$r_{\dot{o}} r_2 m_o$
$r_{\dot{o}} r_2 r_o$
$r_{\dot{o}} m_2 r_o$
$r_{\dot{o}} m_2 m_o$
ATACTIC
$\dot{r}_o r_2 r_o$
$\dot{r}_o r_2 m_o$
$\dot{r}_o m_2 m_o$
$\dot{r}_o m_2 r_o$
THREODIATACTIC
$\dot{r}_o m_2 r_o$
$\dot{r}_o r_2 r_o$
$\dot{r}_o r_2 r_o$
$\dot{r}_o m_2 r_o$
$r_{\dot{o}} r_2 r_o$
$r_{\dot{o}} m_2 r_o$
$\dot{r}_o r_2 r_o$
$\dot{r}_o r_2 r_o$
THREODIISOTACTIC
$\dot{r}_o r_2 r_o$
$r_{\dot{o}} r_2 r_o$
$\dot{r}_o r_2 r_o$
16
14
32
30
ppm
38
36

Figure 2: ^{13}C-NMR spectra of poly(1,2-dimethyltetramethylene)s of different ditacticity, $CDCl_3$, 303 K, OMTS

Table IV gives the chemical shift data extracted from Figure 2. The resonance positions have been assigned as far as possible in the present state. One tendency is evident: When the nucleus under resonance is situated within a m_o diad up to eight signals are distinguishable for each C atom.

Table III: ^{13}C-NMR shifts, δ, and shift differences, $\Delta\delta$, of 3,6-dimethyloctane $CDCl_3$, 303 K, with OMTS as standard

C-atom	meso(m_2) δ	dl(r_2) δ	$\Delta\delta$
CH	34.26_7	34.21_9	0.04_8
CH_2^+	33.47_4	33.42_5	0.04_9
CH_3^{++}	18.68_2	18.55_2	0.13_0

$^+$methylene in 4- and $^{++}$methyl in 3-position

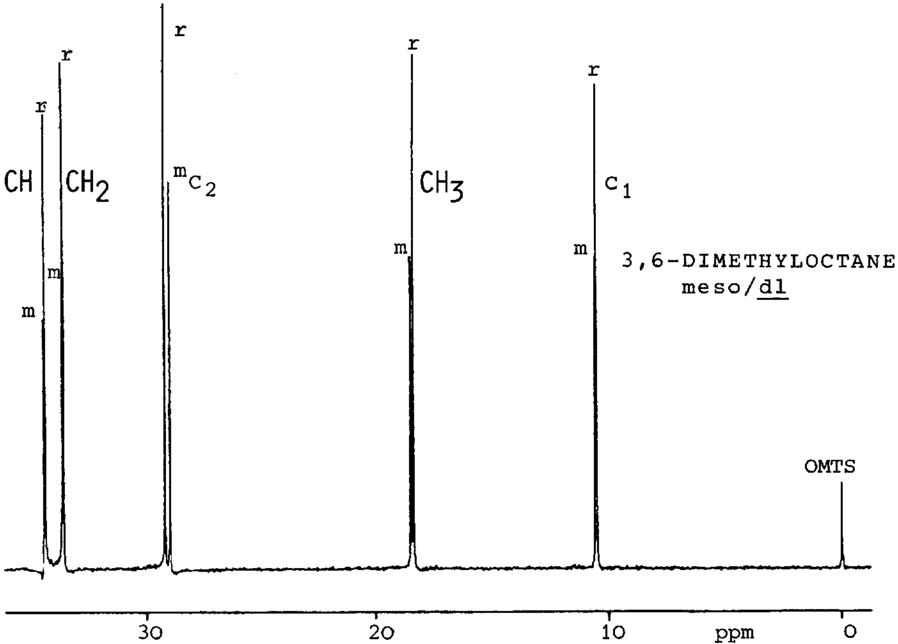


Figure 3: ^{13}C-NMR spectra of 3,6-dimethyloctane, p(dl)>p(m) in $CDCl_3$, 303 K

Table IV: ^{13}C-NMR chemical shifts, δ, of atactic inverted polypropylenes

CH	δ	CH_2	δ	CH_3	δ
$m_2\dot{m}_om_2m_o$	37.65_6	$r_{\dot{o}}r_2m_o$	32.32_4	$m_2\dot{m}_om_2m_o$	15.99_2
	37.44_5	$r_{\dot{o}}r_2r_o$			15.94_3
	37.36_5	$r_{\dot{o}}m_2r_o$			15.87_8
	37.21_5	$r_{\dot{o}}m_2m_o$			15.78_2
	37.13_6	$m_2m_{\dot{o}}m_2m_o$	30.64_0	$\dot{r}_or_2m_o$	13.95_0
	37.07_1		30.49_4	$\dot{r}_or_2r_o$	13.83_0
	36.95_7		30.36_4	$\dot{r}_om_2r_o$	13.74_0
	36.81_3		30.26_7	$\dot{r}_om_2m_o$	13.63_0
$\dot{r}_or_2m_o$	36.61_7		30.15_4		
$\dot{r}_or_2r_o$	36.44_0		29.99_1		
$\dot{r}_om_2r_o$	36.22_9				
$\dot{r}_om_2m_o$	36.14_7				

In the threodiatactic case, however, only two additional signals are observed, which are to be assigned to the change of one of the two h-h diads which are adjacent on both sides.

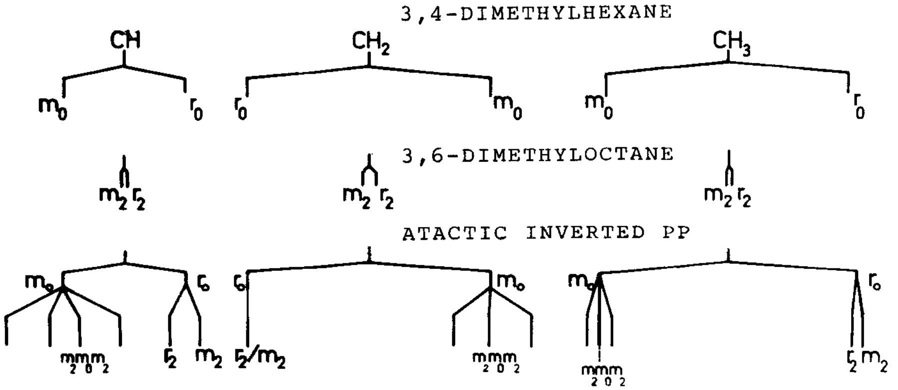


Figure 4: NMR splitting patterns of 3,4-dimethylhexane, 3,6-dimethyloctane and atactic inverted polypropylene in $CDCl_3$ at 303 K, 22.625 MHz, OMTS

As a low molecular weight model enabling the assignment of the complicated polymer spectra 3,4,7,8-tetramethyldecane with different amounts of the diastereomers has been synthesized. Synthesis of this compound as well as detailed informations on further syntheses being discussed in this paper will be presented in a publication being under preparation (MÖLLER and CANTOW).

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