(0.21)(5.6) = 3.4 ppm for the amorphous olefinic carbons in TPBD relative to those olefinic carbons in the crystalline regions.

(25) Solution NMR measurements indicate a level of 28% epoxidation for sample UH29, in good agreement with the amorphous content of 26.7% as determined from the solid-state spectrum. The solution spectrum for UH45 shows an epoxidation of 16.2% as compared to an amorphous content of 26.3% from the solid-state results.[10] At present we cannot offer an explanation for the latter discrepancy.

(26) Komoroski, R. A., private communication; to be published in *J. Polym. Sci., Polym. Phys. Ed.*

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^{13}C-NMR Studies on Ditactic Poly(α-olefins). 1. Poly(1,2-dimethyltetramethylenes) and Their Tetrad Models†

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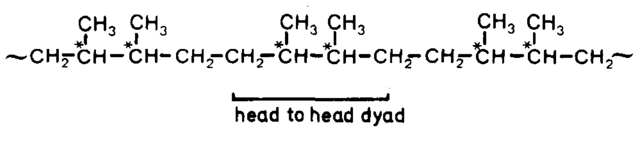
ABSTRACT: Poly(1,2-dimethyltetramethylenes) (head-to-head polypropylenes) were prepared with different tacticities. In addition, low molecular weight compounds representing dyad and tetrad segments of the polymers were synthesized in separate stereoisomeric forms. The 90-MHz ^{13}C-NMR spectra are compared and discussed with respect to their information concerning the stereochemistry. A complete assignment of the signals of atactic poly(1,2-dimethyltetramethylene) is given. The results are analyzed in terms of general aspects of chemical shift effects in aliphatic chain molecules.

The stereochemistry of polymers and the mechanisms of their growth reactions have been studied extensively because of the influence of structural variations on polymeric properties. The addition of a monomer to a growing chain often leads to a variety of stereoisomeric segments in the polymer. Conjugated dienes can react by 1,4 or 1,2 addition, the 1,4 unit may be either cis or trans, and the placement of the residue in the monomeric unit can lead to different relative configurations. In addition to these structural variations some monomeric units can be arranged in a head-to-head:tail-to-tail fashion (HH), in contrast to the "normal" head-to-tail addition (HT). In some polymers HH placements can be found in rather high proportions. Poly(vinyl fluoride) typically can have up to 10% inversions.[1] The polymerization of propylene with specific Ziegler–Natta catalysts can yield head-to-head: tail-to-tail linkages up to 11% as has been shown by ^{13}C-NMR studies.[2,3]

A number of polymers have been reported consisting exclusively of HH placements. The properties often differ significantly from those of the corresponding HT polymers.[4-15] The inverted incorporation of the consecutive monomer units in a HH polymer leads to a broader structural variety than found in HT polymers. HH polymers are ditactic. Generally, inverted asymmetrically substituted polyolefins show NMR spectra different from those of HT polymers. The atoms and bonds adjacent to a nucleus whose signal is observed either are different in structure or are located at different distances.



$$\sim CH_2-\overset{CH_3}{\overset{*}{C}H}-\overset{CH_3}{\overset{*}{C}H}-CH_2-CH_2-\overset{CH_3}{\overset{*}{C}H}-\overset{CH_3}{\overset{*}{C}H}-CH_2-CH_2-\overset{CH_3}{\overset{*}{C}H}-\overset{CH_3}{\overset{*}{C}H}-CH_2\sim$$

Because of this peculiar symmetry of HH polymers, the chemical shift effects of the molecular segments which are adjacent to an atom whose resonance is observed can be distinguished by distance and direction.[16]

The present study is concerned with the preparation and ^{13}C-NMR characterization of HH-polypropylenes [poly(1,2-dimethyltetramethylenes)] of different tacticities. ^{1}H-NMR and ^{13}C-NMR spectra have been previously reported. They do not give evidence of sequence structures more extended than the threo and erythro HH placements.[12-15,17] High-resolution ^{13}C-NMR spectra can give more information for the characterization of the stereochemistry of HH-polypropylenes. The spectra are more complicated than those of HT-polypropylene, but they are also of principal interest for the investigation of chemical shift effects in chain molecules. Because interpretation of the complex ^{13}C-NMR spectra is only possible by comparison with the more distinctive spectra of suitable models, additional stereoregular molecules have been prepared which represent dyad and tetrad segments of the polymers.

Experimental Section

Poly(1,2-dimethyltetramethylenes) (PDTM). All polymerizations were carried out with carefully purified monomers and solvents using high-vacuum line techniques.

(a) Erythrodiisotactic PDTM was prepared according to Natta[18] by the copolymerization of 0.36 mol of *cis*-2-butene with ethylene over a period of 10 h in 70 mL of *n*-heptane at −30 °C. The ethylene was fed continuously to the reactor in a nitrogen stream at a partial pressure of 80 mmHg. The catalyst was prepared from 7.1 mmol of VCl_4 and 17.8 mmol of $Al(n\text{-}C_8H_{17})_3$ in 10 mL of *n*-heptane. The polymer was precipitated in methanol and extracted from the polyethylene fraction with boiling *n*-hexane. The hexane fraction had a butene proportion of 45%, was partially crystalline, and consisted mainly of alternating butene–ethylene sequences. The molecular weight was 12 500 (vapor pressure osmometry), T_m was 338 K, and T_g was 235 K (DSC).

(b) Erythrodiatactic PDTM. *cis*-1,4-Poly(2,3-dimethyl-1,3-butadiene) was prepared as described by Teh Fu Yen[19] from 0.244 mol of 2,3-dimethyl-1,3-butadiene in 150 mL of *n*-hexane at room temperature over a period of 48 h with 14.6 mmol of $Al(i\text{-}C_4H_9)_3$ and 14.6 mmol of $TiCl_4$ in 30 mL of *n*-hexane. The polymer was precipitated in a methanolic HCl solution and reprecipitated from toluene. Complete hydrogenation could be

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† Dedicated to Professor W. H. Stockmayer in honor of his 70th birthday.

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accomplished stereospecifically by repeated treatment with diimine;[20] 17 g of the polymer was dissolved in 500 mL of boiling toluene, and 0.3 mmol of *p*-toluenesulfonyl hydrazide (TSH) was added in small portions over a period of 48 h. The solution was precipitated while still hot in hot methanol. The resulting reprecipitated polymer had a molecular weight of 5300 (vapor pressure osmometry) and a T_g of 240 K (DSC).

(c) **Threodiatactic PDTM.** *trans*-1,4-Poly(2,3-dimethyl-1,3-butadiene) was prepared in the same way as the cis polymer, except that the Al:Ti ratio of the catalyst was changed to 1:4 instead of 1:1.[21] Hydrogenation to threo PDTM was done with TSH as described above. The polymer had a molecular weight of 6300 (vapor pressure osmometry) and a T_g of 240.5 K (DSC).

(d) **Threodiisotactic PDTM.** *trans*-2,5-Poly(*trans,trans*-2,4-hexadiene)[22] was prepared by adding 0.122 mol of *trans,-trans*-2,4-hexadiene to a solution of 3.6 mmol of Et_2AlCl and 0.36 mmol of freshly crystallized $Co^{II}(acac)_2$ in 50 mL of *n*-hexane and polymerized for 48 h at room temperature. Hydrogenation to threodiisotactic PDTM was accomplished with TSH as described above. The final polymer had a molecular weight of 7200 (vapor pressure osmometry) and a T_g of 244 K (DSC). A melting transition could not be observed.

(e) **Atactic PDTM.** Atactic *trans*-2,5-poly(2,4-hexadiene)[23] was polymerized cationically with 0.12 mol of 2,4-hexadiene in 120 mL of toluene and 5 mmol of $BF_3{\cdot}OEt_2$ at −20 °C for 48 h. The polymer was precipitated in methanol. For hydrogenation, 5 g of the polymer was dissolved in 200 mL of benzene with 300 mg of Pd on $CaCO_3$ (5%) and kept under hydrogen at a pressure of 5 atm for 12 h at 70 °C. The catalyst was separated by filtration and the polymer precipitated in methanol. The molecular weight was 17 500 (vapor pressure osmometry) and the T_g was 243 K (DSC).

3,4,7,8-Tetramethyldecane. 1-Bromo-2,3-dimethylpentane (0.23 mol) was added under nitrogen to 0.34 mol of sodium covered with dry diethyl ether. The solution was warmed until the reaction started. After 3 h the unreacted sodium was destroyed with ethanol. After the addition of water the reaction product was extracted with ether, washed with an aqueous solution of NH_4Cl, and dried over $MgSO_4$. The product was distilled under vacuum ($bp_{0.5mm}$ 54 °C, yield 53%).

***threo*-3,4-*threo*-7,8-Tetramethyldecane.** (a) **4,5-Dimethylcyclohex-1-ene** was prepared by Wolff–Kishner reduction[24] of 0.58 mol of 2-methyl-1,2,3,6-tetrahydrobenzaldehyde with 3.76 mol of KOH and 2.64 mol of hydrazine hydrate in 800 mL of glycerol (bp 124 °C, yield 63%).

(b) **3,4-Dimethylhexanedioic Acid.** 4,5-Dimethylcyclohex-1-ene (0.36 mol) was added to 1 L of a 0.5% KOH/water solution with 1 mol of $KMnO_4$. The temperature was not allowed to exceed 50 °C. After 1 h the solution was briefly refluxed, and the precipitated MnO_2 was filtered off and carefully extracted. The collected filtrate was neutralized with HCl. After evaporation of the water, $CHCl_3$ was added to the solid residue to extract the diacid (yield 68%). The crude product (36 g) was dissolved in 60 mL of an aqueous 50% methanol solution. The solution was placed on a reverse-phase column (Waters Prep LC 500) in 10-mL portions. At a flow rate of 0.25 mL/min the *dl* fraction and the meso fraction were separated in a 40/60 methanol/water solution. The meso compound eluted before the *dl* diastereomer.

(c) ***dl*-3,4-Dimethylhexanedioic Anhydride.** Acetic anhydride (1.1 mol) was added to 0.11 mol of the *dl* diacid and heated to 100 °C for 1 h. The acetic acid and the acetic anhydride were evaporated and the dimethylhexanedioic anhydride was fractionated under vacuum ($bp_{0.1mm}$ 80–90 °C, yield 70%).

(d) **Dimethyl *threo*-2,3-*threo*-6,7-Tetramethylsebacate.** Methanol (50 mL) was reacted with 0.5 g of potassium with strict exclusion of water. To this solution was added 76 mmol of the diacid anhydride dissolved in 20 mL of methanol, and the mixture was warmed for 2 h on a water bath. The solution was diluted with 60 mL of methanol, and a Kolbe electrolysis was carried out with two Pt electrodes at −5 °C at a voltage of 12 V and a current of 0.7 A.[25] Afterward the solution was acidified with concentrated acetic acid, and the volatile portions were evaporated. The solid residue was dissolved in diethyl ether, washed with aqueous $NaHCO_3$ solution and water, and dried over $MgSO_4$. The ether was evaporated and the crude product reacted further (yield 40%).

(e) ***threo*-3,4-*threo*-7,8-Tetramethyldecane-1,10-diol.** The tetramethylsebacic acid dimethyl ester (27 mmol) was dissolved in 15 mL of ether and added to a solution of 2 g of $LiAlH_4$ in 30 mL of ether. The mixture was refluxed for 2 h and afterward added to a 2 N HCl/ice mixture. The product was extracted overnight in a liquid–liquid extractor with ether, and the ether solution was washed with $NaHCO_3/H_2O$ and water and dried over $MgSO_4$. Finally, the ether was evaporated (yield 97%).

(f) ***threo*-3,4-*threo*-7,8-Tetramethyldecane-1,10-diol Tosylate.** The diol (26 mmol) was reacted in 20 mL of $CHCl_3$ with 52 mmol of toluenesulfonyl chloride and 12 g of pyridine, as described elsewhere.[26]

(g) ***threo*-3,4-*threo*-7,8-Tetramethyldecane.** The ditosylate (22 mmol) was reduced with 45 mmol of $LiAlH_4$ in THF. The product was fractionated under vacuum ($bp_{0.5mm}$ 50–57 °C, yield 30%).

***meso*-3,4-Dimethylhexane.** (a) ***cis*-4,5-Bis(hydroxymethyl)cyclohex-1-ene.** The dimethyl ester of *cis*-1,2,5,6-tetrahydrophthalic anhydride (1.5 mol) was dissolved in 800 mL of absolute THF under inert gas. A solution of 60 g of $LiAlH_4$ in 1.8 L of THF was added while the reactor was cooled with ice. Afterward the solution was refluxed for 2 h and then carefully added to a mixture of 2 N HCl and ice. The THF was evaporated and the product extracted in a liquid–liquid extractor with ether. The ether solution was dried over $MgSO_4$, and after evaporation of the solvent the product was fractionated under vacuum ($bp_{0.5mm}$ 135–147 °C, yield 62%).

(b) ***cis*-4,5-Bis(ditosylmethyl)cyclohex-1-ene.** The diol[26] (0.9 mol) was reacted in 500 mL of $CHCl_3$ with 1.8 mol of TsCl and 3 mol of pyridine. After workup, the chloroform solution was concentrated and the ditosylate crystallized in the cold (yield 54%).

(c) ***cis*-4,5-Bis(iodomethyl)cyclohex-1-ene.** The ditosylate (0.3 mol) was dissolved in 100 mL of $CHCl_3$, and 0.05 mol of tetrabutylammonium iodide and 0.8 mol of NaI were added to the solution, which was then stirred vigorously for 48 h. The chloroform solution was washed with NaS_2O_3/water and water and dried over $MgSO_4$. Afterward the solvent was evaporated and the crude product distilled on a high-vacuum line ($bp_{10^{-4}mm}$ 80–90 °C, yield 54%).

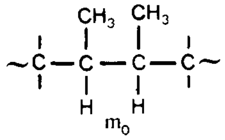
(d) ***cis*-4,5-Dimethylcyclohex-1-ene.** 4,5-Bis(iodomethyl)-cyclohex-1-ene (0.1 mol) was dissolved in 100 mL of THF and combined with a solution of 0.2 mol of $LiAlH_4$ in 200 mL of THF under nitrogen. The solution was refluxed overnight and worked up as described above for the other reductions (bp 124 °C, yield 12%).

(e) ***meso*-3,4-Dimethylhexane.** *cis*-4,5-Dimethylcyclohex-1-ene (0.12 mol) was oxidized with $KMnO_4$, and the *meso*-3,4-dimethylhexanedioic acid was reduced to *meso*-3,4-dimethylhexane as described above for the tetramethylsebacic acid (bp 117 °C, yield 0.3 g).

All ^{13}C-NMR spectra were ^1H-broad-band decoupled and were recorded with a Bruker WH 90 spectrometer at 22.63 MHz. Usually the spectral width was 1000 Hz with 8 K data points. The ^{13}C pulse was 6 μs and the acquisition time 4 s. NMR stabilization was obtained by locking on the ^2H signal of $CDCl_3$. Octamethylcyclotetrasiloxane was used as reference. Octamethylcyclotetrasiloxane has a chemical shift of +0.75 ppm compared to Me_4Si at 303 K in $CDCl_3$. The temperature was kept at 303 K during recording. Signal intensities are given as calculated from the peak area by the computer of the spectrometer.

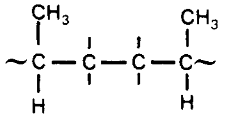
Results and Discussion

Four types of dyads must be distinguished in a HH-polypropylene molecule. In the following discussion the meso HH dyad (erythro) and the meso TT dyad will be signified by m, and the racemic HH dyad (threo) and the racemic TT dyad by r. HH and TT dyads will be distinguished by the index 0 or 2, counting the number of methylene groups inbetween the asymmetric carbon atoms. This is shown below by means of Fischer projections.



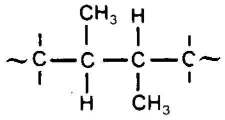
$\sim C-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-C\sim$

m_0



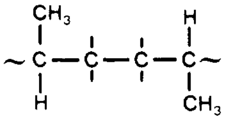
$\sim C-\overset{CH_3}{\underset{H}{C}}-C-\overset{CH_3}{\underset{H}{C}}\sim$

m_2



$\sim C-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-C\sim$

r_0

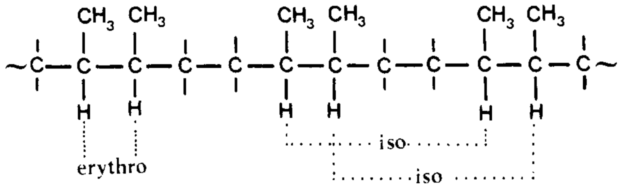


$\sim C-\overset{CH_3}{\underset{H}{C}}-C-\overset{H}{\underset{CH_3}{C}}\sim$

r_2

Theoretically, six configurations are possible, which are stereoregular to different degrees: $(m_0m_2)_n$, $(m_0r_2)_n$, (r_0m_2), $(r_0r_2)_n$, (m_0 and m_2 or $r_2)_n$, and (r_0 and m_2 or $r_2)_n$.

For nomenclatural purposes the polymer is regarded as an alternating copolymer with two types of subunits differing in their orientation. Consequently, the following shows a segment of an erythrodiisotactic HH-polypropylene:



$\sim C-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-C-C-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-C-C-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-C\sim$

HH-polypropylenes can be synthesized by three different routes:

(1) By copolymerization of ethylene and *cis*-2-butene

$$CH_3CH{=}CHCH_3 + CH_2{=}CH_2 \rightarrow -[CH(CH_3)CH(CH_3)CH_2CH_2]_n-$$

(2) By hydrogenation of 1,4-poly(2,3-dimethyl-1,3-butadiene)

$$-[CH_2C(CH_3){=}C(CH_3)CH_2]_n- \rightarrow -[CH_2CH(CH_3)CH(CH_3)CH_2]_n-$$

(3) By hydrogenation of 2,5-poly(2,4-hexadiene)

$$-[CH(CH_3)CH{=}CHC(CH_3)]_n- \rightarrow -[CH(CH_3)CH_2CH_2CH(CH_3)]_n-$$

Route 1 yields a polymer which consists mainly of erythrodiisotactic HH-polypropylene segments, although we could not avoid the incorporation of blocks of polyethylene to a small extent.[27]. Syn-specific hydrogenation of poly(dimethylbutadiene) leads to an erythrodiatactic HH-polypropylene in the case of *cis*-poly(dimethylbutadiene) and to a threodiatactic HH-polypropylene in the case of *trans*-poly(dimethylbutadiene). The hydrogenation of the poly(hexadiene) does not affect the relative configurations of the asymmetric carbon atoms. Thus, we obtained an atactic HH-polypropylene from an atactic 2,5-poly(2,4-hexadiene) and a threodiisotactic HH-polypropylene from poly(hexadiene) polymerized with a $Co^{II}[acac_2]/Et_2AlCl$ catalyst,[22] as we will show. Erythro- and threo-disyndiotactic HH-polypropylenes could not be realized.

In order to assign unambiguously the ^{13}C-NMR signals of the polymers with respect to the threo- and erythro configuration of the HH dyad, we synthesized 3,4-dimethylhexane in its pure meso form, starting from *cis*-1,2,5,6-tetrahydrophthalic acid. 3,4-Dimethylhexane is the simplest molecule which represents the structure of the HH dyad. For the investigation of stereochemical effects beyond the threo and erythro placements, 3,4,7,8-tetramethyldecane was used. This molecule represents a tetrad segment of HH-polypropylene. It was synthesized as a mixture of the diastereomers in proportion to their statistical probability and as a mixture in which the threo placements were enriched to 74%.

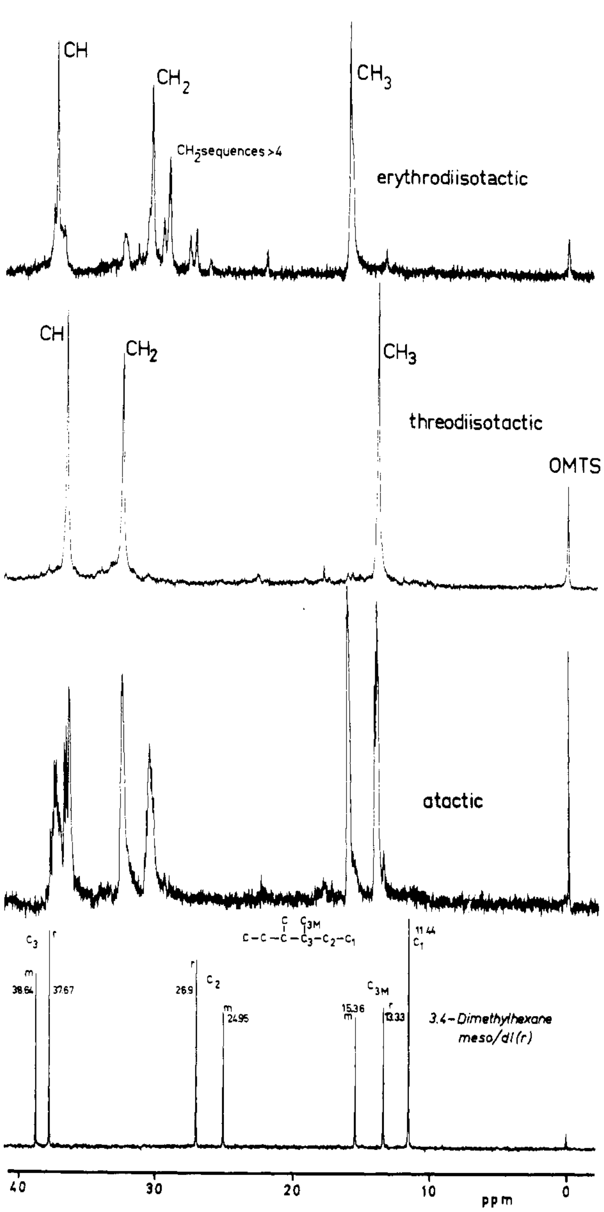


Figure 1. ^{13}C-NMR spectra of poly(1,2-dimethyltetramethylene) samples of different tacticities in comparison to *meso/dl*-3,4-dimethylhexane.

Figure 1 shows the ^{13}C-NMR spectra of the atactic, the erythrodiisotactic, and the threodiisotactic HH-polypropylenes in comparison with the spectrum of the meso/*dl* mixture of 3,4-dimethylhexane. It is evident that the CH_3, CH_2, and CH signals of the polymer split into two subgroups each. This is caused by the nonequivalence of erythro and threo configurations of the HH dyads.

We know the assignment of the 3,4-dimethylhexane resonance signals with respect to the meso and *dl* configurations by comparison with the spectrum of pure *meso*-3,4-dimethylhexane. Chemical shift differences due to the relative configurations of the adjacent asymmetric carbons are very similar for the polymer and the model compound. Therefore, we can assign the subgroups in the polymer spectrum correspondingly. The *cis*-butene/ethylene copolymer turns out to have only erythro placements, in accordance with the erythrodiisotactic structure deduced from X-ray data.[27] The threo structure of the hydrogenated 2,5-poly(2,4-hexadiene) prepared with the Co^{II}-

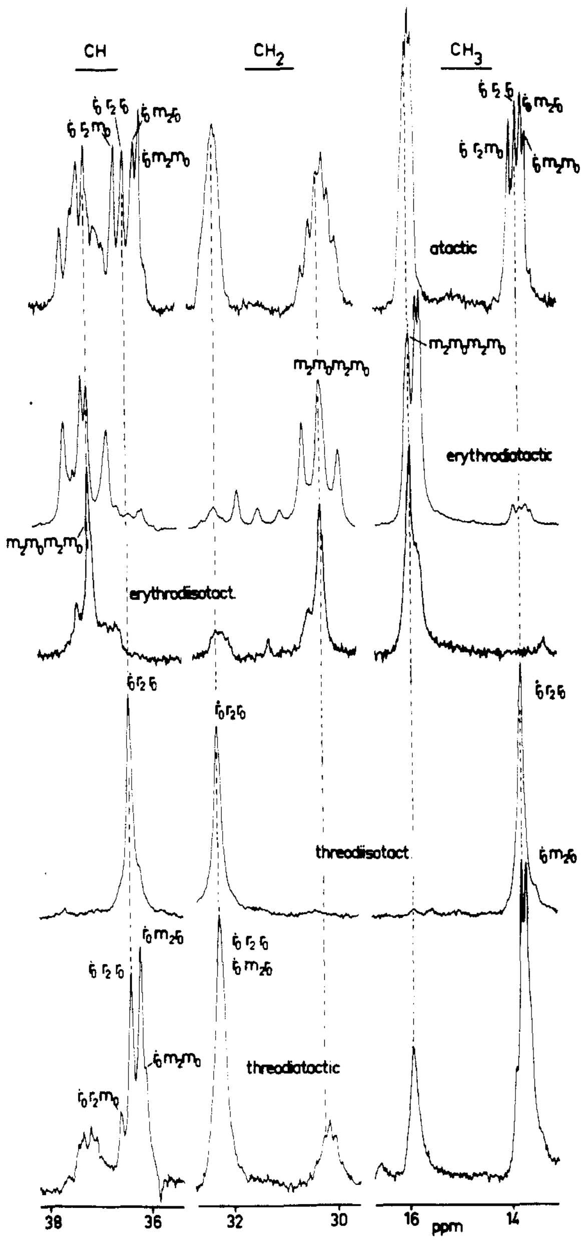


Figure 2. CH, CH$_2$, CH$_3$ ^{13}C-NMR spectra of poly(1,2-dimethyltetramethylene) samples of different tacticities.

[acac$_2$]/Et$_2$AlCl catalyst is clearly demonstrated. When Kamachi et al. first prepared the poly(hexadiene) they could not determine whether it was threo- or erythrodiisotactic.[22] The assignment concerning the erythro and threo placements is also supported by the spectra of the samples made by syn-hydrogenation of *cis*- and *trans*-poly(2,3-dimethyl-1,3-butadiene). To a high extent these samples have only erythro or only threo HH dyads. By comparison of the polymer spectra we could assign the signals as shown in Figure 2. In denoting the configurational sequence, we mark by a dot the position of the carbon atom whose resonance is concerned.

The ^{13}C-NMR signals at the bottom of Figure 2 are from a sample which has mainly threo HH dyads. The less intense signals belong to sequences with erythro placements. The CH and CH$_3$ resonances of sequences which contain only threo HH dyads are split into equally intense signals. No splitting could be observed for the CH$_2$ signal. Also in Figure 2 is shown the spectrum of the sample which has mainly erythro HH dyads. The CH resonance is split into four equally intense signals, and the CH$_2$ and CH$_3$ resonances are split into three signals showing a pattern from four equally intense signals which is not completely resolved. This seems remarkable. In the case of an erythro HH dyad the chemical shifts (especially of the CH resonances) are sensitive to the relative configurations of the two TT dyads on both sides of the observed carbon atom. This results in four signals which belong to the following sequences: $m_2\dot{m}_0m_2$, $m_2\dot{m}_0r_2$, $r_2\dot{m}_0m_2$, $r_2\dot{m}_0r_2$. Splitting of the threo signals is caused only by the relative configurations of one of the adjacent TT dyads. In the spectrum of the threodiatactic sample minor signals can be seen which belong to $\dot{r}_0$–m_0 segments, because the sample contains erythro placements to a small extent. Obviously, also the relative configurations of only one of the adjacent HH dyads are distinguished. Hence we find not more than two signals ($\dot{r}_0r_2$ and $\dot{r}_0m_2$). As we will discuss later, this effect must be explained by the conformations of the respective groups.

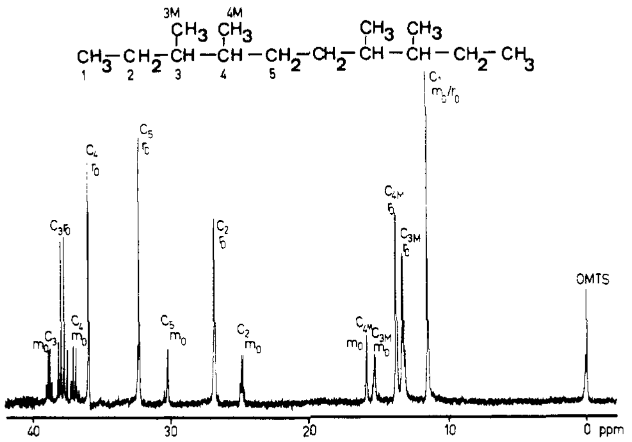


Figure 3. ^{13}C-NMR spectrum of 3,4,7,8-tetramethyldecane with 74% threo CH–CH configurations.

In order to understand the chemical shift pattern better, we synthesized 3,4,7,8-tetramethyldecane as a model compound which represents a longer segment of the inverted polypropylene chain.

In Figure 3 the ^{13}C-NMR spectrum of the 3,4,7,8-tetramethyldecane sample having 74% threo placements is shown. Because of magnetic nonequivalence, seven signals are to be expected for each of the $m_0m_2m_0$, $m_0r_2m_0$, $r_0m_2r_0$, and $r_0r_2r_0$ diastereomers. In the $m_0m_2r_0$ and the $m_0r_2r_0$ forms, all 14 carbons are nonequivalent. As the latter forms have twice the statistical probabilities, we should expect up to eight equally intense signals for each of the seven carbons within the molecule distinguished by constitutional variations, if meso and racemic placements occur with the same frequency. Consequently, for the threo-enriched sample the more intense signals within the subgroups for the carbons distinguished because of constitutional differences belong to the $\dot{r}_0$ HH dyads. In accordance with these considerations the resonances given in Table I were assigned with respect to the threo and erythro placements of both HH dyads in the model compound. The assignment is in agreement with the spectra of 3,4-dimethylhexane and with the shift parameters of Lindeman and Adams.[28] In Table I the intensities are given in relation to the total intensity of the respective threo or erythro resonances.

3,4,7,8-Tetramethyldecane already represents a segment of the polymer long enough that its spectrum should show fine structure comparable to that of the polymer spectrum. The ^{13}C-NMR spectra of the polymers show that carbon nuclei which belong to threo dyads are sensitive only to the relative configurations of one of the adjacent dyads. Therefore, the $\dot{r}_0$ signals of 3,4,7,8-tetramethyldecane

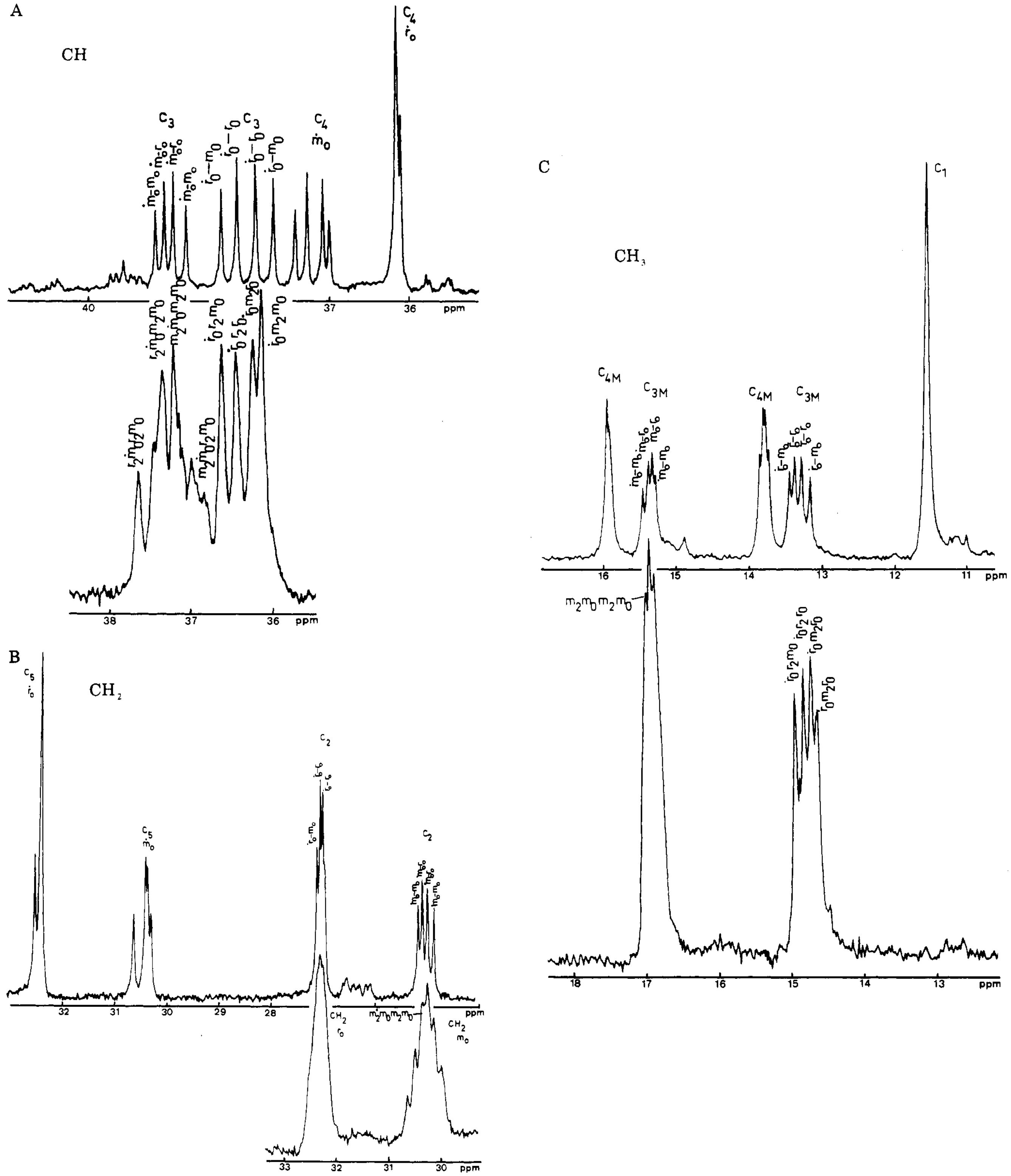


Figure 4. ^{13}C-NMR signals of 3,4,7,8-tetramethyldecane (top) with 50% threo CH–CH configurations in comparison to atactic poly(1,2-dimethyltetramethylene) (bottom). For the relative configurations of the TT dyad of the 3,4,7,8-tetramethyldecane diastereomers no assignment is given in the figure. Instead of m_2 or r_2 a hyphen is given in the denotation. (a) CH signals; (b) CH_2 signals; (c) CH_3 signals.

should show the same splitting pattern as the $\dot{r}_0$ signals of the polymer.

In Figure 4 the CH, CH_2, and CH_3 signals of the atactic polymer and the model compound are shown for comparison. The spectra of 3,4,7,8-tetramethyldecane were obtained from the sample with a 1:1 ratio of erythro and threo placements. Hence it shows a distribution of the configurational sequences, as in the atactic polymer. Surprisingly, the internal CH, CH_2, and CH_3 carbons do not give the same splitting as the corresponding atoms in the polymer, while their resonances appear at similar chemical shifts. The latter fact is due to the constitutional similarity of the carbons in both compounds. However, for carbons belonging to threo placements ($\dot{r}_0$) the signals of the polymer appear in the same order and have shift differences very similar to those of the signals of the corresponding external CH, CH_2, and CH_3 atoms in the model compound. Also the external CH, CH_2, and CH_3

Table I
^{13}C-NMR Shifts and Relative Intensities of 3,4,7,8-Tetramethyldecane with 74% Threo CH-CH Configurations[a]

		chem shift, intensity					chem shift, intensity			
		ppm		$(m_0) < (r_0)$			ppm		$(m_0) < (r_0)$	
	seq[a]	δ	$\Lambda\delta$	exptl	theor	seq[a]	δ	$\Lambda\delta$	exptl	theor
CH(3)	$\dot{r}_0$-m_0	38.35$_1$	0.19$_5$	0.12	0.13	$\dot{m}_0$-m_0	39.17$_7$	0.11$_3$	0.13	0.13
	$\dot{r}_0$-r_0	38.15$_6$	0.22$_6$	0.38	0.37	$\dot{m}_0$-r_0	39.06$_4$	0.11$_4$	0.40	0.37
	$\dot{r}_0$-r_0	37.93$_0$	0.22$_7$	0.38	0.37	$\dot{m}_0$-r_0	38.95$_0$	0.16$_2$	0.35	0.37
	$\dot{r}_0$-m_0	37.70$_3$		0.12	0.13	$\dot{m}_0$-m_0	38.78$_8$		0.12	0.13
CH(4)	$\dot{r}_0$	36.16$_4$	0.04$_9$	0.62		$\dot{m}_0$-m_0	37.42$_7$	0.14$_5$	0.13	0.13
	$\dot{r}_0$	36.11$_5$		0.38		$\dot{m}_0$-r_0	37.28$_2$	0.19$_5$	0.34	0.37
						$\dot{m}_0$-r_0	37.08$_7$	0.08$_1$	0.37	0.37
						$\dot{m}_0$-r_0	37.00$_6$		0.16	0.13
CH$_2$(5)	$\dot{r}_0$	32.53$_4$	0.12$_9$	0.13	0.13	$\dot{m}_0$-m_0	30.60$_6$	0.22$_7$	0.10	0.13
	$\dot{r}_0$	32.40$_5$		0.87	0.87	$\dot{m}_0$-r_0	30.37$_9$	0.03$_2$	0.39	0.37
						$\dot{m}_0$-r_0	30.34$_7$	0.06$_5$	0.40	0.37
						$\dot{m}_0$-m_0	30.28$_2$		0.11	0.13
CH$_2$(2)	$\dot{r}_0$-m_0	27.09$_0$	0.06$_5$	0.10	0.13	$\dot{m}_0$-m_0	25.13$_0$	0.08$_1$	0.15	0.13
	$\dot{r}_0$-r_0	27.02$_5$	0.04$_8$	0.38	0.37	$\dot{m}_0$-r_0	25.04$_9$	0.09$_7$	0.34	0.37
	$\dot{r}_0$-r_0	26.97$_7$	0.03$_3$	0.35	0.37	$\dot{m}_0$-r_0	24.95$_2$	0.07$_0$	0.40	0.37
	$\dot{r}_0$-m_0	26.94$_4$		0.17	0.13	$\dot{m}_0$-r_0	24.88$_2$		0.11	0.13
CH$_3$(4M)	$\dot{r}_0$-m_0	13.85$_3$	0.04$_9$	0.09	0.13	$\dot{m}_0$	15.94$_3$	0.03$_3$	0.45	0.50
	$\dot{r}_0$-r_0	13.80$_4$	0.03$_2$	0.36	0.37	$\dot{m}_0$	15.91$_1$		0.55	0.50
	$\dot{r}_0$-r_0	13.77$_2$	0.04$_9$	0.33	0.37					
	$\dot{r}_0$-m_0	13.72$_3$		0.22	0.13					
CH$_3$(3M)	$\dot{r}_0$-m_0	13.43$_2$	0.06$_5$	0.13	0.13	$\dot{m}_0$-m_0	15.45$_7$	0.08$_1$	0.11	0.13
	$\dot{r}_0$-r_0	13.36$_7$	0.09$_7$	0.39	0.37	$\dot{m}_0$-r_0	15.37$_6$	0.04$_9$	0.40	0.37
	$\dot{r}_0$-r_0	13.27$_0$	0.13$_0$	0.42	0.37	$\dot{m}_0$-r_0	15.32$_7$	0.04$_8$	0.35	0.37
	$\dot{r}_0$-m_0	13.14$_0$		0.06	0.13	$\dot{m}_0$-m_0	15.27		0.14	0.13
CH$_3$(1)		11.53$_6$								

[a] In denoting the configurational sequence, we give no assignment for the relative configuration of the TT dyad. Instead of m_2 or r_2 a dash is given.

carbons which belong to the meso HH dyad ($\dot{m}_0$) of the model compound show very similar splittings to the signals of the corresponding nuclei in the polymer. Hence the situation can be summarized as follows. The chemical shifts of the internal CH, CH$_2$, and CH$_3$ carbons are nearly identical with the chemical shifts of the corresponding polymer resonances. This reflects the constitutional equivalence of those atoms. The fine splitting of the polymer resonances resembles, particularly in case of a threo placement, that of the external CH, CH$_2$, and CH$_3$ signals of the model compounds. Consequently, concerning the information about the configuration, the external carbons of the model compound are in an analogous situation as those in the polymer. We conclude that particularly for the signals of a threo dyad, long-range stereochemical information in the polymer spectrum is dominantly not given with regard to relative configurations of the next-nearest adjacent asymmetric carbons but with regard to the dyad on the opposite side.

A consistent assignment is now possible for the signals of carbons within a threo dyad by comparison of the polymer spectra with those of 3,4,7,8-tetramethyldecane. In Figure 5 we also give a complete assignment for the signals of carbons within an erythro dyad. The relative configurations of the TT dyads on both sides of the observed nuclei are taken into account, but we could not take into account the relative configuration of the second adjacent HH dyad. In contrast to the threo case, the relative configurations of the next HH dyad, which is nearer to the observed carbon atom, are not of negligible influence on its chemical shift. This can be seen also in the spectrum of the internal CH, CH$_2$, and CH$_3$ groups in 3,4,7,8-tetramethyldecane. The resulting configurational splitting in the polymer spectrum leads to partial overlapping of the signals. Therefore the assignment is not as conclusive as for the carbons within a threo dyad. In Table II the chemical shifts and relative intensities of the atactic HH-polypropylene spectrum are given with the corresponding configurational symbols. The intensities were calculated from the peak areas and are compared with intensities calculated under the assumption of Bernoullian statistics and equal probability of the relative configurations:

$$P(r_0) = P(m_0) = 0.5$$

$$P(r_2) = P(m_2) = 0.5$$

Conclusions

A comparison of the spectra of poly(1,2-dimethyltetramethylene) samples of different tacticities allows a consistent assignment of some of the ^{13}C-NMR signals, as shown in Figure 2. On this basis we draw three conclusions regarding the resonances of the atactic polymer:

1. CH$_3$, CH$_2$, and CH ^{13}C-NMR signals show a distinctive splitting into two subgroups, which can be assigned to erythro and threo placements of the HH dyad in which the observed carbon is located.
2. Carbon atoms within an erythro dyad can see different relative configurations on both sides.
3. Signals of carbons within a threo dyad do not split up to the same degree as those of carbons within an erythro dyad. Apparently, only the relative configurations of the adjacent dyad in one direction of the chain are distinguished. This is most obvious for the CH signals.

Although this conclusion is the most straightforward argument conveivable to explain the splitting pattern, the difference between the erythro and the threo case appeared puzzling. We therefore synthesized 3,4,7,8-tetramethyldecane in order to obtain more information. The spectra

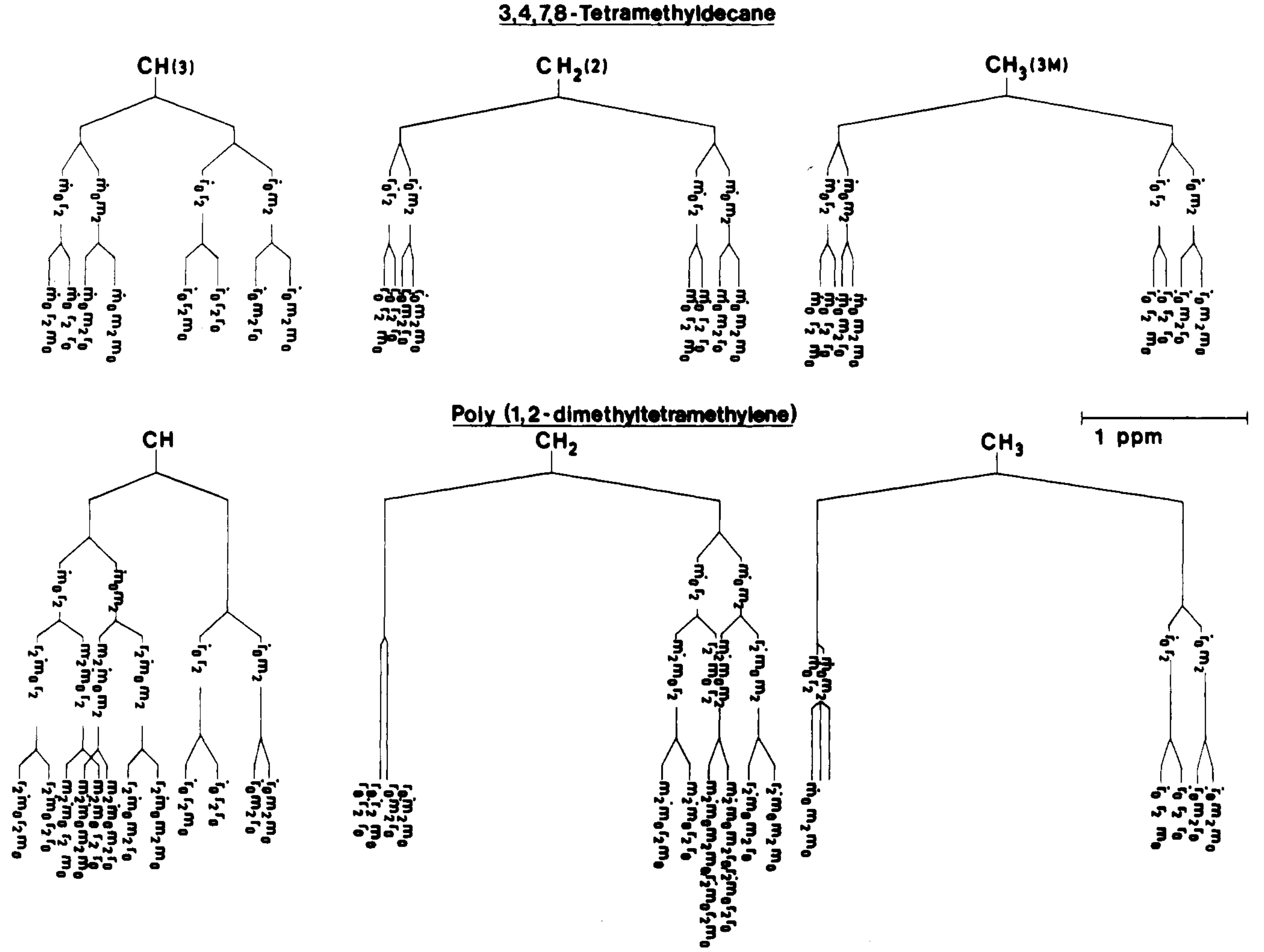
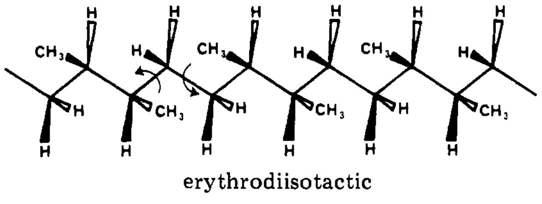


Figure 5. Scheme with the assignment of the configurational sequences to the ^{13}C-NMR signals of 3,4,7,8-tetramethyldecane and atactic poly(1,2-dimethyltetramethylene).

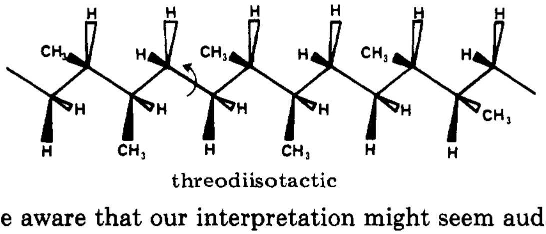
of this model unambiguously show a splitting pattern which is even more astonishing: When the observed nucleus is part of a threo HH dyad, the external CH_3, CH_2, and CH carbons show more pronounced chemical shift differences due to the configurations of the adjacent HH dyad than the internal carbons. This leads us to our fourth conclusion.

4. In case the observed nucleus is part of a threo HH dyad the splitting of the corresponding resonances is caused by the relative configurations of the more distant adjacent HH dyad. This conclusion is consistent with our conclusion 3 but also in contradiction to intuition. We present some arguments in favor of conclusion 4.

The chemical shift of a carbon atom depends mainly on the spatial arrangement of the bonds and atoms in α-, β-, and γ-positions. In the fast-exchange regime of the rotational isomeric states, chemical shifts are averaged over the populations of the conformers. If the relative configuration of an asymmetric carbon atom determines the structure beyond the γ-position, the equilibrium of the rotational isomeric states of the bonds near the carbon under investigation is influenced.[29] It is well established that the gauche conformation of a carbon atom in a γ-position leads to a pronounced upfield shift compared to the anti position. If we take only this anti/gauche effect into account, the following explanation for the CH splitting if offered: changes in the relative configurations of the asymmetric carbon atoms within the next HH dyad predominantly influence the rotational state equilibrium of the $CH-CH_2$ bond in the case of a threo dyad. Configurational splitting is observed for the outer CH atom. In case of erythro dyads relative configurations of the next HH dyad influence the rotational state equilibrium of the $CH-CH_2$ and of the CH_2-CH_2 bond. Configurational splitting is observed for both the CH atoms. This is equivalent to the fact that configurational differences can be detected in both directions along the chain.



erythrodiisotactic



threodiisotactic

We are aware that our interpretation might seem audacious and surely needs further support. But it may be justifiable to point out the unique opportunity HH polymers offer. Because of their peculiar symmetry the origin of chemical shift effects can be located by distance as well as by direction. Thus variations of the conformational state equilibria of the bonds adjacent to a certain nucleus can be located too. Obviously, the situation is different

Table II
^{13}C-NMR Shifts and Relative Intensities of Atactic Poly(1,2-dimethyltetramethylene)

	seq	chem shift, ppm	intensity	
			theor	exptl (±0.05)
CH	$\dot{r}_2m_0r_2m_0$	37.65_6	0.125	0.14
	$\dot{r}_2m_0r_2r_0$	37.44_5	0.125	0.12
	$\dot{m}_2m_0r_2m_0$	37.36_5	0.125	0.19
	$\dot{m}_2m_0m_2m_0$	37.21_5	0.125	0.13
	$\dot{m}_2m_0r_2r_0$	37.13_6	0.125	0.05
	$\dot{m}_2m_0m_2r_0$	37.07_1	0.125	0.06
	$\dot{r}_2m_0m_2r_0$	36.95_7	0.125	0.18
	$\dot{r}_2m_0m_2m_0$	36.81_3	0.125	0.13
	$\dot{r}_0r_2m_0$	36.61_7	0.25	0.25
	$\dot{r}_0r_2r_0$	36.55_0	0.25	0.25
	$\dot{r}_0m_2r_0$	36.22_9	0.25	0.23
	$\dot{r}_0m_2m_0$	36.14_7	0.25	0.26
CH_2	$\dot{r}_0$	32.32_4	1.00	1.00
	$\dot{r}_2m_0m_2m_0$	30.64_0	0.125	0.10
	$\dot{r}_2m_0m_2r_0$	30.49_4	0.125	0.14
	$\dot{r}_2m_0r_2m_0$, $\dot{m}_2m_0m_2m_0$	30.36_4	0.25	0.21
	$\dot{m}_2m_0m_2r_0$, $\dot{r}_2m_0r_2r_0$	30.26_7	0.25	0.26
	$\dot{m}_2m_0r_2r_0$	30.15_4	0.125	0.18
	$\dot{m}_2m_0r_2m_0$	29.99_1	0.125	0.11
CH_3	$\dot{m}_2m_0r_2$	15.99_2	0.25	0.27
	$\dot{m}_2m_0m_2$	15.94_3	0.25	0.23
	$\dot{r}_2m_0r_2$	15.87_8	0.25	
	$\dot{r}_2m_0m_2$	15.78_2	0.25	0.50
	$\dot{r}_0r_2m_0$	13.95_0	0.25	0.27
	$\dot{r}_0r_2r_0$	13.83_0	0.25	0.19
	$\dot{r}_0m_2r_0$	13.74_0	0.25	0.31
	$\dot{r}_0m_2m_0$	13.63_0	0.25	0.23

in case of a HH dyad and a TT dyad. Hence it would be useful to check our considerations by model calculations. Unfortunately, the only published RIS model for HH–TT-polypropylene uses unreasonable interaction parameters. Asakura et al.[30] assumed most stable CH–CH bond conformations, which were shown later to be unfavorable.[31-33] Furthermore, chemical shift calculations published for H–T-polypropylene are based on a γ-gauche effect of -5.3 ppm[34-36] or of about -5 ppm for methyl groups and -3.5 ppm for methylene groups.[37-39] However, slow-exchange measurements in solution, as well as in the solid state by means of the CP-MAS technique, of HH-polypropylene and its low molecular weight model compounds[40-42] showed a γ-gauche effect of -8 ppm for both the methylene and the methyl carbons.

RIS calculations for HH-polypropylene using the experimental data of the above cited references[31-33,40-42] are in progress, and we hope we can soon report further results.

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