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Micro- and Macroconformation of Macromolecules

1. Microconformation of Inverted Polypropylenes from Slow Exchange ^{13}C-NMR Spectra of Low Molecular Weight Compounds

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Dedicated to Prof. C.I. Simionescu on the occasion of his 60th birthday

SUMMARY

Configurative as well as conformational variations with respect to the polymer structure yield comparable effects in the chemical shift of ^{13}C- NMR signals. With the example of the head- to head diad within the isomeric polypropylenes, it is demonstrated with the aid of corresponding low molecular weight model compounds that the conformational informations in the ^{13}C - NMR spectrum can be used for the determination of the rotational isomers. For the meso- head-to head diad the temperature dependence of the methyl group coalescence signals can be interpreted with the aid of the slow exchange spectra of the low molecular model compounds. The consequences of the microconformations on the macroconformation of the macromolecules are discussed.

INTRODUCTION

It is well known that chain conformation has strong influence on polymer properties. Quite all important properties of a polymer are governed by the spatial arrangement within the chain, as chemical reactivity, glass transition, crystallization behaviour, thermal expansion, adhesion, stress- strain curve and melt viscosity.

In many papers it has been demonstrated that the overall shape of a macromolecule (the macrodimension) is determined by the chemical structure (constitution as well as configuration) of a polymer. Within the period of the last few years, neutron scattering experiments 1) have verified FLORY's conclusion 2) that macromolecules exhibit their unperturbed dimensions under Θ- conditions in solution as well as in the melt and in the glassy amorphous state. Those unperturbed macrodimensions are determined by the short range rotational isomeric effects. The excluded volume is being eliminated and longe range interactions are of no influence. Specific polymer-solvent interactions should be absent also. The unperturbed macrodimensions have to be dependent on the temperature, which follows from the fact that the conformations within the macromolecular chain are not isoenergetic. If for instance in a typical asymmetrically substituted vinyl polymer the anti- conformer is lower in energy than both the isoenergetic gauche conformers, the macrodimensions will contract with increasing temperature, because the population of the more compressed higher energy gauche conformers is increasing.

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Experimental data have shown however that even under pseudoideal Θ-conditions in solution specific polymer- solvent interactions are sometimes influencing the macrodimensions $^{3)}$. Furthermore, a critical analysis of the macrodimensions determined in the solid state by neutron scattering shows that those are about ten percent higher in average than the unperturbed macrodimensions in solution. Neutron scattering can not yield conclusions concerning the microdimensions at segmental level consisting of some repeating units in the macromolecule because of the wavelengths employed in the experiment. 20 to 30 Å seems to be the limit of resolution at this time. Consequently it seems to be worthwile to look for methods for analyzing the microconformational range. NMR measurements are in the position to give information concerning the microconformations in solution as well as in the solvent free rubbery state.

It is the purpose of this paper to present microconformational data obtained from ^{13}C- NMR chemical shift measurements and its temperature dependence. Investigations of the slow exchange spectra of low molecular weight model compounds being representative for the structure of head- to head polypropylene (H-H) have been interpreted in order to yield conclusions on the populations of conformers which are present in the macromolecules.

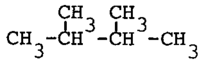
RESULTS AND CONCLUSIONS

The chemical shift of a ^{13}C- signal is depending significantly on the spatial arrangement of the neighbouring groups of the nucleus under observation. In the spectra of methyl substituted cyclohexane molecules a pronounced gauche- effect of the carbons in γ- position is well known $^{4)}$. The conformers A and B exist with two discrete chemical shifts δ_A and δ_B. If the velocity of the transition between A and B is small as compared with the frequency difference between the signals δ_A and δ_B these signals are resolved. If the velocity, however, exceeds the signal difference, one single coalescence signal occurs. Its chemical shift is the weighted average over the populations of the conformers which occur with the signals δ_A and δ_B : $\delta_{coal} = x_A\delta_A + x_B\delta_B$.

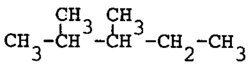
For the C=N- rotation in polyamides the activation energy of the rotational barriers is about 50 kJ. Therefore with the usual spectrometers at room temperature one detects the discrete signals of the conformers. One is in the position to determine their populations from the intensities. However, for the inverted polypropylenes investigated in this paper, the activation energy for the rotation around the chain bonds is within the region of 10- 20 kJ. Consequently, slow exchange, where the conformers have discrete signals, can be reached only at very low temperatures below 100 K, even with high resolution superconducting instruments. Such measurements, however, are not realizable on the macromolecules themselves, because the cooperative type of chain motions causes broader and less exactly analyzable signals. Furthermore, at such low temperatures, the athermal solutions required are hardly realizable. Therefore measurements on inverted polypropylenes are restricted to the fast exchange range. The populations of conformers occuring in the macromolecules exist according to BOLTZMANN's theorem. Changing the temperature shifts the equilibrium of the conformers thus influencing the chemical shift of the coalescence signal.

A direct determination of the discrete slow exchange signals of the conformers, however, is possible on low molecular weight compounds, which represent segments of the corresponding macromolecule, and which have model character concerning conformation and chemical shift consequently. The reason that we have chosen inverted polypropylenes and their segmental model for our approach is a twofold one. First a broad variety of configurations are realizable for this ditactic type of macromolecule. Second, because of the non- equivalence of bonds succeeding each other, influences on the nuclei under investigation can differ with respect to direction and to distance, in contrast to normal head- to tail polymer.

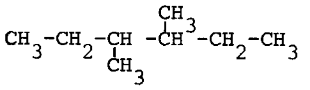
The smallest models being representative for the isomeric inverted polypropylenes are the 3,4- dimethyl hexanes. Because of the two asymmetric methine carbons it occurs in two diastereomer types, RS and SR = meso, RR and SS = dl. Thus these isomers represent the isotactic and the syndiotactic head- to head diads of the polypropylenes. 2,3- dimethyl butane and 2,3- dimethyl pentane are more simple models, which turn out to be usefull for the assignment of signals and for the interpretation of the data:



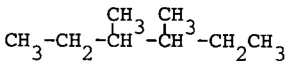
$CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$



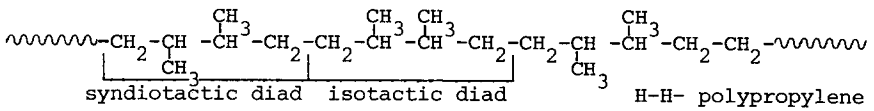
$CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_2-CH_3$



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



$CH_3-CH_2-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_2CH_3$



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

It may be noted that because of the two adjacent chiral centers head- to head polypropylene may exist in four ditactic forms, erythro- and threo- diisotactic and erythro- and threo- disyndiotactic.

With the model alkanes cited above, we succeeded to measure ^{13}C- NMR- spectra under conditions of slow exchange, at 90,51 MHz and at temperatures down to 83 K. When compared with our measurements published before [5)], major improvements concerning the resolution could be achieved for the 2,3- dimethyl pentane and for the isomeric 3,4- dimethyl hexanes by choosing 1- monodeutero ethane instead of 1- monodeutero propane as the solvent. No more overlapping occured between peaks arising from the alkanes and the solvent.

In Figure 1 the NMR- spectrum of 2,3- dimethyl butane is shown in the region of fast as well as of slow exchange. At 210 K one finds two signals, the one from the equivalent methyl carbons and the other from the two methine carbons, with an intensity ratio of 2/1. In the slow exchange at 85 K one detects five discrete signals, which have to be assigned to the gauche and to the anti- conformer. The denomination gauche and anti is related to the position of the hydrogen atoms at the methine carbons. We will show later on that for the polymers another definition has to be applied. From the figures of the conformers it is evident that in the anti conformer the methine carbons C_1 as well as the four methyl carbons C_2 are magnetically equivalent, with the consequence of the two 2/ 1-

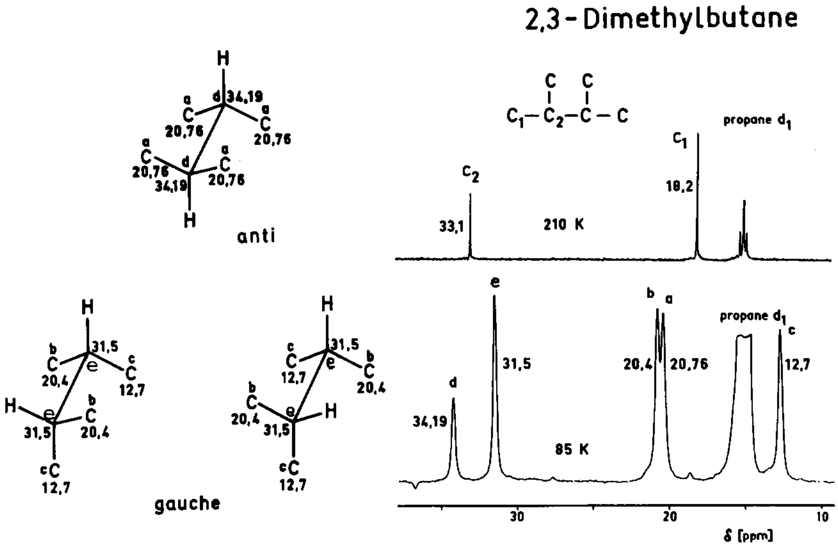


Figure 1: Fast and slow exchange ^{13}C- NMR spectra of 2,3- dimethyl butane, staggered anti and gauche conformers

intensity signals for the anti conformer. In the gauche conformation, however, every two of the four methyl carbons are equivalent. Note that the methyl carbons signed with b are situated within practically identical magnetic environment as the methyl carbons in the anti conformer. Consequently, the double signal at 20 ppm is assigned to methyl carbons a and b. The resonance found for the methyl carbons c in the gauche conformation is situated at higher field, because they are influenced by one γ- carbon more in gauche position. Thus a ratio of 2/ 1 is concluded for gauche to anti conformation. Consequently both the methine carbon signals, d and e, can be assigned unequivocally +). The assignment of the methyl signals a and b at 20,4 and 20,76 ppm can be established from their intensity ratio.

Figure 2 presents the ^{13}C- spectra of 2,3- dimethyl pentane in monodeutero ethane as solvent. In the region of fast exchange the signals can be assigned according to LINDEMANN and ADAMS 6). Carbons C_1 and C_{2M} are magnetically unequivalent because of the chiral C_3 carbon. (C_{iM} means the carbon of the methyl group bond to the C_i in the chain). The assignment of the 15,3 and 19,8 ppm signals to the carbons C_1 and C_{2M} is possible by the aid of knowing the most

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+) Unfortunately in a foregoing short letter 5), due to a slipping error, the nominations d and e were interchanged. As a consequence, the equivalent signals have to be corrected for 2,3- dimethyl pentane and for the 3,4- dimethyl hexanes too, as done now in this paper. Thus the other gauche conformer shows up to be the most stable in both cases.

stable conformers as derived below. The spectrum at 105 K shows the transition towards slow exchange, which is reached definitely at 83 K. With the exception of the C_3 signal at 38 ppm, all signals are split into doublets of unequal intensity. Two gauche and one anti conformation have to be taken into consideration for the assignment. Comparing with 2,3- dimethyl butane the influence of the additional C_5 carbon on the chemical shift can be taken into account on the base of the data of LINDEMANN and ADAMS. Thus the signals of the gauche$^+$ conformer of the 2,3- dimethyl pentane are calculated from the spectrum of the 2,3- dimethyl butane: C_1 = 12,5 , C_2 = 29,0 , C_{2M} = 20,4 , C_3 = 38,5 , C_{3M} = 10,2 and C_4 = 28 ppm. The higher intensity signals are in excellent agreement with the calculated ones. Consequently, they have been assigned to the gauche$^+$ conformation. Analogously, the less intensive signals - 32,1 , 19,5 , 16,7 , 13,1 and 11,1 ppm - are assigned to the gauche$^-$ conformer. No signals have been detected for the anti conformer.

Figure 3 gives the spectra of the 3,4- dimethyl hexanes. Because of the two chiral carbons two diastereomers exist, the meso and the dl one. They both show well resolved caolescence signals, which again can be interpreted according to LINDEMANN and ADAMS. The pure meso compound has been synthesized in order to make an unequivocal assignment with respect to the configuration.

With decreasing temperature the signals of the meso isomer show a strong exchange broadening, whereas the dl isomer exhibits minor broadening. Below the coalescence temperature the meso signals are splitting pairwise, whereas the dl signals shift only slightly their position. Such a small coalescence broadening is typical for the situation where two discrete signals of very different intensity arise. Then the situation of the signals below and above coalescence do not differ significantly. The assignment of the signals at 85 K has been acheived by comparison with the spectra of 2,3- dimethyl butane and 2,3- dimethyl pentane. One finds that both - meso and dl 3,4- dimethyl hexane - are occuring below 100 K in one single conformation only, the dl- isomer in the gauche$^+$, the meso in the gauche conformation. For meso gauche$^+$ and gauche$^-$ are mirror images and are consequently identical. The meso conformer signals are split with 1/1 intensity, because the carbons of identical configuration within the molecule are no more equivalent in the gauche conformation.

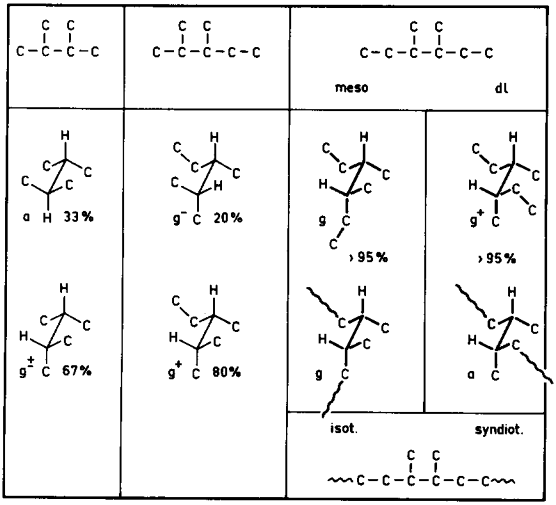

Table I: Populations of the low molecular weight models for the H- H- polypropylenes. Definition of the conformers for low and high molecular weight molecules

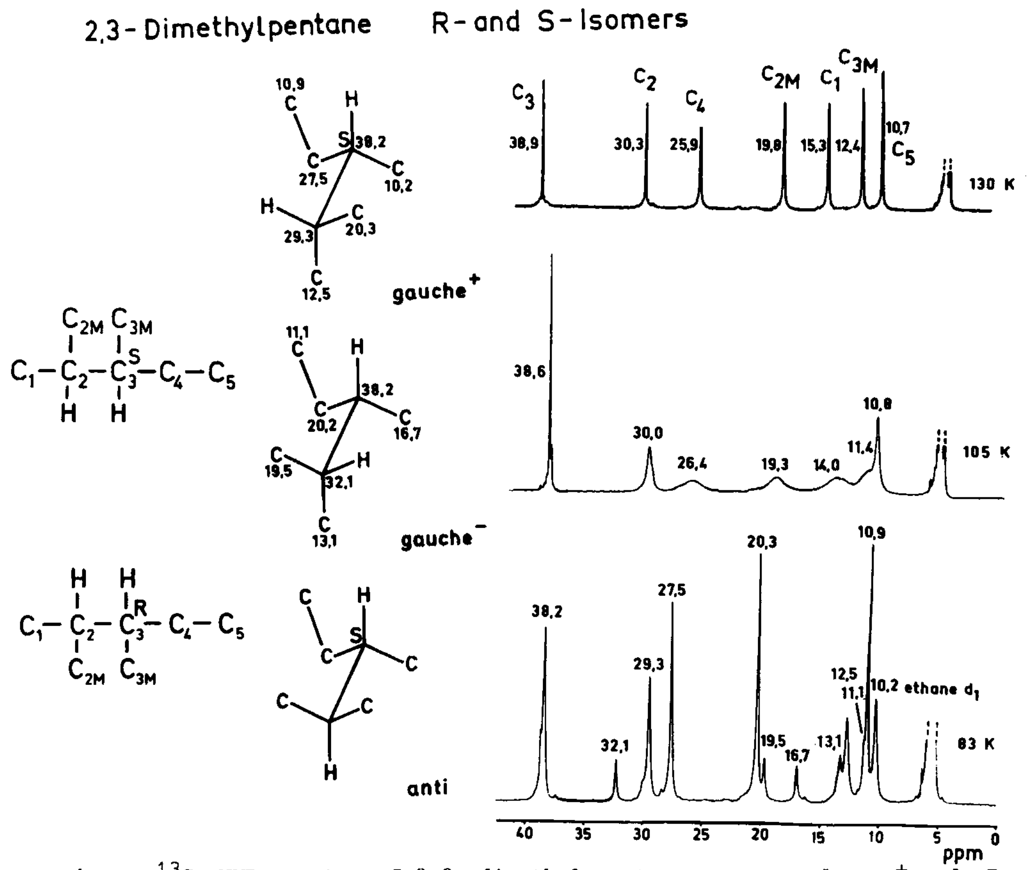

Figure 2: Fast and slow exchange ^{13}C- NMR spectra of 2,3- dimethyl pentane; staggered a, g^+ and g^- conformers

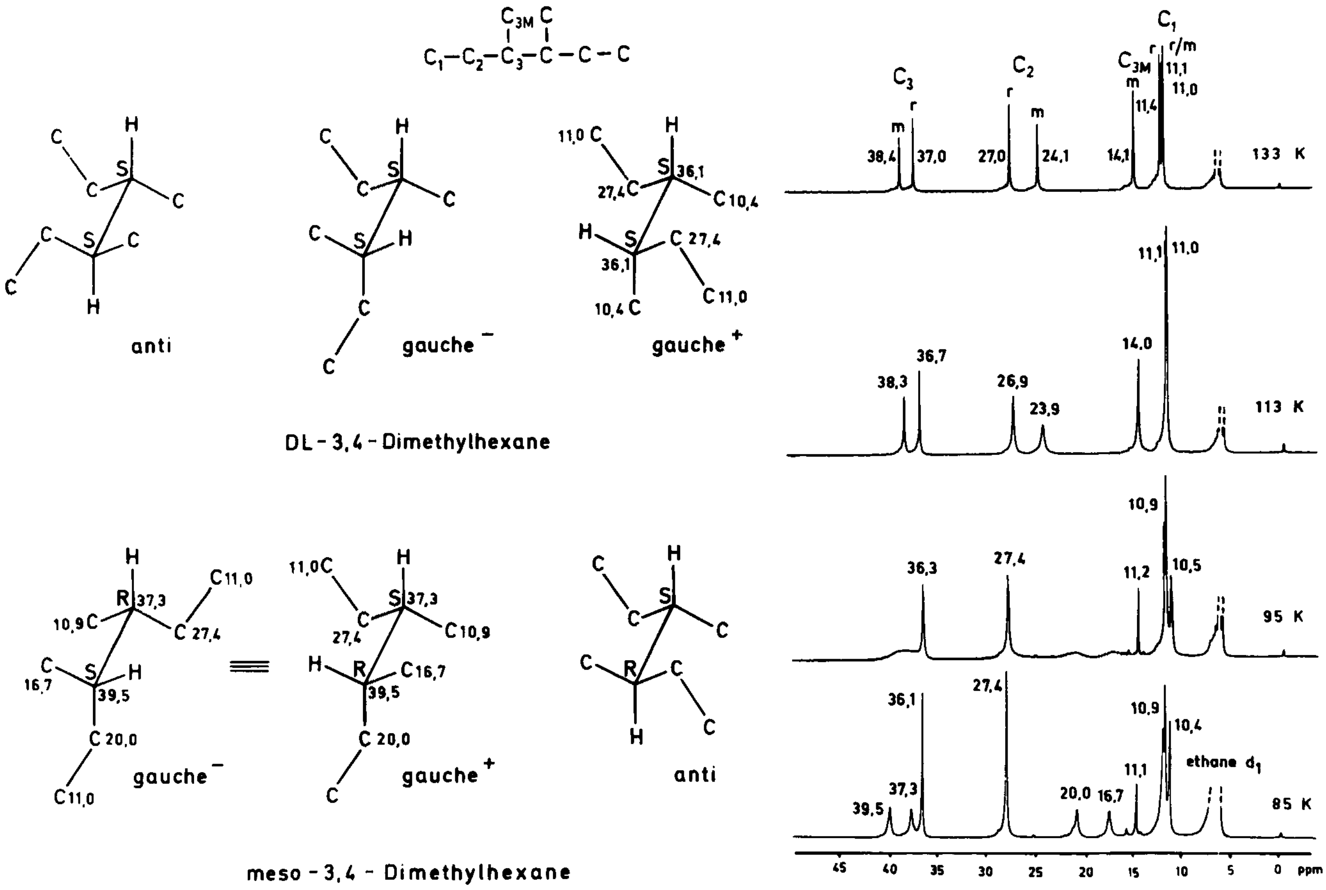

Figure 3: Fast and slow exchange ^{13}C- NMR spectra of meso- and dl- 3,4- dimethyl hexane; staggered conformers

As stated before in the organic chemistry the definition of the conformation is related to the situation of the hydrogen atoms. For a polymer, however, we have to relate the conformation to the situation of the macromolecular chain. This situation is demonstrated in Table I. Thus for gauche$^+$ as the most stable conformer for the low molecular weight dl compound, anti turns out to be the most stable microconformer within syndiotactic inverted polypropylene. For isotactic H-H- polypropylene, however, as well for its representative low molecular weight model - meso 3,4- dimethyl hexane - gauche is the most stable conformer. If one assumes that the macrodimensions of the macromolecules can be calculated by adding up the effects of the short subunits, the gauche tendency of the subunits with increasing temperature will induce a corresponding tendency to the syndiotactic head-to head chain, namely to decrease the unperturbed macrodimensions. The macroconformation of isotactic inverted polypropylene on the other hand will exhibit a tendency to increase with the temperature, because the higher energy anti conformation of the subunits increase. For a definite analysis, however, one has not only to take into account the relative situation of the methyl side groups. The conformational situation around the methine- methylene as well as of the methylene- methylene bonds will also change with temperature. For the latter type of bonds it is highly probable that they will induce a stiffening effect to the macromolecular chain with decreasing temperature because of increasing anti- tendency of the CH_2- CH_2- subunits, in parallel with the polyethylene situation. This would assist the effect of decreasing the macroconformation of syndiotactic H-H- polypropylene with increasing temperature and counteract the increasing macroconformation tendency of isotactic inverted polypropylene. The influence of the conformation around the methyl substituted methines, however, will be dominant.

Work is under way to analyze the temperature dependence of the populations of the conformations around these other bonds in order to make definite predictions on the temperature dependence of the macroconformations of the inverted polypropylenes of different configuration. Direct measurements on the macroconformations are also planned. They should show, to which extent an influence of neighbouring subunits will exhibit additional influence, i. e. whether erythro- and threo-diisotactic inverted polypropylene will exhibit different temperature dependence of the unperturbed macrodimensions. Finally, the experimental conclusions will be compared with the results of semiempirical conformational energy calculations 7).

From the temperature dependence of the coalescence signals and from the discrete signals of the conformers in the slow exchange region it can be concluded that the energy difference between the conformers is increasing with the length of the molecule under consideration, whereas the minimum energy shift differences are practically invariant. The quantitative numbers will be reported in the subsequent paper as well as the rotational barriers between the conformers. Furthermore, an approach to determine the populations of the conformers in polymers by measurements under fast exchange conditions only will be proposed.

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