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Micro- and Macroconformation of Macromolecules

4. Microconformation of Erythro-Ditactic Inverted Polypropylenes and of Their Low Molecular Weight Analogs from Fast Exchange NMR-Measurements

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SUMMARY

From ^{13}C- NMR chemical shift measurements under fast exchange conditions it is concluded that meso- 4,5- dimethyl octane as well as meso- 5,6- dimethyl decane are representative low molecular weight models for erythro-diisotactic inverted polypropylene. The macromolecule and its models exhibit identical temperature dependence of the chemical shift of the methyl carbon and, consequently, identical temperature dependence of the populations of the conformers of the head-to head diad and identical energy differences between the competing anti and gauche conformers. This fact seems to be remarkable because the macromolecule has to move in a cooperative manner at a segmental level, whereas the models may move freely in an isotropic manner. As a further consequence of the experimental findings all erythro- type inverted polypropylenes may be represented by the low molecular weight 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 are discussed.

INTRODUCTION

Recently in this journal we have reported 1) 2) effects of chain microconformation on the temperature dependence of the chemical shift of fast exchange ^{13}C- NMR signals of coiled macromolecules and their low molecular weight segmental models. For inverted polypropylenes we derived conclusions on the rotational states of the head-to head bond. The temperature dependence of the methyl group ^{13}C- NMR signal of erythro- diisotactic head-to head - tail-to tail polypropylene has been compared to that of low molecular weight models representing the head-to head diad, 2,3- dimethyl butane, 2,3- dimethyl pentane and meso- 3,4- dimethyl hexane. The temperature

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dependence of the chemical shift has been interpreted in terms of the dependence of the populations of the conformations around the CH-CH - bond on temperature. For 2,3- dimethyl butane and meso- 3,4- dimethyl hexane we could verify the chemical shift of the conformers under slow exchange conditions. Thus we have demonstrated that the conclusions derived from the fast exchange measurements are consistent. For the energy gap per mol between anti and gauche conformers we concluded 360 J for 2,3-dimethyl butane and 1880 J for meso- 3,4- dimethyl hexane. For the polymer we have calculated 4100 J assuming that in the macromolecular chain two low energy rotamers are competing in a temperature dependent manner.

The crucial question, however, remained open, namely wether the different energy gap between the conformers of the meso- 3,4- dimethyl hexane and of the macromolecules is caused by an insufficient length of the low molecular weight model or wether it is a specific macromolecular effect.

MEASUREMENTS AND DISCUSSION

In order to clarify this question we have carried out fast exchange NMR measurements on meso- 4,5- dimethyl octane and additionally on meso- 5,6- dimethyl decane, which offer representative models with one and with two more methylene groups on each side when compared with meso- 3,4- dimethyl hexane. Figure 1 represents the plot of the ^{13}C- NMR chemical shifts of the methyl carbon signals for the macromolecule and its models versus the inverse temperature, in the coalescence region. For the meso- 3,4- dimethyl hexane the slow exchange data are given additionally.

It is evident that there is no significant difference in the temperature dependence of the chemical shift between erythro- diisotactic inverted polypropylene and its "longer" models, meso- 4,5- dimethyl octane and meso-5,6- dimethyl decane. Consequently the temperature variant balance of the competing rotamers around the head-to head diad is concluded to be identical for the macromolecule and its models. Apparently the ditactic macromolecule does not show up conformational influences on the methyl group chemical shift arising from the adjacent disubstituted groups separated by two methylene groups from each other. Because their relative configuration is irrelevant concerning the chemical shift, all erythro-type head-to head sequences - erythro- disyndiotactic and erythro- atactic - should show up identical temperature dependence of the CH_3- chemical shifts like the erythro- diisotactic macromolecule. The experimental proof is given in Figure 1, where the chemical shifts of an erythro-atactic polymer coincide the data of the erythro- diisotactic one.

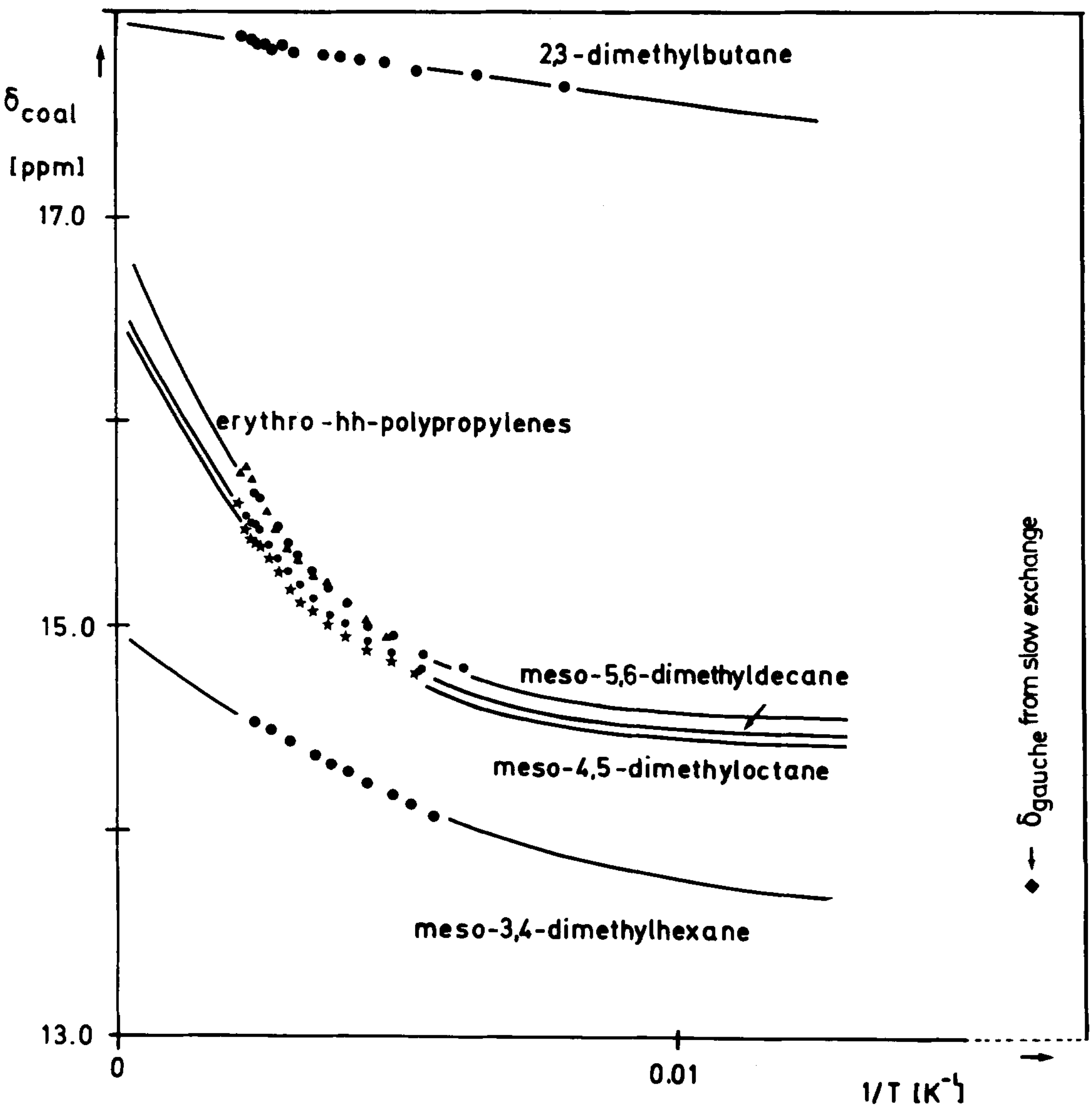


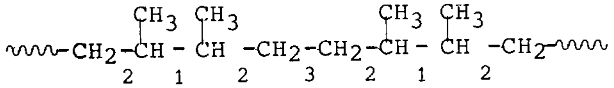
Figure 1: Chemical shift δ_{coal} for the metyl carbons versus 1/T. From top to bottom: 2,3- dimethyl butane (●), erythro- diisotactic(●)and erythro- atactic (▲) inverted polypropylene, meso- 5,6- dimethyl decane (o), meso- 4,5-dimethyl octane (✱)and meso- 3,4- dimethyl hexane (●). Chemical shift δ for the g-conformer of meso- 3,4- dimethyl hexane, from slow exchange data, is marked (◆)

It may be worthwile to note that the macromolecules and their representative low molecular weight models exhibit identical temperature dependence of the conformers populations, irrespective the fact that the latter can move freely in an isotropic manner, whereas the former have to carry out cooperative motions at segmental level. Thus concerning the populations of the conformers around the disubstituted bond no macromolecular effect exists.

The difference in the energy gap between the macromolecules and their short model, meso- 3,4- dimethyl hexane, seems to be due to the different effect of the bonds adjacent to the CH-CH - bond in the small molecule. Because these parts of the molecule have endgroup character the conformational freedom is higher than for the macromolecular chain. This may explain that only the longer model molecules are satisfying models for the macromolecules. Slow exchange measurements on these longer model molecules are in progress in order to further elucidate the problem of microconformation at segmental level. Furthermore spin- lattice relaxation investigations may yield more insight into the mode of motion of the macromolecules when compared with their representative models.

At this time theoretical models for the chain dynamics include the assumption that the conformers engaged in the cooperative crankshaft motions are isoenergetic. The data presented may enhance to develop motion models, where competing effects arising from conformers with differing energy are engaged.

Finally consequences of our conclusions on the microconformation of erythro- type inverted polypropylenes concerning their unperturbed macroconformation may be discussed. Such macromolecules exhibit three types of bonds. By the temperature dependence of the conformational balance of all of them the macroconformation is built up.



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As demonstrated by the NMR- investigations gauche is the lowest energy conformer for the CH- CH - bond in the erythro- type macromolecules. Thus the increase of the anti- conformer induces a component for a coil expansion with increasing temperature. Semiempirical atomistic calculations are in progress, which take into account three- bond systems [3]. Thus the influence of the neighboured 2- type bonds may be included into the analysis of the conformational balance. The energy difference between the conformers around the CH_2-CH_2 - bond (type 3) finally should be similar to that of polyethylene, around 2 kJ/mol. Than the temperature dependence of the unperturbed macrodimensions should be calculable by combining the findings of independent investigations, NMR measurements and semiempirical atomistic three- bond calculations. It seems to be highly probable that the macrodimensions of erythro- type inverted polypropylenes will increase slightly with increasing temperature. Threo- type macromolecules, however, should shrink with increasing temperature, because anti is the dominant conformation around the CH-CH - bond at low temperature [2]. Thus, by preparing configurational copolymers with an appropriate ratio of erythro- and threo- subunits, macromolecules with temperature invariant macrodimensions may be realizable. They should exhibit, consequently, no energy contribution to their elastic behaviour in the rubbery state. Such quasi- isoenergetic macromolecules, as the consequence of an internal conformational balance, have been reported by us recently: statistical 1,4- polybutadienes containing cis- and trans-subunits 4).

Another point of scientific interest may be the glass transition behaviour of the inverted polypropylenes. The heigths of the rotational barriers are decreasing from the 1- type to the 2- and the 3- type bond. The temperatures of broadening of the respective NMR- signals may yield information concerning those barriers arising from intramolecular effects. Combination with findings from mechanical- dynamic investigations may offer a chance to separate intra- and intermolecular influences which, in combination, cause the glass transitions.

EXPERIMENTAL

The ^1H broad band decoupled high- resolution nuclear magnetic resonance spectra were obtained in the same way as reported before 2).

4,5- dimethyl octane and 5,6- dimethyl decane were synthesized as mixtures of the meso- and the d,l- diastereomers in the way described for the 4,5- dimethyl octane.

By the reaction of 0,36 moles bromomagnesium- pentane- 2 with 0,29 moles pentanone- 2 in 150 ccm of diethyl ether 4,5- dimethyl octanol- 4 was synthesized. The product was worked up in the usual way. By destilling the crude 4,5- dimethyl octanol- 4 over 2 ccm of 89 % phosphoric acid 19 g of 4,5- dimethyl octene- 4 were obtained (b.p. 160- 165°C). The 4,5- dimethyl octene- 4 was hydrogenated by the reaction with diimide and solved in 350 ccm toluene. 45 g p- toluenesulfonyl were added, and the mixture was refluxed under N_2 for 24 h. The volatile components were separated by evaporation and condensation in a high vacuum chamber and fractionated then by destillation over a 100 mm spinning band column. 6 g of 4,5- dimethyl octane (b.p. 155°C) were obtained finally.

In the same way 5,6- dimethyl decane was synthesized from 2- bromohexane and hexanone- 2 (b.p. 197- 198°C).

The indication of the ^{13}C- NMR signals to the diastereomers was possible by comparison with the spectra of 3,4-dimethyl hexane 2).

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