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8. Magic Angle ^{13}C-NMR Investigation on Linear *n*-Alkanes and Highly Mobile Phase Cyclotetracosane as Models for Solid State Polyethylene

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SUMMARY

The proton enhanced magic angle ^{13}C-NMR spectrum of cyclotetracosane exhibits one sharp signal only at room temperature indicating that all carbons within the ring have identical average conformational surrounding at the NMR time scale. A highly mobile pseudorotating phase is concluded. The average ratio of the gauche and of the anti conformers has been calculated from the chemical shift of these cyclotetracosane carbons applying the anti conformer chemical shift of n-alkanes and that of the gauche conformer derived from solution slow exchange spectra of meso 4,5-dimethyloctane. Thus, polyethylene spectra of EARL and VANDERHART could be interpreted in terms of the anti-gauche ratio within the amorphous folds of polyethylene. The conformational balance within the amorphous region of polyethylene is compared with that of erythrodiisotactic poly(1,2-dimethyltetramethylene).

INTRODUCTION

It is known since the sixties that cycloalkanes exceeding a certain length are crystallizing in a manner that two parralel relatively undistorted strands are bridged by narrow loops. An attractive model thus is offered which may simulate the noncrystalline amorphous region situated between the folded lamellae formed in melt or solution crystallized polyethylene. Neutron scattering experiments at intermediate angles 1) offer the chance to get insight into segmental dimensions. YOON and FLORY just succeeded 2) to analyze the scattering envelope in terms of amorphous folds in polyethylene and in polypropylene. They concluded that adjacent reentry of the loops is higly improbable.

Whereas in neutron scattering the effects arising from crystalline as well as from amorphous regions overlap, proton enhanced NMR under magic angle condition yields well resolved resonances for both regimes as demonstrated for semicrystalline poly(1,2-dimethyltetramethylene) in the preceeding paper 3). In the following we try to demonstrate that a quantitative analysis of the balance of the rotamers being present within the amorphous loops of polyethylene may be effected applying slow exchange data derived from low molecular weight model compounds. Spectra by EARL and VANDERHART have been evaluated by this approach 4).

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EXPERIMENTS AND DISCUSSION

In preceeding papers we have reported that chemical shift measurements in solution, with the ^{13}C nucleus as indicator, can deliver precise results on the temperature dependence of the conformational balance of macromolecules, with ditactic poly-(1,2-dimethyltetramethylene)s as examples $^{5)}$. A first chance for conformational analysis in the solid state has been offered by BRUKER, Karlsruhe, Dr. FÖRSTER, which enabled the evaluation of crystalline and amorphous regions in diisotactic poly(1,2-dimethyltetramethylene) in the solid state at ambient temperature.

Thus, PE-MAS measurements have been carried out at 303 K, 75.42 MHz ^{13}C, with pentatriacontane and tetratetracontane, as models for the all-anti chains within PE lamellae, and with cyclotetracosane the model containing loops. The cyclic sample had been synthesized by metathesis reaction of cyclodecene and subsequent hydrogenation $^{6)}$.

Figure 1 shows the solid state PE-MAS ^{13}C spectra of the cycloalkane and both the linear alkanes. The chemical shifts indicated are related to TMS in $CDCl_3$ solution. They result from the chemical shifts of the adamantane solid phase signals when compared with those of the samples measured. The latter were assumed to be equal to the adamantane shifts when compared with TMS in $CDCl_3$ solution. The solid state chemical shifts may be compared directly with the corresponding shifts in solution, consequently.

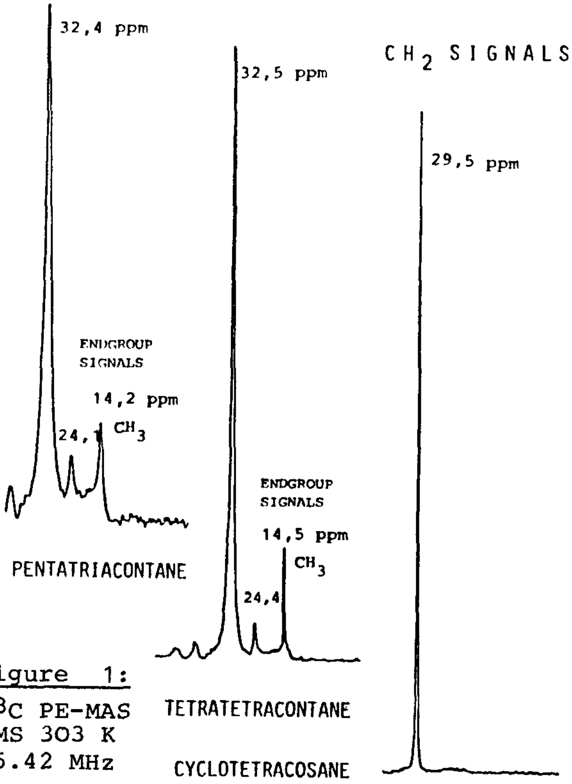

Figure 1:
^{13}C PE-MAS
TMS 303 K
75.42 MHz

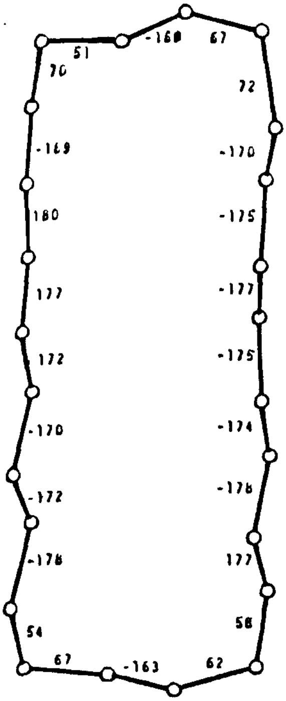

Figure 2: Conformation cylotetracosane -160° C rot. angles indic. GROTH

As expected the signals of both the linear alkanes do not differ irrespective the fact that both exhibit different crystal structure. The conformation of the chain bonds is effective only in the NMR experiment. The cyclic $C_{24}H_{48}$, however, shows up fascinating behaviour at room temperature: One sharp signal only occurs irrespective the fact that X-ray analysis presents one third gauche and two thirds anti conformations, with relatively low distortions of the bond angles 7) (Figure 2). This single sharp resonance of the cyclotetracosane is shifted 3 ppm upfield when compared with the anti rotamers signal of the n-alkanes. This may be interpreted, consequently, that for all C-atoms within the ring all the conformations of adjacent bonds are exhibiting identical gauche-anti populations, with fast transitions between the conformers. Oscillating motions of the respective atoms around differing equilibrium positions would yield three signals for the conformation shown in Figure 2. A broad signal could be understood in this case which may be built up by an overlapping of those three subsignals. Comparison of the linewidth of the cyclotetracosane signal with that of the n-alkanes, however, demonstrates that such an interpretation is unrealistic. Thus, the cyclic molecule exhibits even in the crystalline state high internal mobility. The ^{13}C NMR spectrum of cyclotetracosane clearly indicates that, besides the melt transition, further phase transitions have to be expected which are connected with freezing of those motions. Relevant investigations in the solid state as well as in the melt will be reported in the following paper, which strongly support the conclusions derived from NMR 8). The extreme mobility indicated by the solid state ^{13}C-NMR measurements on cyclotetracosane at ambient temperature is compatible with empirical and theoretical results on pseudorotation in smaller rings, by F. A. L. and R. ANET 9) and by J. DALE 10). Up to now it was not possible to execute temperature dependent ^{13}C solid state measurements with magic angle spinning. Such measurements should yield very exact conclusions concerning the conformations and the dynamic processes in cyclic molecules.

In the following the differing chemical shift of the cycles signal (3 ppm upfield the anti signal of the n-alkanes) and of that of the amorphous part of polyethylene (2.3 upfield according to EARL and VANDERHART 4)) may be discussed. The resonances of the n-alkanes and of the crystalline regions of polyethylene may be assumed to be identical, even if the chemical shift given for the latter by EARL and VANDERHART differ with 2 ppm from our n-alkane values, in consequence of different methods of the determination. This deviation is unsubstantial, however, for the following discussion because it is additive for all signals, crystalline or amorphous.

Because the cyclotetracosane signal shows up higher upfield shift than the signal of the amorphous part of polyethylene it is concluded that the C_{24} paraffinic cycle contains a higher amount of gauche conformers than the amorphous folds of the PE ($\delta^{s}_{PEcr} = \delta^{s}_{C_{44}H_{90}} = 32.5$, $\delta^{s}_{PEam} = 30.2$ and $\delta^{s}_{C_{24}H_{48}} = 29.5$ ppm TMS, ^{s} indicating solid state chemical shift). In $CDCl_3$ solution the cyclotetracosane chemical shift is very similar to that in solid state, 29.4 ppm, whereas the chemical shift of the n-alkanes, the models for polyethylene in solution, is situated downfield the solid state PE_{am} shift at room temperature.

When the chemical shift difference between the anti and gauche rotamers is known the solid state ^{13}C chemical shift of cyclotetracosane can be related to that of the n-alkanes, with p_g the amount of gauche conformation within the cyclic molecule:

$$\delta^{s}_{C_{24}H_{48}} = \delta^{s}_{C_{44}H_{90}} - \Delta\delta_{g-a} \cdot p_g \qquad (1)$$

Effectively, as to be demonstrated in a following paper, it is possible to derive numbers of the conformational chemical shift difference, $\Delta\delta_{g-a}$, from slow exchange measurements on meso and d,l 4,5-dimethyloctane or 3,4-dimethylhexane, resp. An upfield shift of ∿ 7.5 ppm has been found for conformers exhibiting atoms situated gauche with respect to the nucleus observed when compared with those with the γ-C atoms in anti position. Thus, p_g for the cyclotetracosane is concluded ∿ 0.41. This value exceeds the gauche content of 1/3 as derived from the X-ray analysis carried out at -160° C, if one inserts the undistorted bond angles for the chemical shift calculation. Figure 2 demonstrates, however, that those angles are distorted to a certain extent. Thus, deviations of the anti conformers rotational angle systematically would shift downfield somewhat with an apparent increase of the gauche content determined by NMR chemical shift. Furthermore the rotational angles may deviate even more from the stable staggered conformations and specific defect structures may be included within the pseudorotating phase.

Arguing analogously the gauche content within the amorphous phase of polyethylene turns out to be $p_g = 0.31$. The somewhat higher chemical shift of the n-alkanes in solution and of amorphous polyethylene, consequently, may indicate an increased amount of anti situated bonds when compared with the conformational balance within the amorphous folds within semicrystalline polyethylene. At this time it seems to be hazardous, however,to conclude concerning the type of backfolding of the chains within the folded lamellas. Adjacent reentry seems to be higly improbable because of insufficient gauche content within the amorphous region, thus affirming YOON's and FLORY's conclusions from neutron scattering [2]. The transition from the adamantane to the TMS reference, however, includes some incertainity when discussing absolute shift data derived from solid phase and from solution spectra, resp. As a consequence of the method for conversion of the reference bases, however, shift differences caused by other influences than conformational ones should be cancelled essentially, which may be based on differences in density and by specific differences in the magnetic susceptibility and in specific intermolecular interaction in the solid state. Furthermore, the exactness of determining the chemical shift of the C-atoms within the polyethylene chain being adjacent to gauche bonds should be improved. If it succeeds to realize these signal position as exact as that of the C-atoms within the crystalline anti sequences conformational energies should be determinable very exactly.

One interesting detail may be discussed finally, namely that the chemical shift of the solid cyclotetracosane in the pseudorotating status is nearly identical with that of the ring molecule in solution. Evidently the conformational balance is not depending critically wether the molecule shows up its crystalline habitus, with two parallel strands, or its free shape in solution.

In conclusion macromolecules show up comparable chemical shifts in solution as well as in the amorphous molten state. The signals of the crystalline regions are resolved significantly superior. As the consequence of the identical conformations they show up different chemical shifts, which are comparable with the spectra measured in solution under slow exchange conditions. In the glassy amorphous state the mean part of the line broadening observed is the consequence of the differences of the isotropic chemical shifts due to the rotational isomeric polymer segments, beside the fact that amorphous polymers in the glassy state show up broader lines than crystalline ones, $\Delta\nu_{1/2} = 1/T_{2C}\pi$ 11) 12). Solid state NMR under magic angle conditions should develop as a powerfull tool in determining the conformational balance in semicrystalline and amorphous, rubbery as well as glassy, polymers, especially when combined with investigations in solution.

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