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7. Crystalline and Amorphous Phase Conformational Analysis in Semicrystalline Polymers by ^{13}C-NMR Under the Magic Angle

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SUMMARY

By applying high resolution solid state ^{13}C-NMR with proton enhancement and with magic angle spinning technique it is demonstrated that the rotational states in semicrystalline polymers may be analyzed for the crystalline as well as for the amorphous phase. In erythrodiisotactic poly(1,2-dimethyltetramethylene) the signals of the chemically different nuclei could be distinguished in the crystalline and in the amorphous regions. The interpretation of the solid state spectrum is consistent with the solution spectrum of the polymer and with that of the analogous low molecular weight compound, meso 4,5-dimethyloctane, under slow exchange conditions. It is concluded that the crystalline parts of the macromolecular chain exhibit $g^+aaag^-aaag^+$... conformation (gauches for the CH-CH bond), which is in agreement with the X-ray structure analysis by NATTA et al. Another stable conformation derived from semiempirical atomistic calculations could be excluded for the crystalline phase. An estimation of the conformational balance in the amorphous state has been achieved by comparing the relevant shift data of the solid state erythrodiisotactic poly(1,2-dimethyltetramethylene) with those occuring in the fast exchange spectrum measured in solution.

INTRODUCTION

In preceeding papers of this series high-resolution ^{13}C-NMR investigations on ditactic poly(1,2-dimethyltetramethylene)s and on their low molecular weight analogs in solution have been reported 1-3). From ^{13}C chemical shift under fast exchange conditions it has been concluded that meso-4,5-dimethyloctane is the low molecular weight model representative for erythrodiisotactic poly(1,2-dimethyltetramethylene). The temperature dependent populations of the conformers competing within the macromolecule could be related to the fast exchange chemical shift, in agreement with slow exchange data measured on the low molecular weight models. Assignments for all types of carbons within the polymers of different tacticities have been made.

Conventional high-resolution NMR measurements are limited, however, to the solution or the molten state because of sufficient mobility within the flexible chains. Modern solid state NMR-techniques - spinning under the magic angle combined with proton enhancement - allow, however, to resolve the signals of discrete

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rotational isomeric states of molecular segments. By curtesy of Dr. FÖRSTER, BRUKER, Karlsruhe, the chance has been offered to perform solid state ^{13}C-NMR measurements on poly(1,2-dimethyltetramethylene)s on the BRUKER CXP-300 instrument. Because investigation could be carried out at ambient temperature only, partially crystalline erythrodiisotactic poly(1,2-dimethyltetramethylene) was investigated. It offered the chance to analyze discrete signals arising from crystalline as well as from amorphous phase and to correlate them with the solution data.

EXPERIMENTS AND DISCUSSION

Melt and glass transition have been determined 343 and 240 K by differential scanning calorimetry. Figure 1 presents the PE-MAS ^{13}C-NMR spectrum of erythrodiisotactic poly(1,2-dimethyltetramethylene) at 303 K, 75.42 MHz, together with the $CDCl_3$ solution spectrum registered at the same temperature. Both spectra are related to TMS as standard, the originally adamantane related solid state chemical shifts being converted for TMS standard as described later on [4]. Due to the type of synthesis - by cis-butene-2 - ethylene copolymerization - the sample contains longer ethylene sequences besides the head-to-head tail-to-tail propylene sequences. This is visible in the solution spectrum by the signal at 29.91 ppm and by some signals of minor intensity arising from intersteps between hh-tt propylene and ethylene sequences and by non-quantitative stereoregularity. 37.96, 31.11 and 16.75 ppm are the CH-, CH_2- and CH_3-signals for the erythrodiisotactic hh-tt sequences of propylene units.

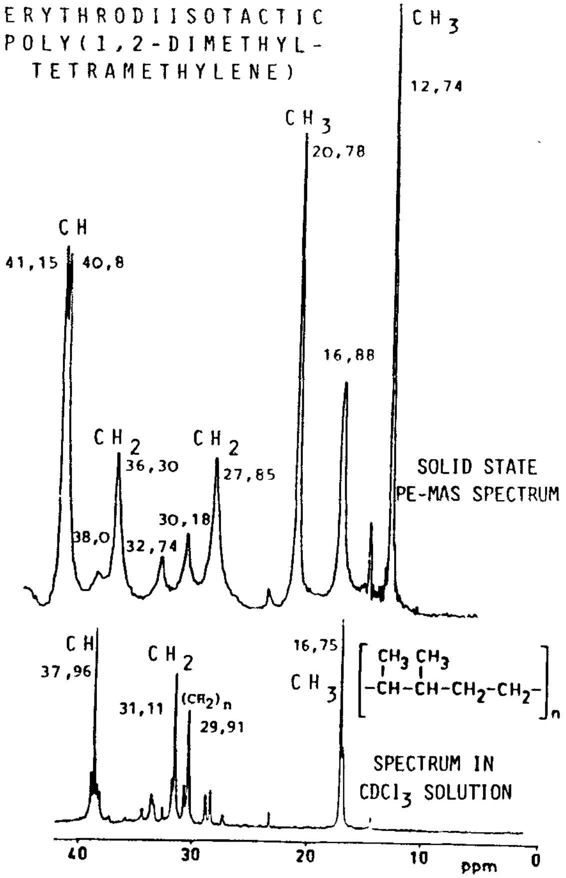

Figure 1: Solid state PE-MAS and $CDCl_3$ solution spectra of erythrodiisotactic poly(1,2-dimethyltetramethylene), 303 K, 75.42 MHz, TMS

As expected the solid state spectrum differs significantly from the solution spectrum. The intensities of signals arising from carbon atoms of different mobility are influenced strongly be the choosen cross-polarization times. Consequently an estimation of the crystalline-amorphous ratio is not possible. The amorphous signals show up generally a little upfield the resonances found in the solution spectrum: 38.0 ppm for CH, 32.74 for CH_2 and 16.88 ppm for CH_3. These signals arising from amorphous regions existing far above the glass transition exhibit much broader profile ($\Delta\nu_{1/2}$ = 40-50 Hz) than the crystalline region signals. The signal at 30.18 ppm has to be assigned to the longer CH_2 sequences. It coincides well with the solid state signal of amorphous polyethylene [1]. The signals arising from the crystalline regions - 41.15, 40.8, 36.30, 27.85, 20.78 and 12.74 ppm - exhibit significantly smaller linewidth mostly ($\Delta\nu_{1/2}$ = 12-15 Hz). The correct assignment of the amorphous and of the crystalline signals could be verified by measurements carried out with different contact times of the ^1H- and ^{13}C-spin systems. The ^{13}C nuclei within the crystalline regions show up longer spin-lattice relaxation times than the ^{13}C nuclei within amorphous regions. Consequently their intensities diminish more with smaller cross-polarization time. This is demonstrated in Figure 2.

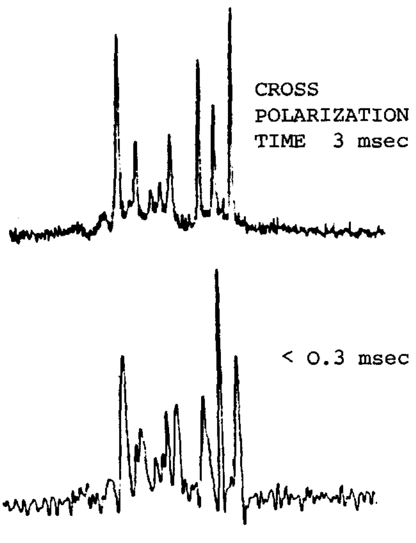

Figure 2: PE-MAS ^{13}C spectra of erythrodiisotactic poly(1,2-dimethyltetramethylene) measured at different ^1H-^{13}C contact time. Conditions like in Figure 1

The signals at 36.30 and at 27.85 ppm are shifted symmetrically upfield and downfield resp. versus the CH_2 signal of the methylene carbon within the amorphous region, 32.74 ppm. Analogously the crystalline region CH_3 signals, 20.78 and 12.74 ppm center the amorphous region signal, 16.88 ppm. Thus they show up the same splitting pattern like the CH_3 and CH_2 signals of meso 4,5-dimethyloctane for the (g) gauche conformation of the CH-CH bond in the slow exchange solution spectrum. This is demonstrated by the scheme in Figure 3. The two remaining signals at 41.15 and 40.80 ppm consequently are those of the CH atoms within crystalline regions. Their shift versus the CH signal of the amorphous region, 38.0 ppm, may be explained only partly by the rotational isomery of the

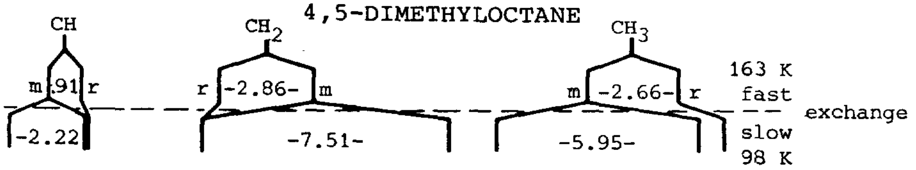

Figure 3: Scheme of the chemical shift of 4,5 dimethyloctane under fast and slow exchange conditions of the CH-CH rotamers

CH-CH bond, which does not influence the position of the C atoms situated γ towards these nuclei. γ-gauche effects for the methine atoms are caused by the rotational isomery around the $CH-CH_2$ and the CH_2-CH_2 bond. Simultaneous downfield shift of both the CH signals has to be interpreted, consequently, by an anti position of both these bonds: The NMR spectrum demonstrates that $(g^{\pm}aaa)_n$ is the conformation of the chain within the crystalline region. g^+ and g^- cannot be distinguished. It appears plausible, however, to argue that g^+ and g^- position have to alternate within the sequence because of the need of an ordered lattice: $g^+aaag^-aaag^+$.. This is exactly the conformation which was calculated from X-ray data by NATTA, CORRADINI et al. 5) for erythrodiisotactic poly-(1,2-dimethyltetramethylene), and which is shown in Figure 4.

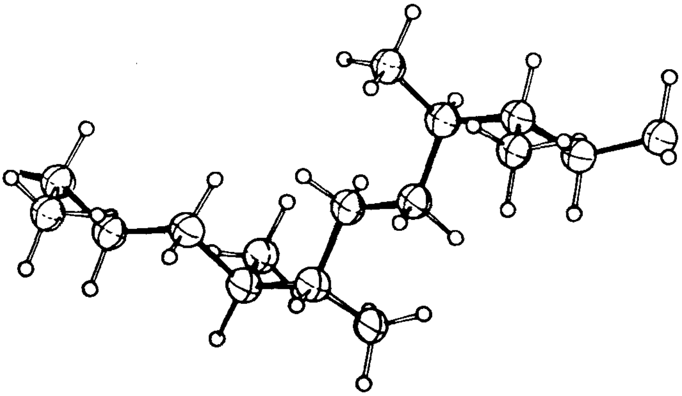

Figure 4: $g^+aaag^-aaag^+$... conformation of erythrodiisotactic poly(1,2-dimethyltetramethylene) according to X-ray structural analysis (NATTA, CORRADINI et al.) and according PE-MAS ^{13}C-NMR analysis (this paper)

Besides this conformation semiempirical atomistic calculations of the most stable conformations of single chains performed by BECK 6) gave another possible conformation, $g^+ag^+g^+g^+a$...., according to Figure 5. This conformation can be excluded by the solid state NMR experiments. Downfield shift of both the CH_2 signals and upfield shift of one CH signal should occur.

The agreement of the conclusions from the ^{13}C-NMR specrum with the results of the

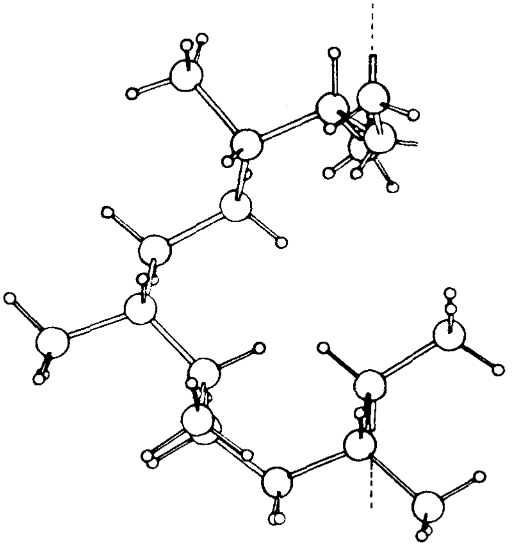

Figure 5: $g^+ag^+g^+g^+a$... conformation (6.1 helix) of erythrodiisotactic poly(1,2-dimethyltetramethylene) according to semiempirical atomistic calculations (BECK)

X-ray structural analysis demonstrates the capability of high resolution ^{13}C-NMR solid state spectroscopy for the analysis of sequences in macromolecules. Its limitation may be due to the fact that NMR offers insight only into small regions. It seems to be advantageous,however, that the information concerning the sequential arrangement is not depending on the type of crystal structure. The analysis is not limited to crystal regions. Signals of different conformers are resolved only, if the exchange is slow in comparison with the time scale of NMR spectroscopy. Temperature dependent measurements will offer excellent additional chances for structural analysis of one- and two-phase polymers. Furthermore chances are offered by relevant relaxation experiments and by line shape analysis with the aim to get information concerning the dynamics of macromolecular motions at a segmental level.

Finally, the chemical shift data of the CH_2 and the CH_3 resonances of the amorphous regions in the erythrodiisotactic inverted polypropylene may be discussed shortly. Both are situated nearly in the midle of the corresponding signals which arise from the crystalline phase, with a small downfield deviation for the methyl and a somewhat greater upfield deviation for the methylene resonance. The conclusion that the conformation in the amorphous regions would be similar to that in the crystalline domains would be allowed only under the assumption that the $CH-CH_2$ and the CH_2-CH_2 bonds are arranged all in anti also in the amorphous state. The CH signal of the amorphous part, however, demonstrates that this is not the case. It is situated a little upfield the corresponding signal in solution, thus indicating that the conformational situation in the solid amorphous state is similar to that in solution. Because all signals in the amorphous part of the solid state spectrum, CH_2, CH_3 and CH, are shifted somewhat upfield when compared with the signals in solution, one may conclude that in the amorphous parts all bonds have a more pronpunced anti tendency than, at the same temperature, in solution. This seems to be plausible for the erythrodiisotactic poly(1,2-dimethyltetramethylene), which probably contains a relatively high concentration of tie molecules in the amorphous phase. Partly they may arise from the longer methylene sequences, which are excluded from the crystalline phase and which exhibit anti conformation preferently. Effectively, no crystalline signal arising from such sequences can be detected. In contrast, for higly crystalline ZIEGLER type polyetylene an increased gauche content within the amorphous part between the well developed folding lamellas has been concluded by corresponding solid state ^{13}C-NMR investigations, as reported in the following paper 4). It may be noticed, however, that the conclusions made concerning the conformational balance within the amorphous phase include certain incertainity, due to the transition from the adamantane to the TMS reference 4). Temperature dependent measurements in the solid state may offer more precise insight into the average conformations within amorphous parts of semicrystalline polymers.

Generally, solid state PE-MAS solid state NMR - including other nuclei besides ^{13}C - seems to develop as a very promising tool in analyzing fixed as well as mobile conformations within amorphous and partly crystalline homo- and copolymers, with inclusion of segmented copolymers. It is not limited, in principle, to polymers exhibiting one crystalline phase only. Competing crystalline states, e. g. those containing helices, should be analyzable with the aid of discrete signals.

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