

**TEMPERATURE DEPENDENT MAGIC ANGLE  
SPINNING<sup>13</sup>C-NMR STUDIES OF SEMICRYSTALLINE  
POLYMERS – POLYETHYLENE AND N-ALKANES**

by

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**INTRODUCTION**

In the foregoing paper<sup>1</sup> we were concerned with the question in which way conformational mobility and intermolecular packing effects are reflected in solid state NMR-

data. Low molecular weight cyclic models for polyethylene and polydimethylsiloxane, cyclododecane and octamethyltetrasiloxane, were studied for this purpose. Comparison with the solution spectra gave evidence that in the case of octamethyltetrasiloxane, the conformational mobility is

determined significantly by the molecular packing in the crystal, while packing effects are negligibly small for cyclododecane.

Cyclic low molecular weight models may offer further insight regarding the transition between crystalline and amorphous phases with respect to the conformational characteristics of the loops<sup>2,3</sup>. Linear low molecular weight models yield corresponding information concerning the situation of the chain ends. It is the aim of the following investigations to discriminate conformational and interchain influences, at the example of polyethylenes and n-alkanes.

## RESULTS AND DISCUSSION

Figure 1 presents the <sup>13</sup>C-NMR spectrum of polyethylene at 300 K. The crystalline peak is separated by 1.8 ppm from amorphous one.

Low molecular weight polyethylenes and n-alkanes offer additional insight at a molecular level by the resonances due to the terminal methyl group and the two adjacent methylene groups.

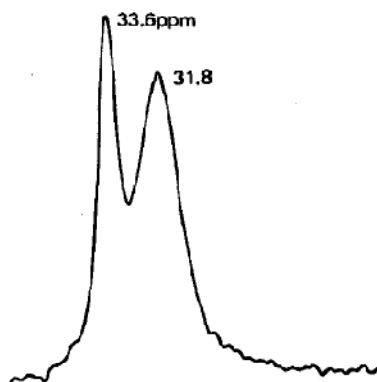


Fig. 1 MAS <sup>13</sup>C-NMR spectrum of PE, 300 K

Figure 2 shows the situation for n-hexatriacontane at 300 K. Besides the resonance for the all-anti crystalline part – at 33.6 ppm like for polyethylene – resonances are visible for the -CH<sub>3</sub>, for the -CH<sub>2</sub>-CH<sub>3</sub> and for the -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> group.

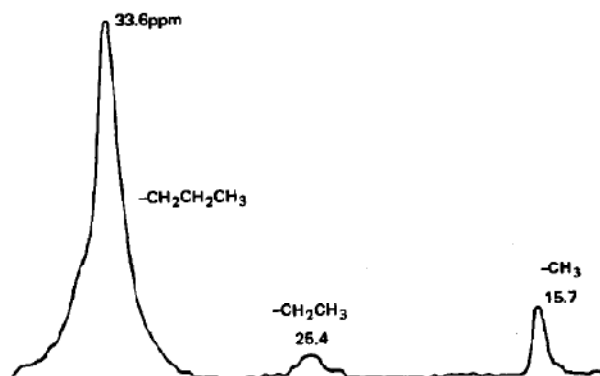


Fig. 2 CP-MAS <sup>13</sup>C-NMR spectrum of n-hexatriacontane, 300 K, contact time 3 sec.

As indicated by Figure 3, lower trace, the resonances for -CH<sub>3</sub> and -CH<sub>2</sub>-CH<sub>3</sub> of the n-hexatriacontane are splitted, when increasing the temperature to 333 K. At even higher temperatures near the melting point (349.3 K), the -CH<sub>3</sub> downfield signal finally disappears. The CH<sub>2</sub>-CH<sub>3</sub> signal behaves similarly at slightly higher temperature. This phenomenon has been observed for samples up to C-48.

However, melt crystallized, carefully annealed (388 K) n-octahexacontane (C-168), which exceeds the critical folding length, shows up the double peak even at 300 K, far below the melting point of 397 K (middle trace). In addition, irrespective of its monodispersity, an 'amorphous' shoulder arises. Low molecular weight polydisperse polyethylene with a similar M<sub>w</sub> like n-C-168 (upper trace) shows up similar behaviour, with a better resolved 'amorphous' resonance.

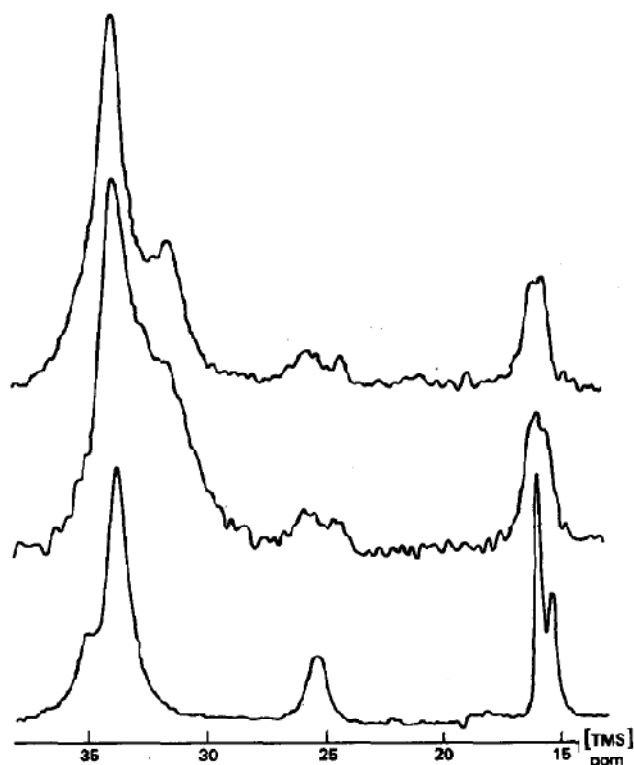


Fig. 3 CP-MAS <sup>13</sup>C-NMR spectra, contact time 3 m sec

Upper trace:  
Polyethylene  
M<sub>w</sub> = 2200, 300 K  
Middle trace:  
n-C<sub>168</sub>H<sub>338</sub>, 300 K  
Lower trace:  
n-C<sub>36</sub>H<sub>74</sub>, 333 K

The NMR data on n-hexatriacontane may be explained by changes in the molecular surrounding of the outer groups. In the pseudohexagonal solid state the mobility of the chains is enhanced. Flip-flop-screw motions are possible with the consequence of an increasing roughness of the lamellar surfaces. The splitting of the signals may be caused by differing conformational situations of terminal groups

situated near the surface of the crystal and of more distant ones. No longer loose ends than  $-\text{CH}_2-\text{CH}_2-\text{CH}_3$  occur at 333 K as concluded from the absence of an 'amorphous' peak indicating groups longer than  $-\text{[CH}_2\text{]}_3-\text{CH}_3$ .

Melt crystallized n-octahexacontahectane builds up 'fringes' longer than  $-\text{[CH}_2\text{]}_3-\text{CH}_3$  apparently at room temperature. Splitted signals for the terminal groups and 'amorphous' resonance arising from the longer pendant groups enable a consistent interpretation. Kinks within the crystalline regions as a source for the 'amorphous' peak can be excluded, because spin-lattice relaxation studies indicate a high mobility of the latter component, which is comparable with that of the amorphous region of high molecular weight polyethylene. The amorphous part in melt crystallized n-C-168 is estimated around 2% from dipolar decoupled experiments under conditions, where the crystalline part is fully relaxed. Fringes  $-\text{[CH}_2\text{]}_3-\text{CH}_3$  and longer contribute to this signal. If one takes into account the additional pendant groups, which do not exceed  $-\text{[CH}_2\text{]}_2-\text{CH}_3$ , the total amount of fringes may add up to around 5%. Their average length is about  $-\text{[CH}_2\text{]}_4-\text{CH}_3$ , consequently.

The conclusion of the existence of a small amorphous part in melt crystallized n-octahexacontahectane is consistent with the data from the longitudinal acoustic vibrations in the Raman spectrum. A crystal thickness of 213 Å has been found here<sup>4</sup>, which coincides with the length of the fully extended chains. Taking into consideration the experimental error in deriving the crystal thickness from Raman data, effective dimensions of the crystallites from 202 Å are acceptable.

NMR studies on solution crystallized n-C-168, where Raman and X-ray low angle data gave indication for folding<sup>4</sup>, are in progress.

## CONCLUSIONS

Magic angle spinning <sup>13</sup>C-NMR studies have been carried out on n-hexatriacontane, n-octahexacontahectane and low

molecular weight polyethylene in order to elucidate the conformational characteristics of loose ends in polyethylene. The NMR-data on n-hexatriacontane near the melting point may be explained by changes in the molecular surrounding of the outer groups. In the pseudohexagonal solid state the mobility of the endgroups is enhanced, with the consequence of an increasing number of loose ends with a maximum length of  $-\text{[CH}_2\text{]}_2-\text{CH}_3$  on the lamellar surface.

n-Octahexacontahectane is a linear model for polyethylene, which exceeds the critical folding length of the latter. However, at room temperature the melt crystallized, carefully tempered sample shows up a crystal thickness of about 202 Å, with amorphous fringes of an average length around  $-\text{[CH}_2\text{]}_4-\text{CH}_3$  as concluded from the 'amorphous' peak and from the signals of the terminal groups. Polydisperse low molecular weight polyethylene with a similar  $M_w$  like the n-C-168 exhibits similar characteristics like the monodisperse model, besides a more developed amorphous part which indicates a minor amount of the longest fringes and some loops, eventually, when compared with those in n-octahexacontahectane.

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## REFERENCES

- 1 D. Emeis, H.-J. Cantow and M. Möller, *Polymer Bull.* in press.
- 2 H.-J. Cantow, D. Emeis, W. Gronski, A. Hasenhiendl, D. Lausberg, M. Möller and Y. Shahab, *Makromol. Chem., Suppl.* 7, 63 (1984).
- 3 M. Möller, W. Gronski, H.-J. Cantow and H. Hoeker J. *Am. Chem. Soc.* 106, 5093 (1984).
- 4 K.-S. Lee, Dissertation Freiburg (1984).