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Pulsed NMR Measurements on Polyethylene Melts

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Summary

NMR measurements were carried out for studies on polyethylene fractions in the melt using Hahn´s spin echo technique and the MW4 pulse sequence. The decays of transverse magnetization M(t) and the line shape function S(f) are discussed.

1. Introduction

Depending on molecular weight the transverse proton magnetization M(t) of polyethylene (PE) melts is observed to possess more or less nonexponential behaviour. A nonexponential correlation function is expected because of the complicated, mostly anisotropic motions in a melt. So the line shape S(f) (the fourier transform of M(t)) may be described by a socalled super-Lorentzian (SL) line shape function (DOSKOCILOVA,SCHNEIDER 1979) containing static contributions especially in its wings, which cannot be averaged out in the NMR time scale (residual dipolar broadening). Only with fast sample rotation around the magic angle (DOSKOCILOVA 1979) the static contributions may be removed. Exponential behaviour of M(t) means a Lorentzian line shape of S(f).

In this study was examined with the help of the MW 4 pulse sequence whether multiple pulse methods of high resolution in solids are able to average out these contributions and in this way allow to observe slow molecular motions. Simultaneously measurements with Hahn´s spin echo technique were carried out.

The method of free induction decay (FID) and the line shape function S(f) of the FID are not suitable for studies on PE melts. H_0 inhomogeneities within the sample due to the structure of the PE melt produce line broadenings of the proton magnetic resonance line up to two orders of magnitude (BACHUS,KIMMICH 1982).

For nonexponential relaxation functions the often discussed time constant T_2 for the decrease of M(t) does not contain all possible information. This information would be available with a detailed line shape analysis (SCHNEIDER 1979). As a ‚fast´ method of line shape analysis the factor A was introduced. A is equal to the width of the spectra at S(f=0)/10 divided by the width of the spectra at S(f=0)/2 and dependent on M_w and the pulse distance parameter τ of the MW4 pulse sequence. From theoretical formulas we get the following relations:

$A_{\text{Gaussian}} = 2 \quad A_{\text{Lorentzian}} = 3 \quad A_{\text{super-Lorentzian}} > 3$

The more nonexponential the relaxation function the greater will be factor A.

This nonexponential relaxation behaviour can be quantitatively described by means of two components.

A precise characterization of these two components was carried out with the three component model of molecular motion (KIMMICH,KOCH 1980;HILLER in preparation). The following assumption was made:

The long and the short component are mainly affected by fast and slow thermal motions, respectively. This concept allows a very good description of the experimental results and supplies different molecular weight dependences of molecular parameters. The time decay constants of these two components are T_{2l} and T_{2S} and their contributions to the total time decay curve of the transverse magnetization M(t) are p_l and p_S . We have the following relations:

$$\frac{1}{T_2} = \frac{1}{T_{2S}} - \frac{1}{T_{2l}} \qquad M(t) = p_S\, M_S(t) + p_l\, M_l(t)$$

2. Basic assumptions

2.1. Hahn's spin echo technique

Unlike the FID this method (HAHN 1950) is not sensitive to H_0 inhomogeneities (caused by magnet and sample shape and substance internal inhomogeneities).

It has the disadvantages that each echo demands a separate measurement dependent on echo distance parameter 2τ and τ cannot be made so small as it would be necessary. This means, that for small times in $M_H(t)$ and for large frequencies in $S_H(f)$ information will be lost.

Explanation: $M_H(t)$ is the envelope of the Hahn spin echoes and $S_H(f)$ is its fourier transform. Under our measuring conditions the effect of echo damping due to self diffusion may be neglected. The self diffusion coefficient D_S of PE melts is $0{,}8 \cdot 10^{-12} \ldots 0{,}7 \cdot 10^{-11}$ m²/s (FLEISCHER 1983). T_{2H} is the time decay constant of $M_H(t)$.

2.2. MW4 pulse sequence

This is a method of high resolution in solids (GRÜNDER 1974) which with a single measurement directly provides the complete time decay curve $M_M(t=4\tau)$ of the envelope of echoes dependent on the pulse distance parameter τ . It is not sensitive to H_0 inhomogeneities (in the same sense as in 2.1.) and allows the investigation of very slow thermal motions. T_{2M} is the time decay constant of the echo envelope. The fourier transform of $M_M(t)$ is $S_M(f)$.

3. Experimental

The following PE fractions were investigated at 423 K:

Sample	M_w	M_w/M_n	Sample	M_w	M_w/M_n
LDPE 1	6420	1,27	HDPE 1	8720	1,26
2	22400	1,19	2	13500	1,21
3	76800	1,10	3	20000	1,22
			4	42400	1,34
			5	52400	1,36
			6	70100	1,11

3.1. Measurements of relaxation times

These measurements were carried out with a pulse spectrometer SXP 4/100 (Bruker Analytik GmbH) at 88 MHz. The magnetization decays of the MW4 method $M_M(t)$ and Hahn's spin echo technique $M_H(t)$ were investigated. The MW4 measurements were made with the pulse distance parameter τ varied.

3.2. Studies of line shape

In order to consider the fourier transform of $M_M(t)$ and $M_H(t)$ $S_M(f)$ and $S_H(f)$ measurements were accomplished with the solid state spectrometer FKS 178 (Zentrum für wissenschaftlichen Gerätebau der Akademie der Wissenschaften der DDR) at 60 MHz.

4. Results and discussion

4.1. Results of relaxation time measurements

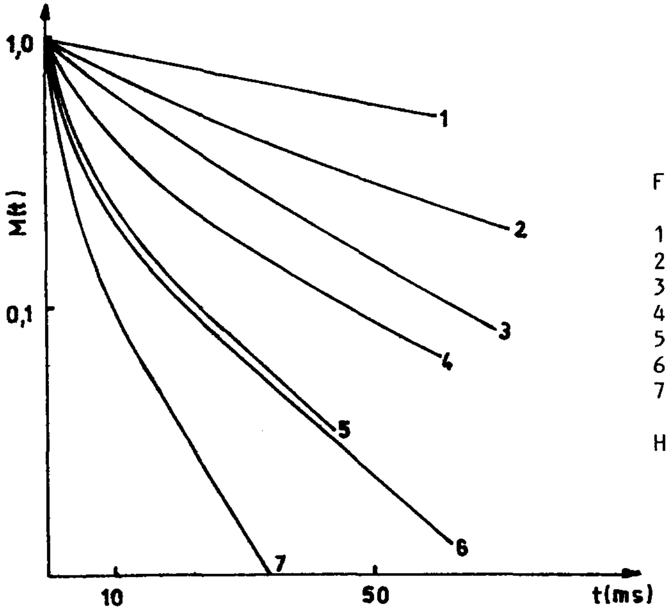

Fig.1a: $M_H(t)$

1	M_w =	2740
2		8720
3		13500
4		20000
5		42400
6		52400
7		71000

HDPE

All observed decays of transverse magnetization are nonexponential. Figure 1 represents the decay curves $M_H(t)$ and $M_M(t)$ dependent on molecular mass and Figure 2 shows $M_M(t)$ dependent on pulse distance parameter τ .

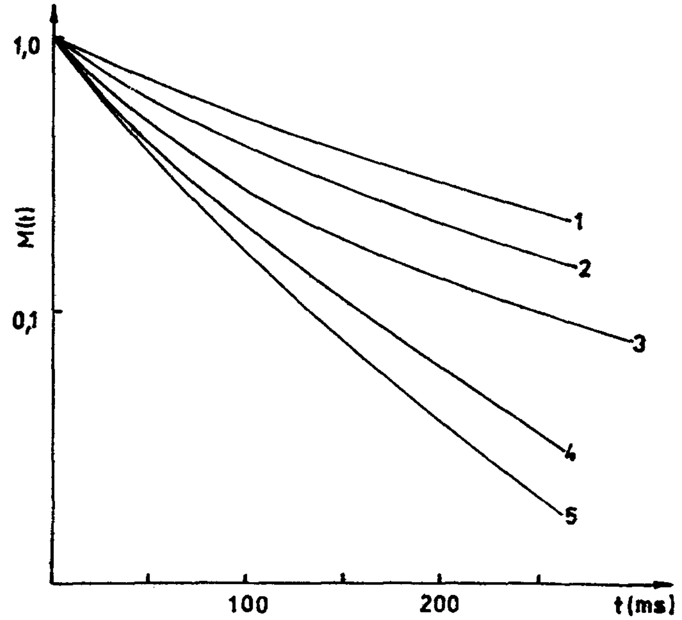

Fig.1b: $M_M(t)$

1 M_w = 8720
2 13500
3 20000
4 42400
5 70100

HDPE

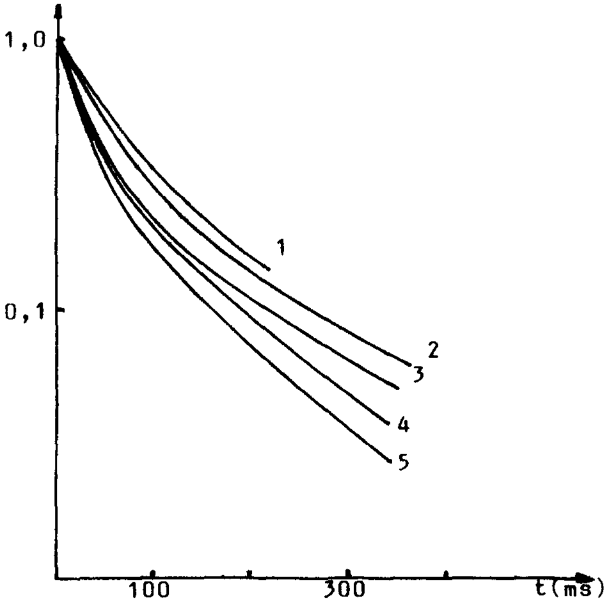

Fig.2: $M_M(t)$

1 τ = 6 μs
2 10 μs
3 40 μs
4 120 μs
5 400 μs

HDPE

Table 1 contains the results of the MW4 measurements and Table 2 those of the measurements with Hahn's spin echo technique.

TABLE 1

	τ = 10 μs				τ = 200 μs			
Sample	T_{2Ml}	p_l	T_{2Ms}	p_s	T_{2Ml}	p_l	T_{2Ms}	p_s
HDPE 2	247	0,44	58	0,56	211	0,44	54	0,54
3	204	0,36	40	0,64	177	0,34	26	0,66
4	91	0,54	28	0,46	95	0,33	14	0,67
5	95	0,50	40	0,50	99	0,29	15	0,71
6	89	0,38	40	0,62	86	0,19	11	0,81

Time decay constants T_{2Ml} and T_{2Ms} [ms] and the contributions p_l and p_s of the long and the short component to $M_M(t)$ dependent on M_w and the pulse distance parameter τ .

TABLE 2

Sample	T_{2Hl}	p_l	T_{2Hs}	p_s
HDPE 1	59	0,66	16	0,34
2	32	0,71	13	0,29
3	35	0,40	8	0,60
4	19	0,27	3,7	0,73
5	19	0,27	3,5	0,73
6	10	0,26	1,8	0,74

Time decay constants T_{Hl} and T_{2Hs} [ms] and the contributions p_l and p_s of the long and the short component to $M_H(t)$ dependent on M_w .

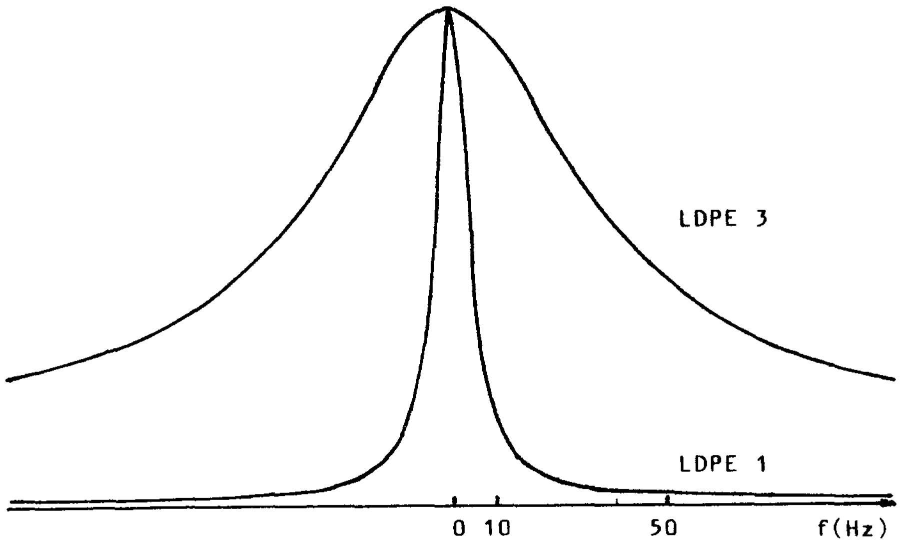

Fig. 3: Fourier transform $S_H(f)$ of $M_H(t)$

4.2. Results of line shape analysis

Table 3 contains the results of Hahn's spin echo measurements and Table 4 those of the measurements with the MW4 pulse sequence. Figures 3 and 4 show $S_H(f)$ dependent on M_w and $S_M(f)$ for different M_w- and τ-values.

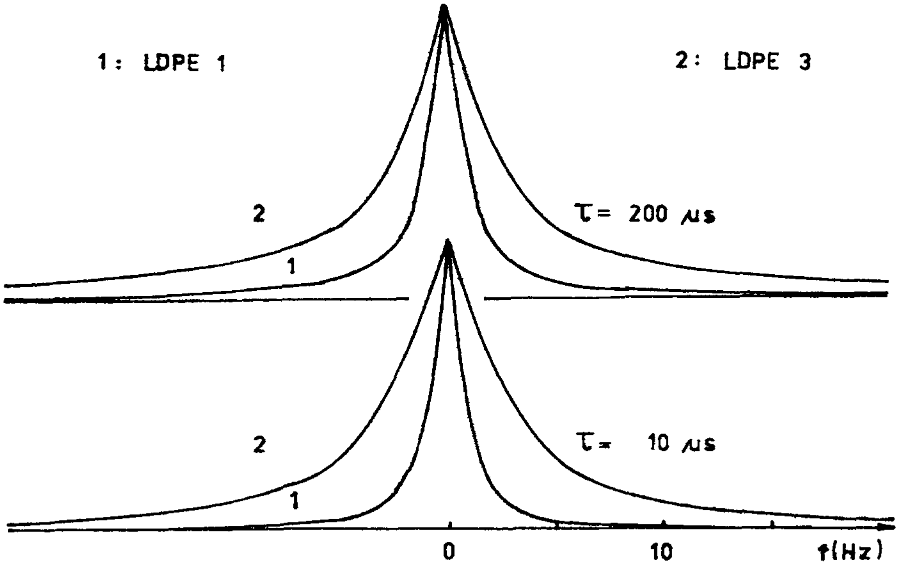

Fig. 4: MW4 line shapes $S_M(f)$ of samples LDPE 1 and LDPE 3

TABLE 3

Sample	LDPE 1	LDPE 2	LDPE 3	HDPE 1	HDPE 2
A	3,8	4,7	6,4	3,6	4,1
$\Delta f_{1/2}$	8	39	95	7	17

Factor A and $\Delta f_{1/2}$ [Hz] for $S_H(f)$ ($\Delta f_{1/2}$ = width of the spectra at $S(f=0)/2$)

4.3. Discussion

Our results show that with higher M_w $S_H(f)$ will be more super-Lorentzian (increasing factor A, Table 3, Fig. 3). The reason is that with increasing molecular weight the static contributions contained in the wings of the line shape will be greater (stronger anisotropy of motion (KIMMICH, BACHUS 1982)). Such a behaviour of $S_H(f)$ conforms to a more nonexponential character of $M_H(t)$ with increasing M_w (Table 2, Fig. 1). That means in contrast to p_l the p_S values rise and T_{2HS} and T_{2Hl} become shorter.

If τ is small enough the static contributions are averaged out in the MW4 line shape $S_M(f)$ and the lines change to a Lorentzian line shape (Fig. 4, Table 4). The averaging effect vanishes if τ has higher values.

The lines will be super-Lorentzian (increasing factor A), but A(LDPE) is smaller than A(HDPE) for comparable molecular weights. However, the pulse distance parameter τ = 10 µs is too long to average out the static contributions completely.

The same tendencies are seen for $M_M(t)$ dependent on τ and M_w (Tables 1 and 2,Fig. 2). The part of the short component p_s will be more nonexponential and the static contributions are better recognized. T_{2Ms} and T_{2Ml} have no clear dependencies on τ .

Both methods of measurement we used provide a line broadening with increasing M_w (decrease of molecular mobility). The MW4 method provides narrower lines with increasing τ (Table 4).

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