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Determination of Polymer Crystallinity from Proton Solid-Echo NMR Measurements

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SUMMARY

The decomposition of the solid-echo curves of crystalline polymers into the crystalline and the amorphous component is discussed. The crystalline component is experimentally determined by using a special method of measurement. The amorphous component is assumed to correspond to a distribution of correlation times.

INTRODUCTION

Lineshape studies of crystalline polymers are based on WILSON and PAKE's work in 1953. This method, however, did not succeed because of its rather arbitrary decomposition procedure which yielded a crystalline fraction that is not in agreement with x-ray crystallinity. Therefore, subsequently several papers appeared which tried to improve the method of decomposition. For example, we suggested to decompose the spectrum into three components (BERGMANN and NAWOTKI, 1967, BERGMANN, 1973, BERGMANN, 1978), a method which resulted in an excellent agreement of NMR and x-ray crystallinity. However, this method suffered from the impossibility to prove experimentally the existence of the two amorphous components. In addition, it was difficult to predict theoretically two amorphous mobilities. An interpretation by two distinct amorphous phases (BERGMANN and NAWOTKI, 1967, MANDELKERN, 1975) does not seem to be possible (BERGMANN, 1978).

In the meantime, we succeeded in improving the separation procedure by finding more suitable lineshapes for the crystalline and the amorphous component: The crystalline component was determined experimentally by a new method. The amorphous component was based on a distribution of correlation times, instead of the two discrete ones used earlier (BERGMANN and NAWOTKI, 1967, BERGMANN, 1973, BERGMANN, 1978). This will be reported in the following.

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EXPERIMENTAL

Materials: The investigated materials were commercial polymers. With the exception of PA 6.10 and PETP, 1 mm thick pressure-moulded sheets were slowly cooled from the melt, dried and filled into a spectrometer tube under nitrogen atmosphere which was then sealed. PA 6.10 was quenched in a CO_2/heptane mixture, annealed at 205 °C for 1 h and quenched again in ice-water in order to produce well-ordered crystals with α-structure. PETP was quenched in ice-water and annealed for 16 h at 200 °C.

Apparatus: The proton NMR-measurements were performed at 60 MHz by means of the Bruker spectrometer CXP. The H_o-field inhomogeneity corresponded to the decay to 1/e of a water signal in 6 ms. The H_o-field was regulated to $2 \cdot 10^{-8}$ with respect to time constancy. The distance of the two 90°-pulses of the solid-echo measurements (POWLES and STRANGE, 1963), each of 1.5 µs length, was 6 µs. The probe assembly and the receiver were modified with respect to band width and dead time in such a way that the solid-echo signal was precisely identical to the Fourier transform of the broadline-spectrum of HDPE at room temperature.

X-ray crystallinity: The x-ray crystallinities were determined by the modified (HABERKORN et al., 1979) method of HERMANS and WEIDINGER (1961). The crystallinity of LDPE was determined from the density (HENDUS and ILLERS, 1967).

SPECTRAL ANALYSIS

For the analysis the solid-echo signals were digitized with a time increment of 0.2 µs by use of a fast analog-digital-converter and an averager. In order to record the crystalline component correctly, the 2000 points obtained were smoothed by computation and concentrated to 60 points, where the points in the range $t < 70$ µs were four time denser than the rest. The analysis of the solid-echo curves was performed according to the method of least squares by comparing them with the shape discussed below by means of iteration of the curve parameters.

Crystalline component: In cases where the amorphous phase shows a smaller relaxation time $T_{1\rho}$ than the crystalline one, the shape of the crystalline component G_c can be measured by a combination of the solid-echo and the $T_{1\rho}$-techniques. The principle of the method consists in the removal of the amorphous magnetization by the $T_{1\rho}$-experiment and the ensuing observation of the remaining crystalline magnetization. The method is explained in Fig. 1,

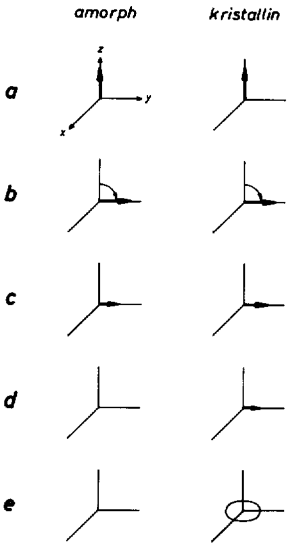

Fig. 1 : Method to measure the crystalline component by a combination of solid-echo and $T_{1\rho}$-techniques

where the magnetizations of both phases are separated by reason of clearness. At the beginning, the magnetization vector of both phases is turned by a 90°_x-pulse from the z- to the y-axis (Fig. 1a, 1b). Then the spin-locking pulse (SOLOMON, 1959, FARRAR and BECKER, 1971) is switched on. It causes a reduction of the magnetization with the time, and for the amorphous phase faster than for the crystalline one (Fig. 1c). In Fig. 1d the case is shown where the magnetization of the amorphous phase has vanished, but that of the crystalline phase is still maintained. Now the spin-locking pulse is switched off, and after a 90°_y-pulse the solid-echo signal of the crystalline component is observed.

As an example, Fig. 2 shows the progressive removal of the amorphous component of HDPE at 310 K, as the duration d of the spin-locking pulse is varied. For d=0 the normal solid-echo signal, i.e., the sum of the amorphous and the crystalline component, is observed. With increasing d the fraction of the amorphous component progressively decreases, until

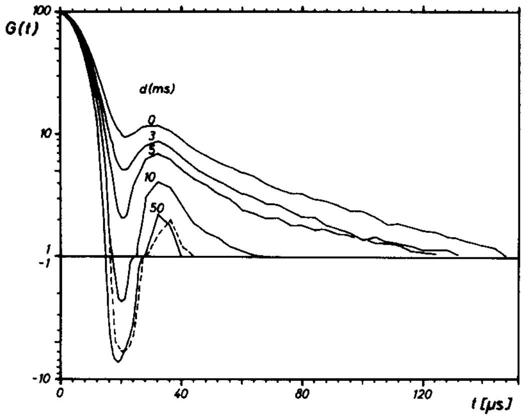

Fig. 2 : Elimination of the amorphous component of HDPE at 310 K with the progressively increasing spin-locking time d. For comparison, solid-echo signal of HNO_3 treated HDPE (---)

at d=50 ms only the crystalline component is left. In order to prove that the signal for d=50 ms in fact is that of the crystalline component, the solid - echo signal of a HDPE sample, the amorphous phase of which had been removed by treatment with nitric acid (PALMER and COBBOLD, 1966), is shown as well. Apart from the time-scaling factor s=1.07 (which probably is a consequence of the imperfection of the spectrometer) both curves are identical.

Amorphous component: The shape of the amorphous component is supposed to follow the equation

$$G_a(t) = \frac{\Sigma\exp\left[-(y_i/\alpha)^2\right]\cdot\exp\left\{-\omega_p^2\tau_{ci}^2\left[\exp(-t/\tau_{ci})-1+t/\tau_{ci}\right]\right\}}{\Sigma\exp\left[-(y_i/\alpha)^2\right]} \quad (1)$$

with

$$y_i = \ln(\tau_{ci}/\tau_{cm}) \ . \quad (2)$$

Eq. 1 is a modification with respect to a Gaussian distribution of correlation times τ_c of the equation

$$\ln G(t) = -\omega_p^2\tau_{ci}^2[\exp(-t/\tau_{ci})-1+t/\tau_{ci}] \quad (3)$$

derived for the shape of a simple motional process with an exponential correlation function (KUBO and TOMITA, 1954). ω_p^2 is the second moment of G_a, τ_{cm} the medium correlation time, and α the width of the distribution. The sum ranges from i=1 to n. The upper and the lower y-limit were chosen to be such that the probability was 10 % of the maximum value. In eq. 1 G_a consists of a sum of KUBO-TOMITA-curves which are supposed to be equidistant with respect to y_i. n is to be chosen so great that G_a is independent of n. In this case the distribution used cannot be distinguished from a continuous distribution. Eq. 1 is able to reproduce adequately the shape of amorphous polymers (BERGMANN et al., to be published). A molecular model of eq. 1 will be discussed elsewhere. A comparison of this shape with the "two-component" shape introduced by us before (BERGMANN and NAWOTKI, 1967, BERGMANN,1973, BERGMANN, 1978) shows that the continuous distribution of eq. 1 has been approximated by two discrete correlation times.

RESULTS AND DISCUSSION

In Table 1 for seven polymers the crystallinities w_c from NMR are compared with those found by x-rays. w_c (NMR) was determined at the specified temperature, w_c (x-ray) at room temperature. The spin-locking time d for the measurement of the crystalline component ranged from 10 to 150 ms. For most polymers Tab. 1 shows an agreement of w_c within the limits of error. These limits were ± 2 % for w_c (x-ray). The error with regard to w_c (NMR) mainly depends on α. The greater error in conjunction with the broader distribution is explained by the greater difficulty to distinguish the immobile amorphous from the crystalline protons in these cases.

TABLE 1

Comparison of crystallinities determined by NMR and x-rays for seven polymers

polymer	density g/cm^3	T K	w_c (%) NMR	x-ray	d ms	$\omega_p\tau_{cm}$	α
HDPE	0.963	310	74±1	75	100	0.7	1.1
LDPE	0.918	300	47±1	43	30	0.4	1.9
PP	0.918	310	79±1	78	50	0.3	1.0
PP	0.899	310	60±2	57	50	0.3	1.3
POM	1.424	310	72±1	67	150	0.5	0.0
PA 6.10	1.098	370	44±3	52	30	0.3	1.8
PETP	1.410	400	51±3	60	10	3	3.1

The temperature, at which w_c (NMR) was measured, was chosen to be such that the error of w_c was minimized. That means that a) within the range of the solid-echo curve not distorted by the H_o inhomogeneity ($t \lesssim 300\ \mu s$) the signal decays to 1-3 % of its initial ordinate. At the same time the condition b) $\omega_p\tau_{cm} \lesssim 1$ has to be fulfilled, i.e., at least half of the distribution must be mobile ($\omega_p\tau_{ci} < 1$) to make the amorphous component separable. Despite the small difference in the lineshapes of the immobile amorphous ($\omega_p\tau_{ci} > 1$) and the crystalline protons, the amorphous component in case $\omega_p\tau_{cm} \lesssim 1$ is still separable, owing to the symmetrical shape of the Gaussian distribution. According to Tab. 1 the condition b is fulfilled in all cases except PETP for which an exceptionally great α-value is obtained. In this case, an increase of the temperature would fulfill condition b, but violate condition a. The solution of this problem and a more detailed discussion of the NMR results will be presented in a future publication.

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REFERENCES

BERGMANN, K. and NAWOTKI, K.: Kolloid Z.Z. Polymere 219, 132 (1967)
BERGMANN, K.: Kolloid Z.Z. Polymere 251, 962 (1973)
BERGMANN, K.: J. Polymer Sci., Polymer Phys. Ed. 16, 1611 (1978)
FARRAR, T.C. and BECKER, E.D.: "Pulse and Fourier Transform NMR", 1971
HABERKORN, H., ILLERS, K.H., and SIMAK, P.: Coll. Polym. Sci. 257, 820 (1979)
HENDUS, H. and ILLERS, K.H.: Kunststoffe 57, 193 (1967)
HERMANS, P.H. and WEIDINGER, A.: Makromol. Chemie 44-46, 24 (1961)
KUBO, R. and TOMITA, K.: J. Phys. Soc. Japan 9, 888 (1954)
MANDELKERN, L.: J. Polymer Sci., Symposium No. 50, 457 (1975)
PALMER, R.P. and COBBOLD, A.J.: Makromol. Chemie 74, 174 (1966)
POWLES, J.G. and STRANGE, J.H.: Proc. Phys. Soc. (London) 82, 6 (1963)
SOLOMON, I.: C.R. Acad. Sci. Paris 248, 92 (1959)
WILSON, C.W. and PAKE, G.E.: J. Polymer Sci. 10, 503 (1953)

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