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Straining Mechanisms of Hard Elastic Fibers Obtained by Broad Line Nuclear Magnetic Resonance Measurements

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SUMMARY

Broad line NMR measurements give information on energy-elastic processes during straining of hard elastic fibers, as there are the shearing of the crystalline regions and transformation of parts of the crystalline into amorphous. The amount of these parts is proportional to straining and recrystallizes again, dependent on temperature and time. Sheared crystalline regions relax within few days, even at very low temperature (-175°C, -12o°C). In the case of isotactic polypropylene the mobility of various groups depends not directly on the temperature but on the nearest neighbour distances. Thus methyl groups in the sheared crystalline regions even at -175°C undergo hindered rotation.

INTRODUCTION

Hard elastic fibers (HEF) show high elasticity and elastic recovery, even at very low temperatures (-19o°C) (PARK and NOETHER, 1975), where the amorphous chains are frozen. There are various models proposed: energy-elastic models (NOETHER and WHITNEY, 1973, PARKand NOETHER, 1975, CLARK, 1973) based on small angle x-ray and mechanical measurements, a model with entropy effects (GÖRITZ and MÜLLER, 1975) obtained from calorimetric measurements, or models which combine both effects (SPRAGUE, 1973) and tray to explain the outstanding mechanical behaviour of the material.

HEF can be made from almost all semicrystalline polymers. This fact was the reason of investigating the changes in the structure and the chain mobility in the crystalline and amorphous regions during straining, to obtain the answer on the question which processes are important for such a behaviour of the material.

Our previous measurements (ČAČKOVIĆ et al., 1978, LOBODA-ČAČKOVIĆ et al., 1979), using broad line nuclear magnetic resonance (NMR), on 6o% at -6o°C strained isotactic polypropylene HEF have shown that by straining the crystallinity decreases from 72 to 6o%. This new generated amorphous part has recrystallized only if the temperature was higher than about -2o°C. From this reason the sample 6o% strained at room temperature showed no change in the crystallinity. From small angle x-ray measurements (HOSEMANN and ČAČKOVIĆ, 1981)

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we know that this part is transformed into bundles of molecules which connect the crystalline lamellae. To obtain the dependence of the percentage of the new generated amorphous part on the straining the 3o% straining was done.

The retractive force of HEF shows two different ranges in temperature dependence (PARK and NOETHER, 1975). For this reason the straining of the sample was done at two temperatures, which belong to these two ranges.

EXPERIMENTAL

Samples: HEF of isotactic polypropylene (PP) were prepared for measurements as previously described (LOBODA-ČAČKOVIĆ et al., 1979). The samples were strained 3o% at -6o°C (sample I) and 3o% at -11o°C (sample 1). Care was taken that the samples did not warm up before the NMR measurements, which were done successively at -175°C (samples I and 1), at -12o°C (samples II and 2) and so on. The numbers on Figure 4 denote the sequence of the NMR measurements.

Apparatus: The measurements were performed on a Varian V-42oo B and a WL 112 broad line spectrometer. The samples were held at a constant temperature within ±1°C during measurements. 5 till 1o spectra were detected at each temperature.

RESULTS AND DISCUSSION

Spectra: The analysis of the spectra was carried out by using a method developed previously for polyethylene, paraffins and isotactic PP (LOBODA-ČAČKOVIĆ et al., 1969, PHAOVIBUL et al., 1974, LOBODA-ČAČKOVIĆ et al., 1979).

The shapes of the spectra at -175°C on Figs.1 and 2 are different, depending on strain, straining temperature and on processes going on at low temperature in the strained sample. This fact supports our method of analysis and opposes the method where the shape of the low temperature spectrum was taken as the shape of the rigid or crystalline component at higher temperatures (BERGMAN, 1973).

At -175°C (Figs.1 and 2) the spectra can be separated into two components. Component α is the derivative of a box shape convoluted with a Gaussian and has a line width of about 14 Gauss (Fig.1). This component is generated by rigid protons. Component β_1 is the derivative of a Gaussian, has a line width of about 5 Gauss and is generated by protons which undergo hindered rotation. From -12o°C (Fig.3) up to -3o°C the spectra have similar shape and consist also of two components. At room temperature the spectra consist of two additional components β_2 and γ of the protons undergoing micro-Brownian motion. These two components are the derivatives of Lorentzian absorption lines and have line widths of about 1 Gauss and o.1 Gauss respectively. Such spectra are published previously (LOBODA-ČAČKOVIĆ et al., 1979).

Processes: In Table 1 the percentages and line widths of distinct components at various temperatures are listed. In Table 2 the mobility of CH_3, CH_2 and CH groups, depending on the temperature, straining and processes going on in the strained state of the samples is pointed out.

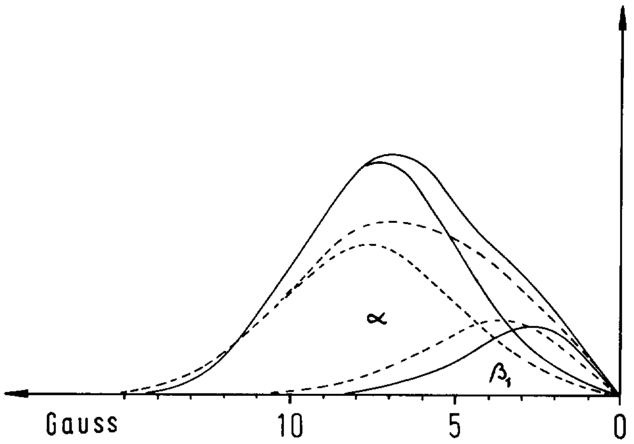

Figure 1: Spectra at -175°C of sample 3 (——) and sample I (---) separated in α and β_1 components. Modulation amplitude: 1.25 Gauss, amplification: 8o (for ——) and 5o (for ---). The same spectrum as for sample I is obtained for sample 4a.

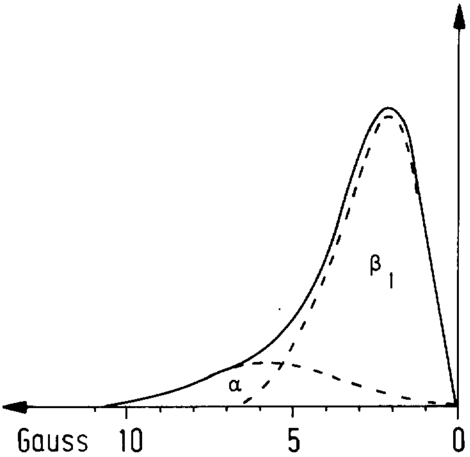

Figure 2: Spectrum of sample 1 at -175°C separated in the α and β_1 component. Modulation amplitude: 1.25 Gauss, amplification: 8o.

TABLE 1

Rigid (α) and Three Mobile Fractions (β_1, β_2 and γ) of the NMR Spectra and Line Widths ΔH_i of the Corresponding Components, Dependent on Temperature[a])

Sample	α	β_1	β_2	γ	ΔH_α	ΔH_{β_1}	ΔH_{β_2}	ΔH_γ	Spectra (Figures)
	%				Gauss				
I	83.4±o.3	16.6±o.3			14.3	6.4			1
II	73.o±o.8	26.8±o.7			12.4	5.4			3
1	33.4±1.7	66.6±1.7			1o.6	3.7			2
2	78.o±o.4	22.o±o.4			12.6	5.4			3
3	91.3±o.5	8.8±o.7			14.5	5.4			1
4	86.9±o.4	13.2±o.4			15.o	6.o			similar to Fig.1
4a	83.o±o.5	17.3±o.7			14.5	6.o			1
5	73.3±o.8	26.8±o.7			12.4	5.3			3
6	73.1±o.8	26.5±o.5			12.6	5.o			similar to Fig.3
7	77.o±o.3	23.o±o.4			12.1	4.8			similar to Fig.3
8	73.o±o.8	26.9±o.8			12.4	4.8			similar to Fig.3
9	85.5±o.3	14.4±o.3			14.1	5.9			similar to Fig.1
1o	72.6±o.4	27.3±o.4			12.5	5.o			similar to Fig.3
11	74.1±o.7	25.9±o.7			12.4	4.8			similar to Fig.3
12	71.2±o.4	22.4±o.3	6.o±o.2	~o.4	11.7	4.4	1.o	o.15	published previously

a) The dependence on the temperature is denoted by the number of the sample corresponding to Fig.4.

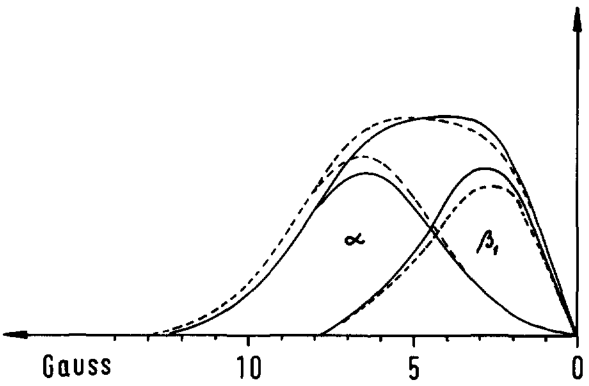

Figure 3: Spectra at -12o°C of sample II (——) and sample 2 (---) separated in α and β_1 components. Modulation amplitude: 1.25 Gauss, amplification: 5o. The same spectrum as for sample II is obtained for sample 5. At temperatures higher than -12o°C up to about -2o°C the spectra differ only quantitatively from these two.

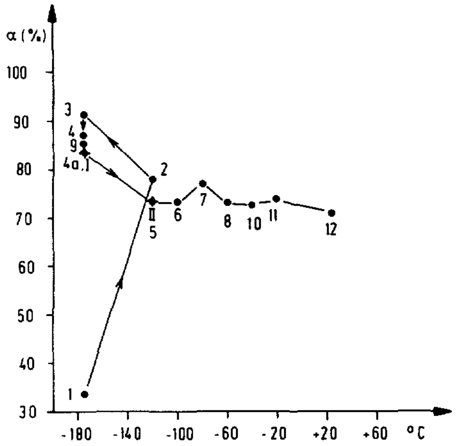

Figure 4: Component α of the rigid protons as a function of temperature. Successive measurements of sample 3o% strained at -6o°C (+): samples I and II, and of sample 3o% strained at -11o°C (●): sample 1, 2, 3 and so on.

TABLE 2

Effects of Straining and of Temperature of Measurements$^{a)}$

Sample$^{b)}$	Rigid groups$^{c)}$, % (α comp.)	Mobile groups$^{c)}$, % (β_1 and β_2 comp.)
I (4a)	66(all c-groups)+ +11.4(CH_2a)+5.6(CHa)	34/2(CH_3a)
II (5, 6)	66(all c-groups)+ +5.6(CHa)	17(CH_3a)+11.4(CH_2a)
1	66/2(all CH_2c and CHc)	66/2(CH_3c)+17(CH_3a)+ +11.4(CH_2a)+5.6(CHa)
2	66(all c-groups)+ +6(CH_2a)+5.6(CHa)	17(CH_3a)+5.4(CH_2a)
3	66(all c-groups)+ +8(CH_3a)+11.4(CH_2a)+ +5.6(CHa)	17/2(CH_3a)
7	72(all c-groups)+ +4.7(CHa)	28/2(CH_3a)+9.3(CH_2a)
8 (1o, 11, 12)	72(all c-groups)	28(all a-groups)
9	72(all c-groups)+ +28/2(all CH_2a and CHa)	28/2(CH_3a)

a) The crystallinity of the unstrained sample 71.7±o.8% (LOBODA-ČAČKOVIĆ et al., 1979) is needed for calculation of percentages of various groups.

b) The dependence on the temperature is denoted by the number of the sample corresponding to Fig.4.

c) c are the groups in the crystalline and a in the amorphous regions.

On Fig.4 the component α against the temperature of measurement is drawn. From the previous work on unstrained samples and strained at -6o°C we know that at -175°C only CH_3 amorphous groups are mobile and all other groups rigid (LOBODA-ČAČKOVIĆ et al., 1979). Thus the unstrained sample, with a crystallinity of 72%, has at -175°C α=86%. The decreasing of the α value to 83% for sample I means the decreasing of the crystallinity to 66%; 6% of the crystalline becomes amorphous during 3o% straining. We know already that by 6o% straining the decrease was about 12%. At -12o°C the CH_2 amorphous groups become also mobile and the sample II (Fig.3) shows a decrease of α to 73%.

Sample 1 (Figs.2 and 4, Tables 1 and 2), which is strained at -11o°C, shows one additional effect. The α component is only 33%. This is explained as decreasing of crystallinity by 6%, that is to 66%, and that all CH_3 groups, also in the crystalline regions, are now mobile. This can happen, if the crystallites in the lamellae are sheared to such an extent that distances between the chains enlarge. Moreover, all amorphous groups get mobile. The second moments of the α (ΔH^2_α) and β_1 ($\Delta H^2_{\beta_1}$) component and the total second moment (ΔH^2) at -175°C for samples 1 and I support the mentioned processes. Sample 1 has an unusually small ΔH^2_α value of $13G^2$, in comparison with about $24G^2$ for sample I. $\Delta H^2_{\beta_1} = 3G^2$ for sample 1 and is smaller than that of $9G^2$ for sample I. ΔH^2 is $6.4G^2$ and $22G^2$ respectively. These values can be explained again with sheared crystalline regions and that all amorphous groups are mobile in sample 1.

After a few days at the low temperature (samples 2 - 4a, Figs. 3 and 1) the crystalline regions relax and sample 4a has the same α as sample I. But this relaxation is accompanied by the tightening of some amorphous chains. Thus at -12o°C, in sample 2 (Fig.3), the crystalline regions are relaxed, CH_3 crystalline groups are again rigid and also about 5o% of CH_2 amorphous groups. At -175°C (sample 3, Fig.1) additionally the corresponding 5o% of CH_3 amorphous groups are rigid and contribute to the α component. From sample 3 (Fig.1) up to sample 4a (Fig.1) at -175°C the tightened amorphous chains relax again.

The 6% crystalline material transformed remains amorphous up to -1oo°C. Increasing of α to 77% in sample 7 (at -8o°C) indicates the recrystallization of these 6%. Sample 9 (again at -175°C) proove the recrystallization process; α=86%, as obtained previously for the unstrained sample (LOBODA-ČAČKOVIĆ et al., 1979). On -6o°C (sample 8) decreasing of α to 73% means that the CH amorphous groups become mobile and up to room temperature (samples 1o - 12) the α component is equal to that of the unstrained sample. The latter result prooves that the entropy-elastic model does not hold, because the α component of strained samples does not increase.

From these results and from previously published work (LOBODA-ČAČKOVIĆ et al., 1979) we can summarize the processes during straining:

- From crystalline regions material is transformed into amorphous.
- The amount of transformed material is proportional to straining and stays amorphous at very low temperatures.
- This new generated amorphous part recrystallizes even at low temperature (for instance -8o°C), depending on time.
- By straining at very low temperature (-11o°C), as an additional effect, the crystalline lamellae become distorted and relax with time, also at low temperature (-12o°C).
- The amorphous chains play an inferior role, if any.
- The mobility of various groups in amorphous and crystalline regions depends not directly on temperature, but on conformation and distance of the neighbouring chains, which result from the straining conditions and temperature.
- Because the retractive force has the same temperature dependence for -6o°C and 25°C, either the transformed crystalline part is amorphous (at -6o°C) or crystalline (at 25°C) has no influence on the retractive force. But the shearing of the crystalline lamellae, which happens by straining at temperatures lower than about -8o°C, has an influence; the retractive force changes its temperature dependence.

- The straining processes of HEF are energy-elastic.
- From small angle x-ray scattering we have obtained that bundles of molecules of 5oÅ diameter appear, with an average mutual distance of about 115Å, connecting the lamellae. From NMR measurements the amount of the material transformed from the crystalline regions gives us the hint that these bundles are situated over the whole fold surfaces of the lamellae.

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