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Analysis of side group motion in *O*-acetyl-starch using regioselective 2-*O*-acetyl-starches by means of dielectric spectroscopy

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Abstract

The complex dielectric constant of *O*-acetyl-starches with regioselective and the statistical distribution of substituents at the anhydroglucose unit (AGU) are measured in an extended frequency range from 10 mHz to 2 MHz and in the low temperature range from −120 to 0°C. The experimentally determined relaxation spectra are evaluated with the well-known model function of Havriliak–Negami for relaxation processes. In the case of 2-*O*-acetyl-starch two significant relaxations are detected which are associated with the orientational motion of the methylolgroup at the AGU and the acetylgroup in position C-2. The activation energies are 48 and 60 kJ/mol, respectively. Owing to that assignment of relaxations at the AGU with acetylation in position C-2 has proved that it is possible to describe further relaxation processes in acetylated amylomaize starch with a statistical substitution pattern. It was found that an additional relaxation process is associated with the dynamics of the acetylgroup at the position C-6 at the AGU and characterized by a lower activation energy of 28 kJ/mol.

From the analytical point of view these results of dielectric spectroscopy analysis demonstrate that the mobility of the side groups depend significantly on the position at the AGU and the type of substituent in their frequency and temperature dependence.

Keywords: Starch; Starch acetate; Amylose

1. Introduction

The measuring of the complex dielectric properties in an extended frequency and temperature range provides an elegant method for the investigation of the molecular dynamics in starches and their derivatives because polysaccharides contain various dipolar groups with different mobilities.

Recently, although more and more papers deal with the dielectric measurements in different polysaccharides and its derivatives, the results are discussed controversially in many details [1–4]. The main causes for this fact and the few investigations of these biopolymers by means of dielectric relaxation spectroscopy (DRS) have to be seen in the very complex supramolecular structure of pure polysaccharides such as intra and intermolecular hydrogen bonds, semicrystallinity, fibrillar supramolecular structure, high variation in the capillary system between fibrils, water content, and in many parameters by chemical isolation treatments from natural sources. In the case of polysaccharide derivatives the kind of chemical functionalization as well as preparation conditions can influence the shape of the dielectric spectra. The existence of water can distort the results significantly [4–6,8]. Therefore, we will restrict our investigations presented to well-dried samples only. Further, explanation of DRS-features of polysaccharide derivatives is restricted, because dielectric relaxation processes on regioslectively substituted substances have never been made. We think that starch derivatives with regular distribution of acetyl groups in the anhydroglucose unit (AGU) can help to distinguish the single relaxation of each dipolar side group.

Generally in all polysaccharides observed there are three types or modes of dielectric relaxation processes. The so-called β- and γ-relaxation at low temperatures (−135 to 0°C): the β-relaxation is associated to the local main chain motion of the polymer and the γ-relaxation to thermal activated side group motion on the AGU. These low temperature relaxations in all polysaccharides are qualitatively similar. In the middle temperature range (0 to +60°C) a further relaxation process (β_{wet}-relaxation-relaxation) exists, which is attributed to motions in regions in a biopolymer–solvent mixing state, especially if the polysaccharides are branched or linked like dextran. This

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Table 1
Distribution of acetyl groups in the repeating unit of starches under investigation

Substances	DS_{Ac}	$DS_{Ac\text{-}C2}$	$DS_{Ac\text{-}C3}$	$DS_{Ac\text{-}C6}$
2-*O*-Ac-AMS	0.34	0.34	0	0
2-*O*-Ac-AMS	0.79	0.79	0	0
2-*O*-Ac-AMS	1.00	1.00	0	0
O-Ac-AMS	1.05	0.35	0.17	0.53

β_{wet}-relaxation-relaxation is very sensitive to small amounts of water or other swelling solvents in the sample [5–8]. In the high temperature range (80–180°C) a further dielectric relaxation process (here called the σ-relaxation) is known, which obviously could not be assigned to any molecular dipolar group orientation. This σ-relaxation is due to the proton hopping in the disordered solid system of the biopolymer [9]. It is strongly related to the dc-conductivity of the polymer system and is also observed in many ionic conducting disordered solids [10–12].

This study is focused on the analysis of the γ-relaxation of regioselectively substituted 2-*O*-acetyl-starches with a different degree of substitution (DS_{Ac}) in comparison with amylomaize starch (AMS) and an acetylated starch derivative ($DS_{Ac} = 1.05$) with statistical substitution pattern. The 2-*O*-acetyl-starches prepared have got a wide range of degree of substitution ($DS_{Ac} = 0.34$, $DS_{Ac} = 0.79$, $DS_{Ac} = 1.00$). On the one hand these derivatives are model substances to investigate the influence of the substituent and on the other hand its position on the AGU to the dielectric spectrum of the side group motion. Therefore the investigation presented deals with the experimental problem to separate the different contributions of dipolar groups on the positions C-2, C-3 or C-6 in the AGU and its assignment in the low temperature relaxation process (γ-relaxation).

The activation energy for the orientational motion of the different side groups was calculated from the temperature dependence of the relaxation times of the relaxation process related. According to the dielectric spectra of acetylated starch the completeness as well as the selectivity of substitution in the AGU can be determined qualitatively.

2. Materials and methods

2.1. Sample preparation

2.1.1. General procedure

The material (amylomaize starch: Hylon VII) used was a gift from the National Starch and Chemical KG and has got an amylose-content of 71%.

The degree of substitution (DS_{Ac}) of starch acetates was determined by means of ^{1}H-NMR spectroscopy after perpropionylation [13,14]. For this reason, 0.3 g starch acetate in 5 ml pyridine was treated with 5 ml propionic anhydride in the presence of 0.5 g 4-dimethylaminopyridine for 20 h at 80°C. The products were precipitated in 100 ml ethyl alcohol, filtered off, washed and dried at 50°C in vacuum. The ^{1}H-NMR spectra were measured with a Bruker AMX 400 spectrometer as 2% solution in $CDCl_3$ at 50°C.

2.1.2. Starch acetate with regioselective 2-O-acetylation

To a solution of 2 g starch in 40 ml dimethylsulfoxide, vinyl acetate and 20 mg disodium hydrogenphosphate was added. The mixture was stirred for 70 h at 40°C. After cooling the residual salt was removed by centrifugation and the solution was poured into 300 ml isopropyl alcohol. The starch acetate (2-*O*-Ac-AMS) precipitated was separated by filtration, washed with 100 ml isopropyl alcohol and dried at 50°C in vacuum [15]. The DS_{Ac} of 2-*O*-Ac-AMS obtained depends on the amount of vinyl acetate used and is summarized in Table 1.

2.1.3. Starch acetate with statistical substitution pattern

Six grams of starch dissolved in 120 ml dimethylsulfoxide was stirred with 3.5 ml acetic anhydride, 5 ml pyridine and 0.4 g 4-dimethylaminopyridine for 20 h at 80°C. The starch acetate (*O*-Ac-AMS) formed was precipitated in isopropyl alcohol, washed and dried at 50°C in vacuum. A DS_{Ac} of 1.05 was obtained (Table 1).

2.2. Dielectric measurements

The real part $\epsilon'(f,T)$ of the dielectric permittivity is also called dielectric store coefficient and the imaginary part $\epsilon''(f,T)$ the dielectric loss coefficient. They were measured in the extended frequency range of 10 mHz to 2 MHz and in the temperature range of −135 to 0°C using the Novocontrol Broadband Dielectric Spectrometer System BDS 4000 with the active sample cell BDC-S. All samples were prepared in an identical manner. First the material is dried at 110°C under vacuum for 20 h and then it is pressed under vacuum with a pressure of 1900 bar into thin discs with a diameter of 30 mm and a thickness of 0.07–0.12 mm in a hydraulic press.

Before inserting into the dielectric spectrometer the sample cell was again pressed under vacuum with 500 bar to effectuate an ideal electrical contact with the gold electrodes and to fill the cell volume completely.

At first the sample was heated to 130°C in the dry nitrogen stream of the thermostat system of the spectrometer to drive out residues of water from the measuring capacitor which might be adsorbed in the course of transport. After that the measurement of the permittivity was started with the lowest temperature. The measurement curves have shown good reproducibility and their overall confidence interval in the real and imaginary part is lower than 5%.

3. Theoretical basis of molecular interpretation and data processing

The dielectric relaxation processes are represented in an

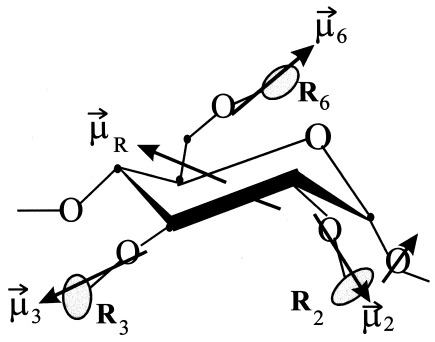

Fig. 1. Dielectric site model of the repeating units of starch and starch-derivatives: R_2,R_3,R_6 are dipolar substituents in the positions 2,3,6, in the AGU μ_R, μ_i ($i = 2, 3, 6$) are effective dipole-moments of the pyranose ring and the side groups, respectively.

empirical form by the Havriliak–Negami equation (HN-equation) [16]. This general relaxation equation includes the special cases of the relaxation expressions of Debye, Cole–Cole and Davidson–Cole [17]:

The complex permittivity measured $\epsilon^*(\omega)$ is a summation over all separable relaxation processes

$$\epsilon^*(\omega) = \epsilon_\infty + \Sigma_i \Delta\epsilon_i^* \tag{1}$$

In this presentation ϵ_∞ means the extrapolated real part to the high frequency end of our measuring window.

For the complex contribution of the *i*th relaxation process the HN-expression is used:

$$\Delta\epsilon_i^* = \frac{\Delta\epsilon_i}{[1 + (i\omega\tau_i)^{\alpha i}]^{\beta i}} \tag{2}$$

This procedure reduces one relaxation process to four relaxation parameters.

The relaxation time $\tau_i(T)$ represents the central position of this process in the time scale.

The relaxation strength $\Delta\epsilon_i(T)$ means a step in the real part of the complex permittivity or equivalently the area below the loss peak $\epsilon''(\log f)$. In general its molecular interpretation is difficult in the case of starches or polysaccharides. In the simple case of rigid dipoles without cross-correlation between the dipolar groups the relaxation strength is expressed as

$$\Delta\epsilon_i \approx \left[\frac{N_i(T)\mu^2}{T}\right] p(\epsilon^*) g \tag{3}$$

where $N(T)$ is the number of dipoles of the type *i* per volume unit, μ the mean effective dipole moment of this polar group *i* and $p(\epsilon^*)$ is the Onsager screening factor to take into account the difference between the external and the internal electrical field [17,18]. The factor *g* means a structural function that describes the structural effect in the summation of the dipole moments. The expression (Eq. (3)) represents a qualitative heuristic formula for $\Delta\epsilon$ in the molecular interpretation of the dielectric results of this type of biopolymers.

The α and the β parameters describe the shape of the relaxation process in the frequency mode. The $\alpha(T)$ parameter means the width and β the asymmetry of the relaxation process in relation to the Debye process. $\alpha = \beta = 1$ applies to the simple Debye process which is typical for small polar molecules in non-polar solvents. Low α values are equivalent to a broad distribution of the relaxation times and low β values represent an asymmetrical distribution in the time scale.

An alternative approach to this empirical HN-representation of dielectric relaxations is to express the broad relaxation process as superposition of continuously distributed

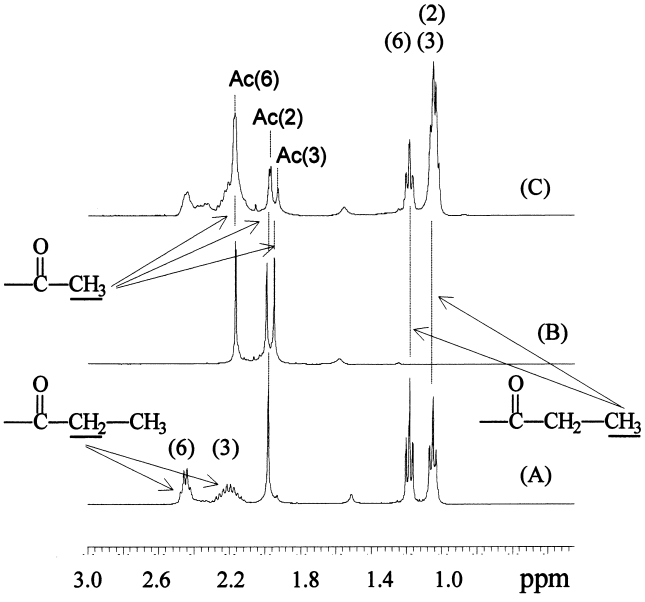

Fig. 2. ^{1}H-NMR spectra at 40°C of (A) regioselective 2-*O*-acetyl amylomaize starch with $DS_{Ac} = 1.00$, (B) tri-*O*-acetyl amylomaize starch and (C) *O*-acetyl amylomaize starch with DSAc = 1, 05 and a statistical substitution pattern. The symbols (2), (3) and (6) means the position of the group in the AGU.

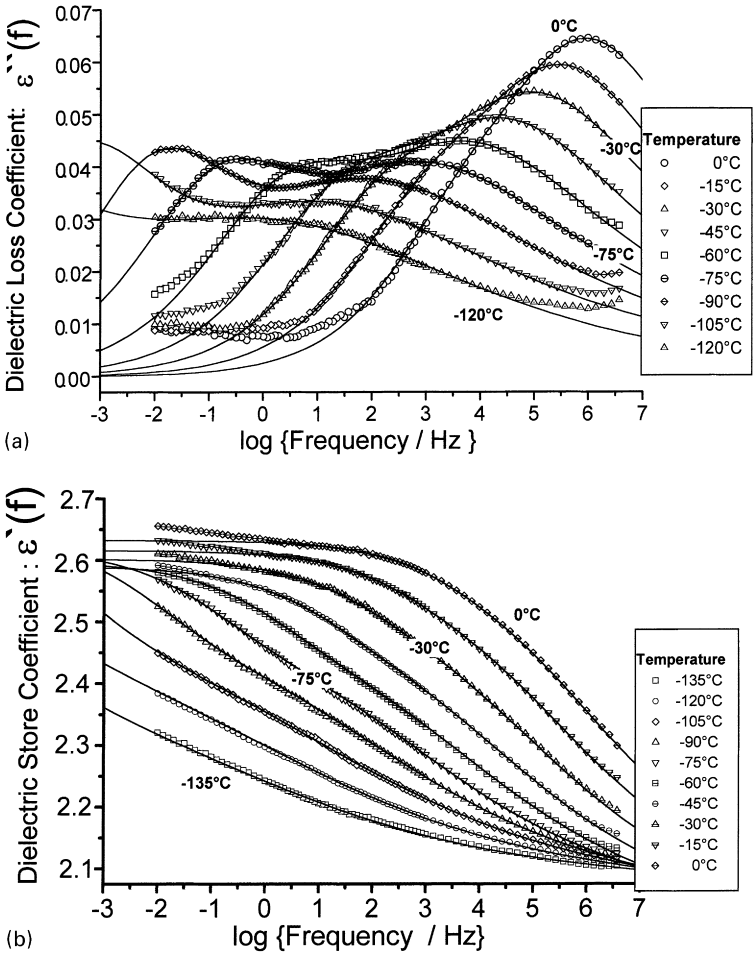

Fig. 3. Dielectric loss spectrum $\epsilon''(f,T)$ (a) and the dielectric store coefficient $\epsilon'(f,T)$ (b) of the regioselective acetyl-starch: 2-*O*-Ac-AMS with a degree of substitution $DS_{Ac} = 1,0$.

Debye relaxations. In this case the result is a distribution function of the relaxation strength $G(\tau)$ and $G(\tau)\,d\tau$ means the intensity of relaxation in the small range of τ to $\tau + d\tau$.

The contribution of the dc-conductivity to the dielectric loss coefficient investigated in this paper can be neglected in the low temperature range.

In the case of starches or generally speaking of polysaccharides the molecular dipole groups of the repeating unit are given in the form of a site model in Fig. 1. The side groups R_2, R_3 and R_6 in the positions C-2, C-3 or C-6 are characterized by the dipole moments μ_2, μ_3 and μ_6, respectively, which can alter in the case of derivatives. The mobility of these polar side groups is different, too. The group in position C-6 (the methylol group in the case of pure starches) is more mobile than the groups in position C-2 or C-3 at the AGU. The motions of these groups are detected with the γ-relaxation.

The dipole-moment μ_R of the glucopyranose ring and the related local main chain dynamic is also measurable in form of the β-relaxation, but is not under investigation in this paper.

4. Results and discussions

4.1. Preparation and structural analysis of 2-O-acetyl starches substituted regioselectively

Recently we have described the possibility to synthesize starch acetates with regioselective distribution of the acetyl group in position C-2 of anhydroglucose unit (AGU). This regioselectivity concerned the different content of acetyl groups only cited at the position C-2 in a range between $DS_{Ac} = 0.1 - 1.0$ [14,15]. The evidence of the substitution pattern of 2-*O*-acetyl starches is given by ^{1}H-NMR spectroscopy after subsequent perpropionylation of all residual hydroxyl groups [13,15]. The ^{1}H-NMR spectrum of the perpropionylated 2-*O*-acetyl starch, $DS_{Ac} = 1.00$, shows only one signal for an acetyl group at 2.00 ppm in comparison to the starch triacetate showing three signals for each position in the AGU (Fig. 2). The chemical shifts of the acetyl signal of all 2-*O*-acetyl starches agreed with the position C-2 in starch triacetate. In contrast to the regioselective 2-*O*-acetyl starch, $DS_{Ac} = 1.00$, a conventional synthesized starch acetate with an approximately equal $DS_{Ac} = 1.05$ has

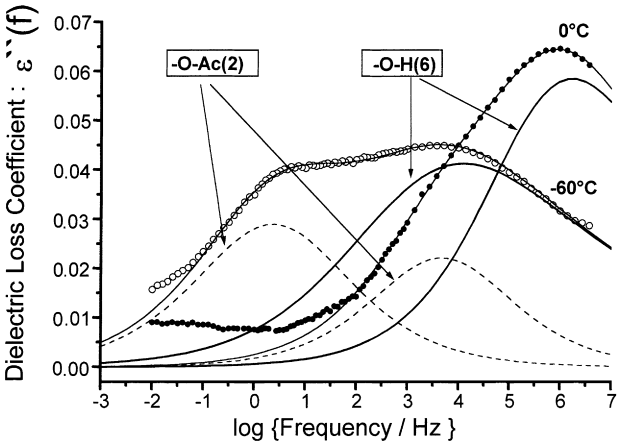

Fig. 4. Dielectric loss spectrum $\epsilon''(f,T)$ of 2-*O*-Ac-AMS with $DS_{Ac} = 1.0$ and the HN-fit-curves of two relaxation processes at two selected temperatures (−60.0 and 0.0°C). (points, experimental values; lines, theoretical curves for the determined fit-parameter).

shown a statistical distribution. In that ^{1}H-NMR spectrum three signals for acetyl groups are found in the positions C-2, C-3 and C-6 like in starch triacetate. The determination of the DS_{Ac} was carried out directly by integrating of the acetyl signals or indirectly by integrating of the propionyl signals [15]. The highest amount of acetyl groups are localized at the primary position C6, followed by C2 and C3 (Table 1).

4.2. Dielectric relaxation in 2-O-acetyl starches with different DS_{Ac}

In Fig. 3a the loss coefficient $\epsilon''(f,T)$ of the regioselectively substituted 2-*O*-acetyl starch, $DS_{Ac} = 1.00$, is shown. In that loss-spectrum two relaxation regions are apparent. These two relaxation processes were not recognized clearly in the store coefficient (Fig. 3b), because these two overlapping relaxation processes are very wide and have nearly the same intensity. Therefore, only the loss curves are used in the following presentations and discussions. The lines in Fig. 3 are the fit results with two HN-functions. To obtain a

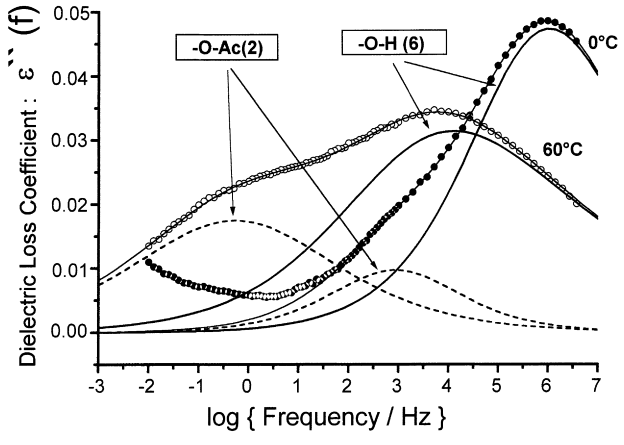

Fig. 5. Dielectric loss spectrum $\epsilon''(f,T)$ of 2-*O*-Ac-AMS with $DS_{Ac} = 0,79$ and the HN-fit-curves (as in Fig. 4).

better understanding for the assignment of relaxations in the loss spectrum and to connect them with motions of specific dipoles (OH-groups or acetyl side groups) in the AGU, the 2-*O*-acetyl starches with different DS_{Ac} and amylomaize starch as starting material was investigated intensively. To demonstrate the loss spectra relaxations at the two temperatures 0 and −60°C only are shown in Figs. 4–6.

As can be seen in Figs. 4–6, the separate two individual relaxation curves can be assigned to the methylol-group in position C-6 (abbreviated as OH(6)) and the acetyl group in position C-2 (abbreviated as OAc(2)) at the AGU. In all the figures the individual HN-fit results are represented as lines. As in pure starches or celluloses the motions of the hydroxyl groups in positions C2 and C-3 are not observable in our frequency range [19,20].

The highest frequency process is established as an orientation process of the methylol group OH(6). In general this relaxation is similar in frequency position and shape to the motion of this side group in the regioselective substituted 2-*O*-acetyl starches and amylomaize starch as well as in all other pure polysaccharides [8].

We intend to publish a fuller account elsewhere [21], which deals with the molecular interpretation of the low temperature relaxation in pure polysaccharides in general, and shall discuss the question whether the methylol-peak can be interpreted as the local chain motion.

The lower frequency loss peak in Fig. 4 is associated with a motion of the acetyl group in position C-2 of the AGU. The mobility of the acetyl group and therefore the shift of its γ-relaxation in the loss spectrum also depend on the position substituted at the AGU. Because of the known substitution pattern of 2-*O*-acetyl starches this result indicates that it is possible to allocate and to investigate the side group motions in different positions at the AGU separately.

To support this interpretation, regioselective acetyl derivatives of amylomaize starch with different degrees of substitution in position C-2 were measured.

The loss curves $\epsilon''(f)$ at the temperatures 0 and −60°C of 2-*O*-acetyl starches, $DS_{Ac} = 0.79$ and $DS_{Ac} = 0.34$, in Figs. 5 and 6 show the γ-relaxations and the HN-fit results of the total and the individual relaxations, respectively. The intensity of the acetyl group relaxation is decreased depending on the lowered DS_{Ac}. The temperature dependence of the relaxation time $\tau(T)$ determined by the HN-fit procedure is represented in Fig. 7 in the form of an Arrhenius plot (log τ vs. 1000 K/T):

$$\tau(T) = \tau_0 \exp\{\Delta E/RT\} \tag{4}$$

Supplementary the relaxation time of the methylol group OH(6) in pure amylomaize starch is drawn. All conformational orientation processes show a thermally activated behaviour with a constant activation energy ΔE. The results are summarized in Table 2. In all samples the methylol group OH(6) is characterized by the same activation energy of 48 kJ/mol. This agrees with findings in the literature for this dielectric side group relaxation in all polysaccharides

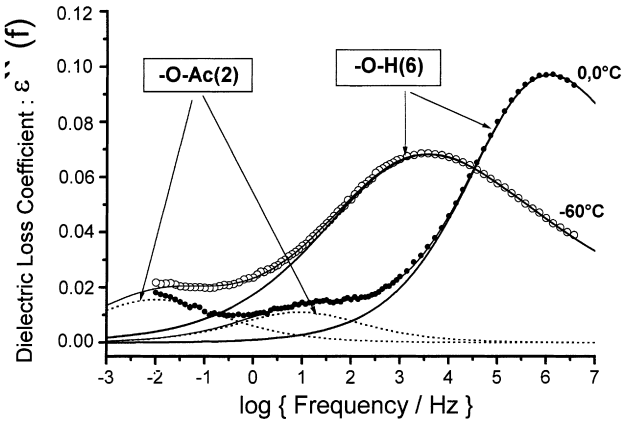

Fig. 6. Dielectric loss spectrum $\epsilon''(f,T)$ of 2-*O*-Ac-AMS with $DS_{Ac} = 0,34$ and the HN-fit-curves (as in Fig. 4).

[1–9,22,23]. The motions of the acetyl group in position C-2 are characterized by an activation energy of 60 kJ/mol similar in all the investigated samples (Fig. 7). The fact that the values of the relaxation times are different depending on the degree of substitution precludes a simple model for this local conformational motion which not only strongly depends on internal energetics (deformations of the shape of the potential curves) but also on environmental local packing effects.

The interpretation of the temperature dependence of the relaxation strength $\Delta\epsilon(T)$ in dependence on the degree of substitution is much more complicated (Fig. 8). In general the intensity of the acetyl polarization is lower than the dielectric effect of the methylol group. This is a result of the lower effective dipole moment of the acetyl group in relation to the hydroxyl group (see Eq. (3)). The experimental temperature dependence on the relaxation strength shows no typical $1/T$-temperature dependence due to the dominance of cross correlation between the dipolar sites in this

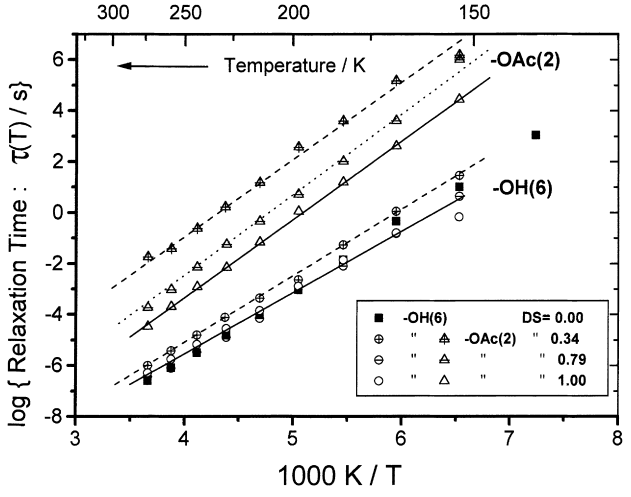

Fig. 7. Temperature dependence on the relaxation times $\tau(T)$ for the two peaks in the dielectric spectra of regioselective 2-*O*-Ac-AMS with different DS_{Ac} from Figs. 4–6 (Arrhenius plot).

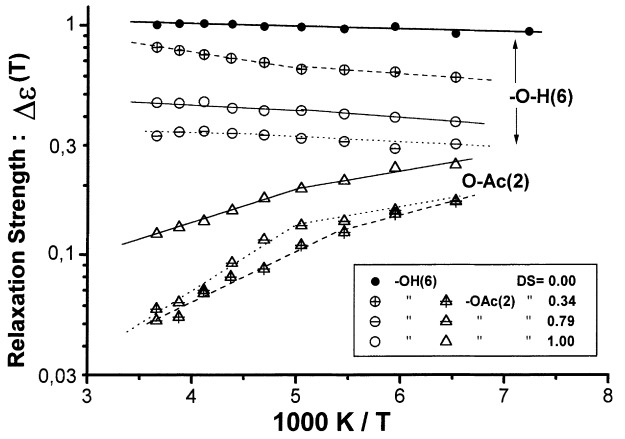

Fig. 8. Temperature dependence on the relaxation strengths $\Delta\epsilon(T)$ for the two peaks in the dielectric spectra of regioselective 2-*O*-Ac-AMS with different DS_{Ac} from Figs. 4–6 (Arrhenius plot).

polymer system. The disordered sequence of the relaxation strength of methylol group polarization to the degree of substitution indicates some local environmental effects, the detailed interpretation of which is impossible at present (Fig. 8). We abstain from the reproduction and discussion of the shape parameters $\alpha(T)$ and $\beta(T)$ in this article because their information is not clearly interpretable at the molecular level.

4.3. Dielectric relaxation in O-acetyl starch, $DS_{Ac} = 1.05$, with a statistical substitution pattern at the AGU

To demonstrate the effect of regioselectivity of substitution in relation to a statistical substitution pattern at the AGU, an *O*-acetyl starch with $DS_{Ac} = 1.05$ was measured and compared with the regioselective 2-*O*-acetyl starches. In Fig. 9, the dielectric loss spectra $\epsilon''(f)$ of all acetylstarches and the pure amylomaize starch are compared at −75°C. The HN-fit is carried out using the three following relaxation processes:

1. the contribution of polarization of the methylol group OH(6);
2. the common indistinguishable contributions of acetyl groups in positions C2 and C-3 at the AGU (abbreviated as OAc(2 + 3));
3. the additional effect of polarization by the acetyl group in position C-6 (abbreviated as OAc(6)) at the AGU.

Position and shape of the γ-relaxation OH(6) is fixed in the fit procedure with values determined in pure starches; only its intensity is fitted as a free parameter.

Caused by the partial substitution of the hydroxyl group in C-6 position by an acetyl group and by the different conformational mobility of the polar acetyl group in comparison to the hydroxyl group (compare Fig. 1), significant differences of the loss-spectrum of the *O*-acetyl starch with the statistical substitution pattern at the AGU in

Table 2
Results of dielectric spectroscopy of amylo-maize starch, regioselective 2-*O*-acetyl amylo-maize starch with different amounts of DS_{Ac} and an *O*-acetyl amylo-maize starch with a statistical substitution pattern

Substances	DS_{Ac}	Side group								
		O–H (6)			*O*-Ac (2) resp. *O*-Ac (2 + 3)			*O*-Ac (6)		
		ΔE_γ kJmol^{-1}	$\tau_o\ 10^{-16}$ s	$\Delta\epsilon$ (−60°C)	ΔE_γ kJgmol^{-1}	$\tau_o\ 10^{-16}$ s	$\Delta\epsilon$ (−60°C)	ΔE_γ kJmol^{-1}	$\tau_o\ 10^{-16}$ s	$\Delta\epsilon$ (−60°C)
Amylomaize starch (AMS)	0.00	51.0	2.6	0.986	–	–	–	–	–	–
2-*O*-Ac-AMS	0.34	50.0	2.7	0.687	60.9	200	0.087	–	–	–
	0.79	48.8	1.0	0.317	63.0	1.6	0.165	–	–	–
	1.00	47.4	4.3	0.424	60.3	1,2	0.176	–	–	–
O-Ac-AMS	1.05	46.7	3.1	0.10	56.0	62	0.303	28.4	810	0.451

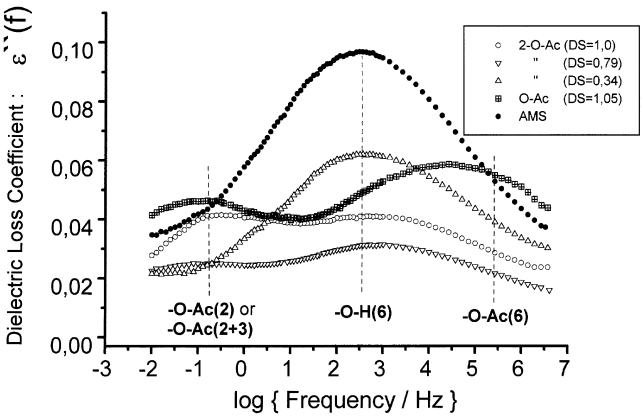

Fig. 9. Comparison of the dielectric loss spectra for pure starch (AMS), regioselective starch-acetates (2-*O*-Ac-AMS) with different DS_{Ac}-values and statistical *O*-Ac-AMS ($DS_{Ac} = 1,05$) (the maxima positions of the individual relaxation processes are marked).

comparison to regioselectively substituted 2-*O*-acetyl starches could be shown in the temperature range of −135 to 0°C.

Fig. 10 shows the experimental data and the HN-fit results for all three individual relaxation processes (lines) at 0 and −60°C. That means, using the dielectric spectroscopy different dipolar groups—like OH and OAc—in the same position at the AGU can be distinguished in the corresponding derivatives of starches and other polysaccharides. However this conclusion presupposes that individual relaxation processes are proved using model polymers with regioselective distribution of the dipolar side groups.

The relaxation strength of the acetyl relaxation in position C-2 increases nearly in a linear way with an increasing number of acetyl groups in this position as shown in Fig. 11. This fact supports the interpretation of the dielectric spectra presented. The decreasing intensity of the γ-relaxation of the methylol group OH(6) with an increasing DS_{Ac},

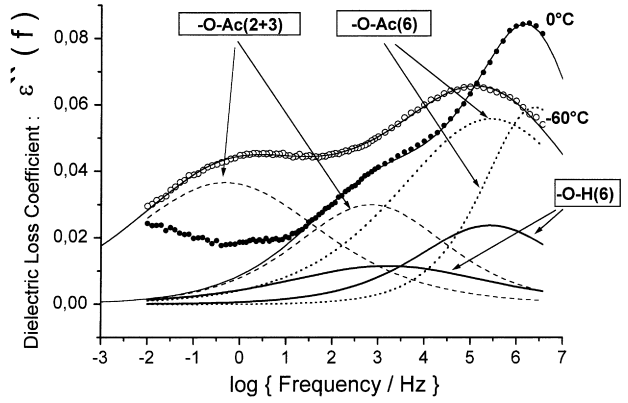

Fig. 10. Dielectric loss spectrum $\epsilon''(f,T)$ of statistical *O*-Ac-AMS with $DS_{Ac} = 1,05$ and the HN-fit-curves for three individual relaxation processes for two selected temperatures (−60°C and 0°C) (points, experimental values; lines, theoretical curves for the individual relaxations).

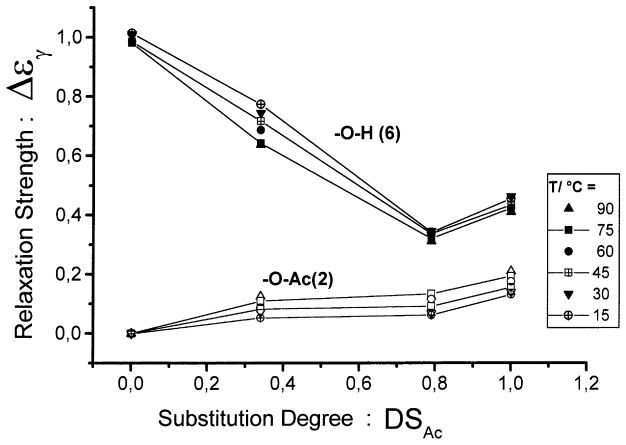

Fig. 11. Influence of the degree of substitution DS_{Ac} to the intensity of the individual side-group-relaxation for 2-*O*-acetyl-AMS ($DS_{Ac} = 0.0$ means pure amylo-maize starch).

but with the same amount of hydroxyl groups in this position, can only be explained with the sensitivity of this orientational dynamics to supramolecular structural effects. The dynamics in position C-2 at the AGU appears to be less sensitive to structural effects; it is illustrated by the nearly linear $\Delta\epsilon$ (DS_{AC}) relation in Fig. 11.

Further, in Figs. 12 and 13 for all individual relaxation processes in the regioselectively 2-*O*-acetyl starch, $DS_{Ac} = 1.00$, and the statistically substituted *O*-acetyl starch, $DS_{Ac} = 1.05$, the relaxation times and the relaxation strength, respectively, are compared. The differences in the activation energies seem to be due to the different dipolar contributions. Therefore the values for the same group in both types of derivatives are similar. All activation energies are summarized in Table 2. In the case of relaxation of the acetyl group in the position C-3 it was not possible to distinguish this motion from the side group in position C-2; at a lower frequency that process is described as OAc(2 + 3) relaxation (Table 2).

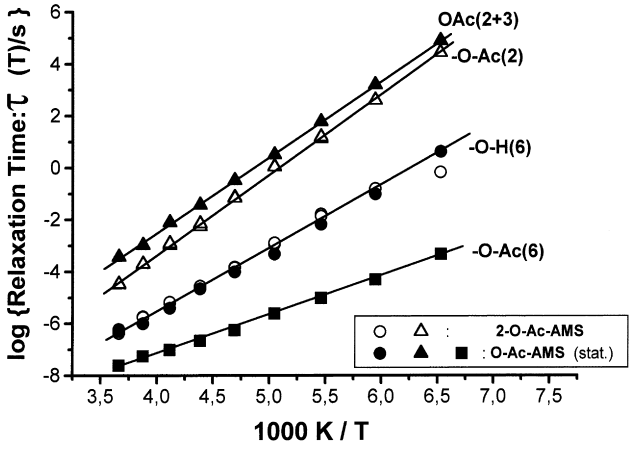

Fig. 12. Arrhenius plot of the relaxation times $\tau(T)$ of the statistical *O*-Ac-AMS in comparison to the regioselective 2-*O*-Ac-AMS of nearly the same.

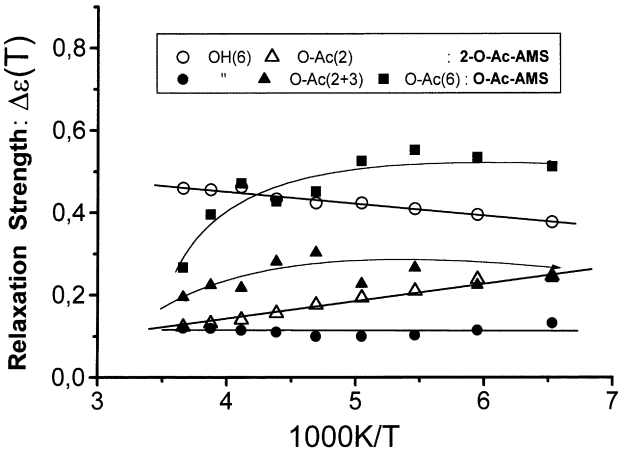

Fig. 13. Temperature dependence on the relaxation strengths $\Delta\epsilon(T)$ for the statistical *O*-Ac-AMS in comparison to the regioselective 2-*O*-Ac-AMS of nearly the same.

5. Conclusions

In well-dried acetyl-starches different γ-relaxation processes are observed by the dielectric measurements in the low temperature range of −135 to 0°C.

The γ-relaxations can be assigned to the side group motion (acetyl group) at the AGU which are clearly influenced by the position at the AGU and the type of the substituent. The acetyl groups in position C-2 and in position C-6 are characterized by relaxation processes with a drastic shift in frequency and in their activation energies of 60.0 and 28.4 kJ/mol, respectively. This is caused by the differences in the degrees of freedom in the conformational motion of the dipolar side group in position C-6 in relation to the groups in position C-2 or C-3 at the AGU.

The relaxation process of the methylol group OH(6) has got an activation energy of 48.0 kJ/mol also found in pure cellulose and cellulose derivatives with methylol groups OH(6) in the low temperature range. The intensity of this motion is very sensitive to local packing effects in the biopolymer, whereas the relaxation time and its activation energy are not very sensitive to morphological influences.

Having the same DS_{Ac}, the dielectric spectra of statistical *O*-acetyl starch and regioselective 2-*O*-acetyl starch can be distinguished. In general three different dielectric low temperature relaxation processes are found and assigned to the methylol group in position C-6 and to acetyl groups in position C-2 as well as positions C-2 and C-3 and position C-6 (abbreviated as OH(6), OAc(2), OAc(2 + 3) and OAc(6), respectively) (Figs. 4 and 12).

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