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The influence of the type of substituents on the polymer dynamics of different regioselective 2-*O*-esters of starch using dielectric spectroscopy

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Abstract

The dielectric relaxation spectra of different regioselective 2-*O*-acyl-esters of amylomaize starch with a degree of substitution DS = 1 were measured in an extended temperature (−135 to 0 °C) and frequency range (0.01 Hz to 3 MHz). For all starch esters, two relaxation processes were found, which are from the type of a secondary relaxation (constant activation energy). One process can be assigned to the local backbone motion of the polymer and the other one with the ester side group motion in position C2 at the anhydro glucose unit. The dynamic parameters of both relaxations were determined and compared. The double bond in the crotonoyl-ester side group has a little influence on both the segmental and the side group motion in relation to the butanoyl-ester. The bulky benzoyl-ester side group shows an inverse influence on the local chain dynamics than the alkyl-ester side group. © 2001 Published by Elsevier Science Ltd.

Keywords: Starch; Starch derivatives; Polymer dynamics

1. Introduction

In our first paper [1], we have reported how regioselective acetylation of amylomaize starch in the position C2 at the anhydro glucose unit (AGU) affects the polymer dynamics by using dielectric spectroscopy in solid state. Finally, the main results were two relaxation processes can be separated in well-dried samples, which are related, on the one hand, to the local chain motion or the segmental motion of the polymer backbone (this relaxation is called β-relaxation) and, on the other hand, to the side group motion of the substituent at the AGU. These investigations were continued by measuring the influence of low water contents and the type of starches on the dielectric response [2]. In this paper, a short review of the literature concerning the dielectric investigations on starch and starch derivatives can also be found. The interpretation of the β-relaxation as local chain process used in this paper and in our article [2] is different from the first paper [1] and it was justified in Ref. [3] in detail. The main arguments for this are: (i) This process has been found in all pure well-dried and wet polysaccharides and, especially, in dextrane not containing methylol side groups too. (ii) In all polysaccharide derivatives investigated and, especially, also in all 6-O-derivatives, this process was found with similar dynamic parameters. (iii) Finally, the decrease in the relaxation strength $\Delta\varepsilon'$ of the β-relaxation with increasing degree of substitution (DS) found in the papers [1,4] can be convincingly explicated by assuming a backbone dynamics for this relaxation.

Within the scope of investigation of the dynamics in polysaccharides and its derivatives using the dielectric relaxation spectroscopy, we have now investigated the influence of the type of substituent for starch esters regioselectively derivatized in position C2 at the AGU. These 2-*O*-acyl-starches are good model substances for this project. The preparation of these starch derivatives with a defined DS in position C2 at the AGU between DS = 0.1 and 1.0 [5–7] is well investigated and it can be well handled practically. Crosscorrelation of side group and chain motion and intensity reduction of the dielectric response by decorating the polymer backbone with bulky acyl-esters as side groups are sufficiently low for these derivatives. Crosscorrelation means, in this context, connection between different motion modes. In our interpretation, it is assumed that bulky substituents can only reorientate relatively to the backbone, if a segmental motion of the chain takes place simultaneously. The low relaxation time of the γ-relaxation is also mainly controlled by the slow local chain motion. Intensive decoration of the chain by bulky substituents at high DS (DS > 1–1.5 depending on the particular system) also increases the

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stiffness of the polymer chain resulting in a decrease of its polarizability. Therefore, the relaxation processes of side groups at the AGU and the segmental motion of the chain backbone are well separable, if this crosscorrelation is sufficiently weak. This is exactly our finding obtained from all our investigations on derivatives of polysaccharides (see Ref. [8]). It is a general result of our investigations of both starch esterified (acetyl-starch [2]) and cellulose derivatives (acetyl-cellulose [8]; tosyl-cellulose [9]) that for higher DS values the intensity of dielectric relaxation processes is reduced intensively and it is difficult to separate the dielectric spectrum into individual relaxation processes.

2. Materials and methods

2.1. Sample preparation

2-*O*-acyl-starches (DS = 1.0) were prepared as described in Refs. [5,7] recently. The primary structure of these well-designed starch esters (see Fig. 1) had been investigated by multi-dimensional NMR spectroscopy. Details are also written in our papers [5,7].

2.2. Dielectric measurements and its interpretation

The complex dielectric permittivity $\varepsilon^*(f,T)$ is given by Eq. (1) where $\varepsilon'(f,T)$ is the real component of the dielectric permittivity (also called store coefficient) and $\varepsilon''(f,T)$ the imaginary component (called dielectric loss coefficient). The dielectric loss factor $\tan\delta(f,T) = \varepsilon''(f,T)/\varepsilon'(f,T)$.

$$\varepsilon^*(f,T) = \varepsilon'(f,T) - j\varepsilon''(f,T) \qquad (1)$$

Both experimental magnitudes available from capacity and loss factor measurement of a condenser filled with sample contain the same information expressed by the Kramer–Kronig rule. An advantage of measuring both spectra simultaneously is, on the one hand, that it does increase the statistical reliability and, on the other hand, the correctness of the correction for dc-conductivity influence on the loss coefficient can be proved well in this way. All samples were well dried at the temperature of 80 °C under vacuum conditions for 24 h. The chemical decomposition under this condition was controlled by comparing the IR spectra before and after this procedure and, in all cases, no decomposition was detected.

The complex dielectric function was measured in the extended frequency range of 10 mHz to 3 MHz and in the temperature range of −135 to +40 °C using the Broadband Dielectric Spectrometer System of Novocontrol.

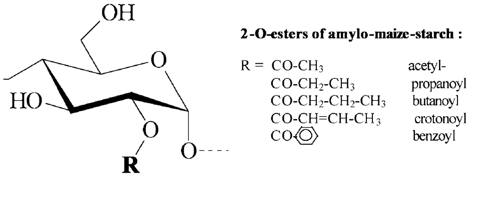

Fig. 1. Chemical structure of the 2-*O*-esters of amylomaize starch with DS = 1.

We assume that the total relaxation is the linear superposition of different separable relaxation processes. These individual relaxation processes and its characteristic parameters were determined using the model function of Havriliak and Negami (HN equation) [10]. This evaluation of the experimental spectra was described in the early papers in detail [2,8]. The HN equation represents the *i*th relaxation process by the following expression:

$$\Delta\varepsilon_i^* = \Delta\varepsilon_i/\left[1 + (\mathrm{i}\omega\tau_i)^{\alpha_i}\right]^{\beta_i} \qquad (2)$$

Each individual relaxation process '*i*' is also represented by four HN relaxation parameters: $\tau_i(T)$, the intensity of the relaxation process $\Delta\varepsilon_i(T)$, the width $\alpha_i(T)$ and the asymmetry $\beta(T)$ of the relaxation process (note that α is not the half-width of the loss curve in the definition of Eq. (2)). The relaxation time τ_i gives the position of the relaxation process in the frequency scale, whereas $\alpha_i(T)$ and $\beta_i(T)$ are shape parameters for this process and are associated with the distribution of the relaxation times. The error of the HN parameter determined by Eq. (2) was estimated between 1 and 8%.

The temperature dependence of the relaxation times was evaluated with the help of Eqs. (3a) and (3b)

$$\tau(T) = \tau_0 \exp\{E_a/RT\} \qquad (3a)$$

$$\tau(T) = \tau_D \exp\{-S_aR\} \exp\{H_a/RT\} \qquad (3b)$$

where E_a is the activation energy, H_a the excess enthalpy, S_a the excess entropy, $\tau_D = h/kT_0 = 1.76\times10^{-13}$ s, R the universal gas constant, k the Boltzmann constant, h the Planck constant and $T_0 = 273.15$ K.

3. Results and discussion

The starch derivatives used are distinguished from usual derivatives by its defined substitution pattern (Fig. 1). Due to the high regioselectivity of esterification in position C2 in the AGU, these 2-*O*-esters of amylomaize starch are excellent model substances for the detailed investigations of the influence of substituent side group on the polymer dynamics in solid state. The electric conductivity was measured simultaneously with the dielectric parameters for all frequencies and temperatures. Its value is necessary for the correction of the conductivity contribution to the dielectric loss coefficient and provides the activation energy for the conductivity process too. On the other hand, the conductivity values provide some good information to detect water residues in the sample and to prove simultaneously chemical decomposition of the derivatives at higher temperatures.

For example, Fig. 2a shows the conductivity spectra for 2-*O*-crotonoyl-starch in an extended temperature range (measured between −135 and +160 °C). The behaviour

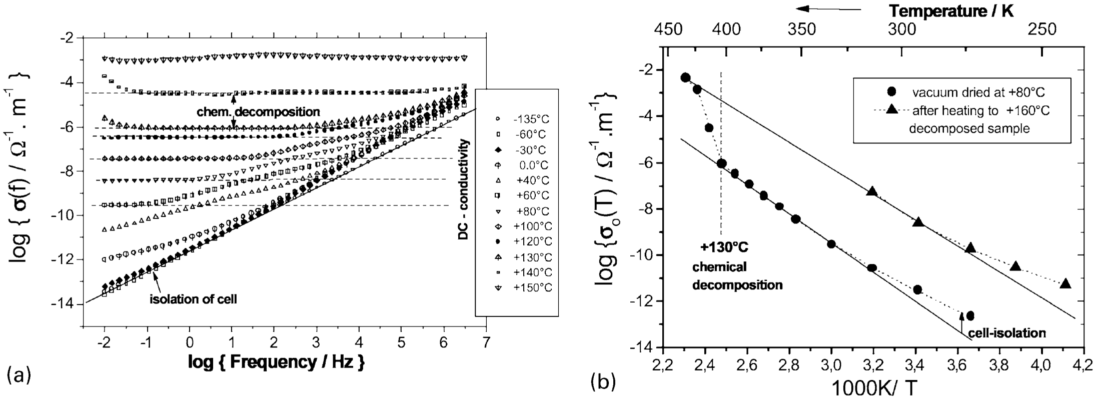

Fig. 2. (a) The conductivity spectra ($\sigma'(f)$ real part of the complex conductivity) measured for 2-*O*-crotonoyl-amylomaize starch ('isolation of cell' means the σ-curve of the empty cell—see text). (b) The activation diagram (Arrhenius plot) of the dc-conductivity of the well-dried sample at +80 °C under vacuum conditions and also for the same sample after heating to +160 °C showing chemical decomposition.

presented in this figure is typical for other starch derivatives investigated: At low temperatures, the conductivity measured is determined by the electrical isolation between the two electrodes of the empty measuring cell (denoted as isolation in Fig. 2). If the loss coefficient of the isolation material $\varepsilon''_{\text{iso}}$ (teflon in our case) is independent of the frequency, it leads to linear increase of the conductivity curves: $\sigma' = \omega\varepsilon_0\varepsilon''_{\text{iso}}$. This behaviour was also measured for the empty cell. The plateau at higher temperatures and low frequencies presents the dc-conductivity (σ_{CD}) of the material measured. In Fig. 2b, these values determined in this way are shown with its temperature dependence. The dc-conductivity makes a sudden change at the temperature of nearly +130 °C caused by chemical decomposition of the substance, which is detected by a mass loss and the variation of colour of the sample too. The partially decomposed substance shows another dc-conductivity, which was reproducibly measured in a following frequency sweep at low temperatures (second curve in Fig. 2b). These simple measurements were used to control the chemical stability of the sample during the heating procedure in the spectrometer. As a result, most samples have been heated only to 80 °C for measuring the dielectric spectra.

A typical example representing all other 2-*O*-esters of amylomaize starch is shown in Fig. 3a–c as experimental isotherms of the loss coefficient spectra (Fig. 3a: $\varepsilon''(f;T)$), the store coefficient spectra (Fig. 3b: $\varepsilon'(f;T)$) and also the spectral results in the form of a Cole–Cole diagram (Fig. 3c: $\varepsilon''(f;T)$ vs. $\varepsilon'(f;T)$) for 2-*O*-butanoyl-amylomaize starch in the whole temperature range, respectively.

From the physical point of view, the information is the same (Kramer–Kronig rule) in both experimentally found magnitudes and Fig. 3a–c, but only in the loss spectra and in the Cole–Cole diagrams, two relaxation processes can be visually distinguished. In each figure, the lines present the HN-fit results for the same set of HN parameters. This result substantiates the consistency of the data experimentally determined in our measurements and the absence of conductivity contributions to the dielectric losses. The relaxation process at higher frequency is associated with the segmental motion in the polymer chain. This local mode of the polymer backbone dynamics is called β-relaxation. The other process, at lower frequencies, we assign to the 2-*O*-ester side group motion relatively to the main chain as it was argued recently in other papers [1,2] in detail. The main arguments for these assignments follow from the comparison of the dynamic parameters of both relaxations found in pure starch (and other polysaccharides) or other starch derivatives and, especially, the linear DS dependence of the γ-peak in the loss spectra of weakly derivatized acetyl starches [2]. In the window of Fig. 3a and in Fig. 3c the two individual processes are separately shown. For all other starch esters investigated, the dielectric spectra are qualitatively similar:

In Fig. 4, different 2-*O*-acylated starch derivatives are compared by its dielectric loss spectra. Its spectra in the whole temperature range are qualitatively very similar to those shown for 2-*O*-butanoyl-starch in Fig. 3a–c. Two relaxation processes can be distinguished again: A dominating relaxation in the high frequency part of the spectrogram was found, which is only slightly shifted in comparison with β-process in pure starch. This small shift depends on the substituent of the special starch derivative. At the low-frequency side of the β-relaxation peak, the γ-process can be separated, which is lower in the intensity and much more dependent on the type of the substituent. It is difficult to find a general relation between the dynamic parameters of the γ-relaxation and the chemical structure of the side group in this actual state of investigation. Nevertheless, the discussion of the individual relaxation parameters gives several indications to the dynamic effects of the different substituent groups: By the HN-fitting of the spectra at all temperatures, the relaxation times for the chain relaxation (β-relaxation) as well as for the side group relaxation (γ-relaxation) were determined. Its temperature dependence is presented in Fig. 5 in the form of an activation plot

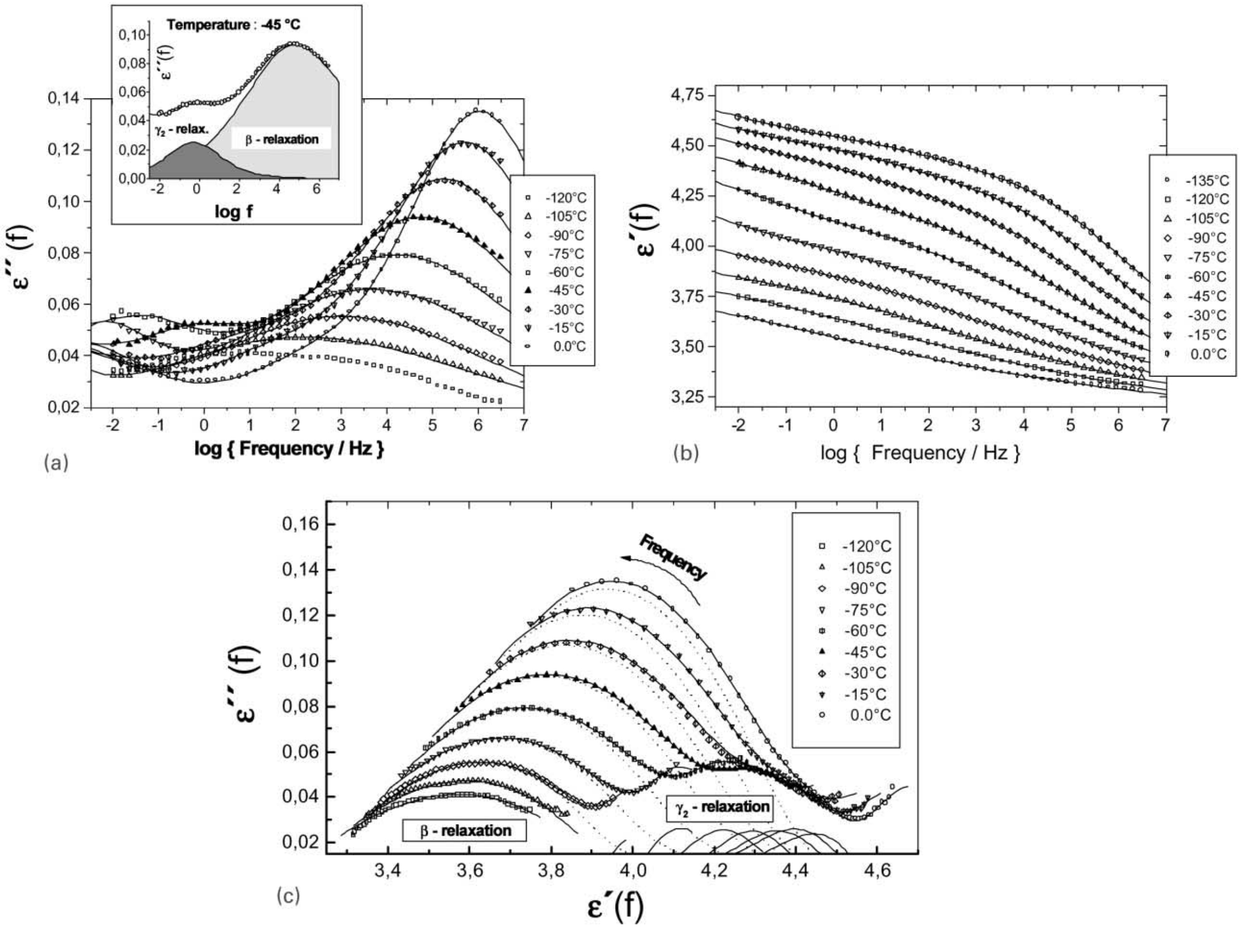

Fig. 3. Dielectric spectral results for 2-*O*-butanoyl-amylomaize starch: (a) dielectric loss spectra $\varepsilon''(f;T)$, window: loss spectrum at the temperature of −45 °C separated into the β- and γ-relaxation; (b) dielectric store spectra: $\varepsilon'(f;T)$; (c) Cole–Cole representation of the dielectric spectra: $\varepsilon''(f;T)$ vs. $\varepsilon'(f;T)$.

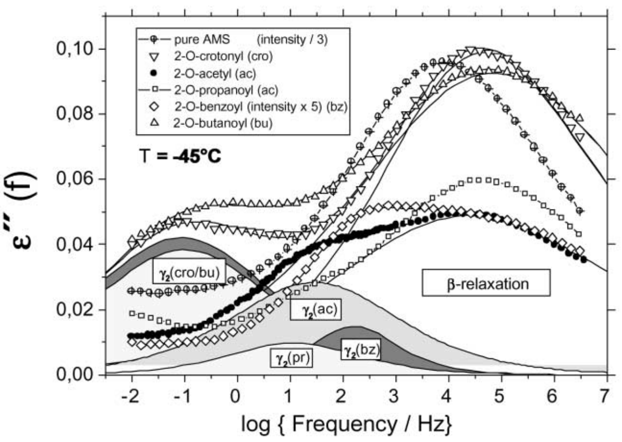

Fig. 4. Comparison of the dielectric loss spectra for following 2-*O*-esters of amylomaize starch and pure AMS at the temperature of −45 °C: 2-*O*-acetyl- (ac), 2-*O*-propanoyl- (pr), 2-*O*-butanoyl- (bu), 2-*O*-crotonoyl- (cro) and 2-*O*-benzoyl-starch (bz) (the individual γ-relaxations are highlighted).

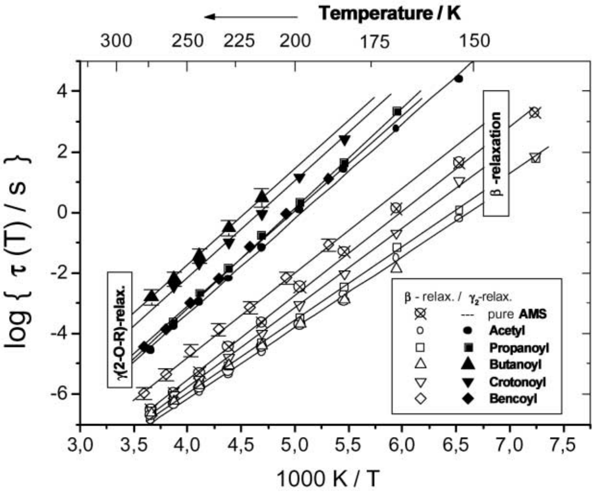

Fig. 5. Activation plot (Arrhenius diagram) of the relaxation times $\tau(T)$ calculated for all 2-*O*-esters of starch investigated and for pure amylomaize starch as reference.

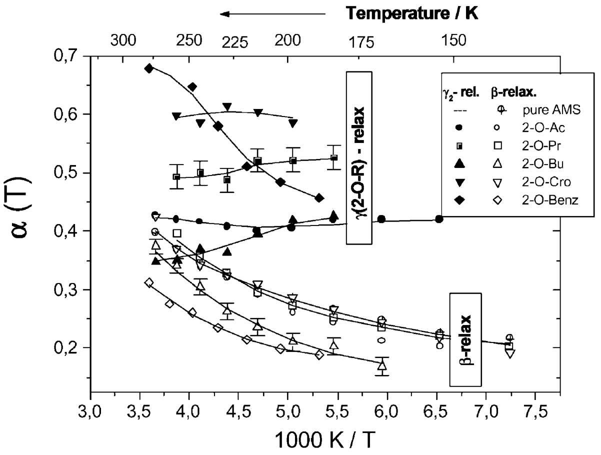

Fig. 6. Relaxation width $\alpha(T)$ of the relaxation times calculated for all 2-*O*-esters of starch and for pure amylomaize starch as reference.

(Arrhenius plot): log τ vs. $1/T$. Both relaxation processes are well separated in this picture and both show an Arrhenius-like behaviour. The other HN parameters of the two dynamic processes detected as relaxation width $\alpha(T)$ (distribution parameter of the relaxation time) and relaxation intensity $\Delta\varepsilon(T)$ (relaxation strength) are shown in Figs. 6 and 7, respectively. The activation energies $E_a(\beta)$ and $E_a(\gamma)$ for all derivatives were calculated from the slope of relaxation time curves in the Arrhenius diagram as well as the pre-exponential factors $\tau_0(\beta)$ and $\tau_0(\gamma)$ using Eqs. (3a) and (3b). All parameters are summarized in Table 1. A systematic relationship between activation energies and the structure of the side group esters could not be found in these examples of derivatives. For the selected temperature of −60 °C, Table 1 contains also the intensity HN parameters $\Delta\varepsilon$ and the relaxation width HN parameters α for the two motion processes separated.

All measurements of these figures confirm that the two dynamic processes—the local main chain motion (β-relaxation) and the side group motion of the *O*-ester group in position C2 of the repeating unit (γ_2-relaxation)—have

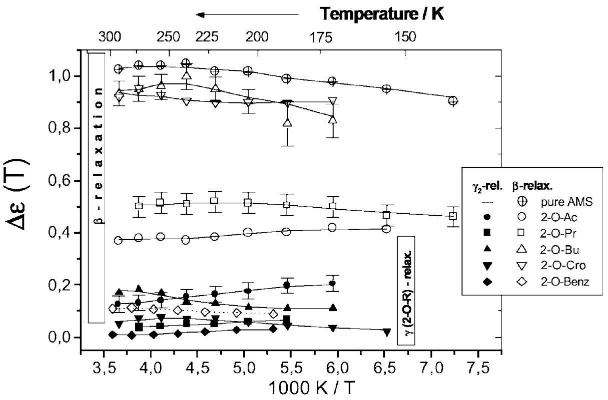

Fig. 7. Relaxation strength $\Delta\varepsilon(T)$ of the relaxation times calculated for all 2-*O*-esters of starch and for pure amylomaize starch as reference.

Table 1
HN-fit parameters at one temperature and the activation energies E_a and the pre-exponential factor τ_0 for all 2-*O*-esters of amylomaize starch investigated

No.	Substance, 2-*O*-esters	β-Relaxation				γ-Relaxation			
		$E_a \pm 1.5\%$ (kJ/mol)	$\tau_0 \pm 20\%$ (10^{-16} s)	$\Delta\varepsilon(-60\,°C) \pm 15\%$	$\alpha(-60\,°C) \pm 3\%$	$E_a \pm 10\%$ (kJ/mol)	$\tau_0 \pm 30\%$ (s)	$\Delta\varepsilon(-60\,°C) \pm 15\%$	$\alpha(-60\,°C) \pm 3\%$
0	AMS	53.7	0.18	1.02	0.31	–	–	–	–
1	2-*O*-acetyl-AMS	45.0	2.7	0.38	0.29	61.0	7.9×10^{-17}	0.17	0.40
2	2-*O*-propanoyl-AMS	45.5	3.6	0.52	0.28	63.0	4.4×10^{-17}	0.05	0.52
3	2-*O*-butanoyl-AMS	43.0	14.1	0.95	0.27	54.7	6.3×10^{-13}	0.13	0.40
4	2-*O*-crotonyl-AMS	49.2	0.90	0.90	0.31	53.2	6.9×10^{-14}	0.073	0.60
5	2-*O*-benzoyl-AMS	52.2	2.7	0.10	0.22	66.6	1.0×10^{-17}	0.024	0.51

clear different dynamic properties. The side group dynamics is more Debye-like ($\alpha = 1$) expressed by higher α-values like the segmental chain dynamics and for polymers it shows less pronounced characteristic widening of the relaxation processes in the frequency scale (Fig. 6). Qualitatively, all relaxation width (α) of the β-relaxation shows a similar decrease with a reduction of temperature. In contrast, the side group dynamics shows nearly constant α-values in the whole temperature range, except the benzoyl group. Furthermore, the relaxation time of the γ-relaxation is distinctly longer than for the β-relaxation with an activation energy, which is higher than for the local chain dynamics (Fig. 5 and Table 1). Our interpretation is that the side group motion is correlated with the segmental motion by sterical and other interaction effects, because a local motion of the polymer chain is necessary for a reorientation of a side group as argued before. The differences of the pre-exponential factors for the relaxation time between the different samples of 2-*O*-acyl-starches, and also in comparison with the τ_0-value for pure starch are not clear. Nevertheless, the butanoyl and the crotonoyl side group dynamics show a similar Arrhenius plot. The double bond of the crotonoyl group gives more stiffness for this side group than the single linkage of the butanoyl group. The surprising result was there is no influence on the dynamics of these side groups. The bulky benzoyl group is characterized by an appreciably different side group dynamics (see $\alpha(T)$—course in Fig. 6). The influence of this substituent on the chain dynamics is significantly different from the effect of the alkyl ester side groups. Only in the case of benzoylation in position C2, an increase of the relaxation time is observed. In all other cases, the relaxation time of the β-process decreased by esterification. Further explanations could be expected, if the DS in position C2 is varied. The dynamic effects in the side group and also in the main chain should depend on the DS value as shown recently [2].

Finally, some general remarks should be added: The intensity of the dielectric response of starch is reduced after derivatization in all cases. The same effect was observed for cellulose derivatives [9]. Only for substituents with a flexible spacer and end groups having a large dipolar moment like cyanoalkyl groups, dielectric effects are observed, which are stronger than in the case of the pure polysaccharide [11,12]. Therefore, the bulky benzoyl group owing a low permanent dipole moment yields the lowest relaxation strength of the β- and the γ-relaxation of all starch derivatives investigated.

4. Conclusions

Regioselective 2-*O*-esters of amylomaize starch are excellent model substances for the investigation of derivatization effects on the polymer dynamics of polysaccharides. In this context, the 2-*O*-esters of amylomaize starch were investigated using dielectric relaxation spectroscopy. Only secondary relaxations can be found in these polysaccharide derivatives in the solid state. Two dynamic processes are typical for the low-temperature spectra: the β-relaxation can be associated with the local chain motion and this dynamics is only slightly affected by derivatization in relation to the segmental motion in pure starch. Considering the β-relaxation, the bulky benzoyl side group has an inverse influence on the local chain dynamics than the alkyl-ester side groups. The reason for this result cannot be explained at present. Therefore, in future, investigations must be extended to further derivatives containing side groups with similar chemical structure and, additionally, extended measurements of the DS dependence of the dielectric response are necessary.

In the case of the γ-relaxation, which is associated with the side group motion relative to the polymer backbone, the following results can be emphasized: for the crotonoyl and the butanoyl ester, similar dynamics were found. That means, the double bound in the alkyl chain has a small influence on the segmental and the side group motion too. This result is important in view of the fact that the double bound increases the stiffness of the side group. On the other hand, the bulky and stiff phenyl group of the benzoyl-ester produces significantly different dynamic effects in the polymer. In general, the side group motions found have a more Debye-like character indicating that the polymeric character is less pronounced for this motion. On the other hand, the crosscorrelation between the side group motion and the chain motion of the polymer determines the relatively long relaxation time of the γ-relaxation.

All interpretations of our experimental results are consistent with the different experimental facts for pure polysaccharides and cellulose derivatives too. However, the assignments of the different relaxation processes found in the dielectric spectroscopy are only an indirect argumentation by comparing different chemical model substances. For a fundamental evidence of the molecular assignment of the different dielectric relaxation peaks, other methods should be carried out, for instance, dynamic solid-state NMR spectroscopy. Nevertheless, the dielectric spectroscopic results presented show that the dynamic analysis used leads to a lot of new information about the complex biopolymeric dynamics of starch and starch derivatives in solid state.

Acknowledgements

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