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Influence of the *p*-toluenesulphonylation of cellulose on the polymer dynamics investigated by dielectric spectroscopy

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Abstract

Cellulose *p*-toluenesulphonates (tosyl cellulose) were studied by dielectric spectroscopy. Two relaxation processes were observed for samples of low degrees of substitution (DS) in the low temperature range (−130 to 0 °C). These are related to the local chain and the tosyl substituent motion, β- and γ-relaxations, respectively. For DS values higher than 1.4, the dielectric spectra no longer could be separated into the individual processes, because the dielectric response became reduced in intensity and its distribution in the frequency scale was broadened by cross-correlation of different motions between the modes of the substituents and the segmental motions of the chain. Significantly, different local chain (β-relaxation) behaviour was found for derivatives of DS ≈ 0.9 with block-like and random distribution of substituents along the backbone. The dynamic behaviour of the tosylated polymers is compared with other cellulose derivatives and revealed similar qualitative behaviour, but the type of the substituents at the anhydroglucose unit has a characteristic influence on the dynamic parameters of the relaxation time, the activation energy related and the shape parameter of the relaxation processes.

Keywords: Cellulose; Derivatives; Dielectric relaxation; Local dynamics

1. Introduction

In past decades, many papers focused on dynamic properties of polysaccharides and low molecular weight saccharides in order to receive a more complete picture of the properties than it has been possible with commonly used techniques for characterisation of these polymers. Recently, dielectric spectroscopy in the solid state has also been applied to cellulosics (Liedermann & Lapcik, 1996; Montes & Canaille, 1999; Noel, Parker, & Ring, 2000; Saad & Furuhata, 1997). One major advantage of this method is that it comprises an extended range in the time scale (10^{-8}–10^{+3} s) connected with good resolution even with commercial equipment.

The dielectric relaxation spectroscopy (DRS) separates various dynamic processes according to different rates of molecular orientations in a polymer. The processes are accompanied with changes in the mean dielectric polarisation state of the material. The prerequisite of applicability is that the repeating units own a permanent dipolar moment. This is fulfilled for all polysaccharides with hydroxyl- and methylol-side groups as dipolar units in the repeating unit. Moreover, the pyranose ring has also an own dipolar moment. Derivatisation modifies the dipolar structure of the repeating unit, changes the mobility of both the side groups and the backbone, and modifies the hydrogen bond system of the biopolymer.

The assignment of the dynamic processes, registered by the DRS, to molecular reorientation motions were controversially discussed in the past, but the following interpretation has recently gathered more and more agreement (see also Butler and Cameron, 2000; Meißner, Einfeldt, & Kwasniewski, 2000; Ozawa, Mikami, Nitta, & Shinmura, 1989; Scandola, Ceccorulli, & Pizzoli, 1991; Veeravazhuthi, Narayandass, & Maangalaraj, 1998). The main relaxation, measured in the low temperature range (−120 to 0 °C), is related to the local backbone or segmental motion of the chain. This process will be called β-relaxation. The motion of the side groups on the repeating unit forms the γ-relaxation. All these relaxations are secondary processes in the notation of polymer physics and are described by Arrhenius behaviour in the activation

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Table 1
Reaction conditions, DS-values and solubility of products for the reaction of cellulose with Tos-Cl

Sample number	Starting cellulose	Path of synthesis	Molar ratio AGU/Tos-Cl	DS_{Tosyl}[a]	Solubility[b]
1	Bacterial cellulose	Homogeneous	1:1.4[c]	0.55	Swells in DMSO, DMA
2	Cotton linters	Homogeneous	1:1.2[c]	0.89	DMSO, DMA, swells in dioxane, THF
3	Spruce sulphite pulp	Via reactive microstructure	1:20:10[d]	0.9	–
4	Cellulose powder Avicel	Homogeneous	1:1.8[c]	1.43	Acetone, DMSO, DMA, dioxane, THF
5	Spruce sulphite pulp	Homogeneous	1:3[c]	1.8	See sample 4 and in $CHCl_3$, CH_2Cl_2
6	Cellulose powder Avicel	Homogeneous	1:4.5[c]	2.30	See sample 5

[a] DS determined on the basis of the sulphur analysis.
[b] DMSO = dimethyl sulphoxide, DMA = dimethylacetamide, THF = tetrahydrofuran.
[c] With triethylamine as base using 2 mol triethylamine/mol Tos-Cl.
[d] Molar ratio AGU/NaOH/Tos-Cl.

diagram ($\log\{\tau\}$ vs. $1/T$) for the relaxation time τ. The primary relaxation (α-process), which is related to the glass transition, was not found in dielectric spectra with well-dried polysaccharides and samples with low water contents (<15% w/w water).

First result of the dielectric spectroscopy of polysaccharides and their derivatives were given by Einfeldt and co-workers (Einfeldt, 1999; Einfeldt, Kwasniewski, Klemm, Dicke, & Einfeldt, 2000; Einfeldt, Meißner, & Kwasniewski, 2001a; Einfeldt, Meißner, Kwasniewski, & Einfeldt, 2001b). For weakly derivatised polysaccharides (DS < 1.4), the side groups produce a well separable relaxation process in addition to the backbone motion. Especially for starch derivatives, the intensity of this γ-relaxation was found to be determined by the degree of substitution (DS) and the type of the substituent (Einfeldt et al., 2000; Einfeldt et al., 2001b). Its position on the repeating unit has also influenced by the dynamic response.

Homogeneous *p*-toluenesulphonylation (tosylation) of cellulose provides convenient access to valuable cellulosic polymers with regard to their film- and membrane-forming properties. They are good starting products for various subsequent modifications in order to design highly advanced materials based on the renewable resource cellulose (Heinze, 1998; Heinze & Rahn, 1999), and therefore, the tosylation is sometimes denominated as functionalisation.

In this paper, we present results from tosyl cellulose focusing on the following questions:

1. Is the dynamics of main chain (β-relaxation) and side group (γ-relaxation) influenced by the DS?
2. Does the distribution of substituents, within the anhydroglucose repeating unit (AGU) and along the chain, have an influence on the relaxation processes in dielectric spectroscopy?
3. Are the results from cellulose tosylates comparable to those from other cellulose derivatives?

2. Experimental

2.1. Materials

As starting celluloses, spruce sulphite pulp (FLUKA), cotton linters (Temming AG, Glückstadt/Germany) and bacterial cellulose from *Acetobacter xylinum*, synthesised in the laboratory of the university in Jena, were applied. All samples were dried in vacuum at 100–105 °C. LiCl, *N*,*N′*-dimethyl acetamide (DMA) and *p*-toluenesulphonyl chloride (Tos-Cl) were purchased from FLUKA. The LiCl had to be treated for 2 h at 120 °C under vacuum to obtain an anhydrous material (Table 1).

2.1.1. Common procedure of p-toluenesulphonation

Both the preparation of the cellulose solutions and the homogeneous *p*-toluenesulphonation of the polymer with Tos-Cl were carried out according to a previously published prescription (Rahn, Diamantoglou, Klemm, Berghmans, & Heinze, 1996).

The investigated samples in this study had values of DS = 0.55 for the sample prepared from bacterial cellulose with a molar ratio Tos-Cl:AGU of 1.8:1; and DS = 0.89 prepared from cotton linters with a molar ratio Tos-Cl:AGU of 1.2:1. DS values higher than 1.4 were prepared with molar ratios of Tos-Cl:AGU > 1.8:1.

Iodination of the samples with anhydrous NaI in acetylacetone revealed a preferential tosylation at the C-6 position of the AGU (Rahn et al., 1996). The samples were soluble in a number of organic solvents.

2.1.2. p-Toluenesulphonation of cellulose to non-random substitution along the chain

Cellulose in the form of 1.5 g of spruce sulphite pulp dissolved in DMA/LiCl (2.5 wt%) was treated with 7.4 g of solid NaOH powder (particle size <1 mm) and suspended in 15 ml DMA at 10 °C. During the addition of solid NaOH, the solution becomes a gel-like mixture with suspended NaOH particles, which do not dissolve during the reaction. Tos-Cl (17.6 g) was added stepwise. After reaction for 5 h at 10 °C, the mixture was precipitated into 200 ml of water. Purification was carried out by washing with water and suspending the polymer in ethanol and acetone. After evaporation of these solvents, the sample was dried at 50 °C in vacuum. The yield was 81% (2.26 g) and the DS = 0.9 (based on sulphur analysis). Thus, the prepared sample was insoluble in common organic solvents and water.

The FTIR (KBr)-results expressed in cm^{-1} are 3520 (ν OH), 3077 (ν C–$\mathrm{H}_{\mathrm{arom}}$), 2890 ($\nu$ CH), 1560, 1500, 1453 (ν C–$\mathrm{C}_{\mathrm{arom}}$), 1365 ($\nu_{\mathrm{as}}$ SO_2), 1177 (ν_{s} SO_2), 815 (δ C–$\mathrm{H}_{\mathrm{arom}}$).

2.1.3. Other derivatives

Films of cellulose formate with a DS of 0.4 were kindly provided by Prof. Dr W. Oppermann/University of Stuttgart. Hydroxypropyl cellulose (HPC) and hydroxyethyl cellulose (HEC), chitin and chitosan, cyanoethyl cellulose, and 3-amino-3-desoxy cellulose were commercial products of the CarboMer Corporation (USA). Regioselective 2,6-*O*-thexyl-dimethylsilyl celluloses (2,6-*O*-Thx) were synthesised according to a procedure of Koschella, Heinze, and Klemm (2001). For details concerning synthesis and analysis of the substitution pattern on the level of the AGU, see Klemm and Stein (1995), Klemm, Stein, Heinze, Philipp, and Wagenknecht (1996).

2.2. Dielectric measurements

The complex dielectric function $\varepsilon^*(f,T)$ can be split into the dielectric store coefficient $\varepsilon'(f,T)$ (real part of $\varepsilon^*(f,T)$) and dielectric loss coefficient $\varepsilon''(f,T)$ (imaginary part of $\varepsilon^*(f,T)$) (see Böttcher and Bordewijk (1978).

$$\varepsilon^*(f,T) = \varepsilon'(f,T) - \mathrm{j}\varepsilon''(f,T) \tag{1}$$

(j is the imaginary unit: $\mathrm{j}^2 = -1$).

Both quantities are available by capacity measurement of a condenser filled with the sample. They provide the same information as is expressed by the Kramer–Kronig rule (Landau & Lifshitz, 1955). The advantage of simultaneously measuring both spectra is an increase in the statistical reliability. Furthermore, the influence of the direct current (dc)-conductivity of the sample and its correction for the experimentally determined loss coefficient can be checked and examined.

The complex dielectric function was measured in the extended frequency range of eight decades from 10×10^{-3} to 3×10^{6} Hz and in the temperature range of -135 to $+40$ °C. A Broadband Dielectric Spectrometer System from Novocontrol was used. The measuring condenser (C_{o}) had plane disc geometry. The empty capacitance was calculated by

$$C_{\mathrm{o}} = \varepsilon_{\mathrm{o}}A/d \tag{2}$$

with the help of the electrode area $A = \pi R^2$ and the distance d between the electrodes, where $2R$ is the diameter of the plane parallel circular electrode system and ε_{o} the permittivity of the vacuum. The real and the imaginary part of the complex permittivity of the sample result from the equivalent parallel circuit elements R and C of the sample filled capacitor, and is given by the relationships

$$\varepsilon'(f,T) = C(f,T)/C_{\mathrm{o}} \tag{3a}$$

$$\varepsilon''(f,T) = R^{-1}(f,T)/C_{\mathrm{o}} \tag{3b}$$

The contribution of the dc-conductivity to the dielectric loss coefficient could be neglected for well-dried samples in the low temperature range ($T < 0$ °C). Only in the case of medium and high temperatures ($T > 0$ °C) or for wet cellulose, the experimental loss coefficients had to be corrected by the dc-conductivity contribution using the equation

$$\varepsilon''(f) = \varepsilon''_{\mathrm{exp}}(f) - \sigma_{\mathrm{o}}f^n/\varepsilon_{\mathrm{o}}2\pi f \tag{4}$$

$\sigma_{\mathrm{o}}f^n$ describes the weak frequency dependence of the dc-conductivity of the amorphous material, and this was simultaneously measured by the dielectric spectrometer.

The total experimental error of these dielectric coefficients was estimated to range between 10 and 20% and originated from uncertainties in determining the thickness and the spatial inhomogeneity of the sample. The errors only influence the intensity parameter of the relaxation processes, but do not affect the dynamic parameters, i.e. the relaxation times and their distribution. The error of the circuit components R and C amounts to <1–2%. All samples were dried at 110 °C in vacuum. To obtain a better sample homogeneity, the material was pressed under vacuum at 1900 bar resulting in thin sheets of $2R = 30$ mm in diameter and $d =$ 0.07–0.13 mm in thickness. The thickness of each sample was measured with a micrometer screw. These sheets were inserted into the measuring capacitor and, once more pressed at a reduced pressure of 500 bar. This procedure gave a good and reproducible electrical contact of the polymer with the metallic electrode. The measuring capacitor was flushed by dry nitrogen gas from the thermostat system. The measurements always started at the lowest temperature and moved on step by step to higher temperatures (temperature steps 15 or 20 °C). The accuracy of temperature control was ±0.1 °C.

2.3. Evaluation of the dielectric spectra

A common model for an individual relaxation process in the frequency domain is the relaxation model-function of Havriliak and Negami (HN-function) (Böttcher & Bordewijk, 1978; Havriliak & Negami, 1966; McCrum, Read, & Williams, 1991). For the complex contribution of the *i*th relaxation process, the HN-expression is

$$\Delta\varepsilon_i^* = \Delta\varepsilon_i/[1 + (\mathrm{j}\omega\tau_i)^{\alpha_i}]^{\beta_i} \tag{5}$$

This general relaxation equation includes the special cases of the relaxation expressions suggested by Debye, Cole–Cole, and Davidson–Cole, respectively.

Application of this relationship allowed the description of

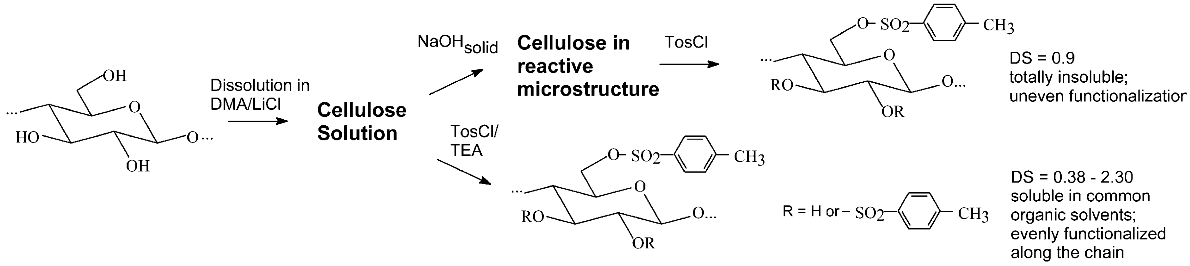

Fig. 1. Scheme for the different reaction paths of cellulose *p*-toluenesulphonation.

each relaxation process 'i' by four relaxation parameters: the relaxation time $\tau_i(T)$ represents the central position of the process in the time scale and is approximately inverse to the maximum frequency: $\tau_i(T) \approx 1/(2\pi f_{\max,i})$ (exact if $\beta_i = 1$, which corresponds to a symmetrical relaxation process). The relaxation strength (or intensity) $\Delta\varepsilon_i(T)$ is the step in the real part of the complex permittivity or, adequately, the area below the loss peak $\varepsilon''(\log f)$. The $\alpha(T)$-parameter characterises the width and β the asymmetry of the relaxation process. A Debye process is characterised by $\alpha = \beta = 1$.

The error of the HN-parameters consists of a random error, between 1 and 3% depending on the intensity of the relaxation process, and a systematic error. The latter one arises from the fact that the four HN-parameters are not independent of each other. Furthermore, in cases of overlapping relaxation processes or if the process is not well located in the measuring window of our spectrometer, the relaxation is not fully determined by the experiment. In these cases, we fixed the β-parameter at values, which were extrapolated from the temperature dependence of this parameter that was found from spectra at temperatures with well-defined HN-parameters. By variation of the β-parameter and determination of the mean square error of the fit procedure, we estimated an upper limit of the confidence interval for the parameters, which are presented in this paper.

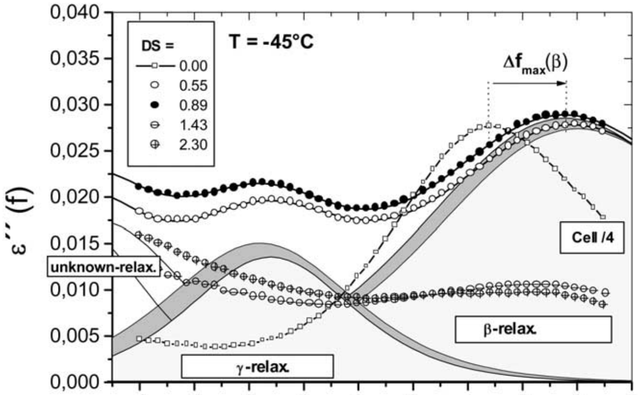

Fig. 2. Dielectric loss spectra at $T = -45$ °C from tosyl cellulose of different DS and random distribution of substituents, at the repeating unit and along the chain.

3. Results and discussion

3.1. Influence of the DS on the dielectric response

In a first set of experiments cellulose *p*-toluenesulphonates (tosyl cellulose) were investigated, which were prepared via the homogeneous reaction path (see Fig. 1). These samples are characterised by a preferential substitution of the C-6 position randomly distributed along the polymer chain. The dielectric measurements of these samples with different DS show the results of Fig. 2.

Three relaxation processes can be distinguished for samples of low DS (DS < 1.2). The fast relaxation can be assigned to sequential motions in the chain (β-relaxation). Additional processes are related to the totality of all side group motions (γ-process). At low frequencies, an additional process of unknown origin appeared. For higher DS than DS > 1.2, the intensity of the dielectric response was strongly reduced, and it became difficult to separate individual processes. Apparently, at high DS-values the voluminous and stiff tosyl-side groups coat the glucose chain such that the polymer chain becomes strongly hindered in its reorientation to the applied electrical field. The side groups are also impeded in their mobility by a coupling of the side group and segment chain motions.

For all investigated samples, the temperature dependence of the two relaxation processes could be presented by straight lines in the Arrhenius plot for the relaxation time (Fig. 3) and by a characteristic temperature dependence of the two other HN-parameters, both reliably found. The intensity $\Delta\varepsilon(T)$ (upper inset) and the width of the relaxations (lower inset in Fig. 3) are also presented. In cases, where a separation in two processes was possible for the low DS, the activation plots for the relaxation times of the segmental chain motion exhibited almost the same form and gave nearly the same activation energy of $E_a(\beta) = 38.5 \pm 1.5$ kJ/mol. The values are reduced compared to cellulose with $E_a(\beta) = 45 \pm 2$ kJ/mol. The side group motion, generated by the tosyl-groups, showed similar energetic properties, but had very different τ_o-values (see Fig. 3 and Table 2). The relatively high values of the pre-exponential factor τ_o for the side group dynamics of these low-substituted derivatives have to be interpreted such that for this low DS, the side group dynamics follow nearly Debye behaviour. This means low co-operativity or weak

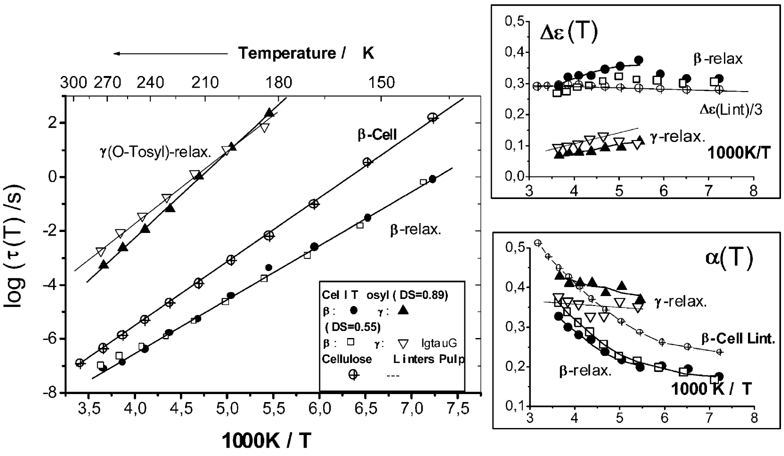

Fig. 3. HN-fit parameters for weakly substituted tosyl-cellulose ($DS_{tos} = 0.55$ and 0.89) in comparison to non-derivatised cellulose. Left inset: Activation or Arrhenius plot of the relaxation times ($\tau(T)$) for local backbone dynamics (β-relaxation) and side group motion (γ-relaxation). Upper right inset: Intensities of both relaxation processes ($\Delta\varepsilon(T)$). Lower right inset: Width parameter of both relaxation processes ($\alpha(T)$).

coupling to the segmental motion (compare Eq. (6b) in Section 3.3).

The sudden change in the DS-dependence of the dielectric properties in the DS-range between 1.2 and 1.4 appears in a different light, if the solubility of tosyl celluloses with different DS-values in various solvents (Fig. 4) is taken into consideration.

With increasing chemical polarity of the solvent, the solubility of the low DS tosyl derivatives improves (Heinze & Rahn, 1996; Heinze & Rahn, 1997). As demonstrated by Fig. 4, there occurs an abrupt change in the solubility at DS-values between 1.3 and 1.5. This fact can be interpreted by an increase of accessibility for the solvent molecules due to structural or morphologic changes (e.g. heterogeneities), when the DS becomes high. The hindered segmental mobility in the chain also correlates with the dielectric local chain polarisablity in the same DS-range. As a general result, a similar DS-dependence can be stated for the chemically based solubility and the physical property of the chain dynamics.

3.2. Influence of the substitution pattern along the chain on the dielectric response

A fundamental question is the influence the distribution of substituents along the chain has on the chain dynamics. Two tosyl derivatives of cellulose with DS of 0.89 and 0.90, respectively, were studied and compared with each other. The samples were prepared according to the two different reaction paths as shown in Fig. 1. The cellulose tosylate with DS = 0.9 was obtained from a conversion under the influence of powdered NaOH, which was expected to lead to a statistical uneven, more block-like pattern of substituents along the chain. This sample was insoluble in most common organic solvents even for the remarkably high DS. The second sample of DS = 0.89 was obtained by homogeneous derivatisation and should therefore have a random pattern of tosyl groups along the chain.

Fig. 5 compares the dielectric loss spectra for these two cellulose tosylates. The dielectric spectra for these derivatives are clearly different. The side group motion, shown in Fig. 6 as activation plot, is independent of the distribution of substituents along the chain, while the backbone dynamics is more cellulose-like for the derivatised obtained by the conversion to a block-like microstructure, in contrast to results for the derivative with random distribution.

For the block-like derivatised chain, this result can be interpreted in that these chain sequences are contained in non-substituted cellulose structures. The HN-α parameters (relaxation width) also show a systematic change in the order of cellulose > block-like > randomly substituted derivatives (inset of Fig. 6). This experimental result clearly

Table 2
HN-parameter of the different dynamic processes determined by dielectric spectroscopy for tosyl-cellulose

Tosylate DS	β-Relaxation				γ-Relaxation			
	E_a (KJ/mol)	log τ_o (s)	$\Delta\varepsilon$ (−60 °C)	α (−60 °C)	E_a (KJ/mol)	log τ_o (s)	$\Delta\varepsilon$ (−60 °C)	α (−60 °C)
Error	± 0.6	± 0.3	0.06	0.02	± 1.5	± 0.5	0.015	0.03
0.55 (statistically)	38.2	−14.6	0.31	0.25	51.9	−12.5	0.13	0.33
0.89 (statistically)	38.7	−14.6	0.34	0.23	60.5	−14.9	0.09	0.39
0.90 (block-like)	44.8	−15.7	0.37	0.27	53.6	−15.4	0.07	0.47
< 1.4	DRS-spectra not separable in separate relaxation processes							

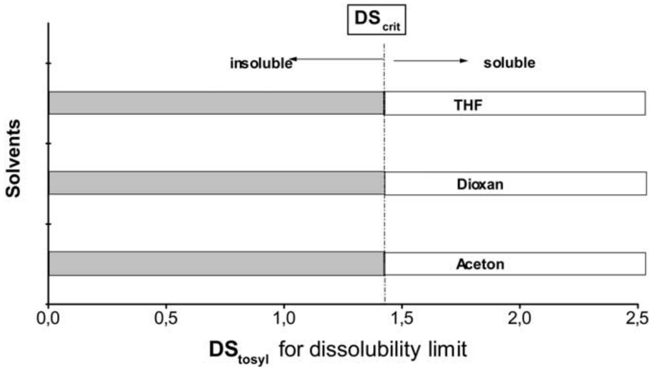

Fig. 4. DS-dependence of solubility for tosyl-celluloses in three solvents at $T = -45$ °C. An abrupt change in solubility at near DS = 1.42 was found.

demonstrates the effect of the special procedure for the cellulose derivatisation. In addition to a change in solubility, it also modifies the dielectric chain dynamics in the solid state.

3.3. Comparison of the tosylates with other types of cellulose derivatives

The effect of chain modification by derivatisation on the polymer dynamics of cellulose was found similar for the tosylate and other derivatives. In Fig. 7, the results from various other, not regio-selectively substituted cellulose derivatives, are summarised in the form of activation plots for the relaxation time.

Again two different relaxation processes can be distinguished by two groups of straight Arrhenius-lines, one for the local segment motion of the chain (β-relaxation) and another one for the side group motion (γ-relaxation). The occurrence of the β-process in all derivatives, and also for substituents in position C-6 at the AGU, supports the conclusion that this process is related to the local chain dynamics and not to the motion of the methylol group in non-substituted polysaccharides and its derivatives (compare Meißner et al., 2000). However, this local chain dynamics is modified by the type of substituents. For comparison, the relaxation time from non-derivatised cellulose is also shown in Fig. 7. In chitin and chitosan, the change of the chain motion is weak, but becomes strongest for cellulose formate. The group of γ-processes, representing the side group motion, display nearly the same slopes (activation energy), but a large variation in the pre-exponential factor τ_o of the Arrhenius relationship:

$$\tau(T) = \tau_o \exp\{E_a/RT\} \tag{6a}$$

$$\tau(T) = \tau_D \exp\{-S_a R\}\exp\{H_a/RT\} \tag{6b}$$

where E_a is the activation energy, H_a the excess enthalpy, S_a the excess entropy, $\tau_D = h/kT_o = 1.76 \times 10^{-13}$ s, R the universal gas constant, k the Boltzmann constant, h the Planck constant, and $T_o = 273.15$ K.

Eq. (6b) was derived by Eyring and co-workers from thermodynamic arguments (Glasstone, Laidler, & Eyring, 1941). It correlates the deviation of the pre-exponential factor τ_o from the Debye τ_D-value to excess entropy due to reorientation in the relaxation process. High entropy

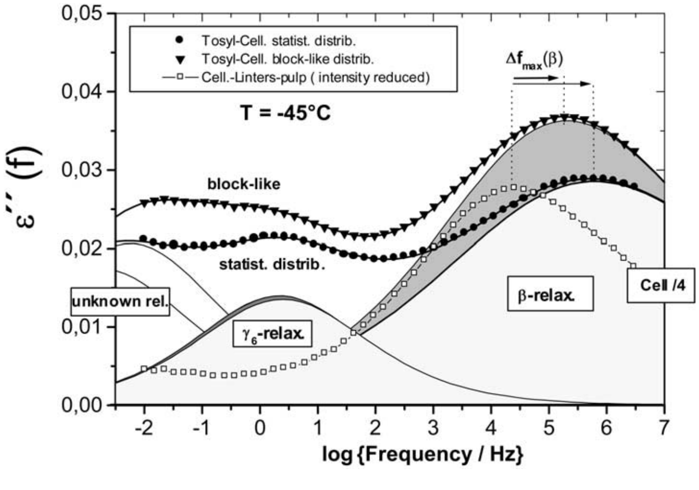

Fig. 5. Dielectric loss spectra of tosyl cellulose with nearly the same DS (0.89 and 0.90, respectively), but random and block-like distributions of substituents along the chain for $T = -45$ °C. The individual relaxation processes are shown by lines and marked by different grey tones.

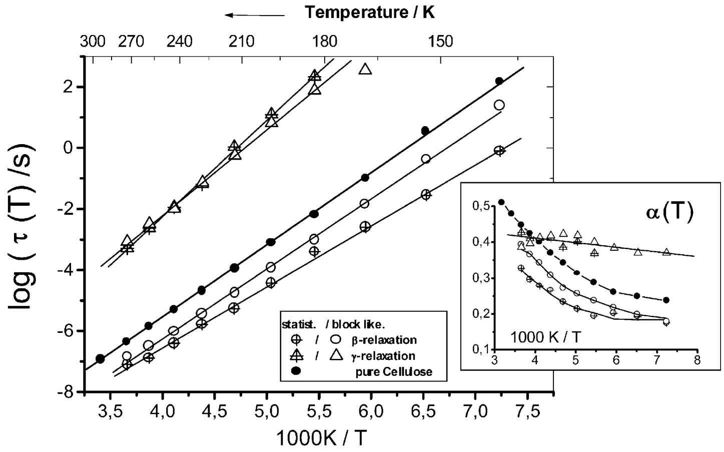

Fig. 6. Activation plot of the relaxation times for the local main chain (β-process) and the tosyl-side group dynamics (γ-relaxation) of randomly and block-like distributed substituents along the backbone and, in addition of non-substituted cellulose (Linters sulphate pulp). Right inset: Relaxation width $\alpha(T)$ for the individual relaxations.

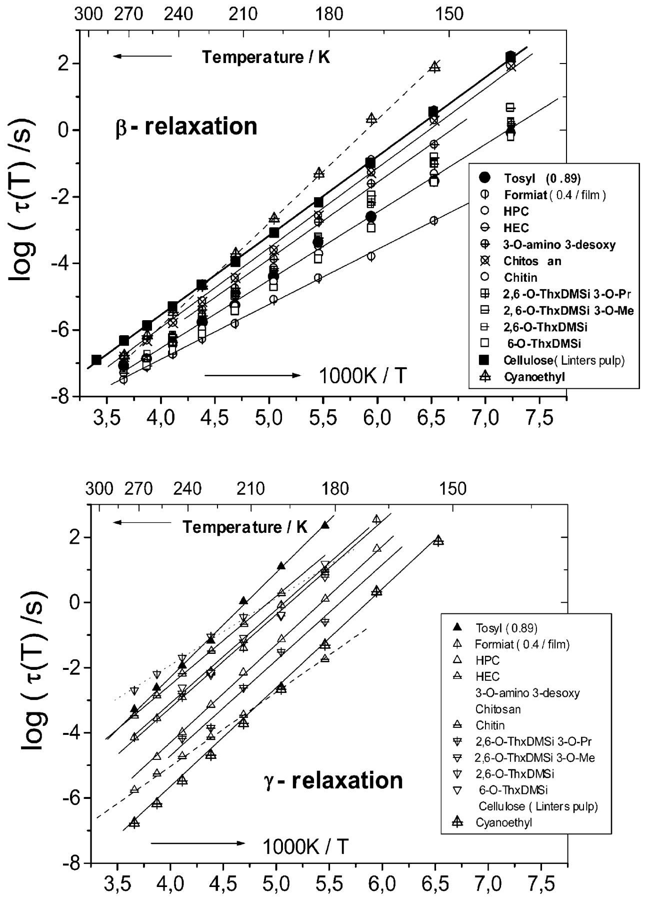

Fig. 7. Activation plots for the relaxation time for various cellulose derivatives with random distribution of the substituents at the AGU and along the chain (Tosyl (0.89)—*p*-touenesulphonate with DS = 0.89; HPC—hydroxypropyl cellulose; HEC—hydroxyethyl cellulose; ThxDMSi—thexyl-dimethylsilyl-; Pr—propyl-; Me—methyl-; Cyanoethyl—cyanoethyl-cellulose).

values can be interpreted to arise from co-operativity of the orientational motion of neighboured side chains. The obtained results mean that large side groups (hydroxyalkyl-, tosyl-, thexyl-groups) lower the activation energies for the chain dynamics in comparison to cellulose and derivatives with small side groups (formate-, amino-acetyl- or amino-groups). The latter show contrary influence. The pre-exponential factors of the β-relaxations are similar in all investigated samples, with the exception of the formate derivative, which, however, was measured as film (see also Table 3). In most cases, the activation energies of the side-group motion are higher than for the segmental motion. The pre-exponential factors for the two alkylcelluloses and the cyanoethyl cellulose are lower than for the other substances. This result indicates a cross-correlation of the side group motion with the chain motion in the solid state. The reorientation of side groups is coupled to the motion of the chain. For thexyl-dimethyl-silyl celluloses (Thx-cell) and aminoacethyl cellulose (chitin), the picture of the pre-exponential factors does not fit the outlined scheme, but there is a hint for a lower co-operativity of the motion with these low polar ether-side groups which cannot yet be discussed in detail, because to this end measurements at various DS have to be performed.

For the cyanoethyl cellulose, the dielectric spectra could not be separated into the β- and γ-processes. This failure is caused by the large dipole moment of the cyano side group and the flexible ethyl-group spacer. The corresponding Arrhenius curve is situated between the β- and the γ-relaxations and shows also a different value for the activation energy than for the other derivatives.

The study of the substituent effects on the polymer dynamics of starch derivatives (Einfeldt, Kwasniewki, Dicke, Klemm, & Einfeldt, 2001c) revealed similar behaviour and supports the results from the cellulose derivatives presented in this paper.

Table 3

HN-parameter of the dynamic polymer properties of cellulose derivatives were discussed in this paper (notation of samples as in Fig. 7)

Substance		β-Relaxation				γ-Relaxation			
Name	Chemical structure	E_a (kJ/mol)	log τ_o (s)	$\Delta\varepsilon$ (−60 °C)	α (−60 °C)	E_a (kJ/mol)	log τ_o (s)	$\Delta\varepsilon$ (−60 °C)	α (−60 °C)
	Error	± 0.6	± 0.3			± 1.5	± 0.5		
Tosylate (DS = 0.89)		38.7	−14.6			60.5	−14.9		
Formate (DS = 0.4 (film))		31.4	−13.4			55.7	−14.9		
HPC		38.1	−14.7			58.5	−16.6		
HEC		39.3	−14.7			48.4	−12.6		
Cell Linters pulp		45.6	−15.1						
3-*O*-amino-3-desoxy		45.2	−15.8						
Cyanoethyl		–	–			57.5	−17.8		
Chitosan		48.2	−15.0						
Chitin		46.1	−15.2			42.6	−13.9		
2,6-*O*-Thx 3-*O*-Pr		41	−15.1			51.6	−15.4		
2,6-*O*-Thx 3-*O*-Me		42.6	−15.4			51.1	−13.8		
2,6-*O*-Thx		40.3	−14.8			41.9	−10.7		
6-*O*-Thx 2,3-*O*-Me		39.3	−15.1			53.8	−14.3		

4. Conclusions

DRS presents a possibility to estimate local chain and side group motions in various cellulose derivatives. Block-like and random substitution patterns along the backbone could clearly be distinguished from each other by their β-relaxations (segmental motions). Tosyl celluloses of low DS < 1.4 show significantly different behaviour than the higher substituted derivatives. In the latter case, it was impossible to separate the β- and γ-relaxations. Dielectric spectroscopic from other cellulose derivatives resulted in qualitatively similar behaviour, but the type of substituent at the AGU had a characteristic influence on the absolute values of the dynamic parameters.

The present results are considered as a first step to a comprehensive investigation of the effect of substituents and their distribution along the chain on the local chain dynamics. In particular, the coupling of the side group with segmental motions is of special interest. We know already of the strong influence of water traces in these polysaccharides, which makes it imperative to carefully control the water content if consistent results about this substituent dependence are to be established.

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