

## RESEARCH ARTICLE

# Determination of the degree of substitution of cellulose esters via ATR-FTIR spectroscopy

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**Abstract**

Cellulose derivatives are promising bio-based polymeric materials with possible applications ranging from thickening agents and stabilizers to optical films. The precise determination of their degree of substitution (DS) is crucial, as the DS substantially influences the material properties of such cellulose derivatives. Herein, the applicability of attenuated total reflection-Fourier transform infrared for DS determination of cellulose esters was investigated. Sixteen cellulose acetates with DS ranging from 0.41 to 2.99 were synthesized and three acetyl group-specific vibrational signals were evaluated quantitatively in reference to the cellulose anhydroglucose unit vibration  $\nu(\text{C}-\text{O})_{\text{AGU}}$ . A non-linear correlation for the absorbance intensity with the DS was observed and the data was fitted based on a newly developed model with correlation coefficients  $R^2$  between 0.958 and 0.998, depending on the evaluated signal. This DS determination method is simple and efficient, since it does not need any prederivatization or extensive sample preparation and can furthermore be applied to non-soluble samples. In order to widen the scope, eight cellulose butyrates, six cellulose laurates and six cellulose benzoates with different DS were synthesized and the DS determination method could be analogously applied to these cellulose esters, but a separate calibration for the different esters was found to be necessary.

**KEYWORDS**

cellulose acetates, cellulose benzoates, cellulose butyrates, cellulose esters, cellulose laurates, degree of substitution, infrared spectroscopy

## 1 | INTRODUCTION

A wide variety of cellulosic materials with different properties can be obtained via chemical modification of cellulose, such as etherification, nitration, phosphorylation, or esterification.<sup>1–5</sup> Besides the type of modification, the properties of the resulting material also strongly depend on the degree of substitution (DS), which is defined as

the average value of substituents per anhydroglucose unit (AGU) and can vary between 0 and 3. Therefore, an accurate determination of the DS is crucial in order to evaluate structure–property relationships and design the related targeted material properties.

For this purpose, several DS determination methods were developed. The most common method for cellulose esters is the titration method, which is based on

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hydrolysis in alkaline solution with subsequent titration as a quantification method of ester moieties.<sup>6–9</sup> However, this method is limited to cellulose esters and is furthermore a destructive method and very time- and labor-intensive, requiring comparably large sample amounts. Alternatively, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy is a very useful method for DS determination as it is a direct, non-destructive method and applicable to a broad range of cellulose derivatives.<sup>10–21</sup> One of the main limitations of this method is the necessity for solubilization, which is especially challenging for cellulose derivatives with a low DS, which are often insoluble in common organic solvents. Furthermore, it is limited to cellulose derivatives with substituents that show signals in the <sup>1</sup>H NMR spectrum that do not overlap with those of the AGU protons that are typically used as reference for DS calculations. Another method for DS determination via NMR spectroscopy involves derivatization of the unreacted hydroxyl groups of the cellulose sample with, for example, a phosphorous-containing reactant, followed by quantitative <sup>31</sup>P NMR spectroscopy. This method was introduced by Kilpeläinen et al.<sup>22</sup> in 2010 and was initially proposed as a DS determination method for chloroform-soluble cellulose esters. However, several examples demonstrated the applicability to almost any class of cellulose derivatives, with the prerequisite of chloroform-solubility having been expanded by adjusting the derivatization procedure.<sup>23–28</sup> Nonetheless, solubility issues in combination with time consuming sample preparation remain the major limitation of this method. Further procedures for DS determination involving gas chromatography,<sup>29,30</sup> UV–Vis spectroscopy,<sup>31</sup> or elemental analysis<sup>14,32–34</sup> were developed, but most of them are time-consuming or limited by their applicability or precision.

Fourier transform infrared (FTIR) spectroscopy is a promising and often-used technique for the analysis of cellulose derivatives, as solid samples can be analyzed without any pretreatment, preventing the necessity of solubilization.<sup>35</sup> In prior research applying transmission FTIR spectroscopy for DS determination, a linear relationship between the carbonyl band absorbance area and the DS was observed, when commercial cellulose triacetate was used in different mass ratios relative to the used KBr in order to simulate different DS values of cellulose acetate.<sup>31</sup> This technique was shown to facilitate the construction of a calibration curve, as no different cellulose acetates with regularly spaced DS need to be synthesized. However, the examined samples need to be precisely weighed and homogeneously distributed within the KBr disc in the form of a fine powder to gain precise results. Especially cellulose acetates with lower DS (<1.5) cannot be easily ground to a fine powder due to their elastic consistency.<sup>31</sup> The requirement of a homogeneous KBr pellet

with a precisely weighed sample mass can be avoided by referencing the arising carbonyl band in the IR spectrum against a vibrational signal which is not affected by the acetylation. Cheng et al. referenced the carbonyl vibration of the acetyl group to the C—O stretching vibration of the cellulose backbone with mixtures of microcrystalline cellulose (MCC) and cellulose triacetate (CTA) to simulate cellulose acetates with DS ranging from 1.80 to 2.85 and observed a curvilinear relationship between the DS and the carbonyl band absorbance intensity.<sup>36</sup> A similar curvilinear relationship was found by Melo et al. for the DS determination of cellulose acetates via attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy, monitoring the O—H stretching vibration referenced to the C—O stretching vibration.<sup>37</sup> Zhang et al. referenced the carbonyl band against the bridge oxygen antisymmetrical stretching signal of the cellulose backbone for acetylated cellulose nanocrystals with a DS between 0.46 and 1.84, and observed a linear relationship with increasing DS.<sup>38</sup>

Herein, we investigated the application of FTIR spectroscopy via an attenuated total reflection unit (ATR) for the DS determination of cellulose acetates, which facilitates the measurement procedure as no KBr pellet has to be produced. Cellulose acetates with DS values ranging from 0.41 to 2.99 were prepared and used for the construction of a calibration curve, which was then compared to a calibration curve based on mixtures of cellulose triacetate with native cellulose. Furthermore, a plausible fit equation for the curvilinear calibration curve was developed and the applicability of this calibration based on cellulose acetate was investigated for other cellulose esters that is cellulose butyrates, benzoates, and laurates.

## 2 | RESULTS AND DISCUSSION

### 2.1 | Synthesis of cellulose acetates with different DS values

For the DS determination of cellulose acetates using ATR-FTIR spectroscopy, a calibration needed to be recorded in the first step. Therefore, a range of cellulose acetates with different, evenly spaced DS values were synthesized directly in homogeneous solution using the previously established DMSO/DBU/CO<sub>2</sub> switchable solvent system with vinyl acetate as the reactant (Figure 1).<sup>39–44</sup>

This synthetic route enables a precise and direct control of the DS over a very broad range by simply varying the equivalents of reactants.<sup>39</sup> In this way, 16 cellulose acetates were synthesized and their DS was determined using <sup>1</sup>H NMR spectroscopy (DS<sub>1H</sub>) as shown in Figure 2. Trifluoroacetic acid was used as an additive for the <sup>1</sup>H



Sample	DS <sub>1H</sub>	DS <sub>31P</sub>	DS <sub>IR,O-H</sub>	DS <sub>IR,C=O</sub>	DS <sub>IR,C-H</sub>	DS <sub>IR,C-O</sub>	DS <sub>IR,mean</sub> <sup>a</sup>
CA-1	0.41	– <sup>b</sup>	0.24	0.43	0.45	0.36	0.42
CA-2	0.59	– <sup>b</sup>	0.47	0.57	0.53	0.52	0.54
CA-3	0.70	– <sup>b</sup>	0.34	0.64	0.71	0.66	0.67
CA-4	1.11	– <sup>b</sup>	1.12	0.96	1.02	1.03	1.00
CA-5	1.21	– <sup>b</sup>	0.77	1.12	1.21	1.10	1.15
CA-6	1.33	1.44	1.60	1.42	1.54	1.39	1.45
CA-7	1.58	1.58	1.66	1.70	1.76	1.58	1.68
CA-8	1.63	1.64	1.57	1.63	1.63	1.65	1.64
CA-9	2.14	2.12	2.26	2.54	2.39	2.21	2.38
CA-10	2.33	2.31	2.60	2.24	2.23	2.39	2.29
CA-11	2.36	2.24	2.18	2.60	2.45	2.27	2.44
CA-12	2.42	2.34	2.24	2.46	2.32	2.21	2.33
CA-13	2.48	2.41	2.58	2.35	2.35	2.47	2.39
CA-14	2.55	2.46	2.41	2.94	2.66	2.48	2.69
CA-15	2.74	2.83	2.99	2.59	2.88	3.04	2.84
CA-16	2.99	2.96	2.96	3.07	3.08	2.88	3.01

<sup>a</sup>Determined from the DS<sub>IR,C=O</sub>, DS<sub>IR,C-H</sub>, and DS<sub>IR,C-O</sub>.

<sup>b</sup>Not determined due to insolubility.

TABLE 1 Degree of substitution (DS) values of all synthesized cellulose acetates applying different determination methods.

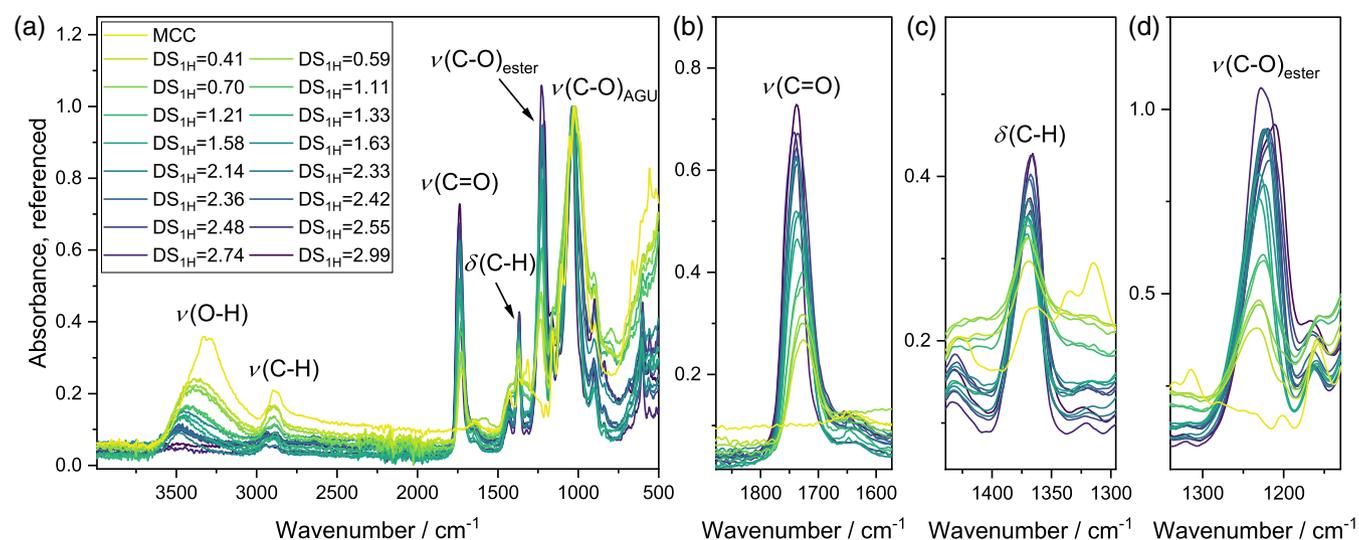


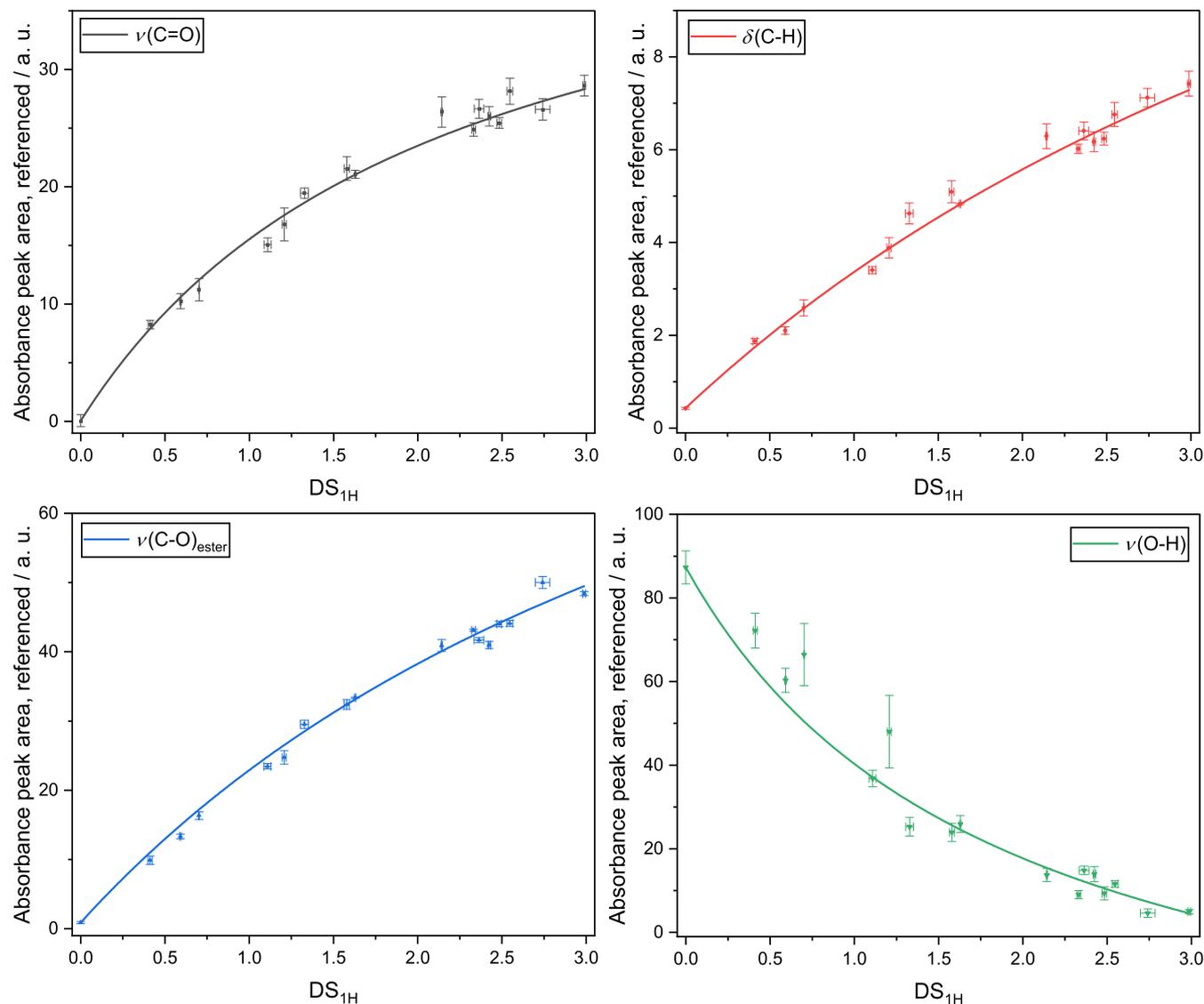
FIGURE 3 Overlaid attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of cellulose acetates with different degree of substitution (DS) values and expanded views of the  $\nu(\text{C}=\text{O})$ ,  $\delta(\text{C}-\text{H})$ , and  $\nu(\text{C}-\text{O})_{\text{ester}}$  vibrations of the acetyl moiety.

ca.  $\tilde{\nu} = 1220 \text{ cm}^{-1}$ . The O—H stretching vibration  $\nu(\text{O}-\text{H})$  at ca.  $\tilde{\nu} = 3325 \text{ cm}^{-1}$  decreases during the acetylation.

The strongest signal of native cellulose is the C—O stretching vibration of the AGU backbone  $\nu(\text{C}-\text{O})_{\text{AGU}}$  at  $\tilde{\nu} = 1030 \text{ cm}^{-1}$  and the intensity of this signal is assumed to not be affected by the degree of substitution. This signal was therefore chosen as the reference and all other signals were examined relative to it. The trend of an increasing absorbance of the three main acetyl related peaks (see above) with an increasing DS is visualized in

Figure 3. Pure and unmodified MCC was used as the reference substance with DS = 0.

For the quantitative evaluation, a baseline correction was applied. The baseline for the carbonyl stretching vibration was chosen as the average value in the range between  $1800$  and  $2000 \text{ cm}^{-1}$ , similar to the correction performed by Da Ros et al.<sup>21</sup> For the C—O stretching vibration, the value at  $1298 \text{ cm}^{-1}$  was taken for the baseline correction (Figures S111–S112). The spectrum of native cellulose exhibits a certain absorbance intensity in



**FIGURE 4** Absorbance peak area of the respective acetyl signal plotted against the degree of substitution ( $DS_{1H}$ ) of cellulose acetate. A non-linear regression was performed based on Equation (1). The absorbance of all samples was determined after being referenced to the  $\nu(C-O)_{AGU}$  vibration. The error bars correspond to the respective standard deviations of a fivefold determination for the absorbance and a triple determination for the  $DS_{1H}$ .

the wavenumber range of all three acetyl group specific signals ( $\nu(C=O)$ ,  $\delta(C-H)$ , and  $\nu(C-O)_{ester}$ ), which can be interpreted as the offset and are quantified by the variable  $c$  in Equation (1). The absorbance intensity of all cellulose acetate samples of the respective acetyl peaks were plotted against the  $DS_{1H}$  and are presented in Figure 4. The  $DS_{1H}$  was determined in triplicates from three different samples of each cellulose acetate batch and the standard deviation was calculated (error bars in Figure 4). The low deviation (ranging from  $\sigma = 0.01$  to  $0.04$ ) indicates high DS homogeneity of the synthesized cellulose acetates.

According to Lambert–Beer’s law, a linear correlation for the absorbance intensity with increasing DS was

expected. However, a curvilinear correlation was observed, which is in accordance with the investigations of Cheng et al. for mixtures of cellulose triacetate and MCC to model cellulose acetates in a DS range of 1.80–2.85.<sup>36</sup> In this previous publication, it was assumed that the Lambert–Beer law has its limitations and is only valid for systems with a low dispersion coefficient or at low concentrations.<sup>36</sup> Nevertheless, the curvilinear relationship can also be explained by another, in our opinion more plausible reason: if the reference peak intensity is influenced in a linear manner with increasing DS, which is in contrast to the previously made assumption, the relationship can be explained with Equation (1).

Cellulose ester	Peak	<i>a</i>	<i>b</i>	<i>c</i>	<i>R</i> <sup>2</sup>
CA	$\nu(\text{O—H})$	$-72.310 \pm 7.320$	$0.540 \pm 0.094$	87.282	0.958
CA	$\nu(\text{C=O})$	$22.738 \pm 1.113$	$0.470 \pm 0.048$	0.062	0.993
CA	$\delta(\text{C—H})$	$3.414 \pm 0.129$	$0.163 \pm 0.028$	0.428	0.998
CA	$\nu(\text{C—O})_{\text{ester}}$	$26.764 \pm 0.940$	$0.216 \pm 0.024$	0.886	0.998
CA-mixtures	$\nu(\text{O—H})$	$-39.668 \pm 1.914$	$0.147 \pm 0.024$	87.282	0.992
CA-mixtures	$\nu(\text{C=O})$	$20.077 \pm 1.104$	$0.391 \pm 0.049$	0.062	0.997
CA-mixtures	$\delta(\text{C—H})$	$5.451 \pm 0.392$	$0.499 \pm 0.078$	0.428	0.997
CA-mixtures	$\nu(\text{C—O})_{\text{ester}}$	$28.396 \pm 1.275$	$0.264 \pm 0.027$	0.886	0.998
CBu	$\nu(\text{C=O})$	$22.039 \pm 2.794$	$0.295 \pm 0.099$	0.062	0.988
CBu	$\nu(\text{C—O})_{\text{ester}}$	$30.098 \pm 4.826$	$0.433 \pm 0.154$	0.886	0.985
CL	$\nu(\text{C=O})$	$16.338 \pm 1.121$	$-0.021 \pm 0.038$	0.062	0.995
CL	$\nu(\text{C—O})_{\text{ester}}$	$12.324 \pm 0.849$	$-0.160 \pm 0.032$	0.886	0.997
CBz	$\nu(\text{C=O})$	$24.333 \pm 1.875$	$0.500 \pm 0.086$	0.062	0.992
CBz	$\nu(\text{C—O})_{\text{ester}}$	$60.093 \pm 10.832$	$1.189 \pm 0.324$	0.886	0.996

**TABLE 2** Results of the non-linear fit for cellulose acetate (CA), cellulose butyrate (CBu), cellulose laurate (CL), and cellulose benzoate (CBz) as well as CAs based on mixtures of cellulose triacetate and cellulose (CA-mixtures).

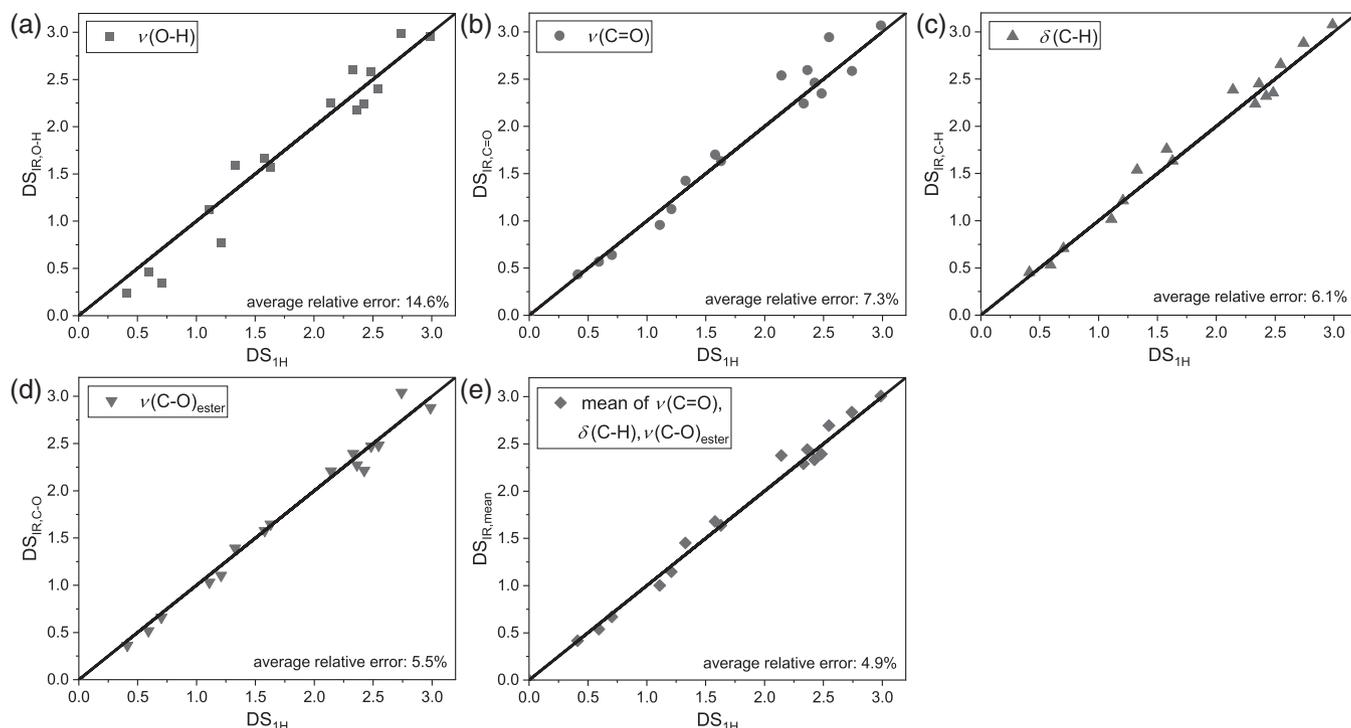
$$A = \frac{a \times \text{DS}}{1 + b \times \text{DS}} + c, \quad (1)$$

*A* is the absorbance, *a* is a peak specific constant quantifying to which extent the respective acetyl signal increases with increasing DS, *b* is a constant quantifying to which extent the reference peak is influenced with increasing DS, and *c* is the offset in *A* from zero, which is caused by the cellulose backbone structure. Two plausible scenarios could influence the reference peak in a linear manner as described by Equation (1): (i) the acetyl moieties cause an additional signal that overlaps with the  $\nu(\text{C—O})_{\text{AGU}}$  signal at ca.  $\tilde{\nu} = 1030 \text{ cm}^{-1}$ , therefore leading to an increase with increasing DS. This correlation is illustrated by a simulation and can be found in Figures S114–S115. (ii) The reference peak  $\nu(\text{C—O})_{\text{AGU}}$  can be seen as a sum of all C—O vibrations on the AGU backbone. Therefore, through acetylation, the C—O stretching vibrations in the AGU are likely shifted, which could lead to a narrower overlap, resulting in a relative increase of the reference peak. The assumption (ii) is strengthened by the fact that the C—O stretching vibration of the AGU at  $\tilde{\nu} = 1030 \text{ cm}^{-1}$  becomes narrower with increasing DS (Figure 3 and Figure S116). With these considerations in mind, the relationship from Equation (1) was used as the fit equation for a non-linear fit applied to the data as shown in Figure 4. The calculated values *a* and *b* from the non-linear fit equation are summarized in Table 2.

The  $\text{DS}_{\text{IR}}$  were then calculated based on the obtained results from these calibration curves (Table 1) and were plotted against the determined  $\text{DS}_{\text{IH}}$  for a comparison of the two methods (Figure 5).

The comparison shows that the highest average relative error was observed for the evaluation of the O—H stretching vibration that is the  $\text{DS}_{\text{IR,O—H}}$  in relation to the  $\text{DS}_{\text{IH}}$ . This can be explained by (i) the comparably broad  $\nu(\text{O—H})$  signal, which leads to higher uncertainties and deviations for the integration of the peak, and (ii) the  $\nu(\text{O—H})$  signal is considerably influenced by water, which can be adsorbed to cellulose acetate samples in varying amounts, depending on the individual DS and the time the sample was exposed to (humid) air. Even though all samples were dried at  $100^\circ\text{C}$  under reduced pressure (30 mbar) for 12 h and immediately measured, the  $\nu(\text{O—H})$  signal resulted in the highest deviations, which is also confirmed by the comparably low correlation coefficient  $R^2$  for the calibration curve of the  $\nu(\text{O—H})$  signal (Table 2). The  $\text{DS}_{\text{IR,O—H}}$  was therefore not considered for further quantitative evaluations. However, in special cases, such as for the determination of historical cellulose acetate objects containing plasticizers (e.g., triphenyl phosphate or diethyl phthalate), the  $\nu(\text{C=O})$ ,  $\delta(\text{C—H})$ , and  $\nu(\text{C—O})_{\text{ester}}$  bands cannot be used due to overlapping peaks from the plasticizers. Melo et al. demonstrated a successful DS determination of historical objects containing plasticizers using the  $\nu(\text{O—H})$  signal.<sup>37</sup> Nevertheless, for pure cellulose acetate samples, the  $\nu(\text{O—H})$  signal was considered unsuitable, as explained before.

The  $\text{DS}_{\text{IR,C=O}}$ ,  $\text{DS}_{\text{IR,C—H}}$ , and  $\text{DS}_{\text{IR,C—O}}$  resulted in similar average relative error values (5.5%–7.3%) in relation to the  $\text{DS}_{\text{IH}}$ . It was found that the arithmetic mean of the  $\text{DS}_{\text{IR,C=O}}$ ,  $\text{DS}_{\text{IR,C—H}}$ , and  $\text{DS}_{\text{IR,C—O}}$  results in an even lower average relative error of 4.9% as can be seen in Figure 5E. This averaging is thus most efficient use of all



**FIGURE 5** Degree of substitution ( $DS_{IR}$ ) determined from the calibration of the respective peak ( $\nu(O-H)$ ,  $\nu(C=O)$ ,  $\delta(C-H)$ , and  $\nu(C-O)_{ester}$ ) compared to the  $DS_{1H}$  of all synthesized cellulose acetates.

information contained in the spectra represents the most accurate means of calibration.

### 2.3 | Comparison of homogeneous cellulose acetates with mixtures of CTA/MCC

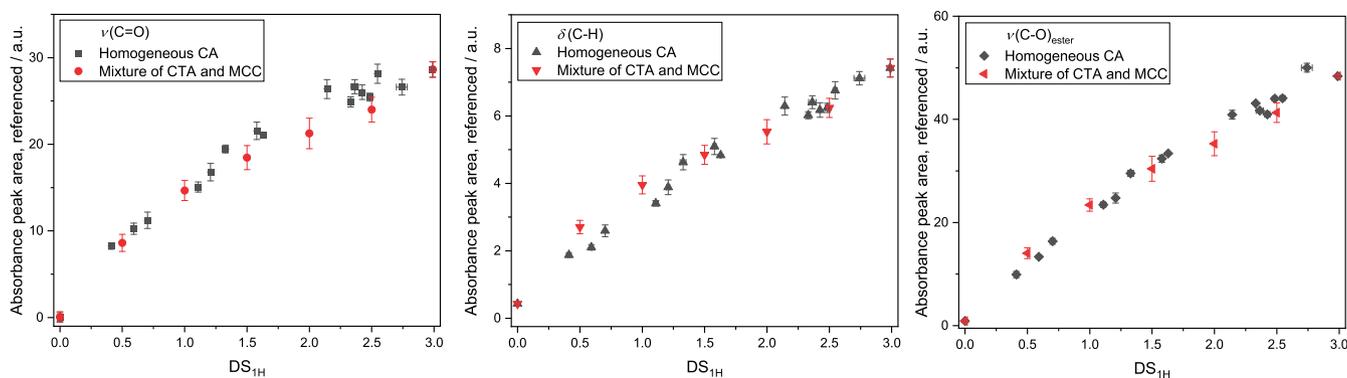
In previous investigations in this field, often mixtures of cellulose acetates (mostly triacetates) with pure, unmodified cellulose were prepared to simulate cellulose acetates with different intermediate DS values.<sup>21,36</sup> These were then used to create calibration curves for cellulose acetate in certain DS ranges. It was often assumed that this procedure is valid, but not confirmed by a suitable comparison to calibrations performed on a broad range of homogeneous cellulose acetate samples with evenly distributed DS values. We thus prepared mixtures of CTA with MCC according to equation (S8) and compared the obtained data to the dataset we observed from homogeneous cellulose acetates (Figure 6). It was found that both methods led to similar results, but the deviations within the five-fold determination for a single sample are considerably higher for the mixtures (with only few exceptions), as can be seen by the error bars that is the standard deviation, in Figure 6. This can be explained by the higher heterogeneity within the sample, which consequently leads to deviations during the FTIR measurement,

especially in the case of ATR-FTIR instruments as the penetration depth of the evanescent wave into the sample is only in the range of few micrometers.<sup>45</sup> This reduces the statistical effect in the measurement of heterogeneous samples and therefore leads to higher deviations for different measurements. Analogous behavior is to be expected for a subsequent measurement of cellulose esters with an inhomogeneous DS distribution within the sample. To increase the accuracy in these cases, the number of different measurements of the individual sample can be increased and the material needs to be finely ground.

### 2.4 | DS determination of other cellulose esters

The calibration curve obtained from cellulose acetates was assumed to be applicable to other aliphatic or aromatic cellulose esters, as the relevant functional groups monitored via ATR-FTIR remain similar. Therefore, a set of cellulose butyrates, laurates, and benzoates with different DS were synthesized and analyzed analogously as the cellulose acetates. All determined DS values are summarized in Table 3.

The absorbance of the two ester moiety signals  $\nu(C-O)_{ester}$  and  $\nu(C=O)$  relative to the reference peak  $\nu(C-O)_{AGU}$  were investigated and plotted against the  $DS_{1H}$  of the respective cellulose esters (Figure 7). A fit



**FIGURE 6** Comparison of homogeneously synthesized cellulose acetates with mixtures of cellulose triacetate (CTA) and microcrystalline cellulose (MCC).

Sample	DS <sub>1H</sub>	DS <sub>31P</sub>	DS <sub>IR,C-O</sub> <sup>a</sup>	DS <sub>IR,C=O</sub> <sup>a</sup>	DS <sub>IR,C-O</sub> <sup>b</sup>	DS <sub>IR,C=O</sub> <sup>b</sup>
CBu-1	0.56	– <sup>c</sup>	0.56	0.62	0.57	0.67
CBu-2	1.03	1.08	0.81	0.96	0.79	1.10
CBu-3	1.34	1.42	1.25	1.47	1.13	1.87
CBu-4	1.62	1.52	1.60	1.45	1.38	1.84
CBu-5	1.62	1.63	1.84	1.77	1.54	2.39
CBu-6	1.75	1.72	1.98	1.45	1.62	1.83
CBu-7	2.37	2.24	2.22	2.39	1.76	3.77
CBu-8	2.42	2.15	2.35	2.38	1.82	3.74
CL-1	1.11	1.13	1.06	1.24	1.07	0.68
CL-2	1.61	1.49	1.65	2.92	1.62	1.29
CL-3	1.68	1.65	1.68	3.05	1.63	1.30
CL-4	2.11	1.83	2.12	6.36	2.05	2.03
CL-5	2.42	2.28	2.55	21.19	2.25	2.49
CL-6	2.47	2.25	2.28	9.09	2.13	2.18
CBz-1	0.76	0.91	0.75	0.80	0.66	1.01
CBz-2	1.02	1.07	1.10	1.18	1.06	1.37
CBz-3	1.36	1.46	1.53	1.65	1.67	1.72
CBz-4	1.86	1.79	1.62	1.74	2.15	1.92
CBz-5	2.25	2.17	2.13	2.29	2.15	1.92
CBz-6	2.38	2.34	2.46	2.65	2.01	1.87

<sup>a</sup>Calculated using a calibration based on the respective ester (CBu, CL, CBz).

<sup>b</sup>Calculated using the calibration based on cellulose acetate.

<sup>c</sup>Not determined due to insolubility.

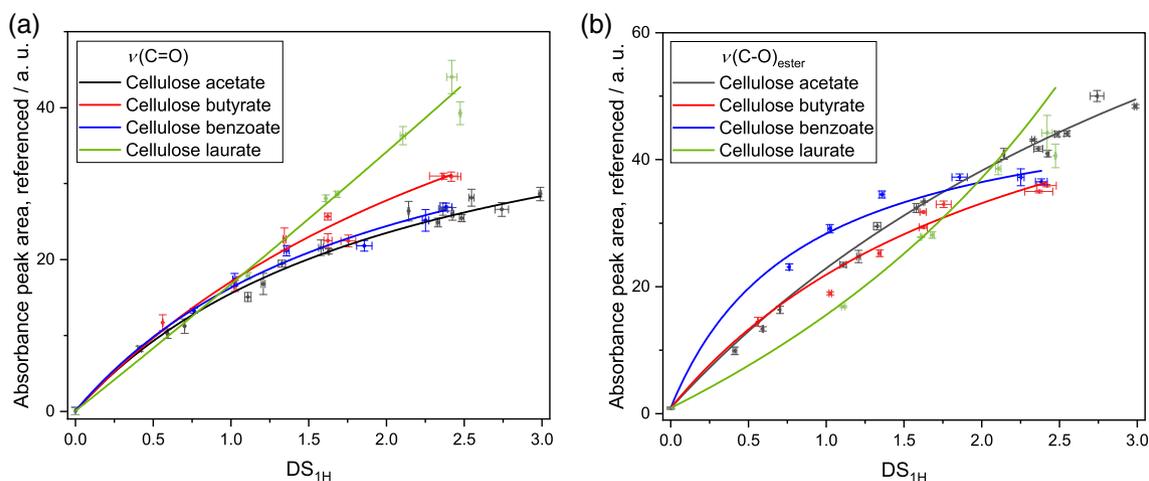
**TABLE 3** Degree of substitution (DS) values of all synthesized cellulose butyrates (CBu), cellulose laurates (CL), and cellulose benzoates (CBz) applying different determination methods.

based on Equation (1) was performed and the calculated values for a and b are summarized in Table 2. The DS<sub>IR</sub> values were then calculated based on the calibration curve from cellulose acetate, as well as on individual calibration curves based on the respective cellulose esters (Table 3).

The fitted curves were compared to the calibration performed for cellulose acetate and high deviations were

obtained for the  $\nu(\text{C}=\text{O})$  vibrational signal (Figure 7A). The  $\nu(\text{C}-\text{O})_{\text{ester}}$  signal absorbance intensities showed a better correlation to the calibration of cellulose acetate, as shown in Figure 7B.

The absorbance intensities are differently influenced for every class of cellulose ester, as can be seen from the fitted curves, as well as from the calculated values for a and b in Table 2. A calibration based on the absorbance



**FIGURE 7** Non-linear fits of the absorbance intensity of the  $\nu(\text{C}=\text{O})_{\text{ester}}$  and  $\nu(\text{C}=\text{O})$  of cellulose butyrate, benzoate, and laurate plotted against the  $\text{DS}_{1\text{H}}$ . The fit of cellulose acetate is shown for comparison, respectively.

intensities of cellulose acetate can therefore not be generally applied to other cellulose esters, even if they are aliphatic and do not bear any other functional groups. A separate calibration is necessary in order to achieve sufficiently precise results. This is confirmed by the fact that the calculated  $\text{DS}_{\text{IR,C-O}}$  and  $\text{DS}_{\text{IR,C=O}}$  values based on a calibration from cellulose acetate differ considerably from the DS values determined via  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, or ATR-FTIR with a calibration based on the respective cellulose ester itself (Table 3). Especially for cellulose laurates, unreliable  $\text{DS}_{\text{IR,C-O}}$  and  $\text{DS}_{\text{IR,C=O}}$  values were obtained when a calibration from cellulose acetate was applied. Generally, the approach of using ATR-FTIR spectroscopy was shown to be applicable to different cellulose esters apart from cellulose acetate, but a separate calibration must be performed for accurate results based on the  $\nu(\text{C}=\text{O})_{\text{ester}}$  absorbance intensity. The presented DS determination method is consequently limited to single substituted cellulose esters and cannot be applied to mixed cellulose esters, like commercially used cellulose acetate butyrates, with sufficient precision.

### 3 | CONCLUSION

The relationship between the DS and the absorbance intensity of different substituent specific vibrational signals in ATR-FTIR spectra was investigated for four different cellulose esters. Sixteen cellulose acetates, eight cellulose butyrates, six cellulose laurates, and six cellulose benzoates with varying DS were synthesized, and their respective DS values were determined via  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy. The determined DS was set into relation to the absorbance intensity of the

$\nu(\text{C}=\text{O})_{\text{ester}}$ ,  $\nu(\text{C}=\text{O})$ , and  $\delta(\text{C}-\text{H})$  vibration of the ester moiety after referencing these signals to the  $\nu(\text{C}-\text{O})_{\text{AGU}}$  of the cellulose AGU. A non-linear correlation was observed and a model was proposed describing this relationship. The presented DS determination method is advantageous in terms of its quick and simple measurement, but especially because of its applicability to non- or poorly soluble samples, as no pretreatment is necessary. As most other DS determination methods rely on soluble samples and the solubility in most cases reduces for cellulose derivatives with lower DS, the presented method is expected to complement existing methods.

## 4 | EXPERIMENTAL SECTION

### 4.1 | Materials

Microcrystalline cellulose (MCC) was purchased from Sigma-Aldrich and was dried at  $100^\circ\text{C}$  under high vacuum for 24 h prior to use. 1,8-Diazabicyclo[5.4.0]undec-7-ene (TCI, >98%) was distilled and stored over molecular sieves. Dimethyl sulfoxide (Acros Organics, dry and stored over molecular sieve), pyridine (Fisher Scientific, >99.5%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Sigma Aldrich, 95%), *endo-N*-hydroxy-5-norbornene-2,3-dicarboximide (Sigma Aldrich, 97%), vinyl acetate (Acros Organics, >99%), vinyl butyrate (TCI, >98%), vinyl benzoate (TCI, >99%), vinyl laurate (Sigma Aldrich, >99%), trifluoroacetic acid (Acros Organics, 99%), and  $\text{CO}_2$  (Air Liquide, 99.995%) were used without further purification. Deuterated solvents ( $\text{DMSO}-d_6$  and  $\text{CDCl}_3$ ) were purchased

from Eurisotop. All other solvents were used in technical grade.

## 4.2 | General procedure for the synthesis of cellulose esters

In a round-bottom flask, cellulose (500 mg, [monomeric unit] = 3.08 mmol) was suspended in 11 mL DMSO followed by the dropwise addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (1.4 mL, 9.25 mmol, 3.0 eq. per AGU). After applying a CO<sub>2</sub> flow through the solution for 20 min at 40°C, a clear solution was obtained and vinyl acetate (0.5–4.5 eq. per AGU) for cellulose acetates, vinyl butyrate (0.7–4.5 eq. per AGU) for cellulose butyrates, vinyl laurate (1.0–4.5 eq. per AGU) for cellulose laurates or vinyl benzoate (0.7–4.5 eq per AGU) for cellulose benzoates was added dropwise. The homogeneous solution was then heated to 60°C and stirred for 4 h. Subsequently, the solution was added dropwise into 50 mL of isopropanol under vigorous stirring. The precipitate was vacuum filtered and washed with isopropanol (2 × 20 mL), suspended in 40 mL isopropanol and heated under reflux 2× for 1–12 h, vacuum filtered and dried. The final product was obtained as a white or yellow solid. Yields ranged from 74% to 99%. Exemplary analytical data for CA-5: ATR-IR (cm<sup>-1</sup>): 3030–3677  $\nu$ (O–H), 2815–2990  $\nu$ (C–H), 1727  $\nu$ (C=O), 1369 methyl  $\delta$ (C–H), 1228 ester  $\nu$ (C–O), 1023 AGU  $\nu$ (C–O). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ <sub>H</sub> ppm: 2.79–5.31 (m, AGU, 7H), 1.69–2.27 (m, CH<sub>3</sub>, 9H).

## 4.3 | DS determination by the <sup>31</sup>P NMR method

The DS was determined by derivatization of the cellulose samples using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (2-Cl-TMDP) as the phosphitylating agent according to a procedure developed by Kilpeläinen et al.<sup>22</sup> An exact amount of 25 mg of each sample was dissolved in 1 mL of pyridine, followed by the addition of 1 mL of CDCl<sub>3</sub>. Next, 2-Cl-TMDP (50  $\mu$ L, 0.63 mmol) was added to the mixture and the solution was stirred for 15 min. Afterwards, the internal standard *endo-N*-hydroxy-5-norbornene-2,3-dicarboximide (100  $\mu$ L, 122 mM in pyridine/CDCl<sub>3</sub> = 3:2, 0.0122 mmol) was added to the mixture, and the solution was stirred for further 10 min. Then, 0.6 mL of the solution was transferred to an NMR tube, and a <sup>31</sup>P NMR measurement was performed. The DS values were calculated according to equation (S1).

## 4.4 | Instruments

### 4.4.1 | Infrared spectroscopy

Infrared spectra (IR) of all samples were recorded using a Bruker Alpha-p instrument with ATR technology in a range of  $\tilde{\nu}$  = 400–4000 cm<sup>-1</sup> with 24 scans per measurement and a resolution of 4 cm<sup>-1</sup>. All samples were dried at 100°C and reduced pressure (30 mbar) for 12 h before the measurement to remove traces of adsorbed water from the sample.

### 4.4.2 | Nuclear magnetic resonance spectroscopy

<sup>1</sup>H nuclear magnetic resonance spectroscopy (NMR) spectra were recorded using a Bruker Avance DRX instrument at 500 MHz with 16 scans and a delay time *d*<sub>1</sub> of 5 s at 298 K. The chemical shift was reported in ppm and referenced to the solvent signal of DMSO-*d*<sub>5</sub> at 2.50 ppm and CHCl<sub>3</sub> at 7.26 ppm. <sup>31</sup>P NMR spectra were recorded using a Bruker Avance DRX instrument at 202 MHz (500 MHz <sup>1</sup>H NMR frequency) with 1024 scans, a delay time *d*<sub>1</sub> of 5 s, and 1 s acquisition time at 298 K.

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## CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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## REFERENCES

- [1] T. Heinze, O. A. El Seoud, A. Koschella, *Cellulose Derivatives*, Springer International Publishing, Cham **2018**.
- [2] D. Klemm, B. Heublein, H. P. Fink, A. Bohn, *Angew. Chem. Int. Ed.* **2005**, *44*, 3358.
- [3] K. N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *ACS Sustainable Chem. Eng.* **2019**, *7*, 1826.
- [4] P. Nasatto, F. Pignon, J. Silveira, M. Duarte, M. Nosedá, M. Rinaudo, *Polymers* **2015**, *7*, 777.
- [5] C. W. Saunders, L. T. Taylor, *J. Energy Mater.* **1990**, *8*, 149.
- [6] J. Wu, J. Zhang, H. Zhang, J. He, Q. Ren, M. Guo, *Biomacromolecules* **2004**, *5*, 266.
- [7] O. Jogunola, V. Eta, M. Hedenström, O. Sundman, T. Salmi, J. P. Mikkola, *Carbohydr. Polym.* **2016**, *135*, 341.

- [8] J. Chen, J. Xu, K. Wang, X. Cao, R. Sun, *Carbohydr. Polym.* **2016**, *137*, 685.
- [9] C. Y. Chen, M. J. Chen, X. Q. Zhang, C. F. Liu, R. C. Sun, *J. Agric. Food Chem.* **2014**, *62*, 3446.
- [10] R. Kakuchi, M. Yamaguchi, T. Endo, Y. Shibata, K. Ninomiya, T. Ikai, K. Maeda, K. Takahashi, *RSC Adv.* **2015**, *5*, 72071.
- [11] S. Barthel, T. Heinze, *Green Chem.* **2006**, *8*, 301.
- [12] Y. Cao, J. Wu, T. Meng, J. Zhang, J. He, H. Li, Y. Zhang, *Carbohydr. Polym.* **2007**, *69*, 665.
- [13] Q. Van Nguyen, S. Nomura, R. Hoshino, K. Ninomiya, K. Takada, R. Kakuchi, K. Takahashi, *Polym. J.* **2017**, *49*, 783.
- [14] J. Wolfs, R. Nickisch, L. Wanner, M. A. R. Meier, *J. Am. Chem. Soc.* **2021**, *143*, 18693.
- [15] C. Yuan, W. Shi, P. Chen, H. Chen, L. Zhang, G. Hu, L. Jin, H. Xie, Q. Zheng, S. Lu, *New J. Chem.* **2019**, *43*, 330.
- [16] Y. Guo, L. Li, G. Guo, M. Pei, L. Zhang, H. Xie, H. Sun, Q. Zheng, *Green Chem.* **2021**, *23*, 2352.
- [17] M. Pei, X. Peng, Y. Shen, Y. Yang, Y. Guo, Q. Zheng, H. Xie, H. Sun, *Green Chem.* **2020**, *22*, 707.
- [18] L. P. Hinner, J. L. Wissner, A. Beurer, B. A. Nebel, B. Hauer, *Green Chem.* **2016**, *18*, 6099.
- [19] H. Kono, H. Hashimoto, Y. Shimizu, *Carbohydr. Polym.* **2015**, *118*, 91.
- [20] Y. Tezuka, Y. Tsuchiya, *Carbohydr. Res.* **1995**, *273*, 83.
- [21] S. Da Ros, A. E. Aliev, I. del Gaudio, R. King, A. Pokorska, M. Kearney, K. Curran, *Polym. Degrad. Stab.* **2021**, *183*, 183.
- [22] A. W. T. King, J. Jalomäki, M. Granström, D. S. Argyropoulos, S. Heikkinen, I. Kilpeläinen, *Anal. Methods* **2010**, *2*, 1499.
- [23] Z. Söyler, M. A. R. Meier, *Green Chem.* **2017**, *19*, 3899.
- [24] Z. Söyler, K. N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *Green Chem.* **2018**, *20*, 214.
- [25] K. N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *ACS Sustainable Chem. Eng.* **2018**, *6*, 8826.
- [26] S. Asaadi, T. Kakko, A. W. T. King, I. Kilpeläinen, M. Hummel, H. Sixta, *ACS Sustainable Chem. Eng.* **2018**, *6*, 9418.
- [27] T. Kakko, A. W. T. King, I. Kilpeläinen, *Cellulose* **2017**, *24*, 5341.
- [28] E. Esen, P. Hädinger, M. A. R. Meier, *Biomacromolecules* **2021**, *22*, 586.
- [29] C. S. R. Freire, A. J. D. Silvestre, C. P. Neto, R. M. A. Rocha, *Cellulose* **2005**, *12*, 449.
- [30] G. Samaranyake, W. G. Glasser, *Carbohydr. Polym.* **1993**, *22*, 79.
- [31] R. Casarano, L. C. Fidale, C. M. Lucheti, T. Heinze, O. A. E. Seoud, *Carbohydr. Polym.* **2011**, *83*, 1285.
- [32] J. Peydecastaing, C. Vaca-Garcia, E. Borredon, *Cellulose* **2009**, *16*, 289.
- [33] C. Vaca-Garcia, M. E. Borredon, A. Gaseta, *Cellulose* **2001**, *8*, 225.
- [34] E. Esen, M. A. R. Meier, *ACS Sustainable Chem. Eng.* **2020**, *8*, 15755.
- [35] D.-F. Hou, M.-L. Li, C. Yan, L. Zhou, Z.-Y. Liu, W. Yang, M.-B. Yang, *Green Chem.* **2021**, *23*, 2069.
- [36] P. Fei, L. Liao, B. Cheng, J. Song, *Anal. Methods* **2017**, *9*, 6194.
- [37] S. Nunes, F. Ramacciotti, A. Neves, E. M. Angelin, A. M. Ramos, É. Roldão, N. Wallaszkovits, A. A. Armijo, M. J. Melo, *Herit. Sci.* **2020**, *8*, 1.
- [38] W. Li, G. Cai, P. Zhang, *J. Mater. Sci.* **2019**, *54*, 8047.
- [39] J. Wolfs, M. A. R. Meier, *Green Chem.* **2021**, *23*, 4410.
- [40] H. Chen, F. Yang, J. Du, H. Xie, L. Zhang, Y. Guo, Q. Xu, Q. Zheng, N. Li, Y. Liu, *Cellulose* **2018**, *25*, 6935.
- [41] P. G. Jessop, D. J. Heldebrant, X. Li, C. A. Eckert, C. L. Liotta, *Nature* **2005**, *436*, 1102.
- [42] Q. Zhang, N. S. Oztekin, J. Barrault, K. De Oliveira Vigier, F. Jérôme, *ChemSusChem* **2013**, *6*, 593.
- [43] Y. Yang, L. Song, C. Peng, E. Liu, H. Xie, *Green Chem.* **2015**, *17*, 2758.
- [44] K. N. Onwukamike, T. Tassaing, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *ACS Sustainable Chem. Eng.* **2018**, *6*, 1496.
- [45] R. Minnes, M. Nissinmann, Y. Maizels, G. Gerlitz, A. Katzir, Y. Raichlin, *Sci. Rep.* **2017**, *7*, 1.

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