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A Novel Method for the Determination of Carbonyl Groups in Cellulosics by Fluorescence Labeling. 3. Monitoring Oxidative Processes

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The fluorescence-based CCOA method for determination of carbonyl group profiles in cellulosic substrates was employed to study the mechanisms of various oxidative and degradation processes involving celluloses in greater detail. The approach comprises labeling with the marker carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)ethoxy]amide (CCOA), followed by gel permeation chromatography in DMAc/LiCl with fluorescence, multiangle laser light scattering, and refractive index detection. At first, the CCOA method was applied to study solutions of pulp in *N*-methylmorpholine-*N*-oxide monohydrate (NMMO), as occurring in the production of Lyocell-type fibers. NMMO is a rather strong oxidant that on one hand converts reducing end groups to carboxyl structures, thus lowering the overall carbonyl content, but generates new keto structures along the chain by nonselective oxidation on the other hand. The CCOA method allowed for the first time to distinguish the carbonyl course in different molecular weight ranges. Second, alkalization and aging of pulp, which are used in the industrial preparation of cellulose derivatives, e.g., as an element of the preripening process in viscose rayon production, were investigated. The CCOA method shows a clear reduction of the molecular weight, accompanied by a fast loss of carbonyls in the first phase, which is due to removal of low-molecular weight material by dissolution, and a slow decrease in the second phase, which is caused by further oxidation of carbonyl groups. Also here, differences in the carbonyl course in different molecular weight regions were monitored. Third, electron beaming, proposed as a means of pulp activation, was shown to decrease and narrow the molecular weight distribution, under generation of comparatively low amounts of carbonyls, which, however, are also introduced into high molecular weight, crystalline domains, as shown by a comparison of homogeneous and heterogeneous CCOA labeling approach. Finally, as the fourth application, thermal treatment of cellulose at temperatures between 105 and 165 °C was shown to bring about a small reduction of the molecular weight, which only at higher drying temperatures is accompanied by an introduction of carbonyls over the whole molecular weight range.

Introduction

The fluorescent label carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)ethoxy]amide (CCOA) contains a carbazole-based fluorophore with an ethylene glycol-tethered hydroxylamine anchor group which binds selectively to carbonyl structures in low molecular weight carbohydrates as well as in cellulosic materials. Marker and labeling procedures have been developed in response to a lack of accurate methods for the determination of carbonyl groups, such as keto, 1,2-diketo, and aldehyde structures, especially in pulps and other higher molecular weight carbohydrates. The labeling is carried out as convenient precolumn derivatization in a gel permeation chromatography setup, with multiangle laser light scattering (MALLS), refractive index (RI), and fluorescence detection in the solvent DMAc/LiCl.[1]

The method, which has also been validated,[2] provides not only the overall carbonyl content of a sample as a sum parameter but also carbonyl profiles which most conveniently portray the carbonyl content in relation to the molecular weight in the form of "carbonyl-DS"[3] plots, or changes in the carbonyl distribution in the form of "carbonyl-ΔDS" plots.

In contrast to conventional methods for the net carbonyl content determination in cellulosic materials, the CCOA approach is able to assign carbonyl groups to specific molecular weight regions and is able to report dynamic activities and oppositely acting processes where former approaches would only state unchanged values. This capability makes it a highly powerful tool to study different oxidative treatments of pulps, such as bleaching sequences,[2] and a valuable instrument to evaluate to what extent specific conditions—such as dissolution, storage, irradiation etc.—cause oxidative changes in the cellulosic material. This work, as the third and last part of this series, gives four illustrative examples, which are not only scientifically interesting but

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also industrially relevant: solutions of cellulose in *N*-methylmorpholine-*N*-oxide (NMMO) as used in the Lyocell process; alkalization and aging of pulp in 18% NaOH as the initial step in the viscose rayon production; electron beaming of pulp as a means of activation for further processing to derivatives; cellulose changes as occurring upon prolonged drying and storage of pulp under thermal stress.

Materials and Methods

The general gel permeation chromatography (GPC) setup was as described previously.[1] The GPC system, a modification of the setup described by Schelosky et al.,[4] consisted of MALLS, RI, and fluorescence detectors, with automatic injection and four serial columns. DMAc/LiCl (0.9%, m/V) was used as the eluant. Molecular weight distribution (MWD) and related polymer-relevant parameters were calculated by software programs, based on a refractive index increment of 0.140 mL/g for cellulose in DMAc/LiCl (0.9%, m/V). The following general GPC parameters were used: eluant, DMAc/LiCl (0.9%, m/V); flow, 1.00 mL/min; columns, four PL gel, mixedA, ALS, 20 μm, 7.5 × 300 mm; fluorescence detection, 286 nm excitation, 330 nm emission; injection volume, 100 μL; run time, 45 min.

Activation of Pulp Samples. To achieve a "good" solubility, i.e., dissolution in DMAc/LiCl (9%, m/V) overnight at room temperature, the pulp samples had to be activated, no matter if genuine pulp or labeled pulp had to be dissolved. For a better dissolution in DMAc/LiCl, the pulp samples were activated by solvent exchange (H_2O to ethanol to DMAc) followed by agitating in DMAc overnight and filtration, which produces efficiently activated, i.e., readily soluble samples.

General Procedure for the Determination of Carbonyls in Pulp by Heterogeneous Fluorescence Labeling. A CCOA stock solution was prepared by dissolving the label (62.50 mg) in 50 mL of 20 mM zinc acetate buffer, pH 4.00. Activated pulp, corresponding to 20−25 mg of dry pulp, was suspended in the acetate buffer containing the label (4 mL). The suspension was agitated in a water bath with temperature control for 168 h at 40 °C. The pulp was removed by filtration, activated (see above), and dissolved in 2 mL of DMAc/LiCl (9%, m/V) overnight at room temperature. Samples of the solution were diluted with DMAc, filtered through 0.45 μm filters, and analyzed by GPC directly yielding the carbonyl content in the respective pulp.

Analysis of Pulps. For the analysis of carbonyl profiles in genuine pulps and pulps having undergone modifications or treatments, the general analytical procedure was used. Calibration of the system was done by means of reference pulps, as described previously.[2] For the determination of the overall carbonyl content, the carbonyl peak area was normalized with regard to the injected mass.

Two standard pulp samples were used: a bleached beech sulfite pulp (kappa number 0.79, brightness 88.5% ISO, viscosity (cuen) 546 mL/g) for alkalization, dissolution in NMMO, and thermal stress experiments; a eucalyptus prehydrolysis kraft pulp (kappa number 0.30, brightness 90.5% ISO, viscosity (cuen) 454 mL/g) for e-beam studies.
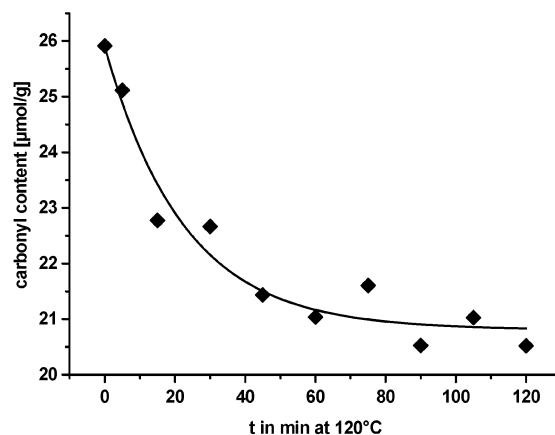

Figure 1. Time course of the total carbonyl content of a beech sulfite (BS) pulp after dissolution and processing in *N*-methylmorpholine-*N*-oxide monohydrate at 120 °C.

Cellulose Solutions in *N*-Methylmorpholine-*N*-oxide (NMMO). Lyocell spinning dopes, based on the milled standard beech sulfite pulp, were obtained from Lenzing AG, Austria. For investigation of thermal stress effects in NMMO, the dope was kept at 120 °C. Every 15 min, a sample was taken, precipitated in deionized water, thoroughly washed with deionized water, and analyzed.

Alkalization. A bleached beech sulfite pulp was suspended in 18.3% NaOH at a NaOH-to-cellulose ratio of 38:1. After the lye was pressed off, the press cake was immediately shredded to provide a large surface area for a uniform reaction with atmospheric dioxygen and was agitated in a tumbler at 42 °C. Alkali cellulose samples (1 g) were taken every hour and suspended in water. The pH was adjusted to 7−8 by 5% acetic acid, and the pulp was washed with deionized water, drained, and analyzed.

Electron Irradiation (e-Beaming). A eucalyptus prehydrolysis kraft pulp was irradiated in air with electron beams (Rhodotron TT 300, 10 MeV) at different dosages (3.1, 15.7, and 22.4 kGy, respectively) and analyzed.

Thermal Treatment. A bleached beech sulfite pulp was dried at different temperatures (room temperature, 105, 130, and 165 °C, respectively) for 12 h in ambient atmosphere. The pulp samples were suspended in water, drained, and analyzed.

Results and Discussion

1. Cellulose Solutions in *N*-Methylmopholine-*N*-oxide (NMMO). Lyocell fibers, having been produced on an industrial scale for about 12 years, represent a comparatively young type of man-made cellulosics. Lyocell formation is based on the direct physical dissolution of cellulose in *N*-methylmorpholine-*N*-oxide monohydrate (NMMO).[5,6] The resulting spinning dope is spun into an air gap and into water to give the final Lyocell product. The dissolution is a derivatization-free process, which means that no additional compounds, such as NaOH and CS_2 in the viscose process or sulfuric acid and acetic anhydride in cellulose acetate production, are required. In addition, the main process chemicals, the solvent NMMO and water, are nearly completely recycled. Due to these features, the Lyocell
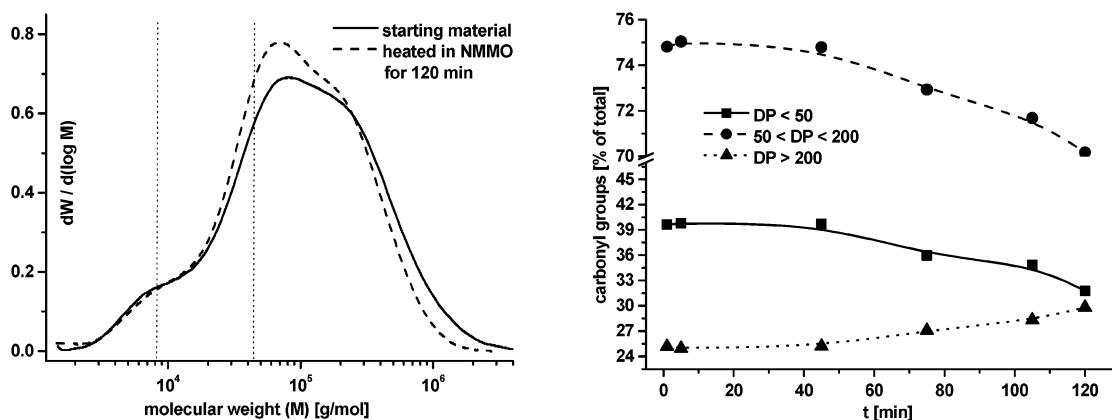
Figure 2. Differential MWD of a beech sulfite pulp, before and after heating in NMMO solution for 120 min. The molecular weights of DP = 50 and DP = 200 are indicated by vertical dashed lines (left). Time course of the overall carbonyl content in three selected molecular weight ranges (right).

process rapidly advances to an ecologically benign, large-scale alternative to viscose rayon production.

The cellulose solvent NMMO is a white crystalline solid at room temperature with a melting point of 84 °C, so that dissolution of cellulose and further processing of the spinning dope requires temperatures of about 100 °C. As NMMO is a relatively strong oxidant—it is frequently used as oxidizing agent in organic synthesis[7]—this quality, additionally intensified by the elevated process temperatures, gives rise to pronounced oxidative stress imposed on the dissolved pulp material. The chemical interaction of oxidizing solvent and pulp continues sufficiently long to cause possible severe effects, e.g., decreased fiber properties, discoloration of the resulting fibers, thermal instabilities of the dope, and even explosions.[8] Thus, the oxidative action of the solvent NMMO on the solute cellulose is a topic of highest importance.

By use of the CCOA method, it was shown that the overall carbonyl content of the pulp decreases continuously upon dissolution in NMMO at 120 °C under Lyocell process conditions. This decrease is relatively small, but significant; see Figure 1. A detailed evaluation, as given in Figure 2, reveals that this overall decrease is a superposition of counteracting processes, regarding regions of different molecular weight. Up to a DP of 50, the amount of carbonyl groups *decreases*. The same is still true for a molecular weight region up to DP 200. However, in high molecular weight material above DP 200, the content of carbonyl groups *increases* moderately.

In the short-chain material with a high relative content of reducing end groups (e.g., one per 50 or 100 anhydroglucose units) a major pathway would be the oxidation of these structures to carboxylic acid residues, analogous to the chemical behavior of model compounds.[8] Possibly, at the same time a minor amount of new carbonyl groups is generated along the chain in unselective oxidation of C-2, C-3, and C-6. This process, however, is largely outweighed by the amount of reducing end carbonyl groups consumed. In the high molecular weight part in contrast, the relative amount of reducing ends is very low (e.g., one per 500 or 1000 anhydroglucose units). Now, the generation of new carbonyl groups becomes predominant, as the consumption of carbonyl groups is negligibly small. The introduction of carbonyl groups, especially into longer chains, is an important
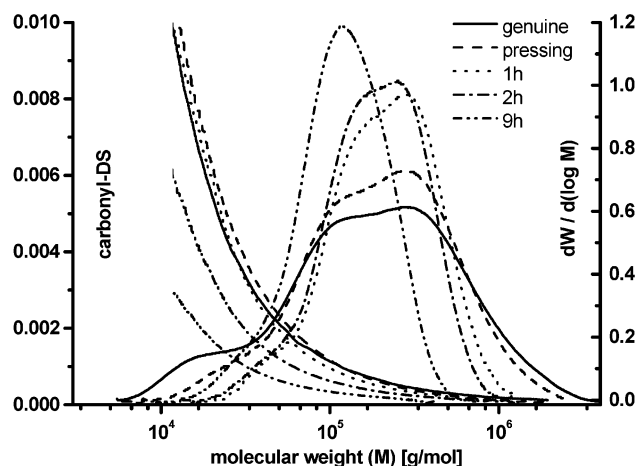

Figure 3. Carbonyl-DS and differential MWD of a beech sulfite (BS) pulp after steeping/pressing and different aging times.
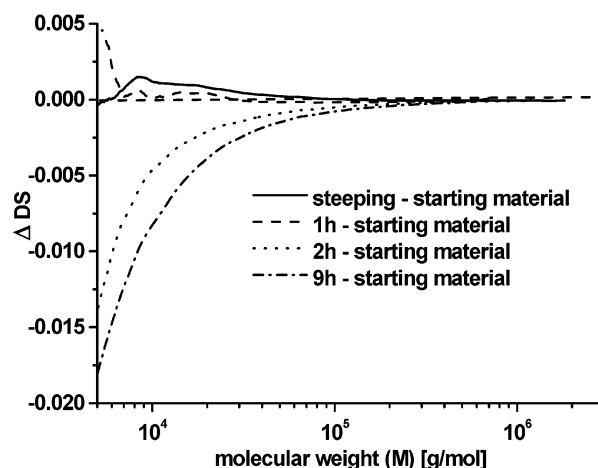

Figure 4. ΔDS plots for a beech sulfite (BS) pulp after steeping and different aging times.

result as carbonyl groups have been demonstrated to be directly correlated with chromophore formation in the Lyocell system.[9,10]

In summary, processing of the beech sulfite pulp sample in NMMO at elevated process temperatures causes a net decrease of the carbonyl content, which is mainly due to the conversion of reducing ends to carboxylic acids. This process is counteracted by a unselective introduction of keto
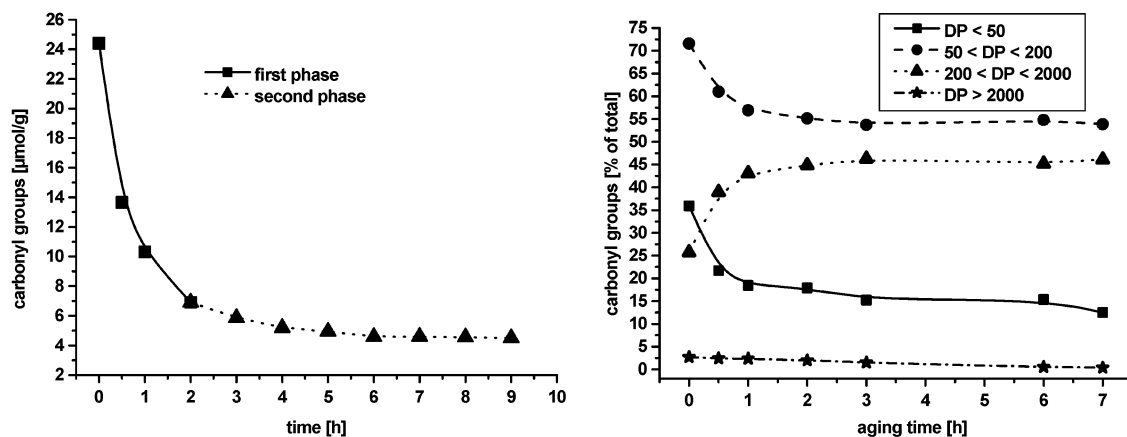
Figure 5. Total carbonyl content of a beech sulfite (BS) pulp after steeping and different aging times. Discernible phases with different rates of carbonyl decrease are indicated by different symbols: squares, rapid decrease due to removal of hemicelluloses and low molecular weight celluloses; triangles, slow decrease due to oxidative removal of remaining carbonyl functions.

groups along the chain, which in turn will play a role in subsequent discoloration effects.

2. Alkalization of Cellulose and Aging of Alkali Cellulose. Alkalization ("steeping") is a crucial process step in the production of cellulose derivatives, where it is mainly employed prior to certain derivatization reactions, such as xanthation in the viscose process or etherification in the production of carboxymethyl cellulose.[11] Especially in the viscose process, the alkalization is used not only to activate the hydroxyl groups but also to free the pulp from impurities such as hemicelluloses. The steeping step involves treatment of bleached pulp with strong alkali hydroxides, mostly 18% NaOH, which converts cellulose into sodium cellulose I. Excess sodium hydroxide is pressed off, and the press cake, consisting of 34−35% cellulose and 15−16% NaOH, is left in the presence of air for several hours, a process which is referred to as aging. In this aging stage appropriate pulp viscosity, i.e., the cellulose DP, is adjusted for further processing to viscose. The changes in the molecular weight distribution are brought about by oxidative processes,[12−14] which involve introduction and conversion of oxidized functions, such as keto and aldehyde groups. The CCOA method now allows for the first time to study these oxidative changes in detail with regard to time course and dependence on the molecular weight.

Figure 3 shows the molecular weight distribution and carbonyl-DS curves of the genuine pulp sample, the pulp after steeping and removal of excess alkali ("pressing"), and the samples after different times of aging. Both the decrease in molecular weight and the intended narrowing of the distribution over time are evident. The overall carbonyl content *decreased significantly* during the alkali treatment (steeping) by about 50%; cf. Figure 3 and Figure 5 (left). In contrast, the carbonyl-ΔDS plot in Figure 4, depicting the difference curve between starting pulp and alkali pulp after steeping, indicated *no significant change* in carbonyls in the pulp, except for the lowest molecular weight part. The overall decrease must consequently be due to a removal of low molecular weight hemicelluloses and celluloses, which were no longer contained in the pulp sample, so that their carbonyl and reducing end groups were thus no longer detected.[15]
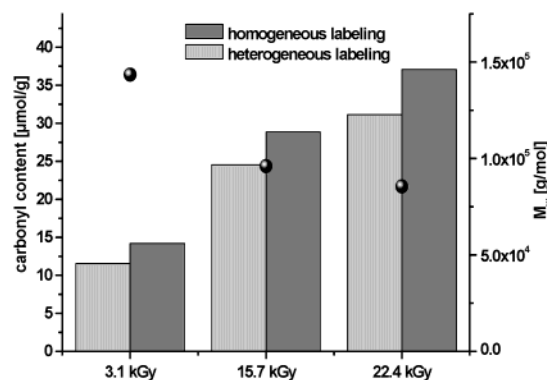

Figure 6. MW (bullets) and overall carbonyl content (bars) of a prehydrolysis kraft pulp, measured along an e-beaming sequence with different dosages. Carbonyl contents were determined according to both the homogeneous and heterogeneous CCOA labeling procedure.

With increasing aging times, the carbonyl content in the pulp decreased further, as proven by the carbonyl-ΔDS plots after 2 and 9 h in Figure 4. The main reason for this loss in carbonyl groups was a progressing oxidation of reducing end groups to carboxyl functions (data not shown) and a removal of keto groups, e.g., by cleavage or rearrangement. After an aging time of 4 h the decline in carbonyls slowed and eventually leveled off at 4 μmol/g; see Figure 5 (left).

A detailed evaluation revealed once more pronounced differences in the reactivity of different molecular weight regions with regard to carbonyl groups newly produced by chain cleavage. In very high molecular material with a DP > 2000, very few carbonyl groups (reducing end groups) are contained, and the amount of these carbonyls decreased very slightly, nearly staying the same; see Figure 5 (right). The relatively large amount of carbonyl groups and reducing end groups in lowest molecular and low molecular weight ranges of DP < 50 and 50 < DP < 200 continuously *decreased* during the aging procedure due to the above-discussed oxidative consumption processes. Intriguingly, the number of carbonyls in the midrange of 200 < DP < 2000 *increased*. Thus, in this region—and only there—oxidative introduction of keto groups overcompensates the oxidative consumption of reducing end groups and other carbonyls, which dominate in the other ranges.
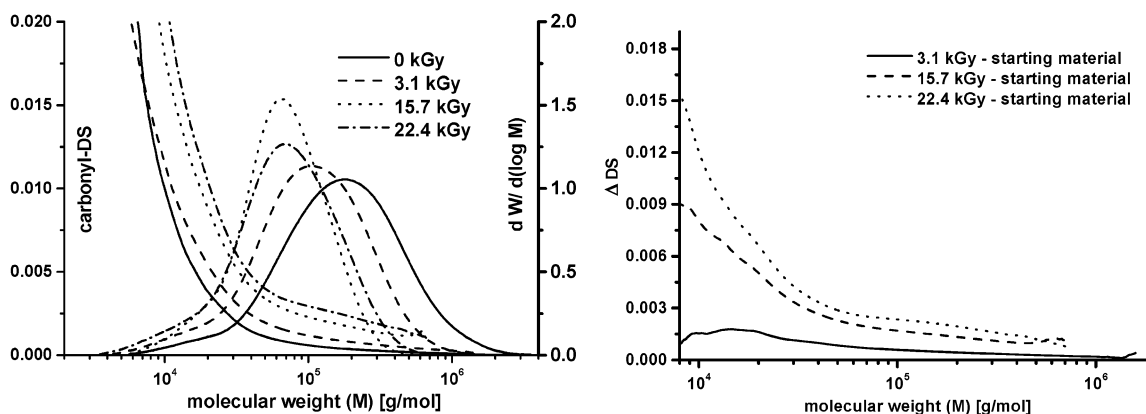
Figure 7. Carbonyl-DS and differential MWD of a prehydrolysis kraft pulp after e-beaming at different irradiation doses (left). Δ DS plots (right).

In summary, application of the CCOA method disclosed two different—more or less consecutive—processes in the alkalization and aging of cellulose under conditions used for derivatization or viscose production: the initial removal of low molecular weight material with a high content of carbonyls by dissolution leaving behind a carbonyl-depleted purified pulp and the subsequent, slower process of oxidative conversion of remaining carbonyl groups to carboxyl groups in the pulp. This confirms the traditional concept of alkalization[12–14] constructed from conventional analytical methods. In the lower molecular weight regions, large amounts of carbonyls are oxidatively removed, in the midrange, generation of new keto groups outweighs this consumption, and in high molecular weight regions, with a very low initial carbonyl amount only a very small decrease was observed.

3. Electron Beaming of Cellulose. Irradiation of pulps with electron beams ("e-beaming") has been proposed[16] as a means of "pulp activation", which means increasing the reactivity of pulp in subsequent process steps, e.g., derivatization. Electron beaming can be used to adjust the molecular weight; it was thought to introduce carbonyl groups into the cellulosic material as "weak spots", which further loosen amorphous areas and even disrupt crystalline regions. The method has later been widely and controversially discussed as to its ability to shape the molecular weight, to introduce carbonyl groups, and to increase pulp reactivity.[17–20]

The CCOA method was employed to address these questions, using a prehydrolysis kraft pulp sample, which had undergone e-beaming of different dosages. The results demonstrated unambiguously that electron beaming introduced carbonyl groups into the pulp, even though the total amount was rather low as compared to oxidative treatments, such as ozone or hypochlorite bleaching. The amount of generated carbonyls increased with irradiation dosage.

In homogeneous solution, the fluorescent label CCOA can readily react with carbonyls in all parts of dissolved cellulose. In the heterogeneous approach, however, highly crystalline areas are not accessible for the marker. As these regions normally do not contain carbonyl functions, both homogeneous and heterogeneous approach generally produce similar carbonyl values, as comprehensively verified.[1] Interestingly, in the particular case of electron beaming the homogeneous and the heterogeneous labeling procedure (cf. part 1 of this
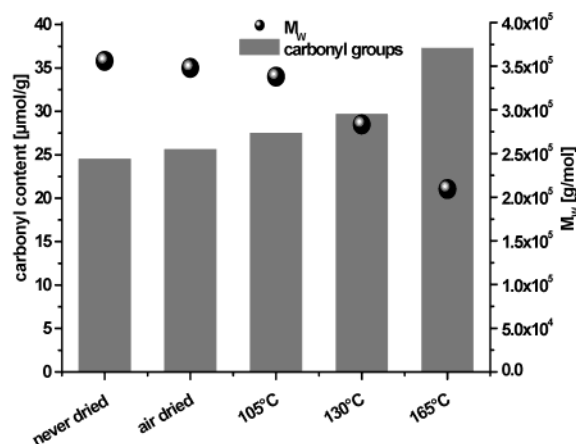

Figure 8. MW (bullets) and overall carbonyl content (bars) of a beech sulfite pulp, measured after drying and dry storage at different temperatures.

series) produced significant differences. The overall carbonyl contents from the homogeneous reaction in DMAc/LiCl were generally higher than the values obtained according to the heterogeneous approach; see Figure 6. This is a clear indication that electron beam irradiation introduces carbonyl groups also into highly crystalline domains of the pulp, as previously suggested.[16] These groups were not accessible for the derivatization reagent under heterogeneous labeling conditions but were well reported by the homogeneous derivatization.

Figure 7 gives the molecular weight distribution and carbonyl-DS curves of the genuine pulp sample and the three irradiated samples. It was evident that both processes, carbonyl generation and chain shortening, were closely interrelated and proceeded simultaneously. Thus, the increase of carbonyl contents with increasing irradiation dose was accompanied by a simultaneous gradual decrease of the molecular weight (Figure 7, left), i.e., both a narrowing and a shift to lower values. Interestingly, carbonyls were also found in regions of rather high molecular weight, in contrast to the majority of conventional oxidation (bleaching) procedures which predominantly affect shorter chain material. Carbonyls are introduced comparatively uniformly above an M_w of 5×10^4, as illustrated by the ΔDS curves. This corroborates the result that carbonyls also had been imported into the highly ordered, crystalline domains of high-molecular weight.
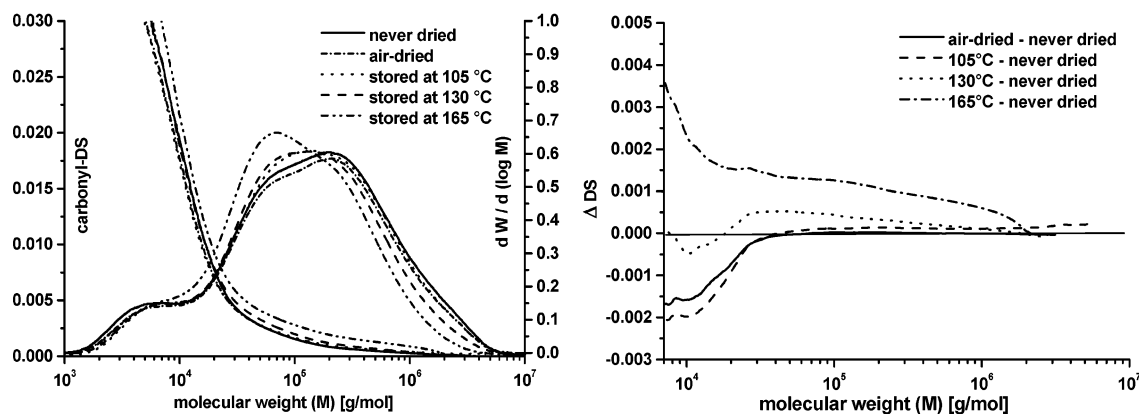
Figure 9. Carbonyl-DS and differential MWD of a prehydrolysis kraft pulp after drying and dry storage at different temperatures.

In summary, the CCOA method was able to prove that e-beaming caused a decrease of the molecular weight with simultaneous generation of carbonyl groups. The content of new carbonyl groups is rather moderate as compared to, for instance, bleaching procedures but encompasses the whole molecular weight range including a nearly uniform introduction into high molecular weight regions. Comparison of the homogeneous and heterogeneous labeling procedure confirmed that carbonyls are also introduced into crystalline domains.

4. Cellulose Drying under Thermal Stress. Intensive drying of pulp, possibly followed by prolonged dry storage at room temperature or even at elevated temperatures, causes a pronounced decrease of pulp reactivity in subsequent derivatization reactions, often described by the rather vague term "hornification".[21−23] This effect causes a decrease in pore volume, accessibility, specific surface area, and reactivity in general, which is largely irreversible, as a rewetting of the dried samples does not restore the previous properties. Chromophore formation and yellowing phenomena are a consequence of thermal treatments; both the influence of water and the crucial role of carbonyls have been established.[24−26] Even though the macroscopic consequences of such thermal treatment procedures are well-known, gaining insight into the complex causes on a molecular level still represents a challenge.

The CCOA method was applied to investigate the changes in a beech sulfite pulp upon drying and dry storage at elevated temperatures. The prevailing conditions caused a minor and rather slow, gradual decrease in the molecular weight (Figure 8 and Figure 9, left), along with a continuous increase of the overall carbonyl content (Figure 8). Only at drastically higher temperatures (165 °C) did the molecular weight shift become pronounced. The ΔDS plots (Figure 9, right) illustrated that air-drying or storage at 100 °C decreased the carbonyl content in the lower molecular weight region. Oxidative processes, which introduce significant amounts of carbonyl structures along the chain, set in at higher temperatures (130 °C) and become pronounced at 165 °C.

Conclusions

The "CCOA method" represents an approach to quantify carbonyl groups relative to the molecular weight in cellulosic

materials. In the present work, it was employed to investigate different oxidative processes affecting cellulose. Care was taken to select topics as diverse as possible to demonstrate the broad applicability of the analytical approach and to choose subjects that are not only scientifically challenging but also industrially relevant. In all four processes studied— dissolution of cellulose in the oxidizing solvent NMMO, alkalization of pulp with aging of the resulting alkali cellulose, electron beaming of pulp, and dry thermal treatment—both the molecular weight distribution and the carbonyl contents changed during the respective treatment. In all cases the CCOA method allowed for a detailed analysis of the time-dependent changes of the carbonyl contents, which frequently affected different molecular weight regions in a different manner.

Outlook. As carbonyl groups play a key role in many cellulose reactions, the CCOA method can reasonably be expected to find further applicability in many fields of cellulose chemistry. In upcoming studies, the CCOA labeling approach will be used to address the mechanism of complex reactions in cellulosic materials, such as differently induced yellowing processes and oxidatively induced strength loss in cellulosic materials. Future work will also concentrate on the development of an analogous, complementary method for *carboxyl* group detection.

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