The Lyocell Process: Cellulose Solutions in *N*-Methylmorpholine-*N*-oxide (NMMO) – Degradation Processes and Stabilizers

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ABSTRACT

Homolytic (radical) reactions in the system cellulose / *N*-methylmorpholine-*N*-oxide (NMMO, 1) involve a primary, nitrogen-centered cation radical (2), and two secondary, carbon-centered radical species (3, 4). Radical formation from NMMO is strongly promoted by transition metal ions.

The main heterolytic (ionic) reactions in Lyocell mixtures are *Polonowski*-type processes, *i.e.*, intramolecular redox processes that lead to the formation of morpholine (6) and HCHO, and the autocatalytic degradation of NMMO catalyzed by carbonium-iminium ions (7).

Both ionic and radical processes cause chain degradation of cellulose and introduction of carbonyl groups, which are important in chromophore formation.

Efficient stabilization of cellulose solutions in NMMO against side reactions and their harmful effects means prevention of both homolytic and heterolytic side reactions, which is mainly accomplished by trapping radicals, formaldehyde, and *N*-(methylene)iminium ions (7). While radical trapping is commonly reflected by the antioxidative capacity (AOC), the effectivity against heterolytic degradation in the Lyocell dope can be expressed by the newly introduced term "formaldehyde trapping capacity" (FTC).

Propyl gallate (PG, 8), the most widely applied Lyocell stabilizer nowadays, acts as phenolic antioxidant, and is finally oxidized to a deeply colored, highly conjugated chromophore (10) *via* ellagic acid (9). It was demonstrated that PG is also a quencher of formaldehyde and *N*-(methylene)iminium ions in the Lyocell dope.

A novel oxa-chromanol derivative, PBD (14), was designed as a stabilizer for Lyocell solutions. In analogy to propyl gallate, PBD acts as scavenger of all three dangerous species, namely radicals, HCHO, and 7. Upon oxidation by radical species, PBD releases acetaldehyde which acts as a very efficient HCHO trap. Both the antioxidative efficiency and the capacity to trap HCHO and 7 are higher for PBD as compared to propyl gallate. In preliminary stabilizer testing, mixtures of PBD and PG proved to be especially effective.

INTRODUCTION

The Lyocell process is becoming more and more important as an eco-friendly, environmentally benign alternative to the viscose (rayon) manufacture, for the production of high-end cellulosic fibers, especially on European and Asian markets. The annual production worldwide amounts to about 100 kt, and is rapidly increasing. In contrast to viscose production, which uses CS_2 and NaOH as derivatization chemicals and sulfuric acid / additives as the spinning bath, the Lyocell process employs only *N*-Methylmorpholine-*N*-oxide monohydrate (NMMO, 1) as a chemical that effects direct dissolution of cellulose without prior derivatization. The spinning is performed into an air gap / water so that no further spin bath chemicals are needed, and the solvent is recycled to more than 99.5 %, even on industrial scale.

Ideally, dissolution of cellulose in the amine *N*-oxide is supposed to be an entirely physical process without any chemical changes being caused in the pulp or in the solvent. However, NMMO – besides having the convenient property of being a cellulose solvent – is a strong oxidant, a solid at room temperature (which requires elevated temperatures to produce a tractable spinning dope) and a rather labile compound. Thus, in real-world processes involving the solvent NMMO and the solute cellulose, numerous chemical processes proceed, which are strongly interrelated and rather complex. (1-4)

The chemical reactions in the Lyocell process have a number of negative effects: increased consumption of NMMO, increased degradation of cellulose (DP loss) with resulting decreased product performance, increased formation of degradation products, which must be removed from the system, increased chromophore formation, and decreased chemical stability of the system, even leading to blasts and explosion, often denoted with the euphemistic terms "fast exothermic process" or "thermal runaway reaction". Especially the chromophore formation implies a number of secondary, undesired side effects, such as temporary or permanent discoloration of the resulting fibers, a reduced bleachability of the fiber material and a high load of dark colored compounds in the spinning dope, which must be continuously removed.

RESULTS AND DISCUSSION

There are three main sets of important side reactions: the complex of homolytic (radical) reactions, Polonowski-type reactions and autocatalytic degradation of NMMO, the two latter belonging to heterolytic (ionic) processes. All homolytic processes start from the primary *N*-centered cation radical 2, which undergoes mesolytic cleavage to two secondary *C*-centered radicals (3, 4). (5) The formation of radicals is strongly promoted by the

action of transition metals, which finally cause formation of *N*-methylmorpholine (NMM, 5) and morpholine (M, 6) from NMMO (Scheme 1). While all transition metals have a pronounced negative effect, iron and copper are especially detrimental, which raises concerns about construction material selection and corrosion issues. The radicals generated from NMMO attack cellulose mainly by hydrogen abstraction from C-2, which leads to introduction of keto groups at this position, and eventually causes chain cleavage by (ionic) β-alkoxy elimination (Figure 1).

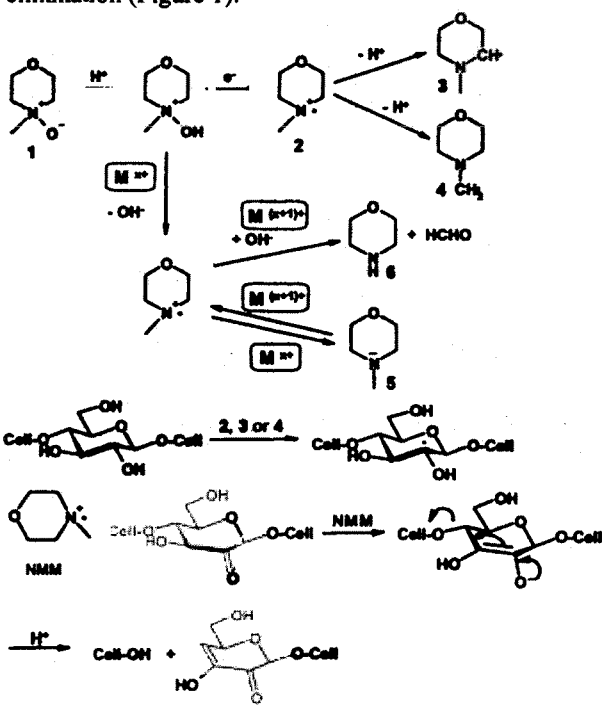

Fig. 1. Radical reactions in the Lyocell system: generation, influence of transition metal ions and action on cellulose.

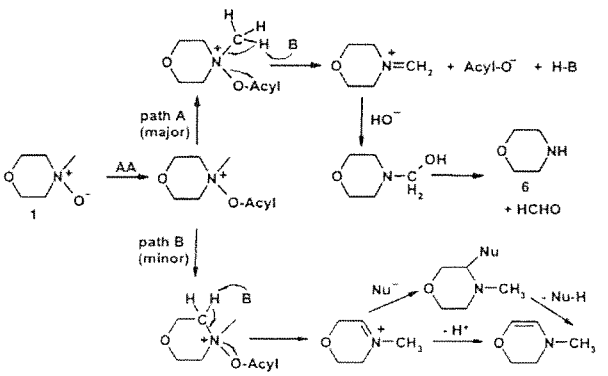

Fig. 2. *Polonowski*-type degradation of NMMO. AA = acylating agent (e.g., gluconic acid or glucuronic acid moieties, formic acid), B = base (e.g. M, NMM), Nu- = nucleophile.

Polonowski-type reactions are induced by *O*-acylation of NMMO. While for preparative purposes, strong acylating agents are used under very mild conditions, the elevated temperatures used in the Lyocell process allow the reactions to proceed with relatively weak acids as inducers, provided that amines are present at the same time. The acid performs the acylation, while the amine promotes the subsequent deprotonation step (Figure 2). Interestingly, byproducts of the Lyocell process, such as gluconic acid, formic acid and other low-molecular weight acids combined with *N*-methylmorpholine (5) and morpholine (6) as amines are able to start *Polonowski* reactions. Finally, morpholine and formaldehyde are produced from NMMO in an intramolecular redox process. (6)

The third main side reaction in the Lyocell systems is perhaps the most important one, as it is the cause of the observed thermal instabilities and "exothermic events". Carbonium-iminium ions (also called *Mannich* intermediates), mainly *N*-(methylene)morpholinium ions (7) formed from 6 and HCHO, are able to degrade NMMO quantitatively into morpholine and HCHO, even if present in catalytic amounts. The reaction starts with an *O*-alkylation of NMMO, with the alkylated intermediate fragmenting into morpholine, HCHO and carbonium-iminium ion in a concerted mechanism. Since the reaction regenerates the carbonium-iminium ions and even produces new ones by reaction of morpholine and HCHO, it is an autocatalytic process, which in addition is highly exothermic and will soon become uncontrollable if the reaction temperature is not carefully controlled (Scheme 3). (7)

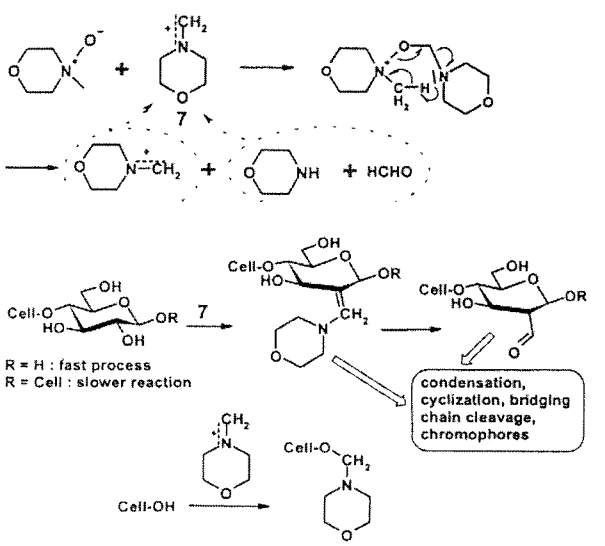

Fig. 3. Autocatalytic degradation of NMMO, catalyzed by carbonium-iminium ions: reaction mechanism and possible reactions of *Mannich* intermediates with cellulose.

The carbonium-iminium ions, once formed, react rapidly with water to form *N*-(hydroxymethyl)-morpholine, and with hydroxyl groups in pulp to form semi-aminals. Only if these reactions cannot compensate the local formation of new carbonium-iminium ions, the reaction with NMMO starts and will almost immediately become unstoppable, causing complete charring of the mixture.

To reduce side reactions in the system and thus to minimize the undesired effects of these processes, stabilizing additives are co-dissolved with cellulose in NMMO. In the early phases of process development in the 1980s, a wide variety of stabilizers – mainly coming from synthetic polymer chemistry – has been proposed: phosphonates, bases, sterically hindered phenols, and also mild reductants.

The need for Lyocell stabilizers to act as radical traps has been known for a long time. The radical trapping effect is reflected by the antioxidative capacity (AOC), *i.e.*, the number of radicals a stabilizer molecule can neutralize. The requirement of Lyocell stabilizers to be a good trap for HCHO and carbonium-iminium ions is a new concept; the effectivity against heterolytic degradation in the Lyocell dope can be expressed by the novel term "formaldehyde trapping capacity" (FTC). (8)

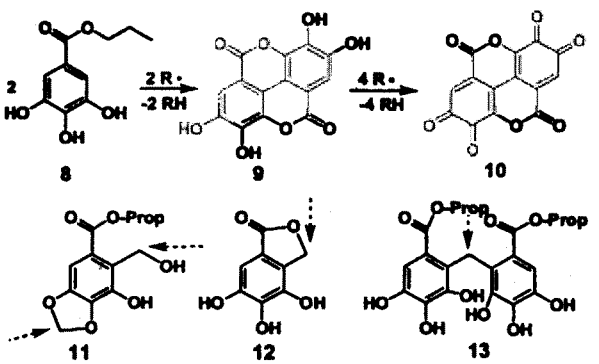

Fig. 4. Radical trapping action of propyl gallate and different HCHO trapping products. Dashed arrows indicate trapped HCHO.

Today, propyl gallate (PG, **8**) is the most frequently and widely applied Lyocell stabilizer. It acts as a phenolic antioxidant, and is finally oxidized to a deeply colored, highly conjugated chromophore (**10**) *via* ellagic acid (**9**) as the intermediate (Figure 4). By isolation and characterization of the respective trapping products it was demonstrated that propyl gallate is also a quencher of formaldehyde (see structures **11-13** in Figure 4) and *N*-(methylene)iminium ions, both in organic solutions of NMMO and in Lyocell dope. PG has a theoretical maximum AOC of 3. The theoretical maximum FTC is 4, whereas the practical value in Lyocell solutions is 2.1. The theoretical and experimental value for trapping of carbonium-iminium ions is 2 and 1.8, respectively. The processes of radical trapping and scavenging of HCHO / **2** are competitive in the case of propyl gallate.

2,4,5,7,8-Pentamethyl-4*H*-1,3-benzodioxin-6-ol (PBD, **14**) is a newly developed stabilizer for Lyocell solutions, the structure of which was derived from vitamin E. PBD acts like a typical phenolic antioxidant by forming a relatively stable phenoxyl radical, which is further oxidized by another radical equivalent to the corresponding *para*-quinone (see Figure 5), thereupon releasing acetaldehyde. The *para*-quinone is unstable and immediately undergoes a quantitative intramolecular rearrangement to an acetophenone. This acetophenone is again able to scavenge two radicals being converted into the final benzoquinoid product **15**. (9) Thus, one molecule of PBD is able to neutralize four radicals (Figure 5).

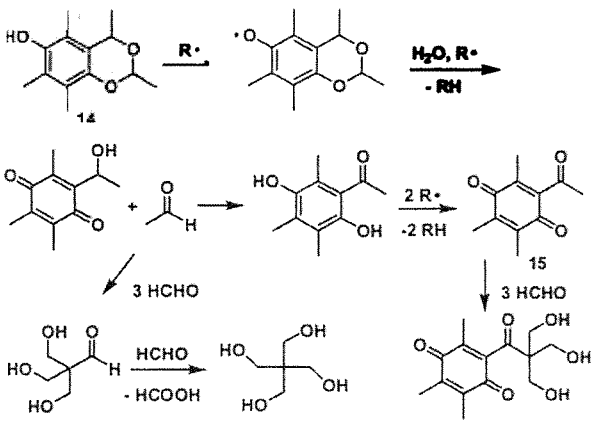

Fig. 5. Radical- and formaldehyde-trapping action of PBD (14).

PBD has a rather high formaldehyde trapping capacity, since the acetaldehyde released upon oxidation of PBD is a very reactive and effective formaldehyde scavenger under Lyocell conditions. Three molecules of HCHO are bound in the aldol-type addition reaction to 3-hydroxy-2,2-bis(hydroxymethyl)-propionaldehyde, a fourth equivalent is consumed upon the subsequent crossed *Cannizzaro* reaction of this intermediate, which gives pentaerythritol. The latter compound, in addition, is a good metal-complexing agent. Under Lyocell conditions, the aldol reaction of acetaldehyde with HCHO is much faster than the oxidation to acetic acid by NMMO. In addition, the quinoid oxidation product is able to consume up to three formaldehyde equivalents in similar aldol additions, so that the overall maximum FTC of **14** amounts to (7). Also the ability of PBD to trap the dangerous *N*-(methylene)morpholinium ions (7) is well developed. In theory, 6 equivalents of **7** would be consumed in *Mannich*-type reactions of acetaldehyde and the benzoquinone **15** (2 x 3 equivalents). The experimental carbonium-iminium ion-trapping capacity of PBD under Lyocell conditions was 4.6.

Thus, PBD offers some major advantages over propyl gallate: first, the oxidation products are much less deeply colored since they do not form large conjugated chromophoric systems as in the case of PG. This might have positive effects on fiber brightness. Second, the antioxidant efficiency is slightly higher (4 versus 3) and third, the FTC is significantly increased (in theory 7 *vs.* 4, experimentally 5.4 *vs.* 2.1), and so is the ability of scavenging carbonium-iminium ions 7 (in theory 6 *vs.* 2, experimentally 4.6 *vs.* 1.8).

In stabilization tests, the time until the start of the exothermic degradation of the reaction mixture was taken as a measure of the stabilizing efficiency, with better stabilizers giving longer stability times. While replacement of PG by PBD had only a relatively small beneficial effect, mixtures of PG and PBD showed a distinct improvement, which indicates a strong synergistic effect between the two stabilizers (Table 1), *cf.* (8). Especially the large improvements achieved by small amounts of PBD added might be interesting in larger-scale applications. In future tests, PBD must now be examined in terms of cellulose DP stabilization.

Table 1. Stabilization of Lyocell mixtures by different stabilizers and stabilizer mixtures.

Stabilizer added [a)]	"t_{onset}" (time until decomposition) [b)]
None	1
0.1 % PG	5.8
0.1 % PBD	6.4
0.1 % (PG + PBD) (1 : 1) [c)]	10.7
0.1 % (PG + PBD) (9 : 1) [c)]	9.9

[a)] the mixture contained 5 ppm Fe(II), no other additives for metal complexation or pH adjustment were added

[b)] times relative to the non-stabilized solution, average of three measurements

[c)] stabilizer concentration in m-%, ratios in mol-%

CONCLUSIONS

From the knowledge about the chemical side reactions in the Lyocell process, five properties of an "ideal" Lyocell stabilizer can be defined. A good stabilizing agent must be able to:

- prevent homolytic reactions by radical trapping ("classic" action of a phenolic antioxidant),
- bind transition metal ions by complexation,
- adjust the pH to non-acidic values to suppress *Polonowski*-type reactions,
- prevent the heterolytic degradation by trapping the catalytically active carbonium-iminium ions,
- trapping of formaldehyde to prevent the formation of *Mannich* intermediates from the beginning.

Complexing metal ions and adjusting the pH value can be accomplished by additives, but trapping reactive intermediates, such as radicals, HCHO and carbonium-iminium ions, must be done by special trapping agents. The efficiency can be expressed by the antioxidative capacity (AOC) and the formaldehyde trapping capacity (FTC).

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