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N-heterocyclic Carbene Catalysed Polymerisation of 2,5-Diformylfuran

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ABSTRACT

The biobased renewable monomer 2,5-diformylfuran is polymerised using various N-heterocyclic carbene (NHC) catalysts in dimethyl sulfoxide (DMSO) affording a low molar mass polymer. It is shown that catalyst structure as well as the temperature and time the polymerization is running have a noticeable effect on its molar mass. The obtained material is characterized by nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). An attempt at chain extension with diamine leads to precipitation of the polymer. This new biobased polymer material might be useful as a sustainable resin.

1. Introduction

As society is becoming more aware of its impact on the environment, there is an increasing motivation to move away from fossil resources. This poses a great challenge for the development of new chemical processes as almost all of the current industrial processes rely heavily on petroleum resources. As it is undesirable for this new feedstock to interfere with the production of food, as well as for economic reasons, this feedstock would preferably originate from agricultural waste streams. These waste streams consist mainly of cellulose, hemicellulose and lignin^[1-3]. In order to be able to produce high purity chem-

icals these polymers have to be broken down into smaller chemicals enabling fractionation and purification. In case of the polysaccharides cellulose and hemicellulose this can be easily achieved by combined acid hydrolysis and dehydration producing 5-hydroxymethylfurfural (HMF) and furfural, respectively^[2,4-7]. For the case of lignin this can be achieved by oxidation to vanillin derivatives or by hydrogenolysis to phenols and various other aromatics^[3,8-10].

Due to the significantly higher yields and easier purification, the furans are currently more appealing from an industrial point of view^[4,11]. Furfural is mainly hydrogenated towards furfuryl alcohol and subsequently polymerized

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to poly(furfuryl alcohol) resins, which find applications in the foundry industry as well as wood preservation^[4]. HMF, however, has a wider range of applications. It can be reduced to produce fuels and fuel additives such as 2,5-dimethylfuran, dodecane...^[3,5]. When oxidized, however, 2,5-diformylfuran (DFF) and 2,5-furan-dicarboxylic acid (FDCA) can be synthesized. The latter has gained a lot of attention as it could be used as a biobased alternative for terephthalic acid in polyester production^[12,13]. DFF has also been used for the synthesis of various polymers such as polyimides^[14,15], polypinacols^[16], urea resins^[17]... Our work focuses on the benzoin coupling for the polymerisation reaction. The analogous polymer bearing benzene rings instead of furan, polybenzoin, has been reported in literature, but to the best of our knowledge the furan analogue, polyfuroin, has not^[18,19].

The benzoin coupling is a C-C coupling reaction transforming two aldehydes into an α -hydroxy ketone. During the reaction a nucleophilic catalyst adds to one of the aldehydes transforming it into a nucleophile itself. This newly formed nucleophile will then add to the other aldehyde after which the catalyst is eliminated. When the reaction was first discovered, a cyanide catalyst was used^[20]. Later it was found that the same reaction could be catalysed by thiazolium species in the presence of base, in a biomimetic reaction^[21]. This was then expanded towards a broad range of N-heterocyclic carbenes (NHC), which have proven to afford higher yields and to be less toxic^[22]. Another advantage of the use of NHC's instead of cyanide is that they can be produced enantiomerically pure allowing for stereocontrol of the reaction products.

2. Materials and Methods

2.1 Instrumentation and Measurements

¹H-NMR measurements were performed in DMSO-d₆ using a Bruker Avance 400 operating at 400 MHz. DSC measurements were done on a TA instruments Q2000 with heating/cooling rates of 10 K/min and isothermal segments of 5 min at the temperature limits. TGA measurements were carried out using a TA instruments Q500 with a heating rate of 10 K/min to 550 °C in nitrogen.

2.2 Synthesis of NHC Precatalysts

Precatalysts **1'** (Figure 1) were made according to literature with exception of the respective hydrazine used^[23]. Purification of these precatalysts could either be achieved by recrystallisation from methanol (**1'a**) or by column chromatography, which produced both pure **1'** as **1**. Precatalyst **1a** was made by deprotection of **1'a** with TMSBr in methanol according to literature^[23].

Precatalysts **2** were also synthesised according to literature procedures^[24]. The procedures were modified with the appropriate hydrazine derivative for synthesising the required precatalyst structure.

Precatalysts **3** were also produced according to literature procedures^[25]. For catalyst **3a** the perchlorate was not purified, but the methanol adduct was synthesised instead. This was not feasible for the other derivatives due to them not forming a precipitate.

Precatalysts **4** and **5** were synthesised according to literature procedures^[26].

To the best of our knowledge the synthesis of precatalysts **1'b**, **1d** and **3b** has not yet been reported in literature. Therefore more detailed synthesis procedures and characterization data of these compounds and ¹H NMR data of the other precatalysts are added in the supplementary information.

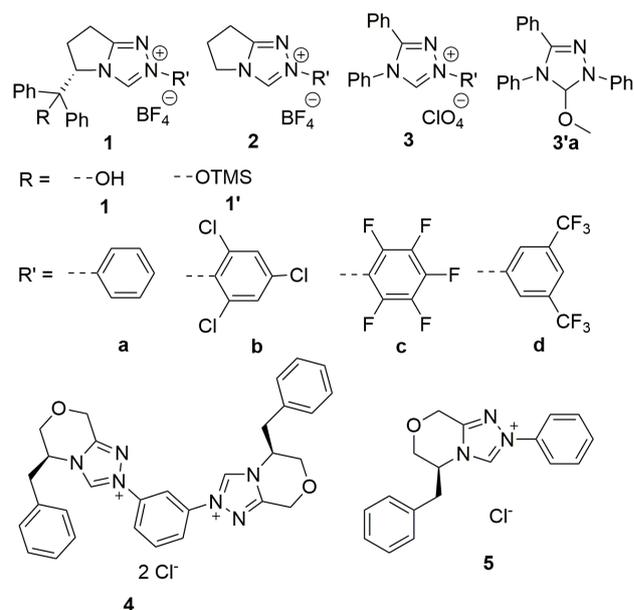


Figure 1. Structures of the NHC precatalysts

2.3 Synthesis of Polyfuroin

A dry Schlenk tube was charged with a stirring bar, 2,5-diformylfuran^[7,27] (248 mg; 2.00 mmol) and NHC precatalyst (0.04 mmol). Three cycles of vacuum-inert gas were applied to the tube and its contents. Subsequently 3 mL of dry, degassed DMSO were added to the tube and it was heated to 40 °C. To start the reaction dry, degassed triethylamine (0.13 mL; 1.0 mmol) was added to the reaction mixture and it was left to stir for 24 h. The reaction was quenched by the addition of a small amount of methanol and subsequently precipitated in 50 mL of 1 mM aqueous HCl. The precipitate was filtered and washed with water before being dried in a vacuum oven at 40 °C.

When catalyst **3'a** was used, the catalyst was placed under vacuum for 24 h at 90 °C. Afterwards nitrogen was let into the tube and it was left to cool to the reaction temperature after which the monomer solution was added to the catalyst.

2.4 Imine Coupling

The (pre-)polymer was dissolved in DMSO. When it was fully dissolved a stoichiometrical amount of diamine was added. This mixture was left to stir at room temperature for 1 h. Afterwards the polymer was precipitated in water, filtered and dried under vacuum.

3. Results and Discussion

3.1 Polymer Synthesis

For the polymer synthesis the choice of solvent is crucial. When an ethereal solvent like THF or 1,4-dioxane are used the polymer precipitates quickly upon formation of very short oligomers. Tests with the monofunctional furfural also led to precipitation indicating that dimers could already come out of solution in these solvents. The precipitation of the polymer leads to shorter chains as further polymerisation is inhibited. More polar solvents such as DMSO or pyridine were able to keep the polymer in solution. Due to the toxicity of pyridine further experiments were only conducted in DMSO. These results are in contrast to those obtained from the polymerisation of terephthaldehyde, where polymerisation in THF afforded higher Mw than in DMSO^[18].

Upon activation of the catalyst by the addition of base, the reaction mixture turns a dark colour (purple-brown). This colour is also present in the final polymer.

From the data in Table 1 it is clear that catalyst type, time and temperature all have an influence on the molar mass of the obtained polymers. Catalysts of the **1'** series slightly outperform the other catalyst structures, but all of them improve when a more electron withdrawing substituent is used on the phenyl ring attached to the nitrogen. Both an increase in the temperature and duration of the polymerisation increase the molar mass of the polymers obtained. The increased molar mass at higher polymerization temperatures could be explained by 2 factors. Either only the increased polymerization kinetics are responsible and the polymerization is stopped closer to its equilibrium or the temperature also affects the equilibrium itself and allows a higher molar mass regardless of polymerization time. The data of longer polymerization times at the same temperature indicate that the polymerization hasn't reached its equilibrium state and the kinetic factor seems more likely, although a shift in equilibrium at higher tem-

perature can't be excluded. What is remarkable, though, is that when the polymerisation is left running for more than 120 h the molar mass decreases again and seems to reach a steady state at around 1500 g/mol.

Table 1. Molar mass and isolated yields of the polymerisations for different catalysts, time and temperature. The polymerisations were carried out in DMSO at a catalyst loading of 2 mol%

Catalyst	Time (h)	Temp (°C)	DPn	Mn (g/mol)	Yield (%)
1a	24	40	3.2	400	75
1'a	24	40	5.6	690	81
1b	24	40	5.6	700	61
1'b	24	40	7.4	920	74
1c	24	40	8.8	1090	77
1d	24	40	30.9	3840	91
2a	24	40	7.1	880	43
2b	24	40	4.3	540	47
2c	24	40	4.4	550	49
3'a	24	40	4.1	510	49
3b	24	40	6.3	790	70
3b	24	50	7.7	950	70
3b	24	60	10.5	1300	71
3b	24	30	5.6	700	68
3b	48	40	12	1490	77
3b	72	40	26.6	3300	77
3b	120	40	36.2	4490	74
3b	144	40	10.9	1310	72
3b	168	40	12.6	1560	78
4	24	40	8.7	1080	75
5	24	40	12	1490	77

3.2 Polymer Characterisation

The first important characteristic is the molar mass of the polymers. Determining this property proved to be a challenge as the polymers only dissolved in viscous highly polar solvents, which were not compatible with our standard columns for SEC (PLgel MIXED). When another column set designed for us with polar solvents was used (PSS Polarsil) adsorption to the column was detected invalidating the results. As an alternative for SEC measurements DOSY measurements were attempted but even at sample concentrations of 10 mg/ml the signal/noise ratio was too low to fit the diffusion coefficient properly and thus no conclusions could be drawn from these measurements. The only remaining option available to us was to estimate the molar mass from concentrated NMR samples via the end-group integration and an assumption of the structure of the polymers. In the ¹H NMR spectrum (Figure 2) the signals from the aldehyde end groups can clearly be dis-

tinguished from the other signals. From this the number average degree of polymerisation (DP_n) can be calculated, under the assumption that the polymer has no branches and has two aldehyde end groups, by the following formula when the integration of the aldehyde protons is set to two:

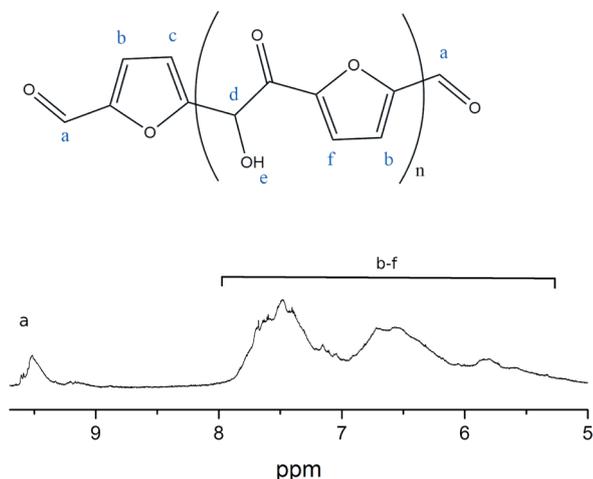


Figure 2. NMR-spectrum of polyfuroin

To assess the thermal stability of the polymer a TGA analysis was carried out under nitrogen atmosphere. The thermogram (Figure 3) shows a small loss of mass already below 100 °C, which can be attributed to the loss of absorbed water. Further loss of mass occurs in two steps each having their highest rate around 260 °C and 430 °C respectively. At the highest temperature of this measurement (550 °C) 51% of the original mass was still left. Visual inspection of the residue shows that it still has the same shape as before the measurement. This suggests that the material does not melt or have a glass transition before thermal degradation sets in.

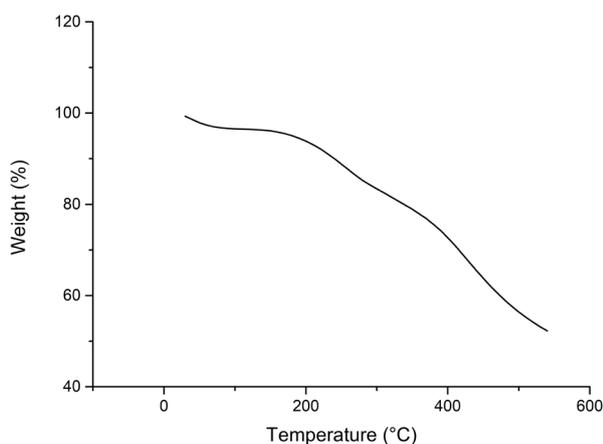


Figure 3. TGA profile of polyfuroin produced using pre-catalyst 1c

To test this DSC measurements were carried out on the

polymer. In the entire thermogram no transition of any kind is visible supporting the hypothesis that the polymer degrades before any thermal transition (Figure 4). This is further supported by the reported values for the T_g of the similar polybenzoin between 112 °C and 150 °C, which are higher than the degradation point found for this polymer^[18].

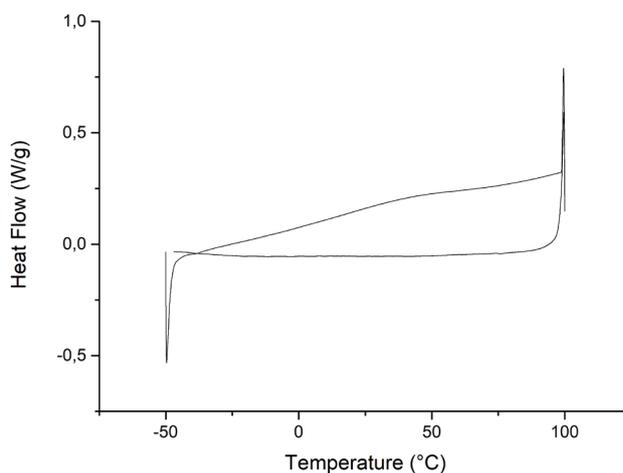


Figure 4. DSC profile of polyfuroin produced using pre-catalyst 1c. The second heating and cooling cycles are shown.

As the low degradation temperature made it impossible to check the crystallinity by thermal measurements, X-ray diffraction experiments were carried out. The main reason for these experiments is to test the hypothesis that the homochiral catalysts can induce sufficient optical homogeneity in the polymer to allow crystallisation. The diffractogram of all polymers, however, did not show any distinct peaks indicating that the material was completely amorphous.

3.3 Imine Coupling of Polyfuroin

When a stoichiometric amount of 1,6-hexamethylenediamine was added to a solution of polyfuroin in DMSO in an attempt to increase its molar mass, a precipitate was formed. This precipitate couldn't be dissolved in either acetone, THF, chloroform, DMSO or DMF. To check if this was an effect of imine coupling of the aldehyde end groups of the polymer, a test reaction was done with DFF instead of polyfuroin at room temperature. This reaction also afforded a precipitate within a few minutes. After workup this polymer was brought into an acidic aqueous solution to hydrolyse the imine and after addition of an organic solvent to dissolve the DFF everything returned back into solution, indicating imine couplings were most likely responsible for the precipitate formation of this polymer. Another possible explanation for the precipita-

tion of the polymer is the formation of an aminal instead of an imine leading to crosslinking of the polymer. The polyfuroin, however, also contains other functional groups making other reactions possible as well.

4. Conclusions

We have shown that the polymerisation of 2,5-diformylfuran by NHC catalysts produces short oligomers that have a low thermal degradation temperature and no detectable crystallinity. The catalyst structure and duration of the polymerisation greatly influence the polymer molar mass. Reaction of the polymer with a multifunctional amine causes it to precipitate either by chain extension or crosslinking.

Author Contributions

Wouter Ruelens: methodology, formal analysis, investigation, data curation, writing – original draft, visualization
Fariba Mafakheri: formal analysis, investigation, writing – review & editing
Viktor Van Lierde: methodology, formal analysis, investigation, writing – review & editing
Mario Smet: conceptualization, resources, writing review & editing, supervision, funding acquisition

Conflict of Interest

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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