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Hydrothermal polymerization towards fully biobased polyazomethines†

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Microwave assisted polycondensation for the synthesis of (partially) biobased polyazomethines in water (hydrothermal polymerization) was investigated for the first time in this study. The polyazomethines prepared *via* this environmentally friendly and simple method show comparable characteristics as the polymers prepared *via* traditional methods in organic solvents.

Polyazomethines (PAz) or poly(Schiff base)s have attracted considerable attention of researchers during the last two decades, due to their interesting characteristic properties such as: high thermal stability, liquid crystalline properties, excellent mechanical properties, metal-chelating ability,[1–3] *etc.* Especially the conjugated aromatic PAz, which usually show special opto-electric conductivity, have valuable potential applications in electrical fields.[4–8]

The strategy to prepare polyazomethines is straightforward, typically through polycondensation from dialdehyde and diamine monomers with the release of water. By derivatization of the monomers, various types of PAz can be expediently obtained. Since the first report in 1923,[9] polyazomethines containing moieties like phenyl,[10] furan,[11,12] ester,[13] ether,[14] silane,[15] thiophene,[16] ferrocene,[17] pyridine,[18] triazole[19] *etc.* were developed successfully. However, most of these azomethine polymerizations were proceeded in solvents like dimethylsulfoxide (DMSO), *N*-methyl-pyrrolidone (NMP), hexamethylphosphoramide (HMPA) or toluene, characterized by high boiling temperatures, non-renewability or even toxicity.[20] As far as we know there is only one report where water was used as the solvent for PAz preparation, however it is only limited to hydrophilic monomers.[21] Recently, hydrothermal polymerization for the synthesis of polyimides was established by Morton[22] and Unterlass.[23–26] Polyimides were obtained efficiently in two hours *via* polycondensation in hot water under pressure using autoclaves or microwave reactors. Moreover, imine-based covalent organic frameworks (COFs) were also realized by this hydrothermal method recently,[27,28] especially the newly published work by Zamora and coworkers providing a simple and green synthetic protocol.[29]

These results were inspiring to make PAz *via* hydrothermal polymerization due to the similarity of the synthesis methods to get PAz, polyimides and imine-linked COFs. They are conventionally prepared *via* condensation reaction in organic solvents with removal of water. Although there are already some studies describing the polycondensation of PAz under high pressure, *i.e.*, from microwave reactors, they were still performed *via* the conventional method with non-renewable organic solvents.[30–34] Furthermore, among these tremendous reports on PAz, only very few of them took biobased monomers into consideration.[34–36] The increasing environmental concerns, along with depleting fossil oil reserves, put higher requirements both on resource renewability and synthetic sustainability of polymer materials.[37] As such, to develop a green and environmentally friendly method to prepare (partially) biobased polyazomethines is a growing demand both in industrial factories and for scientific studies. Herein, we report our preliminary results of the hydrothermal polycondensation towards PAz.

The study was started by comparing different polycondensation methods for the preparation of aromatic PAz with stoichiometric amounts of the common monomers *p*-phenylenediamine and terephthaldehyde (Table 1). Four known conditions were selected from literature[35,38–40] to be compared with catalyst free microwave assisted polycondensation in water. Among the selected conditions, the solvent *N*-methylpyrrolidone (NMP)/$CaCl_2$ was also used in analogy with the procedure to make another class of liquid crystalline polymers, namely polyaramids.[40] $CaCl_2$ is known to improve solubility and acts as a dehydrating agent to capture released water.

All the PAz obtained from the different conditions are yellow or orange solids in accordance with the reported literature. The

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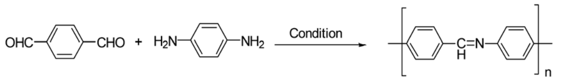
Table 1 Polymerization conditions exploration for PAz synthesis from *p*-phenylenediamine and terephthaldehyde

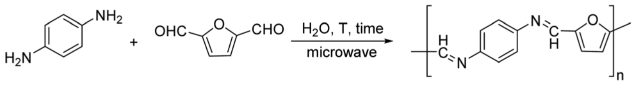


Entries	Conditions	Yield (%)	M_n[a] (g mol^{-1})	$Đ$[a]	Ref.
1	NMP/11 wt% $CaCl_2$, 120 °C, 24 h	91	900	1.5	40
2	NMP/HMPA = 4/1, 120 °C, 24 h	72	900	1.4	38
3	DMSO, 180 °C, 24 h	90	1000	1.6	35
4	Toluene, $ZnCl_2$ (6 mol%), TsOH (2 mmol%), reflux, 12 h	89	800	1.4	39
5	H_2O, 200 °C, microwave, 1 h	98	900	1.5	This work

[a] Measured by GPC in concentrated sulfuric acid (1 mg mL^{-1}) within 72 h.

number average molecular weight (M_n) of the obtained polymers was measured by GPC in concentrated sulfuric acid. Model experiments (p. S8 and S9, ESI†) and NMR studies over time of the polymer (Fig. S8(c), ESI†) indicate that the polymers are stable in H_2SO_4 during the GPC handling time. The results in Table 1 are in line with what is expected from literature.[5,41] Due to the limited solubility of the polymers in the reaction solvents, they precipitate out during reaction what hampers further polymerization and limits molecular weights. FT-IR (Fig. S7, ESI†) confirms the presence of a residual carbonyl peak at 1689 cm^{-1}, typical for a terephthaldehyde end group, referring to traces of aldehyde monomer or low molecular weight polymer with clear visibility of the end groups, similar as observed in literature for PAz.[42,43] NMR analysis further shows that all the aldehyde peaks from the monomer disappeared and shift to a higher ppm in the polymer, indicating that the terephthaldehyde monomer was completely consumed and that low molecular weight polymer with aldehyde end groups was generated. The new peak around 9.82 ppm was assigned as imine and further confirms the polymerized structure (Fig. S8, ESI†). The solvent based procedures resulted in similar molecular weights as the polymerization in hot water at 200 °C (1 h) in the microwave (Table 1 entry 5; IR spectrum in Fig. S7, GPC overlay in Fig. S9, ESI†). The molecular weight results under different conditions were also confirmed by the measurement of the reduced viscosity (η_{red}) in 96% sulfuric acid (Table S2, ESI†).[44,45] Moreover, PAz prepared *via* this green polymerization method have the highest yield due to the simple purification process: polymer is obtained by simply washing the precipitated polymer powder with water and drying after the reaction, without the need to remove high boiling solvents. Hydrothermal polymerization also shows the highest efficiency with the shortest reaction time among all these conditions. All in all, the preliminary experiments indicate the valuable potential of this green polymerization method towards polyazomethines for further investigation.

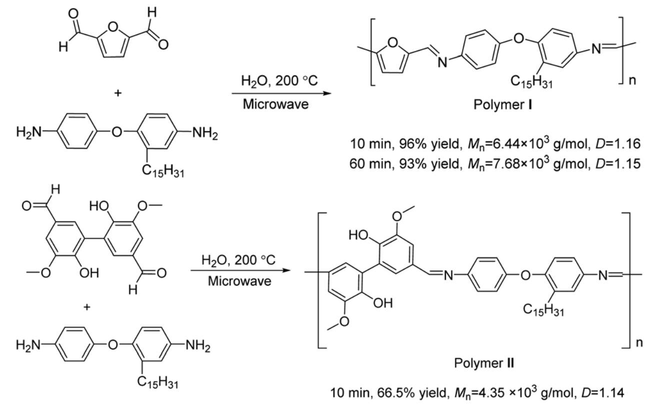
Table 2 Synthesis of partially biobased polyazomethines based on furan-2,5-dicarbaldehyde in hot water



Entries	Time (min)	T (°C)	M_n[a] (× 10^3 g mol^{-1})	$Đ$[a]	Yield (%)
1	1	200	5.56	1.16	95
2	2	200	5.49	1.15	97
3	5	200	5.58	1.16	96
4	10	200	6.12	1.18	95
5	30	200	5.97	1.17	97
6	60	200	6.46	1.26	97
7	90	200	5.85	1.17	91
8	120	200	5.84	1.15	94
9	10	100	5.72	1.19	96
10	10	130	5.71	1.18	96
11	10	160	5.64	1.17	94
12[b]	1440	120	5.39	1.70	75

[a] Determined by GPC with RI detection in HFIP/0.19% NaTFA, calibrated with PMMA standards. [b] Polymerization was performed in NMP/11 wt% $CaCl_2$.

In a next step, hydrothermal polymerization was used to make partially biobased polymers based on a dialdehyde monomer derived from 5-hydroxymethylfurfural (HMF), a versatile biobased building block from carbohydrate sugars[46,47] which is used widely to construct polymer materials.[48] Furan-2,5-dicarbaldehyde (biobased monomer **1**, Scheme S1, ESI†) derived polyazomethines were reported in literature with good properties.[11,12] Moreover, this kind of PAz have a better solubility, which makes it possible to measure their molecular weight with GPC in hexafluoroisopropanol (HFIP with 0.19% NaTFA). The influence of the reaction time and temperature of the hydrothermal polymerization were explored (Table 2). In all cases, PAz were obtained successfully as orange solids. The appearance of new characteristic peaks in the Fourier transform infrared (FT-IR) spectra at 1614 cm^{-1} indicates the successful Schiff-base formation between dialdehydes and diamines (Fig. S10(d), ESI†). NMR spectra also confirm the success of the polymerization from the disappearance of the peaks of the aldehyde group (9.95 ppm) in biobased monomer **1** and the phenyl protons in *p*-phenylenediamine (7.97 ppm), while new aldehyde end groups (10.10 ppm) and distinguished imine bonds (around 9.60 ppm) were generated in the polymers (Fig. S10(e) and (f), ESI†). Moreover these polymers have a very high thermal stability (T_d(5%) = 362 °C; T_d(max) = 390 °C) indicated from TGA, but no T_m or T_g was observed in DSC (Fig. S10(b) and (c), ESI†). At 200 °C, the polymerization was first carried out from 1 min to 120 min (entries 1–8 in Table 2). To our surprise, even after only 1 min reaction time, PAz could be obtained with an M_n of 5.56 × 10^3 g mol^{-1}. With increasing



Scheme 1 Fully biobased polyazomethine synthesis *via* hydrothermal polymerization.

reaction time, the M_n of PAz slightly increases in some cases. Additionally, the obtained polymers became darker upon increase of the reaction time. Considering efficiency and energy saving, 10 min reaction time was selected to explore the influence of temperature. When decreasing the temperature from 200 °C (entry 4 in Table 2) to 160, 130 and 100 °C (entries 9–11 in Table 2), the M_n decreased slightly. Meanwhile, the yields are very high (from 91%–97%) in all cases due to the earlier mentioned simplicity in purification. To further confirm the advantages of hydrothermal polymerization in PAz synthesis, furan-2,5-dicarbaldehyde derived PAz was also prepared using NMP/$CaCl_2$ at 120 °C (Table 2, entry 12). This results in comparable M_n (5.39×10^3 g mol^{-1}) but longer reaction times and lower yield, what further proves the superiority of hydrothermal polymerization to prepare PAz.

After successful synthesis of partially biobased PAz using this green polymerization method, fully biobased PAz were targeted. Polymers based on biobased building blocks generally have a lower CO_2 footprint compared to materials from fossil fuel-based sources. Combined with the hydrothermal polymerization only in water, we aim to make the whole process more sustainable, not only from the preparation point of view but also when considering the raw material sources. We first synthesized the biobased monomers: dialdehyde coming from the lignin derived building block vanillin (biobased monomer **2**, Scheme S2, ESI†)[49] and diamine derived from the cashew nut shell liquid building block cardanol (biobased monomer **3**, Scheme S2, ESI†).[50] The side groups in vanillin (OH, methoxy) and cardanol (long aliphatic chain) decrease the stiffness of PAz and thus enhance the solubility. Both of these monomers were obtained with moderate to high yields (see ESI† for detailed procedure).

With these biobased monomers in hand, hydrothermal polymerization at 200 °C was applied to prepare fully biobased PAz (Scheme 1). FT-IR and ^1H NMR spectra of the monomers and the obtained polymers were performed to confirm the success of polymerization (Fig. S11(g)–(i) and S12(d)–(f)). For polymer **I**, reaction for 60 min gives a higher molecular weight than 10 min reaction time (7.68×10^3 *vs.* 6.44×10^3 g mol^{-1}). For polymer **II**, the M_n is 4.35×10^3 g mol^{-1} and the yield is 66.5%. The lower molecular weight can be correlated with the presence of typical amine and aldehyde carbonyl vibrations in FT-IR (Fig. S12(d), ESI†) due to residual monomer or end groups in low molecular weight polymer. The low yield was caused by the stickiness of the obtained polymer, which complicates work up by precipitation. These two polymers have a high thermal stability with a T_d (5%) of more than 300 °C but do not show a melting point in DSC before degradation. At the same time, Polymer **II** shows a glass transition temperature (T_g) at about 67 °C but no T_g was observed in Polymer **I** (Fig. S11(f) and S12(c), ESI†). These green polymers and their corresponding properties were assumed to provide beneficial information to design more green conductive polymers, imine-based COFs, liquid crystalline materials *etc.*

All in all, the successful synthesis of fully biobased polymers further demonstrates that hydrothermal polymerization is an environmentally benign and simple processing method that is straightforward for the preparation of polyazomethines. Meanwhile several factors such as the formation of a stable conjugated aromatic product, polymer phase separation due to bad solubility and higher pressure for solid-state polymerization[51] are hypothesized to explain the elongation of the polymer chains rather than the hydrolysis of the imine bond in the aqueous medium during hydrothermal polymerization. Further investigations are required to unravel the exact mechanism.

In summary, hydrothermal polymerization was successfully developed for the synthesis of polyazomethines. Within only 10 min microwave assisted polymerization in water, polyazomethines were obtained with excellent yields and comparable properties to the polymers prepared conventionally in organic solvents. Furthermore, this green method was also applied for the preparation of biobased polyazomethines, derived from vanillin, 5-hydroxymethylfurfural and cardanol. These biobased polymers have a high thermal stability and M_n values ranging from 4000 g mol^{-1} to 7000 g mol^{-1}, and could provide useful information to design more sustainable imine-based materials. This green polycondensation method avoids the use of organic solvents and catalysts, ensures high efficiency and affords excellent yield after a simple work up procedure, and as such holds valuable potential for polyazomethine synthesis in both industrial production and scientific studies.

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Conflicts of interest

There are no conflicts to declare.

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