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Short communication

Renewable resources based polymers: Synthesis and characterization of 2,5-diformylfuran–urea resin

Ananda S. Amarasekara *, Dalkeith Green, LaToya D. Williams

Department of Chemistry, Prairie View A&M University, Prairie View, TX 77446, USA

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ABSTRACT

Condensation of renewable resources based monomer 2,5-diformylfuran (DFF) and urea at 110 °C by melting a solid mixture gives a crystalline polymer resin in 90% yield. This resin was characterized by elemental analysis, ^{1}H, ^{13}C and ^{1}H–^{1}H COSY NMR, IR, UV, TGA and DTA. The structural unit of this new material consists of one DFF molecule condensed with two urea molecules at the aldehyde group of DFF. A homologous resin was prepared by using 5,5′-oxydimethylenebis(2-furaldehyde) and urea in 84% yield via a similar procedure and characterized as well.

1. Introduction

In view of declining fossil raw materials and rising oil prices it is necessary to develop renewable resources based feedstock chemicals and new polymeric materials based on these chemicals [1–4]. In recent years there were a number of attempts to utilize biomass derived monomers such as triglycerides [5], 1,3-propanediol [6], furfural [7,8], 2,5-furandicarboxylic acid or its derivatives [9–15] for the preparation of polymers. Acid catalyzed hydrolysis followed by dehydration of several abundant biomass polysaccharides produces furan derivatives such as furfural and 5-hydroxymethylfurfural [16] as the major products. These furans can be considered as practical starting materials useful in the replacement of some fossil raw materials [1,2]. With the recently developed [17] highly efficient preparation method from renewable resources, 5-hydroxymethylfurfural is expected to play a major role in this new generation of chemicals, and the two related oxidation products 2,5-furandicarboxylic acid and 2,5-diformylfuran (DFF, 1) are excellent candidates as monomers for the development novel polymeric materials. In fact 2,5-furandicarboxylic acid has caught the attention of a number of researchers as a potential replacement for terephthalic acid in the future [18].

Grushin has recently shown [19] that DFF can be prepared directly from fructose in a one-pot two step process involving $VOHPO_4$ catalyzed air oxidation of the intermediate 5-hydroxymethylfurfural. Furthermore, we have developed an efficient oxidation method for 5-hydroxym-ethylfurfural to DFF using Mn(III)-salen catalysts and sodium hypochlorite as the primary oxidant [20]. Even though DFF has been used in the synthesis of various useful compounds, including intermediates for pharmaceuticals [21], antifungal agents [22], organic conductors [23] and macrocyclic ligands [24,25] the potential of this symmetrical dialdehyde as a monomer in the preparation of new polymeric materials is a relatively unexplored area. Gandini [26] reported the synthesis of polymeric Schiff bases bearing furan moieties by condensation of DFF with a number of diamines. These compounds exhibited thermal stabilities up to about 260 °C and fully conjugated polymers displayed semiconductivity after doping with iodine.

Aromatic aldehydes are known to condense with two equivalents of amides to give benzylidene-bisamides [27]. Martinez [28] has studied the condensation of furfural with urea by using different molar ratios in aqueous and heterogeneous phases in an attempt to develop a slow

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* Corresponding author. Tel.: +1 936 261 3107; fax: +1 936 261 3117. *E-mail address:* asamarasekara@pvamu.edu (A.S. Amarasekara).

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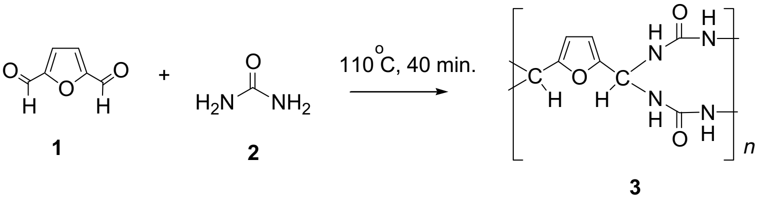

Fig. 1. Synthesis of 2,5-diformylfuran–urea resin (**3**).

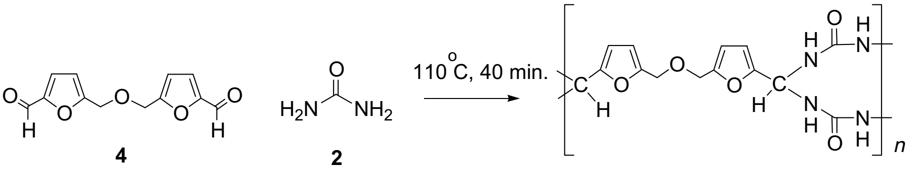

Fig. 2. Synthesis of 5,5′-oxydimethylenebis(2-furaldehyde)–urea resin (**5**).

release nitrogen fertilizer and found that the major product is the difurfuralidinetriurea [28], independent of the furfural urea molar ratio. In this reaction, furfural aldehyde group condenses with two amide nitrogens from two urea molecules. In the present communication we report the preparation and characterization of a relatively insoluble novel polymeric resin by condensation of DFF (**1**) with urea (**2**) as shown in Fig. 1. Further, a homologous polymer was also prepared (Fig. 2) by using 5,5′-oxydimethylenebis-(2-furaldehyde) (**4**) [29] and urea to show the generality of the synthesis. The dialdehyde, 5,5′-oxydimethylenebis(2-furaldehyde) (**4**) can be easily prepared by dimerization of 5-hydroxymethylfurfural in the presence of an acid catalyst [29].

2. Experimental

2.1. Instrumentation and measurements

^{1}H NMR spectra were recorded in DMSO-d_6 on a Varian Mercury plus spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$). ^{13}C NMR spectra in DMSO-d_6 were recorded on the same spectrometer operating at 100 MHz; chemical shifts were measured relative to DMSO-d_6 and converted to δ(TMS) using δ(DMSO) = 39.51. FT-IR spectra were recorded on a Thermo Nicolet IR 200 spectrometer using KBr pellets and UV spectra were recorded on a JASCO V-560 spectrometer using 1 cm cells in spectroscopic grade methanol. Thermogravimetric analysis was carried out in air on a Perkin-Elmer Diamond TG/DTA system. Elemental analysis was performed at QTI Laboratories, NJ, USA.

2.2. Synthesis of 2,5-diformylfuran–urea resin (3)

A mixture of 2,5-diformylfuran [19,20] (38.5 mg, 0.31 mmol) and urea (74.0 mg, 1.24 mmol) was thoroughly grounded together in a pestle and mortar for 2 min. Then the powder was transferred to a glass reaction tube and heated in an oil bath under a nitrogen atmosphere at 110 °C for 40 min. Solid mixture first melted and then solidified to a light brown transparent hard resin. The solid product was allowed to cool and transferred to a centrifuge tube and washed with water (4 × 10 mL), methylenechloride (2 × 10 mL) and cyclohexane (2 × 10 mL). The resulting light brown solid was dried under vacuum to give pure resin (65.6 mg, 90% yield).

Anal. Calc. for $C_8H_8N_4O_3.1.5H_2O$: C, 40.85; H, 4.71; N, 23.82. Found: C, 41.22; H, 4.82; N, 23.62%. IR 3339, 1660, 1525, 1385, 1139, 1021, 796, 582 cm^{-1}. UV(MeOH) 220, 280 nm. NMR and TG/DTA data are shown in Figs. 3 and 4, respectively.

2.3. Synthesis of 5,5′-oxydimethylenebis(2-furaldehyde)–urea resin (*5*)

5,5′-Oxydimethylenebis(2-furaldehyde)–urea resin **5** was prepared by using a procedure similar to the procedure described in Section 2.2. A mixture of **4** [29]

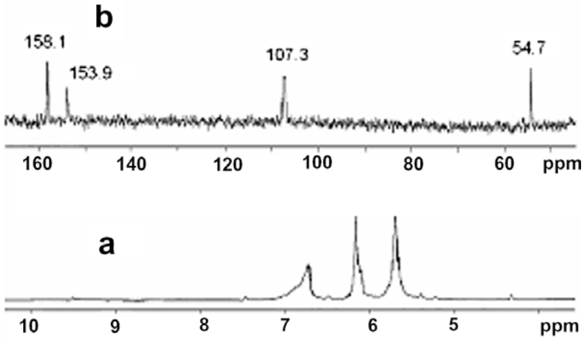

Fig. 3. ^{1}H (a) and ^{13}C (b) NMR spectrums of 2,5-diformylfuran–urea resin (**3**) in DMSO-d_6.

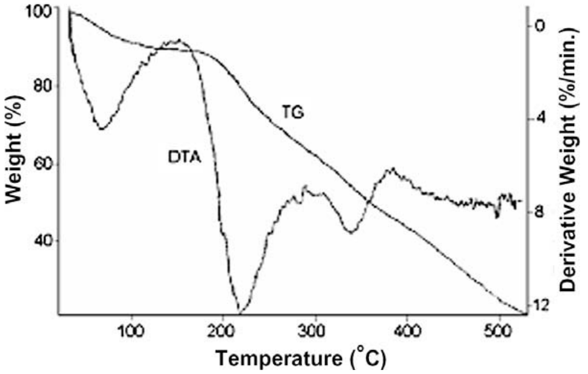

Fig. 4. TG/DTA curves of 2,5-diformylfuran–urea resin (**3**).

(46.8 mg, 0.20 mmol) and urea (48.0 mg, 0.80 mmol) gave pure resin **5** as a brown solid (59.5 mg, 84% yield).

Anal. Calc. for $C_{14}H_{14}N_4O_5.2H_2O$: C, 47.46; H, 5.12; N, 15.81. Found: C, 47.71; H, 5.03; N, 15.86%. IR 3338, 1669, 1524, 1383, 1201, 1135, 1059, 1021, 802, 579 cm^{-1}. ^1H NMR δ 4.37(4H), 5.68(2H), 6.17(2H), 6.36(2H), 6.82(4H). ^{13}C NMR δ 54.9, 63.7, 107.2, 111.2, 151.1, 155.6, 158.1. TG/DTA: two endothermic peaks are observed in the DTA curve at 215 and 350 °C with 24% and 16% weight losses, respectively.

*2.4. Swelling experiment for comparison of the crosslinking densities of **3** and **4***

Polymer resins (**3** or **4**) were cut into thin disks of 10 mm approximate diameter and 2 mm thickness, weighing 0.1–0.15 g. These disks were then weighed (w_i) and immersed in 10–15 mL of toluene in glass vials at room temperature (23 ± 1 °C) for 6 h. Then the swollen disks were removed from the solvent, carefully padded with filter papers to dry the surface and weighed (w_s). The disks were immediately returned to toluene vials and withdrawn after 12, 24, and 48 h of total time, for similar weighings. The percentage degree of swellings after these time periods were calculated using the formula [30]:

$$\text{Degree of swelling}(\%) = (w_s - w_i) \times 100/w_i$$

The experiments were carried out in duplicate for both resins and the results are shown in Table 1.

Table 1
Changes in the degree of swelling (%) with time (h) for polymer resins **3** and **5**.

Polymer resin	Time (h)	Degree of swelling (%)*
3	6	7
3	12	9
3	24	12
3	48	12
5	6	11
5	12	15
5	24	17
5	48	17

Polymer resin disks (diameter ~10 mm, thickness ~2 mm) were used in toluene at room temperature (23 ± 1 °C).

* Average in duplicate experiments.

3. Results and discussion

3.1. Synthesis

Polymer resin **3** (Fig. 1) described in the experiment section was prepared using DFF urea molar ratio 1:4, and this ratio gave the complete reaction of DFF. Earlier attempts using stoichiometric ratio of DFF:urea = 1:2 gave a resin with similar physical appearance, but ^1H NMR of this sample showed unreacted aldehyde functional groups, resulting from partial reaction of DFF. In the 1:4 experiment the crude product was repeatedly washed with water to remove the excess urea, and further washed with methylene chloride and cyclohexane to remove any DFF and soluble oligomers. The DFF:urea = 1:1 condensation product was not observed in the polymerization reaction. This may be due to the high reactivity of the intermediate formed (—CH=N—C(O)—N=CH—) after 1:1 reaction, which readily undergoes aza-Michael additions with urea producing the 1:2 condensation product. The characterized DFF–urea resin **3** is insoluble in water and all the common organic solvents, and only slightly soluble in DMSO and DMF after warming to 45 °C, and dissolves in trace amounts in methanol at room temperature, sufficient to record the UV spectra. The homologous polymeric resin **5** was also prepared (Fig. 2) using dialdehyde (**4**) to urea ratio of 1:4 and purified by washing, as described for **3**. This polymer also showed solubility characteristics similar to **3**.

3.2. Characterization of the polymer resins

3.2.1. NMR spectroscopy

Proton NMR of the polymer resin **3**, recorded in DMSO-d_6 showed three broad peaks at 5.70, 6.17 and 6.75 ppm (Fig. 3a). ^1H–^1H COSY spectrum of this sample indicated a strong cross peak between 6.75 and 6.17 signals, and further the 2D spectrum showed that broad peak at 5.70 ppm is not coupled to any other proton. Upon addition of a drop of D_2O to the NMR tube the intensity of the peak at 6.75 ppm in the ^1H NMR spectrum was significantly decreased, and therefore this peak was assigned as the NH of the amide group (Fig. 3a). With this information and ^1H–^1H COSY spectrum, the peak at 6.17 ppm was assigned to the CH proton in the —NH—CH—NH— fragment. The remaining peak at 5.70 ppm, which is not coupled to any other proton, was assigned to the 3,4 position protons of the furan ring. ^{13}C NMR (Fig. 3b) was recorded using a 5 s relaxation delay, and this spectrum showed four peaks at 54.7, 107.3, 153.9 and 158.1 ppm. High field peak at 54.7 was assigned to —NH—CH—NH carbon by comparison with the ^{13}C spectrum of difurfuilidenetriurea [28], where similar carbon was found to resonate at 54.72 ppm. Two peaks at 107.3 and 153.9 ppm are characteristic [31] of furan ring 3 and 2 position carbons. Carbonyl carbon of the repeating unit (Fig. 1) was assigned to the peak at 158.1 ppm, which is comparable to the carbonyl signal at 157.84 ppm of difurfuilidenetriurea [28].

NMR Spectrums of the homologues resin **5** showed features similar to that of 2,5-diformylfuran–urea resin **3**. For instance, in polymer **5**, CH proton in the —NH—CH—NH—

fragment was observed at 6.17 and NH protons are observed at 6.82 ppm, and the corresponding protons in **3**, resonated at 6.17 and 6.75 ppm. In addition to these signals —O—CH$_2$— ether link protons appeared at 4.37 ppm as a 4H signal. Carbon NMR spectrum of 5 showed two high field signals at 54.9 and 63.7 ppm, corresponding to NH—CH—NH and —O—CH$_2$— ether carbons, and thus respectively, and thus confirming the structure.

3.2.2. IR and UV spectroscopy

FT-IR spectrum of the polymer 3 showed a broad band at 3356 cm^{-1}, and was assigned to the N—H absorption. Carbonyl group and C—N bond absorptions of the new resin were found at 1660 and 1385 cm^{-1}, respectively, whereas the corresponding absorptions for urea are observed at 1683 and 1471 cm^{-1}. These shifts in the IR absorptions further substantiate the bonding of the urea nitrogens to DFF aldehyde carbons. Typical furan ring absorption at 1021 cm^{-1} is also observed in the spectrum, verifying the furan moieties in the resin. UV spectrum of the resin **3** recorded in methanol showed two peaks at 220 and 280 nm, and these absorptions are typical [32] of the furan ring. Related polymeric resin **5** showed the C=O and C—N absorptions at 1669 and 1383 cm^{-1} proving the structural resemblance to 3.

3.2.3. TG/TDA

Thermal analysis of the sample **3** is shown in Fig. 4. Initial weight loss of about 11% in the region of 50–100 °C is due to the crystallized water in the sample. Calculated formula of $C_8H_8N_4O_3$. 1.5 H_2O and the loss of 1.5 H_2O correspond to 11.5%, and agree well with this initial weight loss. Two well defined endothermic peaks are seen in the DTA curve (Fig. 4) at 218 and 338 °C. The first one corresponds to a 22% weight loss, and the second DTA peak is associated with about 15% of weight loss. Similar thermal behavior was reported by Martinez [28] for the furfural-urea condensation compound difurfuralidinetriurea as well, where the two corresponding DTA peaks were found at 200 and 330 °C accompanying 25 and 14% weight losses, respectively. TG/DTA curves of the resin **5** showed thermal behavior comparable to the 2,5-diformylfuran–urea resin **3** further confirming the structural similarity.

3.2.4. Degree of swelling and crosslinking densities of **3** and **4**

Crosslinking nature of the polymer can be confirmed by the swelling experiment using toluene as the solvent. This experiment showed that polymers **3** and **5** reached the equilibrium degree of swellings of 12% and 17%, respectively, after 24 h in toluene at room temperature (Table 1). The polymer resin **3** with lower degree of swelling has a higher crosslinking density when compared with the homologous polymer **5**.

4. Conclusion

We have shown that condensation of renewable resources based monomer, 2,5-diformylfuran with urea by melting a solid mixture without a catalyst produces an insoluble, novel polymer resin in 90% yield. The polymer is shown to have the structural unit **3** with a crosslinked structure by a combination of spectroscopic methods and elemental analysis. Related polymer resin prepared from 5,5′-oxydimethylenebis(2-furaldehyde) and urea in 84% yield is shown to have the structural unit **5**.

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References

[1] Corma A, Iborra S, Velty A. Chem Rev 2007;107(6):2411–502.
[2] Lichtenthaler FW. Acc Chem Res 2002;35:728–37.
[3] Gandini A, Belgacem NM. Polym Int 1998;47(3):267–76.
[4] Klass DL. Biomass for renewable energy, fuels and chemicals. San Diego, CA: Academic Press; 1998.
[5] Sharma V, Kundu PP. Progress Polym Sci 2006;31(11):983–1008.
[6] Umare SS, Chandure AS, Pandey RA. Polym Degrad Stabil 2007;92(3):464–79.
[7] Patel AA, Patel SR. Europ Polym J 1983;19(3):231–4.
[8] Arora PB, Patel HS, Patel SR. Europ Polym J 1987;23(4):307–9.
[9] Afli A, Gharbi S, El Gharbi R, Bigot YL, Gandini A. Europ Polym J 2002;38(4):667–73.
[10] Khrouf A, Boufi S, El Gharbi R, Gandini A. Polym Int 1999:649–59.
[11] Khrouf A, Abid M, Boufi S, El Gharbi R, Gandini A. Macromol Chem Phys 1998;199:2755–65.
[12] Gharbi S, Andreolety JP, Gandini A. Eur Polym J 2000;36:463–72.
[13] Gharbi S, Gandini A. Acta Polym 1999;50:293–7.
[14] Abid M, El Gharbi R, Gandini A. Polymer 2000;41:3555–60.
[15] Gharbi S, Afli A, El Gharbi R, Gandini A. Polym Int 2001;50:509–14.
[16] Lewkowski J. Arkivok 2001;1:17–54.
[17] Román-Leshkov Y, Chheda JN, Dumesic JA. Science 2006;312:1933–7.
[18] Ribeiro mL, Schuchardt U. Editors. Capparelli M, Luiz H, Leao A, Frollini E. Natural Polymers and Composites IV, In: Proceedings from the International Symposium on Natural Polymers and Composites, 4th, Sao Pedro, Brazil, Sept. 1–4, 2002. Sao Carlos: Publisher: Embrapa Instrumentacao Agropecuaria, 2002. p. 192–197.
[19] Halliday GA, Young Jr RJ, Grushin VV. Organic Lett 2003;5:2003–5.
[20] Amarasekara AS, Green D, McMillon E. Catal Commun 2008;9:286–8.
[21] Hopkins KT, Wilson WD, Bender BC, McCurdy DR, Hall JE, Tidwell RR, et al. J Med Chem 1998;41:3872–8.
[22] DelPoeta M, Schell WA, Dykstra CC, Jones S, Tidwell RR, Czarny A, et al. Antimicrob Agents Ch 1998;42:2495–502.
[23] Benahmed-Gasmi AS, Frere P, Jubault M, Gorgues A, Cousseau J, Garrigues B. Synth Met 1993;56:1751–5.
[24] Richter DT, Lash TD. Tetrahedron Lett 1999;40:6735–8.
[25] Howarth OW, Morgan GG, McKee V, Nelson J. J Chem Soc, Dalton Trans 1999:2097–102.
[26] Hui Z, Gandini A. Europ Polym J 1992;28(12):1461–9.
[27] Polya JB, Spotswood TM. Recl Trav Chim Pay B 1951;70:269–76.
[28] Martínez-García A, Ortiz M, Martínez R, Ortiz P, Reguera E. Ind Crops Products 2004;19(2):99–106.
[29] Chundury D, Szmant HH. Ind Eng Chem Prod Res Dev 1981;20:158–63.
[30] Wei X, Malcolm B, Huglin BL, Timothy GJJ. Eur Polym J 2007;43(3):915–27.
[31] Huckerby TN. J Mol Struct 1976;31(1):161–7.
[32] Martinez A, Rodriguez ME, York SW, Preston JF, Ingram LO. Biotechnol Prog 2000;16(4):637–41.