Supplementary Information for "Hydrothermal Polymerization towards Biobased Polyazomethines"

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Experimental Methods

^{1}H- and ^{13}C-H NMR spectra were recorded on a Bruker Avance at 300 MHz for ^{1}H-NMR and 75 MHz for ^{13}C-NMR in $CDCl_3$-d_1, DMSO-d_6, $C_2D_2Cl_4$-d_2 or D_2SO_4-d_2. Chemical shifts are presented in parts per million (δ) relative to DMSO-d_6 (2.50 ppm in ^{1}H- and 39.51 ppm in ^{13}C-NMR respectively), $CDCl_3$-d_1 (7.26 ppm in ^{1}H- and 77.16 ppm in ^{13}C-NMR respectively), $C_2D_2Cl_4$-d_2 (6.04 ppm in ^{1}H-NMR) D_2SO_4-d_2 (11.20 ppm in ^{1}H-NMR). The resonance multiplicities are described as s (singlet), d (doublet), t (triplet) or m (multiplet).

TGA analysis (TA Instruments Q500) was used to determine the thermal stability of the prepared polymers. Around 5 mg of the material (dried overnight under vacuum at 80 °C) was heated at 10 °C/min from 25 °C to 700 °C in a nitrogen atmosphere.

Differential scanning calorimetry (DSC) was performed on approximately 5 mg polymer sample (dried overnight under vacuum at 80 °C) using a Netzsch Polyma 2014 DSC. The polymer sample was first subjected to a heating and cooling cycle to erase the sample history. Then the samples were heated from 25 °C to 250-300 °C (depending on the TGA data) and cooled again at a scanning rate of 10 °C/min under a nitrogen flow of 20 mL min^{-1}.

GPC in HFIP + 0.19% NaTFA was recorded on an Agilent 1260 Infinity LC system with RI detection, relative calibration with PMMA standards, PSS WinGPC UniChrom software, 2 × PSS PFG Micro linear M (7 μm) 4.6 × 250 mm columns + 1 × PSS PFG Micro linear M (7 μm) 4.6 × 30 mm guard column, column oven 40 °C. The GPC samples were prepared by dissolving 5.0 mg of the polymer in 1.5 mL of the solvent. The solutions were filtered over a 0.2 μm PTFE syringe filter before injection.

GPC in H_2SO_4 (1 mg/ml) was measured with a modular HPLC set-up consisting of a pump, autosampler and UV detector. Concentrated sulfuric acid was used as eluent in combination with modified silica columns calibrated with PS standards in THF (600-7,500,000 Da). A UV detector (340 nm) was used in order to determine the molecular weight and dispersity of the polymer.

The reduced viscosity was measured with a Xylem Ubbelohde viscometer (type IIc) in a water bath at 25°C, with polymer solutions of 0.25 w/v% in 96% sulfuric acid (SI Analytics CT 72/2 system, WinVisco software).

Infrared spectroscopy (IR) of samples in the powder form was recorded on a Shimadzu IR affinity-1 Single Reflection ATR or PerkinElmer Spotlight 400 FT-(N)IR microscope..

Hydrothermal polymerization was performed in Biotage Initiator+ Microwave System (maximum power 400 W), with microwave program "initiator 4.1.4", where the target temperature is reached within 2 min and maintained for the set time; after reaction, the temperature is decreased to 50 °C within 4 min. Reactions were performed in pressure tubes equipped with a magnetic stirring bar and closed with a crimp-cap septum.

The water content was checked in a Mettler Toledo Coulometric Karl Fisher titrator C30 using Hydranal-Coulomat AK as anolyte and Hydranal-Coulomat CG-K as catholyte.

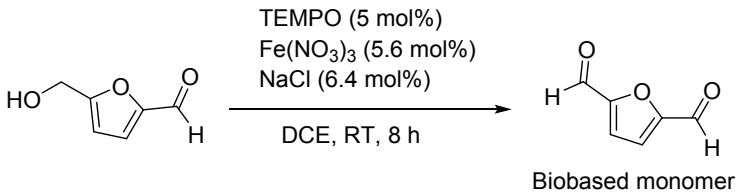
Melting temperatures of organic compounds were measured with a Mettler Toledo MP90 Melting Point System with a heating rate of 10 °C/min.

Materials

5-(hydroxymethyl)furfural > 95.0% was purchased from AVA Biochem BSL AG without further purification. N,N-Dimethylformamide (DMF) AR, tetrahydrofuran (THF) AR, ethyl acetate AR, toluene AR, ethanol AR and dimethylsulfoxide (DMSO) AR were purchased from Biosolve. Zinc chloride ($ZnCl_2$) >99%, *N*-methylpyrrolidone (NMP), dimethylsulfoxide-d_6 (DMSO-d_6), chloroform-*d* ($CDCl_3$), calcium chloride ($CaCl_2$), *p*-phenylenediamine >99% (PPD), K_2CO_3 >99%, NaTFA 97% and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) >99.5% were purchased from Acros Organics. Sodium peroxodisulfate ($Na_2S_2O_8$) ≥98%, hexamethylphosphoramide (HMPA) ≥99%, vanillin ≥99%, $FeSO_4$ heptahydrate ≥99%, cardanol (3-penta decylphenol) ≥90%, hydrazine hydrate 50-60%, Pd/C (10w% loading), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) for synthesis, $Fe(NO_3)_3.9H_2O$ >98%, sulfanilic acid ≥99%, $NaNO_2$ ≥97%, sodiumdithionite for analysis, 1-chloro-4-nitrobenzene 99%, p-toluene sulfonate (TsOH) 95 % and 1,2-dichloroethane 99.8%, D_2SO_4 96-98 wt. % in D_2O were purchased from Sigma-Aldrich. 1,1,2,2-tetrachloroethane-d_2 99.5 % was purchased from Cambridge Isotope Laboratories

NMP/$CaCl_2$ solutions were prepared from the following procedure: $CaCl_2$ was dried under vacuum at 250 °C for several hours. The $CaCl_2$ was allowed to cool down to room temperature under vacuum. Then $CaCl_2$ was combined with dry NMP (obtained from a MBraun SPS-compact solvent purification system) in a glovebag under nitrogen atmosphere. The final $CaCl_2$ concentration was 11 w%.

Monomer synthesis and characterization



Scheme S1: Synthetic route for biobased monomer **1**, furan-2,5-dicarbaldehyde

Biobased Monomer **1** (furan-2,5-dicarbaldehyde) was synthesized according to a literature procedure[1] (Scheme S1).
To a 500 mL beaker hydroxymethylfurfural (HMF, 6.33g, 50.1 mmol, 1.0 eq), TEMPO (0.401g, 2.57 mmol, 5 mol%), $Fe^{III}(NO_3)_3$ (1.132g, 2.8 mmol, 5.6 mol%) and NaCl (0.184g, 3.2 mmol, 6.4 mol%) were added. These compounds were dissolved in dichloroethane (200 mL) and stirred for 8h in the open air. After full conversion was achieved, the reaction mixture was filtered and the residue was evaporated under reduced pressure. The crude product was purified by recrystallization from toluene, followed by a sublimation step at 160 °C.

Yield: 88 %; White or yellow solid. T_m = 115 °C. ^{1}H NMR in ppm (300 MHz, $CDCl_3$) δ 9.88 (s, 2H, C*H*O), 7.35 (s, 2H, C*H* in furan ring). FT-IR wavenumber (cm^{-1}) (Figure S9(h)) = 3123 ν(CH furan) w, 2876 and 2750 ν(CH of CHO) w, 1666 ν(CHO) st, 1562 and 1511 ν(C=C furan) m, 1234 and 1170 ν(C-O-C) st, 955 δ(=CH 2,5 disubstituted Ar) st.

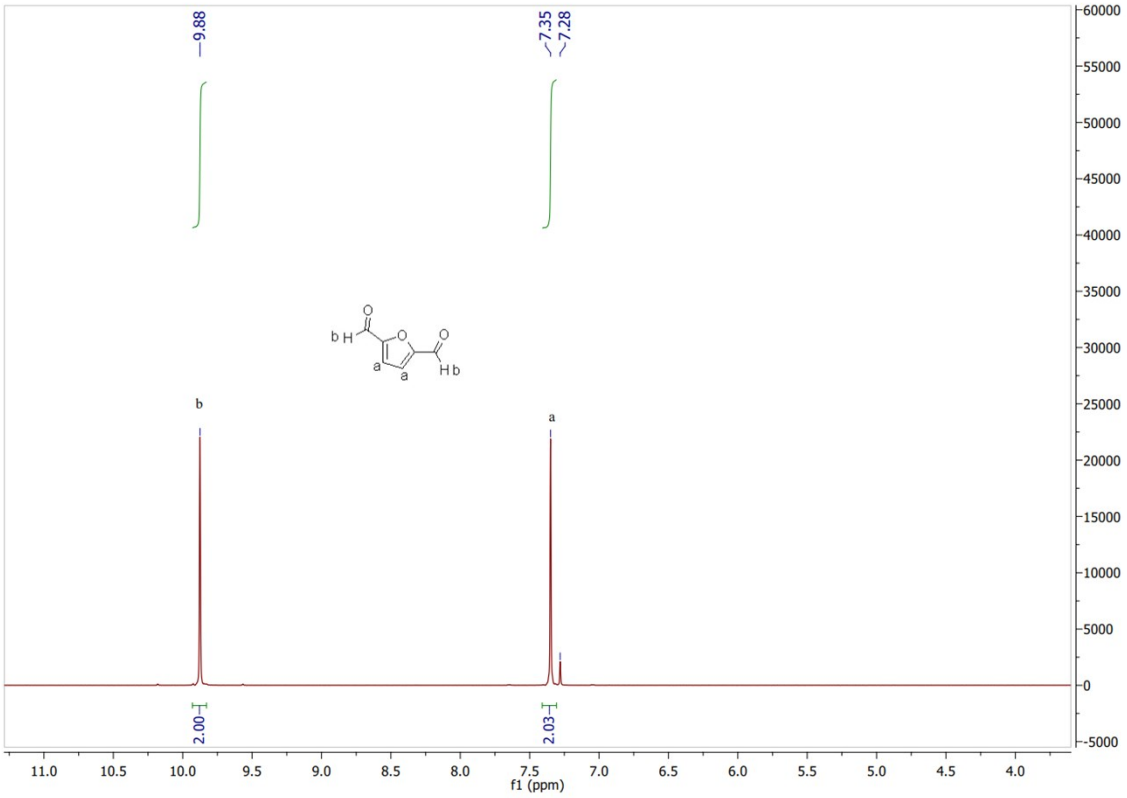
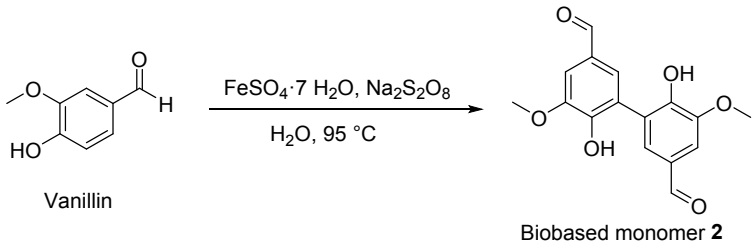


Figure S1. ^{1}H NMR spectrum of biobased monomer **1**, furan-2,5-dicarbaldehyde in $CDCl_3$.



Scheme S2: Synthetic route for biobased monomer **2**, 5,5'-bisvanillin

Biobased monomer **2** (5,5'-bisvanillin or 6,6'-dihydroxy-5,5'-dimethoxy-[1,1'-biphenyl]-3,3'-dicarbaldehyde) was synthesized following a slightly modified literature procedure[2] (Scheme S2).

1.83 g vanillin (12 mmol) was dissolved into 100 mL H_2O at 95 °C under stirring (500 rpm), and then 0.15 g $FeSO_4$•$7H_2O$ (0.54 mmol, 0.2 mol%) was added into the solution. Immediately the solution turned brownish. The cross coupling process was carried out by subsequently adding 1.61 g $Na_2S_2O_8$ (6.76 mmol, 0.56 eq.) and a precipitate was formed directly. The suspension was then further stirred for 5 mins at 95 °C and cooled down to room temperature. The crude product was harvested by vacuum filtration. The solid was dissolved again in 20 mL NaOH (3 M), and then the product was reprecipitated by drop-by-drop addition of around 15 mL 4 M HCl. The final product was harvested by vacuum filtration and further washed three times with hot water, followed by drying in the vacuum oven overnight at 60 °C.

Yield 85%, brown powder, T_m=305 °C (lit. > 270 °C)[2]. Soluble in DMSO, NMP, DMF. ^{1}H NMR in ppm (300 MHz, DMSO-d_6) δ 9.90 (bs, 2H, O*H*), 9.84 (s, 2H, C*H*O), 7.43 (s, 4H, C*H* in benzene ring), 3.93 (s, 6H, CH_3). FT-IR wavenumber (cm^{-1}) (Figure S10(d)) = 3294 ν(OH) br, 1670 ν(CHO) st, 1651 ν(C=C Ar) st, 1454 and 1417 δ(CH_2/CH_3) m, 1253 ν(=C-O-C) and δ(OH) st, 1183 ν(=C-O-C) w, 1139 1,2,4 substituted Ar st, 1038 ν(C-O) m, 879 w and 841 m 1,2,4 substituted Ar.

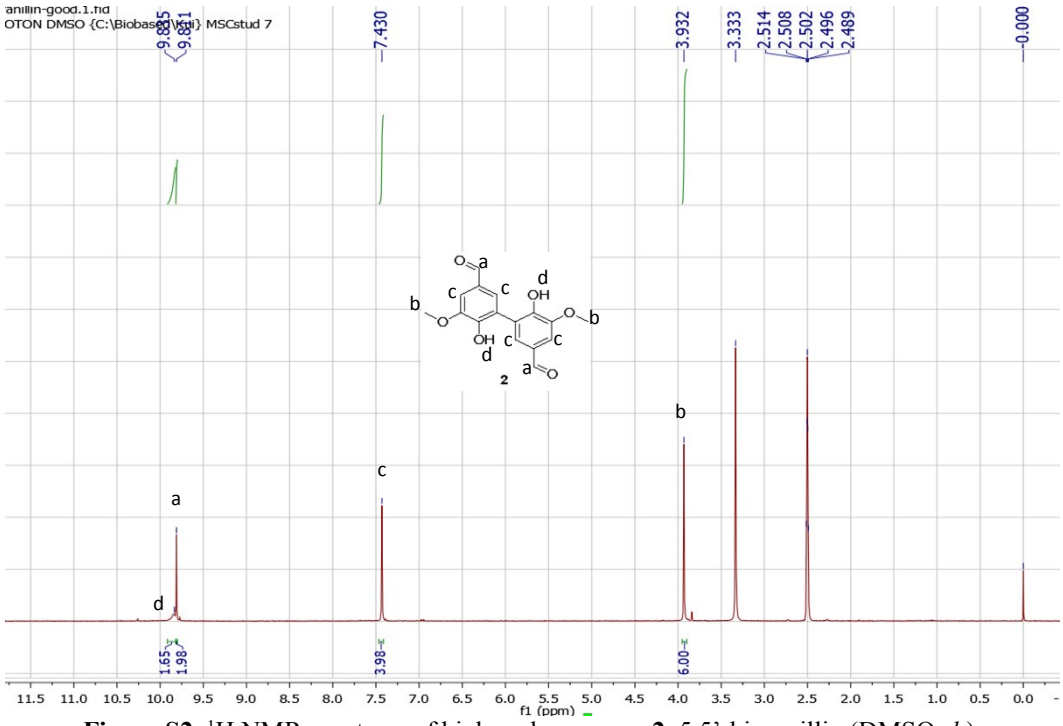
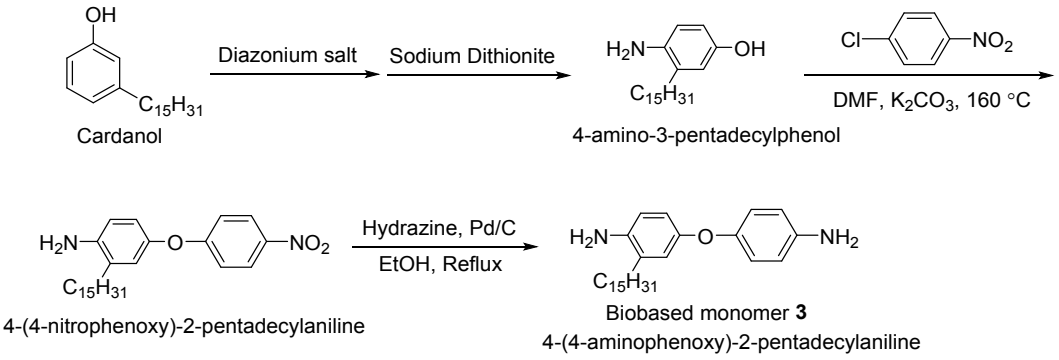


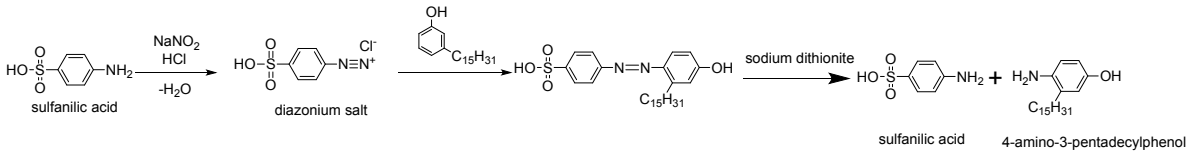
Figure S2. ^{1}H NMR spectrum of biobased monomer **2**, 5,5'-bisvanillin (DMSO-d_6).



Scheme S3: Synthetic route for biobased monomer **3**, 4-(4-aminophenoxy)-2-pentadecylaniline

Biobased monomer **3** was synthesized via a three step procedure according to the a slightly modified version of a reported procedure[3] (Scheme S3).

Step 1: preparation of 4-amino-3-pentadecylphenol



Scheme S4: Synthetic route for 4-amino-3-pentadecylphenol

- Preparation of the diazonium salt: 1.73 g (10 mmol) sulfanilic acid and 0.53 g (5 mmol) sodium carbonate were dissolved in 20 mL distilled water in a flask. The solution was heated to 50 ℃ for full dissolution. Then the solution was moved to an ice water bath. 0.76 g (11 mmol) sodium nitrite ($NaNO_2$) was dissolved in 5 ml distilled water in a beaker. The sodium nitrite solution was poured to the sulfanilic acid and sodium carbonate solution. Then the mixture was added slowly to 2 mL concentrated HCl in a flask. The flask was shaked and the diazonium salt was put into an ice bath for direct use.

- Preparation of the azo compound: 3.04 g (10 mmol) 3-pentadecyl phenol, 2.8 g (50 mmol) KOH and 20 ml ethanol were added into a 250 ml round bottom flask equipped with a magnetic stirring bar and a reflux condenser. After the solid was fully dissolved, the phenol solution was put into an ice bath, and the diazonium salt was added dropwise to the phenol solution with a syringe while stirring. The red dye solution was stirred in an ice bath for 2 hours.

- Azo bond cleavage via reduction process: 5.22 g (30 mmol) sodium dithionite was dissolved in 30-50 mL distilled water. The sodium dithionite solution was added dropwise to the azo solution which was heated at 75 ℃ (the color changed from dark red to orange) and the mixture was stirred for 30 min. 1.8 g (30 mmol) acetic acid in 2 ml distilled water was added to the solution, and reacted for another hour (the color changed to pale tan). The solution was filtered and washed with distilled water. Then the precipitate (yellow crystals) was dried in a vacuum oven at 50 ℃ overnight. The crude product obtained was purified by recrystallization using toluene.

Yield: 79%. Brown solid. T_m=103.7 °C (lit. 104 °C)[3], soluble in DMSO. ^{1}H NMR in ppm (300 MHz, DMSO-d_6) δ 8.21 (s, 1H, O*H*), 6.43 (d, J = 8.4 Hz, 1H, C*H* in benzene ring), 6.38-6.30 (m, 2H, C*H* ortho of OH in benzene ring), 4.12 (s, 2H, -NH_2), 2.33 (t, J = 7.5 Hz, 2H, ArCH_2CH$_2$-), 1.49-1.42 (m, 2H, ArCH$_2$CH_2-), 1.32-1.20 (m, 24H, -CH_2-), 0.85 (t, J = 6.6 Hz, 3H, -CH$_2$CH_3).

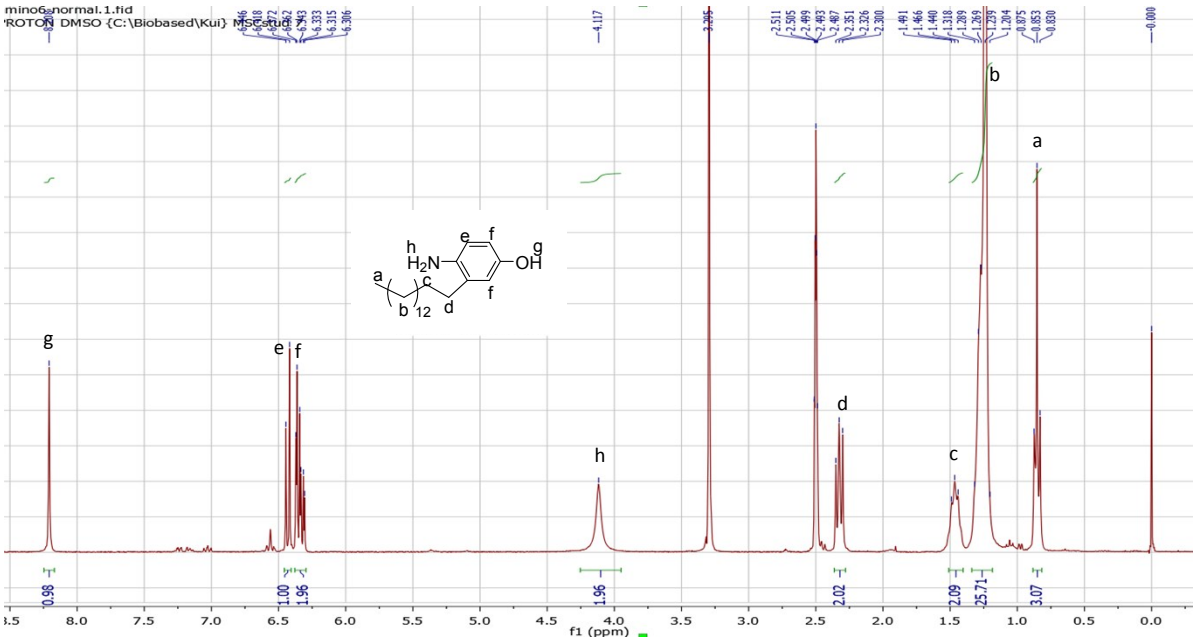
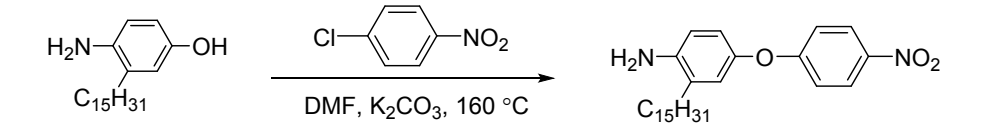


Figure S3. ^{1}H NMR spectrum of 4-amino-3-pentadecylphenol in DMSO-d_6.

Step 2: preparation of 4-(4-nitrophenoxy)-2-pentadecylaniline



4-amino-3-pentadecylphenol

4-(4-nitrophenoxy)-2-pentadecylaniline

Scheme S5: Synthetic route for 4-amino-3-pentadecylphenol

4-amino-3-pentadecyl phenol (1 g, 3.1 mmol), 1-chloro-4-nitrobenzene (0.49 g, 3.1 mmol), potassium carbonate (0.48 g, 3.4 mmol) and N,N-dimethylformamide (20 mL) were added into a 100 ml three-necked round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 3 h at 160 °C under dry nitrogen gas stream. After completion of the reaction, the reaction mixture was cooled to room temperature and poured into water (20 mL). The mixture was extracted three times with ethyl acetate. The collected organic layers were evaporated via rotary evaporation, resulting in a brown liquid. To this liquid, a minimum amount of distilled water was added, giving rise to a yellow precipitate. The yellow solid was filtered, dried and recrystallized from ethanol.

Yield: 86.4%, Yellow solid. T_m = 66 °C (lit. 67 °C)[3], soluble in chloroform. ^{1}H NMR in ppm (300 MHz, $CDCl_3$-*d*) δ 8.17 (d, *J* = 8.4 Hz, 2H, C*H* ortho to NO_2 in benzene ring), 6.95 (d, *J* = 8.4 Hz, 2H, C*H* meta to NO_2 in benzene ring), 6.81-6.72 (m, 3H, C*H* in benzene ring), 3.93 (s, 2H, -NH_2), 2.49 (t, *J* = 7.8 Hz, 2H, ArCH_2CH$_2$-) 1.64-1.59 (m, 2H, ArCH$_2$CH_2-), 1.33-1.25 (m, 24H, -CH_2-), 0.88 (t, *J* = 5.1 Hz, 3H, -CH$_2$CH_3).

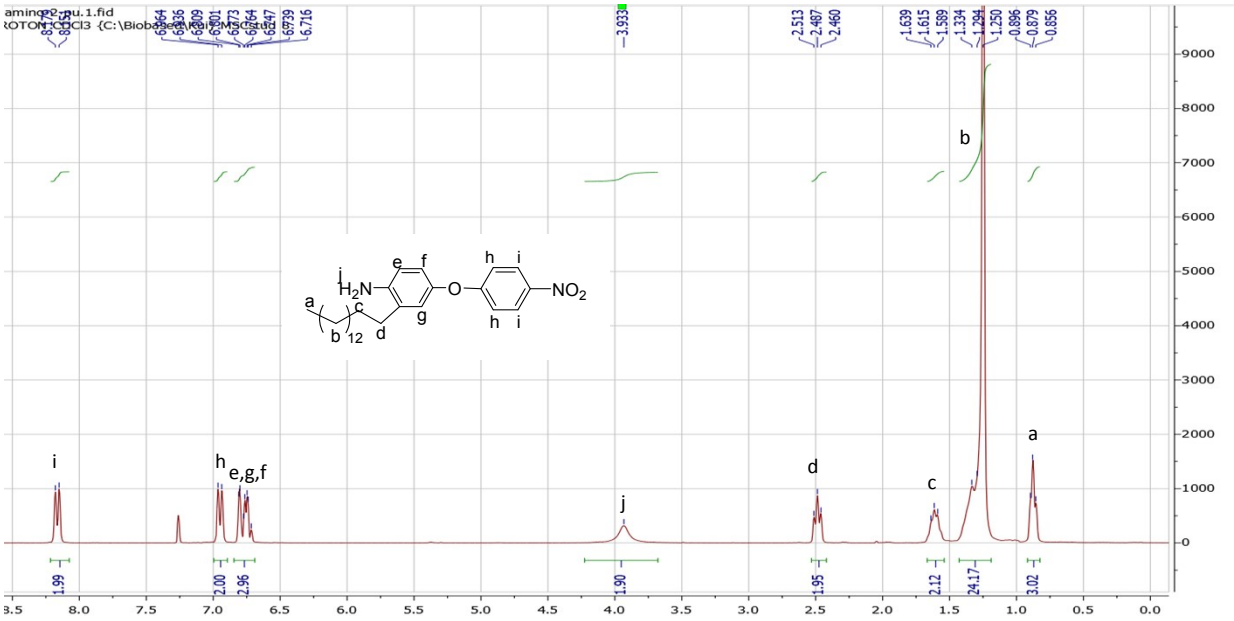
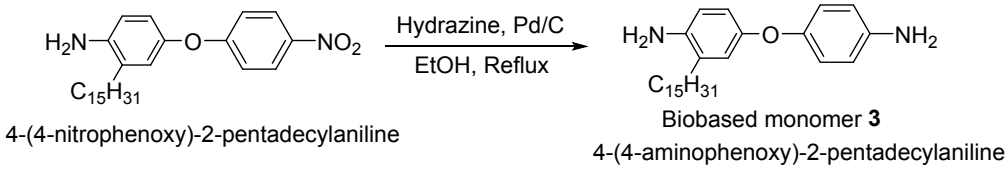


Figure S4. ^{1}H NMR spectrum of 4-(4-nitrophenoxy)-2-pentadecylaniline in $CDCl_3$.

Step 3: preparation of biobased monomer **3**, 4-(4-aminophenoxy)-2-pentadecylaniline



4-(4-nitrophenoxy)-2-pentadecylaniline

Biobased monomer **3**

4-(4-aminophenoxy)-2-pentadecylaniline

Scheme S6: Synthetic route for 4-(4-aminophenoxy)-2-pentadecylaniline

4-(4-aminophenoxy)-2-pentadecylaniline (0.01 g, 0.22 mmol), palladium-on-charcoal (3 wt%, 3 mg) and ethanol (2 mL) were added into a 50 mL round-bottom flask equipped with a dropping funnel and a reflux condenser. To the reaction mixture, hydrazine hydrate (0.34 g, 6.8 mmol) was added dropwise at 80 ℃. After the addition was complete, the reaction mixture was refluxed for 3 h under nitrogen. The hot reaction mixture was filtered to remove palladium-on-charcoal. Upon cooling, yellow crystals precipitated which were isolated by filtration and recrystallized twice from ethanol. The final white powder after drying under vacuum was stored under nitrogen.

Yield: 64%, white solid. T_m = 81 °C (lit. 81 °C)[3], soluble in chloroform. ^{1}H NMR in ppm (300 MHz, $CDCl_3$-*d*) δ 7.00-6.66 (m, 7H, C*H* in benzene ring), 4.58 (bs, 4H, (-NH_2)$_2$), 2.49 (t, *J* = 8.1 Hz, 2H, ArCH_2CH$_2$-) 1.61-1.55 (m, 2H, ArCH$_2$CH_2-), 1.35-1.25 (m, 24H, -CH_2CH_2-), 0.88 (t, *J* = 5.7 Hz, 3H, -CH$_2$CH_3). FT-IR wavenumber (cm^{-1}) (Figure S9(g)) = 3471-3376 ν_{as}(NH$_2$) and ν_s(NH$_2$) w, 2952 ν(CH$_3$) w, 2921 ν_{as}(CH$_2$) st, 2845 ν_s(CH$_2$) st, 1619 δ(NH$_2$) m, 1493 ν(C=C Ar) st, 1455 and 1423 δ(CH$_2$/CH$_3$) m, 1208 ν(C-O-C) st, 835 and 810 δ(=CH Ar).

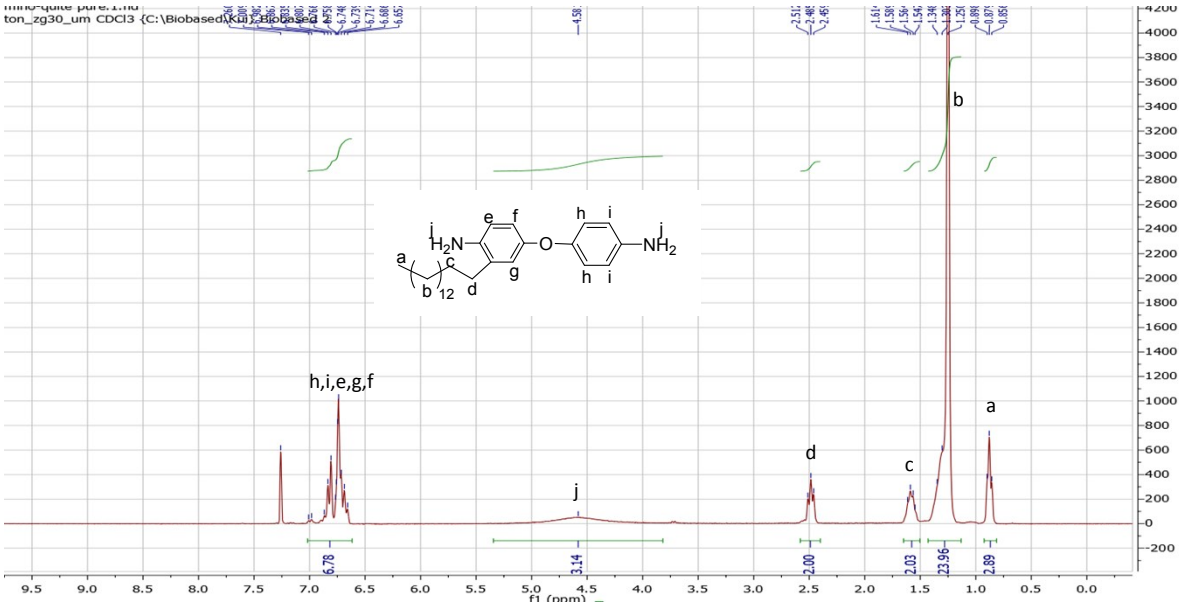
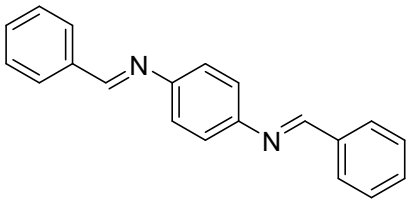


Figure S5. ^{1}H NMR spectrum of biobased monomer **3**, 4-(4-aminophenoxy)-2-pentadecylaniline.

Stability test of model compounds and polymers based on *p*-phenylene diamine and terephtaldehyde in concentrated Sulfuric Acid by NMR

Polymers poly(*p*-phenylene diamine-*co*-terephtaldehyde) were analyzed via GPC in H_2SO_4 (Table 1 in the main text) and via Ubbelohde viscometry in H_2SO_4 (Table S2). In order to prove the validity of this method, the stability of the imine bond upon exposure to H_2SO_4 during the measurement procedure, was evaluated via three methods. First of all, the stability of a low molecular weight model compound based on *p*-phenylene diamine and benzaldehyde was followed via ^{1}H NMR in D_2SO_4. Secondly, the stability of the polymer poly(*p*-phenylene diamine-*co*-terephtaldehyde) itself in D_2SO_4 was studied as a function of time by following the integrals of the aldehyde and imine protons. Finally, the GPC was remeasured in H_2SO_4 as fast as possible within 24 hours, while originally samples were subjected 72 hours to H_2SO_4 upon GPC measurement.



The model molecule was synthesized according to the reported method [4].

The stability test was performed by ^{1}H NMR in the solvent of D_2SO_4 (96-98 wt. % in D_2O), whose water concentration is similar to the solvent in GPC measurement. 5 mg model molecule was dissolved in 0.7 mL D_2SO_4, of which NMR was measured in 10 min, 1 hours, 5 hours, 18 hours, 24 hours and 72 hours. From the spectra recorded at different timepoints, very tiny degradation happened within hours, becoming distinctive after 24 hours and 12% degradation after 72 hours, as can be seen in Tables S1. Degradation peaks were marked in yellow in the NMR spectra of Figure S6.

Table S1. Degradation ratios of model molecule calculated from NMR in D_2SO_4.

Time (hours)	Degradation (%)
5	4.8
18	6.3
24	6.4
48	9.2
72	12

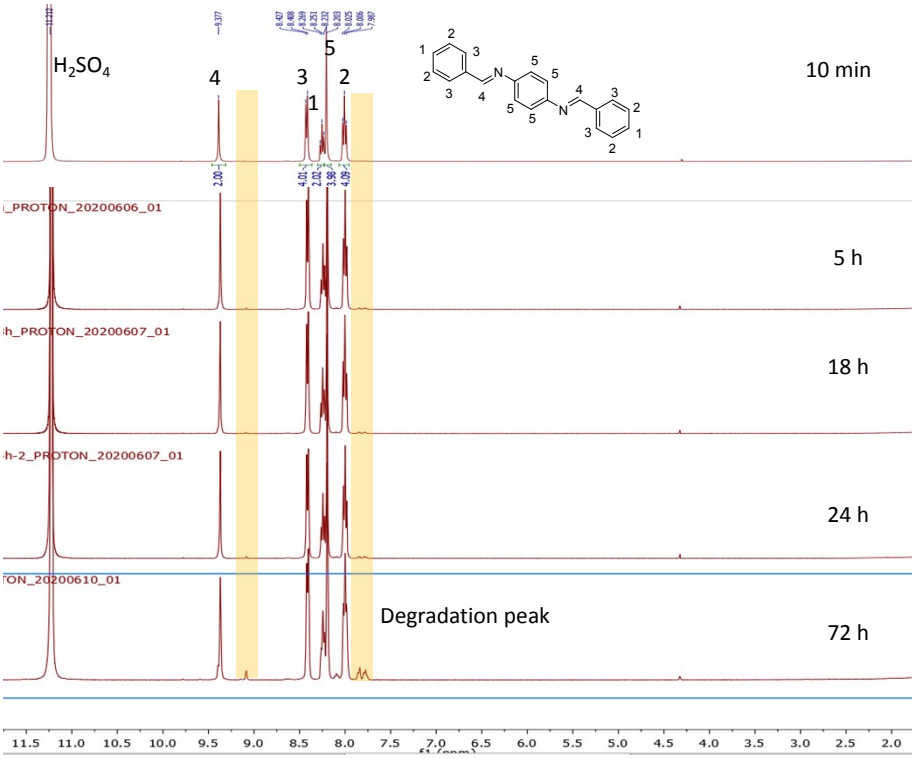


Figure S6. ^{1}H NMR spectrum and assignment of model compound in D_2SO_4 and stability test in different period.

The corresponding polymers were also measured in D_2SO_4 over time, and as could be expected the polymers are more stable than the model compound. It can be derived from Figure S8(c), that the ratio of aldehyde to imine peaks stays constant, even after 17 days.

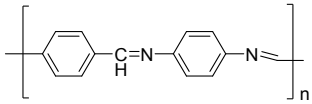
At last, the new GPC measurement where samples are maximally 24 hours exposed to H_2SO_4, shows similar results as the previous ones where samples were 72 hours exposed to H_2SO_4 (Table S2).

Based on these studies, GPC measurements of poly(*p*-phenylene diamine-*co*-terephtaldehyde) in H_2SO_4 was justified.

Polymer synthesis and characterization

General method for hydrothermal polymerization. The dialdehyde (1 eq.) and diamine (1 eq.) were added into a 10 mL pressurized glass vial equipped with a magnetic stirring bar. The air was extracted and nitrogen was refilled into the vial for three times. 5 mL distilled water was added into the vial. The vial was then closed with a crimp-cap septum. The suspension was heated by microwave to 200 °C within 2 min and kept at this temperature for 10 min. The

precipitated product was filtered off on a glass filter and washed with water and ethanol several times. The collected polymer was dried in the vacuum oven at 40 °C for 24 hours.



98% yield. Yellow or orange solid. GPC in H_2SO_4: $M_{n,GPC}$= 900 g/mol, $Đ$=1.5; reduced viscosity at 0.0025 g/cm^3 in H_2SO_4=60 cm^3/g; FT-IR: wavenumber (cm^{-1}) (Figure S6) = 2870 ν_s(=CH) st, 1600 ν(C=N) st, 1486 δ(C=C Ar) st, 1189 $\delta_{in\text{-}plane}$(1,4-substituted aromatic), 841 $\delta_{out\text{-}of\text{-}plane}$(1,4-substituted aromatic); ^{1}H NMR in ppm (300 MHz, D_2SO_4-d_2) δ 10.32 (s, -C*H*O), 9.82 (s,-C*H*=N-), 8.89-8.13 (m, aromatic peaks)

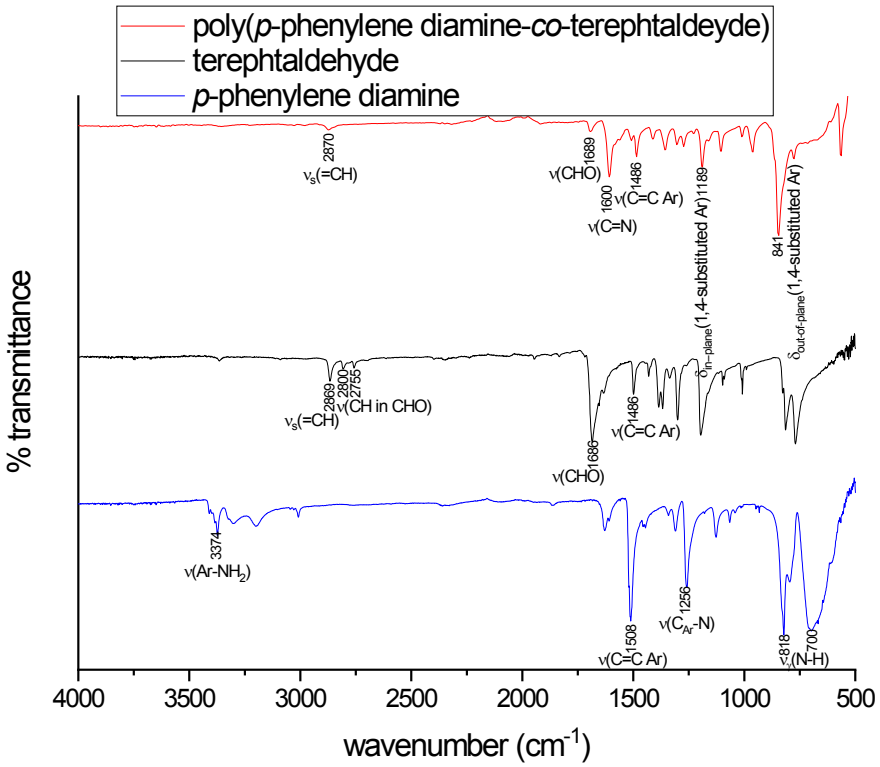
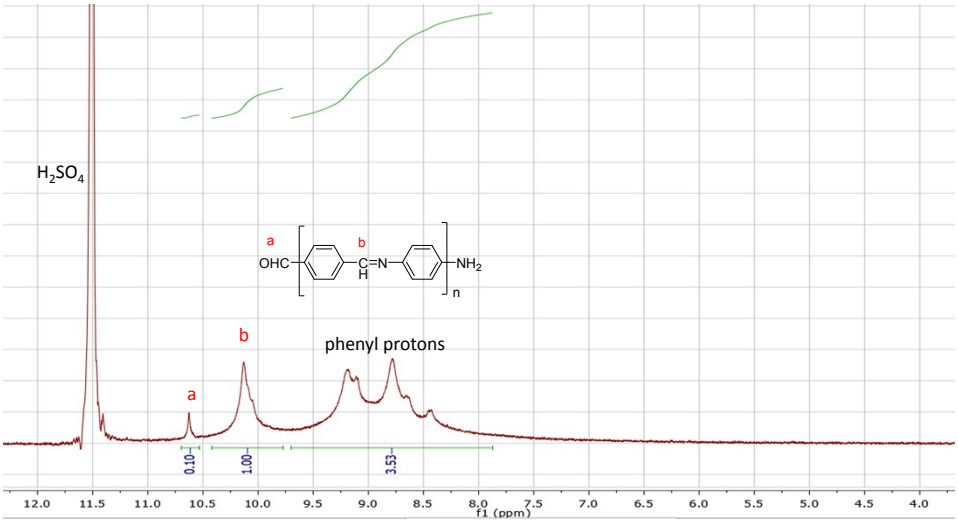
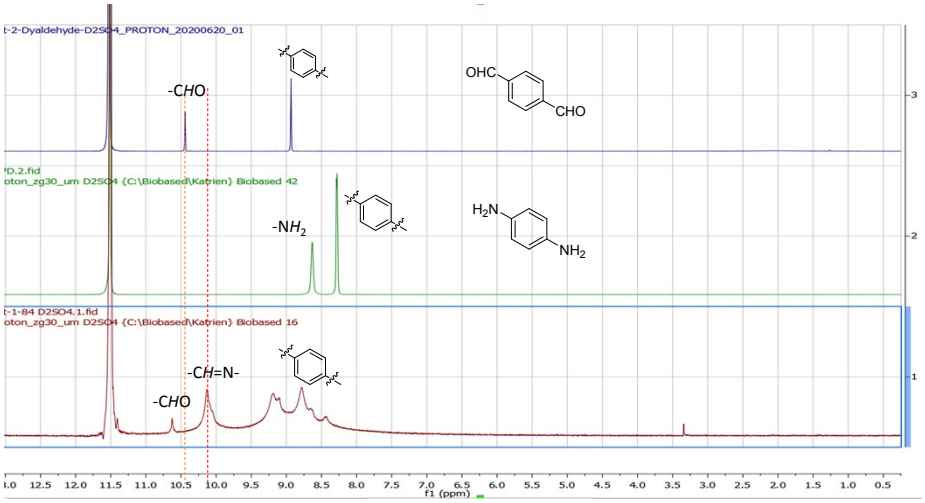


Figure S7. FT-IR spectra of PAz from *p*-phenylene diamine and terephtaldehyde.

(a)



(b)



(c)

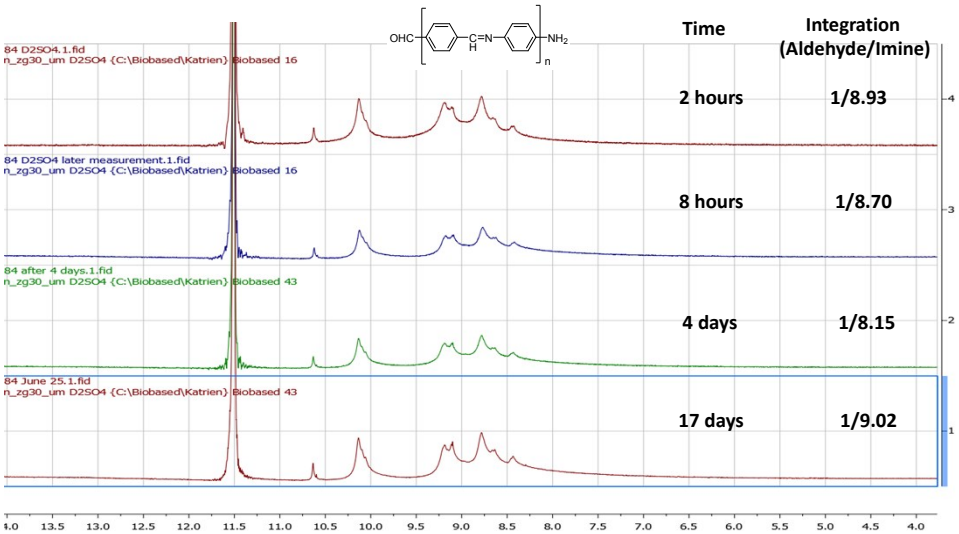


Figure S8. ^{1}H NMR spectrum of PAz from *p*-phenylenediamine and terephthaldehyde in D_2SO_4. (a) peaks and assignment for polymer; (b) comparison of PAz and monomers; (c) stability by comparison of polymer freshly dissolved (2 hours), after 8 hours, after 4 days and after 17 days.

Table S2. Properties of PAz from *p*-phenylenediamine and terephthalaldehyde under different conditions.

Entries	Conditions	Yield (%)	Reduced viscosity η_{red} (cm^3/g)[a]	GPC within 72 h		GPC within 24 h	
				M_n (g/mol)[b]	$Đ$[b]	M_n (g/mol)[b]	$Đ$[b]
1	NMP/11 wt% $CaCl_2$, 120 ˚C, 24 h	91	58	900	1.5	1000	2.0
2	NMP/HMPA=4/1, 120 ˚C, 24 h	72	49	900	1.4	900	1.5
3	DMSO, 180 ˚C, 24 h	90	65	1000	1.6	1000	1.8
4	Toluene, $ZnCl_2$ (6 mol%), TsOH (2% mmol), reflux, 12h	89	46	800	1.4	900	2.0
5	H_2O, 200 ˚C, microwave, 1 h	98	60	900	1.5	1000	1.8

[a] 0.0025 g/cm^3 in 96% sulfuric acid at 25 °C

[b] GPC in concentrated sulfuric acid (1 mg/mL), UV detection at 340 nm, PS standards

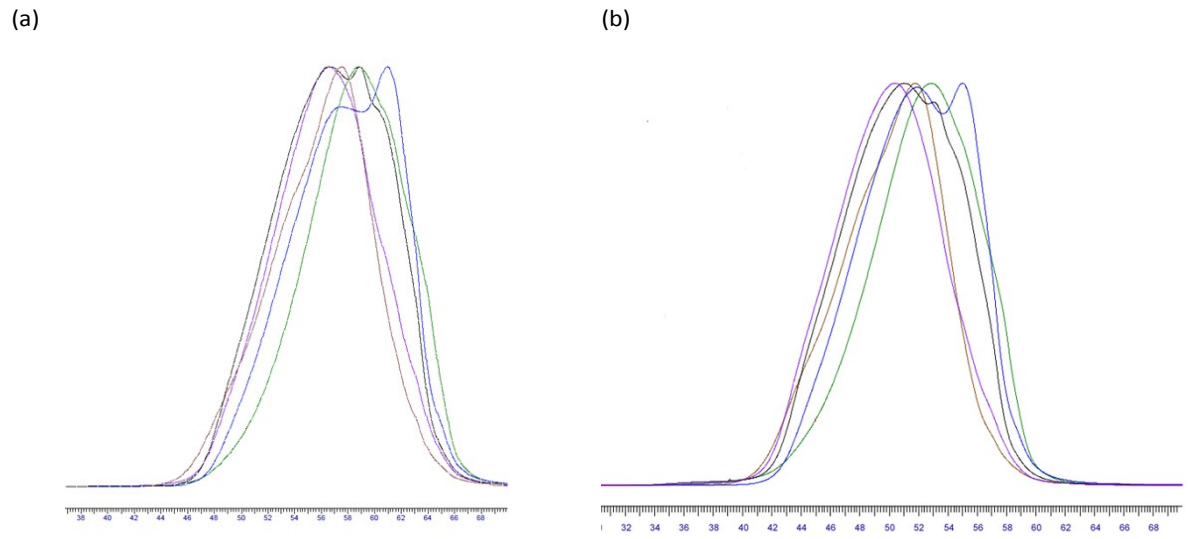
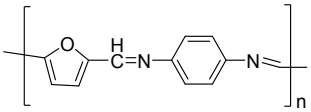
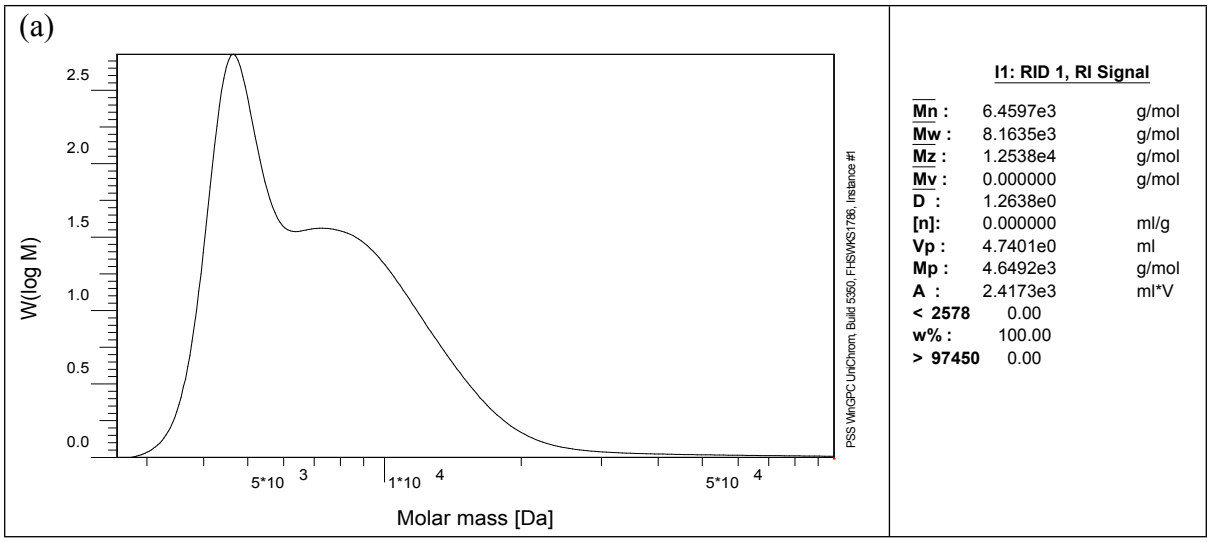


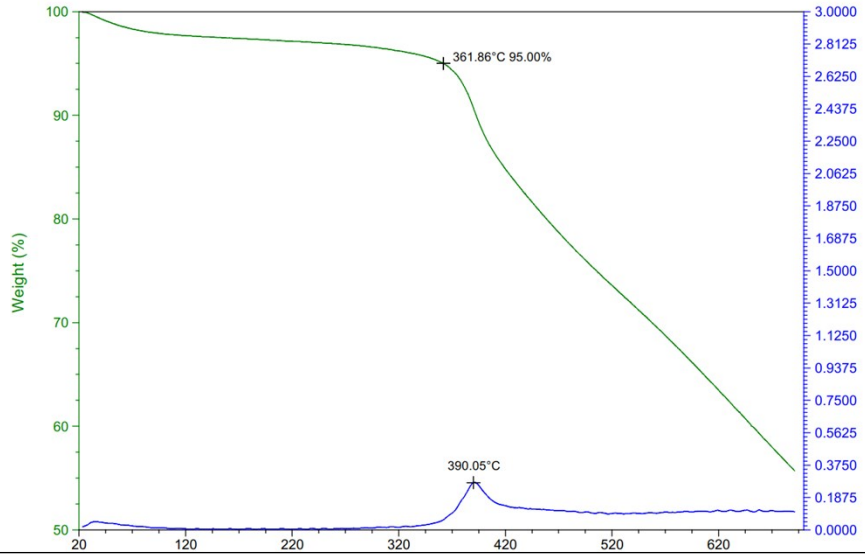
Figure S9. GPC spectra for PAz from *p*-phenylenediamine and terephthalaldehyde (UV detection at 340 nm, H_2SO_4 as eluent, calibrated with PS standards) (**a**) Measured within 72 hours; (**b**) Measured within 24 hours . (1) black line: NMP/11 wt % $CaCl_2$, 120 ˚C, 24 h; (2) blue line: NMP/HMPA=4/1, 120 ˚C, 24 h; (3) brown line: DMSO, 180 ˚C, 24 h; (4) green line: toluene, $ZnCl_2$ (6 mol%), TsOH (2 mmol%), reflux, 12h; (5) purple line: H_2O, 200 ˚C, microwave, 1 h.



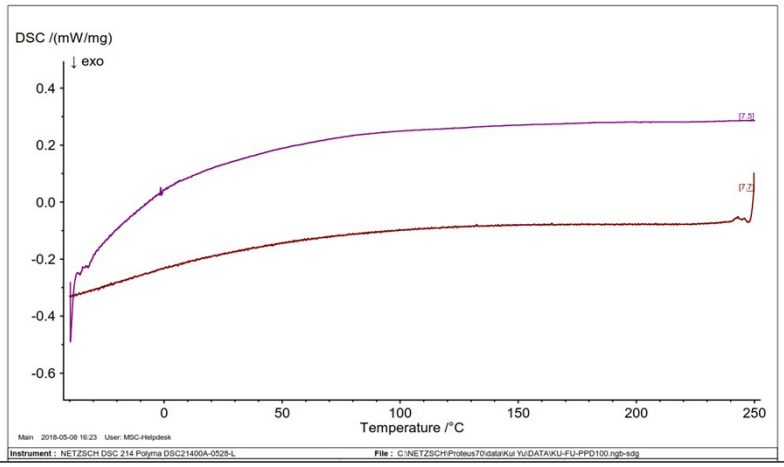
97% yield; reacted at 200 °C for 60 min; orange solid; GPC in HFIP/0.19% NaTFA: $M_{n,GPC}$ = 6.46 × 10^3 g/mol, $Đ$ = 1.26; T_d (5%) = 362 ˚C; T_d (max) = 390 ˚C; no T_m and T_g observed in DSC; FT-IR: wavenumber (cm^{-1}) = 3073 ν(CH furan) w, 1666 ν(CHO unreacted monomer/end groups) w, 1614 ν(C=N) st, 1549-1505 ν(C=C furan) m, 1189 ν(C-O-C) st, 949-835 δ(=CH 2,5 disubstituted furan). ^{1}H NMR in ppm (300 MHz, D_2SO_4-d_2) δ 10.10 (s, -C*H*O), 9.67-9.54 (m,-C*H*=N-), 8.66-8.13 (m, aromatic peaks)



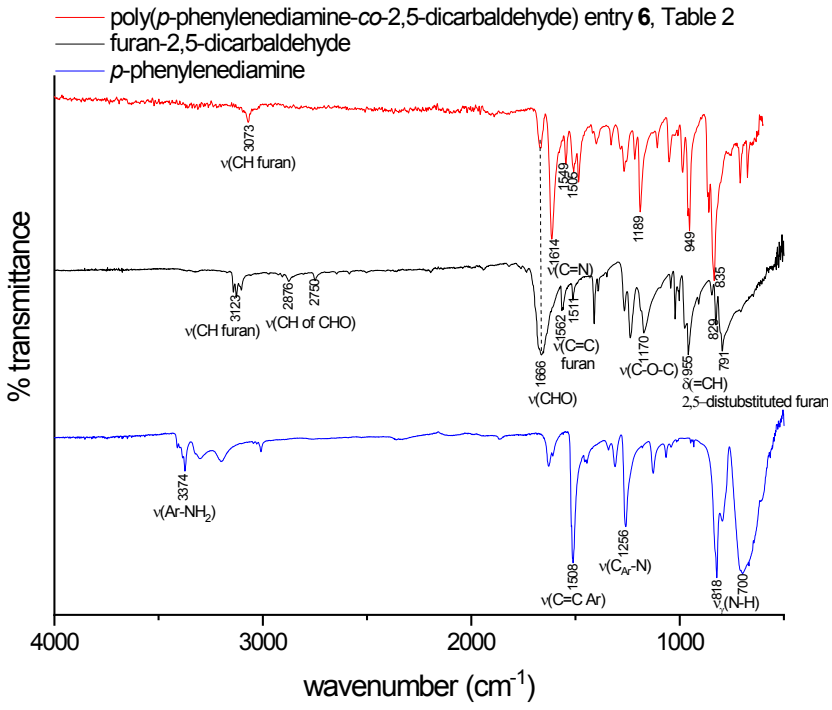
(b)


Weight (%)
361.86°C 95.00%
390.05°C
100
90
80
70
60
50
20
120
220
320
420
520
620
3.0000
2.8125
2.6250
2.4375
2.2500
2.0625
1.8750
1.6875
1.5000
1.3125
1.1250
0.9375
0.7500
0.5625
0.3750
0.1875
0.0000

(c)


DSC /(mW/mg)
↓ exo
0.4
0.2
0.0
-0.2
-0.4
-0.6
0
50
100
150
200
250
Temperature /°C

(d)


poly(p-phenylenediamine-co-2,5-dicarbaldehyde) entry 6, Table 2
furan-2,5-dicarbaldehyde
p-phenylenediamine
% transmittance
3073
ν(CH furan)
1589
1502
1189
949
1614
ν(C=N)
3123
2876
2750
ν(CH furan)
ν(CH of CHO)
1562
1511
ν(C=C)
furan
1170
ν(C-O-C)
955
δ(=CH)
835
829
791
2,5-distubstituted furan
1666
ν(CHO)
3374
ν(Ar-NH2)
1508
ν(C=C Ar)
1256
ν(CAr-N)
818
700
δ(N-H)
4000
3000
2000
1000
wavenumber (cm-1)

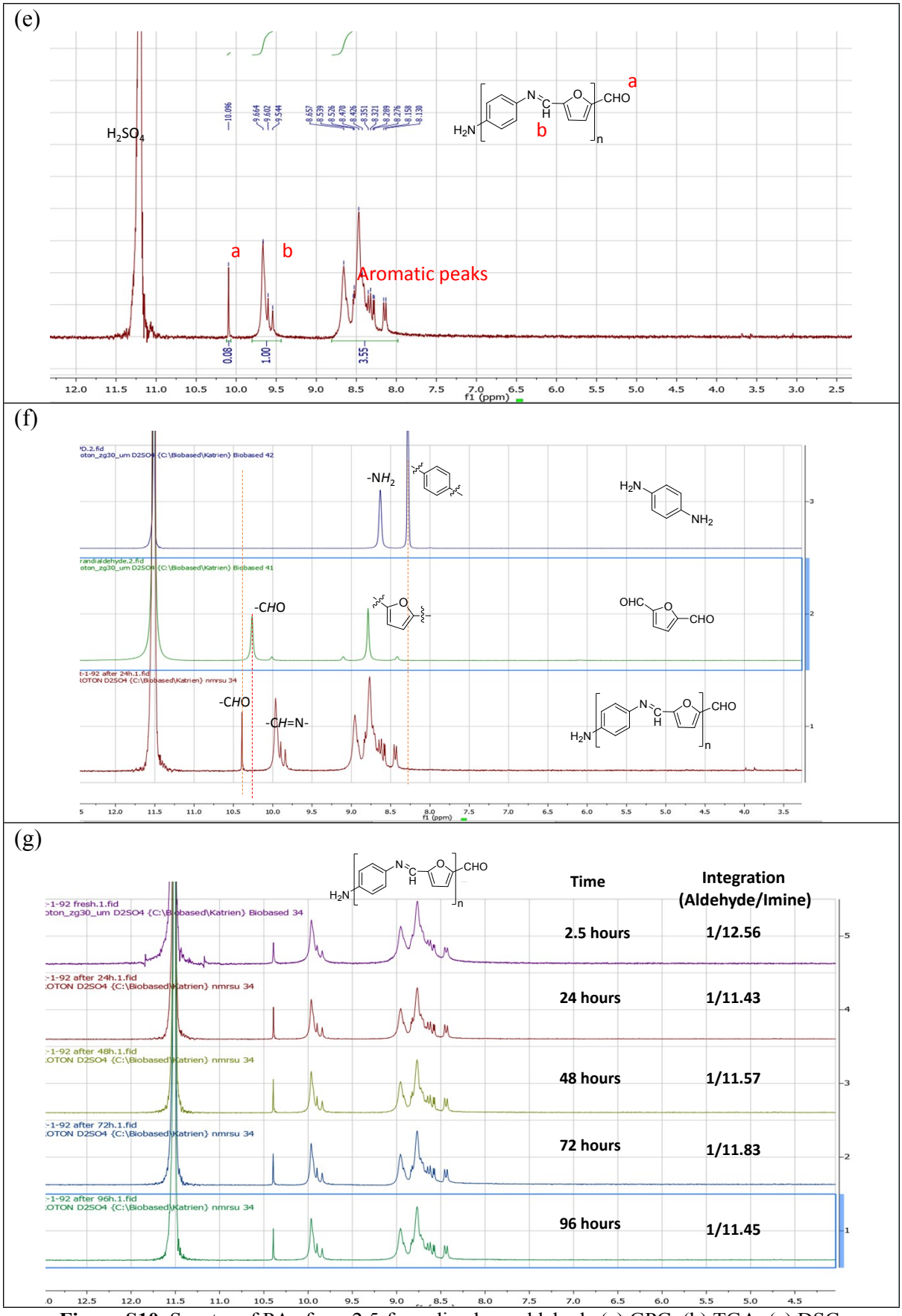
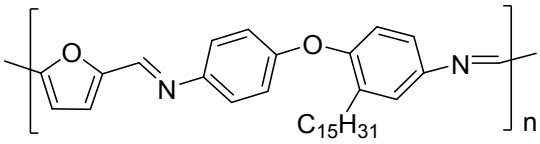


Figure S10. Spectra of PAz from 2,5-furandicarboxyaldehyde (a) GPC; (b) TGA; (c) DSC; (d) FT-IR; (e) ^{1}H NMR assignment of polymer in D_2SO_4; (f) NMR comparison of polymer and monomers in D_2SO_4; (g) PAz stability in D_2SO_4 for 4 days.



Biobased Polymer **I**.

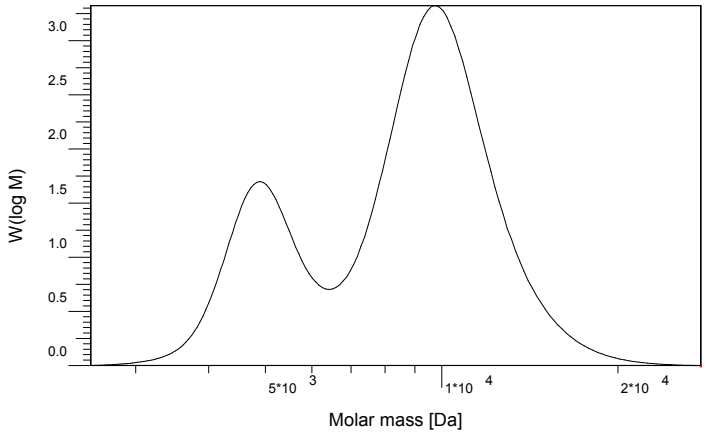
Condition 1: reacted at 200 °C for 60 min; black wax; 93% yield; GPC in HFIP/0.19% NaTFA: $M_{n,GPC}$ = 7.69 × 10^3 g/mol, $Đ$ = 1.15; T_d (5%) = 360 ˚C, T_d (max) = 383 ˚C; no T_m and T_g observed in DSC.

Condition 2: reacted at 200 °C for 10 min; black wax; 96% yield; GPC in HFIP/0.19% NaTFA: $M_{n,GPC}$ = 6.44 × 10^3 g/mol, $Đ$ = 1.16; T_d (5%) = 341 °C, T_d (max) = 381 ˚C; no T_m and T_g observed in DSC.

FT-IR results for both conditions are the same: wavenumber (cm^{-1}) = 2921 $\nu_{as}(CH_2)$ st, 2845 $\nu_s(CH_2)$ st, 1613 ν(C=N) st, 1468 ν(C=C Ar), δ(CH_2/CH_3) st, 1240 ν(C-O-C) st, 955, 829, 797 δ(=CH Ar). ^{1}H NMR in ppm (300 MHz, $C_2D_2Cl_4$-d_2) δ 8.45-8.36 (m,-C*H*=N-), 7.41-6.54 (m, aromatic peaks); 2.86-2.48 (CH_2CH_2Ph); 1.74-1.26 ($CH_2(CH_2)_{13}CH_2$) 0.94-0.89 (CH_3CH_2-).

Condition 1

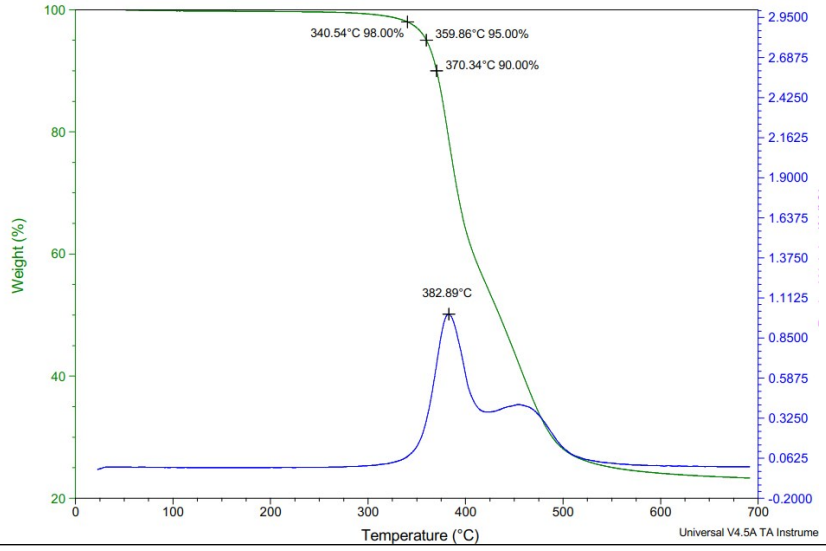
(a)



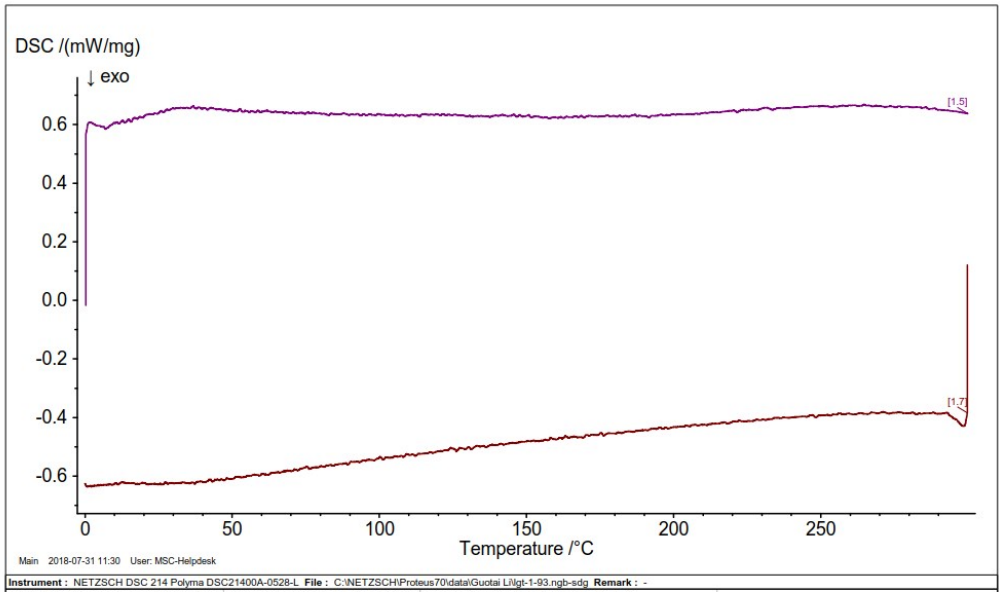
I1: RID 1, RI Signal

Mn :	7.6862e3	g/mol
Mw :	8.8440e3	g/mol
Mz :	9.9560e3	g/mol
Mv :	0.000000	g/mol
D :	1.1506e0	
[n]:	0.000000	ml/g
Vp :	4.4188e0	ml
Mp :	9.7562e3	g/mol
A :	1.0160e3	ml*V
< 2512	0.00	
w% :	100.00	
> 27705	0.00	

(b)

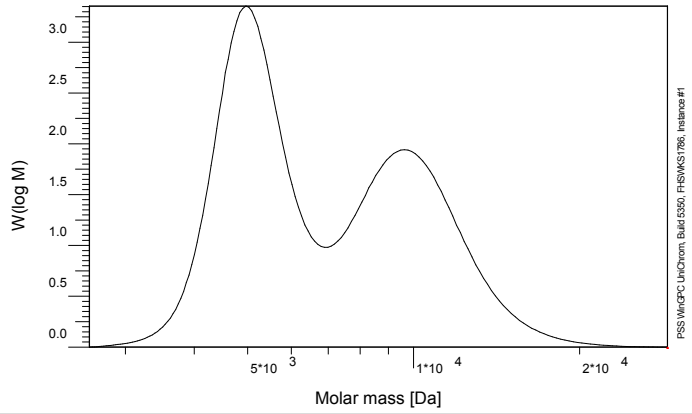


(c)



Condition 2

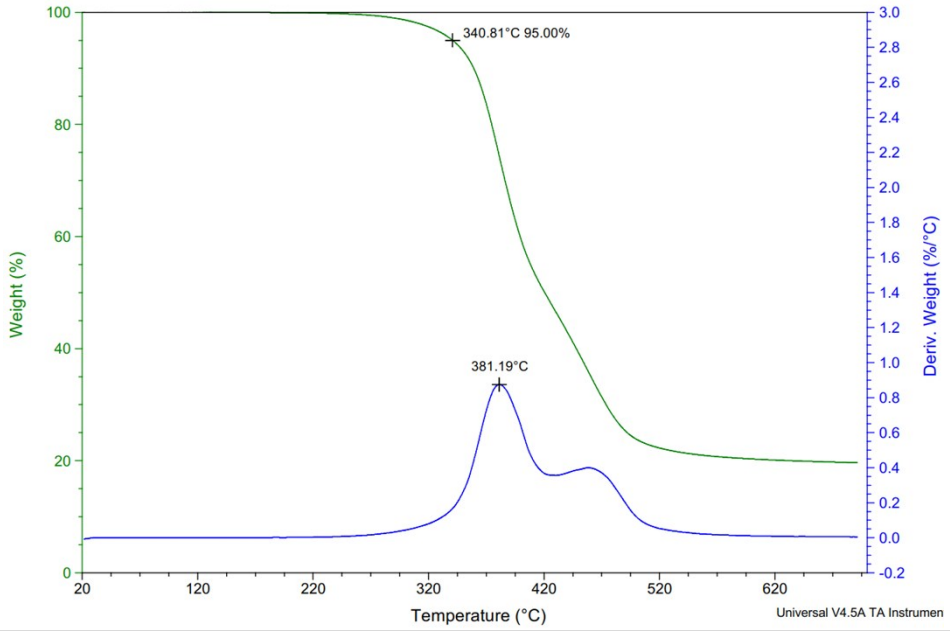
(d)



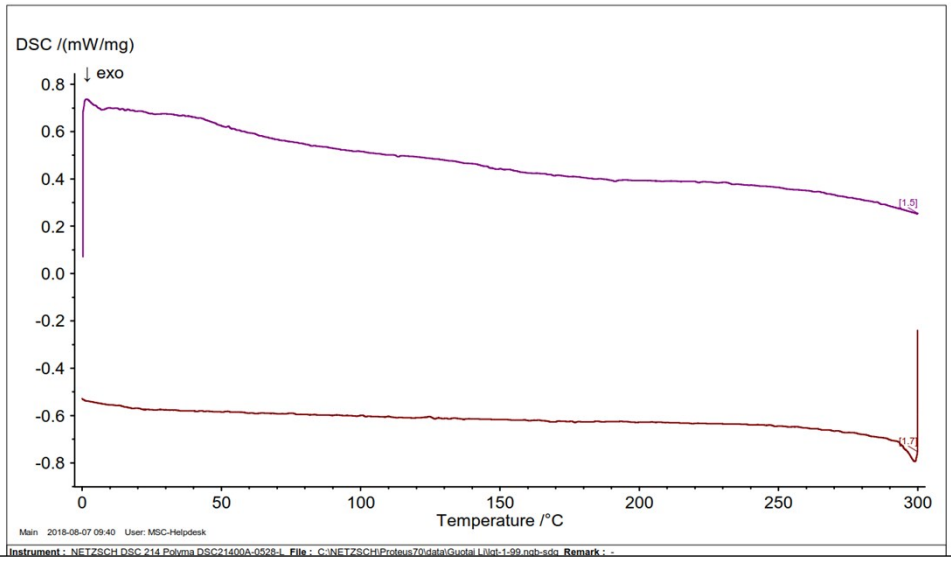
I1: RID 1, RI Signal

Mn :	6.4399e3	g/mol
Mw :	7.4830e3	g/mol
Mz :	8.7733e3	g/mol
Mv :	0.000000	g/mol
D :	1.1620e0	
[n]:	0.000000	ml/g
Vp :	4.6823e0	ml
Mp :	5.0238e3	g/mol
A :	1.0066e3	ml*V
< 2580	0.00	
w% :	100.00	
> 28868	0.00	

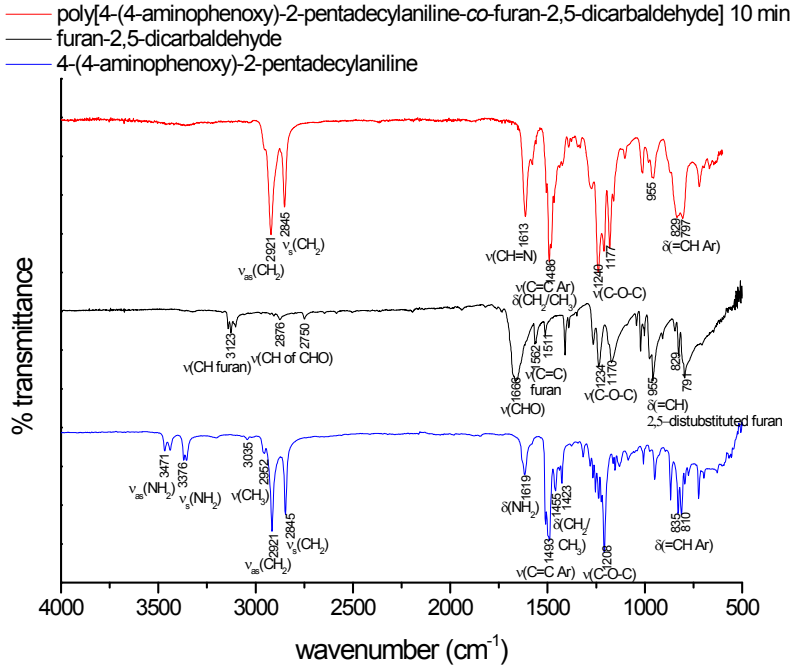
(e)



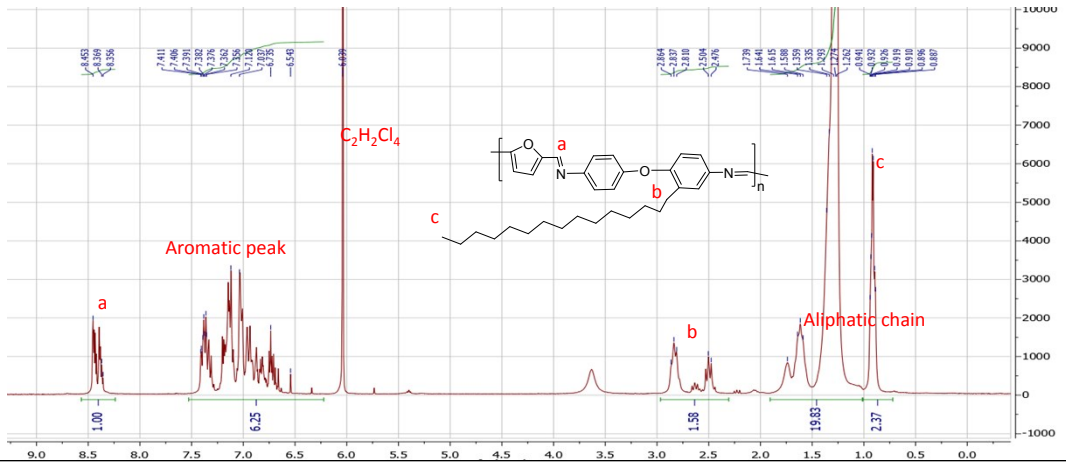
(f)


DSC /(mW/mg)
↓ exo
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
0
50
100
150
200
250
300
Temperature /°C
Main 2018-08-07 09:40 User: MSC-Helpdesk

(g)


poly[4-(4-aminophenoxy)-2-pentadecylaniline-co-furan-2,5-dicarbaldehyde] 10 min
furan-2,5-dicarbaldehyde
4-(4-aminophenoxy)-2-pentadecylaniline
% transmittance
wavenumber (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
νas(CH2)
2921
νs(CH2)
2845
ν(CH=N)
1613
ν(C=C Ar)
1488
δ(CH2/CH3)
1177
ν(C-O-C)
1249
955
829
797
δ(=CH Ar)
ν(CH furan)
3123
ν(CH of CHO)
2876
2750
ν(CHO)
1668
ν(C=C) furan
1562
1511
ν(C-O-C)
1224
1176
955
829
791
δ(=CH) 2,5-distubstituted furan
νas(NH2)
3471
νs(NH2)
3376
ν(CH2)
3035
2852
νas(CH2)
2921
νs(CH2)
2845
δ(NH2)
1619
δ(CH2/CH3)
1455
1423
1493
ν(C=C Ar)
1208
ν(C-O-C)
835
810
δ(=CH Ar)

(h)


C2H2Cl4
a
b
c
n
Aromatic peak
Aliphatic chain
1.00
6.25
1.58
19.83
2.37
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

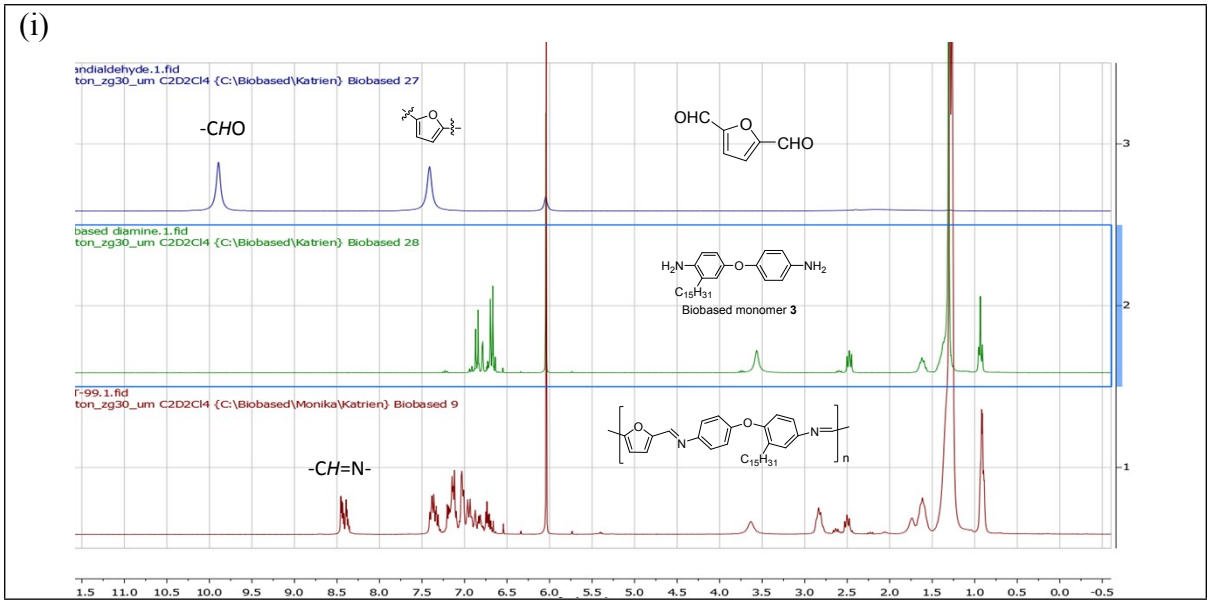
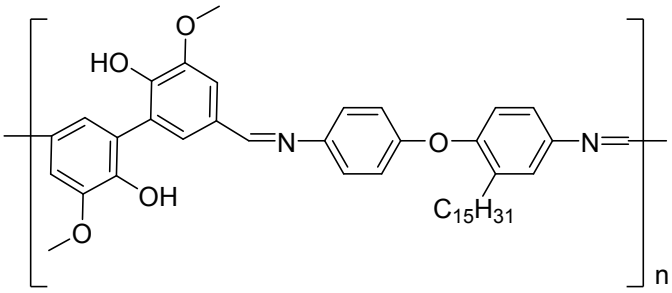
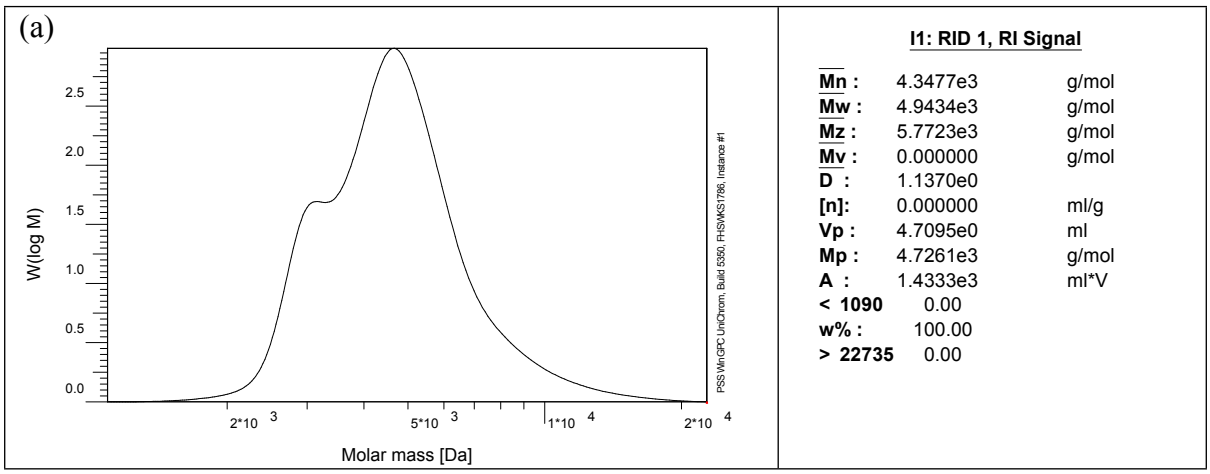


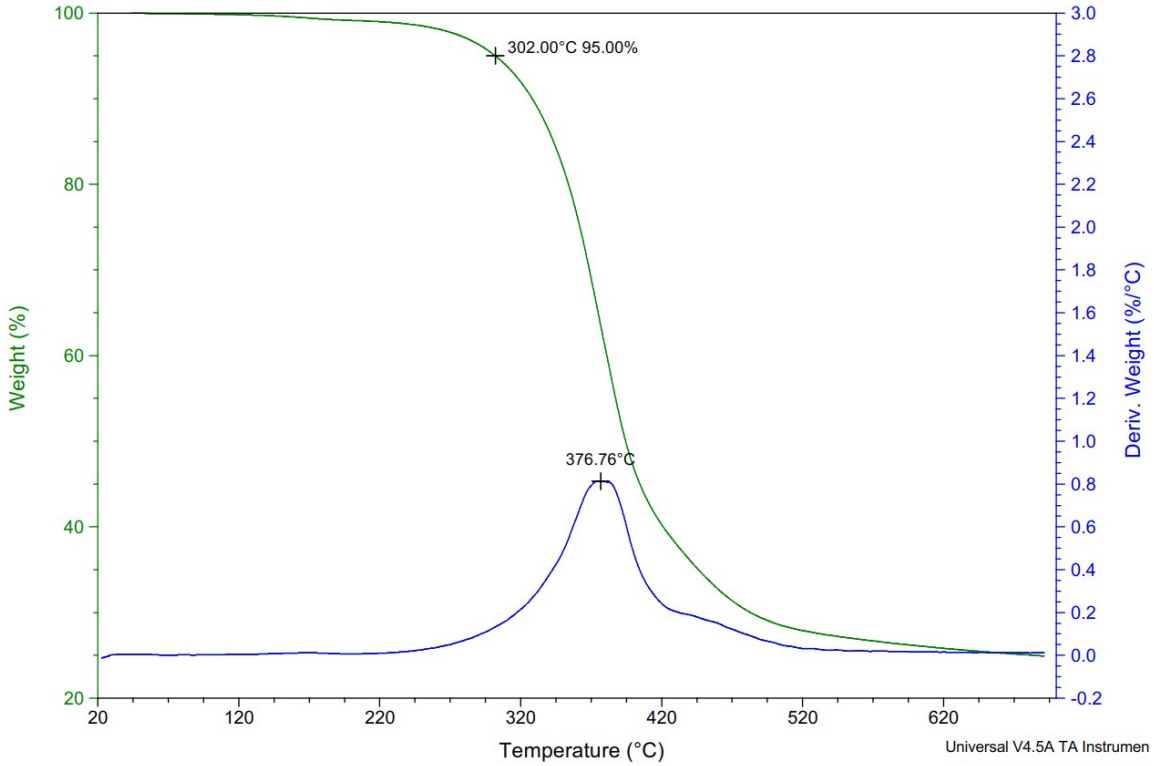
Figure S11. Spectra of biobased PAz polymer **I**. Condition 1: (a) GPC in HFIP/0.19% NaTFA; (b) TGA; (c) DSC. Condition 2: (d) GPC; (d) TGA; (f) DSC; (g) FT-IR; (h) ^{1}H-NMR in $C_2D_2Cl_4$; (i) ^{1}H-NMR comparison of polymer and monomers in $C_2D_2Cl_4$.



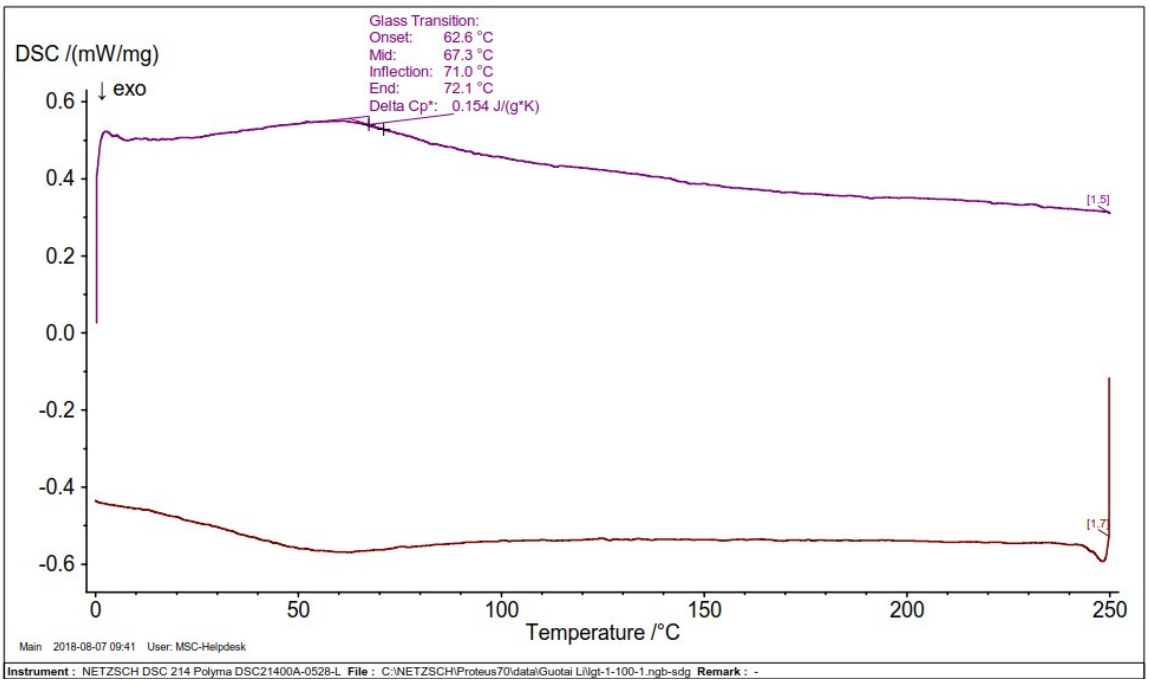
Biobased Polymer **II**, reacted at 200 °C for 10 min; black solid; 66.5% yield; GPC in HFIP/0.19% NaTFA: $M_{n,GPC}$ = 4.35 × 10^3 g/mol, $Đ$ = 1.14; T_d (5%) = 302 ˚C, T_d (max) = 377 ˚C; T_g = 67 °C, no T_m observed in DSC. FT-IR: wavenumber (cm^{-1}) = 3351 ν(OH) w, 2915 $\nu_{as}(CH_2)$ st, 2852 ν(aryl-OMe), $\nu_s(CH_2)$ m, 1676 ν(CHO) w, 1620 ν(C=N) w, 1587 ν(C=C Ar) m and 1492 ν(C=C Ar) st, 1215 ν(=C-O-C), δ(OH) st, 1145 1,2,4 substituted Ar st, 829 δ(=CH Ar) m; ^{1}H NMR in ppm (300 MHz, $C_2D_2Cl_4$-d_2) δ 9.90 (s, -C*H*O), 8.46-8.38 (m,-C*H*=N-), 7.72-6.54 (m, aromatic peaks); 4.10-4.03 (m,-OCH_3); 2.81-2.44 (m, CH_2CH_2Ph); 1.64-1.30 (m, -(CH_2)$_{13}$CH_3); 0.93-0.92 (CH_3CH_2-).



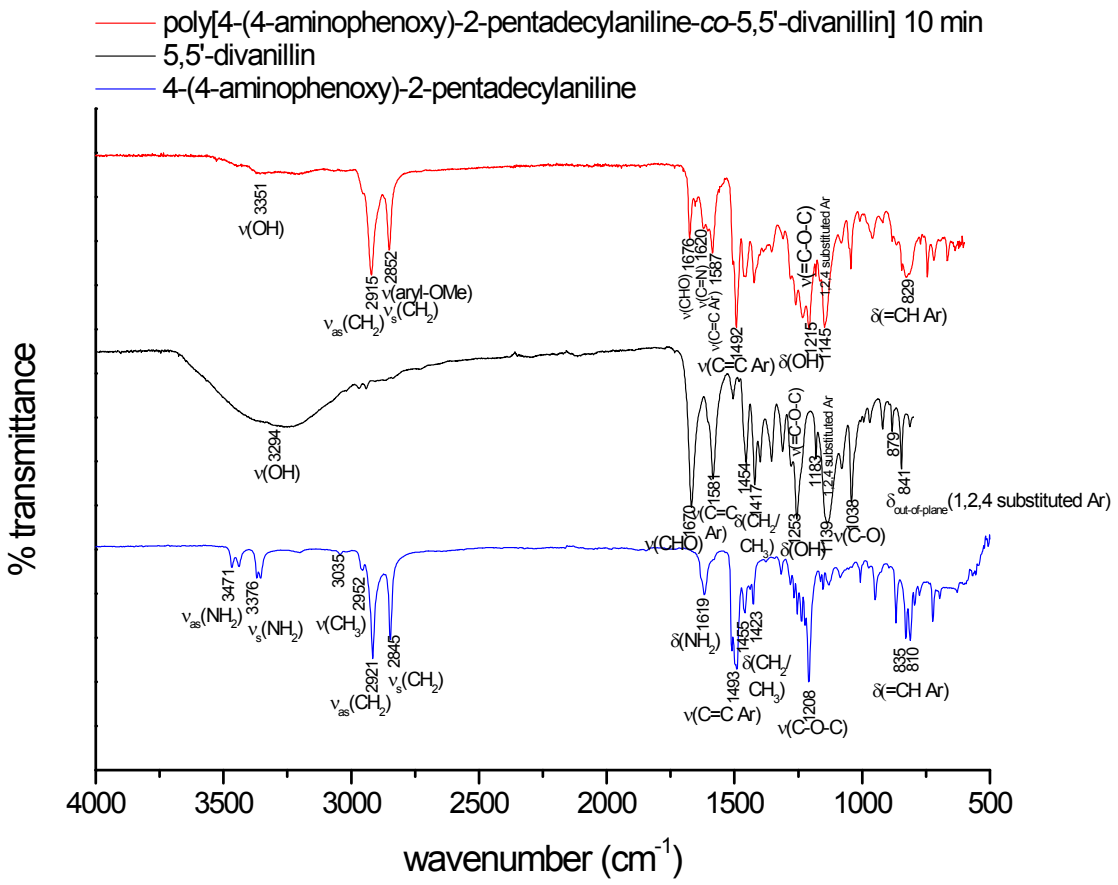
(b)


302.00°C 95.00%
376.76°C
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V4.5A TA Instrumen

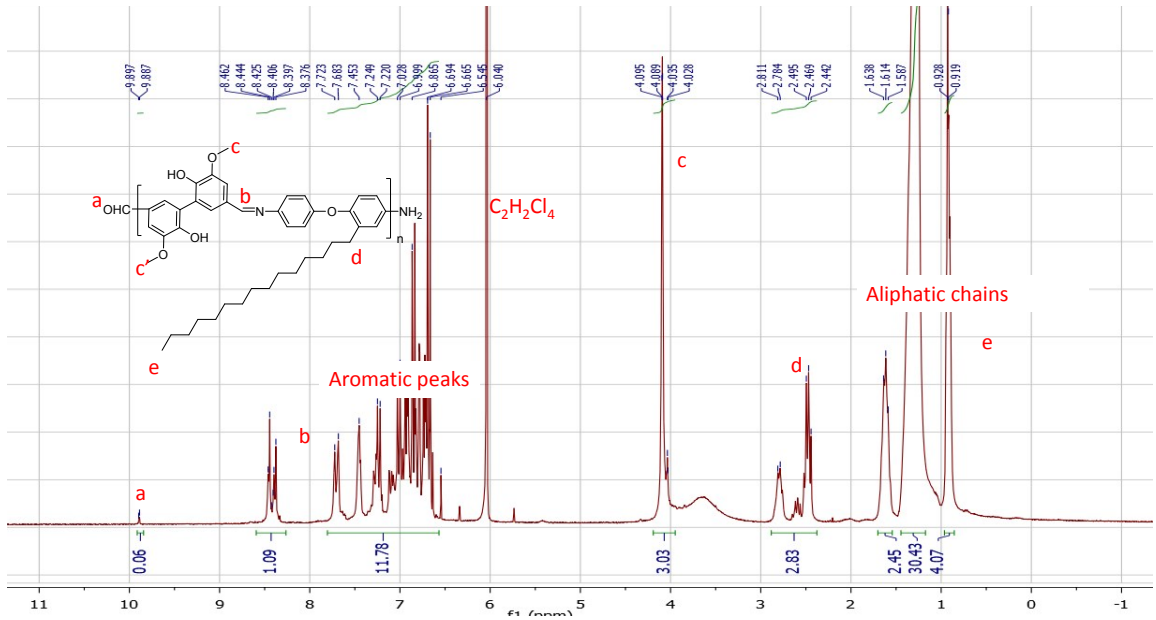
(c)


DSC /(mW/mg)
↓ exo
Glass Transition:
Onset: 62.6 °C
Mid: 67.3 °C
Inflection: 71.0 °C
End: 72.1 °C
Delta Cp*: 0.154 J/(g*K)
[1.5]
[1.7]
Temperature /°C
Main 2018-08-07 09:41 User: MSC-Helpdesk
Instrument : NETZSCH DSC 214 Polyma DSC21400A-0528-L File : C:\NETZSCH\Proteus70\data\Guotai Li\lgt-1-100-1.ngb-sdg Remark : -

(d)


poly[4-(4-aminophenoxy)-2-pentadecylaniline-co-5,5'-divanillin] 10 min
5,5'-divanillin
4-(4-aminophenoxy)-2-pentadecylaniline
% transmittance
wavenumber (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
3351
ν(OH)
2915
2852
νas(CH2)
νs(CH2)
ν(aryl-OMe)
1676
ν(CHO)
1620
ν(C=N)
1587
ν(C=C Ar)
1492
ν(C-C Ar)
1215
1145
ν(=C-O-C)
1274 substituted Ar
829
δ(=CH Ar)
δ(OH)
3294
ν(OH)
1670
ν(CHO)
1581
ν(C=C Ar)
1454
1417
δ(CH2/CH3)
1253
1183
ν(=C-O-C)
1274 substituted Ar
1039
ν(C-O)
879
841
δout-of-plane(1,2,4 substituted Ar)
δ(OH)
3471
νas(NH2)
3376
νs(NH2)
3035
ν(CH3)
2952
2921
νas(CH2)
2845
νs(CH2)
1619
δ(NH2)
1493
ν(C=C Ar)
1455
1423
δ(CH2/CH3)
1208
ν(C-O-C)
835
810
δ(=CH Ar)

(e)


a
b
c
d
e
OHC
HO
OH
NH2
n
C2H2Cl4
Aromatic peaks
Aliphatic chains
0.06
1.09
11.78
3.03
2.83
2.45
30.43
4.07

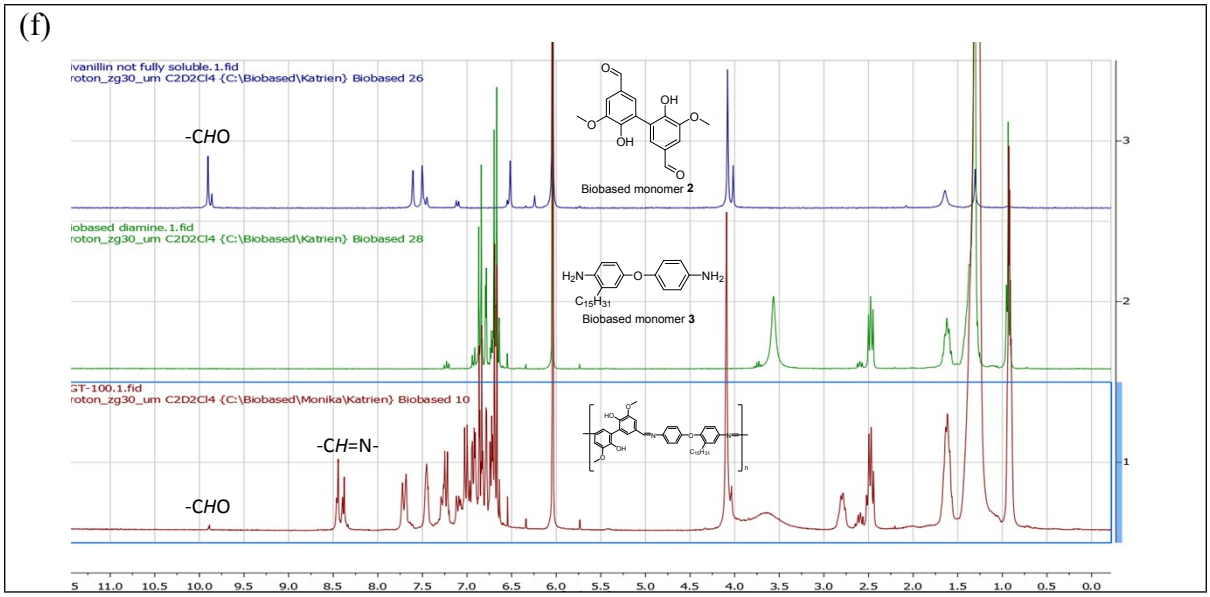


Figure S12. Spectra of biobased PAz polymer **II**. (a) GPC in HFIP/0.19% NaTFA; (b) TGA; (c) DSC; (d) FT-IR; (e) ^{1}H NMR assignment of polymer in $C_2D_4Cl_2$. (f) ^{1}H NMR comparison of polymer and monomers in $C_2D_2Cl_4$.

References

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[3] A. S. More, P. S. Sane, A. S. Patil, P.P. Wadgaonkar, *Polym. Degrad. Stability*, 2010, **95**, 1727-1735;

[4] P.H. Kiviranta, J. Leppänen, S. Kyrylenko, H.S. Salo, M. Lahtela-Kakkonen, A.J. Tervo, C. Wittekindt, T. Suuronen, E. Kuusisto, T. Järvinen, A. Salminen. *J. Med. Chem*. 2006, **49**, 7907–7911