

FigSupplementary information

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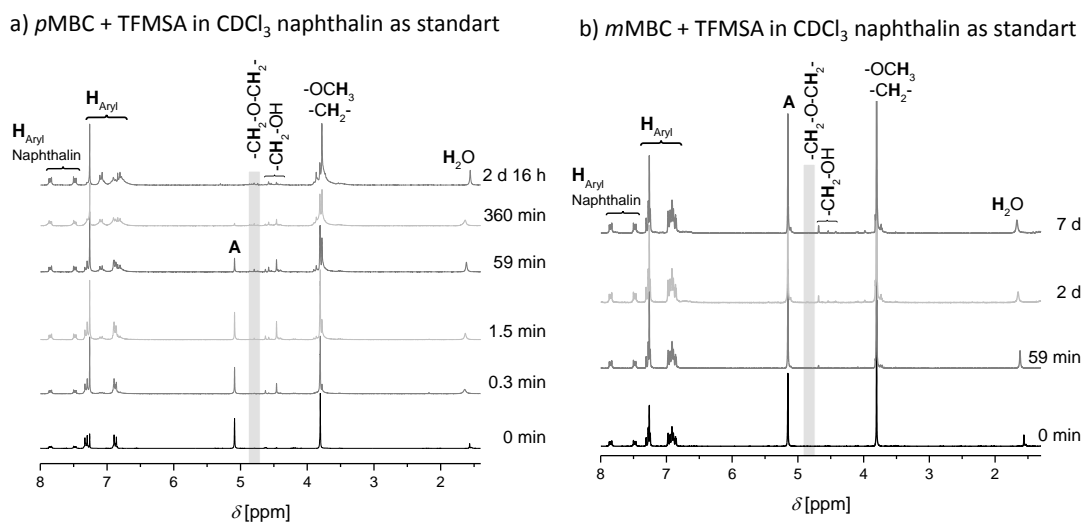


Fig. S 1 Liquid ¹H-NMR spectra of the reaction of a) *p*MBC and b) *m*MBC with trifluoromethanesulfoic acid (TFMSA) in CDCl₃ obtained at different times.

To study the reaction mechanism of the cationic polymerization of carbonates, the reaction was monitored with liquid ¹H-NMR spectroscopy. The polymerization was done at room temperature using trifluoromethanesulfoic acid (TFMSA, tenth mol regarding carbonate). Different time intervals were chosen to take a NMR sample from the reaction mixture. The ¹H-NMR signal **A** (-CH₂- of carbonate) was integrated while calibrating the naphthaline standart and a decrease of carbonate concentration was determined. In ¹H-NMR spectra methylo signals (-CH₂OH) between 4.4 and 4.7 ppm appear. As well traces of methylether bridges (-CH₂OCH₂-) in the region of 4.7 and 4.9 ppm can be detected. The signals of methylenebridges (-CH₂-), which can be found between 3.3 and 4.0 ppm, increases depending on time.

All three carbonates can not be investigated with the same acid catalyst. The least reactive *m*MBC shows no polymerization with trifluoroacetic acid (TFA, pK_a^{aq} ~ 0¹), methanesulfoic acid (MSA, pK_a^{aq} ~ -2¹) and *p*-toluenesulfoic acid (*p*TS, pK_a^{aq} -2.8¹) in solution at room temperature. A strong acid trifluoromethansulfoic acid (TFMSA, pK_a^{aq} ~ -13¹) is nessecary to polymerized *m*MBC. Additionally, reaction time of several days are nessecary and low conversions can be monitored within *m*MBC polymerization. DFC is too reactive for polymerization with TFMSA.

Extensive investigations on molecular structure formation of anisolic resins have not been reported in literature, yet. The assignment of NMR signals were performed according the published NMR data of phenolic resins because anisol as a derivative of phenol can likewise polymerize to methylene bridged anisolic resins. A overview of possible structure units and the chemical shifts in ¹H- and ¹³C-NMR were shown in Table S 1 ²⁻⁷.

Table S 1 Molecular structure units in phenolic resin and the chemical shifts in ^1H and ^{13}C -NMR.

Structure unit	Chemical shift ^{13}C ^1H -NMR [ppm]	Structure unit	Chemical shift ^1H -NMR [ppm]
$\text{C}_{\text{Aryl}}\text{CH}_3$	18	$\text{C}_{\text{Aryl}}\text{CH}_3$	2.3
$\text{C}_{\text{Aryl}}\text{CH}_2\text{C}_{\text{Aryl}}^-$	<i>o,o'</i> -	$\text{C}_{\text{Aryl}}\text{CH}_2\text{C}_{\text{Aryl}}^-$	3.5-4.0
	<i>o,p'</i> -		
	<i>p,p'</i> -		
$\text{C}_{\text{Aryl}}\text{CH}_2\text{-OH}$	58-65	$\text{C}_{\text{Aryl}}\text{CH}_2\text{-OH}$	4.4-4.7
$\text{C}_{\text{Aryl}}\text{CH}_2\text{-O-CH}_2\text{C}_{\text{Aryl}}$	66-72	$\text{C}_{\text{Aryl}}\text{CH}_2\text{-O-}$ $\text{CH}_2\text{C}_{\text{Aryl}}$	4.8
$\text{C}_{\text{Aryl}}\text{OCH}_3$	149-156	$\text{C}_{\text{Aryl}}\text{OCH}_3$	3.7
$\text{C}_{\text{Aryl}}\text{COOH}$	171	$\text{C}_{\text{Aryl}}\text{COOH}$	11
$\text{C}_{\text{Aryl}}\text{CHO}$	194	$\text{C}_{\text{Aryl}}\text{CHO}$	10

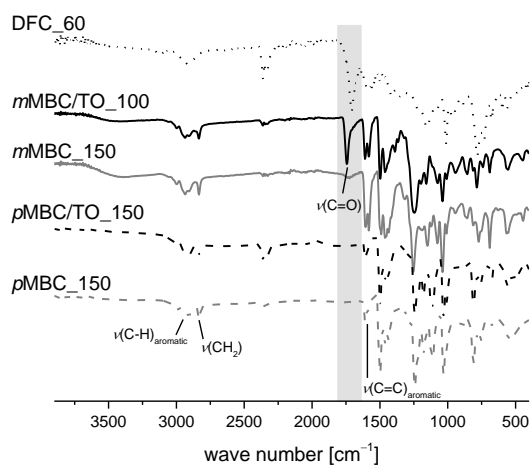


Fig. S 2 ATR-FTIR spectra of anisolic resins and polyfurfuryl alcohol resin obtained by cationic polymerization of *pMBC*, *mMBC* and *DFC*.

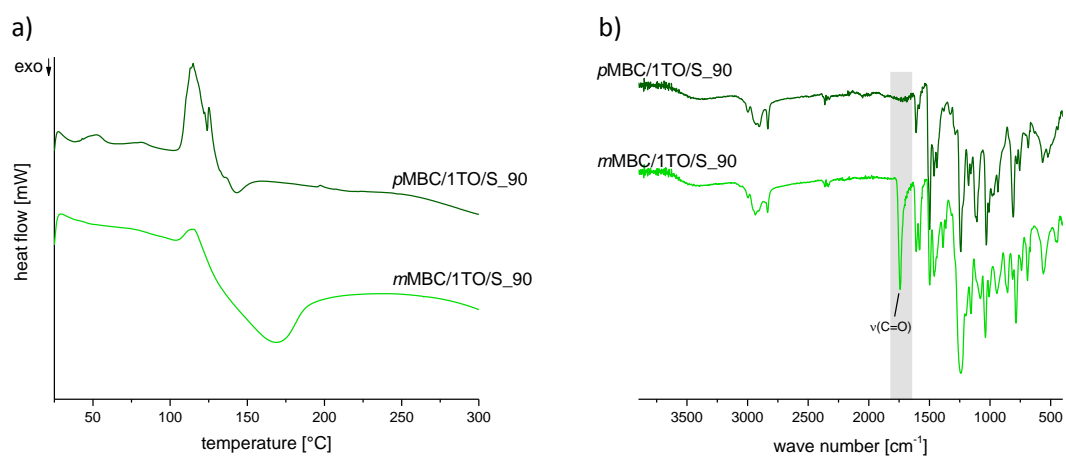


Fig. S 3 DSC measurement a) and ATR-FTIR spectra b) of polymers obtained by cationic polymerization of *pMBC* and *mMBC* with a surfactant (*S*) and trioxane (*TO*) at 90 °C.

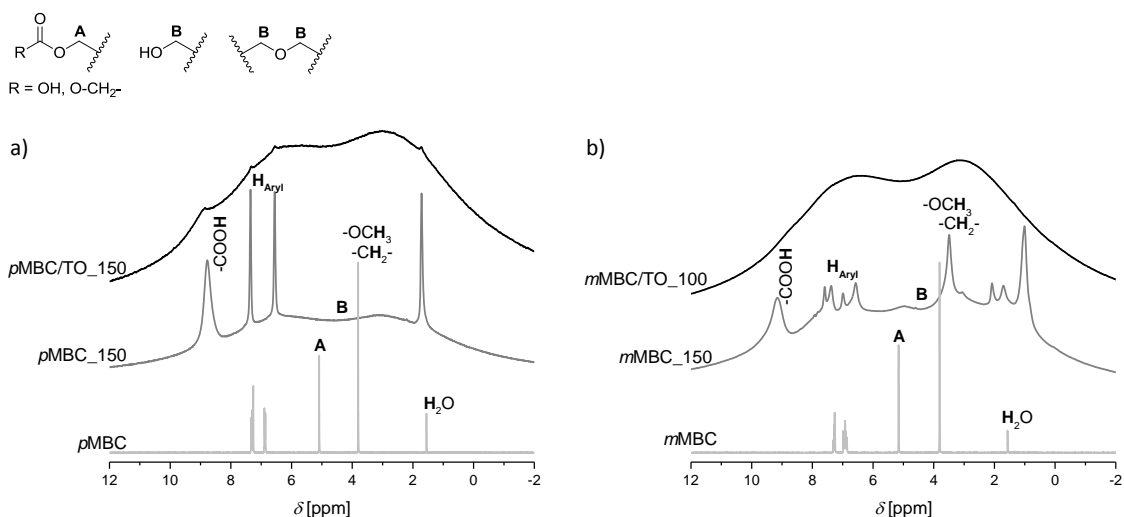


Fig. S 4 Liquid ^1H -NMR of methoxybenzyl carbonates a) pMBC and b) mMBC compared to solid state ^1H -NMR of polymers without and under addition of 1,3,5-trioxane.

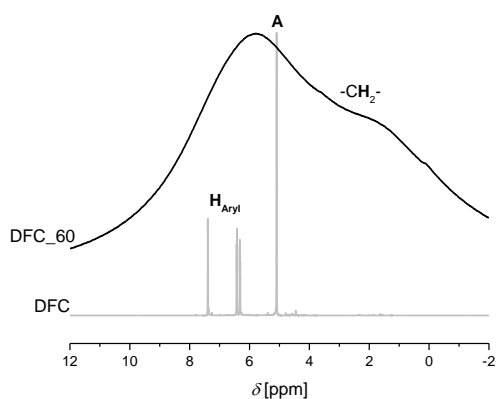


Fig. S 5 Liquid ^1H -NMR of difurfurylcarbonate (DFC) compared to solid state ^1H -NMR of the polymer.

Low condensed polymers of pMBC and mMBC show sharp peaks in ^1H solid state NMR because of the flexibility of structure moieties. In contrast polymers crosslinked with 1,3,5-trioxane (TO) show broad signals. The polymerized DFC exhibit as well a broad signal even without adding a cross linking agent. The reason for this is that furfuryl moiety undergoes many side reactions where crosslinked structures obtained. The low condensed polymers of pMBC and mMBC show sharp signals for aryl, methoxy, methylene and water protons. A signal at 8.8–9.2 ppm may attributed to carboxylic acid protons resulted from a dehydrogenation and oxidation process of methylol species. An exact assignment of signal is in ^1H solid state NMR spectra not possible because a peak broadening and peak shift in solid state.

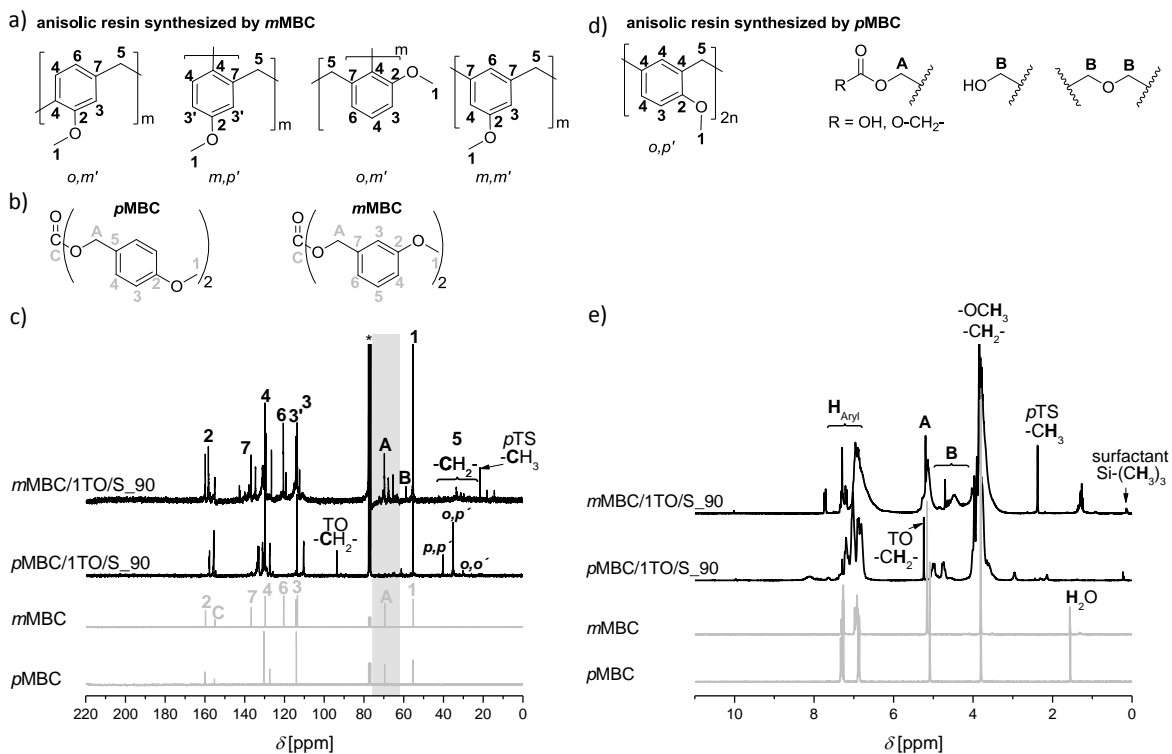


Fig. S 6 c) Liquid ^{13}C - $\{^1\text{H}\}$ -NMR spectra and e) ^1H -NMR spectra of organic carbonates *m*MBC and *p*MBC compared to anisolic resins polymerized with 1,3,5-trioxane at 90 °C. a), b) and d) show the molecular structures of polymers and monomers with the assignment of atoms to signals in spectra.

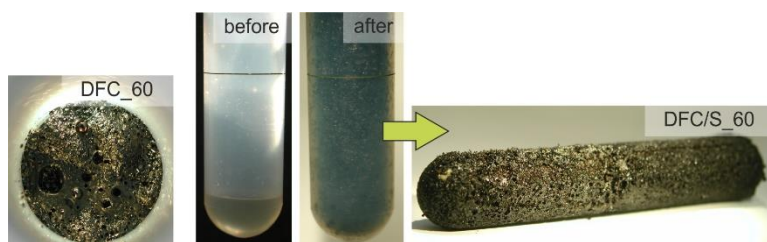


Fig. S 7 Pictures of polyfurfuryl alcohol resins obtained by the polymerization of DFC.

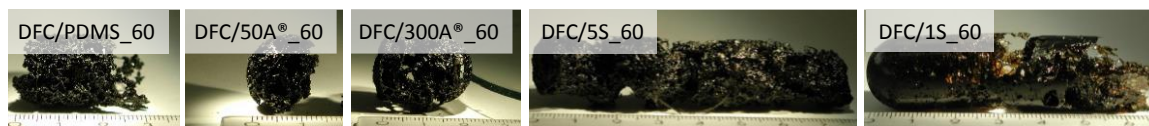


Fig. S 8 Pictures of the polyfurfuryl alcohol resins obtained by the polymerization of each one-gram DFC with 10 mol% pTS, at 60 °C under utilization of different dispersing agents. One percent by weight of a PDMS with 0.8-0.9 % silanol groups, Aerosil Ox_50 with a BET surface of 50 m²/g, Aerosil 300 with a BET surface of 300 m²/g and the polydimethylsiloxane-based surfactant (S) with the designation Dabco® DC 193 was used in each experiment. As well, a polymerization with five percent by weight of Dabco® DC 193 was performed.

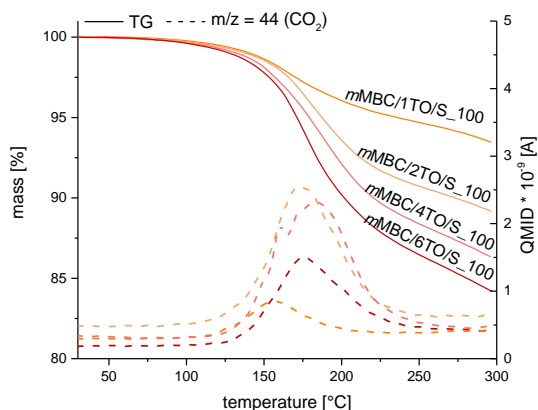


Fig. S 9 TG-MS measurements of polymers obtained by cationic polymerization of pMBC and mMBC at 100 °C. The released CO₂ was detected with mass spectrometry.

Table S 2. Performed experiments under variation of amount of 1,3,5-trioxane with the molar ratios of monomer (n_M) to acid catalyst (n_{pTS}) and curing agent (n_{TO}) and the used mass ratios of the surfactant (m_S). Furthermore, the endorsement of the label indicated the final polymerization temperature. The mass loss of obtained anisolic resins after extraction, curing and pyrolysis.

Sample	molar ratios [mol%]	mass ratios [wt%]	conditions T [°C] / t [h]	mass loss Δm [%]		
				extraction	thermal treatment	
	$n_M : n_{pTS} : n_{TO}$	$m_M : m_S$	T_1	DCM, 3d	250 °C, Ar	800 °C, Ar
pMBC/4TO/S_100	1 : 0.1 : 1	1 : 0.01	100 / 4	89.2	22.7	50.0
mMBC/1TO/S_100	1 : 0.1 : 0.3	1 : 0.01	100 / 4	14.3	6.9	46.3
mMBC/2TO/S_100	1 : 0.1 : 0.7	1 : 0.01	100 / 4	14.1	12.5	38.5
mMBC/4TO/S_100	1 : 0.1 : 1	1 : 0.01	100 / 4	12.9	15.6	37.3
mMBC/6TO/S_100	1 : 0.1 : 1.3	1 : 0.01	100 / 4	10.1	16.6	36.3
pMBC/1TO/S_90	1 : 0.1 : 0.3	1 : 0.01	90 / 4	*	15.0	55.9
mMBC/1TO/S_90	1 : 0.1 : 0.3	1 : 0.01	90 / 4	*	17.1	55.1

* soluble in DCM

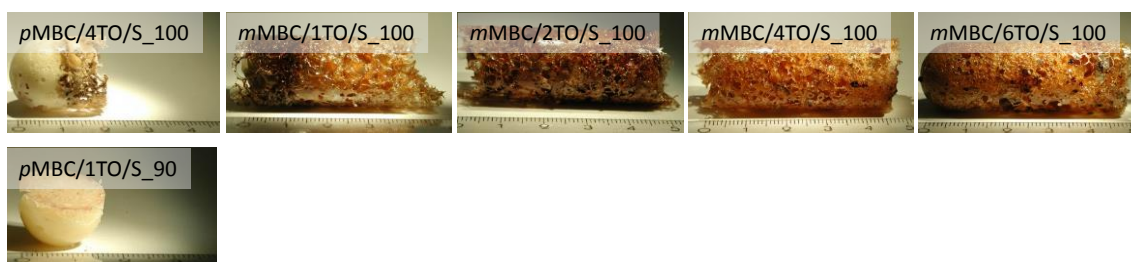


Fig. S 10 Pictures of the anisolic resins obtained by polymerization of mMBC and pMBC with 1,3,5-trioxane.

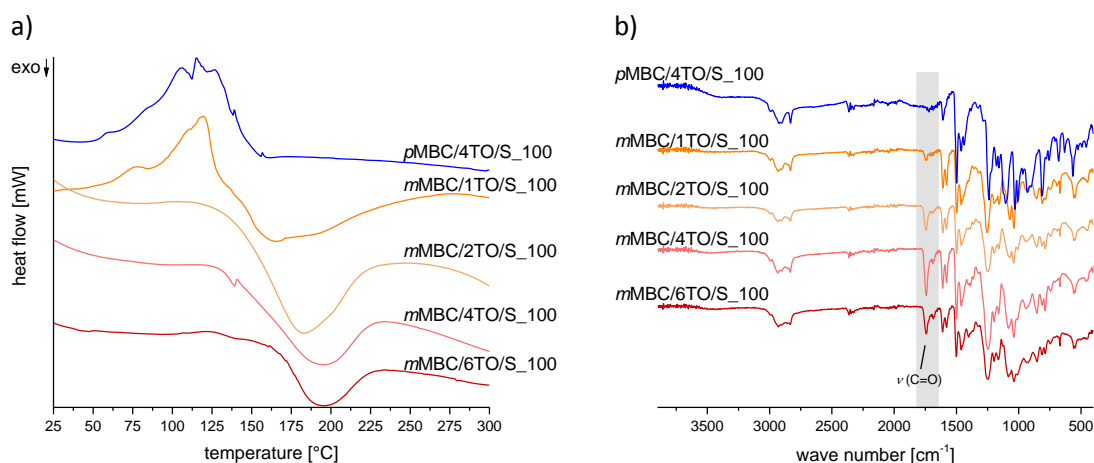


Fig. S 11 a) DSC measurement b) and ATR-FTIR spectrum of polymers obtained by cationic polymerization of *p*MBC and *m*MBC with a surfactant (*S*) and different trioxane (*TO*) contents at 100 °C.

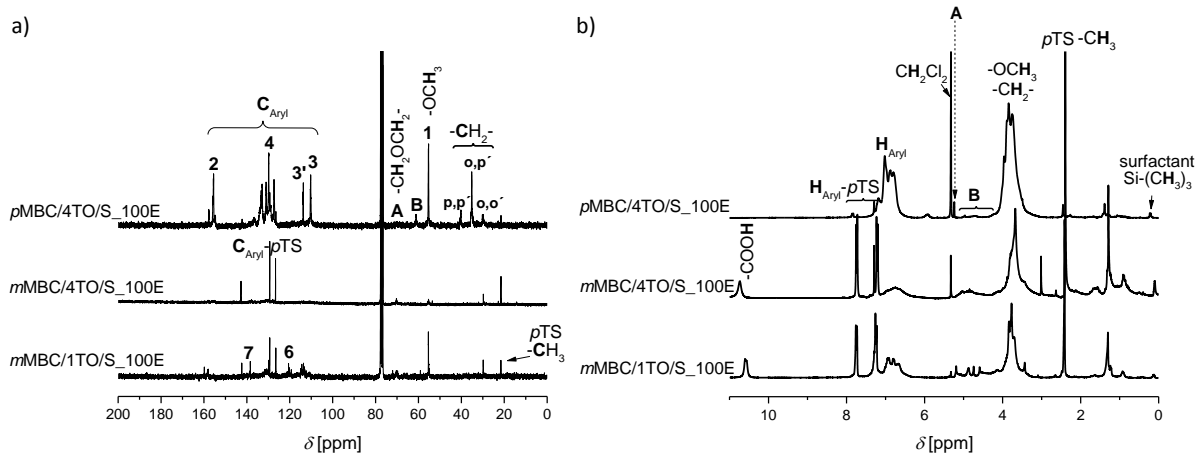


Fig. S 12 a) Liquid $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectra and b) ^1H -NMR spectra of extracts (labeled with E) obtained after extraction with dichloromethane.

The extracts of polymers were investigated by means of ^1H - and $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectroscopy dissolving them in CDCl_3 . The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectra (Fig. S 12a) show signals for methylene (A) (29–42 ppm), methylol (B) (58–63 ppm), methylenether groups (C) (65–75 ppm) and aromatic carbons^{2,3}. The extract of *p*MBC/4TO/S contains of *o,o'*-, *o,p'*- and *p,p'*-methylene linked anisolic resins which can be attributed to signals at 29.8, 35.1 and 40.6 ppm in $^{13}\text{C}\{-^1\text{H}\}$ -NMR, respectively. The *m*MBC/4TO/S_{100E} and *m*MBC/1TO/S_{100E} consists almost of *p*TS which can be seen in strong signals in the ^1H - and ^{13}C -NMR spectra (Fig. S 12a, b). In ^1H -NMR the protons of methylene groups can be found between 3.5–4.0 ppm whereas methylol and methylenether groups situated between 4.4 and 4.8 ppm⁴. The sample *p*MBC/4TO/S_{100E} shows no ether signals in NMR. The amount of methyleneether species in extracts of *m*MBC can not be determined because the signals were overlaid with methylolprotons in ^1H -NMR. Traces of carbonate monomer and surfactant found, too. Additional, in extract of polymers produced with *m*MBC carbonic acid signal were found at 10.7 ppm. Signals for dichloromethane the extraction solvent were found in ^1H -NMR, too.

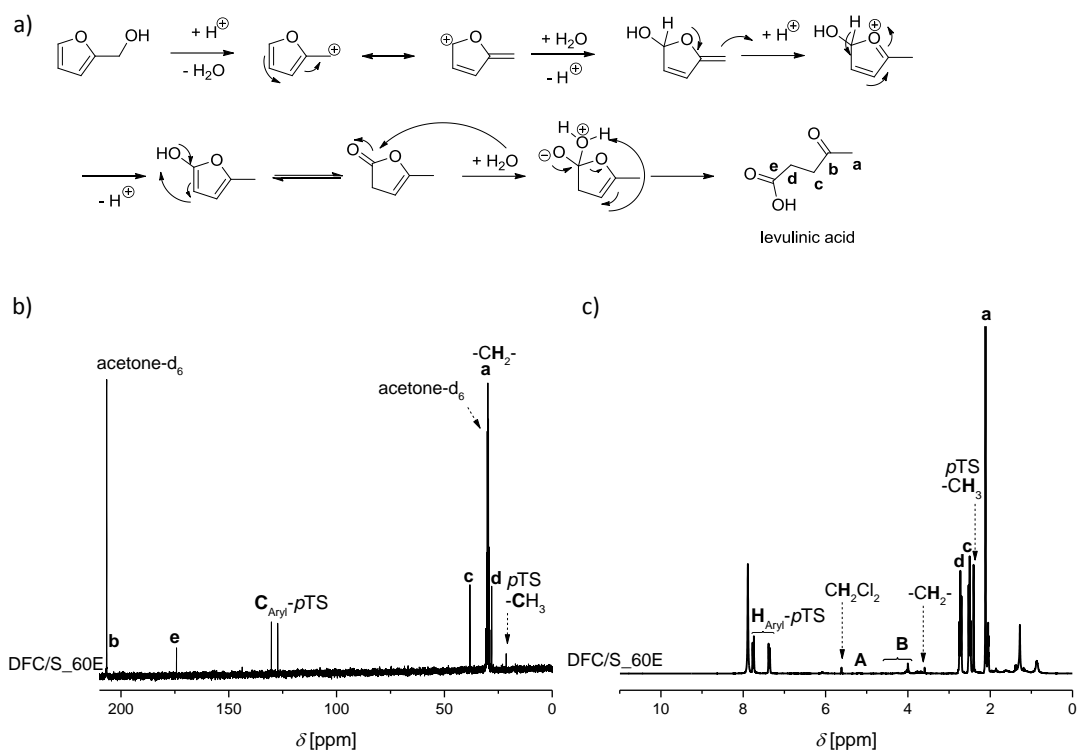


Fig. S 13 a) The mechanism for levulinic acid formation from the reaction of furfuryl alcohol with acids⁸. b) Liquid $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectra and b) ^1H -NMR spectra of extracts (labeled with E) obtained after extraction of DFC/S_60 with dichloromethane.

The polymer DFC/S_60 shows a extractable content of 24.6 %. The liquid $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectra (Fig. S 13b) and ^1H -NMR spectra (Fig. S 13c) of the extract exhibit mainly signals of pTS and levulinic acid. Levulinic acid is a side product of the cationic polymerization of furfuryl alcohol due to a hydrolytic furan ring opening⁸. The mechanism is shown in Fig. S 13a.

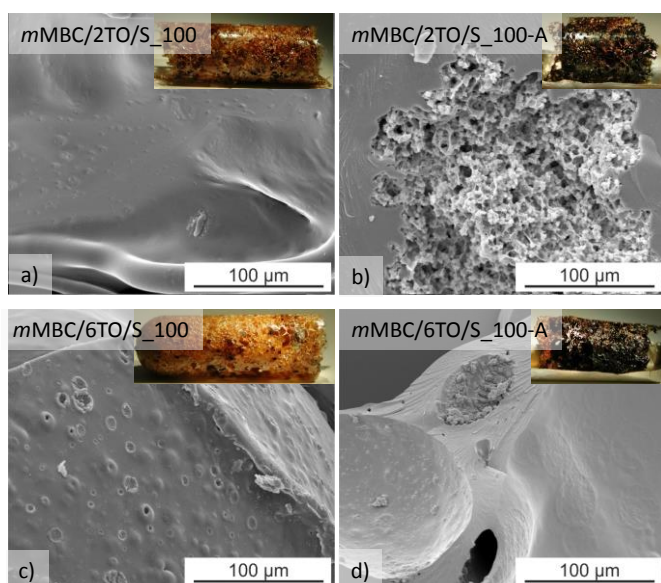


Fig. S 14 SEM images of the anisolic resins obtained by cationic polymerization mMBC at 100 °C with 1,3,5-trioxane. SEM images of the annealed (A) anisolic resins at 250 °C. The inset shows the picture of the polymer foam.

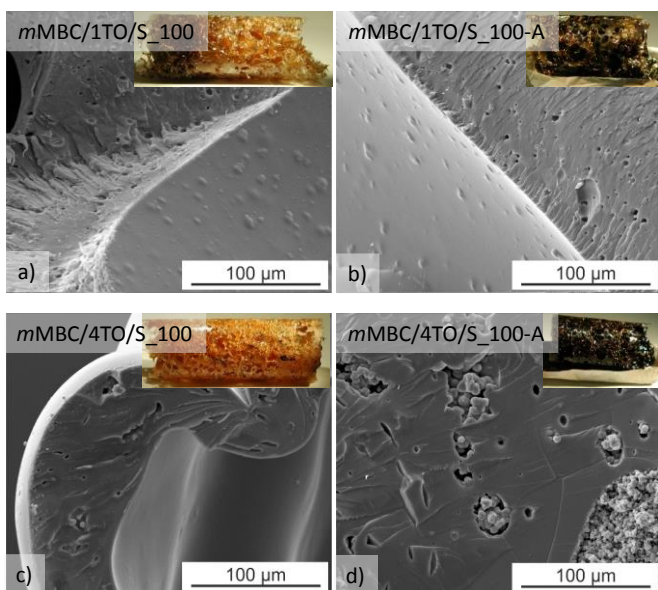


Fig. S 15 SEM images of the anisolic resins obtained by cationic polymerization mMBC at 100 °C with 1,3,5-trioxane. SEM images of the annealed (A) anisolic resins at 250 °C. The inset shows the picture of the polymer foam.

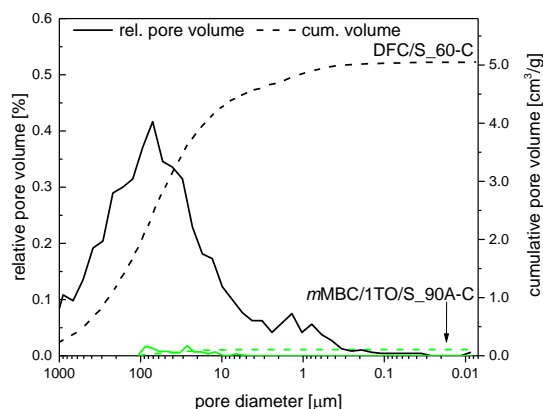


Fig. S 16 The cumulative volume and pore size distribution of DFC/S_60-C and mMBC/1TO/S_90-A obtained by mercury porosimetry measurement.

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