Kinetics of early stages of resorcinol-formaldehyde polymerisation investigated by solution-phase nuclear magnetic resonance spectroscopy

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Abstract

Resorcinol and formaldehyde reactions were quantitatively monitored by means of ^{1}H and ^{13}C NMR spectroscopy at room temperature (293K) before heat treatment leading to formation of organic gels. We found that resorcinol substitution with formaldehyde starts with an initial surprisingly rapid step followed by a more gradual depletion of the reactants. Substituted species with both monomeric and dimeric hydroxymethyl groups were observed immediately after mixing of the reagents with the proportion of formaldehyde-based solution species consumed between 30 and 50%. Substituted resorcinol species can be all accounted for by solution-phase NMR at ambient conditions before they form nanoscale clusters upon heating. It can therefore be expected that the final properties of resorcinol-formaldehyde gels depend not only on the composition of reaction mixtures and duration of the high temperature treatment but also on the manner and period of reagent mixing (a hitherto overlooked synthesis step), as different amounts of alternatively substituted resorcinol can be produced before heat treatment commences.

Introduction

Nanoporous organic gels are of great interest in energy applications as electrodes in double-layer supercapacitors and batteries [1], gas storage [2], capacitive deionization units, catalyst supports and adsorbents [3]. These materials can be obtained by polymerization of phenol, melamine, resorcinol or similar substances substituted with formaldehyde. Resorcinol-formaldehyde gels synthesized via the

sol-gel method have been widely studied since their discovery in the late 1980s [4]. These nanoporous materials are of great interest due to their tunable parameters, which include pore size, electrical conductivity and density [5–7].

The sol-gel synthesis of resorcinol-formaldehyde gels is generally believed to follow the reaction mechanism shown in Figure 1. Formaldehyde reacts with resorcinol and the resulting hydroxymethyl resorcinol derivatives subsequently undergo condensation reactions. The first step is thought to be catalyzed by basic catalysts, such as sodium or potassium carbonates and hydroxides, while the latter one is favoured in acidic conditions and at elevated temperatures [4,8]. The standard preparation procedure includes dissolution of resorcinol and the basic catalyst in water, adding formaldehyde and mixing the solution (typically for 30-60 min) at room temperature prior to temperature treatment at ca. 70-90°C. While it is widely assumed that the reaction takes place at a noticeable pace upon heating, this might not necessarily be the case as some previous investigations noticed that substituted resorcinol species were observed under ambient conditions [9–11]. However, this has not been previously investigated in detail and we are not aware of any quantitative information about the kinetics of resorcinol substitution with formaldehyde at ambient conditions. If such substitution were significant then the manner and period of reagent mixing would be expected to influence the final properties of the resorcinol-formaldehyde gel.

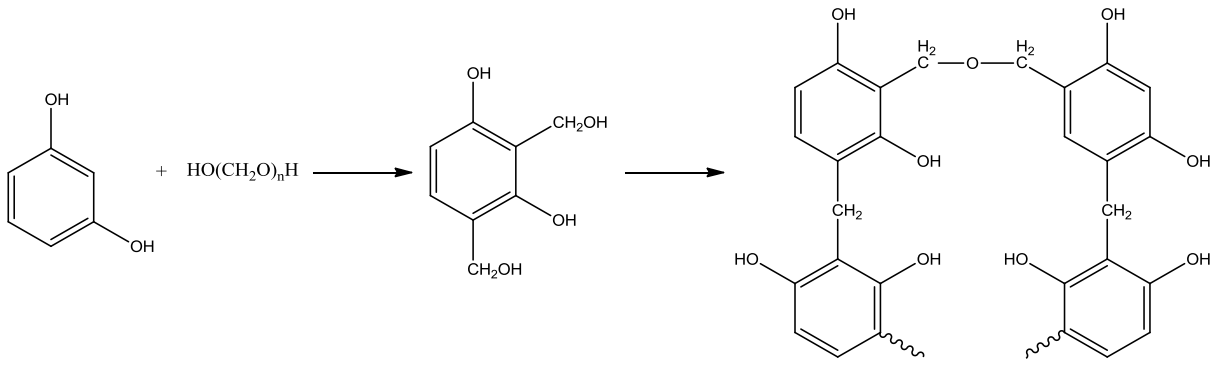


Figure 1. General mechanism of reactions between resorcinol and formaldehyde.

Much effort has been devoted to developing empirical relationships between the final properties of gels - dried or carbonized - and the conditions of the synthesis [4,12–18]. However, there has been

less focus on investigating resorcinol-formaldehyde polymerization and *in situ* observations of the sol-gel process itself. Several papers reported investigations of reacting mixtures during the synthesis [19–22] as well as nanostructure evolution in the early stages of gel formation [22–25]. There were two previously proposed mechanisms concerning gel formation: microphase separation [26,27] or aggregation of primary colloidal particles formed by substituted resorcinol or its oligomers [22]. The mechanism based on microphase separation suggests that the polymeric chains gradually grow until they are too large to be soluble in the reaction environment and thus induce demixing of the reacting solution, leading to formation of two interpenetrating phases. As a result, one of the phases is rich in the formed polymer (insoluble) and the other contains mostly the solvent. The other scenario, which is colloidal aggregation, is based on the idea that primary colloidal particles are formed and subsequently aggregate, forming a space-filling network of interconnected clusters. Dynamic Light Scattering studies revealed monomodal decay time distributions with apparent cluster hydrodynamic diameters reaching about 5 nm in the course of the reaction followed by a rapid growth of these species [22]. More recently, we have studied early stages of gel formation using Dynamic Light Scattering and we found that the size of primary clusters appears to be thermodynamically controlled, where a miscibility limit is reached due to formation of certain reaction intermediates, resulting in nanoscale molecular demixing and thus leading to formation of approximately monodisperse primary clusters, similar to formation of micelles or spontaneous nanoemulsions [24,25].

The chemical nature of reactions between formaldehyde and resorcinol taking place in sol-gel processes has not been studied in great detail. Werstler used ^{13}C NMR to study species present in resorcinol-formaldehyde mixtures [9] and this work is often referred to for ^{13}C NMR peak assignments in this system. More recently, Christiansen used ^{13}C-enriched reactants to follow reactions in this system [28] and Moudrakovski et al. used solid-state NMR to study resulting gels [29]. A recent study by Lewicki et al. [10] used ^{1}H NMR and DSC to monitor resorcinol-formaldehyde polymerization. They noted that the nature of the initially formed substitution species is ill-defined, arguing that since the initial substitution pattern defines the structure of the resulting polymeric gel, only limited control over its structure and properties is possible. We have previously investigated speciation in aqueous

methanolic formaldehyde solutions under conditions used for resorcinol-formaldehyde polymerization and developed a detailed thermodynamic model accounting for polymerization of methylene glycol (hydrated formaldehyde) species in such solutions [30]. This provides us with knowledge and control of formaldehyde-related species as a function of solution concentration and temperature.

In this work we focus on the initial substitution of resorcinol with formaldehyde to investigate the potential to control the starting material for subsequent condensation polymerisation in order to better enable rational design of resorcinol-formaldehyde gels. Surprisingly, we found that substitution of resorcinol with formaldehyde is very rapid under ambient conditions, although neither subsequent condensation nor formation of nanoscale clusters takes place over timescales of hours without further heating. The manner and period of the initial mixing of reagents under ambient conditions is thus a hitherto overlooked synthesis step in resorcinol-formaldehyde polymerization that can be used to control the degree and nature of resorcinol substitution and thus the subsequent crosslinking affecting properties of resulting resorcinol-formaldehyde gels.

Methods and materials

Resorcinol (99 % wt.), formaldehyde (37 % wt., aqueous solution stabilized by methanol, 13 % wt.; the concentration of methanol was determined experimentally using NMR spectroscopy [11]), sodium carbonate (≥ 99.5 wt. %, anhydrous ACS reagent), tetramethylsilane (TMS ≥ 99.9 % wt., NMR grade, ACS reagent) and deuterium oxide (99.9 atom % D) were all purchased from Sigma–Aldrich. Borosilicate glass NMR tubes and matching coaxial inserts containing TMS were used during the experiments. According to the volume specifications provided by the manufacturer (Wilmad), the NMR signal of the substance in the sample compartment should be 8.833 times greater than that of the same substance in the coaxial insert. Experimental validation revealed that the actual ratio was 8.943, and this was taken into consideration in quantitative assessment of the experimental data. The compositions of the reacting mixtures are summarized in Table 1. In all cases, the compositions of the samples were chosen to match specific ratios of the reactants and the diluent. The ratios R/C and R/F stand for resorcinol to catalyst and resorcinol to formaldehyde ratios and are expressed in mol per mol.

The resorcinol to water ratio (R/W) is expressed in grams per milliliter and was kept constant and equal to 0.1.

Table 1. Compositions of investigated reacting mixtures.

Reactants' ratios	Resorcinol [g]	Formaldehyde [ml]	Sodium carbonate [g]	Water/D_2O (7:3 vol) [ml]
R/C=10 R/F =0.33	1.00	2.23	0.0963	10.00
R/C=25 R/F =0.33	1.00	2.23	0.0385	10.00
R/C=50 R/F=0.33	1.00	2.23	0.0193	10.00
R/C=10 R/F=0.5	1.00	1.47	0.0963	10.00
R/C=25 R/F=0.5	1.00	1.47	0.0385	10.00
R/C=50 R/F=0.5	1.00	1.47	0.0193	10.00
R/C=10 R/F=1.0	1.00	0.74	0.0963	10.00
R/C=25 R/F=1.0	1.00	0.74	0.0385	10.00
R/C=50 R/F=1.0	1.00	0.74	0.0193	10.00

All NMR experiments were performed using a three-channel multinuclear Bruker Avance-III 600 MHz NMR spectrometer equipped with a 14.1 T Bruker UltraShield magnet and a TBI-z-[^{1}H, ^{13}C, ^{31}P–^{15}N] probehead operating under TopSpin (version 2.1, Bruker, Karlsruhe) running on a HP XW3200 workstation equipped with Windows XP. Tetramethylsilane (TMS), present as a chemical shift reference standard, was used in a coaxial sample insert, thereby preventing its influence on the kinetics and chemistry of the processes under investigation; ^{1}H and ^{13}C chemical shifts of the respective methyl resonance signal of TMS were set to 0 ppm. In order to aid NMR signal assignment, chemical shifts were calculated using ChemDraw Ultra 12.0 (CambridgeSoft).

Experiments were performed at 293K. The required amounts of de-ionized water and deuterium oxide (at volumetric ratios of 7 to 3) were measured with an automatic pipette into a glass vial. Resorcinol was weighed, transferred into the vial and stirred using a magnetic stirrer for 5 min until fully dissolved. Sodium carbonate was weighed on an analytical scale and transferred to the vial containing dissolved resorcinol. After 10 min of further stirring to dissolve sodium carbonate, the required amount of formaldehyde solution was measured with an automatic pipette and added to the mixture. The vial was sealed and shaken vigorously for about 30 s and then a small volume (0.5 mL) of the mixture was taken to rinse the NMR tube. Once rinsed, the tube was filled with the reacting mixture

and a coaxial tube containing TMS was inserted, allowing excess reacting mixture to spill and ensuring that no air bubbles were trapped. The NMR tube was rinsed with acetone on the outside, labeled and immediately placed into the NMR spectrometer for data measurements. The approximate time between adding formaldehyde and starting the experiment was about 3 min.

In order to facilitate NMR signal assignments, a separate set of 2D [^{1}H, ^{13}C] HSQC and ^{13}C NMR data was collected using a different approach. A reacting mixture prepared as described above, was poured into a glass 50 mL bottle, sealed and heated in an electric oven set to 353K (80°). After 10, 20 and 30 minutes, a 1 mL sample was taken by an automatic pipette, diluted in 3 mL of water-D_2O mixture (7:3 by volume) which was kept in an ice bath to ensure the reacting mixture would be quenched immediately. The solution was then lightly shaken to mix and transferred into a clean and dry NMR tube equipped with a coaxial insert and both ^{13}C and 2D [^{1}H, ^{13}C] HSQC spectra were collected. All NMR measurements were carried out at 293K.

Due to the carbon-based nature of the reactants and the fact that the reaction between them is conducted in an aqueous environment, a preferable tool for qualitative investigation of reactant speciation and resulting product formation would be ^{13}C NMR. We have previously used ^{13}C NMR for quantitative study of equilibrium speciation in formaldehyde methanolic aqueous solutions [30]. However, ^{13}C NMR is less suitable for kinetic studies in these systems due to relatively long data acquisition times required to obtain reasonable signal-to-noise ratio caused by the low natural abundance of ^{13}C. To obtain quantitative ^{13}C NMR data, a large number of transients as well as very long delay times would be required relative to ^{1}H NMR. The addition of relaxing agents such as $Cr(AcAc)_3$ would increase the rate of relaxation of carbon nuclei due to paramagnetic enhancing effects, but these agents can affect pH and may influence the rate or even the mechanism of the reaction being monitored. Nevertheless, ^{13}C NMR spectroscopy is an invaluable tool for identifying the species found in reacting solutions as valuable previous literature shows regarding ^{13}C NMR assignments of resorcinol-formaldehyde reaction products [9,28]. Such data allows us to use 2D [^{1}H, ^{13}C] Heteronuclear Single Quantum Coherence (HSQC) spectra to assign ^{1}H NMR spectra, thereby

enabling the use of ^{1}H NMR data as a much faster technique to monitor kinetics of resorcinol-formaldehyde reactions.

^{13}C NMR measurements were carried out with delay times of 60 s and 1024 transients were collected in each experiment. This time interval was chosen because of a very long relaxation time for several formaldehyde-related species [30]. The resolution of the resulting FID was 1.02 Hz per point. 2D [^{1}H, ^{13}C] Heteronuclear Single Quantum Coherence (HSQC) spectra were acquired over a ^{1}H frequency width of 10.0 ppm centered at 4.89 ppm in 2048 data points with 16 transients for each of 128 t1 increments over a 13C frequency width of 220 ppm centered at 99.00 ppm.

^{1}H NMR spectra comprised of 32 scans, an additional two dummy scans and a delay time set to 1 s, and FID resolution was 0.19 Hz per point. Each spectrum was collected directly after the previous, in order to ensure that the monitoring was almost continuous.

Results and Discussion

Qualitative analysis of the NMR spectra

Figure 2 shows an example 2D [^{1}H, ^{13}C] HSQC NMR spectrum for the reaction mixture after 10 min of temperature treatment at 80°C, where the horizontal (ω2) axis corresponds to the proton NMR chemical shift range and the vertical (ω1) axis corresponds to the carbon NMR chemical shift range. There are four distinguishable regions with NMR signals labeled A-D. Region A contains peaks from carbon and hydrogen atoms in CH_3O- groups, present in methanol and methoxylated oligooxyglycols; in this case only the signal for a methoxylated monomer is visible ($HO\text{-}CH_2\text{-}OCH_3$, methoxy monoglycol, MMG [30]). Region B contains peaks not present in either formaldehyde or resorcinol solutions alone, labeled 1-6, which may overlap with MG ($HO\text{-}CH_2\text{-}OH$, monoglycol [30]) and DG ($HO\text{-}CH_2O\text{-}CH_2\text{-}OH$, diglycol [30]) signals in the ^{1}H NMR spectrum and with MMG and methanol signals in the ^{13}C NMR spectrum. Region C contains signals from species found in formaldehyde solution, such as MG, DG and MMG ([30], as well as a new signal, labeled 7, which again is not present in either formaldehyde or resorcinol solutions alone. Region D contains signals related to carbon atoms C(2,4,5,6) in resorcinol. There are no signals arising from carbon atoms 1 and 3 in the

resorcinol molecule: there are no hydrogen atoms bound to them directly, a requirement for signal observation in 2D [^{1}H, ^{13}C] HSQC NMR spectra. The assignment of all peaks found in the 2D [^{1}H, ^{13}C] HSQC NMR spectrum was based on previous ^{13}C NMR assignments (see below), which also show excellent correlation with calculated chemical shift values. Calculated and measured chemical shifts of signals found in the 2D [^{1}H, ^{13}C] HSQC NMR spectra are shown in Table 2, and the correlation figures are shown as Figure 3.

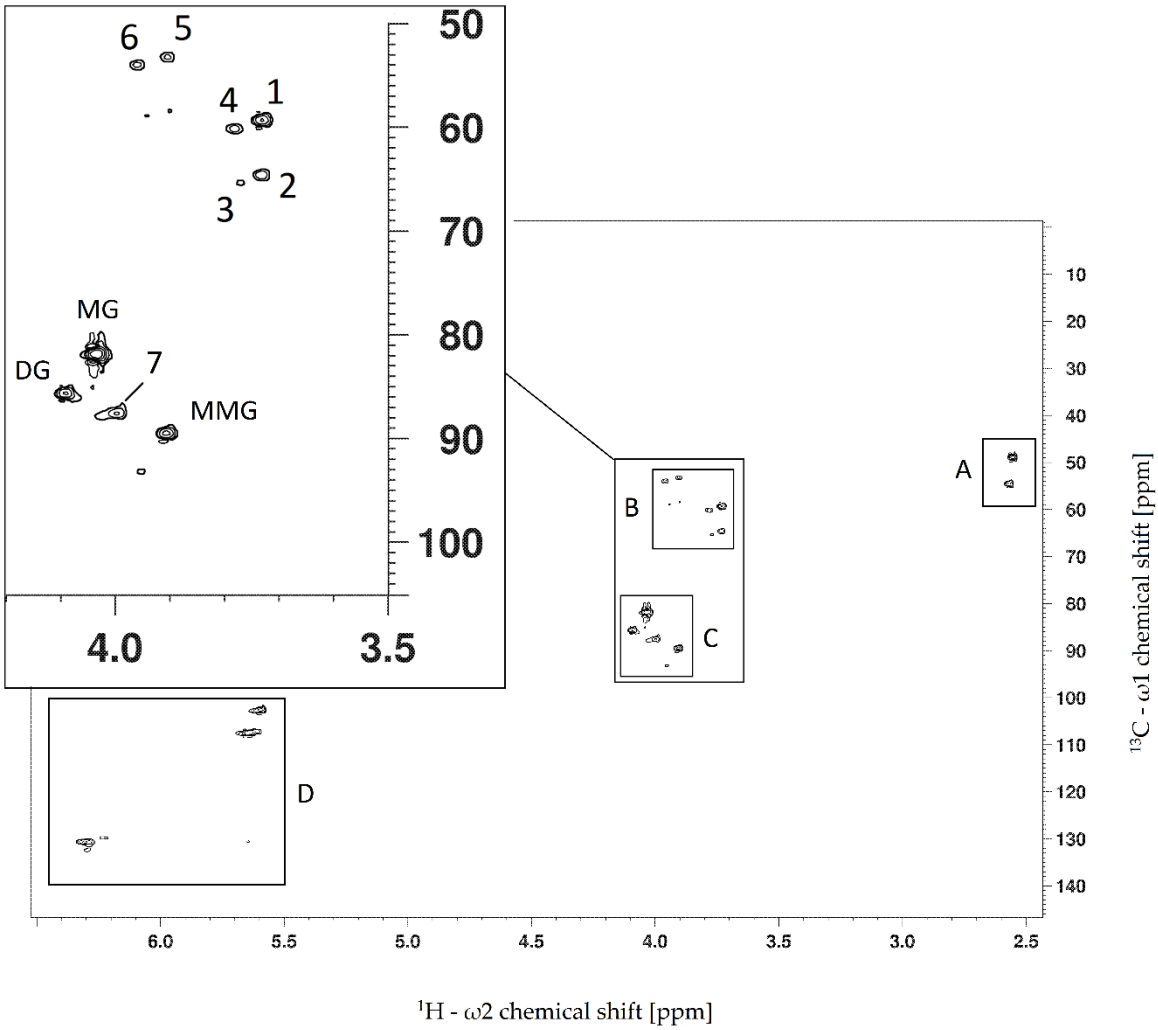
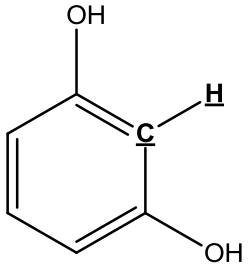
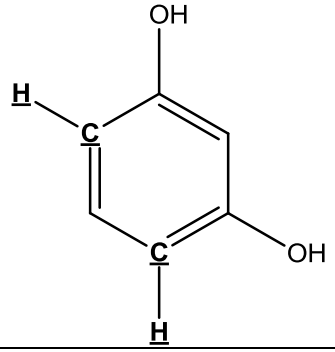
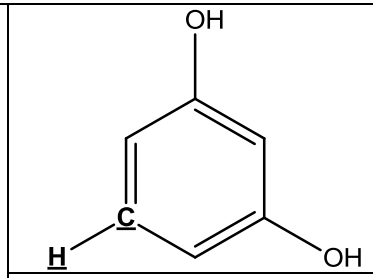
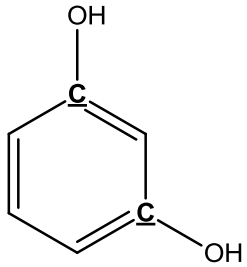
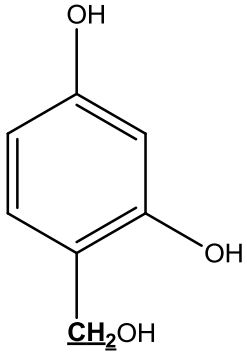
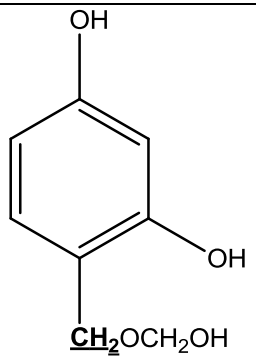
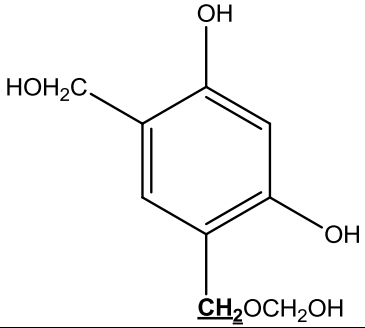
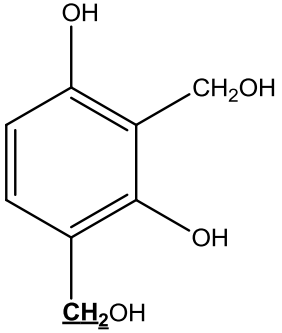


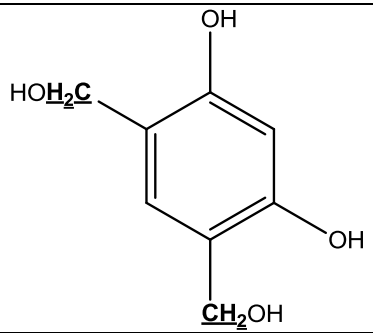
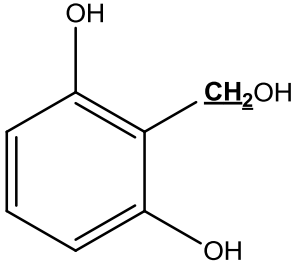
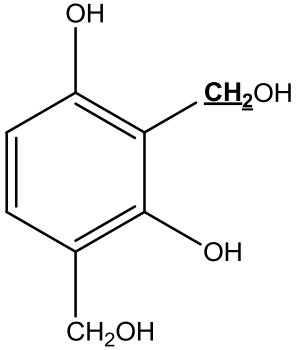
Figure 2. A 2D [^{1}H, ^{13}C] HSQC NMR spectrum collected after 10 min of temperature treatment (80°C, 353K) of a reacting mixture (R/C 200 mol·mol^{-1}, R/W 0.10 g·ml^{-1}, R/F 0.5 mol·mol^{-1}; water-D_2O dilution; see text for details).

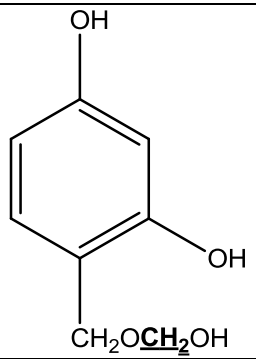
Table 2. Assignment of signals in the 2D [^{1}H, ^{13}C] HSQC NMR spectrum of Figure 2.

Assignment		**^{1}H chemical shift δ_H [ppm]**		**^{13}C chemical shift δ_C [ppm]**		
		Calculated	**Measured (this work)**	**Calculated**	**Measured** (this work)	**Measured** [9]
Formaldehyde	**C**H$_3$-OH	3.39	2.56	46.7	48.9	50.70 (peak C)
	CH$_3$O-CH$_2$-OH	3.30	2.58	55.3	54.6	56.10 (peak D)
	HO**C**H$_2$OH	5.77	4.01	82.0	82.5	83.73 (peak I)
	HO**C**H$_2$O**C**H$_2$OH	5.61	4.08	85.2	85.9	87.29 (peak J)
	CH$_3$O-**C**H$_2$-OH	5.61	3.92	91.4	89.4	91.30 (peak M)
Resorcinol		6.27	5.61	103.6	102.5	104.25 (peak O)
		6.51	5.68	108.5	107.9	109.18 (peak P)

		7.11	6.33	131.5	131.1	132.04 (peak W)
		-	-	159.9	156.8	158.27 (peak DD)
Peak 1		4.61	3.73	59.9	59.3	61.49 (peak F)

Peak 2		4.80	3.73	64.7	64.7	66.50 (peak H)
Peak 3		4.80	3.77	65.0	65.1	67.11 (peak H')
Peak 4	 or	4.61	3.78	60.2	60.4	62.36 (peak F')

						
Peak 5		4.61	3.91	53.6	53.2	57.8-58.8 (peak E)
Peak 6		4.61	3.96	53.9	53.9	n/a

Peak 7		5.61	3.98	88.8	87.9	89.27 (peak K)

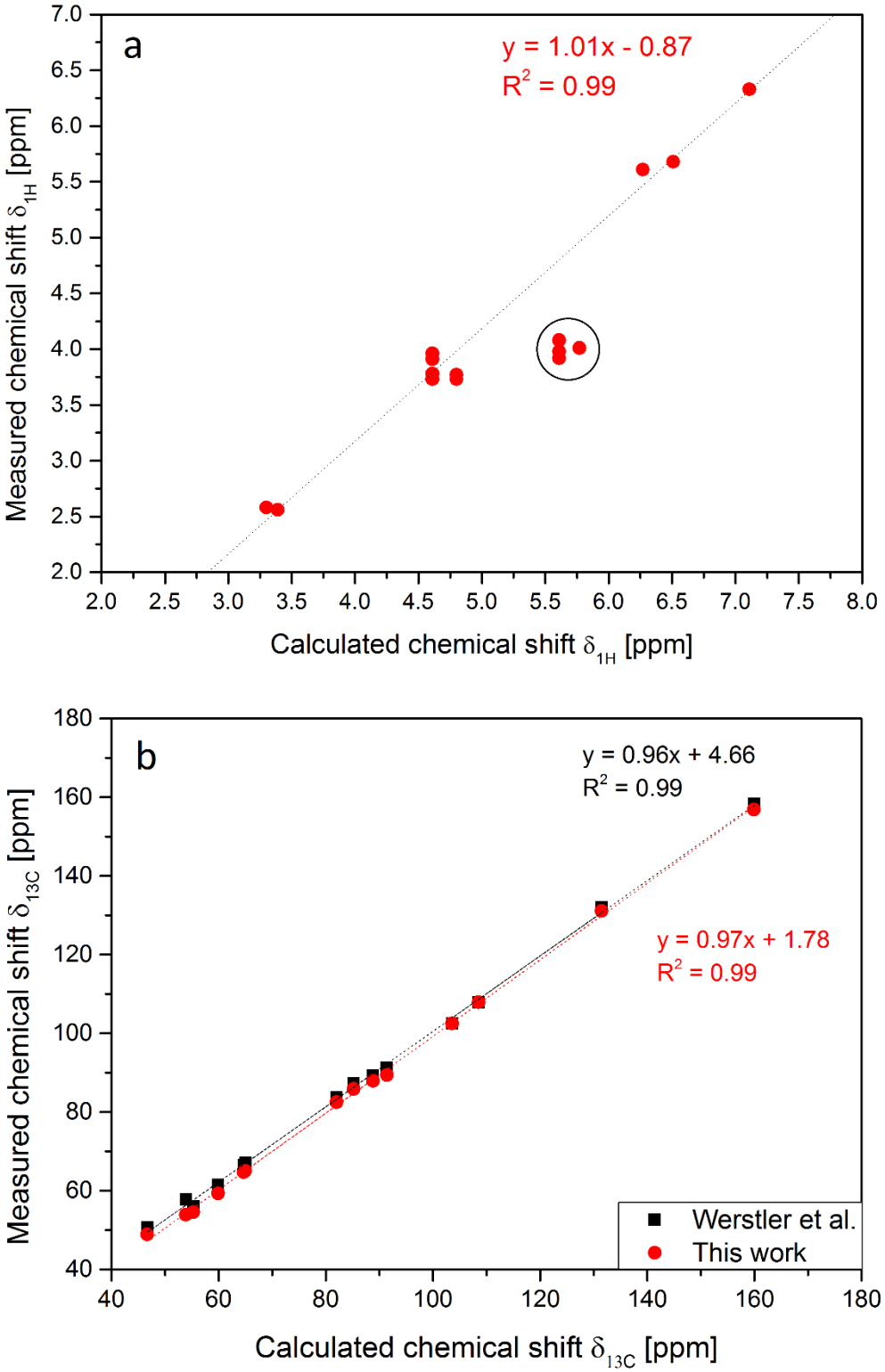


Figure 3. Chemical shift correlations for assignments in Table 2: (a) ^{1}H NMR data and (b) ^{13}C NMR data. Note that in (a) encircled data points are associated with -O-CH_2-O- groups and are excluded from the correlation shown.

^{1}H NMR assignments for species originating from formaldehyde solution are in agreement with those reported previously [10,30]. However, we note that quantitative distribution of formaldehyde-related species reported by Lewicki et al. for DMSO solutions are significantly different from those observed in aqueous methanolic solutions [30]. This may be due to use of DMSO as a solvent rather than water commonly used in sol-gel synthesis which could lead to changed equilibria among these species.

^{13}C NMR assignments shown in Table 2 are consistent with those published previously [9,28,29] with few minor exceptions. New peaks appearing between 50 and 100 ppm are indicative of carbon atoms in hydroxymethyl derivatives of resorcinol. Christiansen attributes peaks at ca. 60 and 65 ppm to carbon in hydroxymethyl group attached to carbons atoms C(4) and C(6), respectively, while the signal at 55-60 ppm is assigned to the same carbon but bound to C(2). It is noteworthy that Christiansen observed these signals after 19 min of the reaction. Werstler assign signals at 57.8-58.8 ppm (their peak E) to carbon atom in hydroxymethyl group bound to C(2) (our peak 5), indicating that it was apparently difficult to determine chemical shift for this species and in fact, these signals are not seen in spectra shown in Werstler's paper. Furthermore this assignment seems to be the only one in the Werstler's paper to be somewhat off the chemical shift correlation (Figure 3b) so we believe that it is not accurate. Similarly, peak G in Werstler's paper is not observed in spectra shown in their paper and neither was this found in our work. We also note that there is a typographical error in Table 1 in Werstler's paper where the compound for peak D should be methoxylated methylene glycol rather than ethanol.

Substitution of resorcinol with hydroxmethyl groups at carbon atoms C(4) and C(6) gives rise to our peak 1 (Werstler's peak F). Both Christiansen and Werstler et al. observed ^{13}C signals at 67.7 and 90.3 ppm [28] and at 66.50 and 89.27 ppm [9], which they assigned to a product of addition of DG (HO-CH_2-O-CH_2-OH) to the resorcinol ring at the C(4) site. Our study confirms the presence of such species, as HSQC spectra contain two corresponding peaks, labelled 2 and 7 (see Figure 2 and Table 2). The corresponding ^{13}C NMR chemical shifts are 64.7 and 87.9 ppm. Presence of these signals and their absence in spectra of non-reacting formaldehyde-water solutions (see [30]) confirms that it is possible to obtain a dimeric hydroxymethyl derivative of resorcinol and not exclusively monomeric

derivatives. The question which remains to be answered is whether DG reacts directly with resorcinol or whether species assigned to peaks 2 and 7 is a product of two consecutive reactions of formaldehyde addition and then further formaldehyde addition to form a hydroxymethyl derivative.

Due to short acquisition times (ca. 2 min) related to high natural abundance of ^{1}H and its relatively short relaxation time compared with the ^{13}C nucleus, ^{1}H NMR spectroscopy is much more suitable for monitoring reaction kinetics than ^{13}C NMR spectroscopy. Having assigned all signals present in the 2D [^{1}H, ^{13}C] HSQC NMR spectrum based on the ^{13}C NMR assignments, we were able to assign the ^{1}H NMR spectra. ^{1}H NMR spectroscopy provides quantitative data of good signal-to-noise ratio in a matter of minutes. One drawback is the presence of water in the reaction, which yields a very strong and broad NMR signal that overlaps with signals from –OH groups in both glycols and resorcinol. Unfortunately, this peak covers a relatively wide chemical shift range and obstructs signals of the CH_2-groups in oligooxyglycols. In most cases deconvolution can solve this problem but this is only possible when the positions of the peaks beneath the –OH peak are known or when its shape indicates their whereabouts [30]. Alternatively, water peak suppression techniques can be used [31]. Another concern is related to the change in chemical shifts with temperature as discussed in our previous work [11,30].

^{1}H NMR spectra of isolated reactants, i.e. formaldehyde and resorcinol in their aqueous solutions, are shown in Figure 4. Peaks from both reactants do not overlap, as formaldehyde-related species give rise to signals at chemical shifts below 5 ppm, while resorcinol hydrogen atoms appear downfield from CH_2 signals, at ca. δ_H = 5.7 ppm and 6.3 ppm.

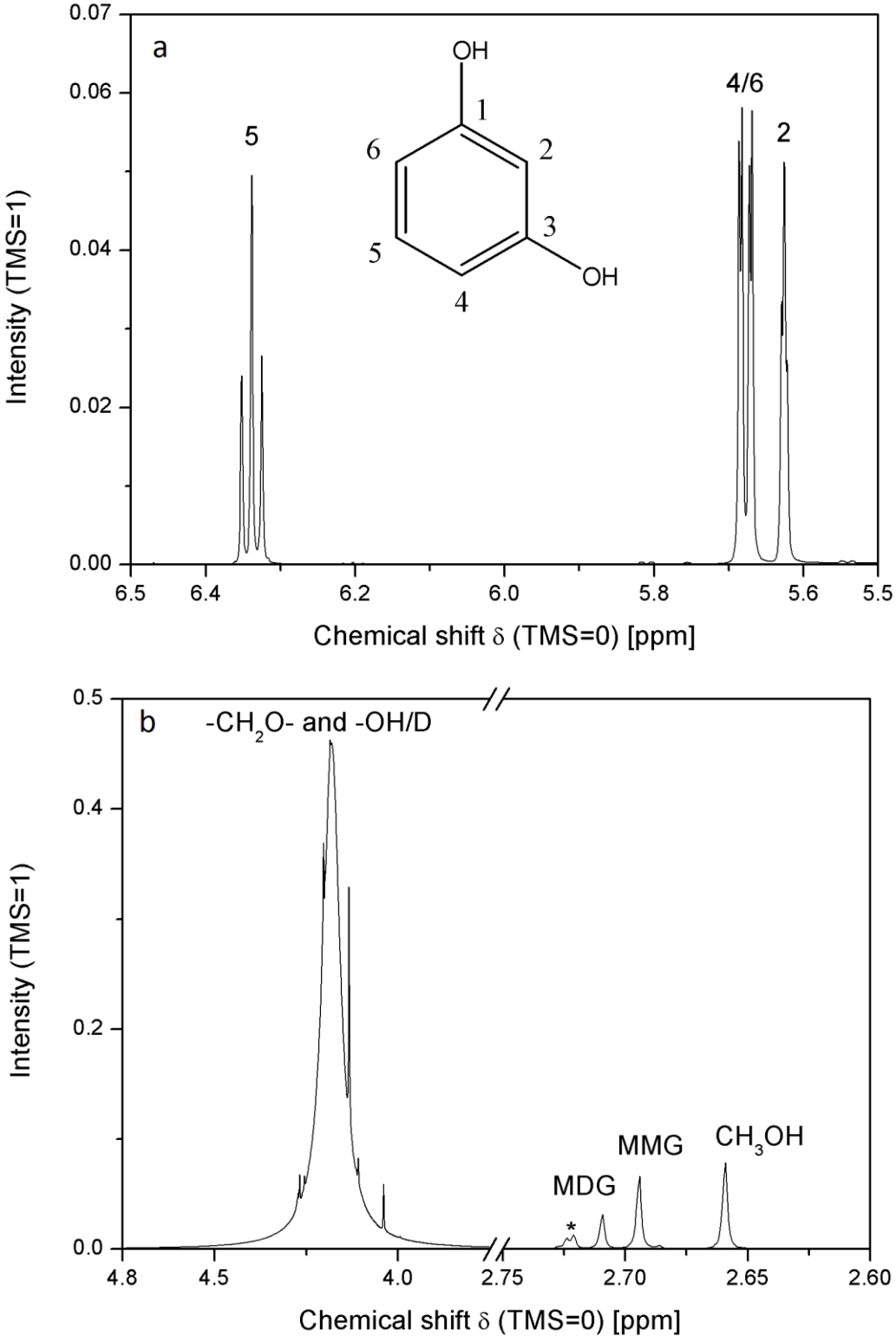


Figure 4. ^{1}H NMR spectra of (a) resorcinol and (b) formaldehyde aqueous solutions in concentrations matching the reaction conditions. In the formaldehyde spectrum, the asterisk denotes oligomeric methoxylated glycols.

In the first stage of the reaction between formaldehyde and resorcinol, hydroxymethyl derivatives are formed, which is reflected by changes in the appearance of the NMR spectra in two regions. The primary change is the one resulting from changing the chemical shift of protons attached to carbons of the resorcinol ring once a proton bound to a neighboring carbon atom is replaced by a hydroxymethyl substitute. Once resorcinol reacts with formaldehyde, the proton bound to one of the available carbons (2, 4 or 6) is replaced by a formaldehyde-related species and a hydroxymethyl derivative is formed. Thus the signal from this proton diminishes in intensity. This substitution results in a change of the immediate neighborhood of the protons attached to the aromatic ring, which leads to changes in their chemical shifts. While this change is subtle and amounts to less than 0.1 ppm, it can still be seen in spectra of good quality. An example of stacked spectra collected for a reacting sample is shown in Figure 5.

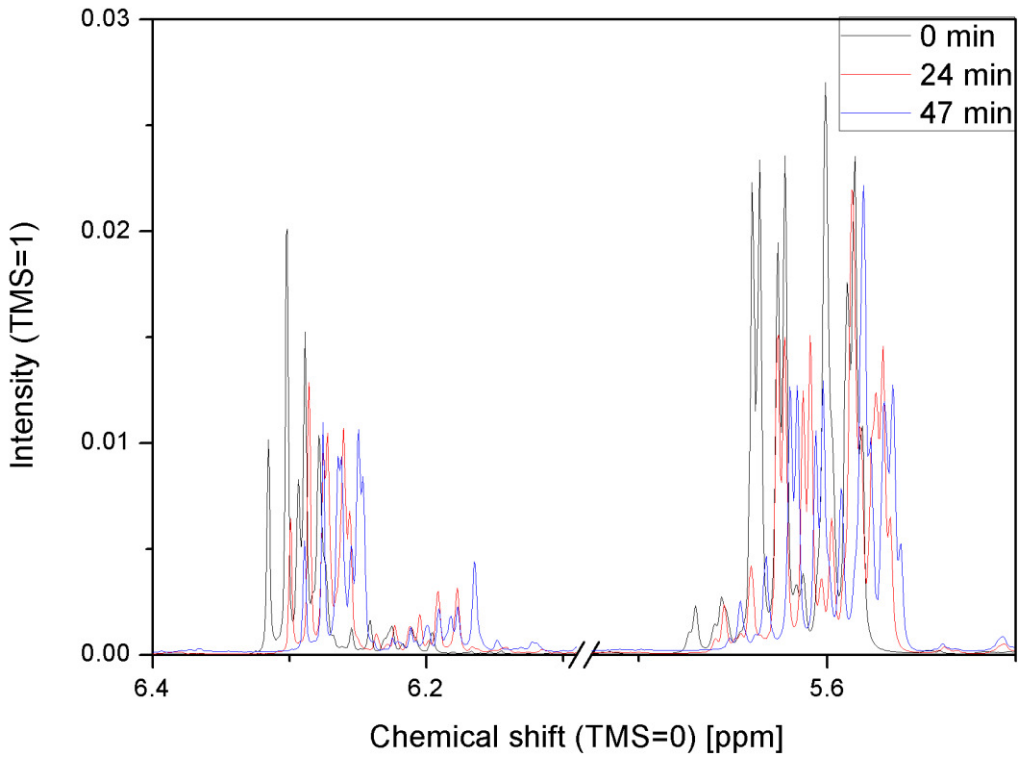


Figure 5. ^{1}H NMR spectra sections corresponding to resorcinol-related peaks collected at the beginning of the reaction, 24 min and 47 min later, while monitoring a reacting mixture in 293K (R/C 10 mol·mol^{-1}, R/W 0.10 g·ml^{-1}, R/F 0.50 mol·mol^{-1}).

Regardless of the position at which the hydroxymethyl group is attached and of the number of the groups attached to the resorcinol molecule, the chemical shift of the protons attached to the aliphatic carbon in this group (R-C**H**$_2$OH) is calculated to be δ_H = 4.61 ppm, which is within the chemical shift region where signals from formaldehyde-related species can be found. Should resorcinol be substituted with DG, the corresponding signal resulting from R-C**H**$_2$OCH$_2$-OH, would be observed at 4.80 ppm (see Table 2).

The next step in the formaldehyde-resorcinol polymerization is condensation of hydroxymethyl resorcinol derivatives, resulting in formation of oxymethylene bridges and in later stages, also methylene bridges. Depending on the type of bridge formed between two condensing molecules, the ^{13}C NMR chemical shift for carbons involved in these bridges is below 70 ppm. Our calculations indicate that carbon atoms in oxymethylene bridges formed between C(2) and C(2) would give rise to signals at 62.1 ppm, C(2) and C(4/6) at 62.1 and 69.7 ppm, while C(4/6) and C(4/6) at 69.7 ppm. Formation of methylene bridges between these carbon atoms would result in signals at 16.5 ppm, 22.7 ppm and 28.9 ppm, respectively. A table summarizing the calculated chemical shifts for various types of substituted resorcinol and their condensation products is presented below (Table 3).

Table 3. Summary of calculated ^{1}H chemical shifts for substituted resorcinol and its condensation products.

Hydroxymethyl derivatives – calculated chemical shift δ_H [ppm]				
Signal assignment	C(2)-CH$_2$OH	C(4)-CH$_2$OH	C(5)-CH$_2$OH	C(6)-CH$_2$OH
C(2)-**H**	-	6.24	6.20	6.24
C(4)-**H**	6.44	-	6.66	6.24
C(5)-**H**	7.04	7.02	-	7.02
C(6)-**H**	6.44	6.24	6.66	-

Condensation products – calculated chemical shift δ [ppm]						
Signal assignment	B					
	R^1-**CH**$_2$-O-CH$_2$-R^2		R^1-CH$_2$-O-**CH**$_2$-R^2		R^1-**CH**$_2$-R^2	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
R^{1}C(2)-B-R^{2}C(2)	4.80	62.1	4.80	62.1	3.96	16.5
R^{1}C(2)-B-R^{2}C(4/6)	4.80	62.1	4.80	69.7	3.96	22.7
R^{1}C(2)-B-R^{2}C(5)	4.80	62.1	4.55	73.1	3.96	28.1
R^{1}C(4/6)-B-R^{2}C(4/6)	4.80	69.7	4.80	69.7	3.96	28.9
R^{1}C(4/6)-B-R^{2}C(5)	4.80	69.7	4.55	73.1	3.96	35.7

Our results show that methylene bridges were not formed during the monitored period of time in our system, as no peaks were detected in the respective section of the spectra. Moreover, it is unlikely that oxymethylene bridges were formed, as all peaks found in the appropriate section of the spectrum were successfully assigned to other species, owing to excellent ^{13}C NMR correlation (Table 2 and Figure 3b) and HSQC results (Figure 2). Both Christiansen and Werstler et al. reported peaks corresponding to methylene bridges at 24.29 and 29.93 ppm [9], as well as at ca. 33-36 ppm [28]. Using solid-state NMR spectroscopy, Moudrakovski et al. [29] reported the presence of methylene and oxymethylene bridges at ca. 24-29 ppm and 50-60 ppm, respectively. Corresponding peaks were observed and assigned in ^{1}H NMR spectra by Lewicki et al. [10], although this region of the ^{1}H NMR spectrum also contains peaks originating from hydroxymethyl resorcinol. Without the support of ^{13}C NMR data, these assignments may be subject to some uncertainty. In our study we focused on the initial stage of the resorcinol-formaldehyde reactions at ambient temperature where we did not observe any signals corresponding to methylene or oxymethylene bridges. We believe that the condensation reaction takes place in further stages of the process where pH decreases [11] and/or temperature is increased in subsequent heat treatment.

Quantitative analysis of experiments at 20°C (293K)

Resorcinol-formaldehyde gel synthesis procedures reported in the literature usually start with mixing reactants at room temperature (for 30-60 minutes) followed by heat treatment at an elevated temperature (up to 363 K) for various periods of time. It can be expected that some reaction may occur before the start of heating but this has not been previously studied in any detail and the potential role of this step in influencing resulting gel properties has been overlooked. In order to examine what processes take place after the addition of formaldehyde at room temperature, i.e. during the typical reactant mixing period, NMR experiments were started immediately after the addition of formaldehyde to resorcinol and sodium carbonate solutions, as described earlier. NMR data accumulation began within approximately 3 minutes from the moment formaldehyde was added. A set of ^{1}H NMR experiments was performed on the reacting mixtures in which the molar ratios of

resorcinol to catalyst (R/C) and resorcinol to formaldehyde (R/F) were varied, while the resorcinol to water (R/W) ratio was kept constant at 0.10 $g \cdot ml^{-1}$. The R/C ratios were chosen to be 10, 25 and 50 $mol \cdot mol^{-1}$. These ratios correspond to the high end of basic catalyst concentrations used in preparations of resorcinol-formaldehyde gels [1,11,24,25].

Formaldehyde is present in aqueous methanolic solutions as a mixture of glycols, oligooxyglycols and their methoxylated forms, as we have described previously [11,30]. Figure 6 shows the δ_H = 3.6-4.2 ppm region of the ^1H NMR spectrum containing signals corresponding to protons of the hydroxymethyl groups. The figure shows a typical proton NMR spectrum taken directly after the addition of formaldehyde to a resorcinol/catalyst mixture. Here MG, DG and MMG correspond to HO-CH_2-OH, HO-CH_2-O-CH_2-OH and HO-CH_2-O-CH_3, respectively [30]. Despite the common view that substitution of resorcinol at room temperature is a slow process, new peaks shown in Figure 6a) are seen after only minutes following the addition of formaldehyde. When compared with signals from the formaldehyde species like MG, the observed signals are relatively intense, indicating that resorcinol substitution with formaldehyde proceeds to substantial conversion almost instantly. We can see new peaks 1-7 in the spectrum shown in Figure 6a) corresponding to substituted resorcinol species shown in Table 2.

The peaks corresponding to hydrogen atoms on the resorcinol ring are present in the δ_H = 5.5-6.5 ppm region of the ^1H NMR spectrum and are shown in Figure 6b). Substitution of resorcinol at a given site affects the chemical shifts of hydrogen atoms at unsubstituted sites, leading to the appearance of new peaks in this region of the spectrum. There are two distinguishable groups of signals: one at δ_H = 5.5-5.8 ppm and at δ_H = 6.1-6.5 ppm. The latter one is assigned to hydrogen atoms at the C(5) sites in both unsubstituted and substituted resorcinol. The former group is assigned to hydrogen atoms present at sites C(2,4,6), in both substituted and unsubstituted resorcinol. Therefore, this region was integrated as a whole and the data then used to determine the equivalent concentration of non-substituted resorcinol denoted as R-C(2,4,6) in this work.

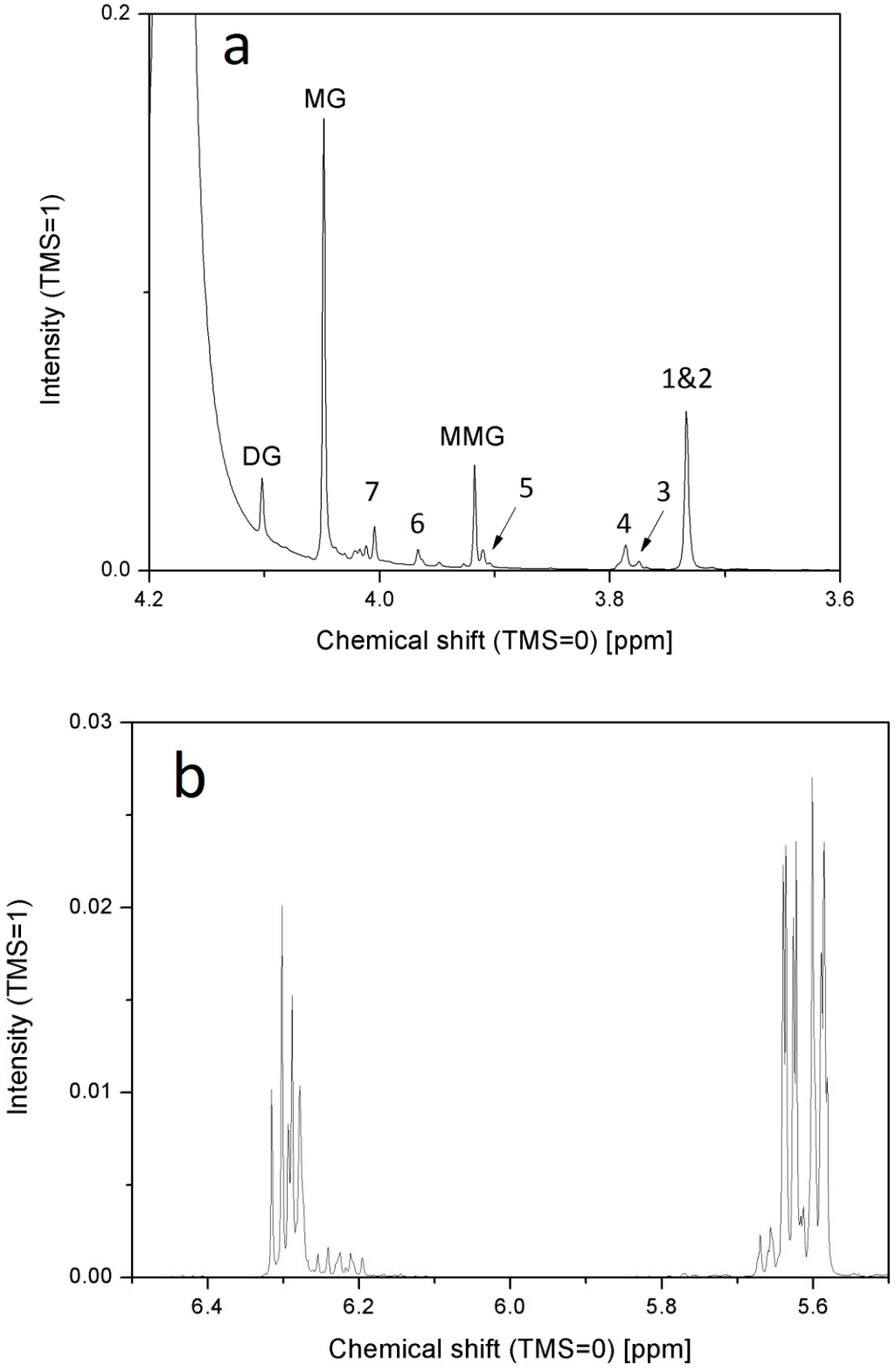


Figure 6. ^{1}H NMR spectrum of a reaction mixture (R/C 10 mol·mol^{-1}, R/W 0.10 g·ml^{-1}, R/F 0.5 mol·mol^{-1}) taken immediately after formaldehyde addition. a) Region corresponding to hydroxymethyl groups. Peaks 1-7 correspond to species in Table 2. b) Region corresponding to resorcinol hydrogens.

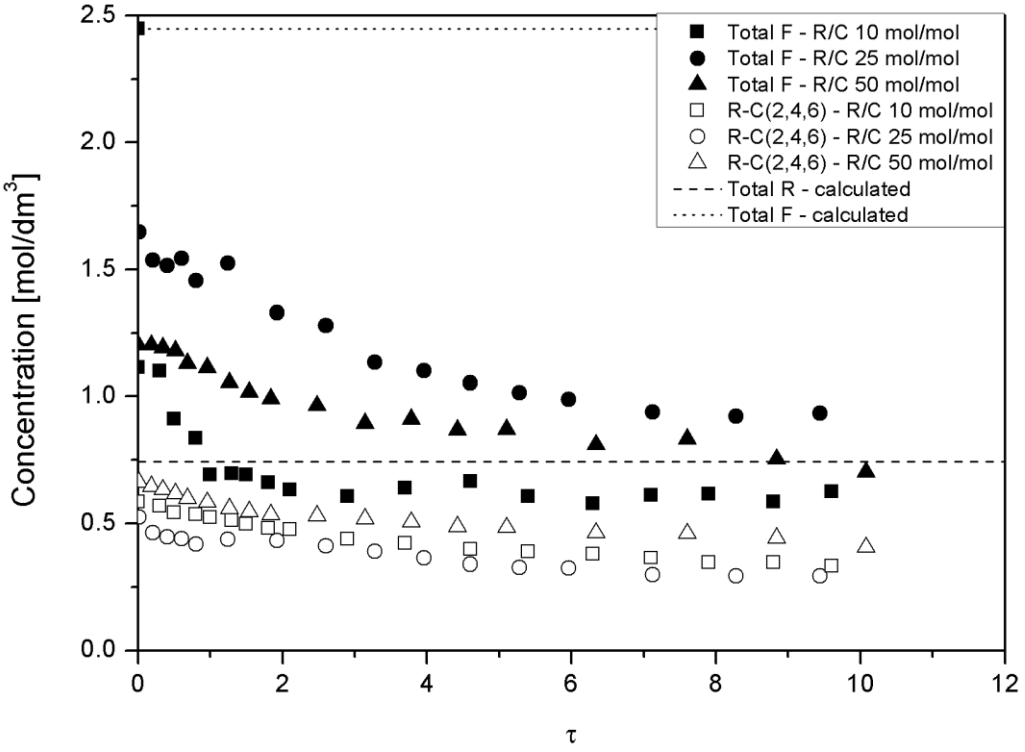
Sodium carbonate is expected to catalyse the reaction of resorcinol with formaldehyde species and the rate of reaction is expected to be proportional to the catalyst concentration. Therefore, we introduce a scaled time $\tau = t/(R/C)$, proportional to the reaction time t multiplied by the catalyst concentration C. Figure 7 shows concentrations of total formaldehyde and resorcinol (in terms of C(2,4,6)) plotted as a function of the scaled time τ.

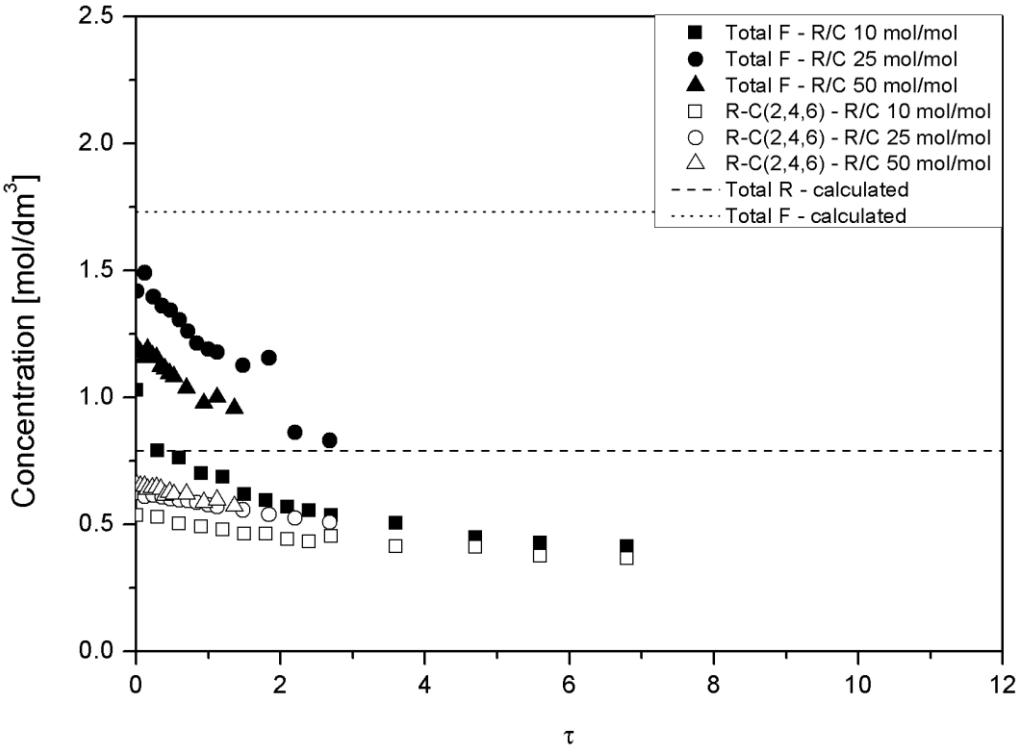
In all cases, we observed a significant drop in the concentration of the reactants within the first minutes of the reaction. As can be seen in Table 4, in every instance the measured concentrations of total unreacted formaldehyde and resorcinol were much lower than the theoretical concentrations in solution before reactions commenced. Since these were recorded within a few minutes from the moment the reactants were mixed, we refer to these differences as "initial drops". These drops amount to as much as 54% of the initial concentration of formaldehyde and up to 32% for resorcinol. This implies that the initial reaction between formaldehyde and resorcinol is, unexpectedly, very fast at room temperature. However, we note that it is not clear whether formaldehyde reacts as an aldehyde (which is present at very low concentrations in equilibrium with glycol species, see [30] and is then replenished via rapid glycol dehydration, or if it reacts as a glycol.

Table 4. Initial drops of total unreacted formaldehyde and resorcinol concentrations observed at room temperature.

R/F ratio [mol/mo]	0.33			0.50			1.00		
R/C ratio [mol/mol]	10	25	50	10	25	50	10	25	50
Total Resorcinol [mol/dm^3]	0.74	0.74	0.74	0.79	0.79	0.79	0.85	0.85	0.85
First datapoint [mol/dm^3]	0.58	0.52	0.66	0.54	0.62	0.66	0.72	0.78	0.82
Initial drop [mol/dm^3]	0.16	0.22	0.08	0.25	0.17	0.13	0.13	0.07	0.02
Total Formaldehyde [mol/dm^3]	2.45	2.45	2.45	1.73	1.73	1.73	0.93	0.93	0.93
First datapoint [mol/dm^3]	1.11	1.65	1.20	1.03	1.42	1.20	0.44	0.52	0.59
Initial drop [mol/dm^3]	1.34	0.80	1.25	0.70	0.31	0.53	0.48	0.40	0.34

After the initial drop, the concentration data appear to follow a uniform dependence on the scaled time, as expected for the catalysed process (assuming that the rate of reaction is first order in the catalyst concentration, which is certainly reasonable).


Concentration [mol/dm^3]
τ
Total F - R/C 10 mol/mol
Total F - R/C 25 mol/mol
Total F - R/C 50 mol/mol
R-C(2,4,6) - R/C 10 mol/mol
R-C(2,4,6) - R/C 25 mol/mol
R-C(2,4,6) - R/C 50 mol/mol
Total R - calculated
Total F - calculated


Concentration [mol/dm^3]
τ
Total F - R/C 10 mol/mol
Total F - R/C 25 mol/mol
Total F - R/C 50 mol/mol
R-C(2,4,6) - R/C 10 mol/mol
R-C(2,4,6) - R/C 25 mol/mol
R-C(2,4,6) - R/C 50 mol/mol
Total R - calculated
Total F - calculated

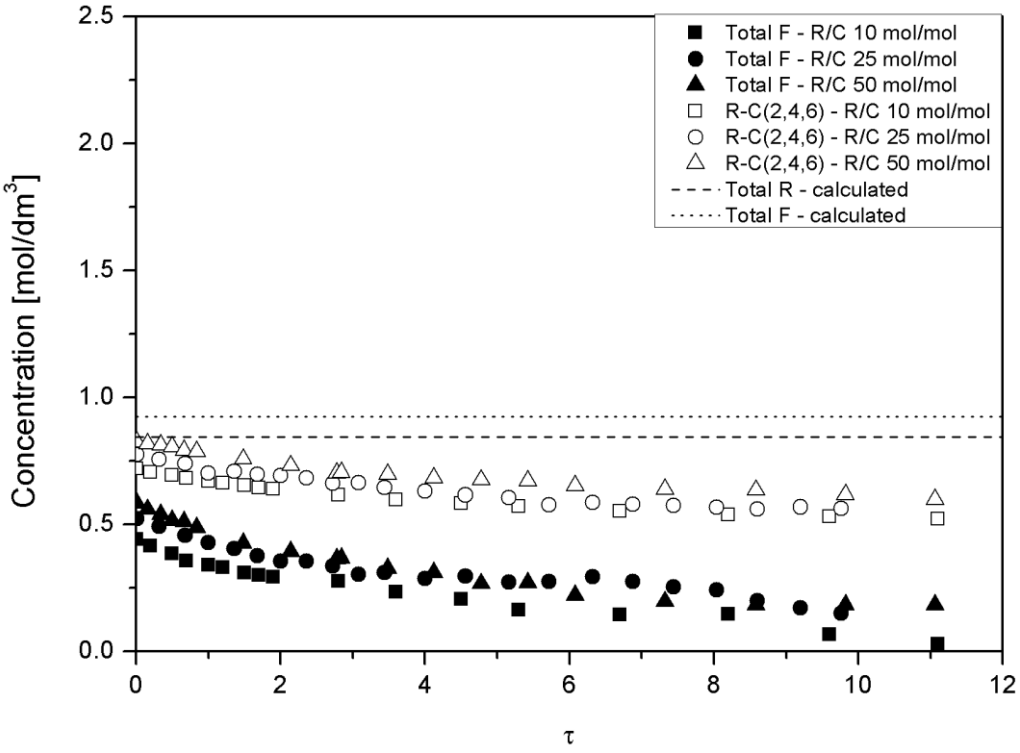


Figure 7. Molar concentrations of total formaldehyde (F) and resorcinol (R) (in terms of C(2,4,6) sites) plotted as a function of the scaled time τ during reaction at 20 °C (293K). The figure shows data for samples with R/F ratios (a) 0.33 mol·mol^{-1},(b) 0.5 mol·mol^{-1} and (c) 1.00 mol·mol^{-1}; R/W = 0.10 g·ml^{-1}.

These observations associated with the formaldehyde species are accompanied by related changes in the resorcinol concentrations. It is possible to identify two regions of data in terms of resorcinol signals: one is associated with C(5) and one with C(2,4,6). The first region contains signals from the proton attached to C(5) in both substituted and unsubstituted resorcinol molecules. The other region contains signals from protons attached to carbons 2, 4 and 6. It is obvious that if a resorcinol molecule is substituted with a formaldehyde-related molecule at e.g. C(2), then the signal from the proton which had been attached at this carbon atom will disappear. The peak is a sum of signals from all molecules present in the sample, those both substituted and unsubstituted at this position. The area of the peak should therefore only decrease rather than disappear completely. At the same time, the signal in the region corresponding to C(5) should not decrease, as protons in that position are not substituted with a hydroxymethyl group. Bearing in mind that the expected substitution due to the presence of two

hydroxyl groups at C(1) and C(3) is in positions C(2,4,6) one would expect the signals in the region related to protons attached to those carbon atoms to decrease in area, while those in the C(5) region should remain constant, and indeed this can be seen in Figure 8. The decrease is indeed small, varying between 5 and 10% with no clear relationship to the catalyst or the reactants concentrations.

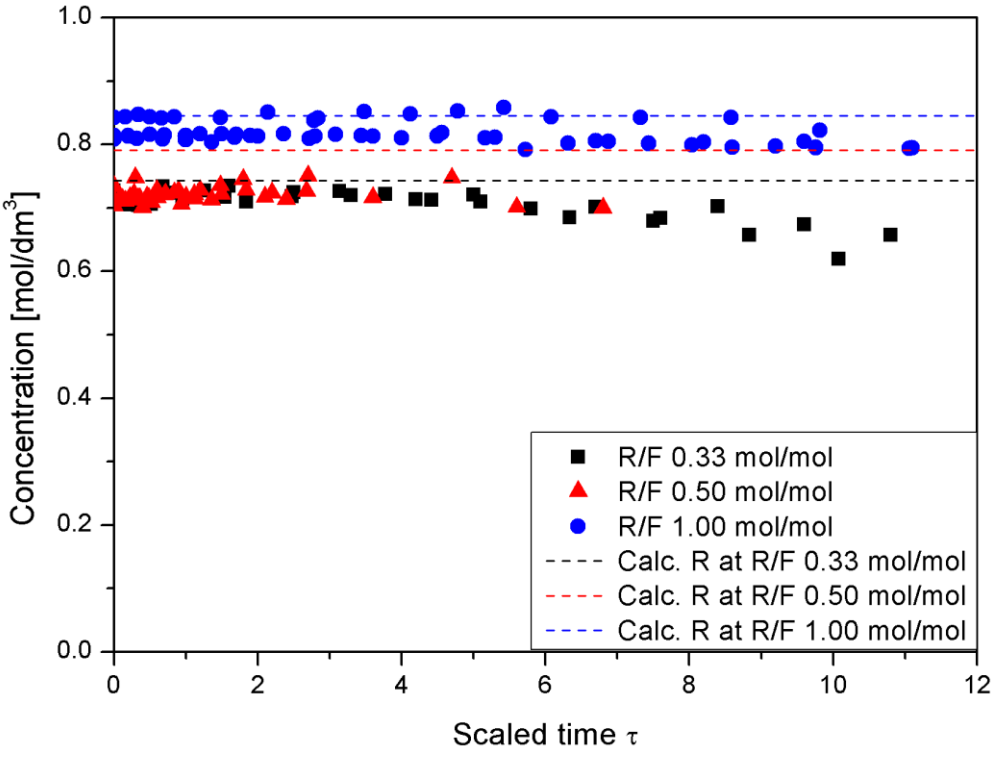


Figure 8. Evolution of resorcinol concentration in terms of R(C5)-H. Conditions: R/C 10, 25 or 50 mol·mol^{-1}, R/F as indicated, reaction carried out at 20°C (293K).

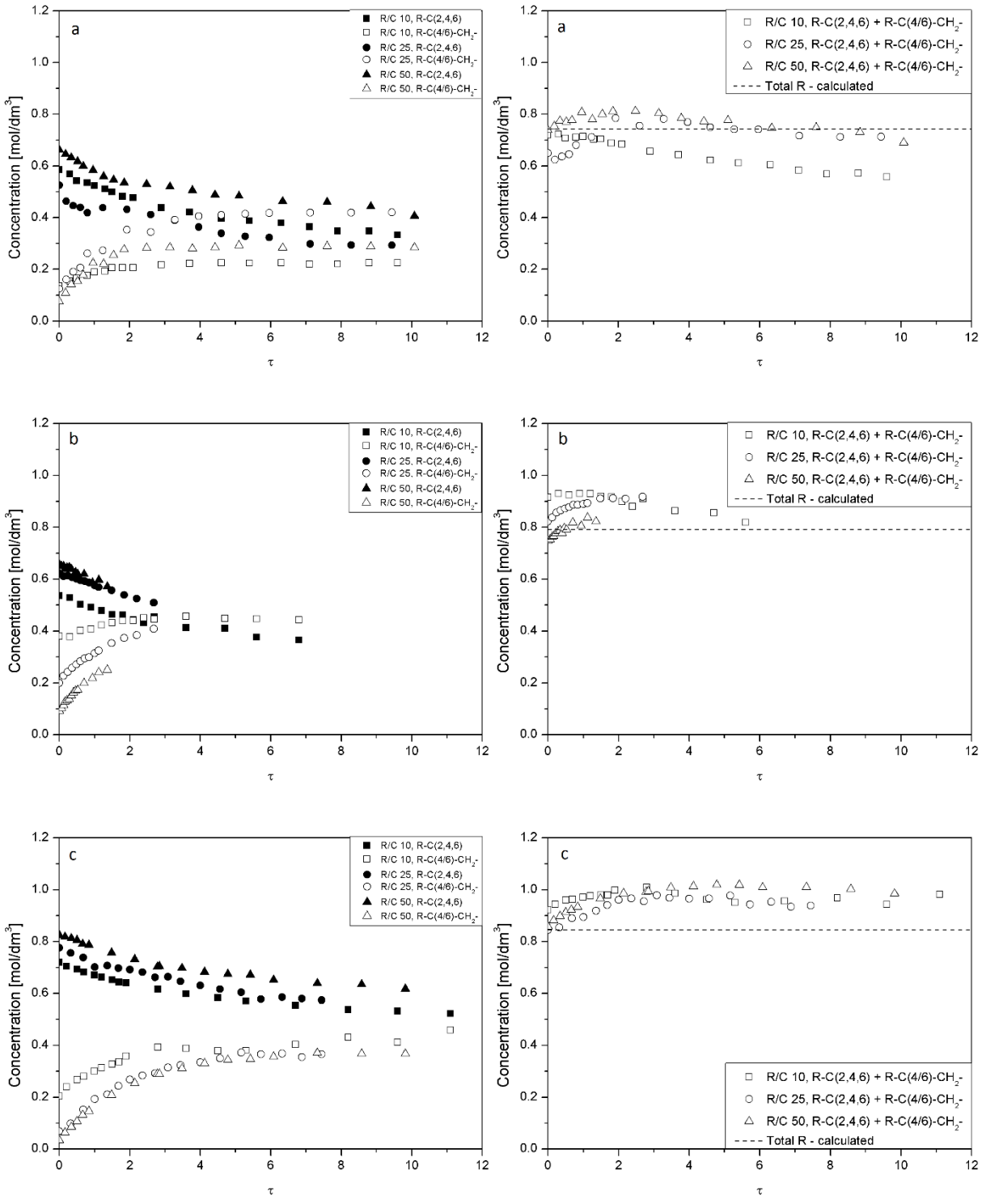


Figure 9. Scaled time evolution of concentration of (left) new product species with the corresponding resorcinol reactant concentrations (in terms of C(2,4,6)) and (right) total material balance of resorcinol as the sum of the unreacted resorcinol (C(2,4,6)) and the reacted resorcinol (hydroxymethyl derivatives, new species). Dashed line corresponds to the theoretical molar concentration of resorcinol

in the reacting mixture. The figure shows data for samples with R/F ratios (a) 0.33 $mol \cdot mol^{-1}$,(b) 0.5 $mol \cdot mol^{-1}$ and (c) 1.00 $mol \cdot mol^{-1}$; R/W = 0.10 $g \cdot ml^{-1}$.

In Figure 9 we show the total concentration of substituted hydroxymethyl sites together with unsubstituted resorcinol sites (on left) and their sum (on right). It is apparent from the data shown in Figure 9 that a substantial amount of substituted species was formed very rapidly after mixing of the reactants and further substitution was dramatically slower. Furthermore, substitution kinetics appeared to be slowing even further as the reaction progressed in line with expected 2nd order reaction kinetics and depletion of reactants.

There are several key points to be drawn based on the discussion of results above obtained by ^{1}H NMR monitoring of the reacting system at ambient temperature. The most significant observation is that within the first few minutes after the addition of formaldehyde into the resorcinol and sodium carbonate solution, the products of the reactions between formaldehyde and resorcinol are present with significant conversion (30-50%) of reactants. Moreover, 2D [^{1}H, ^{13}C] HSQC NMR experiments proved that there is more than just one type of hydroxymethyl derivative and that di-substituted species are present along with mono-substituted derivatives despite the lack of high temperature treatment. It is also clear that the concentrations of reactants further decrease gradually over time, proving that the reaction between formaldehyde and resorcinol does not require elevated temperatures. This is very important when considering the currently used gel preparation methods. Common gel synthesis methods call for approximately 30-60 min of mixing the reactants at room temperature and it has been generally assumed that this period of time is to ensure homogeneity of the mixture rather than to allow significant reaction progress. Often the time during which the sample is subject to heat treatment is referred to as the *reaction time*. This terminology seems to be inappropriate in view of these results. The manner and duration of mixing determines the concentration and the type of hydroxymethyl derivatives (mono- or di-substituted) as these result from competing second order reactions with apparently fast kinetics. Therefore mixtures which then undergo temperature treatment may have different concentrations and different patterns of resorcinol substitutions, which affects the

subsequent condensation and gel formation stages. The implications of this is that it should be possible to control the substitution reaction during the initial mixing stage, for example by gradual addition of formaldehyde to resorcinol solution in a fed batch manner. This should allow for better tailoring of the structure of resulting resorcinol-formaldehyde gels at a molecular level.

Conclusions

In this work we investigated the kinetics of reactions between resorcinol and formaldehyde in aqueous methanolic solutions in the presence of sodium carbonate at room temperature (293K). We monitored the resorcinol substitution reaction *in situ* using solution phase ^{1}H NMR over periods of time typically used for the mixing stage before heat treatment in resorcinol-formaldehyde polymerization.

We assigned all peaks present in both ^{1}H and ^{13}C NMR spectra of the reacting mixtures, using 2D [^{1}H, ^{13}C] HSQC NMR experiments. The latter ones proved formation of seven new signals which can be assigned to newly formed species, namely hydroxymethyl derivatives of resorcinol. These products include resorcinol singly and doubly substituted with -CH_2OH groups, as well as singly substituted resorcinol with a -CH_2OCH_2OH group, corresponding to addition of diglycol to resorcinol, though it is not possible to determine whether it was substitution with diglycol or monoglycol followed by condensation with another monoglycol molecule.

Experiments revealed that the concentrations of both formaldehyde and resorcinol decrease significantly within the first few minutes of the reaction followed by a gradual decrease over a more extended period of time. Surprisingly, this initial drop in reactant concentrations occurs at room temperature and it varies between 30 and 50% across all conditions investigated. This revealed that substitution of resorcinol with formaldehyde takes place nearly instantaneously following addition of formaldehyde to the resorcinol solution in the presence of sodium carbonate.

The main implication of this work is that it may open new hitherto overlooked possibilities to control the substitution of resorcinol with formaldehyde. As the substitution is rapid at room temperature, it could be performed by carefully controlled addition in a fed batch manner to achieve desired

distribution of singly, doubly or triply substituted resorcinol and possibly avoiding substitution with diglycol observed under typical mixing conditions. This would provide better controlled profile of reactants for subsequent polymerisation step and allow for better tailoring of the structure of resulting resorcinol-formaldehyde gels at a molecular level.

Abbreviations used

C – catalyst – sodium carbonate

F – formaldehyde

R – resorcinol

MG – monoglycol – HO-CH_2-OH [30]

DG – diglycol – HO-CH_2O-CH_2-OH [30]

MMG – methoxy monoglycol – HO-CH_2-OCH_3 [30]

FID – free induction decay

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