

# Homogeneous Methylation of Melamine: Mathematical Modeling

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**ABSTRACT:** A novel mathematical model is presented on the methylation of melamine with formaldehyde at 48°C and pH 9.0. The model assumes an instantaneous hydration/dehydration of formaldehyde and the methylation mechanism of Gordon et al. (J Appl Polym Sci 1966, 10, 1153). The 24 kinetic constants were adjusted to experimental measurements by Tomita (J Polym Sci 1977, 15, 2347). The model predicts the evolutions of the comono-

mers and the nine methylated species. This is the first article of a series that aims at developing a detailed model for the industrial synthesis of melamine–formaldehyde resins. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2978–2988, 2007

**Key words:** melamine–formaldehyde resin; polycondensation; mathematical model

## INTRODUCTION

Melamine–formaldehyde (MF) resins are water-soluble oligomers, obtained by methylation/condensation reactions between melamine (M) and formaldehyde (F). Cured at high temperatures and pressures, MF resins are used for producing molded materials, coatings, wood agglomerates, adhesives, and decorative laminates. In the case of decorative laminates, an external  $\alpha$ -cellulose paper is impregnated with the resin, dried, and transformed into a transparent final coating. Even though MF resins have been produced for over 100 years, it is surprising that there are still many unknowns in relation with their reaction kinetics and mathematical modeling.

MF resins are produced in batch stirred-tank reactors. First, M powder is added into formaline (a 37 wt % water solution of F), and the pH is adjusted to 9.0. Then, the mixture is heated up to 90°C, and the methylation/condensation takes place for around 2 h. During the initial heating up period of around 9 min, the temperature is increased from room temperature to around 80°C at 6–8°C/min; and the reaction is heterogeneous since M is scarcely soluble in formaline. The final reaction temperature is reached more slowly, in about seven more minutes. Since most of the methylations occur during the initial heating

up period, it is important to investigate such reactions at temperatures between 40 and 60°C.

The global methylation/condensation has been investigated in many opportunities.<sup>1–18</sup> First, the hydroxymethylation (or “methylation”) is represented by<sup>1,2</sup>



where  $-\text{H}$  is any reactive H of any amine group contained in M or its derived products. Then, a hydroxymethyl group can either react with another reactive H to produce a methylene bridge:



or it can react with another hydroxymethyl group to produce an ether bridge:



Gordon et al.<sup>19</sup> proposed the detailed methylation mechanism in Figure 1. Even though not shown in Figure 1, all forward reactions consume a  $\text{CH}_2\text{O}$  molecule, and all backward reactions regenerate such a molecule. Figure 1 also includes the nomenclature adopted in this work for representing M and each of its nine methylated species. Their main characteristics are presented in Table I. Tomita<sup>20</sup> carried out a series of dilute solution reactions to verify the mechanism of Figure 1. That article constitutes the basis of this work, and it is further reviewed in detail. This work is the first one of a series that aims

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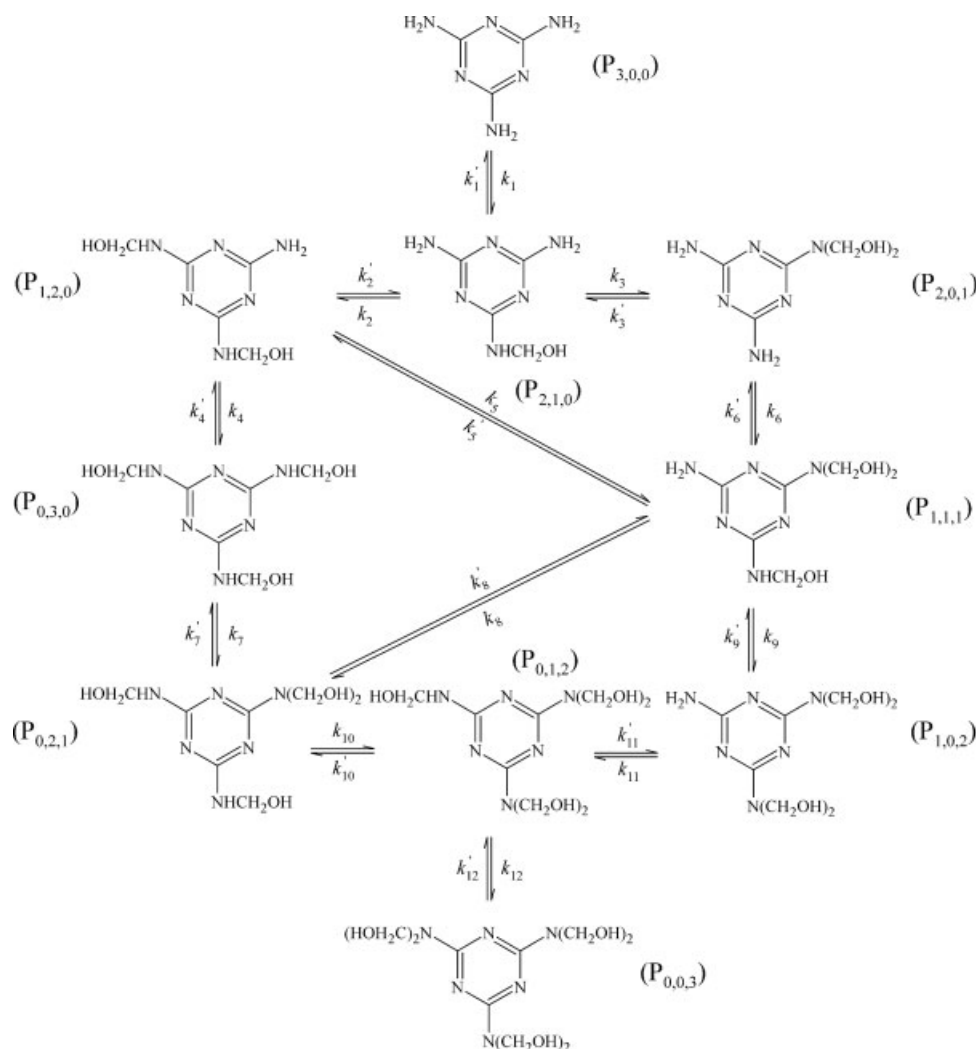


Figure 1 Mechanism for the methylation of melamine, after Gordon et al.<sup>19</sup>

at developing a representative mathematical model for the industrial production of MF resins. In this work, the condensation reactions of eqs. (2) and (3) are avoided by operating at a low temperature and in alkaline conditions.<sup>19,20</sup>

The solubility of M in water is relatively low (0.32 g/100 mL H<sub>2</sub>O at 20°C and 5 g/100 mL H<sub>2</sub>O at 100°C).<sup>21</sup> In this article, dilute M concentrations are imposed to ensure homogeneous conditions. Melamine only reacts with F ( $\equiv$ CH<sub>2</sub>O). However, in water solutions, F mainly exists as methylene glycol:<sup>22</sup>



where  $k_h$  and  $k_d$  are the F hydration and dehydration rate constants, respectively, and  $K_{\text{MG}}$  is the equilibrium constant. Although  $k_h$  depends on the tempera-

ture and pH,  $K_{\text{MG}}$  is only a function of the temperature (in K), as follows:<sup>23,24</sup>

$$k_h [\text{L/mol s}] = [1 + 870 \times 10^{-\text{pH}} + 6.3 \times 10^{(\text{pH}-8)}] e^{(8.962-1913/T)} \quad (5)$$

$$K_{\text{MG}} [\text{L/mol}] = e^{-2.325+2579/T} \quad (6)$$

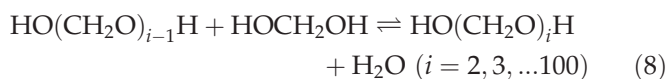
We define the total formaldehyde concentration  $[\text{F}_T]$  through

$$[\text{F}_T] = [\text{F}] + [\text{HOCH}_2\text{OH}] \quad (7)$$

In commercial (formaline) solutions at ambient temperature less than 0.1% of the total F is present as CH<sub>2</sub>O as a consequence of eqs. (4)–(6).<sup>22</sup> Methylene glycol partially polymerizes into poly(oximethylene glycol) or “paraformaldehyde” through<sup>22</sup>

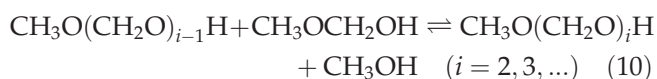
TABLE I  
Molecular Weights and Number of Reactive H's and Methylol Groups Per Molecule, for Melamine and Its Nine Derived Methylolmelamines (See Fig. 1)

$P_{A_0, A_1, A_2}$	$M_{P_{A_0, A_1, A_2}}$ (g/mol)	$f_H$ (No. H/molecule)	$f_{\text{meth}}$ (No. $-\text{CH}_2\text{OH}$ /molecule)
Melamine ( $P_{3,0,0}$ )	126	6	0
Monomethylolmelamine ( $P_{2,1,0}$ )	156	5	1
Dimethylolmelamines ( $P_{1,2,0}$ and $P_{2,0,1}$ )	186	4	2
Trimethylolmelamines ( $P_{0,3,0}$ and $P_{1,1,1}$ )	216	3	3
Tetramethylolmelamines ( $P_{0,2,1}$ and $P_{1,0,2}$ )	246	2	4
Pentamethylolmelamine ( $P_{0,1,2}$ )	276	1	5
Hexamethylolmelamine ( $P_{0,0,3}$ )	306	0	6



At increasing chain lengths, paraformaldehyde becomes increasingly insoluble in water.

Methanol is a typical impurity of F, since it is produced by oxidizing methanol. Furthermore, between 5 and 15% of methanol is sometimes intentionally added into formaline to generate water-soluble hemiformals as follows:<sup>22</sup>



The generation of hemiformals increases the solubility of glycols. This avoids the precipitation of paraformaldehyde by shifting the equilibrium of Eq. (8) toward the left.

In this theoretical work, a mathematical model is developed for the methylation of M in dilute solutions and in the absence of methanol, which is based on the kinetic scheme of Figure 1. The 24 associated kinetic constants were adjusted to the published measurements.<sup>20</sup>

#### Experiments by Tomita<sup>20</sup>

Considering the dilute methylation reactions at pH = 9.0 presented in Tomita,<sup>20</sup> the reactions were car-

TABLE II  
Recipes and Equilibrium Constants for the Methylation Reactions at 48°C and pH = 9.0 Described in Tomita<sup>20</sup>

	$[\text{F}_T]^\circ / [\text{M}]^\circ$						
	1	3	5	7	10	15	30
Recipes							
$[\text{F}_T]^\circ$ (mol/L)	0.0349	0.105	0.168	0.229	0.326	0.473	0.870
$[\text{M}]^\circ$ (mol/L)	0.0332	0.0328	0.0325	0.0322	0.0318	0.0311	0.0291
$[\text{H}_2\text{O}]$ (mol/L)	55.3	55.2	55.0	54.9	54.8	54.5	53.9
Equilibrium constants (L/mol) <sup>a</sup>							
$K_{1,T} = \frac{k_{1,T}}{k'_{1,T}} = \frac{[P_{2,1,0}]}{[P_{3,0,0}][\text{F}_T]}$	26	23	28				
$K_{2,T} = \frac{k_{2,T}}{k'_{2,T}} = \frac{[P_{1,2,0}]}{[P_{2,1,0}][\text{F}_T]}$	13	12	11				
$K_{3,T} = \frac{k_{3,T}}{k'_{3,T}} = \frac{[P_{2,0,1}]}{[P_{2,1,0}][\text{F}_T]}$		0.71	1.0				
$K_{4,T} = \frac{k_{4,T}}{k'_{4,T}} = \frac{[P_{0,3,0}]}{[P_{1,2,0}][\text{F}_T]}$		3.9	4.3	4.4	4.2	4.3	5.2
$K_{5,T} = \frac{k_{5,T}}{k'_{5,T}} = \frac{[P_{1,1,1}]}{[P_{1,2,0}][\text{F}_T]}$		1.8	1.8	2.0	1.7	1.8	1.7
$K_{6,T} = \frac{k_{6,T}}{k'_{6,T}} = \frac{[P_{1,1,1}]}{[P_{2,0,1}][\text{F}_T]}$		30	19				
$K_{7,T} = \frac{k_{7,T}}{k'_{7,T}} = \frac{[P_{0,2,1}]}{[P_{0,3,0}][\text{F}_T]}$			3.2	2.8	2.9	2.9	2.5
$K_{8,T} = \frac{k_{8,T}}{k'_{8,T}} = \frac{[P_{0,2,1}]}{[P_{1,1,1}][\text{F}_T]}$					0.52	0.40	0.48
$K_{9,T} = \frac{k_{9,T}}{k'_{9,T}} = \frac{[P_{1,0,2}]}{[P_{1,1,1}][\text{F}_T]}$					7.2	6.8	7.5
$K_{10,T} = \frac{k_{10,T}}{k'_{10,T}} = \frac{[P_{0,1,2}]}{[P_{0,2,1}][\text{F}_T]}$				1.2	1.3	1.4	1.4
$K_{11,T} = \frac{k_{11,T}}{k'_{11,T}} = \frac{[P_{0,1,2}]}{[P_{1,0,2}][\text{F}_T]}$					18	23	22
$K_{12,T} = \frac{k_{12,T}}{k'_{12,T}} = \frac{[P_{0,0,3}]}{[P_{0,1,2}][\text{F}_T]}$						0.74	0.54

<sup>a</sup> See reaction mechanism of Figure 1.

TABLE III  
Methylation Reactions at 48°C and pH = 9.0, with  $[F_T]^\circ/[M]^\circ = 1, 5, \text{ and } 30$ : Final Weight Fractions and Global Averages. The Measurements<sup>20</sup> Are in Bold Type and the New Model Predictions Are in Parentheses

Weight fractions of	$[F_T]^\circ/[M]^\circ = 1$	$[F_T]^\circ/[M]^\circ = 5$	$[F_T]^\circ/[M]^\circ = 30$
$P_{3,0,0}$	<b>0.614</b> (0.547)	<b>0.089</b> (0.0695)	( $1.14 \times 10^{-4}$ )
$P_{2,1,0}$	<b>0.31</b> (0.333)	<b>0.275</b> (0.221)	(0.00262)
$P_{1,2,0}$	<b>0.077</b> (0.0987)	<b>0.33</b> (0.346)	<b>0.042</b> (0.0295)
$P_{2,0,1}$	(0.00688)	<b>0.031</b> (0.0239)	(0.00204)
$P_{0,3,0}$	(0.00995)	<b>0.156</b> (0.184)	<b>0.163</b> (0.112)
$P_{1,1,1}$	(0.00403)	<b>0.065</b> (0.0740)	<b>0.054</b> (0.0462)
$P_{0,2,1}$	( $6.69 \times 10^{-4}$ )	<b>0.055</b> (0.0652)	<b>0.30</b> (0.287)
$P_{1,0,2}$	( $4.13 \times 10^{-5}$ )	(0.0041)	<b>0.019</b> (0.0201)
$P_{0,1,2}$	( $2.00 \times 10^{-5}$ )	(0.0103)	<b>0.302</b> (0.329)
$P_{0,0,3}$	( $2.70 \times 10^{-7}$ )	( $7.36 \times 10^{-4}$ )	<b>0.119</b> (0.171)
$\bar{M}_n$ (g/mol)	<b>140</b> (141)	<b>182</b> (182)	<b>253</b> (255)
$\bar{M}_w$ (g/mol)	<b>143</b> (143)	<b>187</b> (187)	<b>257</b> (258)
$\bar{f}_{\text{met}}$ (No. $-\text{CH}_2\text{OH}$ /molecule)	<b>0.47</b> (0.49)	<b>1.88</b> (1.88)	<b>4.24</b> (4.30)
$f_H$ (No. H/molecule)	<b>5.53</b> (5.51)	<b>4.12</b> (4.12)	<b>1.76</b> (1.70)
$[F_T]$ (mol/L)	<b>0.0197<sup>a</sup></b> (0.0203)	<b>0.109<sup>a</sup></b> (0.103)	<b>0.742<sup>a</sup></b> (0.746)
$[-\text{NH}_2]$ (mol/L)	<b>0.0843</b> (0.0837)	<b>0.0424</b> (0.0394)	<b>0.0034</b> (0.00379)
$[-\text{NHCH}_2\text{OH}]$ (mol/L)	<b>0.0155</b> (0.0157)	<b>0.0525</b> (0.0526)	<b>0.0443</b> (0.0417)
$[-\text{N}(\text{CH}_2\text{OH})_2]$ (mol/L)	( $2.75 \times 10^{-4}$ )	<b>0.0050</b> (0.00555)	<b>0.0396</b> (0.0415)
$[-\text{H}]$ (mol/L)	<b>0.184</b> (0.183)	<b>0.137</b> (0.131)	<b>0.0511</b> (0.0493)
$[-\text{CH}_2\text{OH}]$ (mol/L)	<b>0.0155</b> (0.0162)	<b>0.0625</b> (0.0637)	<b>0.124</b> (0.125)

<sup>a</sup> Average value.

ried out at three relatively low temperatures (28, 38, and 48°C), and with seven initial comonomer ratios ( $[F_T]^\circ/[M]^\circ = 1, 3, 5, 7, 10, 15, \text{ and } 30$ ). The recipes of the 48°C experiments are listed in Table II. The F solution was prepared by heating commercial para-formaldehyde between 140 and 160°C under nitrogen, and absorbing the produced gas in cool water. The solution was filtered and diluted, yielding a final concentration of 19.8% w/w (as determined by iodometry<sup>22</sup>), and a molar fraction of methanol impurity with respect to F lower than 0.5% (as determined by NMR). Melamine was purified through a series of recrystallization-drying operations. For the 48°C reactions, the equilibrium concentrations were obtained after 4 or 5 h of reaction time. The concen-

trations of unreacted comonomers and of generated methylolmelamines were determined by reverse-phase HPLC. The chromatograph was fitted with a differential refractometer and a  $\mu$ Bondapak C18 column. The carrier solvent was distilled water for the low-substituted methylolmelamines, and a 5% v/v solution of methanol in water for the highly substituted methylolmelamines. The total formaldehyde  $[F_T]$  in eq. (7) was not adsorbed by the column packing, and it was eluted first. The peak assignments were carried out by NMR. The quantitative analysis was based on the peak areas.

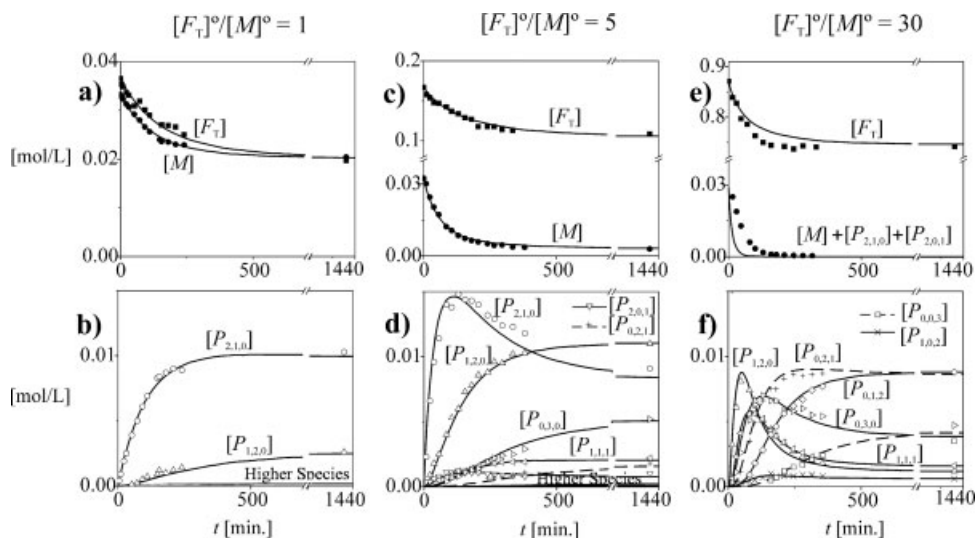
For the reactions at 48°C and pH 9.0, the final results<sup>20</sup> are reproduced in Tables II–IV and Figure 2. The final concentrations and equilibrium constants

TABLE IV  
Kinetic Constants (at  $T = 48^\circ\text{C}$  and  $\text{pH} = 9.0$ ) Proposed by Tomita<sup>20</sup> and Proposed in This Work

Reaction	Tomita <sup>20</sup>		This work		
	$k_{i,T}$ (L/mols)	$k'_{i,T}$ ( $\text{s}^{-1}$ )	$k_{i,Tc}^a$ (L/mols)	$k_i^b$ (L/mols)	$k_i^b$ ( $\text{s}^{-1}$ )
1	0.00147	0.00006	24.25	24.25	0.000067
2	0.00183	0.00015	30.31	9.37	0.000057
3	0.00058	0.00068	9.64	4.00	0.000281
4	0.000833	0.00019	13.78	5.79	0.000080
5	–	–	–	3.44	0.000119
6	–	–	–	21.19	0.000052
7	–	–	–	3.94	0.000084
8	–	–	–	3.64	0.000475
9	–	–	–	0.96	0.000008
10	0.00038	0.00029	6.34	3.80	0.000174
11	–	–	–	2.84	0.000008
12	0.00017	0.00026	2.73	1.23	0.000117

<sup>a</sup> Corrected  $k_{i,T}$  constants with eq. (15).

<sup>b</sup> Final set of constants, after a simultaneous readjustment with eq. (16).



**Figure 2** Investigated methylation reactions at 48°C, pH = 9.0, with  $[F_T]^\circ/[M]^\circ = 1$  (a,b);  $[F_T]^\circ/[M]^\circ = 5$  (c,d); and  $[F_T]^\circ/[M]^\circ = 30$  (e,f). (a, c, e) Comonomers concentrations. (b, d, f) Methylolated species concentrations. The measurements were reproduced from Tomita,<sup>20</sup> and are indicated by the following symbols  $\circ$ :  $[P_{2,1,0}]$ ,  $\triangle$ :  $[P_{1,2,0}]$ ,  $\nabla$ :  $[P_{2,0,1}]$ ,  $\triangleright$ :  $[P_{0,3,0}]$ ,  $\triangleleft$ :  $[P_{1,1,1}]$ ,  $+$ :  $[P_{0,2,1}]$ ,  $\times$ :  $[P_{1,0,2}]$ ,  $\diamond$ :  $[P_{0,1,2}]$ ,  $\square$ :  $[P_{0,0,3}]$ . The curves are the new model predictions.

were presented for all the investigated reactions. However, the time evolutions of reagents and products were only given for the experiments with  $[F_T]^\circ/[M]^\circ = 1, 5,$  and  $30$  (Fig. 2). In the experiment with  $[F_T]^\circ/[M]^\circ = 1$ , only the first two methylolmelamines were isolated [Fig. 2(b)]. In the experiment with  $[F_T]^\circ/[M]^\circ = 5$ , the first six methylolmelamines were isolated [Fig. 2(d)]. In the experiment with  $[F_T]^\circ/[M]^\circ = 30$ , only the last seven methylolmelamines were isolated [Fig. 2(f)]. In addition to the article information,<sup>20</sup> the following measurements were kindly provided to us by Prof. Tomita in a private communication: (a) total F concentration for the reactions with  $[F_T]^\circ/[M]^\circ = 1$  and  $5$  [Fig. 2(a,c)]; and (b) the global concentrations of M,  $P_{2,1,0}$ , and  $P_{2,0,1}$  for the reaction with  $[F_T]^\circ/[M]^\circ = 30$  [Fig. 2(e)].

Considering the equilibrium constants of Table II, in their definitions, the total F concentrations (rather than [F]) were employed. For the experiments with  $[F_T]^\circ/[M]^\circ = 1, 5,$  and  $30$ , Table III presents the final concentration measurements of M and the nine methylolated derivatives (in bold type). By assuming simplified mass balances that neglected the (undetected) contributions by the higher methylolated species, the measurements of Figure 2 were employed by Tomita for adjusting 12 (out of the 24) kinetic constants  $k_{i,T}$  and  $k'_{i,T}$ . The resulting values are presented in Table IV.<sup>20</sup>

### Mathematical model

The mass balances were developed on the basis of the kinetic scheme given in Figure 1 together with the F

hydration reaction of eq. (4). In Figure 1 and Table I, any ringed molecule is represented by  $P_{A_0,A_1,A_2}$ , where  $A_0, A_1,$  and  $A_2$  are, respectively, the number of unreacted amines  $-\text{NH}_2$ ; of generated monohydroxymethylamine groups (or primary methylols)  $-\text{NH}(\text{CH}_2\text{OH})$ ; and of dihydroxymethylamine groups (or secondary methylols)  $-\text{N}(\text{CH}_2\text{OH})_2$ .

The hydration/dehydration reactions of eq. (4) are considerably faster than the methylation/demethylation reactions of Figure 1; and for this reason, the former reactions were assumed instantaneous. In this case, the mass balance for methylene glycol can be written as

$$\frac{d[\text{HOCH}_2\text{OH}]}{dt} = k_h[\text{H}_2\text{O}][\text{F}] - k_d[\text{HOCH}_2\text{OH}] \cong 0 \quad (11)$$

and therefore

$$[\text{HOCH}_2\text{OH}] = \frac{k_h}{k_d} [\text{F}][\text{H}_2\text{O}] = K_{\text{MG}}[\text{F}][\text{H}_2\text{O}] \quad (12)$$

Equations (7) and (12) produce

$$[F_T] = [\text{F}](1 + K_{\text{MG}}[\text{H}_2\text{O}]) \quad (13)$$

To take into account that the reactive species is F rather than F, eq. (13) suggests that the original  $k_{i,T}$  equilibrium constants of Table II and  $k_{i,T}$  forward constants of Table IV can be corrected as follows:

$$K_{i,Tc} \equiv K_{i,T}(1 + K_{\text{MG}}[\text{H}_2\text{O}]) \quad (i = 1, 2, \dots, 12) \quad (14)$$

TABLE V  
Readjusted Equilibrium Constants (at 48°C and pH = 9.0)

Reaction no.	$K_{i,Tc}^a$ (L/mol)							$\bar{K}_{i,Tc}^b$ (L/mol)	$K_i^c$ (L/mol)
	$[F_T]^\circ/[M]^\circ$								
	1	3	5	7	10	15	30		
1	433464	382658	464975					427032	427032
2	216732	199647	182669					199683	199683
3		11812	16606					14209	14209
4		64885	71407	72935	69419	70760	84555	72327	72327
5		29947	29891	33152	28098	29621	27643	29725	29725
6		499119	315519					407319	407319
7			53140	46413	47932	47722	40651	47172	47172
8					119004	111900	121954	117619	117619
9					8595	6582	7805	7661	7661
10				19890	21485	23037	22763	21794	21794
11					297509	378485	357731	258431	334874
12						12177	8781	10479	10479

<sup>a</sup> Corrected  $K_{i,T}$  constants of Table II through eq. (14).

<sup>b</sup> Average  $K_{i,Tc}$  values.

<sup>c</sup> Equilibrium constants adopted in this work.

$$k_{i,Tc} \equiv k_{i,T}(1 + K_{MG}[H_2O]) \quad (i = 1, 2, \dots, 12) \quad (15)$$

where  $k_{i,Tc}$  and  $k_{i,T}$  are the corrected Tomita<sup>20</sup> constants. At 48°C, it is  $K_{MG} = 301.65$  L/mol [Eq. (6)], and therefore  $(1 + K_{MG}[H_2O]) \cong 1.6 \times 10^4$ . The corrected Tomita constants are presented in the fourth column of Table IV, and in columns 2–8 of Table V.

At  $T = 48^\circ\text{C}$  and  $\text{pH} = 9.0$ , the hydration/dehydration constants of F result  $k_h = 1289$  L/(mol s) and  $k_d = k_h/K_{MG} = 4.272$  s<sup>-1</sup> [eqs. (5) and (6)]. The value of  $k_h$  is much larger than  $k_d$  or any of the  $k_{i,Tc}$  values of Table IV; thus justifying the instantaneous hydration/dehydration assumption.

The mathematical model is developed in the Appendix section. It calculates the molar concentration balances of the reagents (M, F, methylene glycol,  $F_T$ , and water) [eqs. (A1)–(A4) and (A14)], and of the nine generated methylolmelamines [eqs. (A5)–(A13)]. The reaction volume was assumed constant, as a consequence of the dilute solution conditions. The following variables were also calculated: number- and weight-average molecular weights of all ringed molecules including M [eqs. (A15) and (A16)]; number average of unreacted hydrogens per ringed molecule  $\bar{f}_H$  [eq. (A17)]; number average of generated methylol groups per ringed molecule  $\bar{f}_{\text{meth}}$  [eq. (A18)]; and global concentrations of amines, hydrogens, mono-, and dihydroxymethylamine groups [eqs. (A19)–(A23)]. The differential eqs. (A1), (A4)–(A14), and (13) were solved by applying a finite differences procedure with time increments of 1 s. The computer program was written in Fortran Power Station. A typical simulation run involved a few seconds in a Pentium 3 PC.

#### Parameter adjustment

The model parameters included the 24 rate constants of Figure 1 and the equilibrium constant of F ( $K_{MG} = 301.65$  L/mol). The final set of rate constants is presented in the last two columns of Table IV. It was adjusted with a two-stage procedure. In the first stage, the equilibrium constants were adjusted to fit the equilibrium measurements of the upper half of Table III. In the second stage, the rate constants were adjusted to fit the time-evolution measurements of Figure 2; except for the global measurements of  $[M] + [P_{2,1,0}] + [P_{2,0,1}]$  in Figure 2(e).

Considering the equilibrium constants adjustment, first, the corrected equilibrium constants  $k_{i,Tc}$  (columns 2–8 of Table V) were averaged, yielding the  $\bar{K}_{i,Tc}$  values of the penultimate column of Table V. Under equilibrium conditions, the generation of hexamethylolmelamine  $P_{0,0,3}$  from the initial monomethylolmelamine  $P_{2,1,0}$  is independent of the reaction path, and therefore the equilibrium constant products  $(K_2 \cdot K_4 \cdot K_7 \cdot K_{10} \cdot K_{12})$ ,  $(K_3 \cdot K_6 \cdot K_8 \cdot K_{10} \cdot K_{12})$ ,  $(K_2 \cdot K_5 \cdot K_8 \cdot K_{10} \cdot K_{12})$ ,  $(K_3 \cdot K_6 \cdot K_9 \cdot K_{11} \cdot K_{12})$ , and  $(K_2 \cdot K_5 \cdot K_9 \cdot K_{11} \cdot K_{12})$  should all coincide. When replacing the  $\bar{K}_{i,Tc}$  values of Table V, its results  $(\bar{K}_{2,Tc} \cdot \bar{K}_{4,Tc} \cdot \bar{K}_{7,Tc} \cdot \bar{K}_{10,Tc} \cdot \bar{K}_{12,Tc}) = (\bar{K}_{3,Tc} \cdot \bar{K}_{6,Tc} \cdot \bar{K}_{8,Tc} \cdot \bar{K}_{10,Tc} \cdot \bar{K}_{12,Tc}) = (\bar{K}_{2,Tc} \cdot \bar{K}_{5,Tc} \cdot \bar{K}_{8,Tc} \cdot \bar{K}_{10,Tc} \cdot \bar{K}_{12,Tc}) = 1.6 \times 10^{23}$ ; but  $(\bar{K}_{3,Tc} \cdot \bar{K}_{6,Tc} \cdot \bar{K}_{9,Tc} \cdot \bar{K}_{11,Tc} \cdot \bar{K}_{12,Tc}) = (\bar{K}_{2,Tc} \cdot \bar{K}_{5,Tc} \cdot \bar{K}_{9,Tc} \cdot \bar{K}_{11,Tc} \cdot \bar{K}_{12,Tc}) = 1.2 \times 10^{23}$ . The last two products were forced to reproduce the initial value of  $1.6 \times 10^{23}$  by readjusting  $\bar{K}_{11,Tc}$  as follows:

$$K_{11} = \frac{1.6 \times 10^{23}}{\bar{K}_{2,Tc} \cdot \bar{K}_{5,Tc} \cdot \bar{K}_{9,Tc} \cdot \bar{K}_{12,Tc}} = 334,874 \text{ L/mol}$$

The final set of equilibrium constants is in the last column of Table V.

Considering the iterative adjustment employed for estimating the 24 rate constants, in all cases, the backward constants were calculated from their corresponding forward and equilibrium constants through  $k'_i = k_i/K_i$ . The initial conditions were determined as follows: (a)  $k_1$  and  $k_2$  were first adjusted to the measurements of experiment  $[F_T]^\circ/[M]^\circ = 1$ , and then readjusted to experiments  $[F_T]^\circ/[M]^\circ = 1$  and 5; (b)  $k_3, k_4, k_5, k_6, k_7$ , and  $k_8$  were adjusted to the measurements of experiment  $[F_T]^\circ/[M]^\circ = 5$ ; and (c)  $k_9, k_{10}, k_{11}$ , and  $k_{12}$  were adjusted to the measurements of experiment  $[F_T]^\circ/[M]^\circ = 30$ . The resulting set of constants was used to initialize the following minimization procedure (that simultaneously readjusted the complete set of rate constants):

$$\min_{k_i (i=1, \dots, 12)} E = \sum_{j=1}^{11} E_j; \text{ with } E_j = \frac{1}{n_j} \sum_{\forall t_i} ([j(t_i)]_{\text{exp}} - [j(t_i)]_{\text{sim}})^2 / [j(t_i)]_{\text{exp}}^2 \quad (16)$$

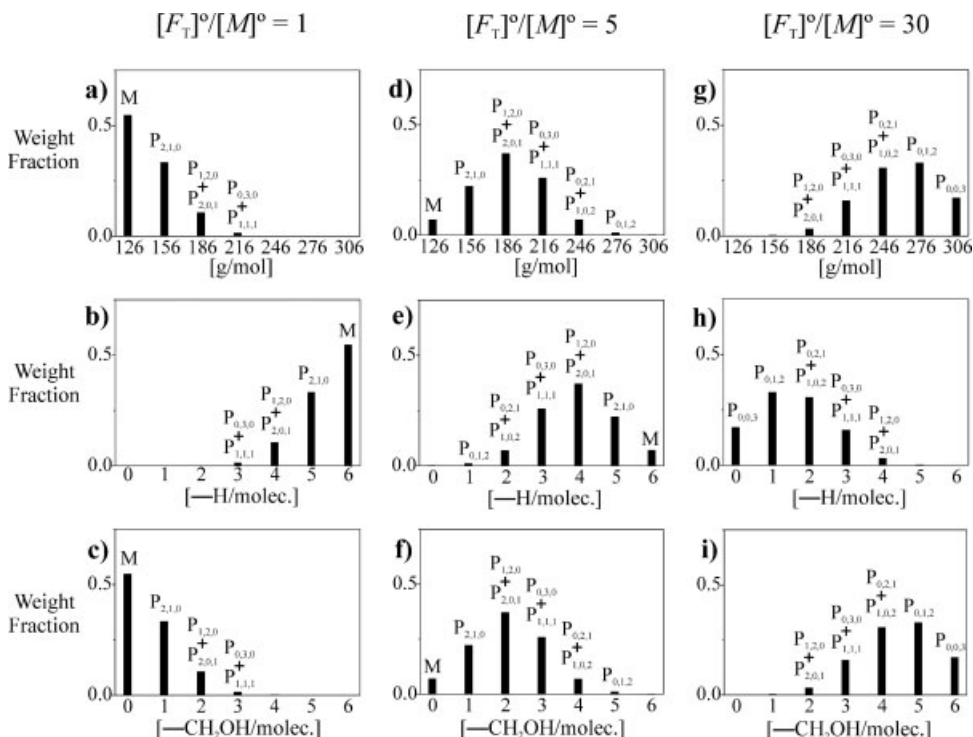
where  $E$  is the total scalar error;  $E_j$  with  $j = 1, \dots, 11$  is the average concentration error for each of the reacting species represented by  $F_T$ ,  $M$ , and the nine methylolmelamines;  $[j(t_i)]_{\text{exp}}$  and  $[j(t_i)]_{\text{sim}}$  are the measured and predicted concentrations of species  $j$

at the discrete measurement times  $t_i$  of Figure 2; and  $n_j$  is the total number of measurements of species  $j$ .

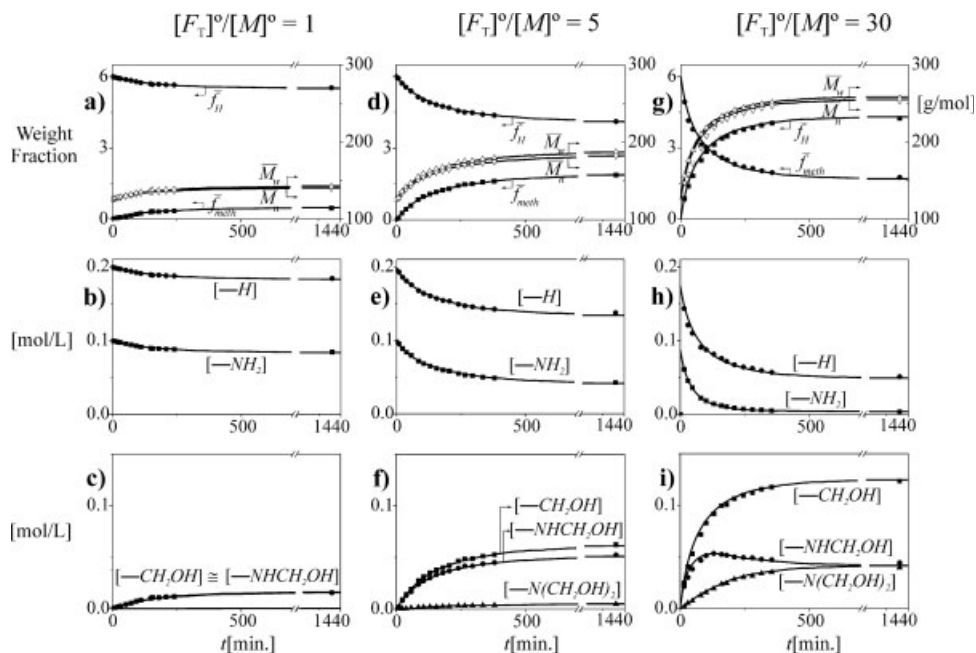
The resulting final set of forward rate constants (penultimate column of Table IV) are several orders of magnitude higher than the available original estimations by Tomita<sup>20</sup> (second column of the same table); due to having replaced the concentrations of  $F_T$  for the (much lower) concentrations of  $F$ . In contrast, the new backward rate constants  $k'_i$  (last column of Table IV) almost coincide with the available rate constants by Tomita<sup>20</sup> (third column of Table IV). Comparing the existing values of  $k_{i,Tc}$  with the corresponding  $k_i$  values (Table IV), both the values are almost coincident for the reaction no. 1, it is  $k_{i,Tc} > k_i$  for reaction nos. 2, 3, 4, 10, and 12. This is a consequence of the fact that the partial adjustments by Tomita<sup>20</sup> did not include the complete set of measurements. Finally, note the large differences between the new forward and backward rate constants  $k_i$  and  $k'_i$ , compared with the more similar values of  $k_{i,T}$  and  $k'_{i,T}$ .<sup>20</sup> The new much lower values of  $k'_i$  with respect to  $k_i$  reduce the correlation between such adjustable parameters, and therefore simplify the numerical resolution.

Simulation results and derived global variables

Table III presents the simulation results for the final equilibrium concentrations, and Figure 2 presents



**Figure 3** Final model predictions for the methylolations at 48°C and pH = 9.0, with  $[F_T]^\circ/[M]^\circ = 1$  (a–c);  $[F_T]^\circ/[M]^\circ = 5$  (d–f); and  $[F_T]^\circ/[M]^\circ = 30$  (g–i). (a, d, g) Molecular weight distributions. (b, e, h) Distributions of H functionalities. (c, f, i) Distributions of methylol functionalities.



**Figure 4** Derived global measurements (in symbols) and model predictions (in continuous curves) for the methylation reactions at 48°C, pH = 9.0, with  $[F_T]^\circ/[M]^\circ = 1$  (a–c);  $[F_T]^\circ/[M]^\circ = 5$  (d–f); and  $[F_T]^\circ/[M]^\circ = 30$  (g–i). (a, d, g) Average molecular weights and average H and methylol functionalities. (b, e, h) Concentrations of total amine groups and hydrogens. (c, f, i) Concentrations of total monohydroxymethylamine, dihydroxymethylamine, and methylol groups.

the dynamic evolutions of reagents and products. A reasonable agreement between measurements and model predictions is observed. The evolutions of  $[\text{HOCH}_2\text{OH}]$  are not presented in the simulation results because they practically coincide with those of  $[F_T]$  in Figure 2(a,c,e).

Figure 3 shows the model predictions for the final (equilibrium) distributions of molecular weights, hydrogen functionalities, and methylol functionalities. Note that the two latter distributions are mirror images of each other.

From the measurements of Figure 2, it is possible to estimate the following derived global measurements: (a) average molecular weights, and average functionalities of H's and methylols through eqs. (A15)–(A18); and (b) global concentrations of unreacted amines, and hydrogens, and of generated monohydroxymethylamines, dihydroxymethylamines, and total methylols through eqs. (A19)–(A23). For the experiment  $[F_T]^\circ/[M]^\circ = 30$ , the individual measurements of  $[M]$ ,  $[P_{2,1,0}]$ , and  $[P_{2,0,1}]$  were not available [Fig. 2(e)], and therefore eqs. (A15)–(A23) could not be directly applied. This problem was overcome with the help of the mathematical model, which provided the fractional contributions of such species toward the total concentration measurements.

The resulting set of derived global measurements is compared with their corresponding theoretical

predictions in Figure 4 and in the lower half of Table III. Again, a very reasonable agreement is observed. As expected, for increasing the  $[F_T]^\circ/[M]^\circ$  ratios, the average molar masses and methylol functionalities steadily increase, while the average H functionality steadily decreases [Fig. 4(a,d,g)]. In addition, the global concentrations of unreacted H and amines steadily decrease [Fig. 4(b,e,h)], while the global concentrations of dihydroxymethylamine, and total methylols steadily increase [Fig. 4(c,f,i)]. Note that the secondary methylols are generated from primary methylols, and for this reason the concentration of primary methylols  $[-\text{NHCH}_2\text{OH}]$  exhibits an increase as shown in Figure 4(i).

## CONCLUSIONS

A new mathematical model was developed for the methylation of M at low temperatures (48°C) and in alkaline conditions (pH 9.0). The model calculates the evolution of reagents and products, and the distributions of molecular weights and functionalities of the ringed molecules.

The kinetic constants were simultaneously adjusted to measurements from the literature.<sup>20</sup> The 12 forward (methylation) constants differed from those originally proposed by Tomita,<sup>20</sup> as a conse-



quence of the relatively low concentration of the truly reactive species (CH<sub>2</sub>O). Unlike Tomita,<sup>20</sup> the forward constants are much larger than the corresponding backward constants. This reduces the correlation between the adjustable parameters, thus simplifying their numerical resolution. The resulting set of parameters is operative for producing a representative mathematical model that can be useful for the optimization and control purposes. However, the resulting kinetic parameters are not necessarily accurate from the chemical point of view, and new improved experiments would be necessary for increasing their accuracy.

In future communications, novel experimental and theoretical investigations on the methylation of M with incipient condensation will be reported.

### NOMENCLATURE

Symbols	Definitions
F	Free formaldehyde (CH <sub>2</sub> O)
F <sub>T</sub>	Total formaldehyde [see eq. (7)]
f <sub>H</sub>	H functionality (number of unreacted hydrogens per ringed molecule)
$\bar{f}_H$	Number-average H functionality
f <sub>met</sub>	Methylol functionality (number of methylols per ringed molecule)
$\bar{f}_{\text{meth}}$	Number-average methylol functionality
k <sub>h</sub>	Rate constant of F hydration (L/mol s <sup>-1</sup> )
k <sub>d</sub>	Rate constant of F dehydration (s <sup>-1</sup> )
k <sub>i,T</sub> (i = 1, 2, ... 12)	Methylation rate constants according to Tomita <sup>20</sup> (L/mol s <sup>-1</sup> )
k <sub>i,Tc</sub> (i = 1, 2, ... 12)	Methylation rate constants after correction through eq. (15) (L/mol s <sup>-1</sup> )
k <sub>i</sub> (i = 1, 2, ... 12)	Methylation rate constants adopted in this work (L/mol s <sup>-1</sup> )
k' <sub>i,T</sub> (i = 1, 2, ... 12)	Demethylation rate constants according to Tomita <sup>20</sup> (s <sup>-1</sup> )
k' <sub>i</sub> (i = 1, 2, ... 12)	Demethylation rate constants adopted in this work (s <sup>-1</sup> )
K <sub>MG</sub>	Equilibrium constant for the hydration/dehydration of F (L/mol)
K <sub>i,T</sub> (i = 1, 2, ... 12)	Equilibrium constants according to Tomita <sup>20</sup> (L/mol)
K <sub>i,Tc</sub> (i = 1, 2, ... 12)	Equilibrium constants after correction through eq. (14) (L/mol)

K <sub>i</sub> (i = 1, 2, ... 12)	Equilibrium constants adopted in this work (L/mol)
M	Melamine (≡ P <sub>3,0,0</sub> )
M <sub>P<sub>A<sub>0</sub>,A<sub>1</sub>,A<sub>2</sub></sub></sub>	Molecular weight of P <sub>A<sub>0</sub>,A<sub>1</sub>,A<sub>2</sub></sub> (g/mol)
$\bar{M}_n, \bar{M}_w$	Number- and weight-average molecular weights of P <sub>A<sub>0</sub>,A<sub>1</sub>,A<sub>2</sub></sub> (g/mol)
P <sub>A<sub>0</sub>,A<sub>1</sub>,A<sub>2</sub></sub>	Any ringed molecule (including M itself), with A <sub>0</sub> unreacted amino groups, A <sub>1</sub> monohydroxymethylamino groups, and A <sub>2</sub> dihydroxymethylamino groups.
t	Time (s)
T	Temperature (°C)
[ ]	Molar concentration (mol/L)

### Superscripts

0	Initial condition
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Authors thank Prof. B. Tomita for kindly providing us with additional measurements not included in Ref. 20.

### APPENDIX: MATHEMATICAL MODEL FOR THE METHYLATION OF MELAMINE

From the kinetic mechanism of Figure 1 and the hydration/dehydration equilibrium of eq. (4), the following mass balances were written for the reagents and products:

$$\frac{d[P_{3,0,0}]}{dt} = -k_1[P_{3,0,0}][F] + k'_1[P_{2,1,0}] \quad (\text{A.1})$$

$$\begin{aligned} \frac{d[F]}{dt} = & k_d[\text{HOCH}_2\text{OH}] + k'_1[P_{2,1,0}] + k'_2[P_{1,2,0}] + k'_3[P_{2,0,1}] \\ & + k'_4[P_{0,3,0}] + k'_5[P_{1,1,1}] + k'_6[P_{1,1,1}] + k'_7[P_{0,2,1}] \\ & + k'_8[P_{0,2,1}] + k'_9[P_{1,0,2}] + k'_{10}[P_{0,1,2}] + k'_{11}[P_{0,1,2}] \\ & + k'_{12}[P_{0,0,3}] - \{k_h[\text{H}_2\text{O}] + k_1[M] + k_2[P_{2,1,0}] \\ & + k_3[P_{2,1,0}] + k_4[P_{1,2,0}] + k_5[P_{1,2,0}] + k_6[P_{2,0,1}] \\ & + k_7[P_{0,3,0}] + k_8[P_{1,1,1}] + k_9[P_{1,1,1}] + k_{10}[P_{0,2,1}] \\ & + k_{11}[P_{1,0,2}] + k_{12}[P_{0,1,2}]\} [F] \end{aligned} \quad (\text{A.2})$$

$$\frac{d[\text{HOCH}_2\text{OH}]}{dt} = k_h[\text{H}_2\text{O}][F] - k_d[\text{HOCH}_2\text{OH}] \quad (\text{A.3})$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = k_d[\text{HOCH}_2\text{OH}] - k_h[\text{H}_2\text{O}][F] \quad (\text{A.4})$$

$$\begin{aligned} \frac{d[P_{2,1,0}]}{dt} = & -k'_1[P_{2,1,0}] + k'_2[P_{1,2,0}] + k'_3[P_{2,0,1}] \\ & + \{k_1[M] - k_2[P_{2,1,0}] - k_3[P_{2,1,0}]\} [F] \end{aligned} \quad (\text{A.5})$$

$$\frac{d[P_{1,2,0}]}{dt} = -k'_2[P_{1,2,0}] + k'_4[P_{0,3,0}] + k'_5[P_{1,1,1}] + \{k_2[P_{2,1,0}] - k_4[P_{1,2,0}] - k_5[P_{1,2,0}]\}[F] \quad (A.6)$$

$$\frac{d[P_{2,0,1}]}{dt} = -k'_3[P_{2,0,1}] + k'_6[P_{1,1,1}] + \{k_3[P_{2,1,0}] - k_6[P_{2,0,1}]\}[F] \quad (A.7)$$

$$\frac{d[P_{0,3,0}]}{dt} = -k'_4[P_{0,3,0}] + k'_7[P_{0,2,1}] + \{k_4[P_{1,2,0}] - k_7[P_{0,3,0}]\}[F] \quad (A.8)$$

$$\frac{d[P_{1,1,1}]}{dt} = -k'_6[P_{1,1,1}] + k'_9[P_{1,0,2}] - k'_5[P_{1,1,1}] + k'_8[P_{0,2,1}] + \{k_6[P_{2,0,1}] + k_9[P_{1,1,1}] + k_5[P_{1,2,0}] - k_8[P_{1,1,1}]\}[F] \quad (A.9)$$

$$\frac{d[P_{0,2,1}]}{dt} = -k'_7[P_{0,2,1}] - k'_8[P_{0,2,1}] + k'_{10}[P_{0,1,2}] + \{k_7[P_{0,3,0}] + k_8[P_{1,1,1}] - k_{10}[P_{0,2,1}]\}[F] \quad (A.10)$$

$$\frac{d[P_{1,0,2}]}{dt} = -k'_9[P_{1,0,2}] + k'_{11}[P_{0,1,2}] + \{k_9[P_{1,1,1}] - k_{11}[P_{1,0,2}]\}[F] \quad (A.11)$$

$$\frac{d[P_{0,1,2}]}{dt} = -k'_{10}[P_{0,1,2}] - k'_{11}[P_{0,1,2}] + k'_{12}[P_{0,0,3}] + \{k_{10}[P_{0,2,1}] + k_{11}[P_{1,0,2}] - k_{12}[P_{0,1,2}]\}[F] \quad (A.12)$$

$$\frac{d[P_{0,0,3}]}{dt} = -k'_{12}[P_{0,0,3}] + k_{12}[P_{0,1,2}][F] \quad (A.13)$$

The total formaldehyde concentration [eq. (7)] is obtained by deriving eq. (7) with respect to time, and replacing eqs. (A.2) and (A.3), yielding:

$$\begin{aligned} \frac{d[F_T]}{dt} = & k'_1[P_{2,1,0}] + k'_2[P_{1,2,0}] + k'_3[P_{2,0,1}] + k'_4[P_{0,3,0}] \\ & + k'_5[P_{1,1,1}] + k'_6[P_{1,1,1}] + k'_7[P_{0,2,1}] + k'_8[P_{0,2,1}] \\ & + k'_9[P_{1,0,2}] + k'_{10}[P_{0,1,2}] + k'_{11}[P_{0,1,2}] + k'_{12}[P_{0,0,3}] \\ & - \{k_1[M] + k_2[P_{2,1,0}] + k_3[P_{2,1,0}] + k_4[P_{1,2,0}] \\ & + k_5[P_{1,2,0}] + k_6[P_{2,0,1}] + k_7[P_{0,3,0}] + k_8[P_{1,1,1}] \\ & + k_9[P_{1,1,1}] + k_{10}[P_{0,2,1}] + k_{11}[P_{1,0,2}] \\ & + k_{12}[P_{0,1,2}]\}[F] \quad (A.14) \end{aligned}$$

The average molecular weights of the ringed  $P_{A_0,A_1,A_2}$  molecules are

$$\bar{M}_n = \frac{\sum_{A_2=0}^3 \sum_{A_1=0}^3 \sum_{A_0=0}^3 [P_{A_0,A_1,A_2}] \bar{M}_{P_{A_0,A_1,A_2}}}{\sum_{A_2=0}^3 \sum_{A_1=0}^3 \sum_{A_0=0}^3 [P_{A_0,A_1,A_2}]} \quad (A.15)$$

$$\bar{M}_w = \frac{\sum_{A_2=0}^3 \sum_{A_1=0}^3 \sum_{A_0=0}^3 [P_{A_0,A_1,A_2}] (\bar{M}_{P_{A_0,A_1,A_2}})^2}{\sum_{A_2=0}^3 \sum_{A_1=0}^3 \sum_{A_0=0}^3 [P_{A_0,A_1,A_2}] \bar{M}_{P_{A_0,A_1,A_2}}} \quad (A.16)$$

where  $M_{P_{A_0,A_1,A_2}}$  is the molar mass of  $P_{A_0,A_1,A_2}$  (Table I).

Any  $P_{A_0,A_1,A_2}$  molecule contains  $(2A_0 + A_1)$  reactive H's and  $(A_1 + 2A_2)$  methylol groups. Thus, the corresponding number-average functionalities are

$$\bar{f}_H = \frac{\sum_{A_2=0}^3 \sum_{A_1=0}^3 \sum_{A_0=0}^3 (2A_0 + A_1) [P_{A_0,A_1,A_2}]}{\sum_{A_2=0}^3 \sum_{A_1=0}^3 \sum_{A_0=0}^3 [P_{A_0,A_1,A_2}]} \quad (A.17)$$

$$\bar{f}_{\text{meth}} = \frac{\sum_{A_2=0}^3 \sum_{A_1=0}^3 \sum_{A_0=0}^3 (A_1 + 2A_2) [P_{A_0,A_1,A_2}]}{\sum_{A_2=0}^3 \sum_{A_1=0}^3 \sum_{A_0=0}^3 [P_{A_0,A_1,A_2}]} \quad (A.18)$$

Finally, the global concentrations of unreacted amines and H's, and of generated monohydroxymethylamine groups, dihydroxymethylamine groups, and total methylols are given by

$$[-\text{NH}_2] = 3[P_{3,0,0}] + 2[P_{2,1,0}] + [P_{1,2,0}] + 2[P_{2,0,1}] + [P_{1,1,1}] + [P_{1,0,2}] \quad (A.19)$$

$$[-\text{H}] = 2[-\text{NH}_2] + [-\text{NHCH}_2\text{OH}] \quad (A.20)$$

$$[-\text{NHCH}_2\text{OH}] = [P_{2,1,0}] + 2[P_{1,2,0}] + 3[P_{0,3,0}] + [P_{1,1,1}] + 2[P_{0,2,1}] + [P_{0,1,2}] \quad (A.21)$$

$$[-\text{N}(\text{CH}_2\text{OH})_2] = [P_{2,0,1}] + [P_{1,1,1}] + [P_{0,2,1}] + 2[P_{0,1,2}] + 2[P_{1,0,2}] + 3[P_{0,0,3}] \quad (A.22)$$

$$[-\text{CH}_2\text{OH}] = [-\text{NHCH}_2\text{OH}] + 2[-\text{N}(\text{CH}_2\text{OH})_2] \quad (A.23)$$

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