Methylolation of Melamine with Incipient Condensation. I. Synthesis and Characterization

V. V. Nicolau,[1,2,3] M. Martinelli,[4] M. C. Strumia,[4] D. A. Estenoz,[1] G. R. Meira[1]

[1]INTEC (CONICET and U.N.L.), Güemes 3450, Santa Fe 3000, Argentina
[2]Centro S.A., San Francisco 2400, Córdoba, Argentina
[3]Departamento Química, Fac. Reg. San Fco., U.T.N., San Francisco 2400, Córdoba, Argentina
[4]Departamento Qca. Orgánica, Fac. Ciencias Químicas, U.N.C., Córdoba 5000, Argentina

ABSTRACT: This work investigates five reactions between melamine (M) and formaldehyde (F) at pH = 9.0, and with initial F : M ratios of 2. The samples were analyzed by size exclusion chromatography (SEC), volumetric techniques, and (^{1}H and ^{13}C) NMR. Condensation was quantified by the SEC measurements. In the experiments at 38 and 48°C, condensation was almost negligible, and the reversibility of methylolation reactions determined that equilibriums were reached in the ratios between primary, secondary, and tertiary amines. In the experiments at 60, 70, and 90°C, condensation was significant, but in all cases, the mass fraction of single-ringed species was larger than that of species with two or more rings per molecule. The following were estimated by combining the SEC and volumetric measurements: number-average molecular weights, and average functionalities of reactive H's, methylols, methylene bridges, and ether bridges. The dissolution of M in water was essentially instantaneous. The measurements are employed in the next article of this series for adjusting a novel mathematical model. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1030–1041, 2009

Key words: resins; synthesis; gel permeation chromatography; NMR; molecular weight distribution

INTRODUCTION

Melamine-formaldehyde (MF) resins are oligomers obtained by reaction between melamine (M) and formaldehyde (F) in aqueous medium. They are used as adhesives, for the production of molded articles, and for external transparent coatings in decorative laminates. For this last application, an α-cellulose paper is impregnated with the resin solution in the presence of an acid, the paper is dried, assembled with other impregnated papers, and the resulting "sandwich" is cured under pressure and at temperatures between 140 and 170°C. The degree of crosslinking and chemical reactivity of the external coating strongly depend on the molecular characteristics of the base MF resin.

Base MF resins are synthesized in batch stirred-tank reactors, and with initial comonomer ratios $[F]°/[M]°$ of around 1.7.[1–4] To limit condensation, the pH is maintained between 9.0 and 9.5. (At pH > 10, F decomposes into methanol and formic acid;

this lowers the pH and induces a premature gelation.)

In the initial methylolation stage,[2] free formaldehyde reacts with primary or secondary amines to produce mono- or dihydroxymethylamines:

$$-NH_2 + CH_2O \rightleftarrows -NHCH_2OH \qquad (1)$$

$$-NHCH_2OH + CH_2O \rightleftarrows -N(CH_2OH)_2 \qquad (2)$$

Equations (1) and (2) are often replaced by a global methylolation/demethylolation[1,3]:

$$-H + CH_2O \rightleftarrows -CH_2OH \qquad (3)$$

In contrast, Gordon et al.[2] proposed a detailed methylolation/demethylolation mechanism, with generation of nine single-ringed methylolmelamines. The condensation reactions are[3]:

$$-H + -CH_2OH \rightleftarrows -CH_2- + H_2O \qquad (4)$$

$$2 -CH_2OH \rightleftarrows -CH_2OCH_2- + H_2O \qquad (5)$$
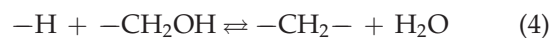
where $-CH_2-$ and $-CH_2OCH_2-$ represent generic methylene- and ether bridges, respectively. More specifically, methylene bridges can be unsubstituted ($-HNCH_2NH-$), monosubstituted ($-HNCH_2NR-$), or disubstituted ($-RNCH_2NR-$). Similarly, ether

bridges can be $-HNCH_2OCH_2NH-$, $-HNCH_2$ OCH_2NR-, or $-RNCH_2OCH_2NR-$.

In water solution, formaldehyde is mainly present as methylene glycol[5]:

$$CH_2O + H_2O \rightleftharpoons HOCH_2OH \qquad (6)$$

with $[HOCH_2OH] \gg [CH_2O]$. Concentrated F solutions (or "formalines") can polymerize into paraformaldehyde and react with methanol to generate hemiformals. Methanol is normally incorporated in commercial F solutions to avoid generation of paraformaldehyde.[5] In dilute solution and in the absence of methanol, the total formaldehyde concentration is:

$$[F_T] = [CH_2O] + [HOCH_2OH] \qquad (7)$$

At the beginning of the F-M reaction (and unless it were carried out in highly dilute solution), only a fraction of the total M is initially dissolved.[6] The following expression was proposed[7] for the water solubility of M (in mol/L) as a function of temperature (in °K):

$$S_M(T) = 0.0794 \left(10^{-1642/T + 5.101} \right) \qquad (8)$$

In our previous publication,[8] a mathematical model was developed for the methylolation of M in dilute solution and in the absence of condensation. It is based on the mechanism by Gordon et al.,[2] and it assumes an instantaneous equilibrium for eq. (6). The 24 associated methylolation/demethylolation kinetic constants were adjusted to measurements of reactions carried out at 48°C and at pH = 9.0.[9]

Several analytical techniques have been used for analyzing MF resins.[1,2,5,10–22] For reactions carried out at 35, 40, and 70°C; and pH between 3 and 10.6, Okano and Ogata[1] combined the results of the iodometric and sulfite methods[5] for estimating the concentrations of F_T and global methylols. These methods are also applied in this work, and are described further below. Gordon et al.[2] used a modified sulfite method[10] for determining the evolution of $[F_T]$ along a series of methylolation/demethylolations.

For reactions at pH > 8 and T > 70°C, several publications have analyzed the reaction products by ^{13}C-NMR[11–17] and ^{1}H-NMR.[14,15,18] Drawbarn et al.,[11] De Breet et al.,[12] and Tomita and Ono[13] directly analyzed the oligomers mixture by ^{13}C-NMR, employing dimethylsulfoxide (DMSO-d$_6$) as solvent. In contrast, Ebdon et al.[14,15] first isolated several reaction mixture components by preparative HPLC (with a water-methanol mixture as mobile phase), and then analyzed each of the isolated components by NMR. For reactions carried at 50°C, pH = 8.3, and $[F_T]°/[M]°$ between 0.5 and 16, Ebdon et al.[14] identified seven simple-ringed methylolamelamines,

with only two remaining undetected: *N,N*-dimethylolmelamine and *N, N, N′,N′*-tetramethylolmelamine. Analyzing the HPLC fractions with two or more azine rings per molecule by ^{13}C-NMR, Ebdon et al.[15] detected both methylene and ether bridges, and determined the relative amounts of primary, secondary, and tertiary amines. In addition, the ratio of secondary to primary amines was estimated by ^{1}H-NMR.[15] Analyzing resins obtained under similar reaction conditions by ^{13}C-NMR, Braun and Legradic[16] and De Breet et al.,[12] detected ether bridges but not methylene bridges. Taken from Refs.,[11–15] Table I summarizes the ^{13}C and ^{1}H signal assignments.

Scheepers et al.[17] analyzed by ^{13}C-NMR the condensation of low methylolmelamines at 90°C; determining the evolutions of $-NHCH_2OH$, $-N(CH_2OH)_2$, $-HNCH_2NH-$, $-HNCH_2NR-$, and $-HNCH_2OCH_2NH-$. The following groups remained undetected: disubstituted methylene bridges ($-RNCH_2NR-$), monosubstituted ether bridges ($-HNCH_2OCH_2NR-$), and disubstituted ether bridges ($-RNCH_2OCH_2NR-$). The experiments were as follows: (a) freeze-dried mixtures of low methylolmelamines were dissolved in DMSO-d$_6$ (16.6% w/w); with toluene as internal standard; (b) the solutions were loaded into sealed NMR tubes and were heated at 90°C; and (c) samples were taken and analyzed along the curing process. The concentrations of $-NHCH_2OH$, $-HNCH_2NH-$, and $-HNCH_2NR-$ were estimated from the peak areas around 64, 47, and 52 ppm, respectively. Unfortunately, $-N(CH_2OH)_2$ and $-HNCH_2OCH_2NH-$ appear superimposed at 68.5 ppm (Table I). For this reason, two indirect methods were employed for first determining $[-HNCH_2OCH_2NH-]$, and then $[-N(CH_2OH)_2]$ from its difference with the total 68.5 ppm signal. The first method is totally based on the ^{13}C spectra, and it assumes a reaction scheme where: (a) unsubstituted ether bridges are produced by reaction between two $-NHCH_2OH$; (b) unsubstituted methylene bridges are produced by reaction between $-NHCH_2OH$ and $-NH_2$; (c) methylolations are neglected because the condensations were carried out in the absence of F; and (d) monosubstituted methylene bridges are not produced by reaction between two $-NHCH_2OH$ groups because the areas under azine carbons bearing primary and secondary amines were seen to remain constant along the condensations. The concentration of $-HNCH_2OCH_2$ $NH-$ was obtained from:

$$[-NHCH_2OH]^0$$
$$= [-NHCH_2OH] + [-HNCH_2NH-]$$
$$+ 2[-HNCH_2OCH_2NH-] \qquad (9)$$

where $[-NHCH_2OH]^0$ is the initial concentration of secondary amines, and $[-NHCH_2OH]$ and

TABLE I
NMR Analysis of MF Resins: Frequency Assignments (in ppm) at Several Measurement Temperatures

		Dawbarn et al.[11]	Breet et al.[12]	Tomita and Ono[13]		Ebdon et al.[14]	Ebdon et al.[15]
		(25°C)	(70°C)	(25°C)	(100°C)	(25°C)	(25°C)
(a) 13C Spectra: Azine rings	NH_2 C=	167.4[a] 167.2[b] 167.0[c] –	165.7	167.2	166.9	167.21[a] 166.97[b] 166.79[c] 166.79[e]	
	$NH(CH_2OH)$ C=	166.3[b] 166.0[c] – 165.8[d] – –	166.3	166.5	166.1	166.05[b] 165.78[c] 165.64[e] 165.51[d] 165.48[f] 165.46[g]	
	$N(CH_2OH)_2$ C=	– 165.2[f] 165.2[g] 165.2[h]	–	166.2	165.6	165.00[e] 164.66[f] 164.65[g] 164.59[h]	
Methylol groups	$-NHCH_2OH$	64.5	64.7	64.8	64.5	–	64
	$-N(CH_2OH)_2$	68.7	–	–	–	–	68–69
	$-N(CH_2-)CH_2OH$	–	–	69.8	69.5	–	–
Methylene bridges	$-NHCH_2NH-$	–	–	47.3	47.3	–	47
	$-N(CH_2-)CH_2NH-$	–	–	52.2	52.1	–	52
	$-N(CH_2-)CH_2N(CH_2-)-$	–	–	–	–	–	58
Methylene ethers of methyl groups	$-NHCH_2OCH_3$	–	72.9	73.0	72.5	–	73
	$-N(CH_2-)CH_2OCH_3$	–	77.3	77.4	76.6	–	77
Ether bridges	$-NHCH_2OCH_2NH-$	–	69.9	69.8	68.6	–	68–69
	$-N(CH_2-)CH_2OCH_2NH-$	–	–	73.0	73.3	–	72
	$-N(CH_2-)CH_2OCH_2N(CH_2-)$	–	–	–	–	–	–
Hemiformals of methylol groups	$-NHCH_2OCH_2OH$	67.4	–	69.8	68.6	–	–
	$-N(CH_2-)CH_2OCH_2OH$	71.6	–	73.0	73.3	–	–
	$-NHCH_2OCH_2OH$	85.6	–	–	86.2	–	–
	$-N(CH_2-)CH_2OCH_2OH$	85.6	–	–	86.2	–	–
Methanol	CH_3OH	–	49.3	50.7	48.4	–	–
Methoxy groups	$-CH_2OCH_3$	–	55.0	55.3	54.5	–	55
Methylene glycol and derivatives	$HOCH_2OH$	84.4	83.8	–	82.1	–	82
	$HOCH_2OCH_2OH$	–	86.9	–	85.2	–	–
	$HOCH_2OCH_3$	–	–	–	89.5	–	–
	$H(OCH_2)_nOCH_2OCH_3$	–	–	–	93.9	–	–
(b) ^1H Spectra:	$-NHCH_2OH$					7.31–746[f]	7–8
	$-NH_2$					–	6–7
	$-N(CH_2OH)_2$					5.37[f]	5.4
	$-NHCH_2OH$					5.21[f]	5.2
	$-N(CH_2OH)_2$					4.97[f]	5.0
	$-NHCH_2OH$					4.67[f]	4.7

Reproduced from Refs. 11–15.
[a] Melamine.
[b] Monomethylolmelamine.
[c] N, N′-dimethylolmelamine.
[d] N, N′, N″-trimethylolmelamine.
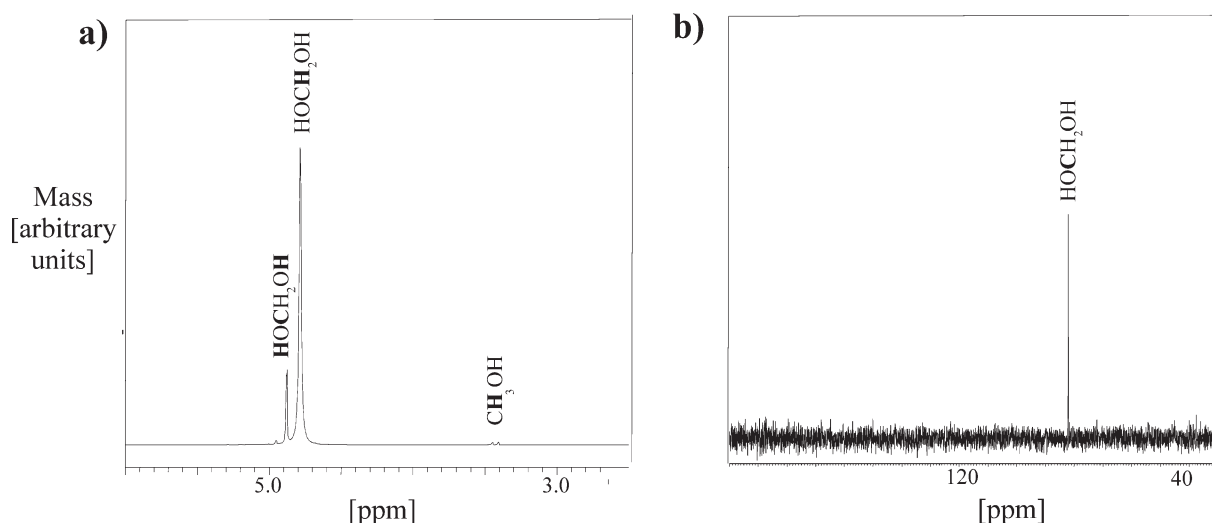[e] N, N, N′-trimethylolmelamine.
[f] N, N, N′, N″-tetramethylolmelamine.
[g] Pentamethylolmelamine.
[h] Hexamethylolmelamine.

[$-HNCH_2NH-$] were determined as mentioned earlier. The second method estimates [$-HNCH_2O$ CH_2NH-] from the difference between the concentration of condensation water (as determined by ^1H-NMR), and the concentration of methylene bridges (as determined by ^{13}C-NMR). The calculation assumed the presence of the following methylene bridges: $-HNCH_2NH-$ and $-HNCH_2NR-$; where the last group is generated by reaction between $-NH_2$ and $-N(CH_2OH)_2$.

Figure 1 NMR analysis of the initial F solution. The ^{1}H spectrum (a), and the ^{13}C spectrum (b) show negligible amounts of methanol, hemiformals, or paraformaldehyde.

Analyzing F-free solutions of single-ringed methylolmelamines in DMSO, Duliban et al.[18] employed ^{1}H-NMR for investigating the intramolecular rearrangements that take place when the solutions are heated or stored for several months at ambient temperature.

On several occasions,[13,19–22] size exclusion chromatography (SEC) has been employed for analyzing MF resins. In spite of the low solubility of MF resins in tetrahydrofurane (THF), this solvent was still employed (in combination with polyvinyl acetate gel columns) by first transforming the original resin into the trimethylsilated derivative.[19] Direct SEC fractionations of MF resins have been carried out with the following systems: (a) dimethylformamide (DMF) solvent combined with alkylated dextran gel columns (Sephadex LH-20)[20–22]; and (b) dioxane with a full set of six poly(styrene-divinylbenzene) columns.[13]

In this article, five reactions between M and F at pH = 9.0 and at temperatures between 38 and 90°C are analyzed by volumetric techniques, SEC, and NMR.

MAIN EXPERIMENTS

The following chemicals were employed: (a) melamine (purity 99.8%, from Agrolinz Melamine International GmbH, Austria); (b) paraformaldehyde (Cicarelli, Argentina); (c) a 2N solution of NaOH (Anedra proanalysis, purity 97%); (d) a 1N solution of Na_2SO_3 (Cicarelli proanalysis, purity 98%); (e) 0.1 and 2N solutions of HCl (Cicarelli proanalysis, conc. 36–38.5%); (f) a 0.1N iodine solution (Anedra proanalysis); (h) $Na_2S_2O_3.5H_2O$ (British Drug Houses, proanalysis); (g) DMF (Sintorgan spectroscopic grade); and (h) deuterated dimethylsulfoxide

(DMSO-d_6 Sigma Aldrich spectroscopic grade, purity 99.9%).

Prior to each reaction, the F solutions were prepared by depolymerization of solid paraformaldehyde. To this effect, the polymer was washed with deionized water, filtered under vacuum, and dried for a few minutes at 50°C. Then, 53 g of the solid was loaded in 100 mL of pure water, and the depolymerization was carried out until completion, at 70°C and pH = 10.0. The initial F concentrations were determined via the sulfite method,[5] and they all resulted between 7 and 8 mol/L. The initial F solutions were also analyzed by NMR (Fig. 1). The ^{1}H-NMR spectrum [Fig. 1(a)] shows a minimal contamination by methanol (see small peak at 3.47 ppm corresponding to the three methyl H's of methanol). The ^{13}C-NMR spectrum [Fig. 1(b)] exhibits a large peak at 82.1 ppm (due to methylene glycol carbons), but not observed are methylene signals of paraformaldehyde at 85–90 ppm and hemiformal methoxy signals at 55 ppm (Table I). Thus, the F solutions were considered essentially free of impurities.

Kinetics of melamine dissolution

Three experiments were carried out to estimate the rate of dissolution of M in water at 50°C and pH = 9.0 ± 0.5. In all cases, 12 g M were added into 135 g of water, and the pH was adjusted with the NaOH solution. The dissolution periods of Exps 1–3 were 20 s, 15 min, and 30 min, respectively. After such periods, the mixtures were filtered under vacuum with Filtrak paper N° 42, and dried until constant weight for 2 h at 120°C. The concentrations of dissolved M were obtained from the difference between the initial and undissolved M masses. For Exps 1–3, the dissolved M concentrations resulted 1.170, 1.092,

and 1.128 g M/100 g H_2O, respectively. These (essentially constant) values are close to the estimate via eq. (8) at 50°C of 1.041 g M/100 g H_2O. Thus, the dissolution of M was considered as essentially instantaneous with respect to the rates of reaction.

Main reactions

Five reactions were carried out at 38, 48, 60, 70, and 90°C (Table II). In all cases, the pH was adjusted to 9.0 ± 0.5 by addition of the NaOH solution, and the initial comonomers ratio was fixed at $[F_T]°/[M_T]° \cong 2$ (a typical industrial value). However, the absolute values of $[F_T]°$ and $[M_T]°$ were about 10 times lower than in industry (Table II); and this was to reduce the amount of initial undissolved M, while simultaneously increasing the reaction times. Table II also presents the initial concentrations of dissolved M ($[M_d]°$), as estimated through eq. (8). According to such estimates, Exps. 1–4 were all initially heterogeneous, whereas Exp. 5 was homogeneous throughout. Errors are to be expected however, because eq. (8) does not include the effect of the other reaction components (i.e.: F, methylene glycol, and methylolated species).

The reactor was a 2 L stainless-steel Parr 4522M fitted with a stirrer, an electric heating jacket, an internal cooling coil, a temperature indicator, a manometer, and valves for feeding the reagents and for extracting the samples by internal pressurization with Argon. First, the reactor was charged with water and M in powder under stirring, and the pH was adjusted to 9.0. Then, the mixture was heated to the final desired reaction temperature, and the reaction was started by loading the F solution at pH = 9.0, and preheated at the same temperature.

The reaction samples were rapidly cooled in ice water, and the following were measured: (a) $[F_T]$ by the sodium sulfite method[5]; and (b) $[F_T]+[—CH_2OH]$ by the iodometric method[5] (see Table II and Fig. 2). Some of the reaction samples were additionally analyzed by: (a) SEC (see mass chromatograms in Fig. 3, and numerical estimates in Table III); and (b) ^1H and ^{13}C-NMR (see spectra of Exp. 3 in Fig. 4, and ^1H-NMR estimates in Table III). The reaction samples taken for the instrumental measurements were frozen and lyophilized (to eliminate water and F), and the dry powders were freeze-stored until their analyses. Table III presents the sample masses before and after lyophilization. The final sample of Exp. 5 (taken at 1535 min) was discarded, because an insoluble condensate was observed over the stirrer and internal coil. Instead, the sample at $t = 1350$ min was adopted as the final sample of Exp. 5.

MEASUREMENTS AND DISCUSSION

SEC measurements

The chromatograph was a Waters Breeze fitted with a W2414 differential refractometer and a Shodex KD 802.5 column. The carrier solvent was DMF at 1 mL/min, and the system was operated at 40°C. The dry samples were dissolved in DMF (0.1% w/w), and the injection volumes were 80 μL. Unfortunately, a direct molar mass calibration was impossible, due to the lack of melamine-like standards. Also, indirect calibrations with PEG standards provided inconclusive results, due to the large structural differences between the linear standards and the ringed oligomers.

Consider the chromatograms of Figure 3. In all cases, the low-conversion samples exhibit single peaks (R_1) that are indicative of single-ringed species. The final samples of Exps 1 and 2 exhibit small second peaks (R_2), that correspond to double-ringed species [Fig. 3(a,b)]. The final samples of Exps 3–5 also contain triple-and-higher ringed molecules (R_3) [Fig. 3(c–e)]. The mass fractions (w_i) of species with 1-, 2-, and 3-or-more azine rings per molecule were determined from the areas under R_1, R_2, and R_3 (Table III).
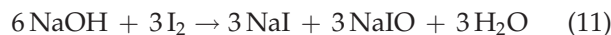
Volumetric measurements

The concentration of total formaldehyde was determined via the sodium sulfite method.[5] First, the total formaldehyde contained in 5 mL of reaction mixture was consumed with an excess (25 mL) of a cold 1N sodium sulfite solution through:

$$CH_2O + Na_2SO_3 + H_2O \rightarrow HCH(NaSO_3)OH \tag{10}$$
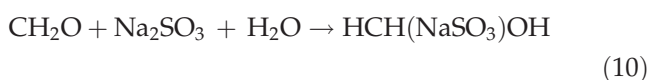
The technique provides $[F_T]$ rather than $[CH_2O]$, because all the consumed CH_2O is almost instantaneously replaced via eq. (6).[23] Then, $[F_T]$ was quantified by direct titration of the generated NaOH with the 0.1N HCl solution in the presence of thymolphtalein. During this operation, the product of eq. (10) was maintained cold to prevent hydrolysis of the methylolmelamines in acid medium.

The added concentrations of F_T and $—CH_2OH$ were determined via the iodometric method.[5] First, sodium hypoiodite NaIO was *in situ* generated, as follows:

$$6\,NaOH + 3\,I_2 \rightarrow 3\,NaI + 3\,NaIO + 3\,H_2O \tag{11}$$

and the generated NaIO consumes both F and the methylol groups through:

$$CH_2O + NaIO + NaOH \rightarrow HCOONa + NaI + H_2O \tag{12}$$
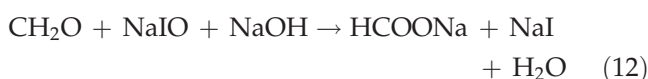
TABLE II
Experiments 1–5: Reaction Conditions and Volumetric Measurements. All the Reactions Were Carried Out at:
$$pH = 9.0 \pm 0.5;\ [F_T]^{\circ}/[M_T]^{\circ} = 2.0;\ \text{and}\ [H_2O] = 53.5\ \text{mol/L}$$

(a) Reaction Conditions

	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
T	$38 \pm 1°C$	$48 \pm 1°C$	$60 \pm 1°C$	$70 \pm 1°C$	$90 \pm 1°C$
$[F_T]^{\circ}$	0.409 mol/L	0.399 mol/L	0.407 mol/L	0.421 mol/L	0.405 mol/L
$[M_T]^{\circ}$	0.202 mol/L	0.200 mol/L	0.201 mol/L	0.202 mol/L	0.202 mol/L
$[M_d]^{\circ}$	0.0526 mol/L[a]	0.0768 mol/L[a]	0.118 mol/L[a]	0.164 mol/L[a]	0.300 mol/L[a]

(b) Volumetric Measurements

Exp. 1 ($T = 38 \pm 1°C$)

Time (min.)	$[F_T]$ (mol/L)	$[F_T] + [-CH_2OH]$ (mol/L)
0	0.409	
2	0.374	0.394
20	0.365	0.399
58	0.331	0.397
90	0.313	0.407
131[b]	0.268	0.402
174	0.234	0.402
1470[b]	0.0674	0.405
1560	0.0636	0.402
2820	0.0636	0.405
4260	0.0562	0.407
4375[b]	0.0562	0.397

Exp. 2 ($T = 48 \pm 1°C$)

Time (min.)	$[F_T]$ (mol/L)	$[F_T] + [-CH_2OH]$ (mol/L)
0	0.399	
2	0.330	
20	0.309	0.397
61	0.187	0.382
95	0.137	0.387
129[b]	0.107	0.397
212	0.0786	0.402
1370[b]	0.0749	0.407
1440	0.073	0.407
1520	0.0749	0.407
1605	0.0749	0.402
2833	0.0655	0.405
2880	0.0711	0.397
3025[b]	0.0711	

Exp. 3 ($T = 60 \pm 1°C$)

Time (min.)	$[F_T]$ (mol/L)	$[F_T] + [-CH_2OH]$ (mol/L)
0	0.407	
2	0.354	
19[b]	0.191	0.410
37	0.125	0.425
59	0.110	0.410
69	0.107	0.410
139	0.105	0.410
1370[b]	0.0992	0.410
1510	0.105	0.405
1680	0.0955	0.394
2825	0.0936	0.384
2970	0.0917	
3030[b]	0.0880	0.379

Exp. 4 ($T = 70 \pm 1°C$)

Time (min.)	$[F_T]$ (mol/L)	$[F_T] + [-CH_2OH]$ (mol/L)
0	0.421	
2	0.343	
20[b]	0.154	0.410
37	0.125	0.412
55	0.118	0.415
65	0.118	0.415
92	0.116	0.405
134	0.116	
153	0.116	0.410
1360[b]	0.110	0.364
1425	0.110	0.359
1500	0.107	0.354
1595	0.0992	0.349
1905[b]	0.103	0.351

Exp. 5 ($T = 90 \pm 1°C$)

| Time (min.)	$[F_T]$ (mol/L)	$[F_T] + [-CH_2OH]$ (mol/L)
0	0.405	
2	0.262	0.377
19[b]	0.150	0.413
38	0.135	0.407
74	0.139	0.402
93	0.132	0.402
1350[b]	0.0711	0.163
1535	—[c]	—[c]

[a] Initial conc. of dissolved M according to eq. (8).
[b] Sample further analyzed by NMR and SEC (Table 3).
[c] Discarded value because of the presence of an insoluble condensate.
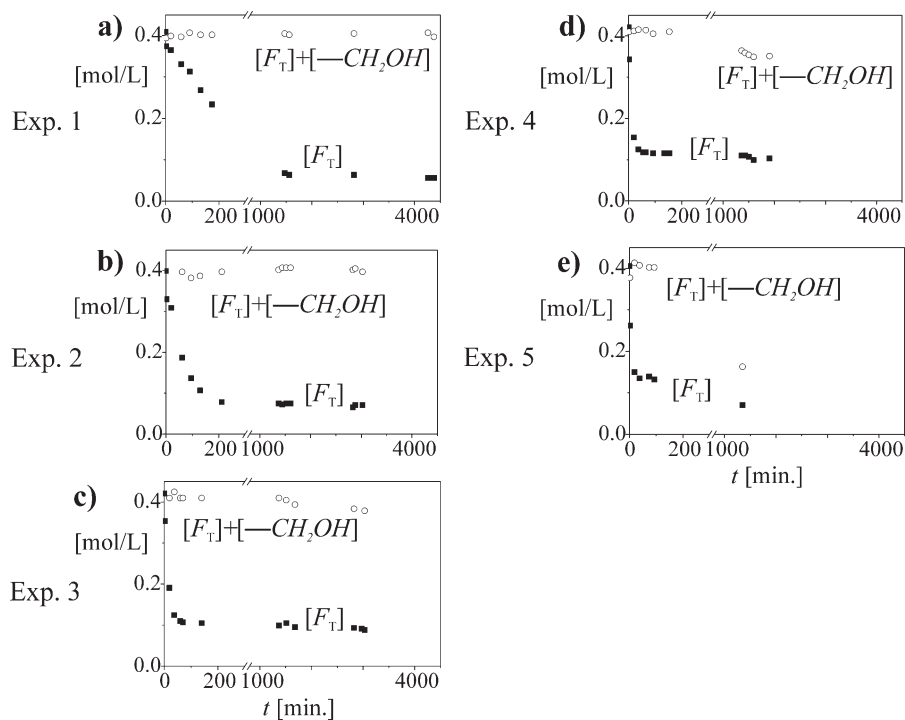
Figure 2 Experiments 1–5: time evolutions of $[F_T]$ (■) and $[F_T] + [-CH_2OH]$ (○). Note the two different scales employed in the time axes.
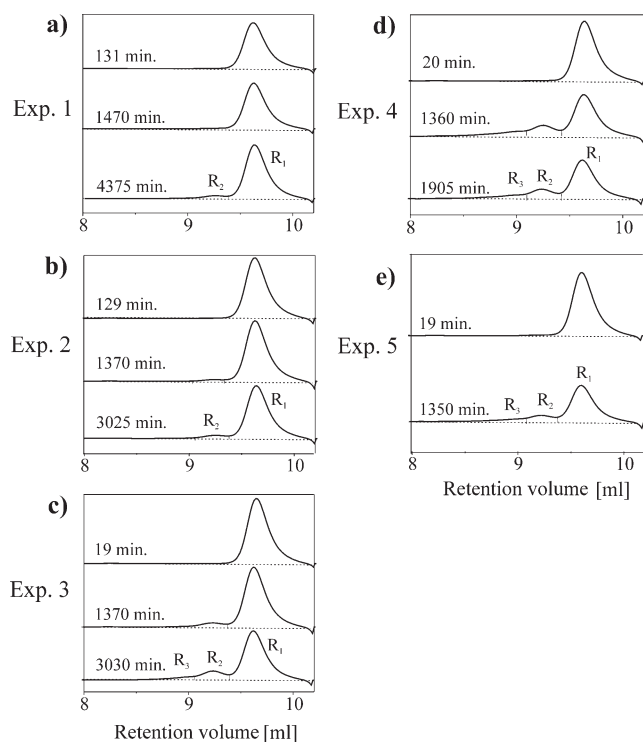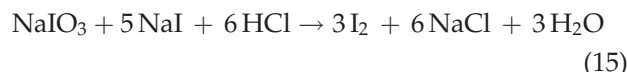

Figure 3 Experiments 1–5: size exclusion chromatograms of samples obtained at three reaction times. Peaks R_1, R_2, and R_3 indicate single-, double-, and triple-or-more ringed species.
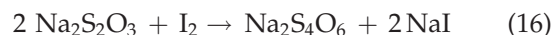
$$2 -CH_2OH + 3\,NaIO + 2\,NaOH$$
$$\rightarrow 2 -C(OH)ONa + 3NaI + 3H_2O \quad (13)$$
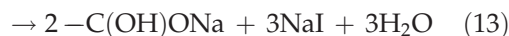
Then, the excess of hypoiodite is decomposed into sodium iodure (NaI) and sodium iodate ($NaIO_3$) under acidic conditions:

$$3\,NaIO \rightarrow 2\,NaI + NaIO_3 \quad (14)$$

and the produced NaI regenerates free I_2 through:

$$NaIO_3 + 5\,NaI + 6\,HCl \rightarrow 3\,I_2 + 6\,NaCl + 3\,H_2O \quad (15)$$

Finally, the free I_2 is titrated with the $Na_2S_2O_3$ solution:

$$2\,Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\,NaI \quad (16)$$

and ($[F_T] + [-CH_2OH]$) is determined by back-titration; that is, by subtraction of the required titration volume from the titration volume employed for a blank reagent without sample.[5] The experimental procedure was as follows. First, 1 mL of sample, 25 mL of a 0.1N iodine solution, and 4 mL of 2N NaOH were loaded into an Erlenmeyer. The mixture was maintained at room temperature for 10 min, and 4.5 mL of the 2N HCl solution were added to liberate the generated iodine. The liberated iodine was titrated with a 0.1N sodium thiosulfate solution (prepared from the corresponding salt); and 2 mL of

TABLE III
Experiments 1–5: Estimates of the Instrumental Measurements at Three Reaction Times

		Sample volume $(V_L)^a$ (L)	Lyoph. Mass (L) (g)	SEC			¹H NMR			Titration only			Titration/SEC				
Exp N°	Time (min)			w_1^b	w_2^b	w_3^b	$\frac{[-NHCH_2OH]}{[-NH_2]}$	$\frac{[-N(CH_2OH)_2]}{[-NCH_2OH]}$	$\frac{[-N(CH_2OH)_2]}{[-NCH_2OH]}$	$\overline{M}_n^{\,d}$ (g/mol)	$\overline{f}_{met}^{\,d}$ (#/molec.)	$\overline{f}_H^{\,d}$ (#/molec.)	$\overline{M}_n^{\,e}$ (g/mol)	$\overline{f}_{met}^{\,e}$ (#/molec.)	$\overline{f}_H^{\,e}$ (#/molec.)	$\overline{f}_{MB}^{\,e}$ (#/molec.)	$\overline{f}_{EB}^{\,e}$ (#/molec.)
1	131	0.00791	0.244	1	–	–	–^{c}	–^{c}	–^{c}	147	0.666	5.33	145	0.628	5.37	–	–
	1470	0.00791	0.296	1	–	–	1.78	0.0204	0.0209	177	1.67	4.33	172	1.52	4.48	–	–
	4375	0.00786	0.288	0.938	0.062	–	1.73	0.0184	0.0200	–	–	–	184	1.57	4.42	0.0293	0.00438
2	129	0.00772	0.287	1	–	–	1.47	–	–	170	1.40	4.60	162	1.21	4.79	–	–
	1370	0.00768	0.314	0.971	0.029	–	1.64	0.0177	0.0182	–	–	–	170	1.30	4.70	0.0113	0.00420
	3025	0.00776	0.265	0.938	0.062	–	1.68	–	–	–	–	–	186	1.69	4.36	0.0300	0.00370
3	19	0.00974	0.346	1	–	–	1.60	0.0174	0.0185	158	1.09	4.91	154	0.945	5.06	–	–
	1370	0.00977	0.385	0.921	0.065	0.014	1.65	–	–	–	–	–	179	1.27	4.75	0.0333	0.0130
	3030	0.00946	0.357	0.790	0.138	0.071	1.79	–	–	–	–	–	208	1.41	4.88	0.103	0.0363
4	20	0.00788	0.316	1	–	–	1.58	–	–	166	1.28	4.72	156	0.994	5.01	–	–
	1360	0.00745	0.273	0.689	0.181	0.130	1.81	–	–	–	–	–	228	1.11	5.18	0.155	0.0728
	1905	0.00731	0.245	0.722	0.176	0.102	1.76	–	–	–	–	–	222	1.39	5.01	0.141	0.0547
5	19	0.00780	0.253	1	–	–	1.83	0.0182	0.0202	164	1.30	4.70	166	1.33	4.67	–	–
	1350	0.00773	0.074	0.757	0.131	0.112	–^{c}	–^{c}	–^{c}	–	–	–	239	1.69	4.38	0.163	0.00860

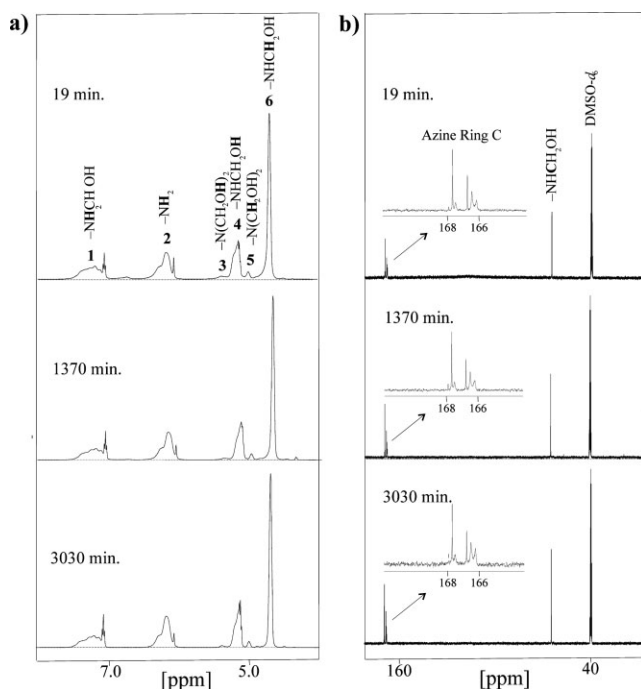^{a} Estimated from the sample mass, assuming a solution density of 1 g/mL.
^{b} Mass fractions of single-, double-, and triple-ringed molecules (see Fig. 3).
^{c} Discarded estimate.
^{d} Estimated through eqs. (18–20).
^{e} Estimated through eqs. (41–45).

Figure 4 Samples of Exp. 3, at three reaction times: (a) ^{1}H spectra; and (b) ^{13}C-NMR spectra. In the ^{1}H spectra, peaks 3, 4, 5, and 6 are potentially contaminated by (methylene or ether) bridge signals.

a soluble starch indicator were added after the solution turned into a pale yellow.

The results are in Table II and in Figure 2. As expected, the rate of consumption of F_T increases with the temperature. In Exps. 1 and 2 with negligible condensation, all the reacted CH_2O is transformed into $—CH_2OH$, and ($[F_T]$ + $[—CH_2OH]$) remains essentially constant [Fig. 2(a,b)]. The following can be written:

$$[F_T]^\circ = [F_T] + [—CH_2OH] + [—CH_2—]$$
$$+ 2[—CH_2OCH_2—] \quad (17)$$

where $[F_T]^\circ$ is total initial formaldehyde. In the absence of condensation, eq. (17) reduces to: $[F_T]^\circ = [F_T] + [—CH_2OH]$; and an equilibrium is reached due to the reversibility of methylolation reactions. In the presence of condensation, $[—CH_2—]$ + 2 $[—CH_2OCH_2—]$ builds up at the expense of $[—CH_2OH]$; and ($[F_T] + [—CH_2OH]$) falls along the reaction [Fig. 2(c–e)].

In the absence of condensation, several average properties were calculated from the estimates of $[F_T]$ and $[—CH_2OH]$; with $[—CH_2OH]$ obtained from the difference between ($[F_T] + [—CH_2OH]$) and $[F_T]$. The number-average molecular weight of the single-ringed molecule mixture (that includes M) is

obtained from $[F_T]$ and the global initial concentration of M ($[M_T]^\circ$) through:

$$\overline{M}_n = \frac{M_M [M_T]^0 + M_F \left([F_T]^0 - [F_T]\right)}{[M_T]^0} \quad (18)$$

where M_M (= 126 g/mol) and M_F (= 30 g/mol) are the molar masses of M and F. In addition, the average methylol and hydrogen functionalities of single-ringed molecules ($\overline{f}_{meth}$ and $\overline{f}_H$, respectively) were found from $[—CH_2OH]$ and $[M_T]^\circ$, as follows:

$$\overline{f}_{meth} = \frac{[—CH_2OH]}{[M_T]^0} \quad (19)$$

$$\overline{f}_H = \frac{[—H_T]}{[M_T]^0} \quad (20)$$

with:

$$[—H_T] = 6[M_T]^0 - [—CH_2OH] \quad (21)$$

where $[—H_T]$ is the total concentration of unreacted H's.

NMR measurements

The NMR spectrophotometer was a 400 MHz Brücker (Avance II), and the measurements were taken at ambient temperature. The samples were prepared by dissolving 35 mg of lyophilized resin in 0.7 mL of DMSO-d_6. For Exp. 3, Figure 4 presents the ^{1}H and ^{13}C spectra at three reaction times. The second analytical sample of Exp. 5 taken at 1350 min presented dissolution problems. This produced low-resolution ^{1}H spectra, and therefore, their estimates were discarded (Table III). ^{1}H-NMR estimates of the first sample of Exp. 1 were also discarded because of technical errors.

The ^{1}H spectra provided quantitative information (Table III). Special software (HNMR predictor 5.0 by ACD labs) was used to simulate the spectrum of protons in (methylene and ether) bridges. Double-ringed molecules with several types of methylene or ether bridges were simulated; and the results were as follows: (a) proton signals from un-, mono-, and disubstituted methylene bridges appear in the ranges ([5.65–5.0] and [5.0–4.80]), ([5.60–5.05] and [5.05–4.85]), and [5.60–5.0]; respectively; and (b) proton signals from un-, mono-, and disubstituted ether bridges appear in the ranges [5.15–4.60], ([5.45–4.75] and [4.20–4.0]), and ([5.60–4.90] and [4.20–3.95]), respectively.

The ^{1}H spectra [Fig. 4(a)] do not show signals in 4.20–3.95 ppm, and this suggests negligible amounts of mono- and disubstituted ether bridges. The concentrations of $—NHCH_2OH$, $—NH_2$, $—N(CH_2OH)_2$,

$-NHCH_2OH$, $-N(CH_2OH)_2$, and $-NHCH_2OH$ were quantified from the areas A_i ($i = 1, \ldots, 6$) [see Fig. 4(a)]; and to this effect the peaks were integrated in the ranges [7.65–7.00], [6.55–6.00], [5.50–5.30], [5.30–5.05], [5.05–4.91], and [4.80–4.60], respectively. Even though bridge signals were not expected to affect the signals from $-NHCH_2OH$ and $-NH_2$, they could however interfere with those of $-N(CH_2OH)_2$, $-NHCH_2OH$, $-NHCH_2OH$, and $-N(CH_2OH)_2$.

Following Ebdon et al.,[15] the ratio of secondary to primary amines was estimated through:

$$\frac{[-NHCH_2OH]}{[-NH_2]} = \frac{A_1}{(A_2/2)} \quad (22)$$

Consider the results for $[-NHCH_2OH]/[-NH_2]$ in Table III. The following can be noted: (a) the final values remain essentially constant in the last two samples of Exps. 1 and 2 with negligible condensation; and (b) the value of the third sample of Exp. 4 is lower than that of the second sample; possibly due to condensation reactions and/or to the generation of tertiary amines.

For the samples with negligible condensation, the ratio of tertiary to secondary amines was independently estimated through:

$$\frac{[-N(CH_2OH)_2]}{[-NHCH_2OH]} = \frac{1}{2}\frac{A_3}{A_4} \quad (23)$$

and

$$\frac{[-N(CH_2OH)_2]}{[-NHCH_2OH]} = \frac{1}{2}\frac{A_5}{A_6} \quad (24)$$

The results of eqs. (23) and (24) are also shown in Table III. As expected, the estimates are reasonably close to each other.

Consider the ^{13}C spectra of Figure 4(b). The peaks at 167 and 64 ppm correspond to Carbon atoms contained in azine rings and secondary amines, respectively. Not observed were methylene bridge signals at 47 ppm nor ether bridge (or secondary methylol) signals at 69 ppm. Thus, ^{13}C-NMR did not provide information on the chemical nature and/or on the concentration of condensation bridges. Possible reasons for the absence of bridge signals are: (1) the measurements were taken at ambient temperature, while higher resolutions are expected at 90–100°C[13,17]; and (2) the sample preparation did not include a preconcentration stage by HPLC of the double- and higher-ringed species.[14,15]

Estimates obtained by combination of the volumetric and SEC measurements

For the more general case of non-negligible condensation, volumetric and SEC measurements were combined for estimating $\overline{M}_n$, $\bar{f}_{meth}$, $\bar{f}_H$, $\bar{f}_{MB}$, and $\bar{f}_{EB}$ (where $\bar{f}_{MB}$ and $\bar{f}_{EB}$ are, respectively, the average numbers of methylene and ether bridges per molecule). The assumptions were as follows: (1) negligible concentration of species with more than three rings per molecule; (2) only unsubstituted (methylene and ether) bridges are present; (3) the H's of unsubstituted (methylene and ether) bridges remain nonreactive; (4) the average ratios of methylene to ether bridges are identical in double- or triple-ringed molecules; and (5) the average number of methyols per molecule are proportional to the number of feasible H atoms per molecule (i.e.: six in single-ringed molecules, eight in double-ringed molecules, and 10 in triple-ringed molecules). Hypothesis N° 4) can be written:

$$\frac{\bar{f}_{MB_2}}{\bar{f}_{EB_2}} = \frac{\bar{f}_{MB_3}}{\bar{f}_{EB_3}} \quad (25)$$

where $\bar{f}_{EB_2}$, $\bar{f}_{EB_3}$, $\bar{f}_{MB_2}$, and $\bar{f}_{MB_3}$ are the average ether and methylene bridge functionalities in the fractions of double- and triple-ringed molecules. Hypothesis N° 5 implies that:

$$[-CH_2OH]\frac{6[R_1]}{6[R_1] + 8[R_2] + 10[R_3]} = [R_1]\bar{f}_{meth_1} \quad (26)$$

$$[-CH_2OH]\frac{8[R_2]}{6[R_1] + 8[R_2] + 10[R_3]} = [R_2]\bar{f}_{meth_2} \quad (27)$$

$$[-CH_2OH]\frac{10[R_3]}{6[R_1] + 8[R_2] + 10[R_3]} = [R_3]\bar{f}_{meth_3} \quad (28)$$

where $[R_i]$ ($i = 1, 2, 3$) are the molar concentrations of single-, double-, and triple- ringed molecules. These concentrations were obtained through:

$$[R_i] = \frac{Lw_i}{\overline{M}_{n_i}V_L}; \ (i = 1, 2, 3) \quad (29)$$

where w_i ($i = 1, 2, 3$) are the mass fractions of species with 1-, 2-, and 3-or-more rings per molecule as determined by SEC; L is the total mass of lyophilized sample; and V_L is the corresponding sample volume (Table III).

Call $\overline{M}_{n_i}$, $\bar{f}_{meth_i}$, and $\bar{f}_{H_i}$ ($i = 1, 2, 3$) the average molecular weights and functionalities of species with 1-, 2-, and 3- rings per molecule. These averages are interrelated through:

$$\overline{M}_{n_1}[g/mol] = 120 + 31\bar{f}_{meth_1} + \bar{f}_{H_1} \quad (30)$$

$$\overline{M}_{n_2}[g/mol] = 240 + 31\bar{f}_{meth_2} + \bar{f}_{H_2}$$
$$+ 16\left(1 - \bar{f}_{EB_2}\right) + 46\bar{f}_{EB_2} \quad (31)$$

$$\overline{M}_{n_3}[\text{g/mol}] = 360 + 31\overline{f}_{\text{meth}_3} + \overline{f}_{H_3} + 32\left(1 - \overline{f}_{EB_2}\right)$$
$$+ 92\overline{f}_{EB_2} \quad (32)$$

$$\overline{f}_{\text{meth}_2} = 2\overline{f}_{\text{meth}_1} - (1 + \overline{f}_{EB_2}) \quad (33)$$

$$\overline{f}_{\text{meth}_3} = 3\overline{f}_{\text{meth}_1} - 2(1 + \overline{f}_{EB_2}) \quad (34)$$

$$\overline{f}_{H_1} = 6 - \overline{f}_{\text{meth}_1} \quad (35)$$

$$\overline{f}_{H_2} = 8 - \overline{f}_{\text{meth}_2} \quad (36)$$

$$\overline{f}_{H_3} = 10 - \overline{f}_{\text{meth}_3} \quad (37)$$

where 31, 16, 46, and 120 are, respectively, the molecular weights of $-CH_2OH$, $-HCH_2H-$, $-HCH_2O$ CH_2H-, and C_3N_6 (i.e.: M without the six amine H's). Replacing eqs. (33)–(37) into eqs. (30)–(32), one obtains:

$$\overline{M}_{n_1}[\text{g/mol}] = 126 + 30\overline{f}_{\text{meth}_1} \quad (38)$$

$$\overline{M}_{n_2}[\text{g/mol}] = 234 + 60\overline{f}_{\text{meth}_1} \quad (39)$$

$$\overline{M}_{n_3}[\text{g/mol}] = 342 + 90\overline{f}_{\text{meth}_1} \quad (40)$$

From the measurements of $[-CH_2OH]$, w_i ($i = 1$, 2, 3), L, and V_L, eqs. (26), (27), (29), and (33)–(40) enable to estimate $\overline{f}_{\text{meth}_i}$, $\overline{f}_{H_i}$, $\overline{M}_{n_i}$, $[R_i]$ ($i = 1, 2, 3$), and $\overline{f}_{EB_2}$. The global averages are given by:

$$\overline{M}_n = w_1\overline{M}_{n_1} + w_2\overline{M}_{n_2} + w_3\overline{M}_{n_3} \quad (41)$$

$$\overline{f}_{\text{meth}} = \frac{\overline{f}_{\text{meth}_1}[R_1] + \overline{f}_{meth_2}[R_2] + \overline{f}_{\text{meth}_3}[R_3]}{[R_1] + [R_2] + [R_3]} \quad (42)$$

$$\overline{f}_H = \frac{\overline{f}_{H_1}[R_1] + \overline{f}_{H_2}[R_2] + \overline{f}_{H_3}[R_3]}{[R_1] + [R_2] + [R_3]} \quad (43)$$

$$\overline{f}_{MB} = \frac{\overline{f}_{MB_2}[R_2] + \overline{f}_{MB_3}[R_3]}{[R_1] + [R_2] + [R_3]} \quad (44)$$

$$\overline{f}_{EB} = \frac{\overline{f}_{EB_2}[R_2] + \overline{f}_{EB_3}[R_3]}{[R_1] + [R_2] + [R_3]} \quad (45)$$

Finally, the number average chain length $\overline{r}_n$, and the molecular weight of the "effective" repetitive unit $\overline{M}_{\text{eff ru}}$, are given by:

$$\overline{r}_n = \overline{f}_{MB} + \overline{f}_{EB} + 1 \quad (46)$$

$$\overline{M}_{\text{eff ru}} = \frac{\overline{M}_n}{\overline{r}_n} \quad (47)$$

Accurate estimates of $[-CH_2OH]$ are vital for acceptable errors in the derived averages. Errors of $\pm5\%$ in $[-CH_2OH]$ induce the following relative errors: 1.73 and 2.21% in $\overline{M}_n$, 2.32 and 3.57% in $\overline{f}_H$, 6.18 and 7.02% in $\overline{f}_{\text{meth}}$, 3.36 and 6.80% in $\overline{f}_{MB}$, 23.15 and 120.25% in $\overline{f}_{EB}$. Thus, errors in $[-CH_2OH]$ strongly propagate into $\overline{f}_{EB}$. Other sources of errors may be due to the model hypotheses. For example, an important fraction of species with four or more rings per molecule would induce errors by defect in the number-average molecular weights and the bridge functionalities.

Consider the results of Table III. In the absence of condensation, $\overline{M}_n$, $\overline{f}_{\text{meth}}$, and $\overline{f}_H$ obtained through eqs. (41)–(43) are close to the direct titration estimates via eqs. (18)–(20). In the first sample of Exp. 1, methylolation was incomplete because neither $\overline{f}_{\text{meth}}$ ($\cong 0.63$) nor $\overline{f}_H$ ($\cong 5.37$) had reached their final quasi-equilibrium values. In Exps 1 and 2, the final product essentially consisted of single-ringed molecules of the following average characteristics: $\overline{f}_{\text{meth}}$ $\cong 1.6$; $\overline{f}_H \cong 4.4$; $\overline{f}_{\text{meth}} + \overline{f}_H \cong 6$; $\overline{f}_{MB} \cong 0.03$; $\overline{f}_{EB}$ $\cong 0.004$; $\overline{r}_n \cong 1.03$; and $\overline{M}_{\text{eff ru}} \cong 180$ g/mol (where $\overline{M}_{\text{eff ru}}$ is the "effective" repetitive unit molar mass). The results of Exps 1 and 2 are similar due to the common initial F : M ratios. In Exps 4 and 5 with condensation, the final values of $\overline{f}_{\text{meth}}$ and $\overline{f}_H$ are similar to those of Exps 1 and 2; while higher values are observed for $\overline{f}_{MB}$; $\overline{f}_{EB}$; $\overline{r}_n$; and $\overline{M}_{\text{eff ru}}$.

CONCLUSIONS

The dissolution of M in water is almost instantaneous with respect to the reaction rates, and SEC proved efficient for quantifying the mass fractions of single-, doubled, and triple-or-more-ringed species. Condensation is negligible at the beginning of the reactions, and under such conditions, ^{1}H-NMR proved appropriate for estimating the relative amounts of primary, secondary, and tertiary amines. With negligible condensation, the volumetric techniques provide relatively direct estimates of the average molar masses and functionalities of the single-ringed mixture.

Even though ^{13}C-NMR proved inadequate for detecting bridge formation, the combination of volumetric and SEC measurements produced (gross and indirect) estimates of the average molar masses and bridge functionalities.

The given set of measurements is employed in the second part of this series for adjusting a novel mathematical model that estimates the distributions of

molecular weights and functionalities of the evolving reaction mixture.

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