Modeling of Polymerization Reactions using CCREACS

CCREACS can be used to simulate condensation polymerization reactions comprising multifunctional reagents.

The polycondensation is a step-growth polymerization, which involves the elimination of a small molecule, frequently water but which may also be, for example, carbon dioxide, ammonia or hydrochloric acid, during the polymer forming reaction between the functional groups. However, in many such polymerizations, notably polyurethane formation, no small molecule is eliminated (condensed) out.

Typical examples of condensation polymerization are:

- Polyesterification
- Polyamidation
- Phenol-, urea-, and melamine – formaldehyde formation
- Epoxy resin formation

The modeling technique evolved for CHEMCAD CCREACS program package operates with the number average molecular weights of the growing polymer molecules. These molecules are divided into subgroups. The subgroups are identified by their functional groups.

CCREACS handles the user defined differential equations describing the time depending number average molecular weight. Differential equations for mole number of growing polymer molecules and differential mass balance equations for separated subgroups should be specified.

This short brochure outlines the kinetic treatment of condensation polymerization by a simplified example of amino resin formation.

Amino Resin

Amino resins are condenses formed when carbonyl compounds react with compounds containing amino, imino, or amide groups, liberating water. A very large number of carbonyl- and nitrogen-containing compounds yield condenses of relatively low molecular weight. The type of interaction is determined by the functional groups.
Formaldehyde, urea (and melamine) have become the most important compounds.

Amino resin production consists of two stages: ***hydroxymethylation*** and ***condensation***.

Hydroxymethylation is carried out industrially in an alkaline or slightly acidic solution. Hydroxymethylation reactions are reversible and establish equilibrium. The following equations illustrate the process for formaldehyde plus urea:

Monohydroximethylurea:

$$H_2N\text{-}CO\text{-}NH_2 + CH_2{=}O \leftrightarrow H_2N\text{-}CO\text{-}NH\text{-}CH_2\text{-}OH$$

Dihydroximethylurea:

$$H_2N\text{-}CO\text{-}NH\text{-}CH_2\text{-}OH + CH_2{=}O \leftrightarrow HO\text{-}CH_2\text{-}HN\text{-}CO\text{-}NH\text{-}CH_2\text{-}OH$$

The condensation is catalyzed by H+. Condensation can take place by different routes:

R1:

$$(X\text{-}R1\text{-}OH)+(H\text{-}R2\text{-}X) \rightarrow (X\text{-}R1\text{-}R2\text{-}X)+H_2O \quad \& X = H \text{ or } OH$$

R2:

$$(X\text{-}R1\text{-}CH_2\text{-}OH)+(HO\text{-}R2\text{-}X) \rightarrow (X\text{-}R1\text{-}R2\text{-}X)+H_2O+CH_2{=}O \quad \& X = H \text{ or } OH$$

R3:

$$(X\text{-}R1\text{-}OH)+(HO\text{-}R2\text{-}X) \rightarrow (X\text{-}R1\text{-}O\text{-}R2\text{-}X)+H_2O \quad \& X = H \text{ or } OH$$

Further condensation leads to longer chains of the basic unit – N – CO – N – CH2 – .
| |
Basically we can divide the “monomers” and the growing chains into following subgroups:

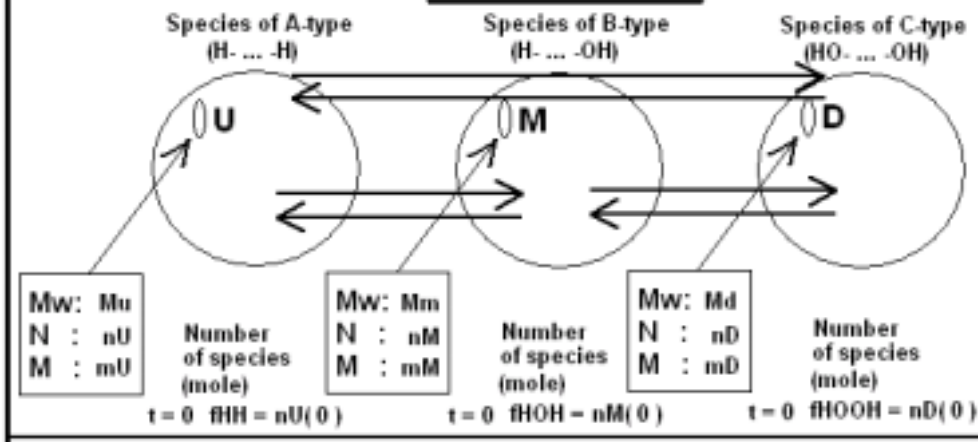
Species with function groups (H – … – H)
Species with function groups (HO – … – H)
Species with function groups (HO – … – OH)

The kinetic model of polycondenzation should describe all possible reaction routes.
The following tables illustrate the main steps of this modeling procedure for urea – formaldehyde system.

Table 1 – 2: Overview of modeling philosophy and of possible reactions
Table 3 – 4: Fundamental steps of model building
Table 5: Numerical example solved with theoretical kinetic data
Figures 1 – 2: Graphical representation of simulation result.

Note: The simplified numerical example consists of 18 differential equations and 3 parameters of reaction rate. (The full model needs ~ 60 DE and 10 kinetic parameters.)

System Specification



POLYCONDENSATION

REACTIONS	PRODUCT
Group 1:	Subgroups:
(... -H) + (HO- ...) =>	(H- ... -H) (H- ... -OH) + W (HO- ... -OH)
Group 2:	Subgroups:
(... -CH2-OH) + (HO- ...) =>	(H- ... -H) (H- ... -OH) + W + F (HO- ... -OH)
Group 3:	Subgroups:
(... -OH) + (HO- ...) =>	(H- ... -O- ...-H) (H- ... -O- ...-OH) + W (HO- ... -O- ...-OH)

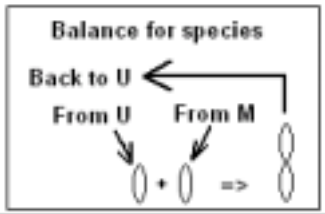
Specification of reaction system: Stoichiometry & Rate

Example: Reaction (Group1/Subgroup1):

Bt + At => At + W
M + U => U(M + U - W) + W

on mass base: $M => c\_1 * U + c\_2 * W$ (kg) $c\_1 = \frac{Mm - Mw}{Mm}$ $c\_2 = \frac{Mw}{Mm}$

on mole base: $M => c\_1 * U + c\_2 * W$ (kmol) $c\_1 = \frac{Mm - Mw}{Mu}$ $c\_2 = 1$



on mole base: $d[fHH]/dt = 0$

$d[fHOH]/dt = -R11$ fHOH => nfHOH

bond (not active)

R1 = ?

R11 = k11 * [fHH] * [fHOH]

To the correct solution we should take into account that

$Mu \triangleq Mu(t)$, $Mm \triangleq Mm(t)$, and $Md \triangleq Md(t)$

Calculation Sequence

k-1 (t = 0)

initial state is specified

dt → CHEMCAD MODEL

k (t = t + dt)

Calculated data:

nU_k, nM_k, nD_k
fHH_k, $fHOH_k$, $fHOOH_k$ & $Mu_k = \left(\frac{nU * Mu(0)}{fHH}\right)_k$, $Mm_k =$, $Md_k =$

dt → CHEMCAD MODEL

k + 1

Calculated data: ...

Main Components	Code	Name / Structure	Function Groups			Type
Urea	U	H2N-CO-NH2	(H-H)			At
Formaldehyde	F	CH2=O				
Hydroximethylation		**Equation / Main Product**				
Monohydroximethylurea	M	*H2N-CO-NH2 + CH2=O <=> H2N-CO-NH-CH2-OH* H-**NH**-**CO**-**NH**-**CH2**-OH	(H-OH)			Bt
Dihydroximethylurea	D	*H2N-CO-NH-CH2-OH + CH2=O <=> <=> HO-CH2-HN-CO-NH-CH2-OH* HO-CH2-**NH**-**CO**-**NH**-**CH2**-OH	(HO-OH)			Ct
Polymerization Polycondensation		**Equation / Main Product**	**Function Groups**	**Product 2**	**Product 3**	**Type**
Reaction 1 (first step)	**ID**					
(X-R1-OH)+(H-R2-X)		*(X-R1-R2-X)+H2O & X = H or OH*				
(H-OH)+(H-H)	1 *	H-**NH**-**CO**-**NH**-**CH2**-NH-CO-NH-H	(H-H)	H2O		[At]
(HO-OH)+(H-H)	2 *	H-**NH**-**CO**-**NH**-**CH2**-**NH**-**CO**-**NH**-**CH2**-OH	(H-OH)	H2O		[Bt]
(H-OH)+(H-OH)	3	H-**NH**-**CO**-**NH**-**CH2**-**NH**-**CO**-**NH**-**CH2**-OH	(H-OH)	H2O		[Bt]
(HO-OH)+(H-OH)	4 *	HO-CH2-**NH**-**CO**-**NH**-**CH2**-**NH**-**CO**-**NH**-**CH2**-OH	(HO-OH)	H2O		[Ct]
Reaction 2 (first step)						
(X-R1-CH2-OH)+(HO-R2-X)		*(X-R1-R2-X)+H2O+CH2=O & X = H or OH*				
(H-OH)+(HO-H)	5	H-**NH**-**CO**-**NH**-**CH2**-NH-CO-NH-H	(H-H)	H2O	CH2=O	[At]
(H-OH)+(HO-OH)	6	H-**NH**-**CO**-**NH**-**CH2**-**NH**-**CO**-**NH**-**CH2**-OH	(H-OH)	H2O	CH2=O	[Bt]
(HO-OH)+(HO-OH)	7	HO-CH2-**NH**-**CO**-**NH**-**CH2**-**NH**-**CO**-**NH**-**CH2**-OH	(HO-OH)	H2O	CH2=O	[Ct]
Reaction 3 (first step)						
(X-R1-OH)+(HO-R2-X)		*(X-R1-O-R2-X)+H2O & X = H or OH*				
(H-OH)+(HO-H)	8	H-**NH**-**CO**-**NH**-**CH2**-O-**CH2**-**NH**-**CO**-**NH**-H	(H-O-H)	H2O		[At]
(H-OH)+(HO-OH)	9	H-**NH**-**CO**-**NH**-**CH2**-O-**CH2**-**NH**-**CO**-**NH**-CH2-OH	(H-O-OH)	H2O		[Bt]
(HO-OH)+(HO-OH)	10	HO-CH2-**NH**-**CO**-**NH**-**CH2**-O-**CH2**-**NH**-**CO**-**NH**-CH2-OH	(HO-O-OH)	H2O		[Ct]

*** Used in DEMO example**

Fundamental Types	Short Code	Species	Name
(H-H)	At	U	Urea
(H-OH)	Bt	M	Monohydroximethylurea
(HO-OH)	Ct	D	Dihydroximethylurea
		F	Formaldehyde
		W	Water

Fundamental Reactions	ID	Short Code	Product	Theoretical Equation (Coded)	Theoretical Equation (Species)
R1					
(H-OH)+(H-H)	1 *	Bt + At	At	Bt + At -> At + W	M+U=U(M+U-W)+W
(HO-OH)+(H-H)	2 *	Ct + At	Bt	Ct + At -> Bt + W	D+U=M(D+U-W)+W
(H-OH)+(H-OH)	3	Bt + Bt	Bt	Bt + Bt -> Bt + W	M+M=M(M+M-W)+W
(HO-OH)+(H-OH)	4 *	Ct + Bt	Ct	Ct + Bt -> Ct + W	D+M=D(D+M-W)+W
R2					
(H-OH)+(HO-H)	5	Bt + Bt	At	Bt + Bt -> At + W + F	M+M=U(M+M-W-F)+W+F
(H-OH)+(HO-OH)	6	Bt + Ct	Bt	Bt + Ct -> Bt + W + F	M+D=M(M+D-W-F)+W+F
(HO-OH)+(HO-OH)	7	Ct + Ct	Ct	Ct + Ct -> Ct + W + F	D+D=D(D+D-W-F)+W+F
R3					
(H-OH)+(HO-H)	8	Bt + Bt	At	Bt + Bt -> At + W	M+M=U(M+M-W)+W
(H-OH)+(HO-OH)	9	Bt + Ct	Bt	Bt + Ct -> Bt + W	M+D=M(M+D-W)+W
(HO-OH)+(HO-OH)	10	Ct + Ct	Ct	Ct + Ct -> Ct + W	D+D=D(D+D-W)+W

* Used in DEMO example

ID	Code	Name	Molecular Weight	Comment	
1	FHH	(H-H) active moles	1.00E-08	FHH = nU(0)	Number of moles of A-type in the initial charge
2	NFHH	(H-H) bonded moles	1.00E-08		
3	FHOH	(H-OH) active moles	1.00E-08	FHOH = nM(0)	Number of moles of B-type in the initial charge
4	NFHOH	(H-OH) bonded moles	1.00E-08		
5	FHOOH	(HO-OH) active moles	1.00E-08	FHOOH = nD(0)	Number of moles of C-type in the initial charge
6	NFHOOH	(HO-OH) bonded moles	1.00E-08		

Note: The molecular weight is zero practically!

Reaction ID		Reaction Nu	Change of mole number U	M	D	Meaning	Reaction Rate (mole base)	Comment
1	*	r11	0	-1	0	FHOH -> NFHOH	r11 = k11 * [FHOH] * [FHH]	r1 = r11
2	*	r12	-1	+1	-1	FHH + FHOOH -> FHOH + NFHOOH	r12 = k12 * [FHOOH] * [FHH]	r2 = r12
3		r13	0	-1	0	FHOH -> NFHOH	r13 = k13 * [FHOH] * [FHOH]	r3 = r13
4	*	r14	0	-1	0	FHOH -> NFHOH	r14 = k14 * [FHOOH] * [FHOH]	r4 = r14
5		r15	+1	-2	0	2*FHOH -> FHH + NFHOH	r15 = k15 * [FHOH] * [FHOH]	r5 = r15
6		r16	0	0	-1	FHOOH -> NFHOOH	r16 = k16 * [FHOOH] * [FHOH]	r6 = r16
7		r17	0	0	-1	FHOOH -> NFHOOH	r17 = k17 * [FHOOH] * [FHOOH]	r7 = r17
8		r18	+1	-2	0	2*FHOH -> FHH + NFHOH	r18 = k18 * [FHOH] * [FHOH]	r8 = r18
9		r19	0	0	-1	FHOOH -> NFHOOH	r19 = k19 * [FHOOH] * [FHOH]	r9 = r19
10		r20	0	0	-1	FHOOH -> NFHOOH	r20 = k20 * [FHOOH] * [FHOOH]	r10 = r11

*** Used in DEMO example**

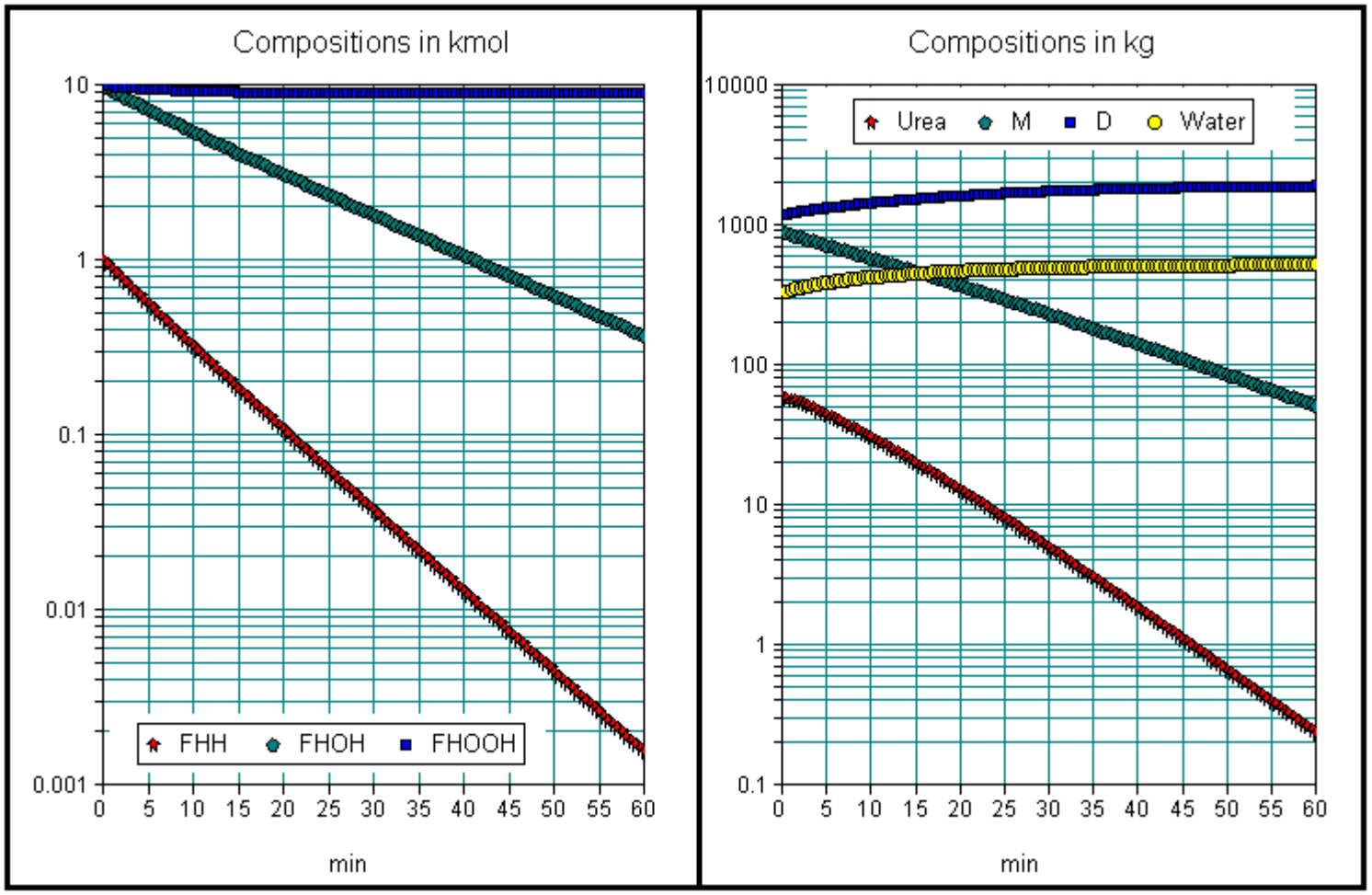
Example with simplified kinetic system

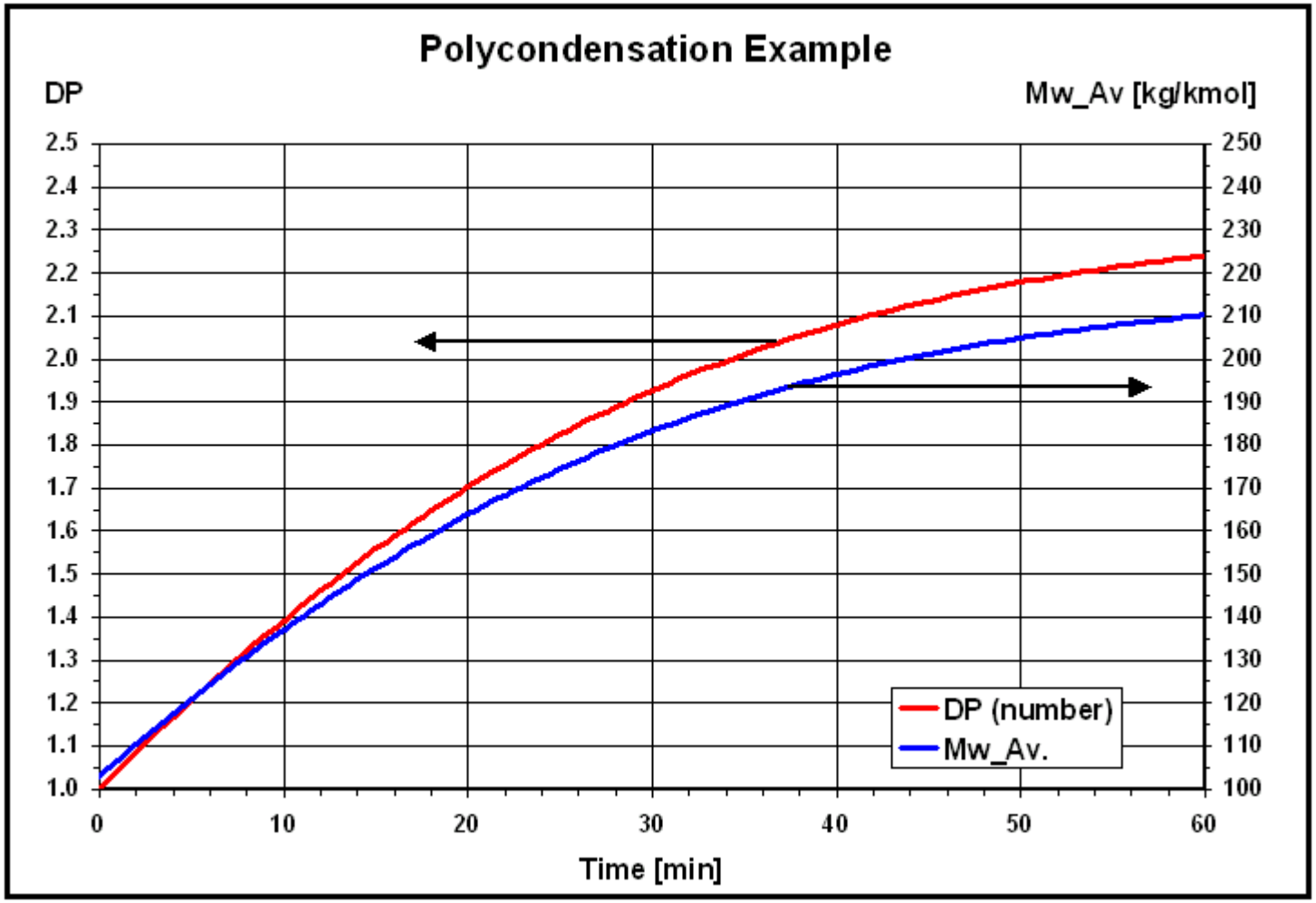
Fundamental data to kinetic parameters			
Mu	60	kg/kmol	
Mm	90	kg/kmol	
Md	120	kg/kmol	
Mw	18	kg/kmol	
Mf	30	kg/kmol	
k11	2.00E-04	m3/kmol s	
k12	4.00E-04	m3/kmol s	
k14	2.00E-04	m3/kmol s	

Item	Initial	At t = 1 hr	Difference
Total kg	2526.1839	2526.1642	0.0197
Species in kg			
U	60.056	0.2353	-59.8207
Formaldehyde	30.026	30.026	0
M	900.8189	51.7823	-849.0366
D	1201.0829	1918.484	717.4011
Water	334.2	525.6364	191.4364
Function groups			
FHH	0	0	0
FHOH	0	0	0
FHOOH	0	0	0

Mole Initial	Mass Initial	Mole At t = 1 hr	Mass At t = 1 hr	Mweight At t = 1 hr
1	60.06	0.0015	0.24	156.8667
10	900.82	0.3720	51.78	139.1997
10	1201.08	9.0015	1918.48	213.1294
21	2161.96	9.3750	1970.50	
Overall		Mw = M/N =	210.1868	2.0416

Item	Initial	At t = 1 hr	Difference
Total kmol	61.5512	56.1044	
Species in kmol			
U	1	0.0039	
Formaldehyde	1	1	
M	10	0.5748	
D	10	15.973	
Water	18.5512	29.1777	
Function groups			
FHH	*1*	***0.0015***	***0.9985***
FHOH	*10*	***0.372***	***9.628***
FHOOH	*10*	***9.0015***	***0.9985***
	21	***9.375***	
Overall	DP = N0/N	2.24	


Compositions in kmol
10
1
0.1
0.01
0.001
FHH
FHOH
FHOOH
0 5 10 15 20 25 30 35 40 45 50 55 60
min
Compositions in kg
10000
1000
100
10
1
0.1
Urea
M
D
Water
0 5 10 15 20 25 30 35 40 45 50 55 60
min


Polycondensation Example
DP
Mw_Av [kg/kmol]
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
0
10
20
30
40
50
60
Time [min]
DP (number)
Mw_Av.