Step-Growth Polymerization, Case Study:

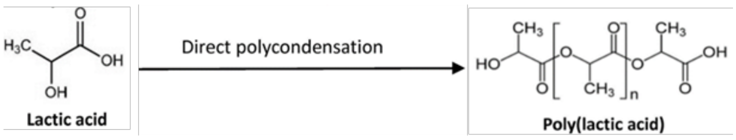
Low MW Poly(lactic acid) (PLA) Production by Melt Polycondensation

Poly(lactic acid) (PLA) is produced via a three step process: polycondensation, backbiting and then Ring Opening Polycondensation (ROP). The bulk-melt Polycondensation, which can be described by the following simplified kinetic scheme:

$$P_1 + P_1 \underset{kd,11}{\overset{kp,11}{\rightleftarrows}} P_2 + W$$

$$P_1 + P_n \underset{kd,1p}{\overset{kp,1p}{\rightleftarrows}} P_{n+1} + W \;\; with\, n > 1$$

$$P_n + P_m \underset{kd,pp}{\overset{kp,pp}{\rightleftarrows}} P_{n+m} + W \;\; with\, n, m > 1$$



The system is fed with pure Lactic Acid (P^0). The backbiting and endbiting reactions, which usually happen and lead to the formation of the Lactide dimer, can be neglected. The experimental setup adopted to simulate the industrial production, represented in Figure 1, is equipped with an isothermal reactor and a distillation column. To remove more efficiently the water by-product and increase the polymer production, a nitrogen flux is injected from the bottom of the reactor.

It is asked to evaluate, by using a **kinetic approach**:

1. The monomer conversion versus time
2. The moments λ_0, λ_1 and λ_2 versus time
3. The molecular weight distribution (MWD) versus time
4. The $\overline{M_n}$, $\overline{M_w}$ and PDI versus time

Finally, it is asked to change the operative parameters (temperature and initial concentrations) to appreciate their influence in the calculated quantities.

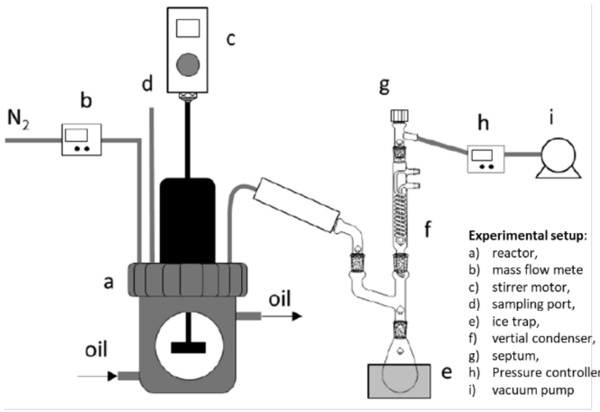


Figure 1

Assumptions:

- Negligible lactide formation
- Constant reaction volume
- Ideal distillation with continuous water removal and no other species (Lactic acid, oligomers, …) stripped in the system; the water in vapor phase (W_{gas}) can be considered as an ideal gas and the water removal due to stripping can be taken into account with the simplified mass transport relation:

$$\varphi = K_a * (W - W_{gas})$$

Parameter	Value / Relation	Unit of measure
$k_{p,11}$	$e^{\left(-\frac{14552}{T}+33.22\right)}$	[1/mol/h]
$k_{p,1p}$	$e^{\left(-\frac{14552}{T}+33.22\right)}$	[1/mol/h]
$k_{p,pp}$	$e^{\left(-\frac{15115}{T}+33.36\right)}$	[1/mol/h]
$K_{eq,11}$	0.33	[-]
$K_{eq,1p}$	0.275	[-]

$K_{eq,pp}$	$\frac{K_{eq,1p}^2}{K_{eq,pp}}$	[-]
K_a	0.5	[-]
$P^0 = LA^0$	1	[mol/L]
W^0	0.1	[mol/L]
T	120	°C
P	1	atm

In addition, use the **combinatorial method** to evaluate:

1. The number distribution versus the conversion
2. The weight distribution versus the conversion
3. The DP_n and DP_w versus the conversion
4. The $\overline{M_n}$, $\overline{M_w}$ and PDI versus the conversion