Circularidade e Engenharia de Polímeros

Polimerização no Estado Sólido (SSP)

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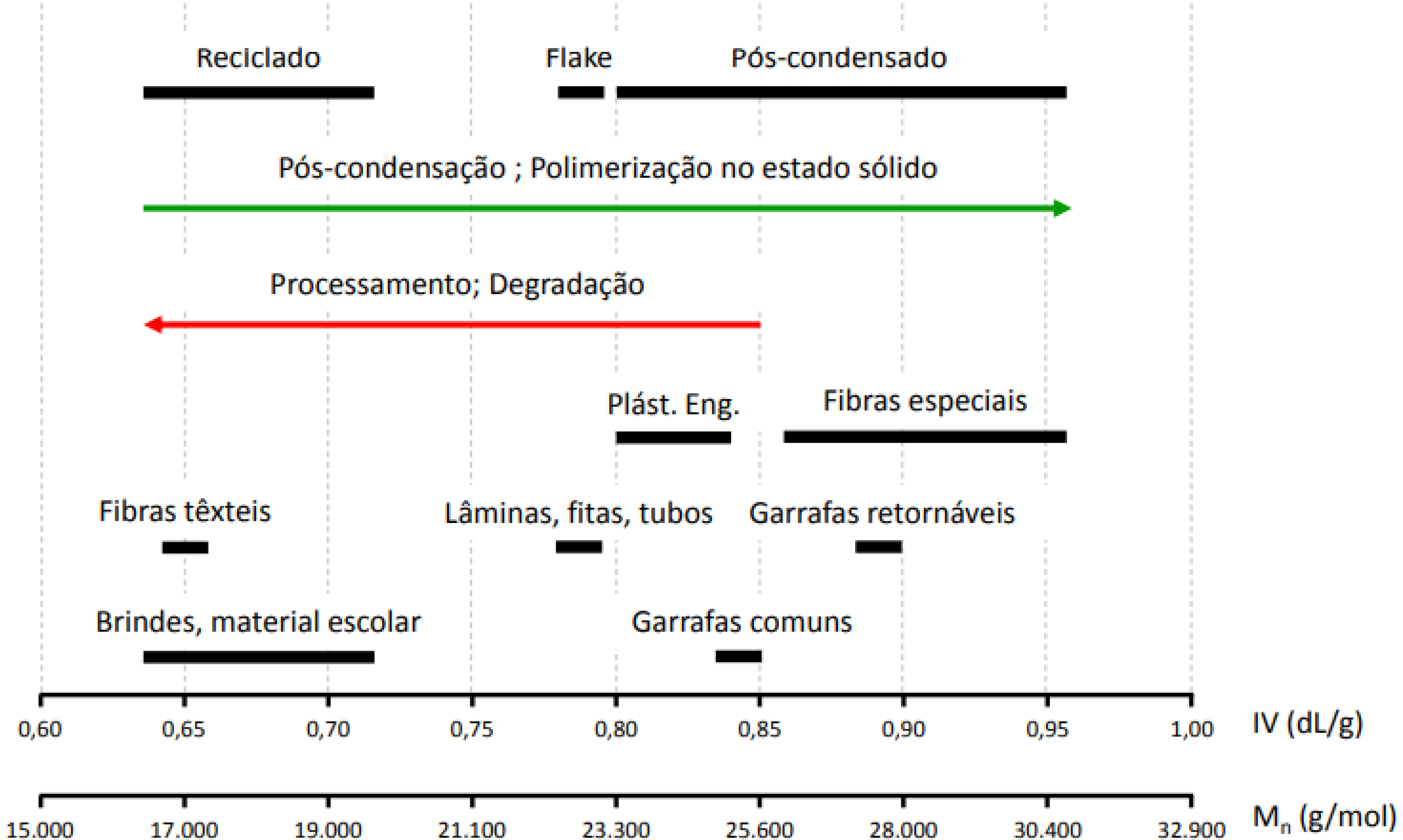
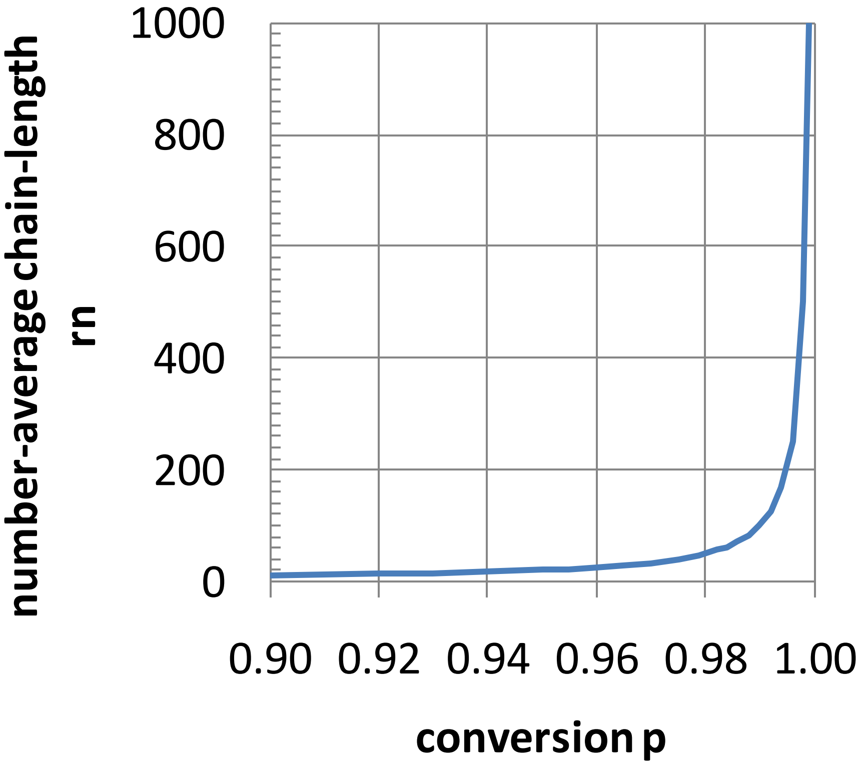
Polimerização no Estado Sólido (SSP) de PET

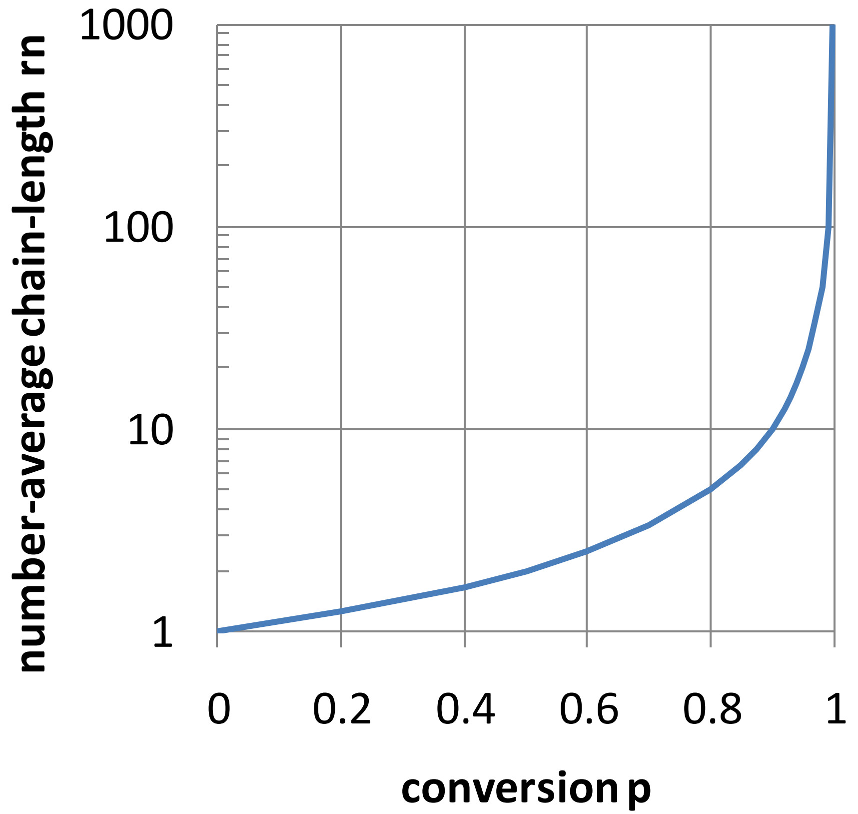


(L.B.Canto, curso Circularidade e Eng. de Polímeros, 2020)

Polycondensation (type AB)

$$\bar{r}_n = \frac{1}{1-p}$$





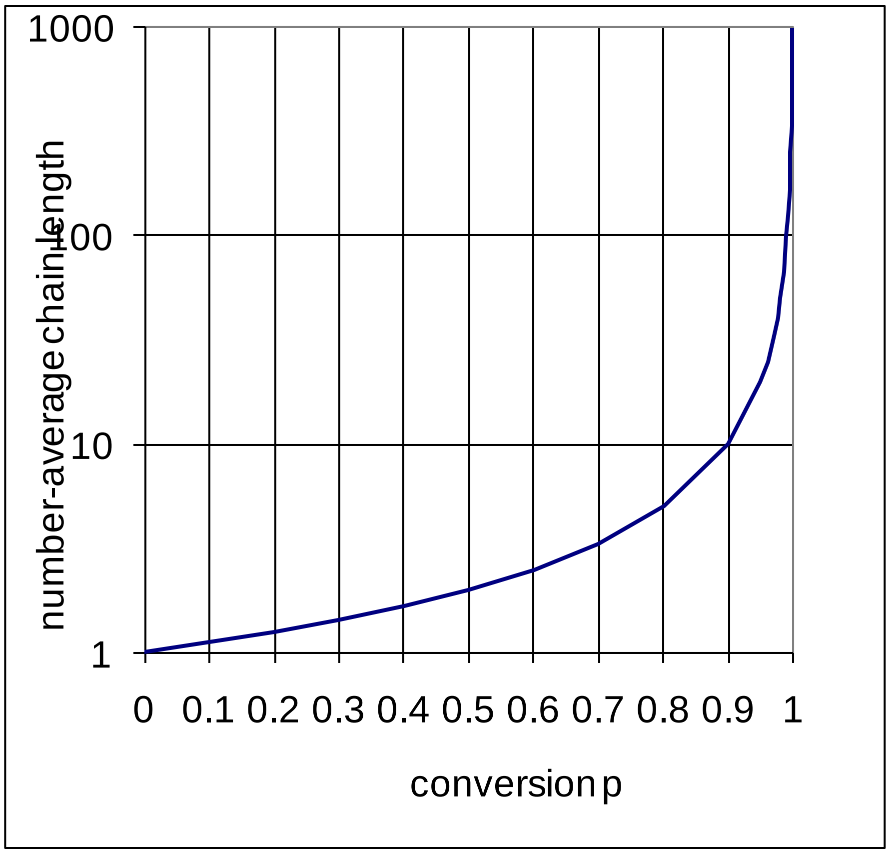
Conversion of end-groups (p) must be > 0.99 for average chain length of 100

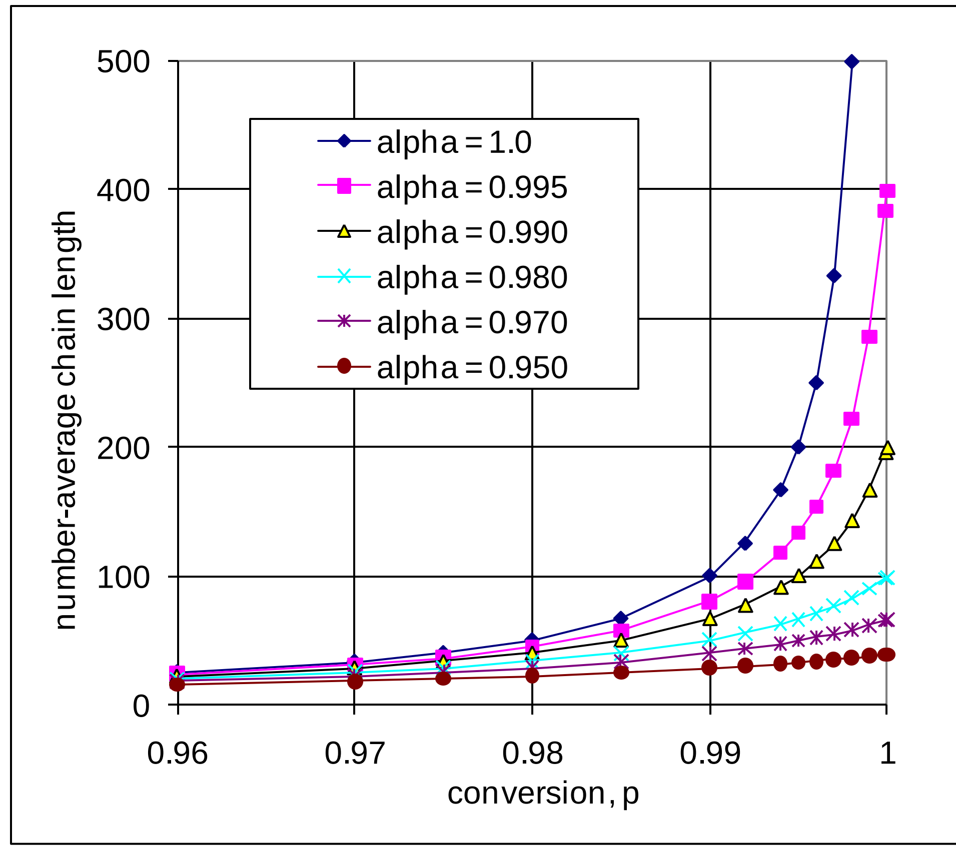
Policondensation AA + BB

Stoichiometric Imbalance (A < B)

AB $\bar{r}_n = \frac{1}{1-p}$

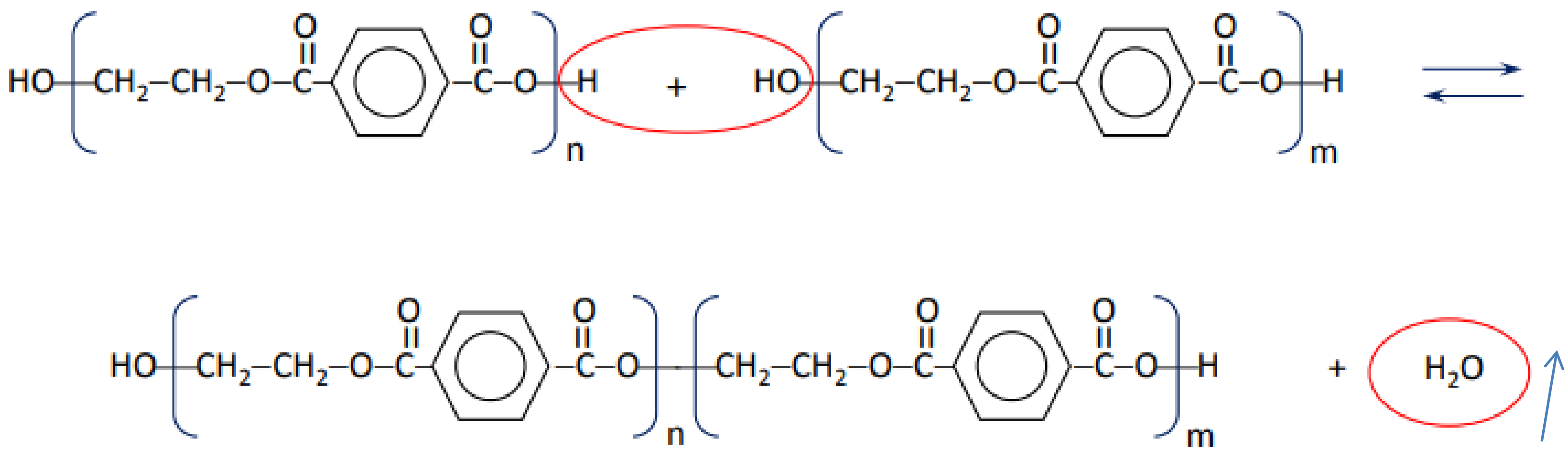
$\bar{r}_n = \frac{1+\alpha}{1+\alpha-2\alpha p}$ **AA+BB**





Monofunctional monomers (AX or BX) => effect similar to stoichiometric imbalance

Polyesterification



$$\sim\!\sim COOH \; + \; \sim\!\sim OH \;\overset{K}{\rightleftharpoons}\; \sim\!\sim CO-O\sim\!\sim \; + \; H_2O$$

- $K \approx 1 \Rightarrow$ equil. conversion $\approx 0{,}5 \Rightarrow$ number-av. chain-lenght ≈ 2

Polycondensation reactors

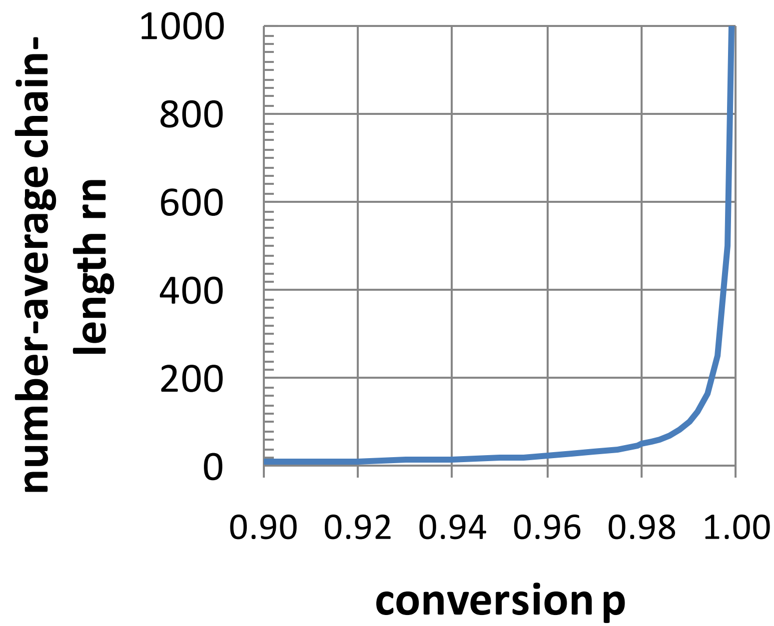
Typical polycondensation processes have three distinct stages:

(a) first stage or prepolymerizer
  (to prepare prepolymer from the monomers)

(b) second stage or polymerizer
  (to polymerize the prepolymer to a moderate molecular weight)

(c) final stage or finisher
  (to reach the polymer up to the final, desired molecular weight)

Each stage is inherently different due to
- kinetic
- mass transfer
- heat transfer
- viscosity problems



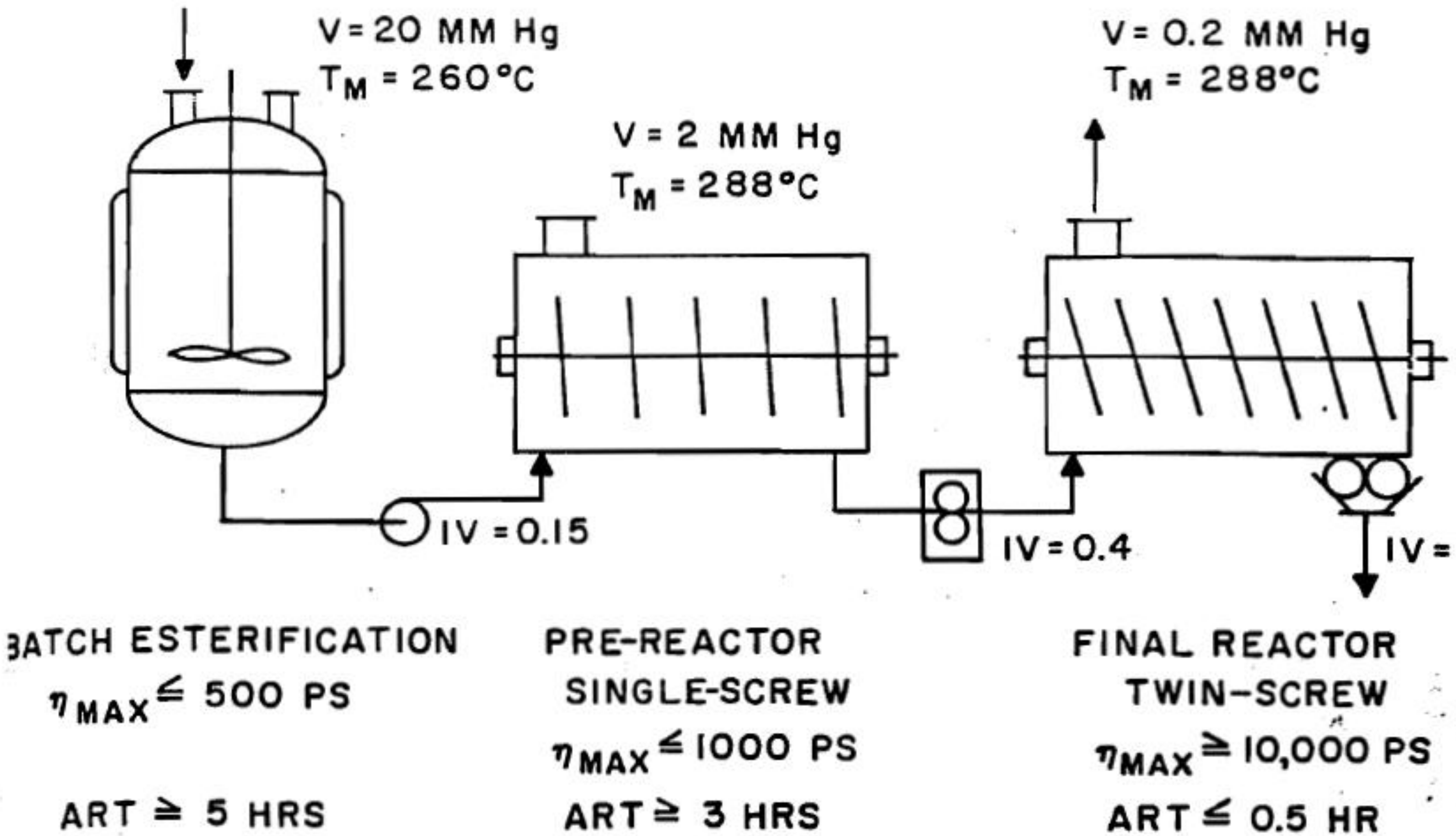


Figure 11. Typical multi-stage polycondensation reactors.

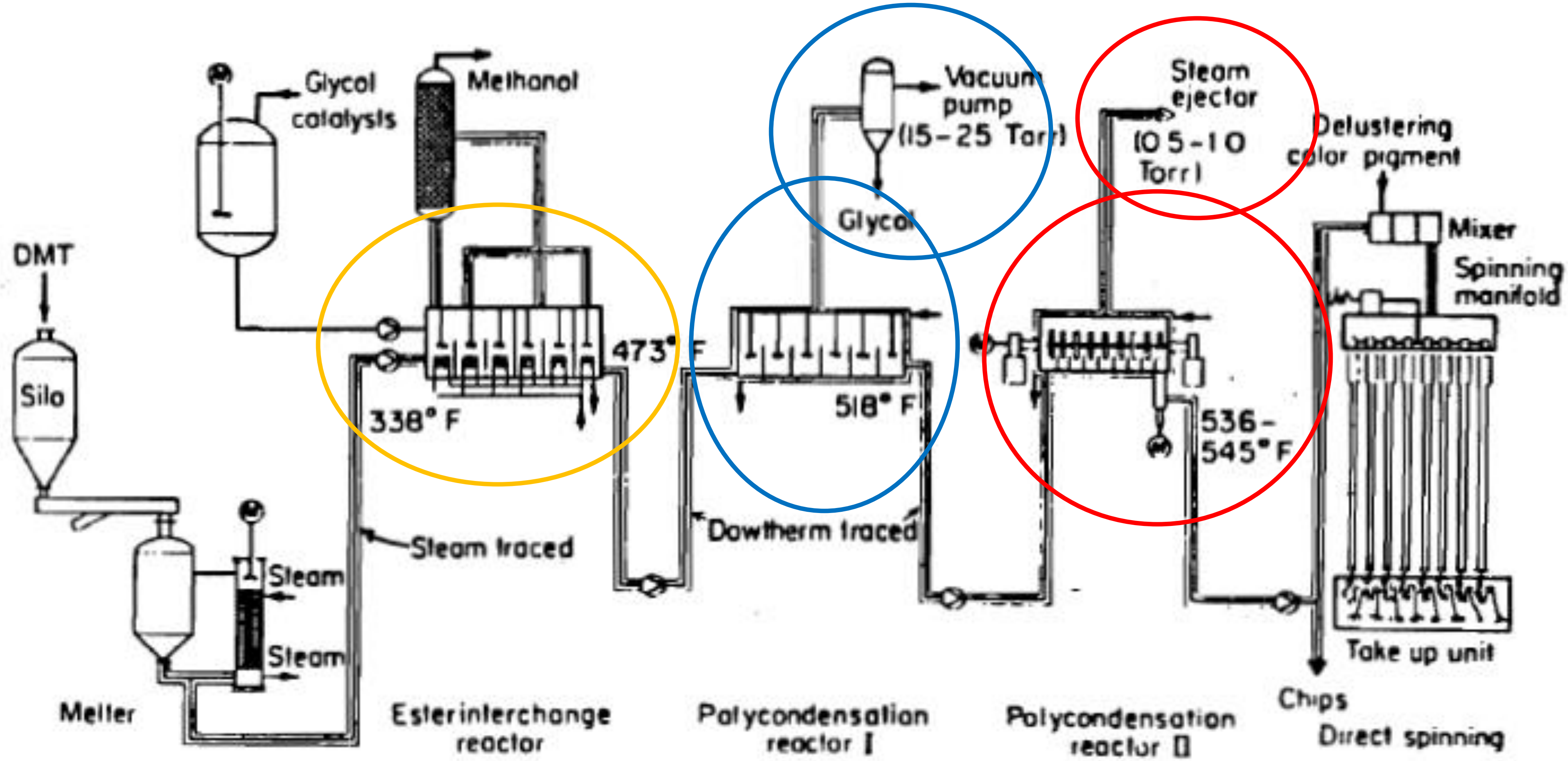
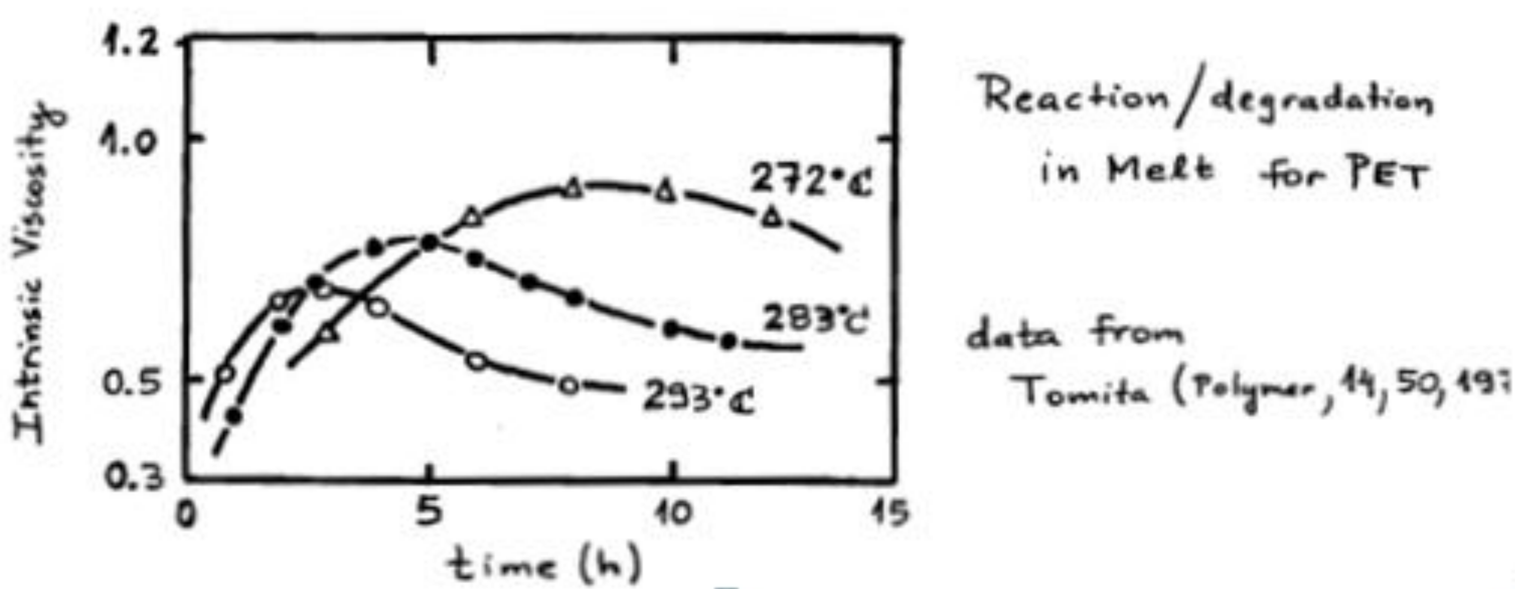


Fig. 2-16 Schematic representation of industrial process for synthesis of poly(ethylene terephthalate). After Ellwood [1967] (by permission of American Chemical Society, Washington, D.C.).

SSP

- High molecular weight polymers (PET, nylon, PBT, etc.)
  - Requires very high conversions ⇒ higher T, longer t ⇒ **degradation**
- Problems in melt polymerization:
  - high viscosity, mixing problems, heat and mass transfer, cleaning
- Lower T to avoid degradation ⇒ **SSP**
  - usually 10 to 50 °C lower then Tm in melt polymerization
  - but T higher than Tg (mobility of end groups)



SSP

- T_g (glass transition) < T_{SSP} < T_m (melting transition)
- end groups still have enough mobility
- polymer as pellets of 1-4 mm (shorter distance for diffusion of small molecules)
- small byproducts removed by either operating the reactor at low pressure (vacuum) or flushing the reactor with an inert gas
- previous thermal treatment to increase crystallinity (to prevent sticking ; however, high crystallinity $\rightarrow$ low diffusivity of end groups and small molecule byproducts)

APPLICATIONS:

- PET for softdrink bottles
- Tire reinforcement cords
- PET recycling

Factors that affect SSP

- Temperature
  - favors end group mobility
  - for PET 210 – 250 °C (T_m = 265 °C)
  - Increase T to speed SSP, but may favor degradation reaction
    - there is an optimum temperature

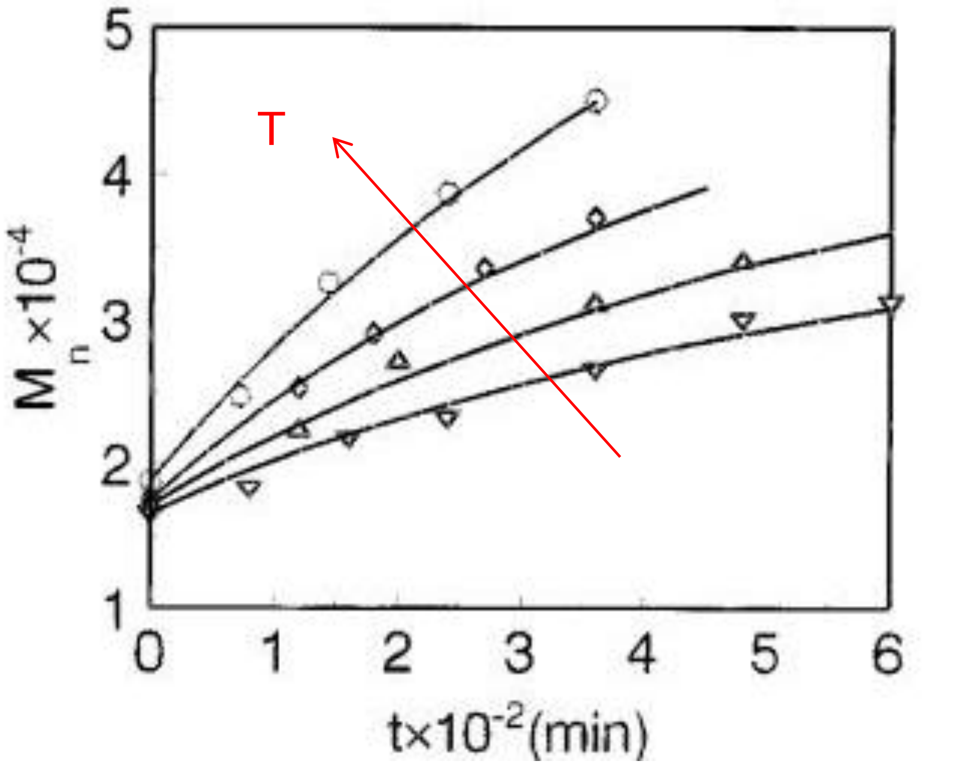


Figure 3. Effect of temperature on the relationship of number-average molecular weight M_n vs time t: (○) T = 245 °C; (◊) T = 235 °C; (△) T = 225 °C; (▽) T = 215 °C. (—) Simulation, experimental at particle size: R = 0.25 mm.

PET
Wu et al., Macromolecules 30(22), 6737 (1997)

- Reaction time
  - SSP requires longer times than in melt polymerization

Factors that affect SSP

- Particle size
  - smaller particles favor diffusion of byproducts
  - too small particles may crystallize too much during drying, making difficult the diffusion of byproducts

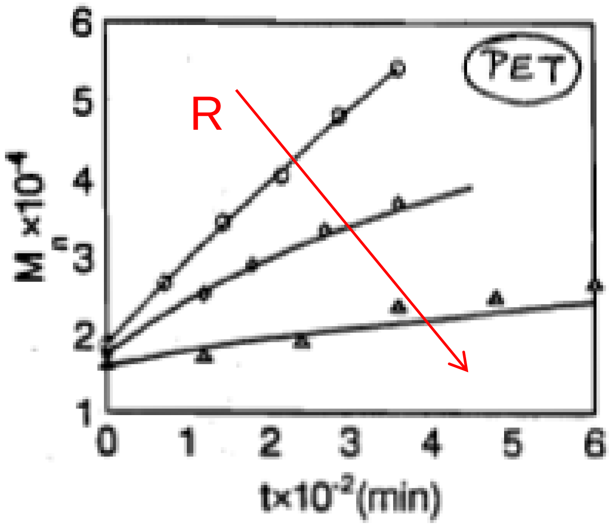
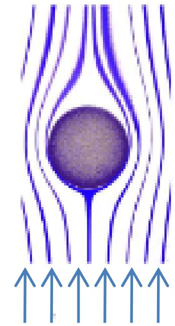


Figure 4. Effect of temperature on the relationship of number-average molecular weight M_n vs time t. (—) Simulation, experimental at temperature T = 235 °C. Particle sizes: (O) R = 0.1 mm; (⊙) R = 0.25 mm; (△) R = 0.5 mm.

from Wu et al, Macromolecules, 30(22), 6737 (1997)

- Gas flow rate
  - reduces the external gas-phase mass-transfer resistance



from Qiu Gao et al. Chem. Eng. Sci, 52(3) p.371 (1997)

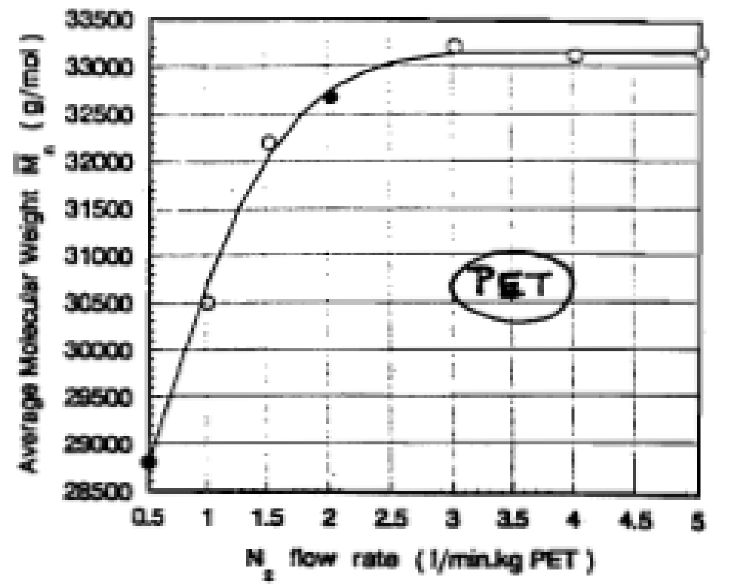


Fig. 1. Influence of nitrogen gas flow rate on SSI (e_0 = 0.0187 mol g^{-1}, x_0 = 0.75 mm, reaction temp T = 225°C, reaction time t = 1800 min).

Factors that affect SSP

- Particle size
  - smaller particles favor diffusion of byproducts
- Gas flow rate
  - reduces the external gas-phase mass-transfer resistance

Variation of MW with particle radius for PBT

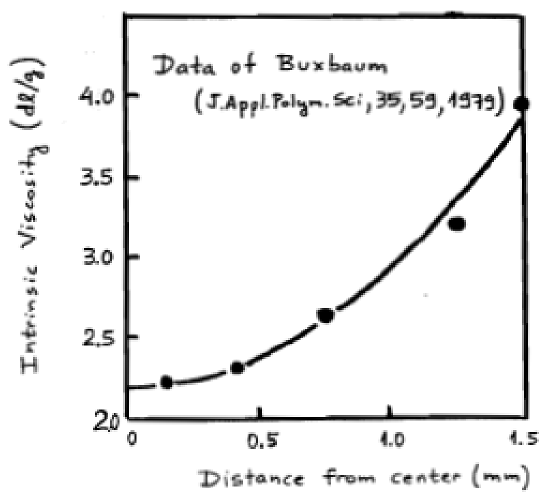


Table 2. Intrinsic viscosity as a function of time at various N_2 flow rates

Flow rate ($l\ min^{-1}\ kg^{-1}$ PET)	Time (min)	Intrinsic viscosity ($dl\ g^{-1}$)			Molecular weight		
		Average	Surface	Core	Average	Surface	Core
2.0	600	0.859	0.887	0.837	25,390	26,400	24,600
	1200	0.963	1.034	0.935	29,180	32,010	28,150
	1800	1.057	1.141	1.007	32,690	35,900	30,800
0.5	600	0.837			24,600		
	1200	0.893			26,620		
	1800	0.953			28,810		

from Qiu Gao et al., CES, 52(3), 371 (1997)

Factors that affect SSP

crystallinity

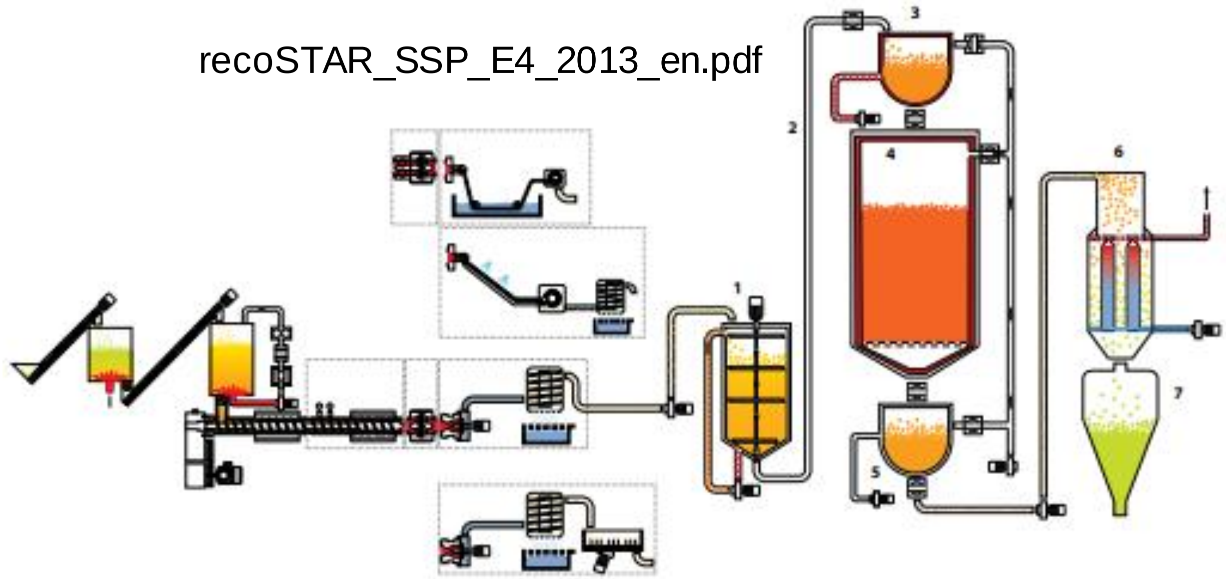
- partial crystallization is induced during drying previously the SSP
  - (to reduce sticking)
- crystalline regions reject condensate and end groups
  - concentrations in amorphous phase increase
  - affecting kinetics and mass transfer
- diffusivity decreases as crystallinity increases
  - polymer crystallites obstruct the diffusion path (tortuosity)

reactor type

SSP may be carried out

- in tumbler dryer, under low pressure (vacuum)
  - (usual in laboratory)
- in moving packed bed (with an inert gas passing through)
- in fluidized bed
- in stirred beds

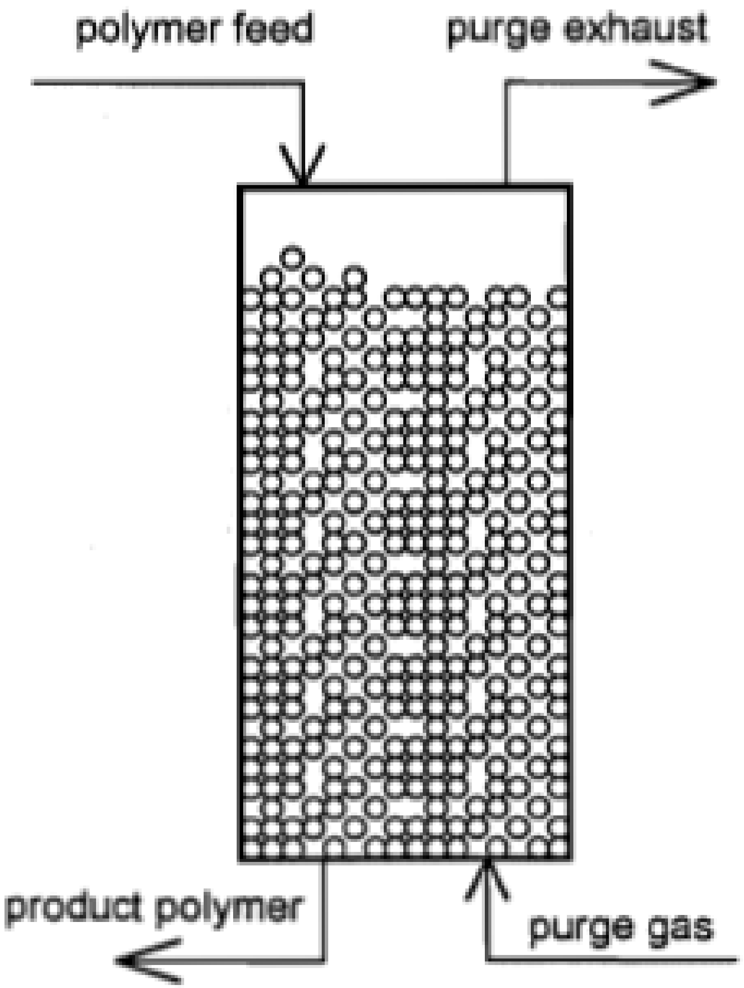
recoSTAR_SSP_E4_2013_en.pdf



1. Crystallizer
2. Vacuum transport
3. Preheating unit
4. SSP reactor
5. Cooling unit/vacuum sluice
6. Energy recovery kit
7. Storage silo

https://docplayer.es/20342585-Nosinyec-fabricacion-de-pellets-desde-botellas-postconsumo.html

Moving packed bed

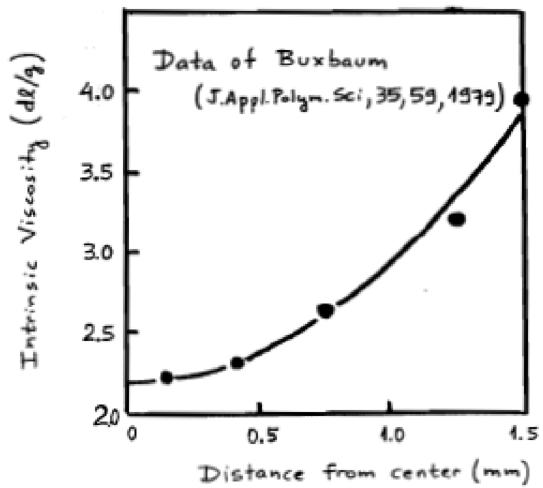


Typical conditions for PET:

- temperature about 230°C
- N_2 as carrier gas
- polym. resid.time about 3 hrs.
- particle size about 2 mm

Model for SSP

Variation of MW with particle radius for PBT



Model equations

condensate concentrations (volatile species)

$$\frac{\partial C_v}{\partial t} = D\nabla^2 C_v + \textit{Reaction terms}$$

b.c. at the particle center $\quad (\partial C_v / dr) = 0$

b.c. at the particle surface $\quad -D\frac{\partial C_v}{\partial r} = k_m(f_{solif,v} - P_{gas,v})$

non-volatile species

$$\frac{dC_k}{dt} = \textit{Reaction terms}$$

D = f(crystallinity) = f(X_c)

conc. in amorphous phase = concentration /(1-X_c)

Reactions terms = h(X_c, catalyst conc., current local conc. in amorphous phase)

Particle is isothermal

Mark-Houwink Eqn. to convert Mw to IV: $\quad IV = k M^a$

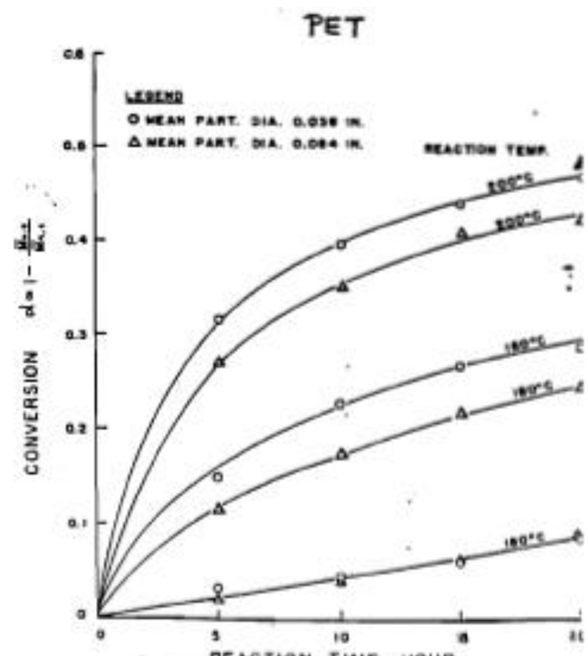
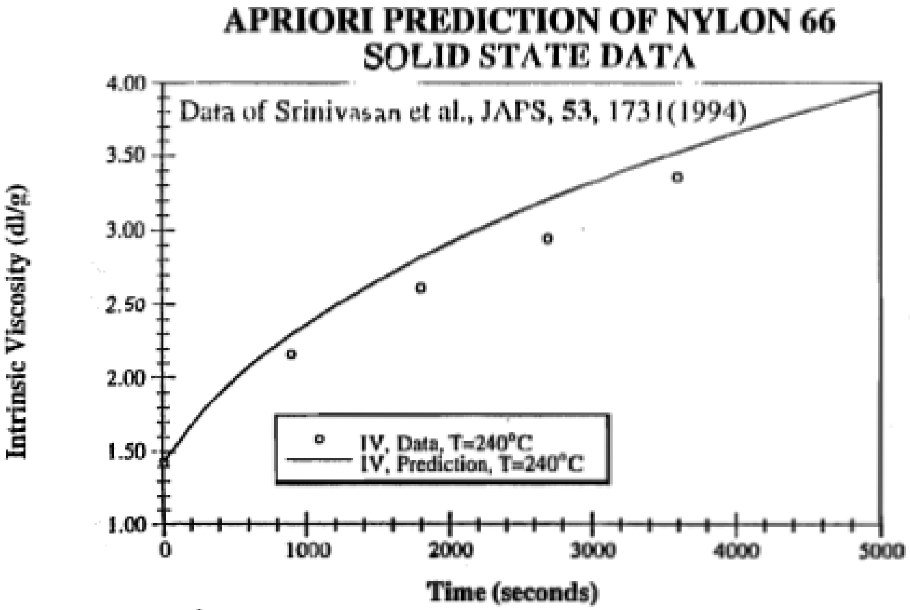
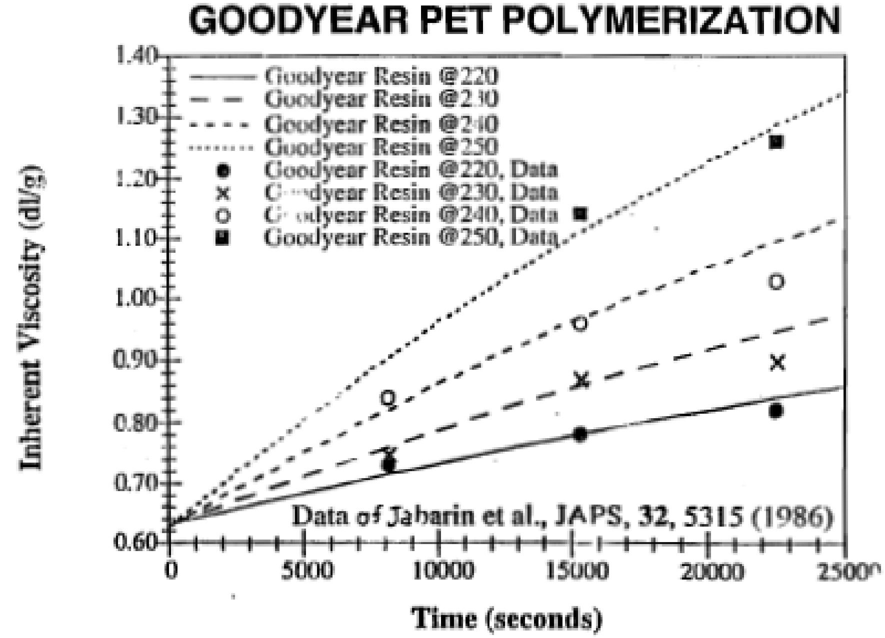
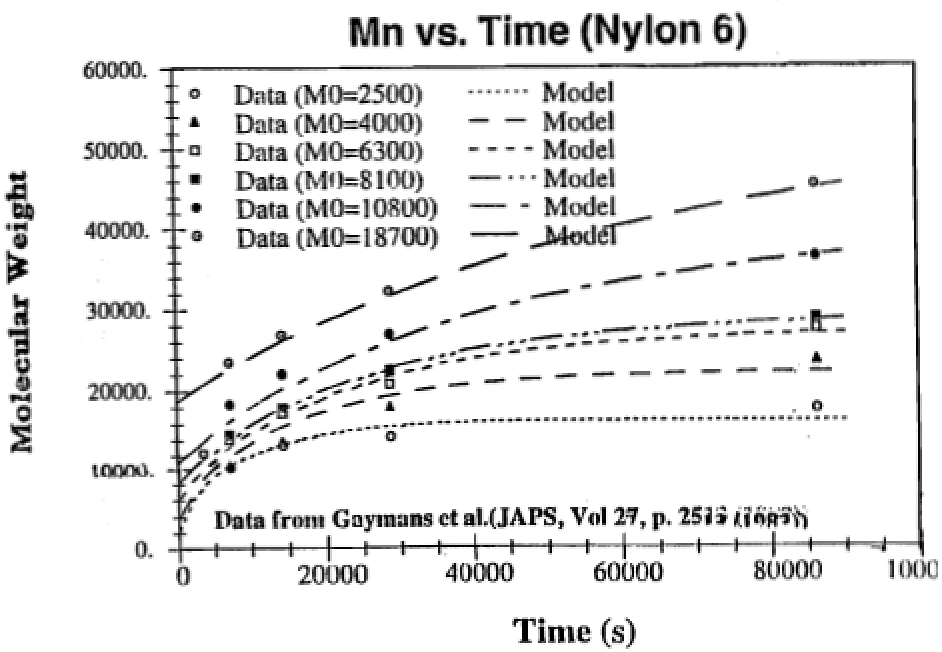
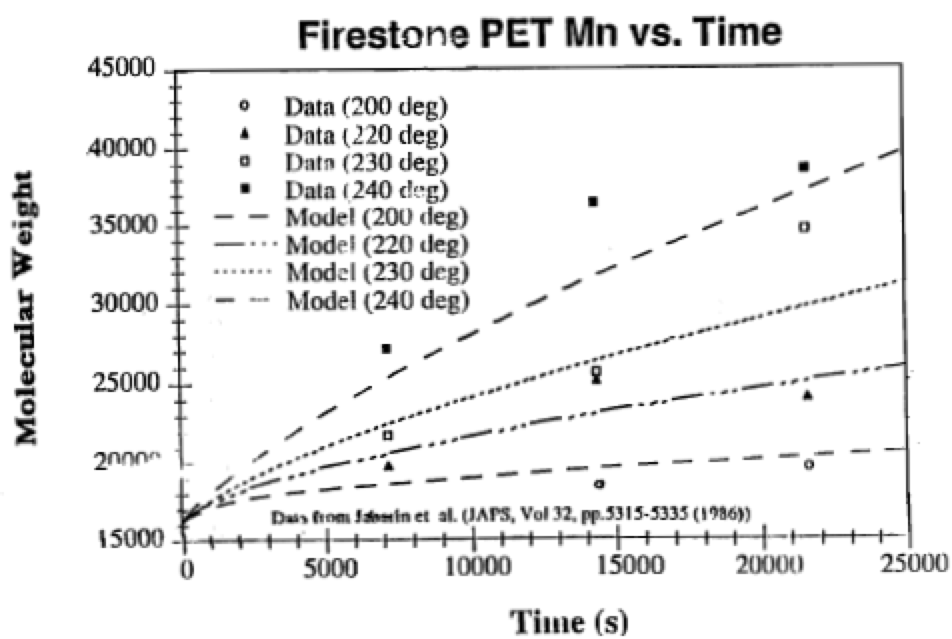


Fig. 7. Conversion vs. reaction time for polyethylene terephthalate.

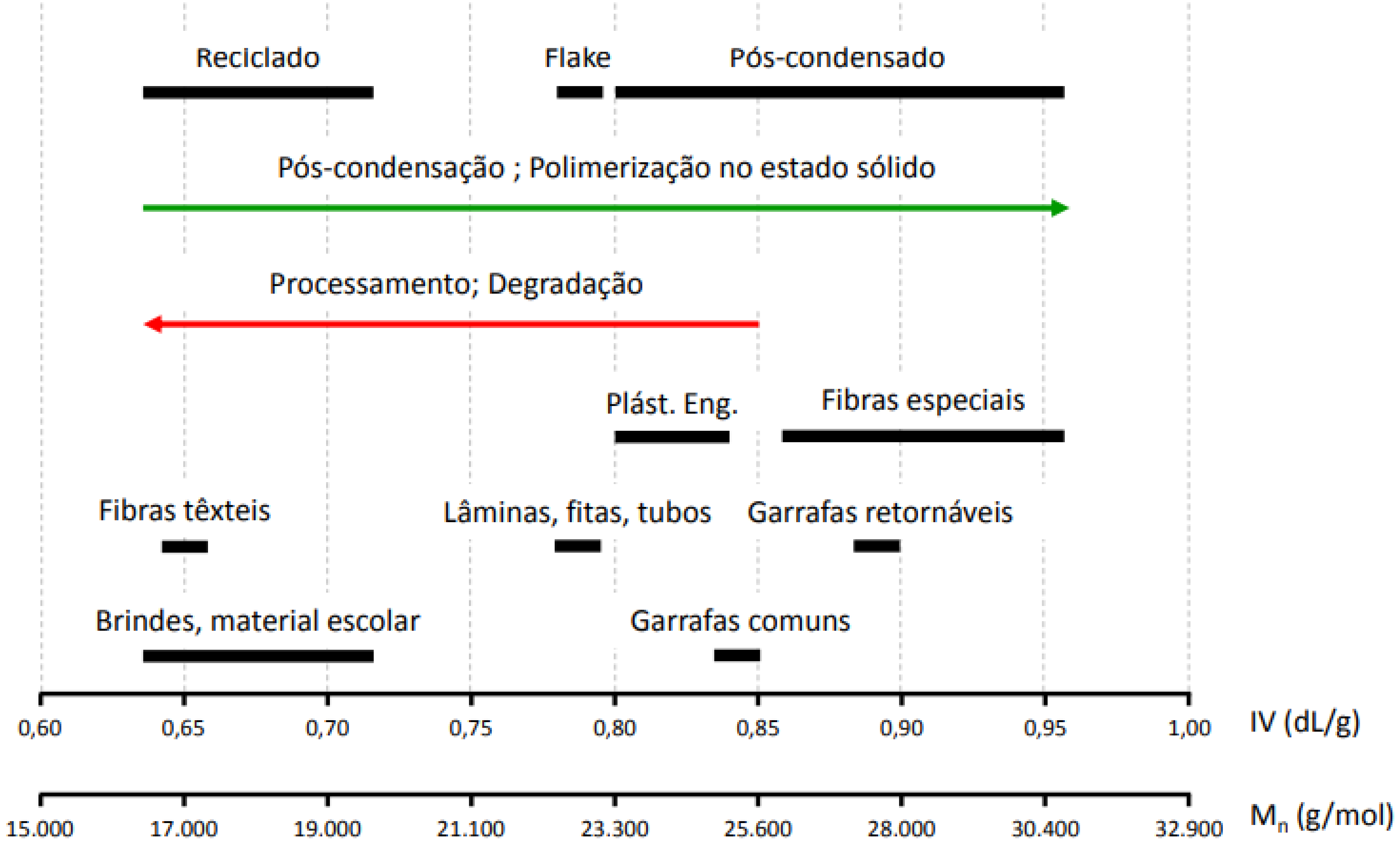

APRIORI PREDICTION OF NYLON 66
SOLID STATE DATA
Data of Srinivasan et al., JAPS, 53, 1731(1994)
IV, Data, T=240°C
IV, Prediction, T=240°C
Intrinsic Viscosity (dl/g)
Time (seconds)
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0
1000
2000
3000
4000
5000


GOODYEAR PET POLYMERIZATION
Goodyear Resin @220
Goodyear Resin @230
Goodyear Resin @240
Goodyear Resin @250
Goodyear Resin @220, Data
Goodyear Resin @230, Data
Goodyear Resin @240, Data
Goodyear Resin @250, Data
Data of Jabarin et al., JAPS, 32, 5315 (1986)
Inherent Viscosity (dl/g)
Time (seconds)
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0
5000
10000
15000
20000


Mn vs. Time (Nylon 6)
Data (M0=2500)
Data (M0=4000)
Data (M0=6300)
Data (M0=8100)
Data (M0=10800)
Data (M0=18700)
Model
Model
Model
Model
Model
Model
Data from Gaymans et al.(JAPS, Vol 27, p. 2513
Molecular Weight
Time (s)
60000.
50000.
40000.
30000.
20000.
0.
0
20000
40000
60000
80000


Firestone PET Mn vs. Time
Data (200 deg)
Data (220 deg)
Data (230 deg)
Data (240 deg)
Model (200 deg)
Model (220 deg)
Model (230 deg)
Model (240 deg)
Data from Jabarin et al. (JAPS, Vol 32, pp.5315-5335 (1986))
Molecular Weight
Time (s)
45000
40000
35000
30000
25000
15000
0
5000
10000
15000
20000
25000

Polimerização no Estado Sólido (SSP) de PET



(L.B.Canto, curso Circularidade e Eng. de Polímeros, 2020)