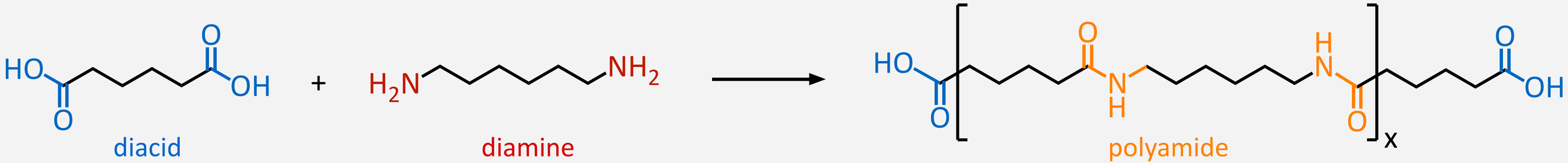
5.2 Step-Growth Reactions

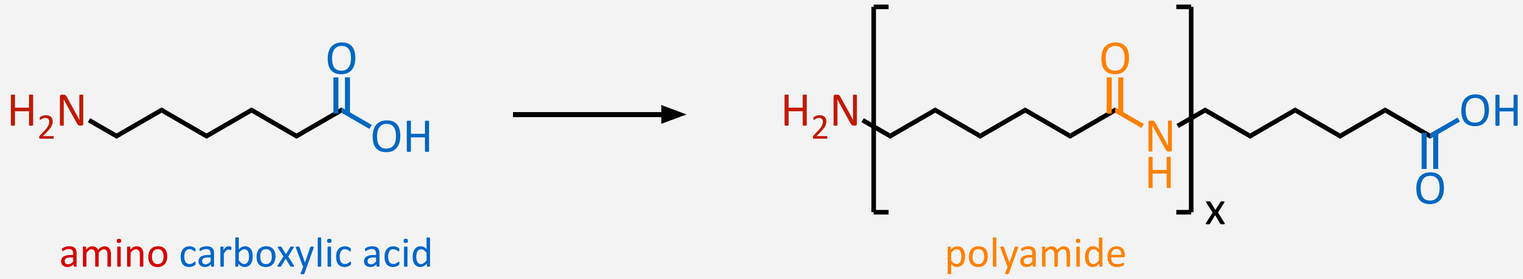
Step Growth Reactions

- every step of polymer growth is an independent organic reaction (e.g., esterification)
- requirement for polymer formation: monomers must be difunctional molecules

  - AA/BB-type: two monomers with two identical, complementary functions each



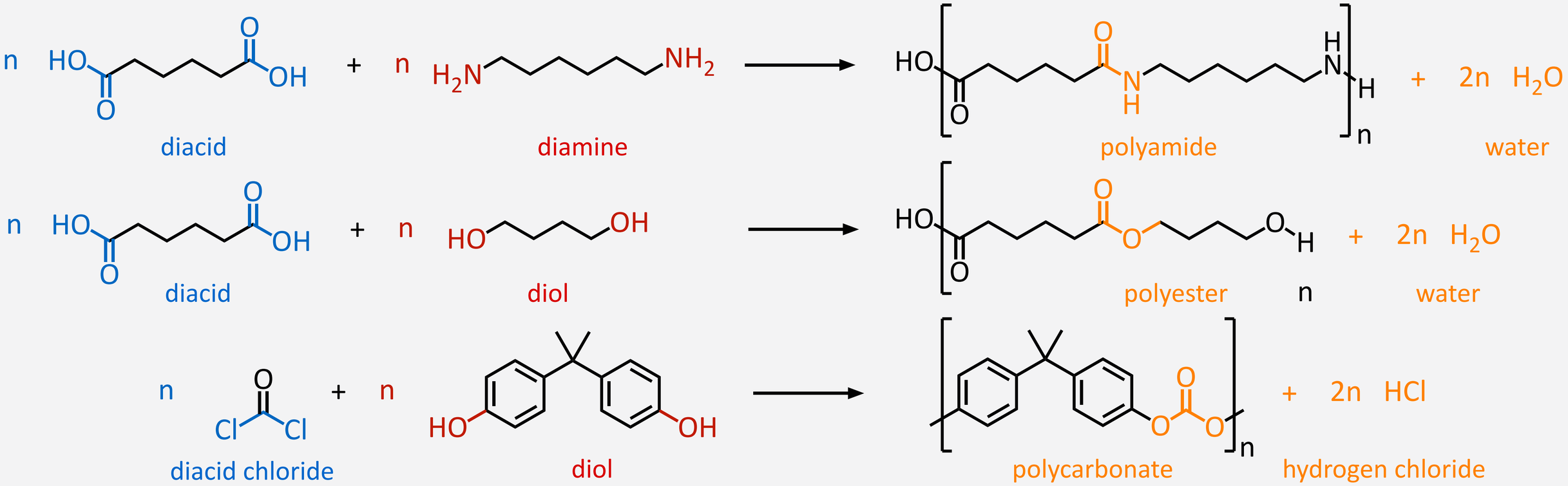
  - AB-type: one monomer with two complementary functions



- end groups always remain active for further coupling reactions
- degree of polymerization is function of the degree of conversion of functional groups

Polycondensations

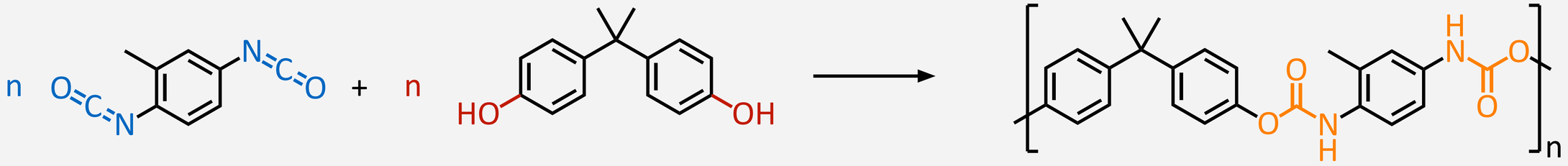
- **polycondensations** are reactions of difunctional molecules under release of a small molecule
- AA/BB-type and AB-type polycondensations are both possible



- problem: each step is an equilibrium reaction, multiplication results in diminishing polymer yield
- relatively “simple” and very efficient coupling reactions are typically employed
- typically performed in “open systems”, under removal of the small moleciule side product

Polyadditions

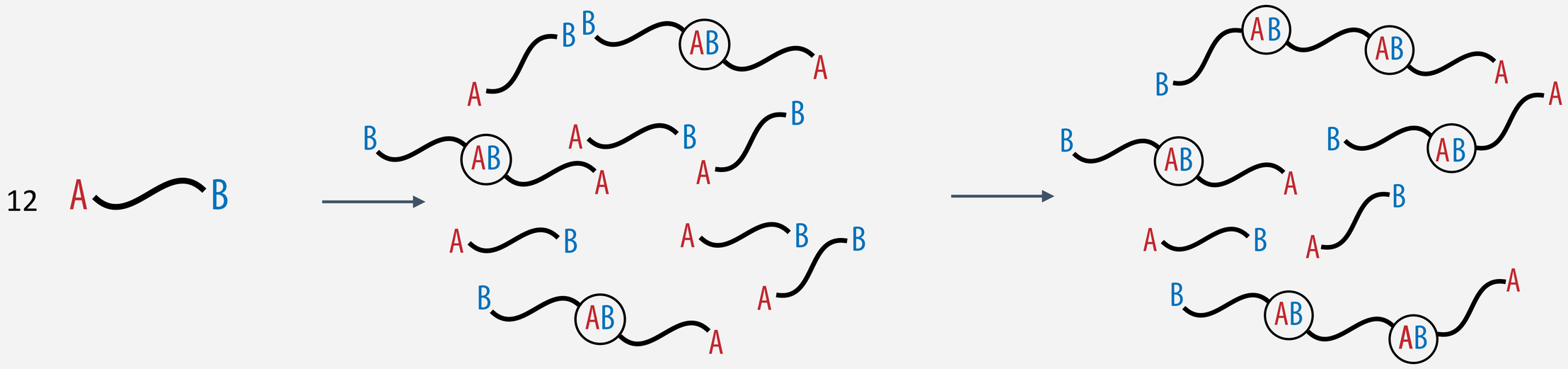
- **polyaddition**: reaction of difunctional molecules **without release of small molecule side-product**



diisocyanate diol polyurethane

- **small molecule elimination already performed during monomer synthesis**
- **high-energy monomers, coupling reactions are inherently efficient**

Origin of Dispersity and Molecular Weight Limitations



0% conversion
$M_n = 1$
$M_w = 1$
$Đ = 1$

25% conversion
$M_n = 1.33$
$M_w = 1.50$
$Đ = 1.13$

50% conversion
$M_n = 2.00$
$M_w = 2.33$
$Đ = 1.16$

- **polymer chain growth is a statistical process, and hence the source of dispersity**
- **dispersity increases with conversion of functional groups**
- **conversion limits molecular weight – high molecular weights require extremely high conversions!**

The Carothers Equation

- in the polymerisation of A-A and B-B type monomers, the resulting number-average degree of polymerization $\overline{X}_n$ relates to the conversion *p* of groups A and B and their stoichiometric ratio *r*

ratio of monomers and functional groups

$$r = \frac{[M_A]}{[M_B]} = \frac{N_{A,0}}{N_{B,0}} \qquad N_{A,0} < N_{B,0}$$

conversion of functional groups

$$p = \frac{N_{A,0} - N_A}{N_{A,0}} = \frac{N_{B,0} - N_B}{N_{B,0}}$$

degree of polymerization

$$\overline{X}_n = \frac{N_0}{N} = \frac{1 + r}{1 + r - 2pr}$$

Carothers Equation

- **perfect stoichiometry and high degree of conversion required for high molecular weight polymers**

Dependence of Molecular Weight on Conversion and Functional Group Ratio

$$\overline{X}_n = \frac{1 + r}{1 + r - 2pr}$$

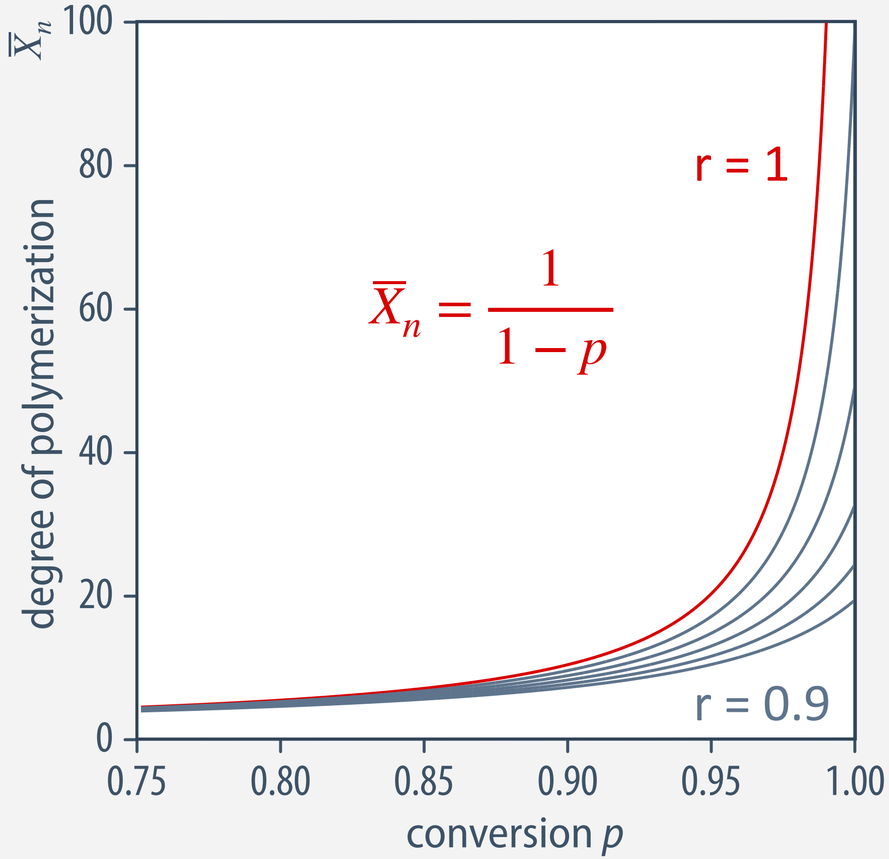
general Carothers Equation

$$\overline{X}_n = \frac{1 + r}{1 - r}$$

for complete conversion (p = 1)

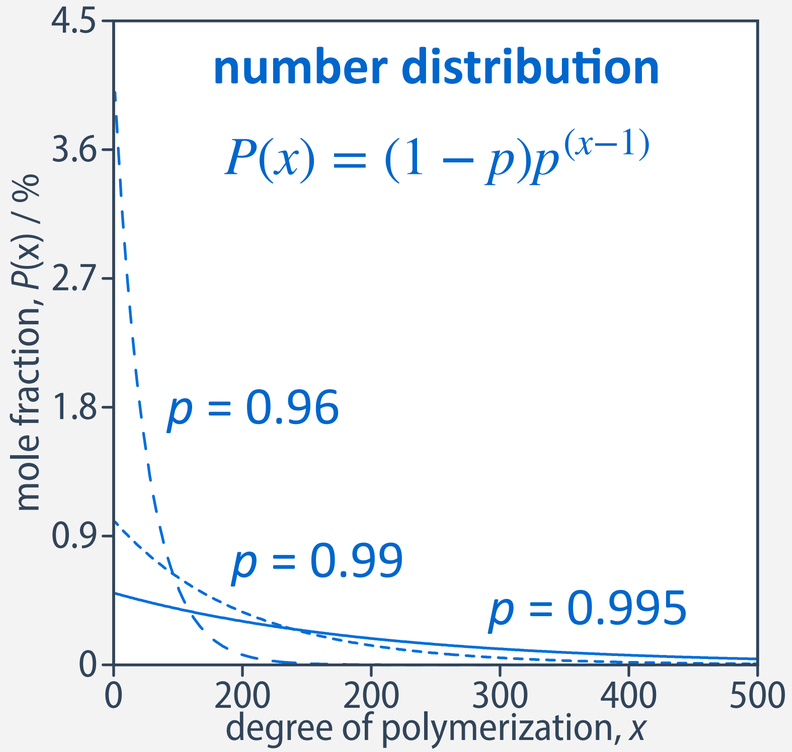
$$\overline{X}_n = \frac{1}{1 - p}$$

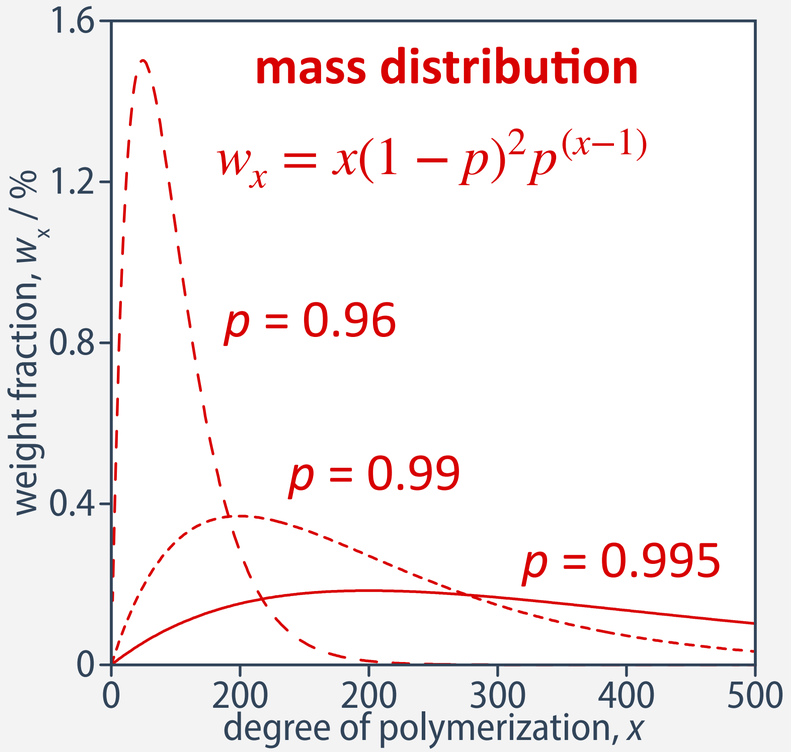
for perfect stoichiometry (r = 1)



- functional group conversions close to unity required for highmolar mass polymers
- significantly reduced molecular weight for any deviation from perfect stoichiometry

Flory-Schulz Distribution





- **at any conversion *p*, the mole fraction of monomer is greater than that of any other species !**
- **mass distribution shows a maximum that moves to higher *x* with increasing conversion *p***

see reader on *Step-Growth Polymerizations*

Summary of the Kinetics of Step Growth Polyreactions

number-average degree of polymerization

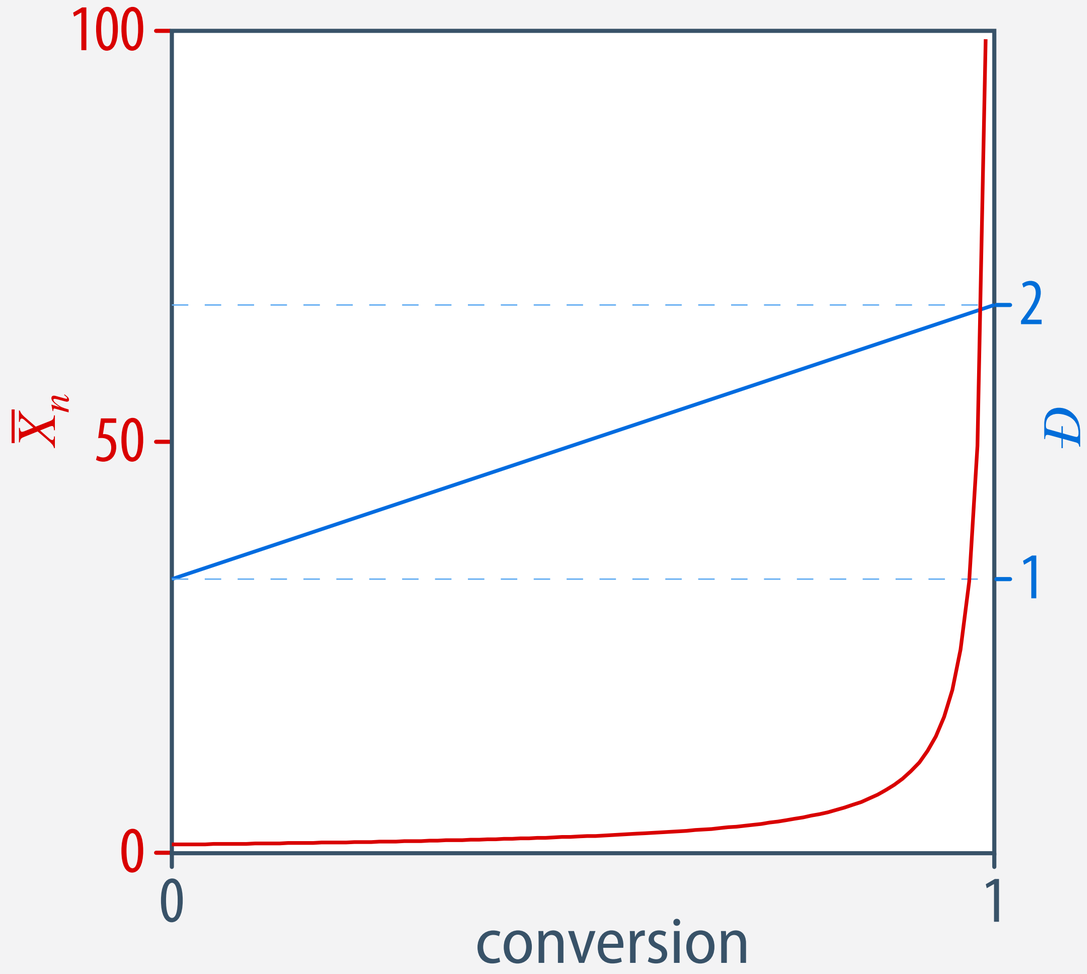
$$\overline{X}_n = \frac{1}{1-p}$$

weight-average degree of polymerization

$$\overline{X}_w = \sum x w_x = \frac{1+p}{1-p}$$

dispersity

$$Đ = \frac{\overline{X}_n}{\overline{X}_w} = 1 + p$$



- **convergence to a dispersity of *Đ* = 2 is diagnostic of a well-behaved step-growth polymerization**