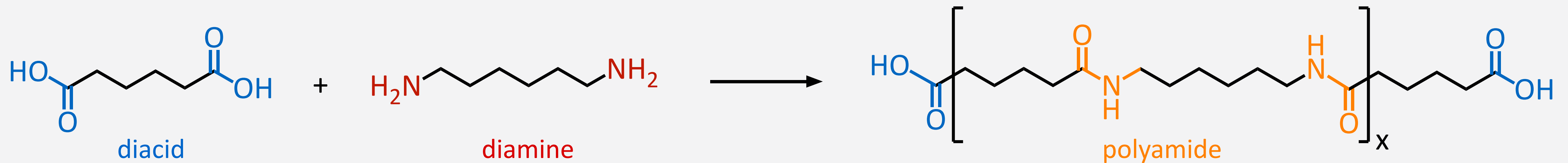


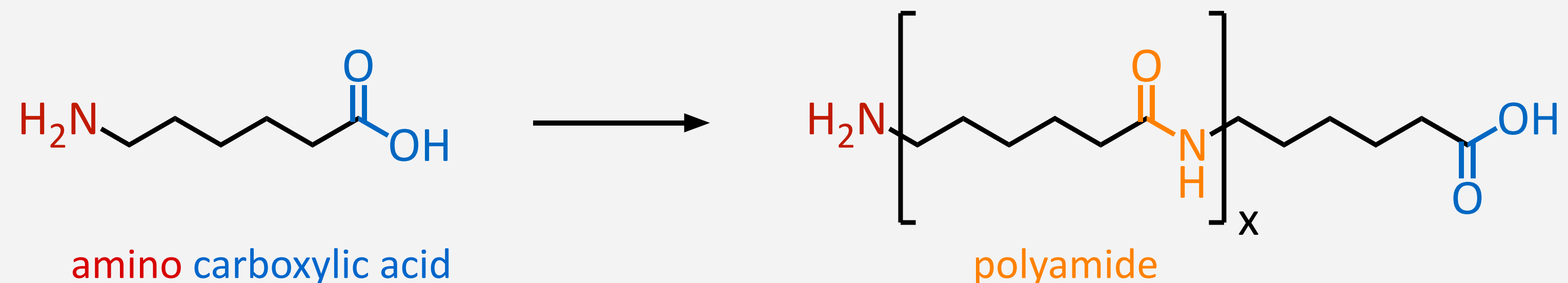
5.2 Step-Growth Reactions

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



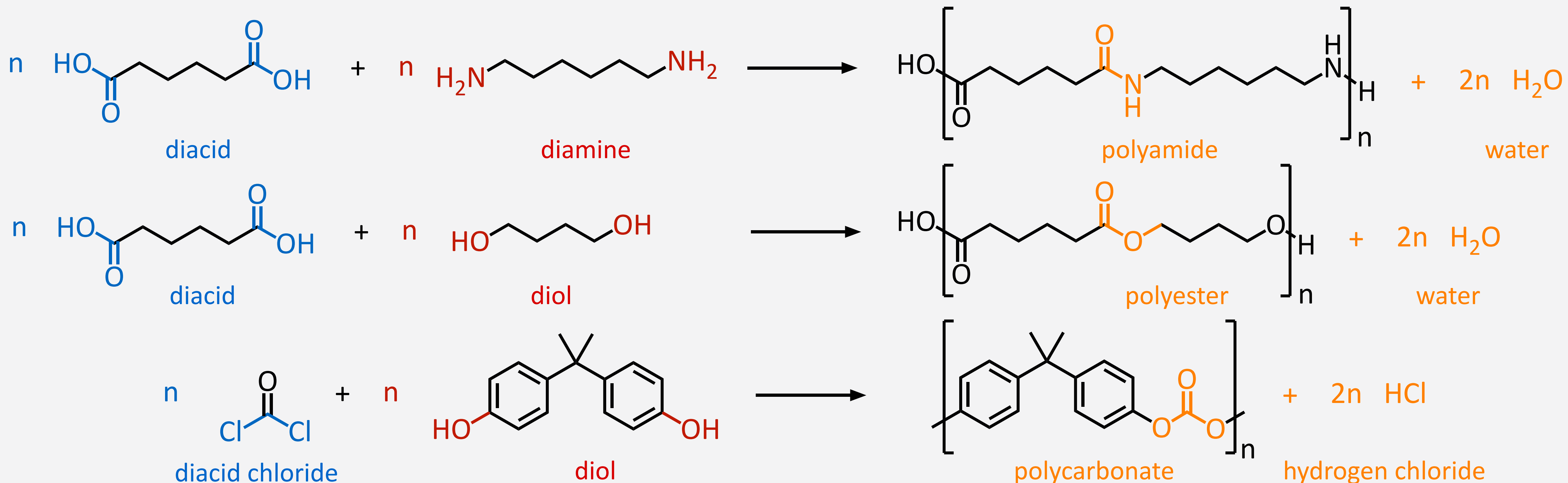
- AB-type: one monomer with two complementary functions



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

Polycondensations

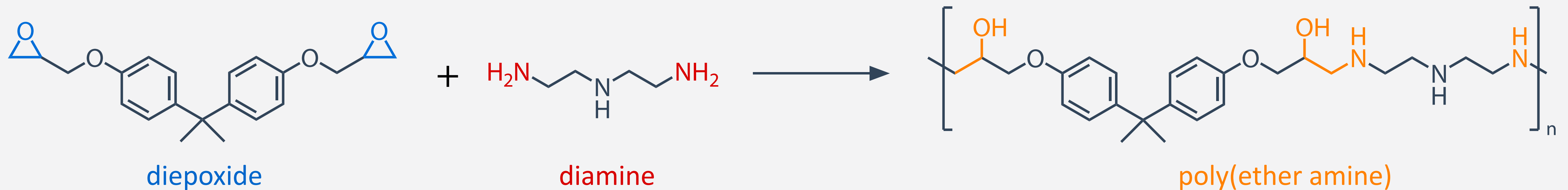
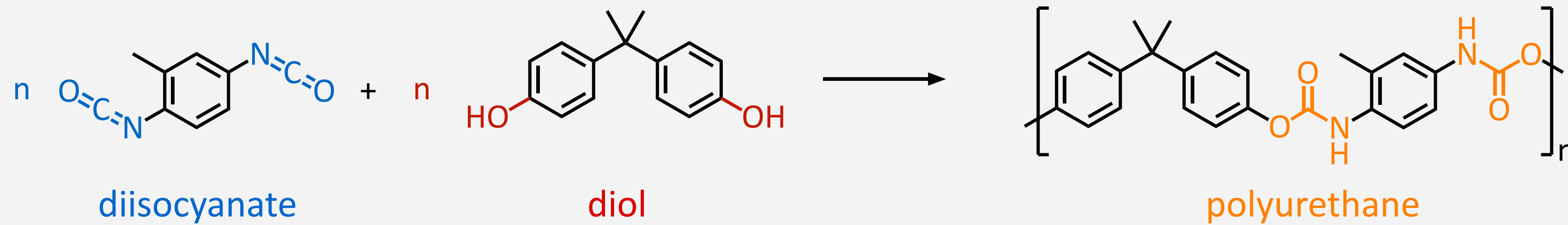
- **polycondensations** are reactions of difunctional molecules under release of a small molecule
- AA/BB-type and AB-type polycondensations are both possible



- **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 molecule side product

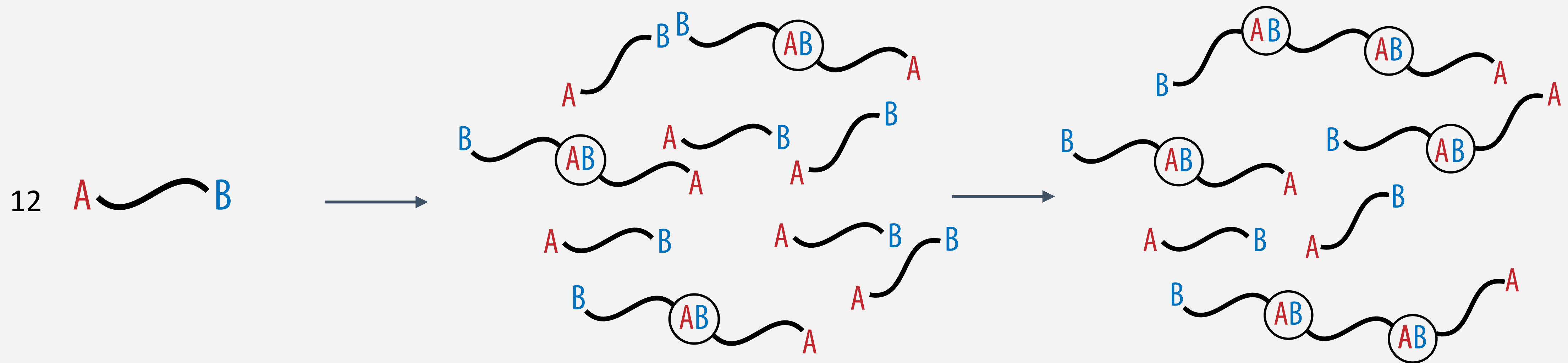
Polyadditions

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



- 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

$$M_n = 1$$

$$M_w = 1$$

$$\bar{D} = 1$$

25% conversion

$$M_n = 1.33$$

$$M_w = 1.50$$

$$\bar{D} = 1.13$$

50% conversion

$$M_n = 2.00$$

$$M_w = 2.33$$

$$\bar{D} = 1.16$$

- 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 molar masses 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 \bar{X}_n relates to the conversion p of groups A and B and their stoichiometric ratio r

ratio of monomers and functional groups

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

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

$$\bar{X}_n = \frac{N_0}{N} = \frac{1 + r}{1 + r - 2pr} \quad \text{Carothers Equation}$$

- perfect stoichiometry and high degree of conversion required for high molar mass polymers

Dependence of Molecular Weight on Conversion and Functional Group Ratio

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

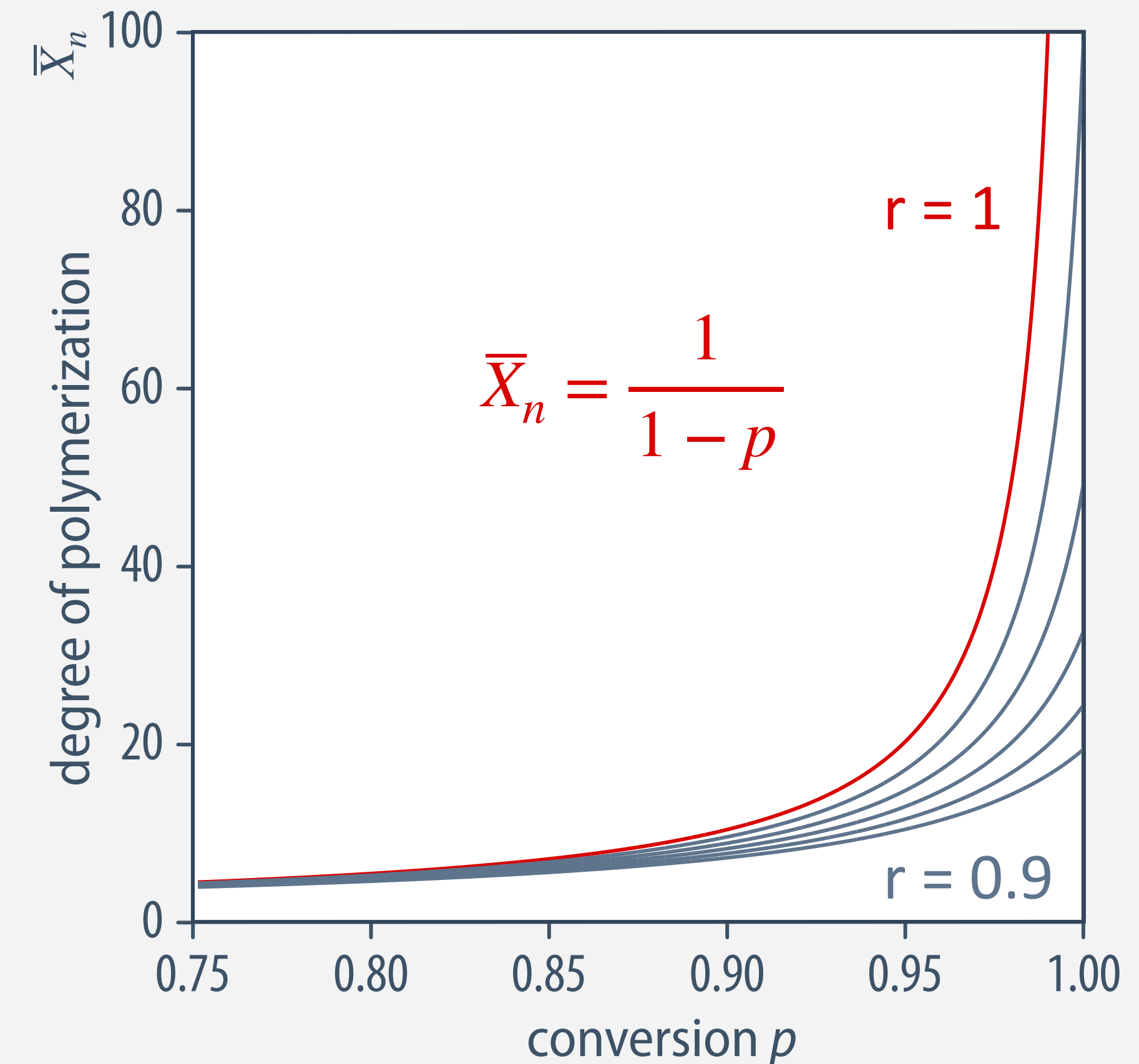
general Carothers Equation

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

for complete conversion ($p = 1$)

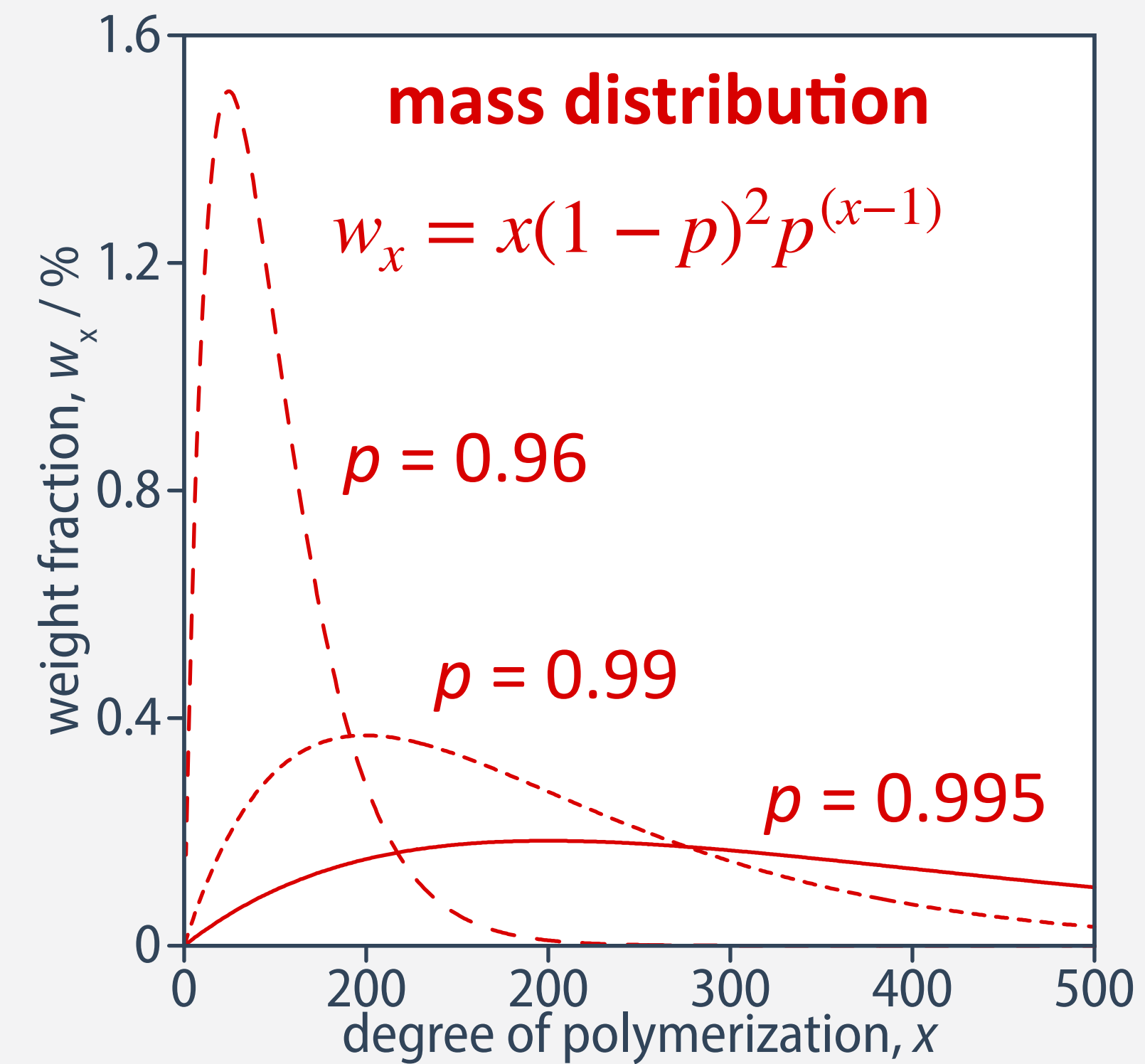
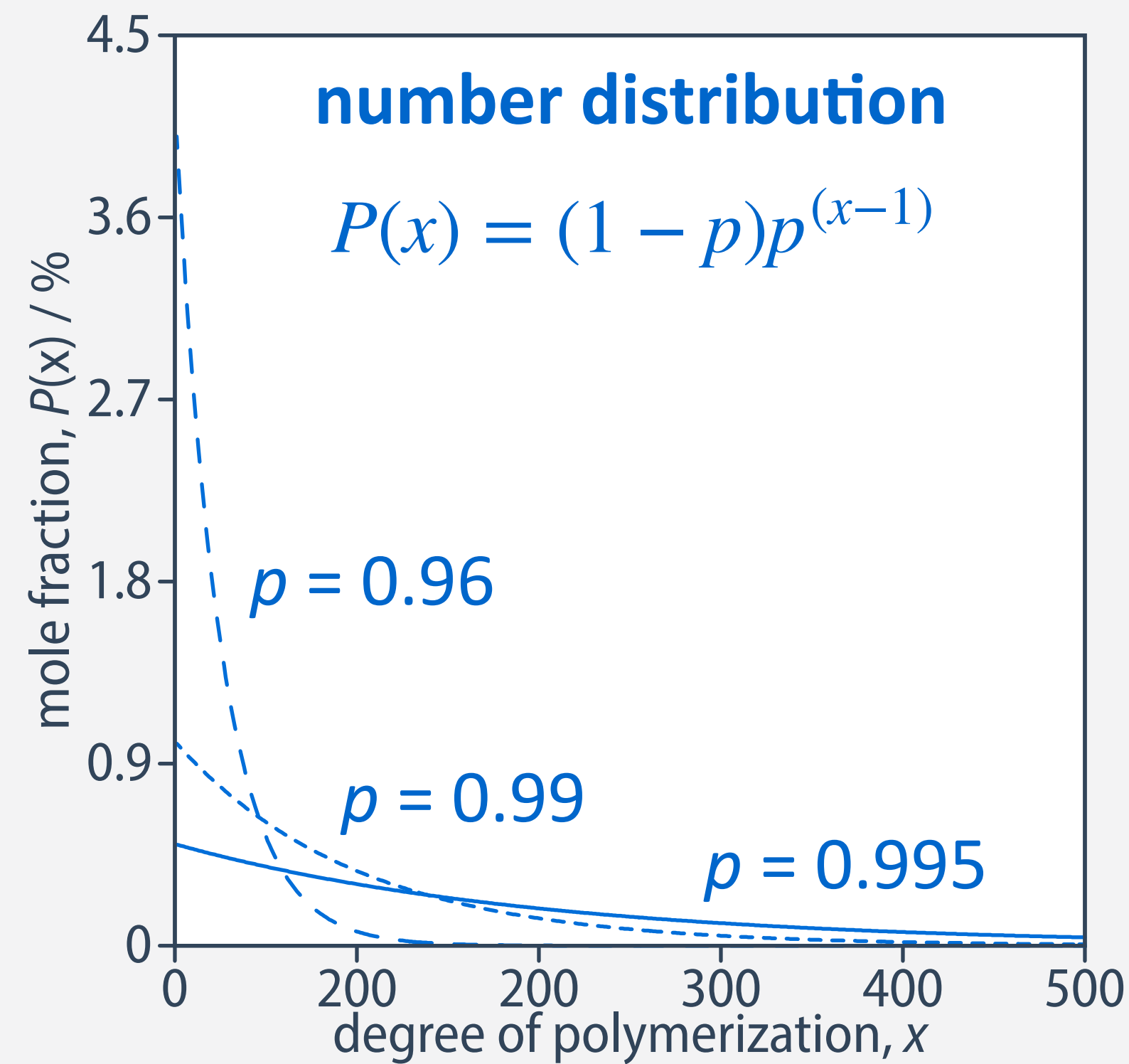
$$\bar{X}_n = \frac{1}{1 - p}$$

for perfect stoichiometry ($r = 1$)



- functional group conversions close to unity required for high molar mass polymers
- significantly reduced molar mass 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

Summary of the Kinetics of Step Growth Polyreactions

number-average degree of polymerization

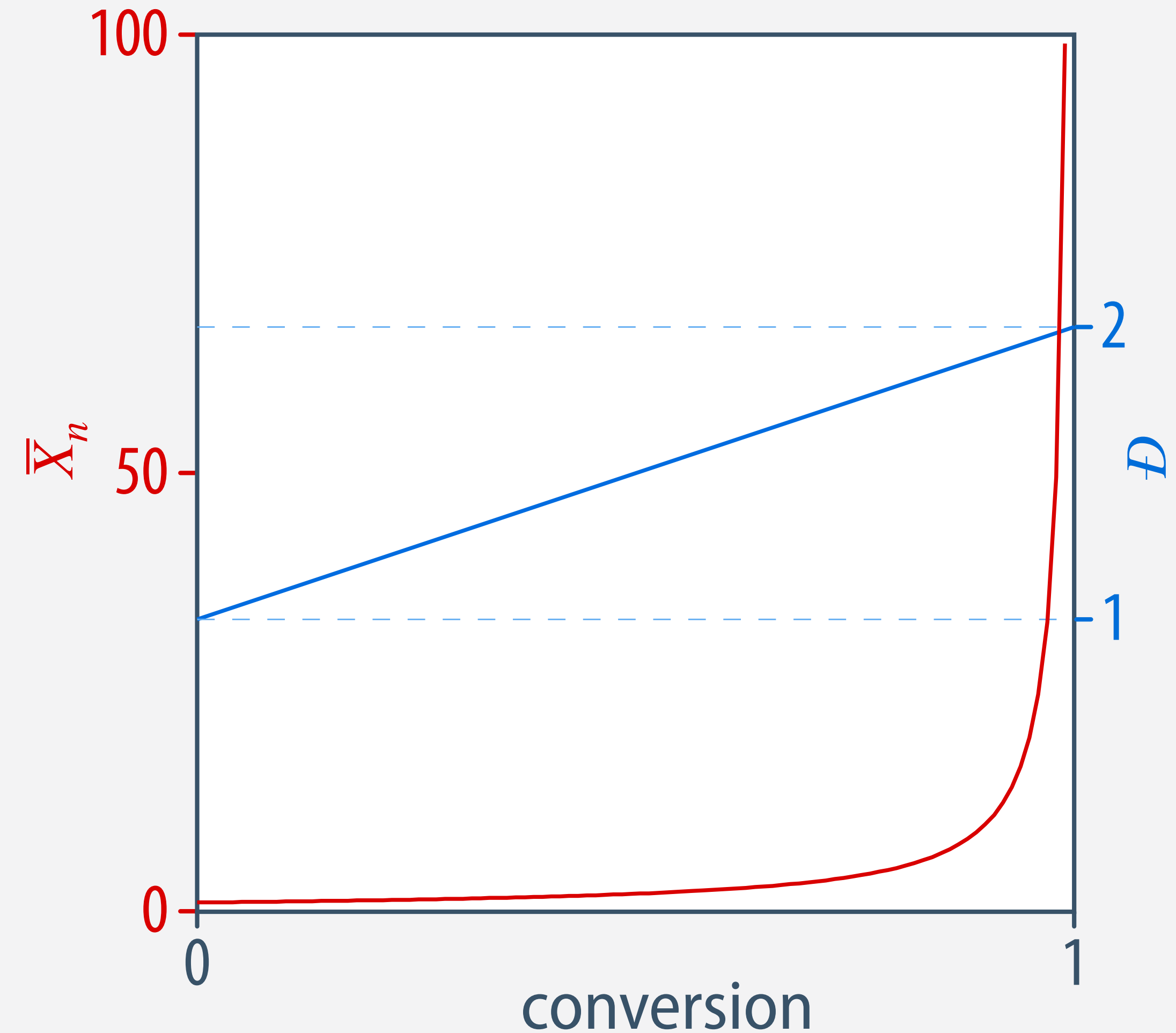
$$\bar{X}_n = \frac{1}{1-p}$$

weight-average degree of polymerization

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

dispersity

$$D = \frac{\bar{X}_w}{\bar{X}_n} = 1 + p$$



- convergence to a dispersity of $D = 2$ is diagnostic of a well-behaved step-growth polymerization

