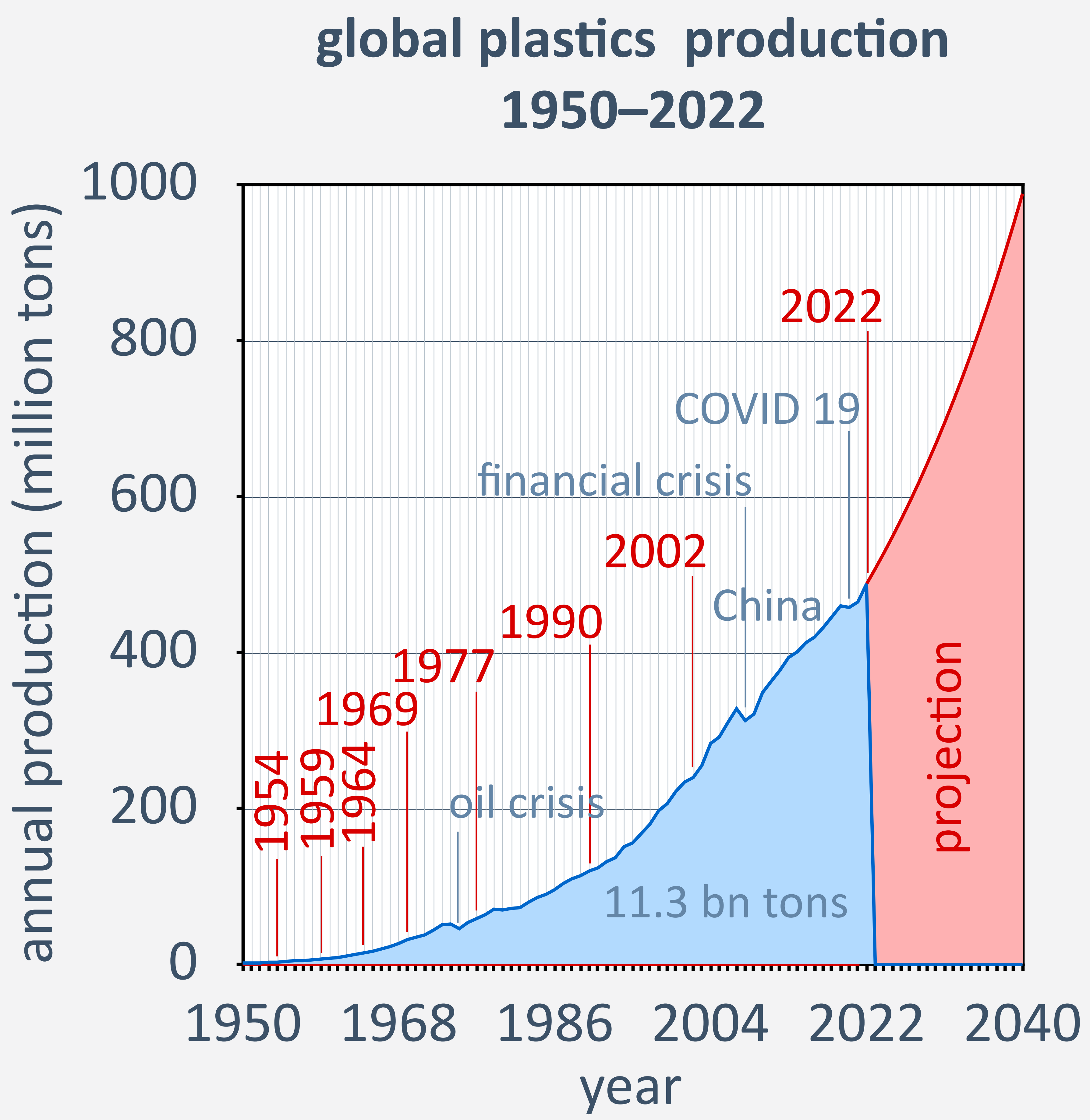
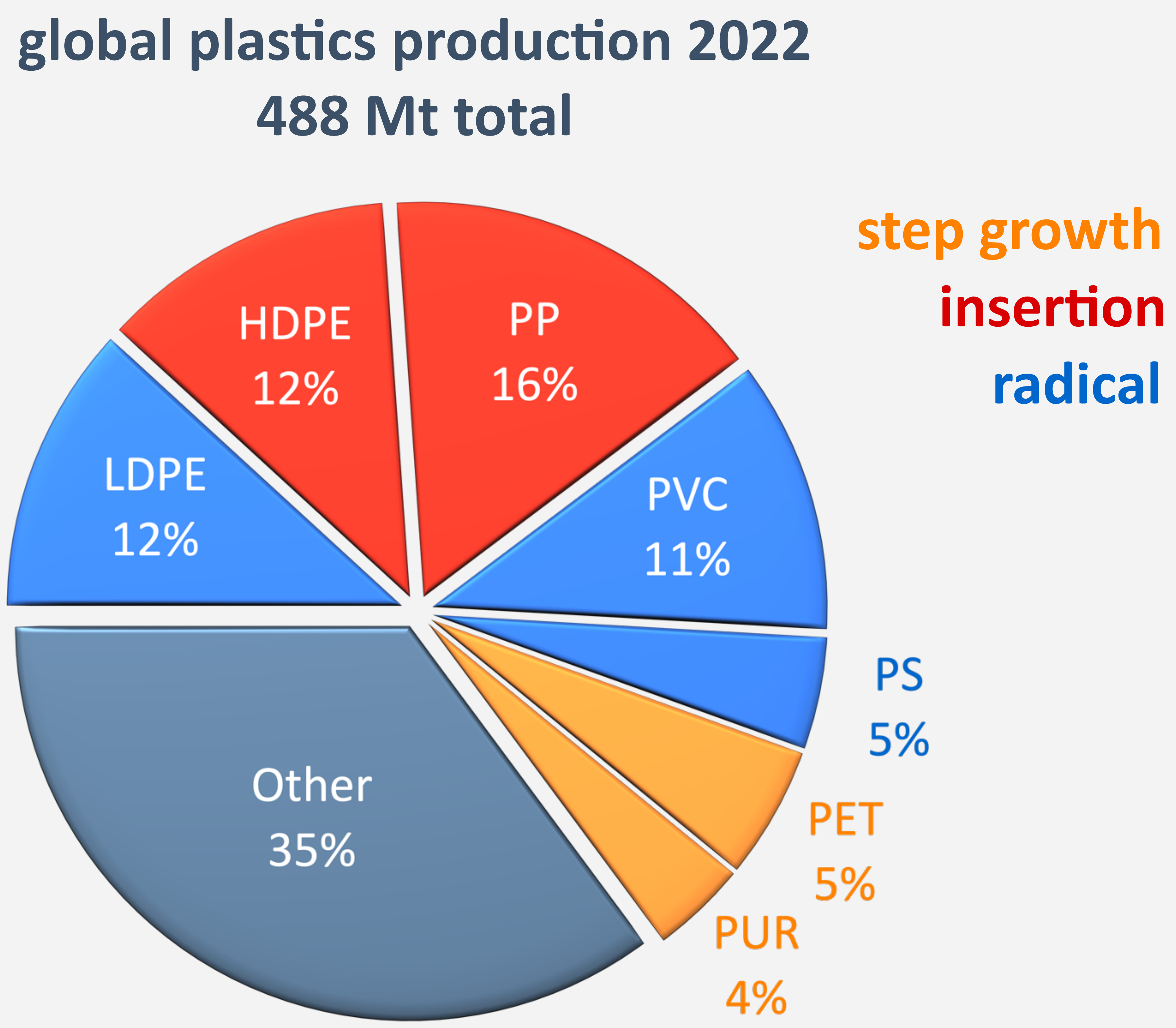
5.5 Polymer Materials

Global Plastics Production



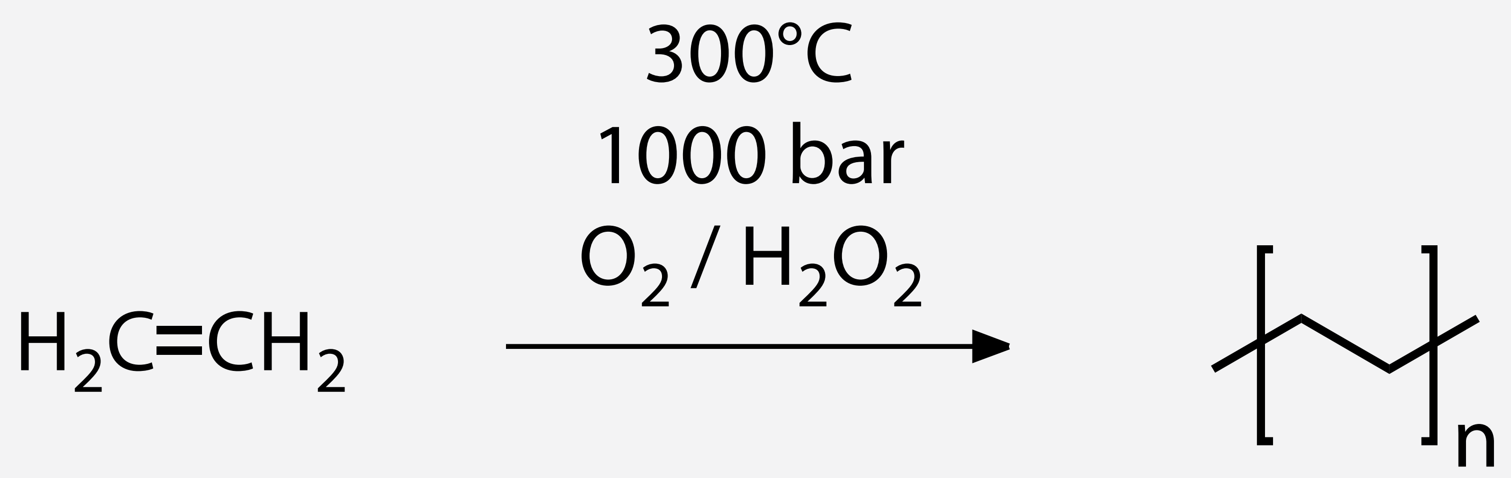


- the "big six" polymers are polyethylene (HDPE, LDPE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS), poly(ethylene terephthalate) (PET), polyurethanes (PUR)

Polyethylene

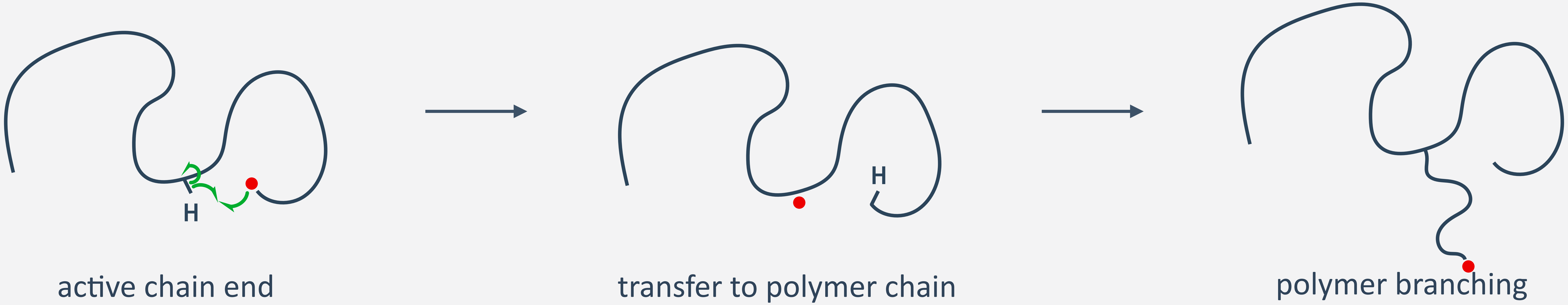
Low-Density Polyethylene (LDPE) by Radical Polymerization of Ethylene

- **free-radical polymerization possible at high temperature and high pressure in the gas phase**



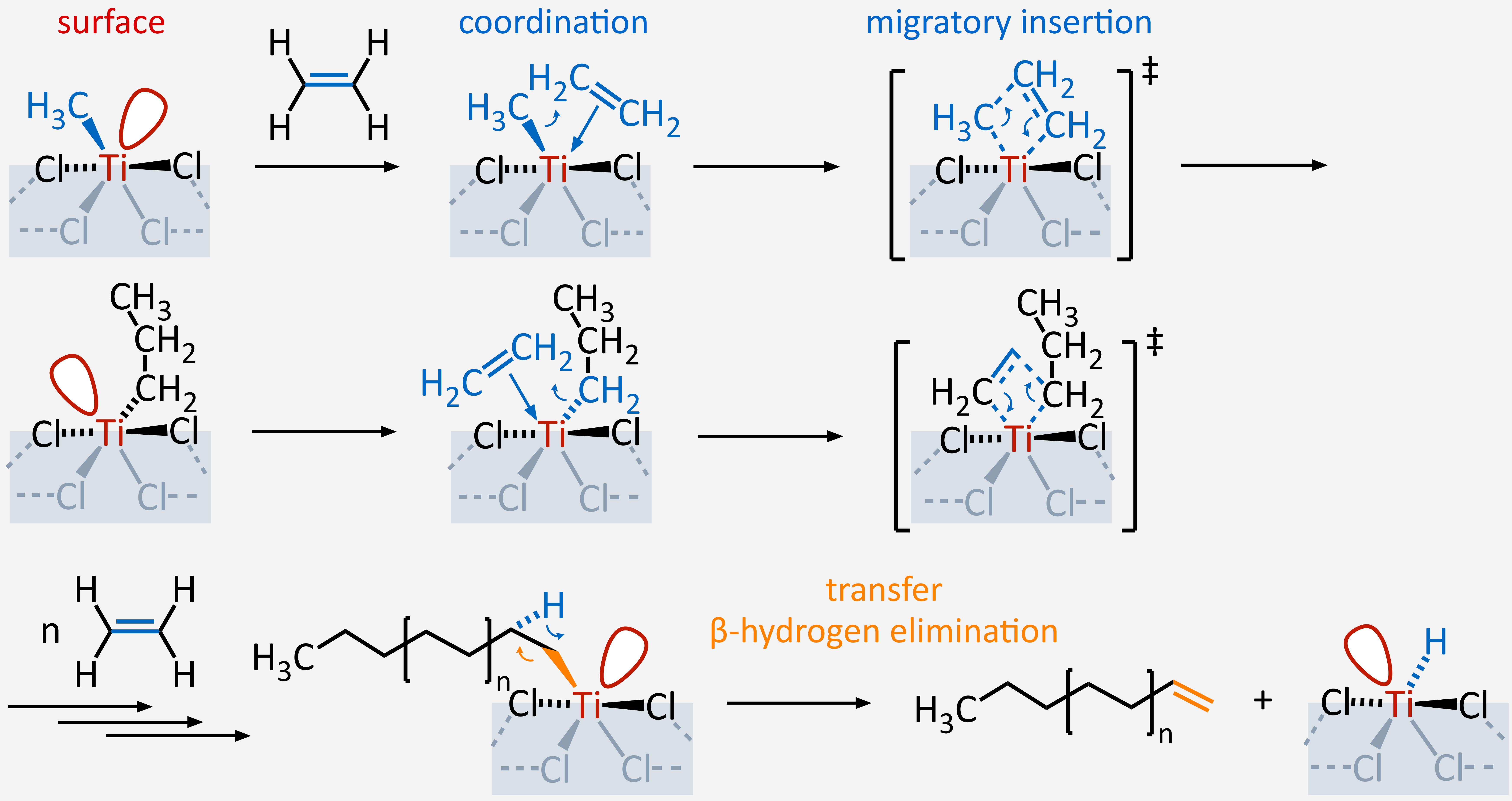
low-density polyethylene (LDPE)
T_g = –100°C; T_m = 105–115°C

  - no electronic stabilization of the radical, requires drastic conditions and promotes side reactions
  - high degree of long-chain branching due to chain transfer (2–4% Me, 0.5% longer branches)



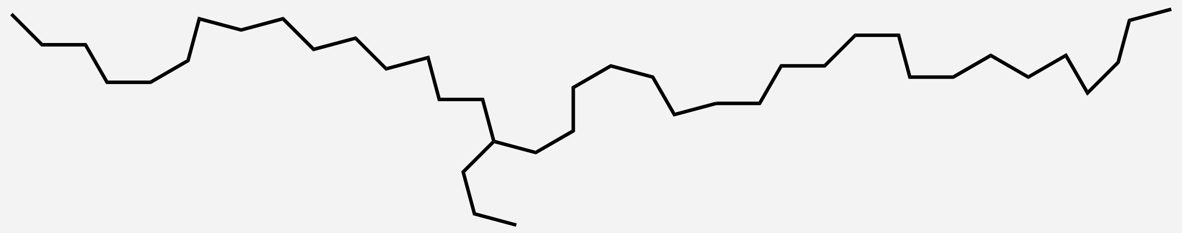
- **long chain branching results in low degree of crystallinity, hence low density and low stiffness**
- **increased entanglement for high melt strength, and (together with low crystallinity) high ductility**

High-Density Polyethylene (HDPE) by Ziegler-Natta Polymerization

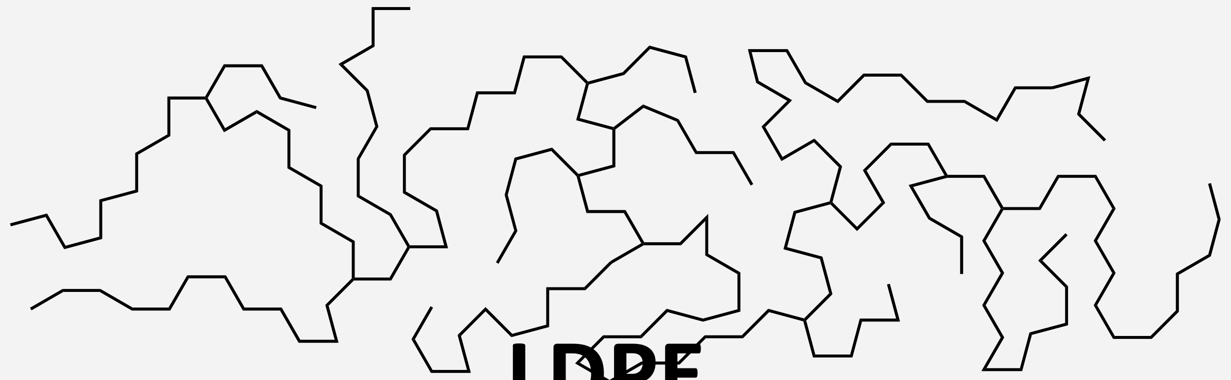


- Cossee Arlman mechanism: **monomer coordination** to **empty coordination site** on surface metal atom
- **migratory insertion** into Mt–C bond, means that **polymer switches coordination site at every step**
- **chain transfer** generates terminal **double bonds** (can result in few branches when polymerized)

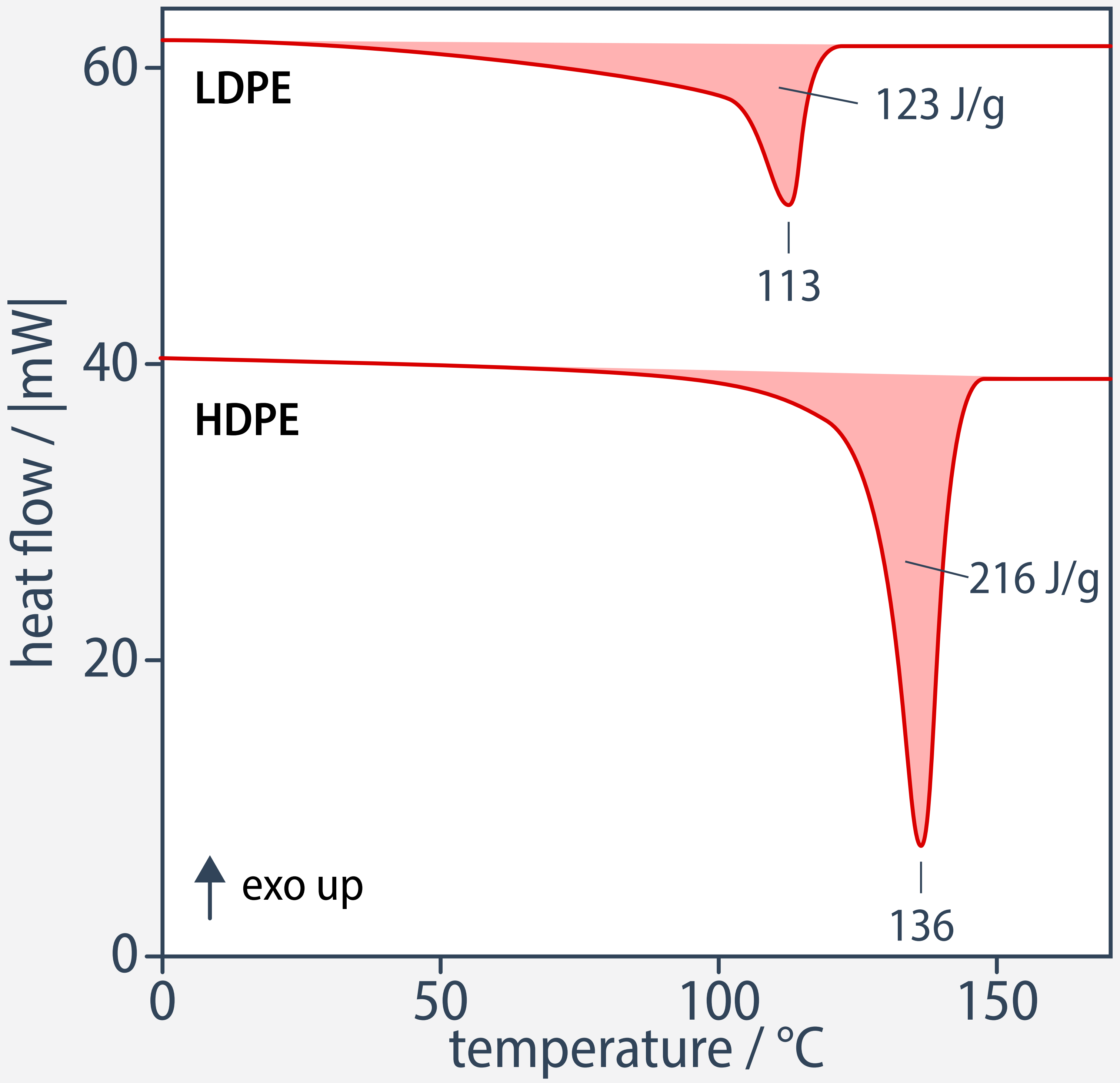
Commercial Polyethylene (PE) Grades

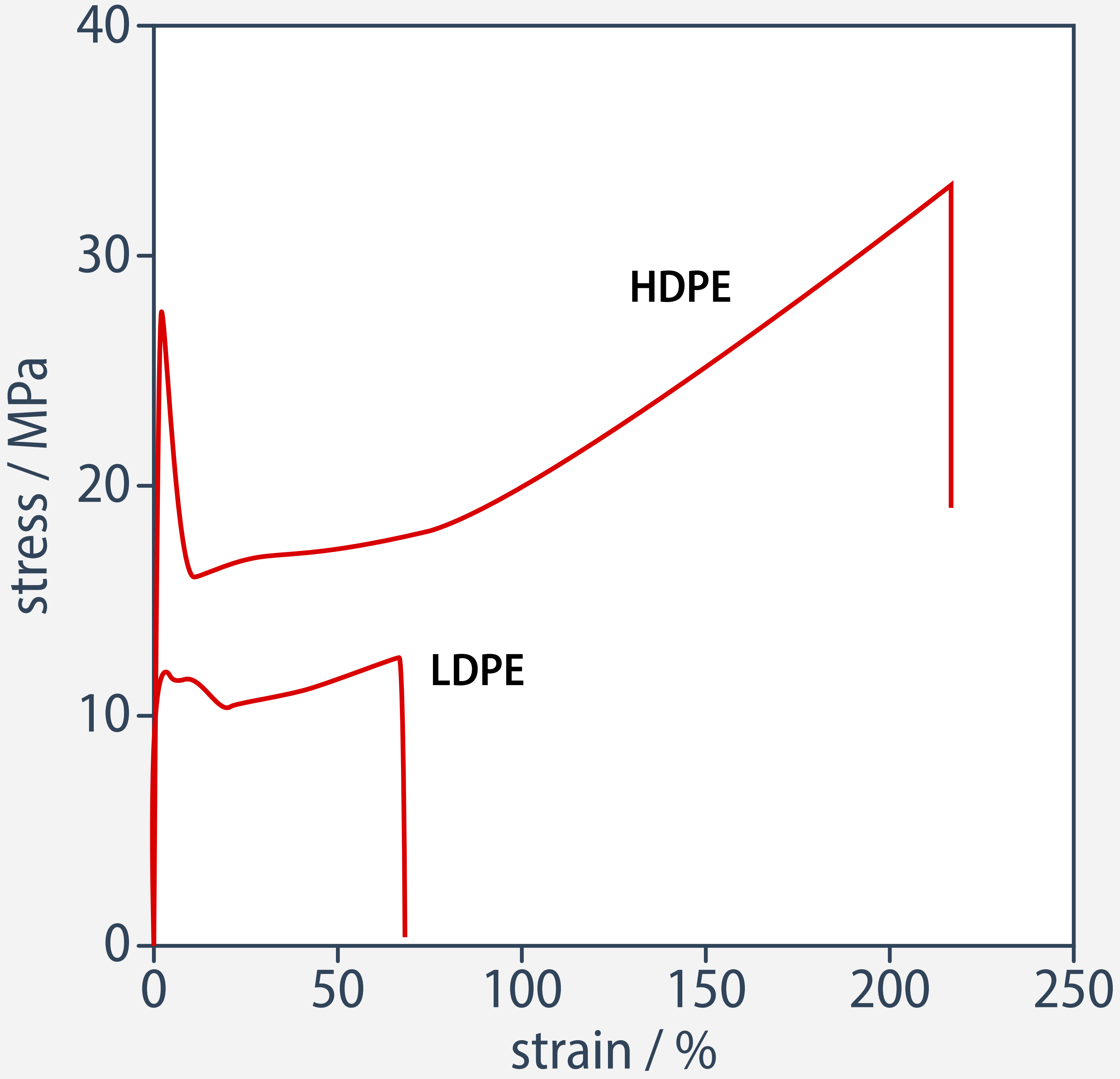


HDPE



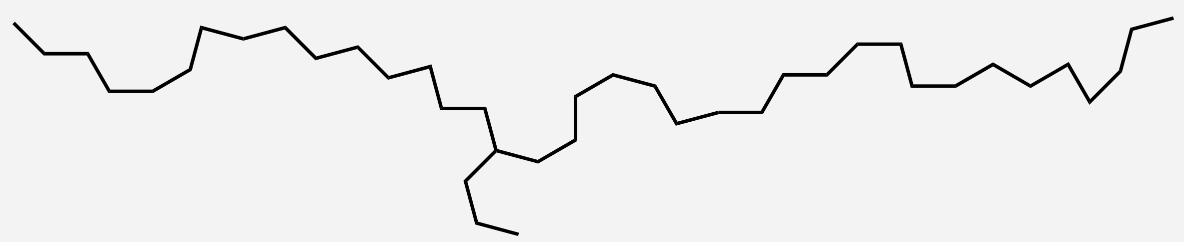
LDPE





- **higher melting temperature, crystallinity, strength and stiffness for HDPE than for LDPE**

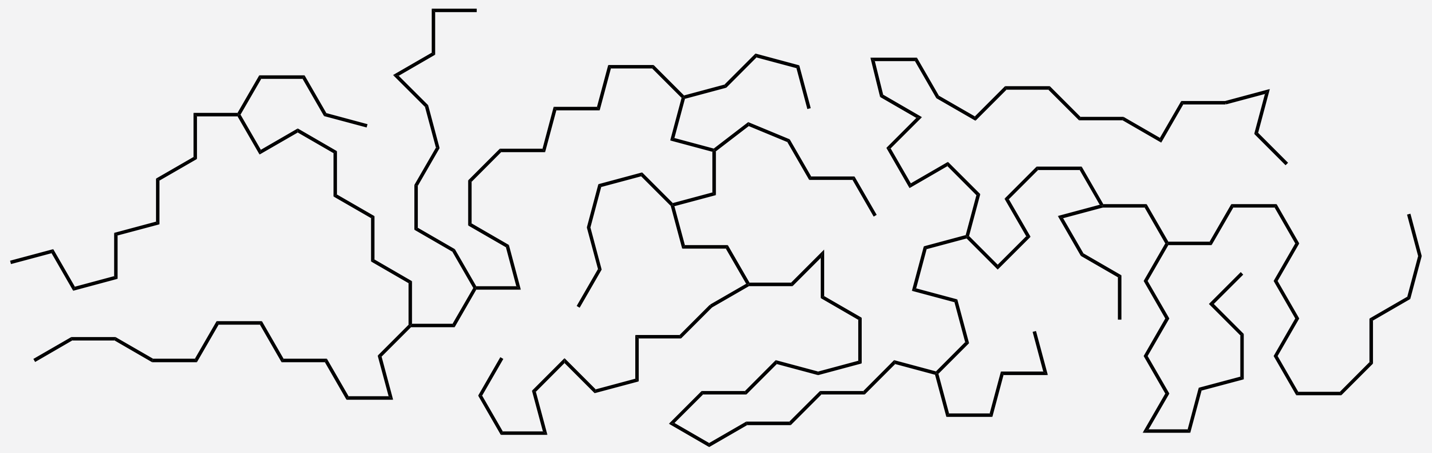
Commercial Polyethylene (PE)



high-density polyethylene (HDPE)

structurally “regular” with few branching points (7/1000 carbons)

packs efficiently, high crystallinity, high density



low-density polyethylene (LDPE)

highly branched with many branching points (60/1000 carbons)

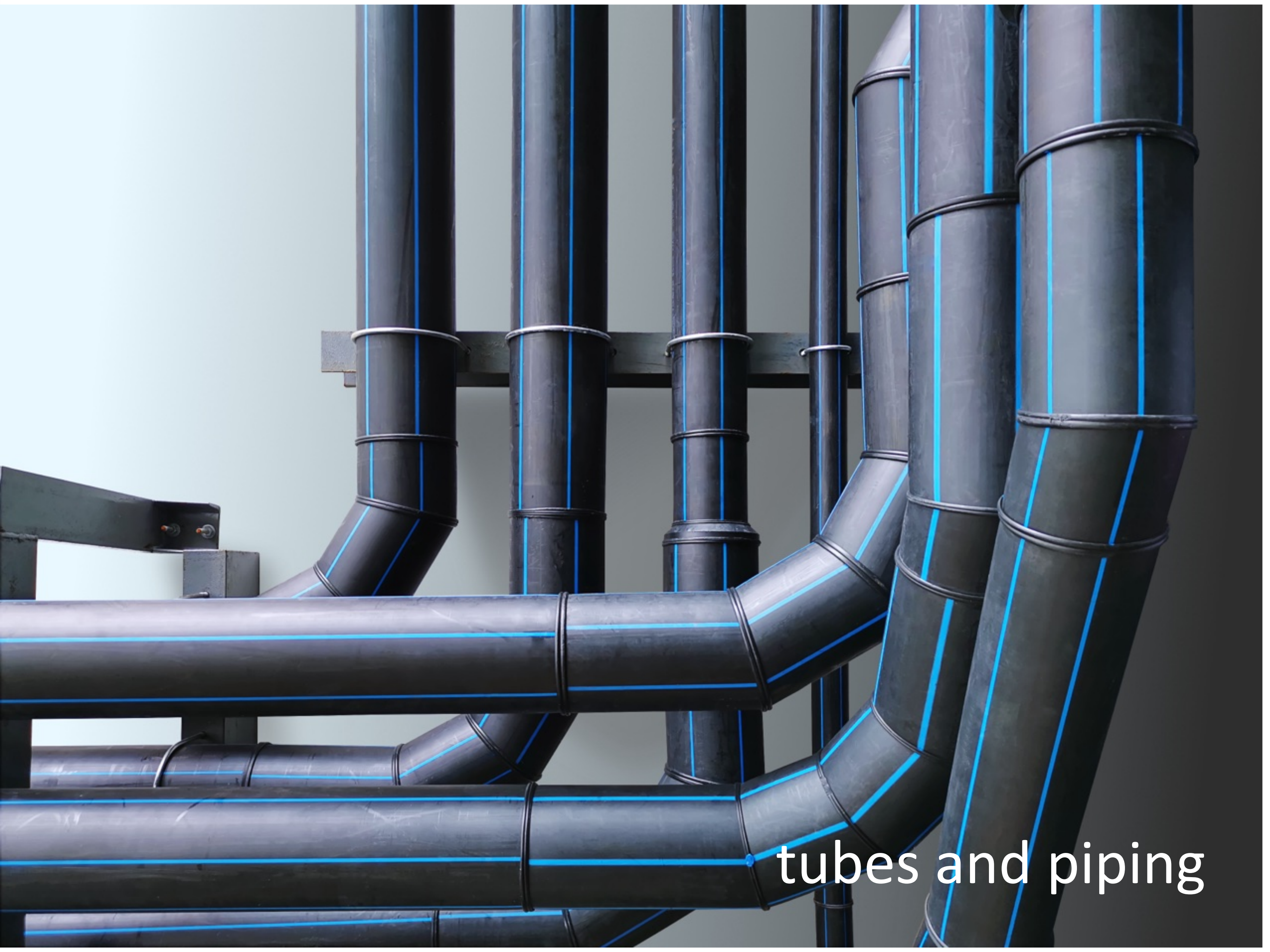
low crystallinity, low density, film forming

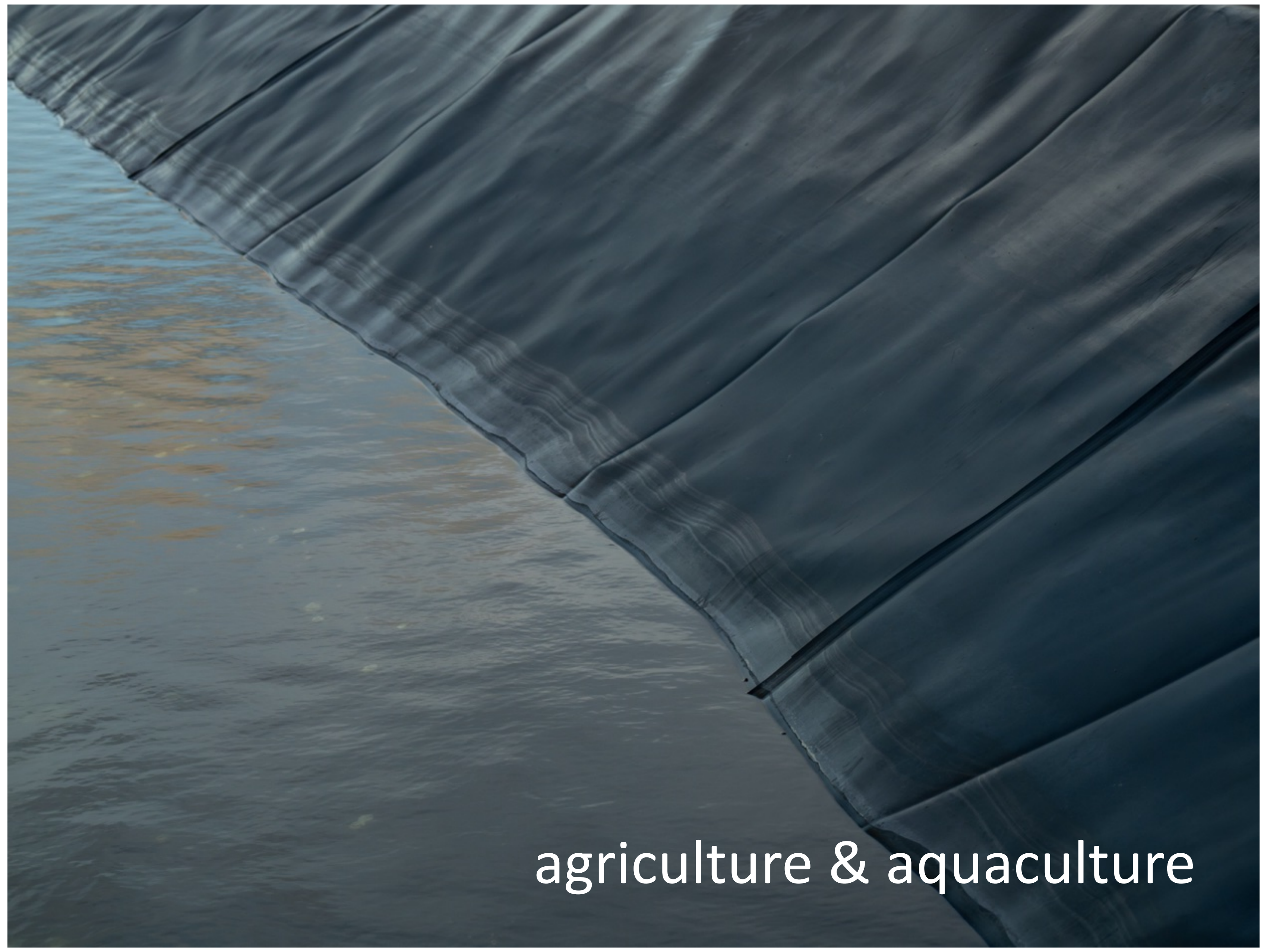
Material	T_m (°C)	T_g (°C)	crystallinity	density (g/mL)	tensile strength (MPa)
HDPE	120-135	-100	70-90%	0.94-0.97	20-37
LDPE	105-115	-100	40-60%	0.92	8-15

- **HDPE and LDPE display vastly different physical properties; separable based on their densities!**

LDPE Applications

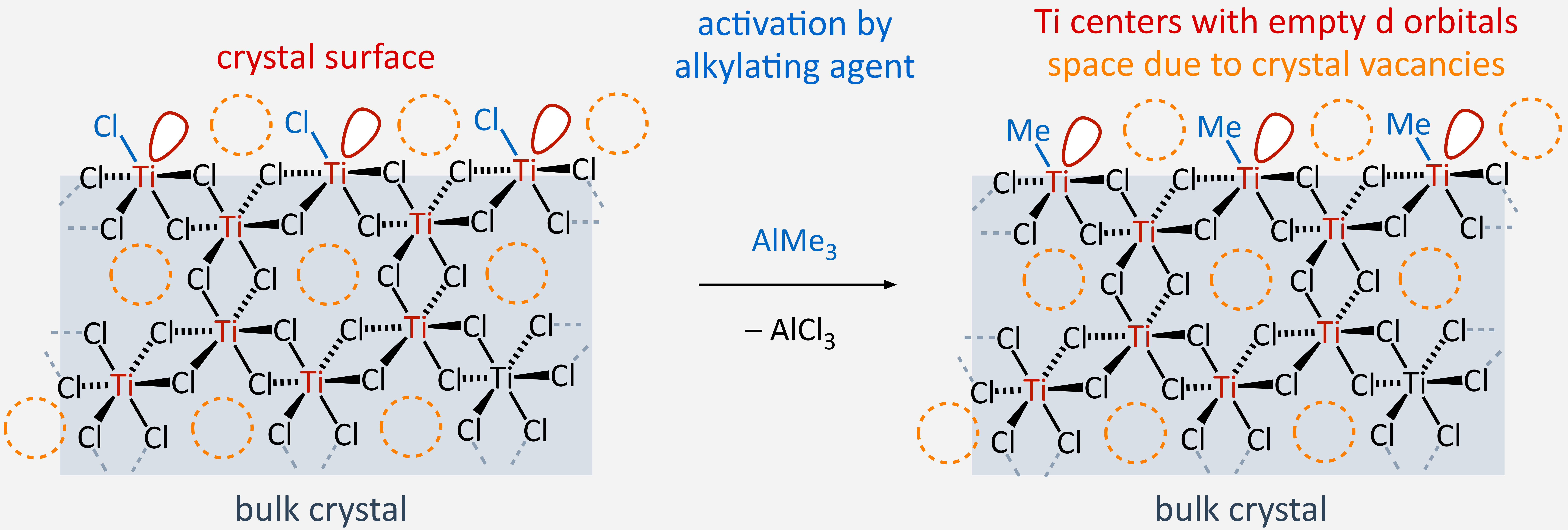
Applications of HDPE





Polypropylene

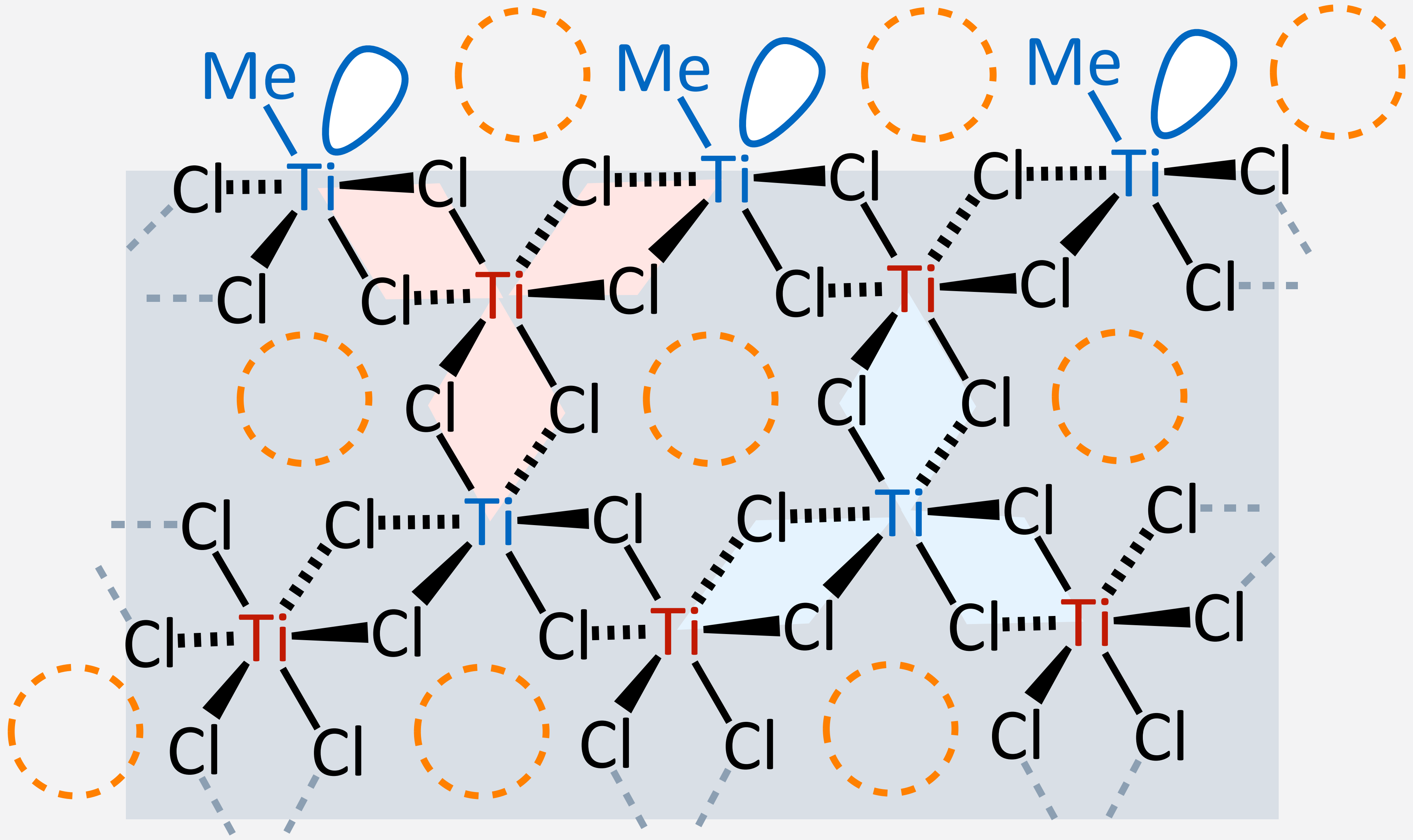
Heterogeneous Catalysts for Ziegler-Natta Polymerization

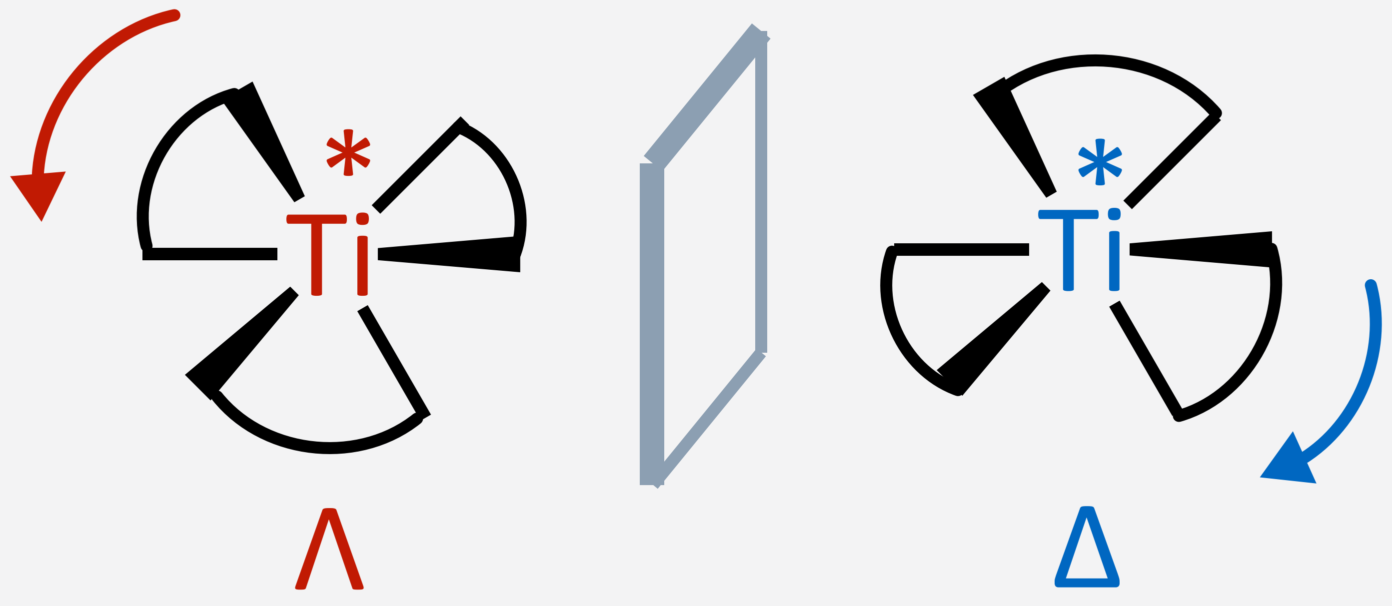


- β-$TiCl_3$ with sheets of edge-connected $TiCl_6$ octahedra with vacancies due to $TiCl_3$ stoichiometry
- 110 crystal surface exposes sheet edges, Ti centers with free coordination site (empty d orbital)
- vacancies near surface Ti centers creates space for monomer to coordinate to empty d orbital
- catalyst activation by alkylation, generates large number of unsaturated & alkylated Ti centers

- **“multisite” catalysts with various types of surface Ti centers & geometries, activity slightly different**

Helical Chirality of Titanium Centers in Ziegler Natta Catalysts

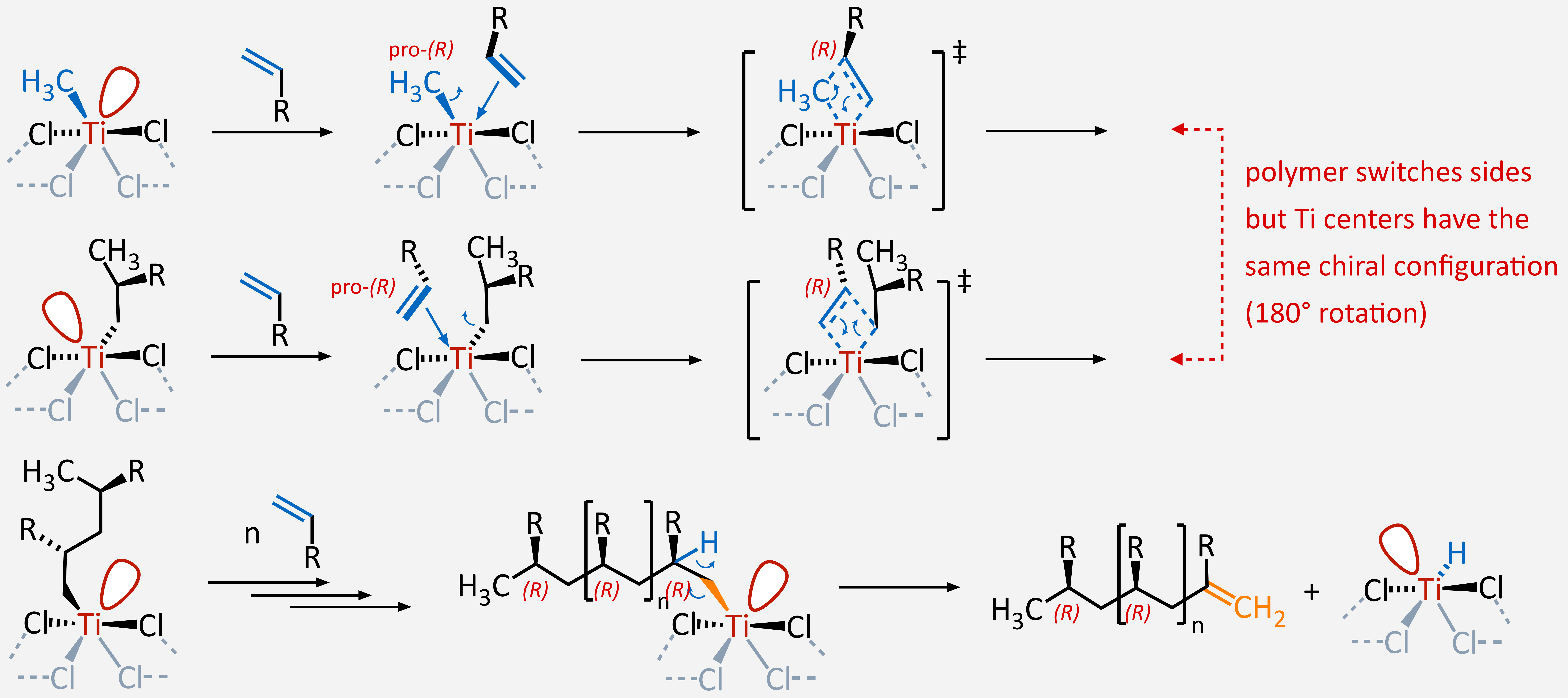




- edge-connected $TiCl_6$ octahedra (three pairs of bridged chlorines) give rise to helical chirality
- crystal is overall achiral contains Ti centers with alternating Λ configuration and Δ configuration
- sheet edge exposed at 110 crystal surface has Ti centers with all the same chirality (Λ or Δ)

- **polymerization-active unsaturated and alkylated surface Ti centers have a chiral environment**

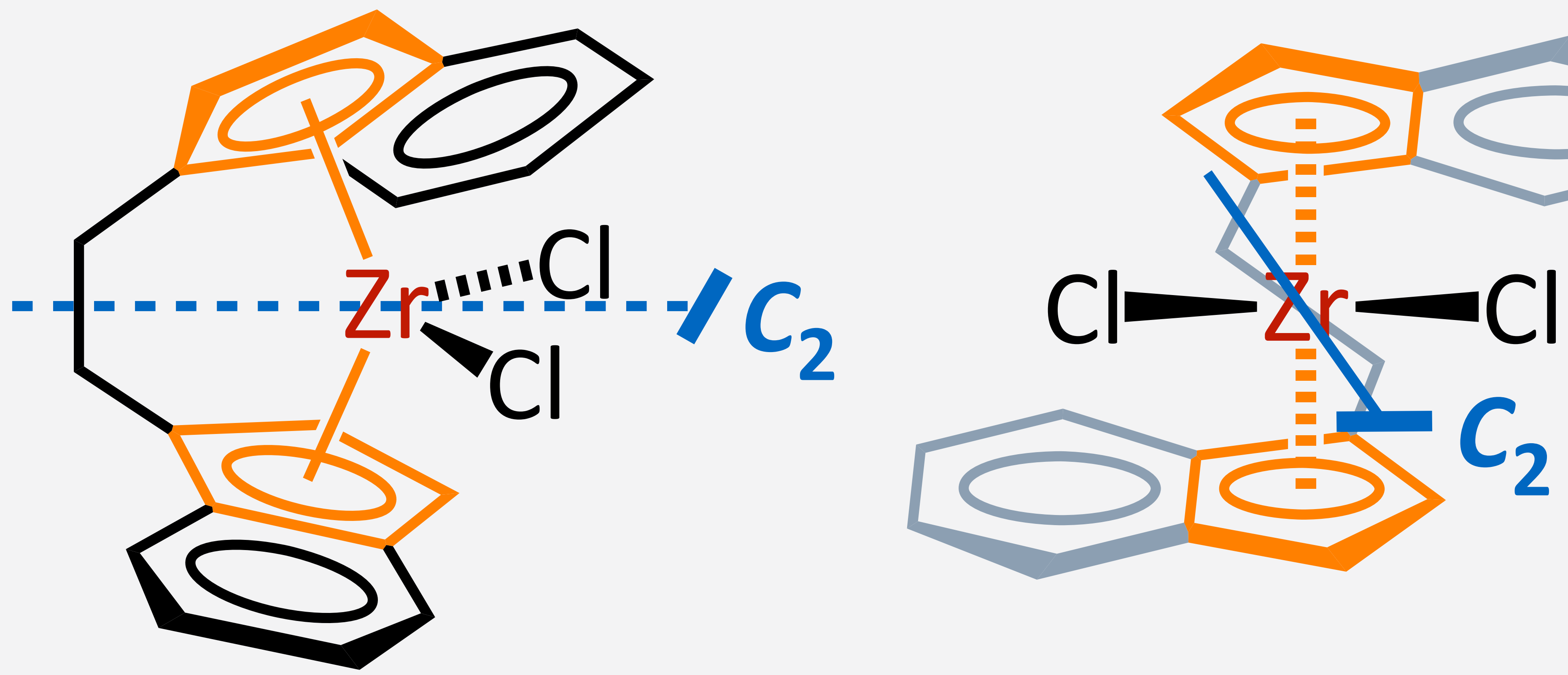
Isotactic Polymerization of Propylene Using Ziegler Natta Catalysts



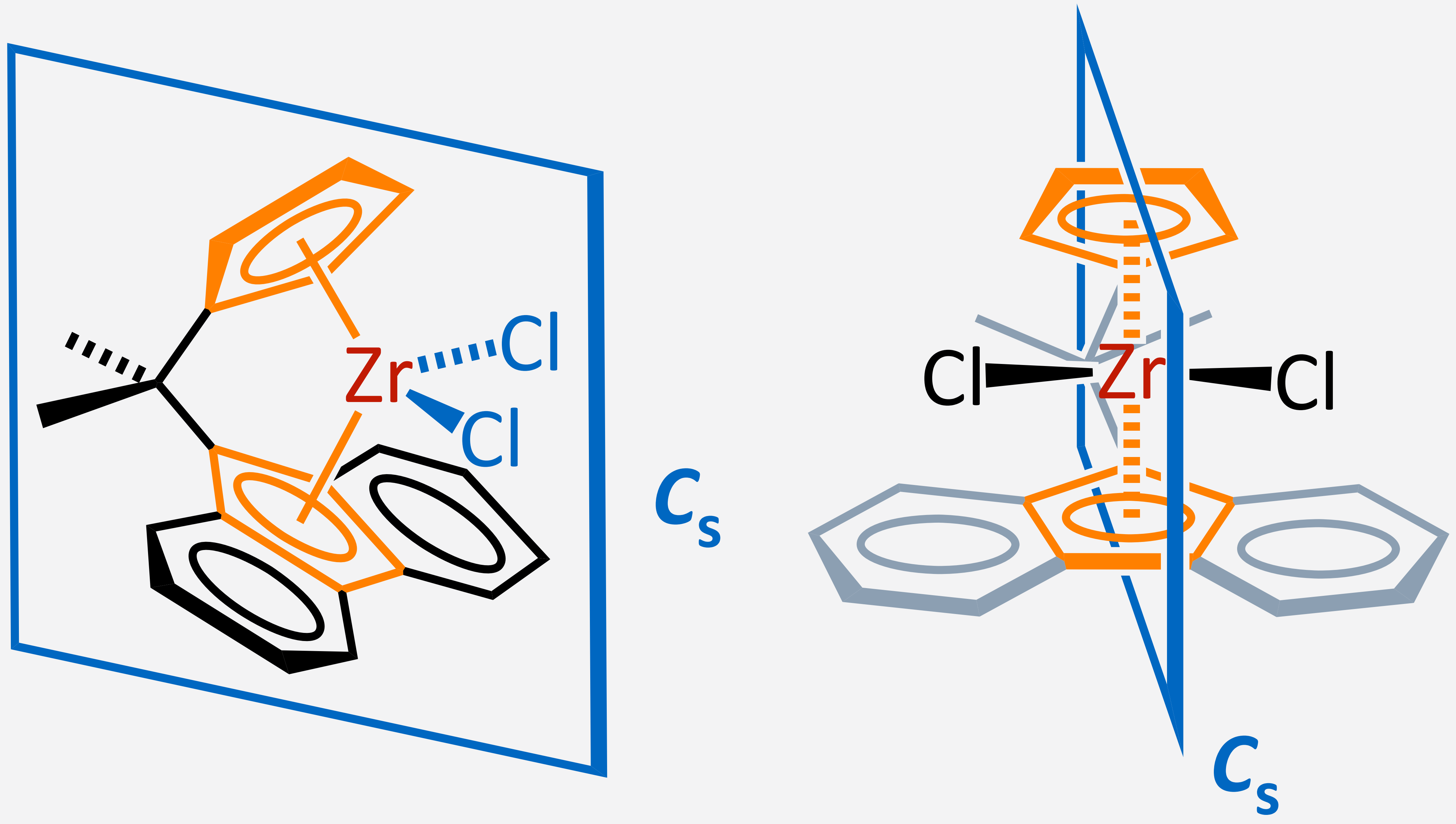
- every insertion step creates a new stereocenter (from planar, achiral monomer)
- Ti centers are racemic mixture of Λ and Δ enantiomers, so absolute stereoconfiguration undefined
- **subsequent steps always create the same stereoconfiguration, resulting in isotactic polypropylene**

Tacticity Control in Metallocene-Catalyzed Propylene Polymerization

- metallocenes are metal complexes with cyclopentadienyl (Cp) ligands
- metallocenes are homogeneous “single site” polymerization catalysts, defined compounds in solution



C_2 symmetric, chiral

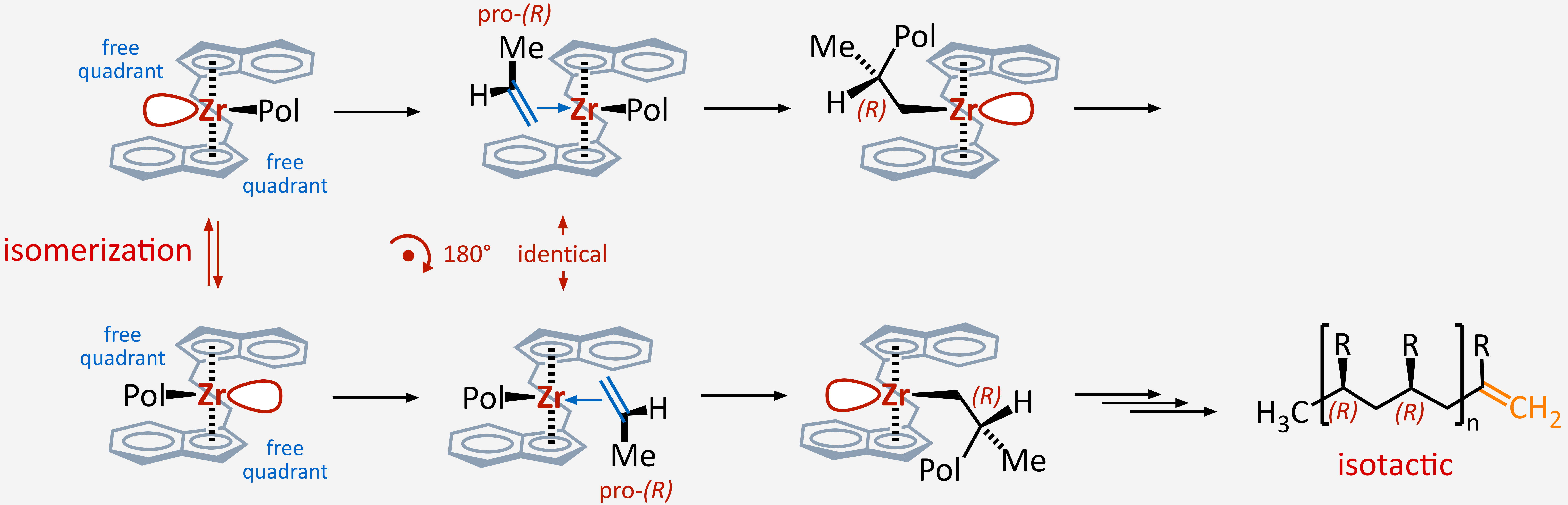


C_s symmetric, achiral

- **most common polymerization catalysts are *ansa*-zirconocenes, with bridged, bidentate Cp ligands**
- **coordination geometry around the metal center allows to control in detail the catalyst symmetry**

Isotactic Polypropylene by Stereoselective Polymerization

- stereoselective polymerization starting from chiral, C_2-symmetric zirconocene catalyst precursors

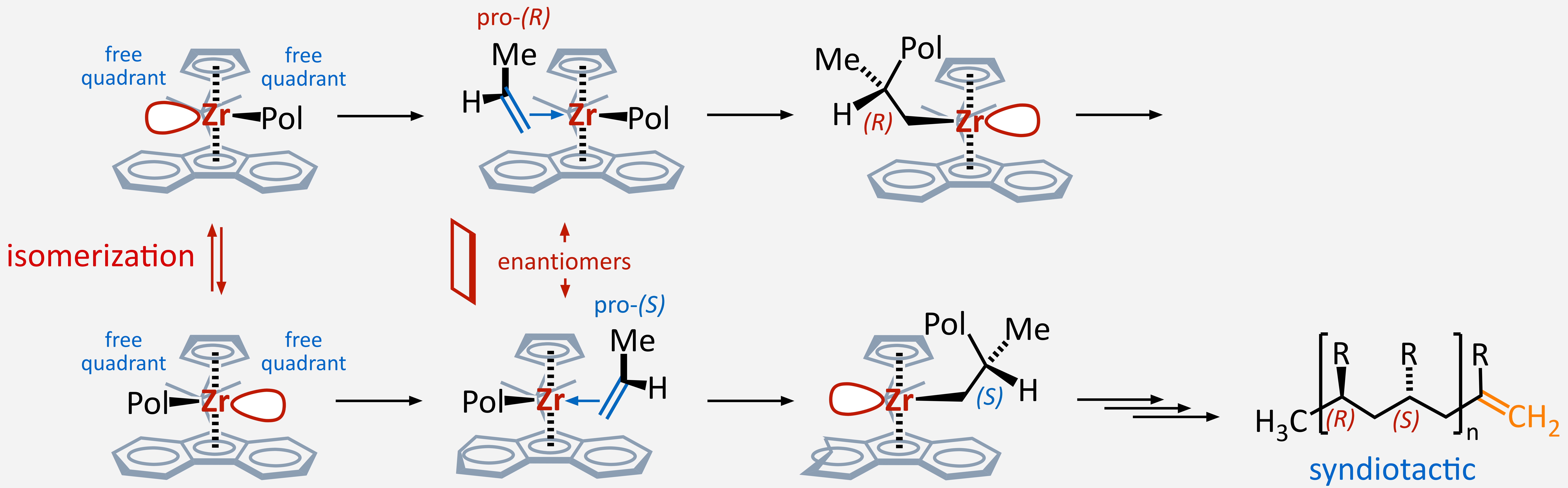


  - monomer coordination with double bond towards zirconium, methyl group in free quadrant
  - two chain positions each enantiotopic but both identical, result in same stereoconfiguration
  - isomerization possible in resting state but results in same configuration, no stereoerrors

- **absolute stereoconfiguration undefined because catalysts typically a racemic mixture**
- **relative stereoconfiguration fixed, all stereocenters have same configuration, isotactic polymer**

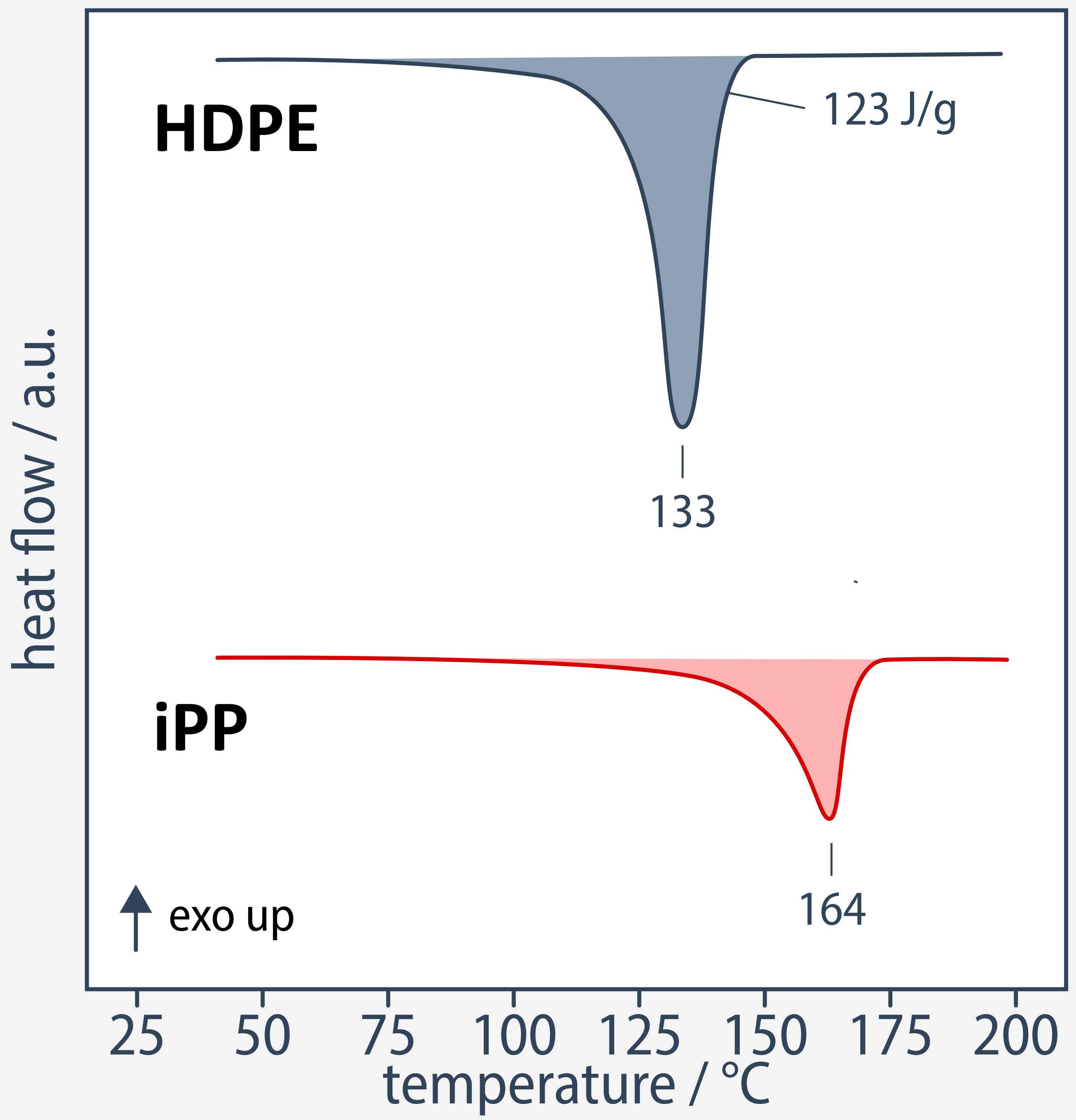
Syndiotactic Polypropylene by Stereoselective Polymerization

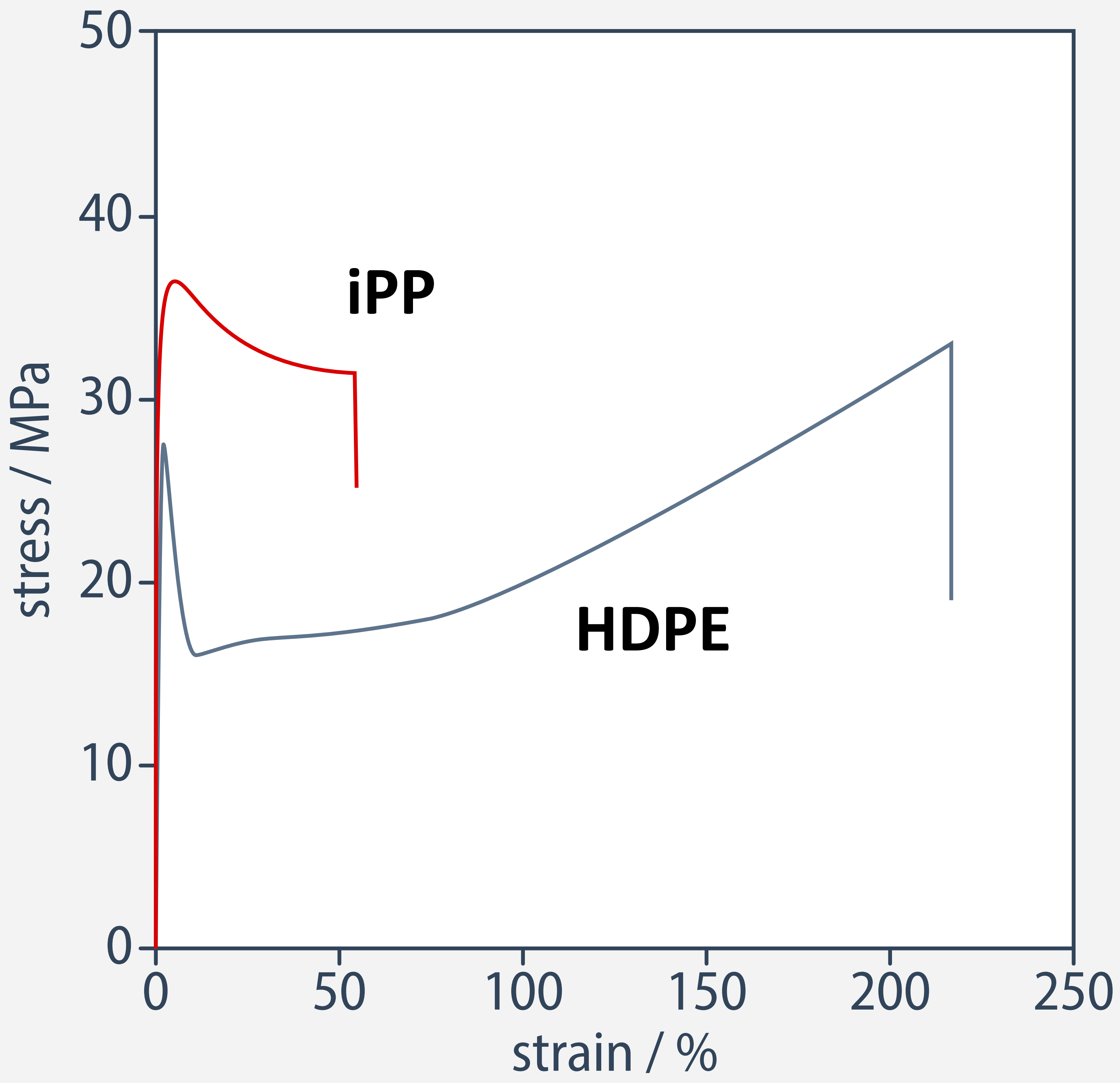
- stereoselective polymerization starting from achiral, C_s-symmetric zirconocene catalyst precursors



  - monomer coordination with double bond towards zirconium, methyl group in free quadrant
  - two chain positions each enantiotopic and enantiomeric, result in opposite stereoconfiguration
  - isomerization possible in resting state, results in opposite configuration and thus stereoerrors
- **absolute stereoconfiguration undefined because catalysts achiral**
- **relative stereoconfiguration fixed, stereocenters have alternating configuration, syndiotactic polymer**

Polypropylene versus Polyethylene





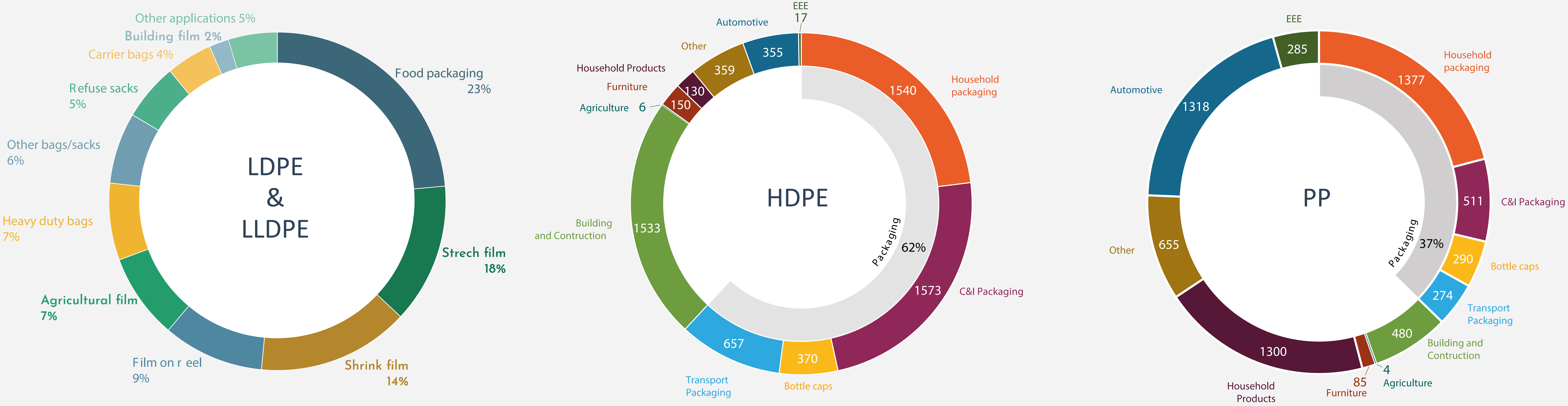
Material	T_m (°C)	T_g (°C)	crystallinity	density (g/mL)	tensile strength (MPa)
HDPE	120-135	-100	70-90%	0.94-0.97	20-37
iPP	160-170	-10	30-60%	0.94	25-40

- **PP offers higher melting temperature, heat resistance, and stiffness, but is less flexible than HDPE**

Applications of PP

Applications of LDPE, HDPE, and PP

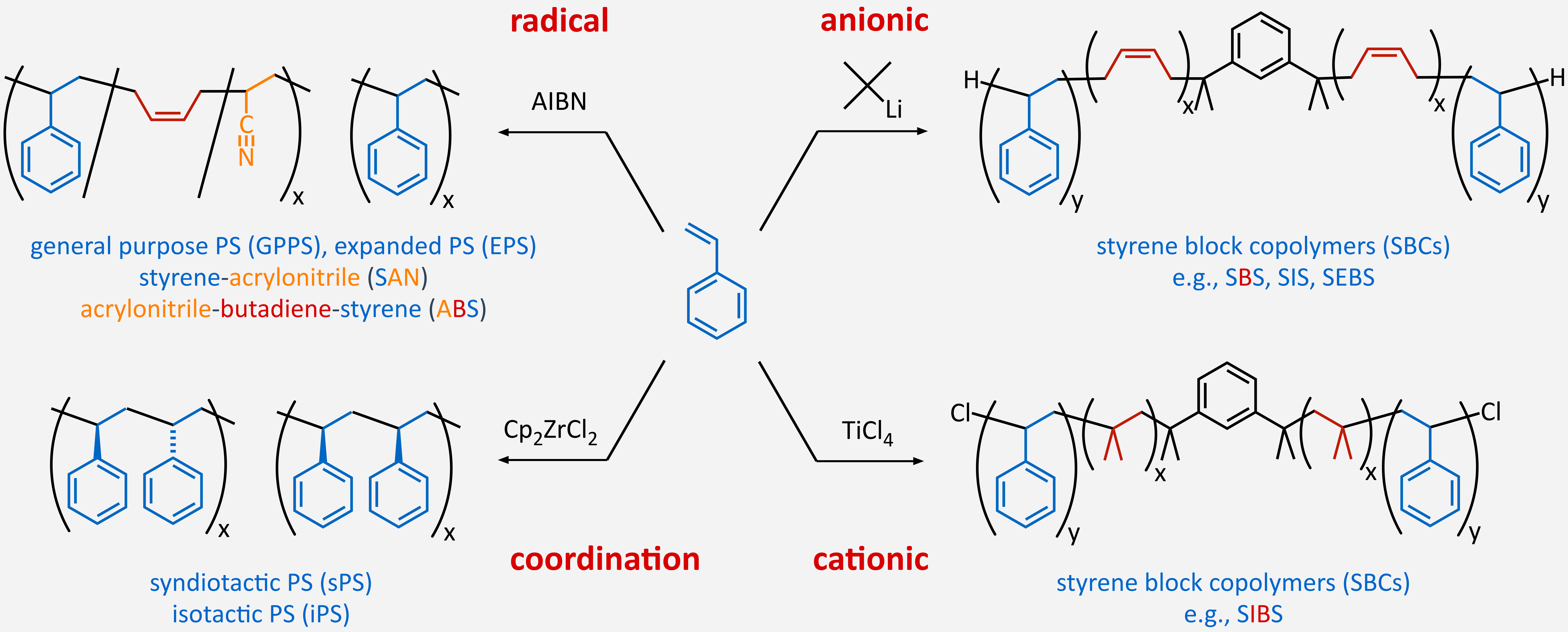
- current market states in Europe (derived from Eurostat data and other studies):



- **LDPE and LLDPE are mostly produced in form of films, used for packaging materials**
- **HDPE and PP mouldable in any shape, hence more diverse applications with packaging dominating**

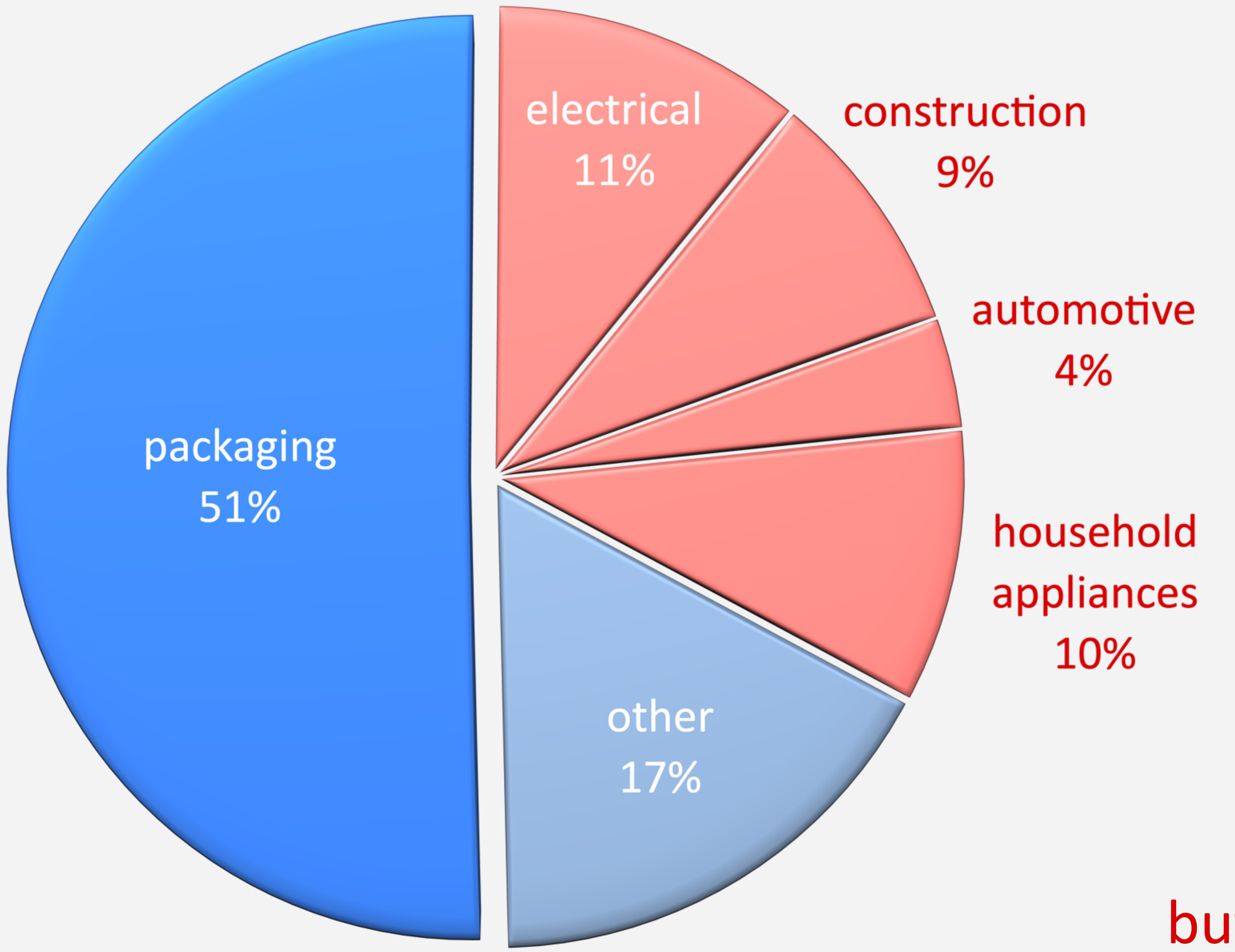
Poly(styrene) and Copolymers

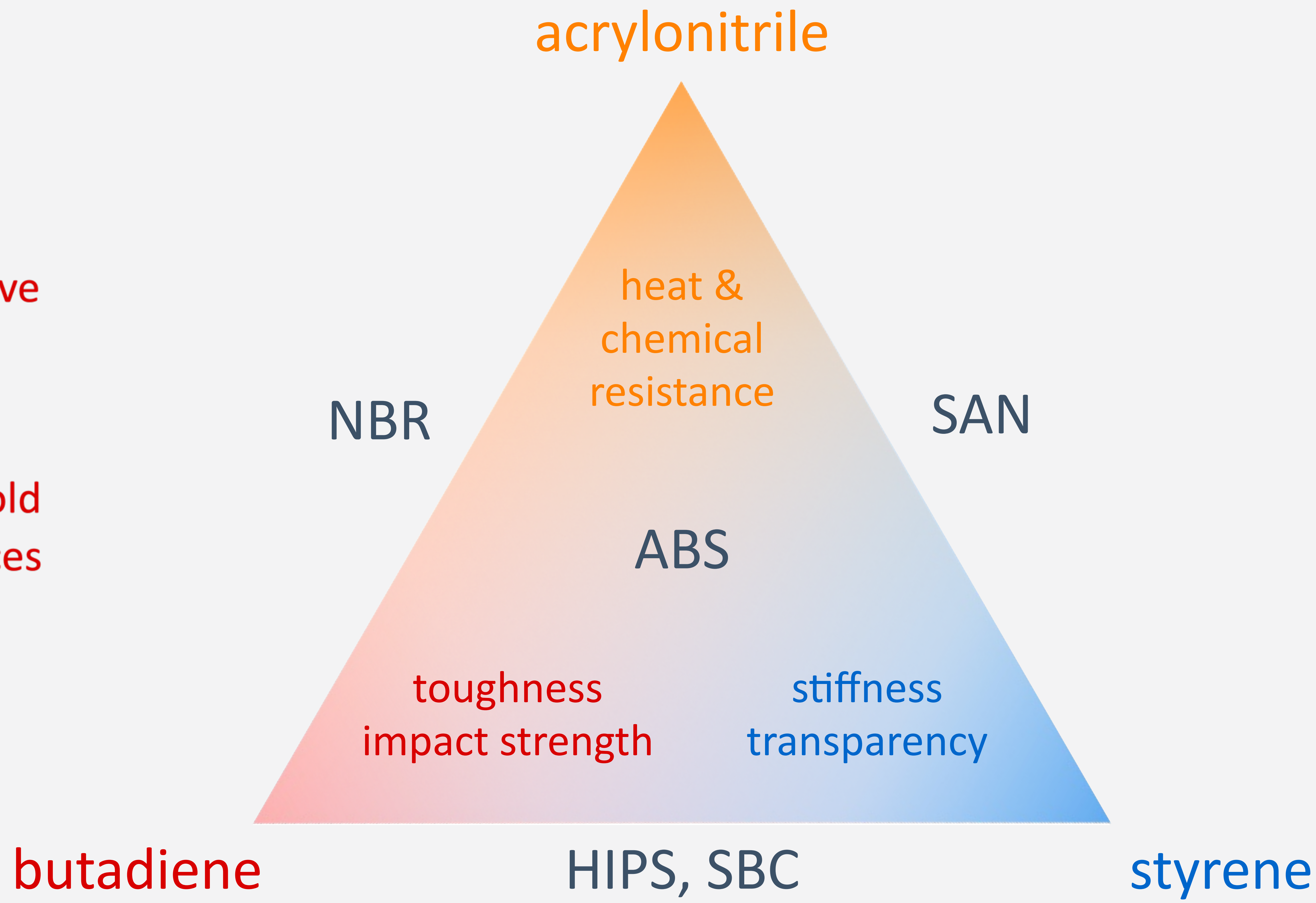
Synthesis of Polystyrene and Copolymers



- **phenyl substituent can serve as both (mostly) +M and –M substituent**
- **styrene can be polymerized by radical, cationic, anionic, and coordination polymerization !**

Applications of Styrenic Materials





- **styrenic materials used in a wide range of applications due to their versatile properties**
- **sustainability concerns due to acrylonitrile and rubber particle content**

Plastics Europe, **2019**; Niessner, *Practical Guide to Structures, Properties and Applications of Styrenic Polymers*, **2013**

General Purpose Polystyrene (GPPS) and Expanded Polystyrene (EPS)

General-Purpose Polystyrene (GPPS)

- completely amorphous, T_g = 100 °C
- thermoplastic, softening at T_g
- high stiffness E = 3.6 GPs, but brittle
- optically highly transparent
- food containers, medical syringes, low-impact packaging

Expanded Polystyrene (EPS) Foams

- processing from PS pellets with foaming agent
- rigid, closed-cell thermoplastic foams
- low density ρ = 10–50 kg/m^3
- vulnerable to organic solvents
- protective packaging, food containers, disposable cups, insulating panels,

General Purpose Polystyrene (GPPS) and Expanded Polystyrene (EPS)

High-Impact Polystrenes(HIPS)

- blend of rubber particles dispersed in continuous PS matrix
- less brittle but loss of transparency, high impact strength
- food containers, refrigerator linings, toys, low-impact appliance housings

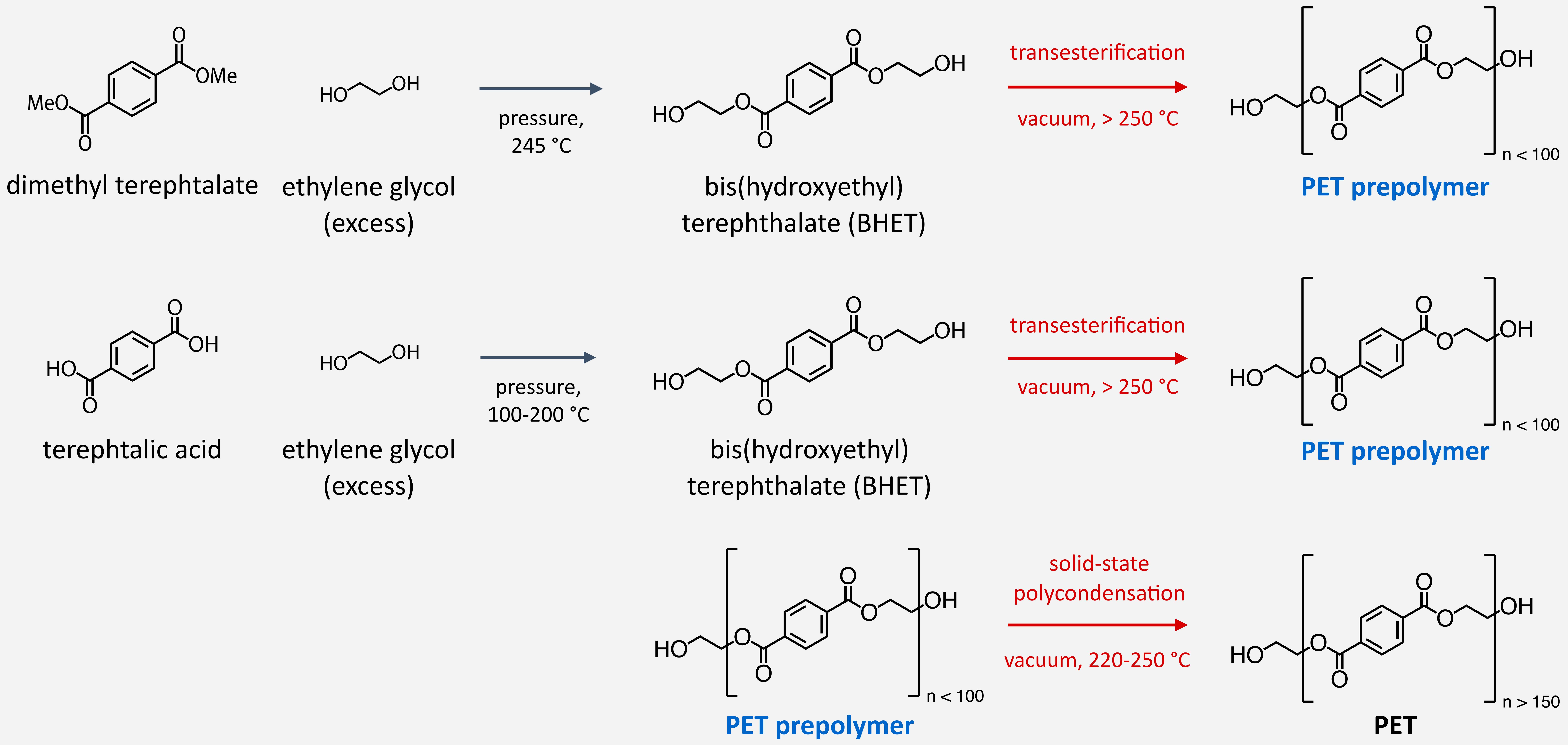
Acrylonitrile-Butadiene-Styrene (ABS)

- radical emulsion polymerization, graft copolymer (P/PAN)-*g*-PB
- higher chemical, heat resistance, impact strength, slow aging, high quality touch
- high-performance applications in automative (dashboards), appliances, toys (LEGO bricks)

Hirayama, Saron, *Polymer* **2018**, *135*, 271–278.

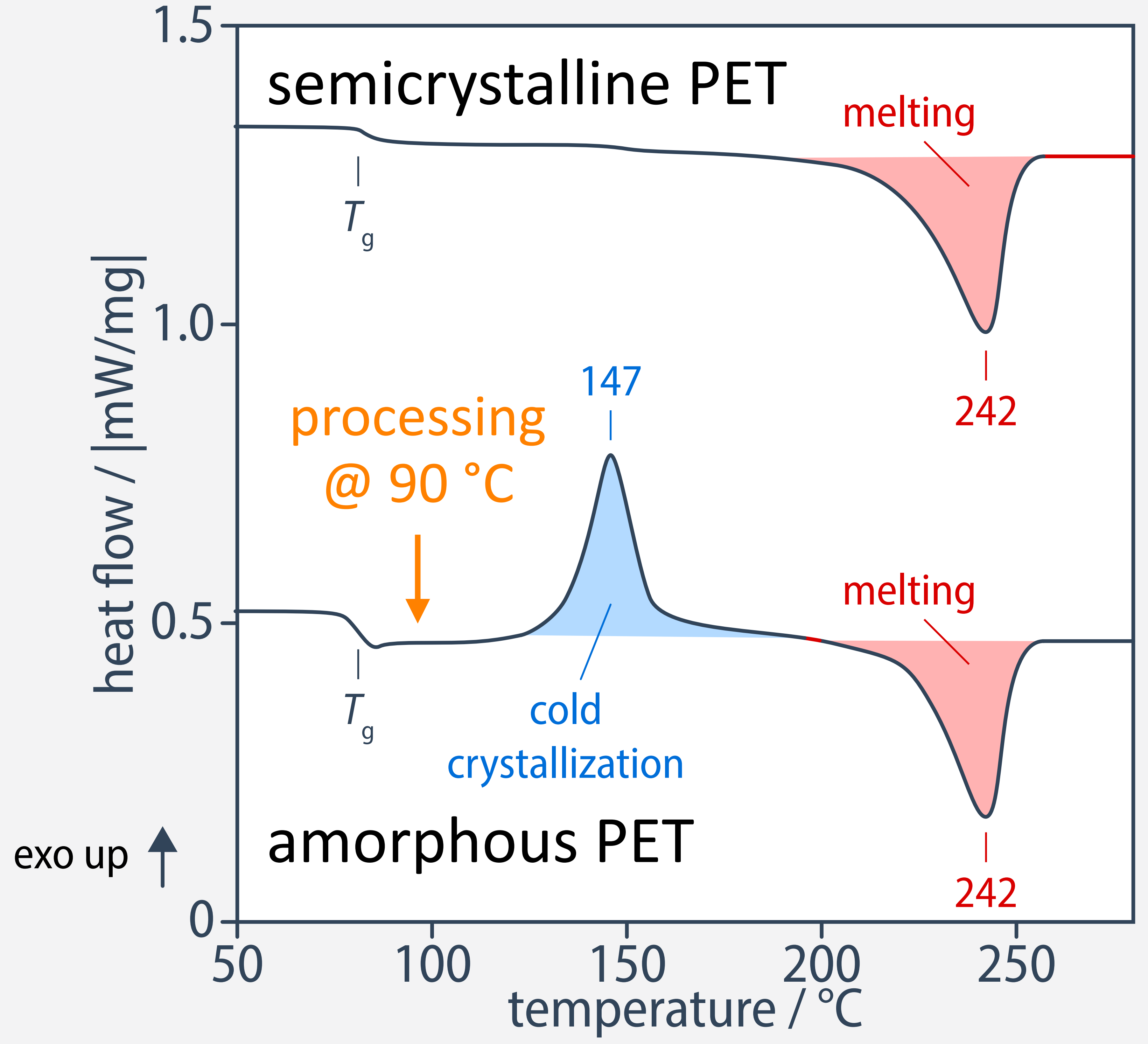
Poly(ethylene terephthalate)

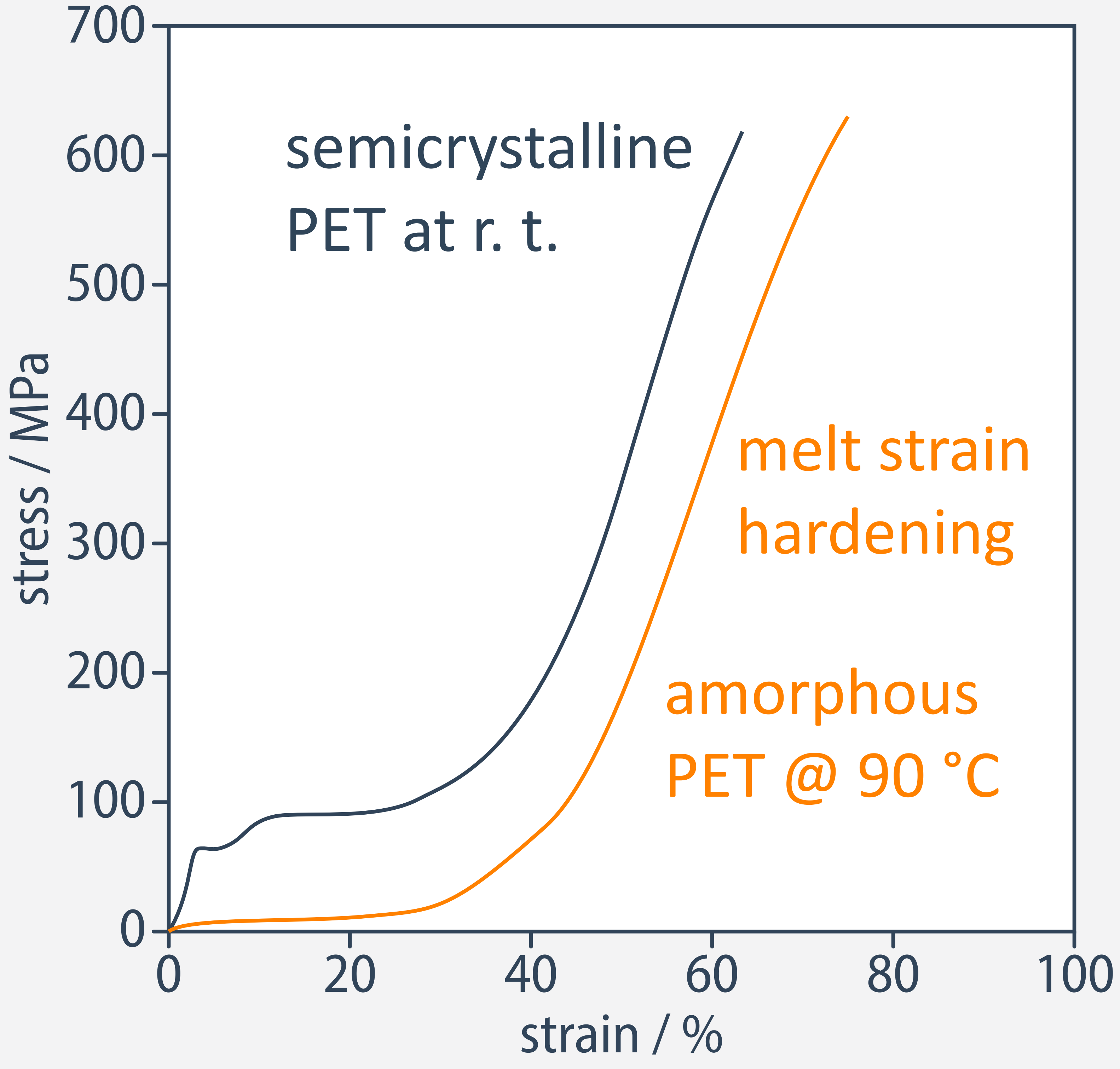
Synthesis of PET



- **PET synthesis via BHET and prepolymer for process efficiency, product quality, and high molar mass**

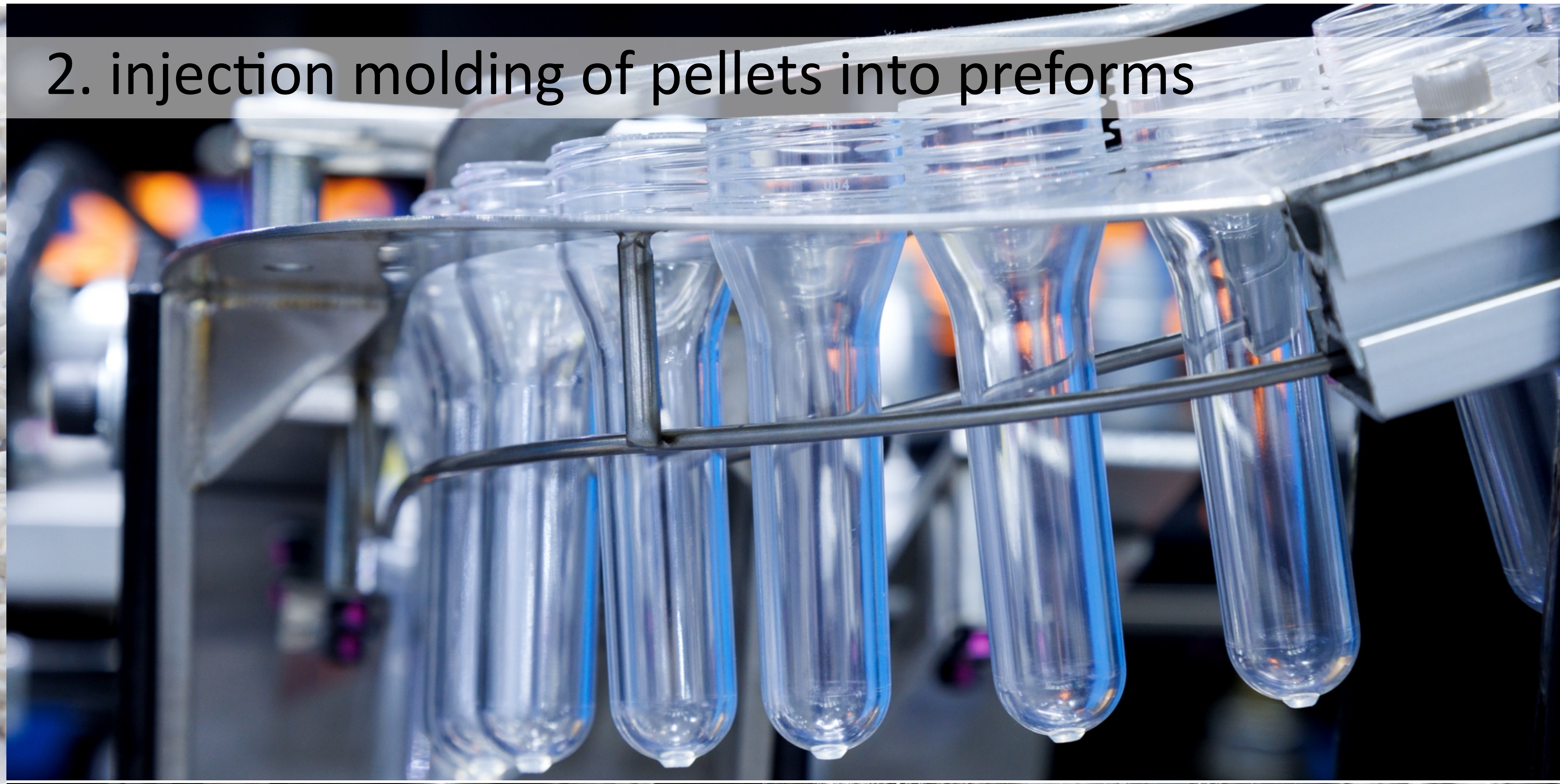
Properties of PET

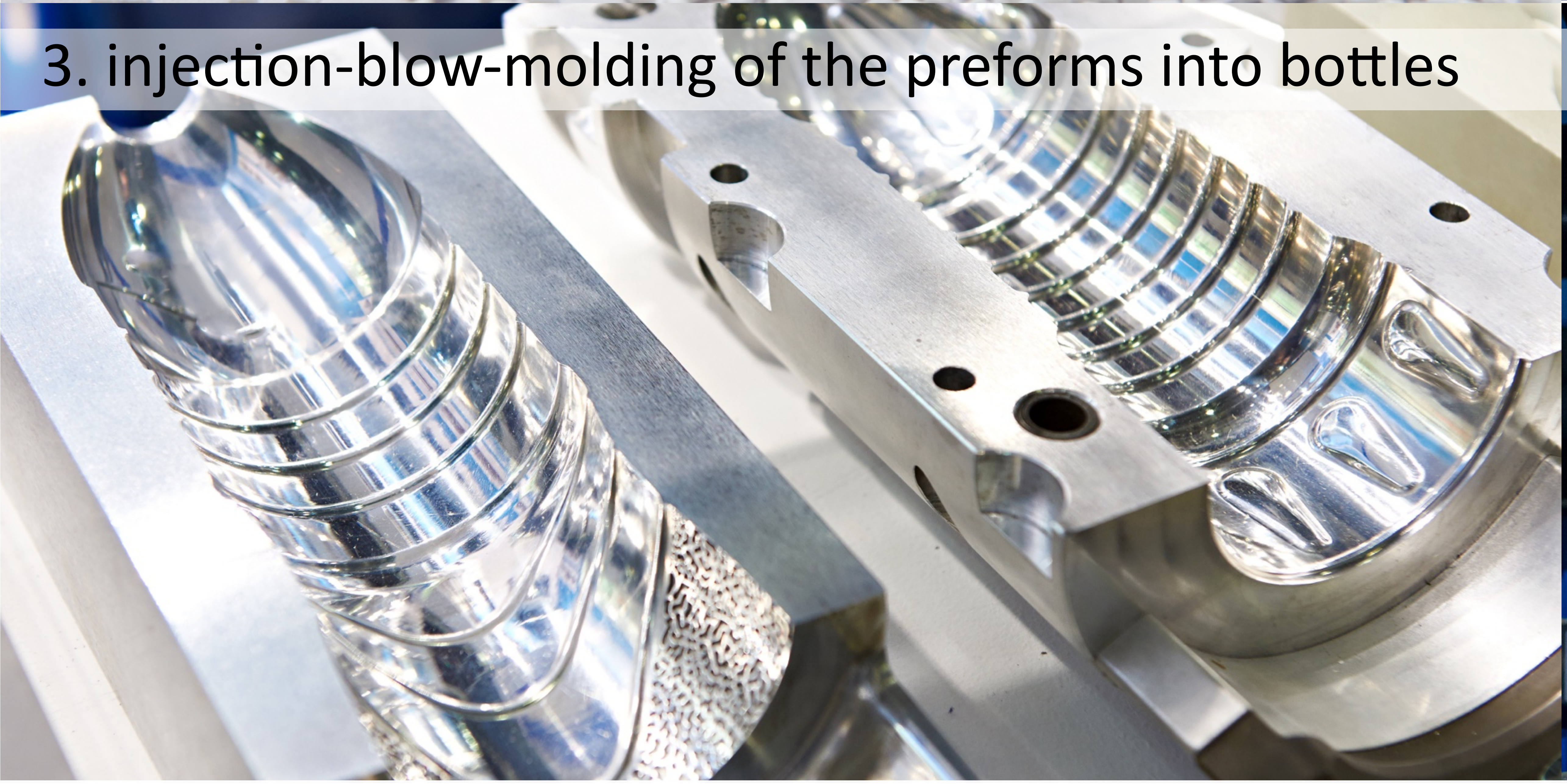




- **PET (T_g = 67–81 ˚C; T_m = 255–260 ˚C) is a semicrystalline, glassy thermoplastic polymer**
- **upon rapid cooling, PET forms an amorphous material that shows cold crystallization upon heating**
- **pronounced melt strain hardening during melt deformation from the amorphous state**

Manufacture of PET Bottles

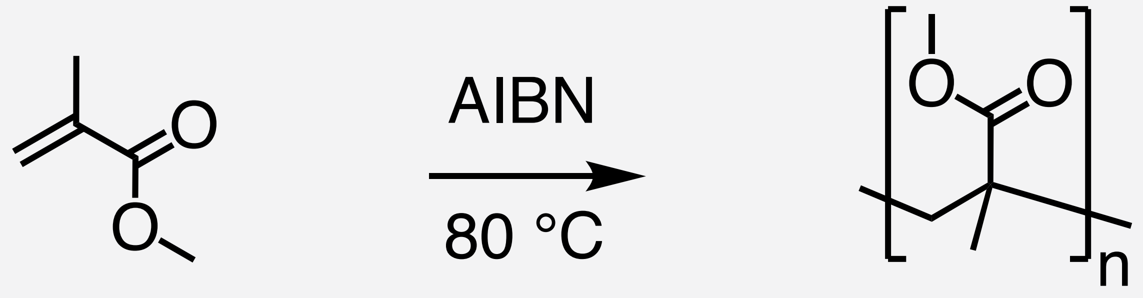




Further Applications of PET

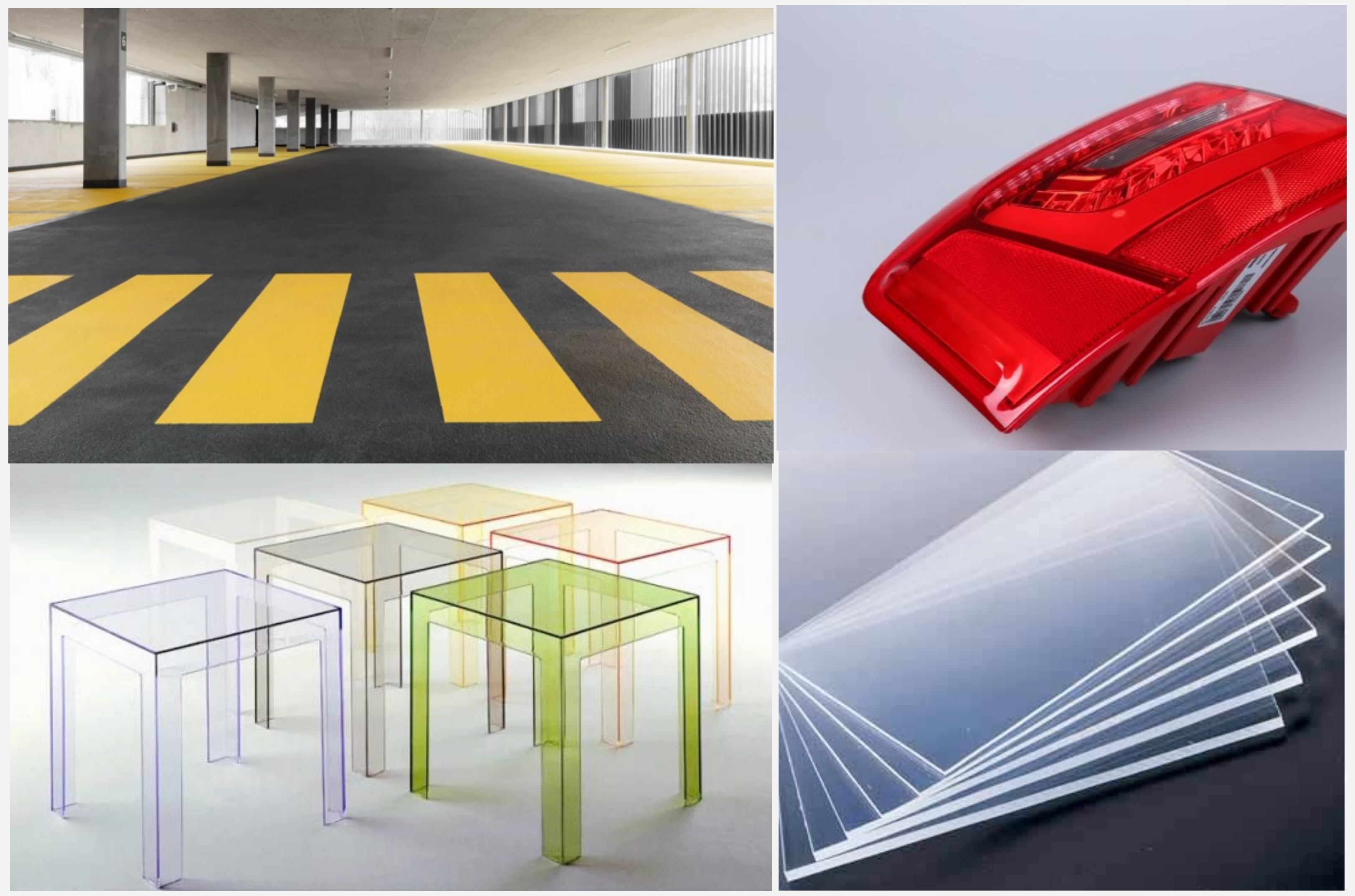
Poly(methyl methacrylate)

Properties and Applications of Poly(methylmethacrylate) (PMMA)



poly(methyl methacrylate)
T_g = 100°C

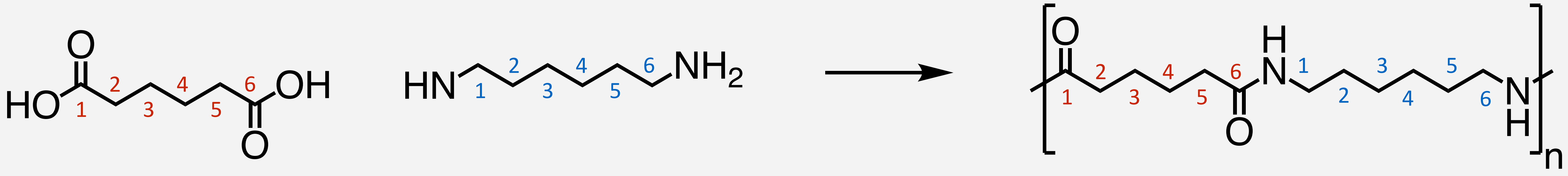
- **Synthesis**
  - PMMA is polymerised by radical polymerization
  - can be polymerised in bulk, solution, emulsion or suspension
- **Properties**
  - amorphous thermoplastic
  - exceptional optical clarity
  - higher impact strength than PS
- **Applications:**
  - glass substitute
  - automotive (motorcycle windshields, panels, fenders)
  - electronics (tv screens, laptops, smartphones display)



Polyamides

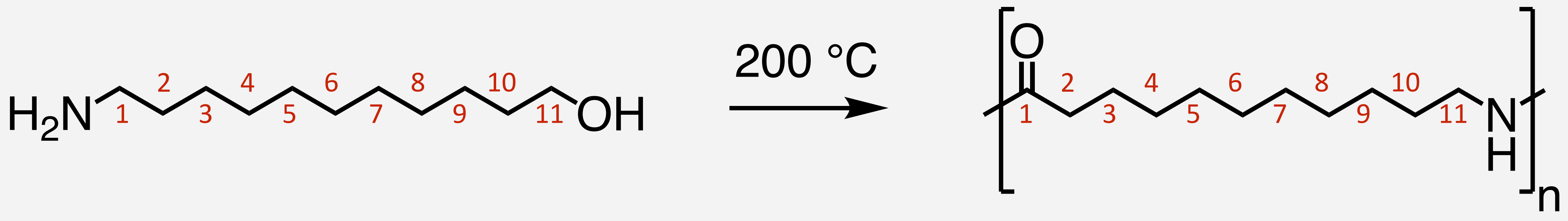
Synthesis of Polyamides (PA)

- synthesis via **AA and BB type monomers** but difficult to ensure stoechiometric conditions



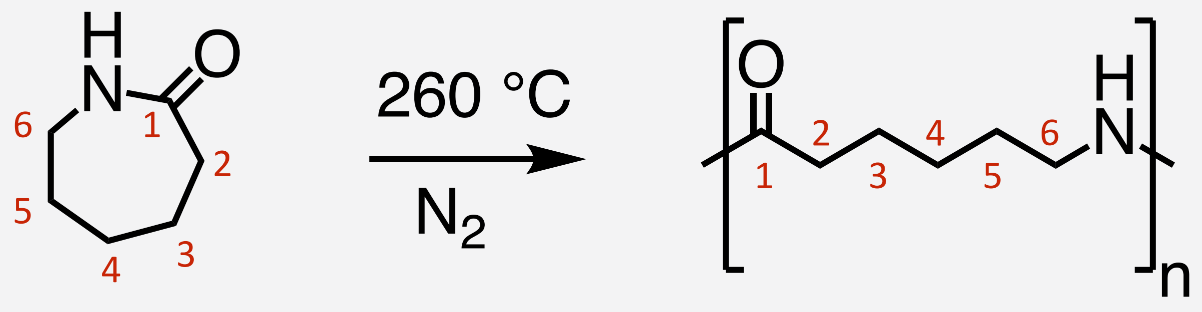
Nylon 6,6 (PA6,6)

- synthesis via **AB type monomers** (ensuring stoechiometry) but storage issues regarding the monomer



Nylon 11 (PA11)

- synthesis via **ring opening polymerization**

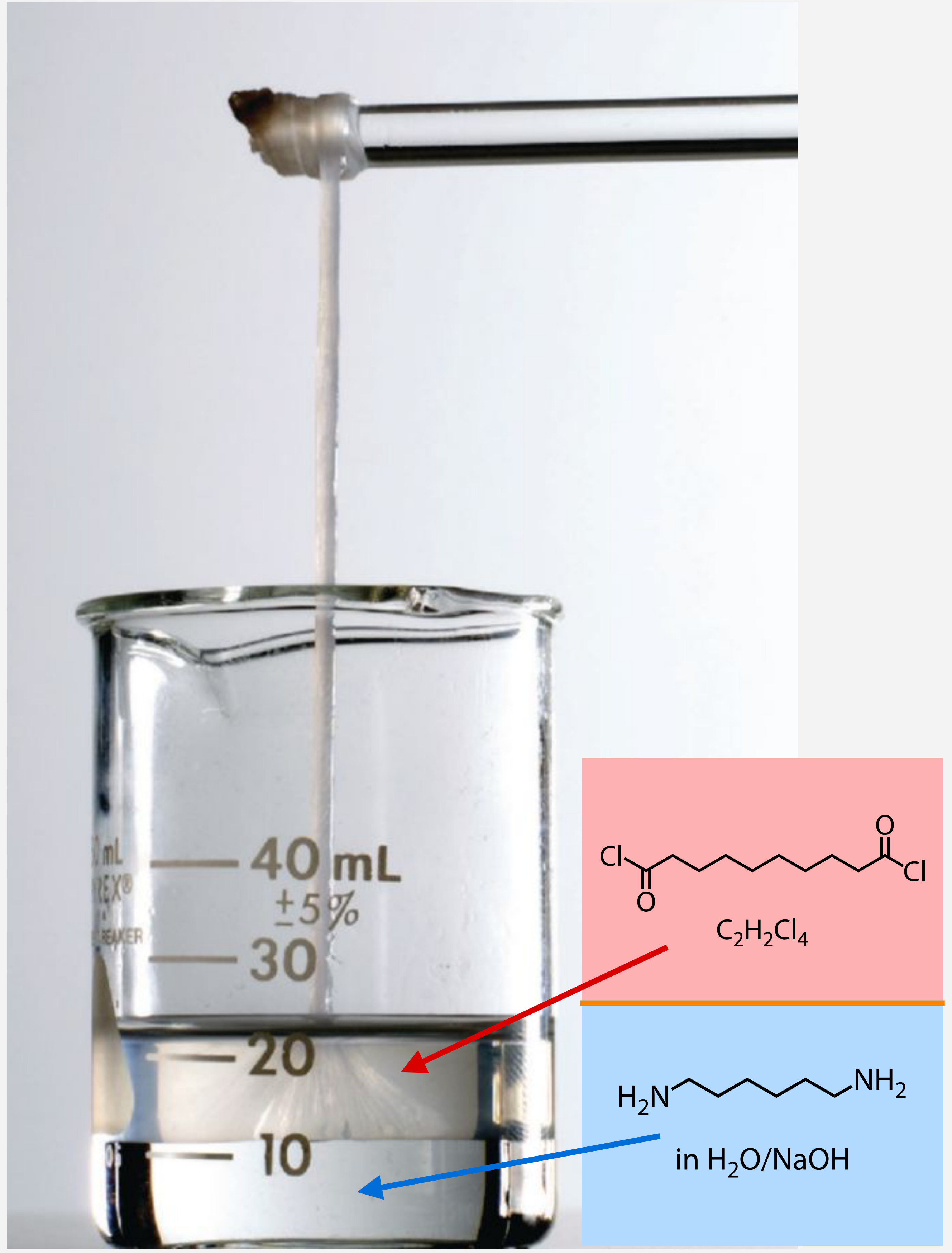


Nylon 6 (PA6)

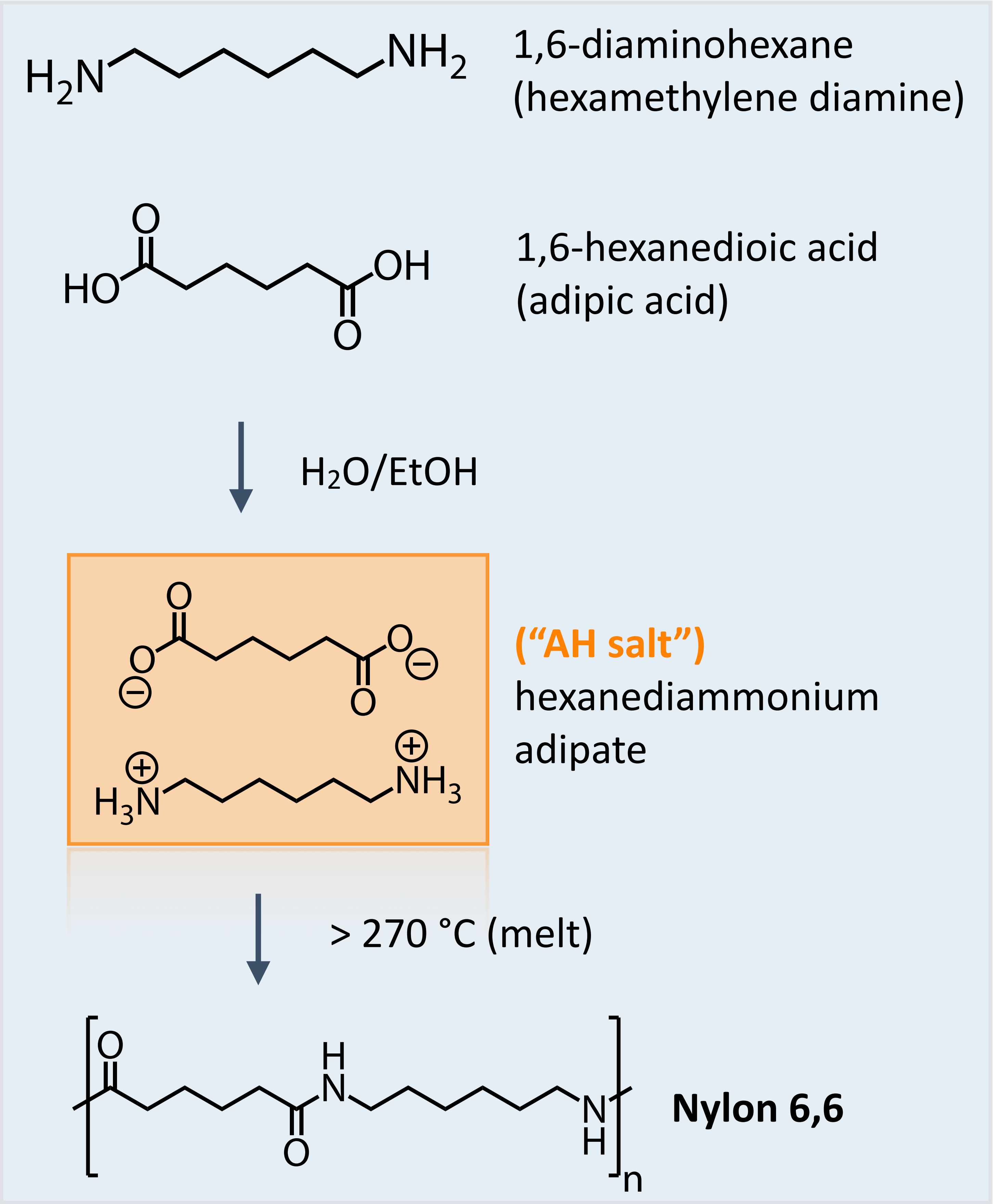
Ensuring Stoichiometric Conditions

- **self-adjusted perfect stoichiometry for technical preparation of nylons and PET**

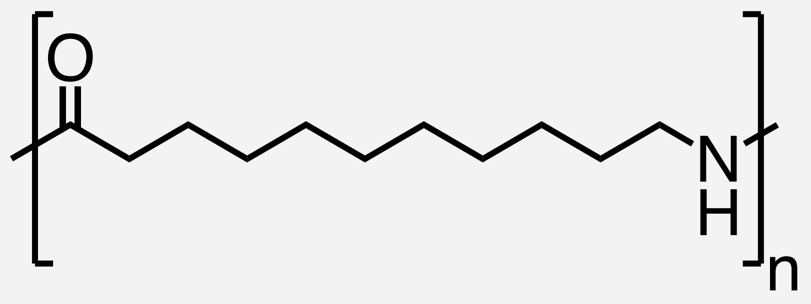
interfacial polymerization
(Nylon 6,10)



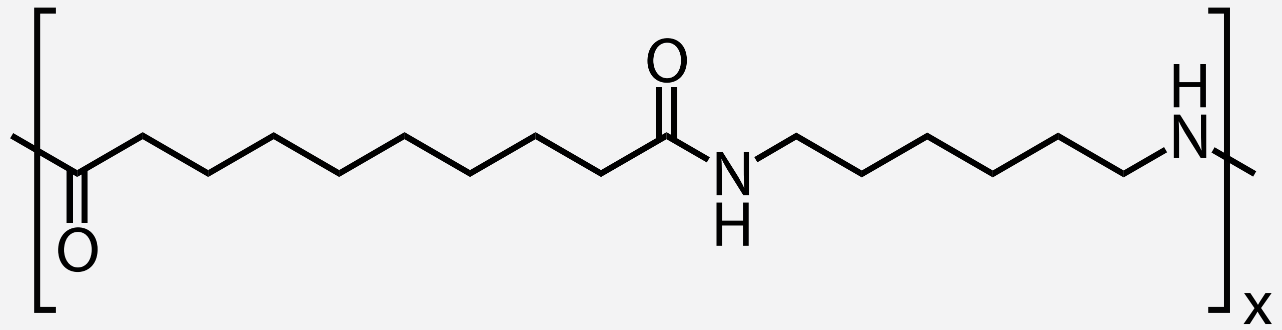
salt dehydration
for melt polycondensation



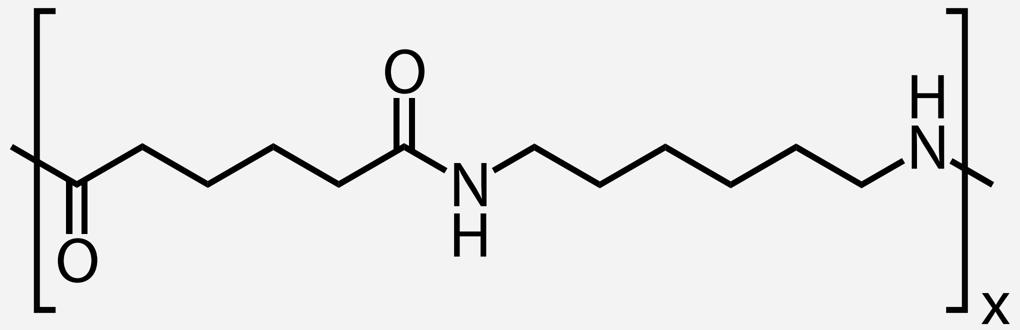
Properties and Applications of Aliphatic Polyamides



Nylon 11
T_g = 45°C; T_m = 185°C

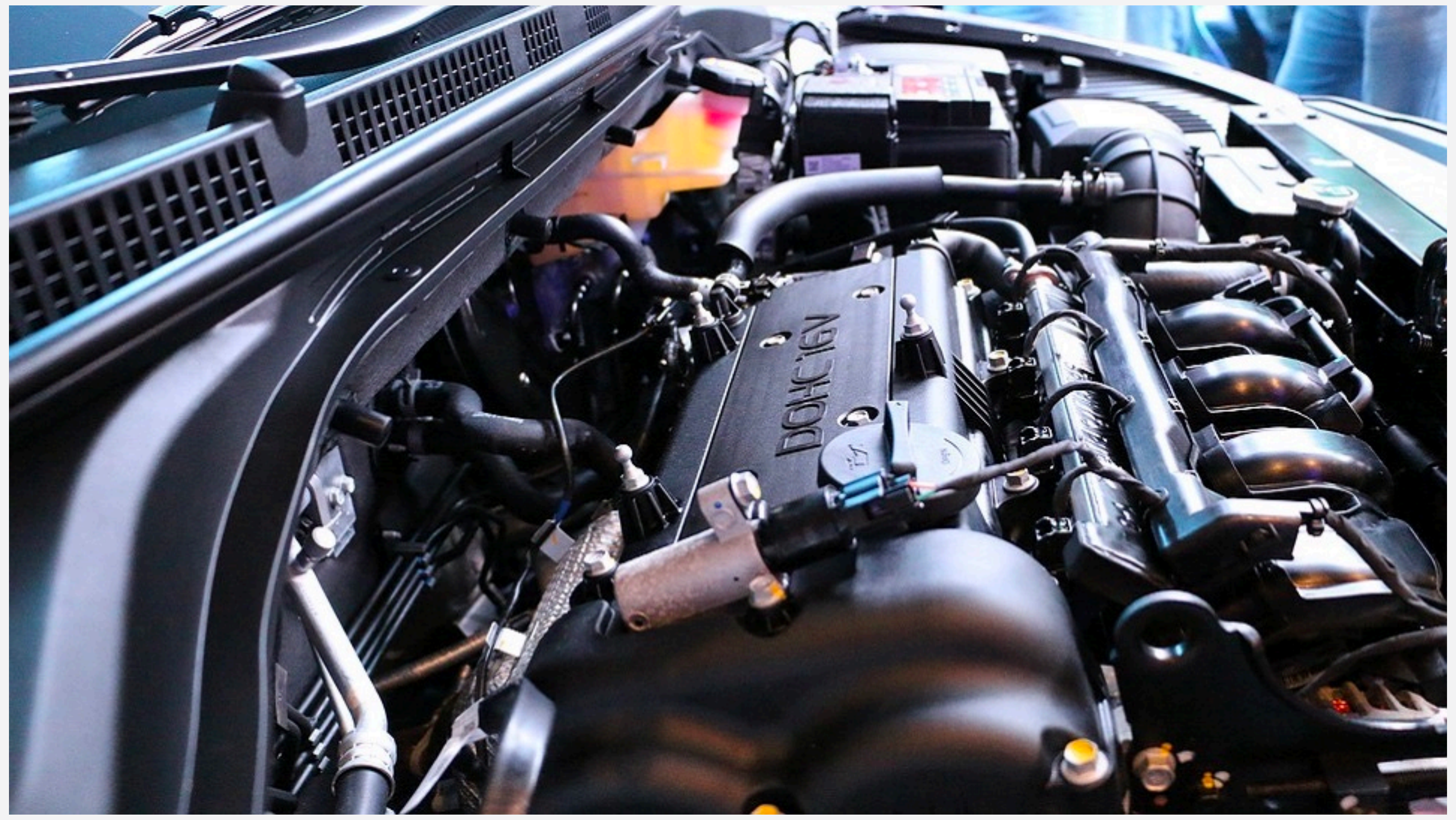


Nylon 6,10
T_g = 55°C; T_m = 215°C

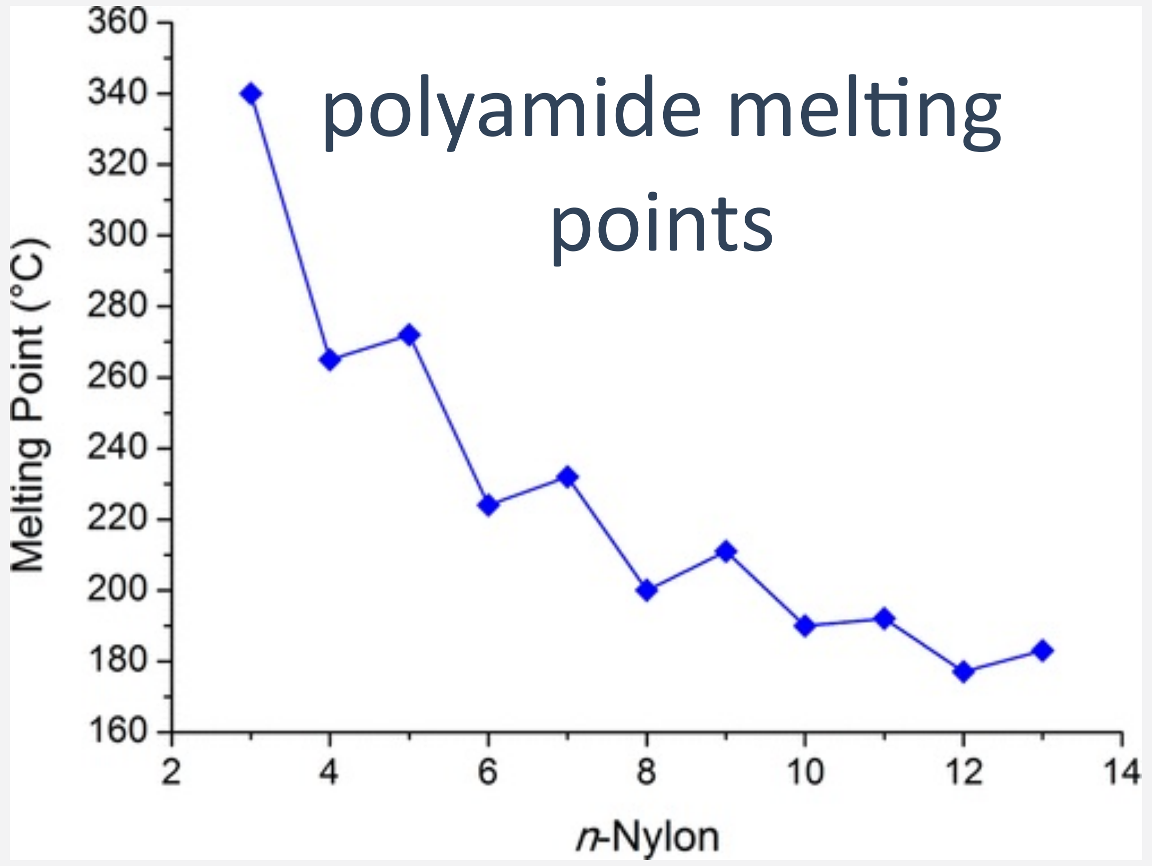


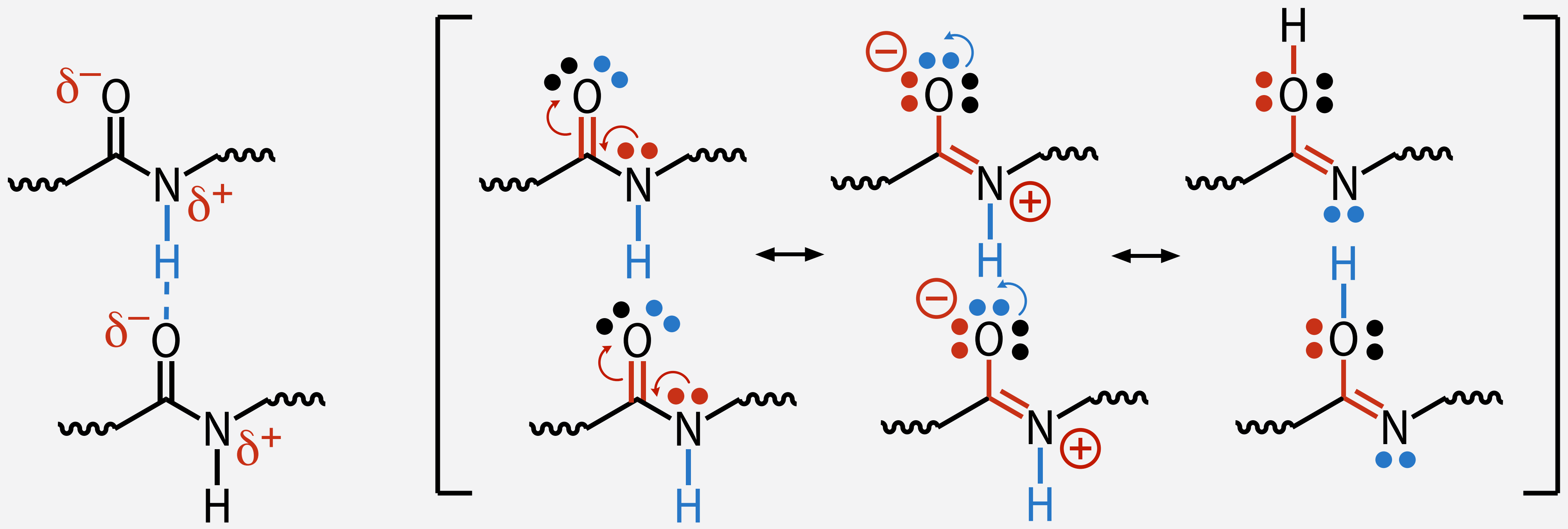
Nylon 6,6
T_g = 70°C; T_m = 255°C

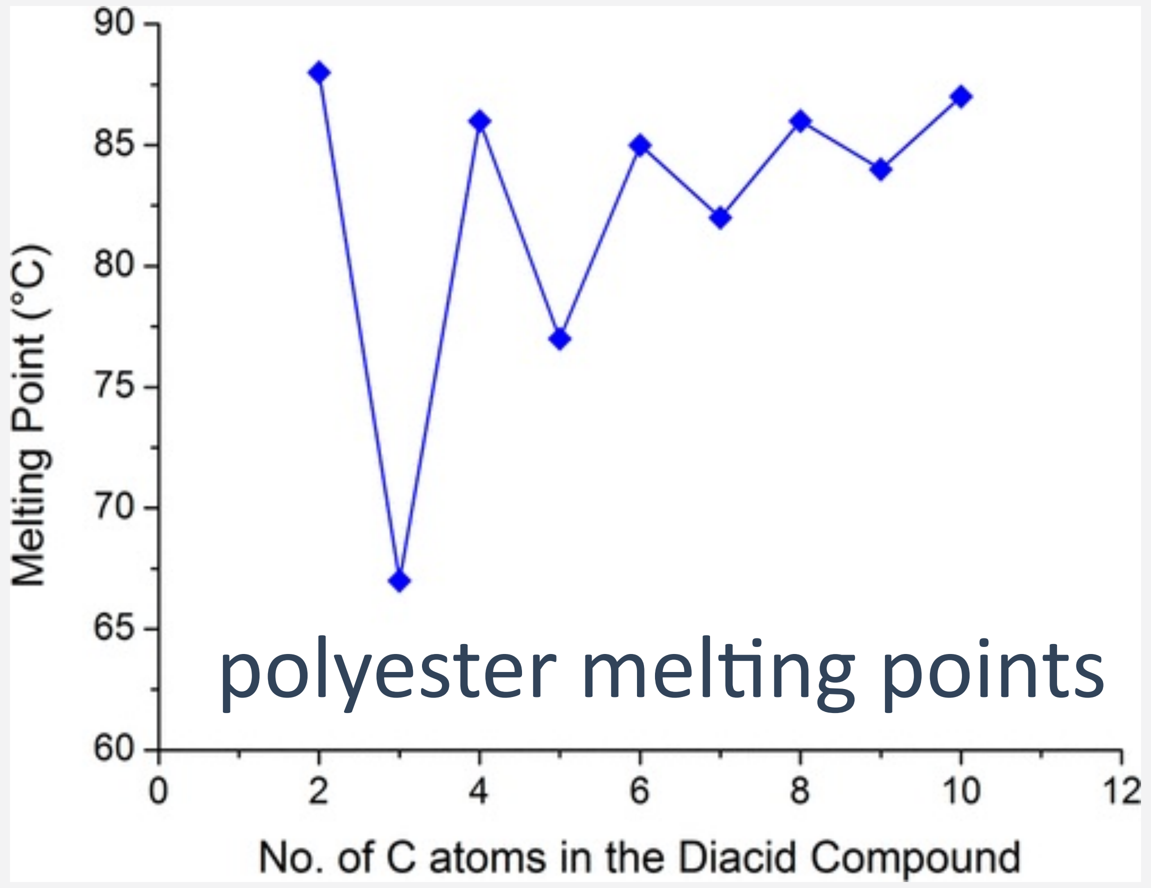
- **Properties**
  - partially to highly crystalline thermoplasts or fibers
  - high strength, toughness, hardness, low wear
  - good electric isolation
  - chemically robust against solvents, acids, bases, oxidants
- **Applications:**
  - machine parts (bearings, gears, conveyor belts)
  - fibers, brush filaments, hosiery
  - electrical components

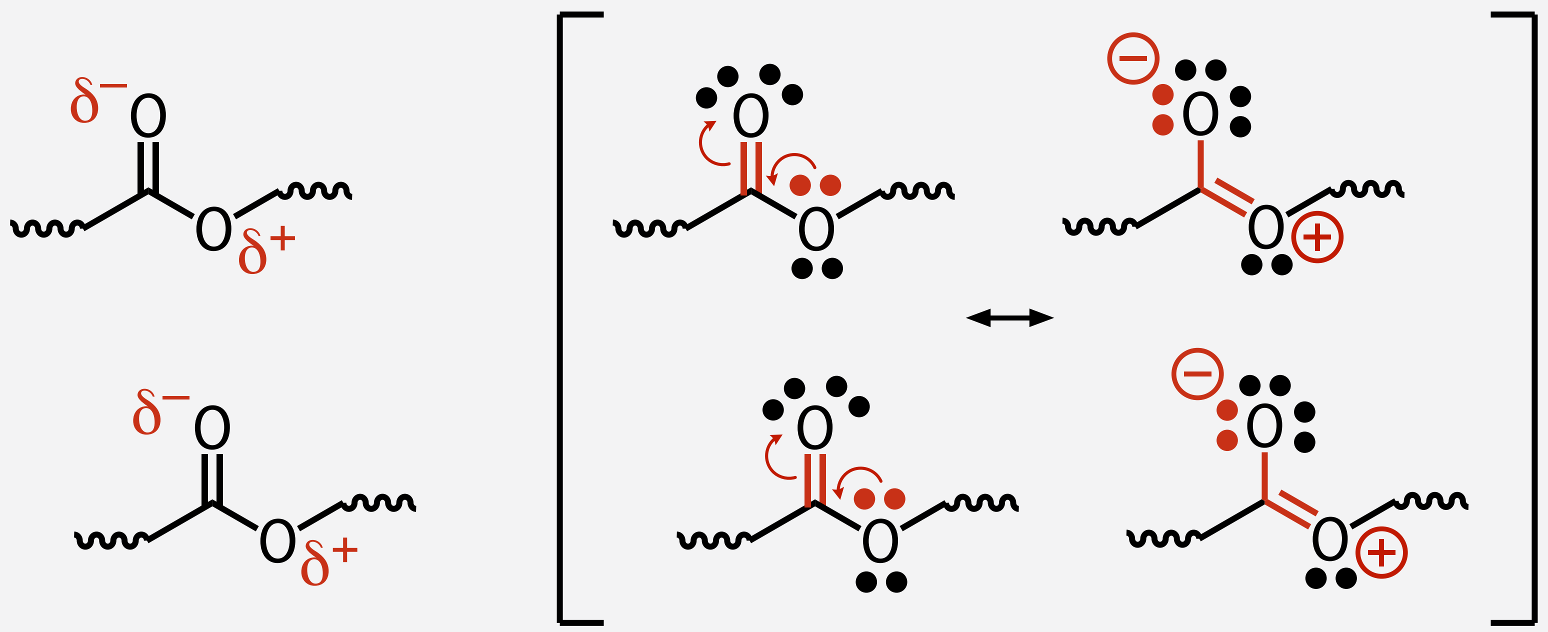


Melting Points of Aliphatic Polyamides and Polyesters



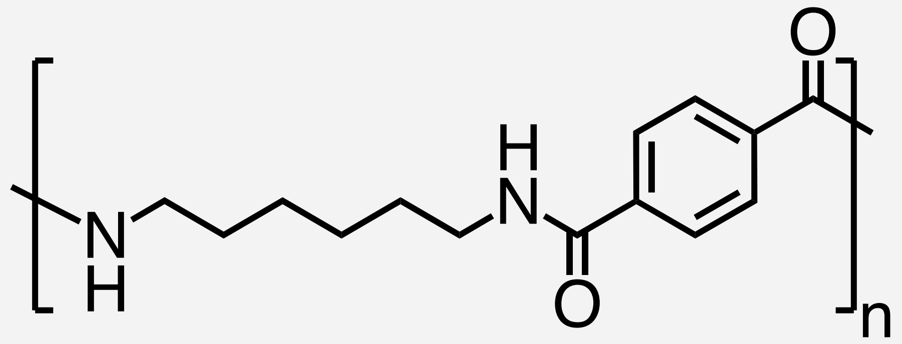






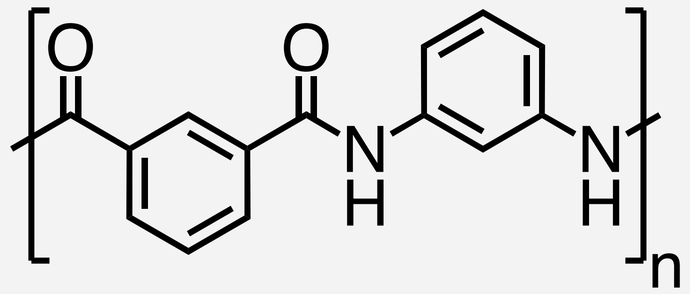
- **hydrogen bonds are the origin of high melting points of polyamides as well as the odd-even effect**

Properties and Applications of Semiaromatic and Aromatic Polyamides



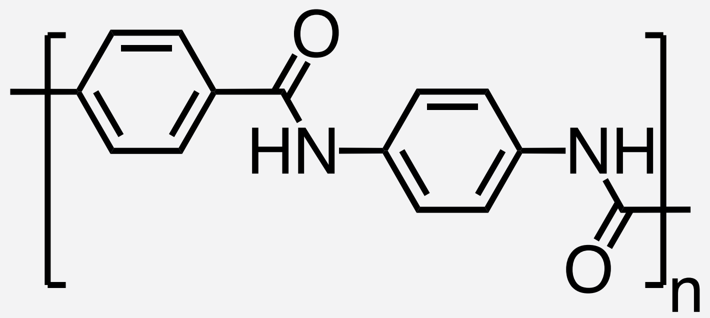
PA6T

T_g = 60°C; T_m = 275°C



Nomex

T_g = 270°C; T_m = 360°C (dec.)



Kevlar

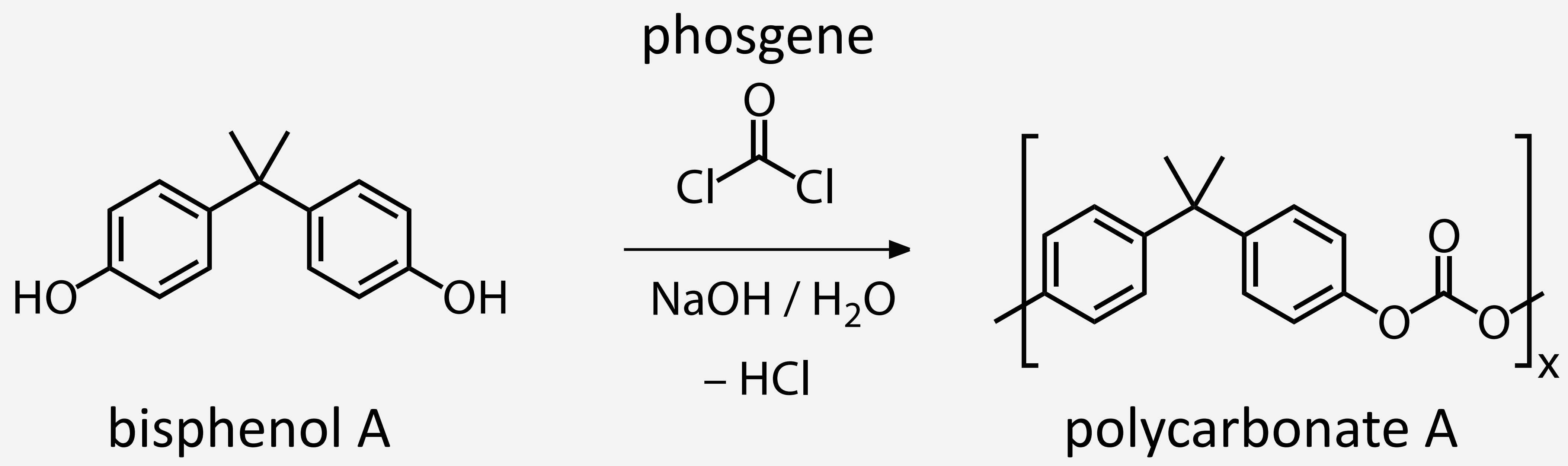
T_m > 400°C (dec.)

- **Properties**
  - higher melting point and glass transition
  - higher strength, chemical, and heat resistance
- **Applications:**
  - aeronautic, aerospatial, military equipment (body-armor)
  - safety equipments (cut-resistant gloves)
  - sports and leisure goods (tennis rackets, skis)

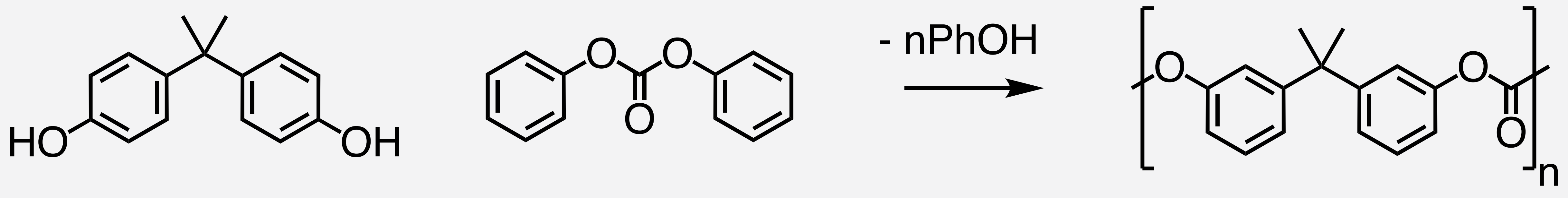
Other Plastics

Synthesis of Polycarbonates

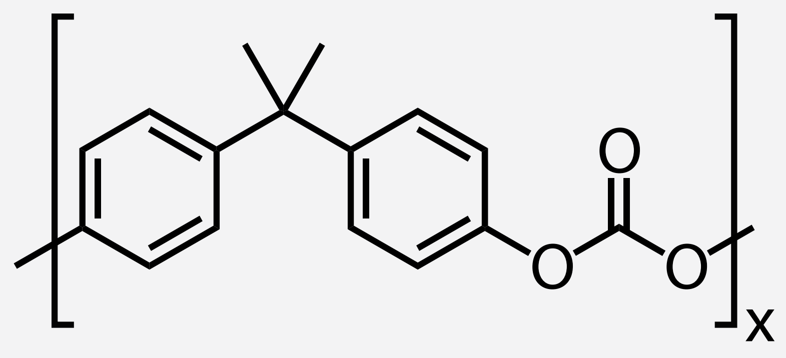
- **step growth polymerization between bisphenol A and phosgene (toxic, volatile)**



- **transesterification of diphenyl carbonate (DPC) with bisphenol A (in bulk)**

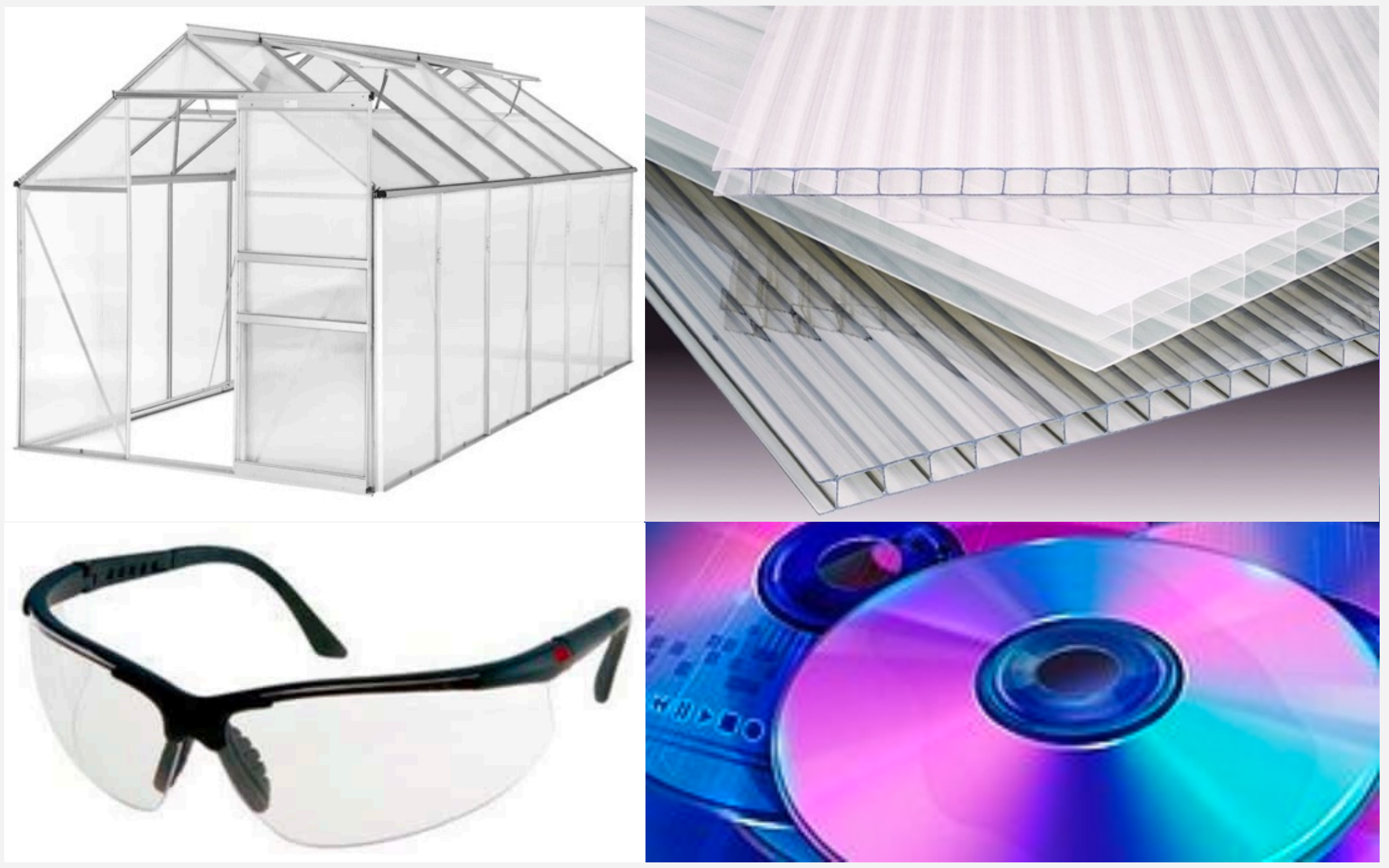


Properties and Applications of Polycarbonates



polycarbonate A
T_g = 150°C

- crystallises very slowly, thus is typically used in its fully amorphous glassy state
- high strength, toughness, hardness, up to 135°C
- highly transparent; good electric isolation, good irradiation stability

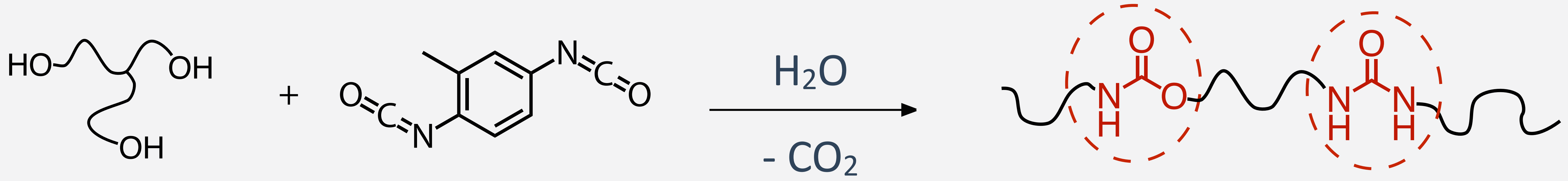


- **Applications:**
- electronic components
- construction materials (domelights, glazing, roofing sheets)
- compact discs, DVDs, blu-rays

Synthesis of Polyurethanes

diol diisocyanate

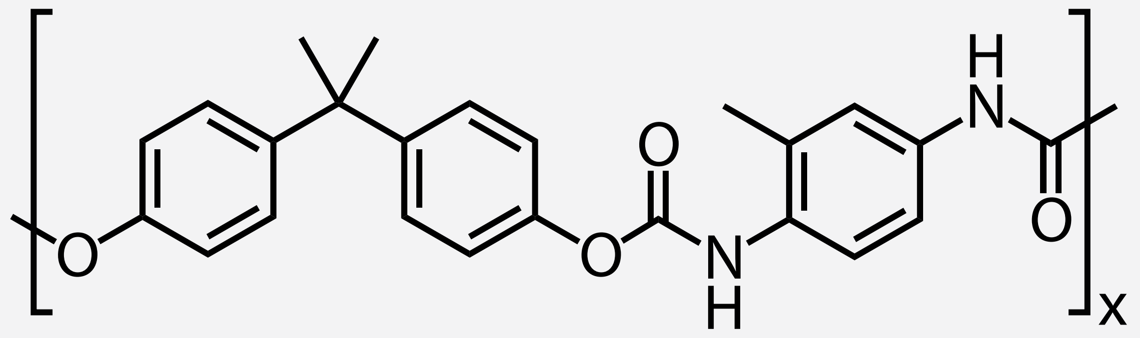
- **step growth polymerization between a diol and a diisocyanate**



polyol diisocyanate urethane linkage urea linkage

- **PU foams are synthesised by polyaddition between a polyol and a diisocyanate in the presence of a blowing agent**

Properties and Applications of Polyurethanes



- chosen polyol molecule has a large influence on the properties and degree of crosslinking in the polyurethane
- when slightly of cross-linking, elastomer with high extensibility
- when highly cross-linked, hard flexible thermoset

- **Applications:**
- automobile parts (seats, headrests, armrests, roof liners, dashboards)
- insulating foam for construction and furniture
- elastomers, adhesives, sealants