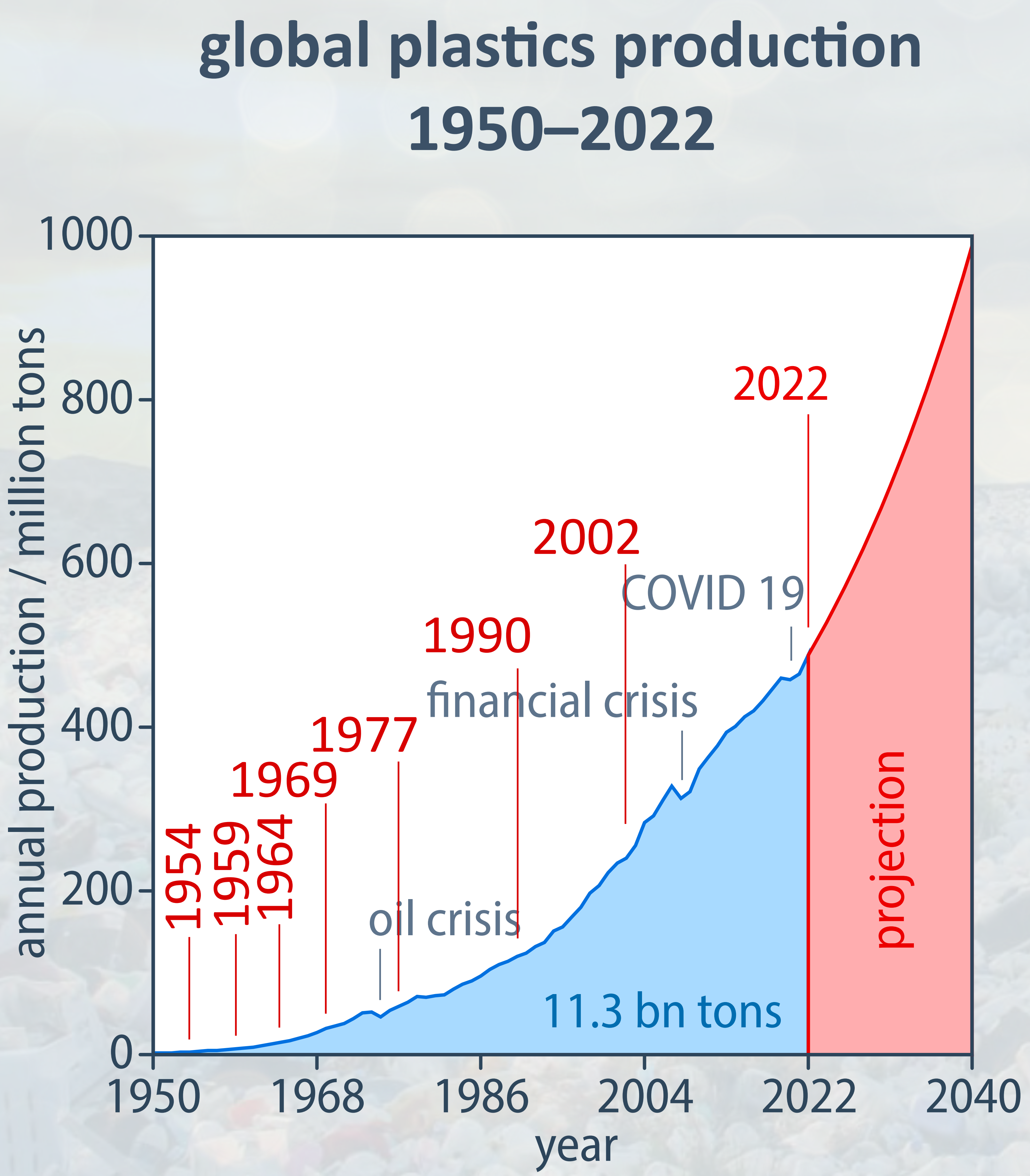
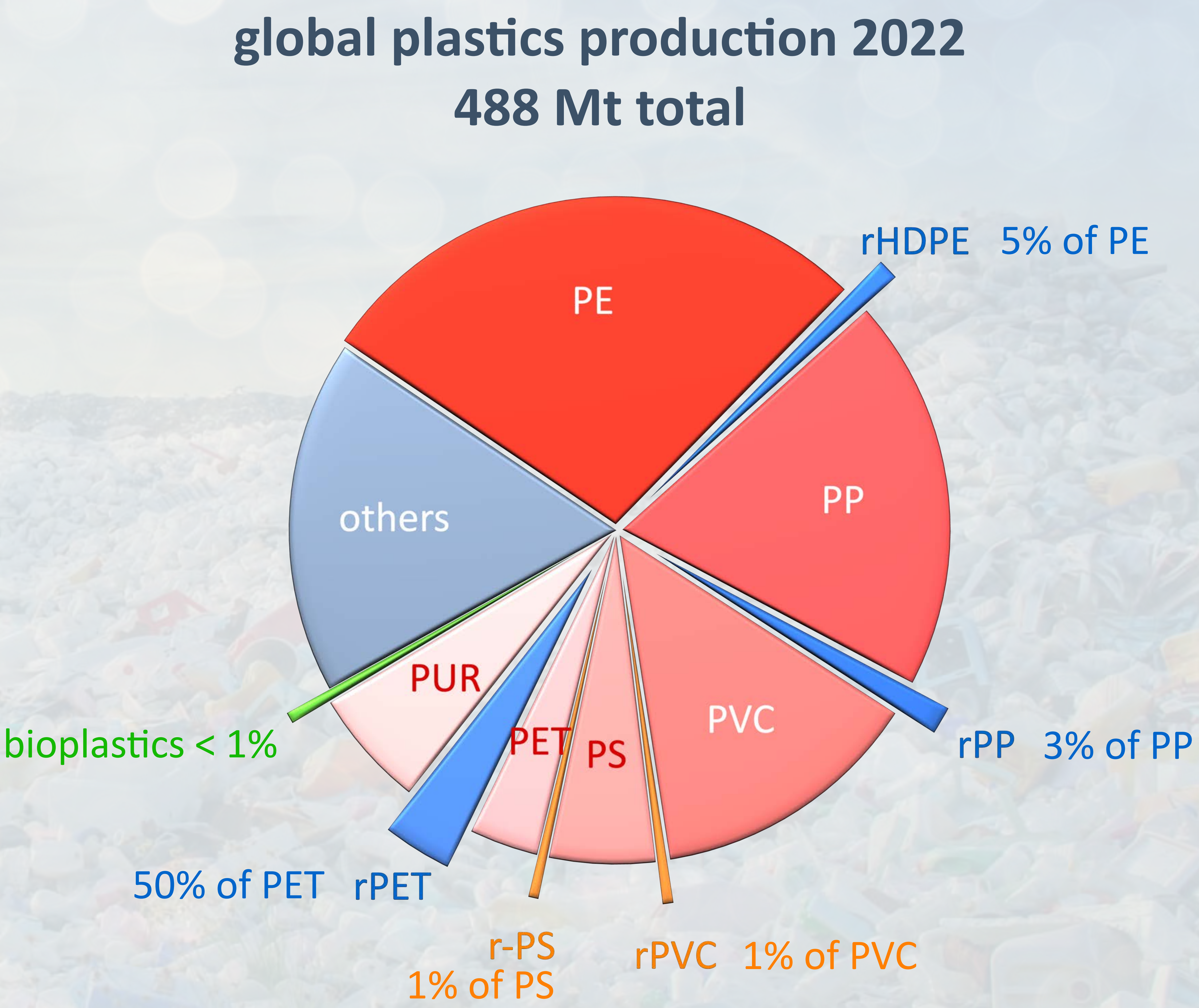
5.5 Polymer Materials

Global Plastics Production & Recycling





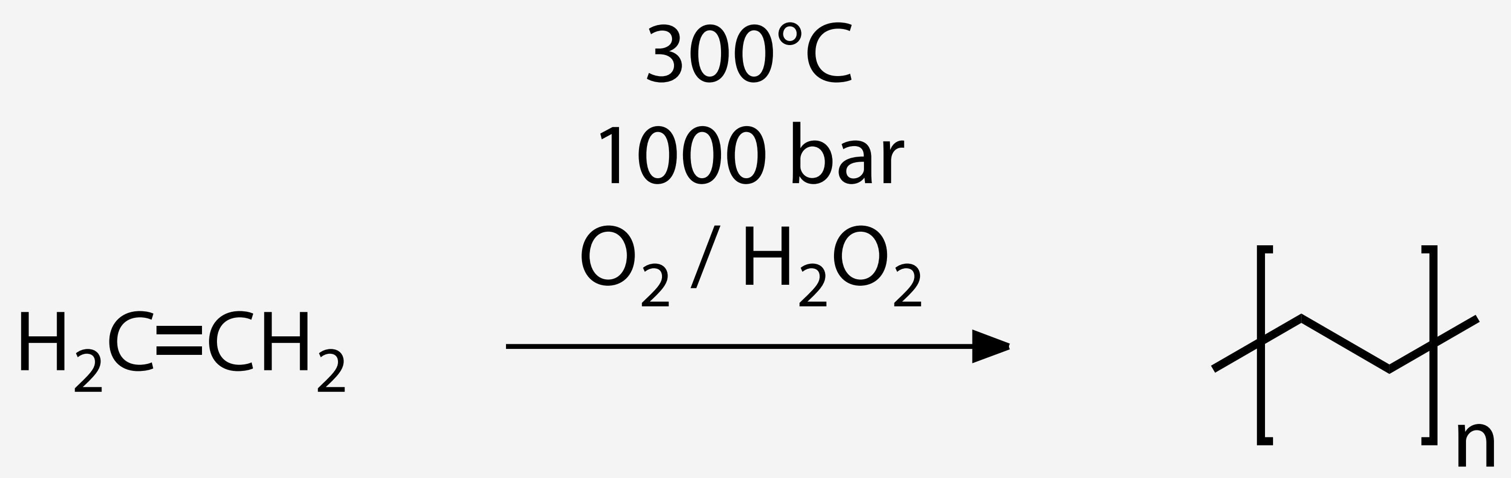
- **just 9% of all plastics recycled, only three open-loop and two closed-loop recycling streams**
- **50% incinerated, 36% landfill, of which half is mismanaged; overall 30% leaked into environment**

Global Plastics Outlook, OECD Report **2022**; Tan, *Commun. Earth Environ.* **2025**, *6*, 257.

Polyethylene (PE)

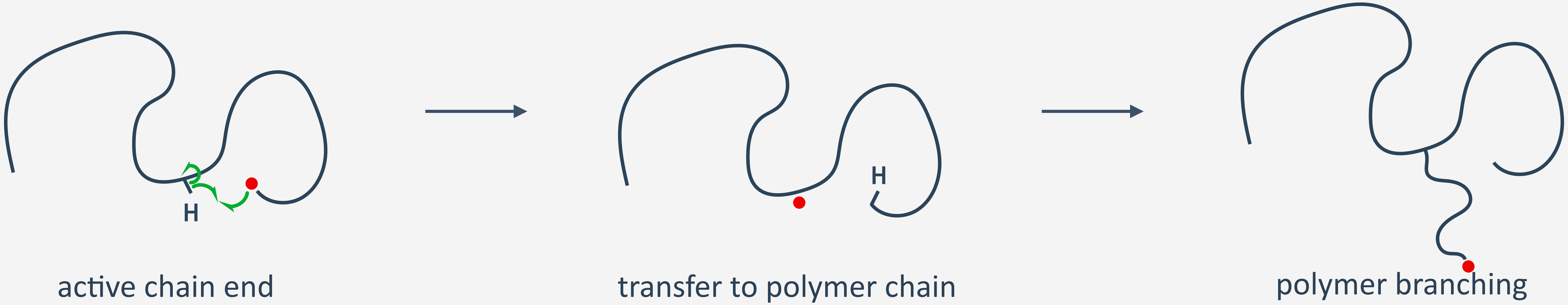
Low-Density Polyethylene (LDPE) by Radical Polymerization of Ethylene

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



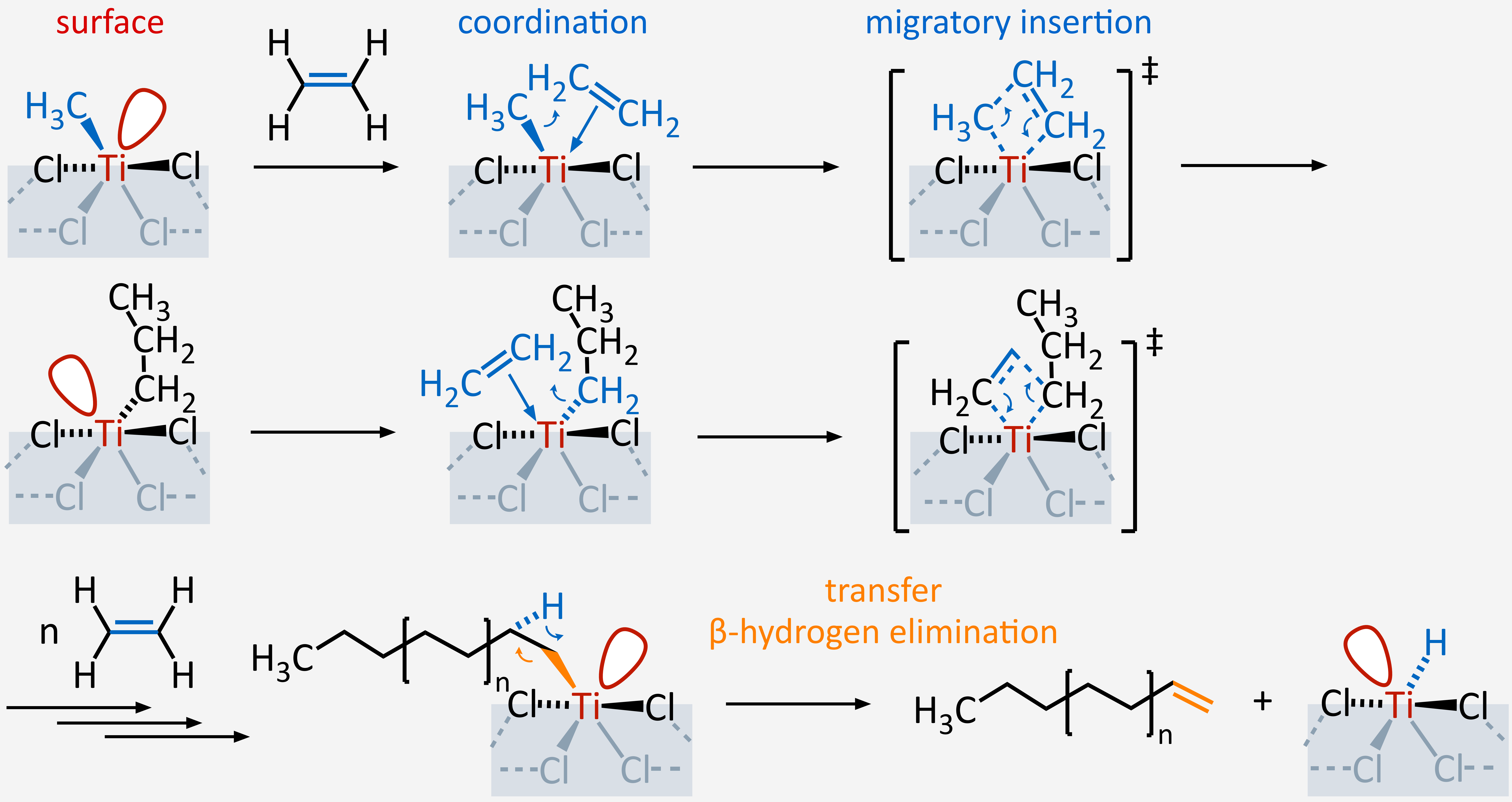
low-density polyethylene (LDPE)
T_g = –100°C; T_m = 105–115°C

  - 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)



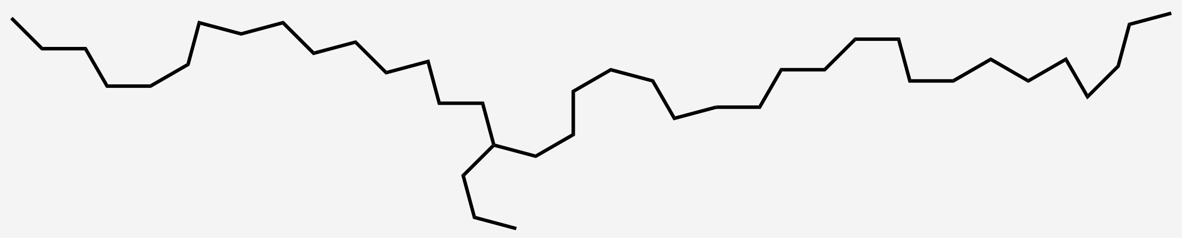
- **long chain branching results in low degree of crystallinity, hence low density and low stiffness**
- **increased entanglement for high melt strength, and (together with low crystallinity) high ductility**

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

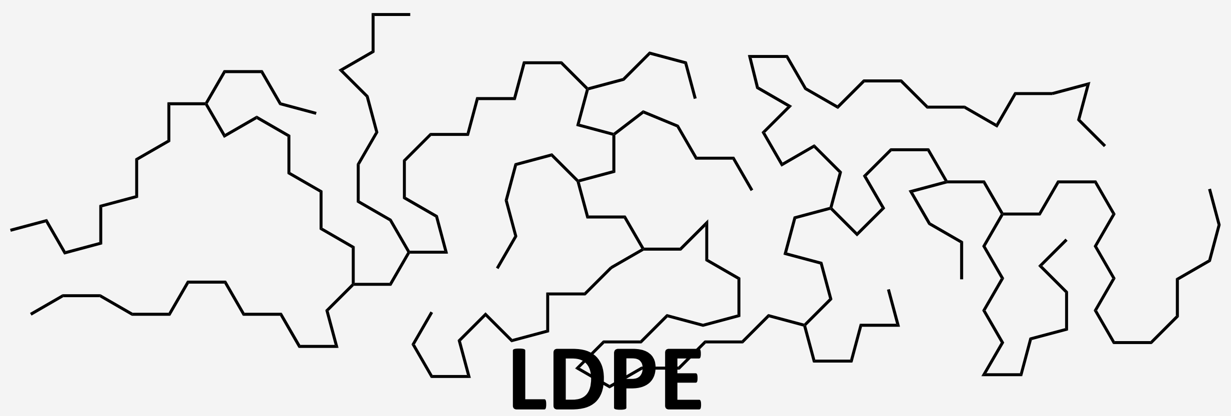


- Cossee Arlman mechanism: **monomer coordination** to **empty coordination site** on surface metal atom
- **migratory insertion** into Mt–C bond, means that **polymer switches coordination site at every step**
- **chain transfer** generates terminal **double bonds** (can result in few branches when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

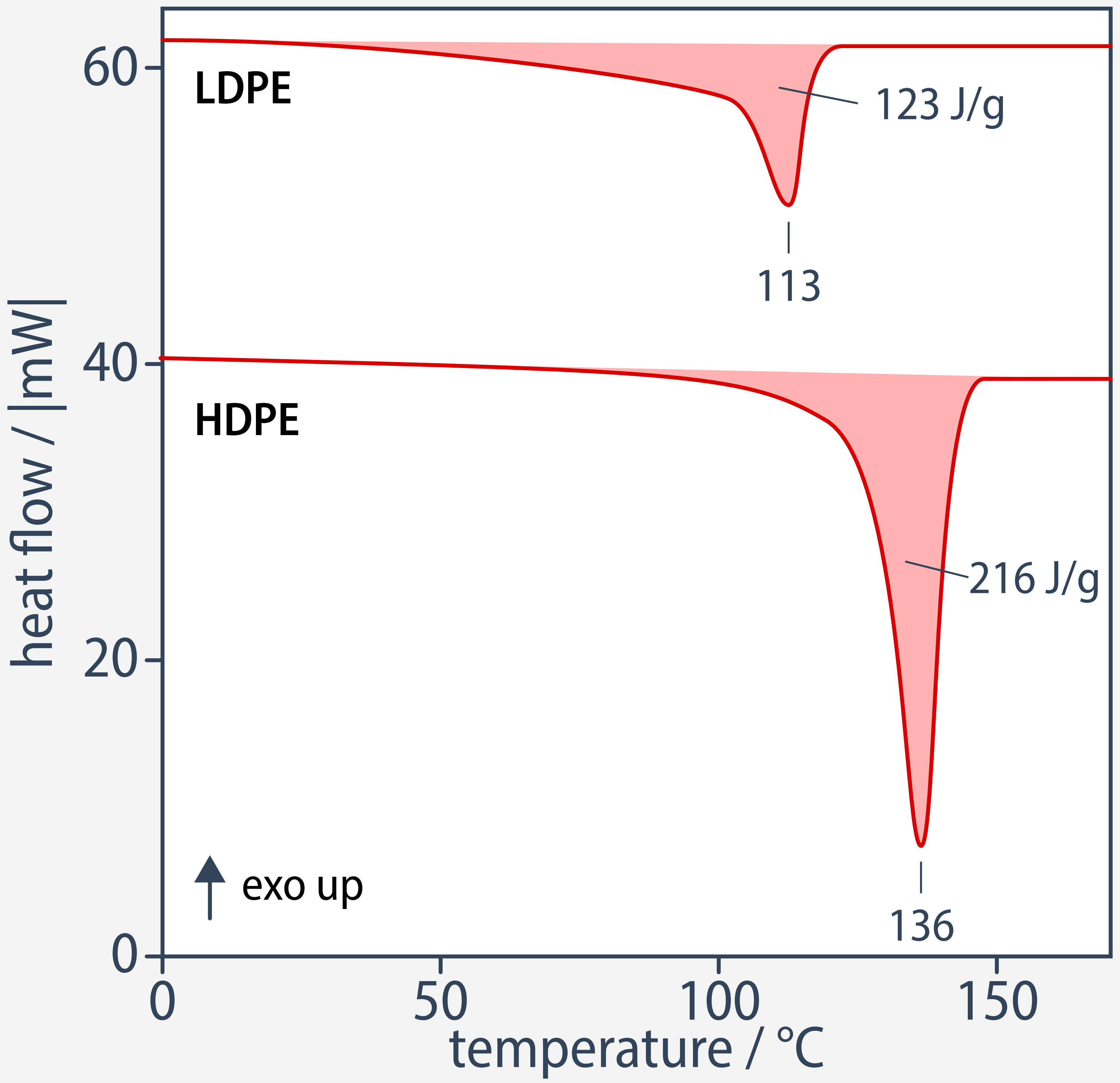
Commercial Polyethylene (PE) Grades

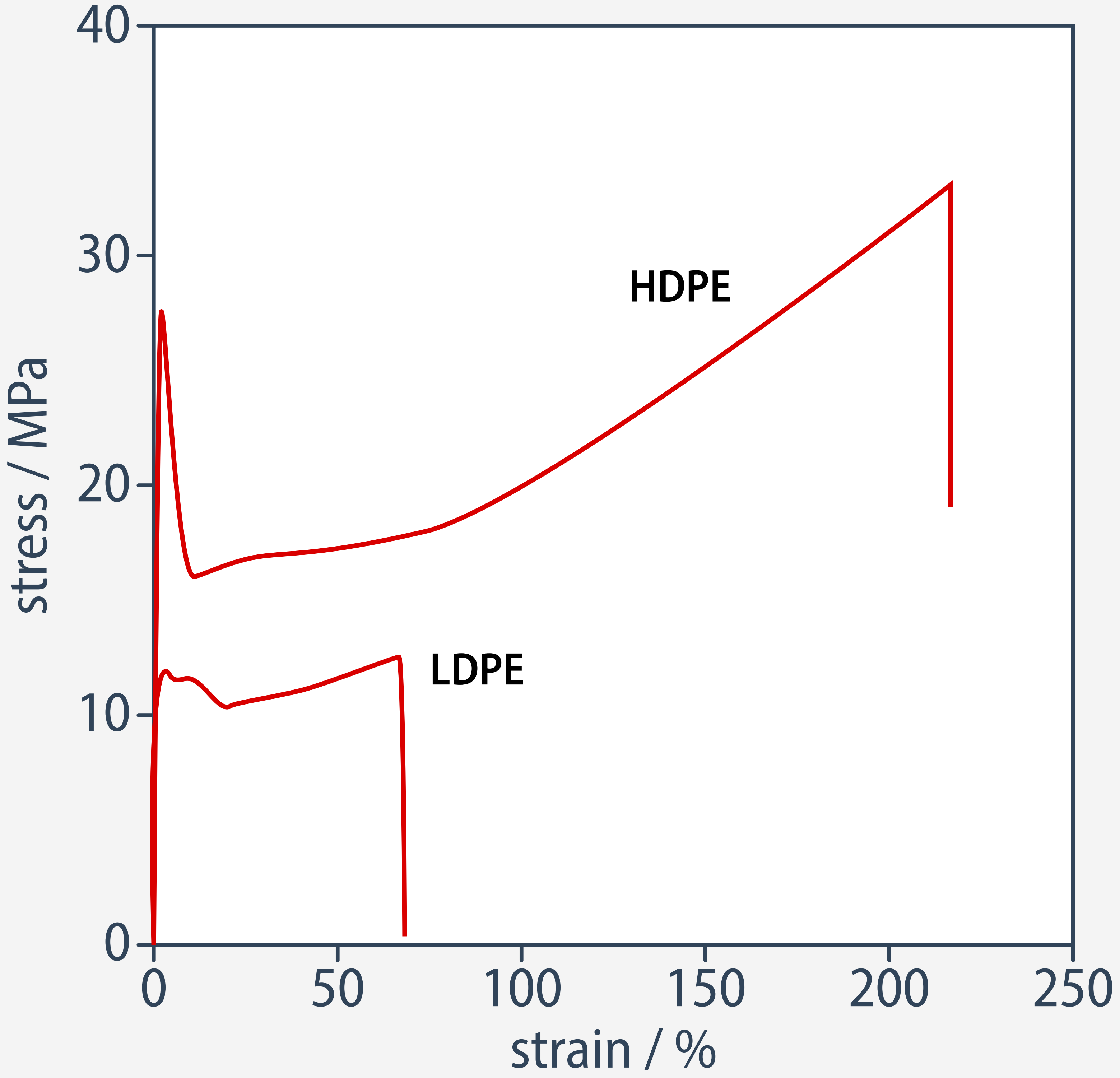


HDPE



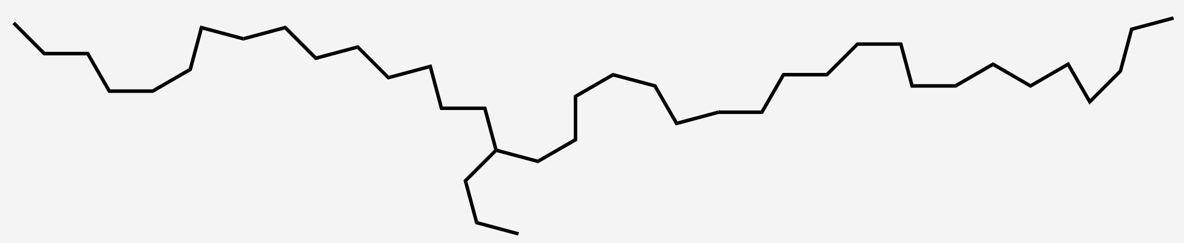
LDPE





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

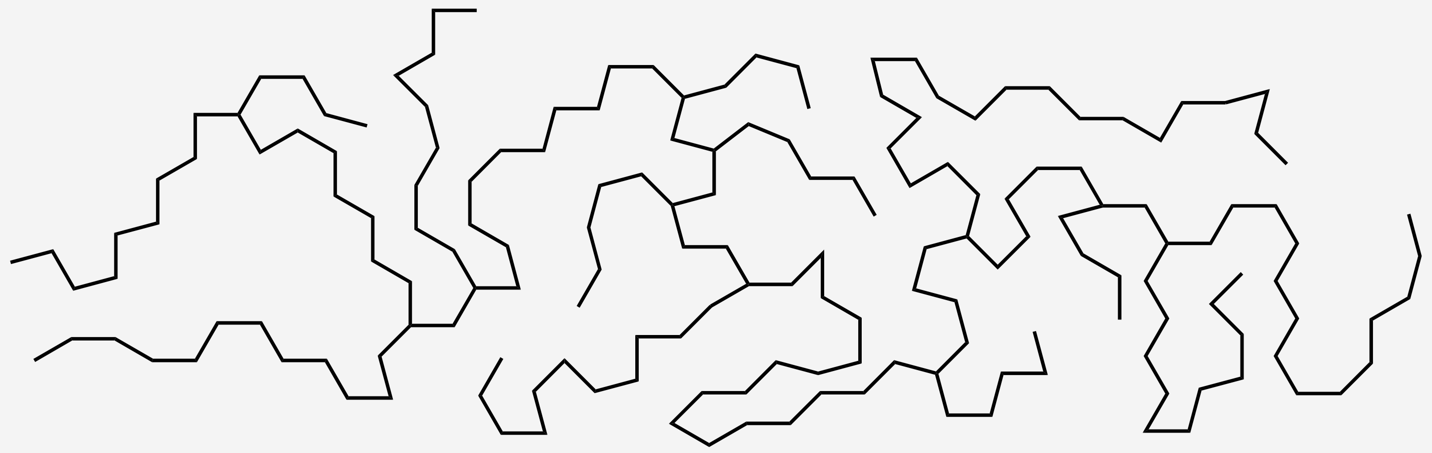
Commercial Polyethylene (PE)



high-density polyethylene (HDPE)

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

packs efficiently, high crystallinity, high density



low-density polyethylene (LDPE)

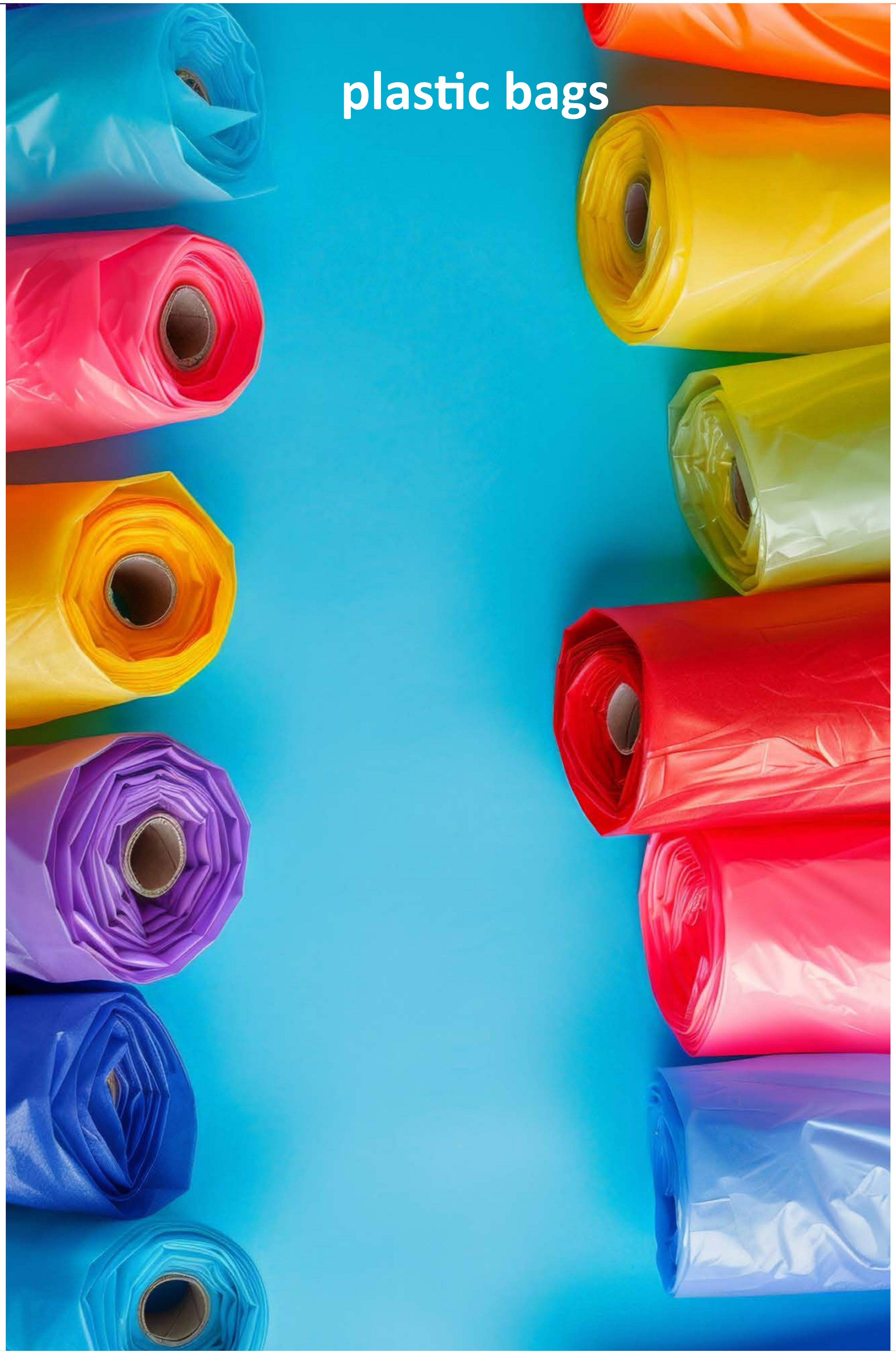
highly branched with many branching points (60/1000 carbons)

low crystallinity, low density, film forming

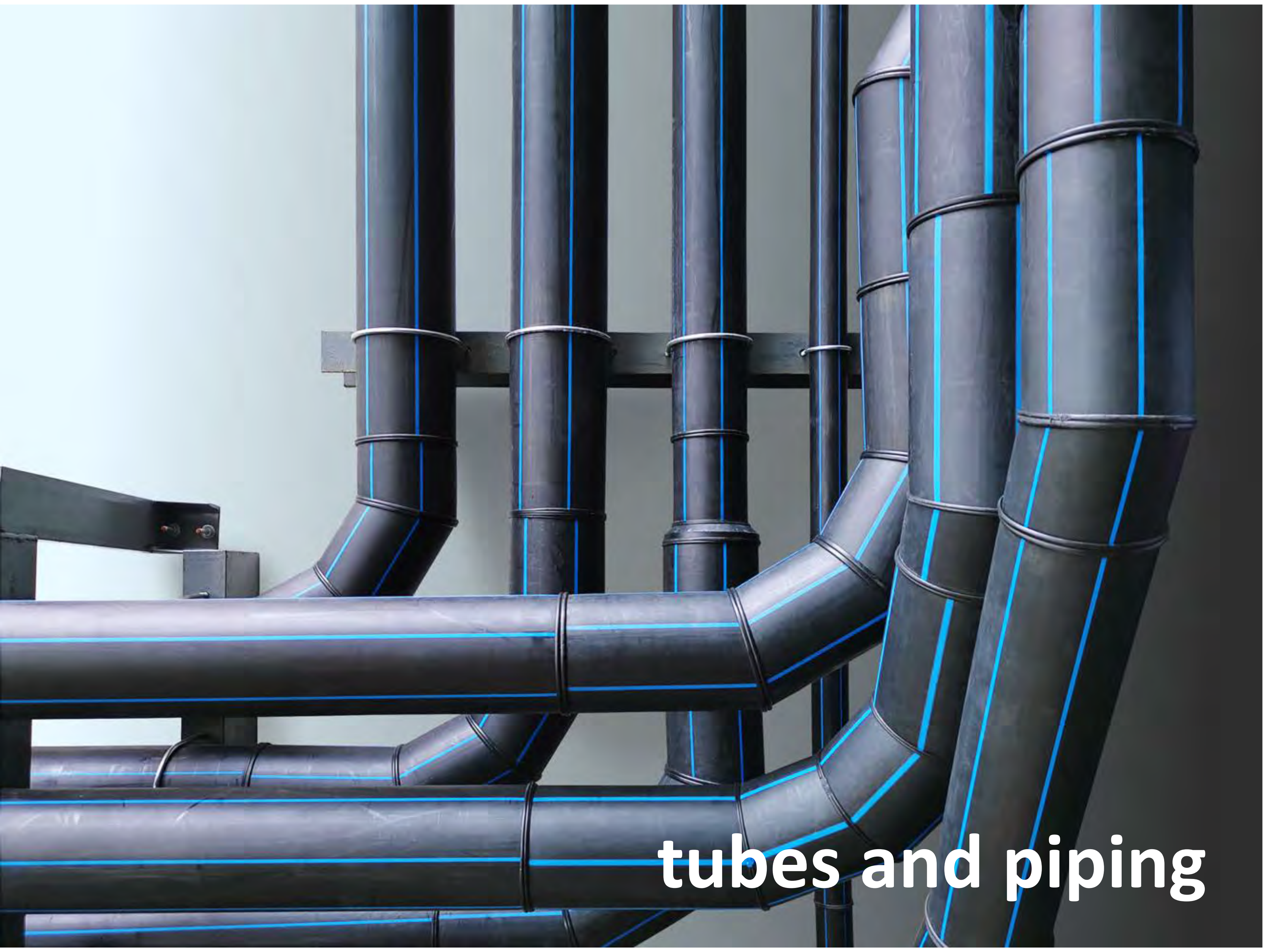
Material	T_m (°C)	T_g (°C)	crystallinity	density (g/mL)	tensile strength (MPa)
HDPE	120-135	-100	70-90%	0.94-0.97	20-37
LDPE	105-115	-100	40-60%	0.92	8-15

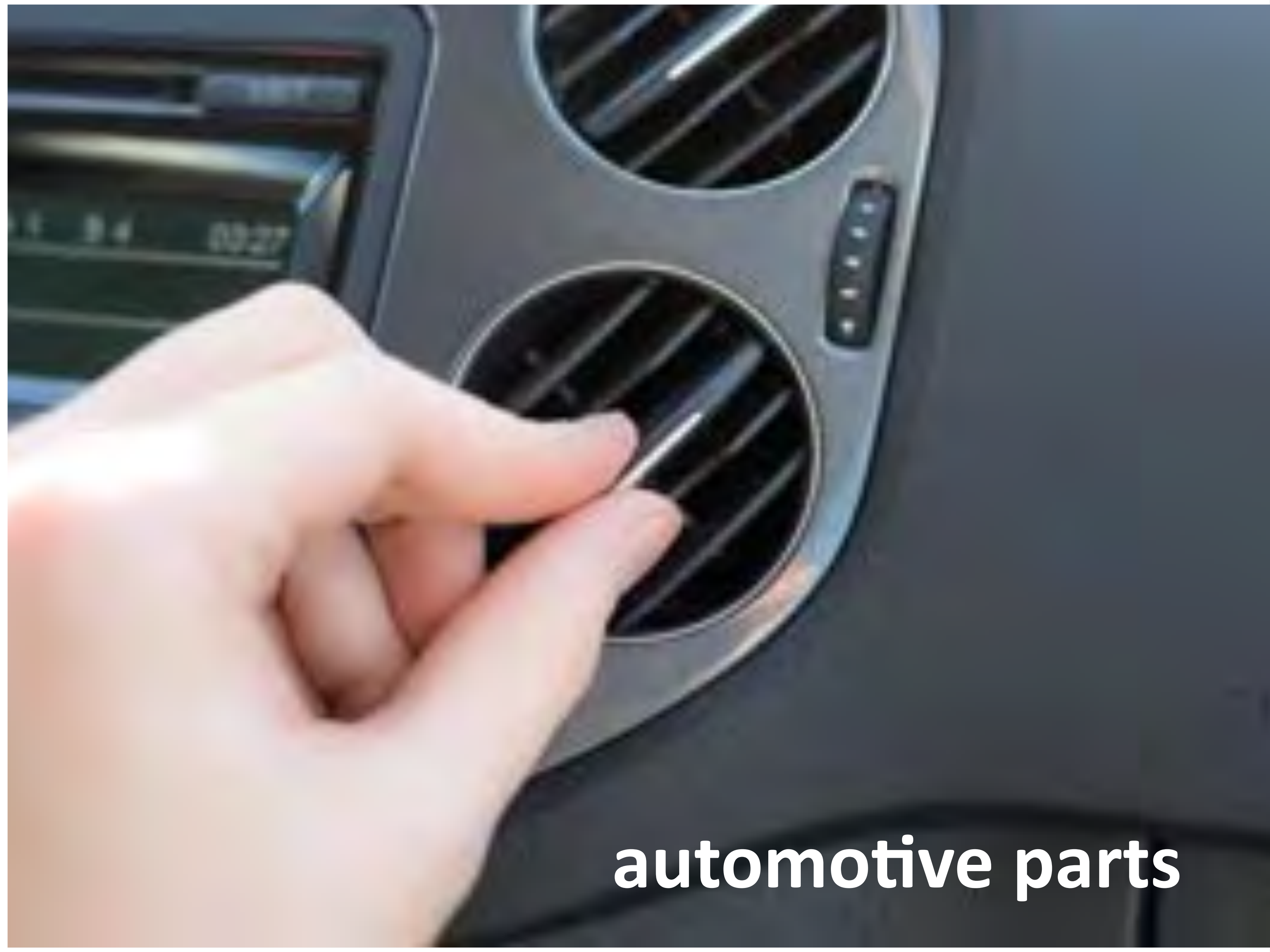
- **HDPE and LDPE display vastly different physical properties; separable based on their densities!**

LDPE Applications



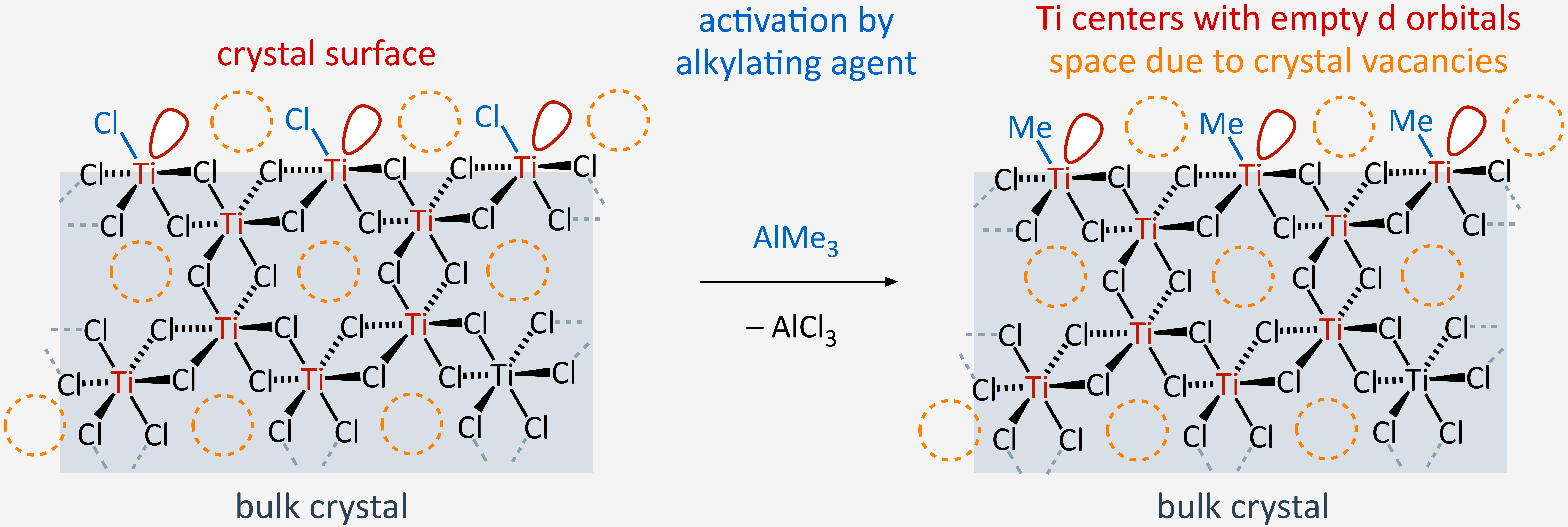
Applications of HDPE





Polypropylene

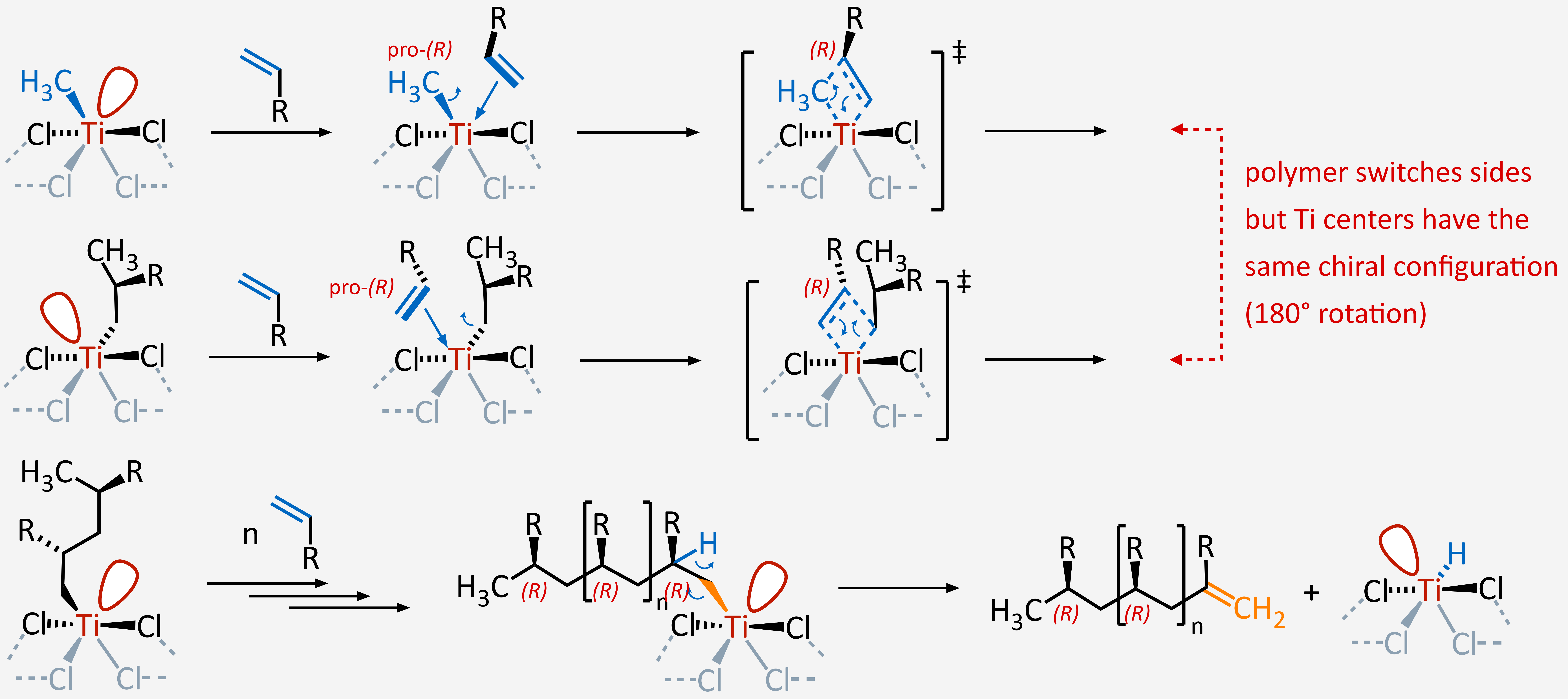
Heterogeneous Catalysts for Ziegler-Natta Polymerization



- 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

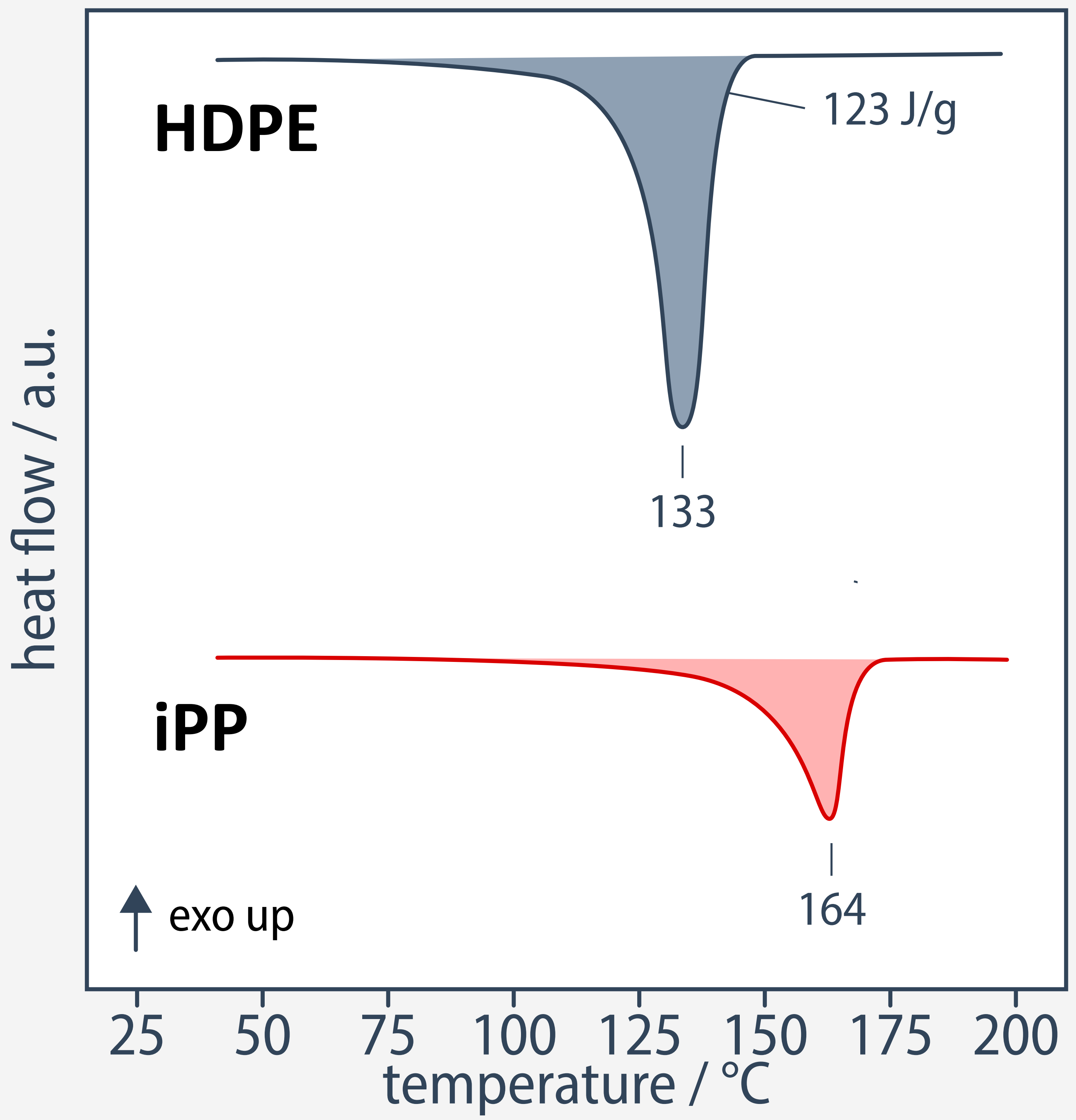
- **“multisite” catalysts with various types of surface Ti centers & geometries, activity slightly different**

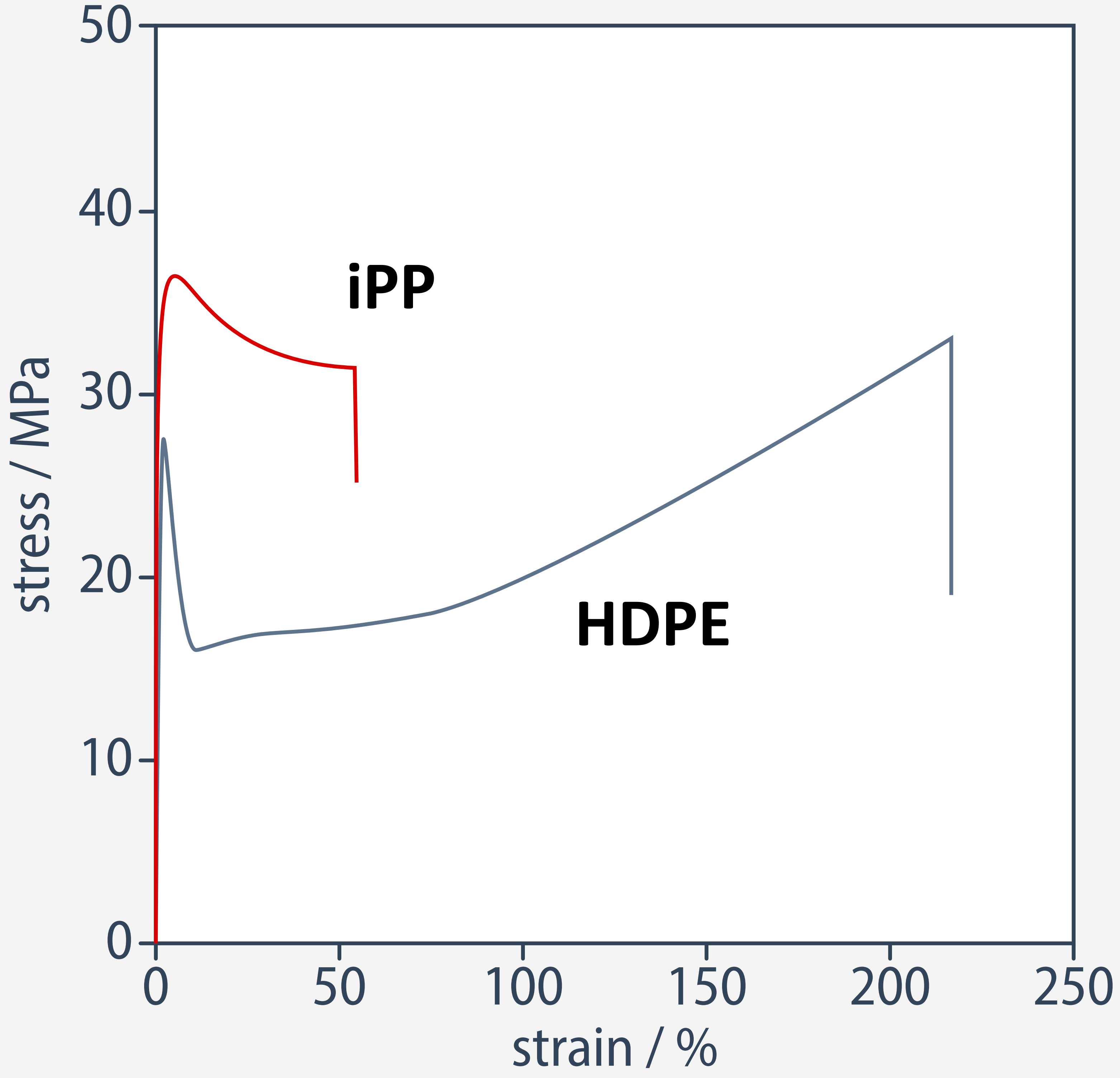
Isotactic Polymerization of Propylene Using Ziegler Natta Catalysts



- **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**

Polypropylene versus Polyethylene





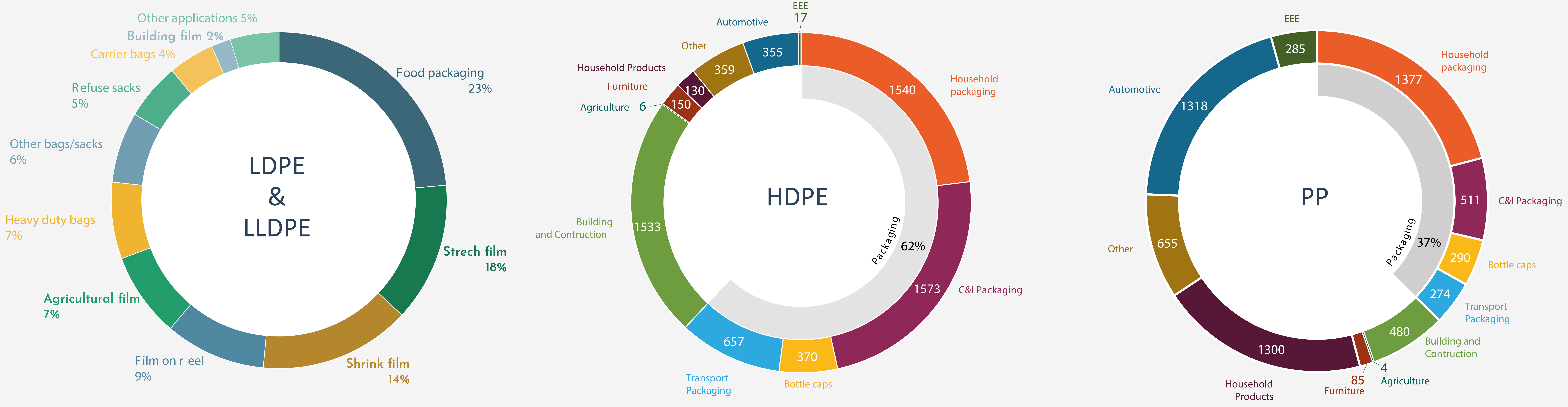
Material	T_m (°C)	T_g (°C)	crystallinity	density (g/mL)	tensile strength (MPa)
HDPE	120-135	-100	70-90%	0.94-0.97	20-37
iPP	160-170	-10	30-60%	0.94	25-40

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

Applications of PP

Applications of LDPE, HDPE, and PP

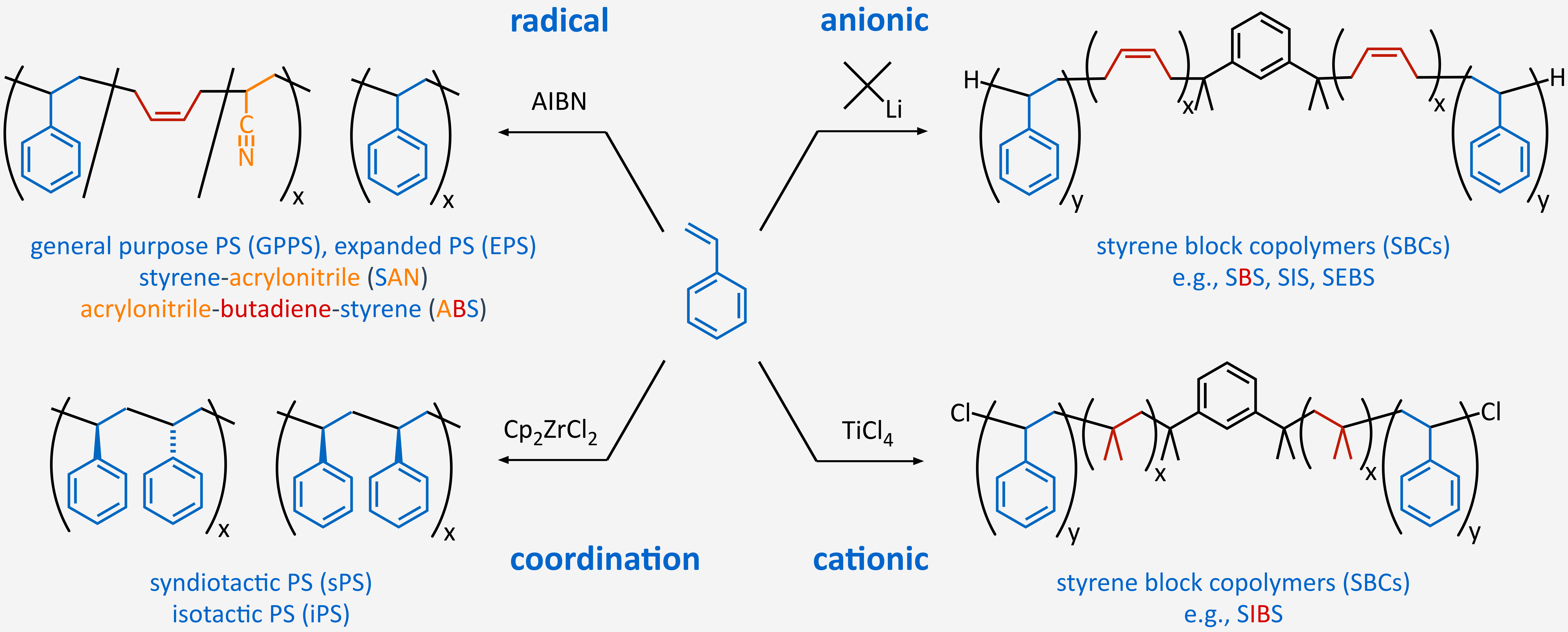
- current market states in Europe (derived from Eurostat data and other studies):



- **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**

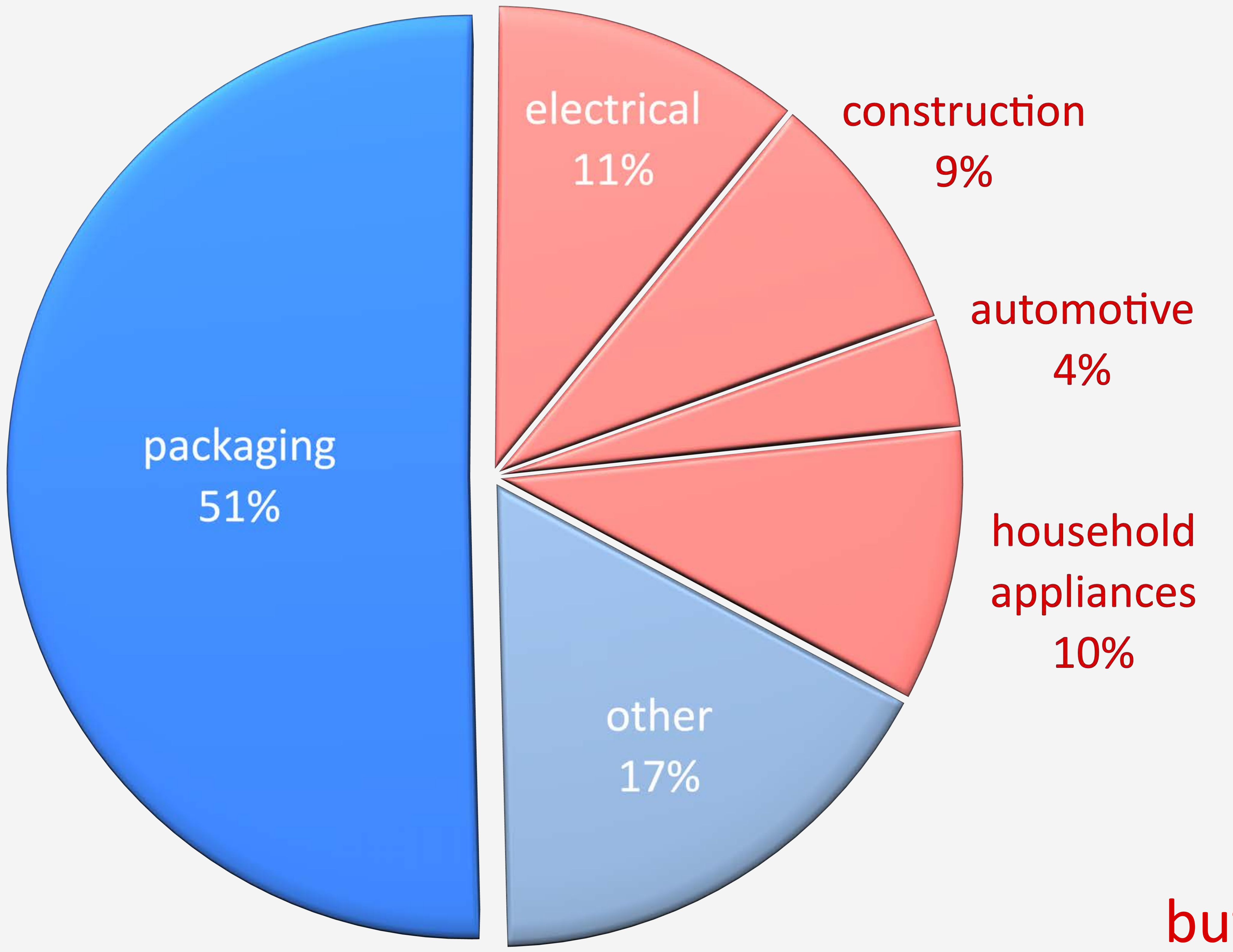
Polystyrene (PS) and Copolymers

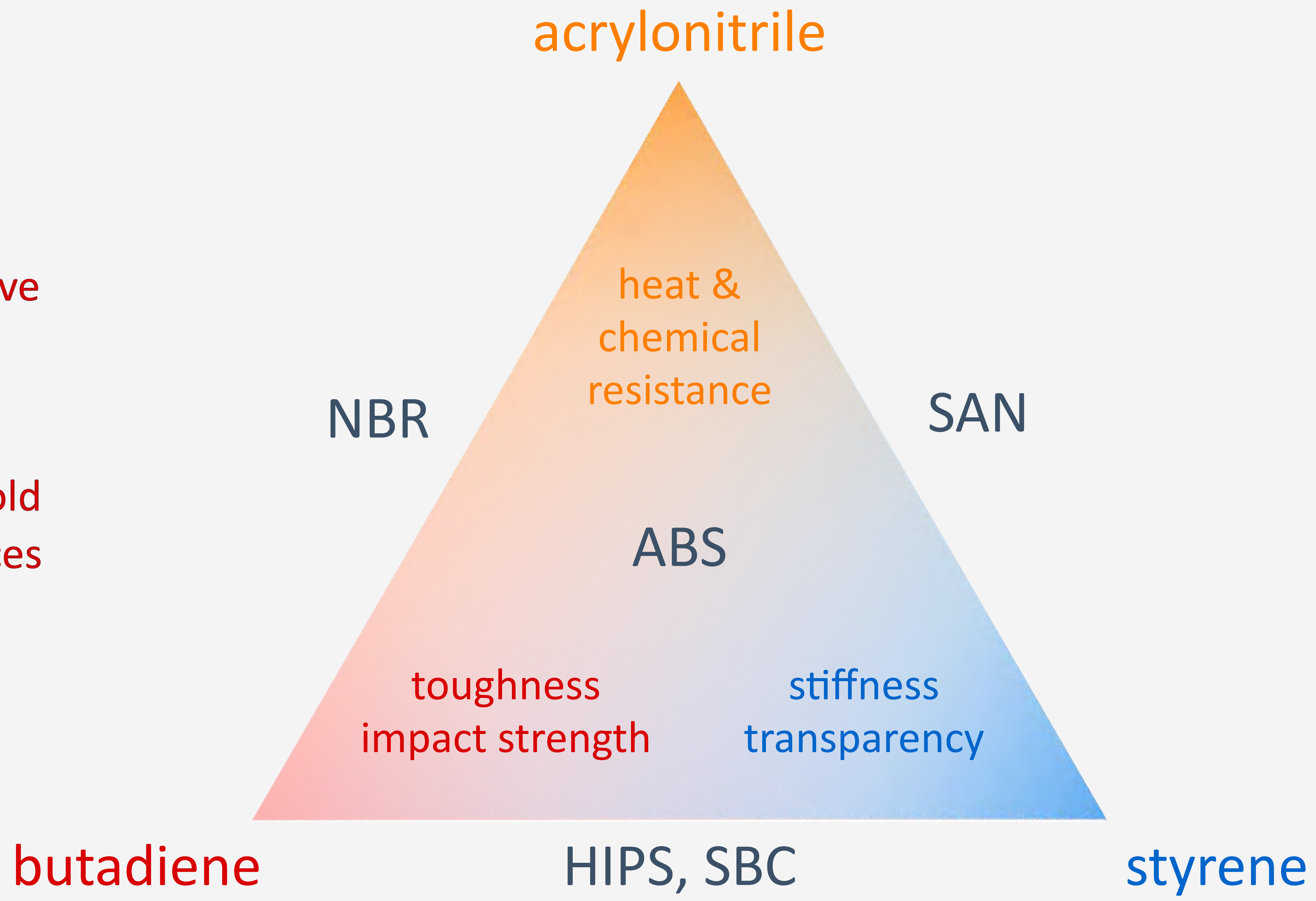
Synthesis of Polystyrene and Copolymers



- 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/m³
- vulnerable to organic solvents
- protective packaging, food containers, disposable cups, insulating panels,

High-Impact Polystyrenes (HIPS) & Acrylonitrile-Butadiene-Styrene (ABS)

High-Impact Polystyrenes (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

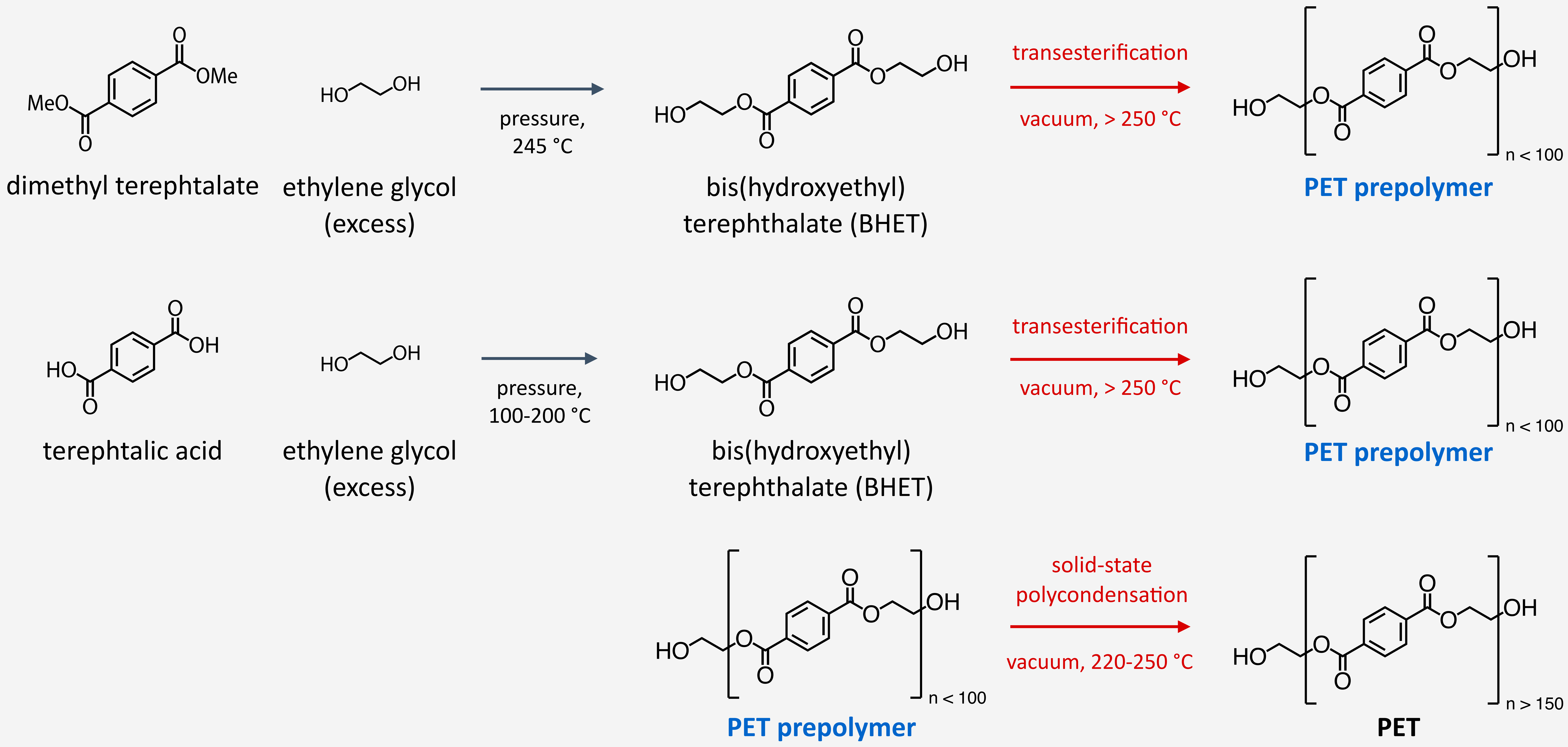
Acrylonitrile-Butadiene-Styrene (ABS)

- 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.

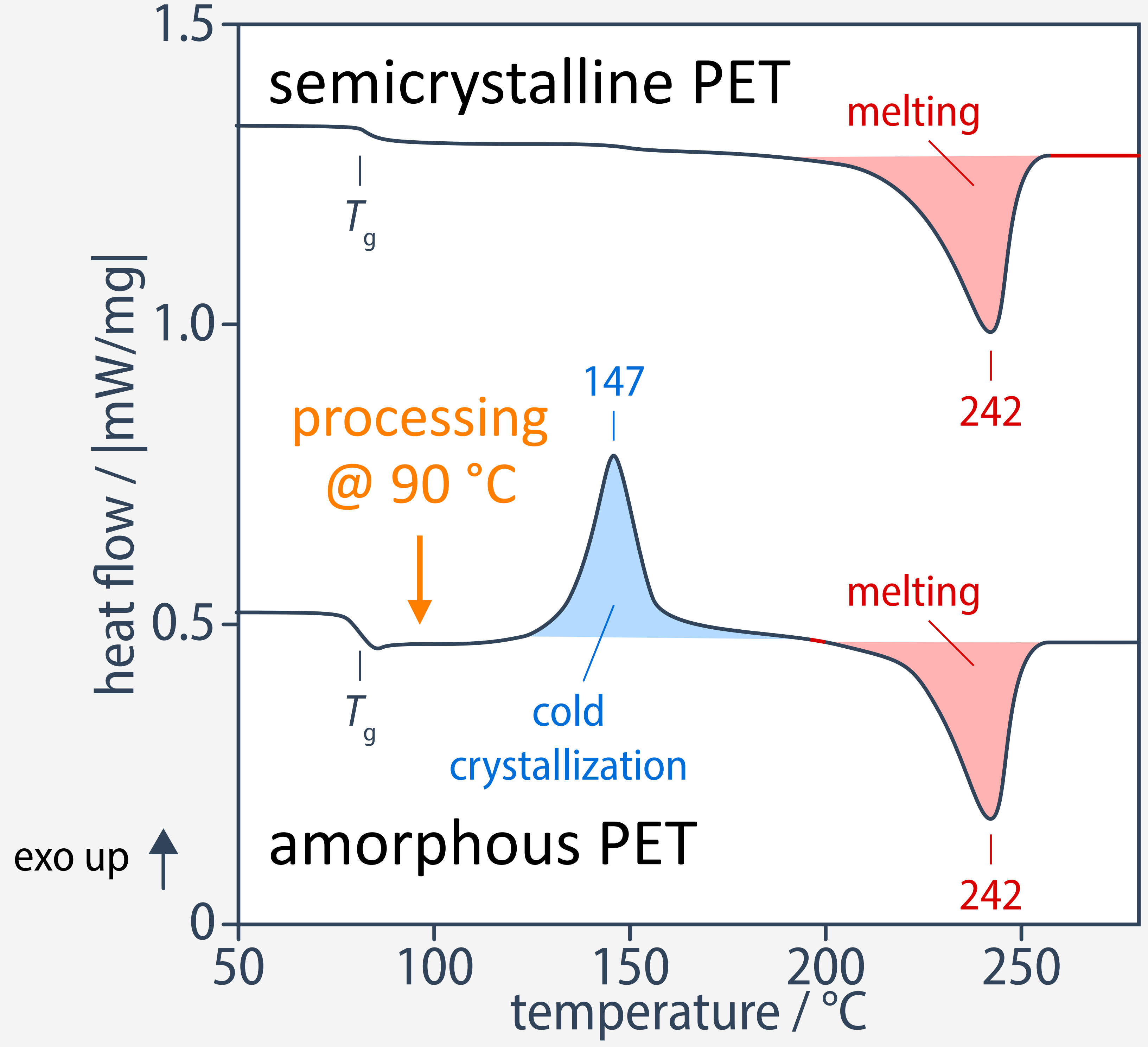
Poly(ethylene terephthalate) (PET)

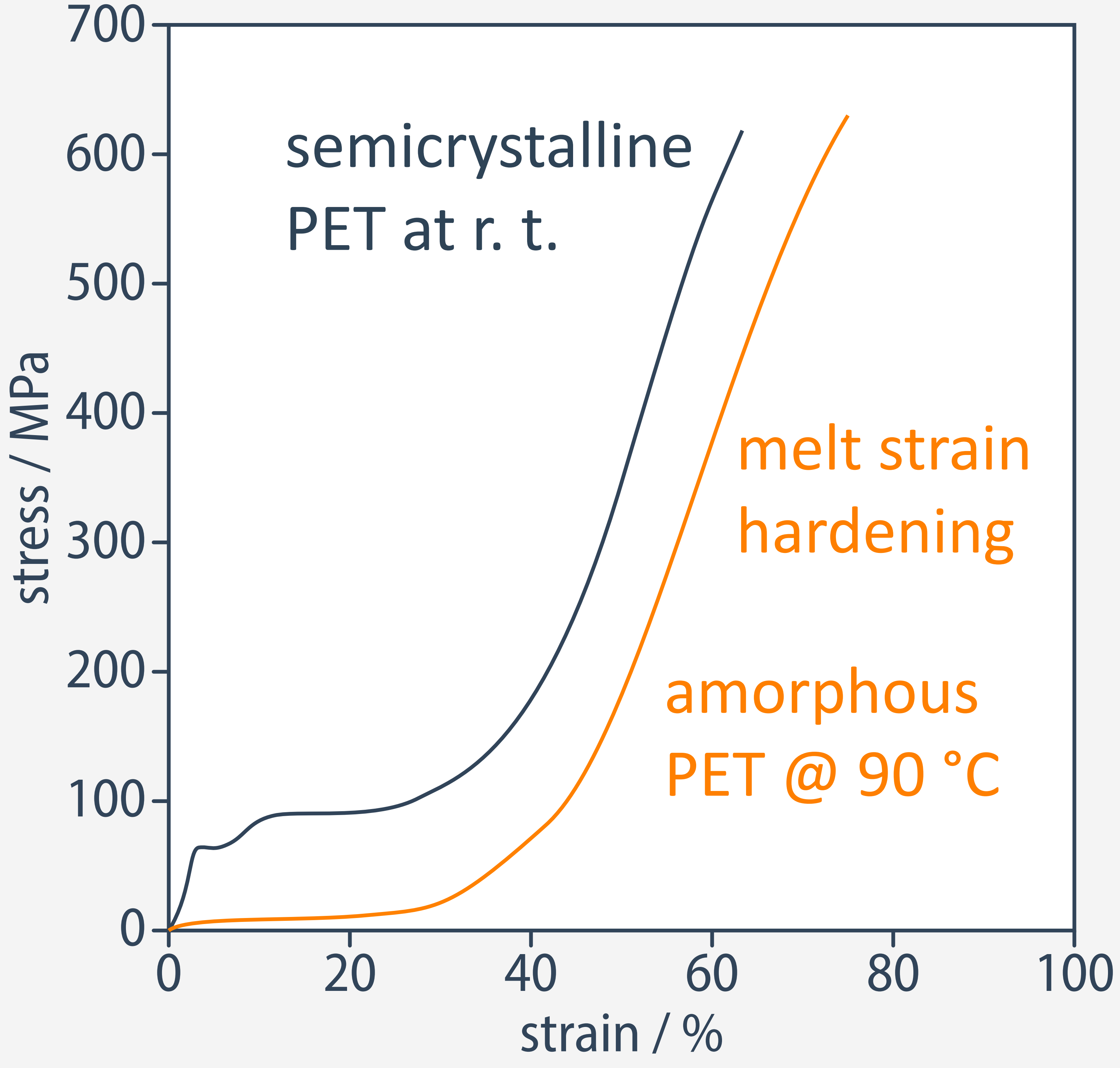
Synthesis of PET



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

Properties of PET

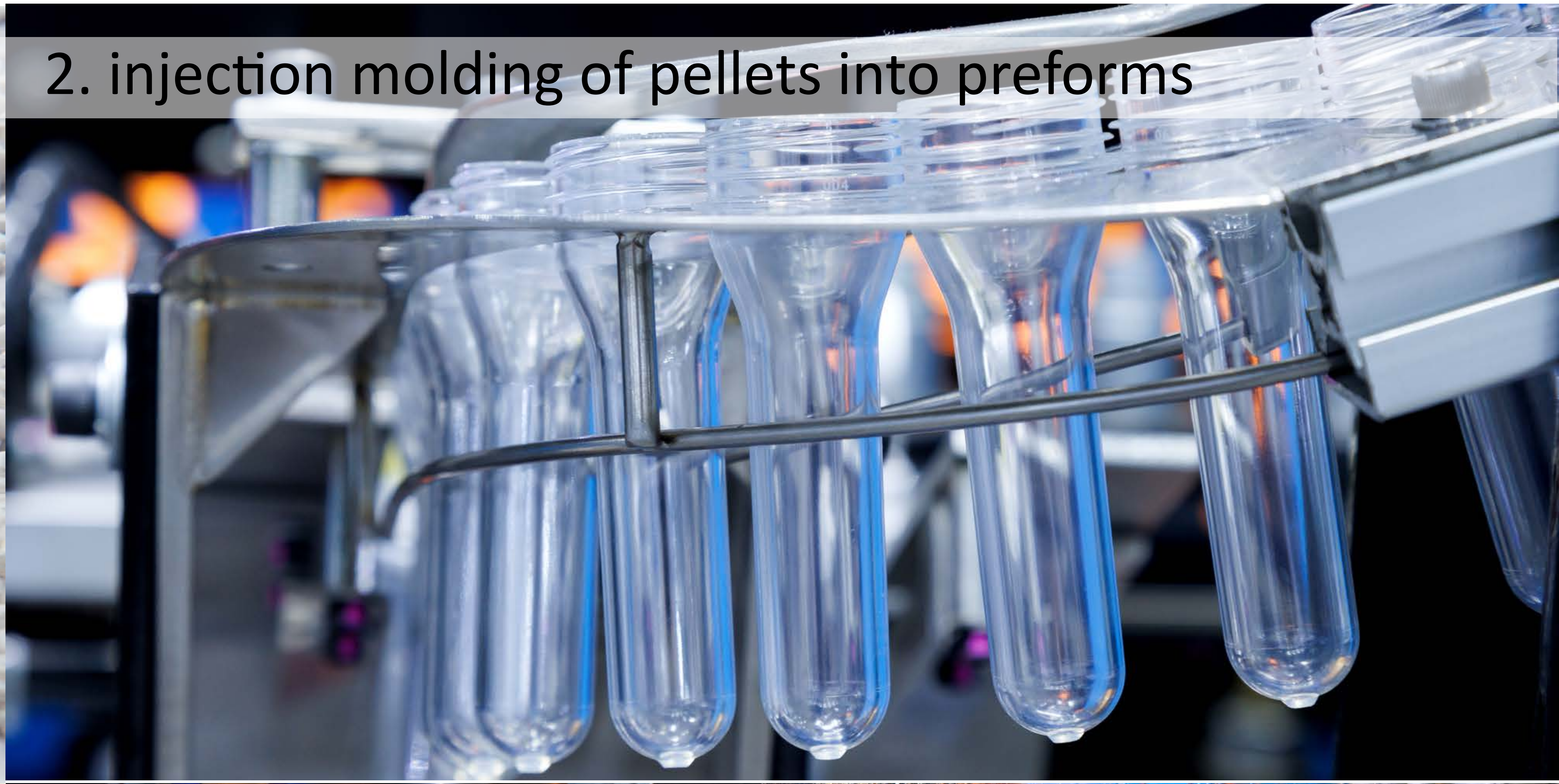




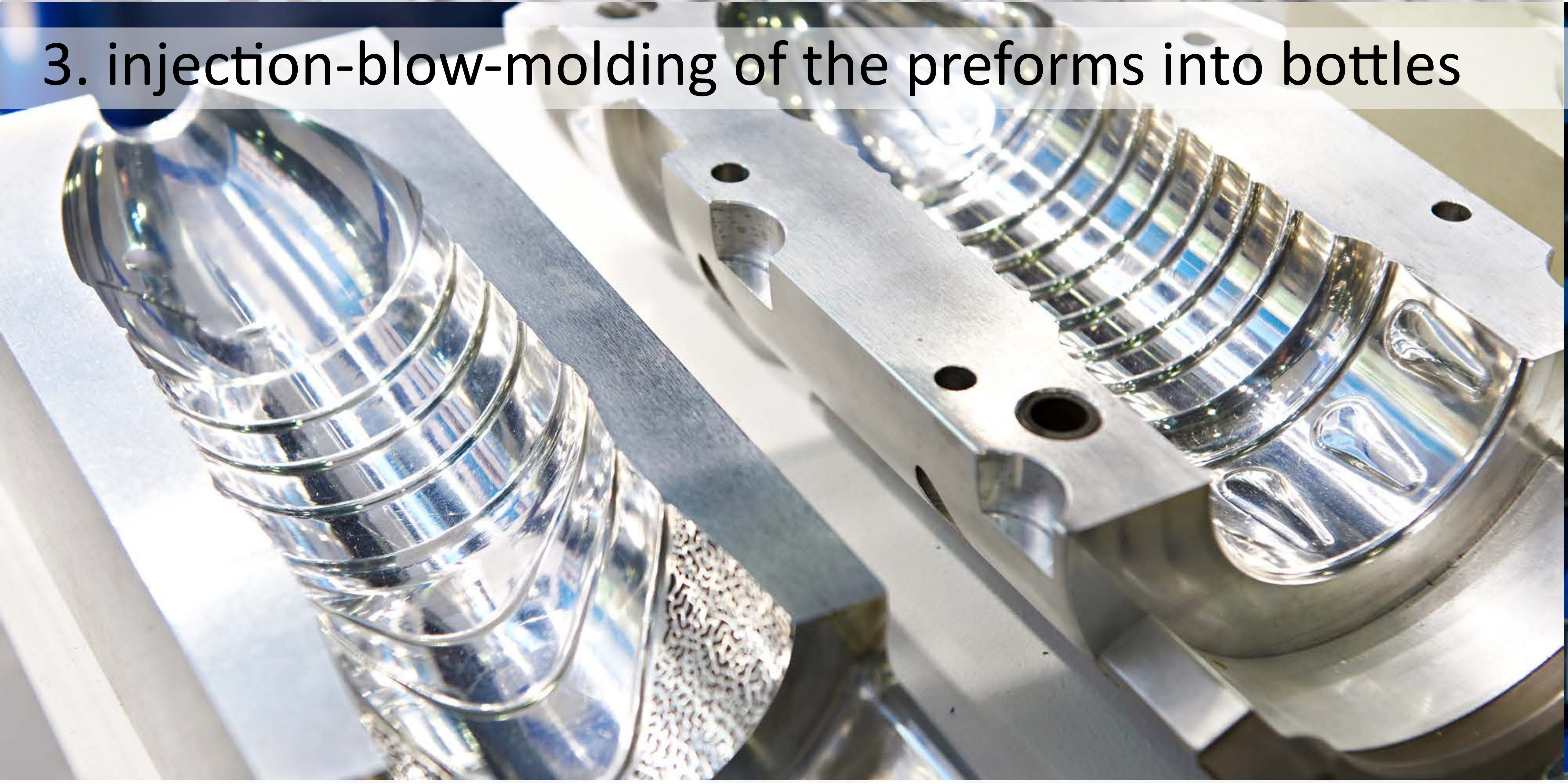
- **PET (T_g = 67–81 ˚C; T_m = 255–260 ˚C) is a semicrystalline, glassy thermoplastic polymer**
- **upon rapid cooling, PET forms an amorphous material that shows cold crystallization upon heating**
- **pronounced melt strain hardening during melt deformation from the amorphous state**

Manufacture of PET Bottles

1. synthesis of PET and extrusion into pellets



2. injection molding of pellets into preforms



3. injection-blow-molding of the preforms into bottles

4. final product

Further Applications of PET