Polymers:
How Long-Chain Molecules Work

FROM MOLECULES TO A BRIGHTER MATERIALS FUTURE

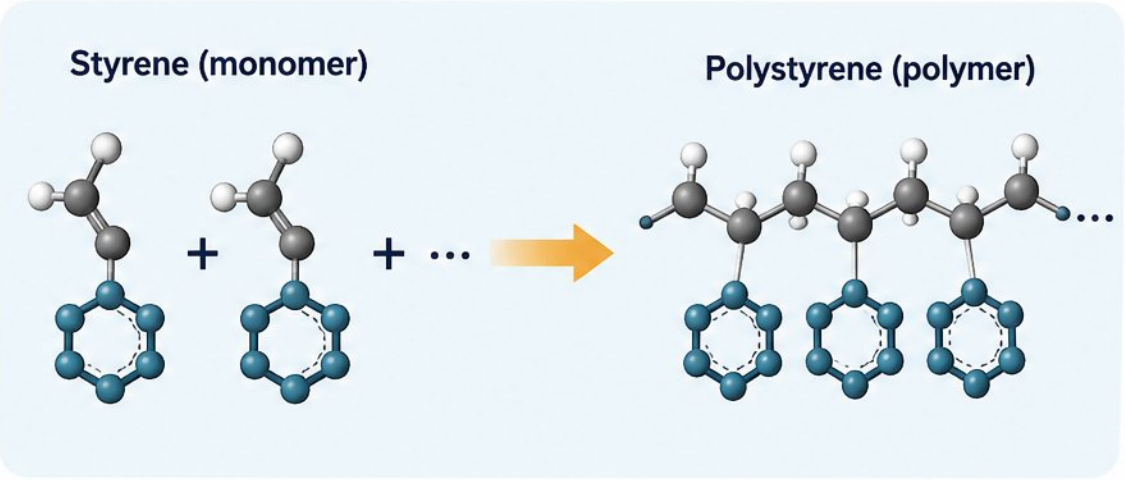


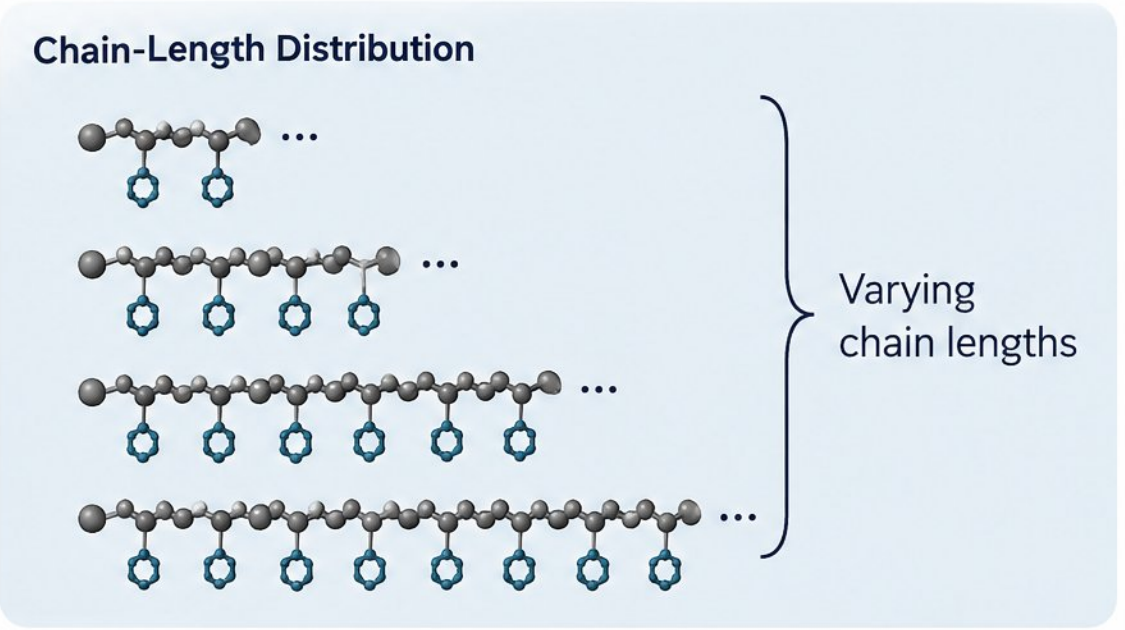
- Polymers are macromolecules built by linking many small repeating units called monomers
- IUPAC: a polymer is a substance of macromolecules with varying molar masses
- Chain chemistry, chain length, architecture, and intermolecular forces shape material properties
- Roadmap: monomer to macromolecule, architecture, thermal behavior, material classes, applications, demos, quick check
- Polymers are everywhere: packaging, textiles, tires, medical devices, composites, DNA, proteins



From Monomers to Macromolecules

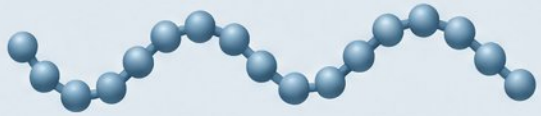
- **Macromolecule:** high molar mass, built from constitutional repeating units
- **Polymer:** a substance of macromolecules with varying molar masses
- **Chain polymerization**: monomers add to active sites (styrene → polystyrene)
- **Step polymerization**: reactions between molecules of all chain lengths
- **Dispersity ($Đ = M_w/M_n$)** describes the breadth of chain-length distribution





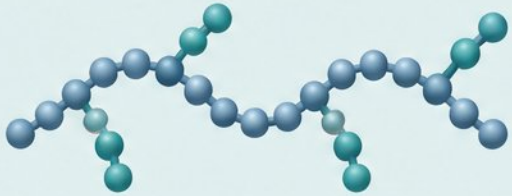
Chain Architecture: Linear, Branched, and Cross-Linked

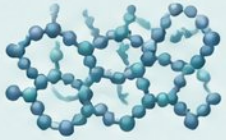
Linear Chains

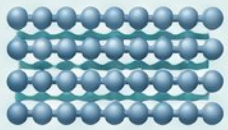


Resemble spaghetti

Branched Chains

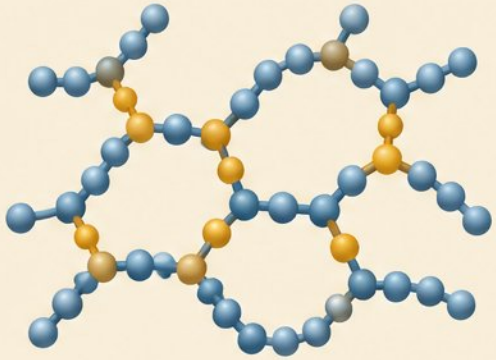






LDPE HDPE

Cross-Linked Chains

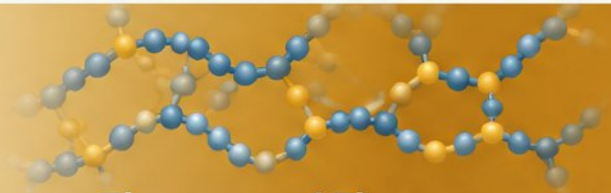


- **Linear chains** resemble spaghetti; weak forces let chains flow when heated—thermoplastic.
- **Branched chains** disrupt packing, lowering density and crystallinity: flexible LDPE vs. tough HDPE.
- **Covalent cross-links** tie backbones together, restricting movement—rigid networks or elastic rubbers.
- **Block copolymers** combine hard domains and soft segments, tuning properties like styrenic TPEs.
- **Entanglements and molar mass distribution** drive melt viscosity, toughness, and processing behavior.



Thermoplastic
Chains can flow

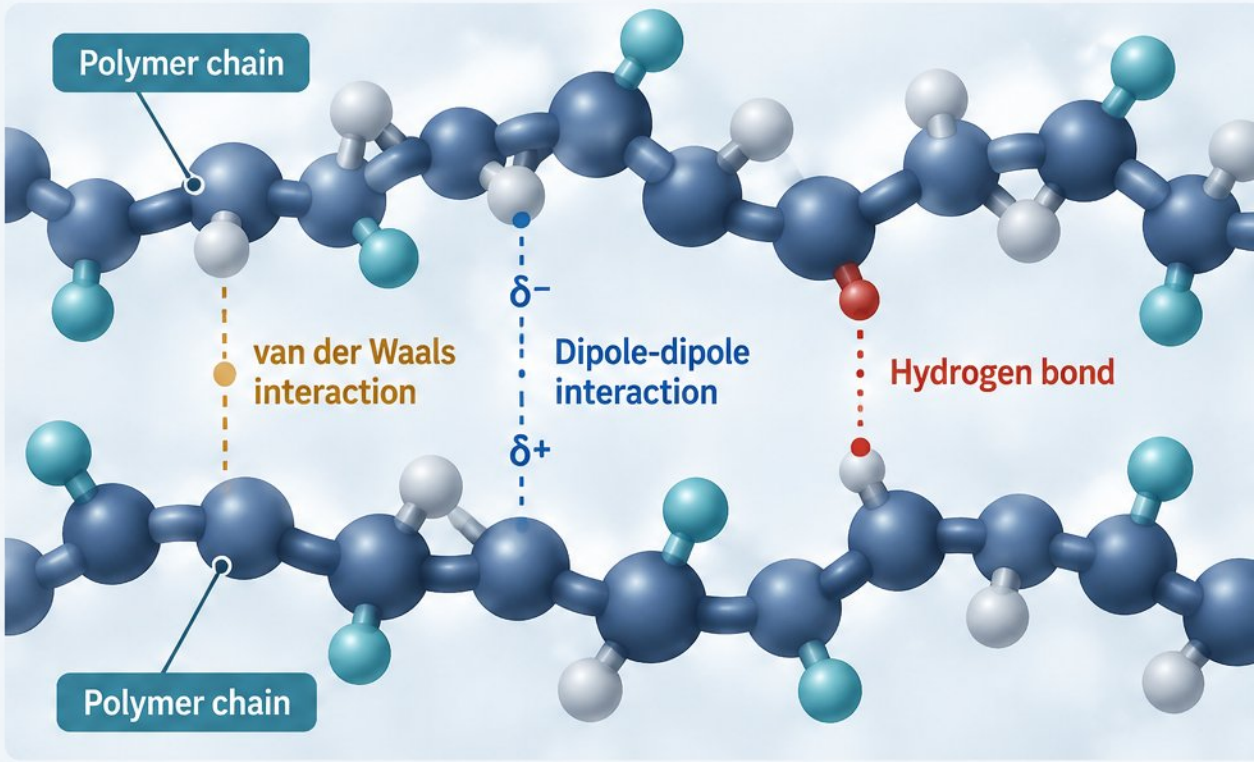
Increasing chain restrictions



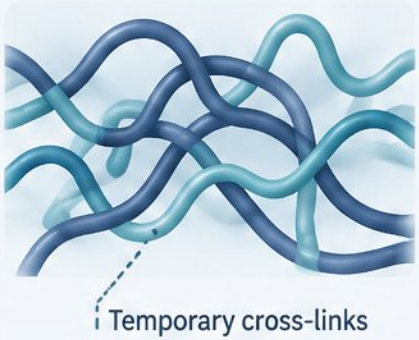
Thermoset / Elastomer
Restricted movement

Intermolecular Forces and Chain Behavior

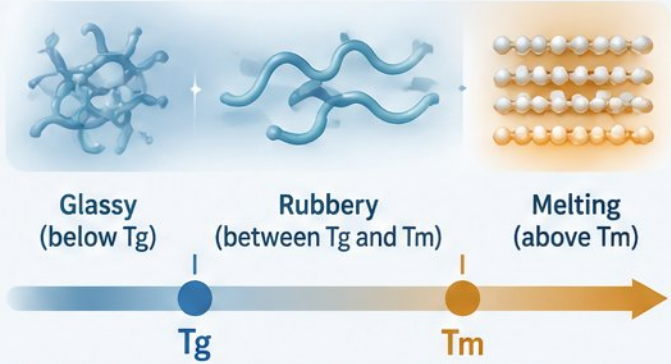
- Weak secondary forces—van der Waals, dipole-dipole, hydrogen bonds—control flexibility and toughness
- These forces are strongest where chains pack closely, as in HDPE
- Chain entanglements act as temporary cross-links, giving melts viscoelasticity
- Tg: glassy-to-rubbery transition; Tm: melting of crystalline regions
- Crystallinity boosts stiffness and barrier; bulky side groups hinder packing
- Short chains, flexible backbones, plasticizers lower Tg; side groups and cross-linking raise it



Chain entanglements



Thermal transitions



Thermoplastics, Thermosets, and Elastomers

DIFFERENT STRUCTURES. DISTINCT BEHAVIOR.

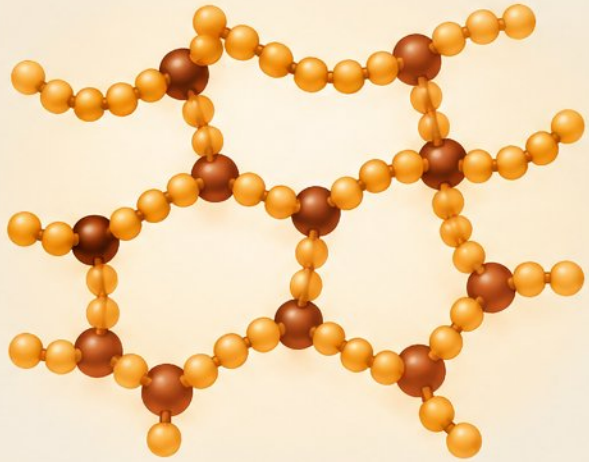
Thermoplastics

FREE CHAINS (MOBILE)



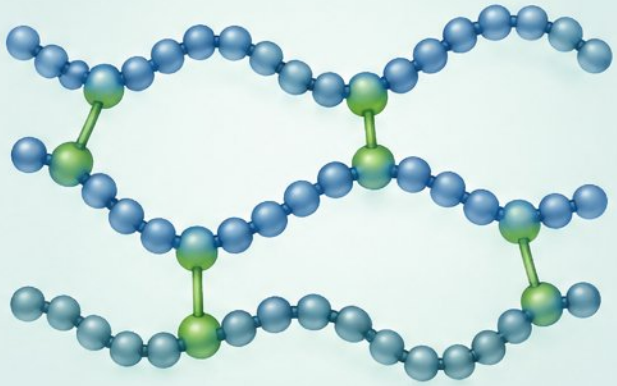
Thermosets

CROSS-LINKED NETWORKS (LOCKED)



Elastomers

LIGHTLY CROSS-LINKED (STRETCH & RECOVER)



- **Thermoplastics:** little or no cross-linking; chains slip in the melt and can be remolded repeatedly
- **Thermosets:** covalently cross-linked networks (epoxy, phenolic, cured silicone); cannot be remelted
- **Elastomers:** lightly cross-linked, low-Tg, amorphous networks that stretch and recover; vulcanization is classic
- **TPEs:** physical cross-links from hard/soft phase separation—rubber-like behavior, thermoplastic processing
- **Processing and recycling** follow chain freedom: molding suits thermoplastics; thermosets need solvolysis or fiber recovery

Structure-Property Relationships in Everyday Materials

Polyethylene

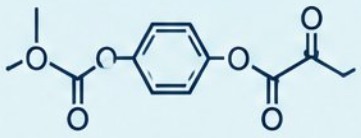




- **Polyethylene:** density and branching tune stiffness—LDPE films flex, HDPE bottles stay tough

PET

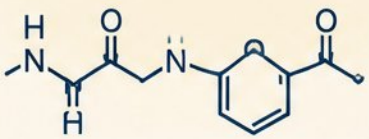




- **PET:** amorphous for clear bottles, drawn semicrystalline for strong fibers

Nylon and Kevlar

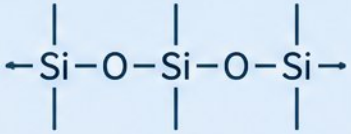




- **Nylon and Kevlar:** hydrogen bonding orders chains; aromatic backbones resist heat

Silicone

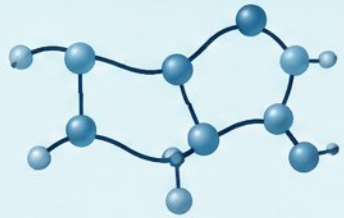




- **Silicone:** flexible siloxane backbone gives very low Tg and wide temperature range

Hydrogels





- Hydrogels: cross-link density and water affinity set swelling and softness

Matrix tool: map chain traits to material outcomes

Real-World Applications and Design Choices

From everyday products to next-generation materials



Packaging

- Packaging: barrier, sealability, recyclability; PHA/PLA blends enter flexible films



Textiles

- Textiles: polyester, nylon, elastane balance strength, stretch, moisture; bio-based fibers cut carbon



Medical

- Medical: resorbable PLA/PGA/PLGA sutures; TPE wearables; silicone thermosets where sterilization matters



Automotive and EVs

- Automotive and EVs: PVC, PC, PU foams, composites; bio-based polyamides in fuel lines



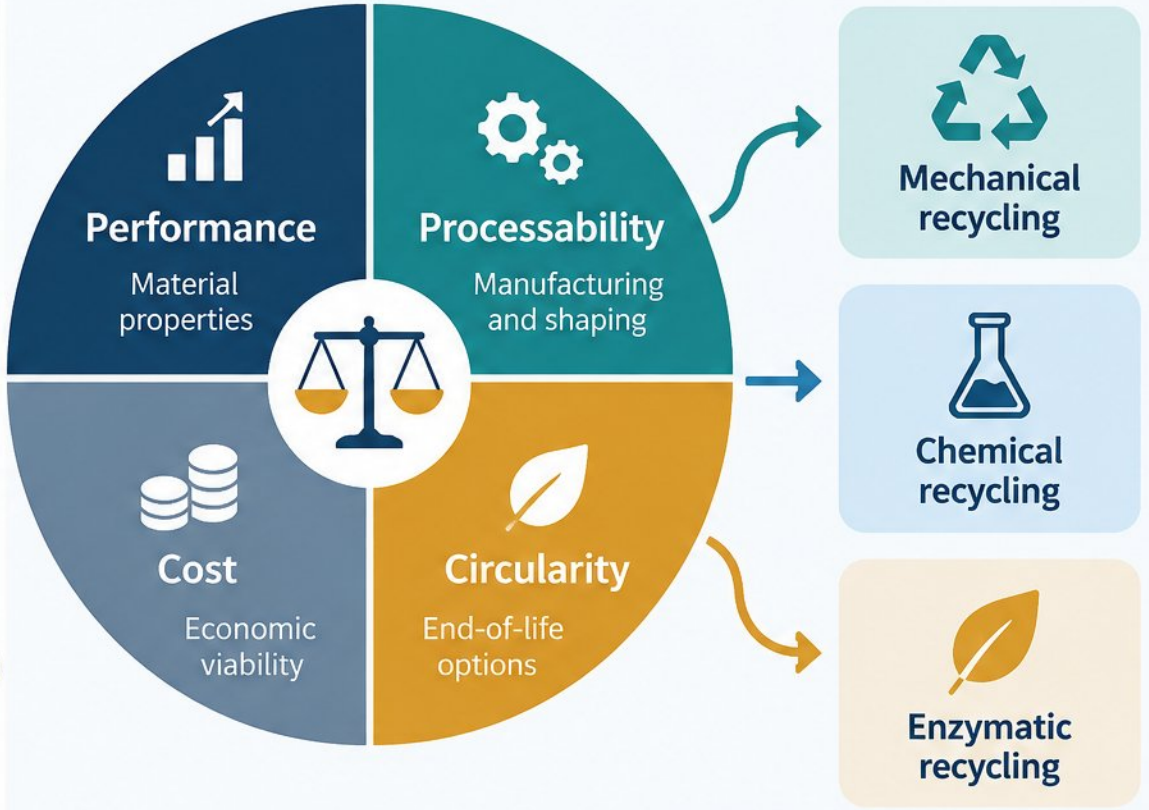
Emerging 2026

- Emerging 2026: bio-based nylon 6,6, design-for-degradation, enzymatic PET recycling, dynamic covalent thermosets

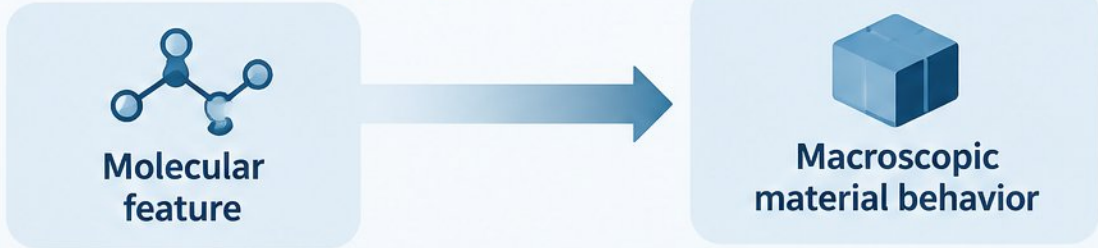
Design Trade-Offs: Performance, Process, Cost, and Circularity

- Every choice balances property, processability, cost, and end-of-life
- Cross-linking adds durability but blocks mechanical recycling; chemical routes break the 3D network
- Solvolysis, catalytic depolymerization, and pyrolysis handle mixed, soiled waste
- Enzymatic PET recycling: PETase/MHETase and FAST-PETase achieve **>90%** depolymerization in under **48** h at 50 °C
- Ester-containing polymers (PET, PLA, PHA) are more recyclable than C–C backbones (PE, PP, PS)
- Policy: extended producer responsibility, recycled-content targets, design for disassembly

Discussion: which material class and end-of-life strategy would your team choose, and why?



Structure to Property



Teaching and Learning Activities

- PVA + borax slime: borate ions cross-link chains into a viscoelastic gel
- Stretch a rubber band slowly vs. sharply to show chain alignment and recoil
- Vary borax (1, 2, 4, 6, 10 mL per 50 mL PVA) and compare bounce, stretch, pour rate
- Classify room objects as thermoplastic, thermoset, or elastomer; debate TPEs
- Read a property table (density, modulus, Tg, Tm) and predict end use





Safety, Materials, and Differentiation for Educators

Materials and Safety

Materials: 4% PVA, 4% sodium borate, cups, stir sticks, food coloring, gloves, safety glasses

Prepare PVA by gentle heating below 80 °C; never let it boil

Borax and PVA irritate eyes; wear goggles, wash hands, discard slime in trash



Adult learners

- Adult learners: link demos to recyclability and part durability; use product teardowns

Traditional students

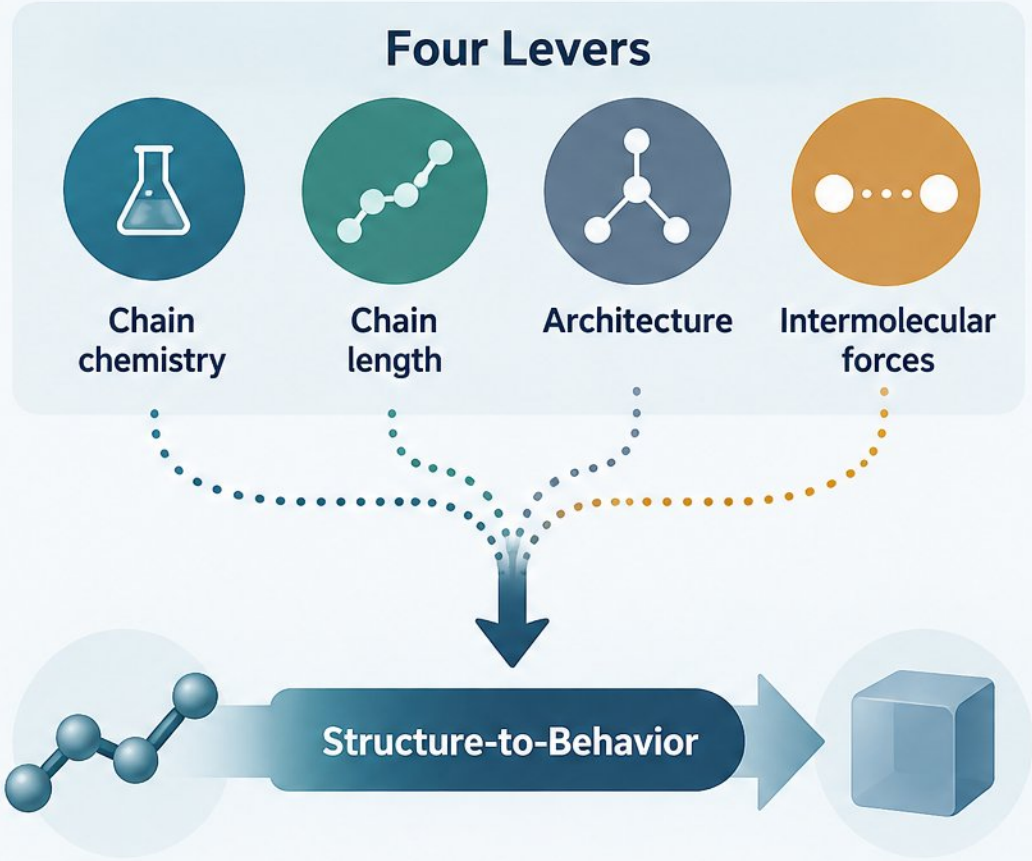
- Traditional students: emphasize prediction, observation, data recording, and vocabulary scaffolds

Misconceptions

- Misconceptions: molecular weight vs. density; cross-linked ≠ unbreakable; not all polymers are plastics

Key Takeaways and Quick Check

- Long chains create many interactions per molecule, amplifying structure effects
- Four levers: chain chemistry, chain length, architecture, intermolecular forces
- Chain freedom and cross-linking separate thermoplastics, thermosets, and elastomers
- Material choice is always a trade-off: property, process, cost, environment
- Quick check: predict flexible, rigid, or stretchy—and cite one structure-property link



Quick check: predict flexible, rigid, or stretchy—and cite one structure-property link

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