Unit 6: Polymers

Engineering Chemistry — DI01000071

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Polymer Definition · Polymerization · Thermoplastics & Thermosets
Elastomers · Conducting Polymers · Biodegradable Polymers

Unit 6 Overview: Polymers

Topics Covered

- Polymer definition & terminology
- Classification of polymers
- Addition polymerization
- Condensation polymerization
- Thermoplastics vs Thermosets
- Important thermoplastics
- Important thermosets (Bakelite, epoxy)
- Elastomers (natural & synthetic rubber)
- Conducting polymers
- Biodegradable polymers
- Fiber-reinforced composites

Exam Weightage

≈20% of paper
(Highest weightage unit)

Frequent PYQ topics:

- Nylon-66 synthesis
- Bakelite preparation (mechanism)
- Natural rubber vulcanization
- Buna-S / Neoprene structure
- Conducting polymers (PANI)
- Biodegradable polymers (PLA)

Polymer: Definition & Key Terms

Definitions

Polymer: Large molecule (macromolecule) formed by repetitive joining of small units

Monomer: Small repeating unit (e.g., ethene, vinyl chloride)

Degree of Polymerization (n): Number of repeat units in polymer chain

Repeat unit: Smallest structural unit that repeats

$M_n = n \times M_0$ (Mol. wt. of repeat unit)

Examples:

- Polyethylene: $n(-CH_2 - CH_2-)$ from ethene
- PVC: $n(-CH_2 - CHCl-)$ from vinyl chloride
- Nylon-66: from hexamethylene diamine + adipic acid

Functionality: Number of reactive sites per monomer

- Di-functional: linear polymer
- Tri-functional: cross-linked/branched

Classification of Polymers

Basis	Type	Examples
Source	Natural	Cellulose, starch, rubber, proteins
	Synthetic	PE, PVC, Nylon, Bakelite
Structure	Linear	HDPE, PVC, Nylon
	Branched	LDPE
	Cross-linked	Bakelite, vulcanized rubber
Thermal behavior	Thermoplastic	PE, PP, PVC, Nylon
	Thermoset	Bakelite, epoxy, polyester resin
Polymerization	Addition	PE, PVC, PTFE, polystyrene
	Condensation	Nylon, polyester, Bakelite
End use	Plastic, elastomer, fiber, coating	—

Addition Polymerization

Mechanism

Requires: Monomer with C=C double bond

Steps: (Chain growth)
1. **Initiation:** Free radical / ion attacks monomer
2. **Propagation:** Chain grows by successive addition
3. **Termination:** Radicals combine / disproportionate

No by-product formed
M_n can be very high (10^5–10^6)

Examples:

$n\mathrm{CH_2{=}CH_2} \xrightarrow{\Delta, P, \text{catalyst}} (-\mathrm{CH_2} - \mathrm{CH_2}-)_n$
Ethene → Polyethylene (PE)

$n\mathrm{CH_2{=}CHCl} \rightarrow (-\mathrm{CH_2} - \mathrm{CHCl}-)_n$
Vinyl chloride → PVC

$n\mathrm{CF_2{=}CF_2} \rightarrow (-\mathrm{CF_2} - \mathrm{CF_2}-)_n$
Tetrafluoroethylene → PTFE (Teflon)

Types: Free radical, cationic, anionic, coordination (Ziegler-Natta)

Condensation Polymerization

Mechanism

Requires: Bifunctional monomers (two reactive groups each)

Mechanism: (Step growth)
1. Two monomers react $\rightarrow$ dimer + by-product 2. Dimer reacts $\rightarrow$ tetramer + by-product 3. Continues until high MW polymer

By-products: H O, HCl, NH , CH OH
MW builds slowly

Example — Nylon-66:

$$nH_2N(CH_2)_6NH_2 + nHOOC(CH_2)_4COOH \xrightarrow{-n\,H_2O} (-NH(CH_2)_6NH\text{–}CO(CH_2)_4CO-)_n$$

Hexamethylene diamine + Adipic acid $\rightarrow$ Nylon-66 + H O

Other examples:

- Nylon-6 (caprolactam ring opening)
- Polyester (diol + diacid)
- Bakelite (phenol + formaldehyde)

Thermoplastics vs Thermosets

Property	Thermoplastic	Thermoset
Structure	Linear/branched	3D cross-linked network
On heating	Softens/melts	Decomposes (burns)
Recyclable	Yes	No
Molding	Repeated	Only once
Solubility	Usually soluble	Insoluble
Strength	Moderate	Very high
Examples	PE, PP, PVC, Nylon	Bakelite, epoxy, urea-formaldehyde
Uses	Bottles, pipes, films	Electrical parts, laminates, adhesives

Thermoset mechanism:
Monomers cure via cross-linking $\rightarrow$ rigid, infusible network formed permanently

Common Thermoplastics:
LDPE, HDPE, PP, PVC, PS, Nylon-6, Nylon-66, PTFE, ABS, PET

Important Thermoplastics

Name	Monomer	Structure	Properties & Uses
LDPE	Ethene	Branched	Soft, flexible; polythene bags, films
HDPE	Ethene	Linear	Hard, rigid; pipes, bottles, containers
PP	Propene	Linear/isotactic	High mp (160°C), fatigue resistant; ropes, carpets
PVC	Vinyl chloride	Linear	Rigid/flexible; pipes, cables, floor tiles
Polystyrene (PS)	Styrene	Linear/atactic	Brittle, transparent; packaging foam
PTFE (Teflon)	TFE	Linear	Very low friction, chemical resistant; non-stick, gaskets
ABS	Acrylonitrile+Butadiene+Styrene	—	Tough, impact resistant; helmets, appliances
PET	Ethylene glycol + TPA	Linear	Strong, transparent; PET bottles, polyester fibers

Polyethylene: LDPE vs HDPE

LDPE

Low Density Polyethylene
Process: High pressure (1000–3000 atm), 100–350°C, free radical

Structure: Highly branched (prevents close packing)
Density: 0.91–0.93 g/cm^3
Crystallinity: 50–60%

Properties: Soft, flexible, translucent
Uses: Cling film, carry bags, squeeze bottles, insulation

HDPE

High Density Polyethylene
Process: Low pressure (6–7 atm), Ziegler-Natta catalyst (TiCl + AlEt)

Structure: Linear (close packing possible)
Density: 0.94–0.97 g/cm^3
Crystallinity: 80–90%

Properties: Hard, rigid, translucent
Uses: Pipes, drums, bottles, chairs

Bakelite: Phenol-Formaldehyde Resin

Synthesis

Step 1: Phenol + HCHO (acid catalyst) → Novolac (linear, brittle)

Step 2: Novolac + more HCHO + hexamethylenetetramine → Bakelite

Mechanism:
Electrophilic substitution at ortho/para positions → methylene bridges form → 3D cross-linked network

Properties:

- Hard, brittle thermoset
- Excellent electrical insulator
- Heat resistant
- Chemical resistant
- Dark brown color

Uses:

- Electrical switches, plugs
- Radio cabinets (historical)
- Handles of pans & irons
- Laminates (Formica)
- Adhesives

Nylon-66: Synthesis & Properties

Synthesis of Nylon-66

Monomers:
Hexamethylenediamine: $H_2N(CH_2)_6NH_2$
Adipic acid: $HOOC(CH_2)_4COOH$

Reaction (Condensation):

$$n\,H_2N(CH_2)_6NH_2 + n\,HOOC(CH_2)_4COOH \xrightarrow{-nH_2O} [-NH(CH_2)_6NHCO(CH_2)_4CO-]_n$$

Properties:

- High tensile strength
- Abrasion resistant
- Good elasticity
- Low coefficient of friction
- Absorbs moisture

Uses:

- Textile fibers (stockings, fabrics)
- Ropes, bristles, brush fibers
- Gears, bearings (engineering)
- Parachute fabric

PVC & Teflon (PTFE)

PVC — Polyvinyl Chloride

$n\mathrm{CH_2{=}CHCl} \rightarrow (-\mathrm{CH_2} - \mathrm{CHCl}-)_n$

Unplasticized (UPVC): rigid, pipes, window frames
Plasticized (FPVC): flexible, cables, floor tiles, hoses

Properties: Flame retardant (Cl), cheap, corrosion resistant
Limitation: Releases HCl on burning (toxic)

PTFE — Teflon

$n\mathrm{CF_2{=}CF_2} \rightarrow (-\mathrm{CF_2} - \mathrm{CF_2}-)_n$

Properties:

- Lowest COF of any solid (0.04)
- Heat resistant (260°C)
- Chemically inert (all acids/bases)
- Non-stick

Uses: Non-stick cookware, lab gaskets, seals, wire insulation

Natural Rubber: Structure & Properties

Natural Rubber

Source: Latex from *Hevea brasiliensis*

Chemical name: cis-1,4-Polyisoprene
Monomer: Isoprene ($CH_2{=}C(CH_3){-}CH{=}CH_2$)

Structure: Long coiled chains; cis configuration gives elasticity

Repeat unit: $(-CH_2-C(CH_3){=}CH-CH_2-)_n$

Properties of Raw NR:

- Highly elastic
- Soft, tacky
- Poor tensile strength
- Affected by heat, cold, solvents
- Ages rapidly (oxidation/ozone)

Limitations requiring vulcanization:

- Becomes brittle in cold
- Sticky and soft in heat
- Dissolves in organic solvents

Vulcanization of Rubber

Vulcanization Process

Discovered by: Charles Goodyear (1839)

Process: Natural rubber + sulfur (3–5%) heated at 140–160°C

Mechanism: Sulfur forms cross-links (S–S bridges) between rubber chains at double bond positions

Rubber–S_x–Rubber cross-links

Hard rubber (ebonite): 30–50% sulfur

Effect of Vulcanization

Property	Improvement
Tensile strength	↑ greatly
Elasticity	Maintained
Hardness	↑
Chemical resistance	↑
Temp sensitivity	↓ (wider range)
Solvent resistance	↑

Synthetic Rubbers: Overview

Name	Monomers	Type	Properties & Uses
Buna-S (SBR)	Butadiene + Styrene (75:25)	Co-polymer	Good abrasion resistance; tyre treads
Buna-N (NBR)	Butadiene + Acrylonitrile	Co-polymer	Oil resistant; fuel hoses, gaskets
Neoprene (CR)	Chloroprene	Homopolymer	Weather, oil, flame resistant; industrial belts, wetsuits
Thiokol	Ethylene dichloride + Na polysulfide	Polysulfide	Oil/solvent resistant; rocket fuel binder, sealants
Butyl rubber (IIR)	Isobutylene + small isoprene	Co-polymer	Gas impermeable; inner tubes, stoppers
Silicone rubber	Dimethyldichlorosilane	Inorganic backbone	Wide temp range (-60 to 250°C); medical, aerospace

NR dominates in tires (natural grip); SBR most produced synthetic rubber worldwide

Buna-S (SBR): Styrene-Butadiene Rubber

Synthesis

Monomers: Butadiene (75%) + Styrene (25%)

Process: Emulsion co-polymerization

Reaction:

$$n\mathrm{CH_2{=}CH{-}CH{=}CH_2} + n\mathrm{CH_2{=}CH{-}C_6H_5} \xrightarrow{\text{emulsion}} (-\mathrm{CH_2} - \mathrm{CH{=}CH} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CHC_6H_5} -)_n$$

Properties:

- Better abrasion resistance than NR
- Good aging resistance
- Less elastic than NR
- Good heat resistance

Uses:

- Automobile tyre treads (most common use)
- Shoe soles, belts
- Floor tiles, hoses

Note: Must be vulcanized for use

Neoprene & Buna-N

Neoprene (Polychloroprene)

Monomer: Chloroprene (2-chlorobutadiene)

$n\mathrm{CH_2{=}CCl{-}CH{=}CH_2}$
$\rightarrow (-\mathrm{CH_2} - \mathrm{CCl{=}CH} - \mathrm{CH_2}-)_n$

Properties:

- Flame retardant (Cl atom)
- Oil & weather resistant
- Good tensile strength

Uses: Wetsuits, industrial belts, hoses, electrical cable jackets

Buna-N (NBR / Nitrile Rubber)

Monomers: Butadiene + Acrylonitrile (15–45% AN)

$(-\mathrm{CH_2} - \mathrm{CH{=}CH} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH(CN)}-)_n$

Properties:

- Excellent oil & fuel resistance (CN groups)
- Poor weather resistance
- Good abrasion resistance

Uses: Fuel hoses, gaskets, O-rings, oil seals, gloves

Conducting Polymers: Introduction

What Are Conducting Polymers?

Conventional polymers are insulators ($\sigma < 10^{-12}$ S/cm)

Conducting polymers: σ up to 10^5 S/cm after doping

Conditions for conductivity:

- Conjugated double bonds (alternating C=C)
- Doping (oxidation/reduction introduces charge carriers)

Discovery: Shirakawa, MacDiarmid, Heeger (Nobel Prize 2000 — Chemistry)

Important Conducting Polymers:

- Polyacetylene (PA) — first, highest conductivity
- Polyaniline (PANI) — most studied, easy synthesis
- Polypyrrole (PPy) — good stability
- Polythiophene (PT)
- Poly(para-phenylene)

Doping types:

- p-type: oxidation (remove electrons)
- n-type: reduction (add electrons)

Polyaniline (PANI): Most Studied Conducting Polymer

Synthesis of PANI

Monomer: Aniline (C H NH)

Method: Chemical or electrochemical oxidation in acidic medium (HCl or H SO)

Oxidizing agent: (NH) S O (ammonium persulfate)

Reaction:
$$nC_6H_5NH_2 \xrightarrow{\text{oxidation}} \text{PANI (emeraldine salt)}$$

Oxidation States:

- **Leucoemeraldine:** Fully reduced, white/colorless, insulating
- **Emeraldine base:** Half-oxidized, blue, insulating
- **Emeraldine salt:** Protonated, green, **conducting**
- **Pernigraniline:** Fully oxidized, violet, insulating

Uses: Anti-corrosion coatings, sensors, supercapacitors, EMI shielding, batteries

Biodegradable Polymers

Why Biodegradable?

Problem: Conventional plastics (PE, PP, PET) persist 100–500 years in environment

Solution: Polymers that degrade via microbial/enzymatic action

Degradation modes:

- Hydrolysis (ester, amide bonds)
- Microbial attack
- Photo-/thermo-oxidative degradation

Important Biodegradable Polymers:

- **PLA (Polylactic acid):** From corn starch; packaging, medical sutures
- **PGA (Polyglycolic acid):** Surgical sutures, dissolves in 2–4 weeks
- **PCL (Polycaprolactone):** Drug delivery, degrades in 2–4 years
- **PHB (Polyhydroxybutyrate):** Bacterial synthesis; packaging
- **Starch-based polymers:** Blends for bags/packaging

PLA: Polylactic Acid

Synthesis of PLA

Route 1: Direct condensation of lactic acid

$n\text{HO-CH(CH}_3\text{)-COOH} \rightarrow [-\text{O-CH(CH}_3\text{)-CO}-]_n + n\text{H}_2\text{O}$

Route 2: Ring-opening polymerization of lactide (cyclic dimer) — gives higher MW

Properties of PLA:

- Transparent, stiff
- Good tensile strength
- Degrades in industrial compost (6–12 months)
- Derived from renewable resources (corn, sugarcane)

Uses:

- Disposable packaging, cups, bags
- Medical: sutures, implants, drug delivery
- 3D printing filament (FDM)
- Agricultural films

Fiber-Reinforced Polymers (FRP) / Composites

What is FRP?

Composite = reinforcing fibers embedded in polymer matrix

Matrix (polymer): Epoxy, polyester, vinyl ester, nylon

Reinforcement:

- Glass fibers (GFRP) — most common
- Carbon fibers (CFRP) — high strength-to-weight
- Kevlar (aramid) — bullet-resistant
- Natural fibers (jute, sisal) — eco-friendly

Properties of FRP:

- High strength-to-weight ratio
- Corrosion resistant
- Design flexibility
- Good fatigue resistance

Applications:

- Aircraft fuselage, wings (CFRP)
- Boat hulls, storage tanks (GFRP)
- Wind turbine blades
- Sports equipment (bicycle frames, tennis rackets)
- Automotive body panels

Epoxy Resins

Synthesis

Most common: DGEBA (Diglycidyl ether of bisphenol A)

Bisphenol A + Epichlorohydrin $\xrightarrow{\text{NaOH}}$ Epoxy resin

Curing: Hardener (amine/anhydride) opens epoxide rings $\rightarrow$ 3D cross-linked thermoset

Mix ratio: Epoxy resin + curing agent (usually 2:1 or 1:1 by weight)

Properties:

- Excellent adhesion
- Chemical & moisture resistance
- Low shrinkage on curing
- Good electrical insulation
- High strength thermoset

Uses:

- Structural adhesives
- Circuit board laminates (FR4)
- Protective coatings/paints
- FRP matrix resin
- Encapsulation of electronics

Polymerization Methods: Comparison

Feature	Bulk	Solution	Emulsion
Medium	Monomer only	Monomer + solvent	Monomer + water + emulsifier
MW of product	High	Lower	Very high
Heat removal	Difficult	Easy (solvent)	Easy (water)
Purity	High	Solvent residue	Surfactant residue
Viscosity	Very high	Moderate	Low
Example	PMMA (cast acrylic), PVC	Solution SBR	SBR, NBR, PVC paste

Feature	Suspension	Notes
Medium	Monomer droplets in water + suspending agent	Bead polymer
MW	High	Good heat transfer
Product form	Beads	Easy separation
Example	Polystyrene beads, PVC suspension	

Glass Transition Temperature (T_g)

Definition

T_g**:** Temperature at which amorphous polymer transitions from glassy (rigid) to rubbery (flexible) state

Below T_g: Chains frozen, brittle, glassy
Above T_g: Chain mobility, rubbery, flexible

T_m**:** Melting point of crystalline region
Note: $T_g < T_m$ always

For rubber: $T_g <$ room temp (hence elastic)

Typical T_g values:

Polymer	T_g (°C)
Natural rubber	-73
Polybutadiene	-85
PVC (rigid)	$+87$
Polystyrene	$+100$
PMMA	$+105$
Polycarbonate	$+147$
Polyimide	$+300$
Nylon-66	$+57$
PET	$+67$

Polypropylene (PP) & Polystyrene (PS)

Polypropylene (PP)

$n\mathrm{CH_2{=}CHCH_3} \xrightarrow{\text{Z-N catalyst}} (-\mathrm{CH_2}-\mathrm{CHCH_3}-)_n$

Tacticity: Isotactic (commercial) — regular structure, crystalline

Properties: mp 160°C, strong, fatigue resistant (living hinge effect)

Uses: Food containers, bottle caps, ropes, carpets, car bumpers

Polystyrene (PS)

$n\mathrm{CH_2{=}CH{-}C_6H_5} \rightarrow (-\mathrm{CH_2}-\mathrm{CH(C_6H_5)}-)_n$

Types:

- GPPS: clear, brittle (CD cases)
- HIPS: impact-modified with rubber
- EPS (expanded): Thermocol — packaging foam

Properties: Rigid, transparent, brittle, cheap

Polyester & PET

Polyester (General)

Formation: Diol + Diacid $\xrightarrow{-H_2O}$ polyester

Linkage: –O–CO– (ester bond)

Alkyd resins: Polyester + oil (used in paints)

Unsaturated polyesters: Cross-linkable; used in FRP (GRP)

PET (Polyethylene Terephthalate)

Ethylene glycol + Terephthalic acid $\xrightarrow{-H_2O}$ $(-O-CH_2-CH_2-O-CO-C_6H_4-CO-)_n$

Properties: Transparent, strong, good barrier to O /CO

Uses:

- Water/soft drink bottles (most common)
- Polyester fibers (Dacron, Terylene)
- Magnetic tape base

Urea-Formaldehyde & Melamine Resins

Urea-Formaldehyde (UF)

Monomers: Urea + Formaldehyde (acid/base catalyst)

Product: Thermosetting resin, colorless/white

Properties:

- Harder than Bakelite
- Light-colored (can be made in any color)
- Good electrical insulation

Uses: Buttons, bottle caps, electrical fittings, plywood adhesive (UF glue)

Melamine Resin (MF)

Monomers: Melamine (C H N) + Formaldehyde

Properties:

- Very hard, scratch resistant
- Heat resistant (dishes, countertops)
- Good surface finish
- Self-extinguishing

Uses: Crockery (melamine dishes), Formica laminates, floor tiles, fire-retardant textiles

Mid-Point Summary: Unit 6

Covered So Far

- ✓ Polymer terminology & classification
- ✓ Addition polymerization (chain growth)
- ✓ Condensation polymerization (step growth)
- ✓ Thermoplastics vs Thermosets
- ✓ LDPE, HDPE, PP, PVC, PS, PTFE, PET
- ✓ Bakelite, epoxy, UF, melamine resins
- ✓ Natural rubber + vulcanization
- ✓ SBR, NBR, Neoprene (synthetic rubbers)

Still To Come

- Nylon-6 (caprolactam)
- Silicone polymers
- Applications comparison tables
- PYQ short & 7-mark questions
- Numericals / structural questions
- Exam tips & common errors
- Revision flash points
- Mind map & unit summary

Nylon-6 vs Nylon-66

Property	Nylon-6	Nylon-66
Monomer	Caprolactam (1 monomer)	Hexamethylene diamine + Adipic acid (2 monomers)
Polymerization	Ring-opening (caprolactam)	Condensation
Linkage	$-NH(CH_2)_5CO-$	$-NH(CH_2)_6NHCO(CH_2)_4CO-$
mp	220°C	265°C
Moisture absorption	Higher	Lower
Mechanical strength	Good	Slightly better
Processing	Easier	More difficult
Uses	Tire cords, fishing lines, bristles	Parachutes, gears, engineering parts
By-product	None	H O

Key fact: Both are polyamides (–CO–NH– linkage); named by carbon count in monomer(s)

Silicone Polymers (Polysiloxanes)

Structure & Synthesis

Backbone: Si–O–Si (siloxane) — inorganic; R groups on Si — organic

Monomer: Dimethyldichlorosilane $(CH_3)_2SiCl_2$

$(CH_3)_2SiCl_2 + H_2O \rightarrow (-Si(CH_3)_2-O-)_n + 2HCl$

Forms: Oils, greases, rubbers, resins

Unique Properties:

- Wide temperature range: -60°C to $+250$°C
- Water repellent (hydrophobic)
- Biocompatible and non-toxic
- Good electrical insulation
- Outstanding weathering resistance
- Low surface tension

Uses: Medical implants, sealants, gaskets, cosmetics, release coatings, aerospace seals

Polymer Additives

Additive	Function	Examples
Plasticizers	Increase flexibility (lower T_g)	DOP (di-octyl phthalate) in PVC
Stabilizers	Prevent degradation by heat/UV	Ca/Zn stearates, HALS
Antioxidants	Prevent oxidative degradation	Hindered phenols, phosphites
Fillers	Reduce cost, improve stiffness	CaCO , talc, silica, carbon black
Flame retardants	Reduce flammability	Brominated compounds, Al(OH)
Colorants	Pigments/dyes	TiO (white), carbon black
Lubricants	Easy mold release, better flow	Stearic acid, wax
Reinforcing agents	Improve mechanical properties	Glass fibers, carbon fibers, clay

Note: Modern polymer products always contain several additives — pure polymer is rarely used directly

Recycling of Polymers

Recycling Codes (Resin ID)

Code	Polymer	Common Use
1	PET	Water bottles
2	HDPE	Milk jugs, pipes
3	PVC	Pipes, cables
4	LDPE	Cling films, bags
5	PP	Containers, caps
6	PS	Foam cups, trays
7	Others	Polycarbonate, ABS

Types of Recycling:

- **Mechanical:** Melt and re-process (thermoplastics only)
- **Chemical:** Depolymerize back to monomers (PET $\rightarrow$ ethylene glycol + TPA)
- **Energy recovery:** Incineration with heat recovery
- **Biodegradation:** PLA composting

Thermosets cannot be mechanically recycled — only ground for filler or energy recovery

Rubber Compounding

What is Rubber Compounding?

Mixing of raw rubber with various ingredients before vulcanization

Ingredients added:

- **Vulcanizing agent:** Sulfur (2–5%)
- **Accelerator:** MBT, CBS (speeds vulcanization)
- **Activator:** ZnO + stearic acid
- **Antioxidant:** Phenyl-β-naphthylamine
- **Filler:** Carbon black (reinforces 3–4$\times$ strength)
- **Plasticizer:** PE wax (for processability)

Importance of Carbon Black:
Carbon black (15–35 phr) is the single most important rubber reinforcing filler:

- Increases tensile strength 3–4$\times$
- Improves abrasion resistance
- Used in ALL tire compounds

Hard rubber (Ebonite):

30–50% sulfur $\rightarrow$ fully crosslinked, rigid, used for bowling balls, battery cases

Copolymers & Polymer Blends

Copolymers

Polymer chain from **two or more** different monomers

Types:

- **Random:** –A-B-A-A-B-B-A– (SBR)
- **Alternating:** –A-B-A-B-A-B–
- **Block:** –AAAA-BBBB– (SBS thermoplastic elastomer)
- **Graft:** Main A chain with B branches (HIPS)

Properties tunable between two homopolymers

Polymer Blends

Physical mixture of $\geq$ 2 polymers (like alloys)

Miscible: Homogeneous (rare) — PS/PPO
Immiscible: Phase-separated (most)

Examples:

- ABS = acrylonitrile + butadiene + styrene blend/copolymer
- PC/ABS blend — dashboards
- Nylon/rubber blends — toughened nylon

Smart & Special-Purpose Polymers

Shape Memory Polymers (SMP):
Return to original shape on heating above T_g
Uses: Medical stents, deployable structures

Hydrogels:
Cross-linked hydrophilic networks that absorb large amounts of water
Uses: Contact lenses, drug delivery, wound dressings, superabsorbent diapers

Ion Exchange Resins:
Sulfonated PS (cation exchanger) or quaternary amine PS (anion exchanger)
Uses: Water softening, deionization, chromatography

Liquid Crystal Polymers (LCP):
Rigid-rod chains with ordered structure; high strength at low weight
Uses: Electronics connectors, aircraft parts

Piezoelectric Polymers:
PVDF — generates voltage on deformation
Uses: Pressure sensors, transducers

Photoresists:
UV-sensitive polymers used in semiconductor lithography (PMMA, novolac + diazonaphthoquinone)

Important Polymers: Properties Summary

Polymer	Type	Mono.	mp/Tg	Key Use
HDPE	TP, addition	Ethene	130°C	Pipes, drums
LDPE	TP, addition	Ethene	110°C	Bags, films
PVC	TP, addition	Vinyl Cl	87°C(Tg)	Pipes, cables
PP	TP, addition	Propene	160°C	Ropes, containers
PTFE	TP, addition	TFE	327°C	Non-stick, seals
Nylon-66	TP, cond.	HDA+AA	265°C	Fibers, gears
PET	TP, cond.	EG+TPA	260°C	Bottles, fibers
Bakelite	TS, cond.	P+HCHO	—	Electrical parts
Epoxy	TS, add.	BPA+ECH	—	Adhesives, FRP
NR (vulc.)	Elastomer	Isoprene	−73(Tg)	Tyres
SBR	Elastomer	Bu+Sty	−60(Tg)	Tyre treads

TP=thermoplastic, TS=thermoset, cond.=condensation, HDA=hexamethylene diamine, AA=adipic acid, EG=ethylene glycol, TPA=terephthalic acid, P=phenol, BPA=bisphenol A, ECH=epichlorohydrin

PYQ Pattern Analysis: Unit 6 Polymers

Frequently Asked Topics

Almost every year (7-mark):

- Nylon-66: monomers, reaction, structure, properties, uses
- Bakelite: preparation mechanism (novolac $\rightarrow$ resole $\rightarrow$ Bakelite), properties, uses
- Natural rubber: structure, limitations, vulcanization (process + effect), uses

Alternate years (7-mark):

- Buna-S: monomers, structure, properties, uses vs NR
- PLA or biodegradable polymers: need, synthesis, types, significance
- Conducting polymers: PANI — synthesis, doping, uses

Short questions frequently:
Classification of polymers, distinguish addition vs condensation, thermoplastic vs thermoset, T_g definition

Previous Year Questions: Short Answer (Unit 6)

2-mark Questions:

1. Define polymer. Give two examples of addition polymers.
2. Distinguish thermoplastic and thermoset with examples.
3. What are biodegradable polymers? Give two examples.
4. Define glass transition temperature (T_g).
5. What is vulcanization? State its effect on natural rubber.
6. What is degree of polymerization?
7. Distinguish addition and condensation polymerization.
8. What are conducting polymers?

3-mark Questions:

1. Describe the preparation and uses of Teflon (PTFE).
2. Explain the synthesis of PET.
3. What are fiber-reinforced composites? Give uses.
4. Explain the doping mechanism in PANI.
5. Compare Nylon-6 and Nylon-66.
6. What are elastomers? Give three examples.

Previous Year Questions: 7-Mark (Unit 6)

Descriptive Questions (7 marks each)

1. Explain the preparation, properties and uses of Nylon-66. Write the repeat unit structure.
2. Describe the formation of Bakelite from phenol and formaldehyde. Give its properties and uses.
3. Explain the structure of natural rubber. What are its limitations? How does vulcanization overcome them?
4. What is Buna-S? Write the monomers, polymerization reaction, and compare its properties with natural rubber.
5. What are conducting polymers? Explain polyaniline (PANI) with its synthesis, oxidation states and applications.
6. Classify polymers. Explain addition and condensation polymerization with suitable examples and distinguish between them.
7. Write a note on: (a) Biodegradable polymers (b) Fiber-reinforced composites.

Structural Questions: Write Repeat Units

Write repeat unit of:

1. Polyethylene (PE)
$(-CH_2 - CH_2-)_n$

2. PVC
$(-CH_2 - CHCl-)_n$

3. Polystyrene
$(-CH_2 - CH(C_6H_5)-)_n$

4. PTFE
$(-CF_2 - CF_2-)_n$

5. Natural rubber (cis-polyisoprene)
$(-CH_2 - C(CH_3)=CH - CH_2-)_n$

Write repeat unit of:

6. Nylon-66
$(-NH(CH_2)_6NHCO(CH_2)_4CO-)_n$

7. Neoprene
$(-CH_2 - CCl=CH - CH_2-)_n$

8. Buna-N (NBR)
$(-CH_2CH=CHCH_2 - CH_2CH(CN)-)_n$

9. PET
$(-O\text{-}CH_2CH_2\text{-}O\text{-}CO\text{-}C_6H_4\text{-}CO-)_n$

10. Silicone
$(-Si(CH_3)_2\text{-}O-)_n$

Numericals: Degree of Polymerization & MW

Solved Examples

Q1. Calculate MW of nylon-66 if degree of polymerization = 200.
Repeat unit: $-[NH(CH_2)_6NHCO(CH_2)_4CO]-$
$M_0 = 6(14) + 2(14) + 2(14) + 2(16 + 12) = 226$ g/mol
$M_n = 200 \times 226 = 45{,}200$ g/mol

Q2. MW of PVC sample = 125,000 g/mol. Find degree of polymerization.
M_0 of repeat unit $(-CH_2 - CHCl-) = 62.5$ g/mol
$$n = \frac{125000}{62.5} = 2000$$

Q3. How many monomer units in polyethylene of MW = 56,000 g/mol?
M_0 of $(-CH_2 - CH_2-) = 28$ g/mol; $\quad n = 56000/28 = \mathbf{2000}$

Common Exam Errors & Tips (Unit 6)

Common Mistakes

- Calling Nylon-66 an addition polymer (it is condensation — amide bond with H O loss)
- Drawing cis-isoprene as trans (must be cis for elastic properties)
- Saying all rubbers are natural (SBR/NBR/Neoprene are synthetic)
- Confusing Buna-S (75% butadiene) with Buna-N (butadiene + acrylonitrile)
- PTFE is addition polymerization (not condensation — no by-product)

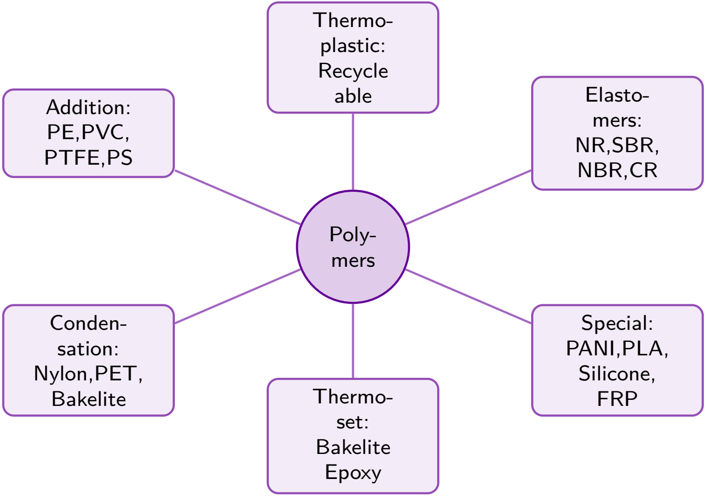
Exam Scoring Tips

- For Bakelite: always describe mechanism (electrophilic substitution) + draw cross-linked structure
- For vulcanization: state % sulfur, temp, duration, and draw S–S bridges
- For Nylon-66: always write both monomers + balanced equation
- Mention trade names where known (Teflon, Terylene, Neoprene)
- 7-mark answers: definition $\rightarrow$ synthesis/structure $\rightarrow$ properties $\rightarrow$ uses (5+ uses)

Revision Flash Points: Unit 6 Key Facts

Term / Polymer	Key Fact
Addition polymerization	No by-product; requires C=C in monomer
Condensation polymerization	By-product (H O, HCl, etc.); bi-functional monomers
LDPE vs HDPE	LDPE: branched, soft; HDPE: linear, rigid
Nylon-66 monomers	HDA (6C amine) + Adipic acid (6C diacid)
Nylon-66 linkage	Amide bond (–CO–NH–); by-product = H O
Bakelite	Phenol + HCHO; thermoset; 3D cross-linked
Natural rubber	cis-1,4-polyisoprene, from Hevea brasiliensis
Vulcanization agent	Sulfur (3–5%); 140–160°C; forms S–S bridges
Buna-S components	75% butadiene + 25% styrene
PANI conducting form	Emeraldine salt (protonated)
PLA degradation	Compostable in 6–12 months (industrial)
T_g of NR	-73°C (well below RT $\rightarrow$ elastic at room temp)
Nobel Prize 2000	Shirakawa, MacDiarmid, Heeger

Unit 6: Polymers — Mind Map



Polycarbonate (PC)

Synthesis

Monomers: Bisphenol A + Phosgene (COCl)

HO-C_6H_4-C$(CH_3)_2$-C_6H_4-OH + $COCl_2$ $\xrightarrow{-2HCl}$ $(-$O-BPA-O-CO$-)_n$

Alternative: Interfacial polycondensation or melt transesterification

Outstanding Properties:

- Optically transparent
- Impact strength $\sim$250$\times$ glass
- $T_g = 147$°C (high heat resistance)
- Dimensional stability
- Good electrical insulation

Uses:

- Bullet-proof glass (laminated)
- CDs, DVDs, Blu-ray discs
- Eyeglass lenses
- Helmets, shields
- Greenhouse panels

Polyacetylene: The First Conducting Polymer

Polyacetylene (PA)

Monomer: Acetylene (HC CH)

$n\text{HC}{\equiv}\text{CH} \xrightarrow{\text{Ziegler-Natta}} (-\text{CH}{=}\text{CH}-)_n$

Forms:
cis-PA (silvery, less stable)
trans-PA (golden, more stable)

Doping: I (p-type) or Na/K (n-type)
Conductivity: up to 10^5 S/cm (metallic!)

Band Theory Explanation:
Alternating single-double bonds $\rightarrow$ conjugated π system $\rightarrow$ overlapping p-orbitals $\rightarrow$ delocalized electrons

Undoped PA: semiconductor
Doped PA: conductor (removes/adds electrons from π band)

Limitations:

- Air-sensitive (oxidizes rapidly)
- Insoluble and infusible
- Difficult to process

Hence PANI preferred for practical use

Polymer Applications by Field

Field	Polymer	Application
Packaging	LDPE, PET, PP	Bags, bottles, wraps, trays
Construction	PVC, epoxy, FRP	Pipes, coatings, structural panels
Automotive	ABS, PP, Nylon, SBR	Dashboards, bumpers, tires
Medical	PTFE, silicone, PGA, PLA	Implants, sutures, drug delivery
Electronics	PC, epoxy, PTFE	Circuit boards, connectors, insulation
Textiles	Nylon-66, PET (Terylene)	Fabrics, ropes, sportswear
Aerospace	CFRP, Kevlar, PEEK	Fuselage, structural components
Agriculture	LDPE, PLA film	Mulch films, greenhouse covers
Consumer goods	PS, PP, ABS, PC	Appliances, toys, housewares

Natural Rubber vs Synthetic Rubber

Property	Natural Rubber	Synthetic (SBR)
Source	Hevea brasiliensis (botanical)	Petrochemical (butadiene+styrene)
Chemical name	cis-1,4-Polyisoprene	Styrene-Butadiene Rubber
Elasticity	Excellent	Good (less than NR)
Tensile strength (unfilled)	Very high	Lower
Abrasion resistance	Moderate	Better than NR
Heat resistance	Poor	Better
Oil resistance	Poor	Poor (NBR needed for oil)
Weather/ozone resistance	Poor	Moderate
Cost	Higher (variable)	Lower, consistent supply
Vulcanization	Required	Required
Main uses	Aircraft tyres, surgical gloves	Car tyre treads (70% market)

Polymer Degradation & Aging

Types of Degradation

Thermal: Chain scission/oxidation at high temp; poly(MMA) depolymerizes cleanly

Oxidative: O /ozone attacks double bonds in rubbers → cracking

Photo (UV): UV breaks C–C bonds; chalking/yellowing of PP, PVC

Hydrolytic: Water cleaves ester/amide bonds; affects PET, nylon

Biological: Microbes degrade bio-based polymers (PLA, PHB)

Mechanical: Fatigue, wear, stress cracking

Stabilization Strategies:

- UV stabilizers (HALS) — absorb/quench UV energy
- Antioxidants — interrupt radical chain oxidation
- Heat stabilizers (Ca/Zn) — prevent HCl elimination in PVC
- Ozone protectants — wax bloom on rubber surface
- Carbon black — UV screen in HDPE pipes

Service life prediction: Arrhenius model; accelerated aging tests at elevated temp

Other Conducting Polymers: PPy & PT

Polypyrrole (PPy)

Monomer: Pyrrole (5-membered N-heterocycle)

Synthesis: Electrochemical or chemical oxidation (FeCl)

Properties:

- $\sigma \approx$ 100–200 S/cm (doped)
- Good environmental stability
- Biocompatible

Uses: Sensors, actuators, corrosion protection, supercapacitors

Polythiophene (PT)

Monomer: Thiophene (5-membered S-heterocycle)

Important derivative: PEDOT (poly 3,4-ethylenedioxythiophene)

PEDOT:PSS:

- σ up to 1000 S/cm
- Transparent conducting film
- Solution processable

Uses: Organic solar cells (OPV), OLEDs, transparent electrodes, anti-static coatings

Polymer Nanocomposites:
Dispersing nanoscale fillers ($<$100 nm) in polymer matrix $\rightarrow$ dramatic property improvements at low loading (1–5%)

Common nanofillers:

- **Nanoclay:** montmorillonite (MMT) $\rightarrow$ barrier, flame retardancy
- **Carbon nanotubes (CNT):** conductivity, strength
- **Graphene:** barrier, conductivity, mechanical
- **Nano-SiO , nano-TiO :** UV protection, scratch resistance

Why Nano?

High surface area: Nano fillers have aspect ratio $>$100 $\rightarrow$ more interface with matrix

Key applications:

- Nylon-6/clay nanocomposite (Toyota, 1990s) — first commercial nanocomposite; engine parts
- CNT-polymer: EMI shielding, lightweight structural
- Graphene-PE: gas barrier packaging

Environmental Impact of Plastics

Problems

- **Persistence:** PE/PP last 400–500 years in soil
- **Microplastics:** Fragments <5 mm enter food chain; found in oceans, drinking water, human blood
- **Marine pollution:** 8 million tonnes plastic/year enter oceans
- **Toxic additives:** Phthalate plasticizers, BPA (endocrine disruptors) leach from PVC, PC
- **Incineration:** HCl from PVC, dioxins from Cl-plastics

Solutions:

- Biodegradable polymers (PLA, PHB)
- Mechanical recycling (PET, HDPE)
- Chemical recycling (pyrolysis, glycolysis)
- Extended producer responsibility (EPR)
- Single-use plastic bans (EU, India)
- Bio-based feedstocks (sugarcane PE, bio-PET)

India context: Ban on single-use plastics <75 micron effective July 2022

More PYQ Short Answer Practice (Unit 6)

Answer in 2–3 lines:

1. Why is LDPE softer than HDPE?
2. Why does natural rubber become brittle in cold and sticky in heat?
3. What is the role of sulfur in vulcanization?
4. Why is Bakelite called a thermosetting polymer?
5. What property makes PTFE non-stick?
6. Why are biodegradable polymers preferred for medical sutures?
7. Distinguish Neoprene and Buna-N based on oil resistance.
8. Why is cis-configuration important in natural rubber?

Model Answers:

1. LDPE has branched chains $\rightarrow$ less crystallinity $\rightarrow$ softer
2. $T_g < -70°C$ $\rightarrow$ chains mobile at RT; heat $\rightarrow$ chains too mobile, flow
3. Sulfur forms S–S crosslinks between chains, restricting slippage
4. Once set (cured), 3D network cannot melt — only decomposes
5. Extremely low surface energy C–F bonds adsorb nothing
6. PGA/PLA degrade inside body $\rightarrow$ no removal surgery needed
7. NBR (nitrile groups) oil-resistant; Neoprene weather/flame resistant but not oil

Additional Numericals (Unit 6)

Practice Problems

Q1. A sample of polystyrene has MW = 104,000 g/mol. Find degree of polymerization.
*(Repeat unit −CH −CH(C H)−: M_0 = 104 g/mol; n = 104,000/104 = **1000**)*

Q2. Nylon-66 has $n = 150$. Calculate MW of polymer.
*(M_0 = 226 g/mol; MW = 150 × 226 = **33,900 g/mol**)*

Q3. What mass of adipic acid is needed to produce 10 g of Nylon-66? (MW of Nylon-66 repeat unit = 226; MW of adipic acid = 146)
1 mol repeat unit requires 1 mol adipic acid
moles of RU = 10/226 = 0.0443 mol
*mass of adipic acid = 0.0443 × 146 = **6.47 g***

Q4. PET repeat unit MW = 192 g/mol. Find n for PET of MW = 96,000 g/mol.
*n = 96000/192 = **500***

Polymer Processing Methods

Process	Polymer Type	Products
Injection molding	Thermoplastics	Caps, toys, housings, car parts (high volume)
Extrusion	Thermoplastics	Pipes, sheets, films, profiles (continuous)
Blow molding	Thermoplastics	Hollow bottles (PET, HDPE, PP)
Compression molding	Thermosets	Bakelite parts, rubber gaskets
Reaction injection molding (RIM)	Thermosets (polyurethane)	Car bumpers, foam seats
Rotational molding	Thermoplastics	Large tanks, playground equipment
Fiber spinning	Nylon, PET, PP	Textile fibers, industrial yarns
Calendering	PVC	Sheet, floor tiles, artificial leather

Polyurethane & Acrylic Polymers

Polyurethane (PU)

Linkage: urethane (−NH−CO−O−)

Polyol + Diisocyanate → PU

Forms:

- Flexible foam (furniture, mattresses)
- Rigid foam (insulation panels)
- Elastomeric (spandex/Lycra fibers)
- Coatings, adhesives

Acrylic Polymers

PMMA (Perspex/Lucite):

nCH =C(CH)COOCH $\rightarrow$ PMMA

- Optically clear (better than glass)
- UV resistant, lightweight
- **Uses:** Acrylic glass, aquariums, signs, aircraft canopies

Polyacrylonitrile (PAN):

- Carbon fiber precursor
- Acrylic fibers (Orlon)

Bio-based & Future Polymers

Bio-based but not biodegradable:

- Bio-PE (from sugarcane ethanol $\rightarrow$ ethylene)
- Bio-PET (30% bio-based MEG from sugarcane)
- Bio-based drop-in replacements — same properties, renewable source

PHB/PHBV (PHA family):
Produced by bacteria (Cupriavidus necator)
Truly biodegradable in soil/marine environments

High cost $\rightarrow$ limited commercial use currently

Emerging Technologies

- **Covalent adaptable networks (CANs):** Thermosets that can be reprocessed (vitrimer)
- **Self-healing polymers:** Repair cracks autonomously (Diels-Alder reversible bonds)
- **4D printing:** Shape memory polymer + 3D printing
- **Protein-based polymers:** Spider silk, elastin mimetics — extremely high toughness

Unit 6: Key Properties & Values for Exam

Fact	**Value / Detail**
Nylon-66 mp	265°C
NR vulcanization	Sulfur 3–5%, 140–160°C, S–S bridges
Buna-S ratio	75% butadiene : 25% styrene
PTFE coefficient of friction	0.04 (lowest of any solid)
PLA degradation time	6–12 months (industrial composting)
PC impact strength	$\sim$250$\times$ ordinary glass
Nobel Prize (conducting polymers)	2000 — Shirakawa, MacDiarmid, Heeger
PANI conducting form	Emeraldine salt (green, protonated)
Carbon black in rubber	Increases tensile strength 3–4$\times$
Degree of polymerization	$n = M_n/M_0$
Thermoset recycling	Not possible (only comminuted for filler)
Bakelite color	Dark brown/black (phenol condensation products)
Nylon type linkage	Amide ($-$CO$-$NH$-$)
PET bottle recycling code	1 (PETE)

Unit 6: Summary & Bridge to Unit 7

Unit 6 Covered

- ✓ Polymer terminology & classification
- ✓ Addition & condensation polymerization
- ✓ Thermoplastics: PE, PP, PVC, PTFE, PS, PC, PET
- ✓ Thermosets: Bakelite, epoxy, UF, melamine
- ✓ Elastomers: NR, vulcanization, SBR, NBR, Neoprene
- ✓ Conducting polymers: Polyacetylene, PANI, PPy
- ✓ Biodegradable: PLA, PGA, PHB

Next: Unit 7 — Water

Topics Ahead:

- Water quality parameters (DO, BOD, COD)
- Hardness of water: types & units
- Softening methods (lime-soda, zeolite, ion exchange)
- Reverse osmosis & membrane processes
- Boiler feed water treatment
- Desalination
- Sewage/wastewater treatment
- Drinking water treatment