0 · Revision Blueprint READ FIRST

★ This unit has **two halves that share one mindset**: make the molecule (synthesis + polymers) and prove what you made (spectroscopy) — both judged against the **green-chemistry** yardstick of doing it with the least waste, energy and hazard.

Side 1 = analysis & sustainability metrics. Side 2 = reactions & polymers. The exam reflex you need: read a structure, predict its spectra; read spectra, deduce the structure; and for any route, judge its *atom economy*.

Most-tested skills: calculate atom economy / E-factor; assign an IR + MS + NMR set to one structure; pick S_N1 vs S_N2; classify a polymerisation; name a greener alternative (solvent, catalyst, feedstock).

SIA → *Two-line discipline: always state degrees of unsaturation first in any structure problem, and always quote the metric (a number) when asked "is this green?" — markers reward the calculation, not the adjective.*

1 · Green Chemistry · 12 Principles ANASTAS & WARNER 1998

The design framework for the whole unit. Memorise the mnemonic **"PRODUCTIVELY"** idea — but really know the high-yield five (★).

1. ★ **Prevent waste** — better than treating/cleaning it up
2. ★ **Atom economy** — maximise atoms of reactant in product
3. Less hazardous synthesis (low toxicity to people/environment)
4. Design safer chemicals (function with minimal toxicity)
5. ★ **Safer solvents/auxiliaries** — avoid where possible
6. Design for energy efficiency — ambient T & P
7. **Renewable feedstocks** not depleting ones
8. Reduce derivatives (protecting groups add waste steps)
9. ★ **Catalysis** > stoichiometric reagents
10. ★ **Design for degradation** — break down after use, no persistence
11. Real-time analysis to prevent pollution
12. Inherently safer chemistry (accident prevention)

Prevention > remediation is the spine: principles 1, 2, 9 do most of the exam work.

1b · Worked · Atom Economy TWO ROUTES

Target = ethanol (C_2H_6O, M_r 46):

Hydration $CH_2{=}CH_2 + H_2O \rightarrow C_2H_5OH$
AE = 46/(28+18) = 100% (addition, no by-product).

Fermentation $C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$
AE = (2·46)/180 = 51% — CO_2 is lost mass, *but* the feedstock is renewable.

⇒ greenness trades AE vs feedstock vs energy. **Quote all three**, don't crown a winner on AE alone.

2 · Sustainability Metrics CALCULATE THESE

Yield tells you nothing about waste. A 100% yield reaction can still be wasteful if half the reactant mass ends up as by-product. That's why we measure *atoms* and *mass*.

ATOM ECONOMY *TROST 1991*

% ATOM ECONOMY

$$AE = \frac{M_r\ \text{desired product}}{\Sigma\ M_r\ \text{all products}} \times 100 = \frac{M_r\ \text{product}}{\Sigma\ M_r\ \text{reactants}} \times 100$$

Theoretical (uses the balanced equation, ignores yield). Addition & rearrangement → 100% AE; substitution & especially **elimination/condensation** lose atoms.

E-FACTOR *SHELDON*

ENVIRONMENTAL FACTOR

E = mass of waste / mass of product
ideal E = 0 (zero waste)

INDUSTRY	TONNAGE	E-FACTOR
Bulk chems	10^4–10^6	<1–5
Fine chems	10^2–10^4	5–50
Pharma	10–10^3	**25–>100**

Smaller-tonnage, higher-value products are the *dirtiest* per kg — pharma is the big target.

PROCESS MASS INTENSITY

PMI & RME

PMI = total mass in / mass product (PMI = E + 1)
RME = mass product / Σ mass reactants × 100

PMI includes **solvent & water** — usually the largest mass in a process, which AE ignores.

3 · Feedstocks RENEW VS DEPLETE

Non-renewable: crude oil, natural gas, coal → cracked to platform chemicals (ethene, propene, BTX = benzene/toluene/xylene). Finite, CO_2-emitting.

Renewable: **biomass** — sugars, cellulose/lignocellulose, plant oils, terpenes. Bio-platform molecules: *ethanol, lactic acid, succinic acid, HMF, glycerol* (biodiesel by-product).

Tension: 1st-gen (food crops) vs 2nd-gen (waste lignocellulose) — the latter avoids the food-vs-fuel problem. Renewable ≠ automatically green (land, energy, processing all count).

3b · CO_2 & C1 Feedstocks WASTE → RESOURCE

Use abundant one-carbon sources as raw material: **CO_2** → urea, cyclic carbonates, salicylic acid, and (with H_2) methanol; **syngas** ($CO + H_2$) → methanol, Fischer–Tropsch hydrocarbons.

Drop-in bio-chemicals = chemically identical to the fossil version (bio-ethene) ⇒ slot straight into existing plants. **Novel** bio-chemicals = new structures (lactic acid → PLA).

4 · Catalysis · Fundamentals PRINCIPLE 9

A catalyst lowers E_a by providing an alternative pathway, is regenerated, and is **not consumed**. It speeds *both* directions equally — so it does **not** shift the equilibrium position or change ΔG/K; it only changes the *rate*.

Why it's green: replaces stoichiometric reagents (less waste), enables milder conditions (less energy), and improves *selectivity*.

SELECTIVITY — 4 TYPES

- **Chemo**selective — one functional group over another
- **Regio**selective — one position/orientation
- **Stereo**selective — one diastereomer
- **Enantio**selective — one enantiomer (asymmetric catalysis)

HOMOGENEOUS VS HETEROGENEOUS

	HOMO	HETERO
Phase	same as reactants	different (usually solid)
Selectivity	**high, tunable**	lower
Separation	hard (energy cost)	**easy, recyclable**
Example	Wilkinson's, Pd	Ziegler–Natta, zeolites

ACTIVITY METRICS

TURNOVER

TON = mol product / mol catalyst
TOF = TON / time = catalyst productivity rate

High TON ⇒ a little catalyst does a lot ⇒ greener.

5 · Catalysis · Types KNOW EXAMPLES

- **Acid/base** — protonation/deprotonation steps
- **Organometallic** — Pd/Rh/Ru; oxidative addition → migratory insertion → reductive elimination cycle
- **Biocatalysis** — enzymes; water, mild T/pH, exquisite enantioselectivity
- **Organocatalysis** — small organic molecules, metal-free (*List & MacMillan, Nobel 2021*)
- **Photoredox** — light drives single-electron steps

Asymmetric hydrogenation (chiral metal complex) and enzyme catalysis are the classic "how to make one enantiomer cleanly" answers.

5b · Worked · TON / TOF HOW GREEN

0.001 mol catalyst makes 0.8 mol product in 2 h:

TON = 0.8 / 0.001 = 800
TOF = 800 / 2 = 400 h^{-1}

Industrial/enzyme catalysts reach TON 10^6–10^9. Real TON is capped by **deactivation** (poisoning, leaching, sintering) — recyclability is the green prize.

6 · Structure Elucidation THE WORKFLOW

Combine the techniques — each answers a different question:

- **MS** → molecular formula & mass (what's the size?)
- **IR** → functional groups (what's attached?)
- **¹H/¹³C NMR** → carbon–hydrogen skeleton (how connected?)

STEP 1 ALWAYS: DBE

DEGREES OF UNSATURATION (IHD/DBE)

DBE = (2C + 2 + N − H − X) / 2
(O is ignored. Ring or π–bond = 1 each.

DBE ≥ 4 ⇒ suspect a benzene ring (3 C=C + 1 ring). C=O = 1, C≡N = 2, C≡C = 2.

SIA → *DBE first, every time — it tells you how many rings/multiple bonds to "spend" before you draw a single line.*

7 · IR Spectroscopy CM⁻¹

Bond stretching frequency ∝ $\sqrt{(k/\mu)}$: **stronger bond & lighter atoms ⇒ higher cm^{-1}**. Read the diagnostic 4000–1500 region; 1500–500 is the "fingerprint".

BOND / GROUP	CM^{-1}	NOTE
O–H alcohol	3200–3550	broad
O–H carb. acid	2500–3300	**v. broad**
N–H amine/amide	3300–3500	1–2 bands
C–H sp^3 / sp^2	<3000 / >3000	key split
≡C–H alkyne	~3300	sharp
C≡N / C≡C	2210–2260	weak/sharp
C=O	**1670–1750**	strong ★
C=C alkene	1620–1680	weak
aromatic C=C	1450–1600	
C–O	1000–1300	strong

C=O fine print: amide ~1650 < acid ~1710 ≈ ketone 1715 < aldehyde 1725 < ester 1735 < acyl chloride 1800. Conjugation lowers C=O by ~30.

7b · Reading an IR Spectrum 3 QUESTIONS

1. **C=O?** strong, sharp 1650–1750 ⇒ carbonyl present
2. **Broad O–H / N–H?** 2500–3550 ⇒ acid/alcohol/amine
3. **C–H above or below 3000?** ⇒ sp^2/aromatic vs sp^3

Tell-tales: aldehyde = C=O + twin C–H (Fermi) ~2720/2820; nitrile = sharp 2250; anhydride = *two* C=O bands.

7c · Distinguish by IR ISOMER TRAP

GROUP	O–H/N–H	C=O
Carb. acid	broad 2500–3300	~1710
Ester	none	1735 + strong C–O
Ketone	none	~1715 only
Amide	N–H ~3300	~1650
Alcohol	broad ~3300	none

8 · Mass Spectrometry M/Z

$M^{+\bullet}$ molecular ion = relative molecular mass. Then bonds fragment to give a pattern of cations.

DIAGNOSTIC RULES

- **Nitrogen rule**: odd M^+ ⇒ odd number of N atoms
- **M+1** ≈ 1.1% × (number of C) — counts carbons
- **Cl**: M:M+2 ≈ 3 : 1
- **Br**: M:M+2 ≈ 1 : 1

COMMON NEUTRAL LOSSES

ΔM	LOST	IMPLIES
15	·CH_3	methyl
18	H_2O	alcohol
28	CO / C_2H_4	carbonyl
29	CHO / C_2H_5	aldehyde
31	·OCH_3	methyl ester
45	COOH	carb. acid

Key fragments: m/z 43 = CH_3CO^+ (acylium), 91 = tropylium (benzylic), 77 = phenyl. **α-cleavage** & **McLafferty** (γ-H transfer, loses an alkene from carbonyls) are the named fragmentations.

9 · ¹H NMR Δ / PPM

Three readings: **shift δ** (environment), **integration** (relative # H), **multiplicity** (neighbours).

SPLITTING

n equivalent neighbours ⇒ **n + 1** peaks
J (coupling constant, Hz) shared by coupled partners

PROTON	Δ PPM
TMS (ref)	0
R–CH_3 / CH_2 / CH	0.8–1.7
C–H α to C=O	2.0–2.6
C–H next to N	2.2–2.9
C–H next to O / X	3.3–4.5
alkene =C–H	4.5–6.5
aromatic Ar–H	6.5–8.0
aldehyde CHO	**9.5–10**
carb. acid COOH	10–12

OH/NH = broad, variable, exchange with D_2O (peak vanishes ⇒ confirms OH/NH).

9b · Coupling Patterns RECOGNISE INSTANTLY

GROUP	PATTERN
–CH_2CH_3 (ethyl)	triplet 3H + quartet 2H
$(CH_3)_2CH$– (iPr)	doublet 6H + septet 1H
–OCH_3 / isolated CH_3	singlet (no neighbours)
para-disubst. ring	2 doublets (AA'BB')

Equivalent H (by symmetry) = one signal & don't split each other. **n+1** counts H on *adjacent* carbons only.

10 · ¹³C NMR + DEPT Δ / PPM

Counts unique carbons (no integration; ¹H-decoupled = singlets). Wide 0–220 ppm range.

CARBON	Δ PPM
alkyl C	0–50
C–N	30–60
C–O	50–90
alkyne C	65–90
alkene / aromatic	100–150
C=O acid/ester/amide	160–185
C=O ketone/aldehyde	**190–220**

DEPT

Edits by # attached H: **CH** & **CH_3 up**, **CH_2 down**, quaternary C absent (the give-away for C=O & substituted aromatic).

COUNTING SIGNALS = SYMMETRY

of signals = # of *chemically distinct* environments. Benzene = 1 ^{13}C; *para*-disubstituted ring = 4 (two pairs equivalent). Fewer signals than carbons ⇒ symmetry — a fast structural clue.

11 · Worked · C_4H_8O PUT IT TOGETHER

MS M^+ = 72. **DBE** = (2·4+2−8)/2 = **1** ⇒ one C=O or C=C/ring.

IR 1715 cm^{-1} strong ⇒ ketone C=O (no broad O–H, no ~2720 aldehyde C–H, no 1735 ester).

¹H NMR triplet 1.0 (3H), quartet 2.4 (2H), singlet 2.1 (3H) ⇒ ethyl + isolated methyl on C=O.

⇒ **butan-2-one**, $CH_3COCH_2CH_3$. MS loss of 15 (→57) and 29 (→43, CH_3CO^+) confirm α-cleavage either side of C=O.

SIA → *Reconcile every piece of data to one structure — if a single peak doesn't fit, the structure is wrong. Examiners build the trap on the one ignored signal.*

11b · Worked · C_8H_8O SPOT THE RING

DBE = (2·8+2−8)/2 = **5** ⇒ benzene ring (4) + one more (a C=O).

IR 1685 (conjugated C=O). **¹H**: 5H multiplet 7.4–8.0 (mono-substituted ring) + singlet 2.6 (3H, CH_3CO).

⇒ acetophenone, $C_6H_5COCH_3$. ^{13}C ~198 (C=O); m/z 105 ($PhCO^+$) & 77 ($C_6H_5^+$) confirm.

Which Technique? RECAP

QUESTION	USE
Mass / formula	MS (M+1, isotopes)
Functional groups?	IR (C=O, O–H, N–H)
# unique C; C type	^{13}C + DEPT
H count & connectivity	¹H (δ, integ, J)
Rings / π count	DBE from formula

Formula Belt SIDE 1

AE = M_r(prod)/ΣM_r(react) ×100
E = waste / product · PMI = E+1
DBE = (2C+2+N−H−X)/2
splitting = n+1 · M+1 ≈ 1.1%·nC
Cl 3:1 · Br 1:1 (M:M+2)

12 · Functional Groups

REACTIVITY MAP

Reactivity lives at the functional group; the carbon skeleton is mostly inert. Two master patterns:

- **Polar / ionic** — a nucleophile (electron-rich, δ–) attacks an electrophile (electron-poor, δ+). Curly arrows go *from* Nu *to* E.
- **Radical** — homolysis, single-electron (fish-hook) arrows; chain initiation/propagation/termination.

Electrophilic carbons: C–X (halide), C=O (carbonyl). **Nucleophiles:** OH^-, RO^-, CN^-, NH_3, enolates, RMgX (carbanion equiv.).

13 · Substitution & Elimination

$S_N1/2$ · E1/2

	S_N2	S_N1
Steps	1 (concerted)	2 (carbocation)
Rate	k[RX][Nu]	k[RX]
Substrate	**1°** > 2°	**3°** > 2°
Stereo	inversion	racemisation
Solvent	polar aprotic	polar protic
Nu	strong	weak ok

E2: concerted, anti-periplanar H & LG, strong base, rate k[RX][base]; **E1**: via carbocation, rate k[RX]. Both follow **Zaitsev** (more-substituted alkene) — except a bulky base (t-BuO^-) gives **Hofmann** (less-substituted).

The fork: strong bulky base + heat ⇒ elimination; good Nu, weaker base ⇒ substitution. 3° + weak Nu/protic ⇒ S_N1/E1 mix.

13b · Nucleophiles & Leaving Groups

RANK THEM

Leaving group best→worst: $I^- > Br^- > Cl^- \gg F^-$; TsO^- & H_2O good. A weak base is a good LG (stable once it leaves); OH^-, RO^-, NH_2^- are poor LGs.

Nucleophilicity ↑ with negative charge & less steric bulk. **Basicity ≠ nucleophilicity**: in polar aprotic they track; in polar protic the bigger, more-polarisable ion wins ($I^- > F^-$).

13c · Carbocation Stability

DRIVES S_N1/E1

Order 3° > 2° > 1° > methyl (hyperconjugation + induction); **benzylic/allylic** are extra-stable (resonance).

An unstable cation **rearranges** (1,2-hydride or alkyl shift) to a more stable one — the classic S_N1/E1 "wrong product" trap.

13d · Mechanism Arrows

METHOD MARKS

- Arrow starts at a **lone pair or bond**, points where electrons go
- **Never** start an arrow at H^+ or a + charge
- Conserve charge & atoms each step
- Double-head = $2e^-$ (polar); fish-hook = $1e^-$ (radical)

14 · Carbonyl Chemistry

C=O

The carbonyl C is **electrophilic** (δ+); O is the basic/nucleophilic end. Two regimes:

ALDEHYDES & KETONES

Nucleophilic addition — Nu adds to C, O becomes O^-/OH. e.g. + RMgX → alcohol; + $NaBH_4$ → alcohol; + H_2O → hydrate; + ROH → acetal; + amine → imine.

CARBOXYLIC ACID DERIVATIVES

Nucleophilic acyl substitution (addition–elimination): Nu adds, then the leaving group leaves, C=O reforms.

REACTIVITY (LG ABILITY)
acyl chloride > anhydride > ester ≈ acid > **amide**
can convert "downhill" only

ENOLATES / ALDOL

α-C–H is acidic (~pKa 20) ⇒ base gives an **enolate** nucleophile → **aldol** (β-hydroxy carbonyl), then *dehydration* to enone. Key C–C bond-forming chemistry.

15 · Named C–C Bond Formation

BUILD THE SKELETON

- **Grignard** RMgX + C=O → 2°/3° alcohol (carbanion adds)
- **Aldol** enolate + carbonyl → β-hydroxy carbonyl
- **Wittig** ylide + C=O → alkene (makes C=C cleanly)
- **Pd cross-coupling** — *Nobel 2010*:

NAME	COUPLES
Suzuki	R–X + R'–$B(OH)_2$
Heck	R–X + alkene
Sonogashira	R–X + terminal alkyne

Cycle: oxidative addition → transmetalation → reductive elimination. Catalytic in Pd, mild, tolerant of functional groups ⇒ **green & widely used in pharma**.

15b · Imines, Acetals & Protecting Groups

CARBONYL + N/O

Carbonyl + 1° amine → **imine** (C=N); + 2° amine → **enamine**. Acid-catalysed, water removed to drive the equilibrium.

Carbonyl + 2 ROH → **acetal** = a protecting group for C=O (stable to base & nucleophiles, removed by aqueous acid). But every protecting group adds steps ⇒ *poor atom economy* (principle 8 — reduce derivatives).

15c · Enols & Conjugate Addition

A & B REACTIVITY

Keto–enol tautomerism: the keto form dominates, but the enol is the nucleophile in α-substitution (halogenation, the aldol).

α,β-unsaturated carbonyl is electrophilic at the carbonyl C (1,2-addition) *and* at the β-C: 1,4 / Michael / conjugate addition. Soft nucleophiles & stabilised enolates favour 1,4.

16 · Oxidation & Reduction

THE TOOLKIT

OXIDATION (ADD O / REMOVE H)

1° alcohol → **aldehyde** (PCC, Swern, TEMPO) → **acid** ($KMnO_4$, CrO_3/Jones). 2° alcohol → ketone. Green oxidants: **O_2, H_2O_2** (by-product = H_2O), catalytic TEMPO.

REDUCTION (ADD H / REMOVE O)

REAGENT	STRENGTH	REDUCES
$NaBH_4$	mild	aldehyde, ketone
$LiAlH_4$	**strong**	+ ester, acid, amide
H_2 / Pd	catalytic	C=C, hydrogenation

Catalytic H_2 is greenest (atom-economic, no metal-hydride waste). Chemoselectivity: $NaBH_4$ leaves esters/acids alone.

GREENER REDOX

Replace toxic Cr(VI) & heavy-metal oxidants with O_2 / H_2O_2 (by-product = H_2O) + catalytic TEMPO; use catalytic hydrogenation or enzymatic reduction over stoichiometric hydrides.

17 · Polymers · Two Routes

CLASSIFY FIRST

	CHAIN-GROWTH	STEP-GROWTH
Monomer	C=C (vinyl)	2 functional groups
Mech.	active centre adds monomer	any two ends react
MW vs time	**high early**	high only near 100%
By-product	none (addition)	small molecule (H_2O)
Examples	PE, PP, PVC, PS, PMMA	nylon, PET, PU

CAROTHERS (STEP-GROWTH)
$\bar{X}_n = 1 / (1 - p)$ · p = conversion
⇒ need p > 0.99 for useful chain length

Addition vs condensation = does it lose a small molecule? Addition keeps every atom (100% AE); condensation expels H_2O ⇒ lower AE.

17b · Copolymers

2+ MONOMERS

Arrangement tunes properties: **random** (–ABBABA–), **alternating** (–ABAB–), **block** (–AAA·BBB–, needs living polymerisation), **graft** (B branches off an A backbone).

Block copolymers self-assemble into thermoplastic elastomers (e.g. SBS rubber) — precision delivered by controlled radical (RAFT/ATRP).

17c · Identify the Route

EXAM REFLEX

Given a monomer or repeat unit:

- A **C=C** & repeat unit = same atoms as monomer ⇒ **addition / chain-growth**
- Two functional ends + a small molecule (H_2O) lost ⇒ **condensation / step-growth**
- **Ester** links in backbone ⇒ polyester (PET); **amide** links ⇒ polyamide (nylon)

18 · Addition Polymerisation

CHAIN-GROWTH

RADICAL (FREE-RADICAL)

1. **Initiation** — initiator (AIBN, BPO) homolyses → R·
2. **Propagation** — R· + monomer → new chain radical, repeats
3. **Termination** — combination or disproportionation of two radicals

Cheap, robust (PE, PS, PVC) but **poor control** of MW/architecture. RAFT / ATRP = controlled "living" radical → narrow Đ, block copolymers (a green/precision advance).

COORDINATION — ZIEGLER–NATTA / METALLOCENE

Transition-metal catalyst inserts monomer stereoregularly ⇒ controls **tacticity** & linearity (HDPE, isotactic PP). Heterogeneous, recyclable catalyst.

19 · Condensation Polymers

STEP-GROWTH

- **Polyester (PET)** — diacid + diol → ester links + H_2O. Bottles, fibres.
- **Polyamide (nylon)** — diacid + diamine → amide links + H_2O.
- **Polyurethane** — diol + diisocyanate (no by-product; addition-type step-growth).
- **Polycarbonate** — bisphenol + carbonate source.

Need **exact stoichiometry & high purity** (Carothers) for high MW. The ester/amide links are also the handle for chemical recycling (hydrolysis/solvolysis back to monomer).

19b · Nature's Step-Growth

BIOPOLYMERS

The largest condensation polymers are biological: **proteins** (amino acids → peptide/amide bonds + H_2O), **polysaccharides** (sugars → glycosidic bonds + H_2O), **nucleic acids** (phosphodiester). All are hydrolysable ⇒ inherently degradable — the design template for sustainable polymers.

19c · Worked · Carothers

WHY PURITY MATTERS

Degree of polymerisation vs conversion p:

p	$\bar{X}_N = 1/(1-p)$
0.90	10
0.95	20
0.99	100
0.995	200

⇒ step-growth needs **near-complete conversion** for useful chain length. A single impurity or stoichiometric imbalance caps M — hence the purity demand.

20 · Polymer Properties

STRUCTURE→PROPERTY

MOLAR MASS

AVERAGES & DISPERSITY
$\bar{M}_n = \Sigma n_i M_i / \Sigma n_i$ (number avg)
$\bar{M}_w = \Sigma n_i M_i^2 / \Sigma n_i M_i$ (weight avg)
$Đ = \bar{M}_w / \bar{M}_n \geq 1$ (dispersity)

Đ = 1 ⇒ perfectly uniform; step-growth ~2; controlled radical → low Đ.

THERMAL & ORDER

- **T_g** glass transition (amorphous softens); **T_m** melts (crystalline)
- **Tacticity** — iso / syndio / atactic; regular ⇒ crystalline, higher T_m
- **Thermoplastic** (linear, re-meltable, recyclable) vs **thermoset** (cross-linked, cannot re-melt) vs **elastomer**

Crystallinity ↑ ⇒ stronger, stiffer, more opaque, higher T_m.

21 · Sustainable Polymers

PRINCIPLES 7 & 10

Bio-based (renewable feedstock): PLA (polylactic acid, from corn/sugar), PHA/PHB (bacterial), starch, cellulose.

Biodegradable ≠ bio-based — they're independent. PLA is both; bio-PE is bio-based but *not* biodegradable. Design for degradation = build in hydrolysable links.

RECYCLING HIERARCHY

- **Mechanical** — remelt/reform (thermoplastics; quality degrades)
- **Chemical** — depolymerise to monomer (PET glycolysis/methanolysis) ⇒ closed-loop / circular
- Energy recovery (last resort)

21b · Structure → Property

QUICK RULES

- **Branching ↓** ⇒ packs tighter ⇒ denser & stronger (HDPE > LDPE)
- **Cross-linking ↑** ⇒ rigid, insoluble thermoset (rubber vulcanisation)
- **Chain length / M ↑** ⇒ higher T_m, strength, viscosity
- **Polar groups / H-bonds** (nylon) ⇒ stronger, higher T_m
- **Plasticiser** ⇒ lowers T_g (rigid PVC → flexible)

21c · Measuring Molar Mass

METHODS

- **GPC / SEC** — size-exclusion; gives the full distribution → $\bar{M}_n$, $\bar{M}_w$, Đ
- **End-group analysis** (NMR/titration) → $\bar{M}_n$ (low MW only)
- **Osmometry** → $\bar{M}_n$; **light scattering** → $\bar{M}_w$

$\bar{M}_w \geq \bar{M}_n$ always ⇒ Đ ≥ 1; broad Đ ⇒ wide spread of chain lengths.

22 · Greener Process Toolkit

PRINCIPLES 5,6,9

- **Green solvents** — water, $scCO_2$, ionic liquids, bio-solvents (2-MeTHF, ethanol); avoid chlorinated & VOCs
- **Biocatalysis** — enzymes; mild, aqueous, enantioselective
- **Flow chemistry** — continuous, better heat/mass transfer, safer, scalable (process intensification)
- **Catalysis > stoichiometric** reagents everywhere
- **Avoid protecting groups** (principle 8 — reduce derivatives)

23 · Worked · Atom Economy

SHOW THE NUMBER

Q. Wittig vs substitution to make an alkene — which is greener by AE?

Wittig expels $Ph_3P{=}O$ (M_r 278) — a *large* by-product ⇒ low atom economy despite high yield. An elimination or a catalytic metathesis keeps more atoms in product.

LESSON
high yield ≠ green. Quote AE/E-factor, then name the by-product driving waste.

24 · Exam Discipline

DON'T LOSE MARKS

- State **DBE** before drawing any structure
- Assign **every** spectral peak — reconcile to one structure
- "Is it green?" ⇒ give a **number** + name the waste
- Mechanisms: **curly arrows from Nu→E**, charges & lone pairs shown
- Classify polymer route *before* drawing the repeat unit
- Don't confuse *yield* with *atom economy*

SIA → *Half the marks here are "show the calculation / show the arrow." Method marks survive even when the final number slips — always write the working.*

25 · Green Metrics Recap

NAME THE TRADE-OFF

METRIC	CAPTURES	MISSES
Atom economy	by-products (theory)	yield, solvent
Yield	conversion achieved	waste atoms
E-factor	real total waste	toxicity
PMI	+ solvent & water	hazard

No single number means "green" — name which trade-off the question tests.

Formula Belt

SIDE 2

$\bar{X}_n = 1/(1-p)$ · $Đ = \bar{M}_w/\bar{M}_n \geq 1$
splitting n+1 · reactivity: RCOCl>ester>amide
S_N2 inversion · E2 anti-periplanar
green: catalysis · renewable · degrade

good luck. revise smart.