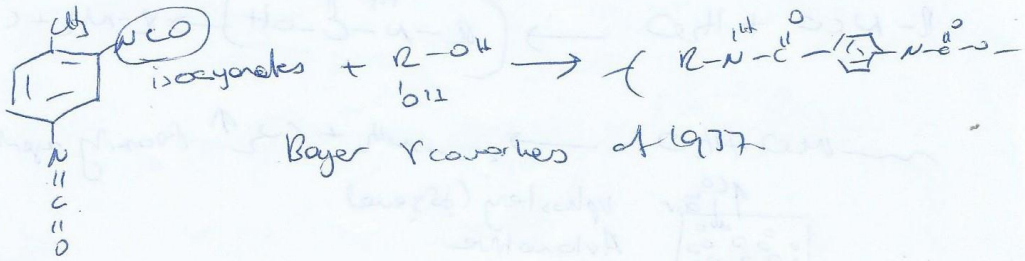
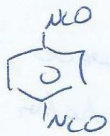
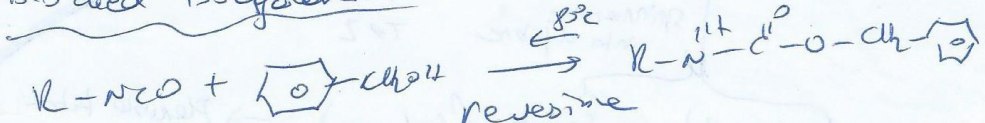
Polyurethane

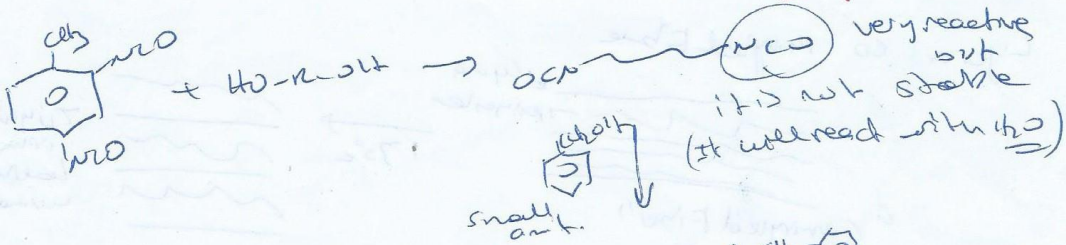


Aromatic  $k_1 \neq k_2$ generally $k_1 > k_2$ (one group reacts it effect other isocyanate group drastically)

R'–OH (1° 1, 2° 0,2, 3° 0,08) → reactivity

Blocked isocyanate

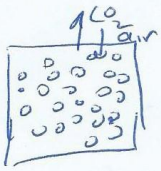




foamed Polyurethane

$R-NCO + H_2O \longrightarrow \left(R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-OH\right) \rightarrow R-NH_2 + CO_2$

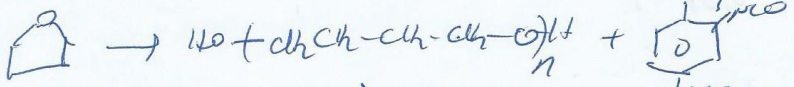
$\sim NCO + H_2O \longrightarrow \sim NH_2 + CO_2\uparrow$ Foaming agent

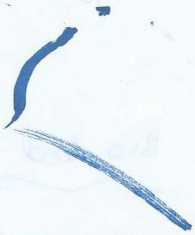


Upholstery (closed)
Automotive
Public places
Aircraft

Flame retardant polyurethane foam. However, It needs flame retardant test because CO_2 concentration changes with times with airs. (First year you can pass it correctly but three years later it would not be)

Polyurethane fibre

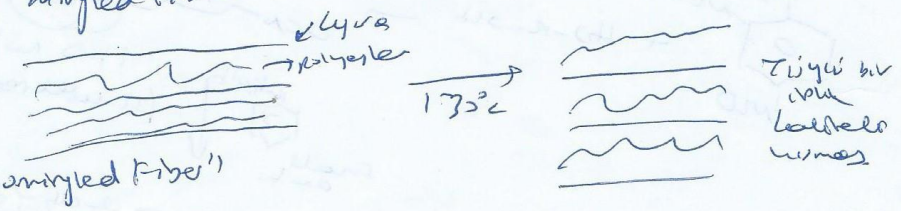




Spinnerette into a fibre

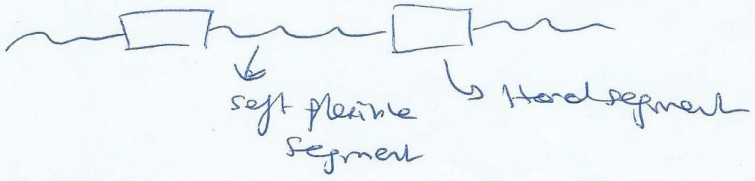
Lycra (Dupont) Spandex (Celanese) → Flexible fibre

Lycra co mingled fibre



("comingled fiber")

Polyurethane 2



Reaction - injection molding is increasing in importance and emphasizes the production of thermoset PU.

liquid monomers mixed together under high pressure → split on to mold.

→ curing occurs in the mold ⇒ most automotive dashboards are RIM products.

Aromatic diisocyanate derived coatings generally offer poor external light stability while aliphatic-derived systems offer good light stability

Yellowing effect of isocyanate

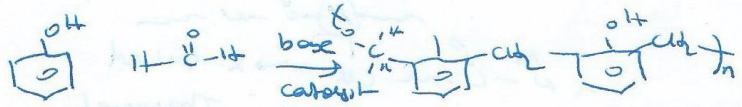
low level of ~~no~~ TDI residue should be present in end product

Formaldehyde Resin (1)

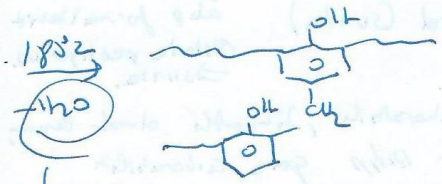
Phenol – Formaldehyde 1909 Backeland

"Bakelite"

Tencere kulpları, eski telefonlar, gitar - gaz fıstıklıları → bakelitten



Linear, sometime liquid, thermoplastic



p position of one chain reacts with $-CH_2OH$ end group of another chain

↳ this water absorbed by fillers, calcite or calcium black

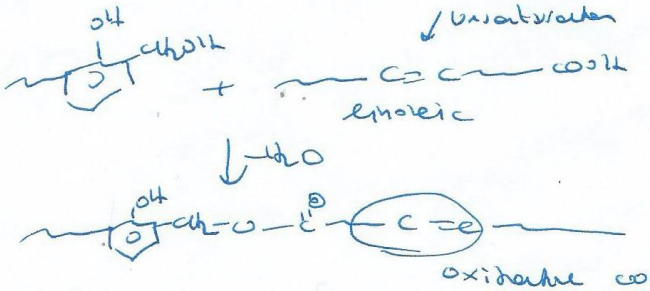
good electrical resistance, excellent flame retardancy

"Bridge lining → fren balatası"

Köprülerde çalışan kişilerde kanser olma oranı yüksek, millet parayı alıp fren yapıyor ⇒ phenol formaldehyde çalışıyor.

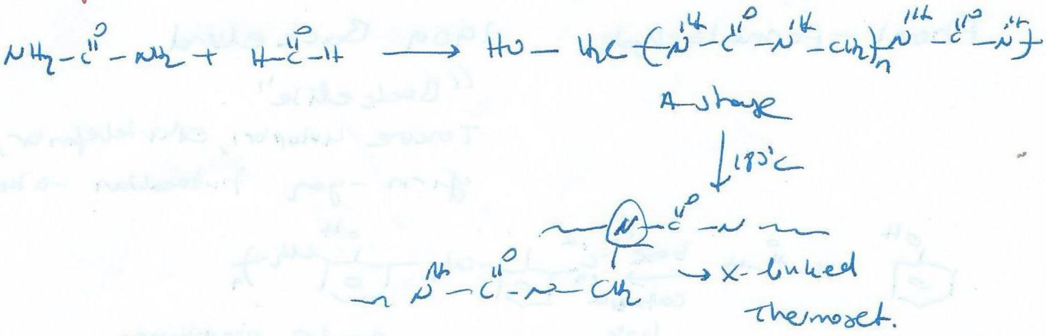
Air cured Phenol Formaldehyde

Stage A



Paint Binder → high temperature paint → over roast, kalorifer, soba boyaları, kanser boyaları

Urea – formaldehyde

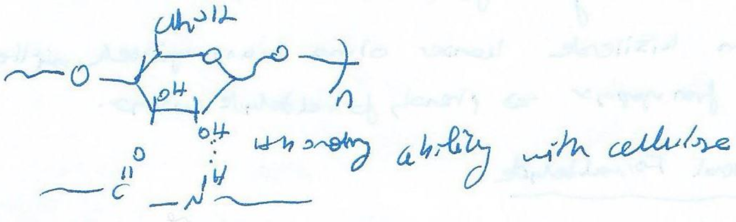


* wood glue → Plywood (kontraplak)
→ Fiber ~~board~~ board (Sunta)

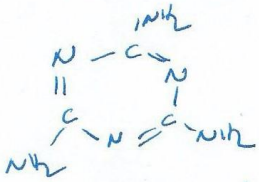
ağaç parçalarını alıp formaldehit resin ile presliyorsun. ⇒ sunta.

Sunta kesilince formaldehyde çıkarabilir, dikkatli olmak lazım, ahşap lambalılar zamanla suntayı kesip gaz çıkarabilir

* Sizing (Apre) for cotton "wash-n-wear"
buruşmaz apre.

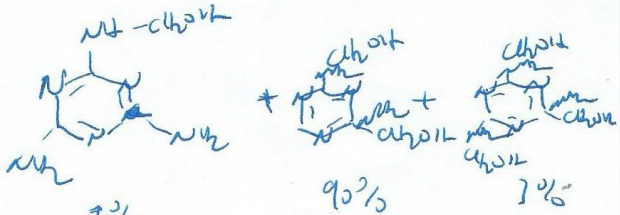


melamine - Formaldehyde



melamine (antibacterial)

1 : formaldehyde 2.3 — 70°C, 4 min



7% 90% 3%

you obtain a mixture

→ liq resin → textile finish (monomethylol conc high, so you get low MWT)

→ thermoset resin → plate (melamin tabulator, trimethylol conc high x-linking high)

melamin formaldehyde → are antibacterial

processing →

prepolymer → dry/ground to powder → mixed with fillers - mica, glass fibres, sawdust, colourants, hardeners

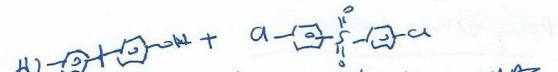
→ heating mold → x-linked occur

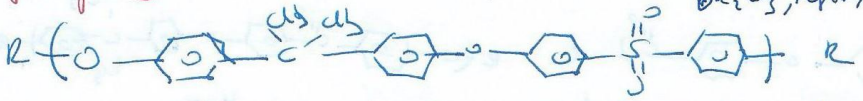
-(CH2-NH-CH2)- links are formed

the fillers are added to reduce the cost and do improve the electrical or mechanical property of the resin

(3)

Polysulfones





Udel, 1966. $T_g \approx 190°C$.

Radel, 1976 Union carbide, $T_g \approx 220°C$

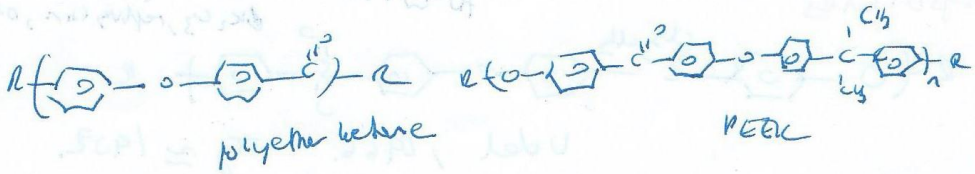
- greater chemical solvent resistance
- greater oxidative stability
- good toughness in comparison to Udel

used in hair dryers, cookware, they are good candidate for hot water and food handling equipment, athletic battery cases, surgical and laboratory equipments, eye support parts, membranes for use in hemodialysis.

Table 4.11. General Physical Properties of PSF

Heat depletion temperature (1,820 kPa, °C)	135
maximum resistance to continuous heat	110°C
Crystalline melting point	190°C
coefficient of linear expansion (cm/cm °C, 10^{-5})	5.0
Compressive strength (kPa)	1.1×10^5
Flexural strength (kPa)	9.6×10^5
Impact strength (Izod: cm N/cm of notch)	21
Tensile strength (kPa)	7.4×10^4
Ultimate elongation (%)	1.1
Density (g/mL)	1.0

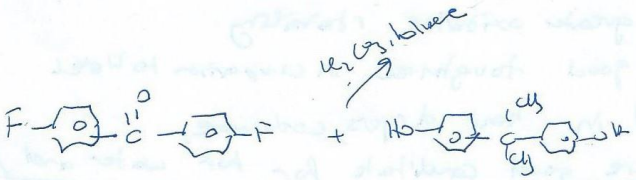
Poly ether ketones



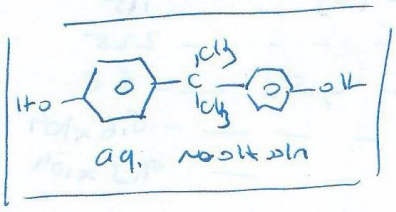
polyether ketone PEEK

→ good thermal stability, good mechanical property, flame resistance, impact resistance and resistance to environment

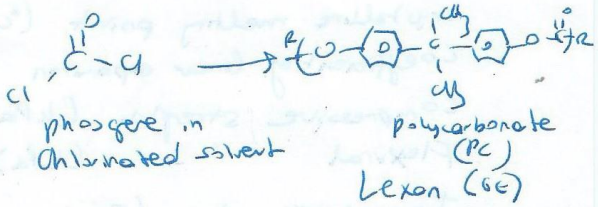
→ Application: compressor plates, valve seats, bearing cages, pump impellers., wire coatings, semiconductor wafer carriers,



Polycarbonate



+



Lexan (GE)
Merlon (Mobay)

residual
Bisphenol A (BPA) may cause neutral and behavioral changes in rats and children.
⇒ banned in baby bottles

20 gr CD weight → 95% is one PC video recording, CD devices. door seals, popcorn cookers, sunglasses lenses, bay blayer.

The moderate inflexibility, lack of ready mobility, and nonlinear structure contribute to PC having a relatively long time constant for crystallization.

Cooling is allowed to be relatively rapid so that most PC products possess a large degree of amorphous nature and account for PC having high impact strength that is important in its use to blunt high impacts and important to CDs to provide a semirigid discs can that can be dropped and not readily shattered.

⇒ Control of the rate of flow and cooling is an important factor in producing CD-quality PC materials → affects the amorphous region

⇒ A high degree of amorphous nature also contributes to the needed optical transparency with amorphous PC having a transparency near that of window glass.

Table 4.1. General Physical Properties of a Polycarbonate

Heat deflection temperature (1,820 kPa, °C)	130
maximum resistance to continuous heat (°C)	115
crystalline melting point (°C)	225
coefficient of linear expansion (cm/cm-°C, 10^{-5})	6.8
compressive strength (kPa)	8.6×10^4
Flexural " (kPa)	9.3×10^4
Impact strength (Izod: cm-N/cm of notch)	530
Tensile strength (kPa)	7.2×10^4
Ultimate elongation (%)	110
Density (g/mL)	1.2

PC → expensive

susceptible long term hydrolysis so that water must be ~~frequently~~ ruthlessly purged

drying process 4 hr at 120°C.

PC → recycling → yellowing index 3,5

virgin → " " 1.8 ⇒ Use for CD materials

CD material application ⇒ Usually MWT 16,000–28,000 Da

- thermal stability
- low levels of chemical impurity
- excellent clarity
- constant mechanical behavior (for reproducibility)

Barrel temp 370°C → injection molding → 138 MPa barrel pressure → mold at 110°C → CD 0,5 mm thick

a thin reflective aluminum layer is sputtered onto the disc.

but most CD/R discs use gold or silver because of their greater reflectivity

a thin acrylic layer is sprayed over the aluminum to protect it

the label is printed on acrylic surface

① Polyester — OH value

Paper → European polymer journal 78 (2016) 46-60 (mercapto-ethanol modified soybean oil)

Hydroxy value (theo.) = 2 × $\frac{56,100}{1036}$ (theoretical molecular weight of MSO with two ME units)

[mg KOH/g]

Hydroxy value (theo.) = 3 × $\frac{56,100}{1114}$ (theoretical molecular weight of MSO with three ME units)

Hydroxyl values (titration) of the polyols were determined by following the ASTM D 1957-86.

Average number of OH functionality per molecule f =

$$\frac{\text{hydroxyl value determined by titration} \times \text{molecular weight of polyol determined by MALDI-TOF}}{56,100}$$

Hydroxyl value = $\frac{(A-B) \times N \times 56,1}{S}$

N → molar concentration of KOH solution

A → with blank with every KOH

B → volume (mL) of KOH used for the titration of sample

S → weight of the sample

→ (acetic anhydride is used) Lonach, Polymer, 2014, 55, 1004.

(Hydroxyl numbers are defined by the mass of KOH in milligrams that is equivalent to the hydroxy content of 1 g of the polyol. (Anal. Chim Acta 541 (2004) pp 313-327.

Functionality = $\frac{\text{molecular weight of reactant} \times \text{OH number}}{56{,}100}$

The Mn, Mw can also be used for chromatography (ASTM D-7134)
(the samples were diluted in acetone and a 10 mg/mL solution of 2,5-dihydroxybenzoic acid in acetone was used as matrix

Addition Polymerization (1)

One monomer is added to the growing chain at a time

m-mer + monomer = (m+1)-mer

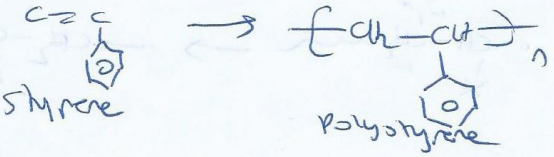
Characteristics: * Free radical
* Ionic → Anionic
Cationic
Living / Immortal (well-defined architecture)

examples

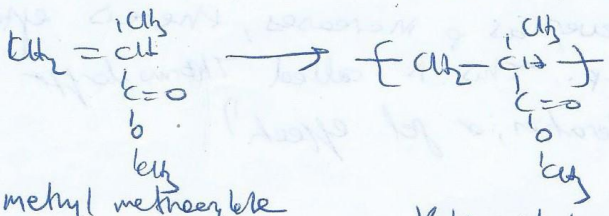
$H_2C=CH_2$ → $\{H_2C-CH_2\}_n$
ethylene → polyethylene

$H_2=CH$ (CH_3) → $\{H_2-CH(CH_3)\}_n$
Propylene → polypropylene

$F_2C=CF_2$ → $\{F_2C-CF_2\}_n$
tetrafluoroethylene → Teflon



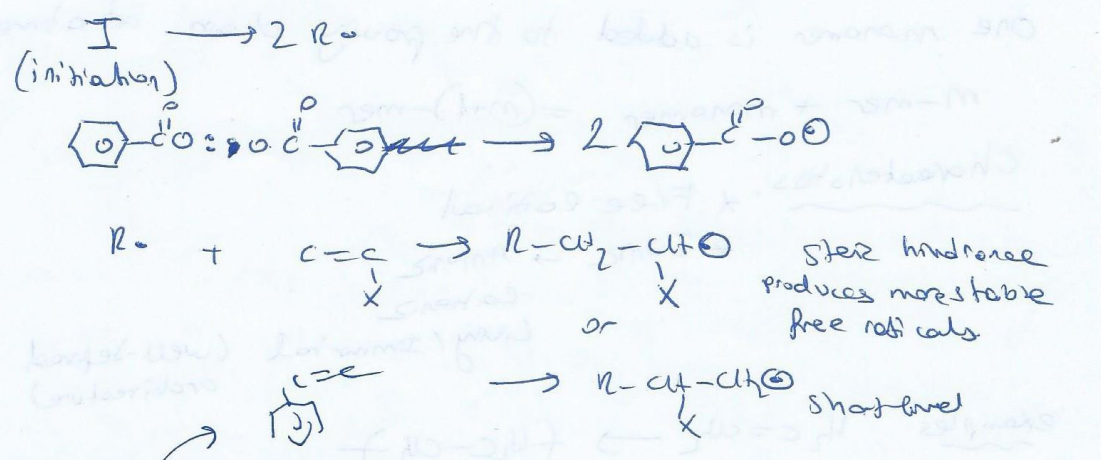
$CH_2=CHCl$ → $\{CH_2-CHCl\}_n$
vinyl chloride → PVC



Process in Addition Polymerization

1. Initiation $R \rightarrow C=C \rightarrow R-C-C\cdot$
2. Propagation $R-C-C\cdot + C=C \rightarrow R-C-C-C-C\cdot$
3. Termination $R-C-C\cdot + R-C-C\cdot$
4. Transfer reaction or active species from one chain to another

Free Radical polymerization

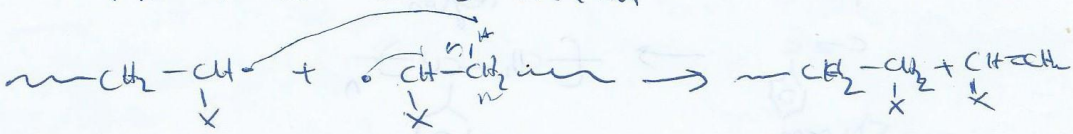


Polystyrene terminates predominantly by combination:

$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{k_{tc}} P_{n+m}$

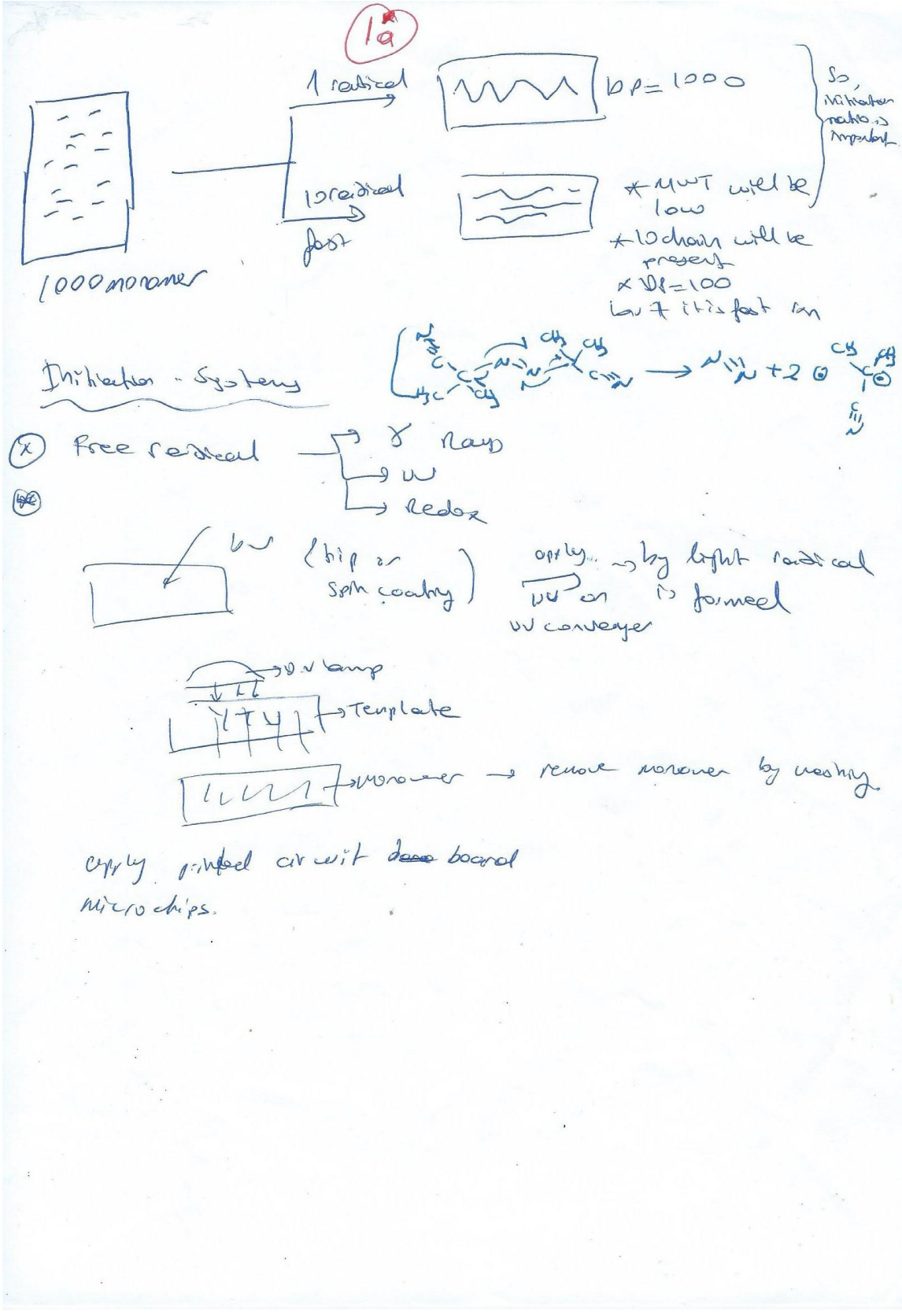
Polymethyl methacrylate terminates predominantly by disproportionation due to the steric hindrance of the methyl methacrylate group.

$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{k_{td}} P_n + P_m$



Auto acceleration

The rate of propagation (R_p) is quite valid at the beginning of the reaction. However, as p increases, there is after a sharp increase in R_p. This is called Thromsdorff-Norrish Effect (or autoacceleration, or gel effect)


1a
1 radical
DP = 1000
So, initiation ratio is important
1000 monomer
1 radical
fast
* MWT will be low
* 10 chain will be present
* PI = 100
isn't it is fast in
Initiation - Systems
Free radical
γ Rays
UV
Redox
UV (dip or spin coating)
apply → by light radical
UV on is formed
UV converger
UV lamp
Template
monomer → remove monomer by washing.
apply printed circuit board
Microchips.

Autoacceleration is due to the increased viscosity. Long, growing chains have greater difficulty diffusing and finding each other to terminate.

⇒ Sharp reduction of k_t.

On the other hand, small monomer molecules can diffuse and find the polymer free radicals to grow.

⇒ Exothermic rxn

* Heat must be controlled
* Explosive rxn.

How one can control the reactions ----⇒ Use dilute solutions

However, the probability of chain transfer increase.

Inhibitors / Retarders

Inhibitors are low concentration radical scavenges that prevent polymerization initiation until all the scavenger is consumed. Retarder is a compound that slows down the rate of reaction

* oxygen is both inhibitor and retarder
* Nitrobenzene is retarder (charge transfer agent that produces less reactive free radical)
  reduces R_p and X_n.

Thermodynamics

$\Delta G < 0$

$\Delta G = \Delta H - T\Delta S$ should be negative for polymerization to take place.

1. ΔH → strongly exothermic rxn
   ΔH_{rp} (enthalpy of propagation) → ~ −160 to −640 kJ/kg
2. ΔS → lose entropy with polymerization
   ΔS → ~ −90 to −120 J/mol·K
   or
   −0.09 to −0.12 kJ/(mol·K)

Usually ΔH is much larger than $T\Delta S$ term.

→ negative ΔG (thermodynamically favorable to polymerize)

Comparison between Stepwise and Chain polymerization

Chain (addition)

* Growth occurs by addition of one unit at a time to the active growing chain end
* Monomer concentration decrease steadily throughout the polymerization
* Polymer chains are formed from the beginning of the polymerization and throughout the process
* Average chain length for reacted species remains approximately constant throughout the polymerization
* As reaction time increases polymer yield increases, but molecular weights remain the same
* Rxn mixture contains almost only unreacted monomer, polymer, and very little growing chain ~~of~~ polymer chain

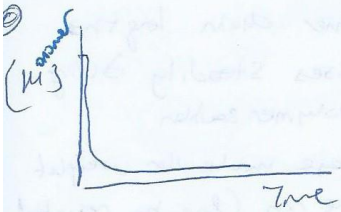
Step (condensation)

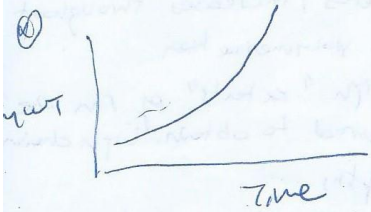
* Any two ~~two~~ molecular units can react
* Monomer disappears early in the reaction
* Polymer chain length increases steadily during the polymerization
* Average molecular weight for the rxn (for the reacted species) increases throughout the polymerization
* High "extents" of rxn are required to obtain high chain lengths
* Rxn system contains various stages, chain lengths, of product present in a calculable distribution

Condensation

* $R-OH + R-\overset{O}{\overset{\|}{C}}-OH$
(Byproduct)

* Polymerization occurs everywhere, "Two monomers can reach".

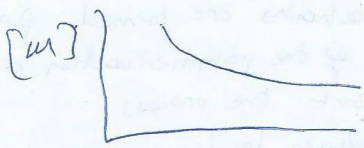


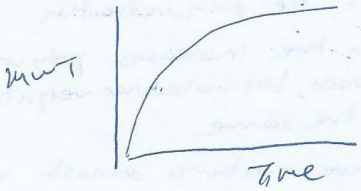


Addition

C=C (reactant)
No byproduct

Polymerization occur only a growing chain.
Two monomers can't reach.





Free radical polymerization cannot be restarted again.
Condensation polymerization can be stopped and restarted.