1) Show the most probable distribution of molecular weight for step polymerizations (demonstration). Mix at high temperature 1 kg of polyester (monodisperse) with M=20000 and 1kg of polyester with M=40000. Calculate the limiting value of Mn and Mw for the resulting blend if transesterification occurs. (11pts)

2) Consider a monomer pair and Alfrey-Prince parameters.

Monomer	Molecular Weight	Q	e
Styrene	104	1.0	-0.8
Acrylonitrile	53	0.6	1.2

Calculate the molar fraction of styrene in the monomer feed at low conversion free radical copolymerization process in order to produce SAN polymer (styrene-acrylonitrile) random copolymer containing 10% by weight of acrylonitrile. (11pts)

3) Show the mathematical expression of elastic retraction force for a single Gaussian molecular chain and comment on the differences with the classical Hook's law. (11pts)

Principles of Polymer Chemistry – 1st session exam
February 7, 2013

Surname name ID number

1- **Copolymerization (10 points)**
Derive the copolymer equation (show all steps) with clear indication of all the simplifying hypotheses.

2- **Crosslinking (10 points)**
A bicomponent polyurethane adhesive is obtained with a mixture of pentaerythritol $C(CH_2OH)_4$ = 1000 g and 1,4 butanediol $HO\text{-}(CH_2)_4\text{-}OH$ = 1000 g as component A, and methylene-bis-diphenyl isocyanate $OCN\text{-}(C_6H_4)\text{-}CH_2\text{-}(C_6H_4)\text{-}NCO$ as component B.
Calculate the amount of diisocyanate needed to have stoichiometric ratio OH/NCO = 1.
Calculate the extent of reaction p at the gel point according to the Carothers equation and the Flory-Stockmayer theory.

3- **Rubber technology (10 points)**
Represent graphically the rheological monitoring of a vulcanization process. Explain how the data can be used to model kinetically the process, and discuss the applicability of the various kinetic (isothermal) equations.

Principles of Polymer Chemistry – July 5, 2013

Surname Name
matricola number

1- **Crosslinking (10 points)**

Show the estimation of the critical extent of ~~gelation~~ reaction at gel point for multifunctional step-growth polyreactions according to Carothers and Flory theories.

~~2-~~ **Copolymerization (10 points)**

A modified PVC grade containing 5% by weight of vinyl acetate is produced by a low conversion random copolymerization of vinyl chloride $CH_2=CH-Cl$ (e=0.20 Q=0.044) and vinyl acetate $CH_2=CH-OCOCH_3$ (e=-0.22 Q=0.026). Calculate the composition of the monomer feed needed to obtain such a copolymer.

3- **Rubber technology (10 points)**

Derive the constitutive equation of rubber elasticity according to the molecular theory model.

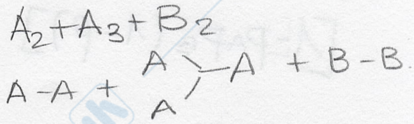
JULY 2013

① Extent of reaction at gel point step-growth polyreactions according to Carothers and Flory theories.

CAROTHERS

$$P = \frac{n^\circ \text{ groups reacted at time } t}{n^\circ \text{ groups at } t=0}$$

Hypothesis: A can only react with B and viceversa.



$A_2 + A_3 + B_2$

$A{-}A + A_3 + B{-}B$

N_0: number of initial molecules
N: number of current molecules

f_{av}: average functionality of the monomer mixture

$$P = \frac{2(N_0 - N)}{N_0 f_{av}}$$

Since the number reacted groups is twice the number of reacted molecules.

$$P = \frac{2(N_0-N)}{N_0 f_{av}} = \frac{2}{f_{av}} \frac{(N_0-N)}{N_0} = \frac{2}{f_{av}}\left(1 - \frac{N}{N_0}\right) = \frac{2}{f_{av}}\left(1 - \frac{1}{x_n}\right) =$$

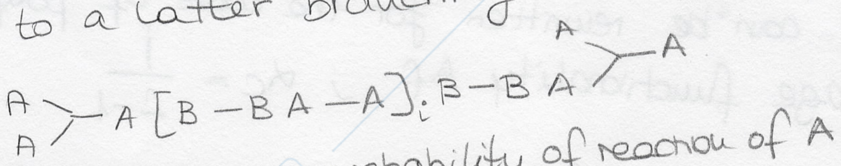
gel point $x_n \to \infty$

$$= \frac{2}{f_{av}} \rightarrow \boxed{P_c = \frac{2}{f_{av}}}$$

FLORY-STOCKMAYER

2 hypothesis
- Reactivity of functional groups independent on M.W.
- No cyclization

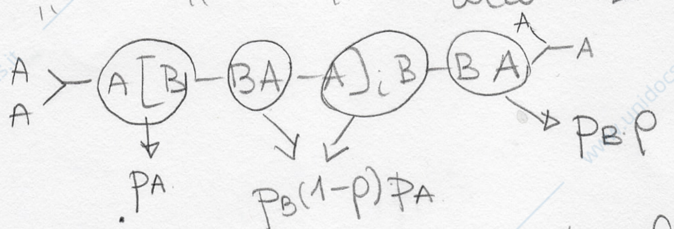
α: branching coefficient: the probability that a group A belonging to a branching (A_3) is connected throug a series of bifunctional links A–B to a latter branching unit A_3



$A_3{-}A[B{-}BA{-}A]_i B{-}BA{-}A_3$

p_A: extent of reaction of A or probability of reaction of A
p_B: probability of reaction of B
ρ: fraction of A groups belonging to A_3

The probability of reaction of B with A_3 is $p_B \rho$
" " " " " with A_2 is $p_B(1-\rho)$



$p_A[p_B(1-\rho)p_A]^i p_B \rho$ → probability of sequence with length i

The same probability extended to all possible chain length is:

$$\alpha = \sum [p_A p_B (1-\rho)]^i p_A p_B \rho = p_A p_B \rho \underbrace{\sum [p_A p_B (1-\rho)]^i}_{\sum X^K \to \frac{1}{(1-X)} \quad X<1} =$$

$$= \frac{p_A p_B \rho}{[1 - p_A p_B (1-\rho)]}$$

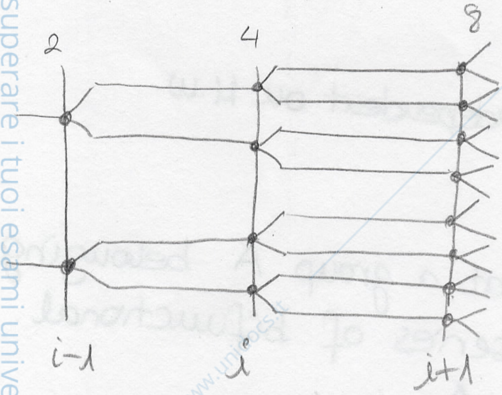
$$p_B = r p_A$$

$$\alpha = \frac{r p_A^2 \rho}{[1 - r p_A^2 (1-\rho)]} \qquad \alpha = \frac{p_B^2 \rho}{[r - p_B^2 (1-\rho)]}$$

If $A = B \rightarrow r = 1 \quad p_A = p_B = p$

$$\alpha = \frac{p^2 \rho}{[1 - p^2 (1-\rho)]}$$

α_c and p_c



During the crosslinking process ($A_2 + A_3 + B_2$) each macromolecular chain terminated with A_3 is able to generate 2 chain at next step, the 4, 8 and so on until cross linking is completed

$$Y_{i+1}/Y_i = 2\alpha$$

Condition for crosslinking $Y_{i+1}/Y_i > 1$

$$\Rightarrow \alpha > 1/2 \text{ and } \alpha_c = 1/2$$

The relation can be rewritten for the case of polyfunctional monomers with average functionality Af ; $\alpha_c = \frac{1}{f-1}$

$$\alpha_c = \frac{1}{f-1} = \frac{p_c^2 \rho}{[1 - p_c^2 (1-\rho)]} \; ; \; p_c = [1 + \rho(f-2)]^{-1/2}$$

② Copolymerization.

PVC / 5% w/w. of vinyl acetate low conversion

— $CH_2=CH-Cl$ ($e=0,20$, $Q=0,044$) ①

$+$

$CH_2=CH-OCOCH_3$ ($e=0,22$, $Q=0,026$) ②

Composition of the monomer feed

$$\begin{cases} r_1 = \frac{Q_1}{Q_2}\exp[-e_1(e_1-e_2)] = \frac{0,044}{0,026}\exp[-0,20(0,20+0,22)] = 1,56 \\ r_2 = \frac{Q_2}{Q_1}\exp[-e_2(e_2-e_1)] = \frac{0,026}{0,044}\exp[+0,22(-0,22-0,2)] = 0,539 \end{cases}$$

Considering 100kg of the copolymer < 5kg of vinyl acetate / 95kg of vinyl chloride

$PM_1 = 12\times 2+3+35 = 62\ g/mol$

$PM_2 = 12\times 4+6+16\times 2 = 86\ g/mol$

$N_1 = \frac{5000\ g}{62\ g/mol} = 80,6$ mol in the copolymer of ① $\rightarrow F_1 = \frac{80,6}{1104,65+80,6} = 0,07$

$N_2 = \frac{95000\ g}{86\ g/mol} = 1104,65$ mol in the copolymer $\rightarrow F_2 = \frac{1104,65}{1104,65+80,6} = 0,93$

$$\frac{1}{F_1} = 1 + \frac{1}{\pi} \Rightarrow \frac{1}{\pi} = \frac{1}{F_1} - 1 = \frac{1}{0,07} - 1 \rightarrow \pi = 0,075$$

$$\pi = \frac{r_1\mu+1}{1+r_2/\mu} \rightarrow \pi\left(1+\frac{r_2}{\mu}\right) = r_1\mu+1 \rightarrow \pi + \frac{\pi r_2}{\mu} = r_1\mu+1 \xrightarrow{\times\mu}$$

$$\rightarrow \mu\pi + \pi r_2 = r_1\mu^2 + \mu \rightarrow r_1\mu^2 + (1-\pi)\mu - \pi r_2 = 0$$

$$\mu = \frac{-(1-0,075) \pm \sqrt{(1-0,075)^2 + 4\cdot 1,56\cdot 0,539\cdot 0,075}}{2\cdot 1,56} =$$

$$= 0,04088\ ; \quad \frac{1}{f_1} = 1 + \frac{1}{\underset{0,04088}{\mu}} \rightarrow f_1 = 0,039$$

$f_2 = 0,96$

PROVA 5 luglio 2013

1- CROSSLINKING

CAROTHERS: $p_c = \frac{2}{f_{av}}$

f_{av}: funzionalità media della miscela monomerica

FLORY: $p_c = \left[1 + \rho\,(f_{av} - 2)\right]^{-\frac{1}{2}}$

ρ: frazione di gruppi A_3 appartenenti ad A_3 rispetto a tutti i gruppi A presenti.

dimostrazioni: vedi foglio 12 (schemi)

2- COPOLYMERIZATION

$CH_2 = CH - Cl$

$e = 0,2$

$Q = 0,044$

(VC) 62 g/mol

95% w

$CH_2 = CH - OCOCH_3$

$e = -0,22$

$Q = 0,026$

(VA) 86 g/mol

5% w

$r_{VC} = \frac{Q_{VC}}{Q_{VA}} \exp\left(-e_{VC}\left(e_{VC} - e_{VA}\right)\right) = 1,556$

? f.

$r_{VA} = \frac{Q_{VA}}{Q_{VC}} \exp\left(-e_{VA}\left(e_{VA} - e_{VC}\right)\right) = 0,539$

~~$r = \frac{[M_1]}{[M_2]} =$~~

$12 + 2 + 12 + 1 + 35 = 62$ g/mol $\quad \frac{95}{62} = 1,53$ moli

$12 + 2 + 12 + 1 + 16 + 12 + 16 + 12 + 3 = 86$ g/mol

$\frac{5}{86} = 0,058$ moli

$f_{VA} = \frac{0,058}{1,53 + 0,058} = 0,0365$

$f_{VC} = \frac{1,53}{1,53 + 0,058} = 0,9634$

f] energia libera di

$F = -T\Delta S$ (a V costante)

$F = -W = -T\Delta S$ $W = \frac{1}{2} K_B N' T \left[\lambda_1^2 + \frac{2}{\lambda_1} - 3\right]$

g] definiamo densità $\rho = \frac{N' M_e}{N_A} \rightarrow N' = \frac{\rho N_A}{M_e}$

sostituendo:

$$W = \frac{1}{2} \overset{R}{\boxed{K_B}\, T \frac{\rho \boxed{N_A}}{M_e}} \left[\lambda_1^2 + \frac{2}{\lambda_1} - 3\right]$$

$$W = \frac{1}{2} \underset{\downarrow}{\boxed{\rho \frac{RT}{M_e}}} \left[\lambda_1^2 + \frac{2}{\lambda_1} - 3\right]$$

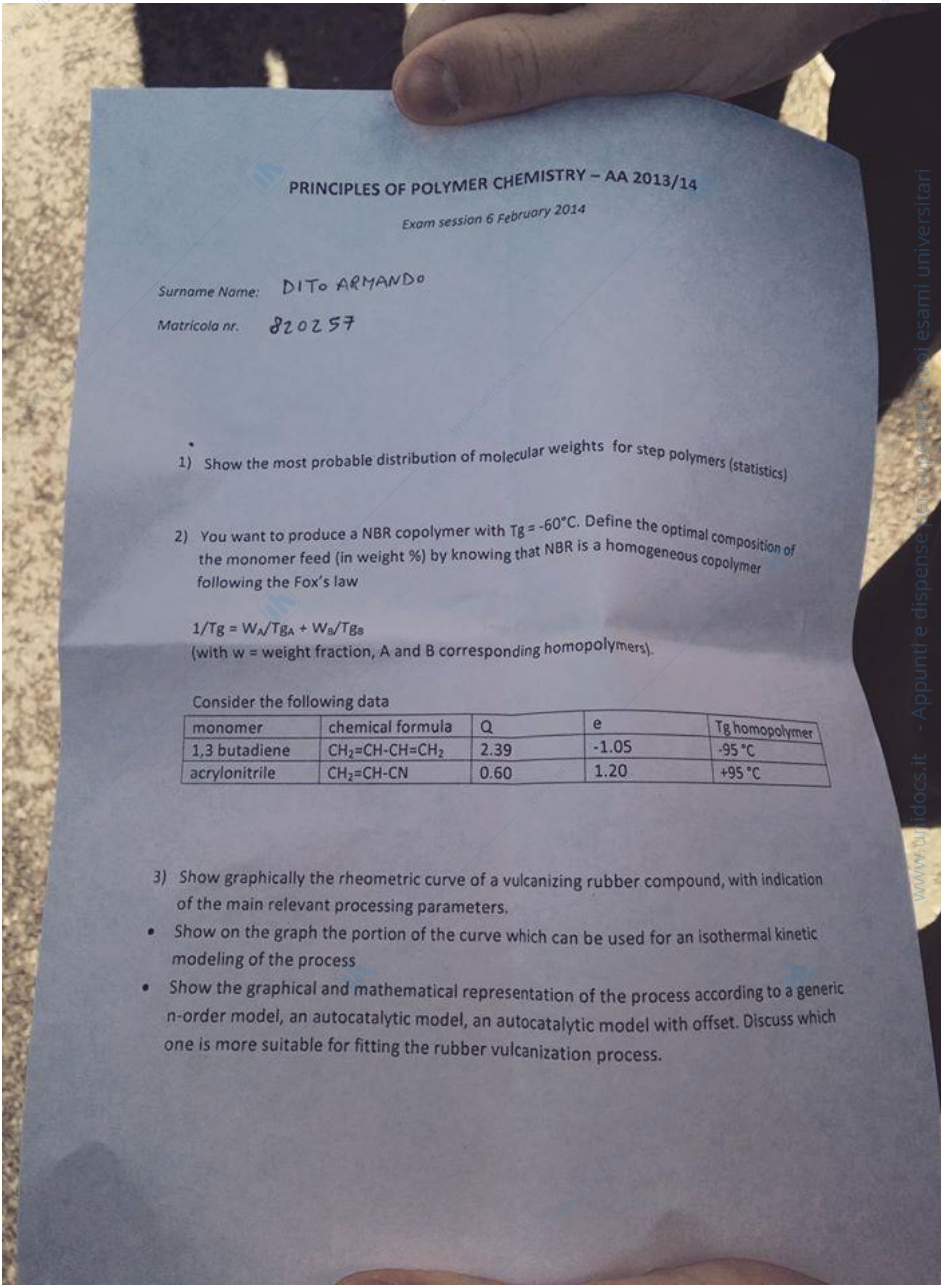
G: modulo della gomma

h] sforzo: $\sigma = \frac{f}{A_0}$ $d\lambda = \frac{dl}{l_0}$

$$\frac{dW}{d\lambda} = \sigma = \cancel{\tfrac{1}{2}} G \left[\cancel{2}\lambda_1 - \frac{1}{\lambda^2}\right]$$

$$\sigma = G\left(\lambda_f - \frac{1}{\lambda_f^2}\right]$$

EQ. COSTITUTIVA GOMME



PRINCIPLES OF POLYMER CHEMISTRY – AA 2013/14

Exam session 6 February 2014

Surname Name: DITO ARMANDO

Matricola nr. 820257

1) Show the most probable distribution of molecular weights for step polymers (statistics)

2) You want to produce a NBR copolymer with Tg = -60°C. Define the optimal composition of the monomer feed (in weight %) by knowing that NBR is a homogeneous copolymer following the Fox's law

$1/T_g = W_A/T_{gA} + W_B/T_{gB}$

(with w = weight fraction, A and B corresponding homopolymers).

Consider the following data

monomer	chemical formula	Q	e	Tg homopolymer
1,3 butadiene	CH_2=CH-CH=CH_2	2.39	-1.05	-95 °C
acrylonitrile	CH_2=CH-CN	0.60	1.20	+95 °C

3) Show graphically the rheometric curve of a vulcanizing rubber compound, with indication of the main relevant processing parameters.
- Show on the graph the portion of the curve which can be used for an isothermal kinetic modeling of the process
- Show the graphical and mathematical representation of the process according to a generic n-order model, an autocatalytic model, an autocatalytic model with offset. Discuss which one is more suitable for fitting the rubber vulcanization process.

PRINCIPLES OF POLYMER CHEMISTRY (AA 2013-14)

Exam session February 26, 2014

Surname ....Name......................................Matricola number.......................................

X **Question 1 (10 pts)**

For most chain polymerizations there is some temperature at which the reaction becomes reversibile i.e.

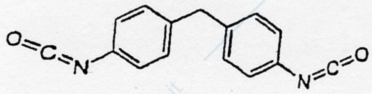
$----M_n^* + M \leftrightarrow ----M_{n+1}^*$

By knowing that a reaction isotherm equation of the type $\Delta G = \Delta G° + RT \ln K$ (K = equilibrium constant) is applicable to the analysis of polymerization-depolymerization equilibria, develop a general relation between T_c (ceiling temperature) and $[M]_c$ (equilibrium monomer concentration) as a function of standard enthalpy and entropy of reaction, $\Delta H°$ and $\Delta S°$.

Comment on the dependence between initial monomer concentration and maximum production temperature in chain polymerizations.

X **Question 2 (12 pts)**

A bicomponent polyurethane is obtained by combination of 100 g of trimethylolpropane $CH_3CH_2C(CH_2OH)_3$ (density at 25°C = 1,08 g/cm^3), and 100 g of 1,6 hexanediol $HO(CH_2)_6OH$ (density at 25°C = 1,16 g/cm^3) and a suitable amount of methylene bis phenyl diisocyanate (density at 25°C = 1,23 g/cm^3).



√ Calculate the amount of diisocyanate for having r = 1.

Estimate the gel time of the polyurethane at ambient temperature by knowing that the kinetic constant is $k_{25°} = 2 \times 10^{-5}$ l/mol.s, and that the polymer undergoes a volume shrinkage of 10% with crosslinking.

X **Question 3 (8 pts)**

Derive the equation of state of elasticity at constant pressure and constant volume, and comment on their applicability to the case of entropic-elastic materials.

PROVA 26 febbraio 2014

1] $\sim M_n^{\bullet} + M \rightleftharpoons \sim M_{n+1}$

$\Delta G = \Delta G° + RT \ln K$ (K: costante di equilibrio) $K = \frac{[M_{n+1}^{\bullet}]}{[M_n^{\bullet}][M]} \sim \frac{1}{[M]}$

? relazione T_c ; $[M]_c$ in funzione di $\Delta H°$; $\Delta S°$

$\Delta G° = \Delta H° - T\Delta S°$

all'equilibrio $\Delta G = 0$

$$0 = \Delta H° - T_c \Delta S° + RT_c \ln \frac{[M_{n+1}^{\bullet}]}{[M_n^{\bullet}][M]} =$$

$$T_c \left[+ \Delta S° + R \ln \frac{1}{[M]} \right] = + \Delta H° \qquad T_c = \frac{\Delta H°}{\Delta S° - R \ln \frac{1}{[M]}} = \frac{\Delta H°}{\Delta S° + R \ln [M]}$$

T_c non è univoca, dipende dalla concentrazione del monomero e, poichè $\Delta H° < 0$ T_c aumenta all'aumentare di $[M]$

2] $CH_3CH_2C(CH_2OH)_3$

100 g

$\rho = 1{,}08$ g/cm³

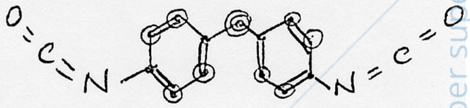
Ⓐ

$HO(CH_2)_6OH$

100 g

$\rho = 1{,}16$ g/cm³

Ⓑ



? g

$\rho = 1{,}23$ g/cm³

Ⓒ

? g_c : $r = 1$

$$r = 1 = \frac{[OH]}{[OCN]}$$

Ⓐ : P.M. $= 12 \cdot 6 + 1 \cdot 14 + 16 \cdot 3 = 134$ g/mol $\qquad \frac{100 \text{ g}}{134 \text{ g/mol}} = 0{,}746$ moli

Ⓑ : P.M. $= 2(1+16) + 6 \cdot (12+2) = \boxed{118}$ g/mol $\qquad \frac{100}{118} = 0{,}847$ moli

$\Rightarrow$ moli OH: $0{,}746 \cdot 3 + \boxed{0{,}847} \cdot 2 = 3{,}932$ = moli NCO

$\Rightarrow \frac{3{,}932}{2} = 1{,}966$ moli di Ⓒ

Ⓒ : P.M. $= (16+12+14) \cdot 2 + 13 \cdot 12 + 10 = 250$ g/mol

$1{,}966 \cdot 250 = 491{,}5$ g

$$P_{c\,FLORY} = \left[1 + \rho(f-2)\right]^{-\frac{1}{2}} = \left[1 + \cancel{3} \frac{0{,}746 \cdot 3}{3{,}932} (3-2)\right]^{-\frac{1}{2}} = 0{,}783$$

$v = Kc^2$ supponendo una cinetica del secondo ordine

February 2014

16

$$\sim M_n^* + M \underset{\xleftarrow{k_{dp}}}{\xrightarrow{k_2}} \sim M_{n+1}^{\bullet}$$

This process can be seen as a competition between propagation (k_2) and depolymerization (k_{dp}). k_2 and k_{dp} increase with T and become equal at the ceiling T. (T_c)

$\Delta G = \Delta G^\circ + RT\ln K_{eq}$

T_c

$[M]_c$

In the equilibrium: $\Delta G = 0 \rightarrow \Delta G^\circ = -RT\ln K_{eq}$

And $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K_{eq}$ (*)

$$K_{eq} = \frac{K_2}{K_{dp}} = \frac{[\cancel{-M_{n+1}^\bullet}]}{([\cancel{-M_n^\bullet}][M])} = \frac{1}{[M]}$$

hypothesis of steady state to macroradicals

(*) $\Delta H^\circ - T\Delta S^\circ = -RT\ln K_{eq}$

$$\Delta H^\circ = +T(\Delta S^\circ - R\ln K_{eq}) =$$

$$= T\left(\Delta S^\circ - R\ln\frac{1}{[M]_c}\right) = T(\Delta S^\circ + R\ln[M]_c) \rightarrow \boxed{T_c = \frac{\Delta H^\circ}{(\Delta S^\circ + R\ln[M]_c)}}$$

Above this temperature is impossible to carry out polymerization.

As $\Delta H^\circ < 0$ if the concentration of the monomer increases, the T_c will increase

(If the T increase the overall reaction rate increase)

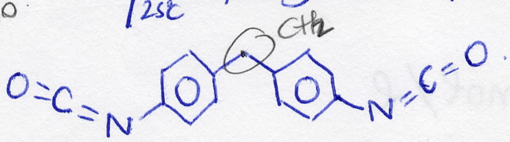
② Polyurethane

- ⓐ 100 g of trimethylpropane $CH_3CH_2C(CH_2OH)_3$ — 1 mol — $F=3$ $\rho_{25°C} = 1{,}08\ g/cm^3$
- ⓑ 100 g of 1,6 hexanediol $HO(CH_2)_6OH$ — $F=2$ $\rho_{25°C} = 1{,}16\ g/cm^3$
- ⓒ ? Methylene bis phenyl diisocyanate $C_{15}H_{10}N_2O_2$ — $\rho_{25°C} = 1{,}23\ g/cm^3$ $F=2$

$\boxed{r=1}$ → ?

⑧

Bifenilo $C_{12}H_{10}$



Polyurethanes: $\sim OH + OCN\sim$ COONH

$$r = 1 = \frac{[OH]}{[OCN]}$$

Ⓐ $P.M = 12\times6 + 14 + 16\times3 = 134\ g/mol \rightarrow N_A = \frac{100\ g}{134\ g/mol} = 0{,}746\ mol$

Ⓑ $P.M. = 2\times16 + 6\times12 + 14 = 118\ g/mol \rightarrow N_B = \frac{100\ g}{118\ g/mol} = 0{,}847\ mol$

Ⓒ $P.M = (16\times2) + (14\times2) + \underbrace{(12\times2)}_{C} + \underbrace{12\times13}_{C} + 10 = 250\ g/mol$

mol OH → $0{,}746\ mol \times 3 + 0{,}847 \times 2 = 3{,}932$ = mol of OCN

$$r = 1 = \frac{[OH]}{[OCN]} \rightarrow mol\ OCN = 3{,}932\ mol \cdot \frac{1}{2} = 1{,}966\ mol\ of\ ⓒ$$

$$1{,}966\ mol\ of\ ⓒ \times 250\ g/mol = \boxed{491{,}5\ g}$$

Gel time · T_R $K_{25°C} = 2 \times 10^{-5}$ l/mol·s $\quad \frac{3+2+2}{3} =$

Polymer undergoes a volume shrinkage of 10% with crosslinking

$$P_{c\,FLORY} = [1+\rho(f-2)]^{-\frac{1}{2}} = \left[1+\frac{0,746\times 3}{3,932}(3-2)\right]^{-1/2} = 0,783$$

$v = Kc^2 \to$ Considering a kinetic equation of 2nd order:

$$\Downarrow$$

$$-\frac{dc}{dt} = Kc^2 \to \frac{1}{c} - \frac{1}{c_0} = Kt \to \frac{1}{1-p} - 1 = ktc_0$$

$$\boxed{c_0} = \frac{[OH]}{V_{TOT}} = \frac{3,932}{0,58179} = \quad mol/l \qquad 1,08\ g/cm^3$$

$= 6,758$ mol/l $\to$ $\qquad \rho = \frac{M}{V}$; $V = \frac{M}{\rho} \to$

$V_a = 92,593\,cm^3 \times \frac{1\,m^3}{(100\,cm)^3} \times \frac{1000\,l}{1\,m^3} = 0,096\,l \to V_a = \frac{100}{1,08} = 92,593\,cm^3$

$V_b = 86,2\,cm^3 \times \frac{1\,m^3}{100^3\,cm^3} \times \frac{1000\,l}{1\,m^3} = 0,0862\,l \to V_b = \frac{100}{1,16} = 86,2\,cm^3$

$V_c = 399,59\,cm^3 \times \frac{1\,m^3}{100^3\,cm^3} \times \frac{1000\,l}{1\,m^3} = 0,39959\,l \to V_c = \frac{491,5}{1,23} = 399,59\,cm^3$

Shrinkage 10% $\to$

$$\to V_{TOT} = 0,58179 - \frac{10}{100}\,0,58179 = 0,523611\,l.$$

$$c_0 = \frac{3,932}{0,523611\,l} = 7,5\ mol/l$$

$$\frac{1}{1-0,783} - 1 = 2\cdot 10^{-5} \cdot 7,5 \cdot t \to$$

$$\to t = \frac{\frac{1}{1-0,783} - 1}{2\cdot 10^{-5} \cdot 7,5} = 24055,3\,s$$

$$\hookrightarrow \boxed{t \sim 6,7\ h}$$

Principles of Polymer Chemistry - exam session of July 9, 2014

Surname Name Matricola nr.

Question 1 (5 points). Explain what is the "gel effect" in free radical polymerizations, and represent it graphically. Suggest how to minimize / avoid this effect.

Question 2 (12 points). A bifunctional polyol (OH groups) with MW 1000 g/mol and density 1.1 g/ml must be stoichiometrically balanced (OH/NCO = 1) and crosslinked with a three-functional polyisocyanate with MW 600 g/mol and density 1.1 g/ml to give a polyurethane adhesive.

- By knowing that the kinetic constant $k_{25°C}$ of the step polyreaction is 5×10^{-4} l/mol.s, calculate the gel time at ambient temperature of the bicomponent polyurethane assuming additivity of volumes.
- How could we extend the gel time of the same adhesive to 150% its initial value without changing the temperature ?
- What's the gel time of a modified adhesive if we decide to crosslink the polyol with a polyisocyanate with an average functionality 2.5? (obtained by premixing the three-isocyanate MW 600 with a di-isocyanate MW 200 in proper amounts – assume density 1.1 g/ml also for the diisocyanate)

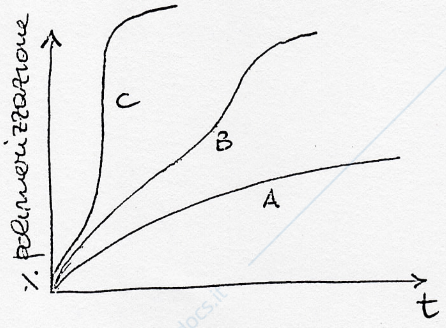
Question 3 (5 points). Calculate the low conversion azeotropic composition for a copolymerization process having $r_1 = 0.7$ and $r_2 = 0.1$. Show graphically the results in form of F_1-f_1 diagram.

Question 4 (8 points). Derive mathematically a suitable expression for the elastic retraction force of single polymeric chain in random coil conformation. Comment on the dependence of such a force on both the deformation and the temperature.

PROVA 1 luglio 2014

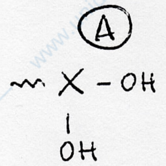
1] <u>GEL EFFECT</u> nella polimerizzazione radicalica

Effetto che si osserva al variare della concentrazione iniziale di monomero $[M]_0$ nella curva resa-tempo: all'aumentare di $[M]_0$ si osserva una variazione di pendenza della curva fino ad arrivare a un valore critico oltre il quale si osservano brusche variazioni che indicano un autoaccelerazione della polimerizzazione.



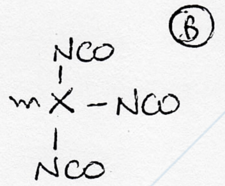
$[M]_{0A} < [M]_{0B} < [M]_{0C}$

2]



$\sim X(-OH)-OH$

$+$



$\sim X(-NCO)(-NCO)-NCO$

NO

M.W. 1000 g/mol

$\rho = 1{,}1$ g/ml

M.W. 600 g/mol

$\rho = 1{,}1$ g/ml

$r = 1$

$K_{25°C} = 5 \cdot 10^{-4} \frac{l}{mol \cdot s}$

? t_{gel}

? $t_{gel\,2} = 150\%\, t_{gel}$

? $f_{av} = 2{,}5$

$$\frac{\frac{X \text{ grammi}}{\text{peso mol}}}{\frac{Y \text{ grammi}}{\text{peso mol } Y}} = 1$$

$[OH] = [NCO]$ $\qquad x = \frac{5}{3} y$

considero 100 ml Ⓐ → $100 \text{ ml} \cdot 1{,}1 \text{ g/ml} = 110 \text{ g}$

$\frac{110}{1000} = 0{,}11$ moli Ⓐ $\Rightarrow 2 \cdot 0{,}11 = 0{,}22$ moli $[OH]$ = moli $[NCO]$

$\frac{0{,}22}{3} = 0{,}073$ moli Ⓑ

$0{,}073 \text{ mol} \cdot 600 \frac{g}{mol} = \frac{43{,}8 \text{ g}}{1{,}1 \text{ g/ml}} = 39{,}81$

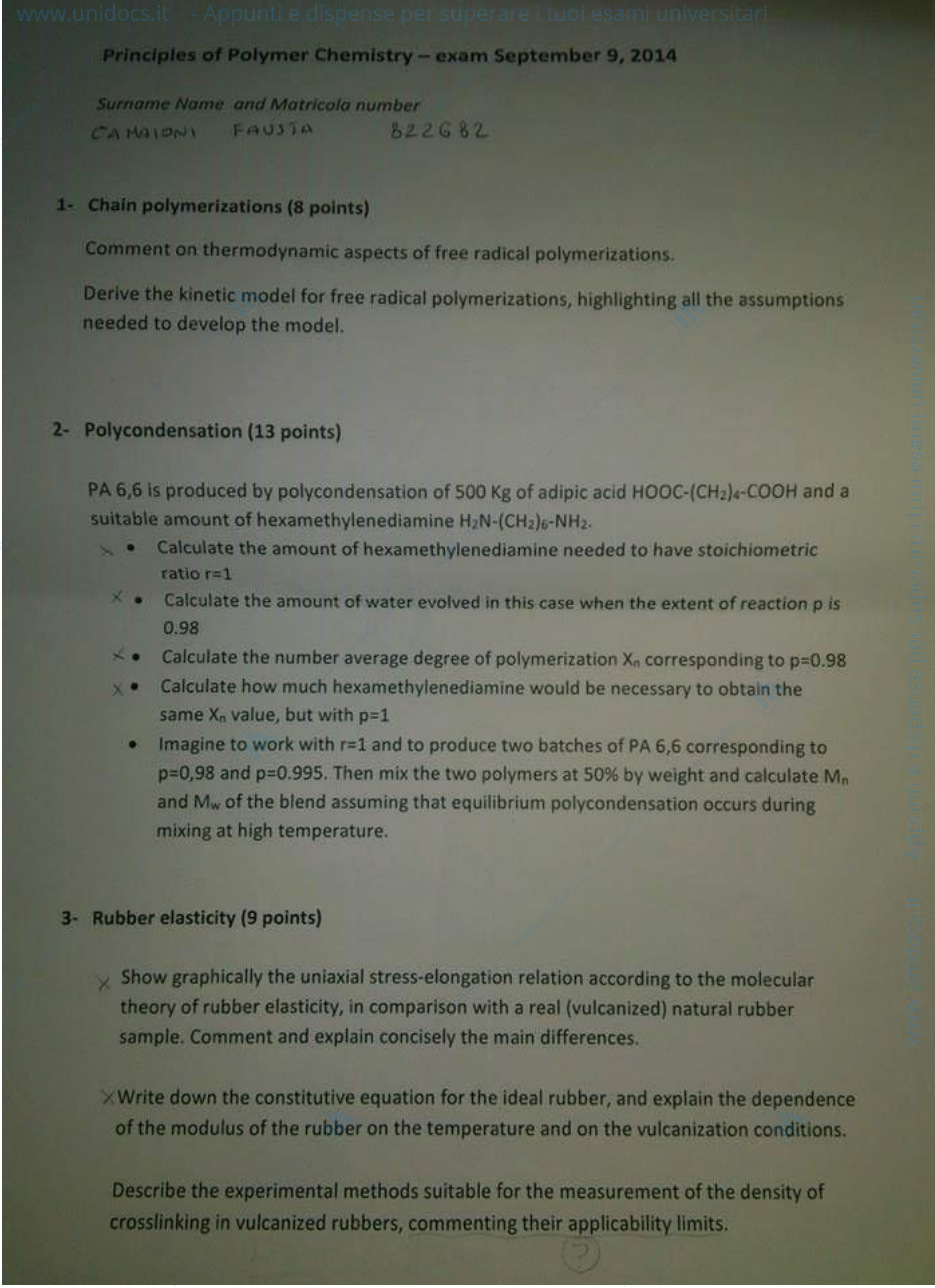
$$t_{gel} = \frac{1}{K C_0}\left(\frac{1}{1-P_c} - 1\right)$$

$$P_c = \left[1+\rho(f_{av}-2)\right]^{-\frac{1}{2}} = \left[1+3\right]^{-\frac{1}{2}} = \frac{1}{2} = 0{,}5$$

$$C_0 = \frac{[NCO]}{\boxed{V_{tot}}} = \frac{0{,}22}{139{,}81} = 1{,}57 \cdot \cancel{10^{3}}$$

$V_{tot} \to 100 \text{ ml Ⓐ} + 39{,}81 \text{ ml Ⓑ} = 139{,}81$

$$t_{gel} = \frac{1}{5 \cdot 10^{-4} \cdot 1{,}57}\left(\frac{1}{1-39{,}81} - 1\right) = -1306{,}7$$



Principles of Polymer Chemistry – exam September 9, 2014

Surname Name and Matricola number

CAMAIONI FAUSTA 822682

1- Chain polymerizations (8 points)

Comment on thermodynamic aspects of free radical polymerizations.

Derive the kinetic model for free radical polymerizations, highlighting all the assumptions needed to develop the model.

2- Polycondensation (13 points)

PA 6,6 is produced by polycondensation of 500 Kg of adipic acid $HOOC-(CH_2)_4-COOH$ and a suitable amount of hexamethylenediamine $H_2N-(CH_2)_6-NH_2$.

- Calculate the amount of hexamethylenediamine needed to have stoichiometric ratio r=1
- Calculate the amount of water evolved in this case when the extent of reaction p is 0.98
- Calculate the number average degree of polymerization X_n corresponding to p=0.98
- Calculate how much hexamethylenediamine would be necessary to obtain the same X_n value, but with p=1
- Imagine to work with r=1 and to produce two batches of PA 6,6 corresponding to p=0,98 and p=0.995. Then mix the two polymers at 50% by weight and calculate M_n and M_w of the blend assuming that equilibrium polycondensation occurs during mixing at high temperature.

3- Rubber elasticity (9 points)

Show graphically the uniaxial stress-elongation relation according to the molecular theory of rubber elasticity, in comparison with a real (vulcanized) natural rubber sample. Comment and explain concisely the main differences.

Write down the constitutive equation for the ideal rubber, and explain the dependence of the modulus of the rubber on the temperature and on the vulcanization conditions.

Describe the experimental methods suitable for the measurement of the density of crosslinking in vulcanized rubbers, commenting their applicability limits.

9

PRINCIPLES OF POLYMER CHEMISTRY

EXAM SESSION OF SEPT.25, 2014

SURNAME NAME:

MATRICOLA NR:

1) Question 1 – Copolymerization (12 points)

When two monomers A and B are copolymerized, an azeotrope copolymer is formed at a ratio of 1 mol of A and 2 mol of B. If monomer A is known not to homopolymerize:

- What polymer composition (expressed as molar fraction of A) will result initially when a mixture of 1 mol of A and 9 mol of B are copolymerized?
- Will the copolymer formed after 50% conversion from an initial mixture of 4 mol of A with 6 mol of B contain more or less of the same amount of A compared to that formed at 1% conversion?

2) Question 2 – Rubber technology (8 points)

Explain the chemistry and process monitoring (graphical representation) of elastomer vulcanization

3) Question 3 – Step polymerizations (10 points)

Derive mathematically the most probable distribution of molecular weights for step-growth polymerizations. (2-5 slides, My notes → 9)

By applying the suitable statistical relations, calculate the weight % of residual monomer for a step-growth polymerization run at r = 1 and p = 0,99.

$r = 1$

$p = 0,99$

$W_x =$

$$X_n = \frac{1+r}{1-r(2p-1)} = \frac{2}{1-(2 \cdot 0,99-1)} = \boxed{100}$$

Septembre 2014

① Copolymerization.

A - B

Azeotrope composition is formed at a ratio of 1 mol A / 2 mol B.

If monomer A is known not to homopolymerize:

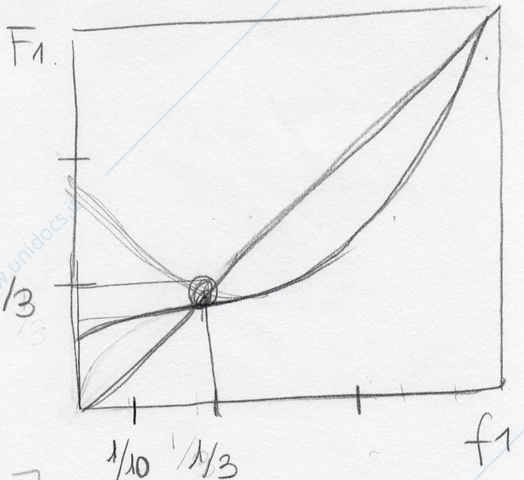
- Polymer composition (molar fraction of A) will result initially when a mix of 1 mol A + 9 mol B.

Azeotrope composition $\boxed{\begin{matrix}\mu = \Pi \\ f_1 = F_1\end{matrix}}$ $\frac{M_A}{M_B} = \frac{-d[M_A]}{-d[M_B]}$

$$\left.\begin{matrix}\frac{1}{f_1} = 1 + \frac{1}{\mu} \\ \frac{1}{F_1} = 1 + \frac{1}{\Pi}\end{matrix}\right\} \quad f_1 = \frac{1}{3} \quad F_1 = \frac{1}{3} \quad \mu = \frac{f_1}{1-f_1} = \frac{1/3}{1-1/3} = \frac{1/3}{2/3} = \frac{1}{2} //$$

$$\Pi = \frac{\cancel{\mu r_1}^{0} + 1}{1 + r_2/\mu} = \frac{1}{1+r_2/\mu} \quad (*)$$

A not homopolymerize → $\begin{cases} r_A = 0 \\ r_B < 1 \end{cases}$ → azeotropic composition



$$\left.\begin{matrix}M_1 = 1 \\ M_2 = 9\end{matrix}\right\} \quad f_1 = \frac{1}{10}$$

$$\mu = \frac{f_1}{1-f_1} = \frac{1/10}{10/10 - 1/10} = \frac{1/10}{9/10} = \frac{1}{9} //$$

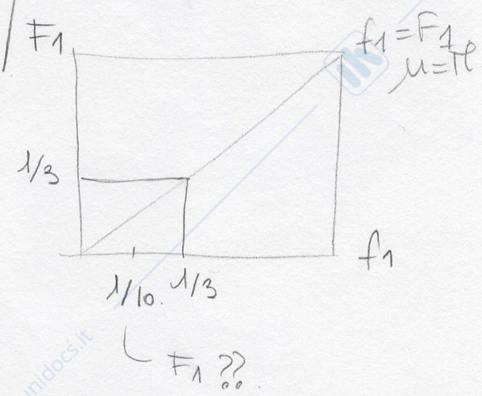
F_1 ?? $\boxed{\Pi = \frac{1}{1+r_2/\mu}} = \frac{1}{1 + \frac{1/2}{1/9}} = \frac{1}{1 + \frac{1}{18}} = \frac{18}{19}$

(*) $\Pi = \frac{1}{1+r_2/\mu} \rightarrow (1+r_2/\mu)\Pi = 1$

$\Pi + \frac{\Pi r_2}{\mu} = 1 \rightarrow$

$\rightarrow \mu\Pi + \Pi r_2 = \mu$

$$r_2 = \frac{\cancel{\mu}(1-\Pi)}{\cancel{\Pi}} = 1 - \Pi = 1 - \frac{1}{2} = \boxed{\frac{1}{2}}$$



$$\frac{1}{F_1} = 1 + \frac{1}{\Pi}$$

$$\boxed{F_1 = 0{,}486}$$

b) After 50% conversion 4 mol A + 6 mol B
$\overset{}{\text{②}}$ ①

Poly. contained more or less of the same amount of A compared to that formed at 1%. ?

cambio indices 1 y 2

50% conversion 4 mol A + 6 mol B. (monomer mixture)

$(f_1)_0 = \frac{6}{10}$ $(f_2)_0 \frac{4}{10}$

$r_1 = 1/2$ $r_2 = 0$

The copolymer formed will be richer in (M_B) since $r_A = 0$. As the conversion increases there will be a drift of the composition of the monomer mixture is progressively enriched by the less reactive (A)

$$1 - \frac{M}{M_0} = 1 - \left[\frac{f_1}{6/10}\right]^{\alpha} \left[\frac{f_2}{4/10}\right]$$

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Principles of Polymer Chemistry - Exam Session of September 28, 2015

Question 1 (score 5).

Explain what is the “gel effect” in free radical polymerizations, and represent it graphically. Suggest how to minimize this effect.

Question 2 (score 9).

A bifunctional polyol (OH groups) with MW 2000 g/mol and density 1.05 g/ml is stoichiometrically balanced (OH/NCO = 1) and crosslinked with a three-functional polyisocyanate with MW 600 g/mol and density 1.1 g/ml to give a polyurethane. By knowing that the kinetic constant $k_{25°C}$ of the step polyreaction is 5 x 10^{-3} l/mol.s, calculate the gel time at ambient temperature of the bicomponent polyurethane assuming additivity of volumes.

Question 3 (score 3)

Control of molecular weight in anionic living polymerizations

Question 4 (score 5).

Calculate the heat evolved during a 300% uniaxial deformation at +20°C of a strip of rubber having dimensions 10x2x80 mm, and density of crosslinking = 10^{-5} mol/cm^3

Question 5 (score 8).

Show graphically the rheological process monitoring of vulcanization, and show the most suitable (isothermal) kinetic models