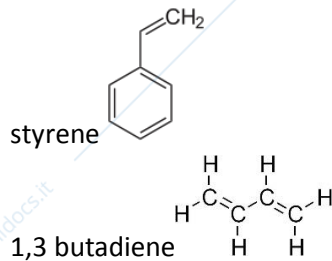


PRINCIPLES OF POLYMER CHEMISTRY – exam session September 7, 2015

Question 1 (score 8)

You want to obtain a styrene-butadiene random copolymer (SBR) with 30% by weight of styrene monomer.



By knowing the appropriate Alfrey-Price parameters ($Q=1$ and $e=-0.08$ for styrene; $Q=2.39$ and $e=-1.05$ for butadiene), calculate the molar fraction of the two monomers in the initial monomer feed.

Draw (approximately) the corresponding F_1-f_1 diagrams.

Question 2 (score 4)

Show the effect of chain transfer agents on molecular weight control in free radical polymerizations

Question 3 (score 6)

Calculate the maximum degree of polymerization that can be achieved through a step polycondensation carried out in a closed system, by knowing the the equilibrium constant $K_{eq} = 45$ and the stoichiometric ratio $r = 0.995$.

Question 4 (score 7)

Show the equation of state of elasticity at constant pressure and constant volume, and obtain a suitable expression for the elastic retraction force in case of a purely entropic-elastic material.

Question 5 (score 5)

Graphical representation and physical interpretation of the Payne effect.

Principles of Polymer Chemistry – exam session July 9, 2015

1- Question 1 (score 6)

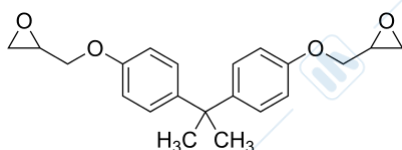
Polymerization of 0.5 mol/l solution of methylmethacrylate monomer (FW = 100.1 g/mol) in an inert solvent at 60°C leads to a polymethylmethacrylate sample with $M_n = 500000$. What concentration of chain transfer (in g/l) will reduce the molecular weight to 100000? ($C_i = 0.270$, FW of chain transfer = 331.65 g/mol, assume there is no chain transfer with the monomer)

2- Question 2 (score 5)

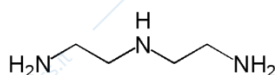
Show the relation among degree of polymerization, stoichiometric ratio and extent of reaction in step polymerizations

3- Question 3 (score 7)

An epoxy resin having the following structure



must be crosslinked with a polyamine having the following structure



Calculate the composition of the stoichiometrically balanced bicomponent formulation (expressed as percentage by weight of the two components), and estimate the conversion at the gel point according to the Carothers and Flory methods.

4- Question 4 (score 6)

Show the expression of the elastic retraction force for a single gaussian chain; comment briefly on the simplifying assumptions introduced.

5- Question 5 (score 6)

The Mooney-Rivlin equation: graphical representation and comparison with behavior predicted by molecular theory of rubber.

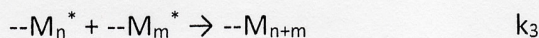
Principles of Polymer Chemistry – exam session February 1, 2016

Surname Name

Matricola Number:

✓ Question 1 (score 5)

Derive a suitable expression of the rate of reaction and the degree of polymerization for a free radical chain polymerization with a pure thermal initiation, according to the following scheme



✓ Question 2 (score 4)

Represent graphically the phenomenon of thermoelastic inversion in rubber materials. Explain briefly how the experiment is realized, and the physical interpretation of results.

✓ Question 3 (score 7)

Given a rubber material with $M_c = 10000$ g/mol and density at $20^\circ\text{C} = 1.1$ g/cm³, calculate:

- ✗ the shear modulus G at 20°C
 - the stress needed to obtain a uniaxial deformation $\lambda_1 = 3$
 - the heat exchanged during the mechanical deformation
- ($R = 8.31$ J/mol.K $k_B = 1.38 \times 10^{-23}$ J/K $N_A = 6.02 \times 10^{23}$ mol⁻¹)

Question 4 (score 8)

You want to produce a polyester resin for coating, by reaction of 1.05 Kmol of ethylene glycol HO-(CH₂)₂-OH and 1 Kmol of succinic acid HOOC-(CH₂)₂-COOH. In order to make easier the following curing process and to improve the coating adhesion to the substrate, it is important that the resin shows some residual -COOH groups.

The polycondensation reaction is stopped after distillation of 35 Kg of water. Calculate:

- ✗ the molecular weight of the polyester produced, neglecting the end groups contribution
- ✗ the residual acidity of the polyester produced, expressed as mmol COOH / g polymer

Question 5 (score 6)

Show graphically and comment briefly how both isotactic and syndiotactic polymers could be obtained through metallocene catalysis (molecular symmetry considerations)

Principles of Polymer Chemistry – exam questions

- ① Show the most probable distribution of molecular weights for step polymerizations (demonstration). After mixing at high temperature 1 Kg of polyester (monodisperse) with $M = 20000$ and 1 Kg of polyester (monodisperse) with $M = 40000$, calculate the limiting value of M_n and M_w for the resulting blend if transesterification occurs

? A mi me queda 30000

- ② Let's consider the following monomer pair and their corresponding Alfrey-Price parameters:

monomer	molecular weight (g/mol)	Q	e
styrene	104	1.0	-0.8
acrylonitrile	53	0.6	1.2

Calculate the molar fraction of styrene in the monomer feed for a low conversion free radical copolymerization process, in order to produce a SAN copolymer (Styrene-Acrylonitrile random copolymer) containing 10% by weight of acrylonitrile

f₁

- ③ Show the mathematical expression of the elastic retraction force for a single Gaussian macromolecular chain, and comment concisely the differences with the classical Hook's law

- ④ A free radical polymerization process is considered with the following data

Temperature = 303 K

Monomer concentration = 0,2 mol/l

Initiator concentration = 0,002 mol/l

$K_{\text{initiation}} = 1 \times 10^{-5} \text{ s}^{-1}$

$K_{\text{propagation}} = 2 \times 10^{+6} \text{ l/mol s}$

$K_{\text{termination}} = 5 \times 10^{+8} \text{ l/mol s}$

Calculate the low conversion average degree of polymerization X_n if termination occurs 50% by combination and 50% by disproportionation?

→ Calculate the average degree of polymerization if the same process is run in presence of a chain transfer agent S (use $[S] = 0,001 \text{ mol/l}$, and $K_{tr} = 5 \times 10^{+3} \text{ l/mol s}$)

I

- ⑤ Obtain the constitutive equation of the ideal rubber according to the molecular theory of rubber elasticity. Show graphically the main deviations from the behavior of the real material, and give an explanation

- ⑥ Show the various steps of the anionic polymerization of styrene in $\text{NH}_3/\text{NaNH}_2$. Show the suitable expressions for the rate of polymerization and the average degree of polymerization X_n

- (7) PA 6,6 is produced by polycondensation of 100 Kg of adipic acid $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ and a suitable amount of hexamethylenediamine $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$. 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 0.95. Calculate the number average degree of polymerization X_n corresponding to $p=0.95$. 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 $p=0.99$ and $p=0.995$. Then mix the two polymers at 50% by weight and calculate M_n and M_w of the blend (neglecting the end groups)
- (8) 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.
- (9) 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.
- ✓ (10) Calculate the azeotropic composition a copolymerization having $r_1=0.3$ and $r_2=0.1$. Show graphically the corresponding F_1-f_1 diagram
- (11) Explain briefly the methods to determine/estimate the reactivity ratios
- (12) A generic cationic polymerization process consists of only three steps (HX is the acid initiator, M is the monomer):
- Initiation
 $\text{HX} + \text{M} \rightarrow \text{MH}^+\text{X}^-$
- Propagation
 $--\text{M}_n\text{H}^+\text{X}^- + \text{M} \rightarrow --\text{M}_{n+1}\text{H}^+\text{X}^-$
- Termination
 $--\text{M}_n\text{H}^+\text{X}^- \rightarrow --\text{M}_n + \text{HX}$ (thermal dissociation)
- Derive the mathematical relations for the the rate of polymerization, and for the average degree of polymerization X_n .
- (13) Two batches of PA 6.6 are prepared by polycondensation of 140 Kg of adipic acid $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ and 110 Kg of hexamethylenediamine $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$. The former batch is stopped after distillation of 32.0 Kg of water, the latter after distillation of 33.5 Kg. Calculate M_n and M_w of the polyamides obtained in both cases, assuming the most probable distribution of molecular weights and neglecting the contribution of end groups. A blend is then made by melt mixing 50% by weight of polymer A with 50% by weight of polymer B; calculate M_n and M_w also for this mixture. What happens to M_n and M_w of the blends if equilibrium transamidation reactions occur during mechanical mixing?

- 14) Explain concisely the role of chain transfer in free radical polymerization with respect to:
- the molecular weight of the final polymer
 - the overall kinetics of polymerization
 - the polymer morphology (i.e. the degree of crystallinity in case of regular structure polymers)
- 15) Show the Carothers and Flory-Stockmayer approaches for the estimation of the critical extent of reaction p_c at gelation in case of polyfunctional step polymerizations. Apply the two models to find p_c for the general case of a monomer mixture made of 0.4 mols of A_3 (trifunctional monomer) + 0.6 mols of A_2 (bifunctional monomer), to be counterbalanced with a proper amount of B_2 (bifunctional monomer), so that the overall stoichiometric ratio $r = A/B = 1$.

EXAM QUESTIONS (POLYMERS)

① Most probable dist. of M.W for step polymerizations

Considering $r=1$ and end group reactivity independent on molecular weight.

$n_x = \frac{N_x}{N}$ The probability of finding a polymer chain of length x is given by its molar fraction.

$1 =$ probability to have at least one monomeric unit

$p =$ probability of reaction.

$1 \cdot p =$ probability to have a dimer.

$1 \cdot p \cdot p =$ probability to have a trimer.

$n_x = p^{(x-1)} (1-p)$ being $(1-p) =$ probability of (further) non-reaction.

$$w_x = \frac{N_x M_x}{N_0 M_0} = \frac{N_x \cdot x \cdot M_0}{N_0 M_0} = \frac{N_x \cdot x}{N_0}$$

$$N_x = n_x \cdot N = n_x \cdot N_0 (1-p)$$

$$= \frac{n_x \cdot N_0 (1-p)}{N_0} = x p^{(x-1)} (1-p)^2 \rightarrow \boxed{w_x = x p^{(x-1)} (1-p)^2}$$

Most probable distribution:

$$\overline{X_n} = \sum_{i=1}^{\infty} n_i x_i = \sum_{i=1}^{\infty} p^{(i-1)} (1-p) \cdot i = (1-p) \sum_{i=1}^{\infty} p^{(i-1)} \cdot i = \boxed{\frac{1}{1-p}}$$

$$\overline{X_w} = \sum_{i=1}^{\infty} w_i x_i = \sum_{i=1}^{\infty} i^2 p^{(i-1)} (1-p)^2 = (1-p)^2 \sum_{i=1}^{\infty} i^2 \cdot p^{(i-1)} = \boxed{\frac{1+p}{1-p}}$$

- Ⓐ 1 Kg PE (monodisperse) $M = 20000$
- Ⓑ 1 Kg PE (monodisperse) $M = 40000$

Calculate the limiting value of M_n and M_w

$$N_A = \frac{1000 \text{ g}}{20000 \text{ g/mol}} = 0,05 \text{ mol}$$

$$N_B = \frac{1000 \text{ g}}{40000 \text{ g/mol}} = 0,025 \text{ mol}$$

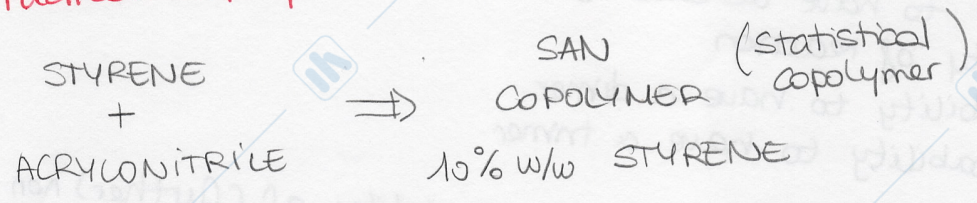
$$M_n = \frac{\sum_{i=1}^2 N_i M_i}{\sum N_i} = \frac{0,05 \cdot 20000 + 0,025 \cdot 40000}{0,05 + 0,025} = 26667 \text{ g/mol}$$

$$M_w = \frac{\sum_{i=1}^2 N_i M_i^2}{\sum_{i=1}^2 N_i M_i} = \frac{0,05 \cdot 20000^2 + 0,025 \cdot 40000^2}{0,05 \cdot 20000 + 0,025 \cdot 40000} = 30000 \text{ g/mol}$$

②

Monomer	Molecular weight g/mol	Q	e
① styrene	104	1	-0,8
② Acrylonitrile	53	0,6	1,2

Molar fraction of styrene in the monomer feed low conversion
 free radical copolymerization SAN copolymer \Rightarrow 10% weight of styrene.
 acrylonitrile.



Reactivity ratios:

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)] \quad ; \quad r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)]$$

$$r_1 = \frac{1}{0,6} \exp[0,8(-0,8 - 1,2)] = 0,336 = \frac{K_{11}}{K_{12}}$$

$$r_2 = \frac{0,6}{1} \exp[-1,2(1,2 + 0,8)] = 0,0544 = \frac{K_{22}}{K_{21}}$$

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} = \frac{r_1 \mu + 1}{1 + r_2 \mu} \rightarrow \text{Instantaneous Composition}$$

$$\mu = \frac{[M_1]}{[M_2]} \Rightarrow \text{Composition of the monomer mixture}$$

SAN 10% w/w of styrene.
 1000g of SAN
 \rightarrow 900g of styrene \rightarrow
 \rightarrow 100g of acrylonitrile \rightarrow
 $n_1 = \frac{900g}{104g/mol} = 8,65 \text{ mol} \Rightarrow$
 $n_2 = \frac{100g}{53g/mol} = 1,89 \text{ mol}$

molar fractions \Rightarrow

$$F_1 = \frac{8,65}{8,65 + 1,89} = 0,82$$

$$F_2 = \frac{1,89}{8,65 + 1,89} = 0,18$$

$$\pi = \frac{-d[M_1]}{-d[M_2]} = \frac{8,65}{1,89} = 4,58 \quad ; \quad \pi = \frac{r_1 \mu + 1}{1 + r_2 \mu} \rightarrow (1 + r_2 \mu) \pi = r_1 \mu + 1$$

$$\Rightarrow \pi + \frac{r_2}{\mu} \pi = r_1 \mu + 1 \rightarrow \mu \pi + r_2 \pi = r_1 \mu^2 + \mu$$

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

$$\mu = \frac{-(1 - \pi) \pm \sqrt{(1 - \pi)^2 + 4 \cdot r_1 \cdot r_2 \pi}}{2 r_1} = \frac{-(1 - 4,58) \pm \sqrt{(1 - 4,58)^2 + 4 \cdot 0,336 \cdot 0,0544 \cdot 4,58}}{2 \cdot 0,336}$$

$$= \begin{matrix} 10,7 \\ -0,07 \end{matrix}$$

5

$\mu = 10,7$; The solution $\mu = -0,07$ it is not valid since it is negative.

$$\frac{1}{f_1} = 1 + \frac{1}{\mu} \rightarrow \frac{1}{f_1} = 1 + \frac{1}{10,7}$$

$f_1 = 0,91$ Molar fraction of styrene in the monomer feed.

④ Free radical polymerization

$T = 303\text{ K}$

$[M] = 0,2\text{ mol/l}$

$[I] = 0,002\text{ mol/l}$

$k_1 = 1 \cdot 10^{-5}\text{ s}^{-1}$

$k_2 = 2 \cdot 10^6\text{ mol/l/mols}$

$k_3 = 5 \cdot 10^8\text{ l/mols}$

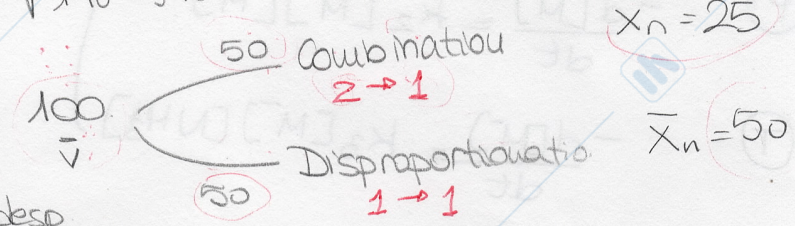
Low conversion average ~~eff~~ degree of polymerization \bar{X}_n 50% combination 50% disproportionation

$$\bar{V} = \frac{V_{prop}}{V_{tem} = V_{iniz}} = \frac{k_2}{\sqrt{k_1 k_3}} \frac{[M]}{[I]^{0,5}} =$$

$$= \frac{2 \cdot 10^6}{\sqrt{1 \cdot 10^{-5} \cdot 5 \cdot 10^8}} \frac{0,2}{(0,002)^{0,5}} = 126491,11$$

$\bar{X}_n = 25$

Combination $\bar{X}_u = 2\bar{V}$
Disproportionation $\bar{X}_n = \bar{V}$



$$\bar{X}_n = \frac{25}{75} \cdot 126491 \cdot 2 + \frac{50}{75} \cdot 126491 = 168654$$

$[S] = 0,001\text{ mol/l}$; $k_{tr} = 5 \cdot 10^3\text{ l/mols}$

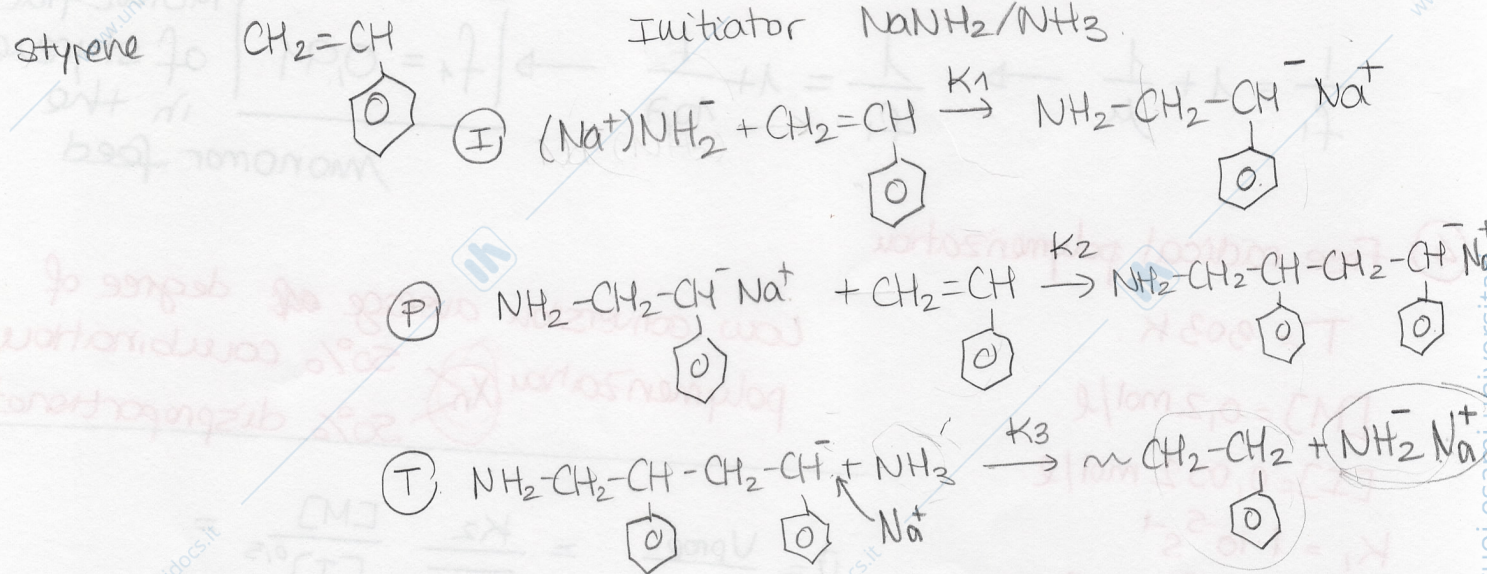
$$\frac{1}{(\bar{V}_n)} = \left(\frac{1}{\bar{V}_n} \right)_0 + \frac{k_{tr}}{k_2} \frac{[S]}{[M]} = \left(\frac{1}{126491} \right) + \frac{5 \cdot 10^3}{2 \cdot 10^6} \frac{[0,001]}{[0,2]} \Rightarrow$$

$$\Rightarrow \bar{V} = 49005,9 \rightarrow \bar{X}_u = \frac{25}{75} \cdot 49005,9 \cdot 2 + \frac{50}{75} \cdot 49005,9 =$$

$= 65341,2$

$\bar{X}_u = 65341,2$

⑥ Various steps of the anionic polymerization of styrene in $\text{NH}_3/\text{NaNH}_2$. Rate of polymerization and degree of polym.



(I) $\frac{d[\text{M}^-]}{dt} = K_1 [\text{I}] [\text{M}]$

(P) $-\frac{d[\text{M}]}{dt} = K_2 [\text{M}^-] [\text{M}]$

(T) $-\frac{d[\text{M}^-]}{dt} = K_3 [\text{M}^-] [\text{NH}_3]$

Steady-state assumption:

$-\frac{d[\text{M}]}{dt} = +\frac{d[\text{M}^-]}{dt}$

$K_1 [\text{I}] [\text{M}] = K_3 [\text{M}^-] [\text{NH}_3]$

$[\text{M}^-] = \frac{K_1 [\text{I}] [\text{M}]}{K_3 [\text{NH}_3]}$

$\bar{V}_p = -\frac{d[\text{M}]}{dt} = K_2 [\text{M}^-] [\text{M}] = \frac{K_1 K_2}{K_3} \frac{[\text{I}] [\text{M}]^2}{[\text{NH}_3]}$

$\bar{X}_n = \frac{\bar{V}_p}{\bar{V}_t} = \frac{K_2 [\text{M}^-] [\text{M}]}{K_3 [\text{M}^-] [\text{NH}_3]} = \frac{K_2 [\text{M}]}{K_3 [\text{NH}_3]}$

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