Polymer chemistry and macromolecular engineering
Fall 2024
Assignment 4

1) What are the main differences between ionic and radical chain polymerization? (state three differences)

Selectivity

- Radicals are not selective,
- Electron releasing substituent Y in cationic polymerization,
- Electron withdrawing substituent Y in anionic polymerization

Nature of the propagating species

- Radical polymerization: single species
- Ionic polymerization: multiple (coexisting) species

-BA	$-B^{+}A^{-}$	$-B^{+}\|\|A^{-}$	$-B^{+} + A^{-}$
Covalent species	*Tight/contact ion pair (charges not separated by solvent)*	*Solvent separated/ loose ion pair*	*Free ions*

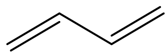
Termination

- Radical polymerization: predominantly via coupling (bimolecular)
- Ionic polymerization: propagating chains react with solvent, counter ion or something else

Kinetics

- Ionic reactions proceed at a very fast rate compared to radical polymerization and therefore, the reactions rates are irreproducible.

2) Consider the cationic polymerization of 1,3-butadiene ([M] = 3 M) using $AlCl_3$ as **co-initiator** and $(CH_3)_3CCl$ as **initiator**. The rate constants for initiation, propagation and termination are $k_i = 60 \times 10^{-3}\ M^{-1}s^{-1}$, $k_p = 2.5\ M^{-1}s^{-1}$ and $k_t = 5 \times 10^{-3}\ s^{-1}$, respectively.



1,3-butadiene

a) The polymerization of 1,3-butadiene can proceed via two different pathways: 1,2–polymerization and 1,4–polymerization. Draw all possible isomeric repeating units of polybutadiene.

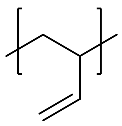
b) Derive the rate of polymerization (R_p) equation.

c) Calculate the degree of polymerization of polybutadiene. Assume that there are no chain transfer reactions occurring.

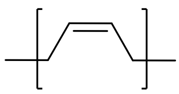
d) Now consider that a transfer agent was added to the reaction at a concentration of 30 mM. The rate constant of the chain transfer to the transfer agent (k_{trs}) is $1.5\ M^{-1}s^{-1}$. What is the new degree of polymerization?

a)

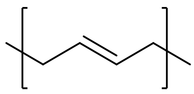
1,2-polymerization



1,4-polymerization



cis-isomer



trans-isomer

b) Initiation:

$$I_{\text{Co-Initiator}} + ZY_{\text{Initiator}} \overset{K}{\rightleftharpoons} Y^+(IZ^-) \quad \text{fast}$$

$$Y^+(IZ^-) + M \xrightarrow{k_i} YM^+(IZ^-) \quad \text{slow}$$

Propagation:

$$HM_n^+(IZ^-) + M \xrightarrow{k_p} HM_nM^+(IZ^-)$$

Termination:

$$HM_nM^+(IZ^-) \xrightarrow{k_t} HM_nMIZ$$

$$R_i = k_i[Y^+(IZ)^-][M] \text{ and } K = \frac{[Y^+(IZ)^-]}{[I][ZY]} \rightarrow R_i = k_iK[I][ZY][M]$$

$R_p = k_p[Y^+(IZ)^-][M]$ → $[Y^+(IZ)^-]$ can be replaced → <u>steady state assumption</u> ($R_i = R_t$)

$$R_t = k_t[Y^+(IZ)^-]$$

Therefore:

$$R_p = k_p \frac{R_t}{k_t}[M] = k_p \frac{R_i}{k_t}[M] = k_p \frac{k_i K[I][ZY][M]}{k_t}[M] = \frac{k_p k_i K[I][ZY][M]^2}{k_t}$$

c) $X_n = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t} = \frac{2.5\ M^{-1}s^{-1} \times 3\ M}{0.005\ s^{-1}} = 1500$

d) $R_i = R_t + R_{trs}$ with $R_t = k_t[Y^+(IZ)^-]$ and $R_{trs} = k_{trs}[Y^+(IZ)^-][S]$

$$R_p = k_p[Y^+(IZ)^-][M]$$

$$X_n = \frac{R_p}{R_t + R_{trs}} = \frac{k_p[Y^+(IZ)^-][M]}{k_t[Y^+(IZ)^-] + k_{trs}[Y^+(IZ)^-]\,[S]} = \frac{k_p[M]}{(k_t + k_{trs}[S])} = \frac{2.5 \times 3}{(5 \times 10^{-3} + 1.5 \times 30 \times 10^{-3})} = 150$$

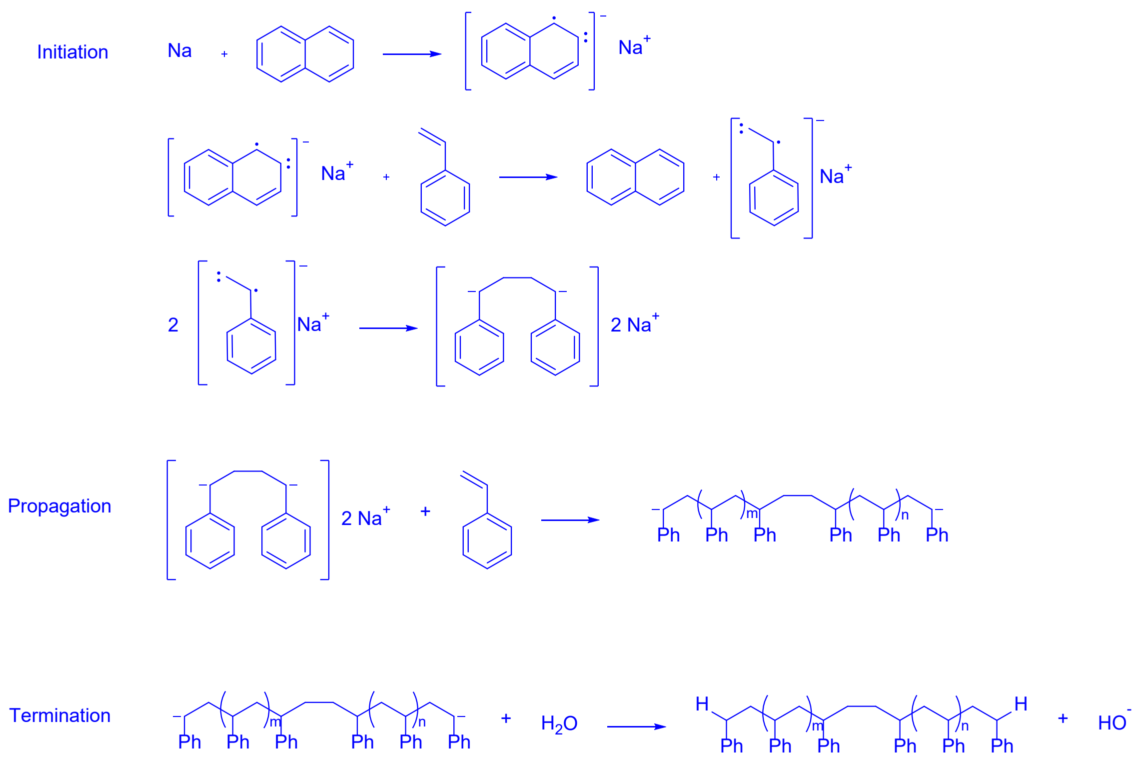
3) For the synthesis of polystyrene, 5 g styrene (M=104.15 g/mol) is dissolved in 250 mL THF. The polymerization is initiated using sodium naphthalene. The concentration of anions initiating the polymerization ([M^-]) is 0.01M. After 2h, the polymerization is stopped at a conversion of p = 0.95 by the addition of water.

a) Illustrate the initiation, propagation and termination of the polymerization.

b) Calculate the dissociation constant of sodium polystyrene, if $k_p^{\pm}$ = 0.3 L mol^{-1} sec^{-1} and k_p^- = 75 L mol^{-1} sec^{-1}.

c) The same reaction is carried out in the presence of 0.05M sodium tetraphenylborate. The parameters of this polymerization are as follows: $k_p^{\pm}$ = 1.5 × 10^{-3} Lmol^{-1}sec^{-1} and k_p^- = 5000 L.mol.sec^{-1}. Calculate the dissociation constant of sodium tetraphenylborate $K_{D\ \text{sodiumtetraphenylborate}}$.

a)



b)

$$R_p = \frac{-d[M]}{dt} = k_p^{app}[M^-][M]$$

$$\frac{-d[M]}{[M]} = k_p^{app}[M^-]\,dt$$

$$\ln\frac{[M]_0}{[M]} = k_p^{app}[M^-]\,t$$

$$p = \frac{[M]_0 - [M]}{[M]_0} \rightarrow [M] = [M]_0\,(1-p)$$

$$\ln\frac{[M]_0}{[M]_0\,(1-p)} = \ln\frac{1}{(1-p)} = -\ln(1-p) = k_p^{app}[M^-]\,t$$

$$\ln(1-p) = -k_p^{app}[M^-]t$$

$$k_p^{app} = -\frac{\ln(1-p)}{[M^-]t} = -\frac{\ln(0.05)}{[0.01M]\times 7200s} = 41.6\times 10^{-3}M^{-1}s^{-1}$$

Anionic polymer chain + counterion is assumed weakly dissociating salt:

$$k_p^{app} = k_p^{\pm} + \frac{(k_p^{-} - k_p^{\pm})[K]^{0.5}}{[M^-]^{0.5}}$$

$$K = [\frac{(k_p^{app} - k_p^{\pm})[M^-]^{0.5}}{k_p^{-} - k_p^{\pm}}]^2 = [\frac{(41.6\times 10^{-3}M^{-1}s^{-1} - 0.3M^{-1}s^{-1})[0.01M]^{0.5}}{75M^{-1}s^{-1} - 0.3M^{-1}s^{-1}}]^2$$

$$= 1.20\times 10^{-7}\mathrm{M}$$

c) Strongly dissociating salt was added to mixture:

$$k_p^{app} = k_p^{\pm} + \frac{(k_p^{-} - k_p^{\pm})K}{[CZ]}$$

$$K = \frac{(k_p^{app} - k_p^{\pm})[CZ]}{(k_p^{-} - k_p^{\pm})} = \frac{(41.6\times 10^{-3}M^{-1}s^{-1} - 0.0015M^{-1}s^{-1})[0.05M]}{(5000M^{-1}s^{-1} - 0.0015M^{-1}s^{-1})}$$

$$= 4.01\times 10^{-7}\mathrm{M}$$