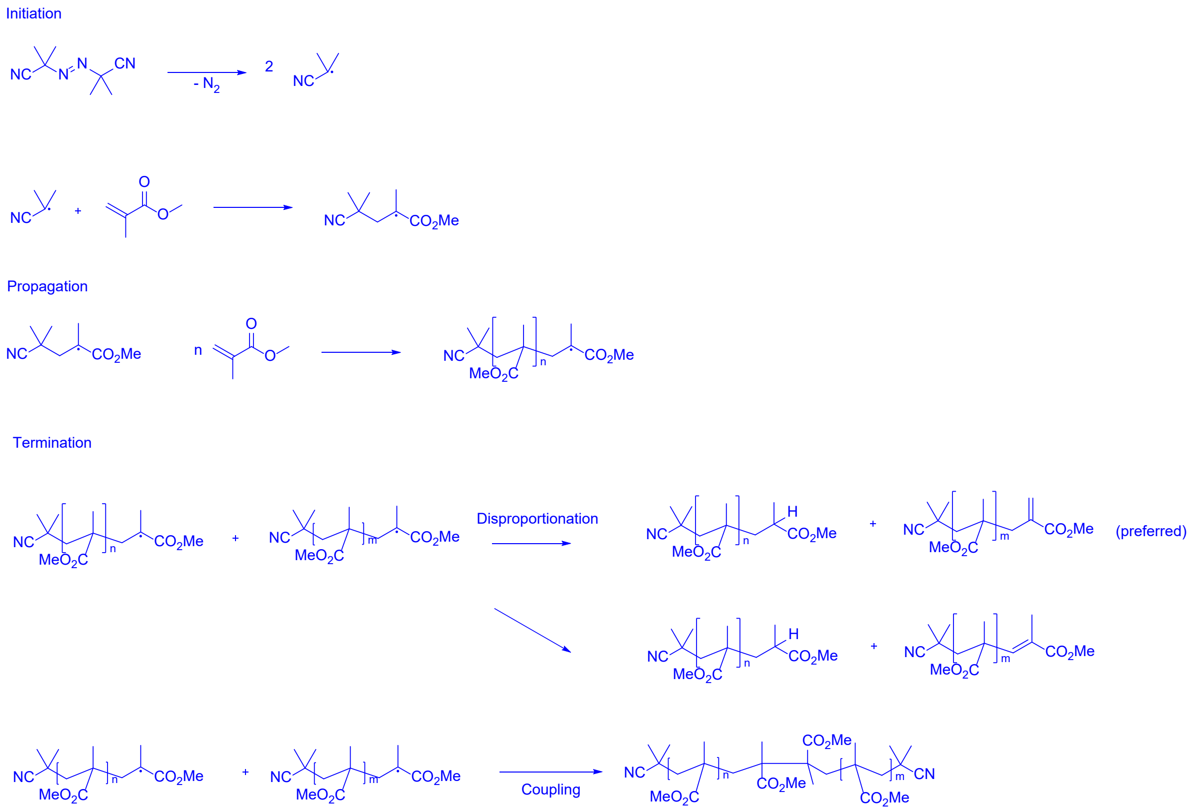
Polymer chemistry and macromolecular engineering
Fall 2024
Assignment 3-Solutions

1. Consider the radical polymerization of methyl methacrylate MMA (1.5 M in toluene) at 70°C. Two polymer chemists decided to run the same polymerization using two different initiators: AIBN (system A) and benzoyl peroxide (system B). All the necessary values are given in the table below. The radical concentrations in both cases are assumed to stay constant during the polymerizations. The molecular weight of methyl methacrylate is 100.12 g/mol.

	[I]	$t_{1/2}$	**[M·]**	k_t	k_p
System A	$4.0 \cdot 10^{-4}$ M	4.8 h	$1.4 \cdot 10^{-7}$ M	$6.3 \cdot 10^{5}$ M^{-1} s^{-1}	476 M^{-1} s^{-1}
System B	$6.0 \cdot 10^{-4}$ M	7.3 h	$1.2 \cdot 10^{-7}$ M	$6.3 \cdot 10^{5}$ M^{-1} s^{-1}	476 M^{-1} s^{-1}

a) Draw the reaction schemes for the initiation, propagation and all possible termination steps of the radical polymerization of MMA (use AIBN as the initiator).



b) Was the initiator of system A or B more efficient?

$$R_i = 2fk_d[I] \rightarrow f = \frac{R_i}{2k_d[I]}$$

$$k_d = \frac{0.693}{t_{1/2}}$$

$$k_{d,\ AIBN} = 4.01 \cdot 10^{-5}\ s^{-1}$$

$$k_{d,\ DBPO} = 2.64 \cdot 10^{-5} s^{-1}$$

$$R_i = 2[M\ \cdot]^2 k_t$$

$$R_{i,\ AIBN} = 2.47 \cdot 10^{-8}\ mol\ L^{-1} s^{-1}$$

$$R_{i,\ DBPO} = 1.81 \cdot 10^{-8}\ mol\ L^{-1} s^{-1}$$

$$\boldsymbol{f}_{\boldsymbol{AIBN}} = \mathbf{0.77}$$

$$\boldsymbol{f}_{\boldsymbol{DBPO}} = \mathbf{0.57}$$

→ **AIBN is a more efficient initiator.**

c) What are the experimental methods to determine the initiator efficiency?

1. Measuring and comparing (a) initiator decomposition and (b) the production of polymer molecules: in case of AIBN N2 evolution or measuring Mn
2. End-group analysis
3. Radical scavengers, for example DPPH
4. Dead-end polymerization

d) The monomer conversion was followed by taking samples of the polymerization mixture after 1 h and 15 h. What monomer conversion values can be expected for system A?

$$R_p = -\frac{d[M]}{dt} = k_p[\mathrm{M}]\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}$$

$$-\frac{d[M]}{[M]} = k_p\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}} dt$$

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}} t$$

$$\frac{[M]_0}{[M]} = \frac{1}{1-p}$$

$$ln\left(\frac{1}{1-p}\right) = k_p\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}} t = 1.27$$

for **t = 1h** → $ln\left(\frac{1}{1-p}\right) = 1.27$ → $\boldsymbol{p} = \mathbf{0.21}$

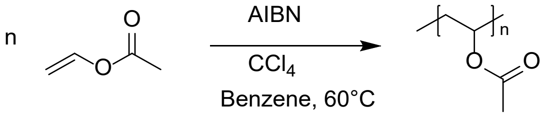
for **t = 15h** → $ln\left(\frac{1}{1-p}\right) = 36.55$ → $\boldsymbol{p} = \mathbf{0.97}$

e) Calculate the kinetic chain length and number average molecular weight of the PMMA polymer (system A) formed at t = 0 assuming that the termination only occurs via coupling.

$$v = \frac{k_p[M]}{2(fk_dk_t[I])^{1/2}}$$
$$v = 4047.2$$
$$\bar{X}_n = 2v = 8094.3$$
$$M_0 = 100.12\ g/mol$$
$$\boldsymbol{\bar{M}_n = M_0\bar{X}_n = 810403\ g/mol}$$

2. As shown in the reaction scheme below, vinyl acetate is polymerized in benzene at 60°C using AIBN as the initiator and carbon tetrachloride as a chain transfer agent. The initial monomer concentration is 150 g/L, initiator concentration 0.98 g/L and the solution density is 0.83 g/cm^3.

What concentration of chain transfer agent should be used to obtain poly(vinyl acetate) with molecular weight of 15'000 g/mol (assuming termination by coupling)? Assume that chain transfer has no effect on the polymerization rate and no chain transfer to initiator occurred.



Use the following data at 60 °C

$k_d = 8.5\cdot10^{-6}\ \frac{1}{s}$; $k_p = 2.34\cdot10^3\ \frac{L}{mol\cdot s}$; $k_t = 2.9\cdot10^7$ L/(mol·s);
$f = 1.0$; $C_M = 2.3\cdot10^{-4}$; C_s (benzene) $= 1.2\cdot10^{-4}$; C_s(CCl$_4$) $= 1.0$

Molecular weight (g/mol): vinyl acetate = 86, AIBN = 164, CCl$_4$ =154 and benzene = 78

The initial concentration of the monomer: $[M]_0 = \frac{150\ g/L}{86\ g/mol} = 1.74\ mol/L$

To calculate the solvent concentration: $[S]_{benzene} = \frac{(830-150)\ g/L}{78\ g/mol} = 8.72\ mol/L$

(the concentration of initiator and chain transfer agent is small and does not significantly change the solvent concentration → can be neglected)

To calculate the initial concentration of the initiator:

$$[I]_0 = \frac{0.98\ g/l}{164\ g/mol} = 5.97\ \cdot10^{-3}\ mol/L$$

The degree of polymerization of the polymerization without accounting for chain transfer reactions, can be calculated from:

$$(\overline{X_n})_0 = \frac{k_p \cdot \ [M]_0}{\sqrt{f\ \ k_d\ \ k_t\ \ [I]_0}}$$

$$= \frac{\left(2.34 \cdot 10^3\ \frac{L}{mol \cdot s}\right)\left(1.74\ \frac{mol}{L}\right)}{\sqrt{1\ \cdot\ \ 8.5 \cdot 10^{-6}\left(\frac{1}{s}\right) \cdot 2.9\ \cdot 10^7\left(\frac{L}{mol \cdot s}\right) \cdot\ 5.97\ \cdot 10^{-3}\,\frac{mol}{L}}} = 3356$$

The desired average degree of polymerization can be calculated from the given molecular weight of the polymer

$$\overline{X_n} = \frac{\overline{M_n}}{M_0} = \frac{15000 g/mol}{86\ g/mol} = 174$$

From Mayo equation, we know that

$$\frac{1}{\overline{X_n}} = \frac{R_i}{2\ R_p} + \ C_M + C_{s(benzene)} \cdot \frac{[S]_{benzene}}{[M]_0} + \ C_{s(CCl4)} \cdot \frac{[S]_{CCl4}}{[M]_0}$$

$$\frac{1}{\overline{X_n}} = \frac{1}{\overline{X_{n0}}} + \ C_M + C_{s(benzene)} \cdot \frac{[S]_{benzene}}{[M]_0} + \ C_{s(CCl4)} \cdot \frac{[S]_{CCl4}}{[M]_0}$$

$$\frac{1}{174} = \frac{1}{3356} + 2.3 \cdot 10^{-4} + 1.2 \cdot 10^{-4} \cdot \frac{8.72\ mol/L}{1.74\ mol/L}\ \ + 1.0 \cdot \frac{[S]_{CCl4}}{1.74\ mol/L}$$

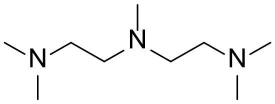
Implies that

$$[S]_{CCl4} = 8.0 \cdot\ 10^{-3}\ mol/L = 8.0\ \cdot\ 10^{-3}\ mol/L \cdot\ 154\ g/mol = 1.23\ g/L$$

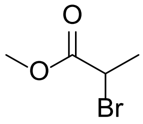
3. In the ATRP process acidic monomers such as acrylic acid can poison the catalyst by complexing with the ligand. Suggest a suitable controlled radical polymerization route to synthesize polyacrylic acid.

Since acrylic acid forms a complex with the ligand (base), the ATRP cannot be conducted in a controlled fashion. One easy way of avoiding this is by protecting the carboxylic acid with a protection group to convert it to an ester group, which will not have the complexation effect. After the polymer with carboxylic groups protected is formed, the desired polymer, polyacrylic acid, can be obtained by deprotection. A different controlled radical polymerization technique to polymerize such acidic monomers could be RAFT polymerization.

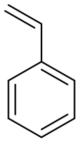
4. Styrene (St) was polymerized by atom transfer radical polymerization (ATRP) using a copper(I) bromide (CuBr) catalyst, *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA) as a ligand, and methyl 2-bromopropionate (MBrP) as an initiator. The initial concentrations of the monomer $[M]_0$ and the initiator $[I]_0$ used for this polymerization were 50 M and 1 M, respectively.



PMDETA

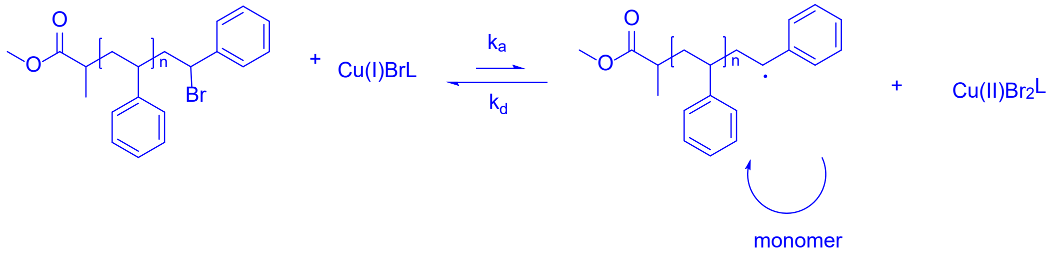


MBrP

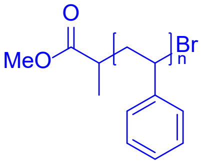


Styrene

a) Illustrate the ATRP mechanism for the polymerization of this monomer.



b) Give the final structure of the polymer including end groups.



c) Calculate the average molecular weight of the polymer formed at 90% monomer conversion (assuming 100% initiator efficiency). Estimate the polydispersity of the polymer. How could you experimentally determine the dispersity?

To calculate the average degree of polymerization, $\overline{X_n}$, for 90% monomer conversion (assuming 100% initiator efficiency);

$$\overline{X_n} = \frac{[M]_0 - [M]}{[I]_0} = \frac{[M]_0 \cdot p}{[I]_0} = \frac{50 \cdot 0.90}{1} = 45$$

$$\overline{M_n} = 45 \cdot 104 = 4680\ g/mol$$

The end groups are $CH(CH_3)COOCH_3$ (87) and Br (80).
Hence total molar mass of the polymer = 4680 + 87 + 80 = 4847 g/mol.
The most rapid and efficient way to calculate the dispersity of a polymer distribution is SEC (size exclusion chromatography), or GPC (gel-permeation chromatography). Other employed methods are MALDI-TOF-MS and end-group analysis with ^{1}H-NMR.
To calculate PDI:

$$PDI = 1 + \frac{1}{\overline{X_n}} = 1 + \frac{1}{45} = 1.02$$

d) How would you explain if the experimental M_W was found higher than the theoretical one?

A higher value of the experimental molar mass would indicate that the initiator efficiency was less than 100%.