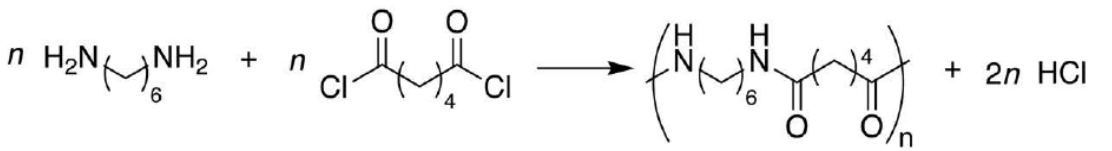
Free-Radical Chain-Growth Polymerization I

16:160:509 – Polymer Chemistry

Lecture 5 to 6

RUTGERS
School of Arts and Sciences
DEPARTMENT OF CHEMISTRY
AND CHEMICAL BIOLOGY

Step-Growth vs Chain-Growth Polymerization

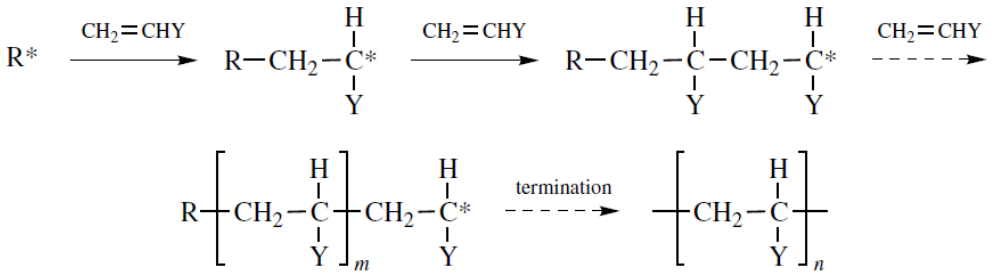


Poly(hexamethylene adipamide), nylon 6,6

In the reaction mixture, we have:

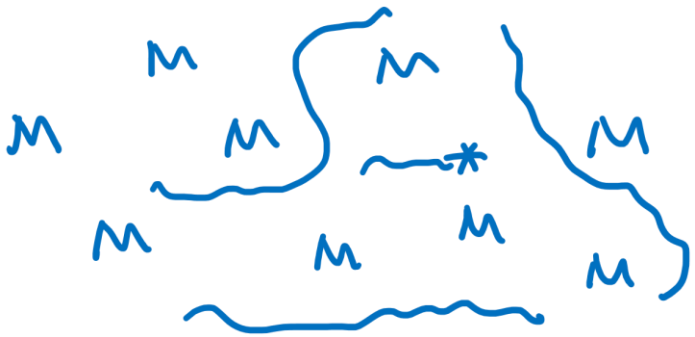
Monomer + monomer ⟶ dimer
Dimer + monomer ⟶ trimer
Dimer + dimer ⟶ tetramer
Trimer + monomer ⟶ tetramer
Trimer + dimer ⟶ pentamer
Trimer + trimer ⟶ hexamer
Tetramer + monomer ⟶ pentamer
Tetramer + dimer ⟶ hexamer
Tetramer + trimer ⟶ heptamer
Tetramer + tetramer ⟶ octamer
etc.

High-MW polymers do not form until very high conversion is achieved.



In the reaction mixture, we have:

- Monomer
- Terminated high-MW polymers
- Growing chains



High-MW polymers form even when conversion is low.

Free-Radical Chain-Growth Polymerization

1. Initiation

$$I \rightarrow I\cdot$$

2. Propagation

$$I\cdot + M \rightarrow IM\cdot \xrightarrow{M} IMM\cdot \rightarrow\rightarrow\rightarrow P_i\cdot$$

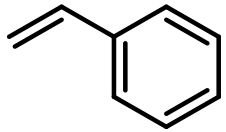
3. Termination

$$P_i\cdot + P_j\cdot \rightarrow P_{i+j} \text{ (dead polymer)}$$

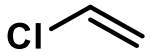
In conventional free-radical polymerization, the lifetime of each propagating chain is short (0.1 to 10 seconds), but radicals are highly reactive species, so hundreds of monomers get added to the propagating chain during this period before the chain gets terminated.

Some monomers used in free-radical polymerization

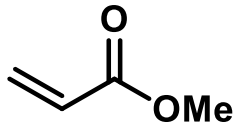
Ethylene



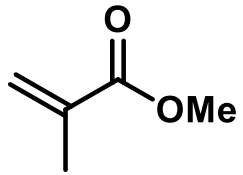
Styrene



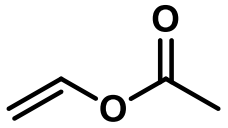
Vinyl chloride



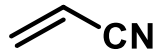
Methyl acrylate



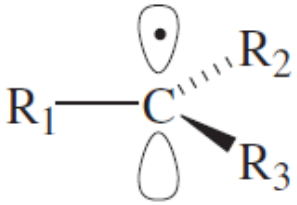
Methyl methacrylate



Vinyl acetate



Acrylonitrile



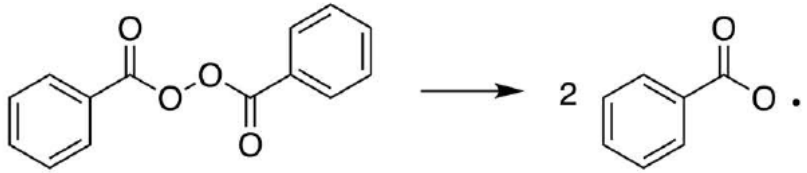
Radical stabilized by EDG

Radical stabilized by EWG

Initiation

Radical initiators are substances that can produce radical species under mild triggering conditions.

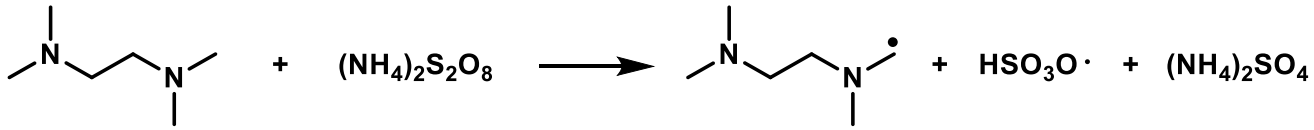
- Thermal radical initiators (we will focus on this type)



Organic peroxide

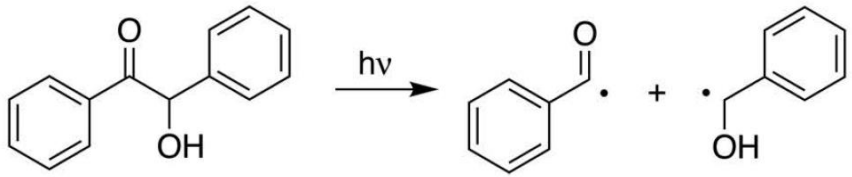
Azobisisobutyronitrile (AIBN)

- Redox radical initiators



TEMED APS

- Photo radical initiators

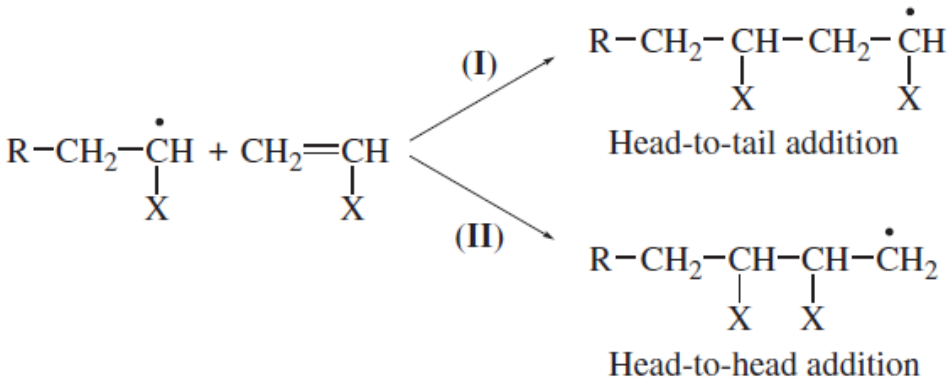


Note that due to numerous side reactions, not all radicals generated from the initiators will initiate polymerization. To quantify this, we define the initiator efficiency, *f*:

$$f = \frac{\text{Radicals incorporated into polymer}}{\text{Radicals formed by initiator}}$$

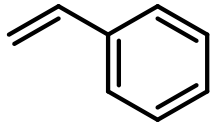
In many experimental situations, *f* lies in the range of 0.3–0.8.

Propagation

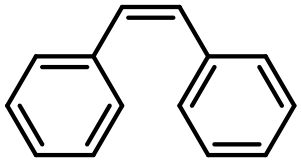


The head-to-tail addition is overwhelmingly predominant (>98–99%) due to:

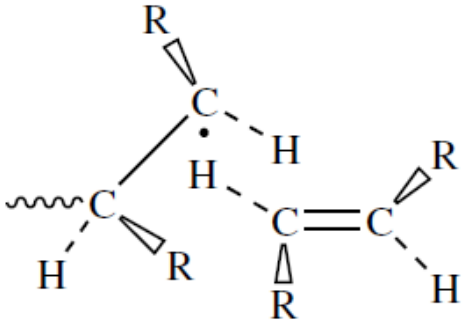
1. Steric reasons (radical species are sensitive to steric factors).
2. Product stability (consider resonance effects).



styrene: very proton to polymerization



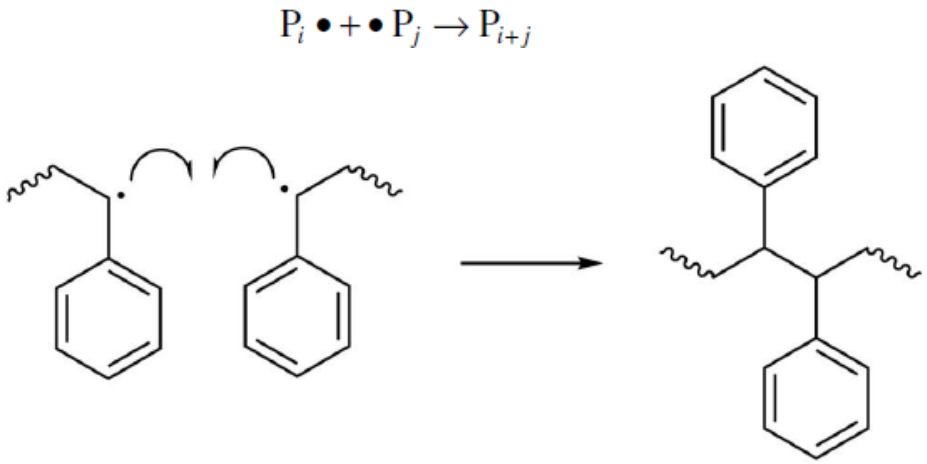
stilbene: impossible to polymerize



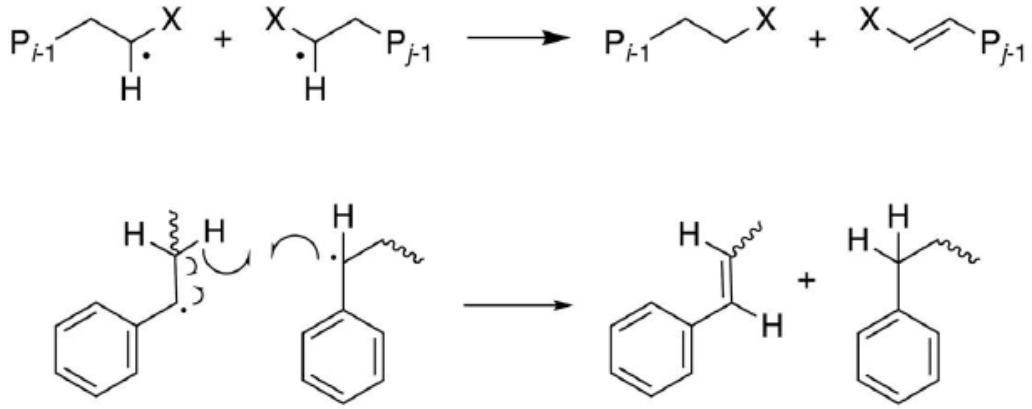
1,2-disubstitution

Termination

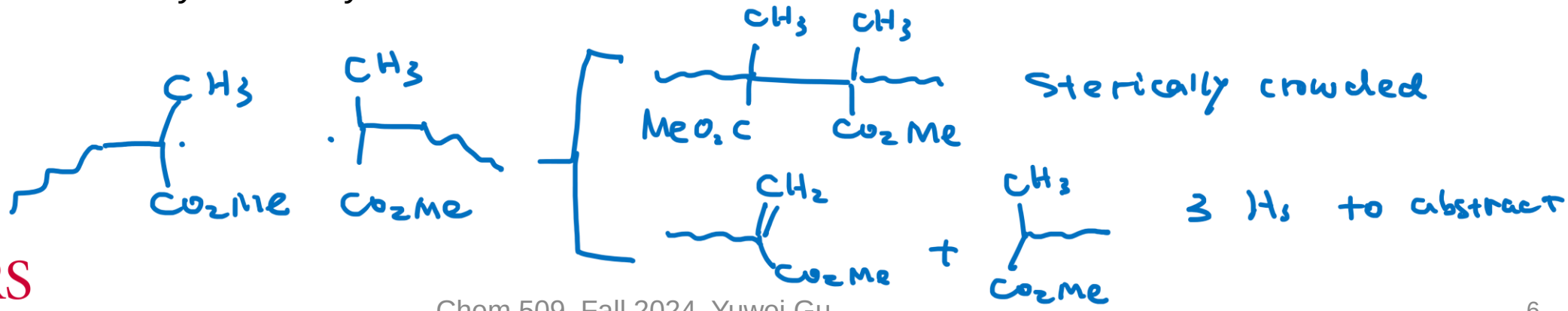
- Termination by combination



- Termination by disproportionation



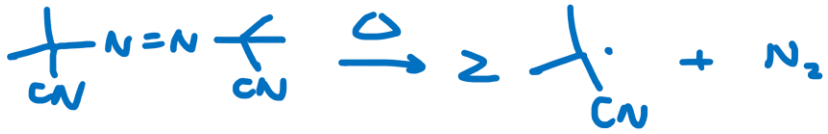
In general, both types of termination reaction take place but to different extents depending upon the monomer and the polymerization conditions. Combination tends to dominate termination in polymerizations of vinyl monomers (CH_2=CHX) such as styrene, whereas disproportionation dominates in polymerizations of α-methylvinyl monomers (CH_2=C(CH_3)X) such as methyl methacrylate.



Kinetics of Free-Radical Polymerization

Let's derive the rate equation for the three stages of free-radical polymerization: initiation, propagation, termination

Initiation: let's focus on thermal radical initiators

$I \rightarrow 2I\cdot$ AIBN:  $+ N_2$

$$-\frac{d[I]}{dt} = \frac{d[I\cdot]}{2\,dt} = k_d[I]$$

Only a fraction (defined as f) of $I\cdot$ react with monomer to initiate polymerization

$I\cdot + M \rightarrow IM\cdot$ $\quad R_i = \frac{d[IM\cdot]}{dt} = f\cdot\frac{d[I\cdot]}{dt} = 2fk_d[I]$

Propagation:

$P\cdot + M \rightarrow PM\cdot$ $\quad R_p = \frac{-d[M]}{dt} = k_p[P\cdot][M]$

Termination:

$P_m\cdot + P_n\cdot$ → P_{m+n} (combination)

→ $P_m + P_n$ (disproportionation)

In either case, we have

$$R_t = \frac{-[P\cdot]}{dt} = 2k_t[P\cdot]^2$$

Kinetics of Free-Radical Polymerization

The expression for R_p involves the concentration of the radical [P•]. How do we derive the radical concentration in the system?

Steady-state assumption: The concentration of highly reactive intermediates quickly reaches a constant, steady-state value during the reaction.

Thus, the rate of radical generation is equal to the rate of radical disapperance

$$\frac{d[IM\cdot]}{dt} = \frac{d[P\cdot]}{dt} \Rightarrow 2fk_d[I] = 2k_t[P\cdot]^2$$

So we get $[P\cdot] = \left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}}$

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

Kinetic Chain Length

Let's define kinetic chain length $\bar{\nu}$ of a radical chain polymerization as the average number of monomer molecules polymerized per each radical that initiates a polymer chain.

Per definition, $\bar{\upsilon} = \dfrac{-d[M]}{d[M\cdot]} = \dfrac{R_p}{R_i} = \dfrac{k_p[M]\left(\dfrac{R_i}{2k_t}\right)^{\frac{1}{2}}}{R_i} = k_p[M]\left(\dfrac{1}{2R_i k_t}\right)^{\frac{1}{2}}$

Thus, $\boxed{\bar{\upsilon} = k_p[M]\left(\dfrac{1}{2\times 2 f k_d[I] k_t}\right)^{\frac{1}{2}} = \dfrac{k_p[M]}{2(f k_d k_t[I])^{\frac{1}{2}}}}$

If termination is exclusively disproportionation: $\bar{X}_n = \bar{\upsilon}$

If termination is exclusively combination: $\bar{X}_n = 2\bar{\upsilon}$

Radical Lifetime

To better visualize a radical polymerization, let's define radical lifetime $\bar{\tau}$ as the average lifetime of a growing radical under steady-state conditions.

Per definition, $\bar{\tau} = \dfrac{\text{average chain length}}{\text{rate of monomer addition to each radical}}$

$$\bar{\tau} = \frac{\bar{v}}{\frac{-d[M]}{dt} / [P\cdot]} = \frac{\bar{v}}{R_p / [P\cdot]} = \frac{\bar{v}}{k_p \cdot [M]} = \frac{k_p \cdot [M]}{k_p \cdot [M]} \cdot \frac{1}{2(f k_d k_t [I])^{\frac{1}{2}}}$$

Thus, we have

$$\bar{\tau} = \frac{1}{2(f k_d k_t [I])^{\frac{1}{2}}}$$

More About These Equations

$$R_p = k_p[M]\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2} \qquad \bar{\nu} = \frac{k_p[M]}{2(fk_tk_d[I])^{1/2}} \qquad \bar{\tau} = \frac{1}{2(fk_tk_d[I])^{1/2}}$$

- Since [M] and [I] may change over time, these equations describe the "instantaneous" values.
- In practice, f (chain end analysis), R_p (spectroscopic methods), $\bar{\nu}$ (molecular weight measurement), $\bar{\tau}$ (rotating sector method, see Page 105 in Lodge) are all measurable quantities, which allows us to determine all the kinetic constants k_p, k_d, and k_t.
- With advanced technique PLP-SEC (pulsed-laser polymerization in conjugation with size-exclusion chromatography), k_p can be measured directly (see Page 267 in Odian).

What conclusions can we draw from these equations?

- Unlike step-growth polymerization, *the molecular weight of free-radical polymerization depends on the concentrations of monomers and initiators*.
- Increasing monomer concentration increases the molecular weight, as there are more monomers available for polymerization
- Increasing initiator concentration decreases the molecular weight, as termination becomes more frequent with the increased radical concentration.
- There is no way to increase polymerization rate and molecular weight simultaneously under a given monomer concentration (the maximum concentration one can achieve is the monomer concentration in bulk).

Let's Put Things Together

$$[P\bullet]_s = \left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2} \qquad R_i = 2fk_d[I] \qquad R_t = 2k_t[P\bullet]^2 \qquad R_p = k_p[M]\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2} \qquad \bar{\nu} = \frac{k_p[M]}{2(fk_tk_d[I])^{1/2}} \qquad \bar{\tau} = \frac{1}{2(fk_tk_d[I])^{1/2}}$$

Below are some relevant values for polymerization of styrene in bulk using AIBN as the initiator at 70 °C:

$k_p = 1.65 \times 10^2$ L mol^{-1} s^{-1}

$k_t = 6.0 \times 10^7$ L mol^{-1} s^{-1}

$k_d = 3.2 \times 10^{-5}$ s^{-1}

$f = 0.6$

[M] = 8.7 mol L^{-1}

[I] = 1.0×10^{-3} mol L^{-1}

$[P\cdot] = \left(\frac{0.6 \times 3.2 \times 10^{-5}}{6 \times 10^7}\right)^{\frac{1}{2}} \times (1 \times 10^{-3})^{\frac{1}{2}} = 1.8 \times 10^{-8}$ mol·L^{-1}

$R_i = 2 \times 0.6 \times 3.2 \times 10^{-5} \times 10^{-3} = 3.8 \times 10^{-8}$ mol·L^{-1}·s^{-1}

$R_t = 2 \times 6 \times 10^7 \times (1.8 \times 10^{-8})^2 = 3.8 \times 10^{-8}$ mol·L^{-1}·s^{-1}

$R_p = 1.65 \times 10^2 \times 8.7 \times \left(\frac{0.6 \times 3.2 \times 10^{-5}}{6 \times 10^7}\right)^{\frac{1}{2}} \times (1 \times 10^{-3})^{\frac{1}{2}} = 2.6 \times 10^{-5}$ mol·L^{-1}·s^{-1}

$\bar{\nu} = \frac{R_p}{R_i} = 684$ $\qquad \bar{\tau} = \frac{\bar{\nu}}{k_p[M]} = \frac{684}{1.65 \times 10^2 \times 8.7} = 0.48$ s

- The concentration of propagating radical species is very low.
- k_t is larger than k_p, but R_p is larger than R_t due to the low concentration of propagating radicals.
- The lifetime of a propagating radical is very short. However, since radicals are very reactive species (large k_p), a significant number of monomers are added to the propagating chains within this short time frame, resulting in a high molecular weight.

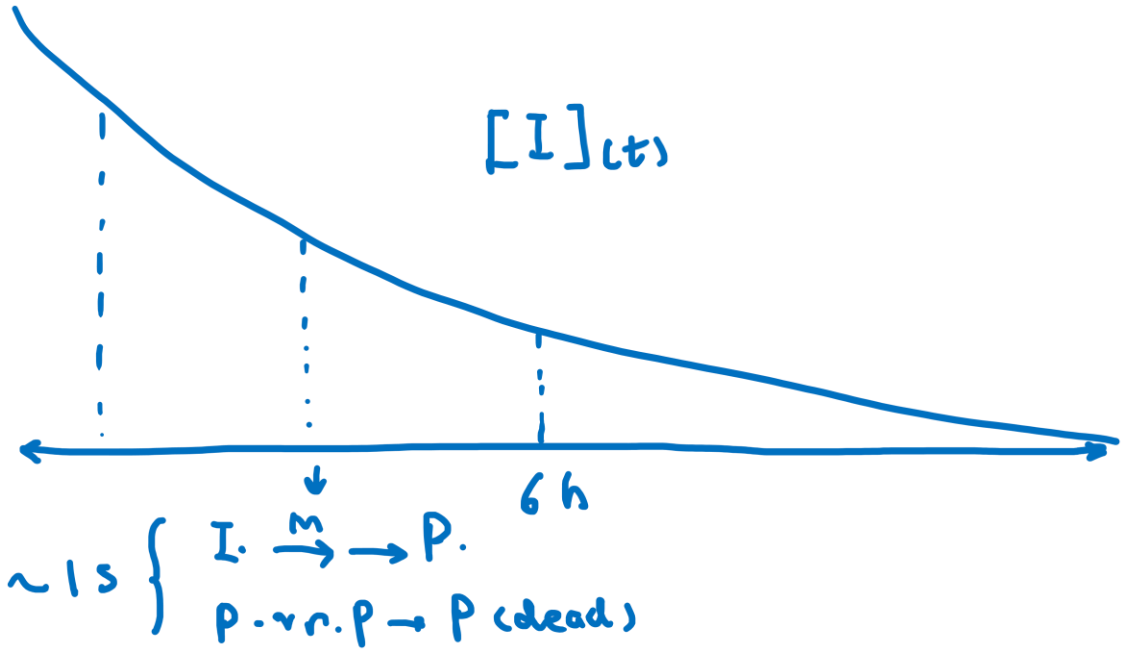
Integral Form of Rate Equations

For thermal radical initiators, we have $\frac{-d[\mathrm{I}]}{dt} = k_d[\mathrm{I}]$

Taking the integral form, we have $[\mathrm{I}] = [\mathrm{I}]_0 e^{-k_d t}$

For AIBN at 70°C, the half-life can be calculated as

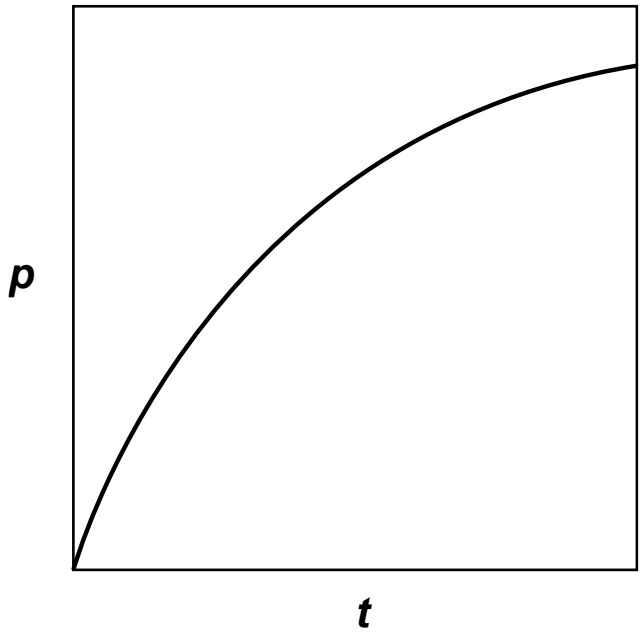
$\frac{1}{2}[\mathrm{I}]_0 = [\mathrm{I}]_0 e^{-k_d t_{\frac{1}{2}}}$ $k_d = 3.2\times10^{-5}\ s^{-1}$ $t_{\frac{1}{2}} = 21660s \approx 6\ h$



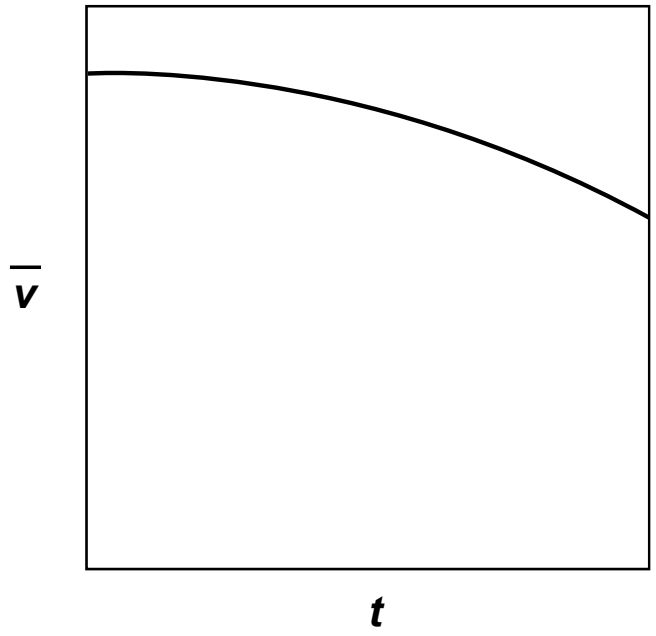
Integral Form of Rate Equations

solve $R_p = \frac{-d[M]}{dt} = k_p[M]\left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}}\left([I]_0 e^{-k_d t}\right)^{\frac{1}{2}}$ gives $[M]_{(t)}$ or $p_{(t)}$

similarly $\bar{v}_{(t)} = \frac{k_p[M]}{2(fk_dk_t)^{\frac{1}{2}}[I]^{\frac{1}{2}}}$ can be derived based on $[M]_{(t)}$ and $[I]_{(t)}$



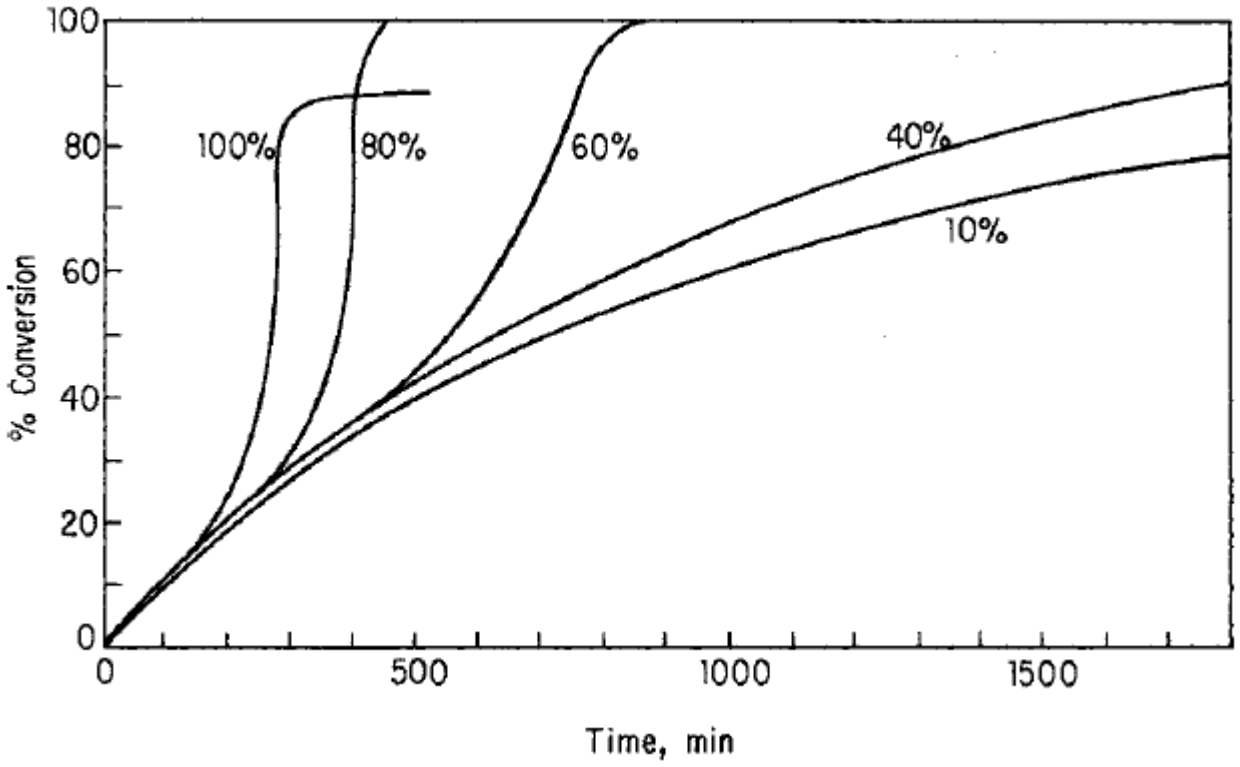
Conversion *vs* time



Average MW *vs* time

However, analysis like this needs to be performed with caution, as the kinetics in actual free-radical polymerization are much more complex than this simple steady-state model depicts.

Autoacceleration (Trommsdorff Effect)



Free-radical polymerization of methyl methacrylate in benzene at various monomer concentrations

- As polymerization progresses, the system becomes increasingly viscous, making the diffusion of large-molecular-weight species more difficult. Since termination involves the reaction of two large-molecular-weight species, k_t decreases over time, while the rate constant for propagation k_p is less affected, as propagation involves only one large-molecular-weight species.

$$R_p \propto \frac{k_p}{k_t^{\frac{1}{2}}} \quad \uparrow \text{ over time}$$

$$\bar{\nu} \propto \frac{k_p}{k_t^{\frac{1}{2}}} \quad \uparrow \text{ over time}$$

Energetic Characteristics of Free-Radical Polymerization

Let's consider how temperature affects R_p

$$R_p = k_p[M]\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}$$

consider how temperature affects $\frac{k_p k_d^{\frac{1}{2}}}{k_t^{\frac{1}{2}}}$, for each $k = Ae^{-\frac{E}{RT}}$

$$\frac{k_p \cdot k_d^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} = \frac{A_p \cdot A_d^{\frac{1}{2}}}{A_t^{\frac{1}{2}}} \cdot e^{-\frac{(E_p + \frac{1}{2}E_d - \frac{1}{2}E_t)}{RT}}$$

$E_d \sim 29 - 36$ kcal/mol

$E_p \sim 5 - 10$ kcal/mol

$E_t \sim 2 - 5$ kcal/mol

$E_p + \frac{1}{2}E_d - \frac{1}{2}E_t \sim 5 + \frac{1}{2}\times 29 - \frac{1}{2}\times 2 = 18.5$ kcal/mol $T \uparrow$, $R_p \uparrow$

How about $\bar{v} = \frac{k_p[M]}{2(fk_tk_d[I])^{1/2}}$

$E_p - \frac{1}{2}E_d - \frac{1}{2}E_t \sim 5 - \frac{1}{2}\times 2 - \frac{1}{2}\times 29 = -10.5$ kcal/mol $T \uparrow$, $\bar{v} \downarrow$

Molecular Weight Distribution

Let's consider the probability (p) that a propagating radical will continue to propagate instead of terminating

$$p = \frac{R_p}{R_p + R_t} = \frac{R_p}{R_p + R_i} = \frac{R_p / R_i}{R_p / R_i + 1} = \frac{\bar{\nu}}{\bar{\nu} + 1}$$

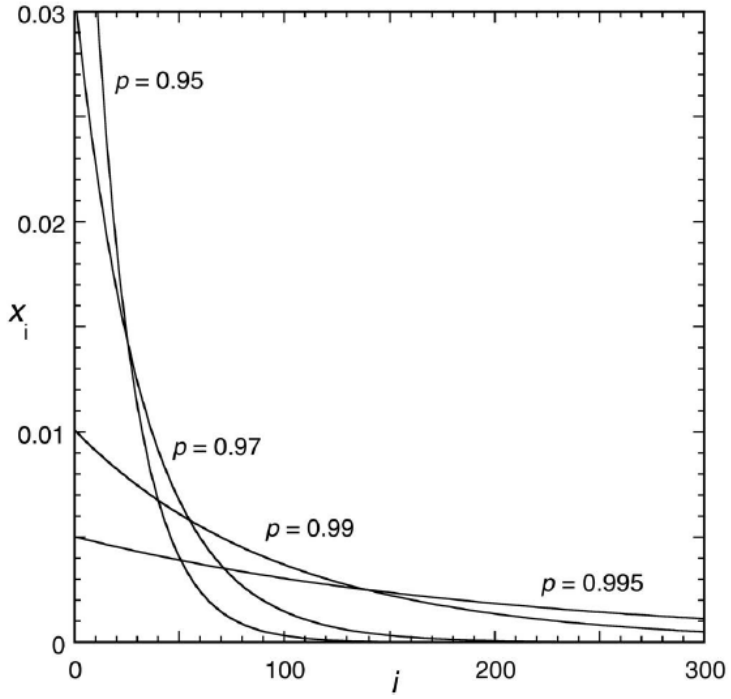
since $\bar{\nu}$ is large, p is close to 1

Therefore, if chain termination is exclusively through disproportionation. we again reach the most probable distribution (same as step-growth polymerization except for the definition of p).

$$x_i = p^{i-1}(1-p) \qquad w_i = i \cdot p^{i-1} \cdot (1-p)^2$$

$$\bar{x}_n = \frac{1}{1-p} = \bar{\nu} + 1 \approx \bar{\nu}$$

$$\bar{x}_w = \frac{1+p}{1-p} \qquad \text{D} = 1 + p \text{ (close to 2)}$$



Molecular Weight Distribution

It gets more complicated when chains terminate through combination

$$P_{i-1}\bullet + P_1\bullet \rightarrow P_i$$

$$P_{i-2}\bullet + P_2\bullet \rightarrow P_i$$

$$P_{i-3}\bullet + P_3\bullet \rightarrow P_i$$

$$\vdots$$

$$P_{i-j}\bullet + P_j\bullet \rightarrow P_i$$

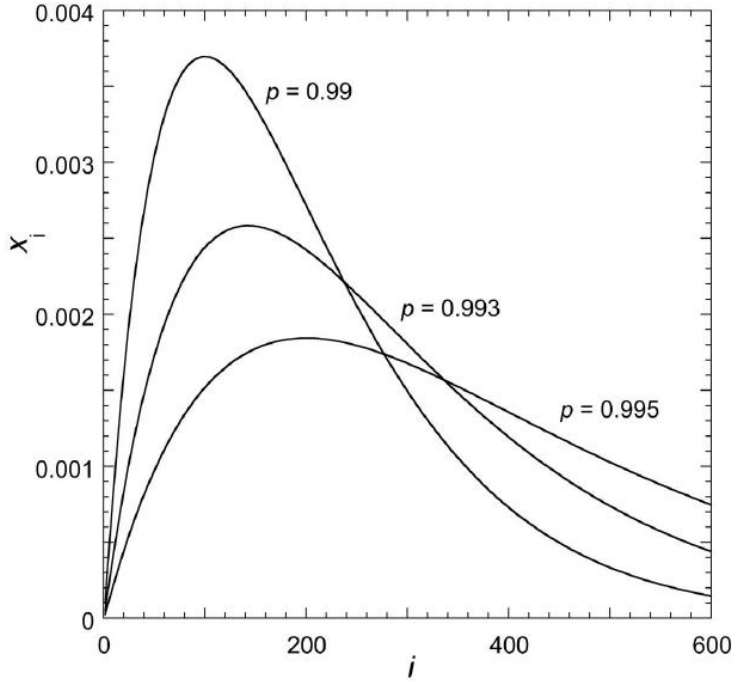
With some math (see Page 109 in Lodge), we can get

$$x_i = (i-1)(1-p)^2 p^{i-2}$$

$$\bar{x}_n = \frac{2}{1-p} \approx 2\bar{v}$$

$$\bar{x}_w = \frac{2+p}{1-p}$$

$$\text{Đ} = \frac{2+p}{2} \quad (\text{close to } 1.5)$$



In practice, since *p* changes as the reactions proceed, along with other factors such as autoacceleration, free-radical polymerization at high conversion often exhibits dispersity much larger than 2 (e.g., as high as 5–10).

Thermodynamics of Chain-Growth Polymerization

So far, we have been assuming that all radical addition events to propagating chains are irreversible. Now, let's consider this process more closely from a thermodynamic perspective.

$$P\cdot + M \longleftrightarrow PM\cdot$$

$$\Delta G = \Delta H - T\Delta S + RT\ln\frac{[PM\cdot]}{[P\cdot][M]}$$

Under steady state, we have $[PM\cdot] \approx [P\cdot]$

$$\Delta G = \Delta H - T\Delta S + RT\ln\frac{1}{[M]}$$

For almost all chain-growth polymerization, we have $\Delta H < 0$, $\Delta S < 0$, so for any given $[M]$, there is a ceiling temperature (T_c), above which $\Delta G > 0$ (i.e. polymerization impossible)

$$T_c = \frac{\Delta H}{\Delta S + R\ln[M]}$$

At T_c, we have polymerization – depolymerization equilibrium.

Thermodynamics of Chain-Growth Polymerization

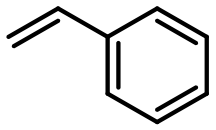
- For any monomer solution of concentration [M] there is a temperature T_c at which polymerization does not occur. Stated another way, the polymerization of a particular monomer solution at a particular temperature proceeds until equilibrium is established, that is, until the monomer concentration decreases to the [M] value corresponding to that T_c temperature.
- While it is clear that each monomer concentration has its own T_c value, it should be noted that the literature often appears to refer only to a singular T_c value that usually refers to the T_c for the pure monomer.

	ΔH	ΔS
Styrene	-73 kJ mol^{-1}	-104 J K^{-1} mol^{-1}
α-Methylstyrene	-35 kJ mol^{-1}	-110 J K^{-1} mol^{-1}

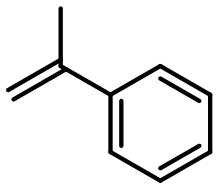
Calculate T_c for styrene and α-methylstyrene at [M] = 1 mol L^{-1} and bulk ($[M]_{st}$ = 8.7 mol L^{-1}, $[M]_{\alpha\text{-mst}}$ = 7.7 mol L^{-1})

For Styrene, at [M] = 1 mol·L^{-1}, $T_c = \frac{-73\times10^3}{-104+8.314\times\ln 1} = 702$ K. At bulk. T_c = 849 K

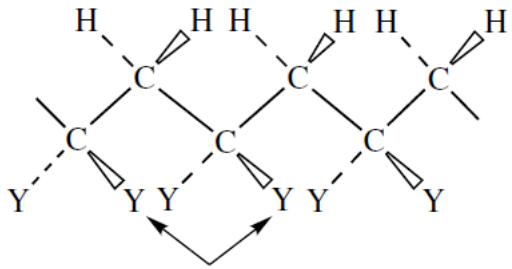
For α-methylstyrene, at [M] = 1 mol·L^{-1}, $T_c = \frac{-35\times10^3}{-110+8.314\times\ln 1} = 318$ K. At bulk. T_c = 376 K



styrene



α-methylstyrene



1,3-Interactions

Chain Transfer

Chain transfer arises when hydrogen or some other atom X is transferred from a molecule in the system to the polymer radical.

$$P_i\bullet + RX \xrightarrow{k_{tr}} P_iX + R\bullet$$

$$R\bullet + M \xrightarrow{k_R} RM\bullet \xrightarrow{k_p} \rightarrow \rightarrow RP_i\bullet$$

- Transfer to initiator, IX: $P_i\bullet + IX \rightarrow P_iX + I\bullet$
- Transfer to monomer, MX: $P_i\bullet + MX \rightarrow P_iX + M\bullet$
- Transfer to solvent, SX: $P_i\bullet + SX \rightarrow P_iX + S\bullet$

		Type of Effect	Effect on R_p	Effect on $\overline{X}_n$
$k_p \gg k_{tr}$	$k_R \simeq k_p$	Normal chain transfer	None	Decrease
$k_p \ll k_{tr}$	$k_R \simeq k_p$	Telomerization	None	Large decrease
$k_p \gg k_{tr}$	$k_R < k_p$	Retardation	Decrease	Decrease
$k_p \ll k_{tr}$	$k_R < k_p$	Degradative chain transfer	Large decrease	Large decrease

The Effect of Chain Transfer on the Kinetic Chain Length

Let's consider how chain transfer affects kinetic chain length $P_i\bullet + RX \xrightarrow{k_{tr}} P_iX + R\bullet$

Chain transfer terminates the propagating chain. So it's one type of termination event

$$\bar{\upsilon}_{tr} = \frac{R_p}{R_t + R_{tr}} = \frac{k_p[M][P\cdot]}{2k_t[P\cdot]^2 + k_{tr}[P\cdot][RX]} = \frac{k_p[M]}{2k_t[P\cdot] + k_{tr}[RX]}$$

$$\frac{1}{\bar{\upsilon}_{tr}} = \frac{2k_t[P\cdot]}{k_p[M]} + \frac{k_{tr}}{k_p}\frac{[RX]}{[M]} = \frac{1}{\bar{\upsilon}} + \frac{k_{tr}}{k_p}\frac{[RX]}{[M]}$$

Define chain transfer constant $C_{tr} = \frac{k_{tr}}{k_p}$

Consider all sorts of chain transfer: to initiator, to monomer, to solvent

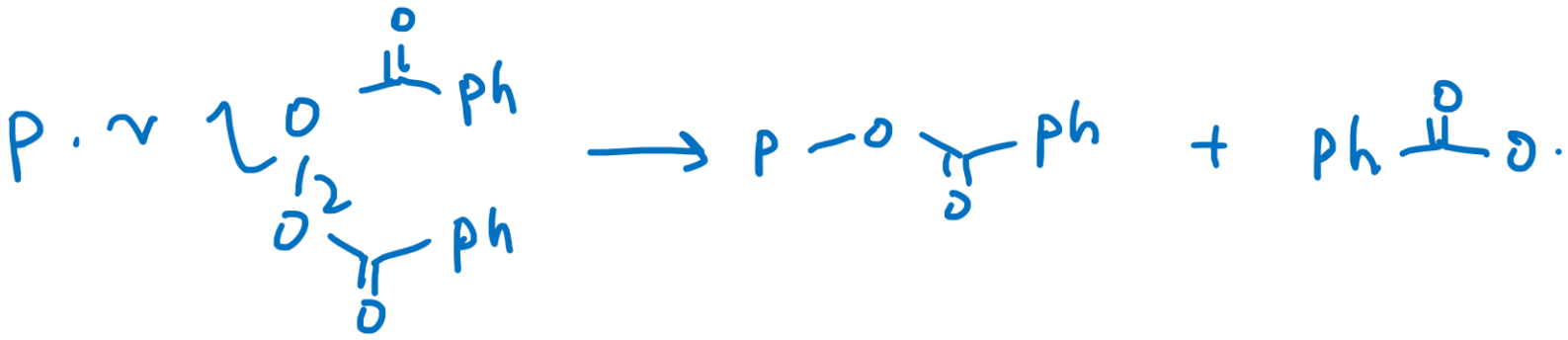
$$\frac{1}{\bar{\upsilon}_{tr}} = \frac{1}{\bar{\upsilon}} + \sum_{\text{all } RX} C_{tr}\cdot\frac{[RX]}{[M]}$$

$C_{tr}\uparrow$, $\bar{\upsilon}_{tr}\downarrow$

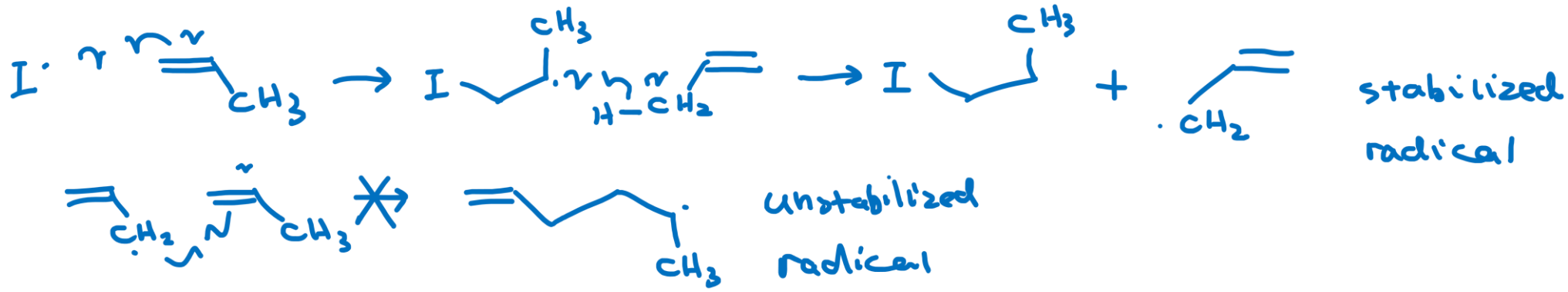
Mayo equation

Some Examples of Chain Transfer

- Chain transfer to initiators is common but usually less of a concern in free-radical polymerization, as the initiator concentration is often very low.

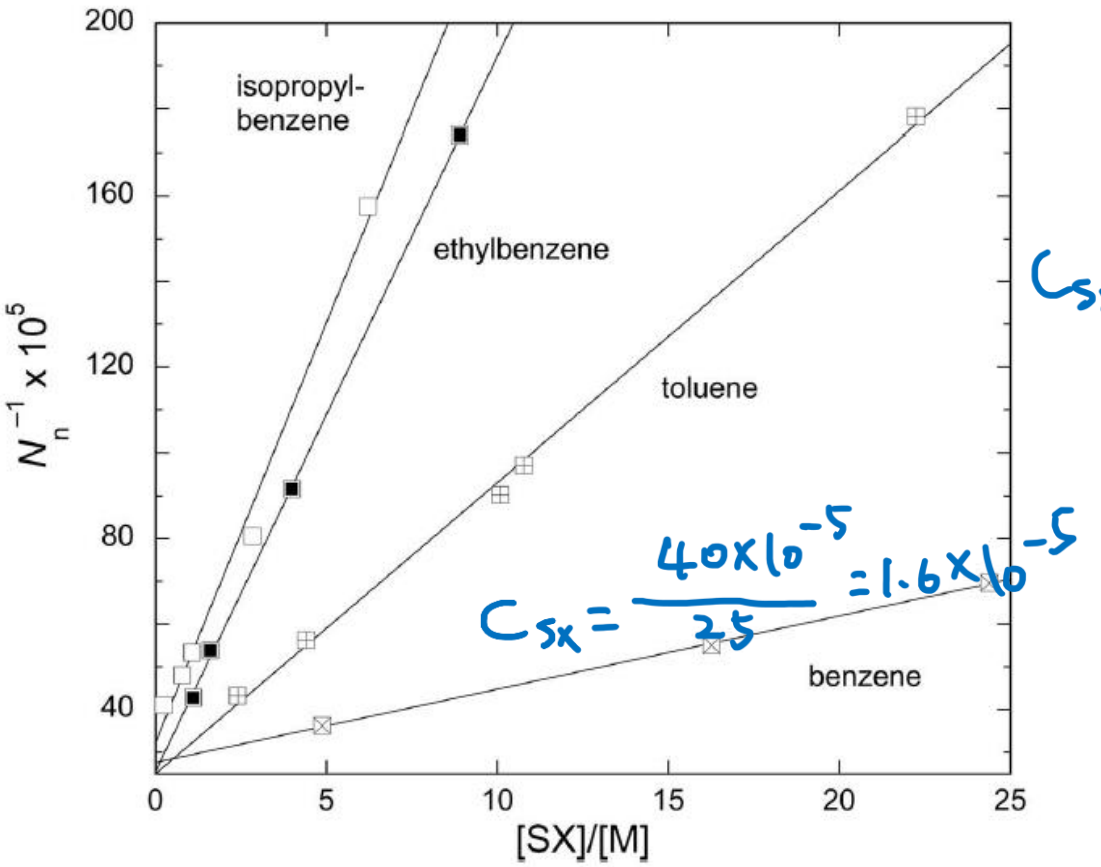


- The chain transfer constant to monomers is usually small. However, degradative chain transfer to the monomer is the reason why free-radical polymerization does not work on α-olefins such as propylene.



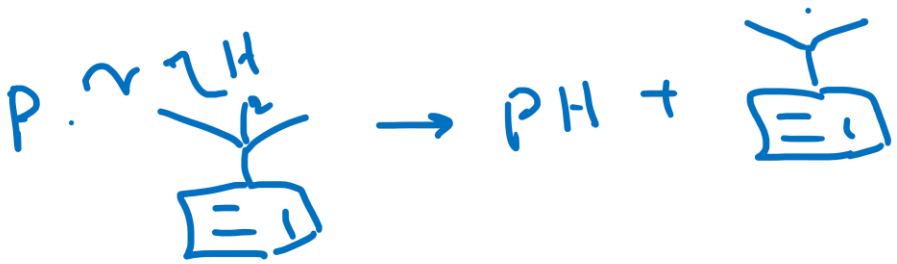
Some Examples of Chain Transfer

- The chain transfer constant to solvents highly depends on the chemical structure of the solvents. Consider the following plots.



$$\frac{1}{\bar{v}_{tr}} = \frac{1}{\bar{v}} + C_{SX}\frac{[SX]}{[M]}$$ C_S is the slope

C_{SX}:



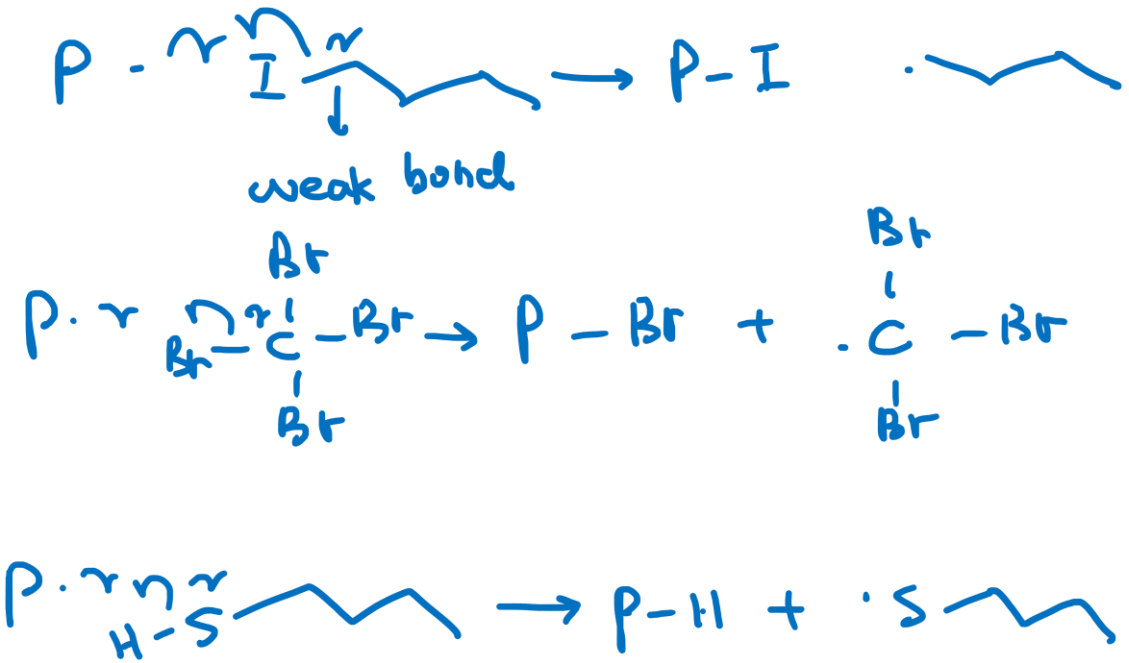
$$C_{SX} = \frac{40\times10^{-5}}{25} = 1.6\times10^{-5}$$

stability:

Polymerization of styrene at 100°C in various solvents

Chain-Transfer Agent

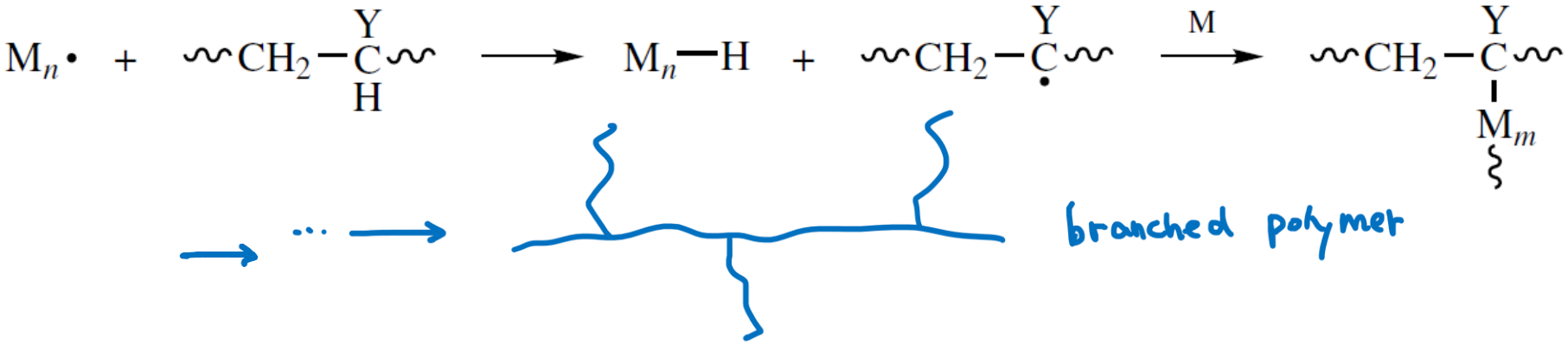
In certain commercial processes it is essential to regulate the molecular weight of the polymer, either for ease of processing or because low molecular weight products are desirable for particular applications such as lubricants or plasticizers. In such cases certain molecules will be deliberately added to the reaction as chain-transfer agents.



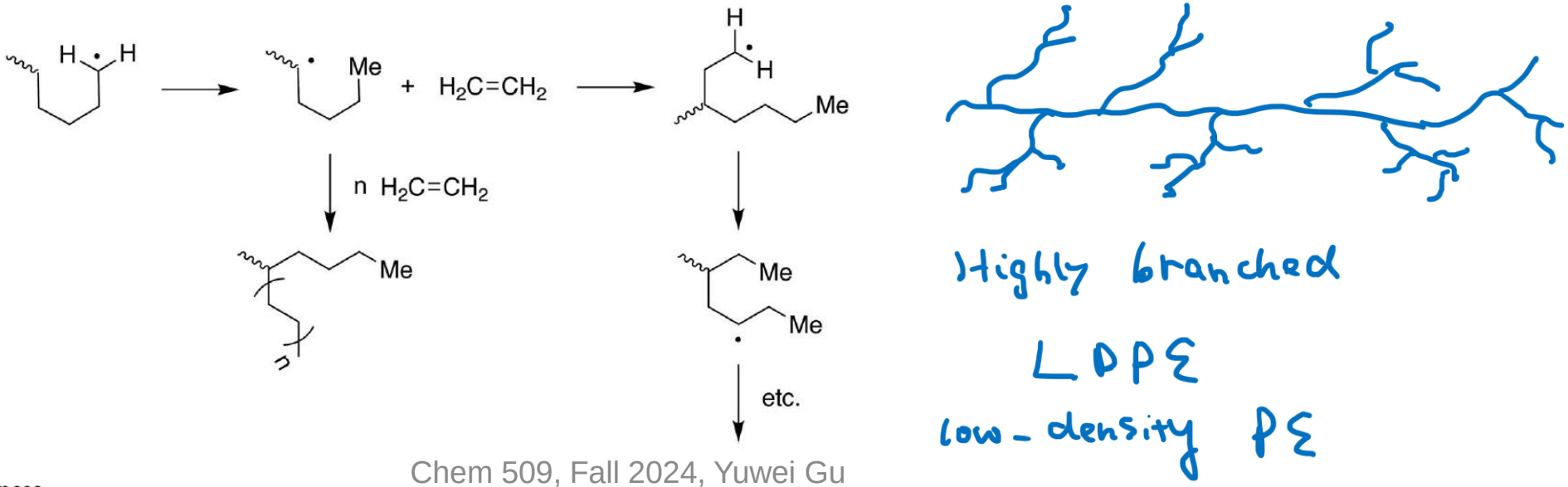
Transfer Agent	$C_S \times 10^4$ for Polymerization of	
	Styrene	Vinyl Acetate
Benzene	0.023	1.2
Cyclohexane	0.031	7.0
Heptane	0.42	17.0 (50°C)
Toluene	0.125	21.6
Ethylbenzene	0.67	55.2
Isopropylbenzene	0.82	89.9
t-Butylbenzene	0.06	3.6
n-Butyl chloride	0.04	10
n-Butyl bromide	0.06	50
2-Chlorobutane	1.2	—
Acetone	4.1	11.7
Acetic acid	2.0 (40°C)	1.1
n-Butyl alcohol	1.6	20
Ethyl ether	5.6	45.3
Chloroform	3.4	150
n-Butyl iodide	1.85	800
Butylamine	7.0	—
Triethylamine	7.1	370
Di-*n*-butyl sulfide	22	260
Di-*n*-butyl disulfide	24	10,000
Carbon tetrachloride	110	10,700
Carbon tetrabromide	22,000	28,700 (70°C)
1-Butanethiol	210,000	480,000

Chain Transfer to Polymers

Chain transfer to polymers does occur, but it does not change the molecular weight, making it difficult to measure. Instead, it introduces branches to polymer chains.

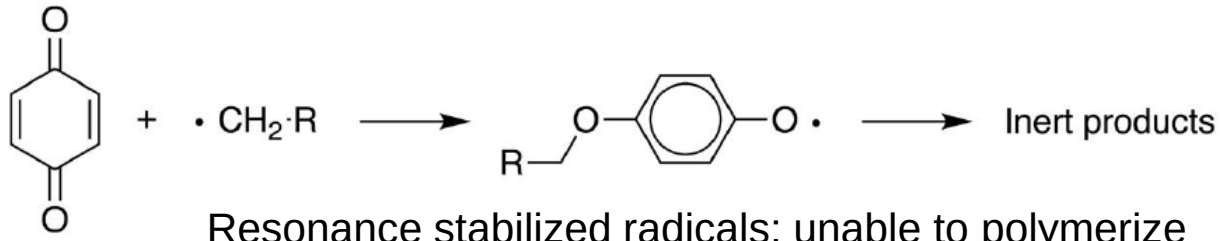


Chain transfer to polymers may also occur intramolecularly. A good example is polyethylene, which features highly flexible chains favoring intramolecular chain transfer through a 6-membered cyclic transition state ("backbiting").



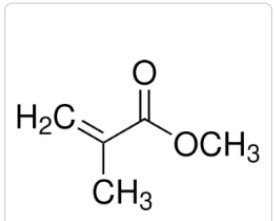
Inhibitors: An Extreme Case of Chain Transfer

- Inhibition of polymerization occurs when chain transfer produces radicals of such low reactivity that no polymerization is possible.

Benzoquinone 

Resonance stabilized radicals: unable to polymerize

- Such inhibitors (sometimes called antioxidants) are added to commercial monomers to prevent their premature polymerization during storage.



M55909 ▶ Sigma-Aldrich.

Methyl methacrylate

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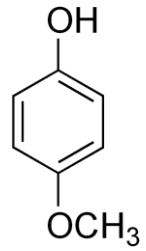
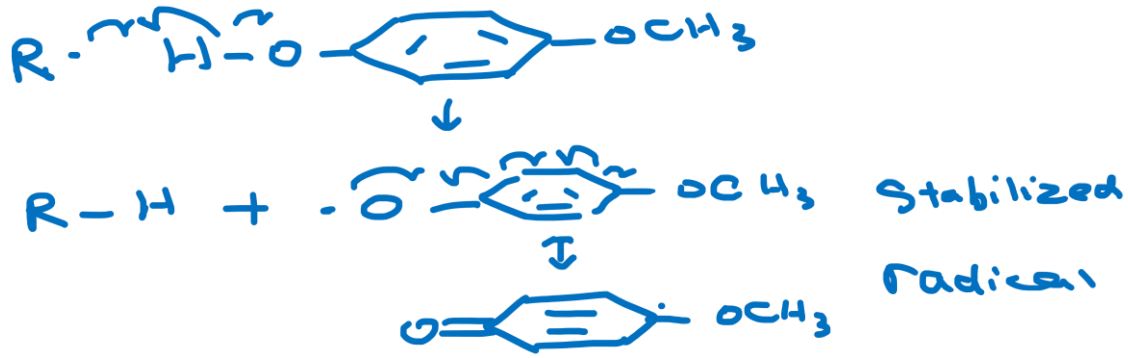
contains ≤30 ppm MEHQ as inhibitor, 99%



MEHQ



- Molecular oxygen is itself a diradical and may inhibit (or even initiate) free-radical polymerization. Therefore, free-radical polymerization is often conducted in a strictly oxygen-free environment.

$$O_2 + M\bullet \rightarrow M - O - O\bullet$$