Controlled Radical Polymerization

Radical Chain Polymerization

1. Initiation

$$I \xrightarrow{k_d} 2R\bullet$$

$$R\bullet + M \xrightarrow{k_i} M_1\bullet$$

R• = initiator radical / primary radical
M_1 • = chain-initiating species
k_d = rate constant for initiator decomposition
k_i = rate constant for the initiation step

2. Propagation

$$M_1\bullet + M \xrightarrow{k_p} M_2\bullet$$

$$M_2\bullet + M \xrightarrow{k_p} M_3\bullet$$

$$M_3\bullet + M \xrightarrow{k_p} M_4\bullet$$

etc., etc.

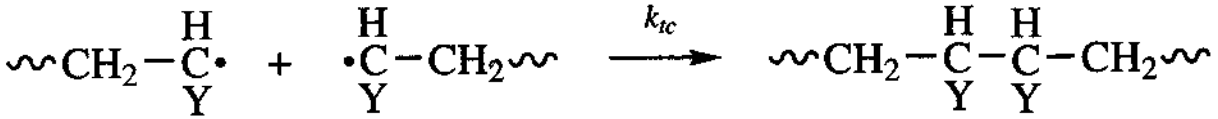
k_p = rate constant for propagation
(10^2-10^4 $L.mol^{-1}.s^{-1}$)

or in general terms

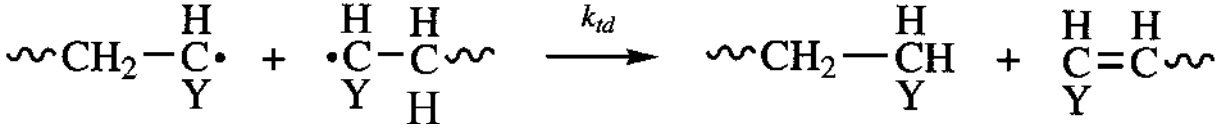
$$M_n\bullet + M \xrightarrow{k_p} M_{n+1}\bullet$$

[concept of equal reactivity of functional groups]

3. Termination



Combination (coupling)



Disproportionation

$$M_n\bullet + M_m\bullet \xrightarrow{k_{tc}} M_{n+m}$$

$$M_n\bullet + M_m\bullet \xrightarrow{k_{td}} M_n + M_m$$

or:

$$M_n\bullet + M_m\bullet \xrightarrow{k_t} \text{dead polymer}$$

k_{tc} = rate constant for termination by coupling

k_{td} = rate constant for termination by disproportionation

with: $k_t = ak_{tc} + (1-a)k_{td}$

- k_t = rate constant for termination (10^6-10^8 L.mol^{-1}.s^{-1})
- a and (1-a) the fractions of termination by coupling and disproportionation, respectively

Macromolecular Engineering

Synthesis of polymers with precise control over molecular weight, composition and topology

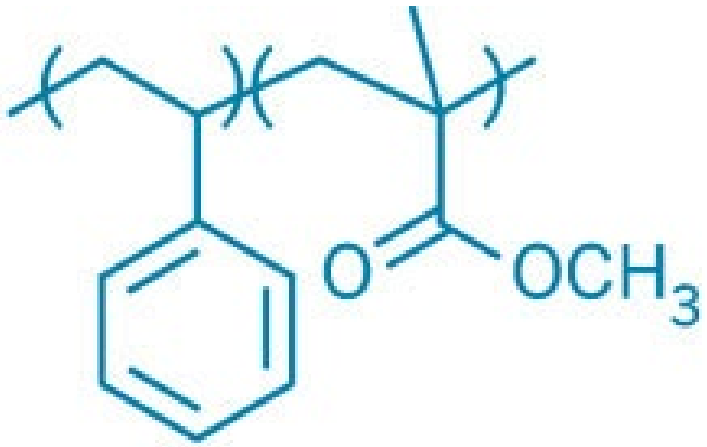
Table 1. Architectural forms of polymers available by living polymerization techniques.

	Polymer	Application
1	OH *Functional ended*	Dispersing agents Synthesis of macromonomers
2	HO OH *α,ω-difunctional*	Elastomers synthesis Chain extension Cross-linking agents
3	*AB Block*	Dispersing agents Compatibilizers for polymer blending
4	*ABA Block*	Thermoplastic elastomers
5	*Graft*	Elastomers Adhesives
6	*Comb*	Elastomers Adhesives
7	*Star*	Rheology control Strengthening agents
8	*Ladder*	High-temperature plastics Membranes Elastomers
9	*Cyclic*	Rheology control
10	*Amphiphilic network*	Biocompatible polymers

Question: Can we achieve this using conventional free radical polymerization ??

O.W. Webster, *Science* **1991**, *251*, 887

Case Study: PS-block-PMMA



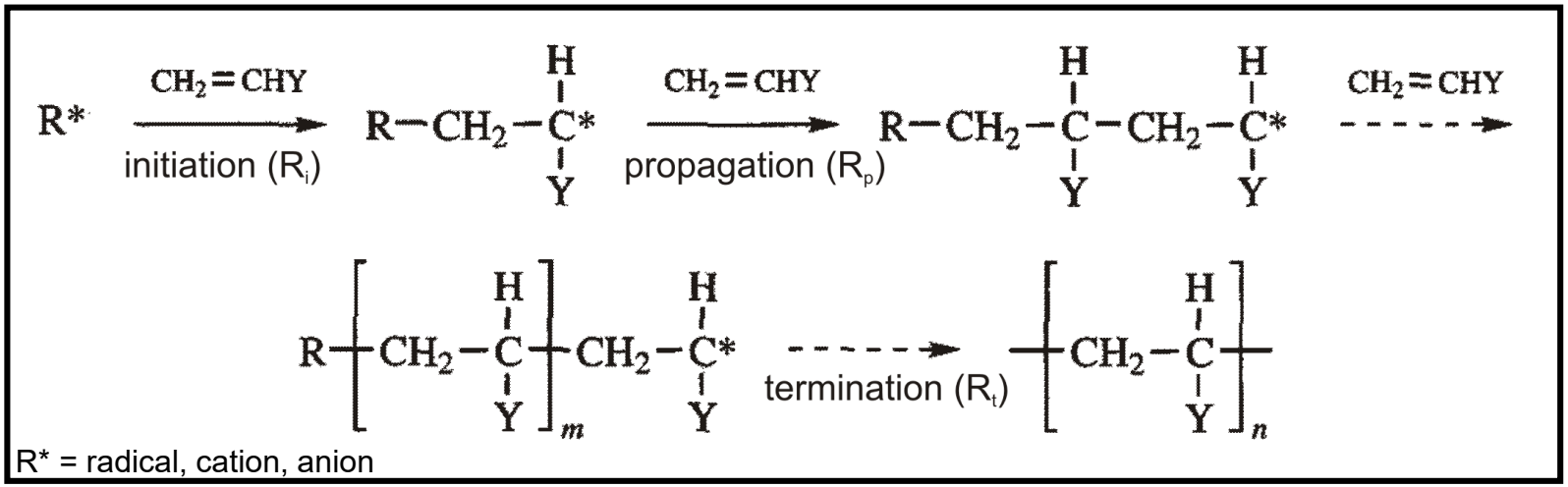
Polystyrene-polymethyl-methacrylate, PS-PMMA

Free radical polymerization

1. Consecutive monomer addition ?

2. Couple PS and PMMA precursors ?

Answer: NO !!



Free radical chain polymerization:

- Initiation is slow compared to propagation and termination ($R_i < R_p, R_t$)
- Chains are very short-lived (< 1 s), due to high chain propagation rates and the existence of termination reactions

As a consequence:

- Relatively broad distribution of chain lengths
- Control over chain length is limited
- Difficult to control polymer composition, functionality and architecture

What Is Needed To Allow Macromolecular Engineering ?

1. Fast and quantitative initiation

All chains start to grow at the same time and $X_n = \Delta[M] / [I]_0$

Consequences:
- Narrow molecular weight distribution
- Precise control of X_n

Since usually X_n = 100 – 1000 and $[M]_0$ = 0.1 – 10 M,
this means $[I]_0 = 1.0 \times 10^{-4}$ – 0.1 M, i.e. relatively high radical concentrations

2. Long-lived polymer chains

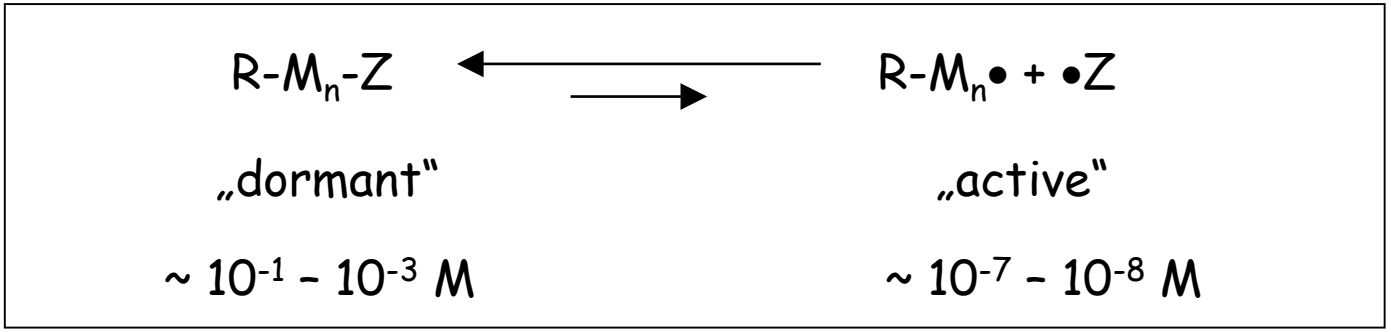
Consequences: Control of end group functionality and polymer architecture

Increasing the lifetime of a polymer chain means reducing the probability for termination to occur.

Since $k_t = 10^6$ L.mol^{-1}.sec^{-1}, this requires $[I]_0 = 10^{-6}$ M,
i.e. relatively small radical concentrations

Fast and quantitative initiation and increasing the lifetime of the growing polymer chains have different demands on $[I]_0$. How can this dilemma be solved?

Polymerization strategies in which a small fraction of active propagating chains is in fast equilibrium with a large fraction of dormant chains, which cannot terminate or propagate



In this way, both requirements can be fulfilled:

1. Low concentration of active radicals prevents termination and increases the lifetime of the growing polymer chains

2. Sufficiently high overall concentration of growing chains allows control of X_n via $\Delta[M]/[I]_0$

-> „Living"/controlled radical polymerization (LRP/CRP)

Characteristics of Living Polymerizations

1. Linear kinetic plot in semilogarithmic coordinates if the reaction is first order with respect to the monomer concentration

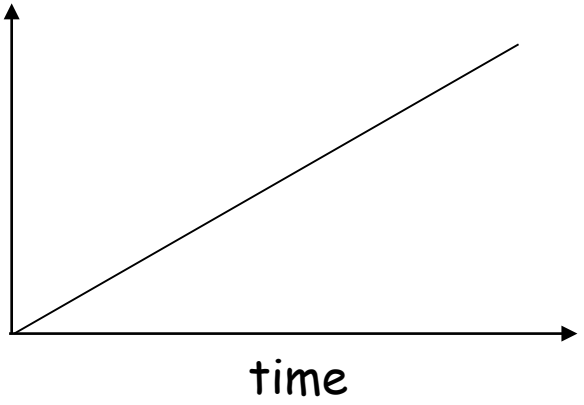
2. Linear evolution of MW with conversion.
   MW < $\Delta[M]/[I]_0$ = transfer;
   MW > $\Delta [M/[I]_0$ inefficient initiation or
   chain coupling

3. Polydispersity M_w/M_n close to Poisson distribution ($M_w/M_n \approx 1 + 1/DP_n$)

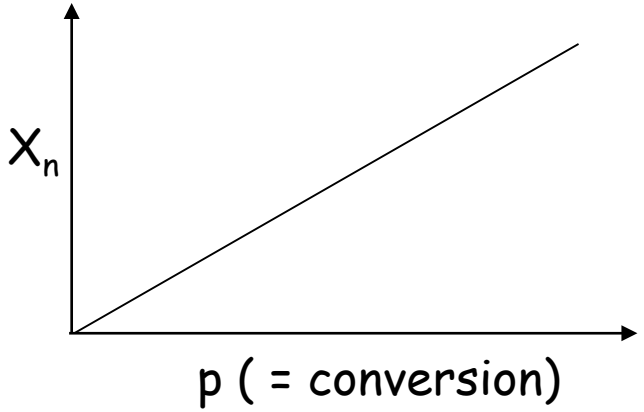
4. End-functionality is not affected by slow initiation and exchange but is reduced when chain breaking reactions become important

Mechanistic Consequences / Characteristics of CRP

1. R_p is first order with respect to [M]



2. $X_n = ([M]_0 - [M])/[I]_0 = p[M]_0/[I]_0$



3. Narrow polydispersity (M_w/M_n)

$M_w/M_n = 1 + 1/X_n$

CRP can be realized in different ways:

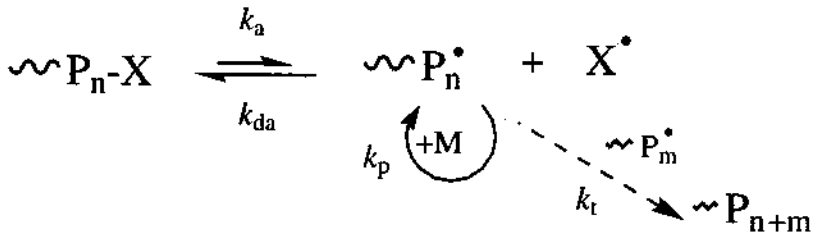
1. Atom-transfer radical polymerization (ATRP)
2. Stable free-radical polymerization (SFRP)

} reversible termination

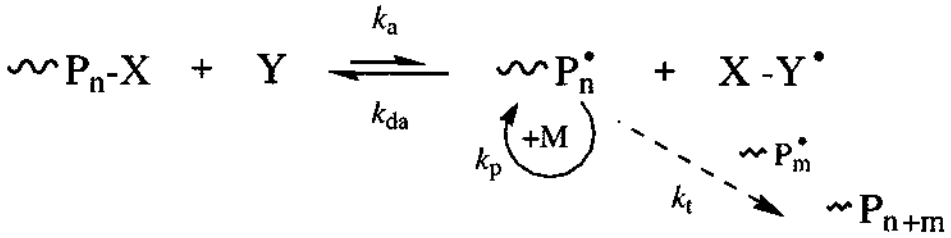
3. Reversible addition-fragmentation transfer polymerization (RAFT)

reversible chain transfer

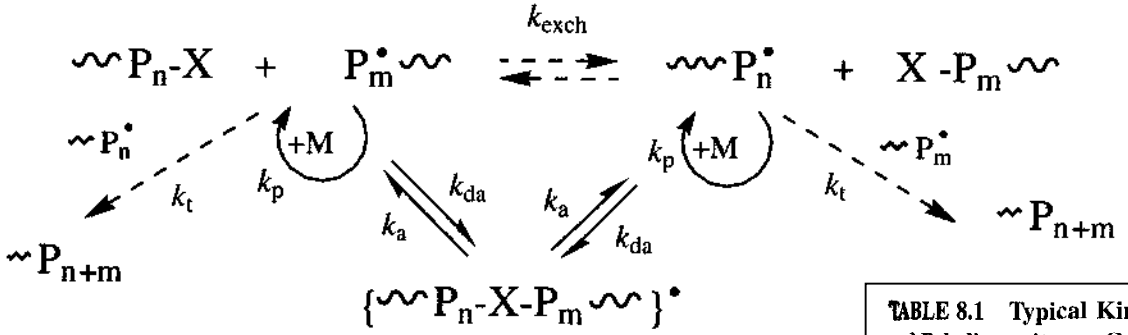
Mechanistic Classification of CRP



NMP/TEMPO



ATRP



RAFT

TABLE 8.1 Typical Kinetic Laws and Dependence of Degree of Polymerization and Polydispersity on Conversion for LRP

No.	Example	Kinetic Law	DP_n	Polydispersity
1	NMP/TEMPO	$R_p = k_p K_{eq}[I]_0/[X^\bullet]$	$DP_n = \Delta[M]/[I]_0$	$M_w/M_n = 1+(2/p-1)(k_p[I]_0)/(k_{da}[X^\bullet])$
2	ATRP	$R_p = k_p K_{eq}[I]_0[Y]/[XY^\bullet]$	$DP_n = \Delta[M]/[I]_0$	$M_w/M_n = 1+(2/p-1)(k_p[I]_0)/(k_{da}[XY^\bullet])$
4	DT[a]/RAFT	$R_p = k_p f k_d (k_t)^{-1/2}([I]_0)^{1/2}$	$DP_n = \Delta[M]/([TA]_0+\Delta[[I]])$	$M_w/M_n = 1+(2/p-1)(k_p/k_{exch})$

[a]Degenerative transfer.

Atom-Transfer Radical Polymerization (ATRP)

Radical generation in ATRP involves an organic halide undergoing a reversible redox process catalyzed by a transition metal compound such as cuprous halide:

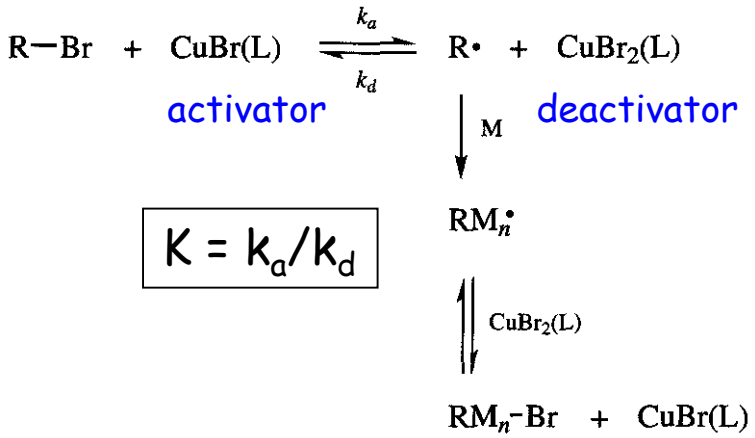
$$[R\bullet] = \frac{K[I][Cu^+]}{[Cu^{2+}]}$$

$$R_p = k_p[M\bullet][M]$$

$$R_p = \frac{k_p K[M][I][Cu^+]}{[Cu^{2+}]}$$

$$\ln\frac{[M]_0}{[M]} = \frac{k_p K[I][Cu^+]}{[Cu^{2+}]}\,t$$

$$\overline{X}_n = \frac{[M]_0 - [M]}{[I]_0} = \frac{p[M]_0}{[I]_0}$$



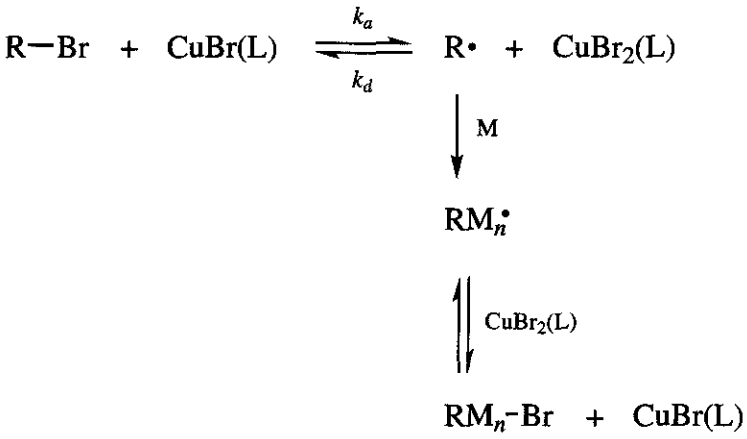
$K = k_a/k_d$

- Fast and quantitative initiation
- Rapid, reversible deactivation

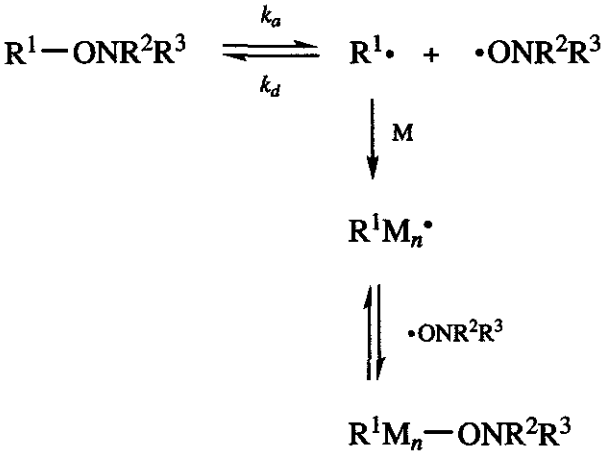
} All propagating chains grow at the same rate and for the same length of time

Stable Free-Radical Polymerization (SFRP)

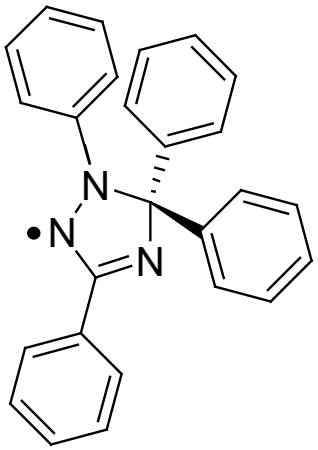
ATRP

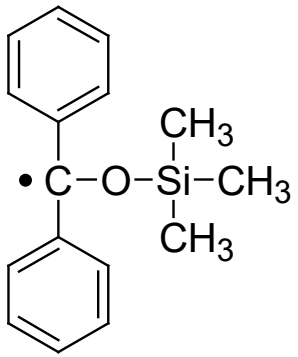


SFRP



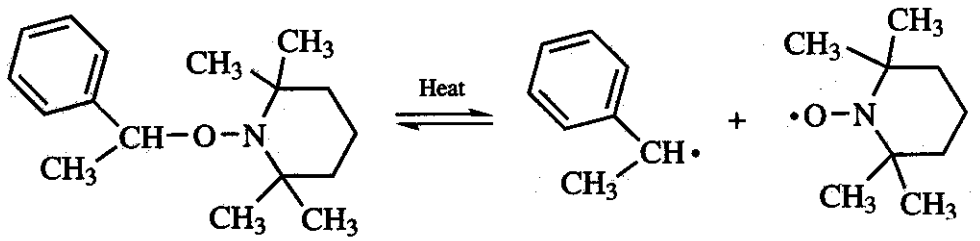
In SFRP, stable radicals such as nitroxide, triazolinyl, and trityl are used as persistent radical (deactivator)





SFRP with nitroxides is referred to as nitroxide-mediated polymerization (NMP)

There are two methods the carry out NMP:
(1) Termal decomposition of alkoxyamines



TEMPO = 2,2,6,6-tetramethyl-1-piperidinoxyl

(2) Use a mixture of a conventional initiator (AIBN, BPO) and a nitroxide radical

Nitroxide-Mediated Polymerization (NMP)

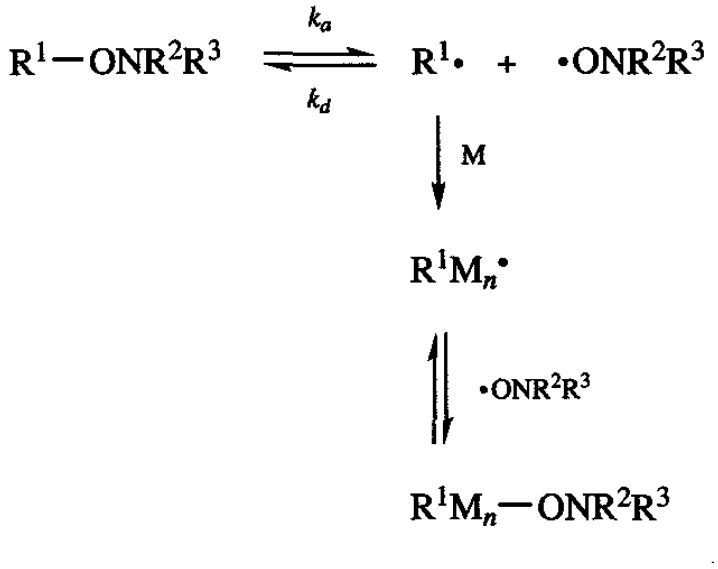
$$[R^1 \cdot] = \frac{K[R-ONR^2R^3]}{[\cdot ONR^2R^3]}$$

$$R_p = k_p[R^1 \cdot][M]$$

$$R_p = \frac{k_p K[M][ONR^2R^3]}{[\cdot ONR^2R^3]}$$

$$ln\frac{[M]_0}{[M]} = \frac{k_p K[ONR^2R^3]}{[\cdot ONR^2R^3]}\mathrm{t}$$

$$\overline{X_n} = \frac{[M]_0-[M]}{[R-ONR^2R^3]} = \frac{p[M]_0}{[R-ONR^2R^3]}$$



The only mechanistic difference in NMP to the ATRP is that there is no activator in NMP, which is present in ATRP (CuBr) that involves in the atom transfer process.

More realistic equations highlighting the mechanism of NMP are more complex due to the increased concentration of the persistent radical ($[\cdot ONR^2R^3]$) with respect to polymerization time.

ATRP versus NMP

ATRP	NMP
Wide range of initiators commercially available	Only a few initiators (either as nitroxides or as alkoxyamines) are commercially available

$K_{ATRP} > K_{NMP}$ and is more easily adjusted by changing initiator, transition metal and ligands (large K = faster polymerization under milder conditions)

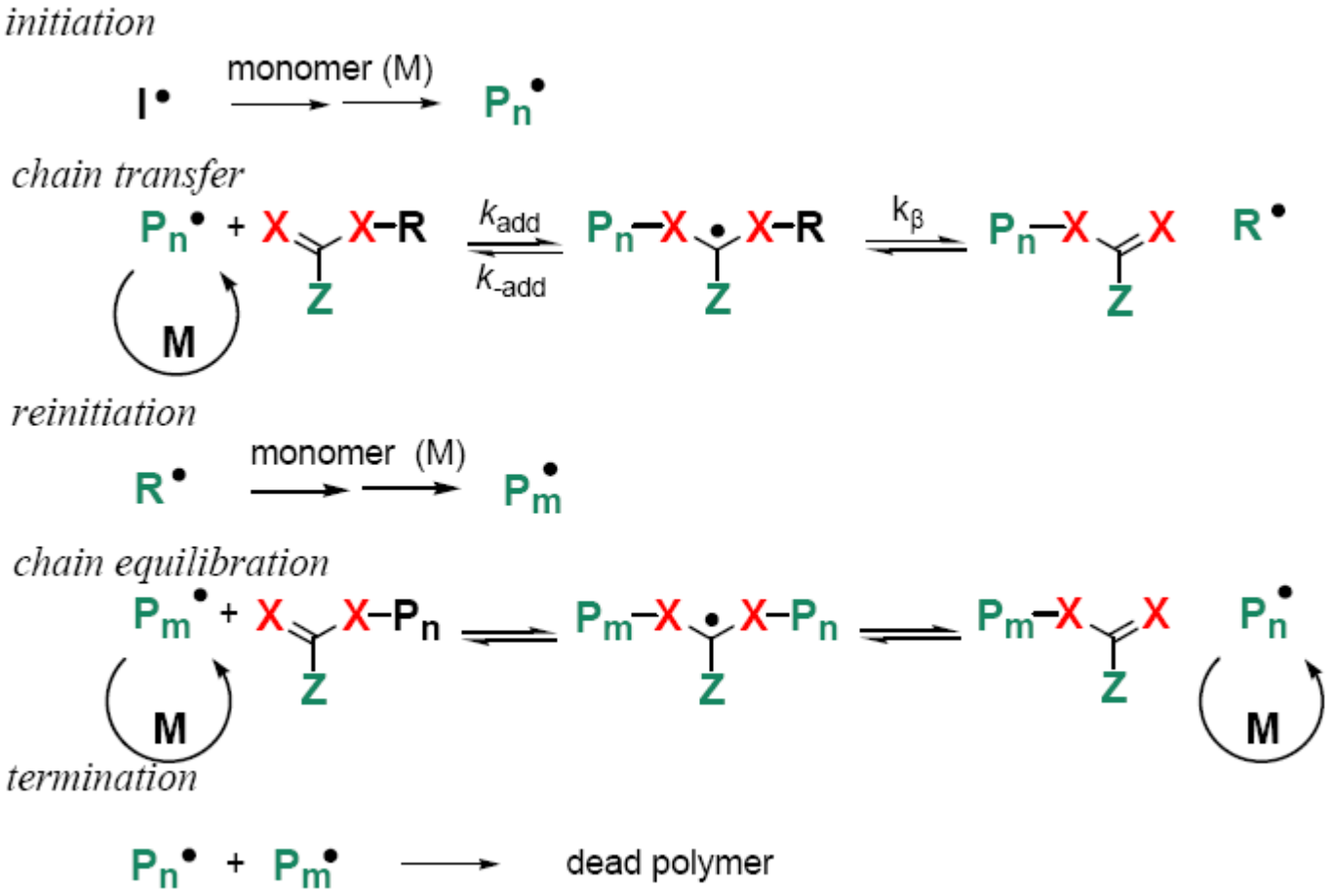
Metal (0.1 – 1%) needs to be removed from reaction mixture

In both ATRP and NMP, control of the reaction through establishment of a steady-state radical concentration that is achieved by the balance between activation and deactivation

Conventional radical polymerization involves a balance between the rates of initiation and termination

Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

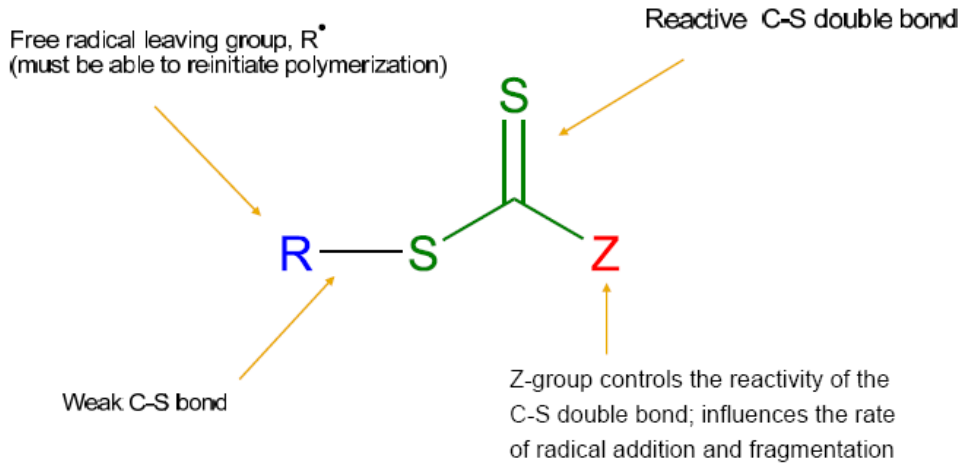
- ATRP and NMP control chain growth by reversible termination
- RAFT controls chain growth via reversible chain transfer



Moad, G.; Rizzardo, E.; Thang, S.H. *Aust. J. Chem.* **2005**, *58*, 379-410.

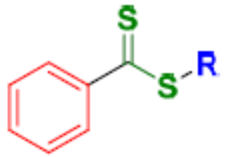
The RAFT agents

General Characteristics:

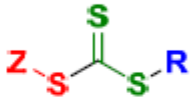


Types of RAFT agents:

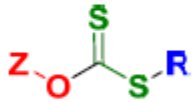
- Dithiobenzoates
  - very high transfer constants
  - prone to hydrolysis
  - may cause retardation when used in high concentrations



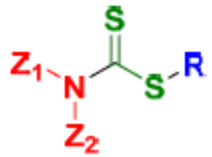
- Trithiocarbonates
  - are readily synthesized
  - high transfer constants
  - cause less retardation and are more hydrolytically stable (than dithiobenzoates)



- Xanthates
  - lower transfer constants
  - more effective with less activated monomers
  - Made more active by electron-withdrawing substituents



- Dithiocarbamates
  - activity determined by substituents on N
  - effective with electron-rich monomers



Moad, G.; Rizzardo, E.; Thang, S.H. *Aust. J. Chem.* **2005**, *58*, 379-410.

Kinetics of RAFT polymerization has not been completely established, and the set of equations trying to predict the kinetics of RAFT polymerization are highly complex.

$$\overline{X}_n \approx \frac{p[\mathrm{M}]_0}{(p'[\mathrm{RAFT}]_0 + 2fp''[\mathrm{I}]_0)} \quad \Rightarrow \quad \overline{X}_n = \frac{p[\mathrm{M}]_0}{[\mathrm{RAFT}]_0}$$

Successful RAFT, i.e. living polymerization, requires high concentrations of RAFT agent compared to initiator ($[\mathrm{RAFT}]_0 \gg [\mathrm{I}]_0$) and large chain-transfer constants

RAFT Pro's	RAFT Con's
• Works with a wider range of monomers than NMP and ATRP • Produced polymers do not contain residual metal	• RAFT agents not commercially available • Polymers contain dithioester end group, which can cause problems in terms of odor and colour

Concluding Remarks

TABLE 8.3 Comparison of NMP, ATRP, and Degenerative Transfer Systems

Feature	Systems NMP	ATRP	Degenerative Transfer (RAFT)
Monomers	Styrenes with TEMPO Also acrylates and acrylamides using new nitroxides NO methacrylates	Nearly all monomers with activated double bonds NO vinyl acetate	Nearly all monomers
Conditions	Elevated T (>120°C for TEMPO) Waterborne systems OK Sensitive to oxygen	Large T range (−30–150°C) Waterborne systems OK Some tolerance to O_2 and inhibitor with Mt^0	Elevated temperatures for less reactive monomers Waterborne systems OK Sensitive to oxygen
End Groups/ Initiators	Alkoxyamines Thermally unstable Relatively expensive Requires radical chemistry for transformations May act as a stabilizer	Alkyl (pseudo)halides Thermally and photostable Inexpensive and available Either S_N, E, or radical chemistry for transformations Halogen exchange for enhanced cross-propagation	Dithioesters, iodides, and methacrylates Less thermally stable and less photo stable Relatively expensive Radical chemistry for transformations (S_N for RI) Color/odor
Additives	None NMP may be accelerated with acyl compounds	Transition metal catalyst Should be removed and recycled	Conventional radical initiator May decrease end functionality May produce too many new chains

Concluding Remarks

There are limitations for all types of LRP:

The occurence of irreversible bimolecular termination of propagating radicals becomes considerable under conditions such as: high monomer conversion, polyfunctional initiators, high initiator concentration and high target molecular weight (about > 100.000)