B.19) CONTROLLED/ “LIVING”/ STABLE RADICAL POLYMERIZATIONS (CRP/ LRP/ SRP), with Emphasis in NITROXIDE-MEDIATED POLYMERIZATIONS

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(Preferred name: CRP, since even though they provide control of MWs and MWDs, chain termination reactions cannot be completely eliminated.)

INTRODUCTION

Advantages of Controlling Polymerization

1. **Molecular weight is a function of conversion; and:** $\bar{r}_\mathrm{n} = \frac{\Delta[\mathrm{M}^0]}{[\mathrm{I}^0]}$

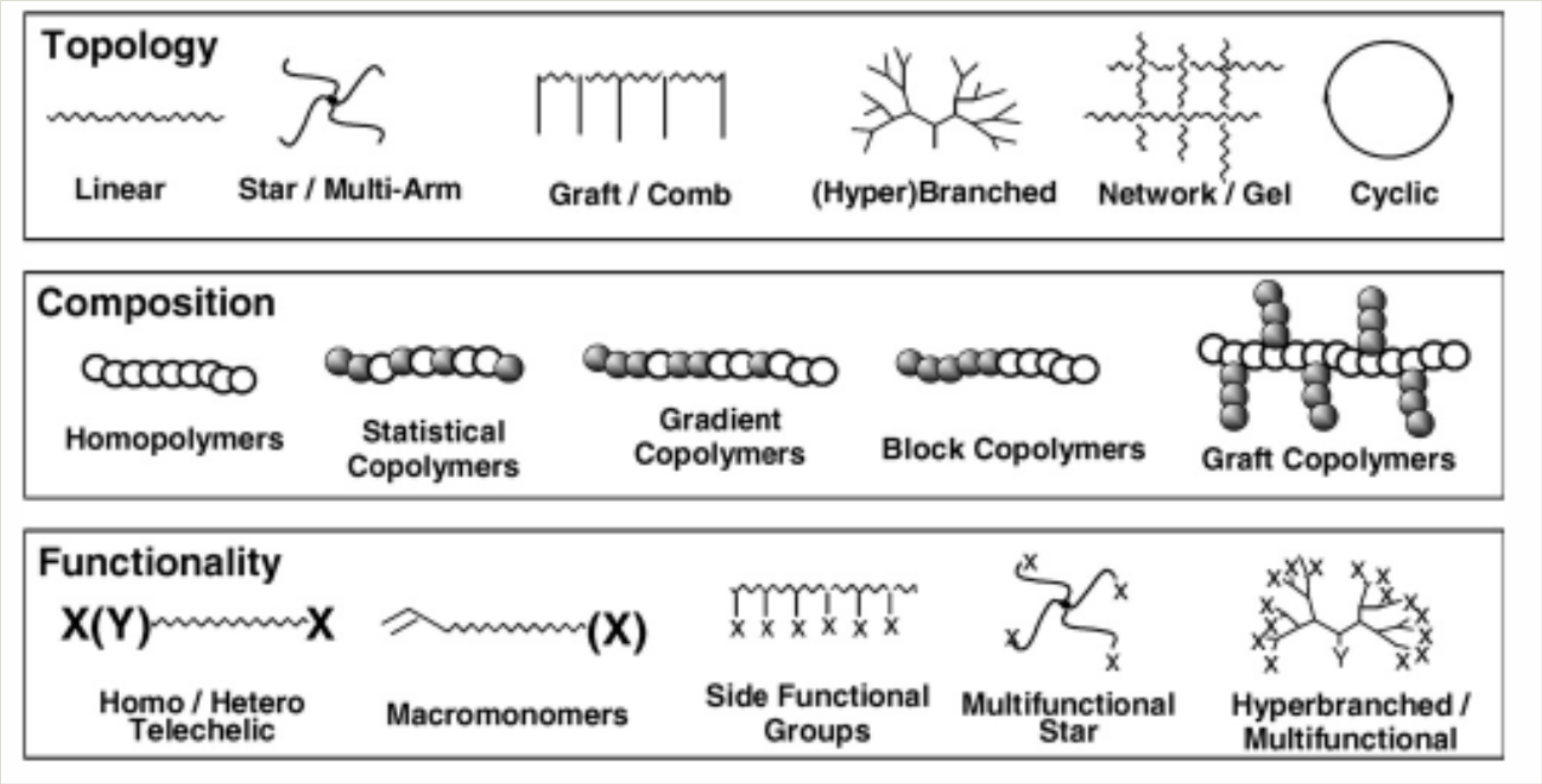
2. **Constant number of polymer molecules that is independent of conversion.**

3. **Narrow molecular weight distribution (as long as all chains grow uniformly, which is not possible at higher molecular weights).**

$$1.01 < \overline{M}_\mathrm{n} / \overline{M}_\mathrm{n} < 1.5 \qquad 200 < \overline{M}_\mathrm{n} < 10^6 \text{ g/mol}$$

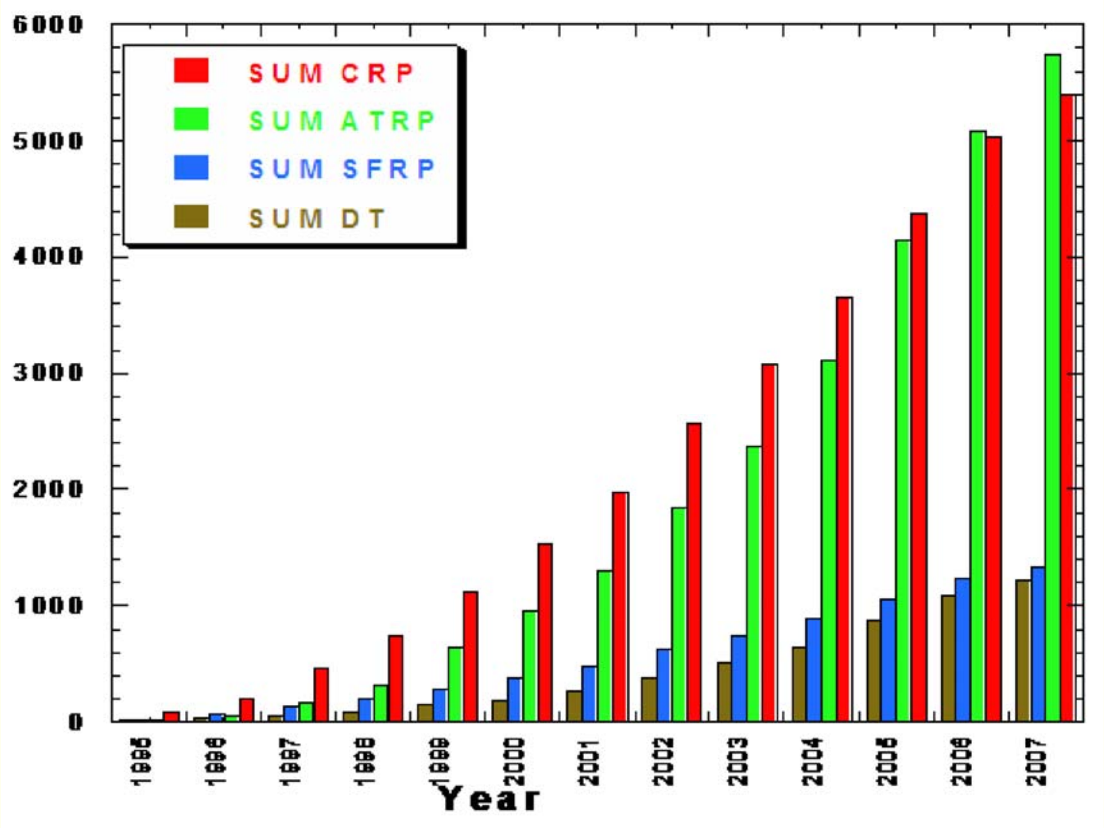
4. **Can control polymer tacticity, topology, and chemical composition.**

5. **Can make end-functionalized (telechelic) polymers.**



Possible Applications: coatings, adhesives, surfactants, dispersants, lubricants, gels, additives, thermoplastic elastomers, electronics, biomaterials.

Cummulative Number of Publications (2007)



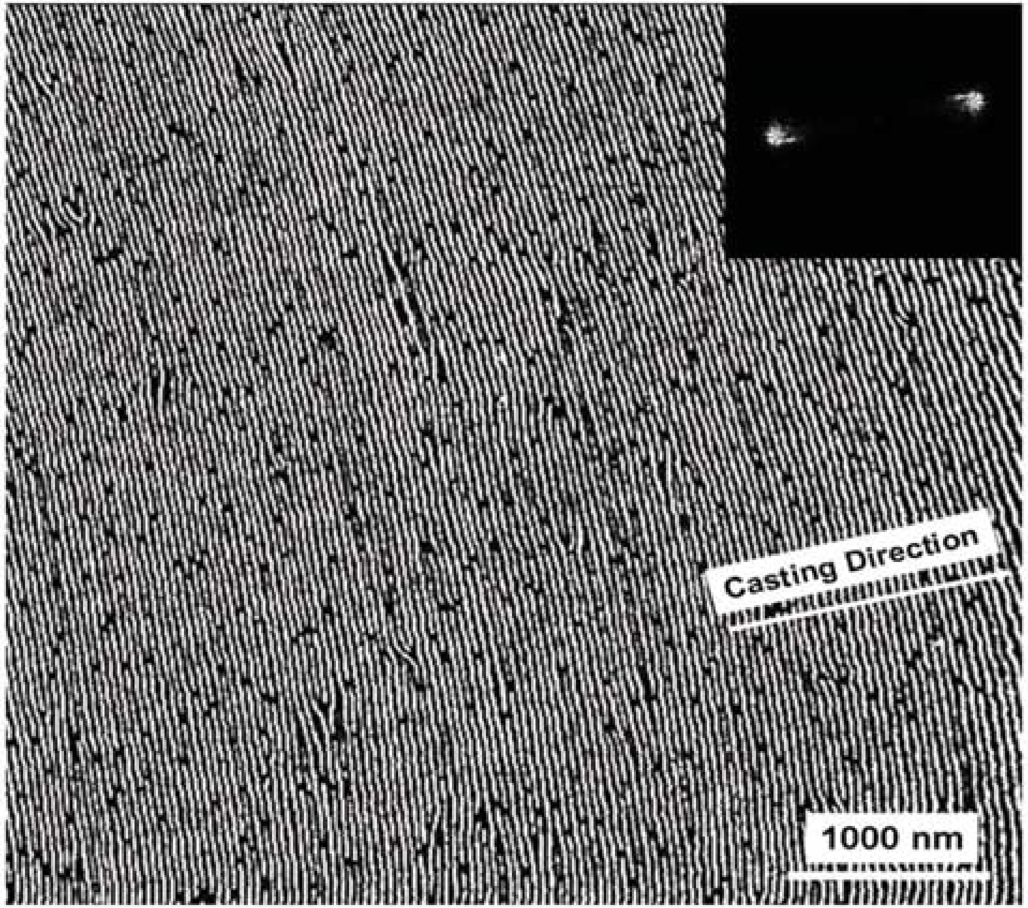
The data displayed is current to August 2007, and was obtained by conducting a search on SciFinder Scholar using the following terms:

1. **"controlled radical polymn" or "living radical polymn" ("SUM CRP" in the figure),**
2. **"ATRP or atom transfer (radical) polymn" (i.e. SUM ATRP in the figure refers to ATRP only, this does not include terms like metal mediated or metal catalyzed radical polymerization),**
3. **"NMP or SFRP or nitroxide mediated polymn or stable free-radical polymn" ("SUM SFRP") and**
4. **"RAFT or reversible addition transfer or degenerative transfer or catalytic chain transfer" ("SUM DT").**

Ex. 1: Poly(BuA-*b*-AN) with 17.5% of PAN

Poly(butyl acrylate-b-acrylonitrile) copolymer with 17.5% polyacrylonitrile:

AFM phase image of a thin film formed by zone casting.



Ex. 2: Four-Armed Star Brush Copolymer

(Both macroinitiator preparation and ‘grafting’ from reaction used ATRP)

AFM image of four-arm star molecular brushes with poly(n-butyl acrylate) side chains on a mica surface.

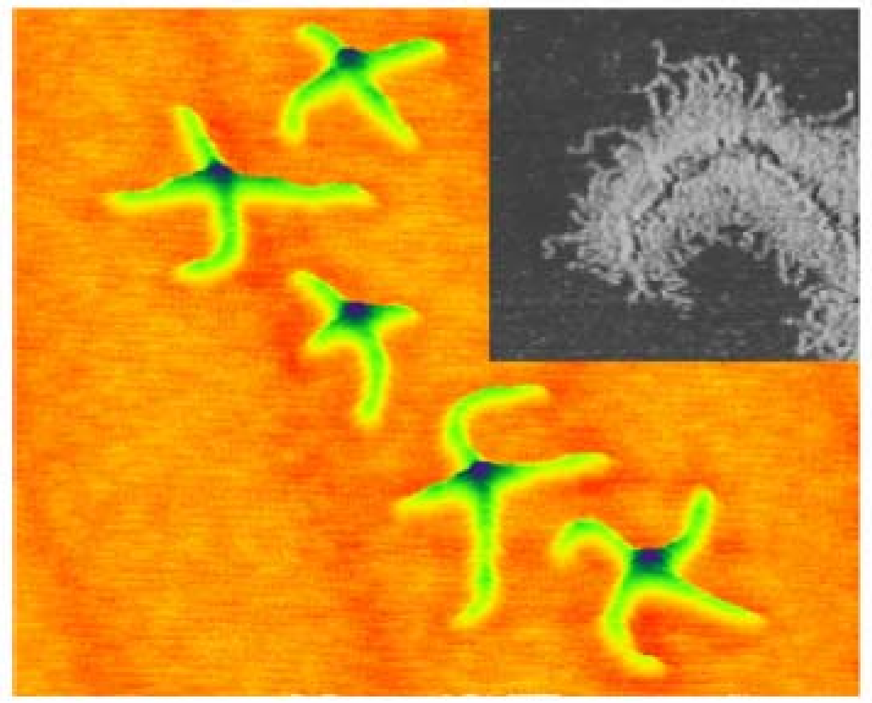
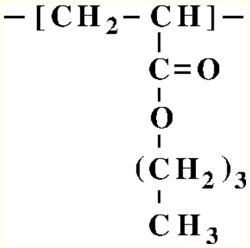


Fig. 16. AFM image of four armed star brushes prepared by ATRP [356].

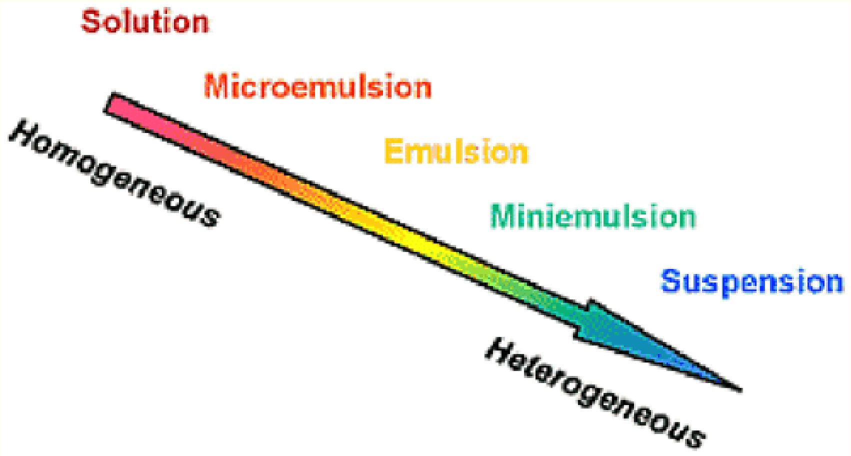
Atomic force microscopy (AFM) image of a poly(n-butyl acrylate) molecular brush on a mica substrate.

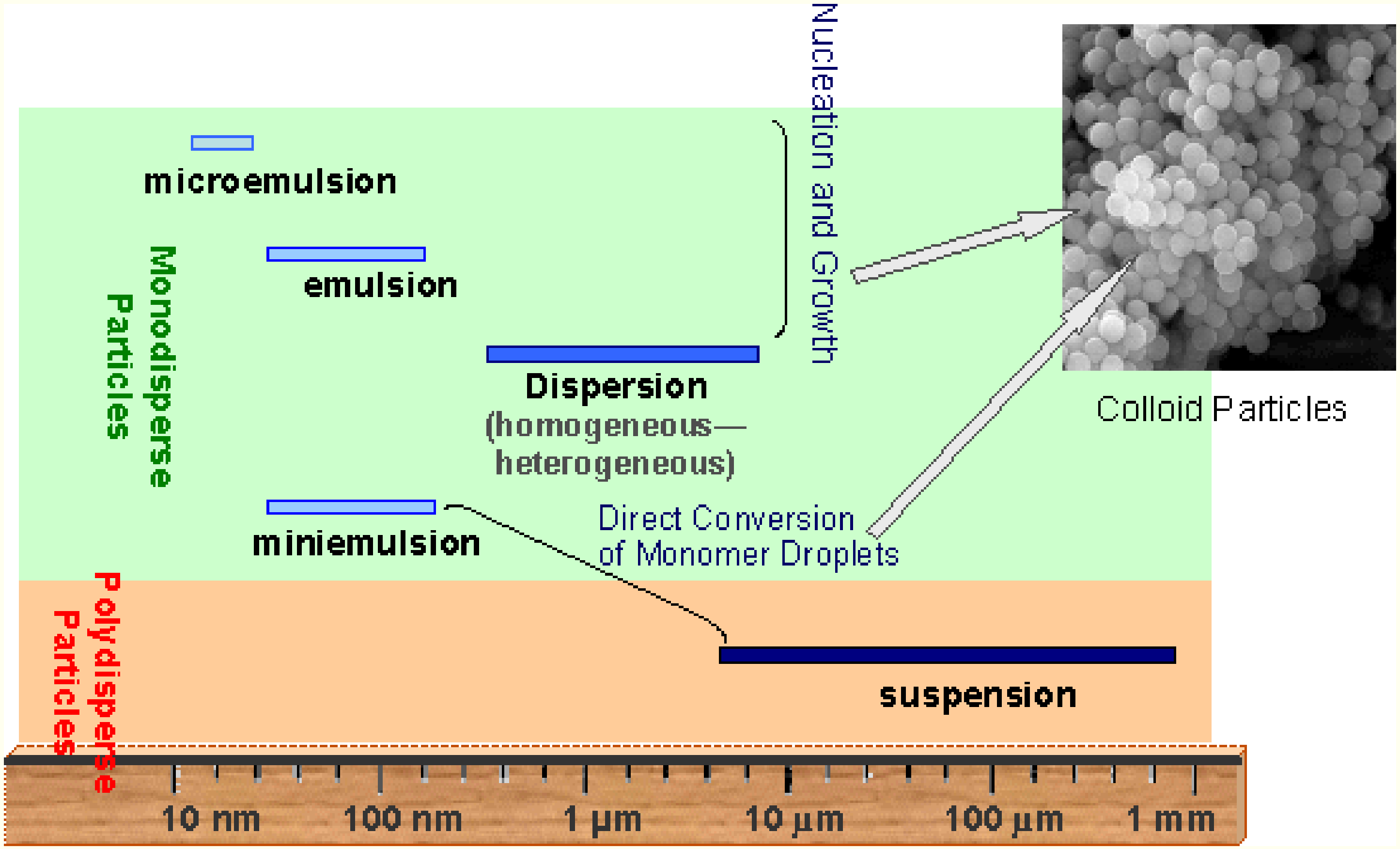


$$-[\mathrm{CH_2-CH}]-\ \ (\mathrm{CH}-\mathrm{C{=}O}-\mathrm{O}-(\mathrm{CH_2})_3-\mathrm{CH_3})$$

CRPs:

Carried out in Homogeneous and Heterogeneous Systems





Review of Conventional Radical *vs.* Living Anionic Polymerizations

Conventional Radical Polymn.

$$\begin{aligned} &I \xrightarrow{K_d} 2\,R^{\cdot}_{in} \\ &R^{\cdot}_{in} + M \xrightarrow{K_i} R^{\cdot}_{1} \end{aligned}$$

Slow and continuous initiation ($k_d \approx 10^{-5}\ s^{-1}$) (halflives ~ 10 hs)

$$R^{\cdot}_{r} + M \xrightarrow{K_p} R^{\cdot}_{r+1}$$

Fast propagation ($k_p \approx 10^{3}\ mol^{-1}\ s^{-1}$)

$$\begin{tikzcd} & P_r + P_s \text{ by disproportionation} \\ R^{\cdot}_{r} + R^{\cdot}_{s} \arrow[ur, "K_{td}"] \arrow[dr, "K_{tc}"'] & \\ & P_{r+s} \text{ by combination} \end{tikzcd}$$

Very fast, and 2nd order w/respect to growing rads ($k_t \approx 10^{7}\ mol^{-1}\ s^{-1}$)

$$\mathbf{R}^{\bullet}_{r} + \mathbf{M} \rightarrow R^{\bullet}_{1} + \mathbf{P}_{r}$$

Fast, and 1st order w/respect to growing rads

Living Anionic Polymn.

$$I + M \xrightarrow{K_I} P^{*}_{1}$$

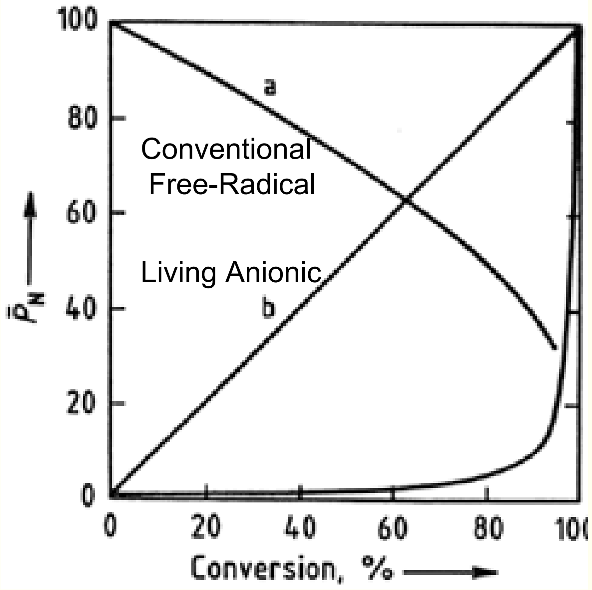
Fast initiation required

$$P^{*}_{r} + M \xrightarrow{K_p} P^{*}_{r+1}$$

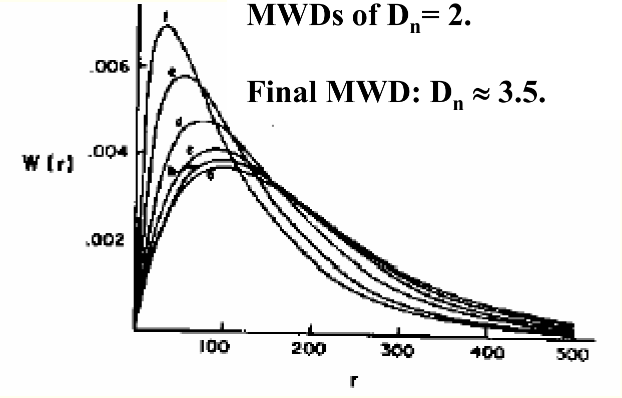
Constant conc. of living ends

	Conventional Radical	Living Anionic
Advantages	• Most compounds with C=C bonds can be either homo- or copolymerized. • Involves more than 50% of all industrial polymerizations. • Polymerization in a wide *T* range (-80 to 250ºC). • Tolerant to water.	• Unsurpassed flexibility for producing 'tailor-made' polymers (i.e.: block copolymers, star copolymers, telechelic polymers, etc.).
Disadvantages	• Macromolecular engineering not feasible (it is impossible to produce block copolymers or controlled arquitectures due to the very fast growth and deactivation of the individual chains). • Requires absence of oxygen. • Final initiator conversion: around 20%. • Impossible to simultaneously control polymerization rate and MWs.	• Stringent reaction conditions (use of ultrapure reagents and in total exclusion of water and oxygen). • Polymerization restricted to relatively few vinyl monomers. • Not easy to produce random copolymers.

MWDs in Ideal Batch Chain-Growth Polymerizations



Ideal Conventional Free-Radical

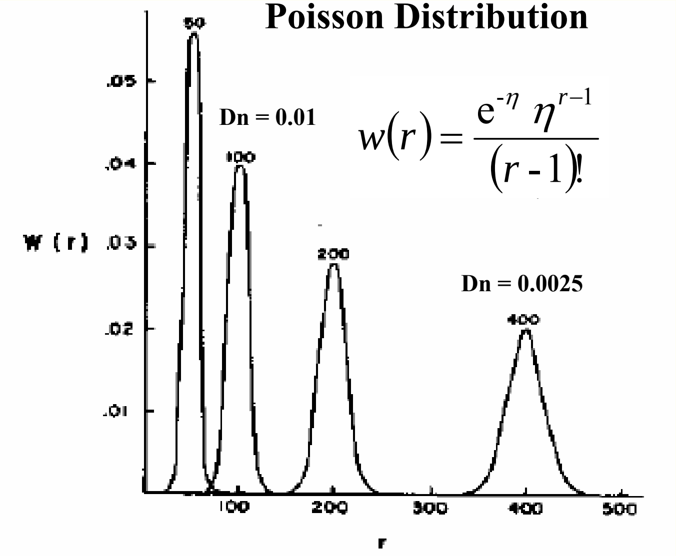


Typically:
Instantaneous "Most Probable" MWDs of D_n= 2.

Final MWD: $D_n \approx 3.5$.

curve	*x*
a	0.01
b	0.10
c	0.25
d	0.50
e	0.75
f	0.90

Ideal Living Anionic (Inst. Initiation)



Poisson Distribution

Dn = 0.01

$$w(r) = \frac{e^{-\eta}\,\eta^{r-1}}{(r-1)!}$$

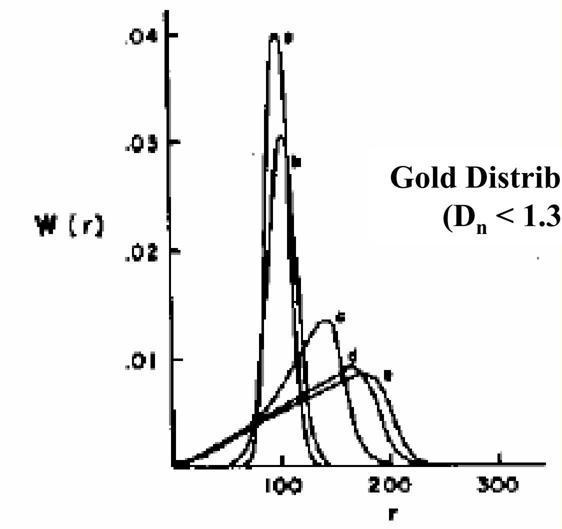
Dn = 0.0025

$$\bar{r}_n = \frac{\Delta[M^0]}{[I^0]} = \eta$$

$$\bar{r}_w / \bar{r}_n = 1 + \frac{1}{\bar{r}_n}$$

Nonideal "Living" Anionic Polymerization in Batch Reactors

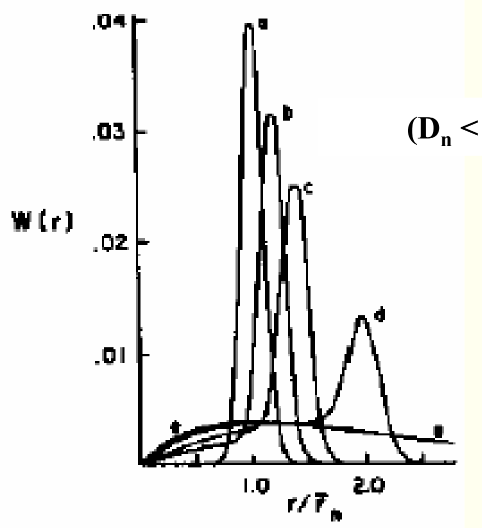
Slow initiation + no termination



Gold Distribution
($D_n < 1.35$)

curve	k_p/k_i
a	1
b	10
c	100
d	1000
e	10000

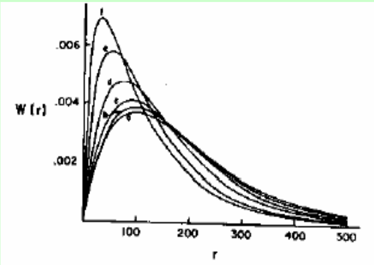
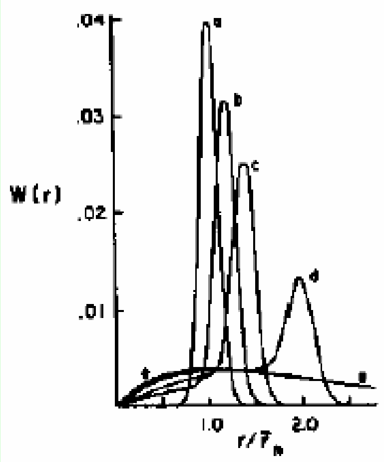
Inst. initiation + slow termination of living ends



($D_n < 2$)

curve	R_t/R_p
a	0
b	0.003
c	0.005
d	0.008
e	0.010

Effect of Reactor Residence Time Distribution

<table>
<tr><th></th><th>Conventional Free Radical</th><th>Living Anionic (slow Ter.)</th></tr>
<tr><td>Batch
or
Continuous
Tubular Reactor</td><td>
</td><td>
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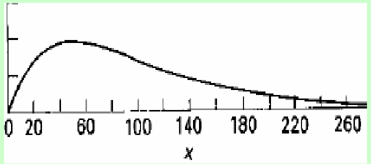
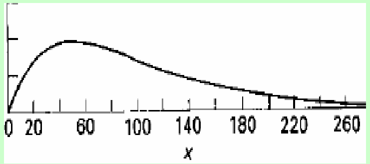
<tr><td>HSTR</td><td>
</td><td>
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CRPs: Ideal *vs.* Nonideal Reactions

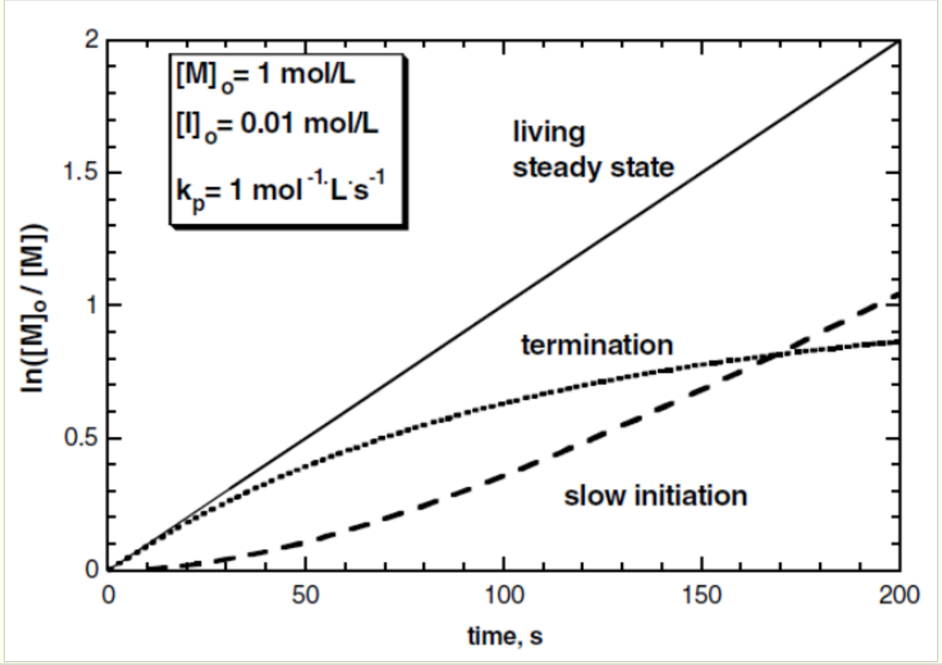
Ideal Living Polymerization with Fast Initiation and Constant Concentration of “Living Ends” ([*P] = constant):**

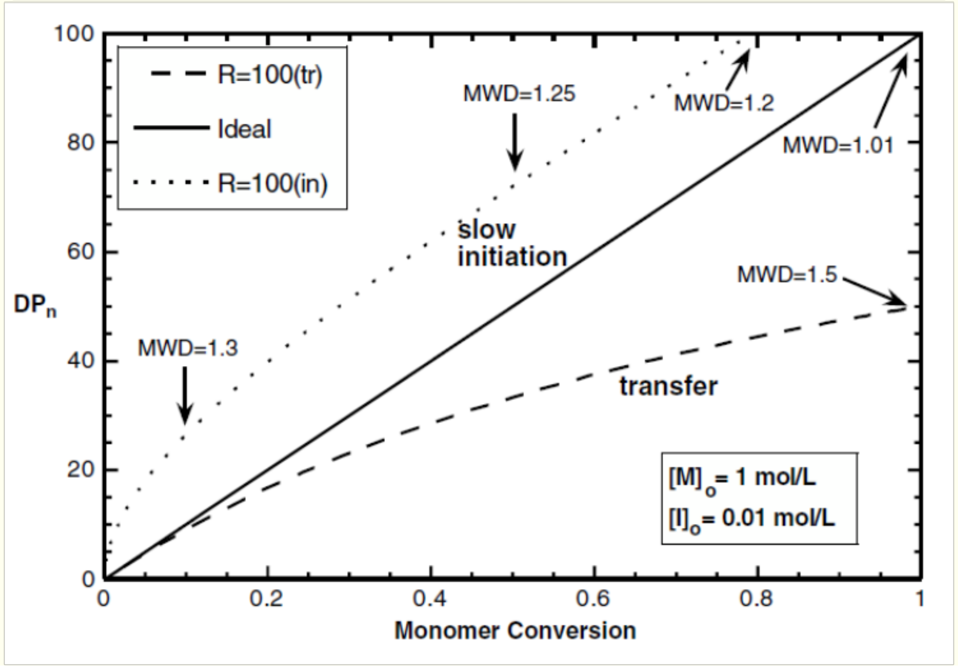
$$R_p = \frac{-d[M]}{dt} = k_p[P^*][M]$$

$$\ln\frac{[M]_0}{[M]} = k_p[P^*]t = k_p^{app}[P^*]t$$

Ideal CRPs: characterized by the linear relationships:

- **ln([M]$_0$/[M] *vs. t***
- **DP$_n$ *vs. x*   (even with deactivation of living ends)**

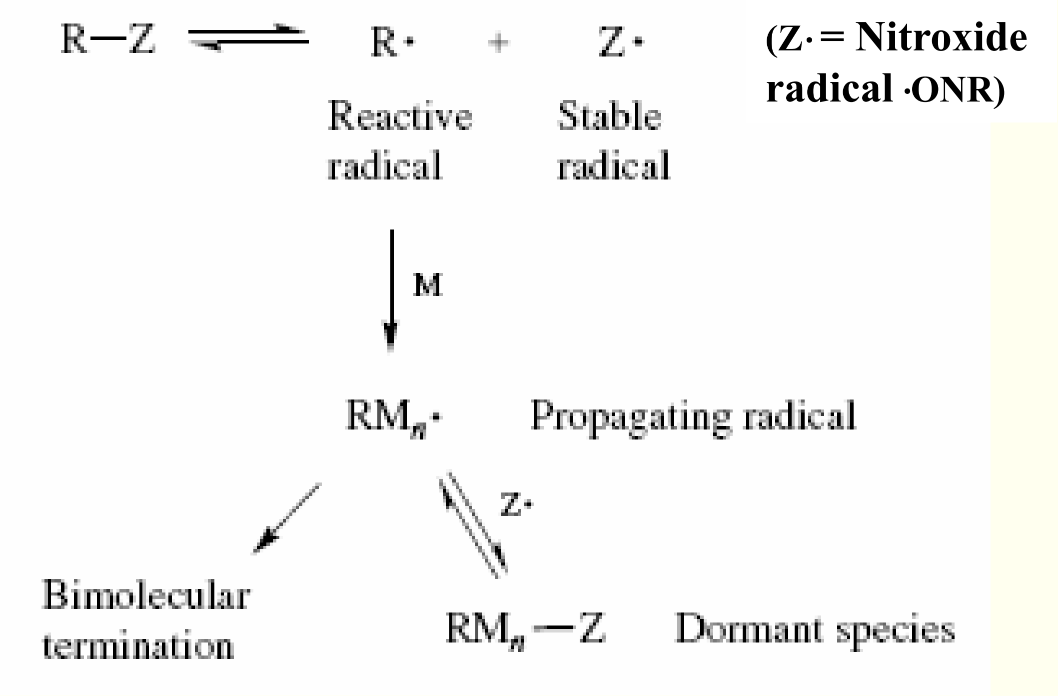




Stable Free-Radical Polymerizations (SFRP)

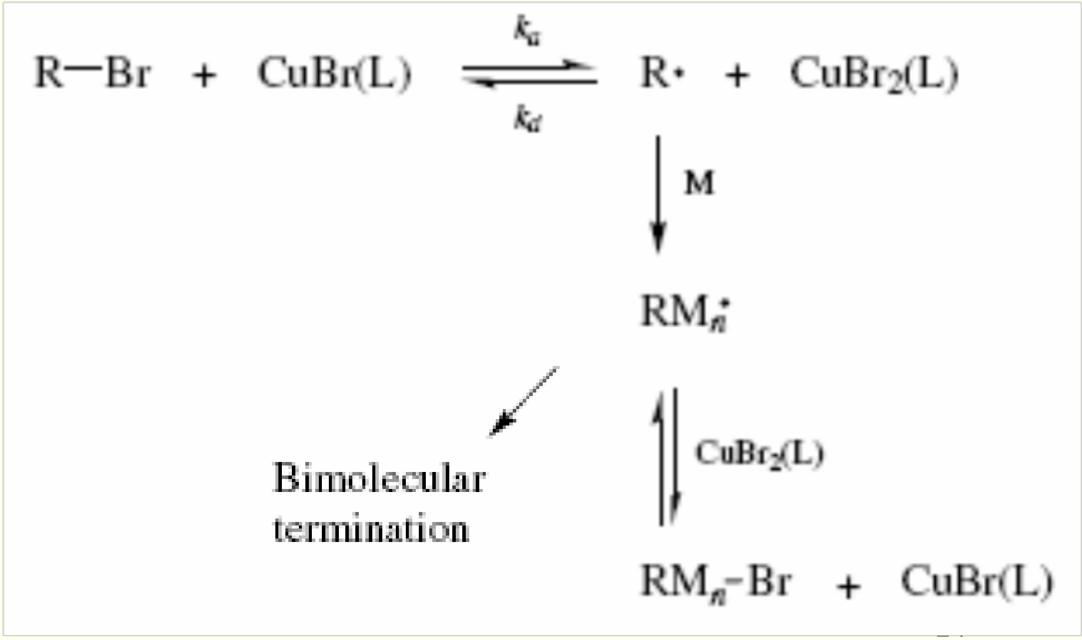
1) Reversible Deactivation by Coupling

e.g.: Nitroxide-Mediated Polymerization (NMP)



2) Reversible Deactivation by Atom Transfer

e.g.: Atom Transfer Reversible Polymerization (ATRP)



Conventional Radical *vs.* CRPs

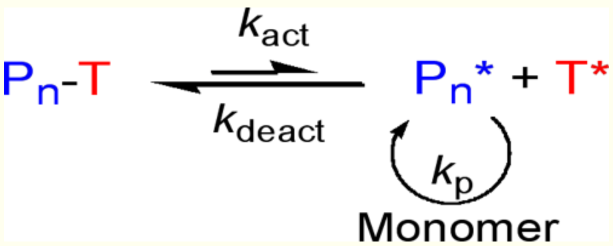
Similarities: **Conventional and CRP's share a common radical mechanism. Therefore, they both can polymerize a similar range of monomers, and produce similar chemo-, regio- and stereo-selectivities.**

Differences:	**Conventional RP**	**Controlled RP**
Generation of radicals	Radicals are formed continuously and irreversively at a small rate.	Radicals are formed reversively, at both the initiation and propagation stages
SS conc. of radicals obtained by balancing:	Similar rates of initiation (Ri) and termination (Rt)	Similar rates of activation and deactiv.; with (Ri, Ract, and Rdeact) >> Rt
Lifetime of growing chain	~ 1 sec	> 1 hour due to active/dormant exchange
Initiation	Relatively slow	Very fast (all chains begin growing reversibly at essentially the same time)
Dead chains	Nearly all	~10 %
Rate of polymerization	Fast	Slower
Termination	Occurs between long-long, long-short, and short-short chains	Between chains of almost the same length

CRPs: Classification according type of main reversible reaction

1) Reversible Deactivation by Coupling

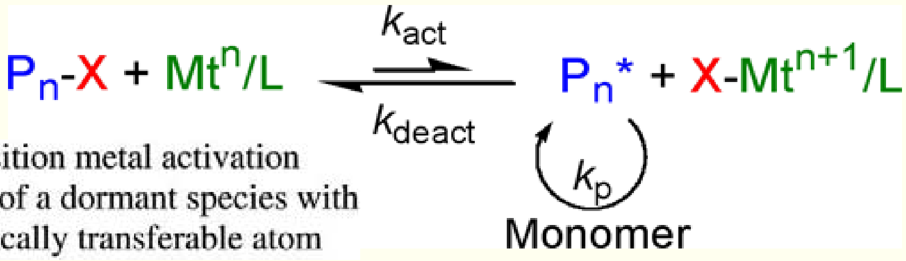
***e.g.*: Nitroxide-Mediated Reversible Polymerization (NMRP)**



T*: stable or "persistent" nitroxide radical (·ONR), that cannot terminate with itself.C

2) Reversible Deactivation by Atom Transfer

***e.g.*: Atom Transfer Reversible Polymerization (ATRP)**



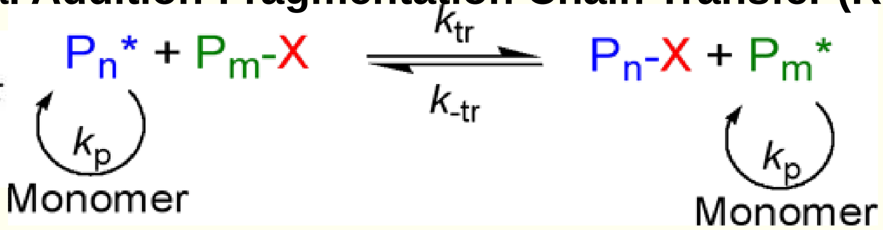
Transition metal activation (k_{act}) of a dormant species with a radically transferable atom

Essentially identical mechanisms of SFRP's

3) Degenerative Transfer

***e.g.*: Radical Addition-Fragmentation Chain Transfer (RAFT)**

Majority of chains are dormant species that participate in transfer reactions (k_{exch}) with a low concentration of active radicals



1) Reversible Deactivation by Coupling

e.g.: Nitroxide-Mediated Polymerization (NMP)

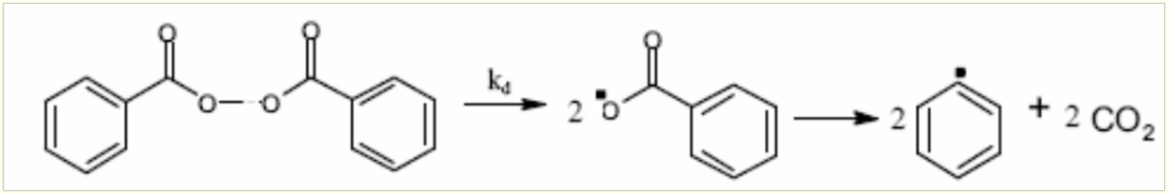
- **Initiation:**

There are two possible initiation mechanisms

1) Bimolecular Initiation

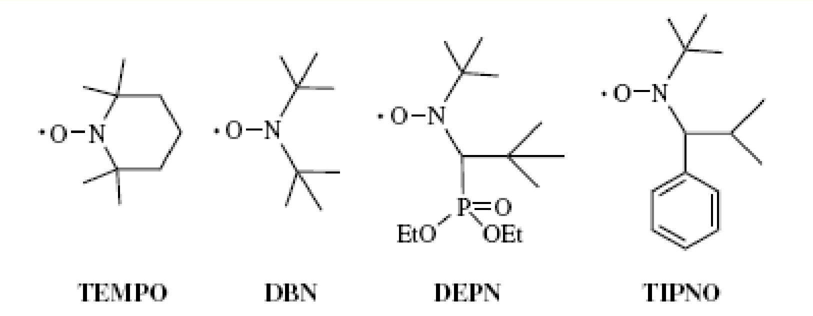
(Mixture of Standard Chemical Initiator + Stable or "Persistent" Nitroxide Radical)

Benzoyl Peroxide decomposition

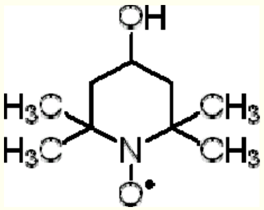


+

TEMPO and TEMPO-Derived Stable Nitroxide Radicals

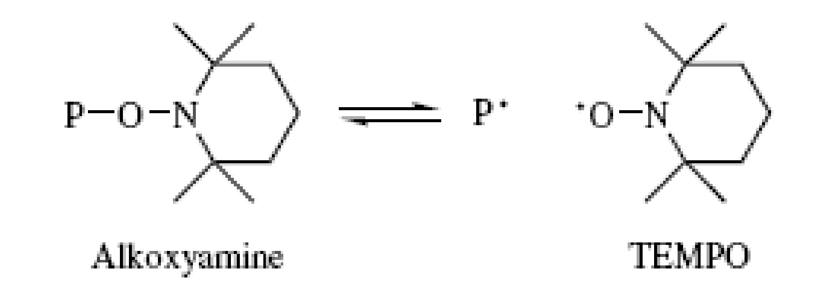


4 OH-TEMPO

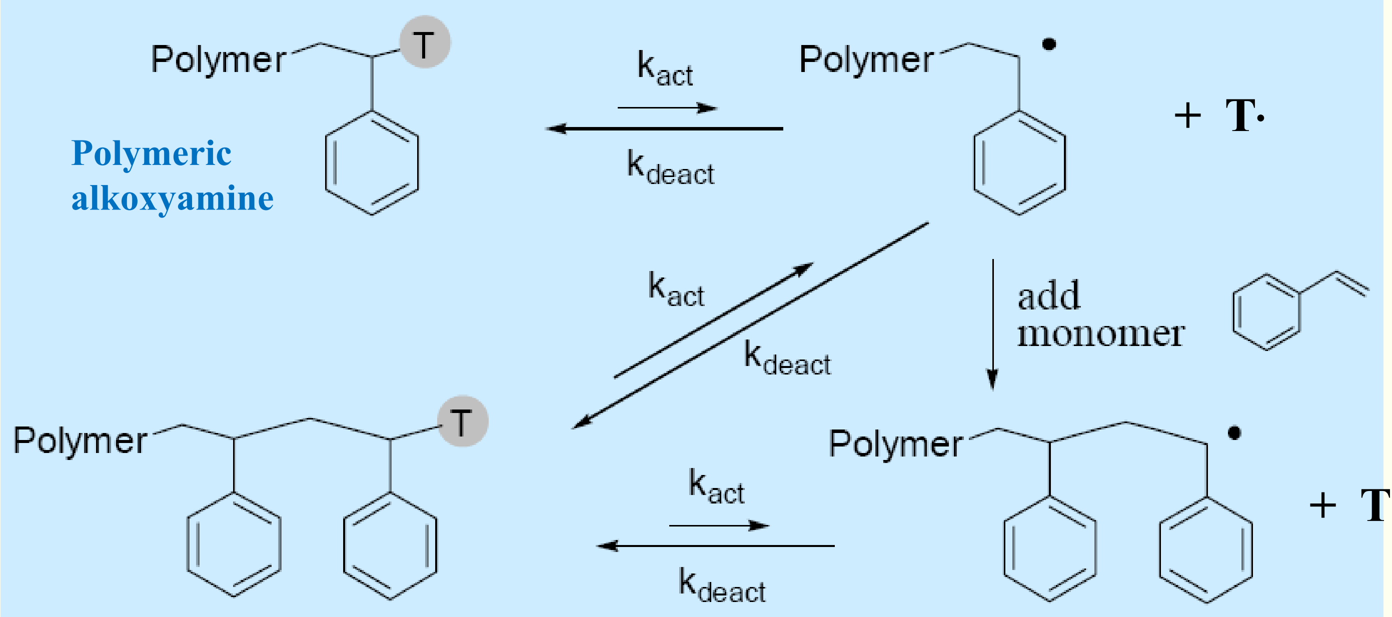


T·

2) Monomolecular Initiation (by Decomposition of an Alkoxyamine Adduct)



- **Propagation**



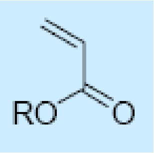
T·: Stable or "Persistent" Nitroxide Radical

2) Reversible Deactivation by Atom Transfer

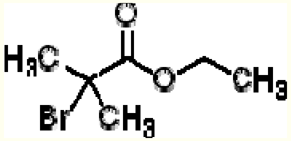
e.g.: Atom Transfer Reversible Polymerization (ATRP)

Polyacrylates with Alkyl(pseudo)halides

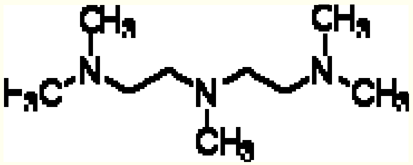
Monomer:
Alkyl acrylate



Initiator:
2-Ethyl Bromide
Isobutirate
(**R-Br**)



Complexing Ligand:
Penta Methyl Diethyl Tetramine
(**PMDETA**)



Catalyst:
Copper Chloride (**CuCl**)

Reinitiation: R-Br + CuCl/PMDETA → R• + BrCuCl/PMDETA

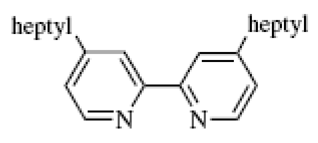
Propagation: R• + M → R-M•

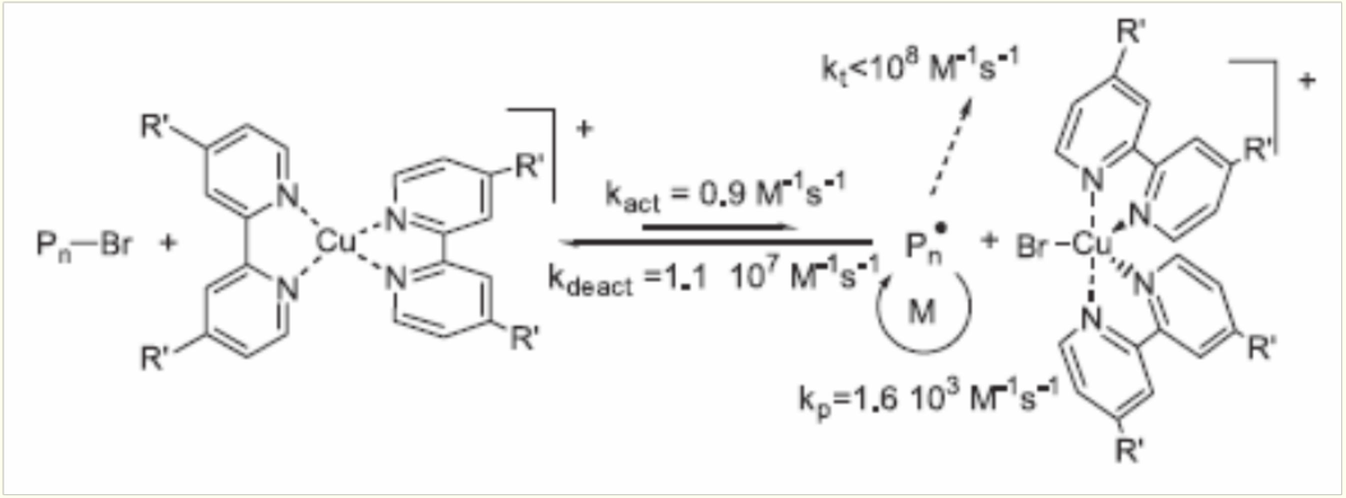
Deactivation: R-M• +BrCuCl/PMDETA ↔ R-M-Br + CuCl/PMDETA

etc.

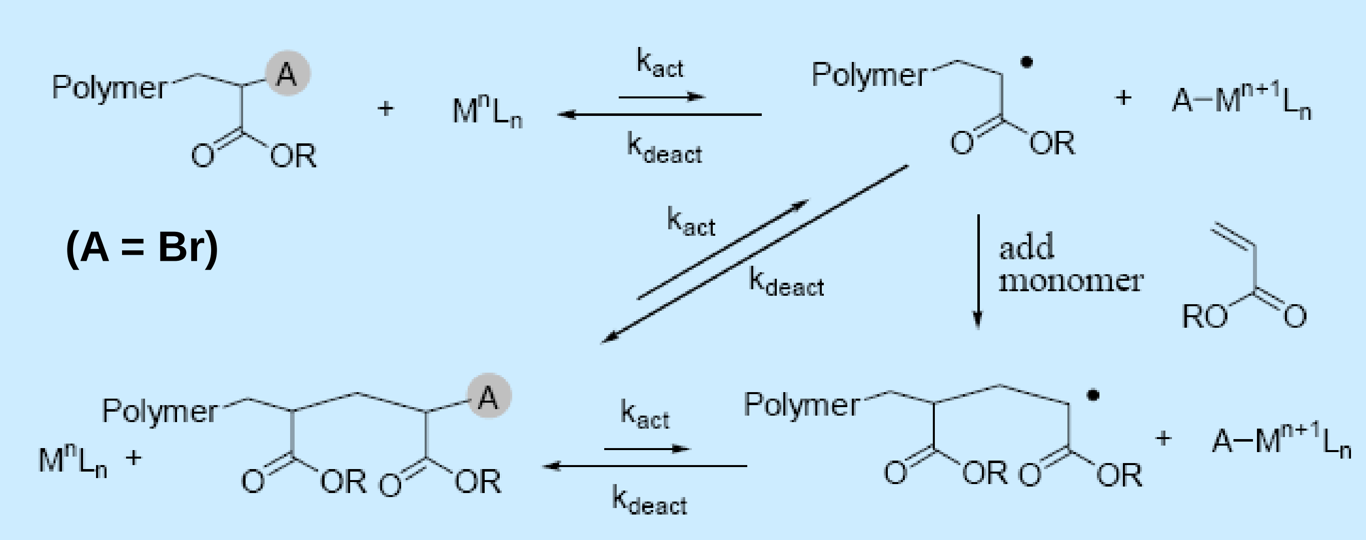
Global Reaction

Complexing Ligand:
Diheptyl Bipyridine





Global Acrylate Polymerization:

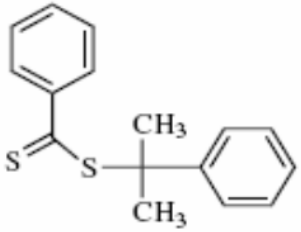


(A = Br)

3) Degenerative Transfer

e.g.: Radical Addition-Fragmentation Chain Transfer (RAFT)

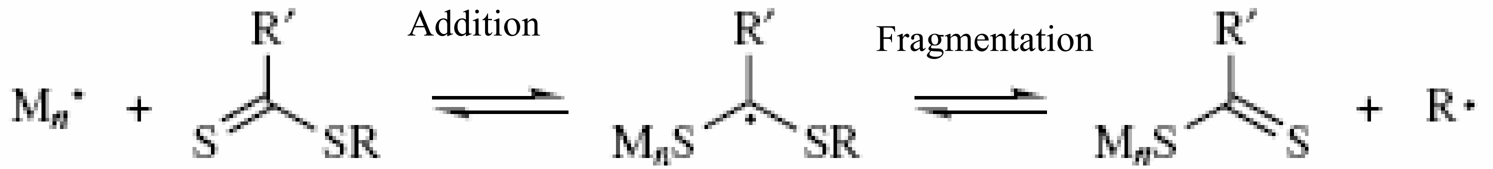
Requires a permanent and slow chemical initiation in the presence of a Ditioester Transfer Agent:



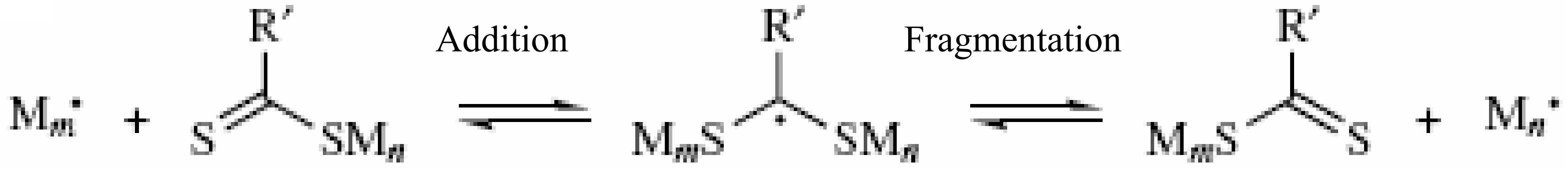
Cumyl dithiobenzoate

$M_n^{\bullet}$: growing radical of *n* repeating units

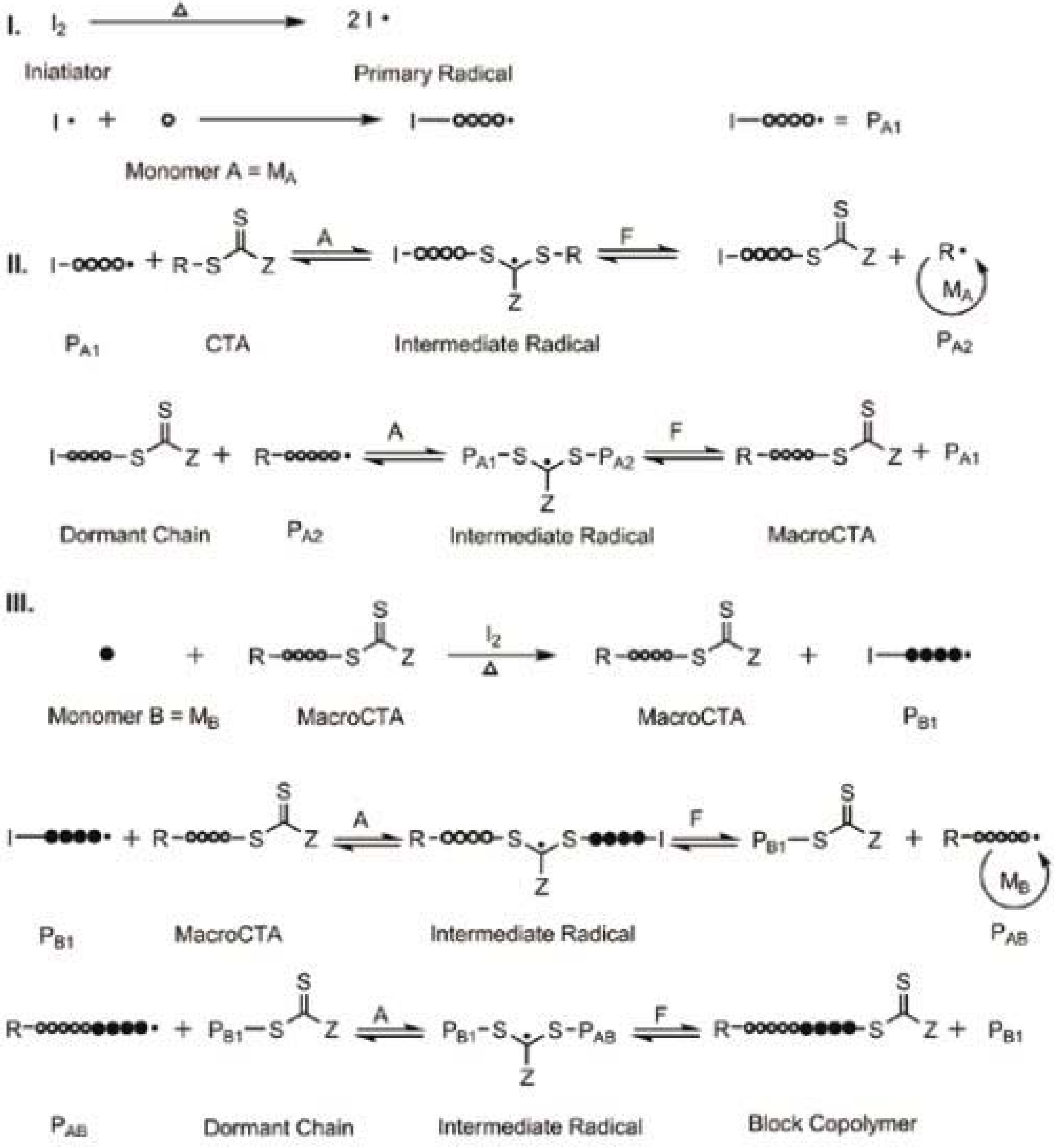
Reinitiation



Degenerative Transfer



Syntheses of Homopolymers and Block Copolymer

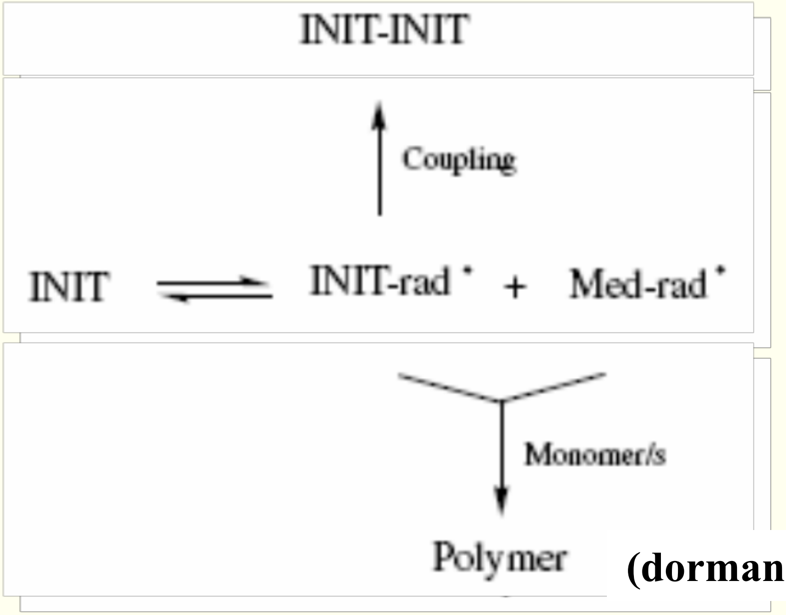


Scheme 1. RAFT mechanism for homopolymerization (I) and (II) and chain extension of a macro CTA (III). A = addition, F = Fragmentation.

	Revers. Deact. by Coupling (NMRP)	**Revers. Deact. by Atom Transfer (ATRP)**	**Degen. Tr. (Rad. Add. Fr. Ch. Tr.)**
Monomers	• Styrene with TEMPO. • Acrylates and acrylamides with new nitroxides. • NO methacrylates.	• Nearly all monomers with activated double bonds. • NO vinyl acetate.	• Nearly all monomers.
Conditions	• High *T* (>120ºC for TEMPO). • Waterborne systems OK. • Sensitive to oxygen.	• Large *T* range (-30 to 150ºC). • Waterborne systems OK. • Some tolerance to O_2 and inhibitor with Mt^0.	• High *T* for less reactive monomers. • Waterborne systems OK. • Sensitive to oxygen.
End groups /Initiators	• **Alkoxyamines:** * Thermally unstable. * Relatively expensive. * May act as stabilizers.	• **Alkyl(pseudo)halides:** * Thermally- and photo-stable. * Inexpensive and available. * Halogen exchange for enhanced cross-propagation.	• **Dithioesters, iodides, and methacrylates:** * Less thermally- and photo-stable. * Relatively expensive.
Additives	• None. NMP may be accelerated with acyl compounds.	• Transition metal catalyst should be removed and cycled.	• Conventional radical initiators. May decrease end functionality and may produce too many new chains.

Stable Radical Polymerizations: Reaction Stages

a) Initiation: Reversible Deactivation and Persistent Radical Effect

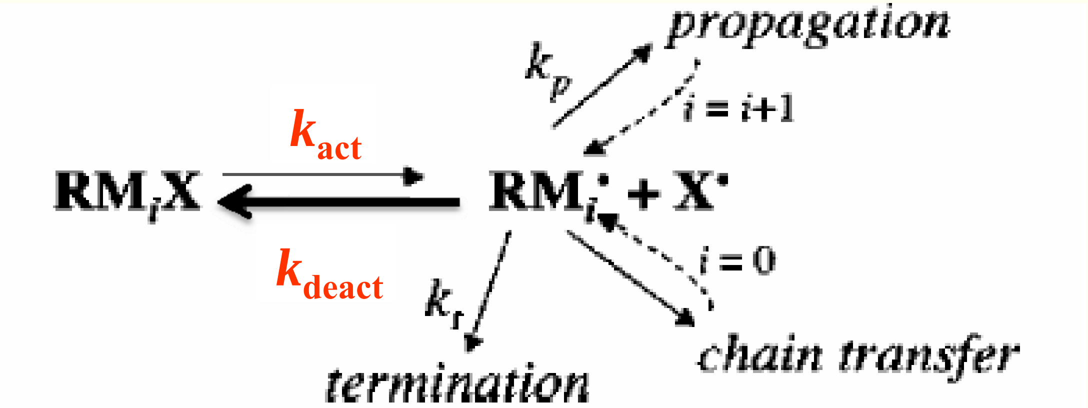


(dormant)

1. **INIT decomposes into Active Radical + Stable Mediating Radical**
2. **Active Radicals reacts with themselves (cage effect) or generate oligomers.**
   Therefore: [Med rad·] > [INIT-rad·].
3. **The increased [Med rad·] is self-limiting, since it increases the formation of the dormant polymer, decreases the amount of radical–radical coupling, and leads to the control of the polymerization process.**

b) Reversible Deactivation of Dormant Species

Dormant Polymer ↔ **Active Radical** + **Persistent Radical**



- **Condition for equilibrium with $[RM_iX] \gg [RM_i^{\bullet}]$ and $k_{act} \ll k_{deact}$:**

$$k_{act}\,[RM_iX] = k_{deact}\,[RM_i^{\bullet}]\,[X^{\bullet}]$$

- **The growing chains increase their chain lengths, while MW dispersity falls.**
- **The accumulation of Persistent Radicals due to termination shifts the dynamic equilibrium to the left, further decreasing polymerization rate.**

c) Termination Reactions

1. Bimolecular Termination of Growing Ends (Disproportionation or Recombination)

- **Bimolecular Termination: second order with respect to radical concentration;**
- **Propagation is first order with respect to radical concentration.**

Therefore, one can make:

Rate of Bimolecular Termination << Rate of Propagation.
by appropriately decreasing radical concentration.

2. Termination of Growing End by Chain Transfer to Monomer

- **Chain Transfer to the Monomer is also first order in the monomer!.**

Thus, CT to monomer will always compete with Propagation as long as monomer exists. This prevents the synthesis of long chain lengths; and for example:

Max. possible N° average chain length: $P_{n,max} = 1/C_m$, with $C_m = k_{fm}/k_p \approx 10^{-4}$
(yielding a "most probable distribution" in this limiting case).

Therefore: for narrow-distributed polymers, the desired chain length must be:

$$\underline{P_{n,design}} \ll \underline{P_{n,max}}$$

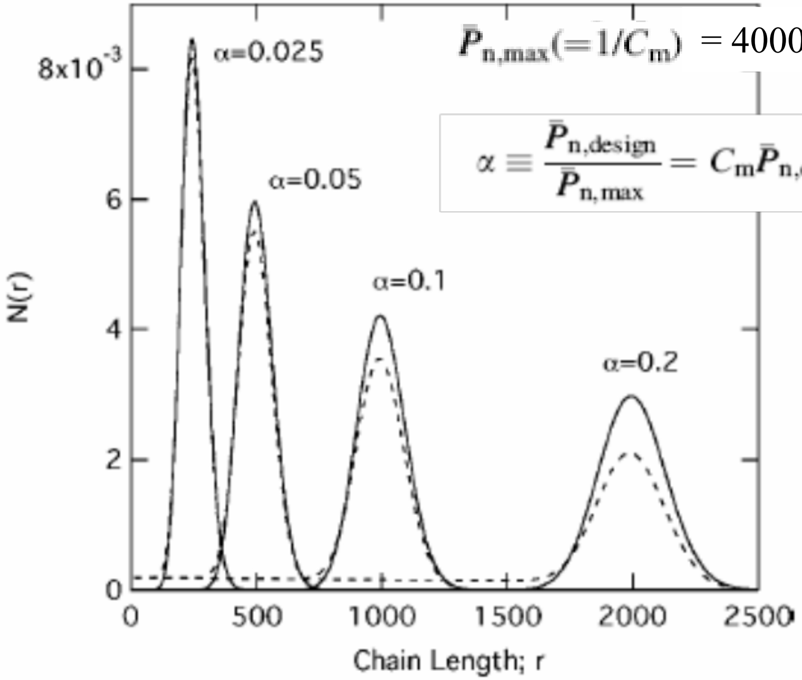
Prerrequisites for LRP

1. Initiation stage should be completed at a low monomer concentration.
2. Relatively low MWs (DP < 1000) should be targeted in order to reduce transfer effects. This requires a high conc. of dormant chains (> 0.02 M in a bulk polymn.)
3. The concentration of propagating radicals should be sufficiently low ([P•] < 10^{-7} M); in order to enable growth of chains to sufficiently high MW before they terminate.

The mismatch [P•] << [P-X] supresses bimolecular termination.

This Persistent Radical Effect is unique for NMP and ATRP, and it is fulfilled by exchange reactions between growing chains in dormant state and minute amounts (< ppm) of propagating free-radicals.

Theoretical MWDs with and without CT to the Monomer (Tobita, 2006)



$\bar{P}_{\mathrm{n,max}}(=1/C_{\mathrm{m}}) = 40000$

$$\alpha \equiv \frac{\bar{P}_{\mathrm{n,design}}}{\bar{P}_{\mathrm{n,max}}} = C_{\mathrm{m}}\bar{P}_{\mathrm{n,design}}$$

Figure 12. Calculated number fraction distribution $N(r)$ development with (dashed) and without (solid) the monomer transfer reactions.

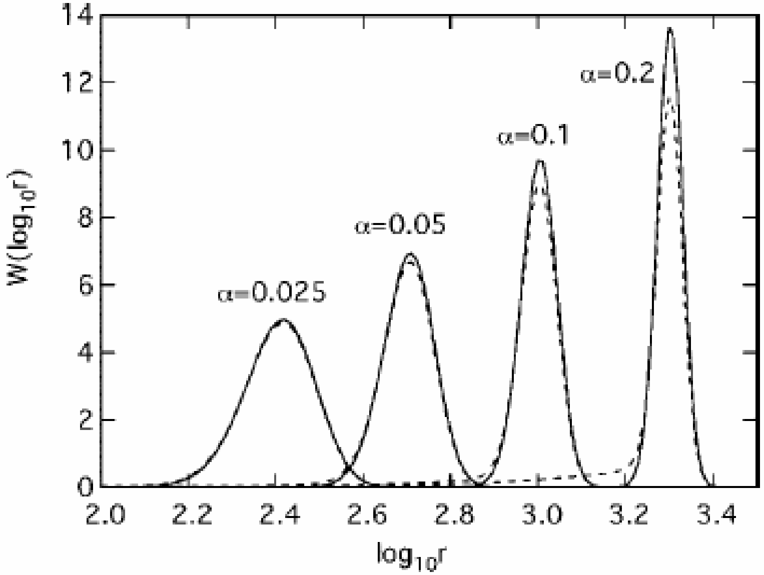


Figure 11. Calculated weight fraction distribution $W(\log r)$ development with (dashed) and without (solid) the monomer transfer reactions.

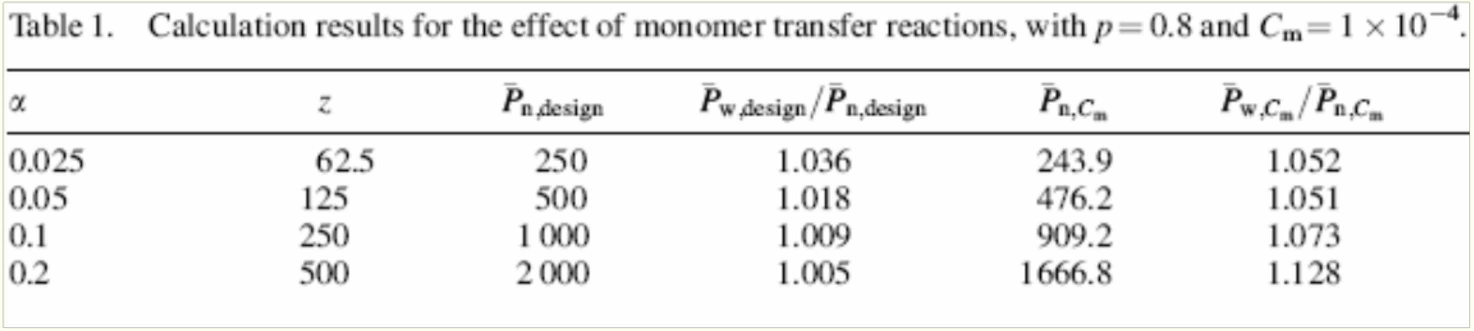


Table 1. Calculation results for the effect of monomer transfer reactions, with $p = 0.8$ and $C_{\mathrm{m}} = 1 \times 10^{-4}$.

α	z	$\bar{P}_{\mathrm{n,design}}$	$\bar{P}_{\mathrm{w,design}}/\bar{P}_{\mathrm{n,design}}$	$\bar{P}_{\mathrm{n},C_{\mathrm{m}}}$	$\bar{P}_{\mathrm{w},C_{\mathrm{m}}}/\bar{P}_{\mathrm{n},C_{\mathrm{m}}}$
0.025	62.5	250	1.036	243.9	1.052
0.05	125	500	1.018	476.2	1.051
0.1	250	1 000	1.009	909.2	1.073
0.2	500	2 000	1.005	1666.8	1.128

Polymerization of Styrene by Nitroxide-mediated Polymerization (NMP)

First paper on NMP (Georges *et al*., 1993)

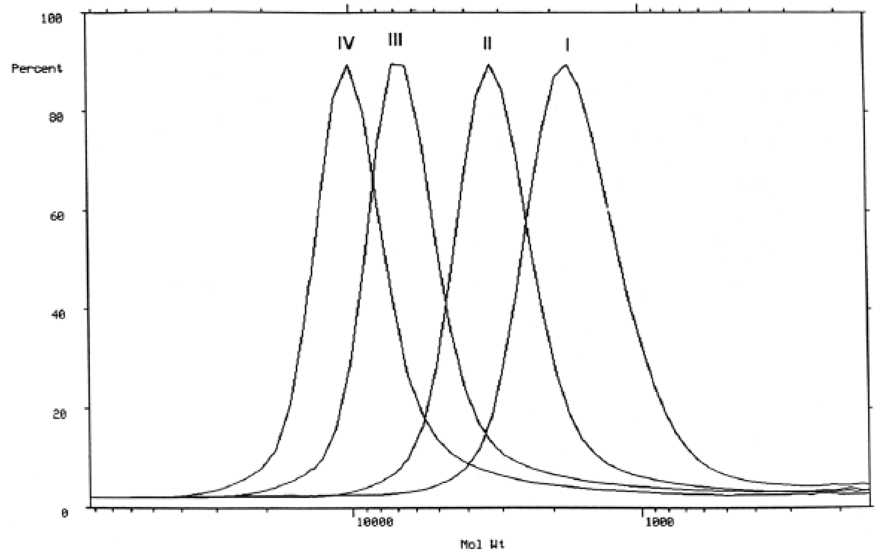


Figure 2. GPCs of polystyrene samples I–IV, from Table I showing the incremental increase of molecular weight with time with no concomitant broadening of the distribution.

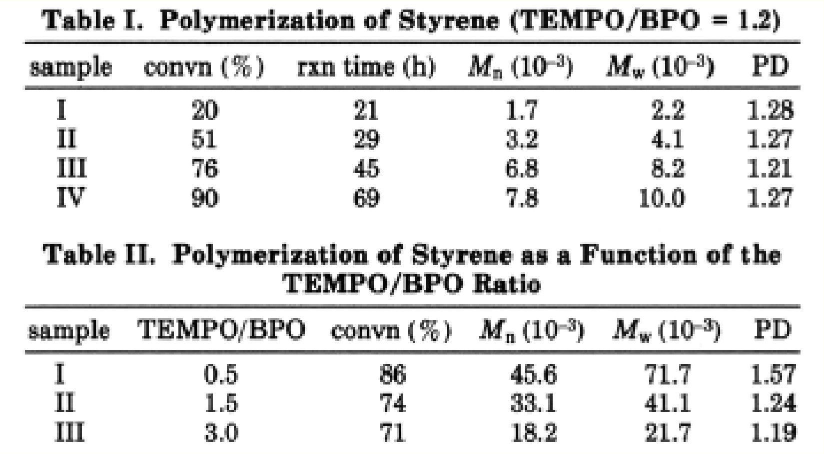


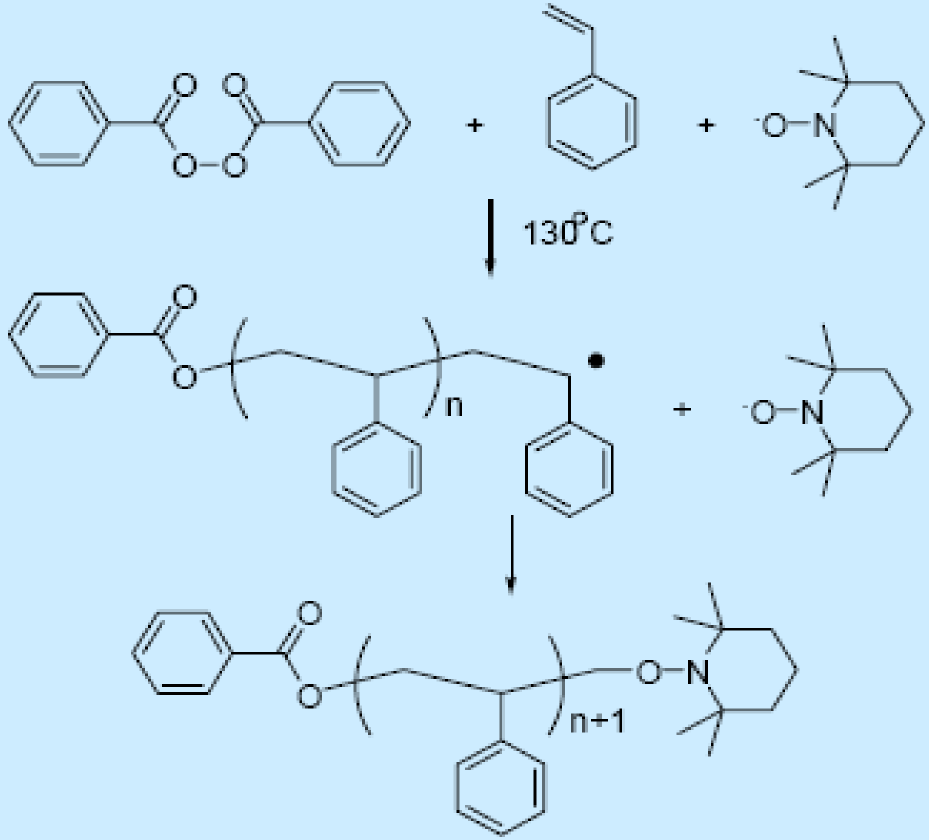
Table I. Polymerization of Styrene (TEMPO/BPO = 1.2)

sample	convn (%)	rxn time (h)	M_n (10^{-3})	M_w (10^{-3})	PD
I	20	21	1.7	2.2	1.28
II	51	29	3.2	4.1	1.27
III	76	45	6.8	8.2	1.21
IV	90	69	7.8	10.0	1.27

Table II. Polymerization of Styrene as a Function of the TEMPO/BPO Ratio

sample	TEMPO/BPO	convn (%)	M_n (10^{-3})	M_w (10^{-3})	PD
I	0.5	86	45.6	71.7	1.57
II	1.5	74	33.1	41.1	1.24
III	3.0	71	18.2	21.7	1.19

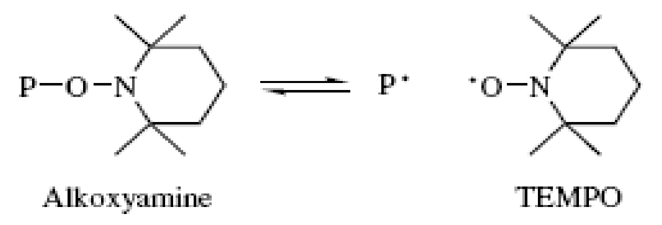
Polymerization of St with ([TEMPO]/[BPO] ≈ 1.2)



Poorly defined nature, unknown initial concentrations

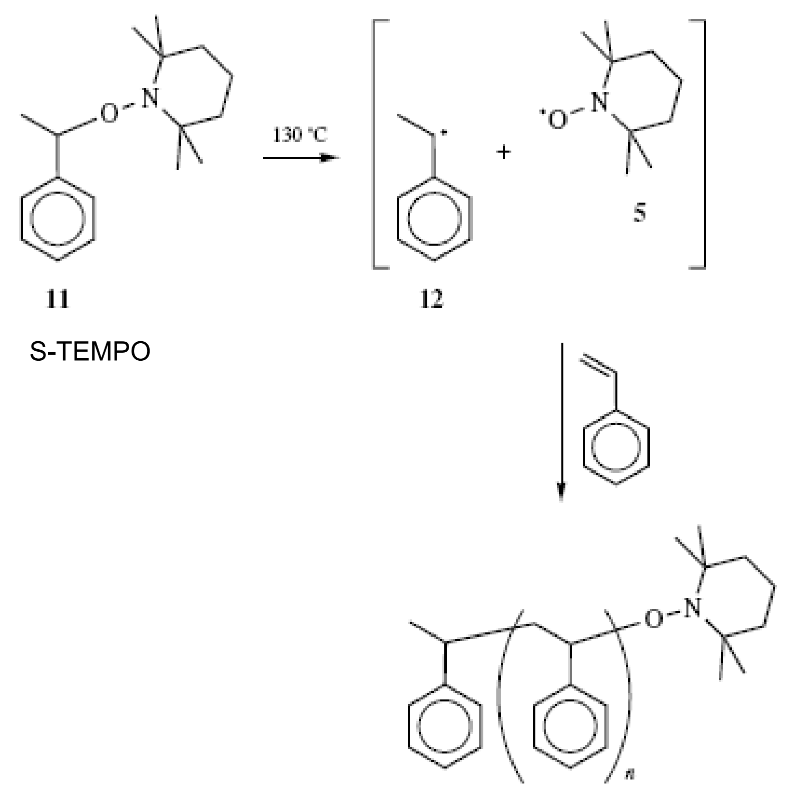
Improved Control *via* Monomolecular Initiation with Alkoxyamines

Initiation with Alkoxyamine



Generates EQUAL AMOUNTS of Active and Stable Radicals (P· and T·)

Polymerization of St with S-TEMPO



Commercial Low Molar Mass Alkoxyamines

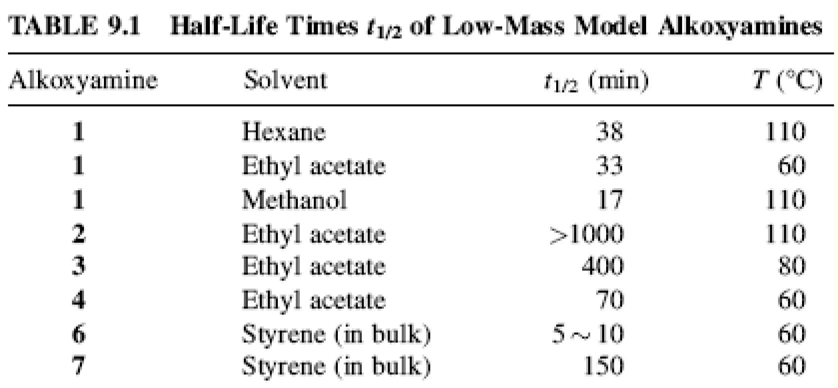
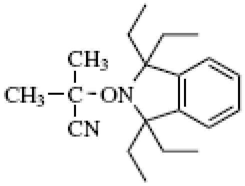


TABLE 9.1 Half-Life Times $t_{1/2}$ of Low-Mass Model Alkoxyamines

Alkoxyamine	Solvent	$t_{1/2}$ (min)	T (°C)
1	Hexane	38	110
1	Ethyl acetate	33	60
1	Methanol	17	110
2	Ethyl acetate	>1000	110
3	Ethyl acetate	400	80
4	Ethyl acetate	70	60
6	Styrene (in bulk)	5 ~ 10	60
7	Styrene (in bulk)	150	60

Nótese la baja T de descomposición y la rápida iniciación del 6: S-TEMPO.



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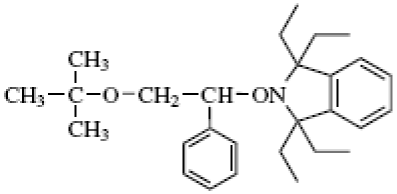

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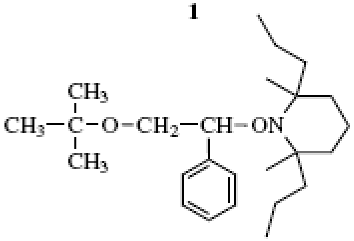

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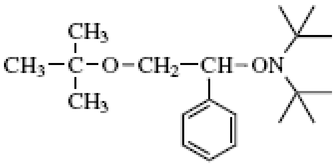

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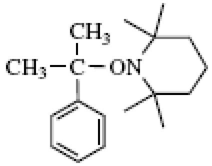

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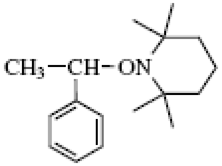
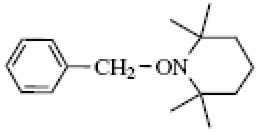


6: S-TEMPO



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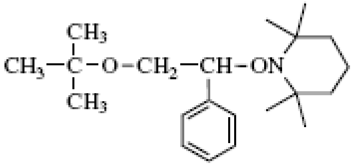

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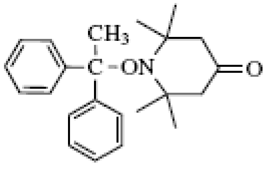

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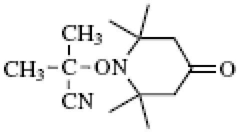

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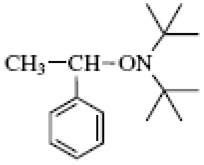
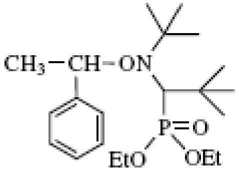
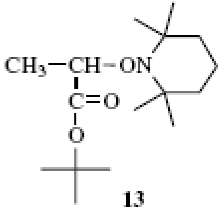


11: S-DBN



12: S-DEPN



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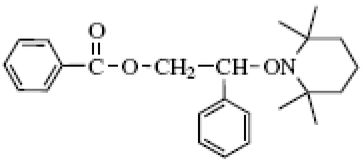
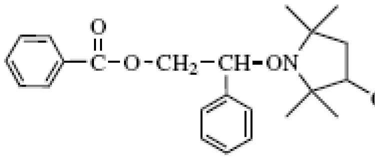


14: BS-TEMPO



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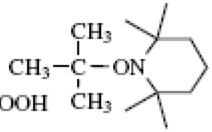
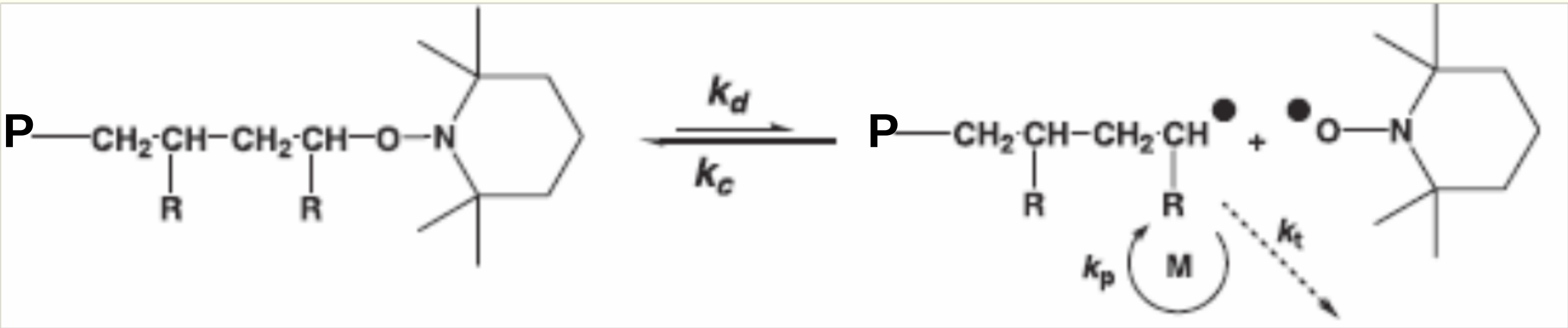


16

Unwanted Reactions in TEMPO-Controlled Polymerization of St

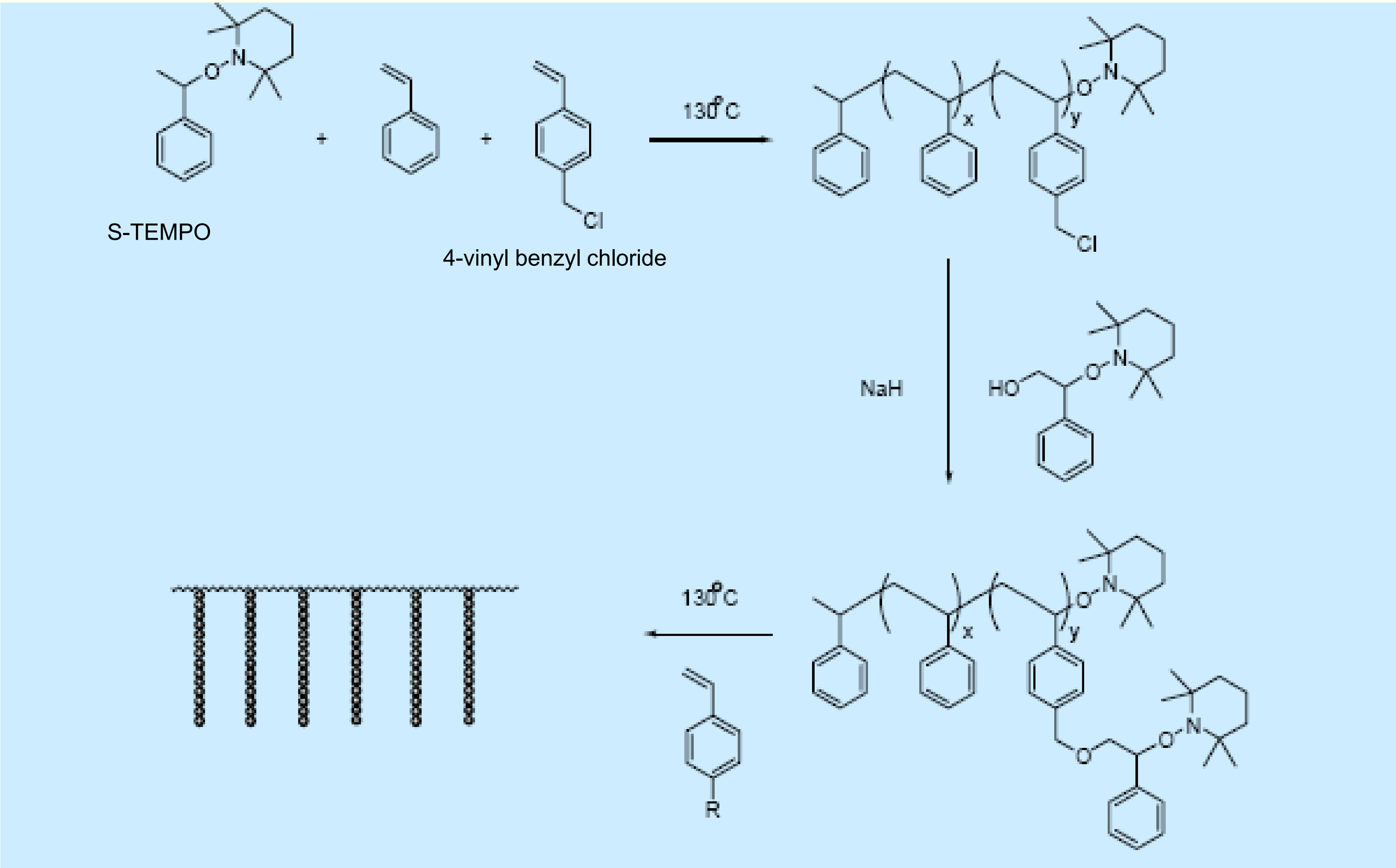


TERMINATION REACTIONS reduce the conc. of active radicals with respect to stable. This shifts the equilibrium toward the left. And this in turn lowers polymerization rate, but also lowers dispersity.

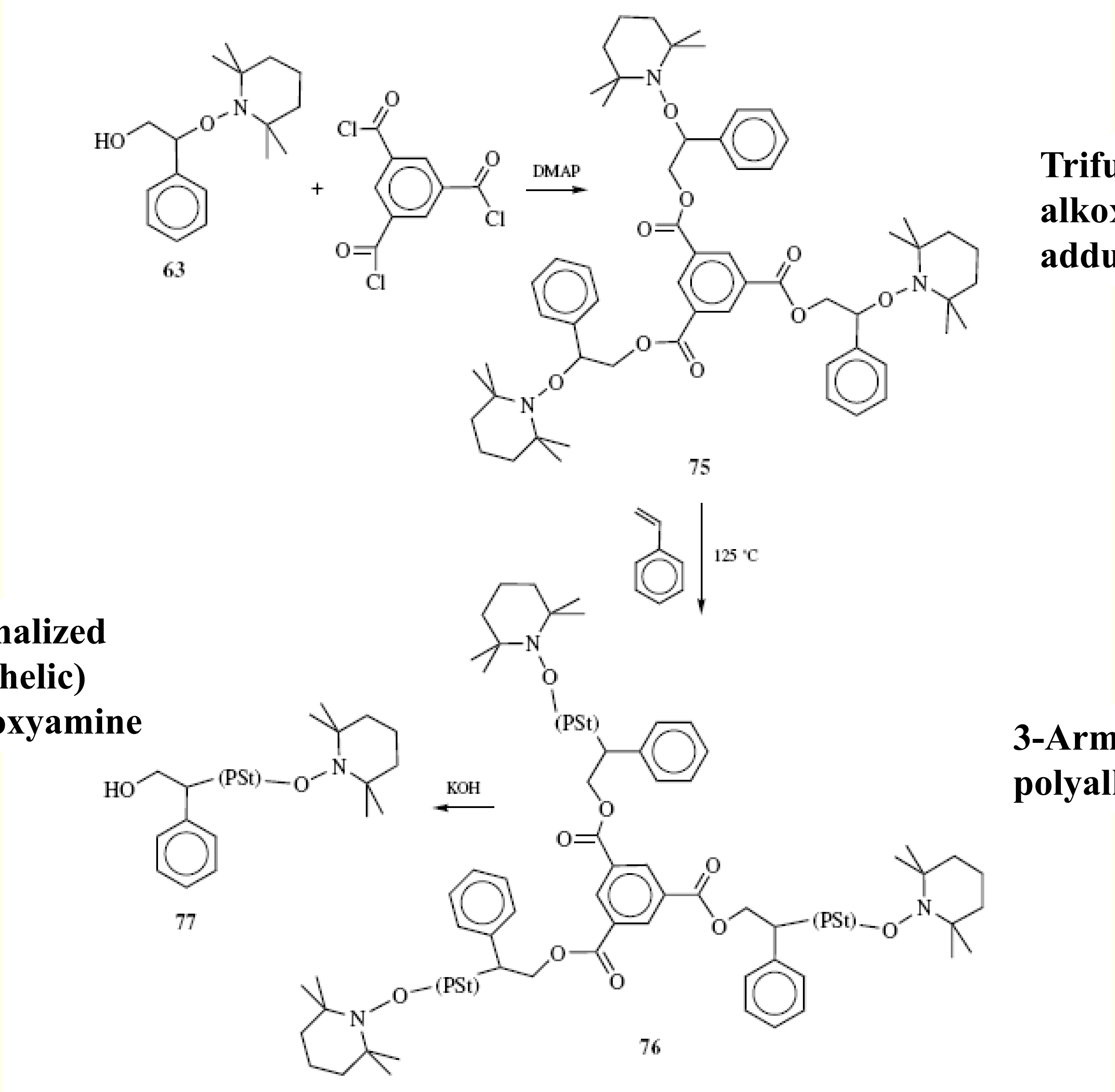
In the polymerization of St, THERMAL INITIATION OF MONOMER generate a tail of low-molar mass material along the reaction; but also maintains polymerization rate without excessive increase in dispersity.

Control of Topology, Composition, and Functionality

a) Special Comb Polymers by Graft Copolymerization



b) Control of Topology and Functionality *via* Alkoxyamine “Building Blocks”



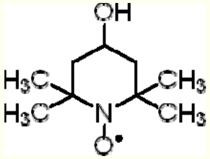
Trifunctional alkoxyamine adduct

3-Armed star polyalkoxyamine

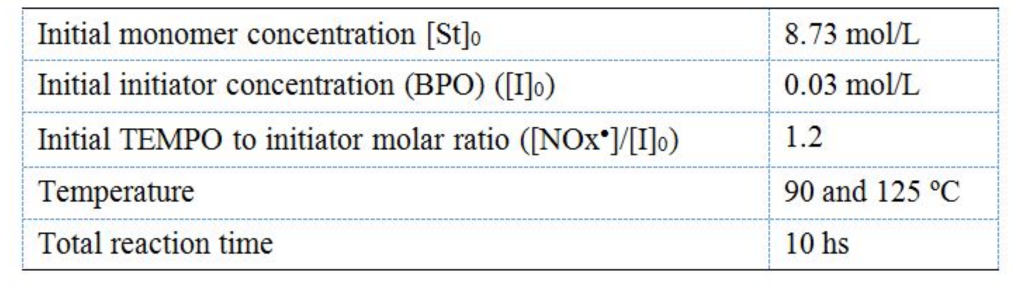
Functionalized (or telechelic) polyalkoxyamine

Nitroxide-Mediated Homopolymerization of Styrene: MATHEMATICAL MODEL

Recipe and reaction conditions



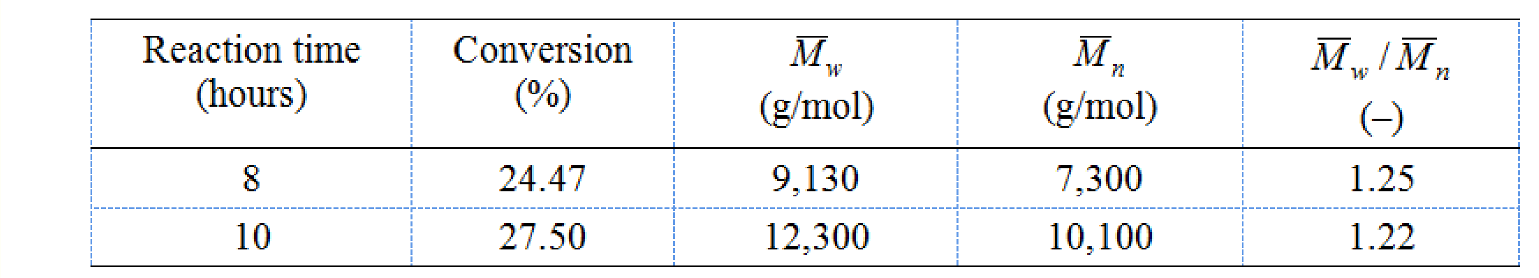
Styrene	**2070.05 g**
BPO (73%)	**8.9555 g**
4 OH-TEMPO (97%)	**5.1565 g**
Volume	**2 L**
Agitation	**250 rpm**



Initial monomer concentration $[St]_0$	8.73 mol/L
Initial initiator concentration (BPO) ($[I]_0$)	0.03 mol/L
Initial TEMPO to initiator molar ratio ($[NOx^\bullet]/[I]_0$)	1.2
Temperature	90 and 125 °C
Total reaction time	10 hs

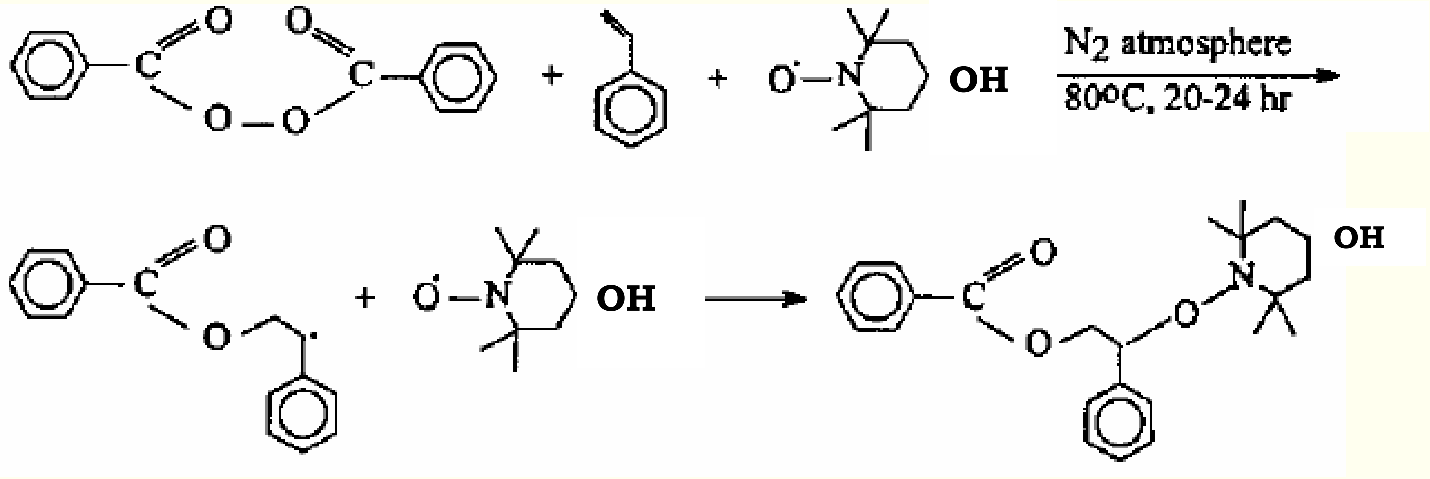
- **1st Stage at 90 °C:** **Synthesis of Alkoxyamine Initiator + Initial Oligomers.**
- **2nd Stage at 125 °C:** **Controlled polymerization.**

Average molecular weights and dispersity of Total Polymer at 8 and 10 hs.



Reaction time (hours)	Conversion (%)	$\overline{M}_w$ (g/mol)	$\overline{M}_n$ (g/mol)	$\overline{M}_w / \overline{M}_n$ (–)
8	24.47	9,130	7,300	1.25
10	27.50	12,300	10,100	1.22

Aim of 1st Stage: “In Situ” Synthesis of Alkoxyamine Initiator

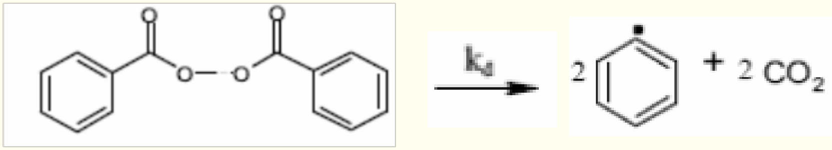


Unfortunately, poor yield (30-40%)
+ wide range of by-products.

Kinetic Mechanism

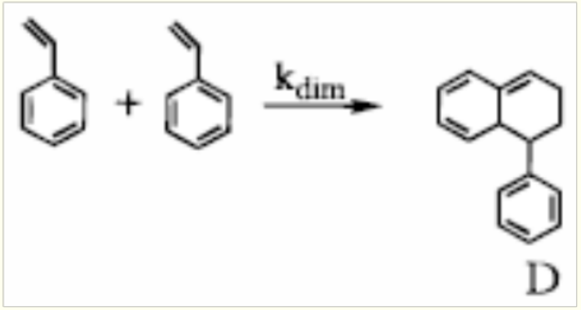
Assumption: Bimolecular Initiation
(Bonilla *et al*., 2002 and Belicanta-Ximenes *et al*. (2007)

Chemical Initiation

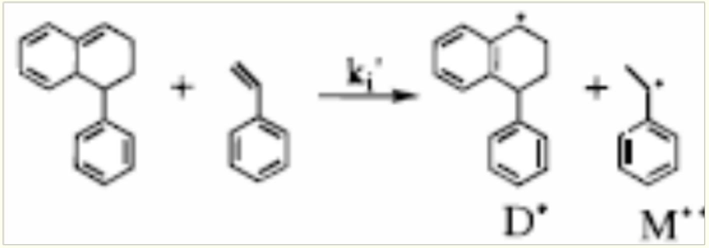


$$I_2 \xrightarrow{k_d} 2\ I^\bullet$$

Thermal St Initiation



$$2\ St \xrightarrow{k_{dim}} D$$



$$St + D \xrightarrow{k_i} D^\bullet + M^\bullet$$

First Propagation Reactions

$$I^\bullet + St \xrightarrow{k_{pi}} R_1^\bullet$$

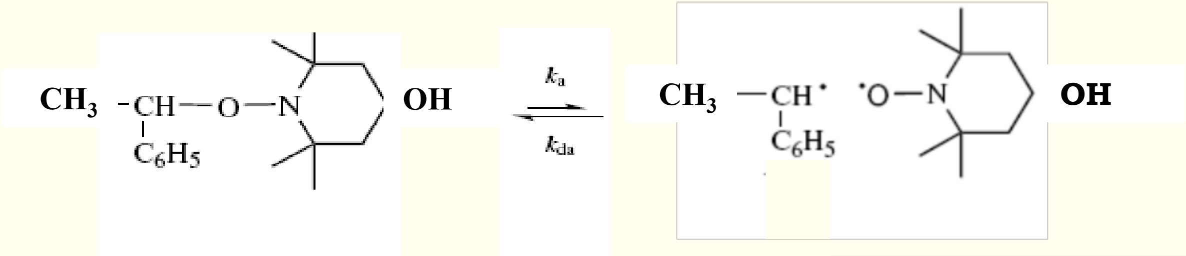
$$M^\bullet + St \xrightarrow{k_{pm}} R_1^\bullet$$

$$D^\bullet + St \xrightarrow{k_{pd}} R_1^\bullet$$

Propagation

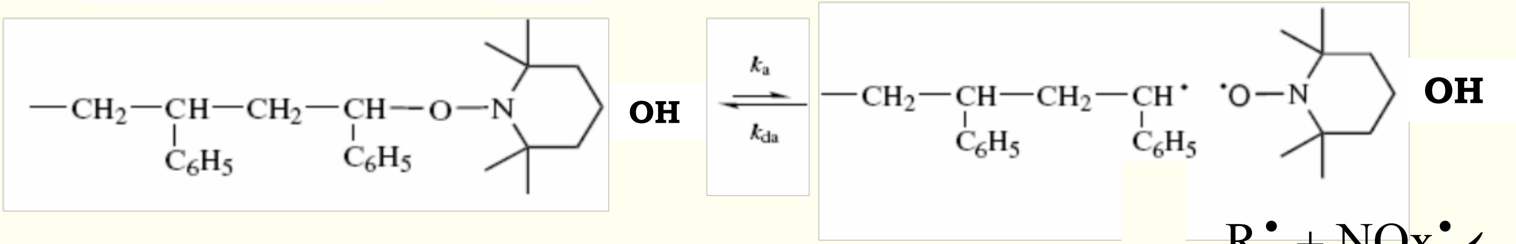
$$R_{r-1}^\bullet + St \xrightarrow{k_p} R_r^\bullet$$

Dormant/Living Exchange



$$M^\bullet + NOx^\bullet \xleftrightarrow[k_a]{k_{da}} MNOx$$

Monomeric
Alkoxyamine



$$R_r^\bullet + NOx^\bullet \xleftrightarrow[k_a]{k_{da}} R_r NOx$$

Conventional Terminations

$$\mathrm{R}^{\bullet}_{r-m} + \mathrm{R}^{\bullet}_{m} \xrightarrow{k_{\mathrm{tc}}} \mathrm{P}_{r}$$

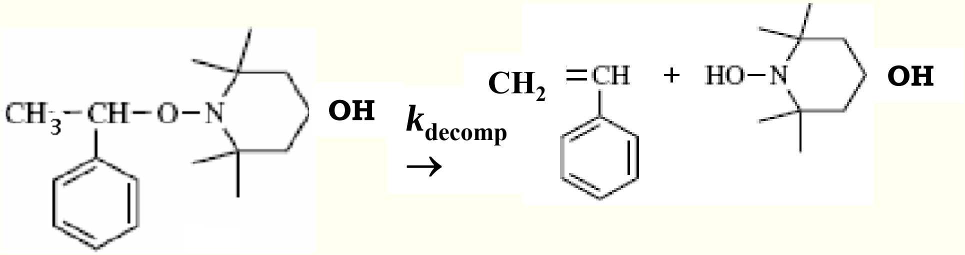
$$\mathrm{R}^{\bullet}_{r} + \mathrm{R}^{\bullet}_{m} \xrightarrow{k_{\mathrm{td}}} \mathrm{P}_{r} + \mathrm{P}_{m}$$

Chain Transfers to Monomer and Dimer

$$\mathrm{R}^{\bullet}_{r} + \mathrm{St} \xrightarrow{k_{\mathrm{fm}}} \mathrm{P}_{r} + \mathrm{M}^{\bullet}$$

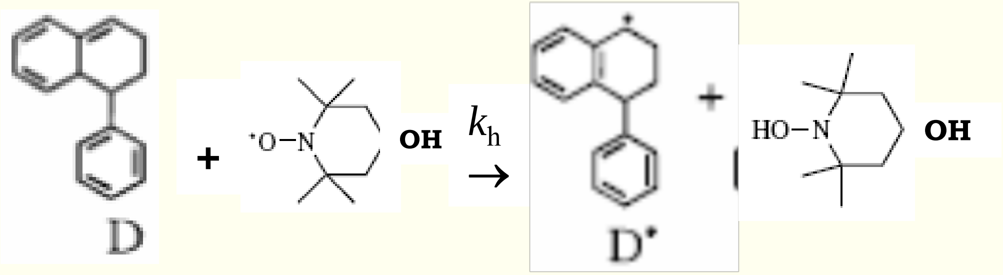
$$\mathrm{R}^{\bullet}_{r} + \mathrm{D} \xrightarrow{k_{\mathrm{fd}}} \mathrm{P}_{r} + \mathrm{D}^{\bullet}$$

Alcoxyamine Decomposition



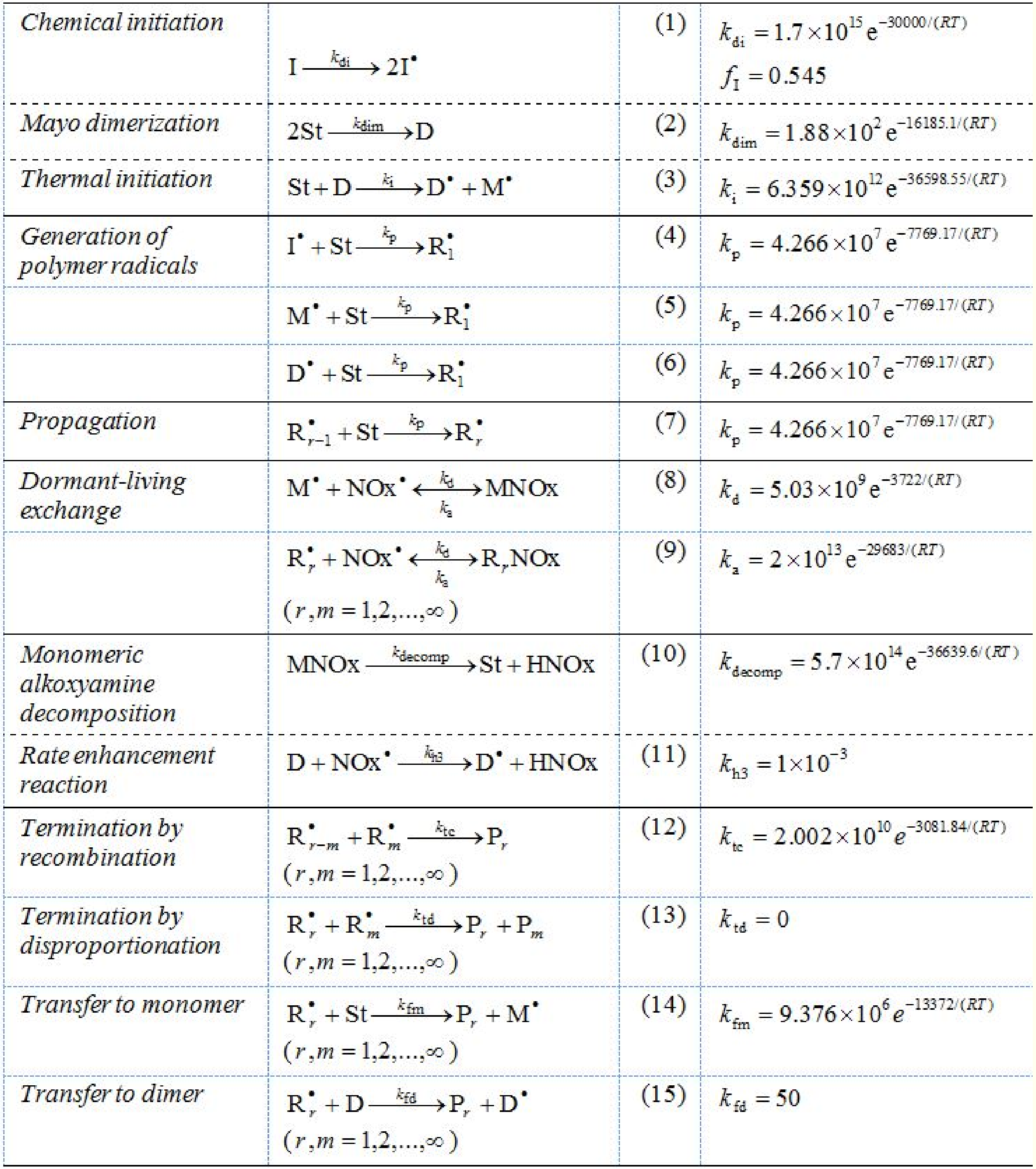
$$\mathrm{MNOx} \xrightarrow{k_{\mathrm{decomp}}} \mathrm{St} + \mathrm{HNOx}$$

Rate Enhacement Reaction



$$\mathrm{D} + \mathrm{NOx}^{\bullet} \xrightarrow{k_{\mathrm{h}}} \mathrm{D}^{\bullet} + \mathrm{HNOx}$$

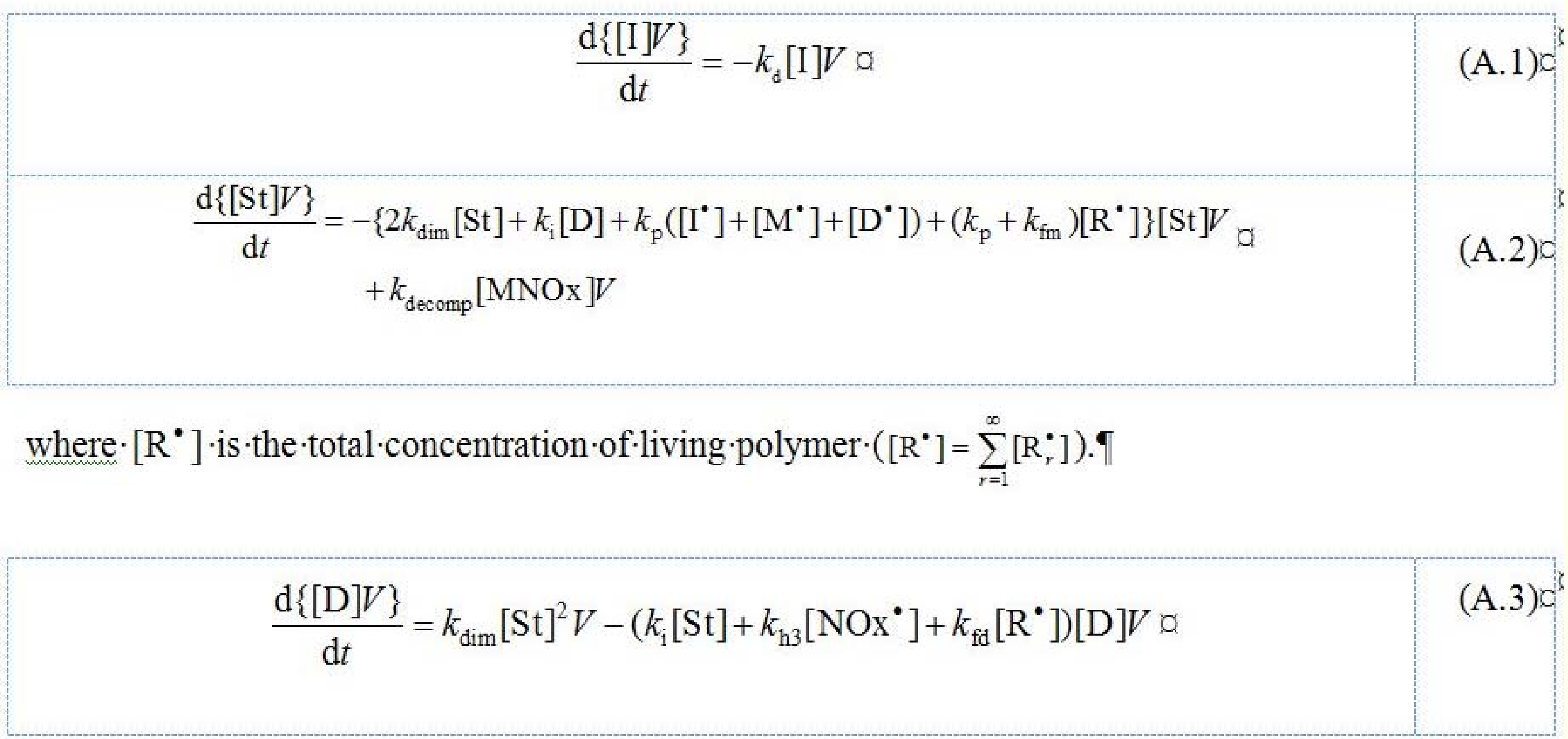
Kinetic mechanism and Arrhenius expressions (Belicanta *et al*. (2007)



Chemical initiation	$\mathrm{I} \xrightarrow{k_{\mathrm{di}}} 2\mathrm{I}^{\bullet}$	(1)	$k_{\mathrm{di}} = 1.7 \times 10^{15}\,\mathrm{e}^{-30000/(RT)}$ $f_{\mathrm{I}} = 0.545$
Mayo dimerization	$2\mathrm{St} \xrightarrow{k_{\mathrm{dim}}} \mathrm{D}$	(2)	$k_{\mathrm{dim}} = 1.88 \times 10^{2}\,\mathrm{e}^{-16185.1/(RT)}$
Thermal initiation	$\mathrm{St} + \mathrm{D} \xrightarrow{k_{\mathrm{i}}} \mathrm{D}^{\bullet} + \mathrm{M}^{\bullet}$	(3)	$k_{\mathrm{i}} = 6.359 \times 10^{12}\,\mathrm{e}^{-36598.55/(RT)}$
Generation of polymer radicals	$\mathrm{I}^{\bullet} + \mathrm{St} \xrightarrow{k_{\mathrm{p}}} \mathrm{R}_1^{\bullet}$	(4)	$k_{\mathrm{p}} = 4.266 \times 10^{7}\,\mathrm{e}^{-7769.17/(RT)}$
	$\mathrm{M}^{\bullet} + \mathrm{St} \xrightarrow{k_{\mathrm{p}}} \mathrm{R}_1^{\bullet}$	(5)	$k_{\mathrm{p}} = 4.266 \times 10^{7}\,\mathrm{e}^{-7769.17/(RT)}$
	$\mathrm{D}^{\bullet} + \mathrm{St} \xrightarrow{k_{\mathrm{p}}} \mathrm{R}_1^{\bullet}$	(6)	$k_{\mathrm{p}} = 4.266 \times 10^{7}\,\mathrm{e}^{-7769.17/(RT)}$
Propagation	$\mathrm{R}_{r-1}^{\bullet} + \mathrm{St} \xrightarrow{k_{\mathrm{p}}} \mathrm{R}_r^{\bullet}$	(7)	$k_{\mathrm{p}} = 4.266 \times 10^{7}\,\mathrm{e}^{-7769.17/(RT)}$
Dormant-living exchange	$\mathrm{M}^{\bullet} + \mathrm{NOx}^{\bullet} \underset{k_{\mathrm{a}}}{\overset{k_{\mathrm{d}}}{\longleftrightarrow}} \mathrm{MNOx}$	(8)	$k_{\mathrm{d}} = 5.03 \times 10^{9}\,\mathrm{e}^{-3722/(RT)}$
	$\mathrm{R}_r^{\bullet} + \mathrm{NOx}^{\bullet} \underset{k_{\mathrm{a}}}{\overset{k_{\mathrm{d}}}{\longleftrightarrow}} \mathrm{R}_r\mathrm{NOx}$ $(r, m = 1,2,\ldots,\infty)$	(9)	$k_{\mathrm{a}} = 2 \times 10^{13}\,\mathrm{e}^{-29683/(RT)}$
Monomeric alkoxyamine decomposition	$\mathrm{MNOx} \xrightarrow{k_{\mathrm{decomp}}} \mathrm{St} + \mathrm{HNOx}$	(10)	$k_{\mathrm{decomp}} = 5.7 \times 10^{14}\,\mathrm{e}^{-36639.6/(RT)}$
Rate enhancement reaction	$\mathrm{D} + \mathrm{NOx}^{\bullet} \xrightarrow{k_{\mathrm{h3}}} \mathrm{D}^{\bullet} + \mathrm{HNOx}$	(11)	$k_{\mathrm{h3}} = 1 \times 10^{-3}$
Termination by recombination	$\mathrm{R}_{r-m}^{\bullet} + \mathrm{R}_m^{\bullet} \xrightarrow{k_{\mathrm{tc}}} \mathrm{P}_r$ $(r, m = 1,2,\ldots,\infty)$	(12)	$k_{\mathrm{tc}} = 2.002 \times 10^{10}\,e^{-3081.84/(RT)}$
Termination by disproportionation	$\mathrm{R}_r^{\bullet} + \mathrm{R}_m^{\bullet} \xrightarrow{k_{\mathrm{td}}} \mathrm{P}_r + \mathrm{P}_m$ $(r, m = 1,2,\ldots,\infty)$	(13)	$k_{\mathrm{td}} = 0$
Transfer to monomer	$\mathrm{R}_r^{\bullet} + \mathrm{St} \xrightarrow{k_{\mathrm{fm}}} \mathrm{P}_r + \mathrm{M}^{\bullet}$ $(r, m = 1,2,\ldots,\infty)$	(14)	$k_{\mathrm{fm}} = 9.376 \times 10^{6}\,e^{-13372/(RT)}$
Transfer to dimer	$\mathrm{R}_r^{\bullet} + \mathrm{D} \xrightarrow{k_{\mathrm{fd}}} \mathrm{P}_r + \mathrm{D}^{\bullet}$ $(r, m = 1,2,\ldots,\infty)$	(15)	$k_{\mathrm{fd}} = 50$

Mathematical Model

Mass Balances for Reagents and Global Products

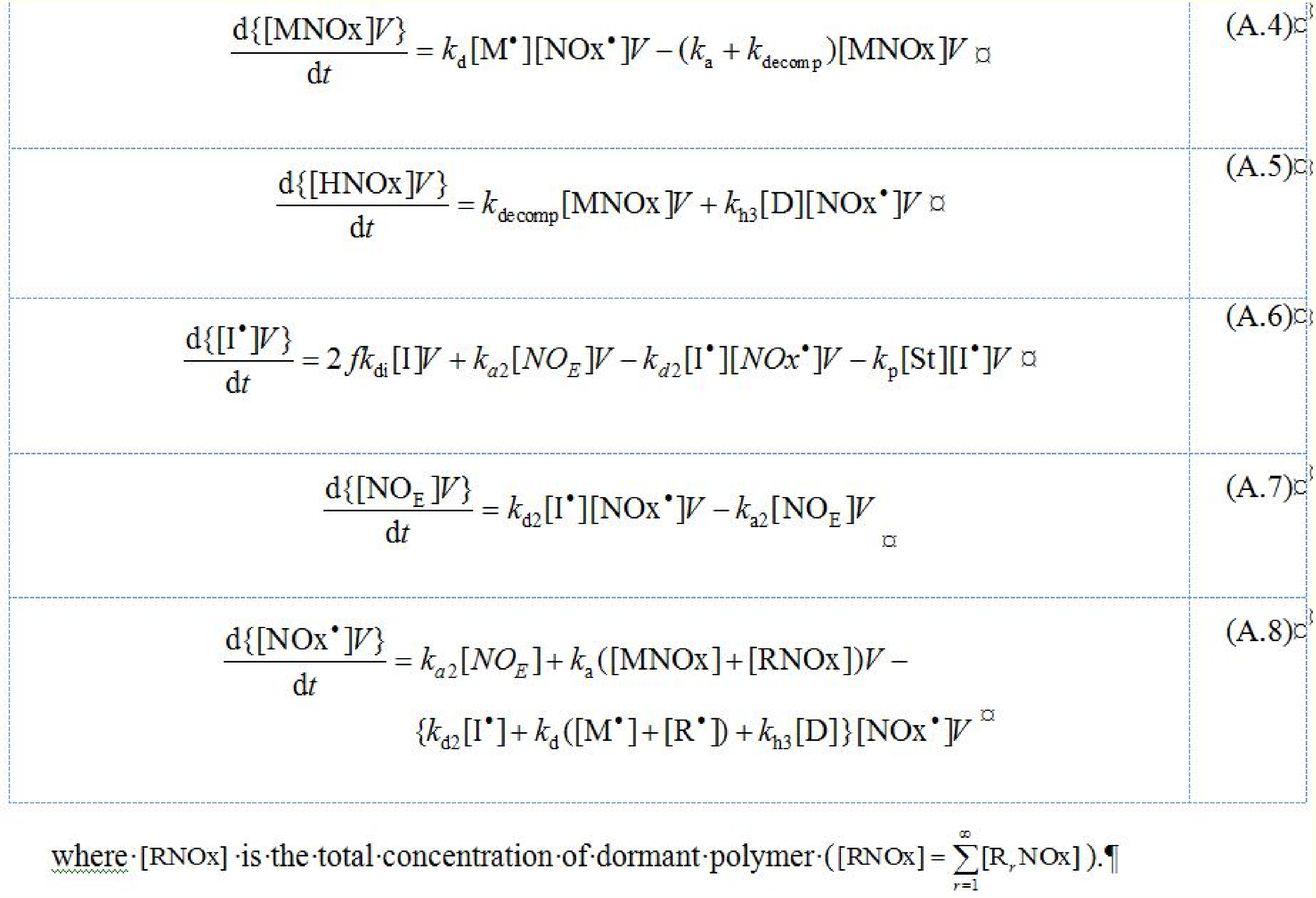


$$\frac{\mathrm{d}\{[\mathrm{I}]V\}}{\mathrm{d}t} = -k_{\mathrm{d}}[\mathrm{I}]V \tag{A.1}$$

$$\frac{\mathrm{d}\{[\mathrm{St}]V\}}{\mathrm{d}t} = -\{2k_{\mathrm{dim}}[\mathrm{St}] + k_{\mathrm{i}}[\mathrm{D}] + k_{\mathrm{p}}([\mathrm{I}^{\bullet}] + [\mathrm{M}^{\bullet}] + [\mathrm{D}^{\bullet}]) + (k_{\mathrm{p}} + k_{\mathrm{fm}})[\mathrm{R}^{\bullet}]\}[\mathrm{St}]V + k_{\mathrm{decomp}}[\mathrm{MNOx}]V \tag{A.2}$$

where $[\mathrm{R}^{\bullet}]$ is the total concentration of living polymer ($[\mathrm{R}^{\bullet}] = \sum_{r=1}^{\infty}[\mathrm{R}_r^{\bullet}]$).

$$\frac{\mathrm{d}\{[\mathrm{D}]V\}}{\mathrm{d}t} = k_{\mathrm{dim}}[\mathrm{St}]^2 V - (k_{\mathrm{i}}[\mathrm{St}] + k_{\mathrm{h3}}[\mathrm{NOx}^{\bullet}] + k_{\mathrm{fd}}[\mathrm{R}^{\bullet}])[\mathrm{D}]V \tag{A.3}$$



$$\frac{\mathrm{d}\{[\mathrm{MNOx}]V\}}{\mathrm{d}t} = k_{\mathrm{d}}[\mathrm{M}^{\bullet}][\mathrm{NOx}^{\bullet}]V - (k_{\mathrm{a}} + k_{\mathrm{decomp}})[\mathrm{MNOx}]V \tag{A.4}$$

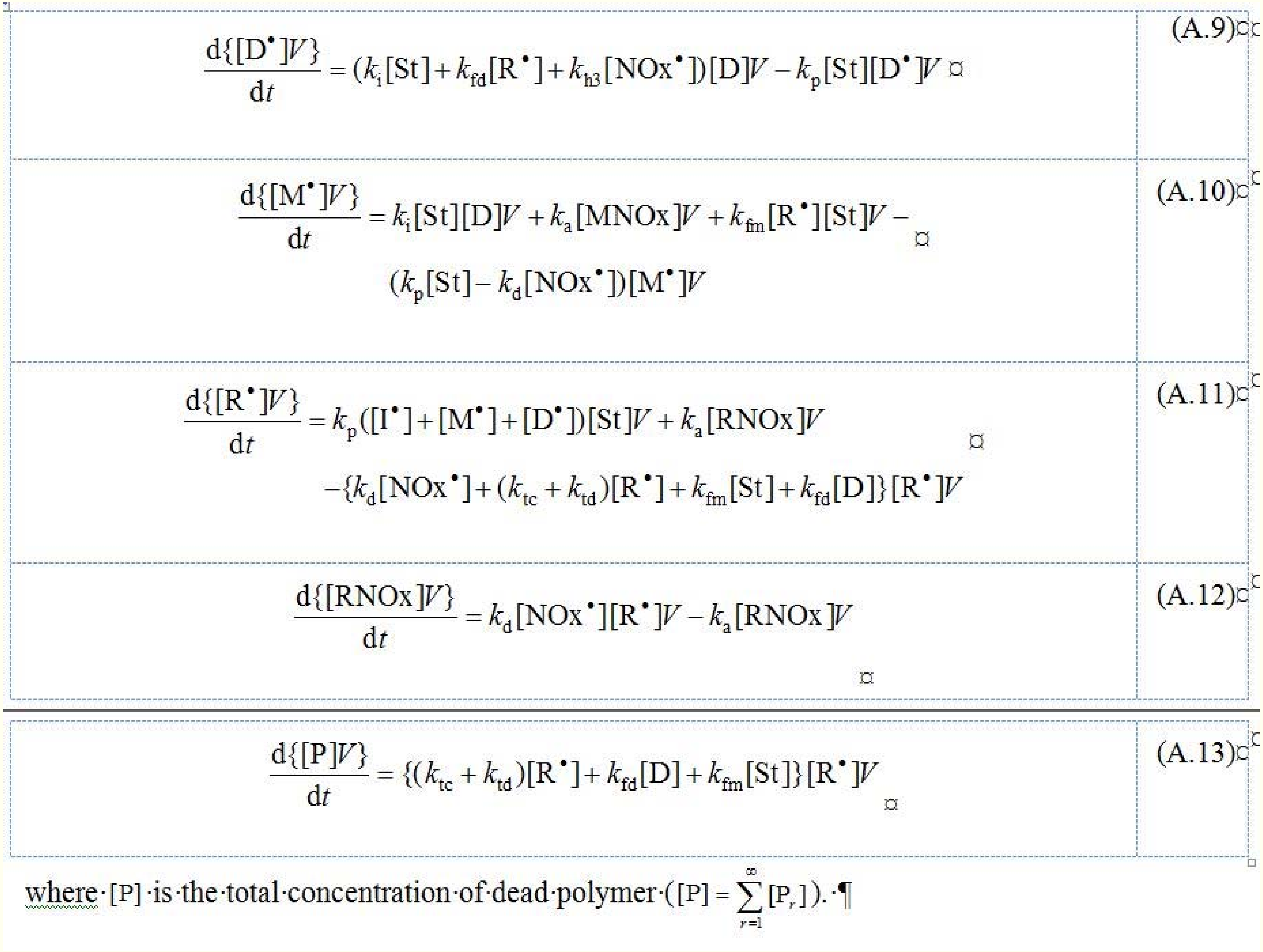
$$\frac{\mathrm{d}\{[\mathrm{HNOx}]V\}}{\mathrm{d}t} = k_{\mathrm{decomp}}[\mathrm{MNOx}]V + k_{\mathrm{h3}}[\mathrm{D}][\mathrm{NOx}^{\bullet}]V \tag{A.5}$$

$$\frac{\mathrm{d}\{[\mathrm{I}^{\bullet}]V\}}{\mathrm{d}t} = 2fk_{\mathrm{di}}[\mathrm{I}]V + k_{a2}[NO_E]V - k_{d2}[\mathrm{I}^{\bullet}][NOx^{\bullet}]V - k_{\mathrm{p}}[\mathrm{St}][\mathrm{I}^{\bullet}]V \tag{A.6}$$

$$\frac{\mathrm{d}\{[\mathrm{NO_E}]V\}}{\mathrm{d}t} = k_{\mathrm{d2}}[\mathrm{I}^{\bullet}][\mathrm{NOx}^{\bullet}]V - k_{\mathrm{a2}}[\mathrm{NO_E}]V \tag{A.7}$$

$$\begin{aligned}\frac{\mathrm{d}\{[\mathrm{NOx}^{\bullet}]V\}}{\mathrm{d}t} &= k_{a2}[NO_E] + k_{\mathrm{a}}([\mathrm{MNOx}] + [\mathrm{RNOx}])V - \\ &\quad \{k_{\mathrm{d2}}[\mathrm{I}^{\bullet}] + k_{\mathrm{d}}([\mathrm{M}^{\bullet}] + [\mathrm{R}^{\bullet}]) + k_{\mathrm{h3}}[\mathrm{D}]\}[\mathrm{NOx}^{\bullet}]V\end{aligned} \tag{A.8}$$

where $[\mathrm{RNOx}]$ is the total concentration of dormant polymer ($[\mathrm{RNOx}] = \sum_{r=1}^{\infty}[\mathrm{R}_r\mathrm{NOx}]$).



$$\frac{\mathrm{d}\{[\mathrm{D}^\bullet]V\}}{\mathrm{d}t} = (k_\mathrm{i}[\mathrm{St}] + k_\mathrm{fd}[\mathrm{R}^\bullet] + k_\mathrm{h3}[\mathrm{NOx}^\bullet])[\mathrm{D}]V - k_\mathrm{p}[\mathrm{St}][\mathrm{D}^\bullet]V \tag{A.9}$$

$$\begin{aligned}\frac{\mathrm{d}\{[\mathrm{M}^\bullet]V\}}{\mathrm{d}t} = {} & k_\mathrm{i}[\mathrm{St}][\mathrm{D}]V + k_\mathrm{a}[\mathrm{MNOx}]V + k_\mathrm{fm}[\mathrm{R}^\bullet][\mathrm{St}]V - \\ & (k_\mathrm{p}[\mathrm{St}] - k_\mathrm{d}[\mathrm{NOx}^\bullet])[\mathrm{M}^\bullet]V\end{aligned} \tag{A.10}$$

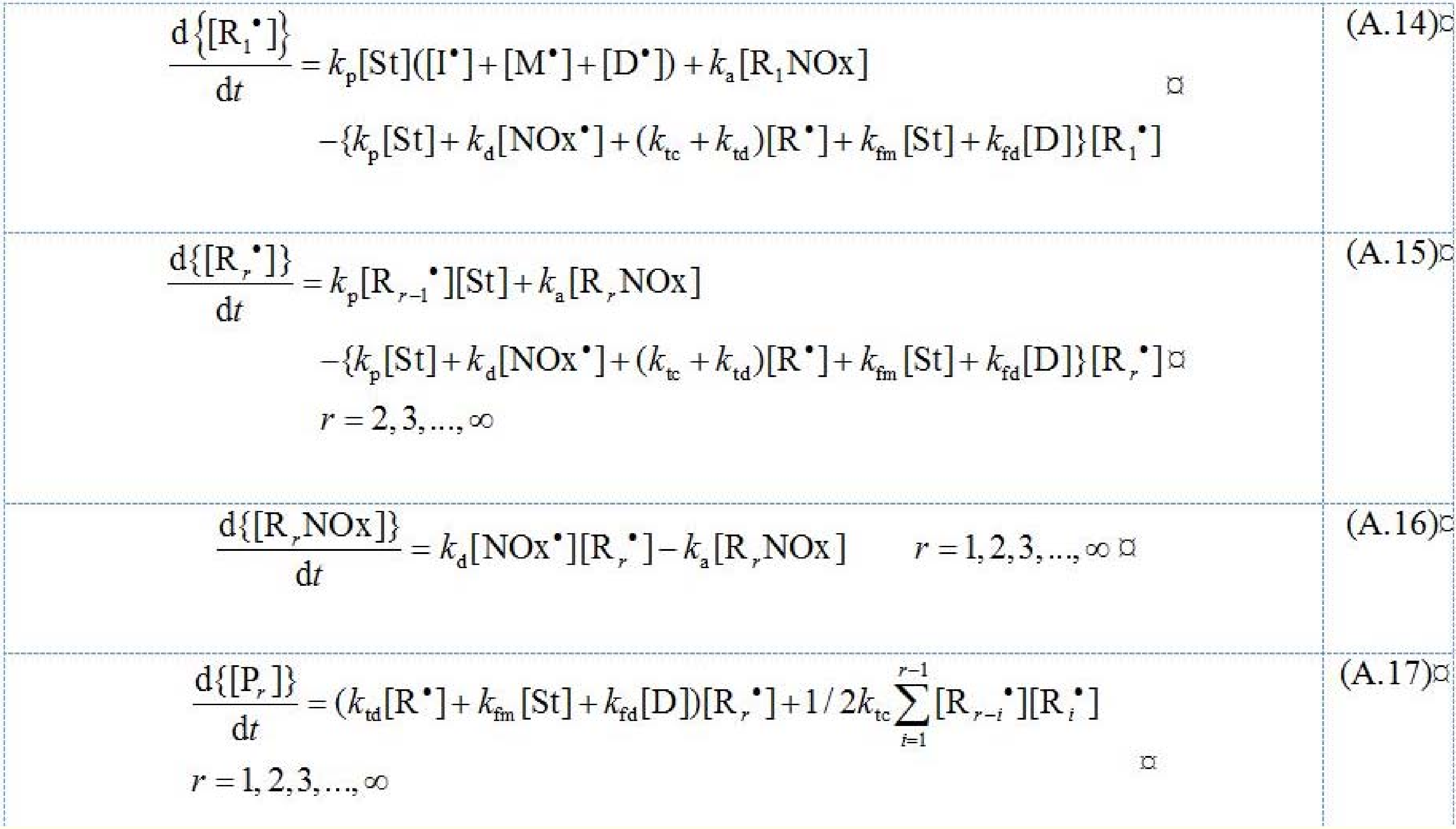
$$\begin{aligned}\frac{\mathrm{d}\{[\mathrm{R}^\bullet]V\}}{\mathrm{d}t} = {} & k_\mathrm{p}([\mathrm{I}^\bullet] + [\mathrm{M}^\bullet] + [\mathrm{D}^\bullet])[\mathrm{St}]V + k_\mathrm{a}[\mathrm{RNOx}]V \\ & -\{k_\mathrm{d}[\mathrm{NOx}^\bullet] + (k_\mathrm{tc} + k_\mathrm{td})[\mathrm{R}^\bullet] + k_\mathrm{fm}[\mathrm{St}] + k_\mathrm{fd}[\mathrm{D}]\}[\mathrm{R}^\bullet]V\end{aligned} \tag{A.11}$$

$$\frac{\mathrm{d}\{[\mathrm{RNOx}]V\}}{\mathrm{d}t} = k_\mathrm{d}[\mathrm{NOx}^\bullet][\mathrm{R}^\bullet]V - k_\mathrm{a}[\mathrm{RNOx}]V \tag{A.12}$$

$$\frac{\mathrm{d}\{[\mathrm{P}]V\}}{\mathrm{d}t} = \{(k_\mathrm{tc} + k_\mathrm{td})[\mathrm{R}^\bullet] + k_\mathrm{fd}[\mathrm{D}] + k_\mathrm{fm}[\mathrm{St}]\}[\mathrm{R}^\bullet]V \tag{A.13}$$

where $[\mathrm{P}]$ is the total concentration of dead polymer ($[\mathrm{P}] = \sum_{r=1}^{\infty}[\mathrm{P}_r]$).

MWDs of Living, Dormant, and Total Polymer



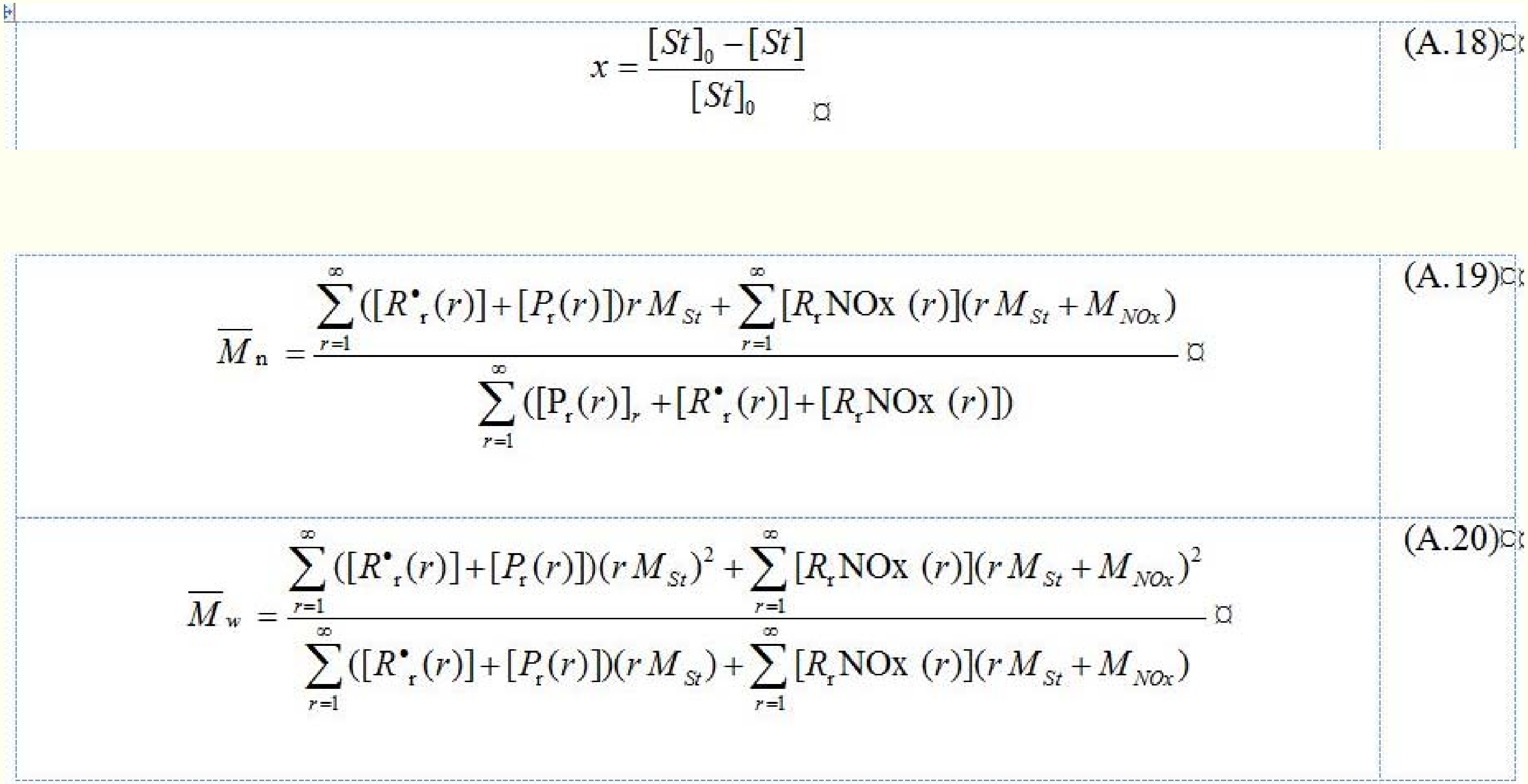
$$\frac{\mathrm{d}\{[\mathrm{R}_1^\bullet]\}}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{St}]([\mathrm{I}^\bullet]+[\mathrm{M}^\bullet]+[\mathrm{D}^\bullet]) + k_\mathrm{a}[\mathrm{R}_1\mathrm{NOx}] - \{k_\mathrm{p}[\mathrm{St}] + k_\mathrm{d}[\mathrm{NOx}^\bullet] + (k_\mathrm{tc}+k_\mathrm{td})[\mathrm{R}^\bullet] + k_\mathrm{fm}[\mathrm{St}] + k_\mathrm{fd}[\mathrm{D}]\}[\mathrm{R}_1^\bullet] \qquad \text{(A.14)}$$

$$\frac{\mathrm{d}\{[\mathrm{R}_r^\bullet]\}}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{R}_{r-1}^\bullet][\mathrm{St}] + k_\mathrm{a}[\mathrm{R}_r\mathrm{NOx}] - \{k_\mathrm{p}[\mathrm{St}] + k_\mathrm{d}[\mathrm{NOx}^\bullet] + (k_\mathrm{tc}+k_\mathrm{td})[\mathrm{R}^\bullet] + k_\mathrm{fm}[\mathrm{St}] + k_\mathrm{fd}[\mathrm{D}]\}[\mathrm{R}_r^\bullet] \qquad r = 2, 3, \ldots, \infty \qquad \text{(A.15)}$$

$$\frac{\mathrm{d}\{[\mathrm{R}_r\mathrm{NOx}]\}}{\mathrm{d}t} = k_\mathrm{d}[\mathrm{NOx}^\bullet][\mathrm{R}_r^\bullet] - k_\mathrm{a}[\mathrm{R}_r\mathrm{NOx}] \qquad r = 1, 2, 3, \ldots, \infty \qquad \text{(A.16)}$$

$$\frac{\mathrm{d}\{[\mathrm{P}_r]\}}{\mathrm{d}t} = (k_\mathrm{td}[\mathrm{R}^\bullet] + k_\mathrm{fm}[\mathrm{St}] + k_\mathrm{fd}[\mathrm{D}])[\mathrm{R}_r^\bullet] + 1/2k_\mathrm{tc}\sum_{i=1}^{r-1}[\mathrm{R}_{r-i}^\bullet][\mathrm{R}_i^\bullet] \qquad r = 1, 2, 3, \ldots, \infty \qquad \text{(A.17)}$$

Conversion and Average Molar Masses of Total Polymer



$$x = \frac{[St]_0 - [St]}{[St]_0} \qquad (A.18)$$

$$\overline{M}_{\mathrm{n}} = \frac{\sum_{r=1}^{\infty}([R^{\bullet}_{\mathrm{r}}(r)]+[P_{\mathrm{r}}(r)])r\,M_{St} + \sum_{r=1}^{\infty}[R_{\mathrm{r}}\mathrm{NOx}\ (r)](r\,M_{St}+M_{NOx})}{\sum_{r=1}^{\infty}([\mathrm{P}_{\mathrm{r}}(r)]_r + [R^{\bullet}_{\mathrm{r}}(r)] + [R_{\mathrm{r}}\mathrm{NOx}\ (r)])} \qquad (A.19)$$

$$\overline{M}_{w} = \frac{\sum_{r=1}^{\infty}([R^{\bullet}_{\mathrm{r}}(r)]+[P_{\mathrm{r}}(r)])(r\,M_{St})^2 + \sum_{r=1}^{\infty}[R_{\mathrm{r}}\mathrm{NOx}\ (r)](r\,M_{St}+M_{NOx})^2}{\sum_{r=1}^{\infty}([R^{\bullet}_{\mathrm{r}}(r)]+[P_{\mathrm{r}}(r)])(r\,M_{St}) + \sum_{r=1}^{\infty}[R_{\mathrm{r}}\mathrm{NOx}\ (r)](r\,M_{St}+M_{NOx})} \qquad (A.20)$$

Measurements and Model Predictions

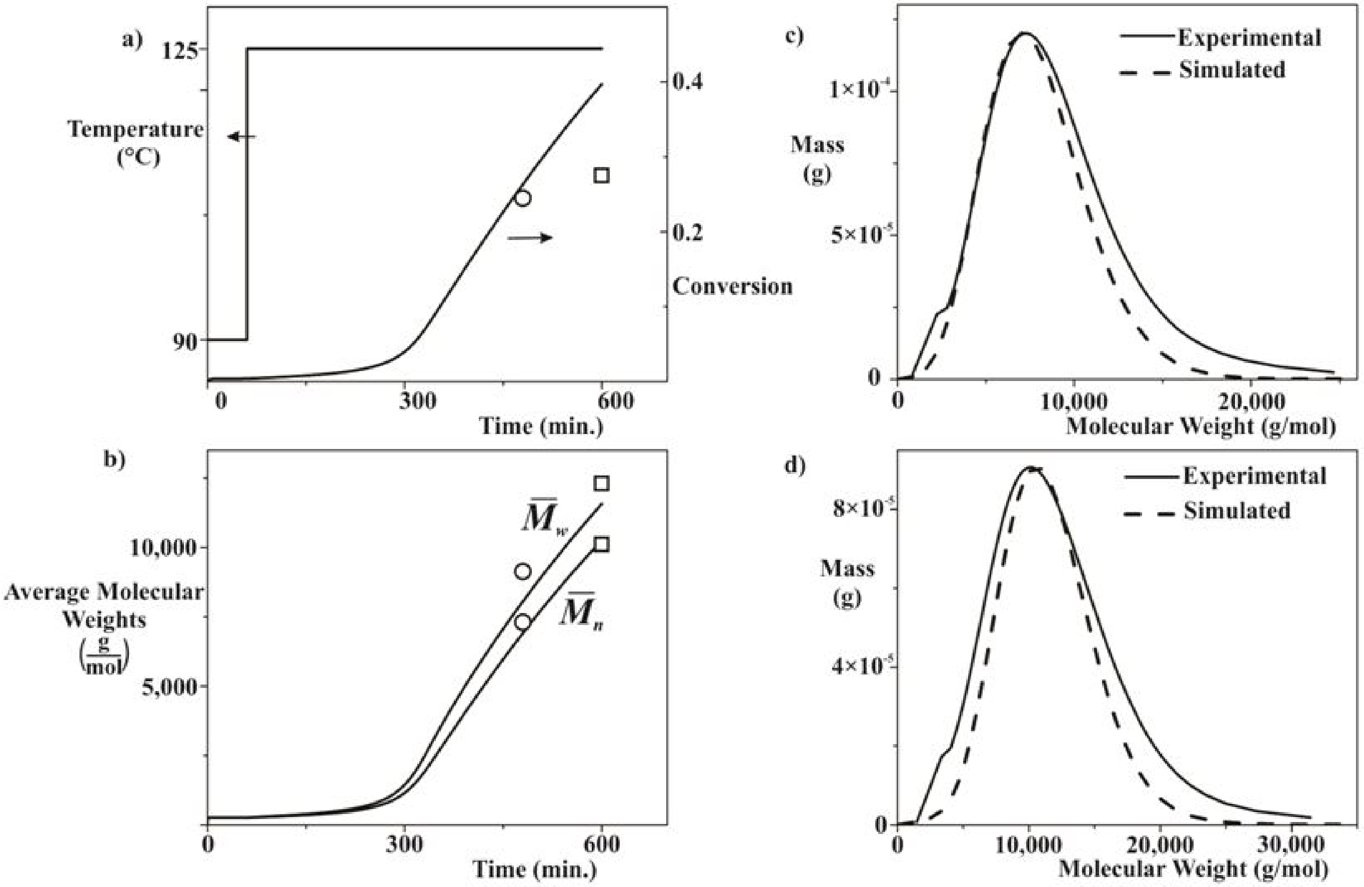


Figure 1: Measurements and model predictions for: a) the monomer conversion; b) the average molecular weights; and c, d) the MWDs at $t = 480$ and 600 min. The measurements of sample 1 are in circles and those of sample 2 in squares.

Ideal/ Nonideal Controlled Polymerization

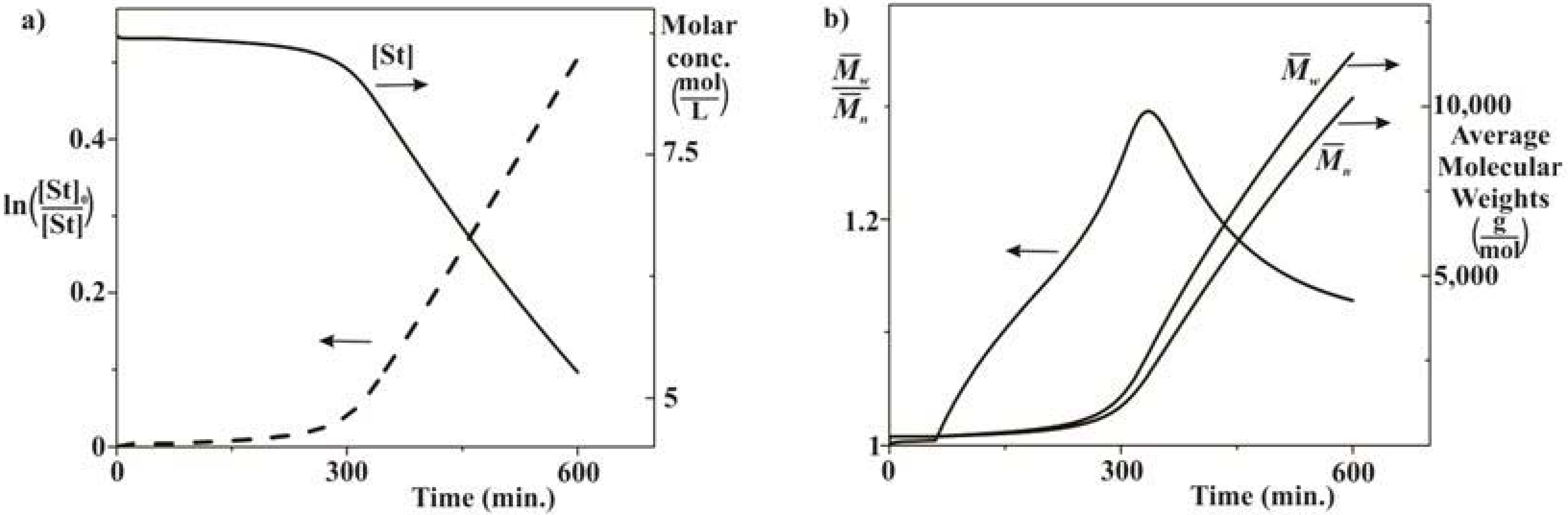


Figure 2: Time evolutions of: (a) monomer concentration and monomer logarithmic conversion; and (b) average molecular weights and dispersity of total polymer.

Polymer Production

Average Molar Masses

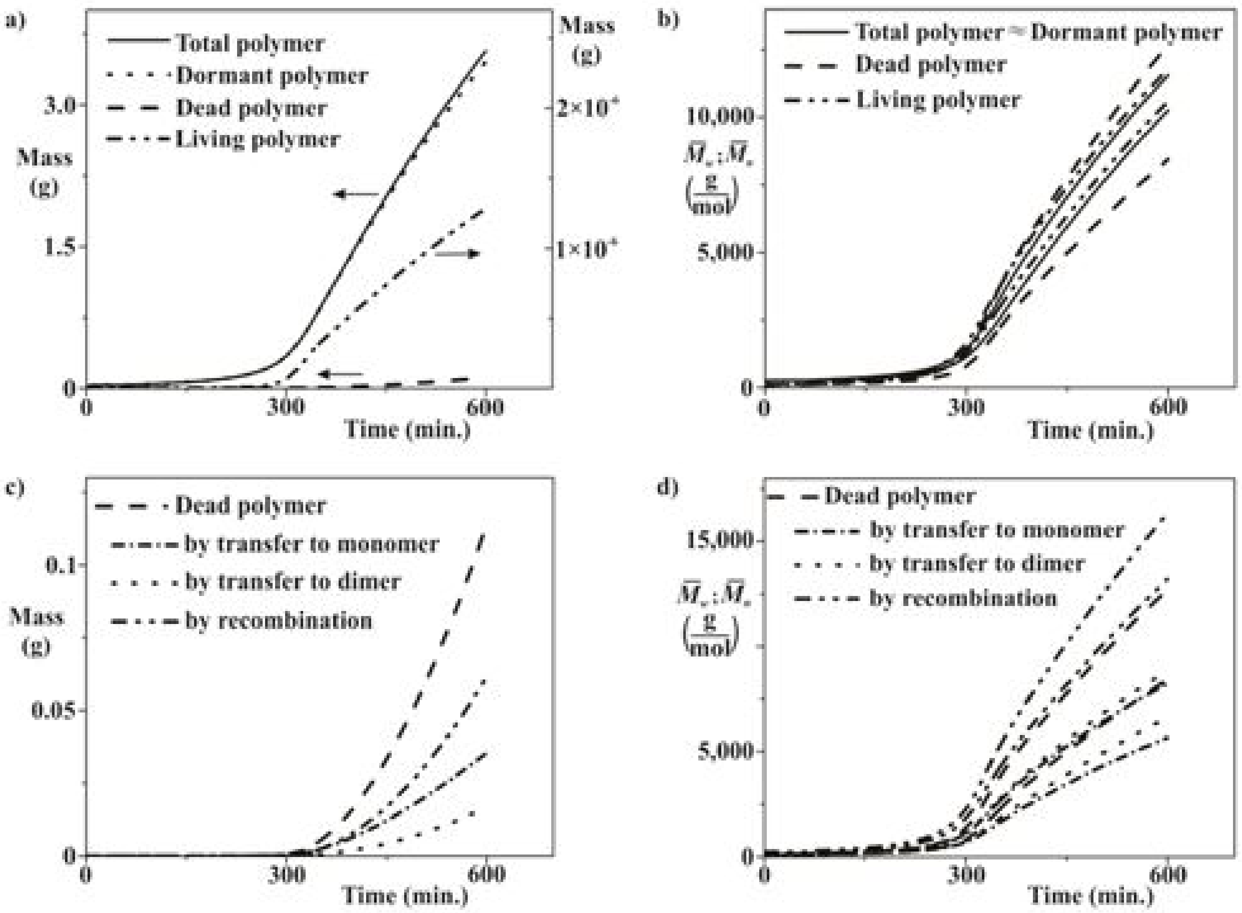
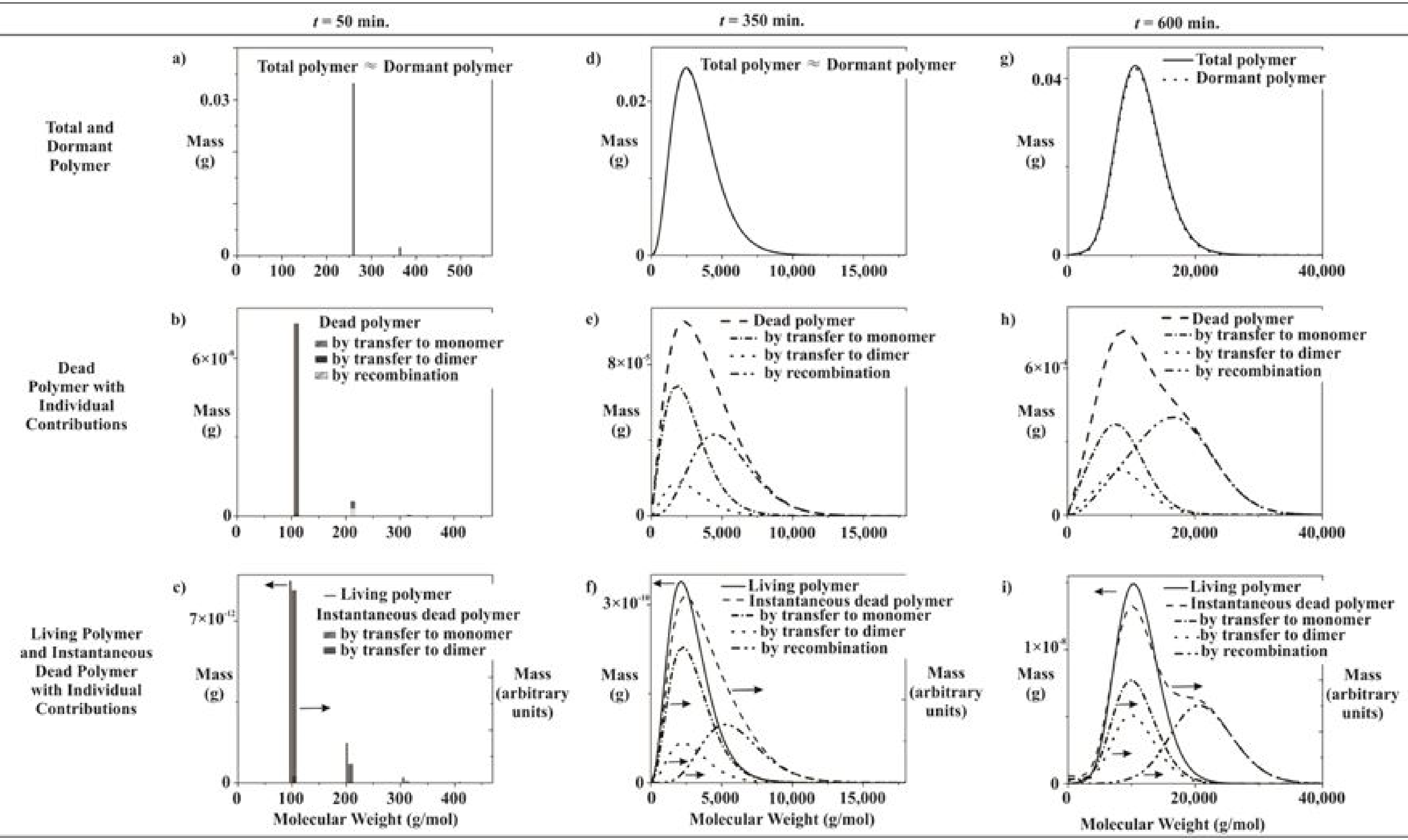


Figure 4: Time evolution of: a) mass concentration of the total polymer and its fractions; b) average molecular weights of the total polymer and its fractions; c) mass concentration of the total dead polymer and its constituents; and d) average molecular weights of the total dead polymer and its constituents.

MWDs of Total Polymer and its Fractions at *t* = 50 min. (a-c); *t* = 350 min. (d-f); and *t* = 600 min. (g-i).
Note the different horizontal scales at the 3 simulated times.



Evolution of Global Active and Stable Radicals

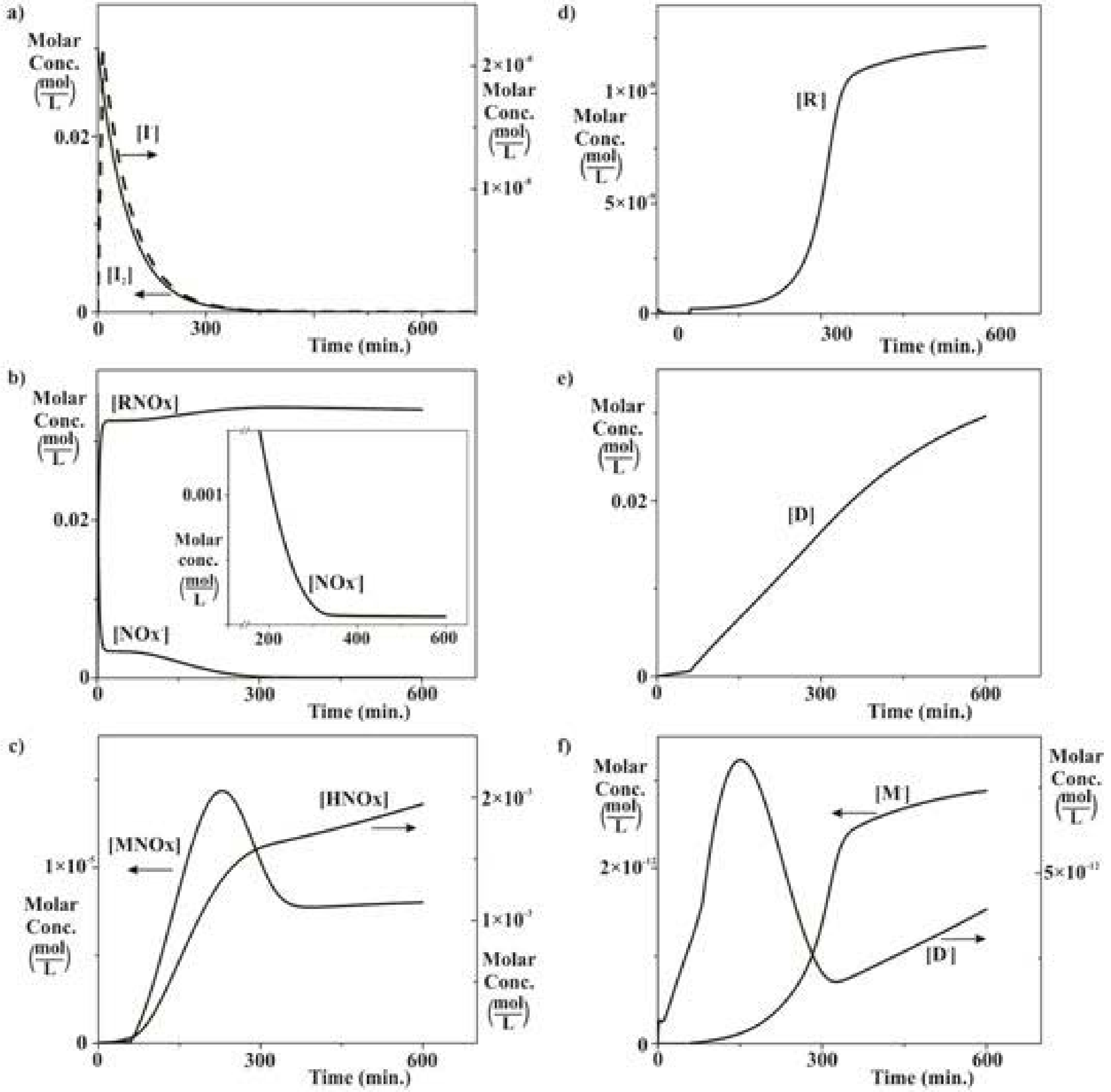


Figure 3: Time evolutions of the molar concentrations of: (a) chemical initiator and initiator radicals at the beginning of the reaction; (b) free nitroxide radicals NOx' and dormant free-radicals RNOx; (c) monomeric alkoxyamine MNOx and deactivated nitroxide HNOx; (d) total free-radicals R; (e) dimer D; and (f) monomer and dimer radicals M' and D', respectively.

CONCLUSIONS

1. CRP processes enable the production of narrow-distributed polymers and block copolymers of relatively low molar masses.

2. An advantage of CRP procedures is the stability of the initiating species. In the case of Nitroxide Mediated processes, the alkoxyamine initiator may be chemically transformed with no deleterious effect on their initiating ability. This enables to prepare not only chain-end-labeled macromolecules, but also permits the introduction of initiating fragments at various surfaces, interfaces, chain ends of dendrimers, and along the backbone of a linear polymer chain.

3. As more and more effort is devoted to controlling structure and function on the nanometer scale, the role of well-defined polymeric materials with controlled size, dispersity and functional groups is critical for the continued evolution of self-assembled materials.