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# Initiating Free Radical Polymerization

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**Summary:** The kinetics and mechanism of the initiation and reinitiation of free radical polymerization is reviewed. The importance of understanding the kinetics, specificity and efficiency of initiation and chain transfer when predicting polymerization kinetics and polymer composition is highlighted. These factors are particularly important when making low molecular weight polymers and in living or controlled polymerization processes. Examples of RAFT polymerization and catalytic chain transfer are provided.

## Introduction

This paper deals with the generation and reaction of small radicals during polymerization. It is primarily concerned with the processes of initiation and chain transfer.

We define initiation of polymerization as that sequence of reactions that commences with the generation of primary radicals from a free radical source (I) and culminates in the production of a propagating radical ($P_1\bullet$). A simplified reaction scheme is shown in Scheme 1.[1]

$$\begin{tikzcd}
I \arrow[r, "k_d f"] & I\bullet \arrow[d, "M"', "k_i"] & & & \\
& P_1\bullet \arrow[r, "k_{p1}", "M"'] & P_2\bullet \arrow[r] & {} \arrow[r, "k_p", "M"'] & P_m\bullet
\end{tikzcd}$$

**Scheme 1**

We may define chain transfer in a similar way as that sequence of reactions that commences with the reaction of a propagating radical ($P_n\bullet$) with a transfer agent (T) and culminates in the production of a new propagating radical (Scheme 2). In either case initiating radicals are those initiator- ($I\bullet$) or transfer agent-derived ($T\bullet$) radicals which add monomer to form propagating radicals ($P_1\bullet$).

$$\begin{tikzcd}
P_n\bullet + T \arrow[r, "k_{tr}"] & P_n + T\bullet \arrow[d, "k_i"', "M"] & & & \\
& P_1\bullet \arrow[r, "k_{p1}", "M"'] & P_2\bullet \arrow[r] & {} \arrow[r, "k_p", "M"'] & P_m\bullet
\end{tikzcd}$$

**Scheme 2**

It is now well established that, in conventional polymerization, the initiation process,

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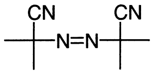
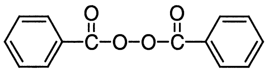
and the specificity of that process, can have a substantial influence on the kinetics of polymerization, the polymer structure and molecular weight distribution, and hence various polymer properties (*e.g.* rheology, long term stability). Although the primary focus in developing living polymerization processes has been on control of termination, it should be clear that there is an equal need to control the specificity and efficiency of initiation or reinitiation.

## Methods of radical generation

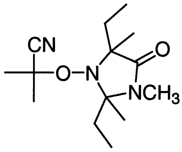
An appreciation of structures of radicals (as formed from initiators and transfer agents) and their effect on the rate and mechanism of radical formation and the rate and specificity of subsequent reactions is critical to the development of an understanding of polymerization. The correct selection of small radical species can determine the outcome of both conventional or non-conventional (i.e. living, controlled) polymerization processes.[1]



**AIBN**



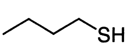
**BPO**



**1**

The most commonly used initiators are azo (e.g. azobisisobutyronitrile, **AIBN**) and peroxy compounds (e.g. dibenzoyl pereoxide, **BPO**). The initiators have traditionally been characterized by a rate constant ($k_d$) for thermal decomposition (often expressed as a half life) and an initiator efficiency ($f$). Compilations of $k_d$ data can be found in commercial literature and in such places as the Polymer Handbook.[2] While it should be recognized that these compilations do not provide a critical review of data, it can also be stated that values of $k_d$ are generally more precise than other kinetic parameters associated with polymerization.[1] Values of $f$ applicable to zero conversion may also be found. However these numbers must be treated cautiously.[1] The initiator efficiency is a variable that depends strongly on process conditions (such as reaction medium, temperature, monomer conversion). Another point to note is that the definition of initiator efficiency is not consistent. In organic free radical chemistry $f$ is simply a measure of the yield of initiator-derived radicals $I\cdot$. In polymer chemistry it generally specifies the yield of $P_n\cdot$. The term thus also embraces terms relating to the specificity whereby $I\cdot$ adds to monomer and perhaps the first few propagation steps.

The last few years has seen the introduction of new classes of initiators for use in living radical polymerization.[3,4] These compounds include alkoxyamines for use in nitroxide-mediated polymerization (NMP) (*e.g.* **1**) and halocompound-metal complex combinations for use in atom transfer radical polymerization (ATRP). The kinetics, mechanism and efficiency of these initiators is the subject of much current research.



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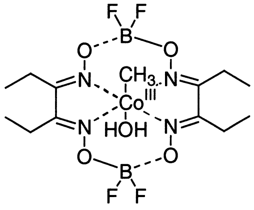

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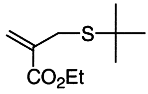

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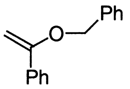

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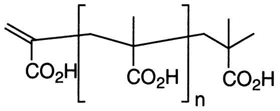

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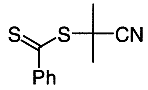


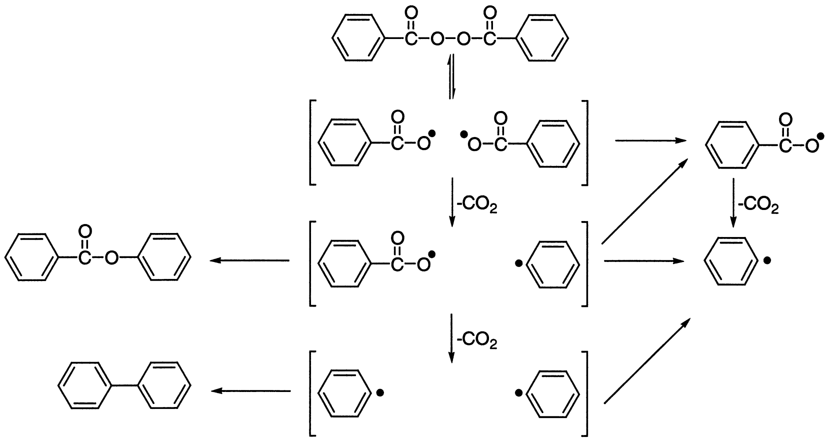
**7**

Conventional transfer agents include thiols (*e.g.* butanethiol **2**), and tertiary amines.[1] Monomers and some solvents may also give chain transfer. A more recent development are cobalt complexes for catalytic chain transfer (e.g. **3**) addition-fragmentation chain transfer agents (*e.g.* allyl sulfide **4** and vinyl ether **5**)[5,6] and various macromonomers[5,7,8] and thiocarbonylthio compounds[9-11] which give reversible addition-fragmentation chain transfer (RAFT) (*e.g.* methacrylic acid macromonomer **6** and cyanoisopropyl dithiobenzoate **7**).

## Mechanisms for initiator decomposition

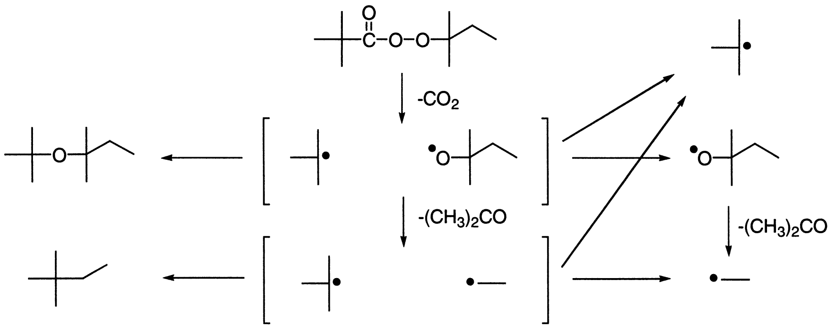
Mechanisms for initiator decomposition (the nature of initiator-derived radicals and extent and type of byproducts formed by cage reaction) are strongly dependent on the initiator structure.[1]

The mechanism for thermal decomposition of BPO is shown in Scheme 3. The rate of decarboxylation is slow, most benzoyloxy radicals escape the solvent cage before decarboxylation. The main cage reaction is reformation of BPO. In bulk polymerization (*e.g.* of styrene, methyl methacrylate (MMA)), few cage byproducts (*ie.* phenyl benzoate or biphenyl) are formed, and the initiator efficiency can be high (>90%),[12] However, the initiator is subject to induced decomposition (see below).



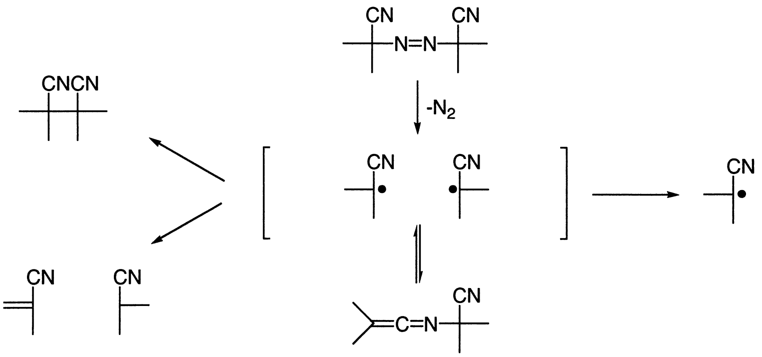
Scheme 3

The major pathways observed for thermal decomposition of *t*-amyl peroxypivalate is shown in Scheme 4.[13] The initiator is thought to decompose by 2-bond scission with formation of *t*-amyloxy and *t*-butyl radicals and a molecule of carbon dioxide. *t*-Amyloxy radicals also undergo rapid β-scission. Thus the predominant initiator-derived species are alkyl radicals. Initiator efficiencies are lower than for BPO (efficiency of radical production is ~53% at 60°C in isopropylbenzene[13]).



Scheme 4

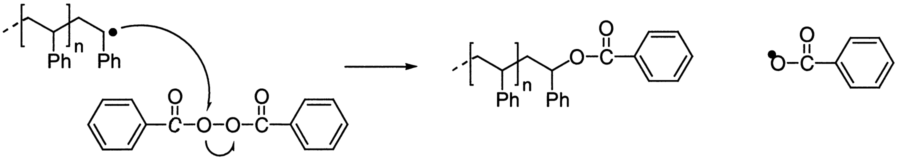
AIBN decomposes with loss of nitrogen to form cyanoisopropyl radicals that combine reversibly to give an unstable ketenimine as the main cage byproduct (Scheme 5).[14,15] At 60°C the ketenimine has a half-life similar to that of AIBN. This complicates the kinetics of decomposition.



Scheme 5

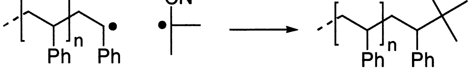
## Side reactions associated with initiation

Other reactions also lead to low initiator efficiency.[1] In the case of azo and peroxy compounds, these include radical induced and various forms of non radical decomposition. Induced decomposition is a major issue with BPO (Scheme 6) and other diacyl peroxides. In styrene polymerization initiated by BPO, much chain termination is by transfer to initiator.[12]

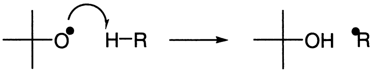


Scheme 6

Primary radical termination is a very minor pathway in benzoyl peroxide initiated polymerization except when very high initiator concentrations are used.[14] The extent of primary radical termination varies inversely with rate of radical addition to monomer – thus it will be more important for cyanoisopropyl (Scheme 7) than for benzoyloxy radical.[16]



Scheme 7



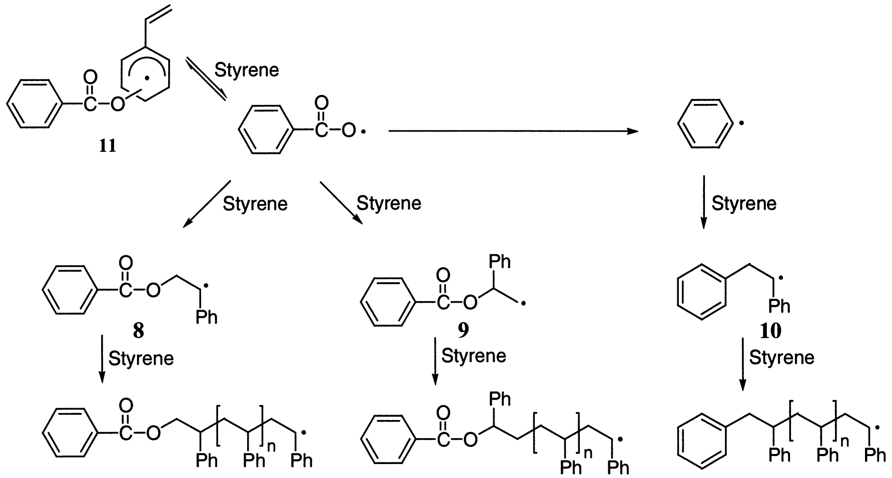
Scheme 8

Primary radical transfer (Scheme 8) may be the major pathway for polymerizations initiated with *t*-butoxy radical sources in solvents, monomers containing aliphatic hydrogens.[17]

## Properties and reactions of initiator-derived radicals

The reactions of initiator-derived radicals with monomers can be complex and involve pathways other than tail addition to the monomer double bond.[1] For example, intermediate products from the reaction of benzoyloxy radicals with styrene are shown in Scheme 9. The initiation pathways shown are established[18] and groups derived from radicals **8-11** have been observed directly in polystyrene formed with benzoyl peroxide initiator by $^{13}$C NMR.[14]

An important question is when does an initiator-derived radical become a propagating radical? Clearly, the cyclohexadienyl radical **11** which does not add further monomer is not a propagating species. Should the radicals **8-10** all be considered as single unit propagating radicals ($P_1$•)?



**Scheme 9**

The primary alkyl radical **9** is likely to display quite different reactivity and specificity to the benzylic radicals **8** and **10**. Furthermore, has been shown that the rate constants the reaction or formation of short chain radicals ($P_1$•, $P_2$•,…) can differ markedly (by more than an order of magnitude in some cases but dependent on radical structure) from those analogous processes involving longer chain propagating species ($P_n$•).[19-22] For example, the rate constants for reactions of monomeric and polymeric propagating species derived from styrene and MMA are compared in the Arrhenius plots shown in Figs. 1 and 2 (values for monomeric radicals are based on Arrhenius parameters taken from Fischer and Radom[19]). It has also been shown that rate constants for radicals $P_1\bullet$ may also vary significantly according to the nature of the penultimate unit (the initiator-derived residue).[19,23]

The impact of these factors on polymerization kinetics and molecular weight distribution will be most noticeable in processes which provide oligomeric products or where oligomeric species play a key role in the reaction mechanism (*e.g.* pulsed laser polymerization,[24,25] particle entry in emulsion polymerization[26]).

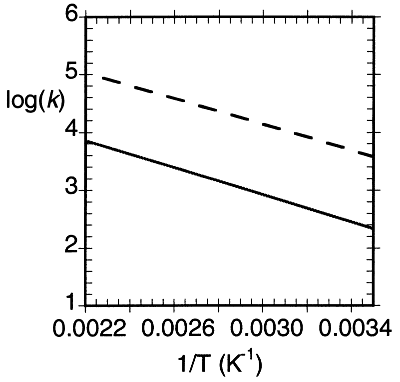


Figure 1. Arrhenius plot for reaction of monomeric (— —) and polymeric PMMA propagating radical (———) adding MMA.

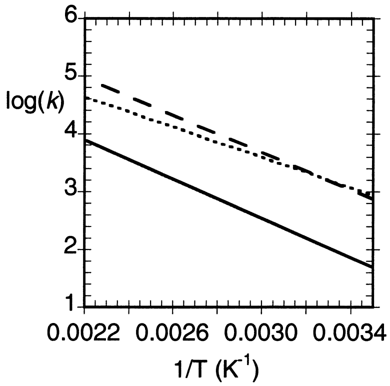
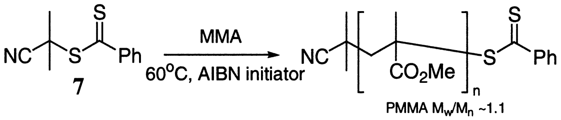


Figure 2. Arrhenius plot for reaction of benzyl (— —), cumyl (-----) and polystyrene propagating radical (———) adding styrene.

## Initiation and reinitiation in RAFT polymerization



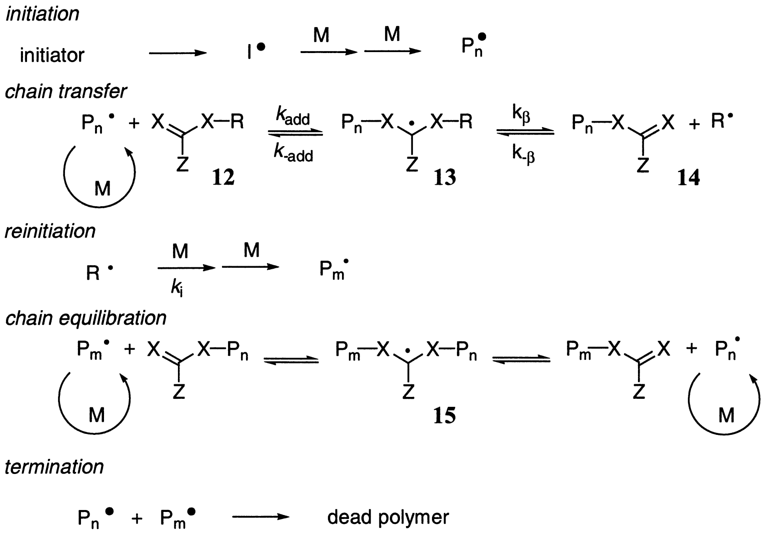
Scheme 10

Polymerization with Reversible Addition-Fragmentation chain Transfer (RAFT polymerization) provides the characteristics of a living polymerization. The overall process results in monomer units being inserted into RAFT agent structure as shown in Scheme 10.[9] Molecular weights can be estimated using the relationship (1):

Calculated Degree of Polymerization ~ [monomer consumed]/[RAFT agent] (1)

The process is compatible with very wide range of monomers and reaction conditions and provides precise control of the polymer architecture, composition and molecular weight distribution. Details are provided in recent papers.[9-11,27-29]

In accord with the proposed mechanism of RAFT polymerization (summarized in Scheme 11)[9] the kinetics have been found to be similar to those of conventional free radical polymerization over a wide range of RAFT agent concentrations. Thus, the rate of RAFT polymerization of (for example) MMA is 0.5 order in initiator and zero order in RAFT agent (see Figure 3). Retardation is only observed with high concentrations of certain RAFT agents (see below).



**Scheme 11**

The rate of consumption of the initial RAFT agent (**12**) is described by equation (2).[30]

$$-\frac{d[\mathbf{12}]}{d[\mathrm{M}]} \approx C_{tr}\frac{[\mathbf{12}]}{[\mathrm{M}]+C_{tr}[\mathbf{12}]+C_{-tr}[\mathbf{14}]} \qquad (2)$$

Where $C_{tr} = k_{tr}/k_p$, $C_{-tr} = k_{-tr}/k_i$, $k_{tr} = k_{add} \times \frac{k_\beta}{k_{-add}+k_\beta}$ and $k_{-tr} = k_{-\beta} \times \frac{k_{-add}}{k_{-add}+k_\beta}$

If $C_{-tr}$ and/or [**14**] is small then the concentration dependence of $C_{tr}$ may be negligible and, if we also make the long chain approximation, equation (2) devolves to equation (3).

$$-\frac{d[\mathbf{12}]}{d[\mathrm{M}]} \approx C_{tr}\frac{[\mathbf{12}]}{[\mathrm{M}]} \qquad (3)$$

which suggests $$C_{tr} \sim \frac{d\ln[\mathbf{12}]}{d\ln[\mathrm{M}]} \qquad (4)$$

The rate of consumption of RAFT agent **12** therefore depends on two transfer constants, $C_{tr}$ ($=k_{tr}/k_p$) and $C_{-tr}$ ($=k_{-tr}/k_i$). It follows that the rate (the apparent transfer constant from equation 4) will decrease with increasing concentration of RAFT agent (**12**) and can also be conversion dependent. The apparent transfer constant of cumyl dithiobenzoate with 0.029 M RAFT agent at low (<20% conversion) is ~9 while that for 0.0058M RAFT agent is ~28 (obtained directly from the lines shown in Figure 4 by application of equation (4)). Equation 2 can be solved numerically and we can show that all data are fit with $C_{tr}$ ~56 and $C_{-tr}$ ~2400 (Figure 4).

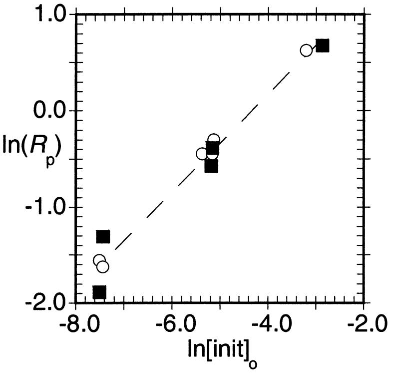


Figure 3. Plot of log (initial $R_p$) vs log (initial initiator concentration). Data are for bulk MMA polymerization at 60°C with AIBN initiator (0.0005-0.04 M) and either cumyl (■) or cyanoisopropyl dithiobenzoate (○) as RAFT agent 0.006-0.03 M . Least squares fit provides slope 0.507, R=0.98655.

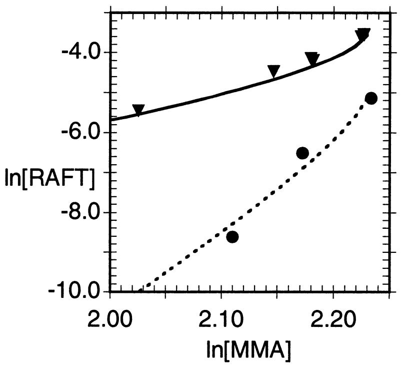
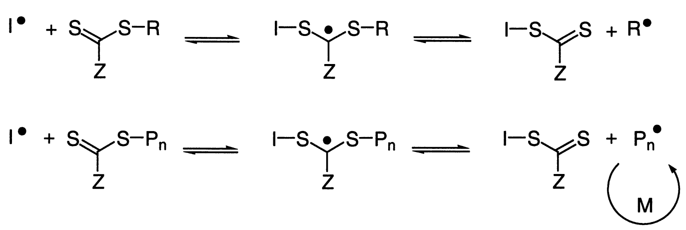


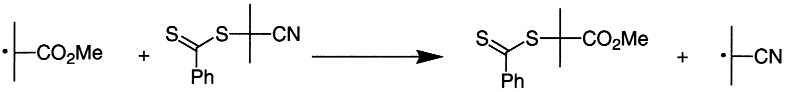
Figure 4. Relative rate of consumption of RAFT agent and monomer in bulk MMA polymerizations at 60°C with AIBN initiator in the range 0.0005-0.04 M and 0.0058 M (●) or 0.029 M (▼) cumyl dithiobenzoate as RAFT agent. Lines are those predicted by equation (2) with $C_{tr}$ ~56 and $C_{-tr}$ ~2400.

Primary radical transfer (Scheme 12) may be seen as an avoidable side reaction that can cause departure from living behavior and potentially some retardation or as a useful synthetic method allowing interconversion of RAFT agents.[10]



Scheme 12

Thus, in MMA polymerization initiated with AIBMe (Scheme 13), the radical **16** may react with the cyanoisopropyl dithiobenzoate (**7**, transfer constant >20)[10] or the polymeric RAFT agent (transfer constant ~140)[31] to form a new less effective RAFT agent (**17**, transfer constant ~2).[10] In this case, the side reaction can be avoided by use of AIBN as initiator.



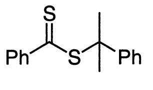
**16** **7** **17**

Scheme 13

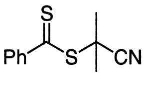
Retardation in RAFT polymerization with cumyl dithiobenzoate has been discussed in several recent papers.[10,32] Based on the RAFT mechanism shown in Scheme 11 we proposed the following as possible explanations for retardation:[10]

a) Slow fragmentation of the adduct (**12**) to the initial RAFT agent (**12**)
b) Slow fragmentation of adduct (**15**) to the polymeric RAFT agent (**14**)
c) Slow reinitiation by the expelled radical (R•)
d) Consumption of the adducts (**13** or **15**) or R• in side reactions - *e.g.* radical-radical termination by combination or disprortionation
e) Specificity for R• to add to RAFT agent rather than monomer.
f) Specificity for the propagating radical ($P_n$ •) to add to RAFT agent rather than monomer.

Retardation in styrene and acrylate polymerization has been discussed in a previous paper.[10] Some data for retardation in MMA polymerization are shown in Figure 5 and in Table 1. Significant retardation is also observed in MMA polymerization in the presence of high concentrations of cumyl dithiobenzoate **18**. This retardation is clearly associated with slow utilization of the initial RAFT agent (as evidenced by the higher than calculated molecular weights). A similar observation was made for styrene polymerizations with cumyl dithiobenzoate.[10] Further evidence that the retardation may be attributed to a property of the initial RAFT agent is the observation that retardation is alleviated with use of RAFT agent with more appropriate ‘R’ (better homolytic leaving group, more effective reinitiation) *e.g.* cyanoisopropyl dithiobenzoate **7**. However, retardation is also reduced when using less active cumyl RAFT agents with ‘Z’ groups that provide less stabilization for the intermediate (**13** or **15**). For example, cumyl dithioacetate **18**, dithiophenylacetate **20**) also give less retardation).



**18**



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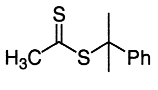

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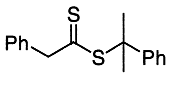


**20**

**Table 1.** Molecular weights and polydispersities obtained in RAFT polymerizations[a]

| time h | [RAFT] M | $\overline{M}_n$ ($\overline{M}_w$ / $\overline{M}_n$) for RAFT agent | | | |
|---|---|---|---|---|---|
| | | **18** | **7** | **19** | Control[b] |
| 1 | 0.13 | 1600 (1.35) | 3500 (1.16) | 2700 (1.38) | 280000 (2.4) |
| 4 | 0.13 | 2000 (1.35) | 4300 (1.14) | 4100 (1.21 | 280000 (2.5) |
| 1 | 0.013 | 31800 (1.25) | 26100 (1.12) | - | 280000 (2.4) |
| 4 | 0.013 | 41600 (1.22) | 32400 (1.14) | - | 280000 (2.5) |

[a] Results are the average obtained in two experiments. Experimental conditions are given in legend to Figure 5.

[b] No added RAFT agent.

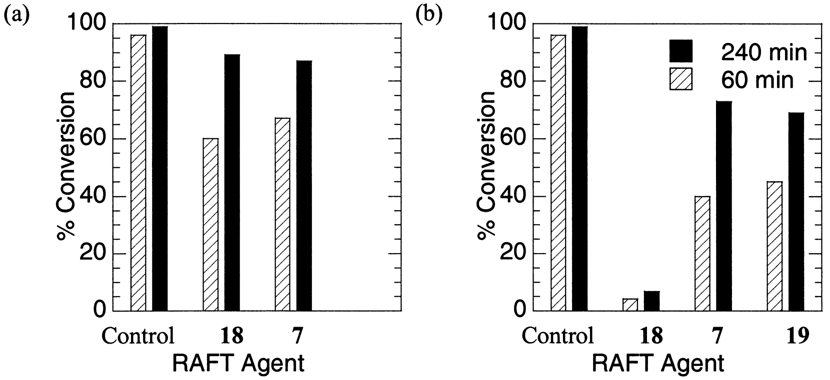


Figure 5. Variation in conversion with RAFT Agent for (a) low (~0.013 M) RAFT agent and (b) high (0.13 M) RAFT agent and reaction times of 60 min (hashed) and 240 min (solid bars). Experiments with azobis(cyclohexanecarbonitrile (0.004 M) initiator and 7.7 M MMA in butyl acetate at 110 °C.

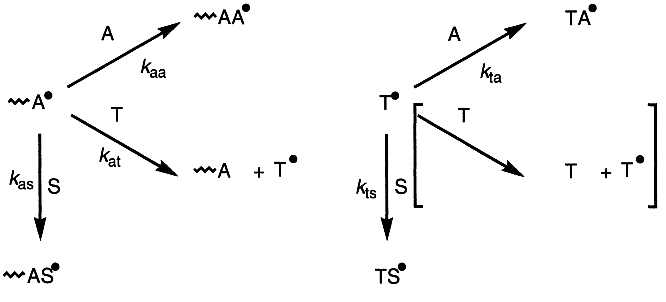
Values of $k_i$[19] for cumyl radical adding to styrene (~3800 M$^{-1}$s$^{-1}$) and MMA (~7800 M$^{-1}$s$^{-1}$ at 60 °C) indicate that cumyl radicals like cyanoisopropyl radicals (4900 and 3300 M$^{-1}$s$^{-1}$ at 60 °C respectively) should be effective at reinitiating styrene and MMA polymerization.

The experimental data thus suggest that retardation is due to slow fragmentation of the adduct (**13**) formed from the initial RAFT agent and/or high $C_{\text{-tr}}$ (i.e. a) in the above list). Kinetic simulation shows that this mechanism can account for the observed molecular weights and rate of polymerization using the method reported previously.[33] Some other possibilities, in particular b)[34] and d)[32] appear inconsistent with the experimental data.

We conclude that to maximize living character (obtain predictable maximum functionality, molecular weight, narrow polydispersity) and minimize retardation it is important to select initiator and RAFT agent (and other reaction conditions) for particular polymerization paying particular attention to the nature of initiating radicals generated.

## Initiation/reinitiation in copolymerization

We have shown that specificity in initiation and chain transfer can have a significant effect on copolymerization.[35,36] The reactions not only determine the polymer end groups, they have a significant effect on the overall composition and the molecular weight distribution.



**Scheme 14**

For sufficiently long kinetic chain lengths, copolymer composition depends only on relative reaction rates (reactivity ratios). There should be no need to know individual propagation rate constants. Contrary to what has been reported,[37,38] this situation also applies in copolymerization with chain transfer (reactivity ratios and chain transfer constants). Binary copolymerization with chain transfer can be treated similarly to ternary copolymerization where one monomer (T) does not homopolymerize[39] to provide equations (5-8) defining the probabilities for finding A, S or T in the polymer.[40]

$$P(\mathrm{A}) \propto [\mathrm{A}]\left\{\frac{R_t[\mathrm{A}]}{r_s}+\frac{[\mathrm{S}]}{r_s}+\frac{R_t[\mathrm{T}]}{1/C_s}\right\}\left\{[\mathrm{A}]+\frac{[\mathrm{S}]}{r_a}+\frac{[\mathrm{T}]}{1/C_a}\right\} \tag{5}$$

$$P(\mathrm{S}) \propto [\mathrm{S}]\left\{\frac{R_t[\mathrm{A}]}{r_a}+\frac{[\mathrm{S}]}{r_a}+\frac{[\mathrm{T}]}{1/C_a}\right\}\left\{[\mathrm{S}]+\frac{[\mathrm{A}]}{r_s}+\frac{[\mathrm{T}]}{1/C_s}\right\} \tag{6}$$

$$P(\mathrm{T}) \propto [\mathrm{T}]\left\{\frac{[\mathrm{A}]}{r_s/C_a}+\frac{[\mathrm{S}]}{r_a/C_s}+\frac{[\mathrm{T}]}{1/C_aC_s}\right\}\left\{R_t[\mathrm{A}]+[\mathrm{S}]\right\} \tag{7}$$

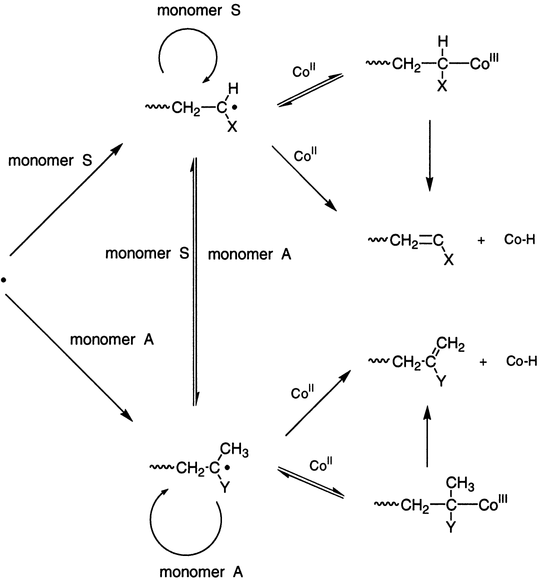
$$P(\mathrm{A}) + P(\mathrm{S}) + P(\mathrm{T}) = 1.0 \tag{8}$$

where $C_a = k_{at}/k_{aa}$, $r_a = k_{aa}/k_{as}$, $R_t = k_{ta}/k_{ts}$ (see Scheme 14) and the other reactivity ratios are similarly defined. .

Note that the fraction of chains that end with monomer A is the fraction of AT 'dyads' ( equation 9) and that the degree of polymerization is simply the inverse of the probability of finding transfer agent 'T' in the chain (10).

$$\frac{P(\mathrm{AT})}{P(\mathrm{AT})+P(\mathrm{ST})} = \frac{P(\mathrm{A})P(\mathrm{A}\,|\,\mathrm{T})}{P(\mathrm{A})P(\mathrm{A}\,|\,\mathrm{T})+P(\mathrm{S})P(\mathrm{S}\,|\,\mathrm{T})} \tag{9}$$

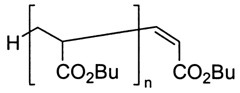
For polymerization with catalytic chain transfer, the expressions need to be modified to take out the contribution from single unit chains formed by chain transfer since these are monomer.[40] $P(1)=P(\mathrm{T}).P(\mathrm{T}|\mathrm{A}).P(\mathrm{A}|\mathrm{T})+P(\mathrm{T}).P(\mathrm{T}|\mathrm{S}).P(\mathrm{S}|\mathrm{T})$.



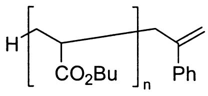
**Scheme 15**

A mechanism for copolymerization with catalytic chain transfer is shown in Scheme 15.[38,41-43] This process offers a route for the synthesis of macromonomers (e.g. **22**) and

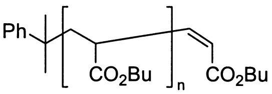
and hyperbranched polymers.[41,45] Clearly, Scheme 15 contains a number of complexities that are not embraced in Scheme 14. There are also other side reactions to consider. Nonetheless, Scheme 14 can take into account all of the kinetically significant events responsible for the chain composition and molecular weight distribution and can be used as a tool for parameter estimation and for gaining an understanding of relationship between the polymer microstructure and the various rate parameters.



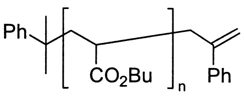
**21**



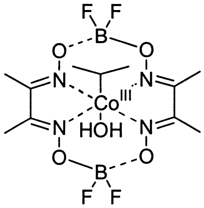
**22**



**23**



**24**



***i*Pr-Co(III)(DMG-BF$_2$)$_2$**

Data for copolymerization of butyl acrylate (BA) with α-methylstyrene (AMS) in the presence of a catalytic chain transfer agent, *i*Pr-Co(III)(DMG-BF$_2$)$_2$, are shown in Figure 6.[40] This reaction provides a mixture of **21-24** as major products at low conversion. Predominantly AMS chain ends (**22**, **24**) are obtained even with 50:1 BA:AMS (see Figure 6). An acceptable fit to the experimental data was obtained with the parameters shown in Table 2. High temperatures (>100 °C) and low conversions (<50%) are advantageous to minimize copolymerization of the macromonomer (lower temperatures and higher conversions may provide a hyperbranched polymer[45]) and minimize homopolymerization of AMS.

**Table 2.** Kinetic parameters used to model BA/AMS copolymerization in presence of *i*Pr-Co(III)(DMG-BF$_2$)$_2$

| Parameter | Value | Parameter | Value |
|---|---|---|---|
| $r_{AMS}$ | 0.3 | $C_{AMS}$ | 100000 |
| $r_{BA}$ | 0.18 | $C_{BA}$ | 200 |
|  |  | $R$ | 1 |

For higher concentrations of *i*Pr-Co(III)(DMG-BF$_2$)$_2$, the molecular weight is determined, not by the transfer agent concentration, but by the number average sequence length for BA. This has the effect of making the system more robust. It means that the outcome of polymerization is less affected by such factors as degradation of the catalyst with reaction time or ineffective degassing.

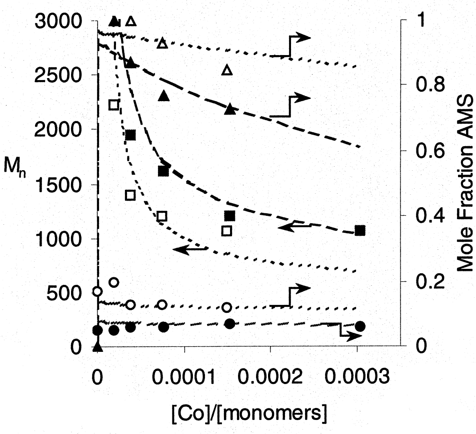


Figure 6. Found and predicted dependence of overall composition (●), end group composition (▲) and molecular weight (■) on concentration of cobalt complex for product of BA-AMS copolymerization in the presence of *i*Pr-Co(III)(DMG-BF$_2$)$_2$ at 125 °C with BA:AMS 50:1 (filled symbols, - - - -) or 25:1 (open symbols, ————).

Selection of initiator and the particular cobalt complex is also important since oxygen centered radicals can cause a reduction in catalyst activity.

## Conclusion

Most recent studies on polymerization kinetics and mechanism have tended to focus on the propagation and termination steps. The examples provided above serve to demonstrate the importance of initiator selection. In living/controlled polymerization process initiator selection assumes even greater importance due to the need to maximize product purity and hence living character.

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