

7. Reversible Addition-Fragmentation Chain Transfer

(RAFT)

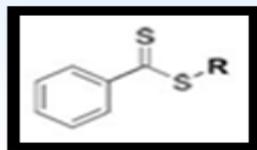
- The **RAFT** process is certainly the most recent of the controlled radical systems.
- **Even** if the concept of atom/group transfer is well-known in organic chemistry.
- **The first** reports about the possibility of performing controlled radical polymerization using dithiocarbonyl compounds only appeared in 1998.

- **The interest** in developing new radical processes with living character for the synthesis of well-defined architectures has allowed an unbelievable growth of this reversible chain transfer mediated process, as shown by the increasing number of publications on the subject.
- **The RAFT** polymerization has several advantages over other CRP techniques.
- **The** most significant advantage is the compatibility of the technique with a wide range of monomers, such as styrene, acrylates, methacrylates and derivatives.
- **This** large number of monomers provides the opportunity of creating well-defined polymer libraries by the combination of different monomeric units.

7.1 Classes of RAFT Agents:

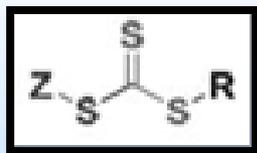
- **Solubility and reactivity** of a **RAFT** agent depend on the **R** and **Z** groups; as a result, different **RAFT** agents are more suitable for specific classes of monomers. The main classes of **RAFT** agents are:

(A) Dithiobenzoates



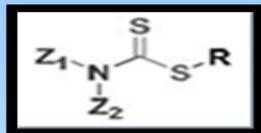
1. Very high transfer constants.
2. Prone to hydrolysis.
3. May cause retardation under high concentrations.

(B) Trithiocarbonates



1. High transfer constants.
2. More hydrolytically stable (than dithiobenzoate).
3. Cause less retardation.

(C) Dithiocarbamates

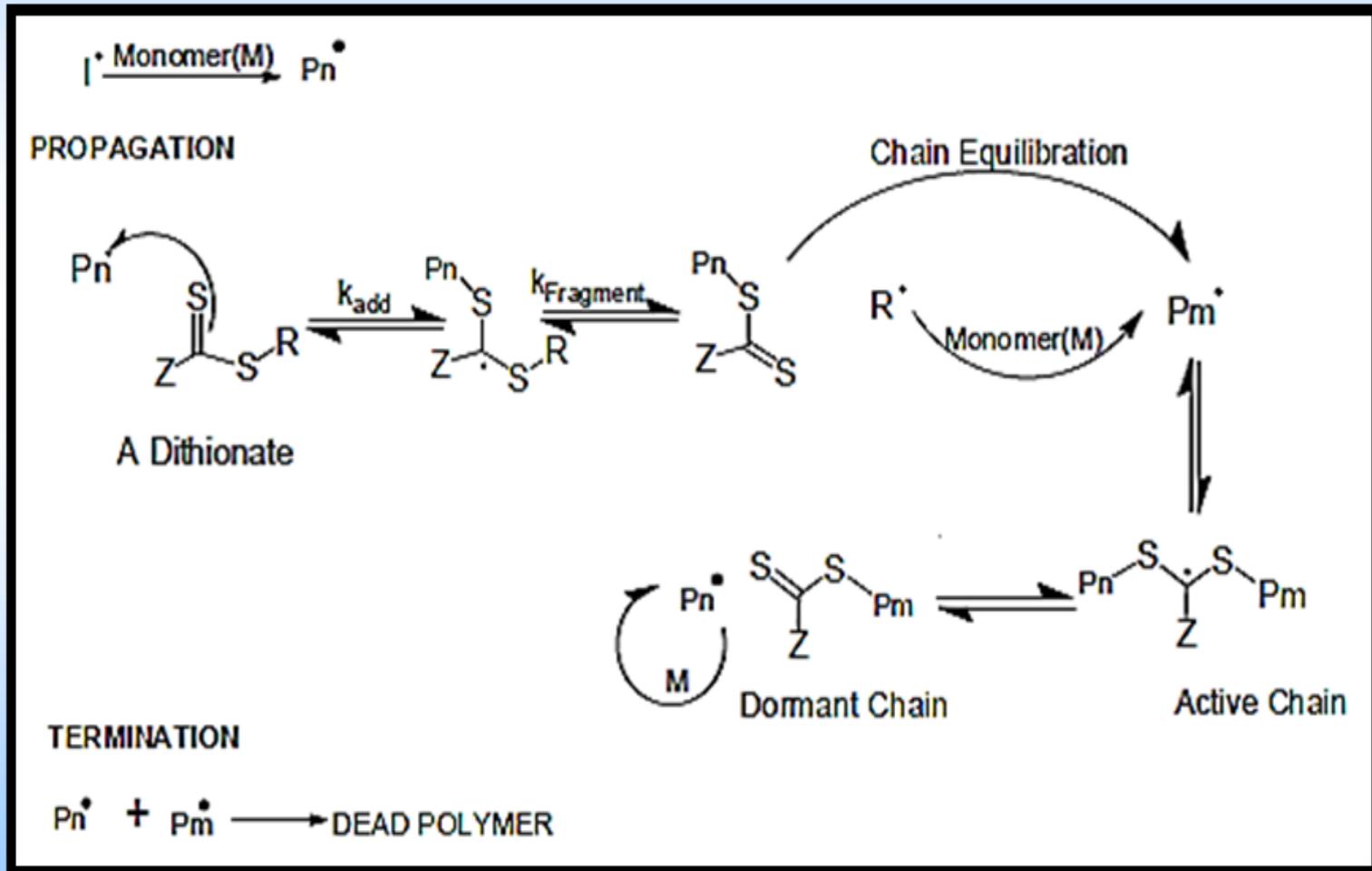


1. Activity determined by substituents on N.
 2. Effective with electron-rich monomers.
- In a RAFT system, the important parameters are:
 1. Choice of the RAFT agent depending upon the monomer to be polymerized,
 2. A high ratio of RAFT agent to initiator consumed, and
 3. A low radical flux during the polymerization.

7.2 Mechanism of RAFT:

- In a **RAFT** mechanism, initiation occurs via the decomposition of the free radical initiator leading to formation of propagating chains.
- **This** is followed by addition of the propagating radical to the RAFT chain transfer agent.
- **Further**, the fragmentation of the intermediate radical occurs, giving rise to a polymeric **RAFT** agent and a new radical.
- **This** radical reinitiates the polymerization to form new propagating radicals.

- **The RAFT** process relies on this rapid central addition fragmentation equilibrium between propagating and intermediate radicals, and chain activity and dormancy.



- The **key** that makes **RAFT** a living polymerization is the choice of the **RAFT** transfer agent.

7.3 Choice of RAFT agent:

- The **RAFT** agent must be chosen such that its chain transfer activity is appropriate to the monomer to be polymerized.
- The **electronic** properties of the activating (**Z**) group and the stereo electronic properties of the leaving (**R**) group determine the chain transfer activity of the **RAFT** agent.
- The **Z** group in the **RAFT** agent must be chosen such that it activates the double bond towards radical addition.
- **but at** the same time not provides a too great stabilization influence on the intermediate radical.

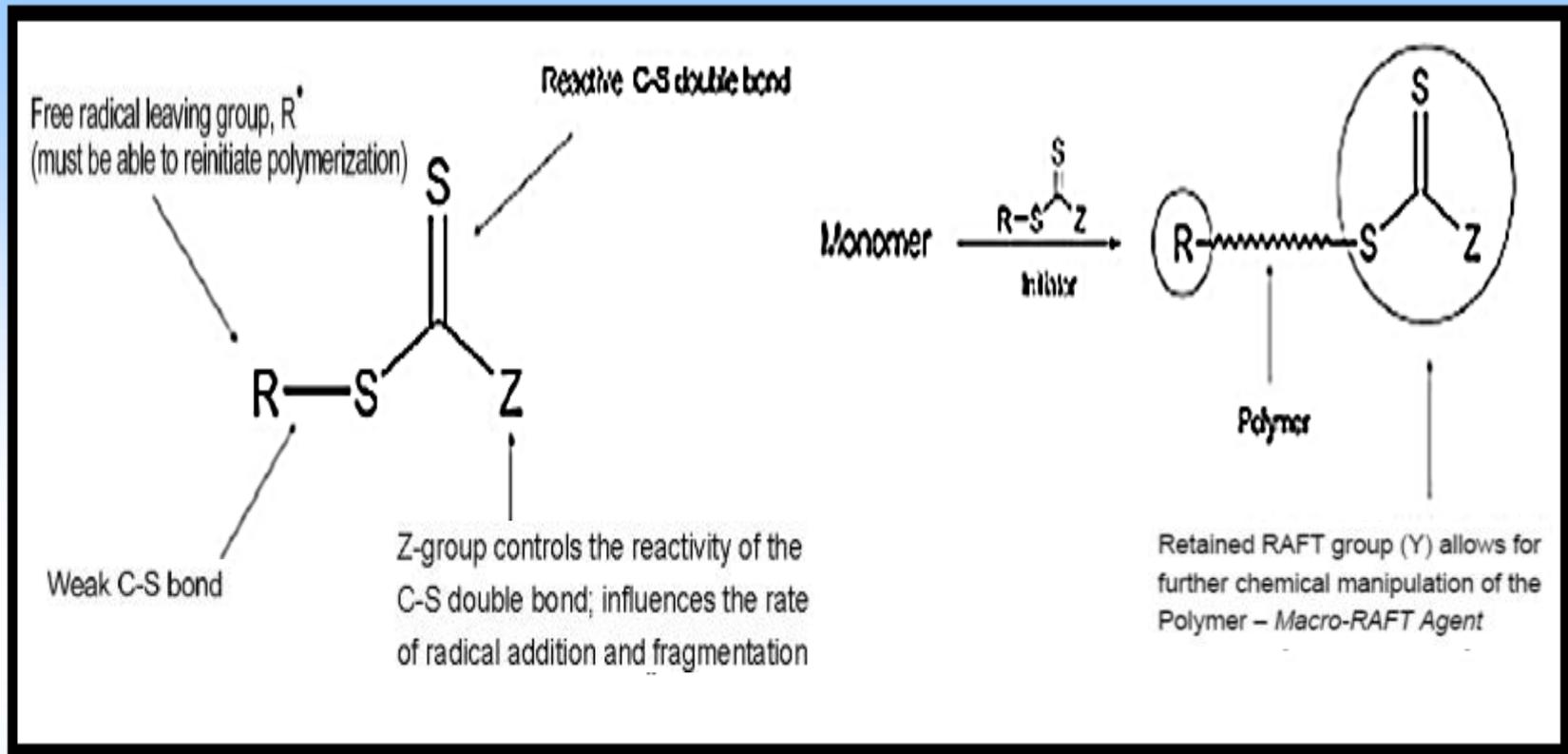
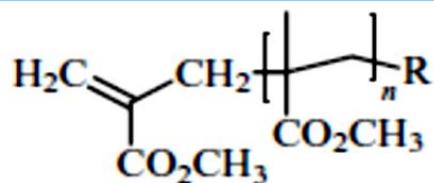
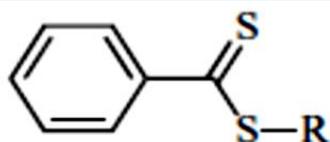


Figure 14: Choice of RAFT agent.

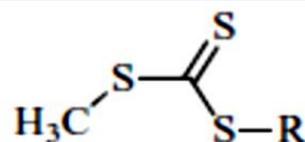
- **The R** group should be a good leaving group, relative to the radical of the propagating species.
- **It should** also preferentially reinitiate the polymerizations.



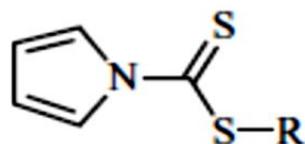
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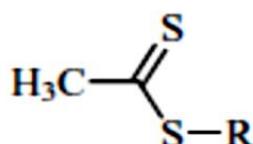
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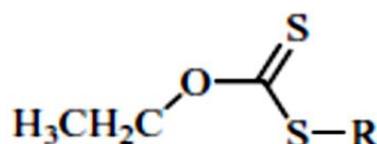
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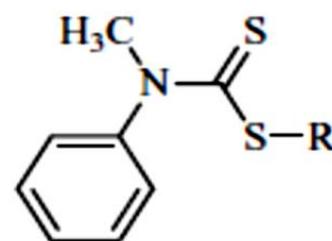
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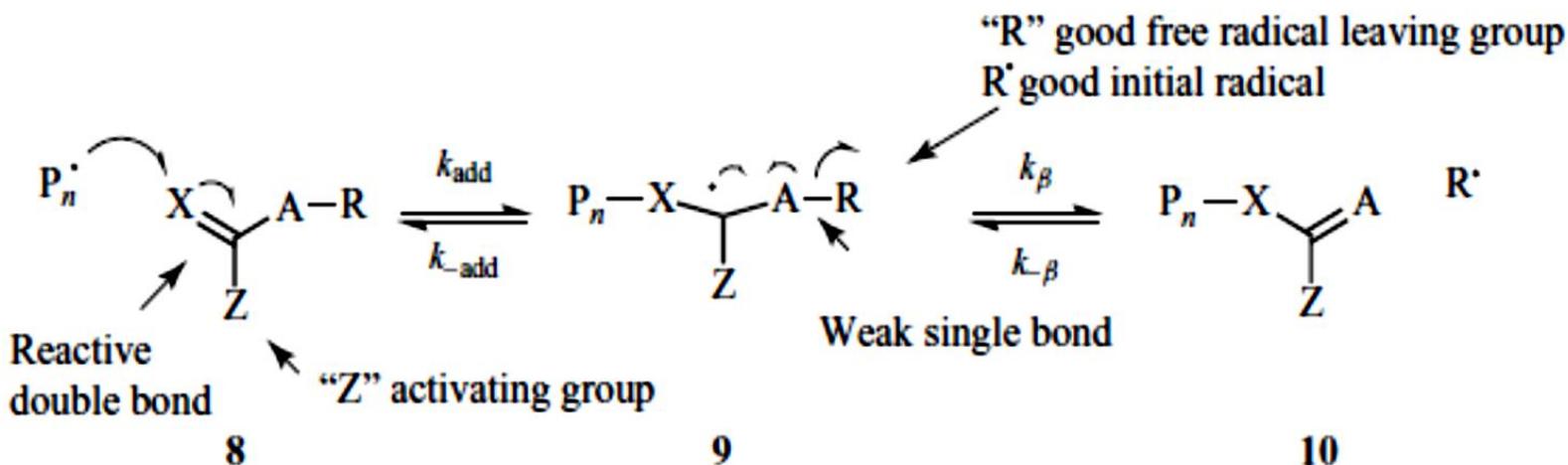
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7.4 Choice of Initiator:

- **The choice** of the thermal initiator is also an important factor in obtaining control over **RAFT** polymerization.
- **High ratios** of the **RAFT** agent to initiator should be employed, so as to maintain a low radical flux.
- **The choice** of the initiator is dependent on its half-life at the desired reaction temperature and its initiation ability relative to the monomer employed.
- **The longer** the half-life of the initiator at the desired temperature, the longer is the duration of radical production and thereby, the **RAFT** polymerization is kept active for a longer time.