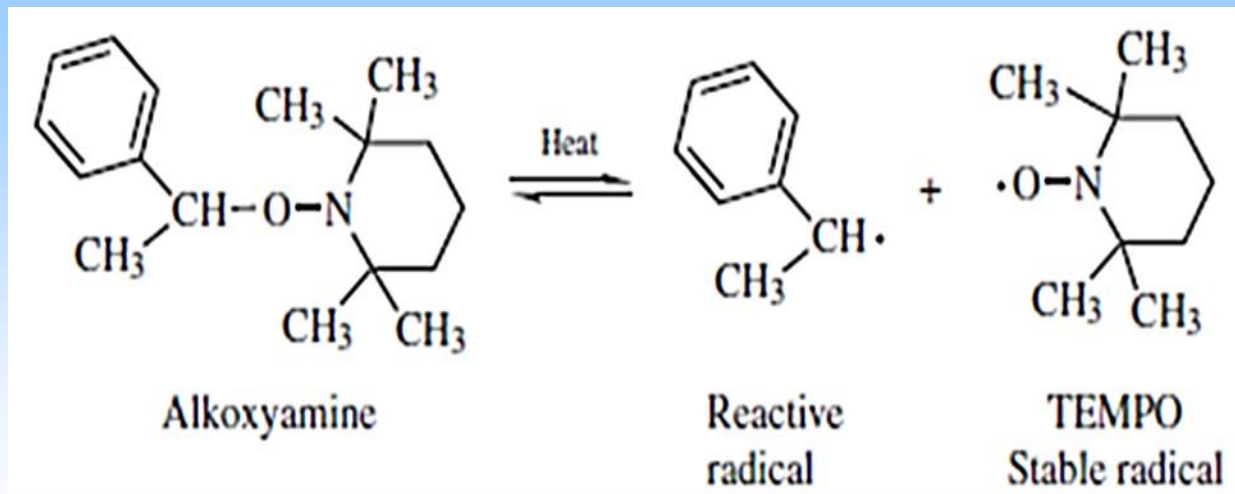


6. Nitroxide Mediated Polymerization:

Stable Free-Radical Polymerization (SFRP)

- **SFRP** with nitroxides is called **Nitroxide Mediated Polymerization (NMP)**, and have regained raising interest.
- **This is** because of the growing number of monomers that nowadays can be polymerized in a controlled manner via this technique.
- **with the** advent of newly designed nitroxide radicals (others than the **TEMPO** radical).



2,2,6,6- **tetra**methyl -1- **piperidin**o xyl (**TEMPO**)

- **However**, the control over the polymerization often arises from equilibria that significantly decrease the reaction times.
- **In NMP**, the control of the reaction is provided by reversible capping and de-capping of the growing (radical) polymer chain by a nitroxide radical.

- **As a result**, the concentration of the growing radical species is decreased and the speed of the polymerization is significantly decelerated, consequently,

1. the polymer chains grow with a uniform speed, and side reactions, like the bimolecular termination, are kept at a minimum, and

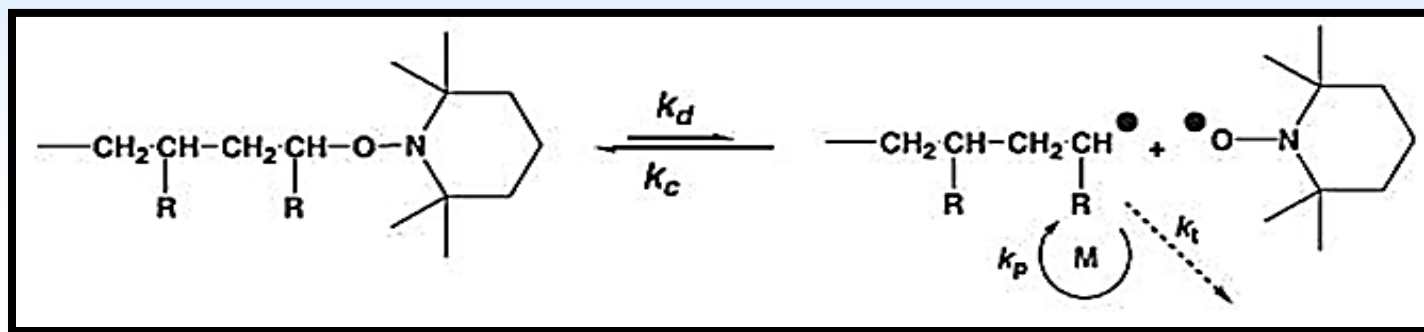
2. the polymers show relatively narrow molecular weight distributions.

- **In order to** gain optimum control over the radical polymerization.

- **one-component** species (decomposing into an initiating radical and a nitroxide radical) have shown to be superior to two-component mixtures, as the latter exhibit the disadvantage of inaccurately specified efficiencies of the initiating radical.

6.1 Basic mechanism:

• **Control** in **NMP** is achieved with dynamic equilibration between dormant alkoxyamines and actively propagating radicals.



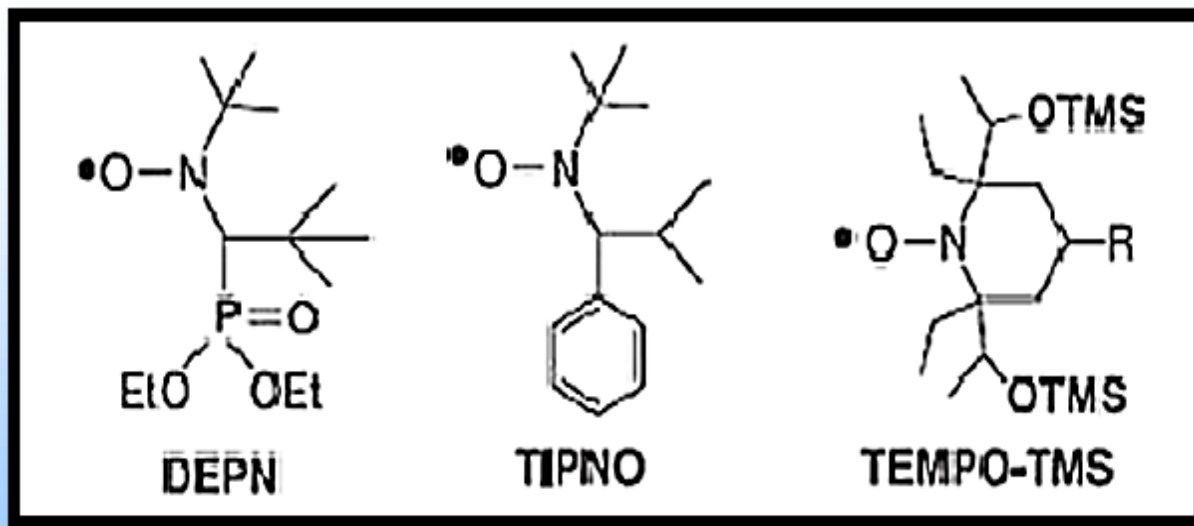
- **In order to** effectively mediate polymerization, **TEMPO** (and other stable free radicals) should react neither with itself nor with monomer to initiate the growth of new chains, and
- **it should not** participate in side reactions such as the abstraction of β -H atoms.

- **The SFRP** equilibrium constant (ratio of dissociation (**k_d**) to cross-coupling/association (**k_c**) rate constant) is generally very small.
- **The values** of **K_{eq}** are often so low that in the presence of excess TEMPO.
- **The equilibrium** become very strongly shifted towards the dormant species and significantly reduces the polymerization rate.
- **While original TEMPO**-based systems were successful at controlling the polymerization of styrene and some of its copolymers.
- **They failed** to mediate polymerization of acrylates and several other monomers for this reason.

6.2 Mediating Species/Initiation Systems

6.2.1 Nitroxides as persistent radicals:

- **TEMPO** efficiently mediates styrene polymerization under the appropriate conditions but fails to mediate polymerization of other monomers with lower equilibrium constants.
- **Other nitroxides** were synthesized in an effort to provide more labile C–O bonds. Three exemplary nitroxide structures:



- **Bulkier nitroxides** can decrease the bond dissociation energy of C–O bonds formed during polymerization.
- **Consequently** increases the proportion of radicals during a polymerization and enables lower polymerization temperatures.
- **Significant steric** bulk was introduced to a TEMPO derivative at the 2,2,6,6- substituents with trans-2,6-diethyl-2,6-bis(1-trimethylsilanoxyethyl)-1-(1-phenylethoxy) piperidine-N-oxy (TEMPO-TMS).
- **The steric effects** of this bulk so effectively decrease the bond dissociation energy of the alkoxyamine that polymerization of butyl acrylate can be successfully mediated at temperatures as low as 70°C.

- **Steric effects** actually prevent the successful control of methacrylate polymerization mediated by nitroxides.
- **Reactive nitroxides** prefer to abstract β -H atoms rather than form alkoxyamines.
- **Less reactive** nitroxides do not cross-couple rapidly enough with growing chains to efficiently control methyl methacrylate (MMA) polymerization.
- **One solution** to this problem involves copolymerizing a small amount of styrene with MMA.
- **Just 10 mol %** styrene has been sufficient to control such copolymerizations.

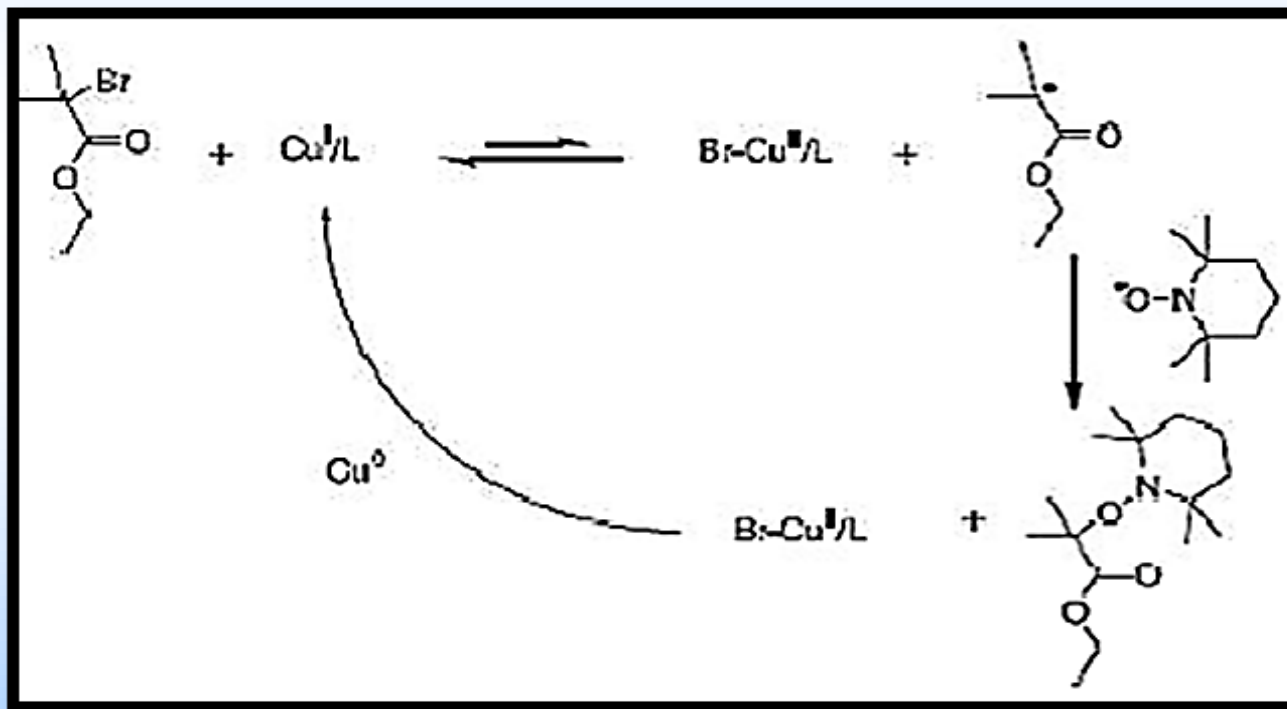
- **However**, further development of nitroxides stabilized by resonance and polar effects will be needed to achieve control in homopolymerizations of pure methacrylates.

6.2.2 Alkoxyamine unimolecular initiators:

- **SFRP** systems can be initiated in two different ways.
 1. Conventional radical initiators can be used in the presence of persistent radicals. Alternatively,
 2. Dormant species can be prepared in advance and used as unimolecular initiators or macro-initiators for block copolymerization.
- **The structure** of these species is based on the alkoxyamine functionality generated at the chain end during NMP.

- **These well-defined** unimolecular initiators permit much better control over polymer molecular weight and architecture than the aforementioned nitroxide persistent radicals used in conjunction with free radical initiators.
- **The exploitation** of alkoxyamines was originally limited by a lack of efficient synthetic procedures for their preparation.
- **Procedures** that often resulted in low yields and a wide range of byproducts.
- **However**, several versatile techniques have since been developed.
- **They** involve the controlled generation and trapping of carbon centered radicals, including single electron transfer reactions associated with ester enolates and enolate anions.

- **Another** simple method involves halogen abstraction from alkyl halides by a Cu catalyst via atom transfer radical addition, and
- **Subsequent** trapping of the alkyl radical by an excess of nitroxide persistent radical.



Scheme 8: Mechanism of the controlled generation and trapping of carbon centered radicals.