Fundamentals for Living Radical Polymerization

- The basics for living radical polymerization can be summarized as follows:

1. Fast initiation as compared to propagation since all chains should begin to grow essentially at the same time and retain functionality.

2. Fast exchange between active and dormant species, so that majority of the growing chains are in the dormant state and only a small fraction is present as propagating free radicals.

3. The propagation rate should not depend on the degree of polymerization

4. The polymerization reaction should be free of termination and transfer reactions.

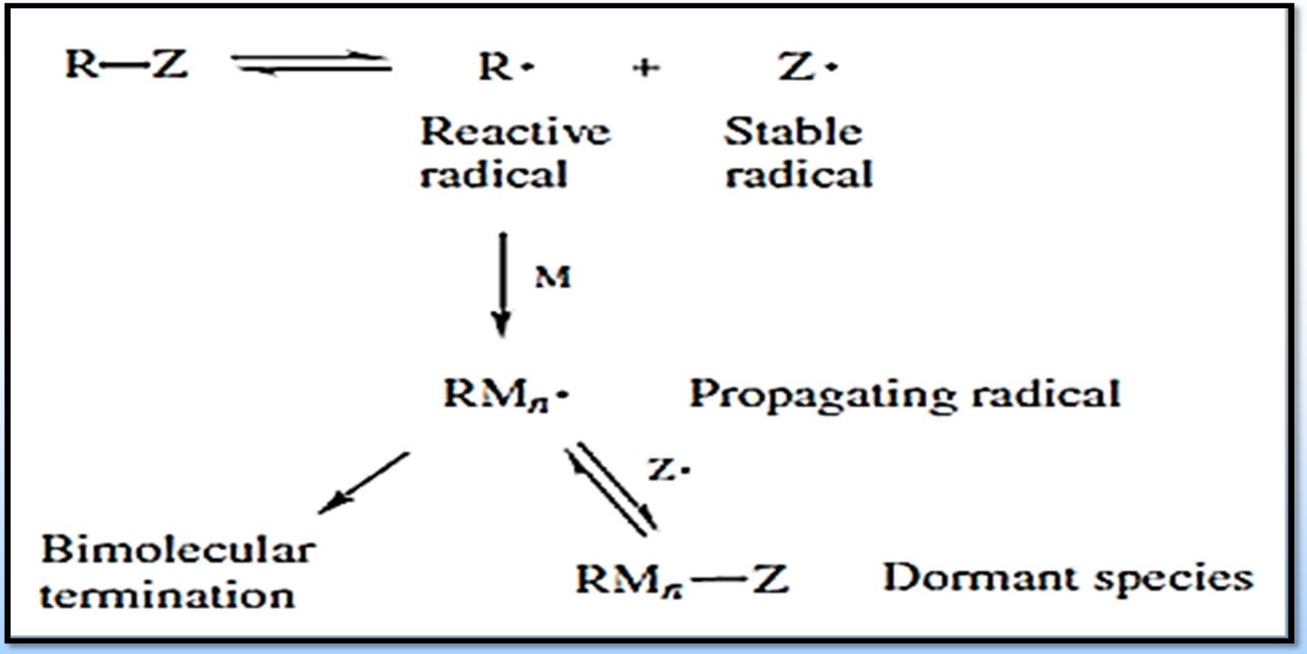
5. Concentration of the propagating radicals should be sufficiently low ([P*] < 10-7 M) to enable chain growth on one hand and reduce termination events on the other.

6. A single type of propagating species must exist; if different propagating species are present, then their inter conversion should be very fast.

7. The number average molecular weight of the polymer should have a linear relation with conversion.

4.2 Advances of LRP than conventional FRP:

- LRP and conventional FRP proceed via the same radical mechanism, exhibit similar chemo-, regio- and stereo-selectivities, and can polymerize a similar range of monomers.
- But Living radical polymerization (LRP) with reversible termination generally proceeds as shown in Scheme 3:



Scheme 3: Mechanism of Living Radical Polymerization.

- However, several important advances of LRP than conventional FRP exist as summarized below.

1. The lifetime of growing chains is extended from <1s in radical polymerization to more than 1h in controlled radical polymerization through the participation of dormant species and intermittent reversible activation.

2. Initiation is slow and free radical initiator is often left unconsumed at the end of a FRP. In most CRP systems, initiation is very fast and near instantaneous growth of all chains can be achieved, which ultimately enables control over chain architecture.

3. Nearly all chains are dead in radical polymerization, whereas in CRP the proportion of dead chains is usually

< 10 %.

4. Polymerization in CRP is often slower than in radical polymerization. However, the rates may be comparable in certain.

5. A steady state radical concentration is established in radical polymerization with similar rates of initiation and termination, whereas in CRP systems based on the persistent radical effect, a steady radical concentration is reached by balancing the rates of activation and deactivation.

6. Termination usually occurs between long chains and constantly generated new chains in radical polymerization

(Fig. 3).

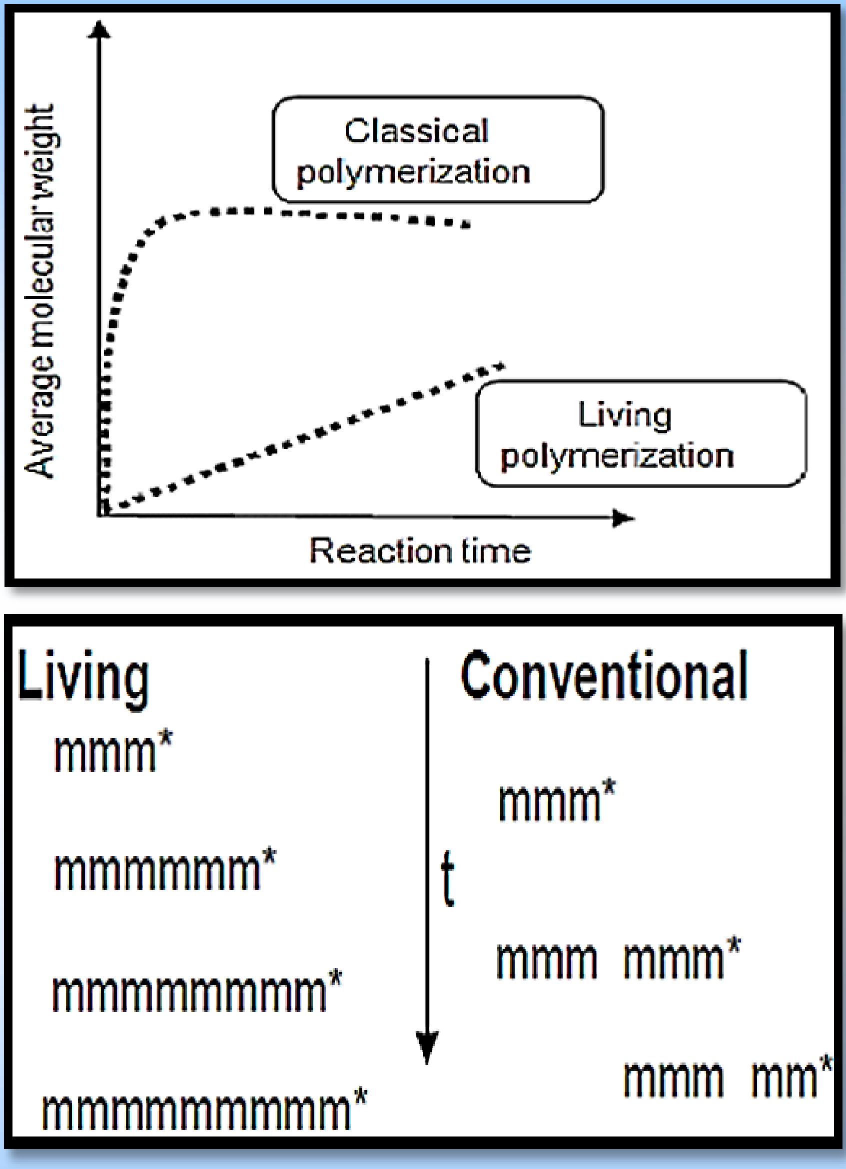


Figure 3: Living vs Conventional free radical polymerization processes.

- In CRP systems based on the persistent radical effect, all chains are short at the early stages of the reaction and become progressively longer, thus, the termination rate significantly decreases with time.

- In FRP processes, new chains are constantly generated by a small amount of conventional initiator, and therefore termination is more likely throughout the reaction.

- Accordingly, in living radical polymerization the rates of initiation, activation and deactivation are much larger than that of termination.

- The exchange between active and dormant chains also enables an extension of the lifetime of propagating chains from ~1s in FRP to >>1h in CRP. This enables synthesis of polymers with different chain topologies (e.g. block, graft).

4.3 Functionality of Living Radical Polymerization:

- Living\‘controlled’ LRP has great potential for the production of polymers of lower molecular weight, but with high degrees of functionality.

- LRP of functional monomers is initiated by functional group containing initiators and transition metal complexes.

.

- The produced polymer contains different functional groups related to monomers and functional groups at the head and tail of living radical polymers.

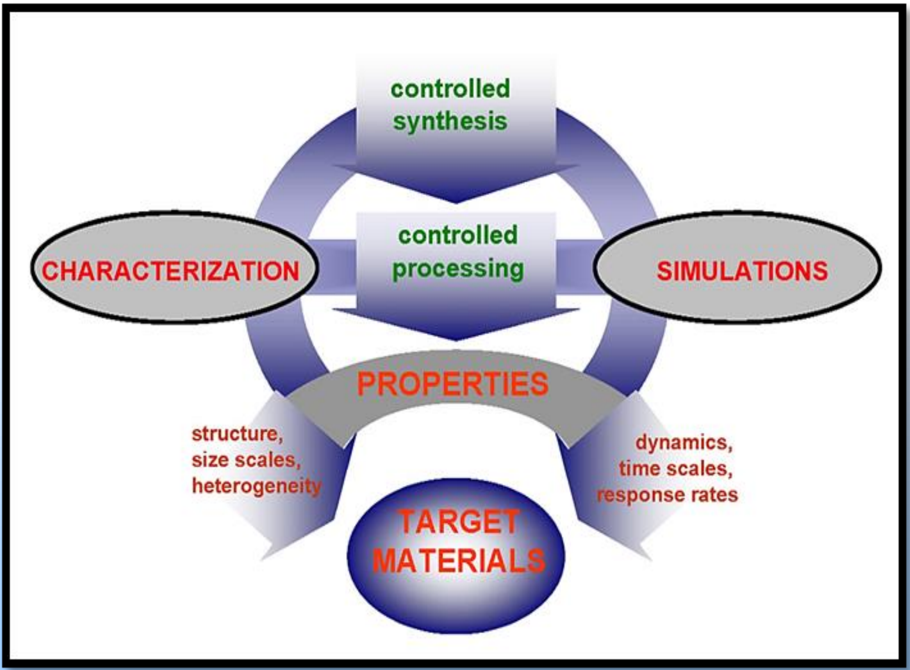
- Precise control of the end groups is readily attained in controlled radical polymerizations

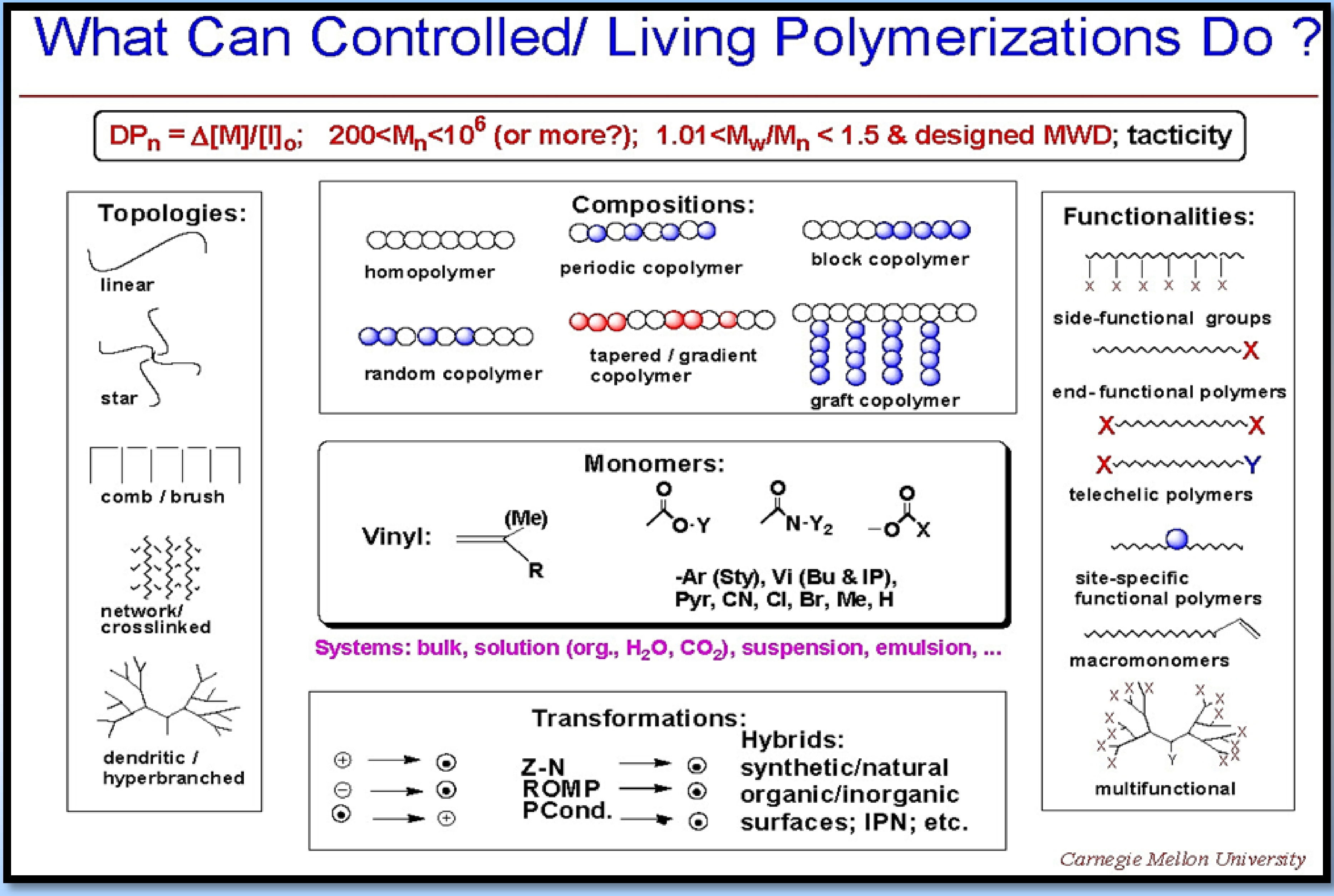
- An example is the preparation of poly(butyl acrylate) with α, ω-hydroxyl groups that can be used as a replacement for poly(ethylene glycol) in polyurethane synthesis.

- **Living “Controlled” radical polymerizations** include:
- **A**tom-**T**ransfer **R**adical **P**olymerization (**ATRP**) and
- **S**table **F**ree-**R**adical **P**olymerization (**SFRP**), which proceed with reversible termination, and
- **R**eversible **A**ddition–**F**ragmentation **T**ransfer (**RAFT**).

4.4 Development of Controlled/"Living" Radical Polymerization

- The most important development concerned with CRP is the Preparation of Functional Materials suitable for different applications.
- One of the ongoing objectives is to explore the scope of CRP for synthesis of novel materials





What Can Controlled/ Living Polymerizations Do ?

$DP_n = \Delta[M]/[I]_o$; $200<M_n<10^6$ (or more?); $1.01<M_w/M_n < 1.5$ & designed MWD; tacticity

Topologies:

- linear
- star
- comb / brush
- network/ crosslinked
- dendritic / hyperbranched

Compositions:

- homopolymer
- periodic copolymer
- block copolymer
- random copolymer
- tapered / gradient copolymer
- graft copolymer

Monomers:

Vinyl:

-Ar (Sty), Vi (Bu & IP),
Pyr, CN, Cl, Br, Me, H

Systems: bulk, solution (org., H_2O, CO_2), suspension, emulsion, ...

Transformations:

Z-N
ROMP
PCond.

Hybrids:
synthetic/natural
organic/inorganic
surfaces; IPN; etc.

Functionalities:

- side-functional groups
- end-functional polymers
- telechelic polymers
- site-specific functional polymers
- macromonomers
- multifunctional

Carnegie Mellon University

Figure 6: Simple plane for what CPR can do.

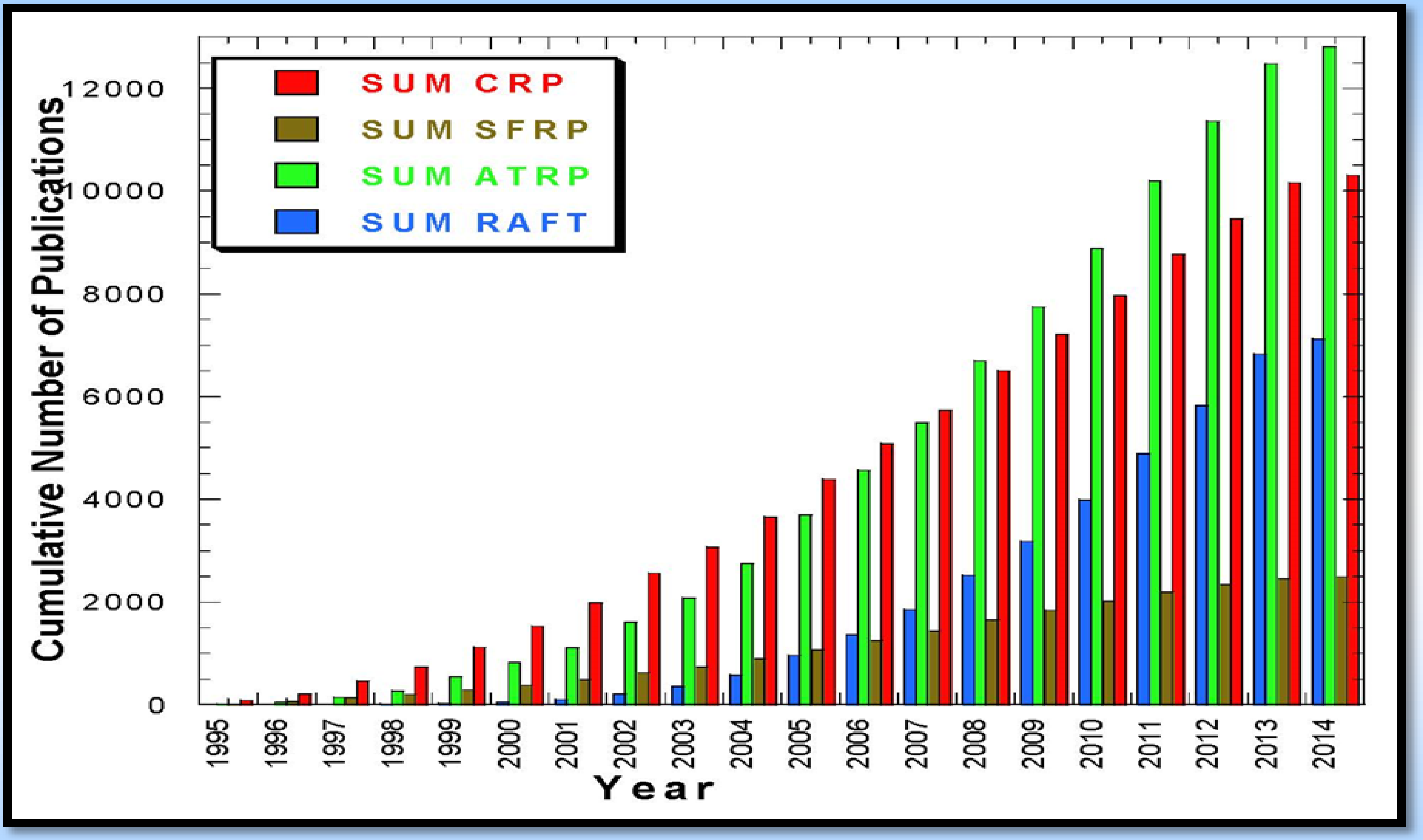


Figure 7: Controlled Radical Polymerization published paper on March 2014.

4.5 Applications of Living Radical Polymerization

- Applications discussed in the literature for materials prepared through LRP range from replacement of existing products in existing markets to novel material concepts.
- Creating new applications such as some very novel approaches to drug delivery through the synthesis of well-defined diblock copolymers by ATRP.
- The block copolymers with a short hydrophobic block (5 < DPn < 9) were explored in detail for the development of new colloidal carriers for the delivery of electro statically charged compounds (e.g., DNA).
- A similar approach has been taken in electronics manufacture where the self-organizing ability of materials prepared by living radical polymerization is being exploited.

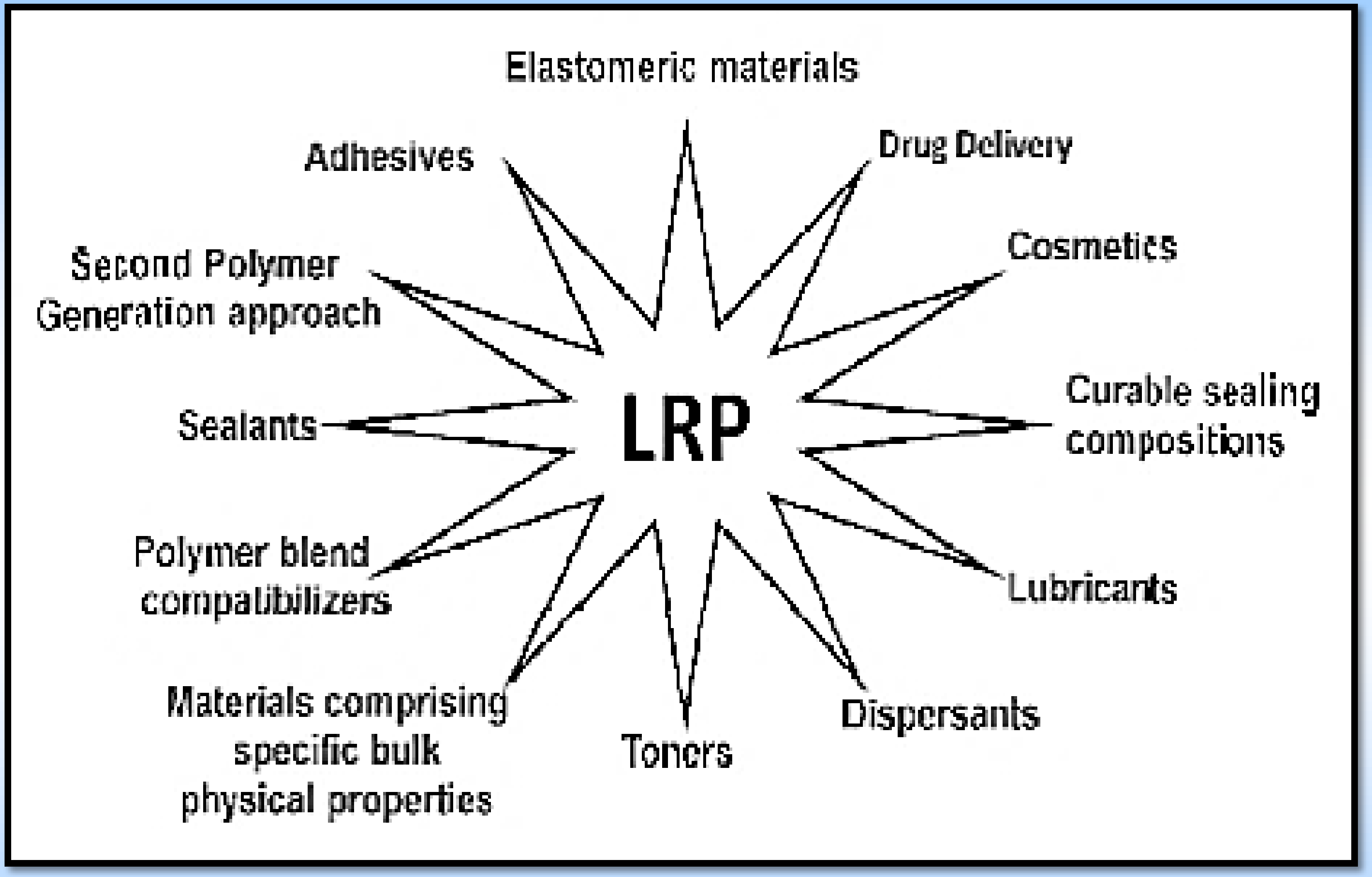
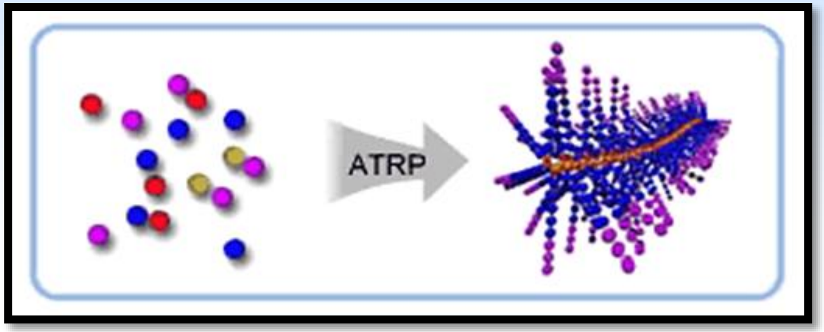


Figure 8: Applications of Living radical polymerization.

- The above applications identified by corporate research, in patents and patent applications.
- Academic workers are also disclosing some new applications.
- Although this has been but a brief review of novel materials prepared using CRP.
- One can easily see that, regardless of the type of CRP employed, these methodologies open the door to a wide range of novel polymers with unique properties.
- Indeed control over polymer sequence distributions continuously expanding and recently multi-block heteropolymer chains with up to 100 blocks in an ordered sequence and controllable block lengths have been reported.
- CRP is among the most rapidly developing areas of chemistry, with the number of publications approximately doubling each year.

5. Atom Transfer Radical Polymerization

- In 1995, two research groups independently reported a similar CRP technique, the Atom Transfer Radical Polymerization (ATRP).



- They were based on catalytic systems used for the atom transfer radical addition reaction (ATRA), or the well-known Kharasch reaction, an efficient method of forming carbon- carbon bonds between organic halides and alkenes.

- The first report by Sawamoto et al., uses $RuCl_2(PPh_3)_3/Al(O\text{-}iPr)_3$ as a catalyst system in the polymerization of MMA initiated by CCl_4.

- The second system reported by Matyjaszewski, et al., is the polymerization of styrene catalyzed by CuCl/2,2’-bipyridyl (bpy) in the presence of 1-phenylethyl chloride as an initiator.

- Since these first reports, there have been many reports on **ATRP** of styrene, acrylates, methacrylates, and acrylonitrile by using various transition metal complexes, including nickel, iron, palladium, and rhodium.

- Compared to other controlled radical polymerization methods, **ATRP** is considered as a very multipurpose method.

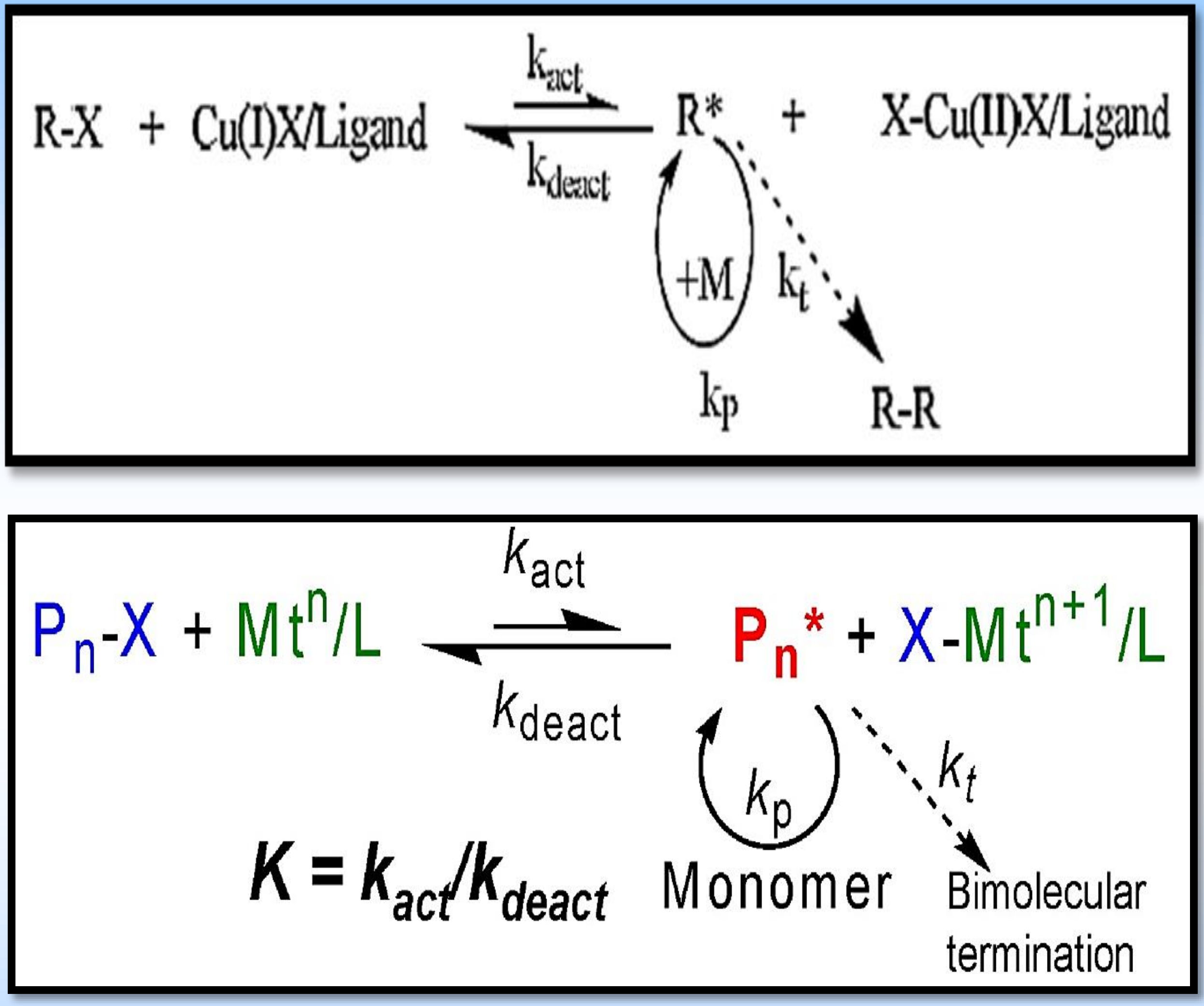
- This method provides control in the polymerization of many different monomers under various reaction conditions.

- It makes possibility to prepare polymers having a wide range of architectures including blocks, grafts, gradient copolymers, stars, combs, branched, and hyper-branched.

- The name **ATRP** comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of polymeric chains.

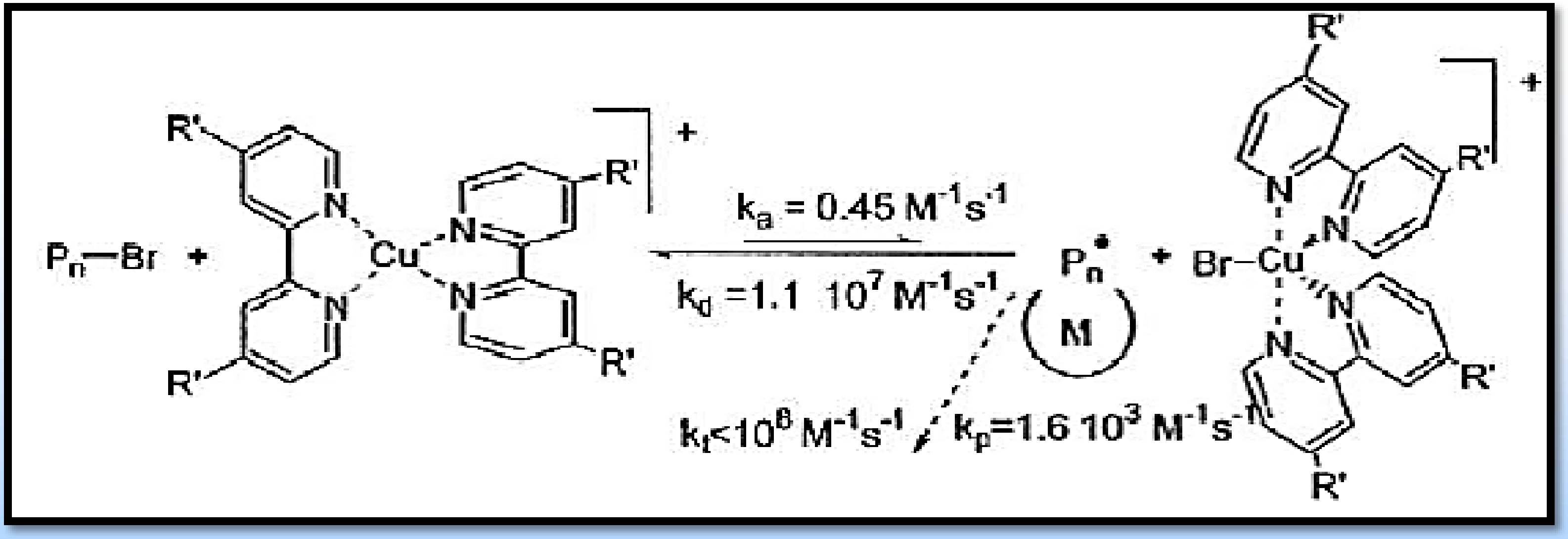
- **ATRP** originates in atom transfer radical addition (ATRA) reactions, which target the formation of 1:1 adducts of alkyl halides and alkenes, which are catalyzed by transition metal complexes.
- The effects of inhibitors and retarders, solvents, and chain transfer agents are the same in **ATRP** as in conventional radical polymerization.

- The concentration of propagating radicals in **ATRP** is obtained as:



Scheme 4: Simplified ATRP Mechanism.

- ATRP is based on the reversible transfer of halogen atoms, or pseudo-halogens, between a dormant species (Pn–X) and a transition metal catalyst (Mnt/L) by redox chemistry.
- In the most studied system, the role of the activator is played by a copper (I) species complexed by two bipyridine ligands and the role of deactivator by the corresponding copper (II) species.



Scheme 5: Values of the rate constant for activation (ka), deactivation (kd), propagation (kp) and termination (kt) for a bulk styrene polymerization at 110°C.

- A successful **ATRP** requires fast and quantitative initiation so that:

  (a) all propagating species begin growth at the same time,

  (b) which results in a narrow molecular weight distribution.

- Rapid reversible deactivation of propagating radicals is needed to maintain:

  (a) low radical concentrations, **and**

  (b) minimize normal termination of living polymers.