5.1 Incorporation of Functional Groups into Polymers (Polymers with Specific Architectures)

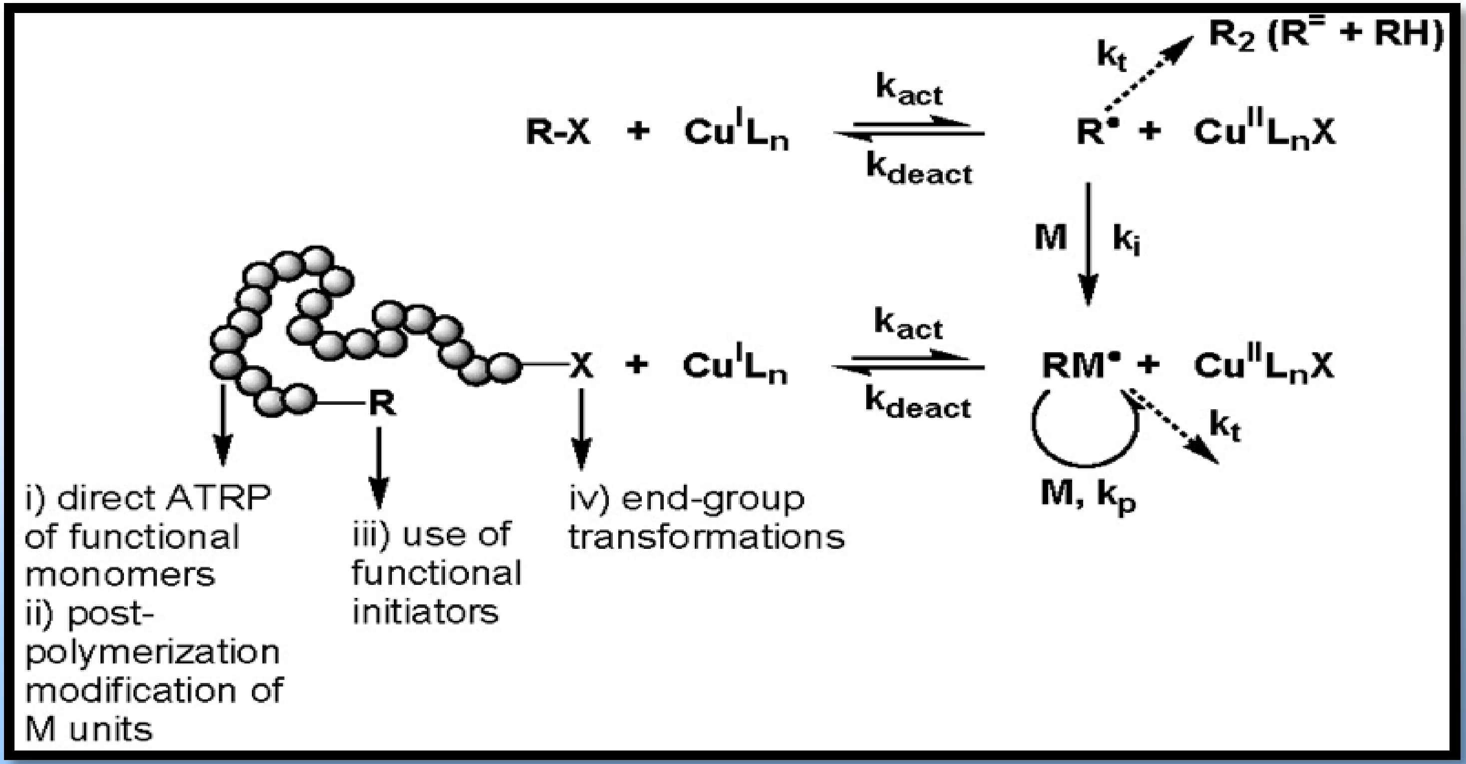
- Functional groups increase the utility of polymers and are fundamental to the development of many aspects of structure-property relationships.

- The functionality present on the monomer units determines the solubility of the polymer in a given solvent.

- One can control the hydrophilicity/phobicity or polarity of a copolymer, and the elasticity or modulus of a material by selecting appropriate monomers.

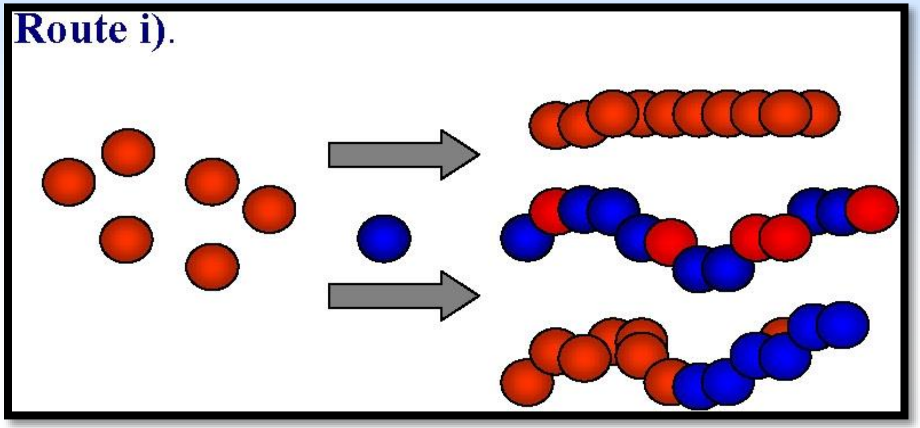
- End functionalized polymers are used for blend compatibilization during reactive processing and in many thermosetting compositions.

- For example, epoxy-functional polymers and functional materials form the basis of the majority of products prepared for dispersant, coating, adhesive, and sealant, etc. applications.
- Four synthetic strategies can be employed for the synthesis of well-defined polymers with site specific functional groups using **ATRP**. They are:



Scheme 6: The four synthetic strategies used

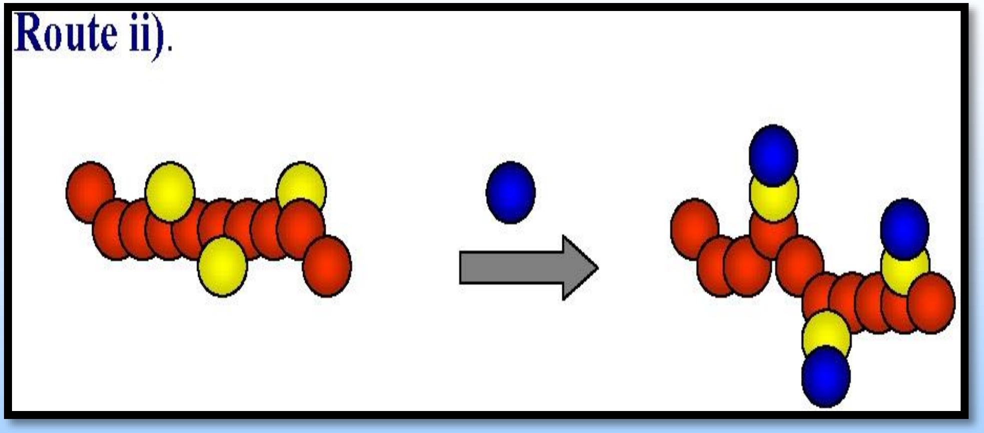
- An obvious approach to functional materials is the direct polymerization, or copolymerization of a monomer containing the desired functionality by the following routes:



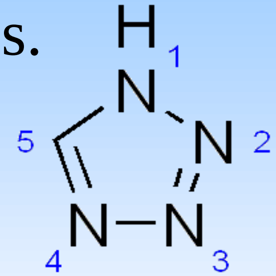
- **ATRP** is generally tolerant of various functional polar groups.

- This route has been successfully used in many instances to form homopolymers, in addition to random or gradient copolymers with controlled distribution of functional monomer units along the backbone, or in specific segments of block copolymers.

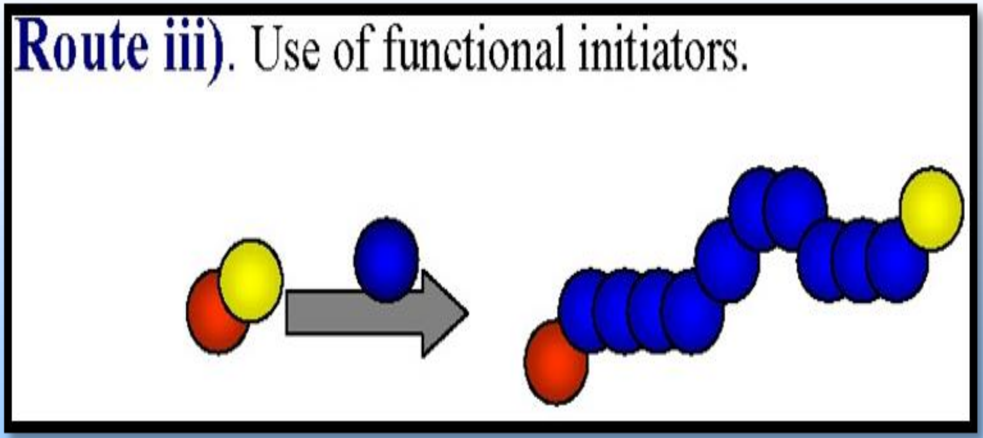
- Some limitation is being addressed especially when strongly coordinating basic, nucleophilic or acidic monomers are used.
- The monomers can react with either the **ATRP** catalyst (leading to its partial or complete deactivation) or with either the alkyl halide-type initiator or dormant polymeric species killing the active chain ends.
- The current synthetic strategy of choice in these cases is to use monomers with "protected" groups that can be transformed into the desired functionality after the polymerization:

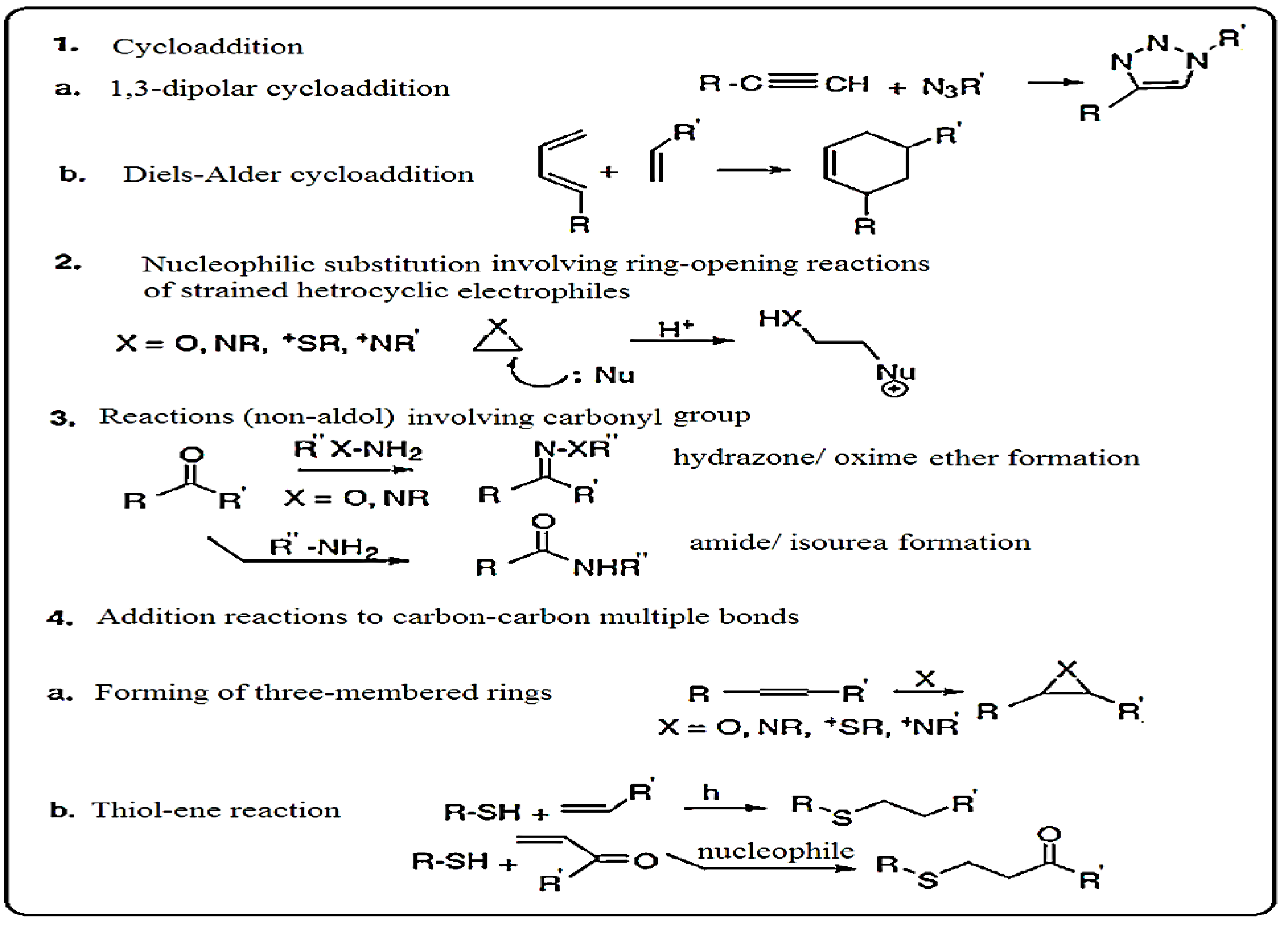


- This approach has been illustrated by the preparation of well-defined polymers with distributed Tetrazole groups.



- Indeed "Click" chemistry-type post-polymerization modifications have been used to introduce various functional groups into polymers prepared by **ATRP**.
- The most obvious way to incorporate a single functionality at the polymer chain end is the use of functional initiators.





1. Cycloaddition

a. 1,3-dipolar cycloaddition

b. Diels-Alder cycloaddition

2. Nucleophilic substitution involving ring-opening reactions of strained hetrocyclic electrophiles

3. Reactions (non-aldol) involving carbonyl group

hydrazone/ oxime ether formation

amide/ isourea formation

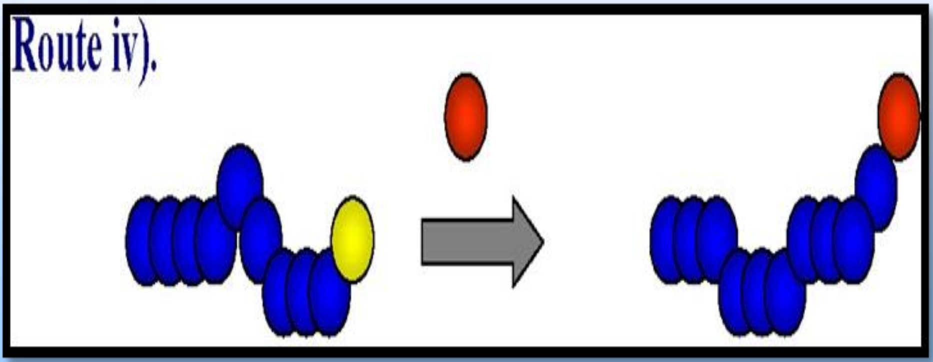
4. Addition reactions to carbon-carbon multiple bonds

a. Forming of three-membered rings

b. Thiol-ene reaction

Scheme (1.5): Categories of click reactions, Dr. Baqer Thesis

- This approach can be used to prepare either homo- or hetero-telechelic polymers.
- Use of a mono-functional initiator with desired functionality leads to direct α-functionalization of the polymer and no post-polymerization modification is required.
- In the vast majority of **ATRP** reactions the active, or growing, polymer chains are halogen-terminated, and can be further used as macroinitiators in chain-extension reactions.
- Or the initial functionality can be viewed as precursors of ω-end-functionalized polymers through end group transformations, route iv).



5.2 Other Functional Monomers Successfully Polymerized by ATRP

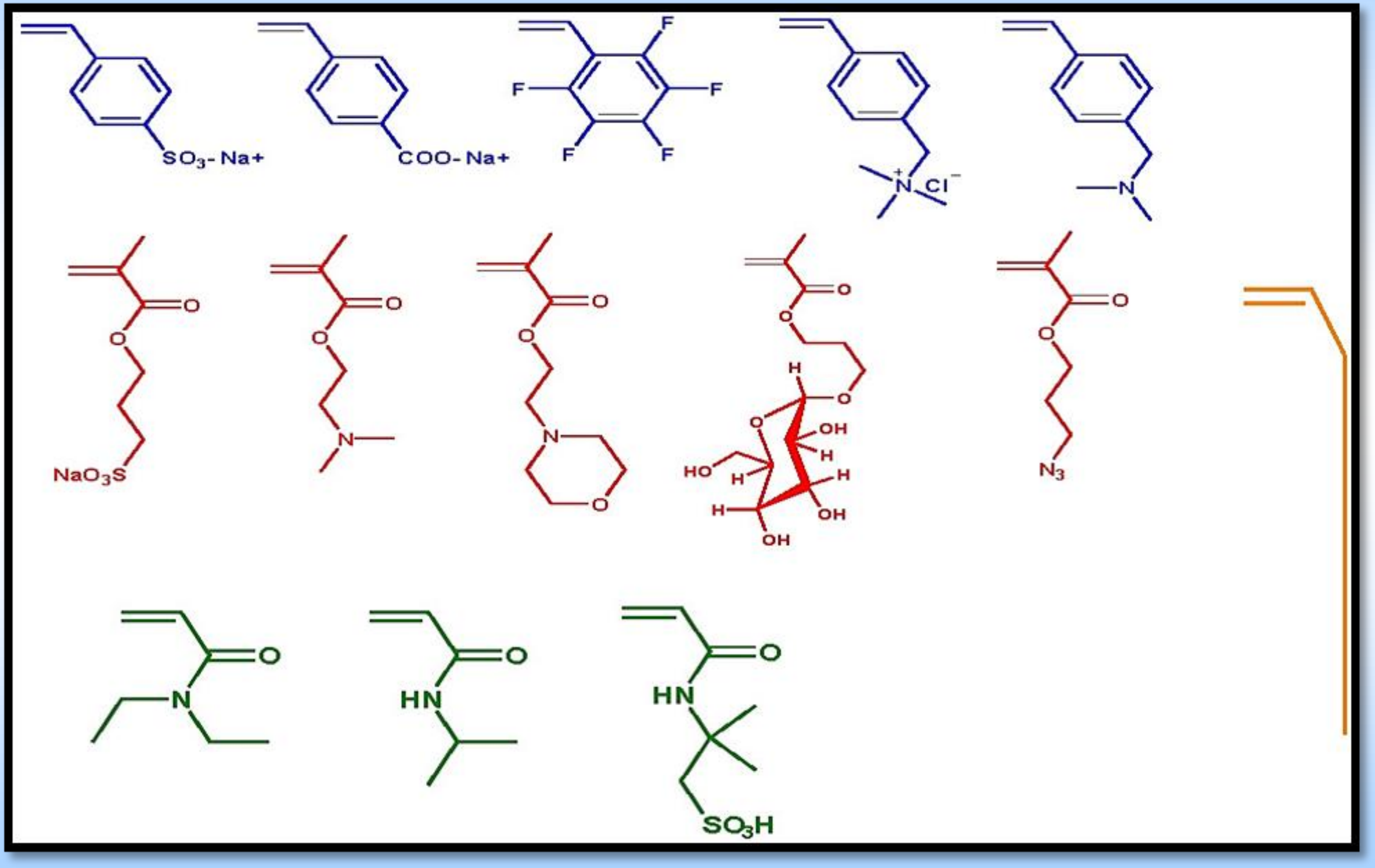


Figure 10: Different monomers polymerized by ATRP

5.3 Components of Atom Transfer Radical Polymerization

- As a multicomponent system, **ATRP** is composed of the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand).
- Sometimes an additive is used. For a successful **ATRP**, other factors, such as solvent and temperature must also be taken into consideration.

5.3.1 Monomers:

- Monomers often have a major effect on the ATRP reaction, several variables can account for the influence of the used monomer, including:

1. The solubility parameters of the monomer and the effects in the copper-complex formation will affect the polymerization in a similar way as the solvent does.

2. The kp of the monomer will affect the polymerization rate.

3. Each monomer used in a polymerization will result in an alkyl halide with a specific redox potential.

4. Some halide containing polymer end-groups can have, beside halogen atom exchange, specific interactions with the copper species present in the reaction.

- Each monomer has its own equilibrium constant (Keq = kact/kdeact) for active and dormant species in **ATRP** even with the same catalyst and conditions.

- The product of kp and Keq determines the polymerization rate.

- Thus, the polymerization will occur very slowly if Keq is too small.

- This could be the plausible reason why polymerization of less reactive monomers like olefins, halogenated alkenes and vinyl acetate are not yet successful.

- Because of this reason, optimal conditions for **ATRP** such as the catalyst type, ligand, solvent, temperature and additives are to be chosen carefully for each monomer.

5.3.2 Initiators:

- In ATRP, alkyl halides (**RX**) are typically used as initiators. Initiation should be fast and quantitative.
- The structure of the **R** group and halide atom **X** must be carefully selected depending on the monomer and catalyst/ligand employed.
- An effective control over the molecular weight and polydispersity index in **ATRP** is achieved if the contribution of side-reactions is low, the initiation rate exceeds, or at least equals, the observed propagation rate and if the initiation is quantitative.
- Many factors can influence the initiation rate, including:

1. The bond strength of the carbon-halide bond:

   The bond strength of R-Cl > R-Br, thus lowering the **ka** of R-Cl.

2. The stability of the formed radicals:

   The stability R* will generally increase with the number of alkyl side-groups on the radical center.

3. The possible formation of anions:

   When the initiators form very electron deficient radicals, outer sphere electron transfer could occur during activation, leading to radical anions susceptible for side reactions.

- Polyhalogenated compounds are established initiators for the use in **ATRP**, i.e. The alky halides used as initiators can contain one or more halogen atoms.

$$M_n = \frac{[M]_o}{[RX]_o} \times \text{Conversion of monomer} \times \text{Molecular weight of Monomer (M)} \quad (1.3)$$

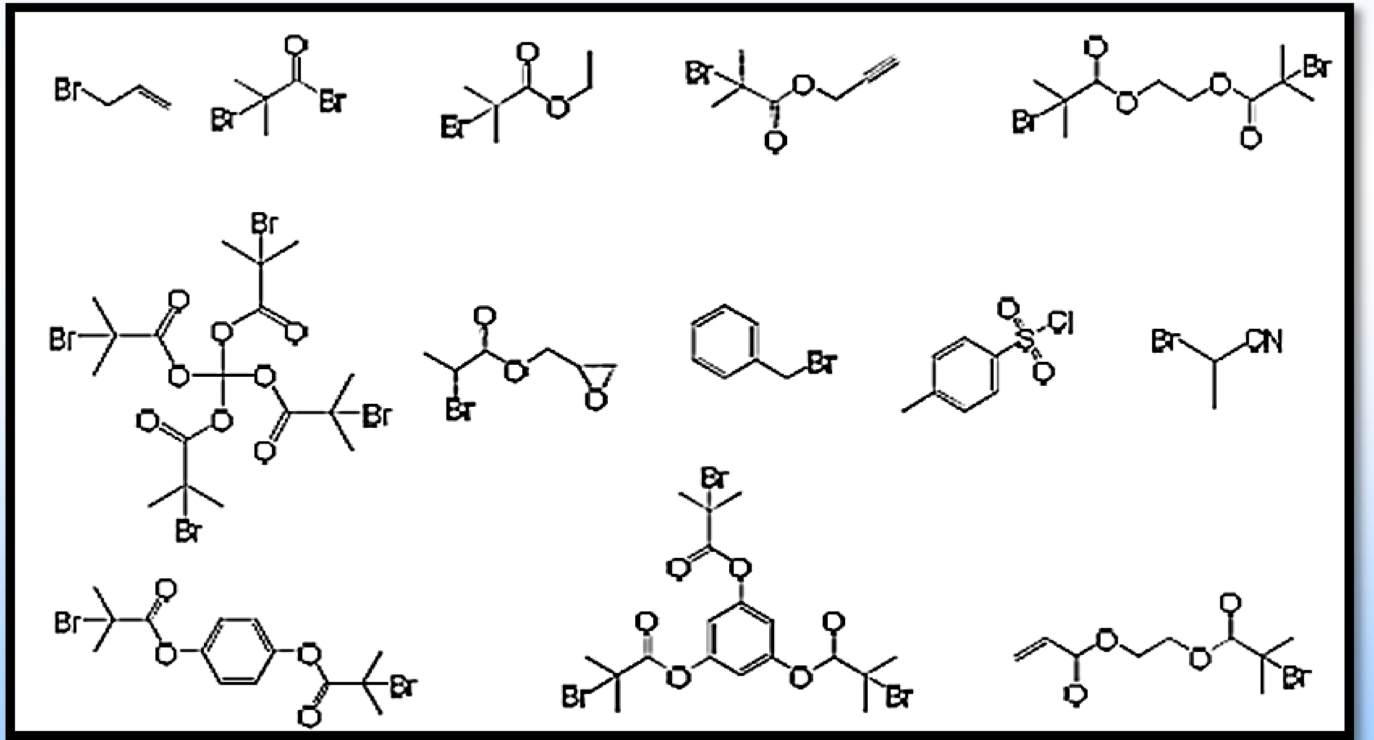


Figure 11: Examples of ATRP initiators

- The alkyl halides used as initiators may also contain various functional groups.

- The main advantages of using functional initiators in the synthesis of polymers via **ATRP** are the following:

1. Direct functionalization.
2. No post-polymerization modification required.
3. Yields telechelic polymers.
4. Multiple applicable functionalities (more than those attainable via nucleophilic substitution of end halogen atom).

5.3.3 Catalyst:

- One of the most important components of **ATRP** is the transition-metal complex, i.e. catalyst.
- It is the key to **ATRP** since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species.
- The role of the transition metals (such as $\mathbf{Cu}^{1+}$) is to abstract halogen atoms from the halogen-terminated inactive polymer chains and is oxidized to $\mathbf{Cu}^{2+}$ via a single electron transfer to generate a growing radical species.
- There also appears to be slow termination reactions of $\mathbf{Cu}^{2+}$ with both the propagating radicals and polymeric halide.

- Many transition-metal complexes used as catalysts for **ATRP**.

- Mostly used catalysts in **ATRP** are transition metal catalysts based on copper, nickel, iron and ruthenium.

- The prerequisites for an efficient catalyst are:

1. Two readily available oxidation states separated by one electron,

2. Reasonable affinity towards a halogen atom

3. Relatively strong complexation with ligand, and

4. An expandable coordination sphere to accommodate a (pseudo) halogen.

- The key to achieve the desired atom transfer equilibrium and the rate of exchange between dormant and active species is the appropriate choice of the catalyst/ligand combination.

- Some important prerequisites for a suitable catalyst are that the metal center should have reasonable affinity towards a halogen.

- and the coordinating sphere around the metal should be expandable on oxidation to selectively accommodate the halide.

- The ligand,
- **should** strongly complex with the catalyst,
- **solubilize** the transition metal salt and
- **adjust** the redox potential of the metal center forming the complex.

- Various transition metals have been studied for the **ATRP** reactions.

- for acrylates, copper(I) bromide was employed, and
- for the methacrylate reactions, copper(I) chloride was used.

- There are several guidelines for an efficient **ATRP** catalyst:

1. Fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously.
2. The equilibrium between the alkyl halide and the transition metal is strongly shifted toward the dormant species side. As a result, the contribution of radical termination reactions to the overall polymerization is minimized.
3. Fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate.
4. Relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate.

5.3.4 Ligand:

- Ligand plays a crucial role in **ATRP** by controlling the solubility of the complex in the reaction mixture.
- It adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer.
- It ensures stability of the complex in different monomers, solvents and temperatures.
- They can fine tune the selectivity’s and force the complex to participate in a one-electron transfer process needed for **ATRP**.

- Various ligands based on nitrogen and phosphorous have been used in **ATRP**.
- Nitrogen based ligands have been particularly successful in copper and iron mediated **ATRP.**
- whereas phosphorous, sulfur, oxygen based ligands have been less effective.
- To go to the higher conversion, one needs to have more deactivator present to completely minimize normal termination, but these results in slower polymerization rates.

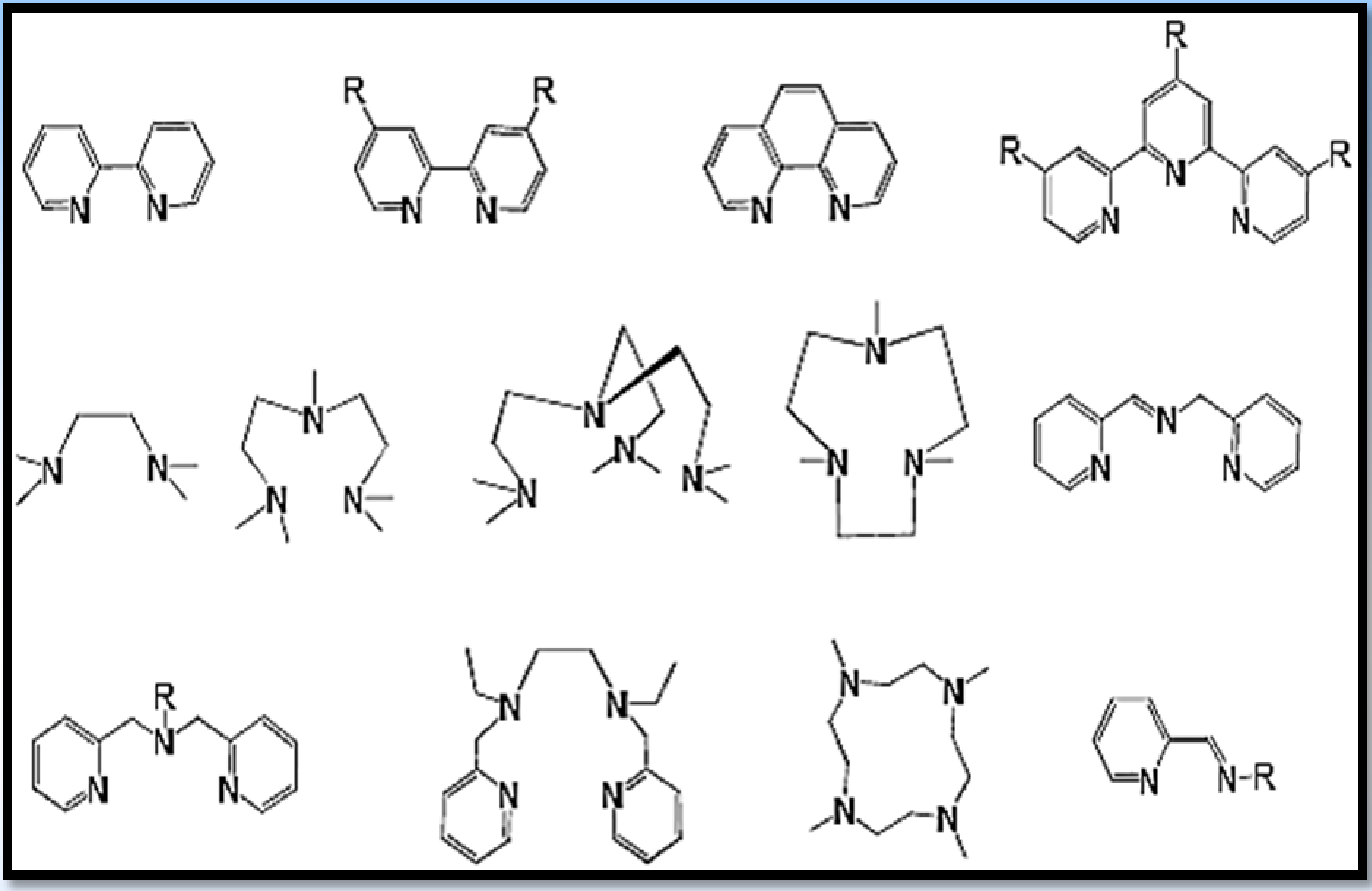


Figure 12: Nitrogen Based Ligands Used for **ATRP.**

- Another important consideration in choosing the ligand is the possible side reactions such as the reaction of amines (especially aliphatic) and phosphines with alkyl halides.

- These side reactions are reduced when tertiary amines are used as ligands and minimum when the ligands are complexed to CuBr.

- Phosphorous ligands have been used in **ATRP** in conjunction with most transition metals such as ruthenium, rhodium, rhenium, nickel, iron and palladium.

- Amongst the phosphorous based ligands (mostly PR3 type), phosphines display a high catalytic activity and good control of the polymerization.

- Recently, cyclopentadienyl, indenyl and 4-isopropyl toluene type ligands were used in ruthenium based ATRP.
- These ligands result in more reactive catalysts than the ones obtained with phosphorous.
- Oxygen based ligands such as phenols and carboxylic acids have also been considered as ligands in **ATRP**.

5.3.5 Solvents:

- The choice of the solvent is as important, since there is a possibility that the structure of the catalyst complex may change in different solvents.

- Which in turn directly influences the atom transfer equilibrium and the polymerization reaction rate.

- Polar solvents are known to improve the solubility of the catalyst complex.

- However, styrene or acrylate monomers are inefficient as the first monomer to form those block copolymers.

- Different solvents (benzene, toluene, xylene, diphenyl ether, ethyl acetate, DMF, ethylene carbonate, alcohol, water, and others) have been used for various monomers.

- Several factors affect the solvent choice.

1. Minimal chain transfer to solvent is one of the basic requirements for selecting a solvent.
2. In addition, interactions between solvent and the catalyst or other components in the **ATRP** system should be considered.
3. Catalyst poisoning by the solvent (e.g. carboxylic acids or phosphines in copper-based **ATRP**, and
4. Solvent-assisted side reactions, which are more pronounced in a polar solvent should be minimized.

5.3.6 Reaction temperature and reaction time:

- In general increasing the temperature in an **ATRP** accelerates the polymerization.
- This is due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant.
- Furthermore, the solubility of the catalyst increases at higher temperatures.
- However, at high temperature the chain transfer and other side reactions such as catalyst decomposition become more pronounced.
- Thus, the optimal temperature for the reaction should be pre-determined based on the particular ATRP system (monomer, catalyst and targeted molecular weight).

- The range of useful reaction temperatures is broad, from 20°C to 150°C.
- At high monomer conversions, the rate of propagation slows down considerably;
- However, the rate of side reactions does not change significantly, as most of them are monomer concentration independent.
- To avoid end group loss, it is suggested that the conversion should not exceed 95%.

5.4 How to Conduct an ATRP

- ATRP can be conducted in bulk, solution or a variety of heterogeneous media including:

  microemulsion, miniemulsion, emulsion, suspension, dispersion and inverse miniemulsion.

- The choice of media primarily depends on solubility issues or heat transfer considerations.

- For example, conditions have to be selected so that the catalyst complex and the product are at least partially soluble in the reaction medium.

- A solvent is required for the polymerization of acrylonitrile since the polymer is not soluble in the monomer, and

- for a room temperature polymerization of a high Tg polymer to avoid verification at high conversion.

- Redox Potential of Copper Complexes for copper based catalysts have been developed for an **ATRP** and it covers a range of seven orders of magnitude.

- Obviously, one cannot select any ligand to form a catalyst complex and assume that the formed catalyst complex is suitable for polymerization of any monomer under any set of conditions.

- A number of starting points that have worked in the literature covering preparation of a range of copolymers using ATRP are provided.

- The conditions posted to provide well defined polymers, but if the run does not go as expected;

- You can/should make adjustments; e.g. add some Cu(II), change the temperature, purge the reaction mix better, add some reducing agent, etc...

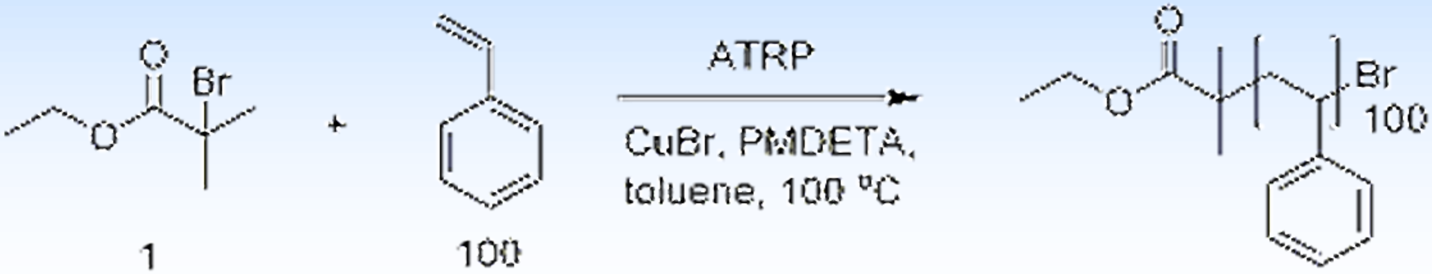
5.4.1Things to Consider Before Conducting an ATRP

- In many of the examples reported in the literature dealing with the preparation of copolymers using ATRP.

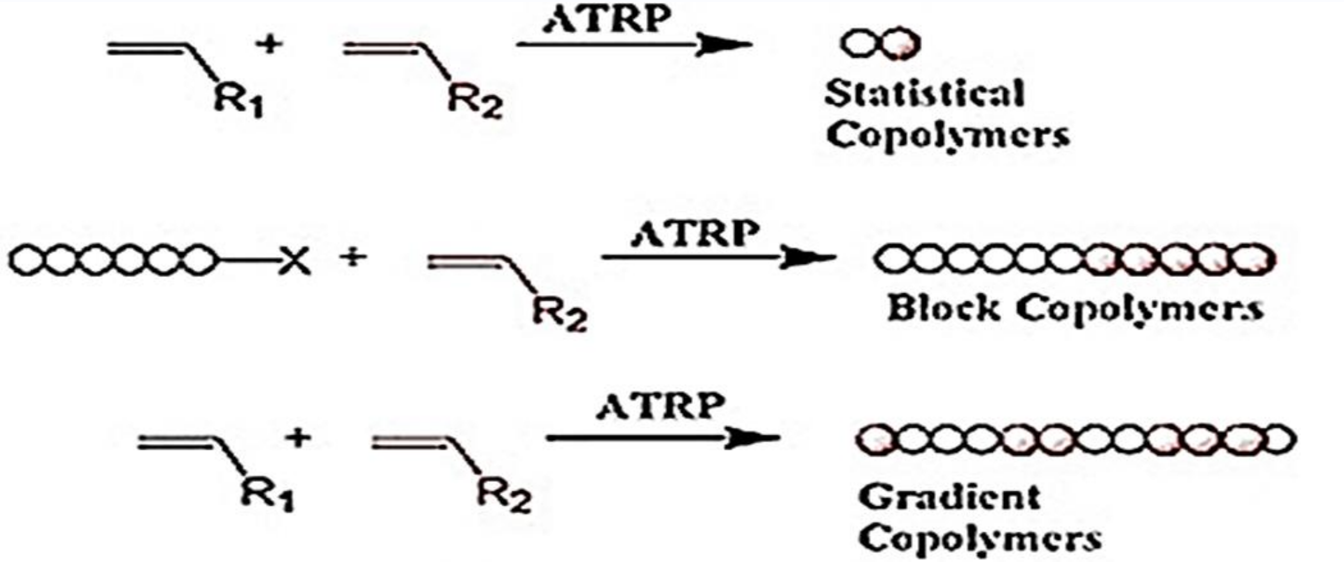
- The monomers and other components of the reaction medium have been subjected to rigorous purification.

- ATRP Examples

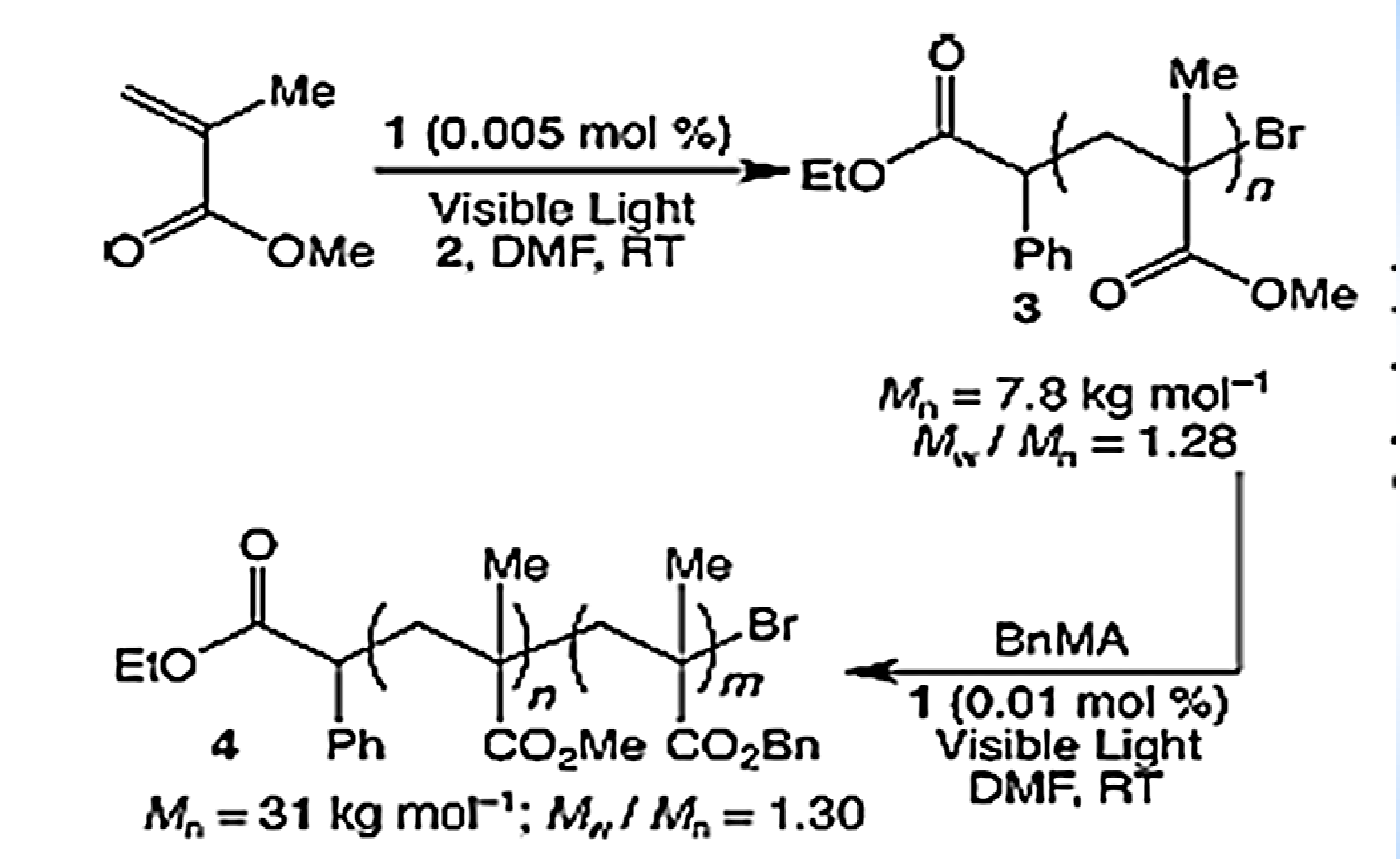
1. ATRP of Styrene



2. ATRP Copolymerization



3. ATRP of A-B Block copolymer



4. ATRP of A-B Block copolymer

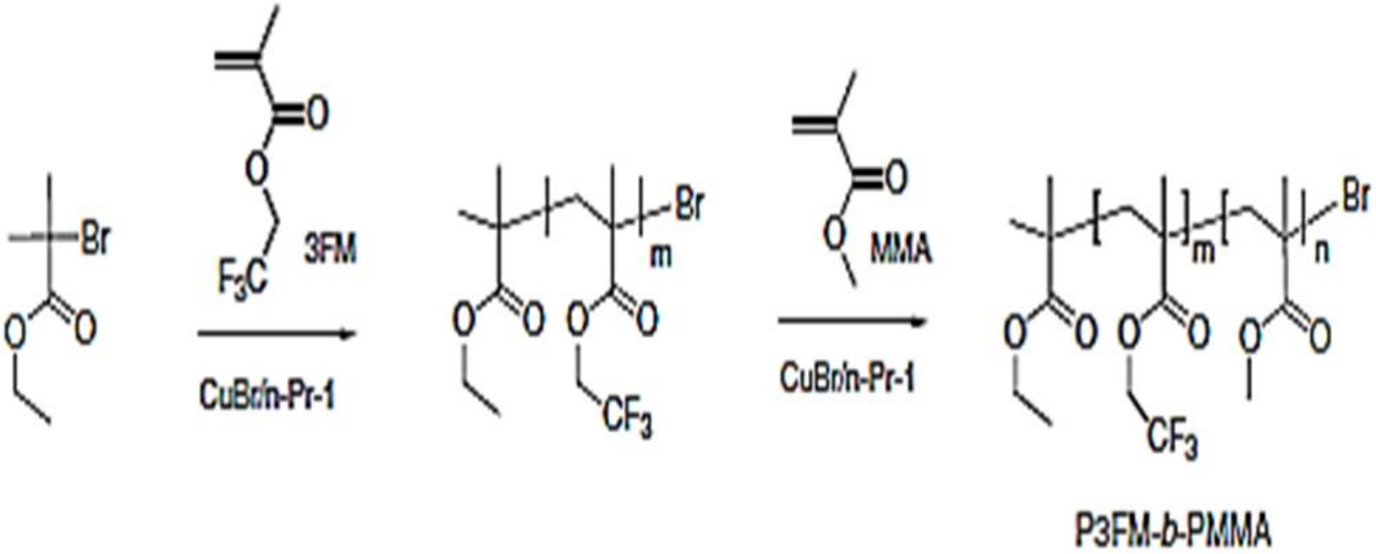


Figure 5.2. Synthesis of block copolymers of 3FM and MMA.

5. ATRP of Triblock copolymer

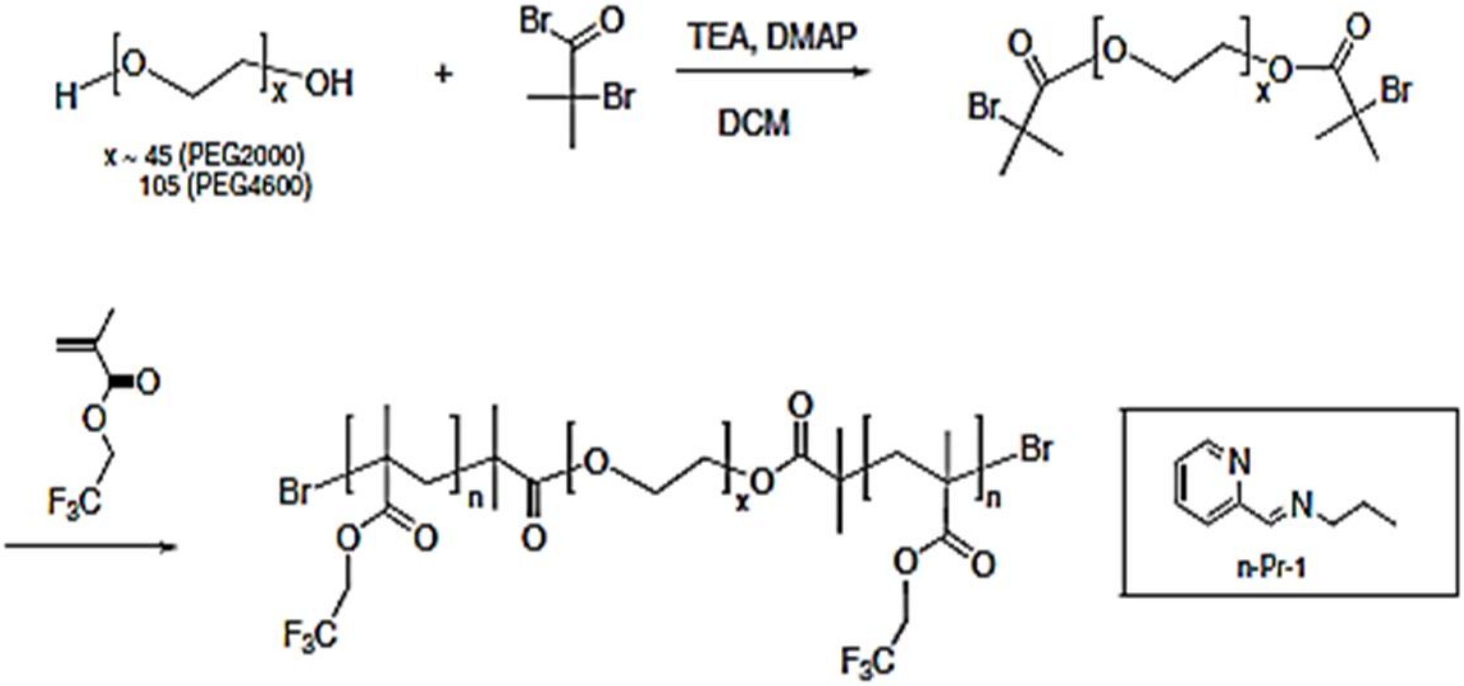
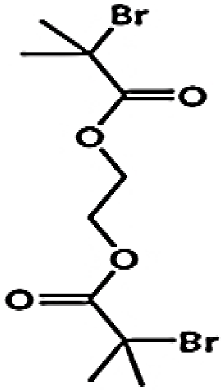
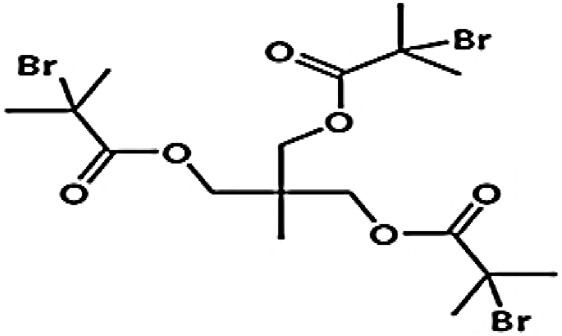


Figure 3.5. Synthesis of triblock copolymers of fluorinated methacrylate 3FM with poly(ethylene glycol) macroinitiators. DCM: dichlormethane, DMAP: 4-dimethylaminopyridine, TEA: triethylamine. Inset: n-Pr-1 ligand.

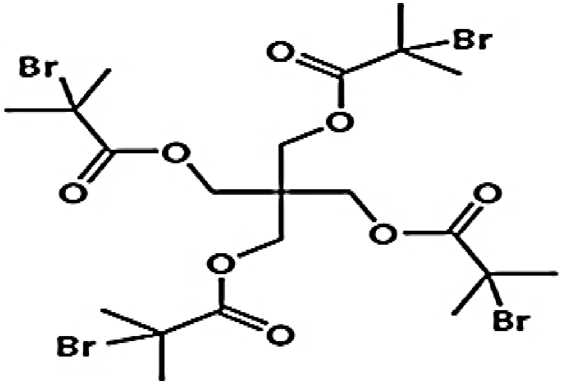
6. Functional initiators for ATRP



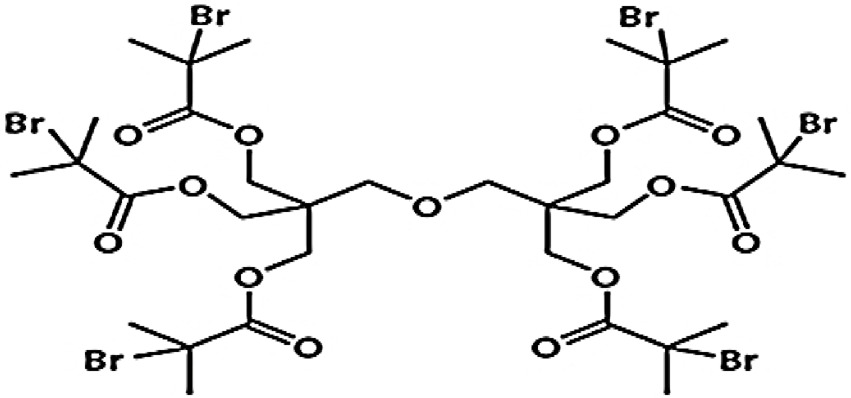
Difunctional initiator
Aldrich Prod. No. 723177



Trifunctional initiator
Aldrich Prod. No. 723185



Tetrafunctional initiator
Aldrich Prod. No. 723193



Hexafunctional initiator
Aldrich Prod. No. 723207

7. Synthesis of ATRP macrointiators

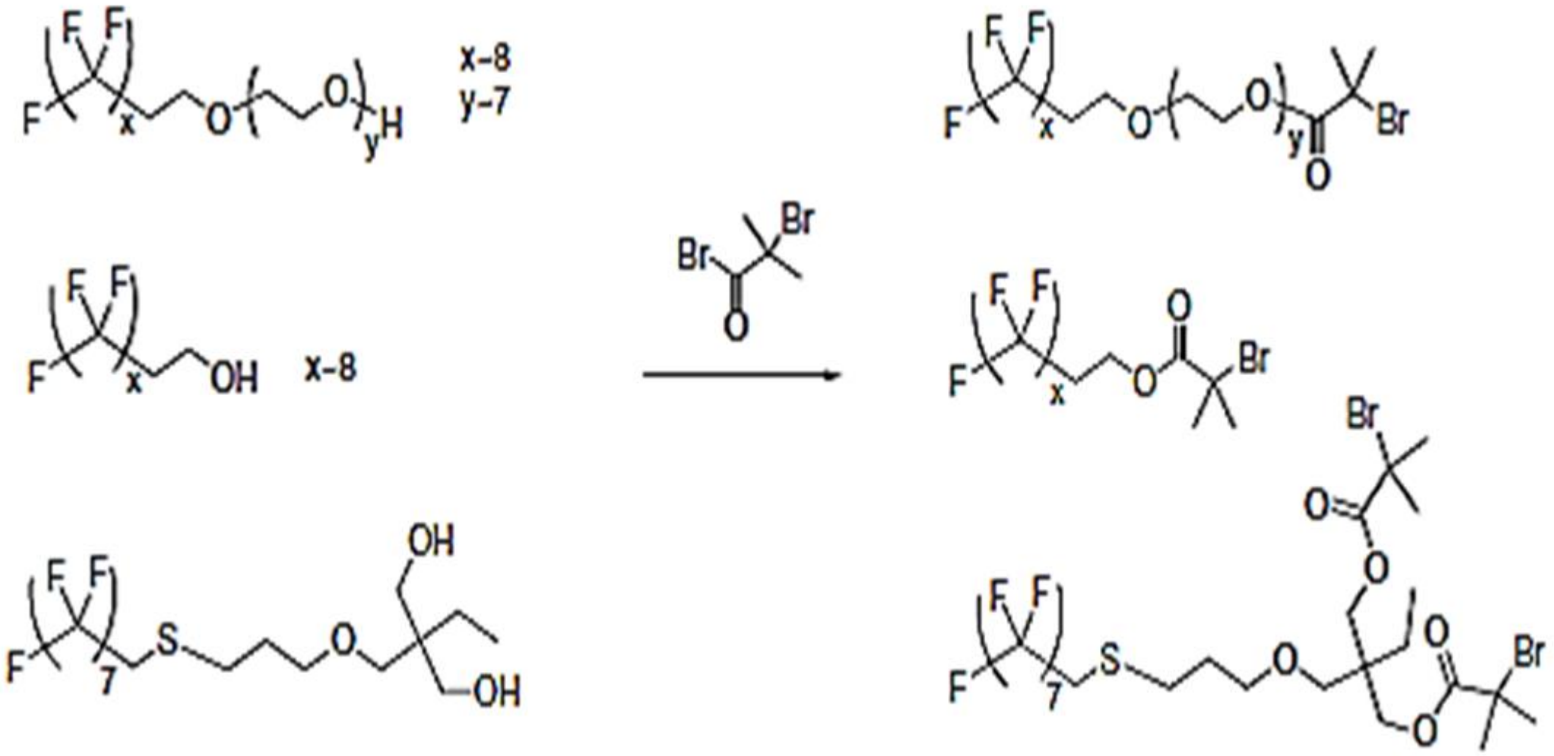


Figure 6.1. Synthesis of fluorinated macroinitiators by transesterification with 2-bromoisobutyryl bromide performed by Perrier *et al.* [20].

8. Synthesis of ATRP macrointiators

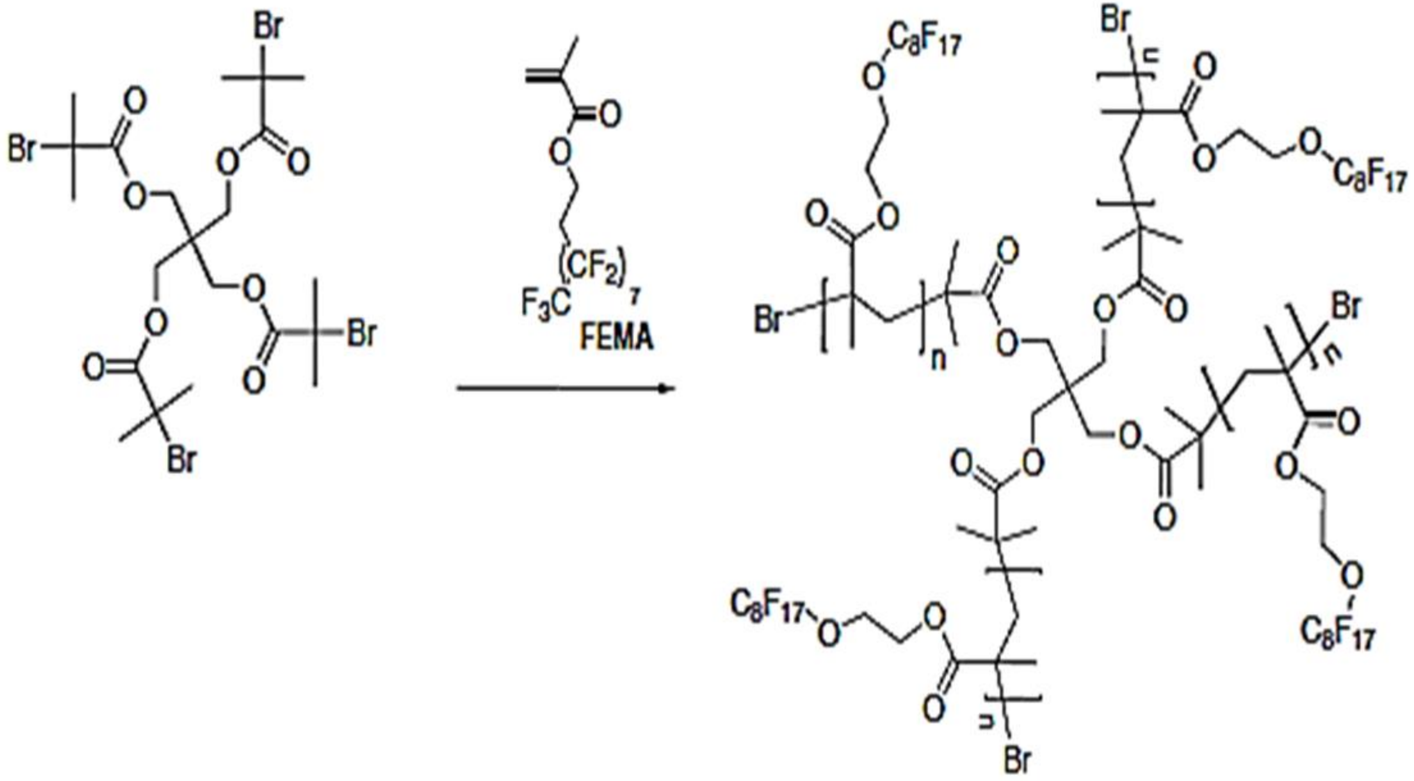
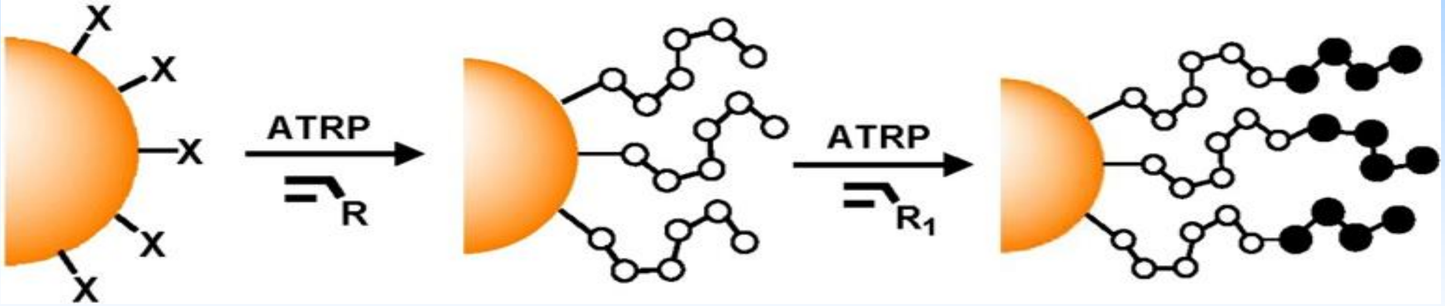
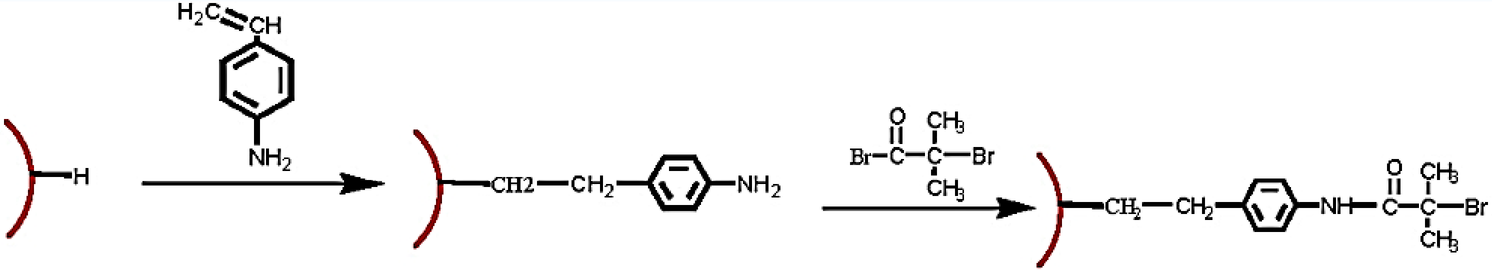


Figure 5.1. Synthesis of tetra-arm star polymer with arms of PFEMA [21].

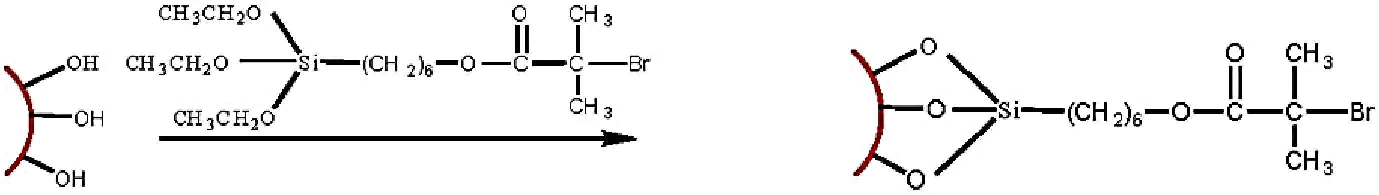
9. Surface ATRP





Si-H

Reference (20)



Reference (21)