POLYMER GRAFTING AND CROSSLINKING

Edited by

AMIT BHATTACHARYA
JAMES W. RAWLINS
PARAMITA RAY

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PREFACE

We are very fortunate to have the opportunity to edit a book in the grafting and crosslinking arena. While several excellent books on polymers are available, our experience in research over the years has revealed the need for a book which emphasizes the basics as well as applied orientation for beginners and those who want to increase their knowledge. An attempt has been made to present the subject lucidly by adopting a non-mathematical approach.

The book covers various mechanistic methods, kinetic factors, analytical evidence, and diverse applications. We extend our appreciation to the numerous publishers who have graciously accorded us permission to use figures and data from their publications.

This book is intended for beginners in this area, advanced students, as well as teachers. It is expected that they possess an adequate background in polymer technology. However, due to the book's wide coverage and simple style, researchers can also benefit from it. The book consists of twelve chapters. All topics have been selected with great care bearing in mind the needs of the students. The first five chapters provide a vivid introduction to the basic concepts. The remaining chapters are devoted to applications.

Needless to say, we owe a great debt of gratitude to our spouses for their encouragement, and to the authors of the various chapters. We are deeply indebted to Dr. P. K. Ghosh, Prof. S. N. Bhattacharyya, and Prof. B. N. Misra for their suggestions and assistance in completing this book. It would have been difficult for us to complete this book without the assistance of our students. Last but not the least, we express our heartiest thanks to readers of the book.

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1

INTRODUCTION

Amit Bhattacharya and Paramita Ray

We deal what we are. This saying serves to introduce the discussions on polymers. A quantum leap in this area brought about the Industrial Revolution in the 19th century. Recognition should be given to Herman Staudinger, who, in 1922, proposed the first explanation that polymers contain long chains of relatively simple repeating units. This date marks a turning point in the history of polymers, for it was then that the term "macromolecule" was first used. Thus the word becomes self-explanatory when broken down: The word "poly" means many, and "meros" means parts. The macromolecular concept was formulated by Staudinger, who received the Nobel Prize in 1953. Polyethylene, for example, is a polymer that contains large numbers of [$-CH_2-CH_2-$] units. In 1970, the first experiments with polyacetylene took place. Polyacetylene is a long string of molecules chained together, with one unit of acetylene repeated over and over again. In 1977, the trio of Mac Diarmid, Shirakawa, and Heeger joined to focus in this arena to revolutionize electronics and received the Nobel Prize in the 21st century.

Polymers play an essential role in the emergence of the modern world. Though started in the middle of the last century, today, the uses of polymer systems are legion. Technology from commodities to rockets is based on productive research on polymers. The polymer industry developed as population growth created increased demands for natural products that could not readily be met because of their limited supplies. "Osmosis" and "reverse osmosis" techniques that regulate life in every aspect are based on polymers.

Abbe Nolet had observed the "osmosis" phenomenon in the year 1748 in pig bladders, with natural polymers. Later on, synthetic ones came to replace natural polymers.

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The history of the “reverse osmosis” membrane started at UCLA in 1959. Samuel Yuster and two of his students, Sidney Loeb and Srinivasa Sourirajan, produced a functional synthetic reverse osmosis membrane from cellulose acetate polymer. The ability to make high-quality biocompatible materials in the biomedical field is at the heart of this revolution.

Traditionally, people in the medical field view polymers as components of devices such as inhalers and catheters, inert bioprostheses, or transdermal patches. Polymers have also proactive role, i.e., they are used as integral parts of therapeutics. New drugs, as well as drug delivery systems based on polymers, have the potential to counter many diseases. The application of synthetic polymers for gene therapy has also been investigated. They may provide a safer way of gene delivery than use of viruses as vectors. Polymeric materials have also been used for biosensors, in testing devices, and for bioregulation.

Textile products made of polymers have always satisfied aesthetic requirements. Synthetic polymers replace natural polymers (e.g., wool and cotton) to help clothe growing populations. The success of aramid fibers has also spawned a variety of other polymer fibers based on nylon, terephthalates, and polyethylene, for example.

Polymers are also identified with insulation. This property has contributed to the enormous success of plastics in insulated shielding for wires and other safety functions. Polymers are also used in the conducting or semi-conducting fields for such things as plastic batteries, light emitting diodes, and sensors.

Polymers touch every aspect of our lives. The nylon toothbrush, the plastic bucket, or the polystyrene umbrella handle are all polymers. Knowingly or unknowingly, every individual today relies on polymers to meet his needs.

Though polymers are legion, sometimes they cannot fulfill the demand, depending on their properties. Improvements in polymers are tremendously important because they will widen the scope of application. There are two main approaches: construction of new molecules that are likely, from their molecular composition, to have the desired properties, and modification of properties of existing large-scale polymers.

Modification of polymers has received greater attention in light of the scarcity of starting materials required for the synthesis of new monomers to deliver better polymeric materials. In other words, modification is essential to meet various challenges, as it is very diffcult to get new polymers. The next generation awaits polymer modification as it opens up new possibilities. Surface and bulk properties can be improved easily by modifying conventional polymers. Sometimes, balancing of properties is needed, and this is possible only through modification of polymers.

Polymer modification is required to bring specific properties to the modified material, such as enhanced thermal stability, multiphase physical responses, compatibility, impact response, flexibility, and rigidity. Modifications make an insoluble polymer from a soluble one or vice versa. Thus polymer modification improves the processibility of the polymers. One of the recent directions regarding polymer modification is intended to avoid their nonbiodegradable nature.

We have already referred to giant molecules and indicated that they are very long molecular chains of carbon atoms, often literally "branched" like a tree or linked together crossways in various directions. These chains can be provided by nature, as in the case of cellulose, or are built up from single short molecules known as "monomers" by uniting them into a chain to give "polymers," which is known as polymerization. When monomers of different kinds are united, the product is known as a "copolymer," and the process of uniting different monomers is copolymerization. Depending on the alignment sequence of different monomers in a polymer chain, copolymers are diversified in their property profiles.

Copolymers with an alternate sequence of monomers are alternating copolymers, whereas random copolymers do not follow any definite sequence in alignment patterns of the constituent monomers. Rarely may we expect any property gain from such compositions. Block copolymers are composed of long sequences (blocks) of one monomer unit, covalently bound to sequences of unlike type. Depending upon the chemical nature of the monomers block copolymers may be di-, tri-, tetra-, or even multi-block.

Generally, blocks are spontaneously self-assembled into a diversity of mesophases with the size scale governed by the chain dimensions. Dissimilar blocks exist as microdomains and exert their properties in the system. Thus glassy microdomains serve to anchor rubbery segments permitting the material to be used as melt processable adhesives and rubbers, i.e., thermoplastic elastomers such as SBS or ABS. Block copolymerization is one of the keys to achieve polymeric products with the desired property profiles.

The prime techniques for polymer modifications are grafting, crosslinking, blending, and composite formation, which are all multicomponent polymer systems. Such materials have attracted considerable attention in the industrial field as they combine a variety of functional components in a single material. Micro- and macrophase separation directly affect the physical and chemical properties in such multicomponent polymers. Graft copolymers are branched macromolecules in which the branches are of a different type from the backbone. They have a variety of potential applications resulting from the wide range of properties available when different polymer chains are connected to form hybrid branched macromolecules.

Multidirectional chain extension of polymers leading to the formation of network structures may be defined as crosslinking and viewed as a stabilization process. Crosslinking may result either through the polymerization of monomers with functionality greater than 2 (by condensation mode) or by covalent bonding between preformed polymer molecules accomplished by irradiation, sulfur vulcanization, or miscellaneous chemical reactions. Crosslinking restricts chains from sliding past one another and generates elasticity in an amorphous polymer. It makes a polymer more resistant to heat, light, and other physical agencies, giving it a high degree of dimensional stability, mechanical strength, and chemical and solvent resistance. The effects of crosslinking on the physical properties of the polymers are primarily influenced by the degree of crosslinking, the regularity of the network formed, and the presence and absence of crystallinity in the polymer. For crystalline polymers there may be a reduction in crystallinity with a low degree of crosslinking as it hinders chain orientation, and the polymer may become softer, more elastic, and have a lower melting point. Crosslinking changes the local molecular packing and leads to a decrease in free volume. This is reflected in an enhancement of glass transition temperature. Improvement in creep behavior also results from crosslinking as it restricts the viscous flow. Hence for property synergism crosslinking is unavoidable in the present arena of polymers.

A macroscopically homogeneous mixture of two or more different polymers may be defined as a polymer blend. The blending of polymers provides a means of producing new materials, which combine the useful properties of all the constituents. Most of the polymers are immiscible. Hence the combination of two arbitrary polydispersed polymers (quasi-binary mixture) exhibits neither a true two-phase nor a single-phase structure. It may appear to have a two-phase morphological pattern whereby both phases contain a different and finite concentration of each polymer or it may have multiphase structure. In both the cases, no definite interface exists between the two adjacent phases. The relative concentration of the constituents in different phases depends upon their intensity of mixing and solubility parameters. The ultimate behavioral pattern of polyblends depends upon extent of phase separation, nature of the predominant phase, character of the dispersed phase, and interaction between the component polymers. Most useful blends have the characteristics of uniform dispersion, i.e., fine discrete particles of one component being uniformly dispersed through the matrix of the other component.

It would be advantageous if the size and size distribution of the domains of the dispersed phase remain practically unaltered over long periods of time, from the conditions of blending to the conditions under which the blend is to be performed. The two main objectives of making polymer blends are to maintain a proper cost performance ratio and reinforcement of properties, i.e., compensation of the demerits of a polymer by blending it with a second one that is rich in the aspects lagging in the initial one. The technology of blending is now advancing at a rapid pace. New blends are constantly being developed and characterized, and blends with metallocene resins, liquid crystal polymers, and biodegradable resins are now available. Blending technology is also proving to be of use in plastics recycling.

A composite, as its name suggests, is made by combining two or more dissimilar materials in such a way that the resultant material is endowed with properties superior to any of its components. These components neither take part in the chemical reaction nor do they dissolve or completely merge with one another. Nevertheless, they remain strongly bonded together while maintaining an interface between one another and act in concert to give a much improved performance. In polymer composites, polymers that are the major components contain different reinforcing materials such as glass fiber, carbon fiber, silica, or mica as minor components. Reinforcement results in increased tensile, flexural, compression, and impact strength; rigidity; size stability; fire retardancy; corrosion resistance; electrical properties; and processibility. Polymer composites have versatile applications from the construction sector to commodity materials.

The two predominant modes of polymer modifications—grafting and crosslinking—are primarily considered in this book. The basic theories and exploration of these techniques in different sectors of human life are described in the following chapters.

2

BASIC FEATURES AND TECHNIQUES

Amit Bhattacharya and Paramita Ray

INTRODUCTION

"Physiosorption," "grafting," and "crosslinking" are the techniques by which the association of monomers and polymers is described. The term physiosorption signifies that it is related to physical attractive forces. The process is a reversible one and is achieved by the end functionalized polymers on to the solid surface or self-assembly of polymeric surfactants, where "grafting" can be described as the covalent attachment process and irreversible. Grafting can be accomplished by either "grafting to" or "grafting from" approaches. In "grafting to" approaches, functionalized monomers react with the backbone polymer to form the grafted one. On the other hand, "grafting from" is achieved by treating a substrate with some method to generate immobilized initiators followed by polymerization. High grafting density polymer also can be accomplished using this technique. The schematic presentation of all the processes is depicted in Figure 2.1A. The "crosslinking" is the association of polymers through a chemical bond. In most cases, the crosslinking is irreversible. It may be intra- and intermolecular (Figure 2.1B).

TECHNIQUES USED

The grafting and crosslinking reactions can be performed by different pathways such as chemical or radiation. The important modes of reactions are discussed in the following.

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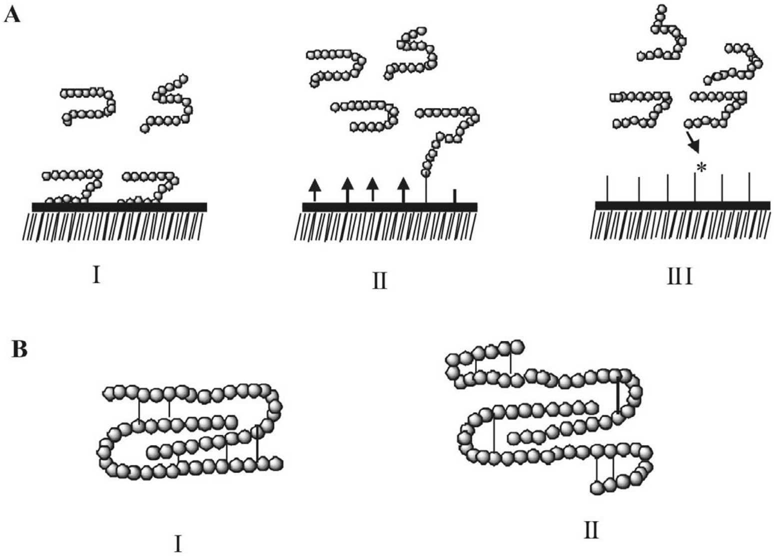


Figure 2.1. A. Schematic diagram of (I) physiosorption, (II) grafting to, (III) grafting from. B. Schematic diagram of (I) intermolecular crosslinking and (II) intramolecular crosslinking.

Chemical Routes

By Redox Reaction The redox reaction is the conventional one to produce the free radicals. There are different redox reagents in which radicals can be generated and relayed to the polymer so that the grafting reaction occurs. The features of the chemical reactions are as follows:

Features:

- Simple to carry out and no constraints in location point of view.
- Feasibility exists at room temperature and also in the aqueous solution.
- Extent of grafting can be controlled by tuning the reaction variables [viz. mixture composition (monomer/initiator), reaction time, and temperature].

The probable reaction pathways are described below.

(I) With Fenton's reagent (Fe^{2+}/H_2O_2) A HO• is generated by the reaction of Fe^{2+} and H_2O_2

$$H_2O_2 + Fe^{2+} \rightarrow HO\bullet + OH^- + Fe^{3+}$$

$$HO\bullet + |-H \rightarrow |\bullet + H_2O$$

(|–H is the polymer and M is the monomer)

The hydroxyl radical has the capability to abstract the hydrogen atom from the polymeric substrate, producing the free radical on it (|•). The monomer molecules that are in the vicinity of the polymeric substrate become the acceptor of the radicals, resulting in chain initiation. Thereafter, they become the free-radical donors to the neighboring molecules. In this way, the grafted chains usually grow. These grafted chains terminate by coupling to yield the grafted copolymer.

Initiation: $|\bullet + \mathrm{M} \rightarrow |-\mathrm{M}_1\bullet$

Propagation: $|-\mathrm{M}_1\bullet + \mathrm{M} \rightarrow |-\mathrm{M}_2\bullet$

$$|-\mathrm{M}_2\bullet + \mathrm{M} \rightarrow |-\mathrm{M}_3\bullet$$

$$\ldots$$

$$|-\mathrm{M}_{n-1}\bullet + \mathrm{M} \rightarrow |-\mathrm{M}_n\bullet$$

Termination: $|-\mathrm{M}_n\bullet + |-\mathrm{M}_m\bullet \rightarrow$ Graft copolymer

Fenton's reagents are used in grafting, but in the crosslinking reaction, they are not used very much. However, crosslinking reaction from the bimolecular reaction of Fe^{2+} and H_2O_2 depends upon the free-radical concentration at once [1].

(II) With Fe^{2+}/Persulphate Persulphate and a ferrous ion act as a source of $SO_4^{-\bullet}$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{-\bullet} + Fe^{3+} + SO_4^{2-}.$$

There are different views regarding the activity of $SO_4^{-\bullet}$. One is that $SO_4^{-\bullet}$ reacts with water to form OH•, subsequently producing free-radicals on the polymeric backbone

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^{-} + OH\bullet$$

$$HO\bullet + |\!-\!H \rightarrow |\bullet + H_2O$$

(|–H is the polymer and M is the monomer)

The propagation and termination steps are similar to the previous example.

An alternate view is that $SO_4^{-\bullet}$ reacts directly with the polymeric backbone to produce the requisite radicals

$$SO_4^{-\bullet} + |-OH \rightarrow HSO_4^{-} + |-O^{\bullet}$$

However, Misra et al. [2] established that during grafting of vinyl monomers onto wool/cellulose, OH• is more reactive than the $SO_4^{-\bullet}$.

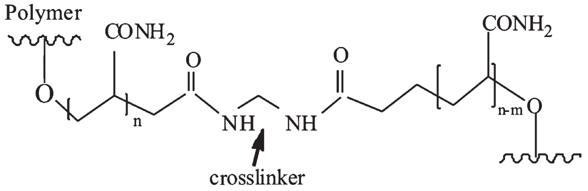


Figure 2.2. Involvement of the crosslinker in the crosslinked polymer.

(III) With Persulfate and Reducing Agent Persulfate and a reducing agent (e.g., sodium bisulphite, thiosulphate, or Ag^+) is also the source of $SO_4^{-\bullet}$, which subsequently produces OH•. $SO_4^{-\bullet}$ has the ability to initiate the polymer free radical directly or indirectly (as in the above example).

Persulfate/Reducing agent M: $S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{-\bullet} + Ag^{2+} + SO_4^{2-}$

Persulfate/thiosulphate: $S_2O_8^{2-} + S_2O_3^{2-} \rightarrow SO_4^{-\bullet} + S_2O_3^{-} + SO_4^{2-}$

Persulfate/bisulphate: $S_2O_8^{2-} + HSO_3^{-} \rightarrow SO_4^{-\bullet} + HSO_3^{\bullet} + SO_4^{2-}$

The $SO_4^{-\bullet}$ and $HSO_3^{\bullet}$ produced in the reaction generate OH• in an aqueous medium (as shown earlier), which forms the free radical on the polymer.

Persulfate-initiated crosslinking occurs in the presence of different crosslinking agents (viz. N, N′ methylene bis acrylamide, NNN′N'tetramethylethyl ene diamine) [3, 4]. The crosslinking mechanism is similar to grafting, except for the crosslinker participation. The involvement of the crosslinker is shown above (Figure 2.2).

(IV) With Fe^{2+}/Hydroperoxides Hydroperoxides and Fe^{2+} comprise another important redox system, with free radicals generated by the interaction between them via thermal decomposition [5]. The activity of a tertiary butyl hydroperoxides –Fe^{2+} system is caused to the formation of a t-butoxy radical arising from one electron transfer between t-butyl-hydroperoxide (TBHP) and Fe^{2+}.

$$\text{t-BuOOH} + Fe^{2+} \rightarrow \text{t-BuO}^{\bullet} + OH^{-} + Fe^{3+}$$

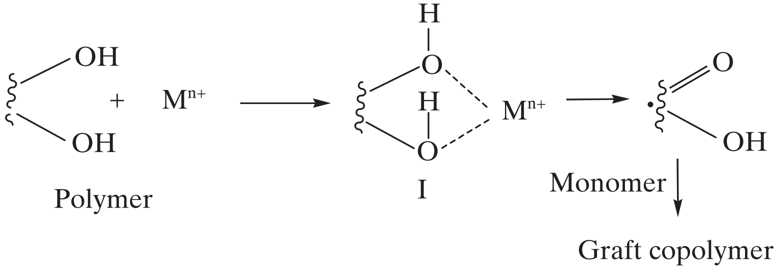
The resulting t-BuO• may participate in hydrogen abstraction to generate OH• and the macroradical on the polymeric backbone:

With monomer (M): $\text{t-BuO}\bullet + M \rightarrow \text{t-BuO-M}\bullet \rightarrow \text{t-BuO-}M_n\text{-M}\bullet$

With polymer (|—H): $\text{t-BuO}\bullet + |\text{—H} \rightarrow \text{t-BuOH} + |\bullet$

With water: $\text{t-BuO}\bullet + H_2O \rightarrow \text{t-BuOH} + OH\bullet$

(V) By Direct Oxidation Unlike the above system, free-radical sites are generated on a polymeric backbone by direct oxidation of the polymeric backbone by certain transition metal ions (e.g., Ce^{4+}, Cr^{6+}, V^{5+} and Co^{3+}) [6–8]. The metal ions with low oxidation potential are the proper choices for the reaction. The proposed mechanism for such processes has been ascribed to the intermediate formation of a metal ion polymer complex of chelate type (I). Such complex formation is not restricted to all polymers especially for cellulose types, where there is a possibility glycol groups may participate in the reaction. The mechanism is as follows:



Grafting through Ce (IV) initiation is feasible in an aqueous medium, but for styrene grafting it is not the proper choice because of its low solubility in water.

Crosslinking through Ce (IV) initiation is possible in the presence of different crosslinking agents. The mechanistic way is similar to the above (through persulfate) [9].

MnO_4^- in the acid medium reduces to Mn^{3+} ions to Mn^{2+}. These highly reactive ions are responsible for initiating graft copolymerization.

$$| -H + Mn(III) \rightarrow \vdash H - Mn(III)\,[\text{complex}]$$

$$| -H + Mn(III) \rightarrow |\bullet + Mn(II) + H^+$$

$$|\bullet + M \rightarrow |\,M\bullet$$

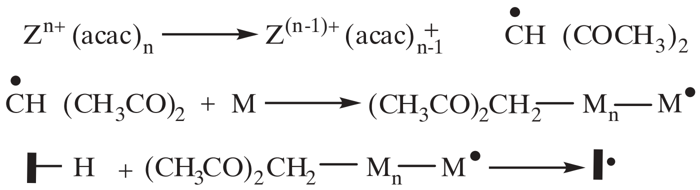
$$Mn(III) + M \rightarrow M\bullet + Mn(II) + H^+$$

$$|M\bullet + nM \rightarrow \vdash M_{n+1}\bullet$$

$$|M_{n+1}\bullet + Mn(III) \rightarrow |M_{n+1} + Mn(II) + H^+$$

$$|\bullet + Mn(III) \rightarrow \text{oxidized product} + Mn(II)$$

(VI) Using Metal Chelates To avoid undesired reactions, controlling redox potential in the form of metal chelates (e.g., Fe(acac)$_3$, Zn(acac)$_2$, Al(acac)$_3$, VO(acac)$_2$:acac:acetyl acetonate) are useful in the grafting reaction. The metal ion forming complex with the monomer decomposes to the free radical, which undergoes a chain transfer to the polymer. The formation of the free radical in the polymer through monomer is sketched below [10, 11], and the grafting reaction is the same as shown in the earlier example.



$$Z^{n+}(\text{acac})_n \longrightarrow Z^{(n-1)+}(\text{acac})^{+}_{n-1} \quad \overset{\bullet}{\text{C}}\text{H}\ (\text{COCH}_3)_2$$

$$\overset{\bullet}{\text{C}}\text{H}\ (\text{CH}_3\text{CO})_2 + \text{M} \longrightarrow (\text{CH}_3\text{CO})_2\text{CH}_2\text{—M}_n\text{—M}^{\bullet}$$

$$\vdash \text{H} + (\text{CH}_3\text{CO})_2\text{CH}_2\text{—M}_n\text{—M}^{\bullet} \longrightarrow \vdash^{\bullet}$$

[Z: metal, (acac)=acetyl acetonate, M: monomer, $\vdash$ H polymer]

(VII) By Indirect Method The secondary free radicals are generated in the system and may ultimately induce the free-radical sites required for grafting [12].

$$\text{Mn}^{4+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn}^{3+} + \text{CO}_2 + \text{CO}_2^{-\bullet}$$

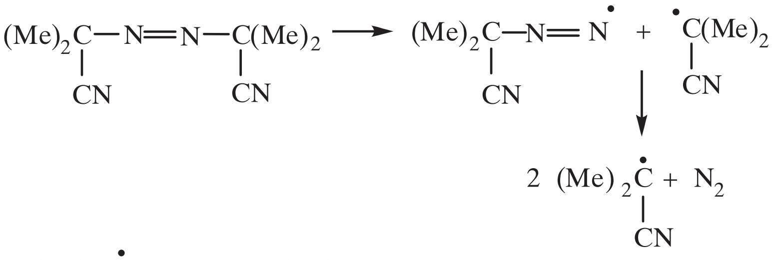
$$\text{Mn}^{3+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn}^{2+} + \text{C}_2\text{O}_4^{-\bullet}$$

V^{5+} in the presence of H_2SO_4 produces secondary $\text{HSO}_4^{\bullet}$, which can induce free-radical sites on the polymeric backbone. The oxidative reaction is as follows:

$$\text{V}^{5+} + \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^{\bullet} + \text{V}^{4+} + \text{H}^+$$

Limitations: The proper selection of the metal ions or oxidative process is a factor, as the higher redox potential of the system has the possibility to react with the monomers that will lead to an increase in homopolymerization. To circumvent this situation, systems with low oxidation potential and polymers of strong reducing agents are preferred.

On heating: Apart from the redox reaction, certain organic compounds (azo, peroxides, hydroperoxides, etc.) [13] are capable of producing free radicals on heating and transferring them to the chain. It is seen that azoisobutyronitrile (AIBN) (I) is not as reactive as benzoyl peroxide (BPO), because of the resonance stabilization of the fragmentation.



$$(Me)_2\dot{C}—CN \longleftrightarrow (Me)_2C—C\equiv N^\bullet$$

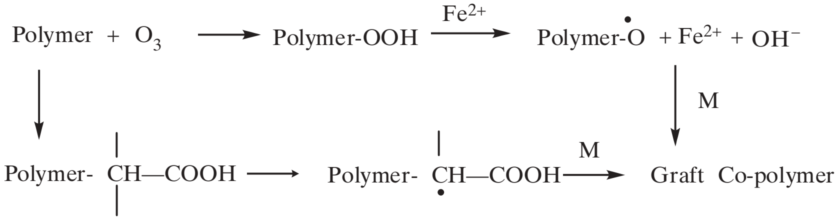
I II

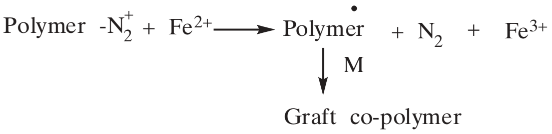
$$(PhCO)_2O \longrightarrow 2\ Ph^\bullet COO \longrightarrow Ph^\bullet + CO_2$$

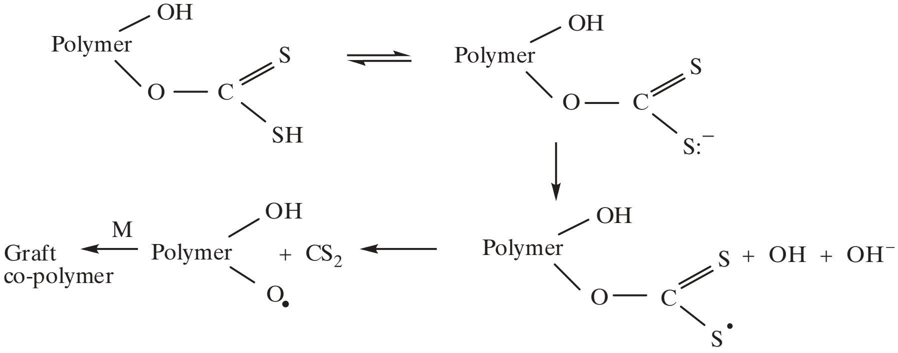
$$(Me)_3COOH \longrightarrow (Me)_3COO^\bullet + {}^\bullet OH$$

Crosslinking is also reported by using different crosslinking agents and initiators; the mechanism is similar to the grafting reaction [14–18].

Chemical pretreatment (e.g., ozonation, diazotization, xanthation) of the polymer backbone may also generate free radicals that provide sites for grafting as follows:







Limitations:

- The conventional free-radical graft polymerization needs continuous initiation.
- The termination step leads to an unreactive polymer.
- The grafted product is of broad molecular distribution.
- The time invariant degree of polymerization.

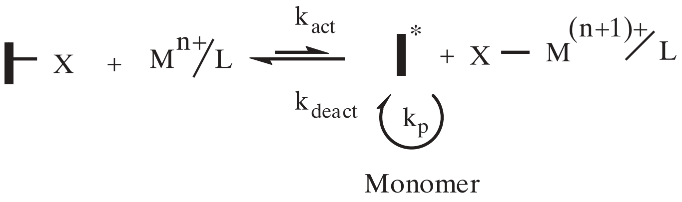
These limitations lead researchers to adopt the following living radical technique.

By Living Radical Formation In this technique, the chain termination step is avoided in two ways: either by increasing the rate of initiation with respect to the rate of propagation or by eliminating chain termination and transfer reactions. The polymer chains grow at a more constant rate, and their chain lengths remain very similar. Thus, it provides polymers that are able to grow whenever an additional monomer is supplied. The conditions are discovered for various types of reactions, e.g., atom transfer, nitroxide mediated, degenerative transfer.

Features:

- It proceeds until all monomers have been consumed. Further addition of a monomer results in continued polymerization.
- In these reactions $R_i << R_p$, where, as for the conventional free-radical grafting, $R_i > R_p$ (R_i and R_p are the rate of initiation and propagation).
- Dynamic equilibrium occurs between a propagating radical and dormant species.
- Mono and/or narrow dispersities of the products are possible.
- Predetermination of molar mass of the grafted/crosslinked polymer molecules is possible.
- Telechelic polymers are easily synthesized by using proper terminating reagents.

(I) Through Atom Transfer The key molecule is the one that contains halogen, positioned in the α-position with carbonyl, alkoxy-carbonyl, cyano, and phenyl groups. The reversible pseudohalogen homolytic transfer between a dormant species, an added initiator, or the propagating dormant chain end, (I-X) and a transition metal complex in the lower oxidation state (M^{n+}/L), occurs to form the propagating radicals (I*) and the metal complex in the higher oxidation state with a coordinated halide ligand [$X\text{-}M^{(n+1)+}/L$]. Activation, deactivation, and propagation, as well as termination steps, are present but as the persistent radical effect (PRE), the radical termination is diminished, and the equilibrium is strongly shifted toward the dormant species [19]. The general reaction is as follows:



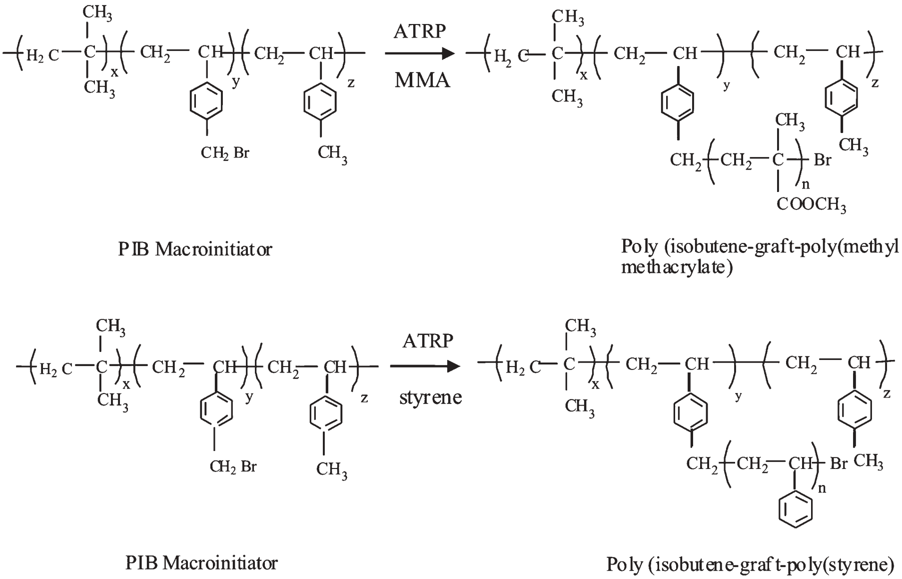
M^n - transition metal, L - complexing ligand, ⊢ Polymer chain, X = Br or Cl

Features:

- Scope for choosing both the initiator and catalyst complex.
- It can occur in solution as well as suspensions.

Polymers prepared by other processes can be functionalized at the terminus or along the backbone and incorporated into an ATRP as a macroinitiator/macromonomer, or simultaneously through use of both a macroinitiator and a macromonomer to improve incorporation of the macromonomers into the polymer leading to well-defined block and graft copolymers [20–25]. Examples related to the grafting of acrylates and styrene to the polymer based on macroinitiators are as follows (Scheme 2.1):

There may be one or multiple initiating sites, leading to chain growth in several directions, which also proves the potential for the preparation of



Scheme 2.1. ATRP reaction to form the graft polymer. Reproduced from *Macromol Chem and Phys*, **202**: 3392 (2001).

molecular brushes, i.e., high grafting density polymer, using a “grafting from” approach. The synthesis of poly (MMA-grad-BPEM)-graft-n-BuA [26] is sketched in Scheme 2.2.

Surface grafting by controlled radical polymerization on the polymeric substrate, colloidal particles and inorganic materials are also possible [27–29]. The examples are displayed in the Schemes 2.3 and 2.4.

Limitations:

- Selection of suitable ligands is critical.
- The reactions preferably conduct in the absence of oxygen, or otherwise some reducing agents [e.g., Cu (0), Sn (EH_2), or ascorbic acid] are essential.

(II) Nitroxide Mediated Free-radical nitroxides [viz. 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO)] are key molecules. The reactions are based on reversible capping of the active polymeric chain end radical with a nitroxide leaving group. The dormant chains are generated by reversible deactivation of growing chains through covalent bond formation. At first, the nitroxide free radical, as well as active growing chain (through homolytic cleavage), forms at high temperature. After that, the reaction occurs with the preformed macromonomers [30–32]. The reaction feature shows that preparation of dendritic polymers [33–35] is possible through this technique. Examples related to the mixture of styrene and p-chloromethyl styrene is presented in the Scheme 2.5. In this case the polymerization mechanism is switched from nitroxide mediated to atom transfer “living free-radical” conditions.

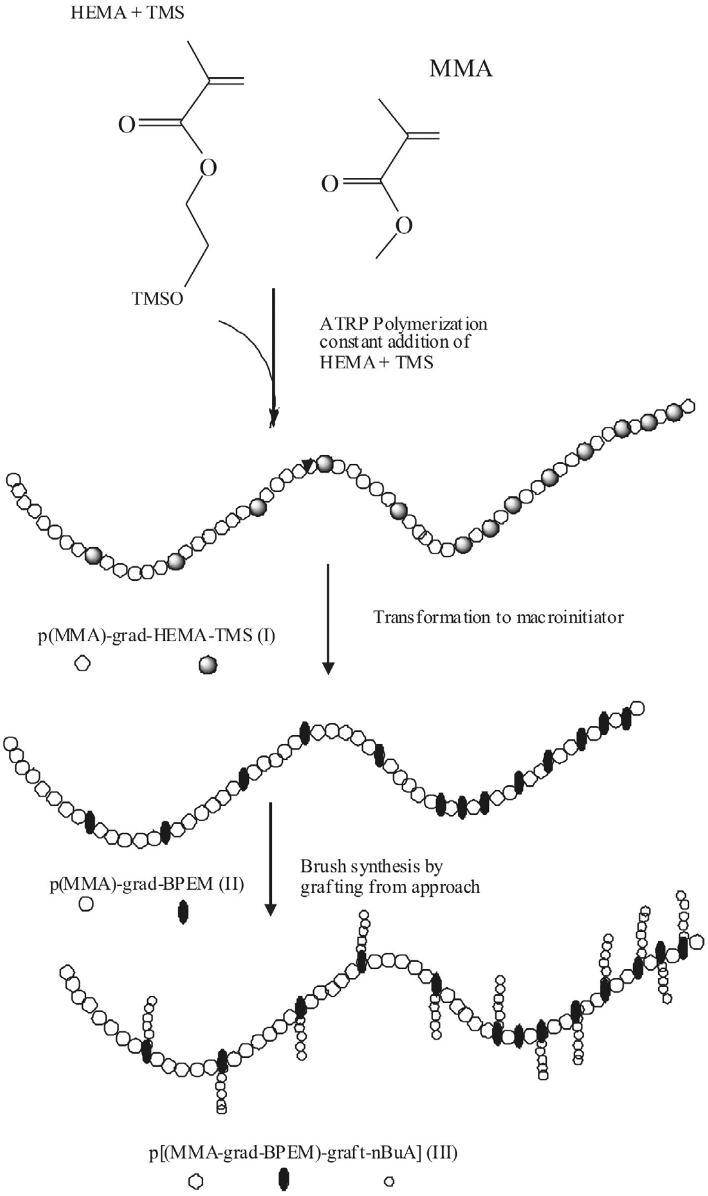
Features:

- Reactions are acceptable with monomers, e.g., styrene, butadiene, methyl methacrylate, styrene sulfonate (aq).
- Reaction feasibility exists when using commercial initiators as well as initiator formed in situ.
- Possibility to introduce stable free-radical adduct to preformed structures including dendrimers, functionalized polymers, and telechelics.
- Narrow molecular weight distribution up to moderate conversions.
- No Trommsdorff (Gel) effect.

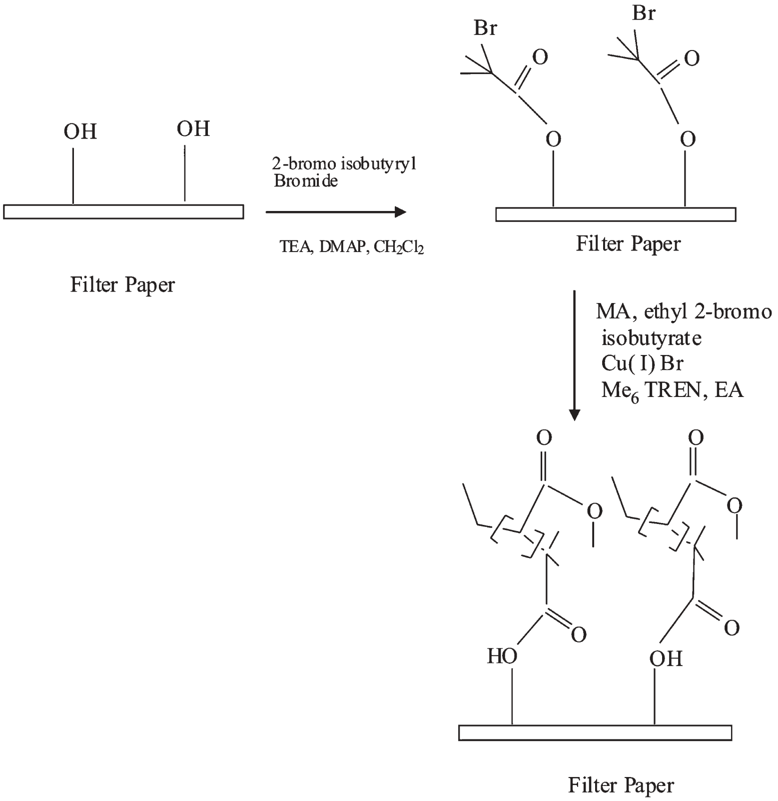
Limitations:

- Monomers (alkyl alkylates, vinyl acetate, vinyl chlorides) do not usually undergo the reaction.
- Loss of molecular weight control at high conversions.
- Very slow rates.

(III) Degenerative Transfer In this mode, the grafting reaction occurs through the chain transfer reagents (alkyl iodides, thiol compounds, and unsaturated

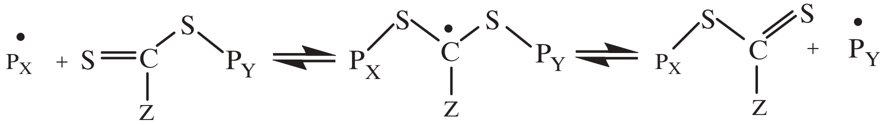


Scheme 2.2. (I) Subsequent synthesis of the macroinitiator precursor. (II) Macroinitiator. (III) Macromolecular brush copolymers. Reproduced from *Macromolecules*, **35**: 3387 (2002).



Scheme 2.3. Schematic presentation of surface grafting on cellulose via controlled living radical polymerization. Reproduced from *J Am Chem Soc*, **124**: 900 (2002).

polymethacrylates). In this mechanism, the polymer (P_x) is attacked by the propagating radical to form the active species and the dormant species.



P_X and P_Y are polymeric chains, $Z=C_6H_5$ and CH_3

This process is also called a reversible addition-fragmentation chain transfer [36, 37]. The synthesis of poly(ethylene-co-vinyl acetate-g-methyl methacrylate) (EVA-g-PMMA) poly(ethylene-co-vinyl acetate-g-styrene) (EVA-g-styrene) based on free-radical polymerization of methyl methacrylate intitiated by AIBN, in the presence of mercapto-modified EVA as chain transfer agent (Scheme 2.6), is the example used in this regard [38, 39].