

# Synthesis of Speciality Polymers through Nitroxide Mediated Living Radical Polymerization

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## Abstract

This paper provides an overview of applications of Nitroxide Mediated Living Radical Polymerization for the synthesis of speciality polymers. Some important factors such as correlation of structure of nitroxides with enhanced control of macromolecular architecture and applications of alkoxyamine initiators are explained. Important mechanistic and kinetic features are also discussed in this paper.

**Keywords:** Nitroxides, TEMPO, 2,2,6,6-Tetramethylpiperidinyloxy, Alkoxyamines, Living Polymerization.

## Introduction

Living Polymerization is a very useful process for synthesizing polymers and this method is widely used in industrial field and academic research. It is used to synthesize large quantity of vinyl based homo-and copolymers annually. It is versatile, can tolerate protic media provides synthetic ease and compatible with large number of functional groups. It is characterized by the absence of chain termination and chain transfer processes in polymerization. The quantitative and fast initiation is the ideal standard for it. It is less sensitive to impurities. The living or nonliving nature of polymerization is dependent on type of monomer, initiator, temperature, solvent etc. Its wide commercial adaptation is also due to its emulsion and suspension techniques which simplify the experimental setup. Living radical polymerization produces polymer with high level of control over molecular weight, polydispersity and chain ends. Traditional free radical polymerization (anionic or cationic polymerization) process contain so many features like poor control on polydispersity, polymer architecture and macromolecular weight, high polydispersity and non-living nature of polymerization. Growing demand of well-defined polymers in all areas is the driving force behind the research in this area [1, 2].

## Historical Evolution

Warrington and Tobolsky in 1955 first used such initiators which can be used for controlled radical polymerization. Otsu coined the term "INIFERTERS" (initiator-transfer agent-

terminator) in 1982. It was the first attempt to make true LFRP technique. Szwarc emphasized the living (non-terminating) nature of polymerization in these words: "Propagation should continue until all monomers are consumed" [3, 4,9].

## Significance of Living Radical Polymerization Technique

The major significance of living polymerization is to give a variety of options for controlling polymer size, architecture, and choice of place of attachment of any functional group in the polymer chain. The absence of chain termination gives the chance for access to macromolecular, multiblock, star, bottlebrush copolymers [5, 6].

## Some Important Types of Living Polymerization

Living Polymerization is mainly of two types. Living Anionic and Cationic polymerization. Szwarc firstly initiate anionic polymerization of styrene. Cationic Polymerization contains a carbenium ion at the chain end and proceeds via a chain growth process. Another interesting polymerization process is Coordination-Insertion polymerization. In which large number of catalysts as like cobalt, zirconium, nickel, chromium etc are involved to make polyolefins [7, 8].

## Nitroxide Mediated Living Free Radical Polymerization

Mediating radicals are primarily required as they can form reversible termination of the propagating chain end but not acting as initiator. It is advanced in comparing to the iniferter formation by Otsu as they have incomplete control over initiation and reversible termination resulting in poor control over polymerization. Success of nitroxide mediating radicals also very much affected by steric hinderance by presence of hetero atoms. A large number of radicals are employed for this function as verdazyl, triphenyls, triazoliny, nitroxides etc. These are some most studied and successful mediating radicals. Nitroxides with associated alkylated derivatives form alkoximes. It is ideal for trapping carbon centre free radicals.

Solomon, Rizzardo and Moad y qtnngf "qp"pkqzkf gu properly with the low temperature typically associated with standard free radical [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 23, 24].

## **Some Important Nitroxides**

### *Aromatic Nitroxides*

The basic structure in aromatic nitroxides is an aromatic ring. TEMPO (2, 2, 6, 6-Tetramethyl-1-piperidinyloxy or 2,2,6,6-Tetramethylpiperidin-1-oxyl) is the one most important aromatic nitroxide mediating radical. Matyjaszewski worked on styrene polymerization and found that rate of polymerization was enhanced by the use of TEMPO derivative. Many TEMPO based derivatives are prepared for improvement of the preparation procedure and yield of polymers. It will give substantial effect because it involved in not only in initiation but in numerous reversible termination and activation steps [19, 20, 21].

### *Alicyclic Nitroxides*

Alicyclic Nitroxides are some more improved nitroxides without the presence of any aromatic ring. Poly (ethylene)oxidemethacrylate (PEOMA) unites with PEO side groups of large number of chain length were synthesized by Nitroxide Mediated Polymerization with a low molecular mass unimolecular alkoxyamine initiator. Abreu et al explained their work the synthesis of Poly (vinyl chloride) by nitroxide mediated polymerization using SGI-based blockbuilder alkoxyamine at low temperature [22, 23, 24, 25].

### *Types of Initiators*

Nitroxides working on the system mainly divided into two classes. First Unimolecular initiator, here alkylated TEMPO (2, 2, 6, 6-Tetramethylpiperidinyloxy) derivatives breakup to supply the initiating radical and the stable radical and in bimolecular system a general free radical initiator such as BPO is used in boundation with TEMPO. However the rate of polymerization is same but Unimolecular initiator give better formation of polymers with controlled molecular weight and polydispersity of resulting polymer. Unimolecular initiators structure for Nitroxide mediating polymerization process was based on the alkoxime functional groups and is attached at the chain end of the propagating polymer in its dormant phase [26, 27, 28, 29].

### *Approaches to Alkoxyamine Nitroxides*

Stable readily functionalized initiators allow the largest degree of control over the produced polymeric structure in living radical polymerization. Various areas of research and nanotechnology benefited by this. Alkoxime is an alkylated derivative nitroxide. Poor yield and large byproducts produces in initial attempt with the reaction of benzoyl peroxide with excess amount of styrene to make a benzylic radical and then by trapping the radical intermediate with TEMPO to produce the benzoyl peroxide adduct. Initially synthesis of alkoxyamines based on carbon centered radicals with trapping of these radical with TEMPO to produce Benzoylperoxide adduct. Various ideas for generation of the radical intermediate have been considered. Benzylic alkoximes, generation of radicals from ester enolates trapped by nitroxides to provide functionalized alkoximes are also made to high yields. Braslau has done reaction by  $\text{Cu}^+$  promoted reaction by single electron-transfer in presence of enolate anions to make carbon centered free radical which can

attached by nitroxides at low temperatures. Lead oxide is used for the oxidation of alkyl hydrazides compounds for the synthesis of alkoxy-amine and with chiral nitroxyl mediating radicals for degree of stereo chemical control on the polymer. Surface modification is also one of the beneficial requirements for polymerization to apply alkoxyamine initiator. It is the first example of living radical initiators using at large number of surface to make covalently added polymer chains. This is here able to moderate the structure, functionality and density etc. The nature of covalent structured surface attachment area permit living free radical initiator to produce polymer brushes to be patterned. Nitroxide mediating process is applicable in general area of Nanotechnology. Two areas of application are the design of "Rasta-resin" and the preparation of functionalized macro porous monoliths hqt use in advance chromatographic separations. The direct synthesis of dispersed nonocomposities shows the capability for surface initiated polymerizations by the productive method of nitroxide-mediated living free radical polymerization [30, 31, 32, 33, 34, 35, 36, 37, 38, 39].

## **Mechanistic and Kinetic Features**

### **Nitroxide Exchange**

Fisher gave the mathematical  $g_{\text{swc}}k_{\text{pu}}v_q$  apply on the polymerization rate and polydispersities of the product polymer by nitroxide exchange and it shows to effectively model LFRP. Turro has shown that the exchange of mediating radical can be used as synthetic tool for placing functional groups at the polymer chain. He developed a facile procedure for preparation of chain end functional group attached macromolecules. His work presents number of advantages, functional group with reactivity can be add under some mild condition, a large number of varieties of differently tagged and structured macromolecules from the same precursor polymer [40, 41, 42, 43].

### **Additives**

The rate of polymerization and termination extent reaction can be manipulated by changing the balance in all reaction and kinetic equations during the radical effect. Continuously addition of initiator or having slow decomposing initiator is needed [44, 45].

### **Elucidation of Living Nature**

The evolution of molecular weight and conversion relation can give the livingness of the process. The relationship between predicted molecular weight and experimental molecular weight gives an idea about the controlled nature of polymerization. Use of the chain end of alkoxyamine to prepare a block copolymer also proves nitroxide mediated process with living nature [46].

### **Emulsion and Related Process**

As like Homogeneous, Heterogeneous system condition eg. Suspension, dispersion, seeded emulsion, batch emulsion, etc. have been studied for better results. The choice of nitroxide is critical here. Second generation nitroxides that work with lower temperature can give positive approach to this reaction

process [47, 48, 49, 50].

### Chain End Degradation

Chain end degradation affects the structural integrity and kinetics of the products by breaking of the alkoxyamine chain end in Nitroxide mediated polymerization. One main pathway is the easy reduction of the mediating nitroxide radical to produce the corresponding hydroxylamine with H-transfer. The termination reaction in preparation of polystyrene containing reaction with unsaturated chain end to reproduce the nitroxide decreasing the living nature of the polymerization and also may vary the total kinetics and proceed for a nonlinear system.

Competitive rate of polymerization and decomposition is present during decomposition of the alkoxyamine attached chain end during polymerization. This reaction is reduced but not totally removed from Nitroxide mediated polymerization. Low polydispersities seen for second generation nitroxides as compared to TEMPO for polystyrene polymerization [51, 52].

### Molecular Weight Control

Hawker using alkoxyamine as initiator produced the molecular weight of polystyrene with great control over molecular weight upto to  $M_n$  values of about 75000. With TEMPO based alkoxyamines and with second generation alkoxyamines upper molecular weight has been increased between 150000 and 200000. At large molecular weight the small amount of terminating species and extraneous radicals quickly becomes significant. It is detected when compared to the low concentration of initiating and propagating radicals attached with the system. This gives result an increasingly nonliving process [53].

### Telechelic and Complex Macromolecular Architecture

Nitroxide mediated polymerization technique was made possible to make telechelic polymers as similar procedure of living anionic process. The numbers of functional group which have been attached in telechelic structure are many useful reactive groups like  $NH_2$  etc. The interconversion of functional group is possible by proceeding chain end of alkoxyamine chemistry by many groups are used to design formation of telechelic system.

### Block Copolymers

Living Radical procedure mainly introduced for preparation of Block copolymers. Vinyl copolymers can be prepared with the traditional fashion sequence. A functionalized alkoxyamine used for termination of polymerization during the preparation of block copolymers. It worked as a macro initiator to form block copolymers. The facile introduction of a functional group or chromophore at the junction point between two blocks is possible that may be used in standard living radical procedure. This can be best explained by the formation of block copolymers based on poly(ethylene glycol). This can be used to polymerize a large number of vinyl monomers to form amphiphilic block copolymers with low polydispersity and accurately controlled molecular weight. For Nonliving block copolymer making proceed to the mixing of living free radical techniques with other process of polymerization which can

form linear block copolymers or graft systems. The preparation of Poly (caprolactone)-b (styrene) copolymers with the process of combination of living ring opening polymerization and nitroxide mediated free radical procedure demonstrate synthetic versatility linked with combining many types of polymerization methods [54, 55, 56, 57, 58, 59].

### Random Copolymers

Living Radical Procedure has one more advantage to prepare Random copolymers. Low Reactive ratio, polymer condition for one monomer is compatible with the second monomer. Nitroxide mediated Condition dg'wugf 'hqt' r tgr ctkpi 'repare random copolymers. Second generation nitroxides improved its preparation. Random copolymers prepared by living polymerization procedure have approximately low dispersity of molecular weight of prepared composition [60].

### Hyperbranched and Dendritic Structure

Many avenues to form special macromolecular architectures that cannot to be made by traditional or anionic polymerization were done by Fréchet in the improvement of self condensing polymerization with the ability to make unimolecular initiators which is reactive. Mediating nitroxides using with polymerizable double bond was discussed by Young. This lead to branch points coupling or knitting together of main polymer chain and with cross link monomer. Nitroxide mediated polymerization is good for choosing monomer and initiator structure to prepare a wide variety of large macromolecular structures like hyper branched and dendritic structure. Chaumont, Sherrington and Fukuda discuss to prepare different hyper branched structure as comparing with traditional polymerization process. Hemery studied on preparation of cyclic polymers. The branch initiating group present during the polymerization may attached in a post-polymerization functionalization step. This is very fruitful to prepare large, highly branched combburst copolymers under mild condition and in limited number of steps. Nicolas said Nitroxide Mediated Polymerization is a radical polymerization with reversible deactivation to grow well defined complex hyperbranched polymers. Living Radical Polymerization of multivinyl monomer towards hyperbranched polymers for biomedical application is also synthesized [61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80]

### Star and Graft Structured Polymers

The decreased concentration of radical centers present at the chain ends gives a number of ways in the synthesis of large complex structure. To make graft or star polymer. polymer with few or no unwanted coupling products gives the number of arms less than 20. Polyfunctional initiator gives best result. Styrene and P-chloromethyl styrene polymerize under living radical condition to give smooth linear copolymer. This polymer reacted with sodium salt of the hydroxyl functionalized composed unimolecular initiator produces variety of graft polymers.

The core first methodology explain the starting of branching firstly before the monomers is going to polymerized and the arm first method taken in reaction of a chain end with a core that contain various types of chemical functionalities. All star

polymers like asymmetric, symmetric and miktoarm stars made from either arm first or core first method. Cross linking with 1, 4-divinyl benzene provides way for large number of arms (10-20) preparation. Many macro initiators with divinyl cross linking agents can react, as like 1, 4-divinylbenzene, ethylene glycol diacrylate to prepare star polymers by nitroxide mediated living radical polymerizations [81, 82, 83, 84, 85, 86, 87, 88, 89].

### Conclusions

Clearly the area of Nitroxide mediated polymerization has been developing year by year. Significant values in every Nitroxide mediated polymerization procedure have to give synthetic chemists with the ability to make different beneficial polymers that were not easy to prepare a decade ago.

Nitroxide mediated living radical polymerization provides the properties of products to be characterized and calculated on the nanoscale. As a result large number of corporation from industry and academic areas making a spectrum of new materials for external evolution. We are now having the capability to change the properties of polymeric materials to the society need.

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