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## Review Article

# Polymeric Pioneers: Revolutionizing Drug Delivery for Precision Therapy

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## ABSTRACT

Polymeric new materials have transformed the world into a revolution in drug delivery. Precision and control have altered therapeutic strategy. The polymer-matrix drug delivery systems have thrown open a new avenue of individualized therapy with methods for controlled, targeted, and sustained release of drugs. These systems amplify bioavailability, cut down side effects, and ensure effectiveness due to specific delivery of drugs to the sites of action. Polymers, whether their background is synthetic or natural, have been engineered to respond to particular stimuli such as pH, temperature, or even enzyme activity, to release drug molecules only in a defined environment, which is very essential in precision therapy in which each patient's individual needs are increasingly catered for. The newly emerged polymeric material-based nanoparticles and micelles have also ensured high efficiency in encapsulating both hydrophobic and hydrophilic drugs, now extending thousands of treatable diseases. Research in polymer drug delivery systems will prove a pioneer foundation for personalized medicine, now moving ground to offering better outcomes for patients at reduced cost with increased patient compliance. Ongoing work in the area of polymeric pioneers has a bright prospect in drug delivery, not as a generalized approach but as a precise and specific patient solution capable of ensuring optimal therapeutic effects and minimizing unwanted consequences.


## INTRODUCTION

Polymeric drug delivery research has been advanced for more than three decades since the 1980s. These involve multi-disciplinary scientific approaches leading to huge advances towards the therapeutic index and bioavailability of drugs at

the site of delivery. Drug delivery systems combine one or more traditional drug delivery systems with technology. They impart the ability to point a very specific place in the body where the drug is released and/or at what rate it is released into the body. Biodegradable and bio-absorbable

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polymers are making the choice of all sorts of new drug delivery systems possible. Bio-absorbable polymers such as hydrogels made of poly (lactic acid) and poly (glycolic acid), as well as their copolymers have been used in formulating the delivery part of the systems. Biodegradable and bio-absorbable polymers provide a safe means to deliver medicine, using a drug delivery system whether it is a biodegradable implant delivering medicine subcutaneously or deep within the body [1]. From the use of polymer carriers to spatiotemporally release therapeutics through pulsatile delivery and implanted reservoir systems, modern drug delivery has a great deal of hierarchical progress. Conventional drug delivery formulations have done wonders in the treatment of diseases, but in specific biological therapeutics, it has proved to be more urgent for intelligent delivery systems. There are tremendous advances which lie in the diffusion-controlled and solvent-activated formulations in drug delivery. Some polymer carriers such as hydrogels have been worked upon for safe delivery of a drug through unfavorable physiological locations. Polymers can be engineered into controlled molecular architectures to elicit preordained responses to external conditions owing to a very good understanding of the underlying mechanisms and the nature of the transitions. Therefore, it is within these classes of polymers that some have emerged as bioactive to impart therapeutic benefit, while some are biodegradable to manipulate release kinetics to prevent accumulation of the carrier. Polymers have been conjugated with pharmaceuticals in order to alter transport or circulation half-life characteristics, permitting passive or active targeting. And lastly, the latest results in drug delivery research using polymers have produced systems of recognition and polymeric carriers that allow cytoplasmic delivery of new therapeutics. This review aims to uniquely cover the whole field of polymers in drug delivery,

covering the basics that are related to drug delivery in certain conceptual contexts and mathematical formulations, and critically reviewing advancements in recent years regarding responsive polymers, polymer therapeutics, and advanced systems designed for molecular recognition or engineered for intracellular delivery of new therapeutics [2].

### **Advantages Of Polymeric Drug Delivery System:**

- **Controlled and Sustained Release:** Engineering polymers to release drugs at a specified constant rate over the years provide continuous availability of the drug and lessen frequent dosing intervals.
- **Targeted Drug Delivery:** Engineering polymers for targeting tissues or cells, such as cancer cells, would result in less impact on the healthy tissue on which the drug has no intended effect
- **Improved Bioavailability:** Poorly soluble drugs containerized in polymers can benefit from better dissolution and bioavailability.
- **Biocompatibility and Biodegradability:** Most of the polymers which used in drug delivery are biocompatible and biodegradable, thereby limiting the accumulation in the body and ensuring safer applications for long durations.
- **Versatility:** Tailored polymeric systems could be capable to deliver a myriad of drugs; these include proteins as well as peptides and small molecules.
- **Reduced Side Effects:** Polymer systems managed release from and targeted drug to certain areas where exposure of healthy tissues to drug would occur, thus minimizing side effects [3].

### **Disadvantages Of Polymeric Drug Delivery System:**

- **Polymeric Drug Delivery:** Complex Manufacturing: Polymer delivery system



development often requires specialized techniques for the preparation and is a lengthy, costlier process.

- **Limited Drug Loading:** Many polymeric systems just don't have the capacity to incorporate and retain the drugs inside the matrix, especially high-dose as well as hydrophobic drugs.
- **Unpredictable Degradation:** The predictable nature of the process could lead to unanticipated inconsistency in drug release profiles.
- **Immunogenicity:** Some polymers just inherently cause immune responses, resulting in inflammation or hypersensitivity reactions.
- **Polymer-Drug Interactions:** Interaction of polymer matrix with the drug could affect stability, release rates, or bioactivity of drugs
- **Regulatory Hurdles:** Most of the polymer systems require testing and approval from the authorities for marketing, especially biodegradable ones<sup>[4]</sup>.

#### **Properties Of Polymeric Drug Delivery System**<sup>[5]</sup>:

##### **Molecular Weight:**

- This has an impact on mechanical strength and drug release profiles.
- High molecular weight polymers usually make stronger slow-release films or matrices.

##### **Solubility:**

- Polymers can have either water-soluble or water-insoluble versions with other solvents.
- This property becomes crucial during drug release profile design.

##### **Biodegradability:**

- An exposure to physiological conditions results in the degradation of certain polymers, leading to drug release in a controlled manner.

##### **Biocompatibility:**

- A requirement for any material introduced into the body.
- A polymer should not induce any inflammatory or immunological response.

##### **Swelling Characteristics:**

- In hydrogel systems, the degree and rate of swelling of the polymer can control drug release.

##### **Thermal Stability:**

- Thermal stability is a requirement for polymers that are used in processes such as tablet coating or hot-melt extrusion.

##### **Viscosity:**

- The viscosity of the polymer solution dictates drug release and processability of the formulation.

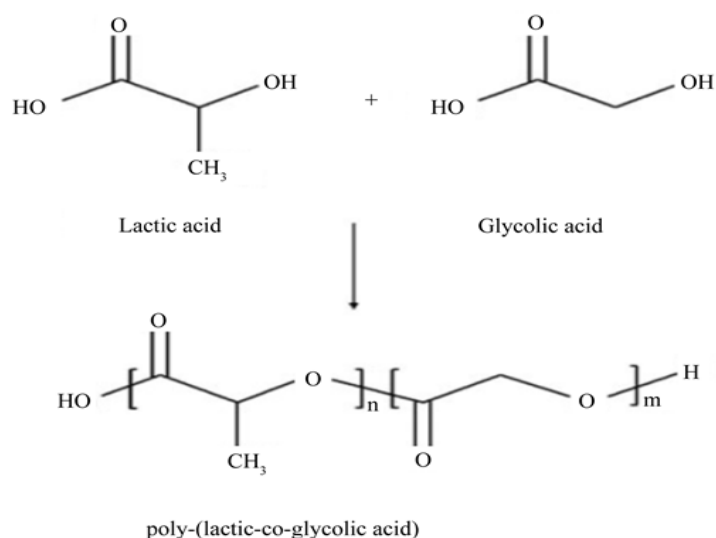
##### **Mechanical Properties:**

- The flexibility, tensile strength, and elasticity indicate the suitability of polymers for various dosage forms

##### **Various Polymers Used in Drug Delivery:**

##### • **PLGA**

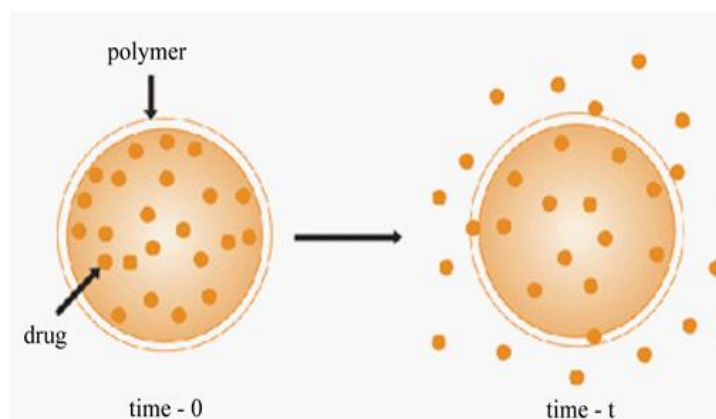
It is probably among the most popularly used biodegradable polymer because of its ability to hydrolyze to give rise to metabolite monomers, namely, lactic acid and glycolic acid. Minimal systemic toxicity is involved with PLGAs since these two monomers are endogenous and normally metabolized in the body through the Krebs cycle, thus providing avenues for the application of PLGA in drug delivery or biomaterial purposes. PLGA-nanoparticles enter cells using both fluid phase pinocytosis and clathrin-mediated endocytosis. The escape of PLGA-nanoparticles from endo-lysosomal compartments into the cytoplasm takes about 10 min after the initiation of cell culture<sup>[6]</sup>.



**Figure 1.1 Structure of Poly- (lactic-co-glycolic acid) (PLGA)**

PLGA is a synthetic biodegradable polymer that is used in drug delivery systems, and it is also known as a "smart polymer" because it has the ability to respond to stimuli. PLGA, a polyester composed of polylactic acid and polyglycolic acid, is one of the most highly characterized biomaterials for drug delivery in terms of design and performance. R and S designations denote asymmetric alpha carbon in polylactic acid classical stereochemical

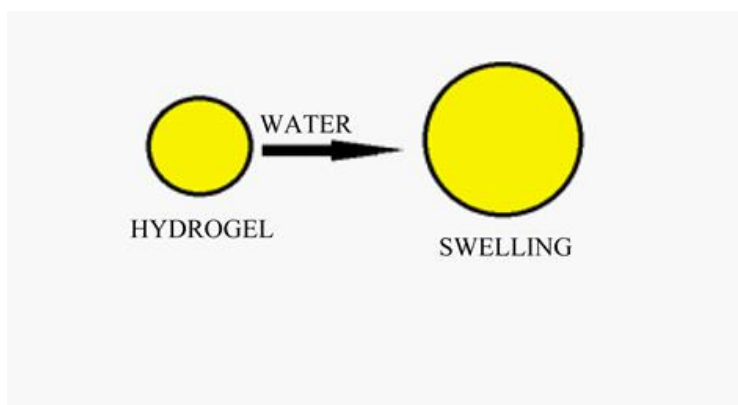
descriptors D and L, whereas their use seems more appropriate in contemporary settings. There are two enantiomeric forms of the polymer PLA: poly D-lactic acid (PDLA) and poly L-lactic acid (PLLA) (Figure 1.1). A common name for poly D, L-lactic-co-glycolic acid is PLGA, where D- and L- lactic acid forms are considered in equal ratio [7].



**Figure 1.2 Diffusion based drug delivery system**

Diffusion controlled drug delivery systems are classified into two types: reservoir systems (or core-shell systems) and matrix systems (one-block or monolithic systems). In reservoir systems, there are three phases, water diffusion, drug dissolution and drug diffusion, that occur in a sequence with an initial phase (Figure 1.2). The drug diffusion phase is the rate-limiting step as in the case of drug

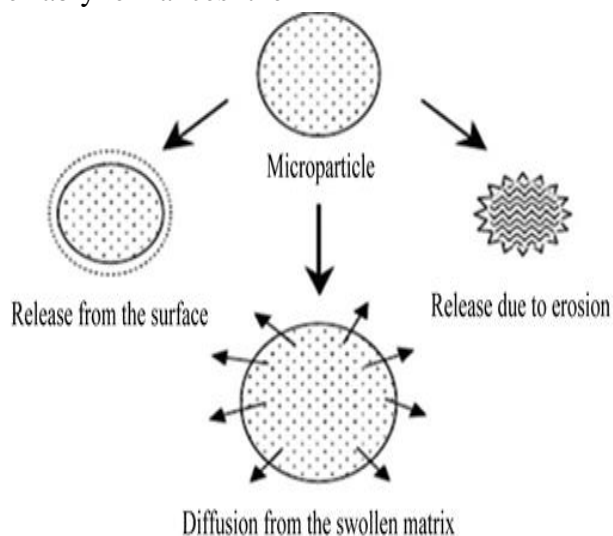
reservoir systems. As this kind of system does not have polymer barriers or boundaries, it shows a high initial drug release rate, followed by a low release rate with the function of the time because of the increasing distance for the accessible drug to diffuse to the surface. It results in dependency of the release rate on the shape and geometry of the drug vehicle [8].



**Figure 1.3 Hydrogel Based Drug Delivery System**

Hydrogels are three-dimensional (3D) networks of polymers built in such a way that they could absorb large amounts of water (up to thousands of times their dry weight) into their hydrophilic structure (Figure 1.3). Hydrogels that are synthetic in nature have shifted more interest to them than hydrogels that are natural-derived since they have a much-improved lifetime and capacity to absorb water than the natural-derived polymers. Nanoparticle usage also enables or preferably enhances the

crosslinking reaction process by either adsorbing or binding to polymer chains. Yet, it modifies the assembly properties of the hydrogel as well. By nature of its porous hydrogel, nanoparticles easily embed within a polymeric 3D-network. This attribute is needed for effective controlled release and may restrict some nanoparticles that serve as carriers for drug molecules and hydrogel functionalization <sup>[9]</sup>.



**Figure 1.4 Various Drug Release Mechanisms**

Another mechanism of drug delivery is swelling in polymers, used extensively for controlling release from a device. Swelling affects the chain mobility through water uptake, which brings the glass transition temperature lower. Drugs are then released only once the hydrogel polymer matrix shows enough flexibility for diffusivity and release rate. Swelling and consequent diffusion over the

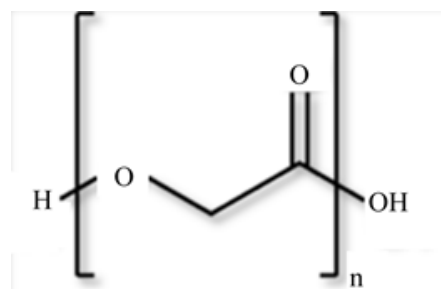
swollen polymer surface will affect water uptake and drug release (Figure 1.4). Diffusion is one of the most essential transport mechanisms for drug-delivery purposes. Diffusion has Brownian motion as the driving force behind it, which is random walking of particles, which could be nano, meso, or micro according to the law of Fick. It can happen over the time when it causes the erosion of



one carrier so that postapplication removal is not required, or it does not remain at the application site. This is also another advantage of use in tissue engineering. Mass loss occurs from a drug-delivery device due to erosion. The material may dissolve in an aqueous solution, while in other cases the material may be a degradable polymer. In this case, the material degrades into water-soluble oligomers, whereby the initial part of matrix erosion starts. There are two forms of erosion: surface and bulk. Surface erosion takes place on the surface of the material, while bulk erosion occurs when materials take a long time to degrade. After some critical degradation has happened, the whole material will be eroded. With surface-eroding polymers, drug release can be controlled through erosion. <sup>[10]</sup>.

- **PGA (Poly Glycolic Acid):**

Poly-glycolide or polyglycolic acid is the linear and the simplest aliphatic polyester. It is rigid and high in crystallinity. It is mostly insoluble in most organic solvents. This is a biodegradable polymer whose fibers exhibit high strength and modulus. Almost identical to those of other polyesters, processing of PGA takes the forms of extrusion, injection, or compression molding. The processing methods used determine properties and degradation characteristics of scaffolds made out of PGA. Glycolic acid, the product of degradation, is a natural metabolite, though its accumulation in tissues at high concentrations may induce local acidities potentially causing tissue damage. Many factors are cited to determine degradation rates in polyesters; one of them is the copolymer ratio, crystallinity and molecular weight, porosity, site of implantation, amount of residual monomer, configurational structure, morphology, and stresses (Figure 1.5).

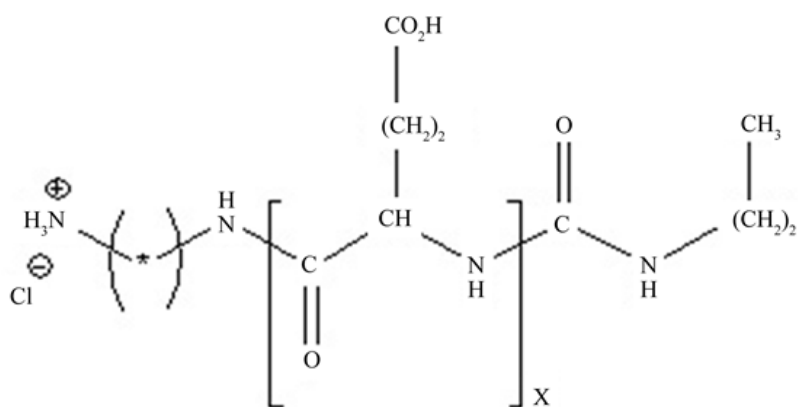


**Figure 1.5 Poly Glycolic Acid (PGA)**

It is a simple aliphatic linear polyester, poly glycolide or polyglycolic acid. PGA is a very stiff and crystalline polymer and is insoluble in most organic solvents. It is a biodegradable polymer having fibers of high strength and modulus. The processing method for PGA is similar to most polyesters, that is through extrusion, injection, or compression molding. Processing techniques impose properties and degradation characteristics of PGA scaffolds. Glycolic acid, the degradation product, is a natural metabolite, but on absorption in high concentrations, this can lead to a local acid concentration, causing damage to tissues. Numerous factors such as copolymer ratio, crystallinity, molecular weight, degree of porosity, implantation site, monomer residual amount, configurational structure, morphology and stresses determine the rate of degradation in polyesters <sup>[11]</sup>.

- **Poly-L-glutamic acid**

Poly ( $\alpha$ -L-glutamic acid) (PGA) is a such a class of synthetic polypeptides comprised of the monomeric unit  $\alpha$ -L-glutamic acid. Polyglutamic acid (PGA) is a polymer of amino acid glutamic acid (GA). Gamma PGA is formed by bacterial fermentation. Gamma PGA has a multitude of potential applications ranging from food to medicine. Water treatment is another application. It is being extensively used as a drug delivery adjuvant in cancer treatment (Figure 1.6).



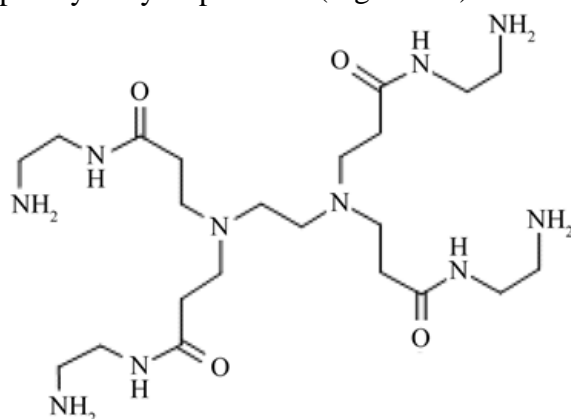
**Figure 1.6 Structure of Poly-L- glutamic acid**

Owing to their intrinsic characteristics comprising biocompatibility, biodegradability, non-immunogenicity, etc., PGA-based nanomaterials are widely used in different biomedical fields such as cancer therapy, wound healing, medical devices, bio-sensing, and tissue regeneration <sup>[12]</sup>.

- **Pamam [Poly (amidoamine)]**

PAMAM, which is short for "polyamidoamine dendrimers," is a completely hydrophilic

hyperbranched polymer, first produced by Tomalia way back in 1979.<sup>19</sup> These dendrimers are synthesized by chemical processes diverging from an ethylenediamine core followed by amidoamine branching structure. This synthesis pattern alternatively leads to amine-terminated full-generation or carboxyl-terminated half-generation dendrimers with each addition step (Figure 1.7).

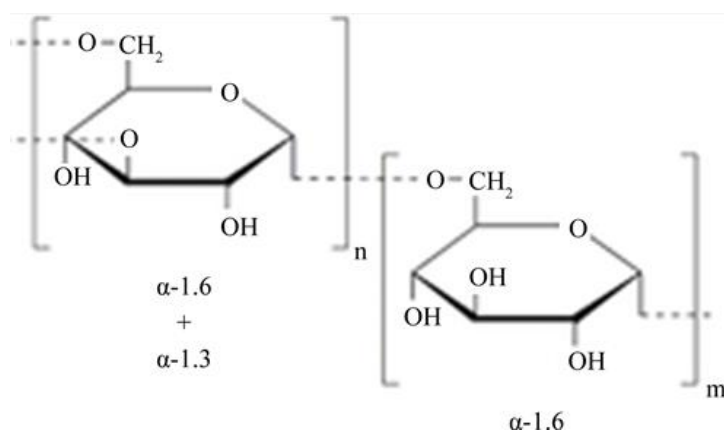


**Figure 1.7 Structure of PAMAM [Poly (amidoamine)]**

The number of functional groups doubles when an increase in generation number occurs while the dendrimer's diameter increases approximately to 1 nm. PAMAM dendrimers have an interestingly low polydispersity because of very tunable and controlled syntheses. Full generation of PAMAM dendrimers contains primary amines on its surface (pKa = 6.85) and tertiary amine groups within its core (pKa = 3.86) <sup>[13]</sup>.

- **Dextran:**

Dextran is defined by *Leuconostoc mesenteroides* which is actually a lactic-acid bacterium without which it is impossible to synthesize dextran using sucrose. It contains a glucan which is (16)-linked and has side chains that are attached to the backbone of 3-positions of glucose units. The straight chain consists of  $\alpha$ -1,6 glycosidic linkages between the molecules of glucose. The branching starts from  $\alpha$ -1,3 linkages (Figure 1.8).



**Figure 1.8 Structure of Dextran**

DEX is the most common type of glycan and it is mainly of three types. There is the first category with a main chain of residues which are  $\alpha$ -D-(1 $\rightarrow$ 6) linked glucose and are independently tiled with  $\alpha$ -D-(1 $\rightarrow$ 2),  $\alpha$ -D-(1 $\rightarrow$ 3),  $\alpha$ -D-(1 $\rightarrow$ 4) branches. This is the second type of the DEX where  $\alpha$ -D-(1 $\rightarrow$ 3) and  $\alpha$ -D-(1 $\rightarrow$ 6) Linear linkage sequences and  $\alpha$ -D-(1 $\rightarrow$ 3) branches are interlaced with each other. Finally, the third and the last type of DEX is formed by completely consecutive  $\alpha$ -D-(1 $\rightarrow$ 6) linear linkages with  $\alpha$ -D-(1 $\rightarrow$ 6) bridges. The molecule configuration of DEX also affects the capacity of the biopolymer to dissolve in the aqueous medium and hence the need for selective modification with hydrophilic and hydrophobic groups. The

compounds having mostly  $\alpha$ -D-(1 $\rightarrow$ 6) charm are the most soluble whereas the DEX having 43%  $\alpha$ -D-(1 $\rightarrow$ 3) side chain is insoluble in water. In terms of molecular structure, DEX is a biopolymer consisting of the higher than 1000 Dalton molecular mass and the linear chain of  $\alpha$  (1-4) and  $\alpha$ -linked D-glucopyranosyl units only. It can also be easily functionalized due to its several hydroxyl functionalities which may be functionalized or bag boned bioactive molecules. The undecorated DEX has also gone through a chemical crosslinking, thermal cross linking to form hydrogels, thin films, nano systems (in the form of a mat or a coating), and so on, for the purpose of controlled release of drugs <sup>[14]</sup>.

#### Classification Of Polymers <sup>[15]</sup>:

Category	Subcategory	Example
Based on Origin	Natural	Chitosan, Alginate, Gelatin
	Synthetic	Poly(lactic-co-glycolic) acid (PLGA), Poly ethylene glycol (PEG), Polycaprolactone (PCL)
Based on Degradability	Biodegradability	Poly(lactic-co-glycolic) acid (PLGA), Poly ethylene glycol (PEG), Polycaprolactone (PCL)
	Non- Biodegradability	Polyethylene (PE), Poly (methyl methacrylate) (PMMA), Polydimethylsiloxane (PDMS)
Based on Drug Release	Diffusion- Controlled	Ethyl-cellulose, Hydroxypropyl methylcellulose (HPMC)
	Erosion- Controlled	Poly(lactic-co-glycolic) acid (PLGA), Polylactic Acid (PLA)
	Stimuli- Responsive	Chitosan, Poly(N-isopropylacrylamide) (PNIPAAm)
Based on Functionality	Matrix- Forming	Hydroxypropyl methylcellulose (HPMC), Poly(lactic-co-glycolic) acid (PLGA)



	Mucoadhesive	Chitosan, Carbopol
	Targeted Delivery	PEGylated Polymers, Nanoparticles

### Application Of Polymer In Drug Delivery System <sup>[15]</sup>:

- Reservoir Systems
- 2. Ocusert System
- 3. Matrix Systems
- 4. Swelling-Controlled Release Systems
- 5. Biodegradable Systems
- 6. Osmotic Control Drug Delivery Systems
- 7. Introduction: Principles of Controlled Drug Delivery
- 8. Progestasert Systems
- 9. Reservoir Design Transdermal Patch
- 10. Matrix Systems
- 11. Stimuli-Responsive Drug Release
- 12. Ultrasound-Responsive Drug Release
- 13. Temperature-Responsive Drug Release
- 14. Drug Release in Response to pH
- 15. Electric Current-Responsive Drug Release
- 16. Polymer-Drug Conjugates

### Novel Technique of Polymerization <sup>[16]</sup>:

Natural polymers like rubber, wood, and silk have existed for quite a long time in the history of mankind. People used these natural polymers to make tools, clothes, etc., whereas in the late 19th century artificial polymers like phenolic resins and polyformaldehyde were developed by researchers. When synthetic polymer technology was first emerging, the researchers were, in essence, involved in synthesizing polymers by chemical reactions. In the 1940s, a combination of chain and step polymerization led to the synthesis of nylon,

while the exploration of catalytic polymerization was next ushered in by the Ziegler-Natta catalyst in the 1950s. Interests in polymer synthesis go back a long way due to the importance of virtually all polymers in many applications.

#### • Atom Transfer Radical Polymerization:

The catalysts are generally transition metal complexes with Cu, Fe, Ru, Ni, or Os using alkyl halides as initiators (R-X). In ATRP, the concept involves the activation of dormant species by the transition metal complexes and the subsequent generation of radicals from such species via an electron-transfer process. The metal is then oxidized to a higher oxidation state. The equilibrium is formed extremely fast in this reversible system, thus favoring the transfer of free radicals to the side with a much less concentration of free radicals. The number of chains will thus depend on the amount of initiator. During the propagation of the growing chains, the active or dormant formation probability is the same for both the chains or the monomers. This gives a method of preparing polymers with similar molecular weights and narrow molecular weight distributions. It's worth noting that ATRP has quite some advantages in being very stable, tolerating many functional groups in the monomer or initiator, including allyl, amino, epoxide, hydroxyl, and vinyl <sup>[17]</sup>. The following diagrams will show chemical equations for some basic ATRP reactions as shown in (Figure 19).

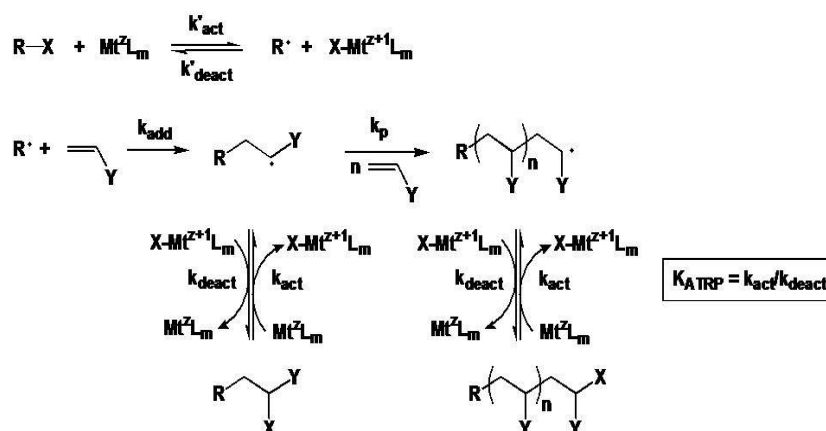


Figure 1.9 Basic equation of ATRP

### • Microfluidic-Assisted Synthesis of Polymer Particles [18]:

There are generally methods in the heterogeneous polymerization that have been used so as to synthesize polymer particles from a few micrometers to a few hundred micrometers, while on other occasions, precipitation with inorganic substances is also a form of syntheses. The two methods might significantly influence the particles' size distribution, one of the major features of the unconventional process, in which particle size, shape and composition can be controlled precisely. The basic concept behind the microfluidics-assisted mechanism is emulsifying two incompatible liquids in a narrow capillary tube, which causes the development of polymer particles smaller by about 2-10% compared with the original droplets. Presently there are two kinds of devices available: (1) Direct polymerization of two incompatible liquids into monomer droplets after emulsification. (2) Continuous flow projection lithography by direct polymerization.

#### 1) Direct polymerization of two incompatible liquids into monomer droplets after emulsification:

There are two different techniques for emulsifying polymerizable liquids. Each method is based on a similar principle, but the first method has both the continuous phase and the dispersed phase flowing within the same tube, while the second separates the two: the continuous phase flows in a tube and

the dispersion flows through a small-sized capillary.

#### 2) Continuous flow projection lithography by direct polymerization:

With this particular method, ultraviolet light is used to bombard the substance, which is then projected thru the objective lens of an optical microscope onto a polymer solution flowing in a microchannel. Essentially any desired shape of the particle can be polymerized and 'printed' in the flowing monomer solution by use of a mask placed on the field cut-off plane of the microscope.

### CONCLUSION:

Polymeric pioneers and their achievements have completely opened doors to this new popular belief in drug delivery from the old barbaric tradition of therapy for precision with high efficiency, a specific reduction in toxicity, and mechanisms of targeted release. Advanced polymeric materials have been utilized to develop highly sophisticated forms of drug carriers: nanoparticles, micelles, and hydrogels, and carefully optimize bioavailability and therapeutic effectiveness. The promise of such designs is enormous in treating complicated diseases such as cancer, neurodegenerative disorders, and autoimmune diseases. Since then, the field will move on: the combination of smart polymers, biomimetic systems, and nanotechnology will enhance precision medicine, ensuring the most personalized treatments with the least side effects.

As always, hurdles remain-scaling up, regulatory approval, and long-term biocompatibility-for a brighter future indeed, as ongoing research and interdisciplinary collaboration propel the next generation of polymer drug delivery systems. This is the process of redefining modern medicine with more appropriate and patient-exclusive therapeutic solutions.

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