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Chapter

Introductory Chapter: Organic Polymer - Graft Copolymers

Arpit Sand and Aparna Vyas

Polymers, high molecular weight compounds, have most essential position in the materials field today even though have been introduction in meaning full logic more recently. In performance, characteristics, and application predictions, polymers offer novelty and usefulness not to be found in other kinds of materials. The rapidity of the all-round developments in polymer science and technology and the unique pace of application development and developments in the design of products and parts and components of polymer processing equipment necessitate fresh efforts in organizing old and established thoughts, ideas, concepts, and practices and updating them in the light of the latest unfolding polymer. Polymer constitutes a diverse range of light- and energy-efficient materials discovered and developed in a large measure out of the sheer necessity of meeting the growing needs and demands of our higher-profile society. The present level of sophistication, growth, and advancements of our expanding society has been made possible in a large measure through continued imaginative and creative efforts of scientists, engineers, and technologists in the polymer field.

In recent years there is a considerable demand for specialty supplies, and there is an increasing affinity to design "intelligent polymers," i.e., specialty polymers, which extend the scope of polymeric materials. Natural polymers have been used throughout the ages. From the beginning man has depended upon animal and vegetable matter for nutrition, shelter, warmth, and other requirements and desires. It is utilized in the field of pharmacology, diagnosis, and artificial respiration and in creation of articles of patient care. Commercially accessible synthetic polymeric materials are long lasting and have noble mechanical properties such as tensile strength and abrasion resistance, but because of the lack of functional groups in them, they resist dyeing and resist chemical reactions. The properties can be further improved by introducing various functional groups into their molecules. This ranges the scope of polymeric materials. Efforts have been made to use readily available natural polymers such as cellulose, proteins, gums and rubber, etc., for making polymers better properties. Copolymerization is an important method for the modification of polymers.

Copolymerization is defined as "a process in which two or more structurally different monomers are incorporated into the same polymeric chain." The properties of polymer produced by copolymerization can be varied over a wide range by adjusting the monomer ratio. Copolymerization involves a chemical reaction between two or more different monomers, which results the formation of following different types of copolymers.

1. Random copolymer

The distribution of the monomer units in the polymer chain does not follow any definite sequence:

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—M_1------M_1------M_2------M_1------M_2------M_1------M_3------

This type of copolymer is produced in bulk, aqueous, suspension, or emulsion using free radical initiators of peroxide type or redox systems.

2. Alternate copolymer

In these copolymers the monomers are arranged in an alternate sequence. These monomer units react with a high degree of order forming a polymer chain having a degree of alteration as

—M_1—M_2—M_1—M_2—M_1—

Special methods are used for manufacturing alternating copolymers. The reactivity of polar monomers can be enhanced by complexing them with metal halide or organo-aluminum halide. These complexed monomers participate in one electron transfer reaction with either an uncomplexed monomer or another electron donor monomer.

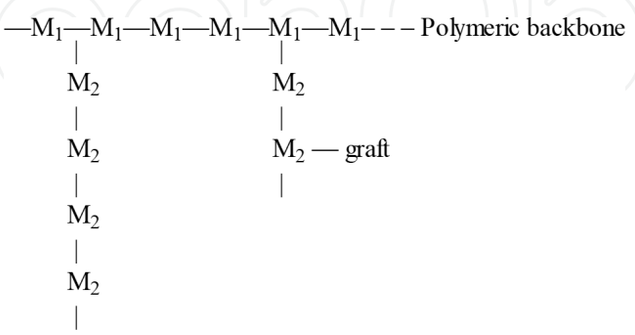
3. Block copolymer

These copolymers are built up of chemically different terminally connected segments. Block copolymers are generally prepared by sequential anionic addition or ring opening or step growth polymerization:

—M_2—M_2—M_2—M_1—M_1—M_1—

4. Graft copolymer

Graft copolymers are branched molecules where the main chain is made entirely of one repeat unit, while branch chains are made of yet additional repeat unit. The structure of such copolymer may be represented as



Schematic representation of graft copolymer

Grafting by most of the known methods includes the attachment of only a small number of side chains on the backbone polymer. During grafting there is little agitation, and, therefore, the bulk properties of polymer undergo little changes. The side chains disturb the uniformity of lattice, and the crystalline content of such polymer becomes smaller with an increasing degree of branching. However, the

most attractive method of modifying the nature of polymer is graft copolymerization.

Graft copolymers are generally prepared by free radical and anionic or cationic initiation process creating the active centers at polymer backbone. The mode of synthesis was first recommended by Flory [1] in 1937. The concept of graft copolymerization was first familiarized by Bandel and Alfrey [2]. Thus, graft copolymer is a macromolecule consisting of a block of constitutional units of backbone and blocks of unit grafts attacked to the backbone.

Random and alternating copolymers, ready by polymerizing two kinds of monomers, possess better properties than constituent homopolymer; on the other hand, graft and block copolymers exhibit many properties that are characteristics of each constituent homopolymer. Conditions are usually so chosen as to retain the desirable properties and to eliminate the less desirable properties of the individual block or graft components. By grafting, some new properties allied with the side chains are added without drastically changing the basic properties of the substrate polymer.

The properties such as thermal stability and improvement in metal ion uptake, viscosity, ion exchange capacity, resistance to biodegradation, flocculation, etc. have been achieved on natural and synthetic polymers over graft copolymerization [1, 3–14]. These modified polymers called as graft copolymers have been found to be useful in oil recovery [15–17].

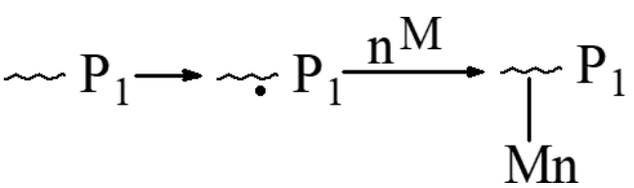
Graft copolymer of vinyl monomers bearing (+ve) charge or episulfide groups onto certain fibers has newly been reported to possess antibacterial activity. Synthetic MMA-grafted polysaccharides have been used as a hydrophilic matrix for controlled release forms [18].

5. Synthesis of graft copolymers

Most of the method of producing graft copolymers involves the use of radical polymerization although ionic graft copolymerizations are also possible. Graft copolymerization can be carried out either in homogeneous or heterogeneous systems depending whether the polymer being grafted and monomer is soluble or insoluble in the solvent being used. Usually grafting can occur by either the "grafting from" or "grafting onto" method as illustrated by the following:

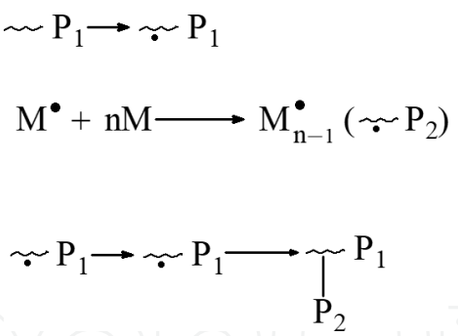
5.1 Grafting from

An active site generated along a polymer backbone starts to propagate monomer and thus produces branches.



5.2 Grafting onto

A growing polymer chain P_2 attacks another polymer P_1.



The preparation of a graft (−ve) copolymer in most cases starts from a homopolymer (A) which is suitably activated, and then the growth of the graft of monomer (B) is initiated. The model must fulfill the following requirements:

1. The copolymer is of poly (A-g-B) type.

2. The probability that a graft will grow on a given unit of the backbone is not contingent on the number or size of the other grafts in the molecule or on the size of the backbone to which it is attached.

The efficiency of grafting is dependent upon several competing reactions:

- Competition between the various species present in the reaction mixture such as monomer, solvent, and backbone for the growing polymer radical, which means that there is competition between chain growth and various chain transfer steps.

- Competition for the initiator radical between monomer and backbone.

- Competition among the terminating process such as disproportionation after the polymer radical has formed.

- Competition among the terminating process in growing grafted species.

If the termination occurs through recombination of rising polymeric chains, it should lower the grafting efficiency. But even though the efficiency of this process is low, it has received considerable use because the reaction is easily carried out. The other reaction parameters, such as concentration of the initiator monomer, temperature, and the time of reaction, affect the grafting efficiency. The nature of the initiating radicals appears to bear a strong influence on the efficiency of grafting.

The graft copolymer is detached from the homopolymer by the solvent extraction method. Often graft copolymer prepared from water-soluble backbone polymers and water-soluble vinyl monomers is also water-soluble. In such cases graft copolymer is precipitated by using appropriate precipitating agent, and homopolymer is also separated. This method of parting has been successfully applied in many systems [19–27]. However, if it is not possible to separate the homopolymer from graft copolymer, such products are referred to as composites. Evidence for grafting in such case has been gotten from turbidimetric studies [27, 28].

5.3 Method of grafting

Combination and characterization of graft copolymers have received considerable interest in recent years due to its industrial importance. The chemistry of graft copolymerization essentially involves the generation of active site on the backbone polymer where appropriate monomer can be grafted. Different methods of activation include:

I. Physical activation

II. Chemical activation

III. Radiation activation

5.3.1 Physical activation

Physical activation contains the application of stress to polymeric backbone swelling it with suitable solvents [7, 29]. Application of stress to polymeric backbone causes segmental motions and molecular flow, which may lead to bond scission and consequent formation of free radicals. Freezing and thawing of the polymer-monomer mixture also make active sites. Free radicals may also be generated by mastication and milling of the backbone polymer. Production of a polymer with pendant basic moieties was performed by grafting dimethylamino-ethylmethacrylate to linear low-density polyethylene (LDPE) in the melt in a batch-type internal mixer.

5.3.2 Chemical activation

This method of activation includes two different mechanisms:

i. Free radical mechanism

ii. Ionic mechanism

5.3.2.1 Free radical mechanism

5.3.2.1.1 Radical initiators

In the existence of radical initiators such as benzoyl peroxide (BPO), azobisisobutyronitrile (AIBN), persulfates ($S_2O_8^{2-}$), etc., grafting of vinyl monomers onto polymeric backbones involves generation of free radical sites by hydrogen abstraction and chain transfer processes as described below:

$$I_2 \rightarrow 2I$$

$$I + \mathrm{PH} \rightarrow P + I\,H$$

$$I + M \rightarrow \mathrm{IM}\ \overrightarrow{\mathrm{nM}}\ I - \mathrm{Mn} - M$$

$$\mathrm{PH} + I - \mathrm{Mn} - M \rightarrow P + I - (M)_{n+1}\text{–}H$$

$$P + M \rightarrow \mathrm{PM}\ \overrightarrow{\mathrm{nM}}\ P - \mathrm{Mn} - M$$

$$P + I - \mathrm{Mn} - M \rightarrow P - (M)_{n+1}\text{–}I$$

where I_2 represents initiator molecules and PH and M are the polymeric backbone and monomer, respectively.

The extent of grafting is dependent on various reaction parameters, such as concentrations of initiator and monomer, reaction time, temperature, etc. The nature of initiator and monomer influences the reactivity of initiator and monomer toward grafting. Misra et al. have observed that during grafting of vinyl monomer onto starch, wool, or rubber, conservative free radical initiators show different reactivity toward grafting.

Although this process is not very efficient, it has received considerable importance because it is industrially important. The major drawback of this process is that it produces considerable amount of homopolymer. Therefore, various radical initiators are employed to graft different vinyl monomers on natural and synthetic polymeric backbones so as to minimize the production of homopolymer.

5.3.2.1.2 Redox systems

In redox systems the free radicals, which initiate polymerization, are generated as transient intermediates in the course of redox reaction. Essentially this involves an electron transfer process followed by scission to give free radicals. A wide variety of redox reactions, linking both organic and inorganic components, are used for this purpose. These reactions take place in aqueous media and occur rather rapidly even at relatively low temperatures. The general mechanism of grafting involves an abstraction of the hydrogen atom from the backbone of the polymeric material by the transient radical formed during the redox reaction, thus generating macro radicals onto which the monomer molecules are added to produce graft copolymer.

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