



TECHNICAL NEWSLETTER

Polymerization - Creating the Chains

Introduction

In a prior newsletter entitled, "Chemical Resistance of Fluoropolymers," the basics of polymer structure in regard to the effect on chemical resistance was briefly discussed. In this current newsletter, we revisit that topic to discuss the mechanisms and methods used to create the long chains that are the basis of all polymers.

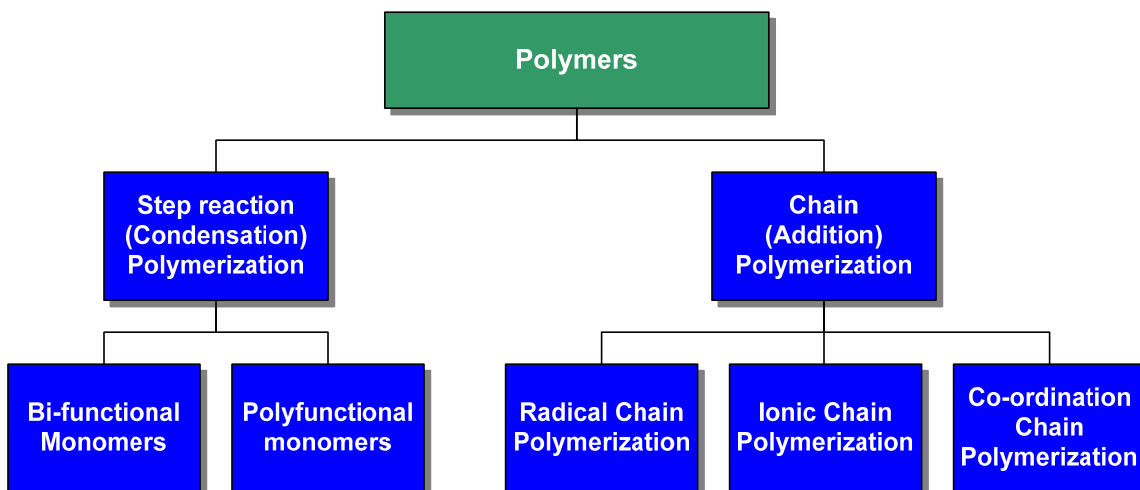
All polymers are long chain molecules made up of many (between 30 and over 100,000) repeated units of a basic building block or monomer. The words monomer and polymer are both made up of Greek words. The "mono" in monomer means single and the "mer" comes from the Greek word meaning part. Therefore, the monomer is a single part. The "poly" in polymer means many. Thus, a polymer is many parts, a collection of repeated parts in a single long chain.

The "mer" is the building block for the polymer. For example, polyethylene is made of repeated parts of ethylene joined together and polytetrafluoroethylene (PTFE) is made up of repeated parts of tetrafluoroethylene joined together in a long chain. The monomer building blocks are joined together by a process known as polymerization and the resulting long chain molecule is the polymer.

General classification of polymer products

The first broad classification of polymerization was suggested in 1929 by Wallace Hume Carothers, the inventor of Nylon, who divided polymerization into the condensation and addition methods. In 1953, Paul Flory changed the emphasis to the actual mechanism of formation. This is where condensation polymers are formed by stepwise condensation of reactive groups and addition polymers are formed from a chain reaction around an active center.

The two basic methods of polymerization used are the step (condensation) and the chain (addition) methods, but these can also be further subdivided as shown below:



The methods of polymerization

The distinguishing features of step and chain mechanisms are:

Step (Condensation) Polymerization	Chain (Addition) Polymerization
<ul style="list-style-type: none"> Any two molecular species present can react. Monomer disappears early in the reaction (i.e. at a degree of polymerization of 10 then < than 1% monomer remains). Polymer molecular weight rises steadily during reaction. Needs long times for high molecular weights. 	<ul style="list-style-type: none"> Only growth reaction adds repeating units one at a time. Monomer concentration decreases steadily during reaction. High polymer formed at once: polymer molecular weight changes little during the reaction. Long time produces high yields but little change in molecular weight.

A comparison of the step and chain methods of polymerization

Step reaction (Condensation) polymerization

The product formed in a condensation reaction is determined by the functionality of the monomers involved (i.e. the average number of reactive groups in each monomer molecule):

- Mono-functional monomers produce only low molecular weight compounds that, while polymers, are not generally processable plastics.
- Bi-functional monomers give linear polymers (i.e. terephthalic acid and ethylene glycol react and produce another bi-functional molecule, polyester).
- Poly-functional monomers (more than 2 functional groups per molecule) produce branched or cross-linked polymers and can lead to either thermoplastic or thermosetting products, depending on the functionality of the reactants. Typical examples of these are nylons



(polyamides), polyesters, alkyds, and phenol-formaldehyde resins. Generally, there are two monomers present and the product is a co-polymer.

Bi-functional monomers

The degree of polymerization (a measure of the numbers of repeat units in the chain) of a condensation polymer can be controlled by varying the time of reaction or by adjusting the temperature. Chilling the polymerizing material at the required degree of polymerization stops the reaction, but subsequent heating can lead to an unstable product. Normally, the reaction is stopped by adjusting the reacting mixture with the addition of a slight excess of one of the bi-functional reactants or by adding a small amount of a mono-functional reagent (i.e. stabilization of nylon by acetic acid). Care is necessary to get high degrees of polymerization since the loss of one ingredient, side reactions, or the presence of mono-functional impurities can reduce the degree of polymerization achieved.

In addition to conventional linear polymer formation, bi-functional monomers can react to give a cyclic product. The type of product is governed by the size of the ring that is formed. If less than 5 atoms or greater than 7 are present, then a linear polymer is usually formed. If a ring of 5 atoms can form, it will occur to the exclusion of a linear polymer. For six and seven, a mixture may be formed. The governing characteristic is the strain involved in forming the valence angles of the ring atoms.

Polyfunctional monomers

The use of a polyfunctional monomer allows the formation of a 3D network from chained branching and cross-linking. These cross-linked polymers have a greater rigidity and when a high degree of cross-linking takes place, the product is rigid and insoluble in most solvents. The point at which this occurs is the "gel point" and divides the mixture into two parts:

1. The gel is an infinitely large polymer network, insoluble in most non-degrading solvents.
2. The solvent remains soluble and can be extracted from the gel.

As the reaction proceeds, the solvent is converted to gel and the mixture is rapidly converted to an elastic material of infinite viscosity. The extent of reaction at which gelation will occur has been theoretically predicted by Carothers.

In many cases, a tri-functional unit is introduced in controlled quantities to a bi-functional mix to promote some cross-linking. Careful control of the quantities of the reactants is necessary to produce an end product with the required properties.



Chain (Addition) polymerization

There are three types of chain polymerization: radical, ionic, and co-ordination. The polymers formed through the chain (addition) method are always thermoplastics because of the essentially linear nature of the reaction. The monomers always contain a double bond and with the exception of fluorinated compounds, always contain the methylene group, CH_2 . The basic monomer is of the form:

$\text{CH}_2=\text{C.R}_1.\text{R}_2$ where R_1 and R_2 are additional groups or for fluorine based monomers: $\text{CF}_2=\text{CF}_2$ or $\text{CF}_2=\text{CClF}$

In this type of reaction, there is generally an active center associated with a single polymer molecule that is responsible for the addition to, and growth of, the chain. Polymer molecules are formed immediately and no species of molecular weight between the monomer and high molecular weight polymer are found. The active center can be one of three types: free radical, cation and anion.

Radical chain polymerization

In this type of chain polymerization a free radical mechanism is involved in splitting the double bond to allow chain building to begin.

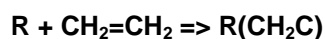
The free radical has an odd number of electrons and thus, an unpaired electron. These can be produced by a variety of methods such as:

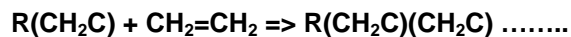
1. Thermal decomposition of organic peroxides, hydroxides, or diazo compounds (e.g. benzoyl peroxide at greater than 70°C decomposes to give benzoate radicals).
2. Photolytic decomposition of covalently bonded compounds (photoinitiation). For example, azobisisobutyronitrile decomposes under UV light in the 3600\AA region. This takes place at temperatures low enough that thermal decomposition does not occur and allows a very controlled source of free radicals.
3. Radiation dissociation of covalent bonds.
4. Redox initiation in aqueous solutions.

The process follows the steps of initiation, propagation and finally termination:

Initiation

When free radicals are generated in the presence of the double bond, the radical breaks the double bond, bonds to the monomer and regenerates another radical. This process continues to form the polymer:





Propagation

The addition can occur in either head-to-tail, head-to-head or tail-to-tail configurations. A random structure containing both arrangements is the normal form. As the polymer radical increases in length, it retains its activity at the growing end and successive monomers are added to propagate the chain. Individual chains are formed in short bursts of activity and not as a continuous process. However, the process of growth is very rapid and in some cases, the growth is explosive.

Termination

Propagation would continue until the monomer was exhausted were it not for the tendency of radicals to react in pairs and thus lose their reactivity. This is somewhat countered by the relatively low concentration of radicals compared with that of the monomer. Termination can occur by:

- Combination or coupling.
- Disproportionation - when this occurs a mix of saturated and unsaturated terminal groups is formed (e.g. PMMA at >60°C).
- Transfer agents - these are able to use up the free radical to prevent further chain growth (e.g. benzoquinone is often added to monomer solutions to prevent spontaneous polymerization and then removed prior to polymerization).

Ionic chain polymerization

In this type of polymerization, an ionic catalyst is used and this may be either a cation or an anion. In general, the three stages of initiation, propagation, and termination are present although the mechanisms are much different. The rate of polymerization is independent of temperature since no energy is needed for initiation and termination cannot occur by disproportionation (like ions repel). Since the termination reaction requires energy, whereas the propagation reaction does not, the degree of polymerization is inversely proportional to temperature.

Initiation of ionic polymerization usually involves the transfer of an ion or an electron to or from the monomer, with the formation of an ion pair. It is thought that the counter-ion of this pair stays closely bound to the ion. Ionic polymerization is usually carried out in an inert non-aqueous media (e.g. toluene) and the catalyst supplies both an ion and a counter-ion. Termination never involves two growing chains, but involves a uni-molecular reaction of a chain with its counter-ion or a transfer reaction leaving a species too weak to propagate.



Monomers with electron donating groups, which supply a high electron density at the double bond, favor polymerization by electron accepting initiators (i.e. cations). Typical catalysts for this are proton donors such as Lewis acids and Friedel-Crafts catalysts. Some examples are H_2SO_4 , HClO_4 , AlCl_3 , BF_3 , SnCl_4 . Monomers with electron abstracting groups, such as vinyl and vinylidene chloride, respond best to electron donors. Typical catalysts include alkali metals, alkoxides, alkyls, aryls, hydroxides and cyanides.

Co-ordination chain polymerization

This technique is sometimes called "stereo-specific" or "stereo-regular" polymerization, but the term "co-ordination polymerization" is used to suggest the existence of a force that governs the orientation with which a monomer approaches the growing end. The mechanism involved may be free radicals or ionic.

In 1953, Karl Ziegler used an organo-metallic catalyst to polymerize ethylene (normally requiring high pressure and temperature) at ordinary pressures and temperatures. The resulting polyethylene proved to be less branched and thus more crystalline and denser than usual. This also gave a higher melting point. Giulio Natta discovered that polymers, such as polypropylene, made using Ziegler catalysts, are different from normal polymers. Instead of the random atactic structure normally found, the groups attached to the carbon backbone were oriented to form a regular pattern. In one type, the side groups were all on the same side of the chain and in the other type there was a regular alternation of direction.

The Ziegler-Natta catalyst is a combination of a metal halide and an organo-metallic compound used in an inert solvent such as hexane (e.g. Titanium tetrachloride (TiCl_4) complexed with trialkyl aluminum ($\text{Al}[\text{C}_2\text{H}_5]_3$) which is used for industrial polyethylene production).

The important thing about co-ordination chain polymerization is that it allows us to make polymers that could not be made using different mechanisms. Using this technique, we can make polymers of a specific tacticity or structure and therefore of specific and very useful properties. Free radical polymerization can only be used to produce branched polyethylene and polypropylene cannot be polymerized at all. Ziegler-Natta catalysts solve this problem to allow the production of linear polyethylene (of specific tacticity and properties) and polypropylene can be polymerized into useful products.

The next major advance was the development of metallocene catalysts that are made up of metal ions and rings of carbon groups. Varying the properties of the metallocene catalyst allows exceptionally close control of the polymerization process and the properties of the resulting



polymer. This can be used to produce polymers with extremely high molecular weights and other tailored mechanical properties. Metallocene catalysts are an emerging phenomenon in polymerization technology.

Monomer	Radical	Cationic	Anionic	Coordination
Ethylene	Polymer formed	Polymer formed	No reaction or oligomers only	Polymer formed
Propylene	No reaction or oligomers only	No reaction or oligomers only	No reaction or oligomers only	Polymer formed
Isobutylene	No reaction or oligomers only	Polymer formed	No reaction or oligomers only	No reaction or oligomers only
Dienes	Polymer formed	No reaction or oligomers only	No reaction or oligomers only	No reaction or oligomers only
Styrene	Polymer formed	Polymer formed	Polymer formed	Polymer formed
Vinyl Chloride	Polymer formed	No reaction or oligomers only	No reaction or oligomers only	Polymer formed
Vinyl Fluoride	Polymer formed	No reaction or oligomers only	No reaction or oligomers only	No reaction or oligomers only
Tetrafluoroethylene	Polymer formed	No reaction or oligomers only	No reaction or oligomers only	Polymer formed
Vinyl ethers	No reaction or oligomers only	Polymer formed	No reaction or oligomers only	Polymer formed
Vinyl esters	Polymer formed	No reaction or oligomers only	No reaction or oligomers only	No reaction or oligomers only
Acrylonitrile	Polymer formed	No reaction or oligomers only	Polymer formed	Polymer formed

Types of chain polymerization for various monomers

Copolymerization

The methods of creating polymers from single monomers or homopolymers are also used to create copolymers. This is where two suitable monomers are polymerized together. The resulting polymer chain contains a mixture of monomer units, but this is not the same as a simple mixture of the two equivalent homopolymers. Even under extreme conditions, many monomers will not polymerize with themselves, but will copolymerize with other compounds (e.g. maleic acid anhydride will copolymerize with SO₂).



In radical addition copolymerization, the copolymer contains mixed repeat units and the product depends on the relative polarizability or the monomer reactivity ratios. A monomer reactivity ratio of < 1 means that the monomer favors addition to the opposite kind of radical. If both monomers do this exclusively, the result is a regular alternating copolymer. If the chain end has no influence on the addition (i.e. a monomer adds equally well to its own or the opposite kind of radical), the result is a random copolymer. If the ratio is > 1 , the monomer favors addition to its own kind and if this happens exclusively then two homopolymers are formed simultaneously. This reactivity depends on the monomer structure. If they have double bonds adjacent to phenyl or methyl groups, the activity is increased. Other groups vary in that some attract electrons away from the double bond and some direct them to it. This results in the double bond being polarized and the distribution of monomer units is affected by this polarization. Monomers with similar bond polarities are random and those with different polarities form alternating polymers.

In condensation copolymerization, there is usually no selective reactivity and the repeat units are randomly distributed in the same proportion as in the initial monomer mixture as in ABBAABBBABABBAAABAB.

In block copolymerization there are runs of one unit alternating with runs of another as in AAAAAAABBBBBBBBBBAAAAAAAAAABBBBBBBB.

In graft copolymerization, there is a backbone of units of one type onto which are grafted units of a different type. Therefore, if a monomer B is addition polymerized in the presence of preformed polymer A, which may be in solution or dispersed, some of B becomes grafted to A. The active centers for this can also be created by irradiation of the stock polymer.

Summary

Producing useful products from monomers involves complex chemistry and careful chemical engineering, but the work of pioneers such as Zeigler and Natta has changed the world in which we live. Natural polymers can be augmented by the chemist who is able to produce tailored products with specific properties. Polymerization is the first step in producing the products that are essential for our modern world.

How Zeus Can Help

With a technical inside and outside sales force backed up with engineering and polymer experts, Zeus is prepared to assist in material selection and can provide product samples for evaluation. A dedicated R&D department staffed with PHD polymer chemists and supported by a world-class analytical lab allows Zeus an unparalleled position in polymer development and customization.



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Zeus Industrial Products, Inc.
3737 Industrial Boulevard
Orangeburg, SC 29118
support@zeusinc.com