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An Analysis upon Concept and Technology of Polymerization: Principles and Mechanisms

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Abstract – The versatility of polymerization resides not only in the different types of reactants which can be polymerized but also in the variations allowed by copolymerization and stereoselective polymerization. Industrial suspension polymerization usually proceeds via a free-radical mechanism to produce polymer beads. The size distribution of the polymer beads is often similar to that of the polymerizing drops in the reactor. That distribution is determined by the operating mechanisms of drop breakage and of drop coalescence. Consequently, the value of the Reynolds Number is significant and a potential change in flow regime must be considered in reactor scale-up. The choice of suspending agent, which can be a watermiscible polymer or a finely divided particulate solid, can affect both the drop size and the properties of the final product. High monomer conversions are attainable but reaction kinetics can be affected by increases in drop viscosity during the polymerization. Drop mixing, which sometimes takes place, can be slow so that non-uniformity occurs in the final product. With copolymerization, complications can arise if the initiator, or one of the monomers, is partially soluble in the continuous phase. Adverse environmental impact of suspension polymerization can be avoided by cleaning and/or recycling of the continuous phase when it leaves the reactor.

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INTRODUCTION

Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules. The small molecules that combine with each other to form polymer molecules are termed monomers, and the reactions by which they combine are termed polymerizations.

There may be hundreds, thousands, tens of thousands, or more monomer molecules linked together in a polymer molecule. When one speaks of polymers, one is concerned with materials whose molecular wights may reach into the hundreds of thousands or millions. There has been and still is considerable confusion concerning the classification of polymers. This is especially the case for the beginning student who must appreciate that there is no single generally accepted classification that is unambiguous. During the development of polymer science, two types of classifications have come into use. One classification is based on polymer structure and divides polymers into condensation and addition polymers. The other classification is based on polymerization mechanism and divides polymerizations into step and chain polymerizations. Confusion arises because the two classifications are often used interchangeably without careful thought. The terms condensation and step are often used synonymously, as are the terms addition and chain. Although these terms may often be used synonymously because most condensation polymers are produced by step polymerizations and most addition polymers are produced by chain polymerizations, this is not always the case. The condensation–addition classification is based on the composition or structure of polymers. The step–chain classification is based on the mechanisms of the polymerization processes.

Differential scanning calorimetry (DSC) belongs to the family of thermal analysis methods. In general thermal analysis is the determination of substance properties in dependence on temperature. Thermodynamic data (heat capacity, phase transition, enthalpy) and kinetic data can be determined by methods of thermal analysis. The greatest advantage of thermal analysis is the easy handling and the output of valuable information from small samples of measured substance.

Other common thermal analysis methods are thermogravimetric analysis and differential thermal analysis. DSC measures the energy needed to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to the same temperature program. There are two types of DSC systems in common use.

1. Power compensation DSC

In this system the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are kept identical by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference.

2. Heat flux DSC

In heat flux DSC, the sample and reference are connected by a low resistance heat flow path (a metal disc) symmetrically. The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference.

The adoption of definite chemical structures for polymers has had farreaching practical applications, because it has led to an understanding of how and why the physical and chemical properties of polymers change with the nature of the monomers from which they are synthesized. This means that to a very considerable degree the properties of a polymer can be tailored to particular practical applications. Much of the emphasis in this paper will be on how the properties of polymers can be related to their structures. This is appropriate because we already have to methods of synthesis of monomers and polymers, as well as to the mechanisms of polymerization reactions.

The special technical importance of polymers can be judged by the fact that half of the professional organic chemists employed by industry in the United States are engaged in research or development related to polymers. The thermal polymerization of 1,3-cyclopentadiene by way of the Diels-Alder addition is not an important polymerization.

Polymerization is generally defined as intermolecular reaction between bifunctional or polyfunctional compounds (covering olefins, diolefins and related compounds) in a manner that makes the process functionally capable of proceeding indefinitely, avoiding formation of ring or cyclic structures. Functional groups or atoms through reactions of which polymerization of different kinds take place are: reactive hydrogen ($–H$), hydroxyl group ($–OH$), halogen atom ($–Cl$, $–Br$), carboxyl group ($–COOH$), amino group ($–NH2$), isocyanate group ($–NCO$), aldehyde group ($–CHO$), double bond ($C = C$) etc.

(a) Functionality Principle: According to the functionality principle and concept, each of the reacting molecules taking part in polymerization must at least be bifunctional, giving the minimum average functionality for the system as 2. For reaction between molecules containing different kinds of functional groups, the average functionality is calculated on the basis of stoichiometric equivalence of the two kinds of mutually reacting functional groups. Thus, for reaction between a dicarboxylic acid and a trihydric alcohol, to strike stoichiometric equivalence of $– COOH$ and $– OH$ groups, the diacid and the triol should be used in a molar ratio of 3 : 2 which would then give the average functionality for the system as 12/5, i.e., 2.4, which is less than the arithmetic average (5/2 = 2.5) for the said functional system. Thus, on the above basis of stoichiometric equivalence of reactive functional groups, a system having a polyfunctional compound (functionality of 3 or more) bearing a given kind of functional group (say, $– OH$) and a related monofunctional compound bearing a different kind of functional group (say, $– COOH$), would give an average functionality less than 2. So, for any system, if one type of reacting molecules are monofunctional then the system would fail to yield polymer molecules. On consideration of functionality, a double bond ($C = C$), bearing two π electrons, would be viewed

as bifunctional and in fact, on thermal or photo activation, the π bond may open up to yield a biradical intermediate.

(b) Basic Features of Step–Growth or Condensation Polymerization: Condensation polymerization of a selected, suitable functional system (also viewed as the monomeric system) allows the monomeric bifunctional or polyfunctional molecules to duly condense inter- molecularly in a manner that permits molecular growth or chain extension reactions to proceed in controlled, distinguishable, steps. The sequence of reactions is normally associated with the formation of a condensed interunit chemical link and liberation of a small byproduct such as H_2O, HCl, etc. at each step; a sequence of step reactions for bifunctional polyesterification

HISTORICAL PERSPECTIVE

Man's quest for new and improved materials has been expanding with time and it can be said to be unending. The materials that have grown into familiarity and acceptance with the ages since the dawn of man's existence on the mother planet, the Earth are: pieces of rocks and stones, sand, soil and various ceramic items; nails, horns, hydes, skins and bones of animals; wood, leaves and plant fibres, covering grass and straw, cotton, coir, jute, hemp, hair, wool and many other fibres of plant and animal origin; silk fibre of insect origin; natural adhesive / film – forming gums and resins (e.g. agar, algies, rosin, shellac etc.); fossil fuels, viz., coal, lignite, natural gas and petroleum; glass and quartz, and metals and alloys extracted from minerals and ores. Polymers, as a class of materials with potential for use as rubbers, resins, plastics and composites, and as adhesives, laminates and coatings came nearly in the end of the chain of discoveries and developments of materials.

Unfolding of the science of polymers and polymer – based materials really had its beginning and headway in the second and third decade of the twentieth century.

Though introduced very late in the chain of materials, polymers occupy a major place and pivotal position in our materials map today. In application prospects and performance characteristics and in property range and diversity, they offer novelty and versatility that can hardly be matched by any other kind of materials. Polymers have gone deep, and far and wide in moulding the present – day human civilization and culture.

Even though scientists, particularly the chemists used to talk about polymers earlier to the early twentieth century, there remained a lot of confusion over the basic understanding of the structures of polymer molecules. It was a common experience for chemists working with polymers that most such materials were very viscous and tacky under melt or solution conditions. One could readily spread the melt or solution into thin films or draw them into fine filaments. In solution, they were recognized more as colloids or associated molecules. Attempts to find their molecular weights from dilute solutions in suitable solvents by cryoscopy often produced irreproducible, doubtful and uncertain and sometimes very high values. For natural rubber, rayon and cellulose derivatives, molecular weights ranging 45,000 – 50,000 or even higher were measured. Such high molecular weight values implied that the relevant polymer molecules were really very large; but this view – point was not favoured or accepted in view of a total lack of structural concept about such large or big molecules. The chemists continued to favour the concept of large associations of much smaller molecules of short – chain or cyclic structures. A state of growing dilemma and confusion imparted fresh impetus to the thinking about the size, shape, complexity, and behavioral patterns of the molecular systems called polymers.

CHAIN – GROWTH (ADDITION) POLYMERIZATION

Chain – growth or addition polymerization is a process by which unsaturated (olefinic, diolefinic, vinylic) monomers are converted to polymers of high molecular weight exhibiting the characteristics of typical chain reactions that takes place very fast. Such very fast, or the so called explosive reactions are typified by three successive, distinguishable stages, viz., (i) triggering off or initiation of the chain process, (ii) propagation of the chain or the chain – growth process, and (iii) cessation of the chain – growth process, commonly referred to as chain termination.

The chain polymerization may be initiated or induced by heat, light or other radiations and by a host of catalysts, called initiators. If induced by light, the process is referred to as photo polymerization. The chain propagation may take place by free radical or ionic (cationic or anionic) mechanisms, depending on the initiator system used and the prevailing polymerization environment.

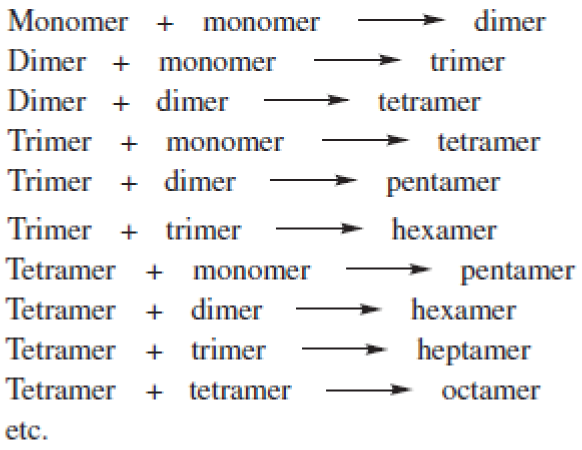
POLYMERIZATION MECHANISM

In addition to the structural and compositional differences between polymers, Flory [1953] stressed the very significant difference in the mechanism by which polymer molecules are built up. Although Flory continued to use the terms condensation and addition in his discussions of polymerization mechanism, the more recent terminology classifies polymerizations into step and chain polymerizations.

Chain and step polymerizations differ in several features, but the most important difference is in the identities of the species that can react with each other. Another difference is the manner in which polymer molecular size depends on the extent of conversion.

Step polymerizations proceed by the stepwise reaction between the functional groups of reactants as in reactions such as those described by Eqs. 1-1 through 1-3 and Eqs. 1-6 through 1-8. The size of the polymer molecules increases at a relatively slow pace in such polymerizations.

One proceeds from monomer to dimer, trimer, tetramer, pentamer, and so on until eventually large-sized polymer molecules have been formed. The characteristic of step polymerization that distinguishes it from chain polymerization is that reaction occurs between any of the different-sized species present in the reaction system.


Monomer + monomer → dimer
Dimer + monomer → trimer
Dimer + dimer → tetramer
Trimer + monomer → tetramer
Trimer + dimer → pentamer
Trimer + trimer → hexamer
Tetramer + monomer → pentamer
Tetramer + dimer → hexamer
Tetramer + trimer → heptamer
Tetramer + tetramer → octamer
etc.

The situation is quite different in chain polymerization where an initiator is used to produce an initiator species R^* with a reactive center. The reactive center may be either a free radical, cation, or anion. Polymerization occurs by the propagation of the reactive center by the successive additions of large numbers of monomer molecules in a chain reaction. The distinguishing characteristic of chain polymerization is that polymer growth takes place by monomer reacting only with the reactive center. Monomer does not react with monomer and the different-sized species such as dimer, trimer, tetramer, and n-mer do not react with each other. By far the most common example of chain polymerization is that of vinyl monomers.

The typical step and chain polymerizations differ significantly in the relationship between polymer molecular weight and the percent conversion of monomer. Thus if we start out step and chain polymerizations side by side, we may observe a variety of situations with regard to their relative rates of polymerization. However, the molecular weights of the polymers produced at any time after the start of the reactions will always be very characteristically different for the two polymerizations. If the two polymerizations are stopped at 0.1% conversion, 1% conversion, 10% conversion, 40% conversion, 90% conversion, and so on, one will always observe the same behavior. The chain polymerization will show the presence of high-molecular-weight polymer molecules at all percents of conversion. There are no intermediate-sized molecules in the reaction mixture—only monomer, high-polymer, and initiator species. The only change that occurs with conversion (i.e., reaction time) is the continuous increase in the number of polymer molecules (Fig. 1a). On the other hand, highmolecular-weight polymer is obtained in step polymerizations only near the very end of the reaction (>98% conversion) (Fig. 1b). Thus both polymer size and the amount of polymer are dependent on conversion in step polymerization.

The classification of polymers according to polymerization mechanism, like that by structure and composition, is not without its ambiguities. Certain polymerizations show a linear increase of molecular weight with conversion (Fig. 1c) when the polymerization mechanism departs from the normal chain pathway. This is observed in certain chain polymerizations, which involve a fast initiation process coupled with the absence of reactions that terminate the propagating reactive centers. Biological syntheses of proteins also show the behavior described by Fig. 1c because the various monomer molecules are directed to react in a very specific manner by an enzymatically controlled process.

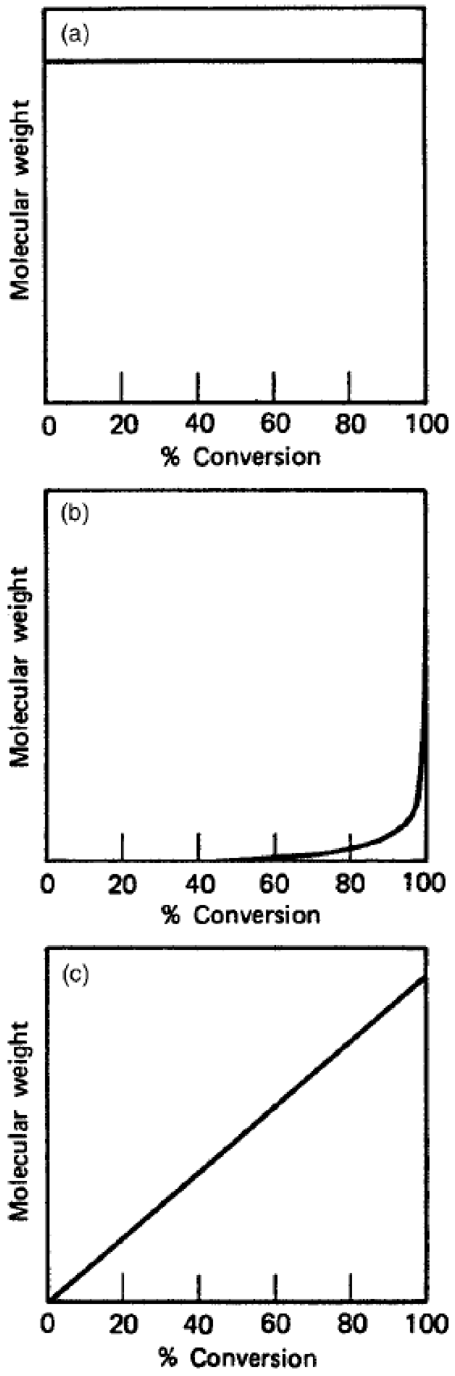


Fig. 1 Variation of molecular weight with conversion; (a) chain polymerization; (b) step polymerization; (c) nonterminating chain polymerization and protein synthesis.

The International Union of Pure and Applied Chemistry [IUPAC, 1994] suggested the term polycondensation instead of step polymerization, but polycondensation is a narrower term than step polymerization since it implies that the reactions are limited to condensations—reactions in which small molecules such as water are expelled during polymerization.

The term step polymerization encompasses not only condensations but also polymerizations in which no small molecules are expelled. An example of the latter is the reaction of diols and diisocyantes to yield polyurethanes (Eq. 1-6). The formation of polyurethanes follows the same reaction characteristics as the formation of polyesters, polyamides, and other polymerizations in which small molecules are expelled.

Ring-opening polymerizations point out very clearly that one must distinguish between the classification of the polymerization mechanism and that of the polymer structure. The two classifications cannot always be used interchangeably. Polymers such as the polyethers and polyamides produced in Eqs. 1-10 and 1-11, as well as those from other cyclic monomers, must be separately classified as to polymerization mechanism and polymer structure.

These polymers are structurally classified as condensation polymers, since they contain functional groups (e.g., ether, amide) in the polymer chain. They, like the polyurethanes, are not classified as addition polymers by the use of Carothers' original classification. The situation is even more complicated for a polymer such as that obtained from E-caprolactam. The exact same polymer can be obtained by the step polymerization of the linear monomer E-aminocaproic acid. It should suffice at this point to stress that the terms condensation and step polymer or polymerization are not synonymous nor are the terms addition and chain polymer or polymerization, even though these terms are often used interchangeably. The classification of polymers based only on polymer structure or only on polymerization mechanism is often an oversimplification that leads to ambiguity and error. Both structure and mechanism are usually needed in order to clearly classify a polymer.

SUSPENSION POLYMERIZATION PROCESSES

Suspension polymerization is used for the commercial manufacture of many important polymers including poly(vinyl chloride), poly(methyl methacrylate), expandable polystyrene, styrene–acrylonitrile copolymers and a variety of ion exchange resins. In suspension polymerization, drops of a monomer-containing phase are dispersed in a continuous liquid phase and polymer is produced inside the drops. In many cases, the monomer contains no diluent and the chemical reactions that occur inside the drops are very similar to those that are found in bulk polymerization. In most suspensions, polymer is formed via a chain reaction mechanism that includes the following steps

$$\text{Initiation:} \qquad I \rightarrow 2A^*$$

$$A^* + M \rightarrow AM^*$$

$$\text{Propagation:} \qquad AM_n^* + M \rightarrow AM_{n+1}^*$$

$$\text{Termination:} \qquad AM_n^* + AM_m^* \rightarrow AM_{n+m}A$$

$$AM_n^* + AM_m^* \rightarrow AM_n + AM_m$$

$$\text{Transfer:} \qquad AM_n^* + T \rightarrow AM_n + T^*$$

Here, M is the monomer and A^* could be an anion, a cation or a free radical. In most industrial processes M is a vinyl compound and a free-radical chain mechanism is used.

Then, the growing polymer chains, AM_n^*, are written as AM_n□. That species has a short life-time (usually << 1 sec) and completed polymer molecules are formed throughout the process. The generation of radicals, A□, is usually induced by thermal decomposition of an organic initiator, I, that is soluble in the monomer. Organic peroxides are often used as initiators. T represents any species that reacts as a chain transfer agent. T can be monomer, polymer, a solvent or a species that is added specifically to function as a chain transfer agent. If T^* is sufficiently active it can behave as A^* and initiate a new polymer chain. In some cases, such as the polymerization of vinyl chloride, chain transfer to monomer is significant and it has a major effect on the average molecular weight of the polymer. Suspension polymerization has been reviewed previously by Yuan et al., Vivaldo-Lima et al., and Arshady.

Although the polymerization chemistry which occurs in the dispersed phase may be similar to that which occurs in the equivalent bulk process it will not be identical unless the monomers and initiator are completely insoluble in the continuous phase and the drop stabilizers (that are usually present) do not participate in the radical reactions. Those conditions are not always satisfied So that complications, which are discussed below, can arise.

In most industrial suspension polymerization agitated batch (or semi-batch) reactors are used and the continuous phase is aqueous. That is advantageous because the process is often exothermic and good heat transfer from the reactor is required. The ratio of surface area to volume is relatively high for small drops so that the rate of heat transfer to the aqueous phase is high. Although drop viscosity may increase substantially, the overall viscosity of the suspension is usually much lower than that which is encountered in the equivalent bulk polymerization. Consequently, agitation of the reactor contents is possible and heat transfer via the aqueous phase to the reactor wall is good. Also, high conversions of monomer to polymer can be achieved inside the drops whereas, in bulk polymerization, increasing viscosity of the polymer-monomer solution often limits the extent of monomer conversion.

Bulk copolymerization may become difficult to control if cross-linking or copolymer precipitation occurs; then, a suspension process may then be the only feasible way in which the copolymerization can be carried out.

Suspension polymerization is particularly useful when the final polymer is required to be in the form of small “beads” (which often have the same size distribution as the drops from which they are formed). However, product contamination can be a problem if the drop stabilizers cannot be removed. Suspension polymerization usually requires larger reactor volumes than bulk processes because the vessels are usually half full with water.

CONCLUSION

Molecular imprinting is a recent new and rapidly evolving technique which allows the creation of synthetic receptors consisting of highly crosslinked porous polymers with recognition properties comparable to the biological systems related to the presence of specific recognition sites complementary in shape, size and functional groups to a target molecule. It is a facile concept, which involves the construction of sites of specific recognition, commonly within synthetic polymers. The template of choice is entrapped within a prepolymerization complex, consisting of functional monomers with good functionality, which chemically interacts with the template. Polymerization in the presence of crosslinking agent serves to freeze these template-monomer interactions and subsequent removal of the template results in the formation of a molecularly imprinted polymer matrix.

In suspension polymerization, control of drop size distribution requires clear determination of the reactor flow regime and an appropriate choice of suspending agent. Partial miscibility of some reaction components with the continuous phase and slow drop mixing can both affect the final polymer properties.

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