1 Introduction to Synthetic Methods in Step-Growth Polymers

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1.1 INTRODUCTION

1.1.1 Historical Perspective

Some of the earliest useful polymeric materials, the Bakelite resins formed from the condensation of phenol and formaldehyde, are examples of step-growth processes.[1] However, it was not until the pioneering work of Carothers and his group at DuPont that the fundamental principles of condensation (step-growth) processes were elucidated and specific step-growth structures were intentionally synthesized.[2,3] Although it is generally thought that Carothers' work was limited to aliphatic polyesters, which did not possess high melting points and other properties for commercial application, this original paper does describe amorphous polyesters using the aromatic diacid, phthalic acid, and ethylene glycol as the diol. As fundamental as this pioneering research by Carothers was, the major thrust of the work was to obtain practical commercial materials for DuPont. Thus, Carothers and DuPont turned to polyamides with high melting points and robust mechanical properties. The first polymer commercialized by DuPont, initiating the "polymer age," was based on the step-growth polymer of adipic acid and hexamethylene diamine — nylon 6,6.[4] It was not until the later work of Whinfield and Dickson in which terephthalic acid was used as the diacid moiety and the benefits of using a para-substituted aromatic diacid were discovered that polyesters became commercially viable.[5]

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In these early days of polymer science, the correlation of structure and property in the newly synthesized structures was a daunting challenge. As Carothers said, "problem of the more precise expression of the relationships between the structures and properties of high polymers is complicated by the fact that some of the properties of this class of substances which are of the greatest practical importance and which distinguish them most sharply from simple compounds can not be accurately measured and indeed are not precisely defined. Examples of such properties are toughness and elasticity" (ref. 6, p. 317).

Today, step-growth polymers are a multi-billion-dollar industry. The basic fundamentals of our current understanding of step-growth polymers from monomer functionality to molecular weight distribution to the origins of structure–property relationship all had their beginnings in the pioneering work of Carothers and others at DuPont. A collection of these original papers offers an interesting and informative insight into the development of polymer science and the industry that it spawned.[7]

1.1.2 Applications

In general, step-growth polymers such as polyesters and polyamides possess more robust mechanical properties, including toughness, stiffness, and higher temperature resistance, than polymers from addition polymerization processes such as polyolefins and other vinyl-derived polymers. Even though many commercial step-growth polymerization processes are done on enormous scale using melt-phase processes, most step-growth-based polymers are more expensive than various vinyl-based structures. This is, at least in part, due to the cost of the monomers used in step-growth polymerizations, which require several steps from the bulk commodity petrochemical intermediates to the polymerizable monomer, for example, terephthalic acid from the xylene stream, which requires oxidation and difficult purification technology. These cost and performance factors are key to the commercial applications of the polymers.

Most of the original application successes for step-growth polymers were as substitutes for natural fibers. Nylon-6,6 became an initial enormous success for DuPont as a new fiber. Poly(ethylene terephthalate) (PET) also found its initial success as a textile fiber. An examination of the polymer literature in the 1950s and 1960s shows a tremendous amount of work done on the properties and structures for new fibers. Eventually, as this market began to mature, the research and development community recognized other commercially important properties for step-growth polymers. For example, new life for PET resulted from the recognition of the stretch-blow molding and barrier properties of this resin. This led to the huge container plastics business for PET, which, although maturing, is still fast growing today.

The remainder of this introductory chapter covers a few general but important parameters of step-growth polymerization. References are provided throughout the chapter if further information is desired. Further details of specific polymers made by step-growth polymerization are provided in subsequent chapters within this book.

1.2 STRUCTURE–PROPERTY RELATIONSHIPS IN STEP-GROWTH POLYMERS

1.2.1 Molecular Weight

Polymers produced by step-growth polymerization are composed of macromolecules with varying molecular weights. Molecular weights are most often reported as number averages, $\overline{Mn}$, and weight averages, $\overline{Mw}$. Rudin, in *The Elements of Polymer Science and Engineering*, provides numerical descriptions of molecular weight averages and the derivation of the molecular weight averages.[8] Other references also define molecular weight in polymers as well as methods for measuring molecular weights.[8–11] Measurement techniques important to step-growth polymers include endgroup analysis, size exclusion chromatography, light scattering, and solution viscometry.

The physical properties of polymers are primarily determined by the molecular weight and chemical composition. Achieving high molecular weight during polymerization is critical if the polymer is to have sufficient thermal and mechanical properties to be useful. However, molecular weight also influences the polymer melt viscosity and solubility. Ease of polymer processing is dependent on the viscosity of the polymer and polymer solubility. High polymer melt viscosity and poor solubility tend to increase the difficulty and expense of polymer processing.

The relationship between viscosity and molecular weight is well documented.[12–14] Below a critical molecular weight, the melt viscosity increases in proportion to an increase in molecular weight. At this point, the viscosity is relatively low allowing the material to be easily processed. When the molecular weight goes above a critical value, the melt viscosity increases exponentially with increasing molecular weight. At higher molecular weights, the material becomes so viscous that melt processing becomes more difficult and expensive.

Several references discuss the relation between molecular weight and physical properties such as the glass transition temperature and tensile strength.[15–17] The nature of thermal transitions, such as the glass transition temperature and crystallization temperature, and mechanical properties are discussed in many polymer texts.[8,17,18] Below a critical molecular weight, properties such as tensile strength and the glass transition temperature are low but increase rapidly with increasing molecular weight. As the molecular weight rises beyond the critical molecular weight, changes in mechanical properties are not as significant. When developing polymerization methods, knowledge of the application is necessary to determine the target molecular weight. For example, polymers used as rigid packaging or fibers require high strength and, consequently, high molecular weights.

Thermoplastic commercial step-growth polymers such as polyesters, polycarbonates, and polyamides are generally made with number-average molecular weights in the range of 10,000–50,000 g/mol. Polymers within this molecular weight range are generally strong enough for use as structural materials yet low enough in melt viscosity to be processable at a reasonable cost.

Thermosetting resins are combined with fibers and other fillers to form composites.[19] Thermosetting resins with low viscosities are necessary to wet fibers or other fillers and to allow efficient processing and application prior to curing. When preparing thermosetting resins, such as unsaturated polyesters, phenolics, and epoxides, it is necessary to minimize viscosity by severely limiting molecular weight.

For example, the molecular weight of unsaturated polyesters is controlled to less than 5000 g/mol. The low molecular weight of the unsaturated polyester allows solvation in vinyl monomers such as styrene to produce a low-viscosity resin. Unsaturated polyesters are made with monomers containing carbon–carbon double bonds able to undergo free-radical crosslinking reactions with styrene and other vinyl monomers. Crosslinking the resin by free-radical polymerization produces the mechanical properties needed in various applications.

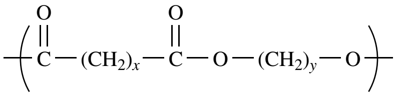
Step-growth polymerizations can produce polymers with a wide range of physical properties. Polysiloxanes made from the step-growth polymerization of silanols have among the lowest glass transition temperatures. Polydimethyl siloxanes have a glass transition temperature near −125°C. On the other hand, step-growth polymerization produces polyimides and polybenzoxazoles with glass transition temperatures of 300°C to over 400°C.[20,21]

Even within a particular class of polymers made by step-growth polymerization, monomer composition can be varied to produce a wide range of polymer properties. For example, polyesters and polyamides can be low-T_g, amorphous materials or high-T_g, liquid crystalline materials depending on the monomer composition.

The dependence of polymer properties on chemical compositions is reviewed in basic polymer texts.[9,10] The backbone structure of a polymer defines to a large extent the flexibility and stability of a polymer molecule. Consequently, a great range of polymer properties can be achieved within each class of step-growth polymers by varying the backbone structure using different monomers.

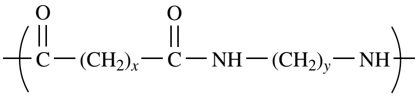
The most common backbone structure found in commercial polymers is the saturated carbon–carbon structure. Polymers with saturated carbon–carbon backbones, such as polyethylene, polypropylene, polystyrene, polyvinyl chloride, and polyacrylates, are produced using chain-growth polymerizations. The saturated carbon–carbon backbone of polyethylene with no side groups is a relatively flexible polymer chain. The glass transition temperature is low at −20°C for high-density polyethylene. Side groups on the carbon–carbon backbone influence thermal transitions, solubility, and other polymer properties.

Nearly all of the polymers produced by step-growth polymerization contain heteroatoms and/or aromatic rings in the backbone. One exception is polymers produced from acyclic diene metathesis (ADMET) polymerization.[22] Hydrocarbon polymers with carbon–carbon double bonds are readily produced using ADMET polymerization techniques. Polyesters, polycarbonates, polyamides, and polyurethanes can be produced from aliphatic monomers with appropriate functional groups (Fig. 1.1). In these aliphatic polymers, the concentration of the linking groups (ester, carbonate, amide, or urethane) in the backbone greatly influences the physical properties.



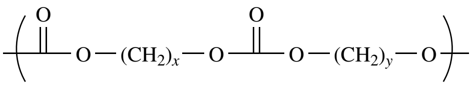
$$-\!\left(\overset{\overset{\textstyle O}{\|}}{C}-(CH_2)_x-\overset{\overset{\textstyle O}{\|}}{C}-O-(CH_2)_y-O\right)\!-$$

Polyester



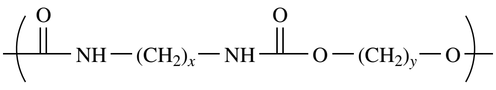
$$-\!\left(\overset{\overset{\textstyle O}{\|}}{C}-(CH_2)_x-\overset{\overset{\textstyle O}{\|}}{C}-NH-(CH_2)_y-NH\right)\!-$$

Polyamide



$$-\!\left(\overset{\overset{\textstyle O}{\|}}{C}-O-(CH_2)_x-O-\overset{\overset{\textstyle O}{\|}}{C}-O-(CH_2)_y-O\right)\!-$$

Polycarbonate



$$-\!\left(\overset{\overset{\textstyle O}{\|}}{C}-NH-(CH_2)_x-NH-\overset{\overset{\textstyle O}{\|}}{C}-O-(CH_2)_y-O\right)\!-$$

Polyurethane

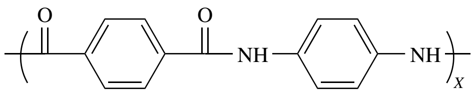
Figure 1.1 Aliphatic step-growth polymers.

Increasing the methylene content increases the melting point, eventually tending toward the T_m of polyethylene at low linking group concentrations. The linear aliphatic polyesters and polycarbonates have relatively low T_g's (-70 to -30°C) and melting points below 100°C. The linear aliphatic polyesters and polycarbonates are not used as structural materials due to the low melting temperatures and limiting hydrolytic stability. Aliphatic polyesters are used as soft-segment polyols in polyurethane production.

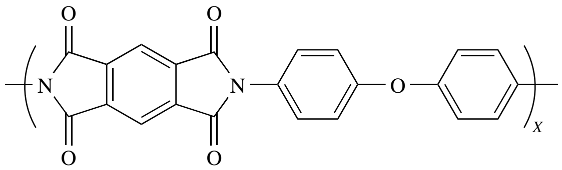
In contrast to the polyesters and polycarbonates, the linear aliphatic polyamides and polyurethanes have high melting points and higher glass transition temperatures as the amide and urethane linking groups participate in intermolecular hydrogen bonding. In Chapter 3 of *Polymer Chemistry*, Stevens discusses the influence of hydrogen bonding in polyamides compared with polyesters.[9] Stevens notes that poly(hexamethylene adipamide) melts at 265°C compared to 60°C for poly(hexamethylene adipate).[9]

Aromatic groups in the polymer backbone bring rigidity and thermal stability to the polymer molecule (Fig. 1.2). Consequently, the demands of high-strength and high-temperature applications are met by polymers with a high aromatic content in the backbone. Polymers with a particularly high aromatic content can show main-chain liquid crystallinity.

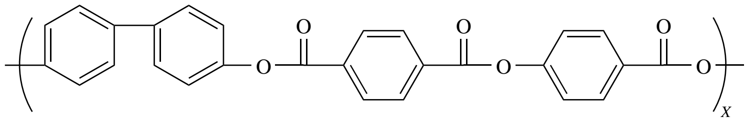
Aromatic polymers are often more difficult to process than aliphatic polymers. Aromatic polyamides have to be processed from very aggressive solvents such as sulfuric acid. The higher melting temperatures and viscosity also make melt processing more difficult. Thermal stability and processing of aromatic polymers can be balanced by the use of flexible spacing groups in between aromatic rings



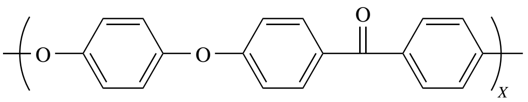
Polyamide



Polyimide



Polyester



Polyetheretherketone

Figure 1.2 Aromatic step-growth polymers.

on a polymer backbone. Hexafluoroisopropylidene, isopropylidene, oxygen, carbonyl, and sulfonyl bridging groups between rings increase opportunities for bond rotation, which decreases T_g's and increases solubility. Also, incorporating nonsymmetrical monomers with meta and ortho linkages causes structural disorder in the polymer chain, improving processability. Flexible groups pendant to an aromatic backbone will also increase solubility and processability.

The following chapters will provide detailed discussions of the structure–property relations with various classes of step-growth polymers.

1.2.2 Polymer Architecture

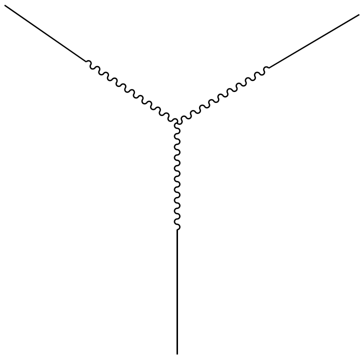
Block copolymers are composed of two different polymer segments that are chemically bonded.[23,24] The sequential arrangement of block copolymers can vary from diblock or triblock copolymers, with two or three segments respectively, to multiblock copolymers containing many segments. Figure 1.3 is a schematic representation of various block copolymer architectures. The figure also includes graft and radial block copolymers. Step-growth polymerization can be used effectively to produce segmented or multiblock copolymers and graft copolymers. Well-defined diblock and triblock copolymers are generally only accessible by chain-growth polymerization routes.

A variety of morphologies and properties can be achieved with microphase-separated block copolymers. Copolymers of hard and soft polymer segments have

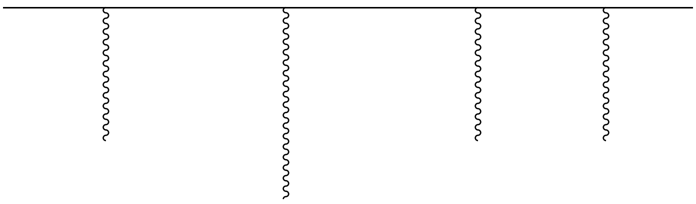
A Homopolymer B Homopolymer

A–B Copolymer

A–B–A Triblock copolymer



Radial or star copolymer



Graft copolymer

Figure 1.3 Various block copolymer architectures.

a variety of properties depending on their composition. Copolymers with small amounts of a soft segment will behave as a toughened glassy polymer while copolymers made predominately of the soft segment will act as a thermoplastic elastomer.

The thermal properties of block copolymers are similar to physical blends of the same polymer segments. Each distinct phase of the copolymer displays unique thermal transitions, such as a glass transition and/or a crystalline melting point. The thermal transitions of the different phases are affected by the degree of intermixing between the phases.

Segmented or multiblock copolymers can be made by combining a functionally terminated oligomer or prepolymer with at least two monomers. To form a segmented copolymer, the backbone oligomer must not be able to participate in interchange reactions with the monomers. For example, combining a polyester oligomer with a diacid and diamine in a melt polymerization might result in interchange reactions between the monomers and the ester linking groups in the oligomer backbone. In this case a random polyesteramide copolymer would be produced instead of a segmented copolymer. Commercial examples of segmented copolymers produced by step-growth polymerization include polyester–polyether, polyurethane–polyether, and polyurethane–polyester copolymers.

Multifunctional monomers with functionality greater than 2 can be used to form three-dimensional polymer structures during step-growth polymerization. Incorporating multifunctional monomers, A_x, with AA and BB monomers results in crosslinking between polymer chains and eventual gelation. The point at which gelation occurs depends on the average functionality of the monomer mixture and the conversion of functional groups.[25]

Adding small amounts of multifunctional monomers results in branching of the main polymer chain. The branched polymer will have a higher polydispersity and melt viscosity than analogous linear polymers. Branching agents are often used to modify the melt viscosity and melt strength of a polymer. Branching in step-growth polymers also changes the relationship between melt viscosity and the shear applied to a melt. Branched polymers tend to undergo a greater degree of shear thinning than unbranched linear polymers.

Monomers of the type A_xB_y are used in step-growth polymerization to produce a variety of polymer architectures, including stars, dendrimers, and hyperbranched polymers.[26–28] The unique architecture imparts properties distinctly different from linear polymers of similar compositions. These materials are finding applications in areas such as resin modification, micelles and encapsulation, liquid crystals, pharmaceuticals, catalysis, electroluminescent devices, and analytical chemistry.

Dendrimers are characterized by highly regular branching following a strict geometric pattern (Fig. 1.4). Dendrimers are prepared in a multistep synthesis often requiring purification between steps. One method of producing dendrimers is known as the divergent method.[29] Using the divergent approach, dendrimer growth starts at the core and proceeds radially out from the center. Each layer is built in a stepwise addition process.

In the convergent method, dendrimer growth begins with chain ends of “surface functional groups” coupling with an AB_y building block.[30] This leads to the next-generation dendron. The process can be repeated to build larger dendrons. Finally, the dendrons can be attached to a polyfunctional core producing a dendritic macromolecule.

Dendrimers produced by divergent or convergent methods are nearly perfectly branched with great structural precision. However, the multistep synthesis of dendrimers can be expensive and time consuming. The treelike structure of dendrimers can be approached through a one-step synthetic methodology.[31] The step-growth polymerization of AB_x-type monomers, particularly AB_2, results in a randomly branched macromolecule referred to as hyperbranch polymers.

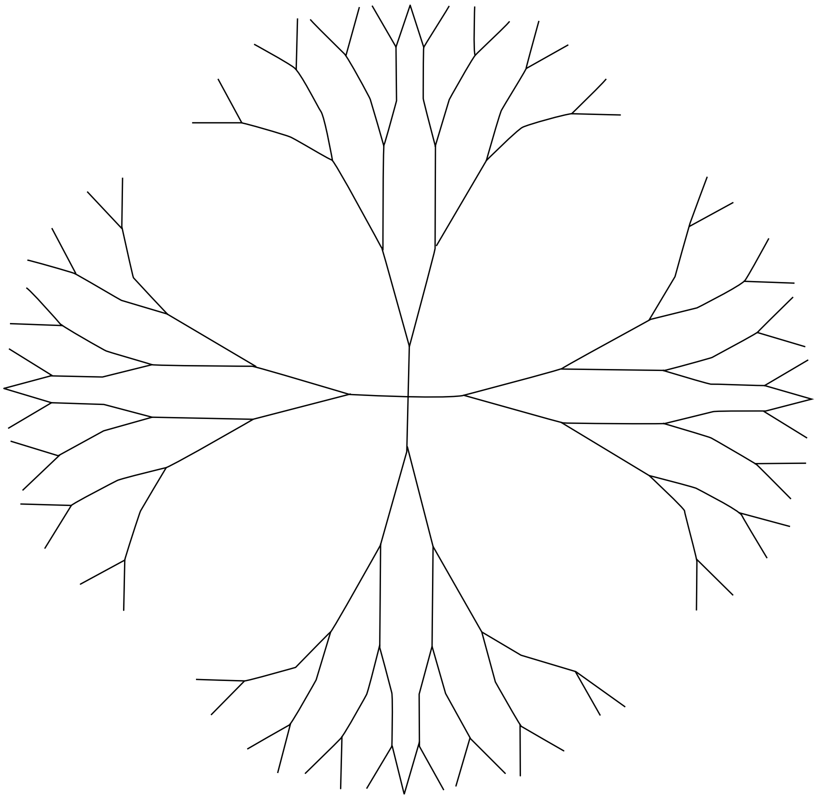


Figure 1.4 Dendrimer structure.

The hyperbranch polymers differ from dendrimers in that perfect branching is not achieved and additional linear units are present in the molecule (Fig. 1.5). The extensive branching in hyperbranched polymers prevents crystallization and results in amorphous materials. Hyperbranched materials are generally brittle with low melt viscosity due to the lack of long chains to form entanglements. These properties can be exploited as functional modifiers in crosslinking resins,[32] thermoplastic processing aids,[33] as well as components in adhesives and coatings.

1.3 SYNTHESIS OF STEP-GROWTH POLYMERS

Many synthetic methodologies have been investigated for the synthesis of high-molecular-weight step-growth polymers. However, only organic reactions that proceed in a quantitative fashion (>99%) are suitable for the preparation of high-molecular-weight linear polymers. The susceptibility of the electrophilic carbonyl to nucleophilic attack has received significant attention in step-growth polymerization processes and is widely utilized in commercially important

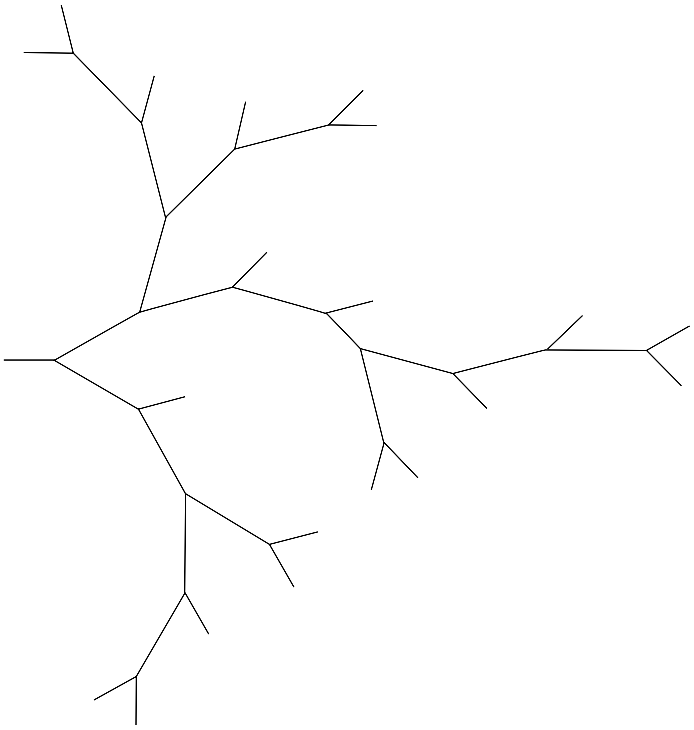


Figure 1.5 Hyperbranch structure.

families of polymeric materials, including polyesters,[34] polyamides, polyimides, polyurethanes, polycarbonates,[35] epoxy resins,[36] and phenol-formaldehyde polymers.[37] Nucleophilic and electrophilic substitution reactions are also employed in the synthesis of many other classes of step-growth polymers. For example, poly(arylene ethers) are synthesized via the nucleophilic substitution of an aryl halide with a diphenol in the presence of a basic catalyst. Diverse polymer families are prepared using nucleophilic and electrophilic substitution reactions in a step-growth polymerization, including aromatic poly(ketones), poly(arylates), poly(phenylene sulfides), poly(sulfones), and poly(siloxanes).[38,39] Transition metal coupling has also received recent attention for the synthesis of high-performance poly(arylenes) or poly(aryl alkenes).[40,41] In addition, nonpolar polymers are readily prepared via recent advances in step-growth polymerization using ADMET polymerization.[42]

A diverse array of polymeric compositions are attainable using step-growth polymerization processes; however, many experimental criteria must be addressed in order to achieve well-defined compositions and predictable molecular weights. In order to achieve high molecular weight in a step-growth polymerization process, the synthetic methodologies described above must meet certain well-established criteria. The following *essential criteria* are often cited for the successful preparation of high-molecular-weight linear polymers:

1. high reaction conversions (>99.9%) as predicted using the Carothers' equation,
2. monomer functionality (f) equal to 2.0,
3. functional group stoichiometry equal to 1.0,
4. absence of deleterious side reactions that result in loss of monomer functionality,
5. efficient removal of polymerization condensates, and
6. accessibility of mutually reactive groups.[43]

Most introductory polymer textbooks discuss the growth of molecular weight for a step-growth polymerization process. High molecular weight is not achieved until high monomer conversions are reached.[44] This is in sharp contrast to free-radical addition polymerizations where high-molecular-weight polymers are produced at relatively low conversions.

The Carothers equation relates the number-average degree of polymerization to the extent of reaction and average functionality of a step-growth polymer. In the Carothers equation, the number-average degree of polymerization, X_n, relates to the extent of reaction, p, and average functionality, f_{avg}, of the polymer system:

$$X_n = \frac{2}{2 - pf_{avg}}$$

The molecular weight of a polymer will be reduced if either the extent of conversion or the average functionality is decreased. At 95% conversion of difunctional monomers, for example, X_n is only 20.[25] The molecular weight is also related to a stoichiometric imbalance, r, which is normally defined to be less than 1.0:

$$X_n = \frac{1+r}{1-r} \quad \text{or} \quad r = \frac{X_n - 1}{X_n + 1}$$

The number-average molecular weight of a polymer may be controlled by offsetting the stoichiometry of two dissimilar mutually reactive difunctional monomers. The polymer will have the same endgroup functionality as that of the monomer used in excess. For a generic polymer made from a difunctional monomer AA with A functional groups and an excess of difunctional monomer BB with B functional groups, r is defined as

$$r = \frac{N_A}{N_B}$$

where N_A is the moles of A functional groups and N_B is the moles of B functional groups. The amount of AA and BB monomer used is then $\frac{1}{2}N_A$ and $\frac{1}{2}N_B$, respectively.

The molecular weight can also be controlled by adding a monofunctional monomer. The monofunctional endgroup, B, has the same functionality as monomer BB. In this case, the moles of A functional groups in the difunctional monomer, AA, is given as N_A and the moles of AA is $\frac{1}{2}N_A$. The moles of B functional group in the difunctional monomer, BB, is given as N_B and the moles of BB is $\frac{1}{2}N_B$. The moles of B functionality in the monofunctional endgroup, B, is given as N'_B which is also equal to the moles of B. The moles of monomers, both mono- and difunctional, containing B functional groups is $\frac{1}{2}N_B + N'_B$. Thus, the stoichiometric imbalance is defined as

$$r = \frac{\frac{1}{2}N_A}{\frac{1}{2}N_B + N'_B}$$

and simplifies to

$$r = \frac{N_A}{N_B + 2N'_B}$$

The derivation of these important equations is described in detail in earlier introductory texts.[25,41–45]

Generally, N_A is assigned an arbitrary value and the values of N_B and N'_B must be calculated. To determine N_B and N'_B, two equations must be solved. The first comes from the above equation, which rearranges to

$$N_B + 2N'_B = \frac{N_A}{r}$$

In order to obtain polymers that are only end capped with the monofunctional end group, the moles of B functional groups must equal the moles of A functional groups. This is expressed in a second equation as

$$N_B + N'_B = N_A$$

By solving these two equations simultaneously, N_B and N'_B can be determined. Figure 1.6 summarizes the impact of the functional group conversion on the molecular weight.[46] High reaction conversion (p) is required to achieve high molecular weight for linear step-growth polymerization processes.[47]

Although most step-growth polymerizations involve the formation of a volatile condensate, this is not a prerequisite for step-growth polymerization, and polyurethane formation is a classic example of a step-growth polymerization that does not form a low-molar-mass condensate.[48] Thus, step growth defines the polymerization process in terms of the basic mechanism, and step-growth polymerization is preferred terminology compared to earlier terms such as condensation polymerization. However, in most instances when a condensate is formed, efficient removal of the condensate using either low pressures (typically 0.1–0.5 mm Hg) or a dry nitrogen purge at high temperatures is required. In addition, efficient agitation and reactor engineering have received significant attention in order to facilitate removal of condensates and ensure accessibility of mutually reactive functional groups. This is especially important in melt polymerization processes where the zero shear melt viscosity (η_o) is proportional to the 3.4 power of the

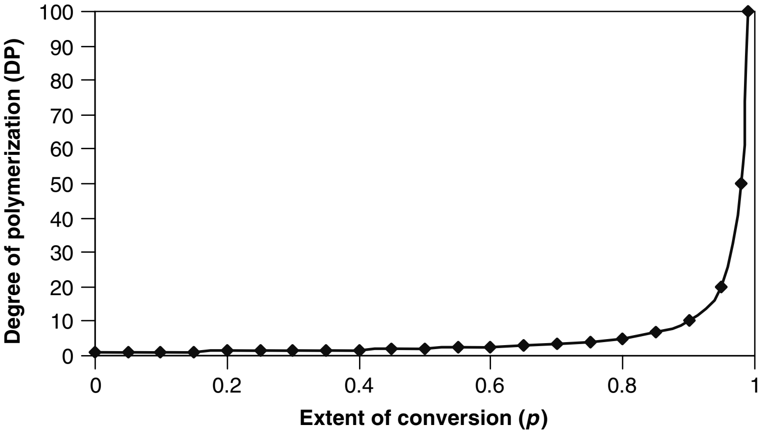


Figure 1.6 Relationship of degree of polymerization to conversion of functional groups in step-growth polymerizations.

weight-average molecular weight.[49] Thus, as molecular weight increases with conversion, the melt viscosity increases dramatically and the requirement for efficient agitation and condensate removal becomes more important.

Linear step-growth polymerizations require exceptionally pure monomers in order to ensure 1 : 1 stoichiometry for mutually reactive functional groups. For example, the synthesis of high-molecular-weight polyamides requires a 1 : 1 molar ratio of a dicarboxylic acid and a diamine. In many commercial processes, the polymerization process is designed to ensure perfect functional group stoichiometry. For example, commercial polyesterification processes often utilize dimethyl terephthalate (DMT) in the presence of excess ethylene glycol (EG) to form the stoichiometric precursor bis(hydroxyethyl)terephthalate (BHET) in situ.

Step-growth polymerization processes must be carefully designed in order to avoid reaction conditions that promote deleterious side reactions that may result in the loss of monomer functionality or the volatilization of monomers. For example, initial transesterification between DMT and EG is conducted in the presence of Lewis acid catalysts at temperatures (200°C) that do not result in the premature volatilization of EG (neat EG boiling point 197°C). In addition, polyurethane formation requires the absence of protic impurities such as water to avoid the premature formation of carbamic acids followed by decarboxylation and formation of the reactive amine.[50] Thus, reaction conditions must be carefully chosen to avoid undesirable consumption of the functional groups, and 1 : 1 stoichiometry must be maintained throughout the polymerization process.

As mentioned previously, the use of multifunctional monomers results in branching. The introduction of branching and the formation of networks are typically accomplished using trifunctional monomers, and the average functionality of the polymerization process will exceed 2.0. As the average functionality increases, the extent of conversion for network formation decreases. In many instances, the trifunctional or higher functional monomers contain reactive groups that are identical to the difunctional monomers. For example, pentaerythritol ($f = 4$) and 1,3,5-benzene tricarboxylic acid ($f = 3$) and trimellitic anhydride ($f = 3$) are commonly used in polyesterification. Many novel families of step-growth polymers are attained through the judicious combination of controlled endgroup functionality, extent of branching, and molecular weight. Hyperbranched step-growth polymers have received significant review in the literature and are an exquisite example of controlled functionality and topology using well-defined monomer functionality.[51]

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