

MOLECULAR WEIGHT DISTRIBUTIONS IN IDEAL POLYMERIZATION REACTORS. AN INTRODUCTORY REVIEW

G.R. MEIRA[†] and H.M. OLIVA[‡]

[†] INTEC (Univ. Nac. del Litoral and CONICET), Santa Fe (3000), Argentina. gmeira@santafe-conicet.gov.ar

[‡] Escuela de Ingeniería Química, Univ. del Zulia, Maracaibo, Venezuela. holiva@luz.edu.ve

Abstract— The ultimate aim of polymerization reaction engineering is the production of polymers with tailor-made properties. An introductory review into this field is presented, with emphasis on the effects on the molar mass distribution (MMD), of the sought combination of polymerization mechanism, reactor type, and reactor control. Three ideal polymerization mechanisms are analyzed: free-radical, “living” anionic, and step-growth. “Living” anionic and step-growth polymerizations are similar in that their growing chains remain reactive while inside the reactor; and for these systems the narrowest MMDs are produced in reactors with narrow residence time distributions (RTD); *i.e.*: batch or continuous tubular reactors. In contrast, in conventional free-radical polymerizations, the polymer molecules grow in a fraction of a second and thereafter remain inactive while inside the reactor. In this case, the RTD does not affect the MMD, and the homogeneous continuous stirred-tank reactors provide the narrowest MMDs. Representative mathematical models of polymerization reactors are useful for: a) quantifying the interrelationships between their numerous inputs and outputs; and b) developing open- and closed-loop strategies for increasing reactor productivity and product quality.

Keywords— Molecular Weight Distribution, Polymerization, Reactor.

I. INTRODUCTION

Synthetic polymers are important materials that find innumerate applications as plastics, composites, rubbers, fibers, adhesives, and coatings. Unlike low molar mass substances where quality is mainly determined by purity, synthetic polymers are mixtures of a large variety of molecular species and morphologies, and therefore are difficult to characterize. The physical properties of polymers (both in the solid and in the melt) depend on complex interrelationships with: a) the molecular structure (described by the distributions of molecular weights, of isomers, of the chemical composition in copolymers, of the molecular topology in long-branched polymers, etc.); and b) the supramolecular morphology (degree of crystallinity, particle size in heterogeneous solids, etc.). “Commodity” thermoplastics and fibers such as polyethylene, polypropylene, PVC, and polystyrene are synthesized in large continuous processes that were mostly developed in the mid-20th Century. In 2007, the World production of synthetic polymers was around 260 million tons, and it is expected to reach 350

million tons by 2015. In volume, the annual production of polymers exceeds that of the 2 most important metals: iron and aluminum. The raw materials for the production of around 95% of all synthetic polymers are non-renewable sources (fossil oil, gas, and coal).

Polymerization Reaction Engineering deals with problems involving the measurement, mathematical modeling, optimization, and control of industrial polymerization processes. It aims at improving both the productivity of the polymerization process and the quality of the produced polymer. Some general references on this area are: Ray (1972), Reichert and Moritz (1989), Hamielec and Tobita (1992), Kiparissides (1996), Ray *et al.* (2004), Yoon *et al.* (2004), Meyer and Keurentjes (2005), Villa (2007) and Asua (2007).

Polymers are high molar mass substances characterized by the repetition (neglecting ends, branch junctions, and other minor irregularities) of one or more types of monomeric repeating units. While homopolymers contain a single type of chemical repeating unit, copolymers contain 2 or more. Polymers may be synthetic or natural (such as proteins, carbohydrates, etc.). In spite of their highly sophisticated structures, natural macromolecules are synthesized at ambient temperature and in mild aqueous media, with the aid of specialized catalysts or enzymes (themselves also polymers). In contrast, synthetic polymers are considerably simpler in their chemical and structural characteristics, are mostly soluble in organic solvents, and their syntheses typically require stringent conditions of pressures, temperatures, and solvents.

The total number of repeating units in a chain is the chain length or degree of polymerization. Most synthetic polymers are linear molecules made up of repeating units of functionality 2. Due to their high molar masses and chain entanglements, polymers are solids at room temperature, but may become viscous liquids between 100 and 300 °C. Their average molar masses are typically between 20,000 and 300,000 g/mol. These values are a compromise between mechanical properties (such as elastic modulus, and tensile strength that all increase with the molar mass), and ease of processability in the molten state, favored by a low melt viscosity (or a low molar mass). In contrast, if the polymer is crosslinked or cured, then the material is essentially a single molecule that unless degraded, it will not flow upon increasing the temperature. “Reactors” for producing crosslinked articles are not stirred, and their shapes provide the shape of the final article (*e.g.*: a mould for producing a