

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Kinetics Modeling for Methyl Methacrylate (MMA) Polymerization

Soh (1980) reviewed some theory in order to measure the propagation rate constant from emulsion polymerization, which styrene and MMA were used for polymerization. The results were compared to some previous literature and showed the comparative values with the conventional methods also.

A mathematical model describing free-radical polymerization reactions exhibiting a strong gel effect was developed by Chiu *et al.* (1982).

The gel effect can be referred to as the autoacceleration, also known as “Norrish-Smith” or “Trommsdorff” effect, for the polymerization rate at intermediate to high conversions. This phenomenon can lead to difficulties ranging from undesired final properties to reactor explosion, since the exothermic nature of the reaction can cause an uncontrolled temperature rise.

They also concluded some theorem used for establishing this model. The developed model describes the polymerization process over the entire course of reaction. The model predictions were compared with literature data on conversion history and product molecular weights for isothermal PMMA polymerization.

A specific model for the termination rate constant with chain length dependence was proposed by Soh *et al.* (1982) and was based on free volume theory and entanglement coupling. Master curves for the characteristics of the reaction rate and molecular weight distribution were presented.

The study of free volume parameters and diffusion-controlled propagation of vinyl polymerization were studied by Soh *et al.* (1982). This study was a part of a series that deals with the bulk polymerization of vinyl

polymers which are soluble in their own monomers over the entire conversion range. The values of the parameters that are necessary to compute the free volume changes accompanying polymerization were determined from viscosity data of concentrated polymer solutions. The theoretical description of the polymerization rate and molecular weight development for bulk polymerization of vinyl monomers over the entire conversion range was also concluded.

The optimization of batch reactors for chain polymerizations exhibiting the gel and glass effects has been a subject of considerable research activity. Vaid *et al.* (1991) studied the optimization temperature histories of MMA polymerization using a kinetic model incorporating gel and glass effects. The minimum end time problem was also studied. They claimed that the optimization algorithm used was efficient and easy to use. Also, it was found that the optimal temperature histories obtained when the desired chain length lies beyond the maxima in the number average chain length ( $\mu_n$ ) vs. time plot differ qualitatively and significantly from those obtained when the desired  $\mu_n$  lies before the maxima.

Ramaseshan *et al.* (1993) reported a technique for the control of bulk polymerization of methyl methacrylate initiated by benzoyl peroxide. The curing profiles of 6-12 hours had been considered incorporating the kinetic features of polymerization which includes a gel effect. They proposed that the influence of the gel effect on the propagation and termination rate constants could be divided into two regions. In the first range the gel effect is independent of conversion while in the latter stage its influence is characterized by Ross-Laurence parameters.

The possibility of assuring a product having constant properties is particularly difficult in batch reactors where during the course of the reaction, concentrations and reactivities of the different species and physical properties of the system undergo large changes. One additional difficulty is given by the

fact that variables that are indices of the final polymer quality are not available in real time. They must be inferred by other intermediate variables (such as conversion and temperatures), which are easier to obtain, by means of a model system.

The global optimization is included in the objectives, in addition to the control of the polymer qualities and the achievement of high productivity (high conversion, short reaction times), and the respect of the operation safety. Main operating variables are: the initial concentration of monomer and initiator, the temperature, the rate of feeding solvent, monomer, and initiator, the use of inhibitor, or chain transfer agents.

A method to determine an optimal temperature profile that guarantees products having controlled molecular weight distribution (MWD) and desired values molecular weight ( $\bar{M}_w$ ) was presented by Scali *et al.* (1995). The optimal temperature profile was determined by imposing that the value of the instantaneous chain length was maintained constant, thus counteracting the effects of the increase of viscosity, which leads to broad MWD.

O'Neil *et al.* (1996) provided critical experiments involving both bulk methyl methacrylate and styrene polymerizations which contradict the widely held belief that the gel effect onset is related to the formation of chain entanglements. By employing experimental conditions which tend to delay or eliminate the formation of chain entanglements by using high initiator and/or chain transfer agent concentrations and addition of low molecular weight polymer prior to reaction, it was shown that the gel effect readily occurs in the absence of entanglements. Delaying the onset of entanglements does not necessarily delay the onset of the gel effect. Furthermore, even under conditions where entanglements are likely to exist, the gel effect onset does not correlate with polymer molecular weight, either of the chains produced or the matrix, in a manner consistent with entanglement arguments. The authors also suggested that although the presented results indicated that the onset of

the gel effect was unrelated to entanglement formation, the kinetics during the gel effect might be affected by entanglements. The experimental test to investigate this issue has been outlined already.

The determination of kinetic and thermodynamic data of free-radical polymerization by adiabatic reaction calorimetry was studied by Mosebach *et al.* (1997). The polymerization of methyl methacrylate in solution, suspension, and emulsion were studied. The results were fit to appropriate mathematical model, for example, the temperature rise and the self-heating rate could be modeled very well for polymerization in solution over the entire range of concentration and, in the case of polymerization in suspension and emulsion, up to a volume fraction of monomer of 20 %. The modeling of molecular weight distribution of polymers produced by polymerization in solution and suspension was satisfactory. For emulsion polymerization, only the order of magnitude of the average molecular weight could be calculated with the model used. The average particle size of the polymer latex formed was calculated rather well. Some of the model equations used for various type of free-radical polymerization were reviewed also.

A mathematical model for the polymerization of methyl methacrylate (MMA) in a batch reactor was developed by Ahn *et al.* (1997). The model includes chain transfers to the monomer and solvent and termination by both combination and disproportionation and also takes into account the density change of the reactor contents and the gel effect. The validity of the proposed model was tested by an isothermal experiment of a batch PMMA polymerization. The experimental results showed that the proposed model could describe the real polymerization system very well in view of both monomer conversion and average molecular weights.

A model-predictive software sensor for on-line estimation of monomer conversion and average molecular weight during bulk polymerization of systems exhibiting a gel effect was developed by Mankar *et*

*al.* (1998). The viscometer-reactor assembly was modified to measure the viscosity of the reaction mass during bulk polymerization of methyl methacrylate (MMA). The viscosity data were curve-fitted using the modified Martin equation. They concluded from the fact that the model tuned with the data obtained under the isothermal reactor operation could be used to predict the viscosity for nonisothermal reactor conditions without further tuning to establishing the efficiency of the software sensor.

## **2.2 Process for Poly(methyl methacrylate) (PMMA) Production**

Kanazawa (1977) claimed that thermal stability of PMMA can be improved by adding a certain amount of selected sulfur-containing compound together with a certain amount of selected surfactant into the starting MMA monomer or a syrup containing soluble polymeric resin in the MMA monomer in casting polymerization.

In order to produce PMMA to be free from impurities and having narrow molecular weight distribution to be suitable as an optical link material in the form of optical fiber or alike, Suka *et al.* (1987) proposed a continuous process for producing PMMA by forcing the feedstock, containing MMA monomer or its copolymer comprising of a precooled monomeric feedstock of MMA mixed with (up to 10 mol%) a highly thermal radical-forming monomer, into a reactor in which a preceding charge was being circulated under pressure. The whole charge was instantaneously mixed and cooled by dint of the sensible heat of the monomeric feedstock, which affected the polymerization within a short time period. The polymerization products were taken out of the reactor, and then the remaining monomers were removed by evaporation in a vacuum vessel.

The single phase blends of polycarbonate (PC) and PMMA were developed by Kyu *et al.* (1988). These blends were prepared by dissolving two polymers in a solvent that have a boiling point about 30 °C, then, solvent was evaporated at temperature about 45 °C. The composition of blends can be maintained from 10 to 80 percent by weight of PC and conversely 90 to 20 percent by weight of PMMA. The blends were contrast to presently known PC/PMMA blends, which are miscible only when the content is nearly all PC or nearly all PMMA. The blends are clear, transparent, and moldable.

The transparent blends of PMMA and bis-phenol A PC was developed by Kambour (1988). The blends were done by solution casting and melt blending procedures. Properties of the blends are combined with preferable properties of both PMMA and PC, such as transparency, high modulus of elasticity, and high degree of scratch resistance from PMMA and superb impact toughness, and good heat resistance from PC. This blends is applicable for making optical disks and other injection moldable articles for which an easy flow PC is needed.

Yasuyuki *et al.* (1989) improved a rapid crosslinking polymerization, which comprises polymerizing a mixture of a monofunctional (unsaturated) monomers, selected from MMA and a monomer mixture comprising predominantly MMA which may partially contain a polymer of the monomer, and a polyfunctional (unsaturated) monomer mixed with (1) a radical polymerization initiator, (2) a sulfur-containing reducing compound, (3) an amine hydrohalogenate or a quaternary ammonium halide, and (4) a copper-containing compound. The final product is PMMA which has high mechanical properties and excellent transparency.

In the casting of PMMA sheet, there were phenomena which cause shifting in color, apparently due to competition for attachment sites on the pigment surfaces by additives such as chain transfer agent and sheet release agent. When such additives replace the dispersants from the pigment surfaces,

the dispersing effect was diminished because the additives are less efficient as dispersants. With diminished dispersing effect, there is more of a tendency for pigment particles to flocculate, leading to color changes. These effects are aggravated by thermal shock from casting cool syrup on a relatively warm metal belt. Delphin *et al.* (1990) found that use of AB dispersants (A is the segment in block copolymer, which is consisting of methacrylic group, and B is the segment in block copolymer which consist of selected monomer units of acrylic and methacrylic groups) made by group transfer polymerization can control the color shift during casting of MMA, containing color pigments and additives, particularly chain transfer agent and sheet release agent.