CHAPTER II

LITERATURE SURVEY

Soh and Sundberg, 1982, referred to study of Balke *et al* (1973) who studied the bulk polymerization of methyl methacrylate (MMA) using AIBN as an initiator at isothermal temperatures of 50, 70, and 90°C. Two methods for determining kinetic parameters from size-exclusion chromatography (SEC) or gel-permeation chromatography (GPC) data had been developed. They are the methods of differential chromatograms and the method of chromatogram heights. They found that the experimental instantaneous differential molecular weight distributions were found to agree well with the predictions by the classical free-radical kinetics theory. The development of conversions, molecular weight averages, and molecular weight distributions before and during the gel effect was explained and was found to related closely to the free volume.
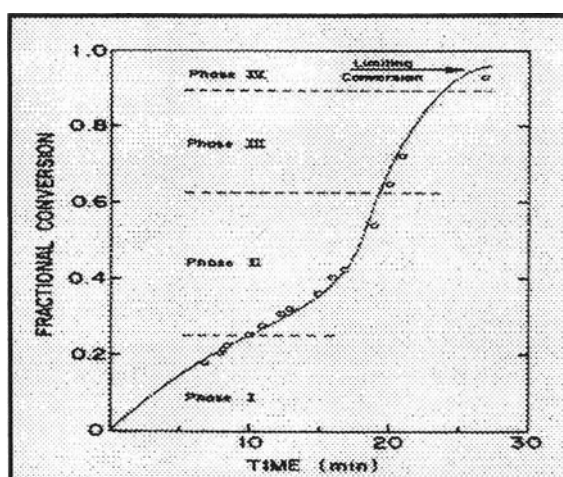

Figure 2.1 Conversion profile for MMA polymerization (at 90°C and 0.3%AIBN) depicting different phases of the reaction (Soh and Sundberg, 1982).
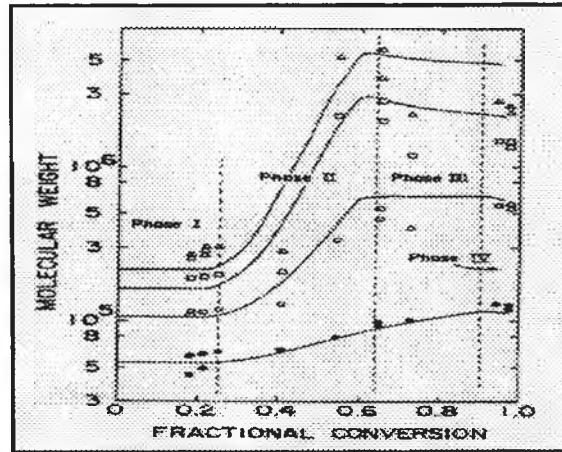
Figure 2.2 Conversion dependence of molecular weight averages for MMA polymerization (at 90°C and 0.3%AIBN) (Soh and Sundberg, 1982). Keys: ● $\overline{M}_n$, ○ $\overline{M}_w$, □ $\overline{M}_z$, △ $\overline{M}_{z+1}$.

In Figures 2.1 and 2.2, they were explained that the polymerization of vinyl monomer soluble in its own polymer consists of four phases of distinctive polymerization behavior. Depending on the monomer type and reaction conditions, one or more of the four phases may be absent. At low conversions, the polymerization rate can be described by conventional kinetics. The cumulative molecular weight averages do not change appreciably, and the molecular weight distribution conform to the Schulz-Flory distribution (Phase I). After a certain conversion, which appears to be independent of initiator level at the same polymerization temperature, the well-known gel effect is observed (Phase II). At still higher conversions, the gel effect disappears. The polymerization rate is fast, but the cumulative molecular weight averages (except for the number average molecular weight) level off or begin to decrease slightly (Phase III). Eventually the deceleration becomes profound, and, when the polymerization temperature is lower than the glass transition temperature of the polymer formed, a limiting conversion is reached beyond which the reaction does not proceed (Phase IV).

In order to improve the thermal stability of the sheet-casted PMMA, Kanazawa (1980) used a sulfur-containing compound for producing a casting plate of PMMA by emulsion polymerization. The process suited with the started monomers

or syrups and the products had an excellent thermal stability and disappeared foam and color.

To describe the effect of gel formation on the free-radical polymerization reaction, a computer model was developed by Chiu *et al.* (1983). Diffusion limitation was shown in an integral part of the chain termination process and also this limitation affected the conversion. Not only temperature and concentration but also molecular weight were important for determining the reaction and diffusion. Moreover, the model also considers the effect of increased glass transition with increasing conversion, which results in the reduction in the mobility of the chain, thus reduction in the diffusion rate, at high conversions.

The optimization of batch reactors for chain polymerizations exhibiting the gel and glass effects has been a subject of considerable research activity. Vaid and Gupta, 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 maximum in the number average chain length (μ_n) vs. time (see Figure 2.3) plot differ qualitatively and significantly from those obtained when the desired μ_n lies before the maximum.

In Figure 2.3, the average chain length of reaction was observed for 60, 70, 80, and 90°C. Even though the cycle time for 90°C is shorter than those for 80, 70, and 60°C, respectively, the average chain length for 90°C is lower than those for 80, 70, and 60°C. Figure 2.4 exhibits the simulated development of monomer conversion with respect to the reaction time for 60, 70, 80, and 90°C, respectively, which clearly confirmed that the polymerization rate at 90°C was the fastest.
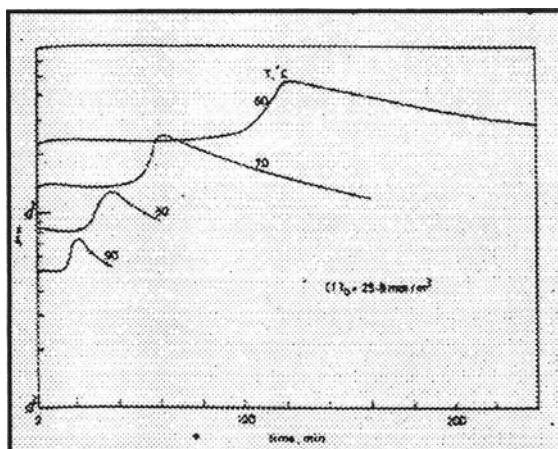
Figure 2.3 μ_n vs. reaction time for an isothermal batch reactor (Vaid and Gupta, 1991).
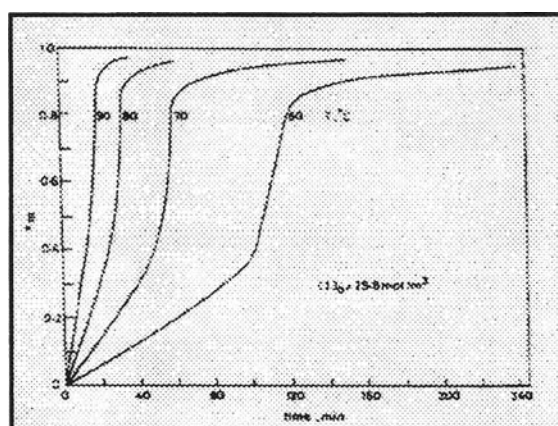

Figure 2.4 Monomer conversion vs. reaction time for an isothermal batch reactor (Vaid and Gupta, 1991).

Ramaseshan *et al.* (1993) reported a technique for controlling bulk polymerization of MMA initiated by benzoyl peroxide. They showed the typical SPI exothermic curve for MMA in Figure 2.5, which reacted with 1% benzoyl peroxide and 10 g. of samples placed in test tubes. Their polymerization time was used for 35 min and the polymerization temperature was 355.2 K (180°F). The calibration curves plotted between conversion and refractive index was observed. It was obtained by relating the densities of the syrup to their conversion assuming a linear

decrease in volume of the reaction mixture with conversion of monomer. Moreover, the experimental results confirmed the fact that during the initial period of polymerization the rate was indeed constant at an optimal isothermal temperature, depending on the overall cycle time. When their parameters compared with Ross-Laurence parameters, they found that the Ross-Laurence parameters overestimate the influence of the gel effect.
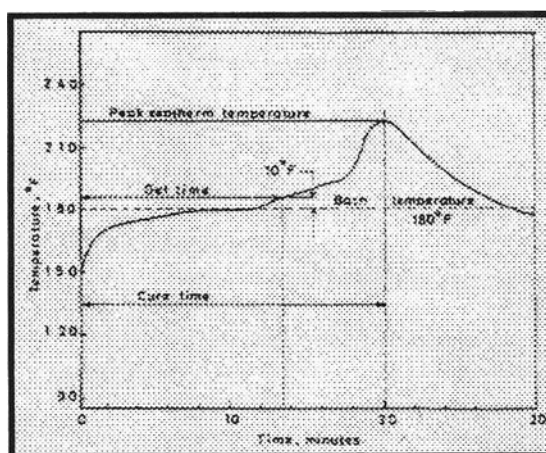

Figure 2.5 Typical SPI exothermic curve for MMA (Ramaseshan *et al.*, 1993).

Actually, the general models cannot be applied to industrial reactors because of their inability to account for non-isothermal effects and semi-batch operating. Recent models had overcome these limitations (Dua *et al.*, 1996).

The degradation behavior of the PMMA blended with propyl ester phoshazene and pure PMMA was compared by Denq *et al.* (1997). The major thermal degradation temperature of blends was greater than pure PMMA.

The sheet modeling process for the production of PMMA involves an isothermal batch reactor followed by Zhou *et al.* (2000). The model showed the ultimate percent of conversion at 98%