# CHAPTER II
LITERATURES

Balke *et al.* (1973) reported on an experimental investigation of the chemical-initiated bulk polymerization of methyl methacrylate by using AIBN as an initiator at isothermal temperature of 50, 70, and 90°C. Two methods of determining kinetic parameters from experimental GPC data had been developed. These were the method of differential chromatograms and the method of chromatogram heights. These experimental instantaneous differential molecular weight distributions were found to agree with theoretical distribution predicted by classical free-radical kinetics. The model of conversions, molecular weight averages, and molecular weight distributions before and during gel effect was explained that they were closely based on their free volume.
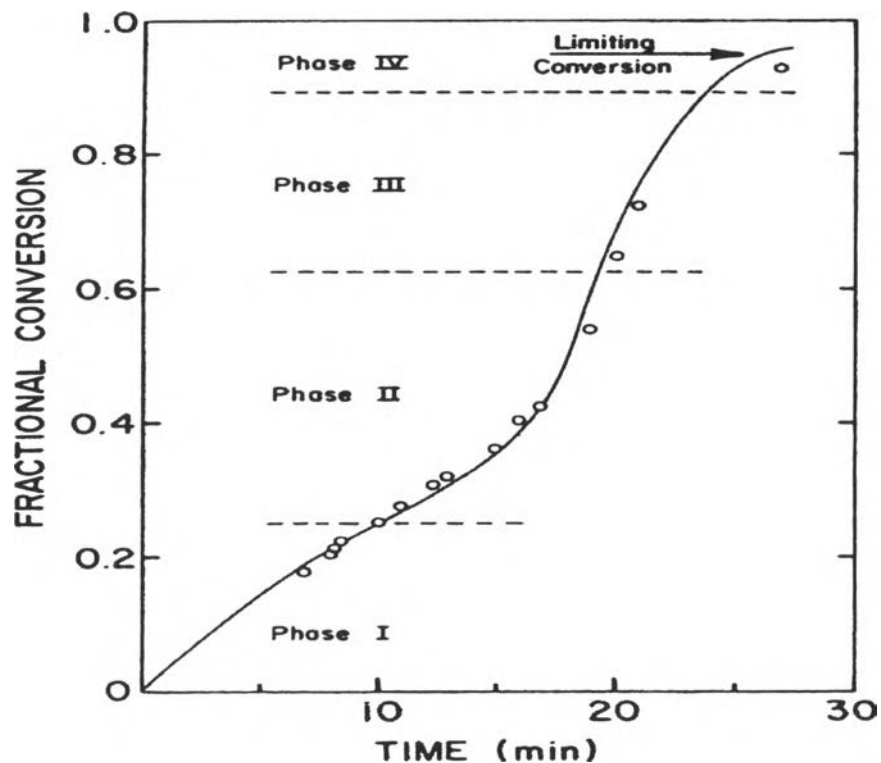
Figure 2.1 Conversion profile for MMA polymerization depicting different phase of reaction at 90°C and 0.30 %AIBN (Soh *et al.*,1982).
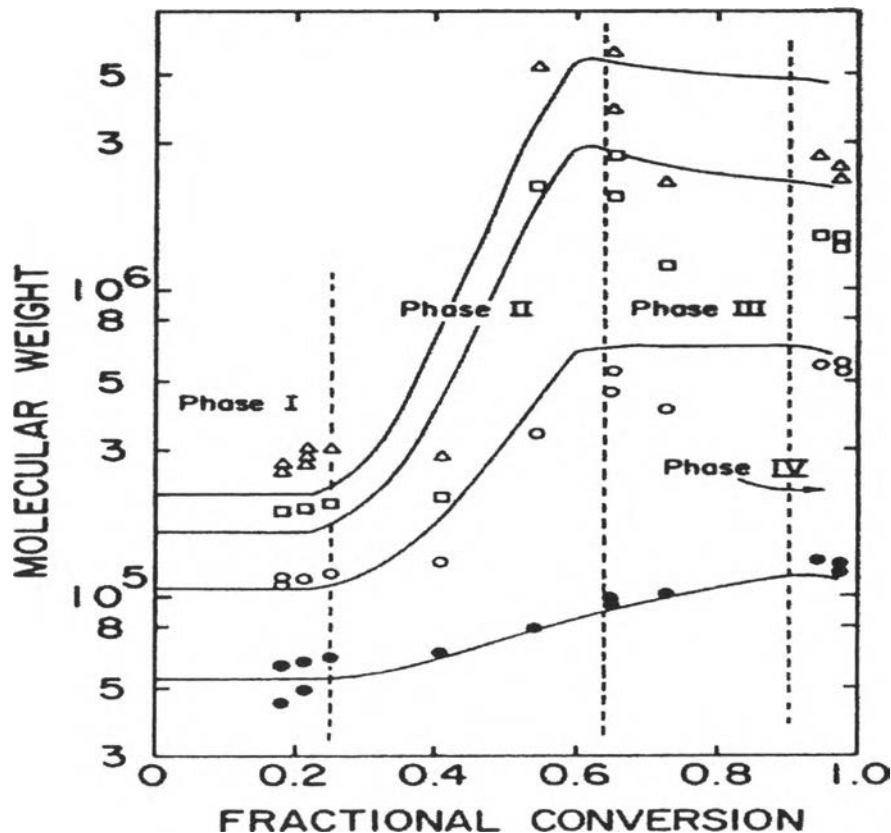
Figure 2.2 Conversion dependence of molecular weight averages for MMA polymerization, $\bullet\ \overline{M}_n$, $O\ \overline{M}_w$, $\square\ \overline{M}_z$, $\triangle\ \overline{M}_{z+1}$, at 90°C and 0.3%AIBN (Soh *et al.*, 1982).

In Figures 2.1 and 2.2, Soh *et al.* (1982) explained that the vinyl polymerization of monomer soluble in its own polymer consists of four phases of distinctive polymerization behavior. Depending on the monomer used or reaction conditions one or more of the four phases may be absent. At low conversion the polymerization rate was described by conventional kinetics, the cumulative molecular weight averages do not change appreciably, and the molecular weight distribution conform to the Schulz-Flory most probably 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 appears to stop. The polymerization rate is fast, but the cumulative molecular weight averages (except 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 process (Phase IV).

In order to improve the thermal stability of the casted PMMA, Kanazawa (1980) used a sulfur-containing compound for producing a casting plate of PMMA by emulsion polymerization. These were the process suited with the starting monomers or syrups and the PMMA had an excellent thermal stability and particularly never foam and is never color ever when heated.

In 1982, the model based on viscosity data of concentrated polymer solution was determined to calculate the free volume changes while polymerization by Soh *et al.* The propagation rate constant and monomeric diffusivity with free volume were postulated that they were related to the friction coefficient of a polymer chain segment and the last equation was also presented the limiting conversion.

Although the kinds of models were explained, a computer model was continuously developed to describe free radical polymerization reaction exhibiting a strong gel effect (Chiu *et al.*, 1983). Diffusion limitation was shown in an integral part of the chain termination process and also this limitation affected to the conversion. Not only temperature and concentration but also molecular weight was the importance of reaction and diffusion. Moreover, the model also considers glass effect, which is only appeared at very high conversion. However, the model predictions were compared with literature data on conversion history and product molecular weights for isothermal PMMA polymerization.

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 maximal in the number average chain length (μ_n) vs. time (see in Figure 2.3) plot differ qualitatively and significantly from those obtained when the desired μ_n lies before the maximal.
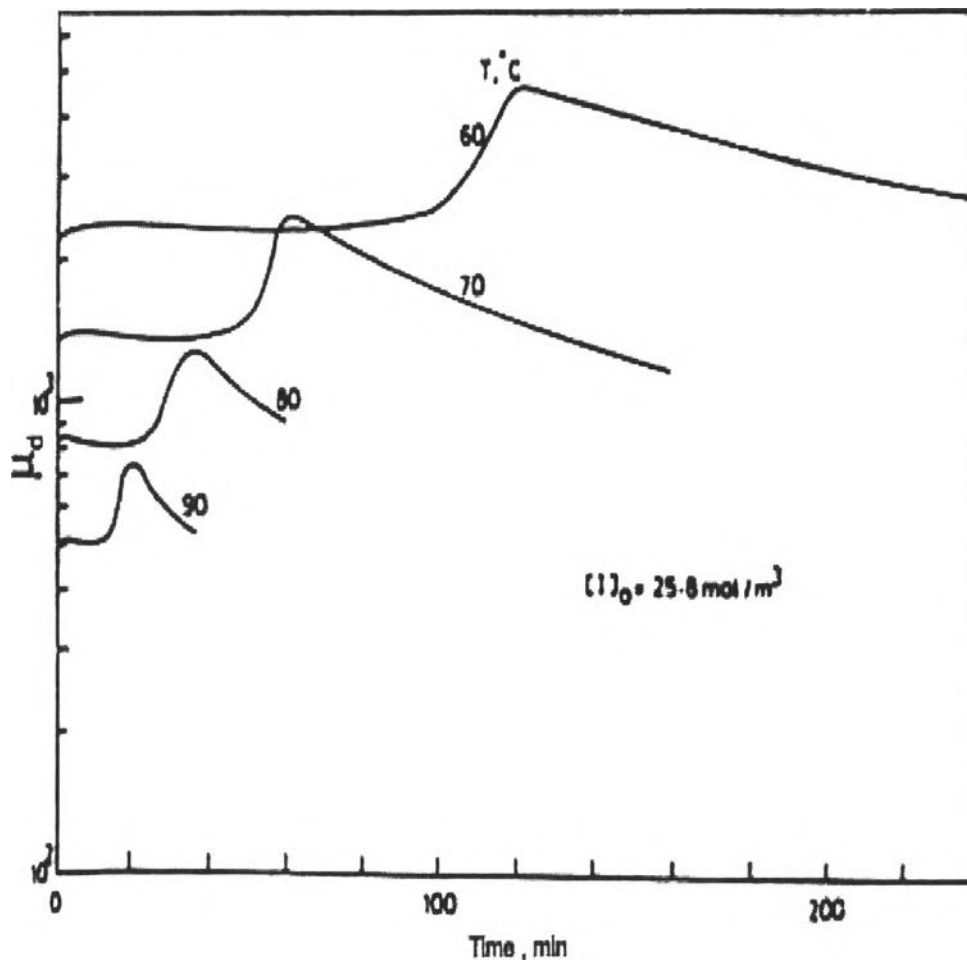
Figure 2.3 μ_n vs. reaction time for an isothermal batch reactor (Vaid *et al.*, 1991).

In the Figure 2.3, the average chain length of reaction was observed at 60, 70, 80, and $90^{\circ}C$. Even though at $90^{\circ}C$, the cycle time is shorter than the cycle time at 80, 70, and $60^{\circ}C$ respectively, the average chain length at $90^{\circ}C$ is lower than the average chain length at 80, 70, and $60^{\circ}C$

And also, the simulation of monomer conversion with reaction time was shown in Figure 2.4. It is confirmation of time at $90^{\circ}C$ that is the fastest the cycle time of reaction.
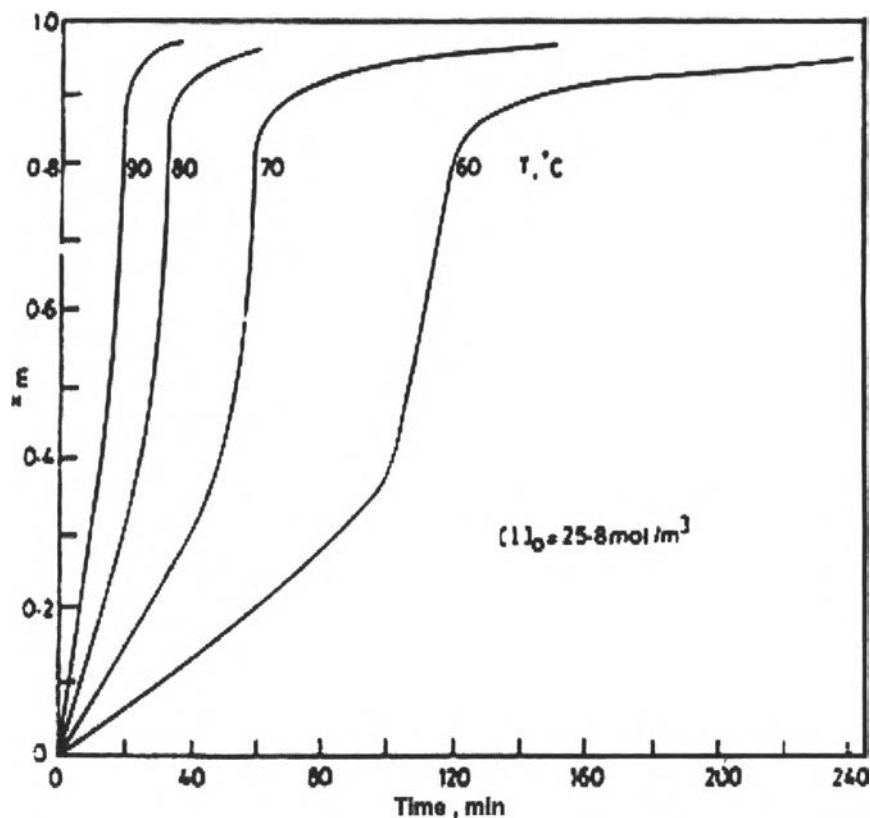
Figure 2.4 Monomer conversions vs. reaction time for an isothermal batch reactor (Vaid *et al.*, 1991).

Ramaseshan *et al.* (1993) reported a technique for the controlled bulk polymerization of methylmethacrylate 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.
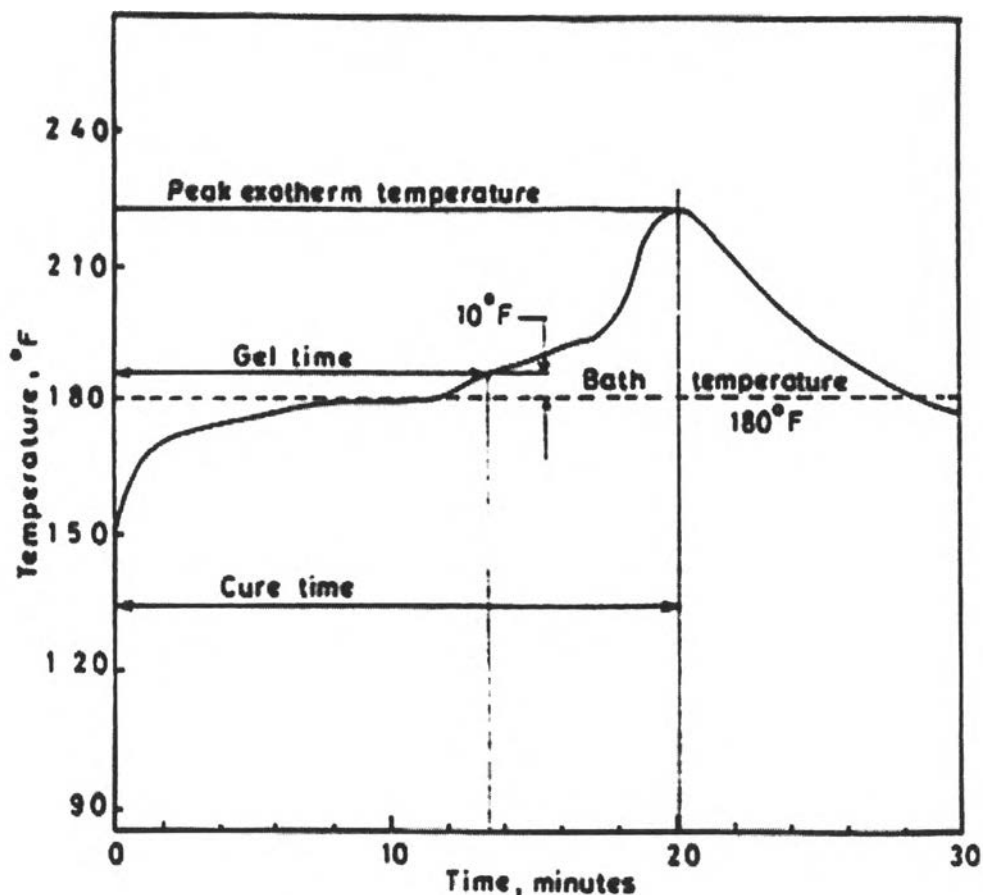
Figure 2.5 The typical SPI exothermic curve for MMA (Ramaseshan *et al.*, 1993).

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).

Bar-long Denq et al., 1997, compared the degradation behavior of the PMMA blended with propyl ester phoshazene and pure PMMA. 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 Fangbin *et al.* (2000). The model showed the relationship between percent conversion, average molecular weight, and thickness of sheet as a function of temperature profile.

PREVIOUS WORK

The effect of the reaction temperature and type of the medium in reaction on the reaction time and mechanical properties was studied by Wanwanichai (2001). The relationship between temperature profile and dynamic percent conversion was studied to confirm that the optimal reaction time could be observed by the temperature profile measurement. In the Figure 2.6 showed the maximum percent conversion was reached after the occurrence of the exothermic polymerization peak. This also holds true for the result obtained for other conditions. Therefore, instead of going through the cumbersome of getting the percent conversion curve in order to determine the observed reaction time, the temperature profile is the easier technique to estimate the observed reaction time.
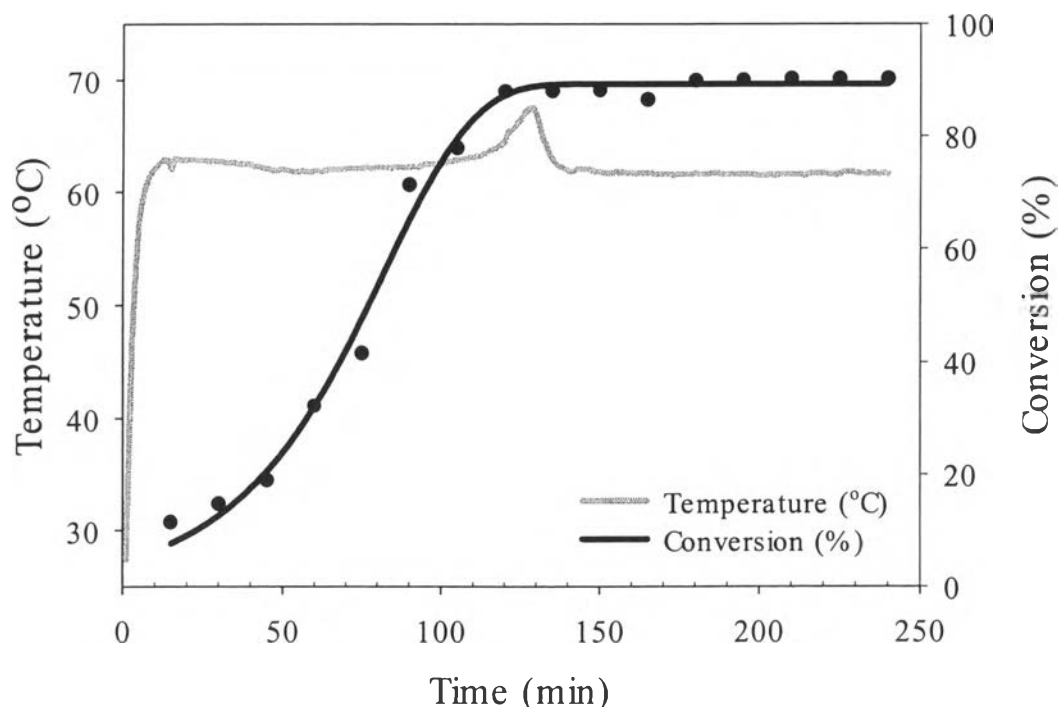
Figure 2.6 Overlay plot of temperature profile and percent conversion for sample polymerized at 62°C with 0.038% ADVN.

In order to reduce the total reaction time of PMMA sheets, the temperature profile of samples polymerized at 60, 62, 65, 68, and 70°C with a fixed initiator concentration of 0.038% ADVN was observed and is shown in Figure 2.7.

Apparently, the reaction time depended strongly on the choice of polymerization temperature. At 60°C, the reaction time was ca. 136 minutes. For 62, 65, 68, and 70°C, they were ca. 128, 112, 93, and 82, respectively. In conclusion, the maximum peak temperature was found to increase, while observed reaction time decreased, with increasing reaction temperature.
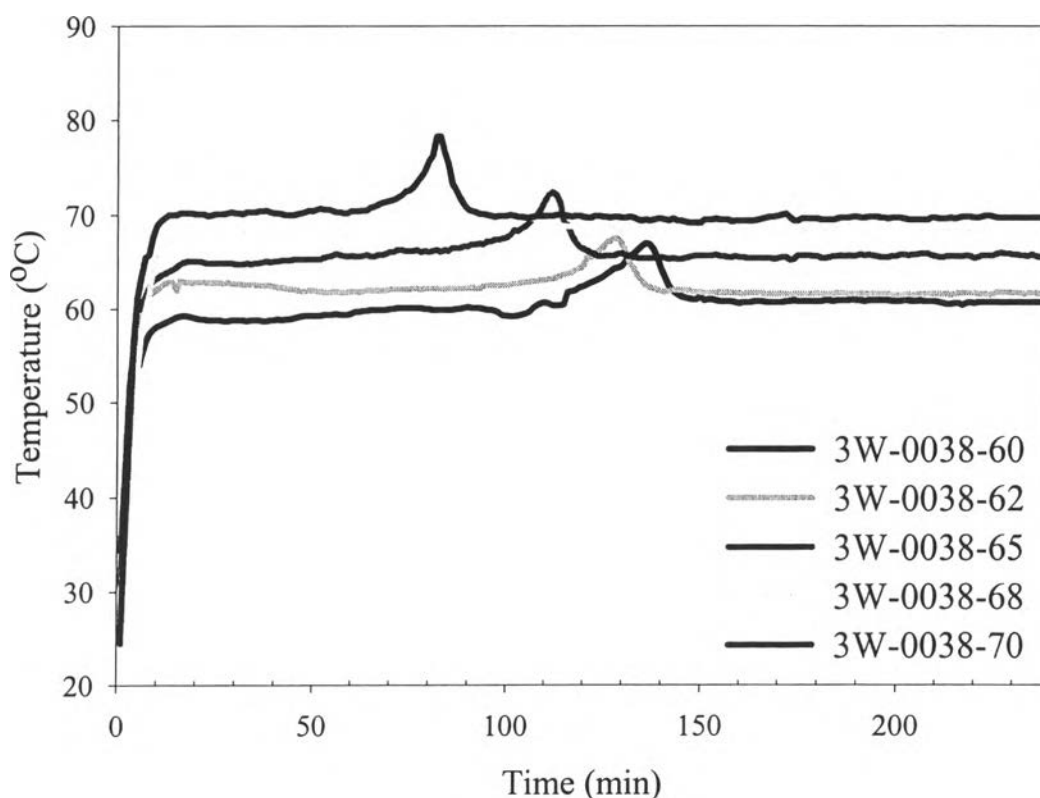
Figure 2.7 Temperature profile of samples polymerized at 62, 65, 68, and 70°C with 0.038% ADVN in water medium.

Figure 2.8 illustrates temperature profiles of samples polymerized at 62, 65, 68, and 70°C with the initiator concentration of 0.038% ADVN. Clearly, when the reaction temperature increased, the reaction time was found to decrease, which is similar to that occurring in the water system.
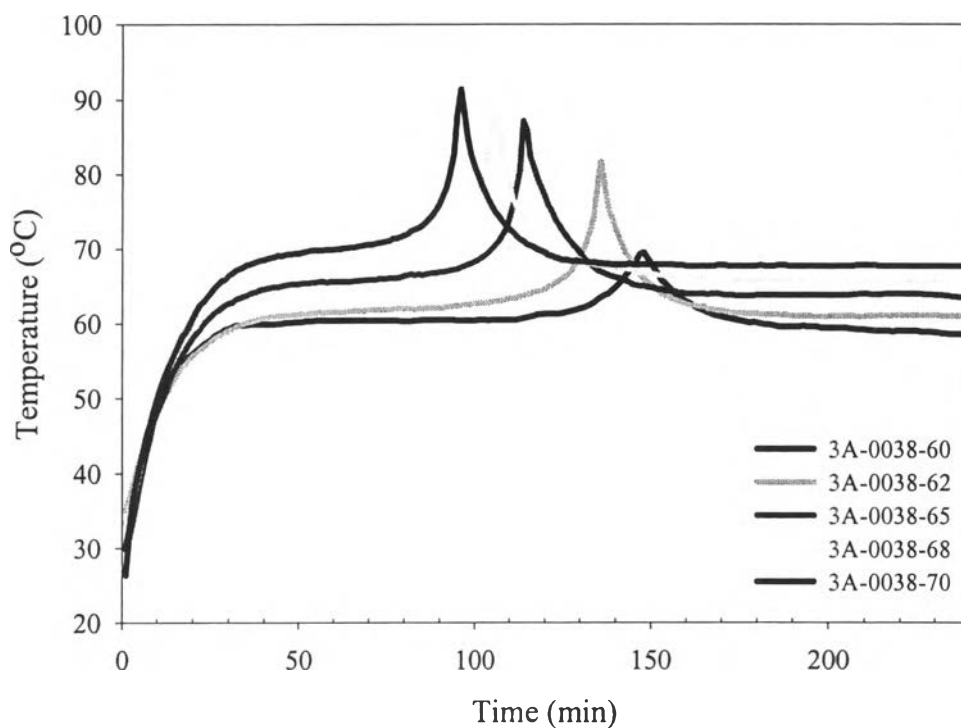
Figure 2.8 Temperature profiles of samples polymerized at 62, 65, 68, and 70°C with 0.038% ADVN in air medium.

In conclusion, both water and air system at a constant initiator concentration, average molecular weights decreased with increasing reaction temperature, while, at a constant reaction temperature, average molecular weights decreased. However, the mechanical properties, which include surface hardness and impact resistant, were found to be unaffected by changes in the reaction temperature.