CHAPTER IV

RESULTS AND DISCUSSION

4.1 Kinetic Rate-Time Profiles

The polymerization rate of $TiCl_4/MgCl_2$ and $Al(C_2H_5)_3$ catalytic system without adding any activator is plotted in Figure 4.1. The rate rises very rapidly to a maximum value and then decreases rapidly with increasing polymerization time.

The initial increase in the rate curve or "induction period" was less than 5 minutes. A number of events can occur (Boor, 1979):

1. The metal alkyl and transition metal surface react to form active centers.

2. Monomer diffusion from the gas cap to the liquid phase and finally to the active centers

3. Polymerization takes place.

4. The catalyst particles begins to break up, exposing new surface and allowing new centers to form.

5. The temperature in the vicinity of the particle centers can become higher than that of the reaction medium if heat transfer is insufficient and chemical reaction at higher temperatures may occur to some extent.

After the polymerization rate reached a maximum, then declined, it appears that with increasing time of polymerization, the decline in
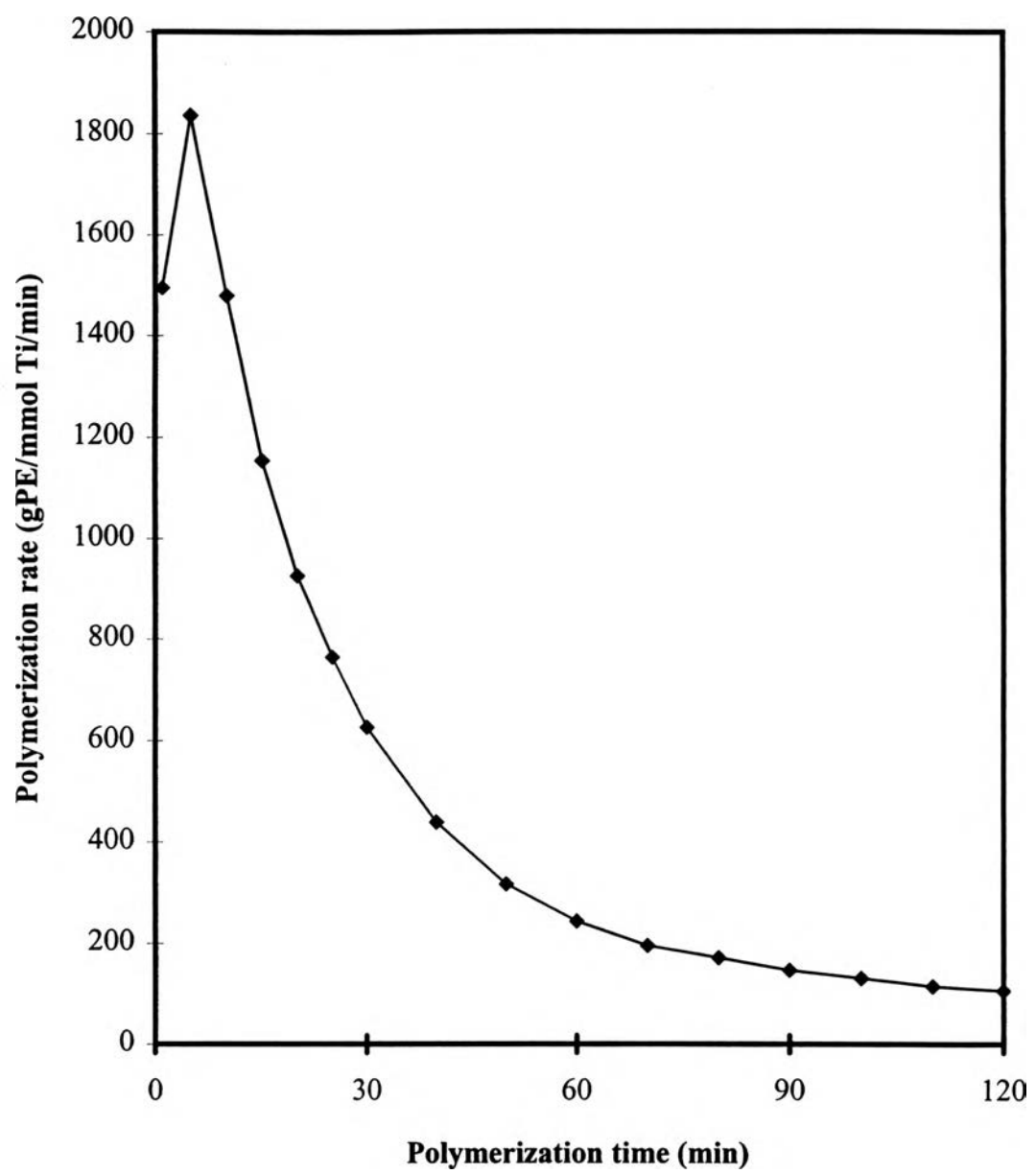
Figure 4.1 Kinetic rate-time profile.

polymerization rate becomes smaller. The decline in polymerization rate has been attributed to a number of factors (Weber et al., 1988):

1. Monomer diffusion limitation due to encapsulation of the catalyst in the semicrystalline polymer.

2. A lower of activity of active centersdue to structural changes.

3. A decrease in the number of active centers by dissolution.

4. Deactivation of catalyst sites.

During the last few years, experimental results have been obtained which substantially deactivation processes 1, 2 and 3. These leave the deactivation of the catalyst sites as the principal cause for decay in the polymerization rate (Weber et al., 1988).

Kollar et al. (1968) concluded that maximum activity for $Al(C_2H_5)_3$-$TiCl_4$ catalyst, when used to polymerize ethylene, occurs when titanium was trivalent. Matsuda et al. (1970) studied the initial rate of ethylene polymerization from the effect of $TiCl_4$ aging or premixing with $Al(C_2H_5)_3$, and found that the initial rate decreased with the aging interval due to over reduction of titanium to lower valence states of titanium. The active sites of polymerization will be titanium ions with a valence higher than two. Baulin et al. (1980) also found that a reduction in the activity of the catalyst can be explained not only by the reduction in the valence of titanium in the active center, but also accumulation in the reaction zone of products of interaction, e.g., alkylaluminium halide.

In this research, we believe that deactivation of catalyst sites due to reduction of more active titanium (III) ions into less active titanium (II) ions is a major cause of the decline in polymerization rate. Monomer diffusion limitations due to encapsulation of the catalyst in the semicrystalline polymer is also a minor cause.

This kinetic rate time profile can be modeled as 1st order exponential decay equation (Fogler, 1992).

1st order decay equation:

$$-\frac{da}{dt} = k_d * a \qquad (14)$$

so

$$a(t) = e^{-k_d*t} \qquad (15)$$

Rate equation:

$$r(t) = r(t = 0) * a(t) \qquad (16)$$

Define initial rate constant

$$r(t = 0) = r_0 \qquad (17)$$

Define deactivation time constant

$$T_d = \frac{1}{k_d} \qquad (18)$$

from equation *(17)*, *(18)* and *(19)* we get

$$r(t) = r_0 \cdot e^{-\frac{t}{T_d}} \qquad (19)$$

For this experiment, we get the initial rate of polymerization (r_0) = 1836.25 gPE/mmol Ti/min and the deactivation time constant (T_d) = 28.7 minutes. The deactivation time constant is the time when the rate is about 37% of initial rate. (When t = T_d then r(t) = r_0 / e).

4.2 Effect of Chloroform (CHCl₃)

From Figure 4.2, it can be seen that the addition of chloroform affected the kinetic rate time profile. The maximum rate was observed at $CHCl_3/Ti$ ratio $c.a.$ 0.1 as shown in Figure 4.3. The productivity; polyethylene produced during polymerization for 2 hours, was plotted against $CHCl_3/Ti$ ratio as Figure 4.4. The maximum productivity was observed at this same $CHCl_3/Ti$ ratio. The productivity as a function of activator per catalyst ratio showed a maximum similar to the findings of Adisson et al. (1994) and Ribeiro et al. (1995) for polymerization of ethylene with supported vanadium catalyst. Adisson et al. (1994) concluded that the main role of the halogenated molecules may be due to their oxidizing character. It allows re-oxidation of the reduced V(II) species formed during the polymerization process, to V(III) and then realkylated by alkylaluminium to become active again and to start a new polymer chain.

In this experiment, we believe that chloroform has reoxidized the Ti(II) inactive species to Ti(III) active species and then the alkylaluminium realkylated these to be active centers. As a consequence, the activity of this catalytic system decays more slowly than without the addition of chloroform. Excess chloroform which is not used to re-oxidize may attach to the active sites and cause a deactivation effect.

The maximum productivity achieved at the optimum $CHCl_3/Ti$ ratio was 540 g or about 28 % more when compared to the system with no activator addition. The $CHCl_3/Ti$ ratio between 0.1 and 0.2 is recommended to be the best range because the slight changes in the $CHCl_3/Ti$ ratio in this range results in little change in productivity.

The exponential decay model *(equation 19)* is applied to these kinetic rate time profiles. The deactivation time and initial rate of polymerization were
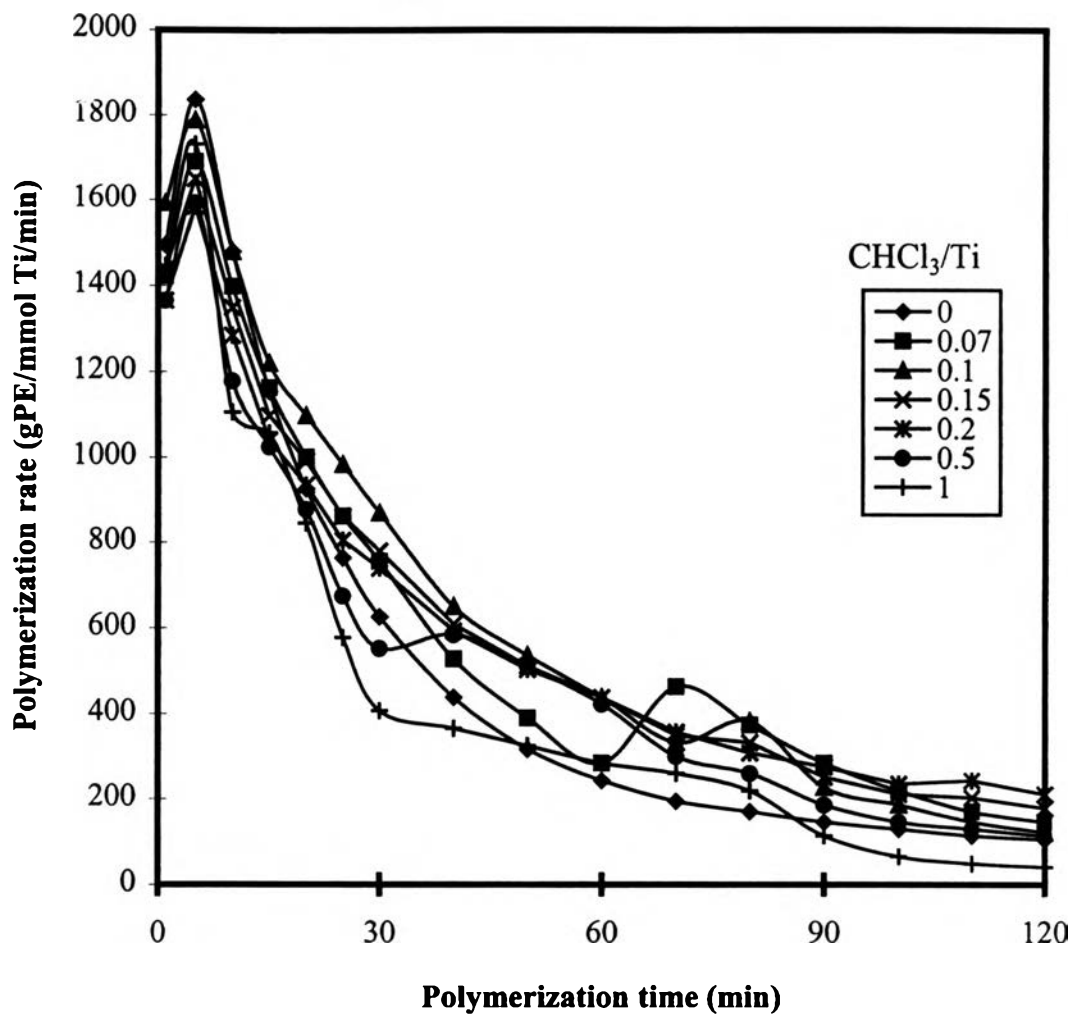
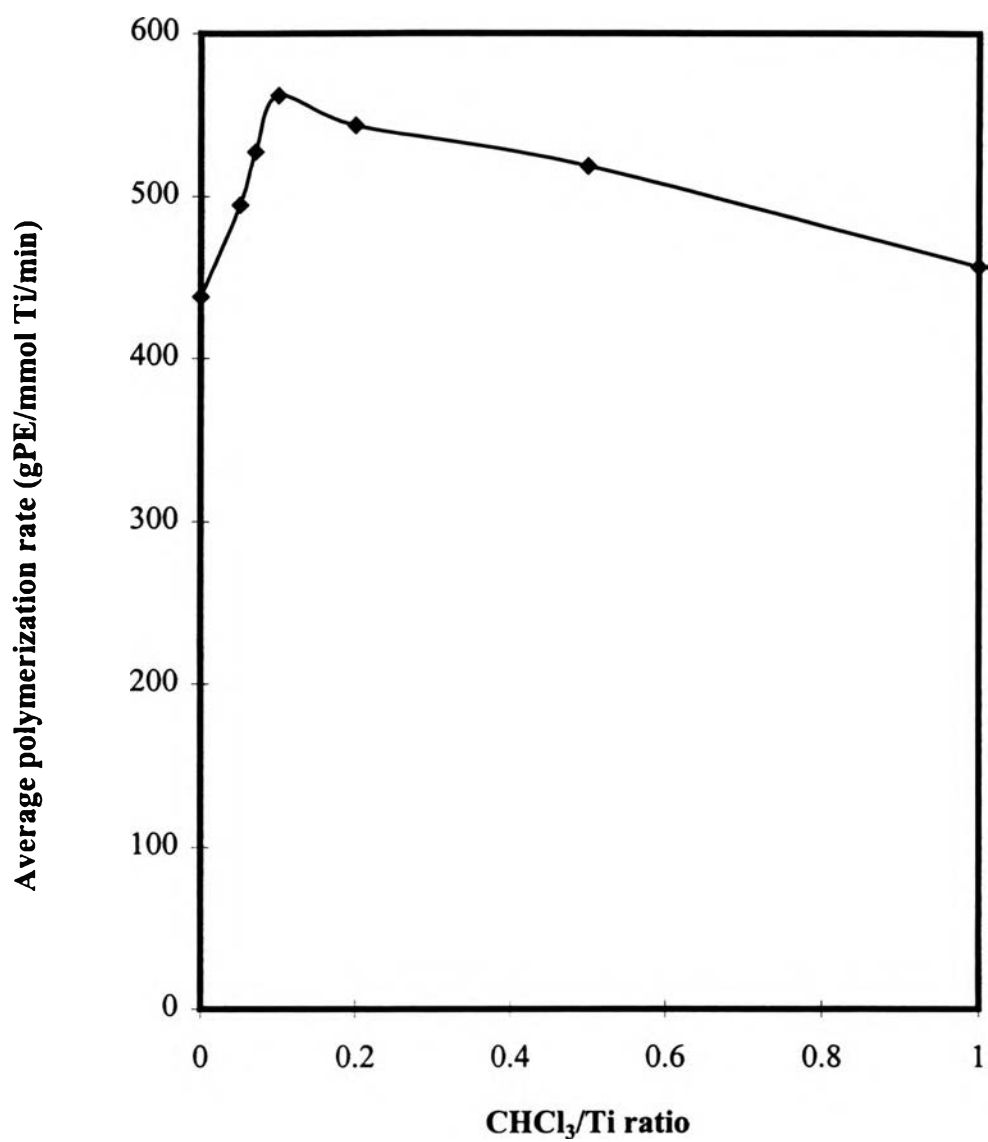**Figure 4.2** Effect of chloroform concentration on kinetic rate time profile.

Figure 4.3 Effect of chloroform concentration on average polymerization rate.
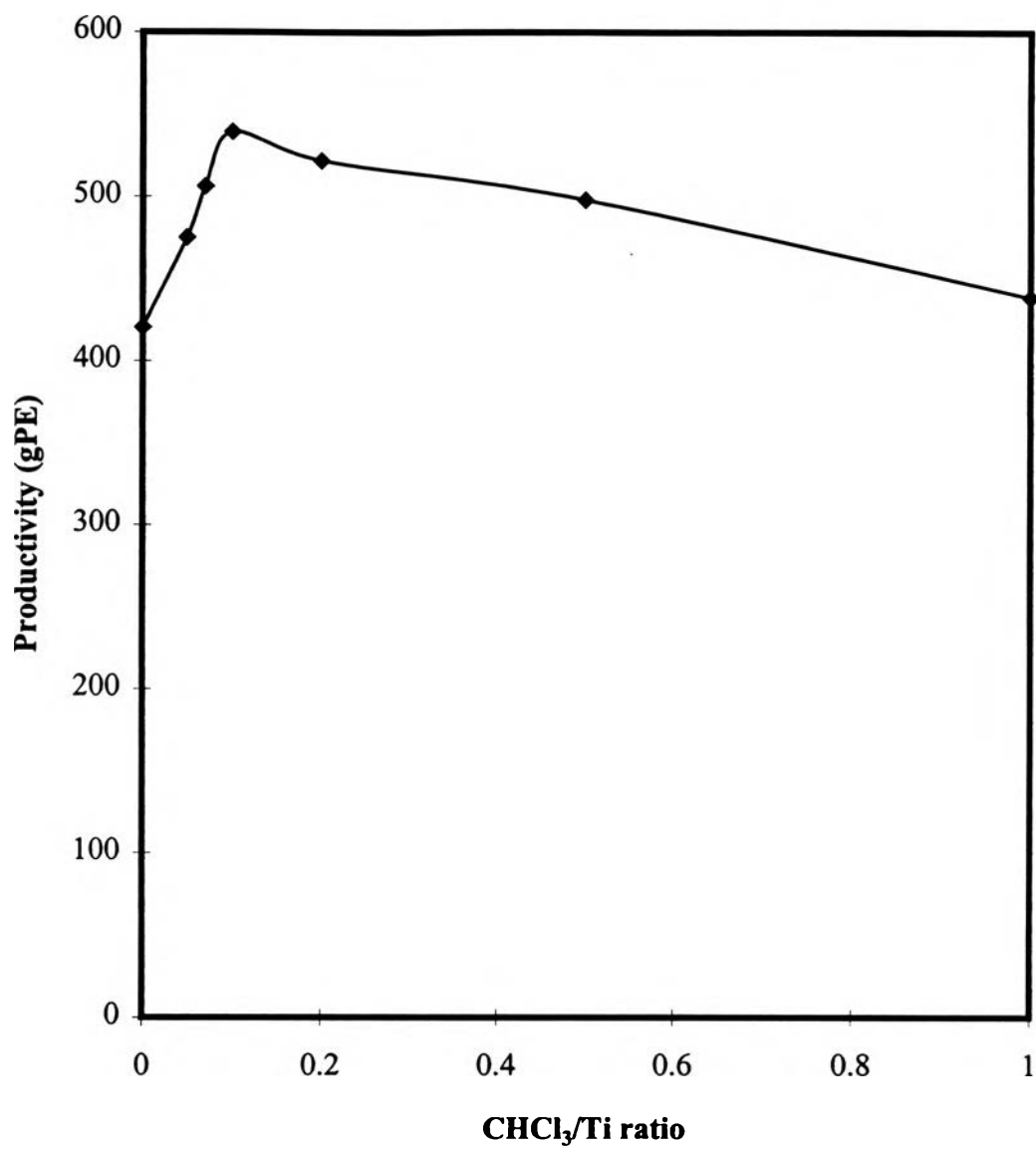
Figure 4.4 Effect of chloroform concentration on productivity.

plotted as shown in Figure 4.5. We observed that initial rates of polymerization at different $CHCl_3/Ti$ ratios to be relatively constant. In contrast, deactivation time constants varied and showed a maximum value at the optimum (*c.a.* 0.1) ratio, which also gave the highest productivity. For this reason, we can conclude that the change in performance of this catalytic system by chloroform is a result of improvement of deactivation or stabilization of the active sites, not an improvement of higher activity or increase in of the active sites.
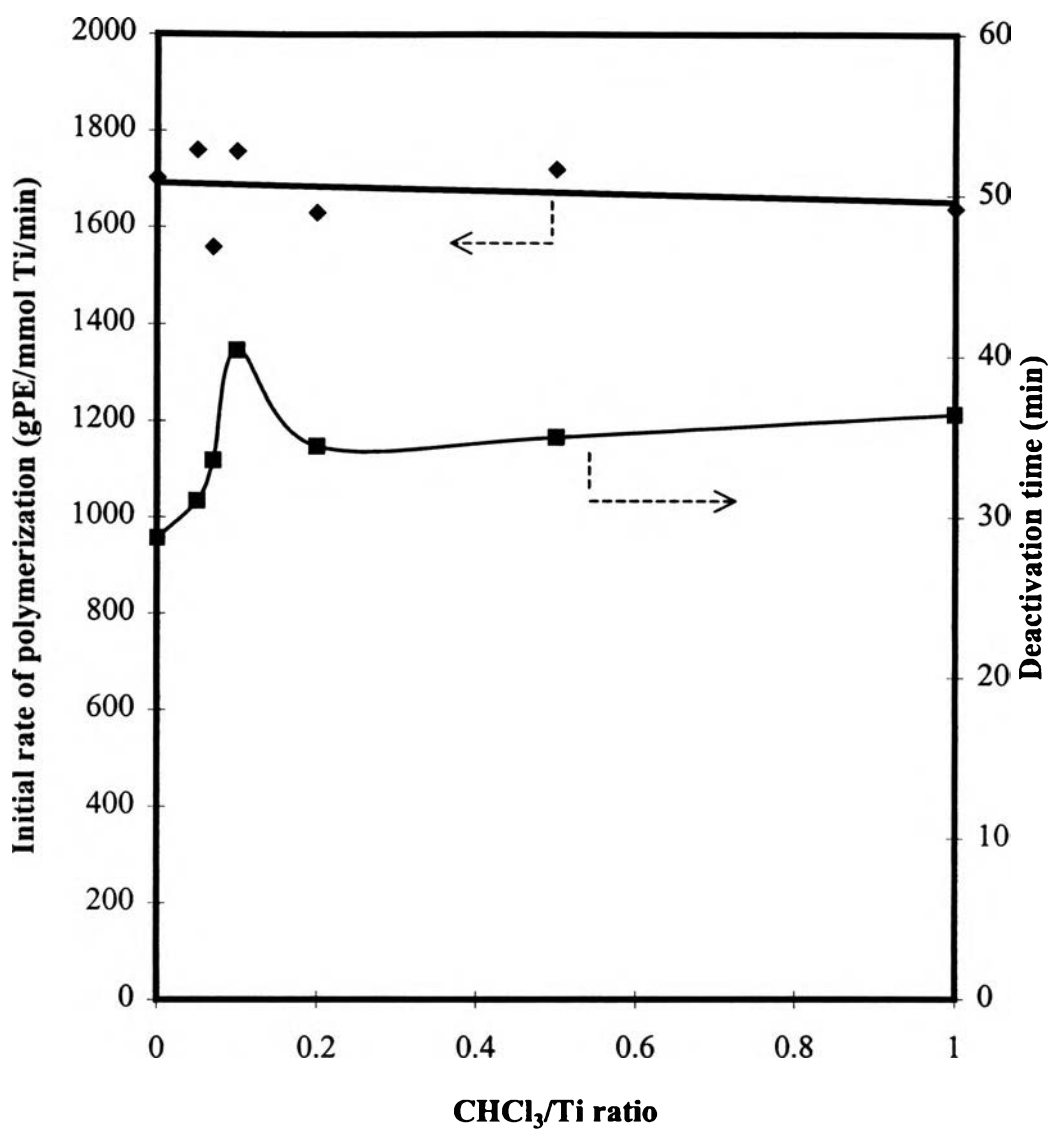
Figure 4.5 Effect of chloroform concentration on deactivation time and initial rate of polymerization.

4.3 Effect of Trichloroethane (CH₃CCl₃)

The effect of trichloroethane on ethylene polymerization with this catalytic system showed a similar effect to that of chloroform as mentioned in section 4.2, but the intensity of the activating effect was less.

Figure 4.6 shows kinetic-rate time profiles affected by trichloroethane concentration. The maximum productivity was observed for a CH_3CCl_3/Ti ratio about the same as for the system with chloroform, as shown in Figure 4.7. The maximum productivity achieved at optimum CH_3CCl_3/Ti ratio was 516 g or 23 % increased compare to the system with no activator addition.

The role of trichloroethane in the polymerization with this catalytic system should be the same as mentioned in the previous part with chloroform. The exponential decay model was also applied to the kinetic rate time profiles. The deactivation time and initial rate of polymerization were plotted against CH_3CCl_3/Ti ratio as shown in Figure 4.8. A similar trend to the effect of chloroform was observed.
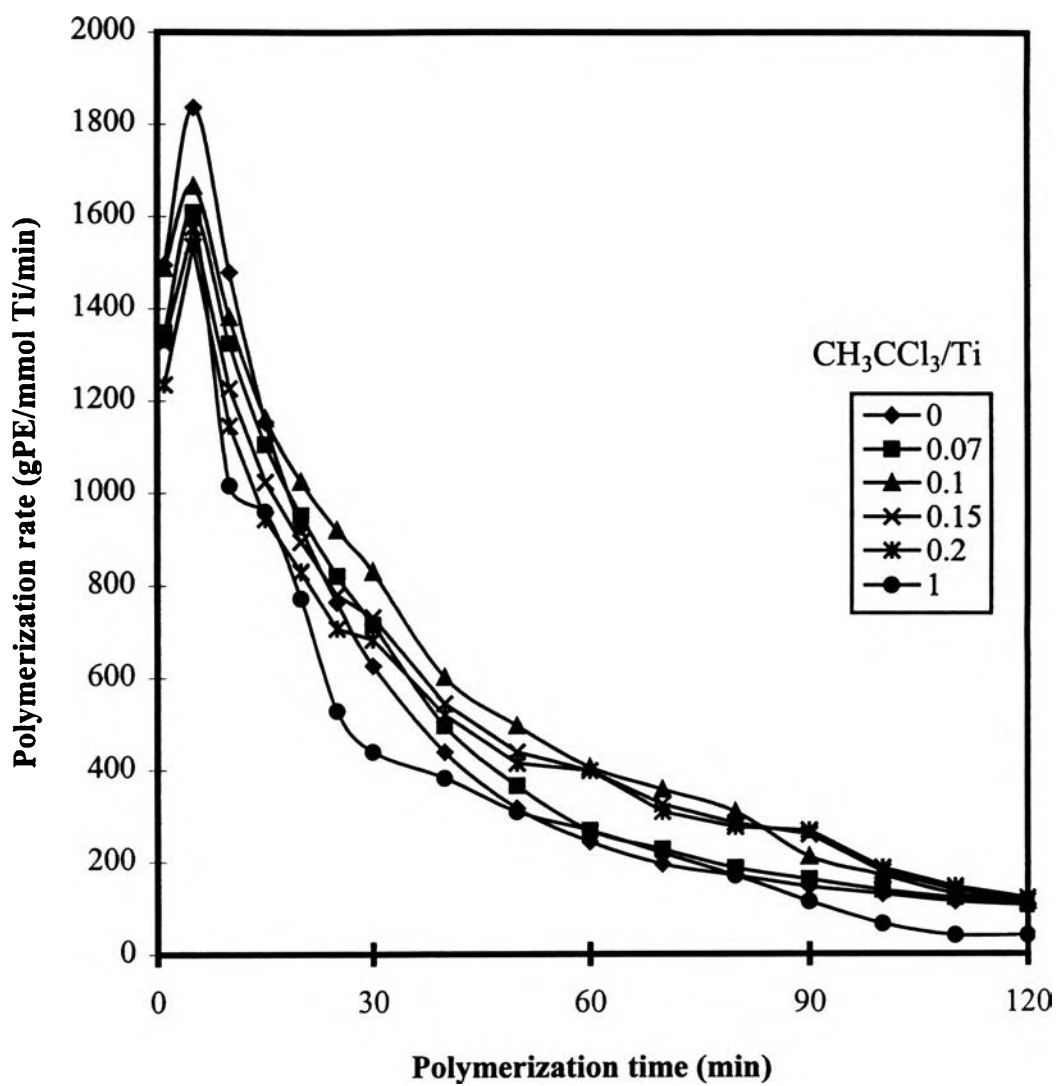
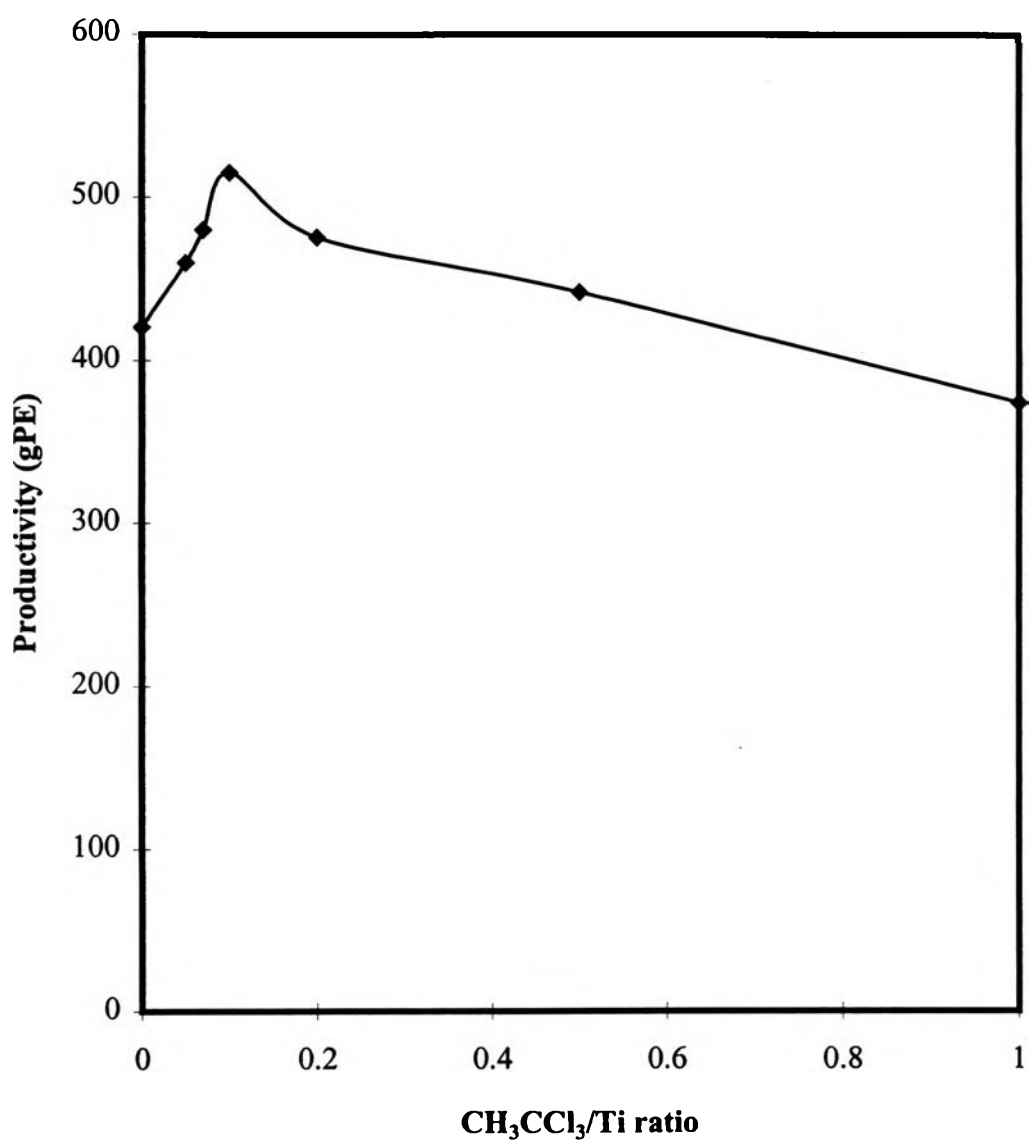**Figure 4.6** Effect of trichloroethane concentration on kinetic rate time profile.

Figure 4.7 Effect of trichloroethane concentration on productivity.
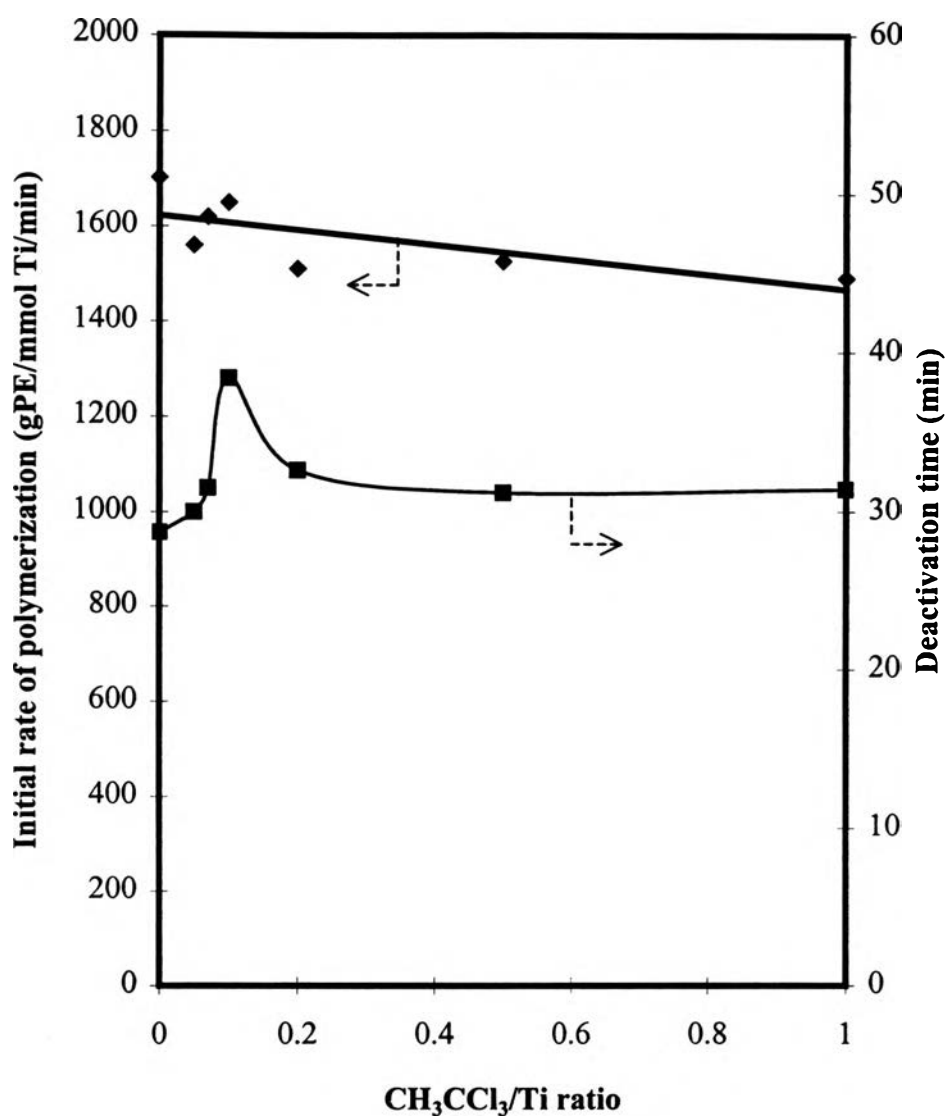
Figure 4.8 Effect of trichloroethane concentration on deactivation time and initial rate of polymerization.

4.4 Effect of Benzylchloride ($C_6H_5CH_2Cl$)

From Figure 4.9, it can be seen that benzylchloride concentration affected the kinetic rate-time profiles. In contrast to chloroform and trichloroethane, benzylchloride did not act as an "activator" but as a "deactivator" or caused deactivation to be more rapid than with no addition. Figure 4.10 shows the effect of $C_6H_5CH_2Cl/Ti$ ratio on productivity of ethylene polymerization with this Ziegler-Natta catalytic system. The deactivation time and initial rate of polymerization were plotted against $C_6H_5CH_2Cl/Ti$ ratio as shown in Figure 4.8.

The proposed mechanism is that the π-electron of benzene ring attach the active site (donor effect), like ethyl benzoate (EB) which using to increase stereospecificity in propylene polymerization is accompanied with a decrease in activity (Kissin, 1985; Tiat, 1989). Another mechanism is the steric effect because the benzyl group is relatively large compared to chloroform and trichloroethane, it blocks sites and decreases monomer reactivity (Kissin, 1981).
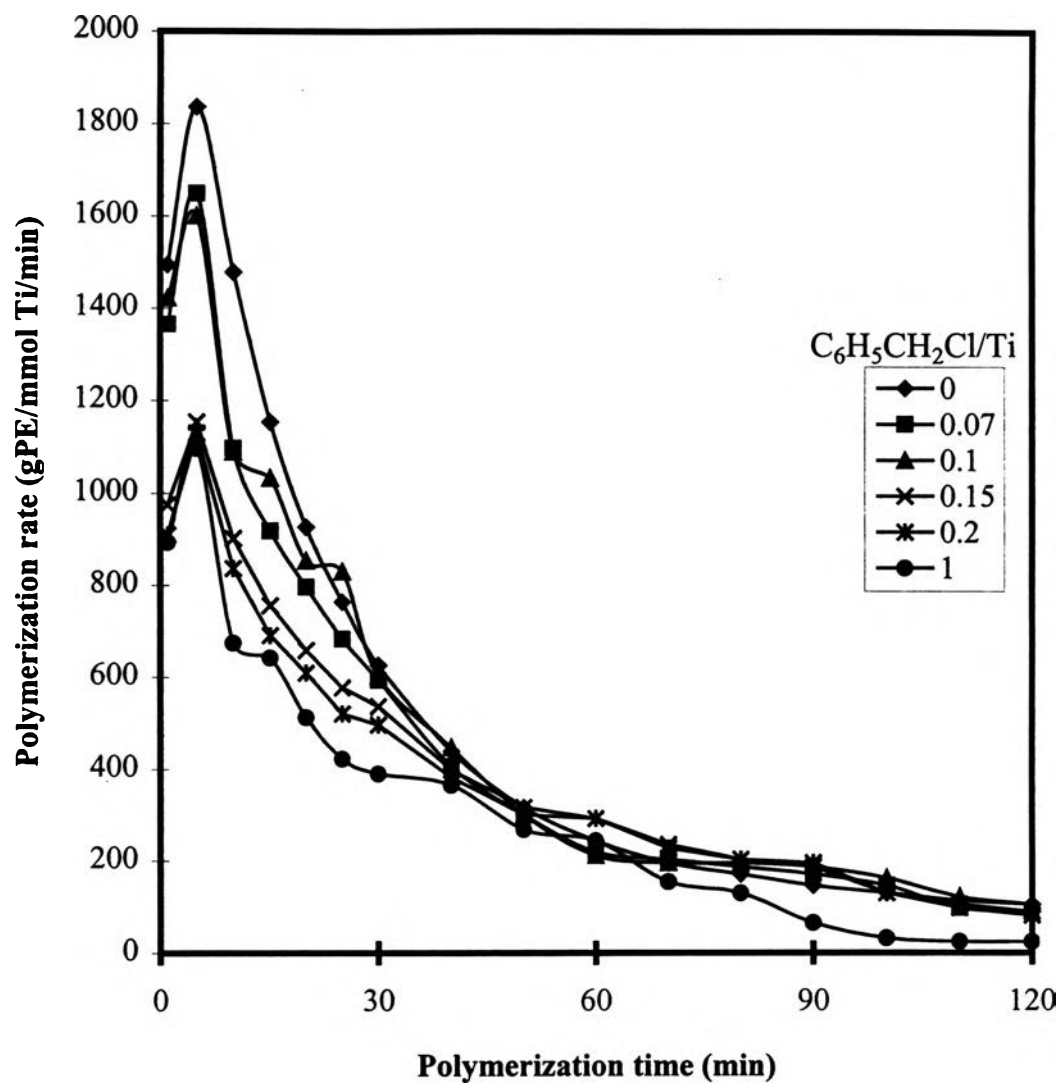
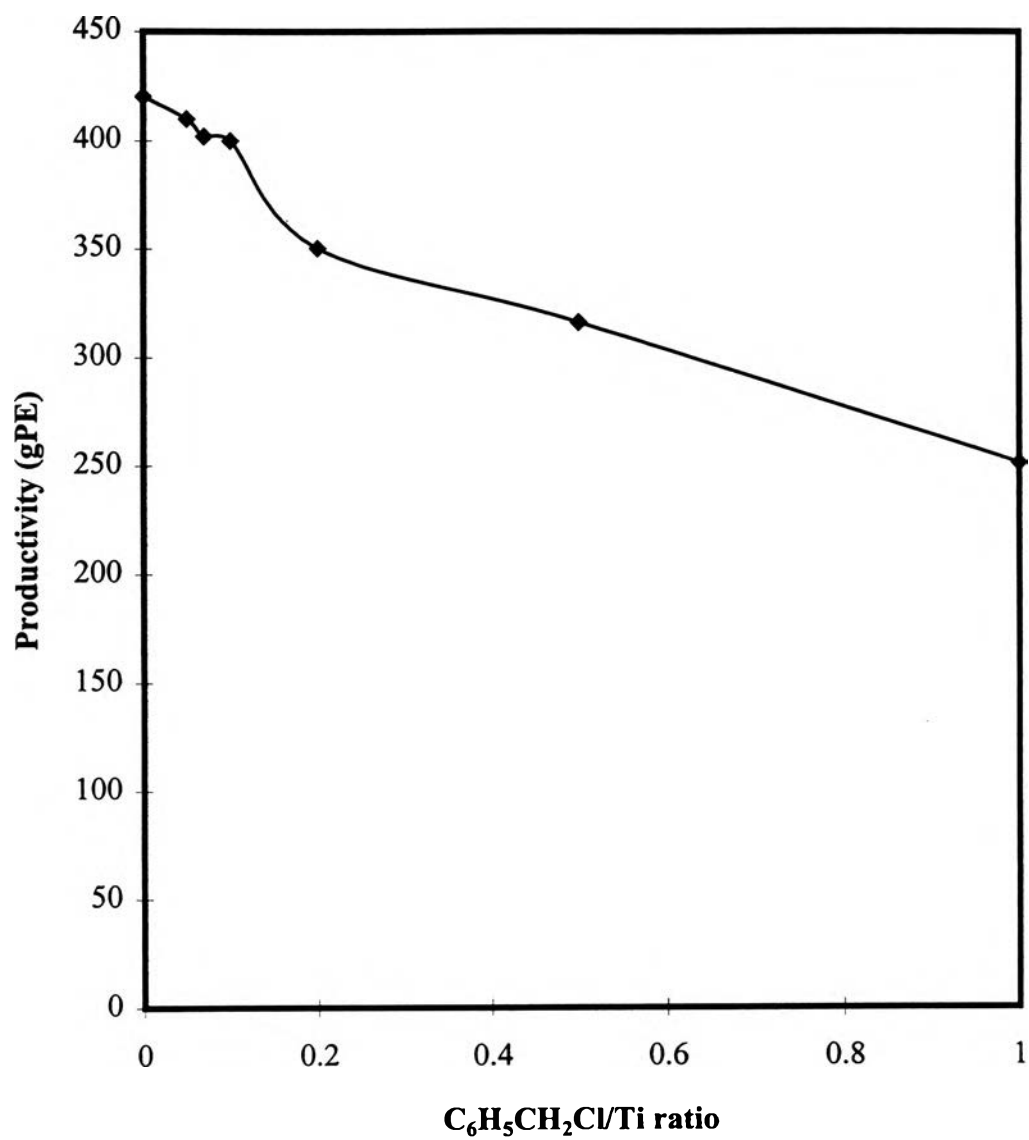**Figure 4.9** Effect of benzylchloride concentration on kinetic rate time profile.

Figure 4.10 Effect of benzylchloride concentration on productivity.
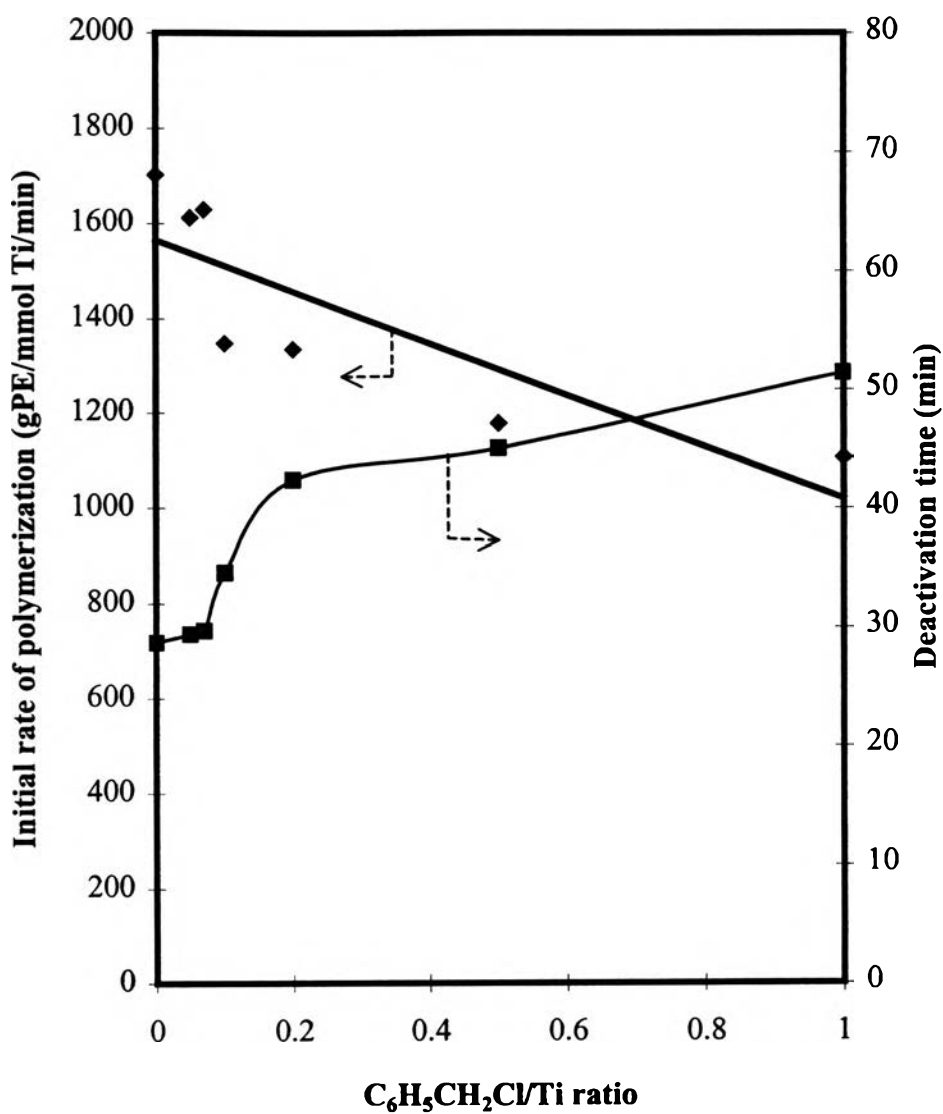
Figure 4.11 Effect of benzylchloride concentration on deactivation time and initial rate of polymerization.

4.5 Effect of Activator Addition Time

In the previous experiments, all activators used were fed into the reactor before polymerization took place. In these topic, the activator feeding as a pulse was started after polymerization was begun. Chloroform which is the most effective activator was studied in detail.

Figure 4.12 shows the effect of time of activator addition on kinetic rate profile and Figure 4.13 shows the effect of time of activator addition on productivity.

Feeding of chloroform at 20 min after the start of polymerization is less effective than feeding before polymerization but feeding at 20 min of polymerization also improved decay rate after the addition.

In the early state of polymerization, chloroform may improve the deactivation behavior of the catalyst site or inhibit type 4 of deactivation (Weber et al., 1988). But when the polymer particles grew up, the decline in polymerization rate may be controlled by monomer diffusion limitations due to encapsulation of the catalyst in the semicrystalline polymer or type 1 of deactivation (Weber et al., 1988). So the chloroform add at this point has only small effect.
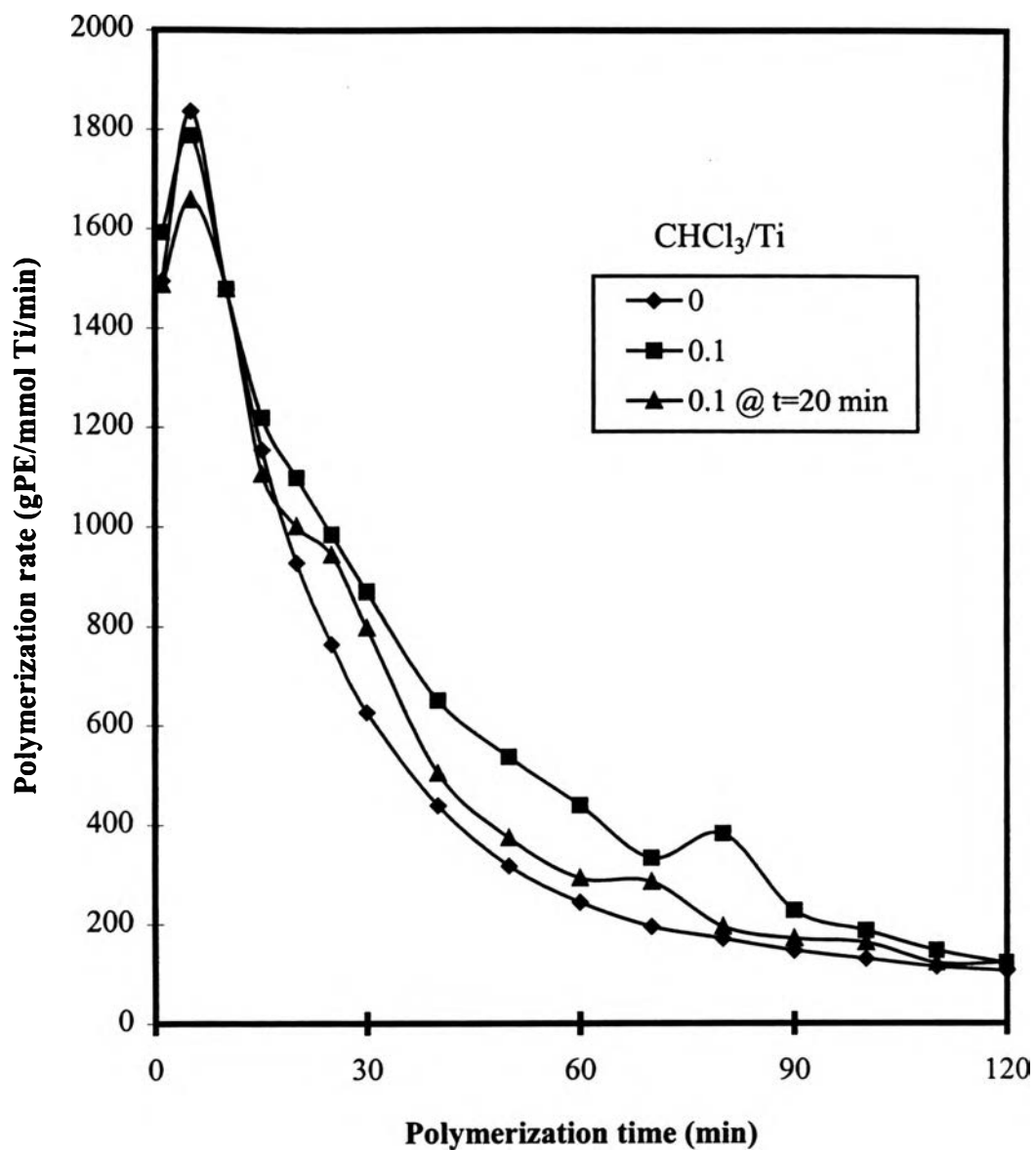
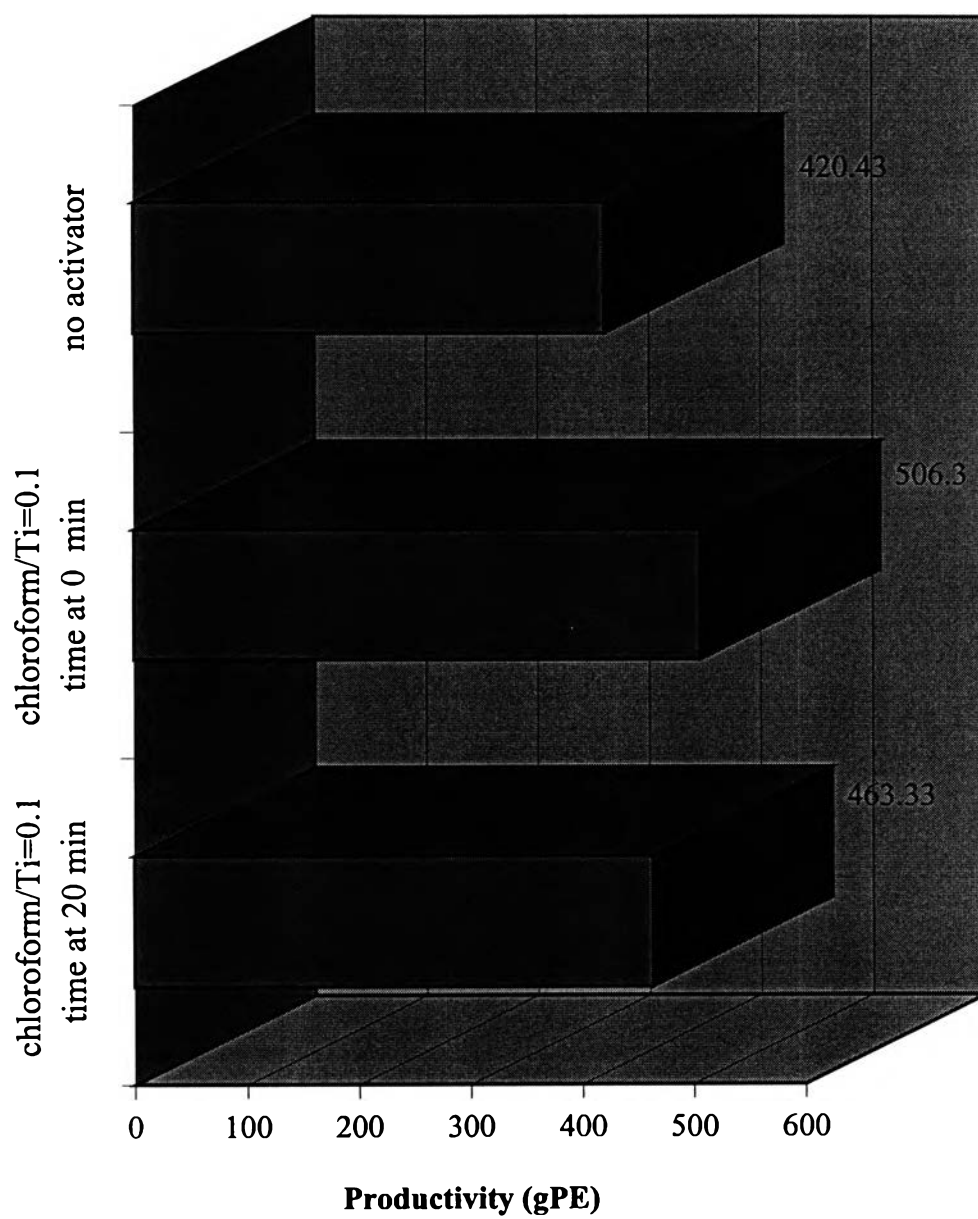**Figure 4.12** Effect of time of activator addition on kinetic rate time profile.

Figure 4.13 Effect of time of activator addition on productivity.

4.6 Effect of Type of Activator

We have already discussed the effect of each type of activator in previous sections. Figure 4.14 shows the effect of type of activator at optimum ratio of each activator per titanium, $c.a$ 0.1 on kinetic rate time profile and Figure 4.15 shows the effect of the type of activator at each ratio on productivity comparing among these three types of activator.

We can observe that chloroform is the best activator, trichloroethane is also good activator but benzylchloride is a deactivator, or poison, to this catalytic system.

4.7 Polymer Characterization

The GPC results of the polyethylene produced by this catalytic system with chloroform activator are shown in Figure 4.16.

It can be concluded that polymer produced with the addition of chloroform is the same quality as without its addition in terms of the MWD. Differences in the polymer produced by vanadium catalyst with activator addition is narrower MWD (Kao et al., 1991; Zoeckler et al., 1988; Beran et al., 1984).
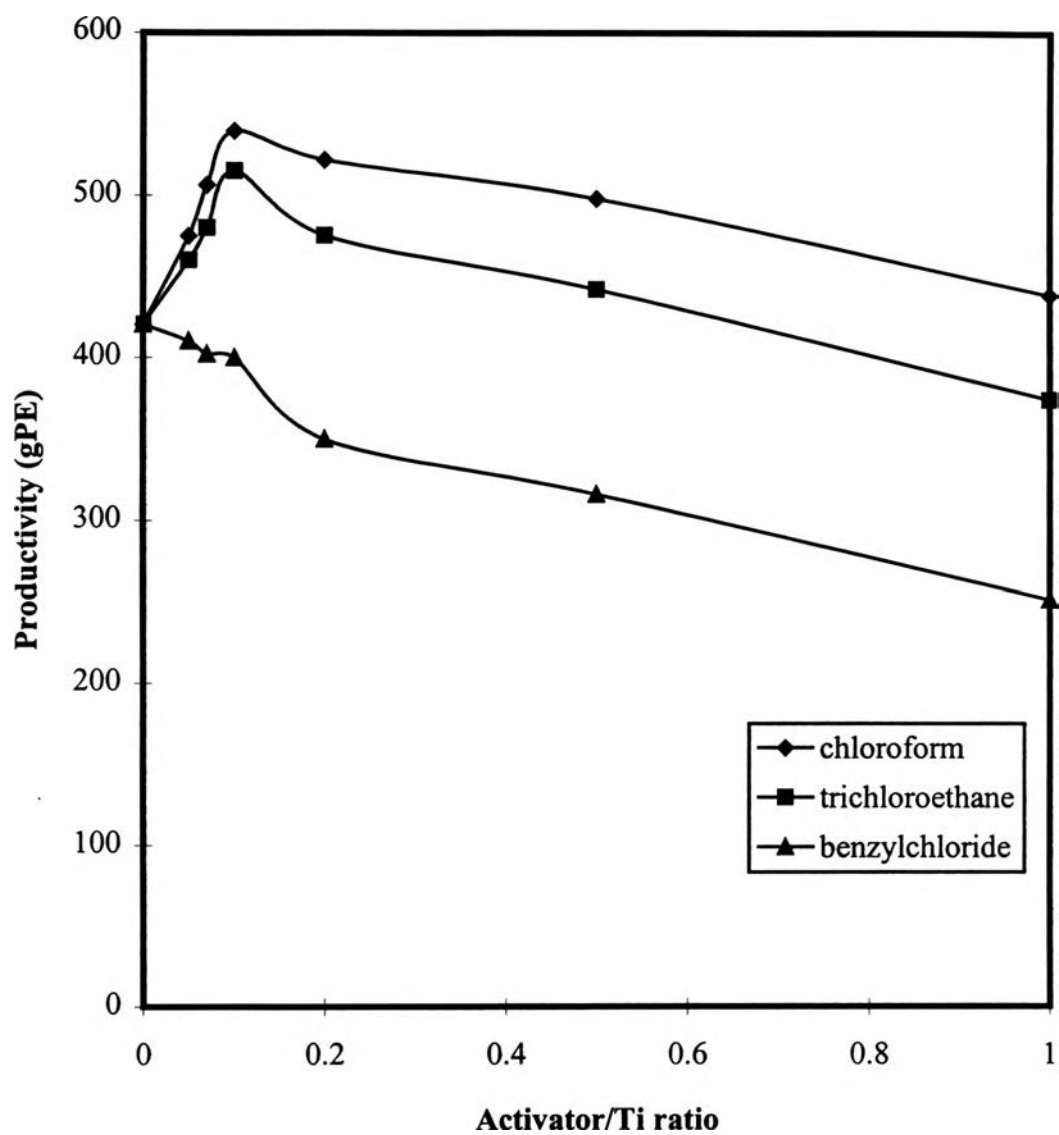
Figure 4.14 Effect of type of activator at optimum ratio on kinetic rate time profile.
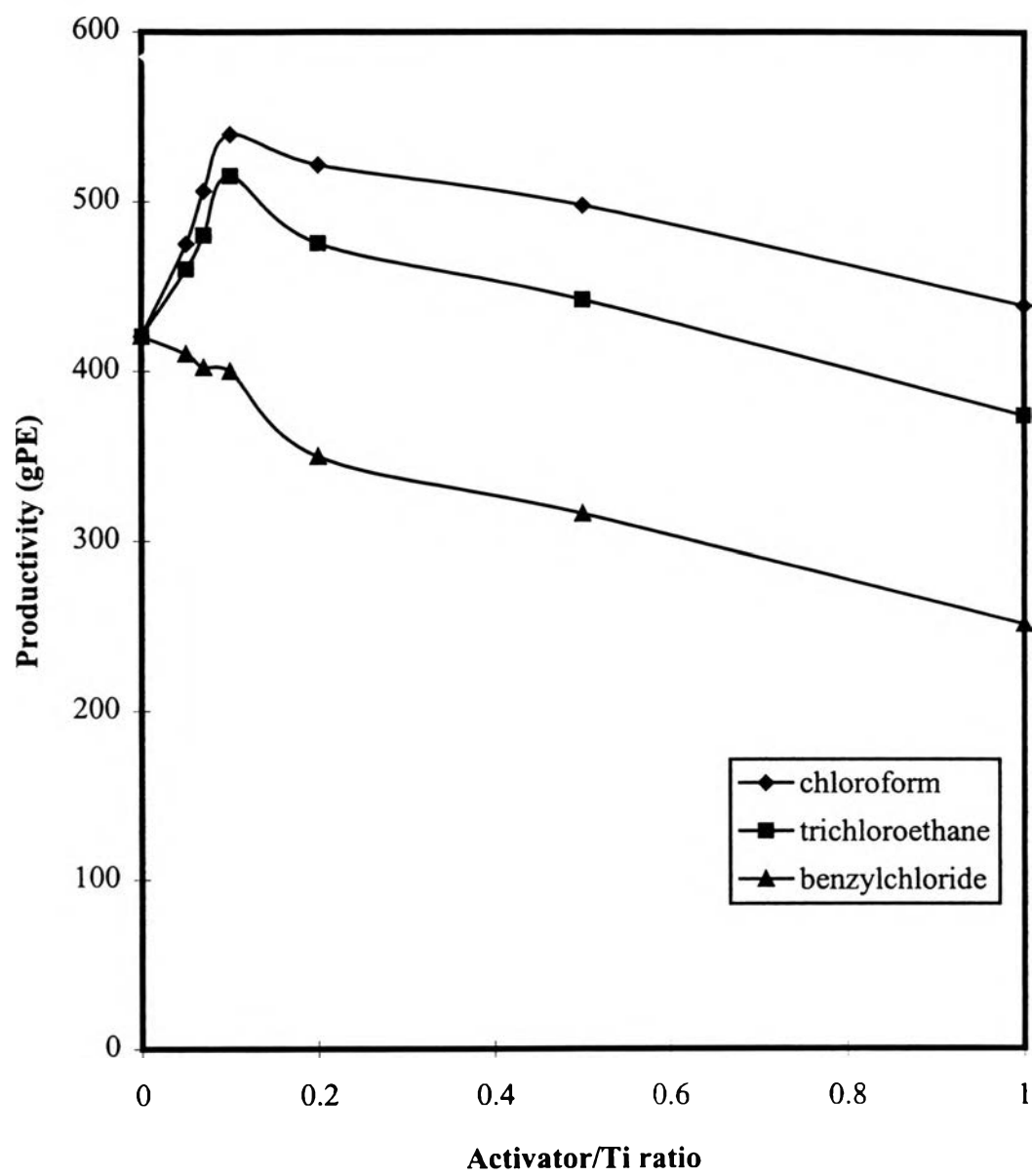
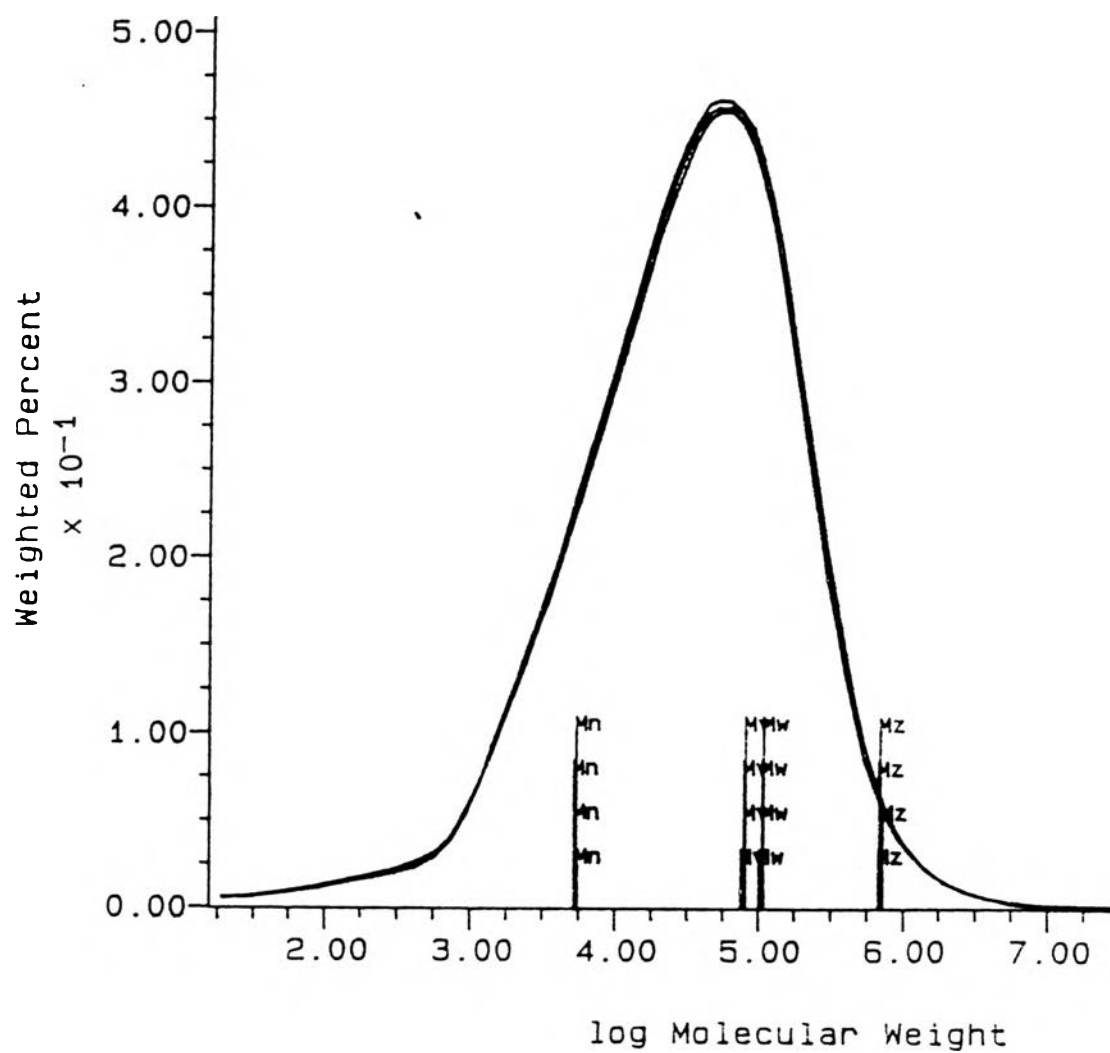**Figure 4.15** Effect of type of activator on productivity.

Figure 4.16 Effect of chloroform concentration on molecular weight distribution of polyethylene.