## CHAPTER IV

## RESULTS AND DISCUSSIONS

### 4.1  Synthesis of Phenyl vinyl ketone (PVK) monomer

In this research work, phenyl vinyl ketone was synthesized using two steps of reactions, Mannich reaction and pyrolysis reaction.

#### 4.1.1  Synthesis of $\beta$-Dimethylaminopropiophenone hydrochloride

$\beta$-Dimethylaminopropiophenone hydrochloride was prepared by Mannich reaction which involved condensation of formaldehyde and secondary amine, dimethylamine hydrochloride, with acetophenone.
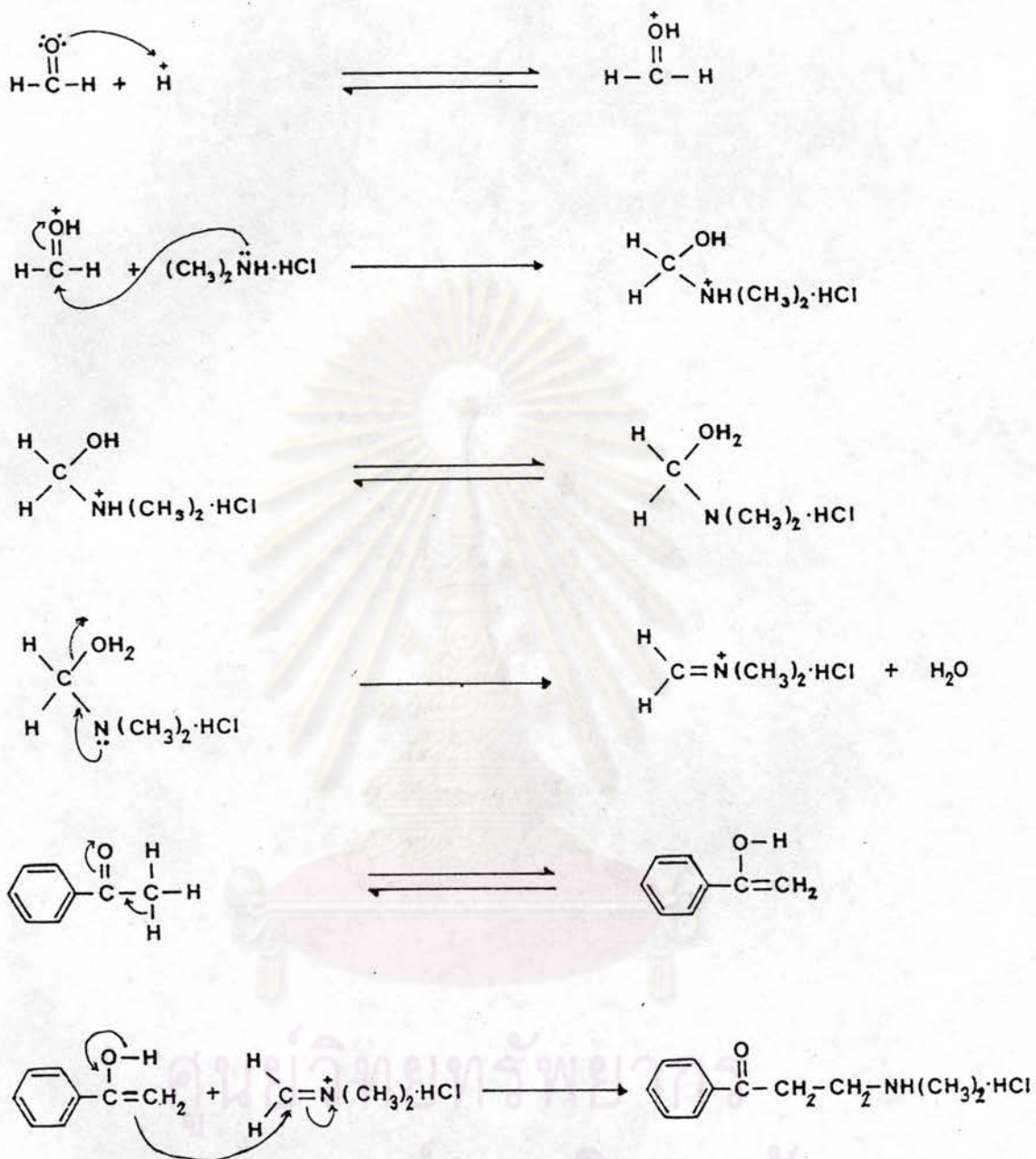
Acetophenone was refluxed with dimethylamine hydrochloride in ethanol and in the presence of paraformaldehyde and trace of hydrochloric acid.
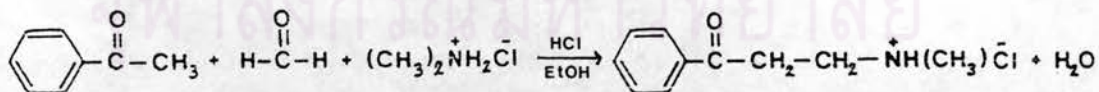
65% yield of white crystal product was obtained after the second recrystallization (m.p 155-156 °C).

The proposed mechanism of this reaction was shown in Scheme 4.1

Scheme 4.1

IR (KBr) spectrum of $\beta$-dimethylaminopropiophenone hydrochloride was exhibited in Figure 4.1. It was clearly shown that $^{+}$NH stretching appeared at $\nu$ 2700-2250 cm$^{-1}$ and C=O stretching at $\nu$ 1675 cm$^{-1}$ which indicated the appearance of the tertiary amine salt ( $R-\overset{\underset{R}{|}}{\underset{|}{N}}H$ ) and carbonyl group in the molecule, respectively. Besides, the absorption band of C-H stretching in aromatic ring and C-H stretching in aliphatic at $\nu$ 3050 cm$^{-1}$ and $\nu$ 2900 cm$^{-1}$ indicated there were aromatic ring and aliphatic moiety in the molecule. The other absorption bands in Figure 4.1 were interpreted in Table 4.1.

Table 4.1 The assignment for the IR spectrum of $\beta$-dimethylaminopropiophenone hydrochloride

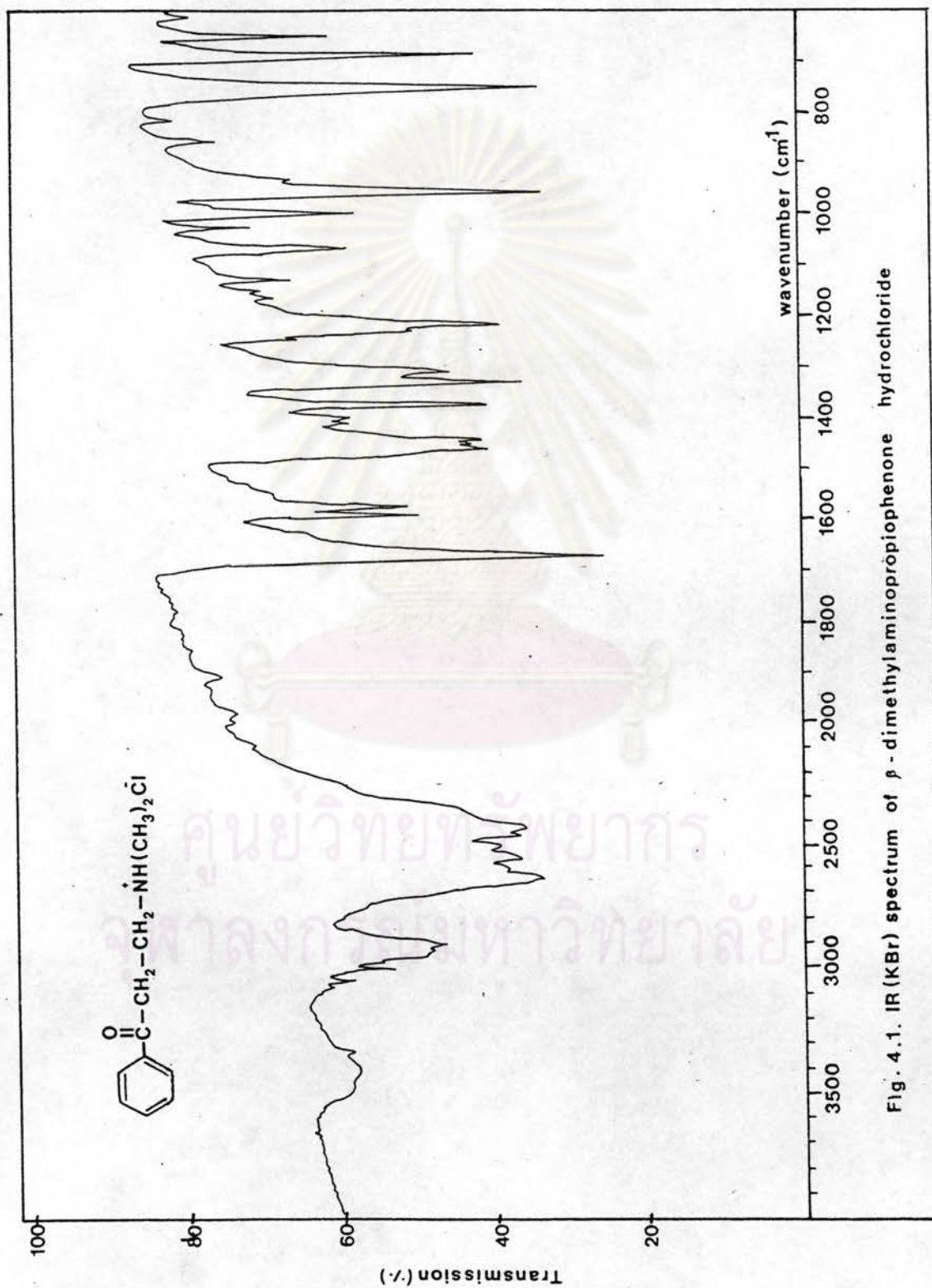| Absorption frequency $\nu$(cm$^{-1}$) | Assignment |
|---|---|
| 3340 | C=O overtone |
| 3050 | C-H stretching in aromatic |
| 2900 | C-H stretching in aliphatic |
| 2700-2250 | $^{+}$N-H stretching ( $R-\overset{\underset{R}{|}}{\underset{|}{N}}H$ ) 3$^{\circ}$ amine salt |
| 1675 | C=O stretching |
| 1600,1440 | C=C stretching in aromatic |
| 1470-1430 | C-H bending ( $\rangle$CH$_2$, -CH$_3$) |
| 1330 | C-N stretching |
| 1220,1020 | C-N vibration |

Fig. 4.1. IR (KBr) spectrum of β-dimethylaminopropiophenone hydrochloride

### 4.1.2  Pyrolysis of $\beta$ -Dimethylaminopropiophenone hydrochloride to phenyl vinyl ketone (PVK)

After drying of $\beta$ -dimethylaminopropiophenone hydrochloride, dimethylamine hydrochloride was easily eliminated by distillation of $\beta$ -dimethylaminopropiophenone hydrochloride under reduced pressure. The yellowish liquid was obtained with b.p 62-63 °C at 2 mmHg and 37% yield.
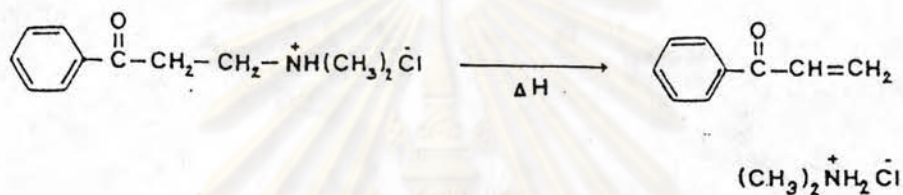


The proposed mechanism of this reaction was shown in Scheme 4.2
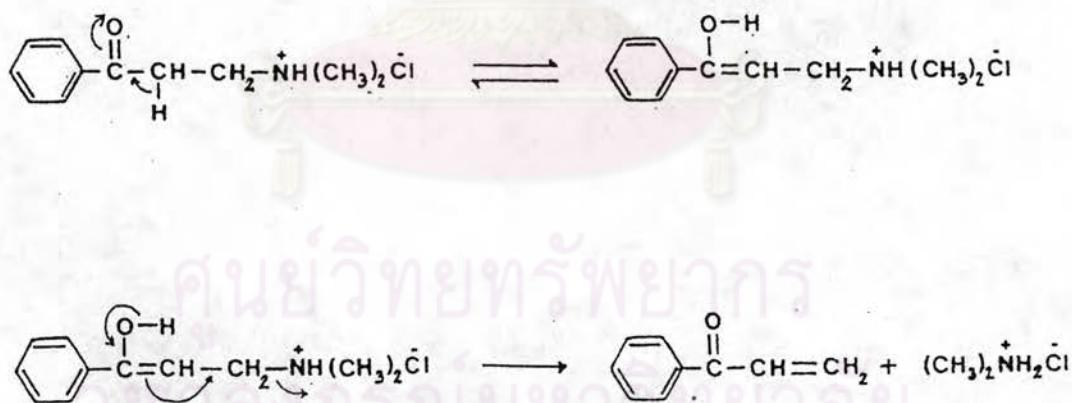


Scheme 4.2

It should be noted here that phenyl vinyl ketone was reactive to light which caused polymerization to yield poly (phenyl vinyl ketone). If this happens, the molecular weight could not be controlled. Therefore, phenyl vinyl ketone and poly(phenyl vinyl ketone) should be prepared and purified in the dark and

hydroquinone which was an inhibitor should be added to $\beta$-dimethylaminopropiophenone hydrochloride before distillation under reduced pressure.

The product could be characterized by spectroscopic technique. IR (NaCl) spectrum was shown in Figure 4.2. The absorption bands at $\nu$ 3050 cm$^{-1}$ and $\nu$ 1670 cm$^{-1}$ indicated aromatic ring and carbonyl group in the molecule, respectively. The absorption band at $\nu$ 1650 cm$^{-1}$ indicated carbon double bond (C=C) conjugated with carbonyl group (C=O).The other absorption bands in Figure 4.2 were interpreted in Table 4.2.

Table 4.2 The assignment for the IR spectrum of phenyl vinyl ketone

| Absorption frequency $\nu$ (cm$^{-1}$) | Assignment |
|---|---|
| 3050 | C-H stretching in aromatic |
| 1960 | |
| 1810 | overtone region of aromatic ring |
| 1770 | |
| 1670 | C=O stretching |
| 1650 | C=C stretching of alkene conjugated with carbonyl |
| 1600, 1440 | C=C stretching of aromatic ring |
| 1400 | =CH$_2$ in plane bending of alkene |
| 990 | =CH out off plane bending of vinyl |

Moreover, the ^{1}H-NMR spectrum (Figure 4.3) for phenyl vinyl ketone also showed the signals at $\delta$ 6.98, 6.48 and 5.92 ppm which corresponded to the olefinic protons (Table 4.3). A double doublet at $\delta$ 6.98 ppm was due to proton $H^c$. It was strongly deshielded by carbonyl group and coupled with proton $H^b$ ($J_{cb}$ = 17.22 Hz) and with proton $H^a$ ($J_{ca}$ = 10.5 Hz). Likewise, a double doublet at $\delta$ 6.48 ppm was due to proton $H^b$ which were coupled with proton $H^c$ ($J_{cb}$ = 17.22 Hz) and the proton $H^a$ ($J_{ab}$ = 1.95 Hz). A double doublet at 5.92 ppm was due to proton $H^a$ which was coupled with proton $H^c$ ($J_{ca}$ = 10.5 Hz) and with the proton $H^b$ ($J_{ab}$ = 1.95 Hz).

Consequently, the ^{1}H-NMR spectrum (Figure 4.3) of this compound confirmed that there was a structure of terminal olefinic group ( $C=CH_2$ ) in the molecule.

In addition, the ^{13}C-NMR spectrum (Figure 4.4) indicated the important carbon signal of carbonyl group (C=O) was at $\delta$ 190.47 ppm. The other signals at $\delta$ 129.85 ppm and 132.24 ppm were the signals of $=^aCH_2$ and $-^bCH=$ , respectively. The other signals were interpreted in Table 4.4.

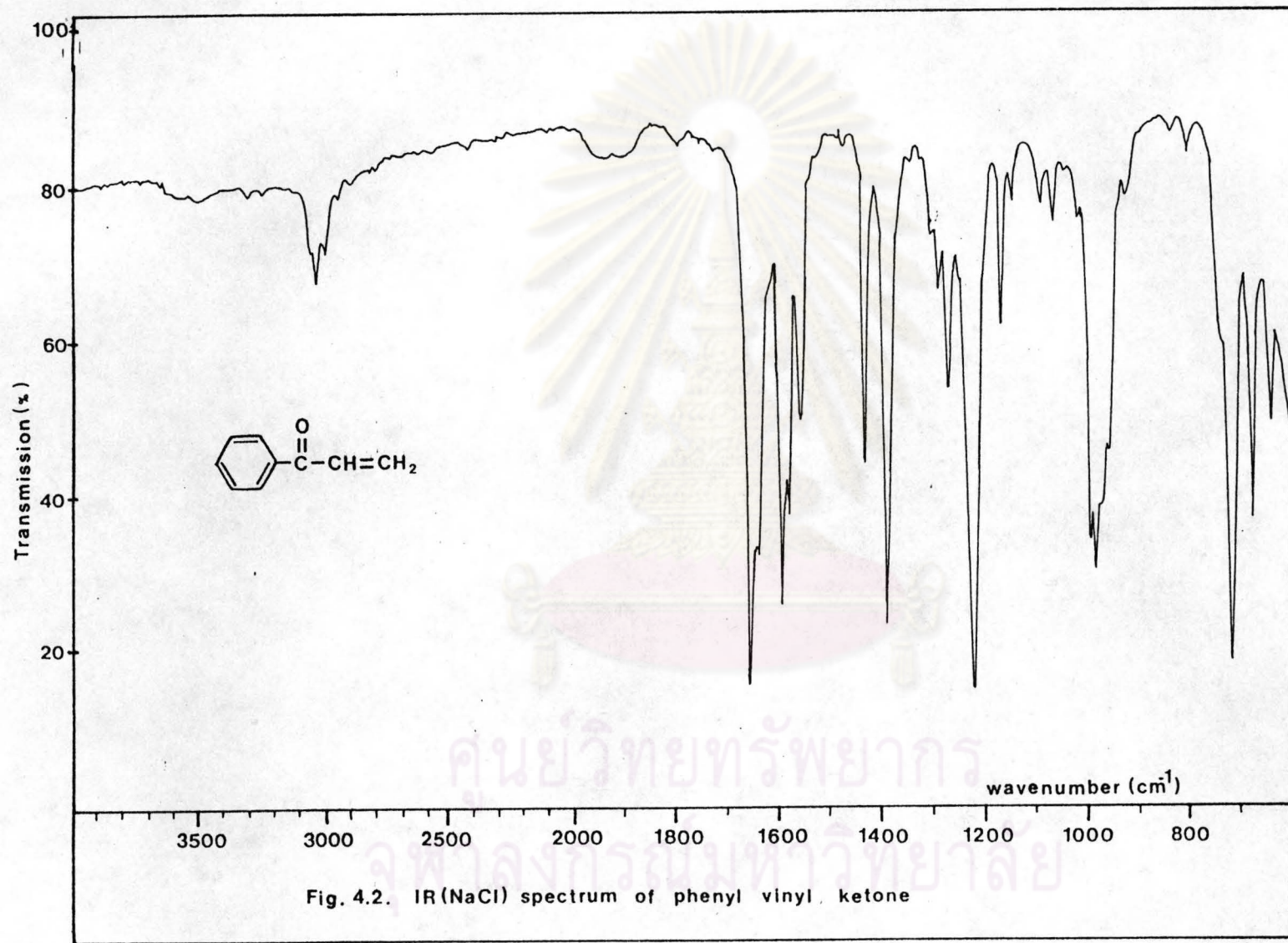**Table 4.3**  The assignment for the ^{1}H-NMR spectrum of phenyl vinyl ketone

| Chemical Shift $\delta$(ppm) | Intensity | Assignment |
|---|---|---|
| 7.86 | Multiplet (2H) | ortho  proton ($H^d$) |
| 7.47 | Multiplet (3H) | meta and para proton($H^e$,$H^f$) |
| 7.29 | | $H^c$⟍    ⟋$H^a$ |
| 7.17 | d.d, 1H($J_{cb}$=17.22 Hz) | $\quad$C=C |
| 7.10 | ($J_{ca}$=10.50 Hz) | ⟋    ⟍$H^b$ |
| 6.98 | | |
| 6.50 | | $H^c$⟍    ⟋$H^a$ |
| 6.47 | d.d, 1H($J_{cb}$=17.22 Hz) | $\quad$C=C |
| 6.31 | ($J_{ab}$= 1.95 Hz) | ⟋    ⟍$H^b$ |
| 6.28 | | |
| 5.92 | | $H^c$⟍    ⟋$H^a$ |
| 5.90 | d.d, 1H($J_{ca}$=10.50 Hz) | $\quad$C=C |
| 5.80 | ($J_{ab}$= 1.95 Hz) | ⟋    ⟍$H^b$ |
| 5.78 | | |

Fig. 4.2. IR(NaCl) spectrum of phenyl vinyl ketone

Fig. 4.3 ¹H–NMR (CDCl₃) spectrum of phenyl vinyl ketone
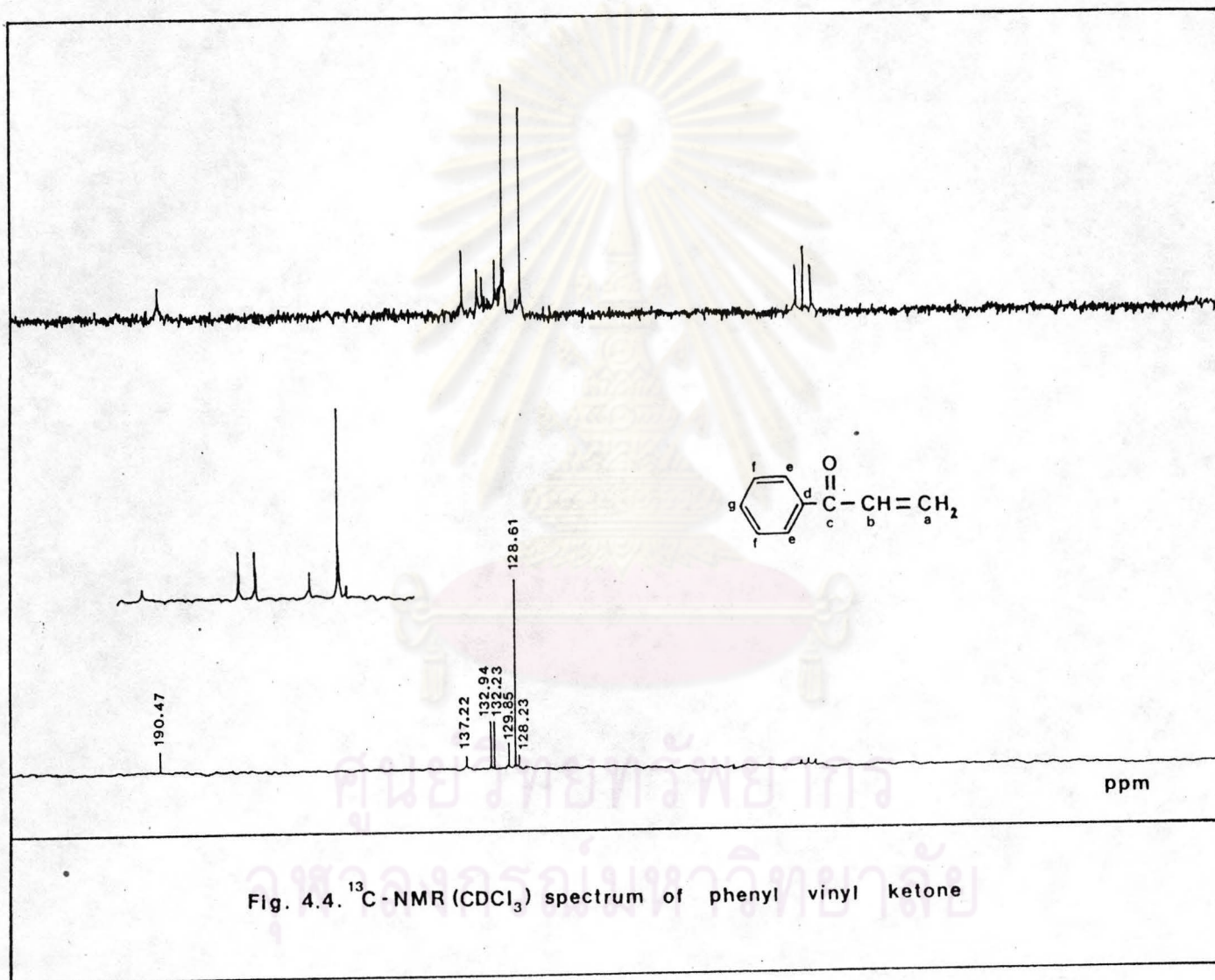
Fig. 4.4. $^{13}$C-NMR(CDCl$_3$) spectrum of phenyl vinyl ketone

**Table 4.4** The assignment for the ^{13}C-NMR spectrum of phenyl vinyl ketone

| Chemical Shift $\delta$ (ppm) | Assignment |
|---|---|
| 128.23 | $-$[e]CH $=$ (aromatic ring) |
| 128.61 | $-$[f]CH $=$ (aromatic ring) |
| 129.85 | $=$[a]CH$_2$ (olefinic group) |
| 132.23 | $-$[b]CH $=$ (olefinic group) |
| 132.94 | $-$[g]CH $=$ (aromatic ring) |
| 137.22 | $-$[d]C $=$ (aromatic ring) |
| 190.47 | $-$[c]C $=$ O (carbonyl group) |

## 4.2 Synthesis of Poly(phenyl vinyl ketone) by Homopolymerization of phenyl vinyl ketone

Phenyl vinyl ketone was homopolymerized in benzene at 50 °C for 3 hours. After the reaction, the solution was more viscous.
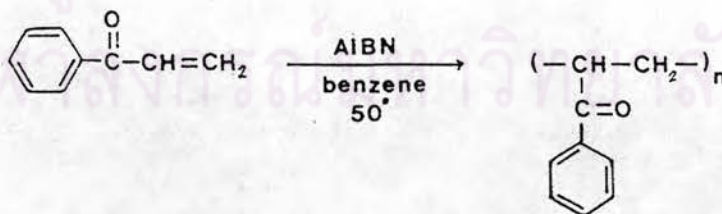


After the third reprecipitation, the white powder was obtained. The white powder product had Tg 87-88 °C (Figture 4.5) and molecular weight about 33,000 and 181,000 were selected for mixing with HDPE.

Poly(phenyl  vinyl ketone) had Tg rather high because  of the  phenyl group in side chain which  decreased  thermobility of polymer  chain  and increased chain rigidity.  The  advantage  of having  high  glass transition temperature is  that  the  polymer will not deform easily under stress and high temperature when  it is mixed with HDPE.

The IR (film and KBr) spectrum of this compound was shown in Figure 4.6-4.7. The absorption band at $\nu$ 1650 cm$^{-1}$  disappeared while  the  absorption  band at $\nu$ 2930 cm$^{-1}$ concurrently appeared comparing  to  IR  spectrum of phenyl vinyl ketone in Figure 4.2. Thus, it indicated that the olefinic group of the monomer  became the aliphatic moiety in the polymer. The C=O stretching  remained at 1680 cm$^{-1}$.  The other absorption bands were assigned in  Table 4.5.

Table 4.5 The assignment for IR spectrum of poly(phenyl vinyl

ketone)

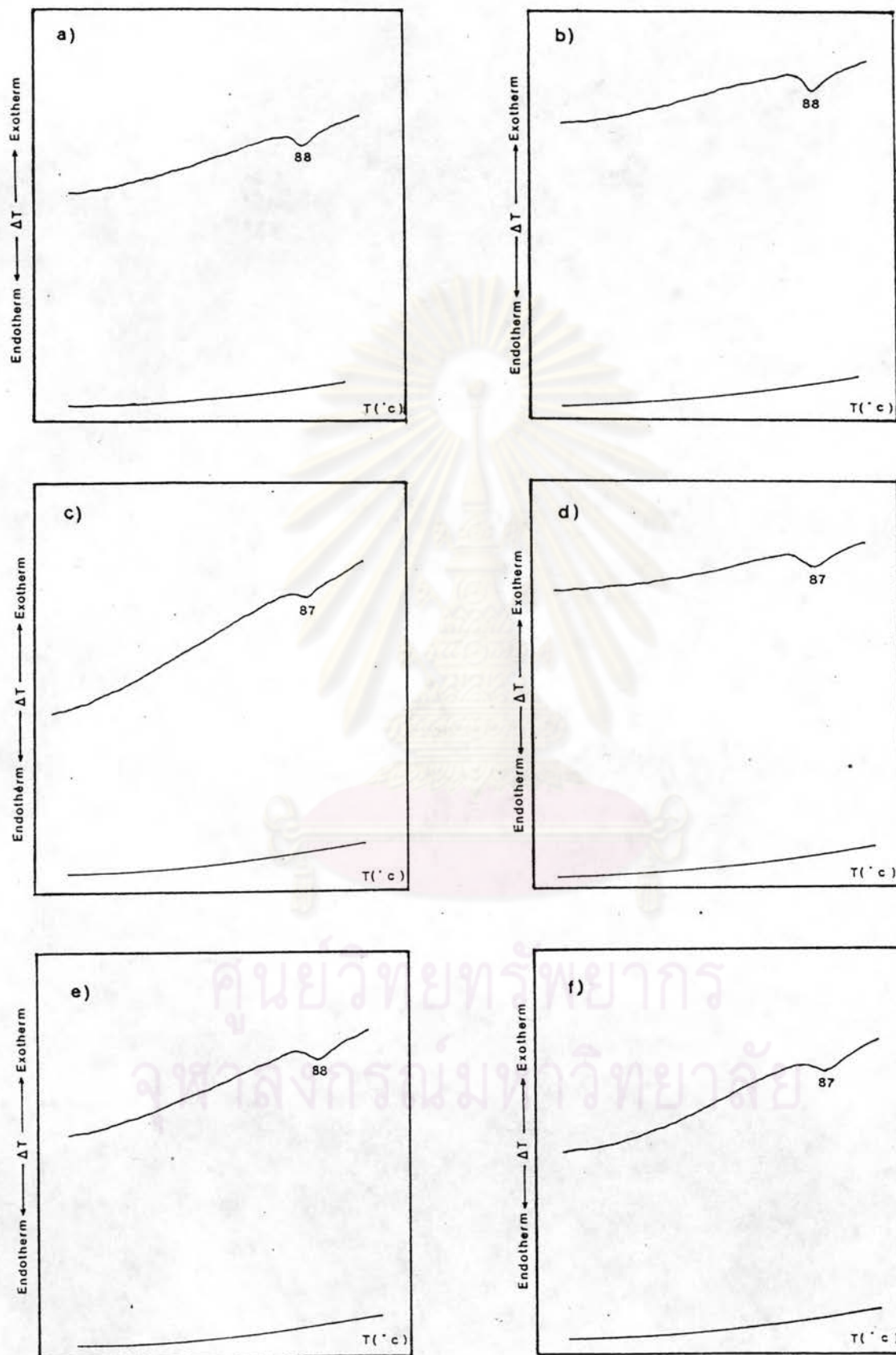| Absorption frequency $\nu$ (cm$^{-1}$) | Assignment |
|---|---|
| 3340 | C=O  overtone |
| 3060 | C-H  stretching in aromatic |
| 2940 | C-H  stretching in aliphatic |
| 1970 |  |
| 1910 | overtone region of |
| 1820 | aromatic ring |
| 1770 |  |
| 1680 | C=O  stretching |
| 1600,1450 | C=C  stretching in aromatic |

Fig. 4.5. Differential thermal analysis thermograms of poly(phenyl vinyl ketone)
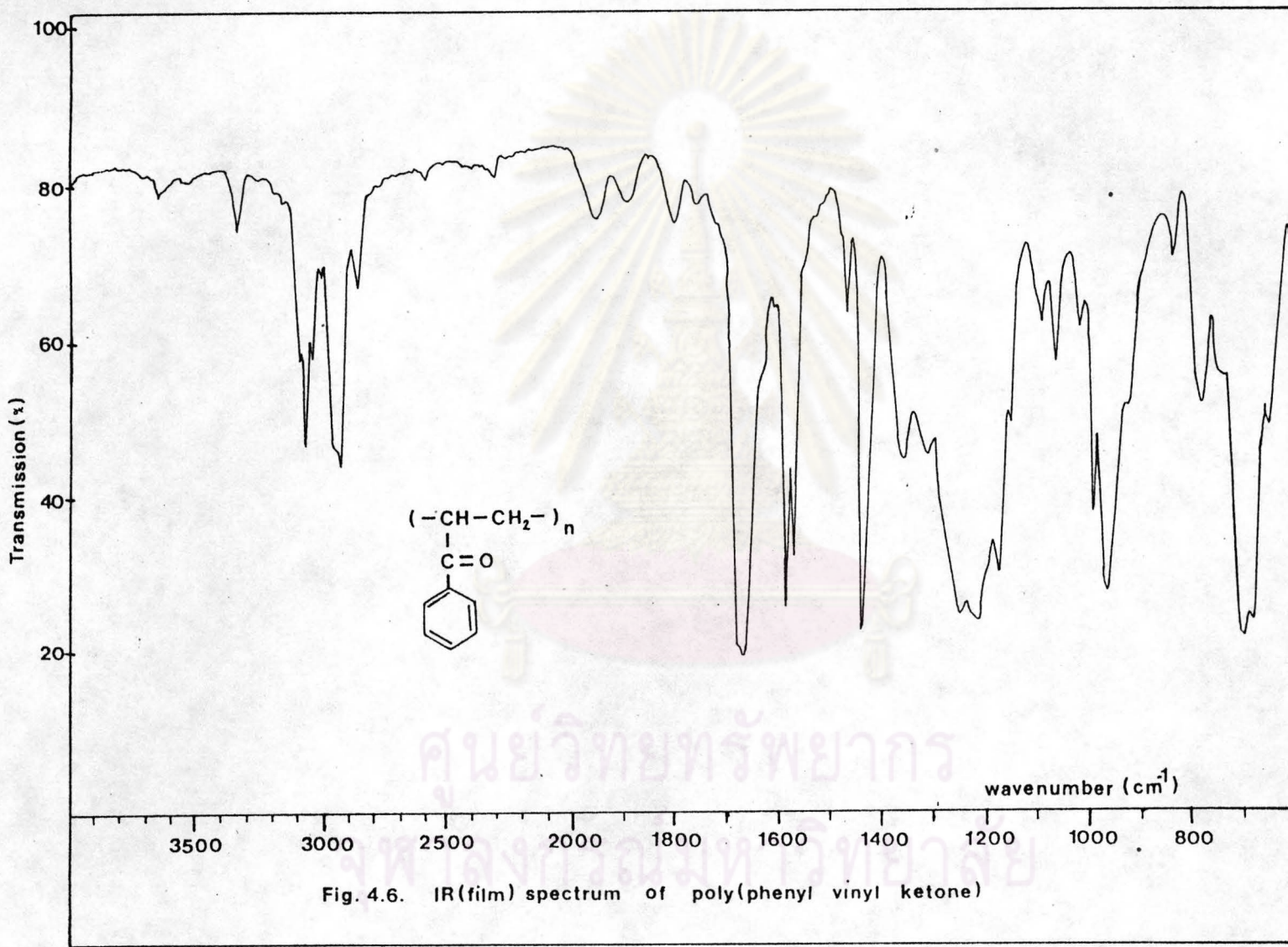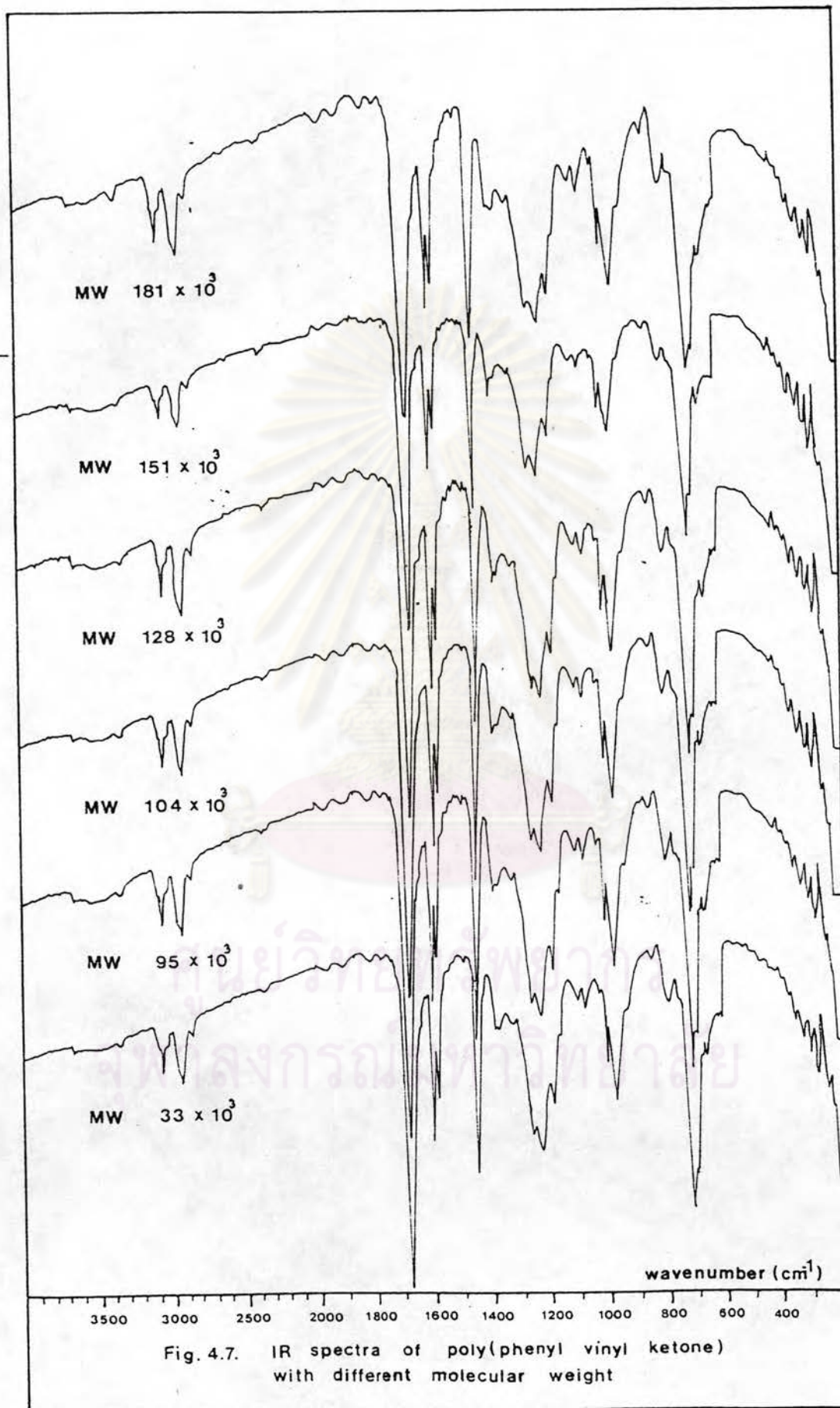batch    a) ,   b) ,   c) ,   d) ,   e) , and   f)

Fig. 4.6. IR (film) spectrum of poly (phenyl vinyl ketone)

Fig. 4.7.  IR spectra of poly(phenyl vinyl ketone) with different molecular weight

## 4.3  Sample preparation

Polyethylene used in this work was commercial film grade high density polyethylene. The films with and without PPVK were obtained by extruding the HDPE in granular form through film blowing machine in which PPVK was being mixed with HDPE in extruder. Usually, 25 kilograms of HDPE must be used. Thus, for 0.1%, 0.5%, 1.0% and 2.0% of PPVK in HDPE film, amount of PPVK needed should be 1,025 grams which was too much to synthesize in the laboratory. Thus, the smallest amount of HDPE as possible was extruded. 1 kilogram of HDPE gaved 0.01 mm thickness film about 80 metres long which was sufficient for degradation testing. Dispersion of PPVK in HDPE film was monitored by comparison of the irradiated samples taken from different portions of the extruded film, which will be mentioned later.

Because of PPVK is white powder, thus there is no effect on color and translucence of the HDPE. The wavelength of photosensitivity is in the range of UV light, because there are carbonyl groups in the PPVK chains. Therefore, degradation of HDPE film with PPVK would be rapid in sunlight but slow under normal illumination.

From a technical point of view, the application of photosensitizers (PPVK) seems more profitable than the synthesis of entirely new polyethylene with phenyl vinyl ketone in the chain because in using sensitizers, photodegradable polyethylene may be produced from different conventional polyethylene.

## 4.4  Natural weathering test

The  effect of poly(phenyl vinyl ketone) (PPVK)  on  HDPE
photodegradation by natural weathering was studied. The HDPE film
with  1.0%  PPVK  was  experimented.  The photodegradation of the
HDPE  films were followed by the determination of their molecular
weight  and  fourier  transform infrared absorption (FTIR) before
and after exposure.

### 4.4.1  Molecular weight measurements

An  immediate  effect of degradation process  is  the
changing  of  the  molecular  weight  of  polymer.  Thus,  the
measurement  of  molecular weight at different time interval is a
means  of  direct  estimation for polymer degradation.  The
molecular  weight  of  unsensitized  and  sensitized HDPE samples
before  and  after exposure was shown in Figure 4.8 and Table 4.6
as  a  function  of  outdoor exposure time.

The  molecular  weight  of  unsensitized  HDPE  film
decreased  from the beginning of outdoor exposure.  The  behavior
of molecular weight of sensitized HDPE film  was similar to  that
of unsensitized HDPE. The greatest reduction in molecular  weight
took  place  in the first 2 weeks from the  beginning  value  and
finally  it  decreased  about 32%. After the  first  8  weeks  it
decreased continuously to a lower molecular weight with  exposure
time.    It can be seen that the molecular weight  of  sensitized
HDPE samples decreased faster than unsensitized HDPE samples.

The molecular weight of HDPE films decreased with exposure time indicated the cleavage of chain into smaller fragments. The higher exposure time was used, the lower molecular weight was resulted.

Table 4.6 Intrinsic viscosity and molecular weight of outdoor exposure HDPE films

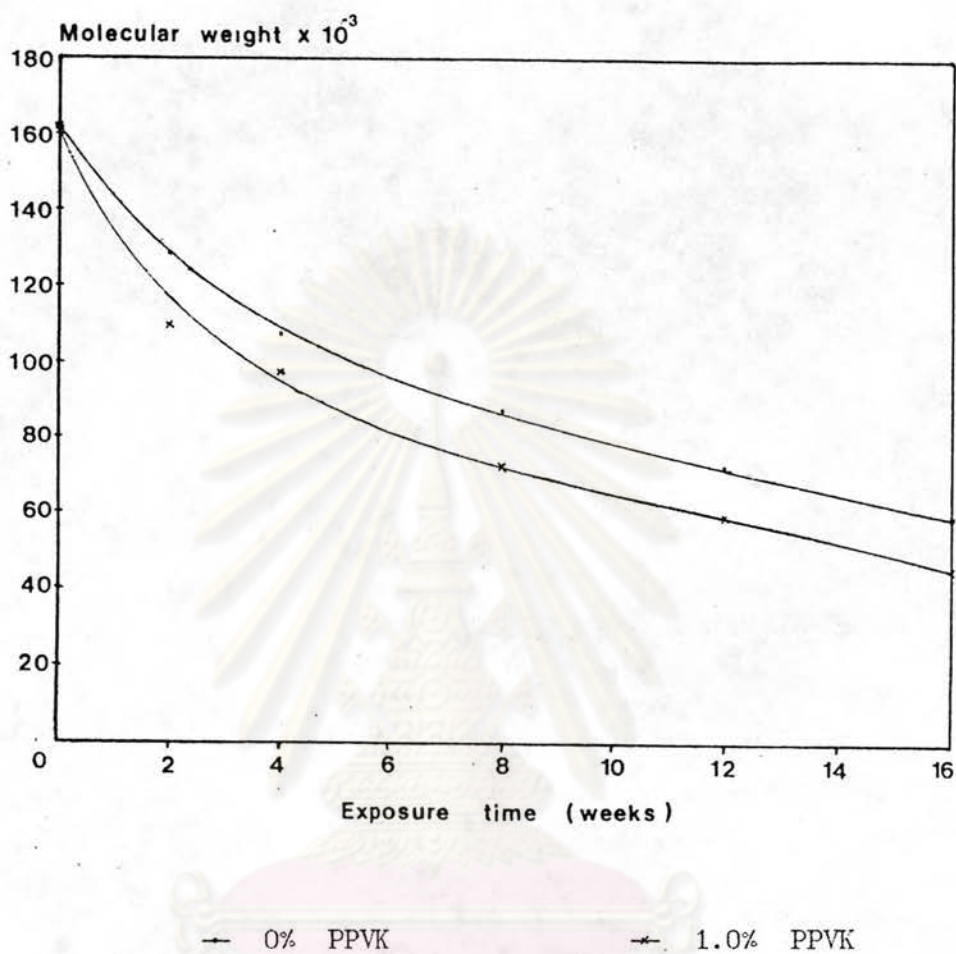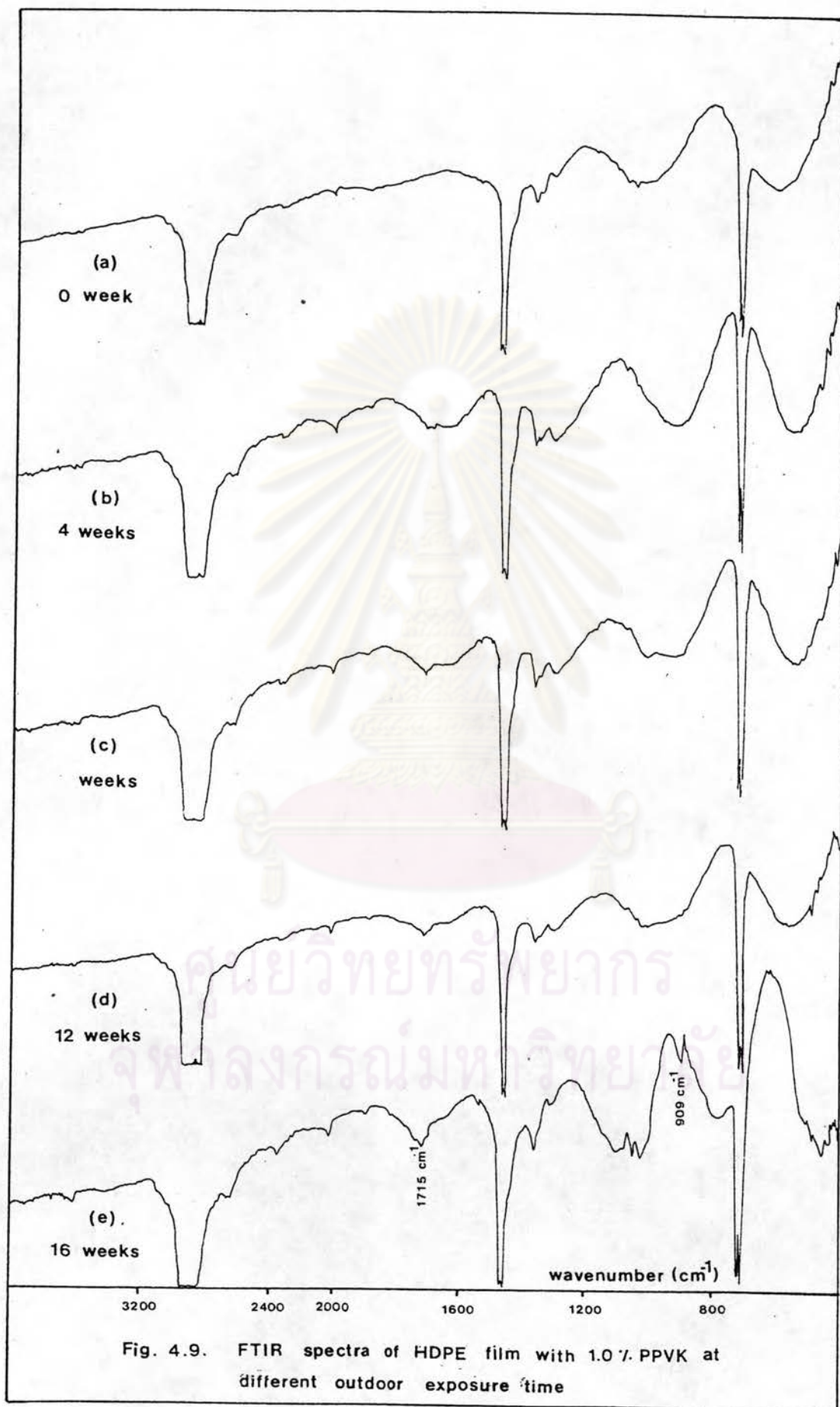| Exposure time (weeks) | Intrinsic viscosity | | Molecular weight $x10^{-3}$ | |
|---|---|---|---|---|
| | 0% PPVK | 1.0% PPVK | 0% PPVK | 1.0% PPVK |
| original | 2.75 | 2.75 | 162.18 | 162.18 |
| 2 | 2.33 | 2.11 | 128.82 | 109.65 |
| 4 | 2.04 | 1.90 | 107.15 | 97.72 |
| 8 | 1.77 | 1.54 | 87.10 | 72.44 |
| 12 | 1.55 | 1.36 | 72.44 | 58.88 |
| 16 | 1.34 | 1.12 | 58.88 | 45.71 |

Fig. 4.8    Molecular weight  of  HDPE  films  as a  function
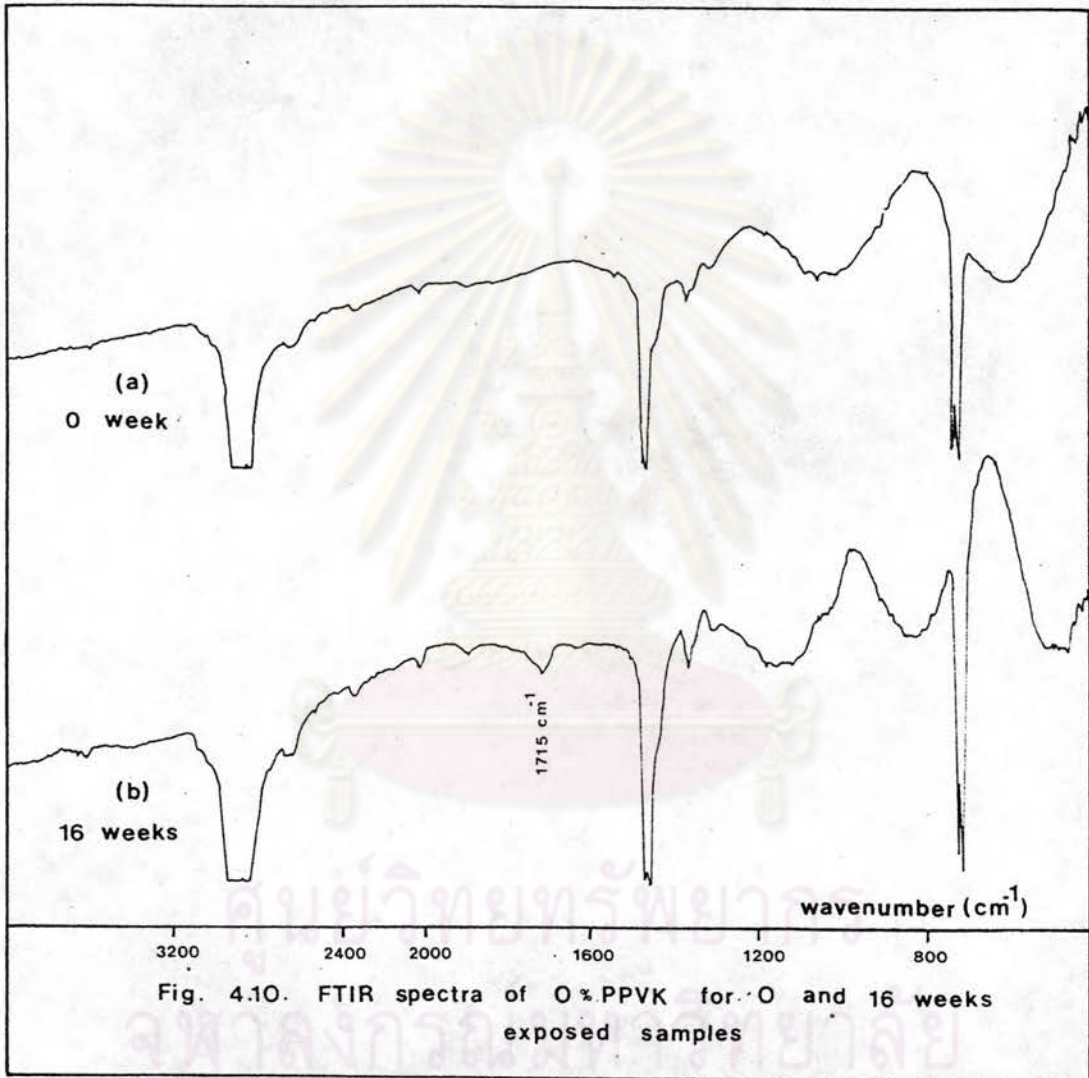            of exposure time at various concentration of PPVK

### 4.4.2 Fourier transform infrared absorption measurement

The FTIR method offers valuable information concerning chemical changes occurred in polyethylene samples. The FTIR spectra of sensitized HDPE samples exposed in natural weathering were obtained and typical spectra were shown in Figure 4.9. Absorption bands at 1715 $cm^{-1}$ and 909 $cm^{-1}$ corresponded to the carbonyl group and the vinyl group in the polymer chains.

FTIR spectrum of HDPE film with 1.0% PPVK before outdoor exposure (Figure 4.9 a) clearly showed no absorption bands at 1715 $cm^{-1}$ and 909 $cm^{-1}$, respectively. This implies that there were no carbonyl and terminal olefinic group in the polymer chains. Figure 4.9 (b), (c), (d) and (e), showed the exposed film for 4, 8, 12 and 16 weeks, respectively. There were absorption band at 1715 $cm^{-1}$ which indicated carbonyl groups in the polyethylene chains. The appearence of carbonyl group was more clearly withthe increasing exposure time. After 16 weeks, the observation of absorption band at 909 $cm^{-1}$ indicated the presence of vinyl groups in the polyethylene chains.

For FTIR spectra of unsensitized HDPE samples exposed in natural weathering were shown in Figure 4.10. FTIR spectrum of HDPE film without PPVK before outdoor exposure (Figure 4.10 a) clearly showed no absorption band at 1715 $cm^{-1}$ which indicated carbonyl groups in the polyethylene chains. When the film was exposed for 16 weeks (Figure 4.10 b) there was absorption band at 1715 $cm^{-1}$ which indicated the presence of carbonyl groups in the polyethylene chains.

Fig. 4.9. FTIR spectra of HDPE film with 1.0 % PPVK at different outdoor exposure time

Fig. 4.10. FTIR spectra of 0 % PPVK for 0 and 16 weeks exposed samples

4.5 Accelerated weathering test by medium pressure
mercury lamp

In parallel with the outdoor exposure test, accelerated
test using medium pressure mercury lamp was carried out for 20
hours. The changes of molecular weight of HDPE films before and
after irradiation were observed for the photodegradation of both
unsensitized and sensitized HDPE films. The following results
were found.

4.5.1 Effect of PPVK concentration

The molecular weight data of both unsensitized and
sensitized HDPE films were shown in Table 4.7 and Figure 4.11.
It can be seen that the molecular weight of unsensitized HDPE
samples decreased from the starting value. The greatest
reduction in molecular weight took place in the first 4 hours
from the beginning of irradiation time and then it decreased
continuously to a lower molecular weight with irradiation time.

The decreasing trend of molecular weight of HDPE
films containing 0.1%, 0.5% and 1.0% by weight of poly(phenyl
vinyl ketone) were similar to that of unsensitized HDPE film.
There was a sudden loss in molecular weight soon after exposure.
Within 4 hours of irradiation it decreased about 50-55 % from the
starting value. After that molecular weight continued to
decrease with time until a point was reached at which the curve
flattened and continued monotonously with irradiation time, at
this stage (after 16 hours of irradiation) the HDPE films became
so brittle but did not break during handling. It was found that
the molecular weight of unsensitized HEPE film decreased slower

than sensitized HDPE films and decreased in the order of HDPE film with 1.0%> 0.5%> 0.1%> 0% PPVK. The HDPE film with 1.0% PPVK was the most degradable as seen in Figure 4.11. The difference of degradation rate among four samples was due to that of the concentration of PPVK. But the difference of degradation rate of sensitized HDPE films at various concentration was small and the effect of PPVK was concentrated mainly in the first stage (the first 16 hours) of the process. The distinct difference between HDPE with 0% and 1.0% PPVK was observed in this study. However, the difference became small at the late stage of irradiation, thus the degradation tended to reach a gradual saturation.

The molecular weight of HDPE films (Thickness of films about 0.020±0.002 mm) containing 0% and 2.0% by weight of poly(phenyl vinyl ketone) were exhibited in Figure 4.12 and the molecular weight data was shown in Table 4.8. The unirradiated HDPE films, both unsensitized and sensitized were white and translucent films and did not contain insoluble material, while the films irradiated only for 4 hours were characterized by the presence of small quantities of insoluble materials and the films changed to yellowish. It was possible that crosslinking reaction occurred in the material, while discoloration was due to oxidation degradation, the structural changed, along with the presence of oxygen. Even if the molecular weight obtained from the films including insoluble materials must be considered inaccurately, a progressive decay of molecular weight was observed.

From Figure 4.12, it can be seen that the decreasing trend of molecular weight of sensitized HDPE film was similar to that of unsensitized HDPE, namely, it decreased about 27% from the starting value within the first 4 hours. After that it decreased continuously with irradiation time. It was found that the degradation rate of sensitized HDPE film was higher than unsensitized one. This phenomenon showed that PPVK affected the lowering of the molecular weight. However the difference of degradation rate of sensitized and unsensitized HDPE films was small.

Table 4.7 Intrinsic viscosity and molecular weight of irradiated
HDPE films (thickness of film about 0.010±0.002 mm.)

| Irradiation time (hours) | Intrinsic viscosity | | | | Molecular weight x10$^{-3}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | 0% | 0.1% | 0.5% | 1.0% | 0% | 0.1% | 0.5% | 1.0% |
| original | 2.75 | 2.70 | 2.73 | 2.75 | 162.18 | 158.49 | 162.18 | 162.18 |
| 4 | 1.76 | 1.74 | 1.69 | 1.63 | 87.10 | 85.11 | 81.28 | 75.86 |
| 8 | 1.58 | 1.47 | 1.37 | 1.28 | 74.13 | 67.61 | 60.26 | 54.95 |
| 12 | 1.41 | 1.33 | 1.24 | 1.17 | 63.10 | 57.54 | 51.29 | 47.86 |
| 16 | 1.19 | 1.14 | 1.10 | 1.08 | 50.12 | 46.77 | 43.65 | 42.66 |
| 20 | 1.08 | 1.06 | 0.98 | 0.09 | 42.66 | 40.74 | 37.15 | 33.88 |

Table 4.8 Intrinsic viscosity and molecular weight of
irradiated HDPE films (thickness of film about
0.020±0.002 mm.)

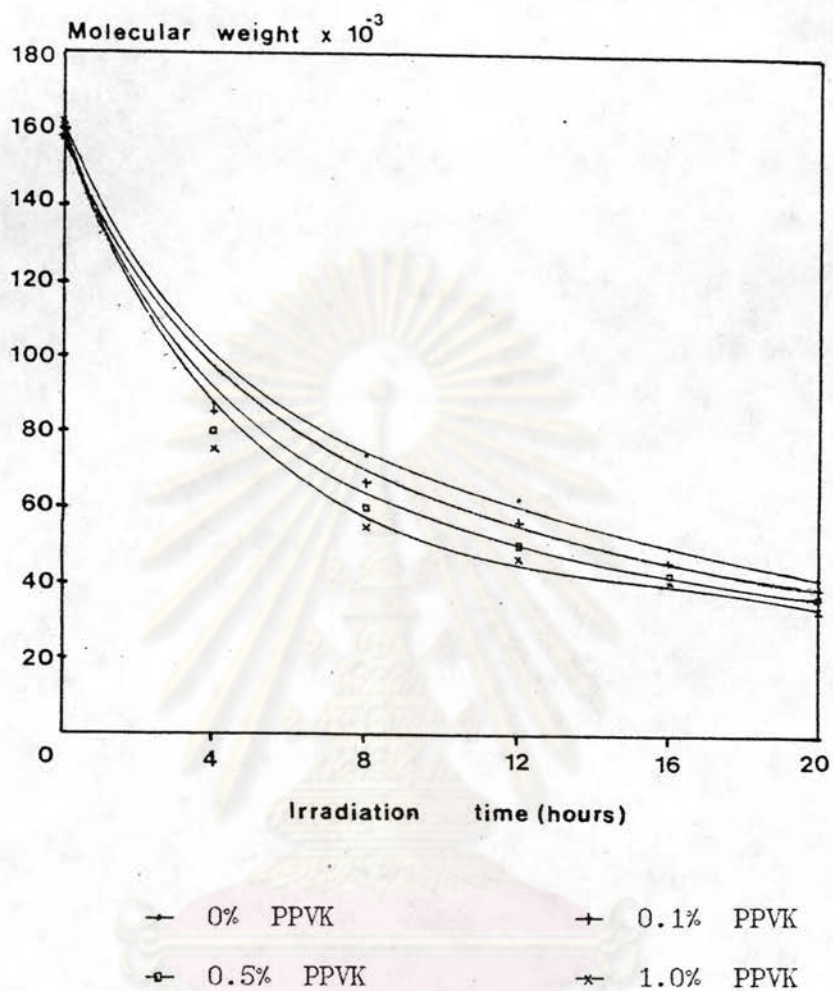| Irradiation time (hours) | Intrinsic viscosity | | Molecular weight x10$^{-3}$ | |
|---|---|---|---|---|
| | 0% PPVK | 2.0% PPVK | 0% PPVK | 2.0% PPVK |
| original | 2.65 | 2.64 | 151.36 | 151.36 |
| 4 | 2.07 | 2.08 | 109.65 | 107.15 |
| 8 | 1.95 | 1.75 | 100.00 | 85.11 |
| 12 | 1.70 | 1.56 | 81.28 | 72.44 |
| 16 | 1.30 | 1.10 | 57.54 | 43.65 |
| 20 | 1.08 | 0.93 | 42.66 | 34.67 |

Fig. 4.11 Molecular weight of HDPE films as a function of irradiation time at various concentration of PPVK (film thickness: 0.010±0.002 mm)
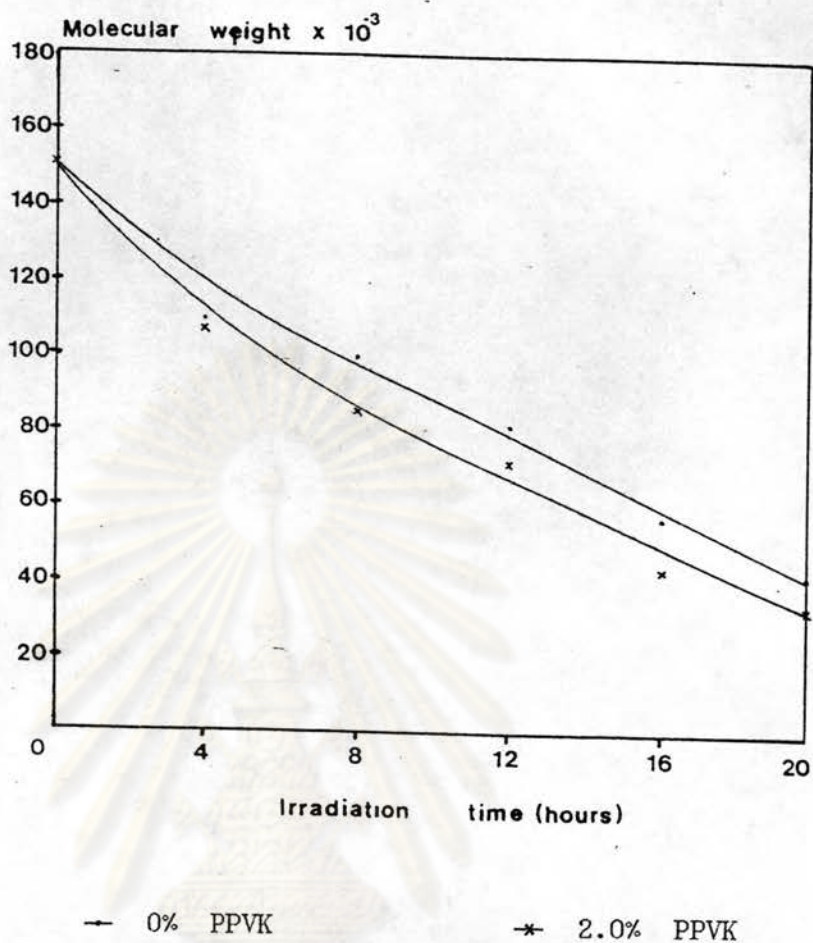
Fig. 4.12 Molecular weight of HDPE films as a function of irradiation time at various concentration of PPVK (film thickness: 0.020±0.002 mm)

### 4.5.2  Effect of film thickness

The unsensitized HDPE with film thickness about 0.010±0.002 mm and 0.020±0.002 mm were selected for this study. The influence on the film thickness was shown in Figure 4.13. The molecular weight data was collected in Table 4.9.
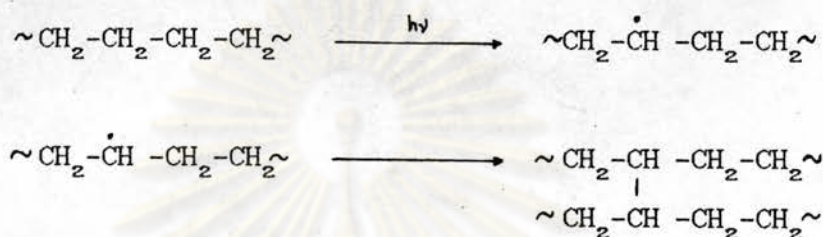
It can be seen that the molecular weight of unsensitized HDPE thinner film decreased about 50% in the first 4 hours from the beginning of irradiation time. While the molecular weight decreased about 27% for the thicker film at the same irradiation period. Afterwards, it decreased continuously to a lower molecular weight with irradiation time. However, after 16 hours of irradiation, the insignificance difference was observed.

As regards to the thickness of the film, the thinner the thickness, the faster the degradation occurred. Besides, the molecular weight decreased, the solubility of irradiated samples also confirmed the faster degradation of the thinner film. Indeed, the clear solution of the irradiated thinner film was obtained, while a cloudy solution obviously appeared for the irradiated thicker one. This could be explained that the extent of oxidation decreased with increasing prenetration depth [22]. This means that photooxidation occurs preferentially at the film surface and that little reaction occurs in the bulk of the samples.

The crosslinking reaction [23], which gave insoluble materials in the case of the thicker film, occurred because the UV light reached only the shallow parts under surfaces.

Accordingly, crosslinking together with the screening effect of the reaction products appearing there, the reaction tended to reach a gradual saturation.

crosslinking reaction:

$$\sim CH_2-CH_2-CH_2-CH_2\sim \xrightarrow{\;h\nu\;} \sim CH_2-\overset{\bullet}{C}H-CH_2-CH_2\sim$$

$$\sim CH_2-\overset{\bullet}{C}H-CH_2-CH_2\sim \longrightarrow \begin{array}{c} \sim CH_2-CH-CH_2-CH_2\sim \\ | \\ \sim CH_2-CH-CH_2-CH_2\sim \end{array}$$

Moreover, it was found that [24] in the case of thinner film containing a stabilizer, the supply of stabilizer from the interior was limited and it might not be able to keep up with the continuous volatilisation and/or leaching occurring at the surface. The thicker film, containing a stabilizer that could also migrate, would have greater reservoirs of stabilizer which could migrate to the surface to lengthen the life of a film.

Table 4.9 Intrinsic viscosity and molecular weight of unsensitized HDPE films (thickness 0.010±0.002 mm and 0.020±0.002 mm)

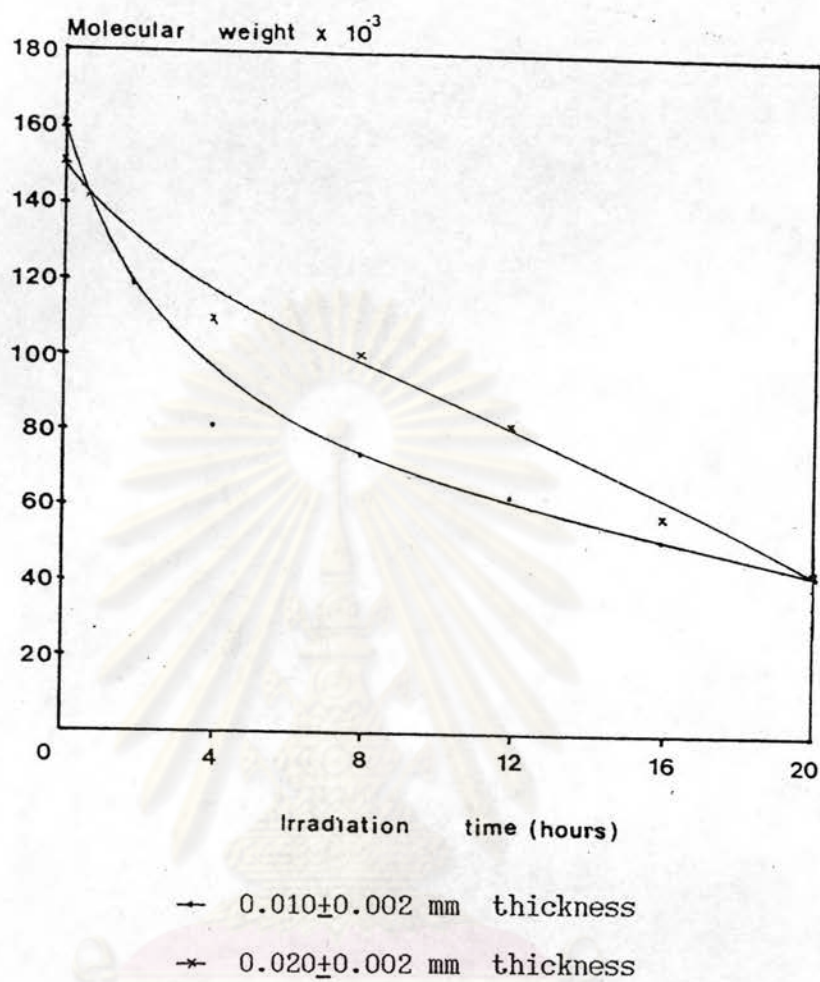| Irradiation time (hours) | Intrinsic viscosity | | Molecular weight x10$^{-3}$ | |
|---|---|---|---|---|
| | 0.01 mm | 0.02 mm | 0.01 mm | 0.02 mm |
| original | 2.75 | 2.65 | 162.18 | 151.36 |
| 4 | 1.76 | 2.07 | 87.10 | 109.65 |
| 8 | 1.58 | 1.95 | 74.13 | 100.00 |
| 12 | 1.41 | 1.70 | 63.10 | 81.28 |
| 16 | 1.19 | 1.30 | 50.12 | 57.54 |
| 20 | 1.08 | 1.08 | 42.66 | 42.66 |

Fig. 4.13    Molecular weight   of HDPE films as a function of
             irradiation time at various of film thickness

### 4.5.3 Effect of the molecular weight of PPVK

Considering the effect of the molecular weight of PPVK on the degradation, the experiment was carried out with HDPE films (thickness $0.010\pm0.002$ mm) containing 0.5% by weight of PPVK of different molecular weights, $10^4$ and $10^5$. Since light absorption was induced by the carbonyl chromophore in PPVK and the number of carbonyl moiety should be the same for both cases, there should not have much difference on degradation of HDPE films. Indeed, the results was very similar as shown in Figure 4.14 and Table 4.10.

However, different molecular weight of PPVK may cause the dispersion problem. The lower molecular weight, the shorter chain lengths, should disperse well in HDPE film. The higher molecular weight, the longer chain lengths, may affect on dispersion in HDPE film because the longer chain lengths, the higher entanglement will be and give the clusters of PPVK in HDPE film.

Table 4.10 Intrinsic viscosity and molecular weight of irradiated HDPE films (molecular weight of PPVK: $10^4$ and $10^5$)

| Irradiation time (hours) | Intrinsic viscosity | | Molecular weight $\times 10^{-3}$ | |
|---|---|---|---|---|
| | PPVK MW $10^4$ | PPVK MW $10^5$ | PPVK MW $10^4$ | PPVK MW $10^5$ |
| original | 2.73 | 2.80 | 162.18 | 169.82 |
| 4 | 1.69 | 1.74 | 81.28 | 85.11 |
| 8 | 1.37 | 1.41 | 60.26 | 63.10 |
| 12 | 1.24 | 1.33 | 51.29 | 57.54 |
| 16 | 1.10 | 1.14 | 43.65 | 46.77 |
| 20 | 0.98 | 0.91 | 37.15 | 33.88 |

ศูนย์วิทยทรัพยากร

จุฬาลงกรณ์มหาวิทยาลัย
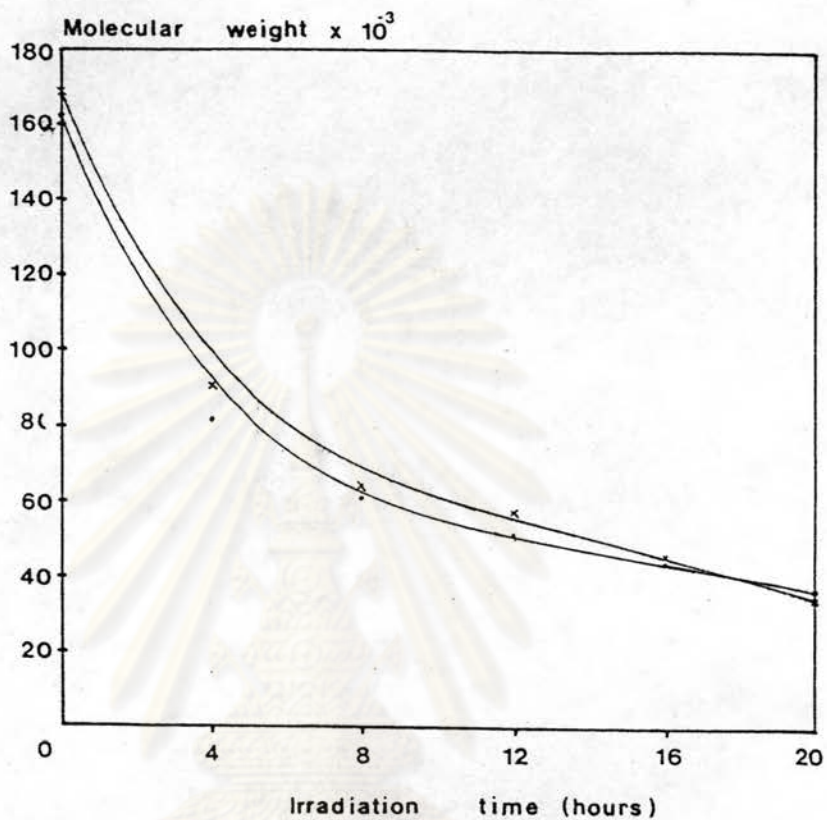
Fig. 4.14  Molecular weight of HDPE films as a function of irradiation time at various PPVK molecular weight.

### 4.5.4  Dispersion of PPVK in HDPE film

In order to study dispersion of PPVK in HDPE film, the film containing 0.5% by weight of PPVK (molecular weight about $10^4$), thickness about $0.010\pm0.002$ mm and 16 hours irradiated film was used. From the data in Table 4.11, it was found that difference in intrinsic viscoisity and molecular weight of the beginning part, the middle part and the end part of HDPE film were not observed. Therefore, PPVK powder was well dispersed in HDPE film. Because of PPVK is a polymer, thus it should be readily incorporate in molten polyethylene and should remain well dispersed in the polyethylene due to the entanglement between PPVK and polyethylene chains.

Table 4.11  Intrinsic viscosity and molecular weight of 16 hour irradiated HDPE films containing 0.5% PPVK (molecular weight about $10^4$)

| Irradiation time (hours) | Intrinsic viscosity | | | Molecular weight $\times 10^{-3}$ | | |
|---|---|---|---|---|---|---|
| | the beginning part | the middle part | the end part | the beginning part | the middle part | the end part |
| 16 | 1.17 | 1.10 | 1.14 | 47.86 | 43.65 | 46.77 |

## 4.6  Proposed Mechanism of Degradation

Under the normal conditions, the mechanisms of chemical changes occuring during the degradation process are believed to be initiated by photo (UV light) energy, which is usually followed by oxidative degradation.

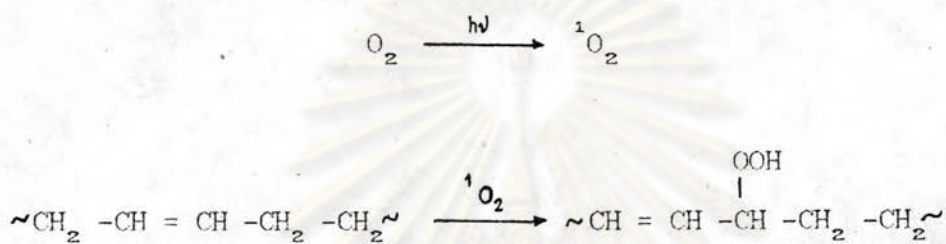### 4.6.1  Unsensitized high density polyethylene

From the results of natural weathering test of unsensitized HDPE films, the molecular weight decreasing with exposure time indicated there was cleavage of chain into smaller fragments, the higher the exposure time, the lower the molecular weight is. It was found that carbonyl groups were formed under HDPE degradation as evidenced by fourier transform infrared absorption. The absorption band of carbonyl group at 1715 $cm^{-1}$ indicated there was initiation through the absorption of energy (UV light) and oxygen ($O_2$) uptake.

Besides, it was found that there were the insoluble materials in the irradiated HDPE films (thickness about 0.02 mm), while insoluble material was not present in the unirradiated one. This indicated that there were cross-linked reaction corresponding with the photooxidation which occurs preferentially at the film surface.

Therefore, the results can easily be explained. The degradation of unsensitized HDPE film take place through incorporation of oxygen and crosslinked reaction which can be seen from Scheme 4.3 [23]. The degradation is most probably associated with the exhaustion of the stabilizing agents present
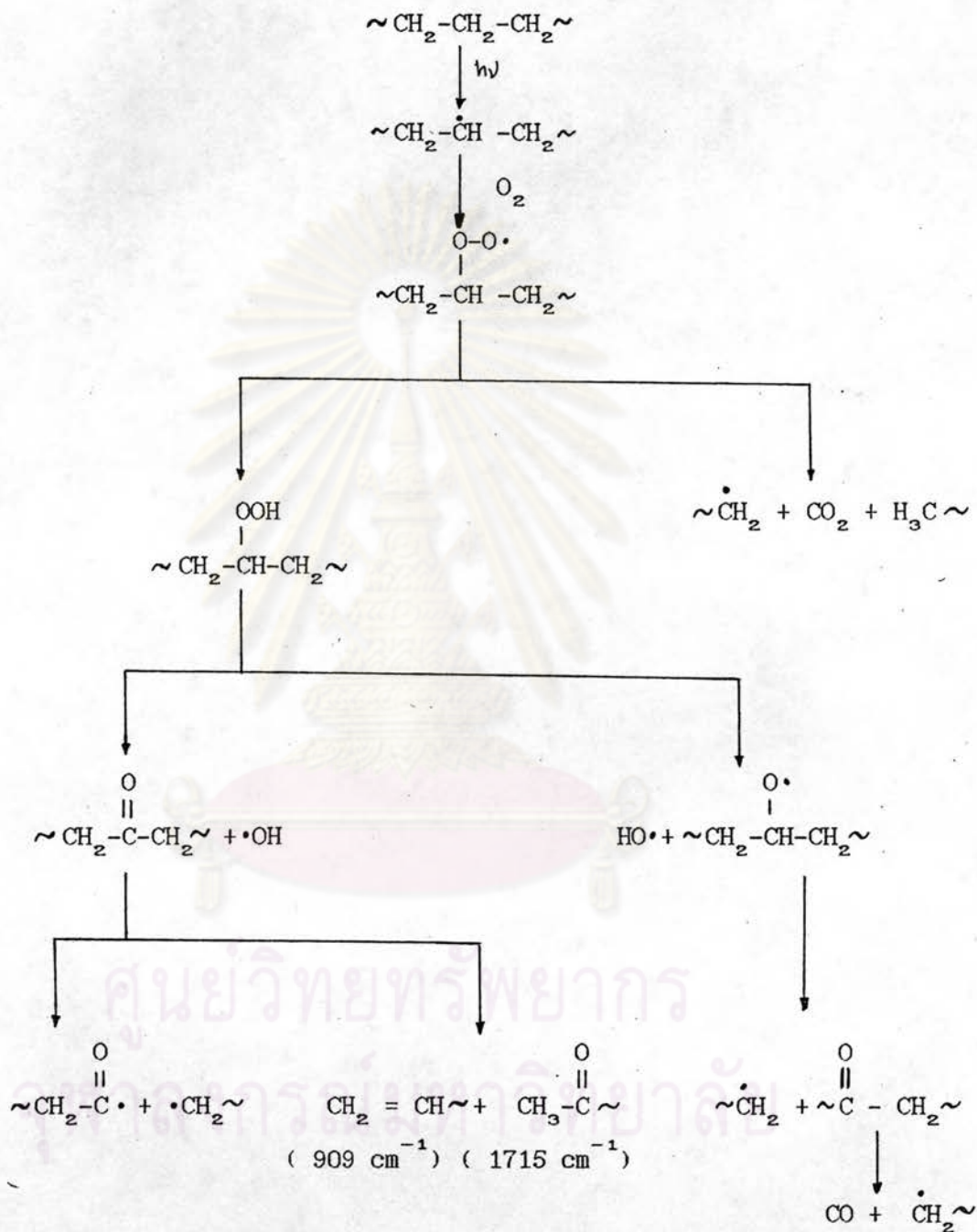
in the original material.

Since a number of double bonds present in commercially processed polyethylene, singlet oxygen may form hydroperoxide as follows:
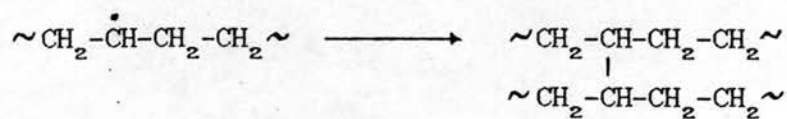
$$O_2 \xrightarrow{h\nu} {}^1O_2$$

$$\sim CH_2 -CH = CH -CH_2 -CH_2 \sim \xrightarrow{{}^1O_2} \sim CH = CH -\overset{\overset{\displaystyle OOH}{\displaystyle |}}{CH} -CH_2 -CH_2 \sim$$

In the presence of air:

$$\sim CH_2-CH_2-CH_2\sim$$

$$\downarrow h\nu$$

$$\sim CH_2-\overset{\bullet}{C}H-CH_2\sim$$

$$\downarrow O_2$$

$$\sim CH_2-\underset{\overset{|}{CH}}{\overset{O-O\bullet}{}}-CH_2\sim$$

$$\sim \overset{\bullet}{C}H_2 + CO_2 + H_3C\sim$$

$$\sim CH_2-\underset{\overset{|}{CH}}{\overset{OOH}{}}-CH_2\sim$$

$$\sim CH_2-\overset{O}{\underset{\|}{C}}-CH_2\sim + \bullet OH$$

$$HO\bullet + \sim CH_2-\underset{\overset{|}{CH}}{\overset{O\bullet}{}}-CH_2\sim$$

$$\sim CH_2-\overset{O}{\underset{\|}{\overset{}{C}}}\bullet + \bullet CH_2\sim \qquad CH_2 = CH\sim + CH_3-\overset{O}{\underset{\|}{C}}\sim$$

( 909 cm$^{-1}$ ) ( 1715 cm$^{-1}$ )

$$\sim \overset{\bullet}{C}H_2 + \sim \overset{O}{\underset{\|}{C}} - CH_2\sim$$

$$\downarrow$$

$$CO + \overset{\bullet}{C}H_2\sim$$

cross-linked reaction:

$$\sim CH_2-\overset{\bullet}{C}H-CH_2-CH_2\sim \longrightarrow \begin{array}{c} \sim CH_2-CH-CH_2-CH_2\sim \\ | \\ \sim CH_2-CH-CH_2-CH_2\sim \end{array}$$
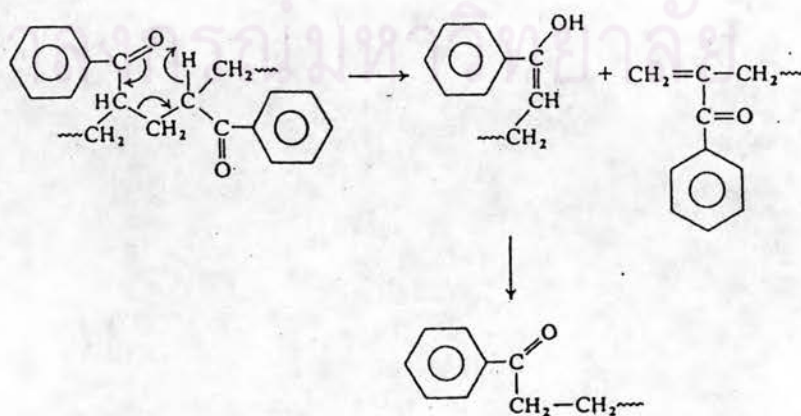
Scheme 4.3

### 4.6.2 Sensitized high density polyethylene

From the results of both natural and accelerated weathering tests, it was found that the degradation rate of sensitized HDPE flims was higher than unsensitized one. The action of PPVK, as a photosensitizer, was concentrated mainly in the first stage of the degradation process. It was clarified that PPVK accelerated the rate of degradation. With regards to the concentration of PPVK, the higher the concentration, the higher the rate of degradation. Besides, it was found that carbonyl and vinyl groups were formed under HDPE degradation and there were insoluble materials in the irradiated samples.

From these results, the mechanisms of degradation of sensitized HDPE films can be proposed as follows.
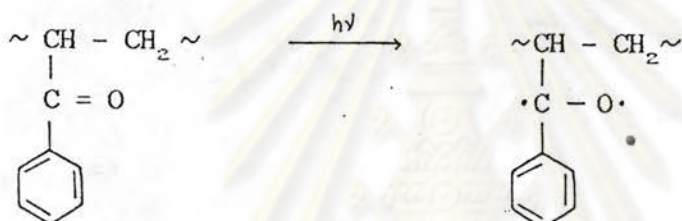
In poly(phenyl vinyl ketone), the aromatic group is the initiating point for Norrish type II cleavage.

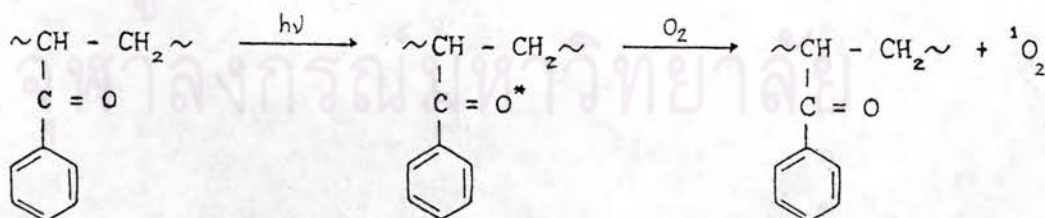And poly(phenyl vinyl ketone) can undergo Norrish type I cleavage
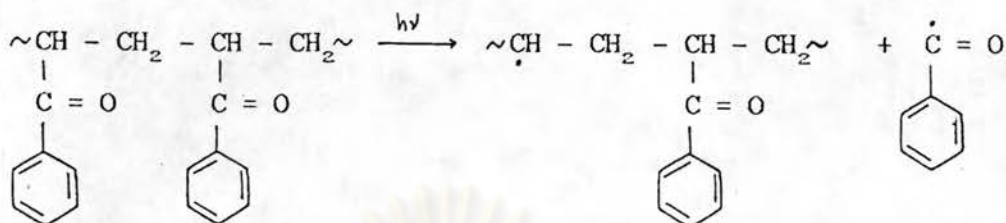


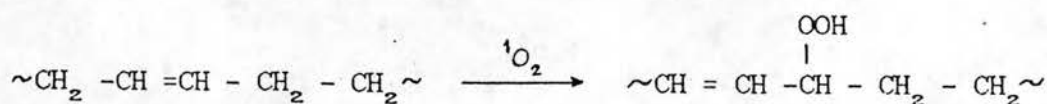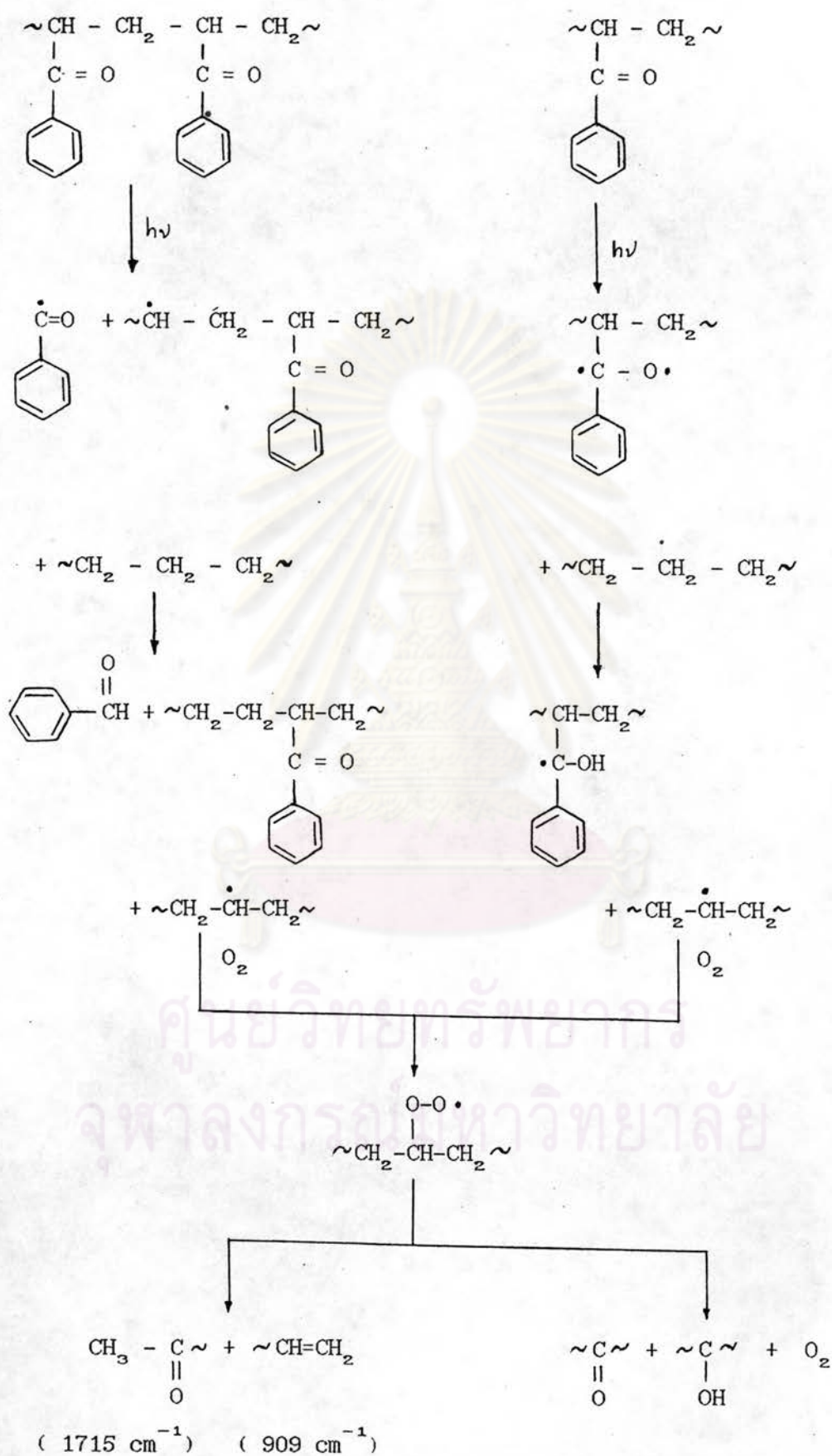and the free radical may be formed as follow



These radicals lead to degradation of polyethylene, as shown in Scheme 4.4.

In the presence of air PPVK may transfer its excitation energy on oxygen molecules and form singlet oxygen.



Initiation may occur by the addition of singlet oxygen to doudle bonds present in polymers.

$\sim CH - CH_2 - CH - CH_2 \sim$

$\sim CH - CH_2 \sim$

$h\nu$

$\dot{C}=O + \sim\dot{C}H - \dot{C}H_2 - CH - CH_2 \sim$

$+ \sim CH_2 - CH_2 - CH_2 \sim$

$+ \sim CH_2 - \dot{C}H - CH_2 \sim$

$O_2$

$O-O \cdot$
$\sim CH_2 - CH - CH_2 \sim$

$CH_3 - C \sim + \sim CH=CH_2$
$\parallel$
$O$

$( 1715 \text{ cm}^{-1} ) \quad ( 909 \text{ cm}^{-1} )$

$\sim C \sim + \sim C \sim + O_2$
$\parallel \qquad \quad$
$O \qquad \quad OH$

Scheme 4.4

cross-linked reaction :

$$\sim CH_2 - \overset{\bullet}{C}H - CH_2 - CH_2 \sim \longrightarrow \begin{array}{c} \sim CH_2 - CH - CH_2 - CH_2 \sim \\ | \\ \sim CH_2 - CH - CH_2 - CH_2 \sim \end{array}$$

$$\begin{array}{c} \sim CH - CH_2 \sim \\ | \\ \bullet C - OH \\ | \\ \bigcirc \end{array} \quad + \sim CH_2 - \overset{\bullet}{C}H - CH_2 \sim \longrightarrow \begin{array}{c} \sim CH_2 \quad \sim CH - CH_2 \sim \\ | \quad\quad | \\ CH - \quad C - OH \\ | \quad\quad | \\ \sim CH_2 \quad \bigcirc \end{array}$$