

## CHAPTER III

### EXPERIMENTAL

#### 3.1 General Information

##### 3.1.1 Instrument

- Infrared Spectrophotometer ; Perkin Elmer 1430.
- Fourier Transform NMR Spectrometer ; Joel, model JNX - FX 90Q.
- Gel Permeation Chromatography ; Pump : Water 510, Refractive Index Detector : Water 410, Injector: Rheodyne with 1 ml loop, Recorder: Servoscribe 1S.
- Melting Point ; BUCH 510.
- Vacuum Oven (Isotemp); Fisher Model 281.
- High Vacuum Pump ; Java - JD 60, Australia.
- Differential Thermal Analysis ; Shimadzu Thermal Analysis Instrument DT-30.
- Fourier Transform Infrared spectrophotometer ; Perkin - Elmer model 1720.
- Film Blowing Machine With Extruder ; Model PE-45-AW.
- Ubbelohde Viscometer ; Schott Gerate ; K = 0.01
- Medium Pressure Mercury Lamp ; Phillips 125 W.
- Exposure Equipments, as recommended in ASTM D1435.
- Weather Cabinet.
- Ultrasonic ; Branson 2200
- Micrometer ; Mitutoyo code no. 7301.

3.1.2 Chemicals and Materials

Dimethylamine hydrochloride	SIGMA
Paraformaldehyde	MERCK
Acetophenone	FLUKA
Conc. hydrochloric acid	MERCK
Hydroquinone	MERCK
Azobis (isobutyronitrile) (AIBN)	
Ethanol	
Acetone	MERCK
Hexane	
Benzene	J.T. BAKER
Decahydronaphthalene	FLUKA
Tetrahydrofuran (THF)	J.T. BAKER
Silicone oil	
Dry ice	
Nitrogen gas	

Commercial film grade polyethylene :

HDPE used in this study is identified as Polene grade A3355 supplied by Thai Petrochemical Industry Co., Ltd. (TPI).

Physical properties of Polene A3355 are listed in Table 3.1

**Table 3.1** Physical properties of Polene A3355 (HDPE)

Physical Property	Test Method	Unit	A3355 (HDPE)
Melt Index (2.16 Kg/190 °C)	ASTM D1238	g / 10 min	0.06
Melt Index (5 Kg/190 °C)	ASTM D1238	g / 10 min	0.25
Density	ASTM D1505	g / cm <sup>3</sup>	0.950
Tensile Strength	ASTM D638	N / mm <sup>2</sup>	> 40
Yield Strength	ASTM D638	N / mm <sup>2</sup>	> 28
Ultimate Elongation	ASTM D638	%	> 1700
Ball Indentation Hardness	DIN 53456	N / mm <sup>2</sup>	> 45
Notched Impact Strength	DIN 53453	mJ / mm <sup>2</sup>	> 12

Source : Thai Petrochemical Industry Co.,Ltd.

### 3.2 Experimental

#### 3.2.1 Synthesis of Phenyl Vinyl Ketone (PVK) Monomer [19]

##### 3.2.1.1 Synthesis of $\beta$ -Dimethylaminopropiophenone hydrochloride (Mannich Reaction)

52 g (0.652 mole) of dimethylamine hydrochloride, 20 g (0.66 mole) of powdered paraformaldehyde and 60 g (48.6 ml, 0.50 mole) of acetophenone were added to 500 ml round-bottomed flask attached to a reflux condenser. 80 ml of ethanol which 1.0 ml of concentrated hydrochloric acid had been added was introduced to the flask. The mixture was refluxed for 2 hours. After the reaction, the solution was poured to a 1000 ml

beaker, 400 ml of acetone was added to the solution and left in a refrigerator overnight. The crystals were filtered, washed with acetone and dried for 24 hours at 80-90 °C. The crude product was recrystallized by dissolving in 100 ml of hot ethanol and 250 ml of acetone was added to the solution. The solid was separated by suction filtration and dried at 80-90 °C for 24 hours. The yield was 65%, m.p. 155-156 °C.

### 3.2.1.2 Pyrolysis of $\beta$ -Dimethylaminopropiophenone hydrochloride to Phenyl Vinyl Ketone (PVK)

An intimate mixture of 21.4 g (0.1 mole) of  $\beta$ -dimethylaminopropiophenone hydrochloride and 0.2 g of hydroquinone was added to a 100 ml two-necked round bottomed flask. The mixture was distilled under reduced pressure at 2 torr; a few crystals of hydroquinone was added to the receiving flask. The crude ketone as obtained at 60-65 °C. Pure phenyl vinyl ketone was obtained by redistillation, b.p 62-63 °C at 2 torr. The yield was 37%.

### 3.2.2 Synthesis of poly (phenyl vinyl ketone) (PPVK) by Homopolymerization of Phenyl Vinyl Ketone (PVK)

The certain amount of phenyl vinyl ketone was dissolved in benzene in a three-necked round bottomed flask and AIBN, an initiator was added. The solution was purged with nitrogen gas for 15 min, then polymerization was carried out under nitrogen atmosphere at 50 °C for 3 hours with stirring rate of 70 rpm. After the reaction, the solution was poured into a large amount of hexane to precipitate the polymer. The resulting polymers were then purified by redissolving in benzene and

reprecipitation from hexane at least twice. The product was white powder obtained with Tg and MW as exhibited in Table 3.2.

Table 3.2 Molecular weight and glass transition temperature (Tg) of poly(phenyl vinyl ketone) (PPVK)

* PPVK (batch)	MW	Tg (°C)	AIBN (% mole)
a	181,000	88	0.9
b	151,000	88	1.0
c	128,000	87	1.1
d	104,000	87	1.2
e	95,000	88	1.3
f	33,000	87	1.5

\* Polymerization was carried out in a 1:2 monomer-benzene mixture (v/v) containing different concentrations of AIBN, as initiator.

PPVK from batch a (higher molecular weight: MW  $10^5$ ) and batch f (lower molecular weight: MW  $10^4$ ) were selected for mixing with HDPE.

### 3.3 Characterization of Chemicals and Polymers

#### 3.3.1 Infrared (IR) Measurement

Infrared (IR) spectra of chemicals and polymers were recorded by using Perkin-Elmer Infrared Spectrophotometer model 1430. The chemical powder was examined by using KBr method. The liquid monomers were recorded as neat samples by using NaCl cell. The polymers could be casted as films, then directly examined.

#### 3.3.2 Nuclear Magnetic Resonance (NMR) Measurement

The  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of monomers were taken by using Fourier Transform NMR spectrometer, Jeol, model JNX-FX 90 Q. The samples were dissolved in  $\text{CDCl}_3$  to make the solution of 5% concentration.

#### 3.3.3 Differential Thermal Analysis (DTA)

DTA thermograms of polymers were obtained with heating rate of  $10^\circ\text{C}/\text{min}$ , and the sensitivity of  $\pm 10 \mu\text{v}$  were selected. The weight of specimens used was milligram. The reliable glass transition ( $T_g$ ) of polymers were obtained.

#### 3.3.4 Gel Permeation Chromatography of Polymers

The molecular weight of polymers were determined by using Gel Permeation Chromatography (Pump: Waters 510; Refractive Index Detector: Water 410; Injector : Rheodyne with 1 ml. loop). 4 columns ( $10^4$ ,  $10^5$ ,  $10^6$  Å and CPD Linear Ultrastyrigel

: Water) were used in serial combination. The samples were dissolved in tetrahydrofuran (THF) as 0.05% w/v solution and filtered through 0.2  $\mu$ m Nylon 66 filter. The recorder was Servoscribe 1 S. The GPC condition were:

sensitivity	4
scale factor	30
flow rate	1 ml/min
detector temperature	45 °C
injection volume	350 $\mu$ l
pressure	$0.5 \times 10^3$ psi
time base	120 mm/hr.

The calibration curve was obtained from the Master's Thesis of Mr. Sumphun Wiriyasathit [20].

### 3.4 Sample preparation

The HDPE film samples were prepared by mixing PPVK with high density polyethylene (see Table 3.3) in a feed hopper and then blow-extruded by having temperatures at zones for HDPE as follow : Feed zone; 180 °C, Compression zone ; 200 °C , Metering zone ; 200 °C and Die zone ; 210 °C.

Table 3.3 Data of HDPE film samples

PPVK		* thickness of films (mm)
MW	percent by weight	
$10^4$	0	0.010±0.002
	0.1	
	0.5	
	1.0	
$10^5$	0	0.020±0.002
	2.0	
$10^5$	0.5	0.010±0.002

\* The thickness of film was measured by Micrometer : Mitutoyo no. 7301.

### 3.5 Sample irradiation

#### 3.5.1 Natural weathering

Natural weathering of HDPE film ( $50 \times 58 \text{ cm}^2$ ) was carried out according to ASTM D1435. The location of the exposure site was Bangkok Thailand (latitude  $13^\circ 44' \text{ N}$  and longitude  $100^\circ 34' \text{ E}$ ). The exposed surfaces of samples were mounted on ASTM  $45^\circ$  rack, facing the equator as shown in Figure 3.1. The exposure was started in April 1991 to July 1991 for 16 weeks.



### 3.5.2 Artificial weathering

The samples (HDPE films ; 6x15 cm<sup>2</sup>) were irradiated in an UV weather cabinet equipped with a medium pressure mercury lamp (HPK 125 w) as shown in Figure 3.2-3.3, by fixing on the sample holders at a distance of 15 cm around the lamp. The irradiated samples were stored in the dark until characterization.

### 3.6 Fourier transform infrared (FTIR) measurement

FTIR spectra of the HDPE films were recorded by using fourier transform infrared spectrophotometer and were used for following the changes in carbonyl group ( >C=O) at about 1715 cm<sup>-1</sup>.

### 3.7 Molecular weight measurement

Molecular weight of polyethylene was determined by the viscosity method. Using decahydronaphthalene solutions and calculated from Mark-Houwink-Sakurada equation;

$$[\eta] = kM^a \quad (3.2)$$

where

[  $\eta$  ] = Intrinsic viscosity

k,a = Constant value that can be obtained from the literature for a given polymer-solvent system [21] as listed in Table 3.4

Table 3.4 Constant value for viscosity average molecular weight calculation [21].

PE	temperature (°C)	$k \times 10^3$ (ml/g)	a
HDPE	135	62.00	0.700

### 3.7.1 Sample solution preparation

0.20 gram of HDPE sample was transferred to a 50 ml volumetric flask. Approximately 30 ml of decahydronaphthalene was added to the flask. The flask was placed in an oil bath maintained at 140°C and shaken once every 10 minutes until HDPE dissolved completely then the solution was added up to 50 ml mark with solvent maintained at 135°C.

The concentration of 0.24, 0.16, and 0.08 g/100 ml were made from the above solution (0.40 g/ 100 ml) .

### 3.7.2 Typical procedure for viscosity determination

Approximately 15 ml of decahydronaphthalene was transferred into an Ubbelohde Viscometer (Figure 3.4) which was permanently positioned in the oil bath (Figure 3.5) which was kept constant at 135 °C until the solution attained thermal equilibrium (about 5 minutes). The liquid level was brought to approximately 10 mm above the upper graduation mark on the viscometer capillary. As the meniscus passed this point, the timer was started and the interval for the solution to drain to the lower mark on the capillary was timed. The efflux time of

the solution was measured at least three times. Three consecutive readings should agree within 0.2 second. The solution was then removed from viscometer.

In the same manner as decahydronaphthalene, three consecutive efflux times of HDPE sample solutions were obtained.



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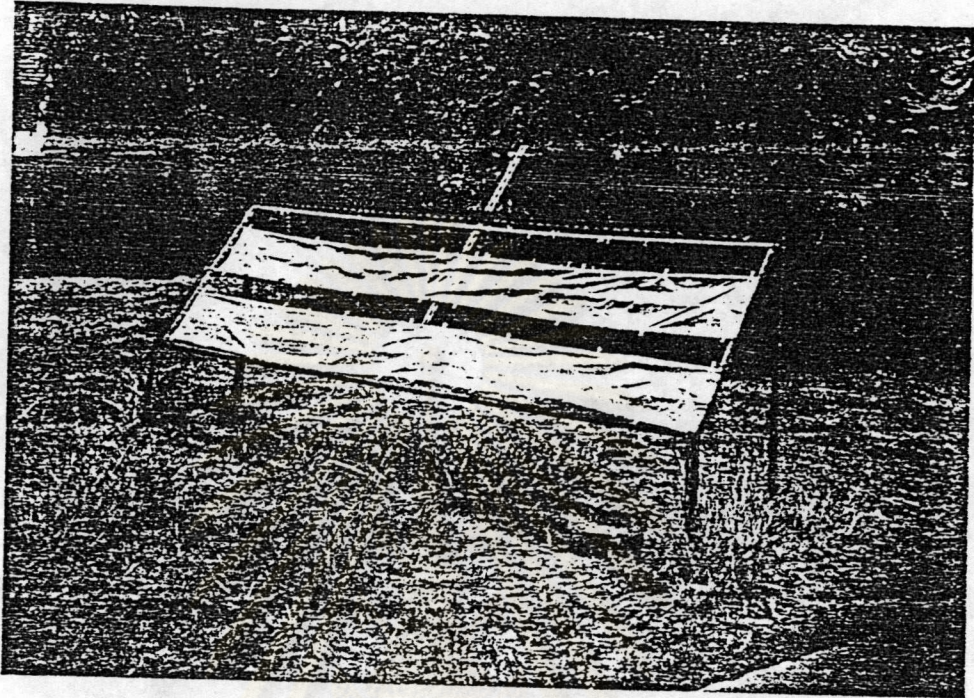


Fig. 3.1 Exposure equipment



Fig. 3.2 Medium pressure mercury lamp

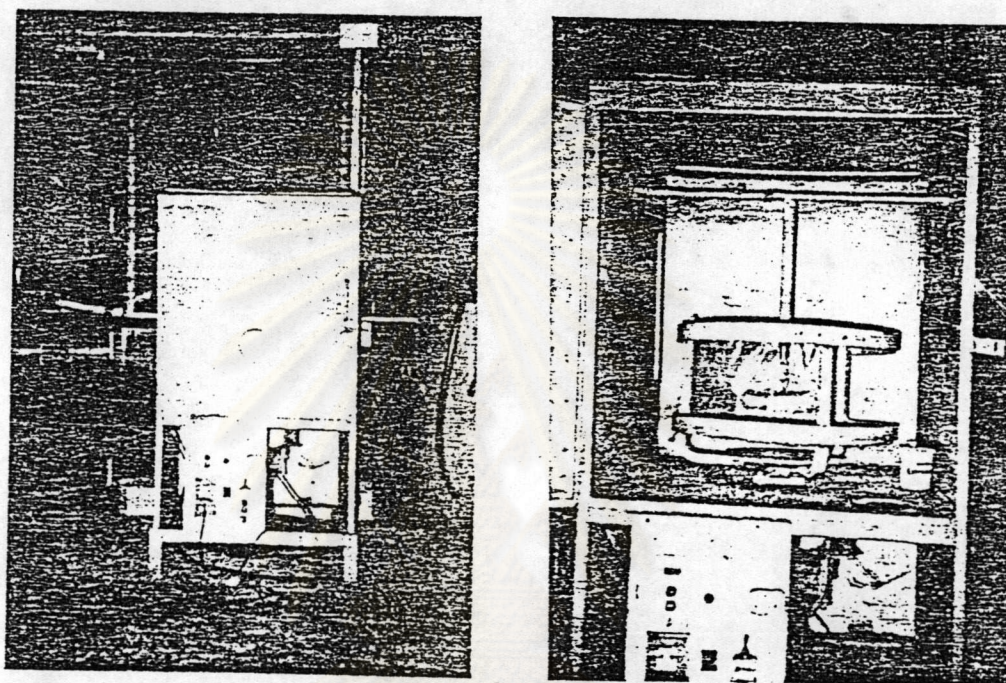


Fig. 3.3. Irradiated cabinet with medium pressure mercury lamp

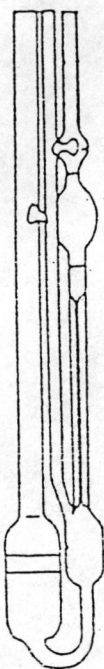


Fig. 3.4 Ubbelohde  
viscometer

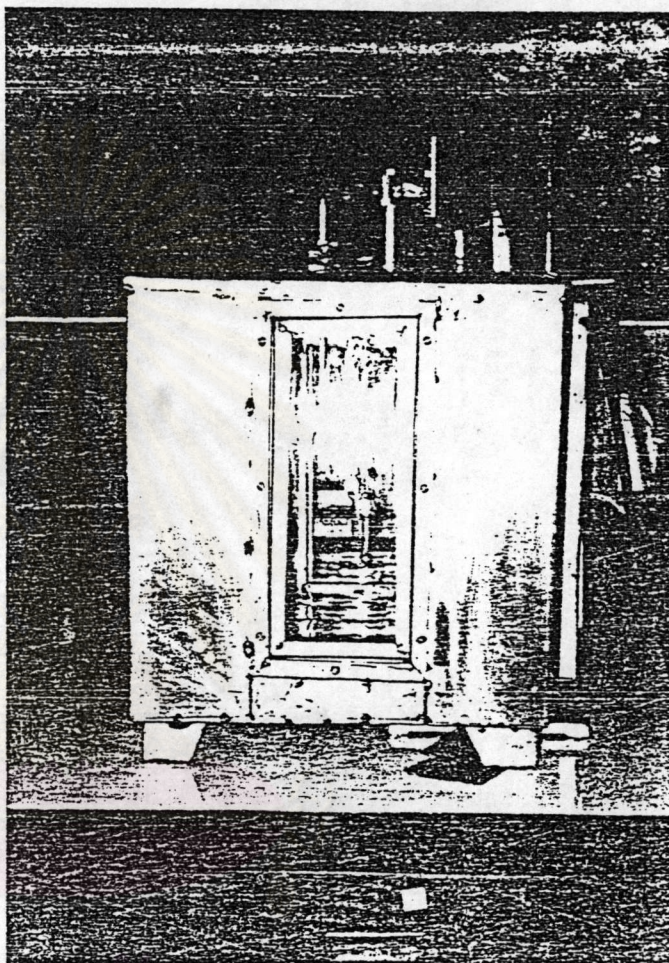


Fig. 3.5. Oil bath