



CHAPTER 3

APPARATUS AND EXPERIMENTAL METHOD

3.1 Reagent and materials

3.1.1 Commercial film grade polyethylene Both LDPE and HDPE used in this study is identified as Polene grade JJ4324 and A3355 respectively supplied by Thai Petrochemical Industry Co.,Ltd. (TPI). Physical properties of the materials are listed in Table 3.1.

3.1.2 Photosensitizers Most of additives were divided into two groups which are presented below:

3.1.2.1 Aromatic ketones have an ultraviolet absorption maximum between 330 and 400 millimicrons [16], as listed in Table 3.2.

3.1.2.1 Aromatic diketones have an ultraviolet absorption maximum between 280 and 330 millimicrons [16], as listed in Table 3.2.

3.1.3 Solvent - decahydronaphthalene (purity >98 %)

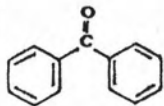
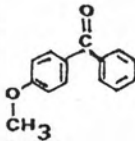
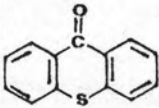
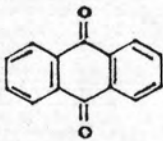
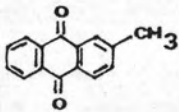
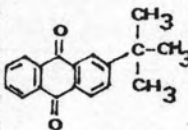
3.1.4 Heat transfer medium - silicone oil

Table 3.1 Physical properties of Polene JJ4324 (LDPE) and A3355 (HDPE)

| Physical property | Test method | Unit | JJ4324 (LDPE) | A3355 (HDPE) |
|--------------------------------|-------------|--------------------|------------------|-----------------|
| Melt index (2.16kg/190°C) | ASTM D1238 | g/10 min | 5.50 | 0.06 |
| Melt index (5 kg/190°C) | ASTM D1238 | g/10 min | - | 0.25 |
| Density | ASTM D1505 | g/cm ³ | 0.922 | 0.950 |
| Tensile strength | ASTM D638 | N/mm ² | >11.0 | >40 |
| Yield strength | ASTM D638 | N/mm ² | >11.0 | >28 |
| Ultimate elongation | ASTM D638 | % | >600 | >1700 |
| Ball indentation hardness | DIN 53456 | N/mm ² | - | >45 |
| Notched impact strength | DIN 53453 | mJ/mm ² | - | >12 |
| Vicat softening temperature | ASTM D1525 | °C | 95 | - |
| Haze | ASTM D1003 | % max. | <6.5 | - |
| Gloss | ASTM 2457 | % min. | >95 | - |
| Impact strength | ASTM D1709B | g | >160 | - |

Source : Thai Petrochemical Industry Co.,Ltd.

Table 3.2 The characterization and properties of photosensitizers [17]

| Photosensitizer | Chemical structure | Character | Melting point, °C | Boiling point, °C |
|-----------------------------|---|----------------|-------------------|------------------------|
| Aromatic ketones | | | | |
| - benzophenone |  | white prisms | 48-49 | 305 |
| - 4-methoxybenzophenone |  | white prisms | 61-64 | 355 |
| - thioxanthone |  | yellow needles | 210-213 | 371-373 (at 715 mm) |
| Aromatic diketones | | | | |
| - anthraquinone |  | yellow needles | 283-287 | 379-381 |
| - 2-methylanthraquinone |  | yellow powder | 177 | 236-238 |
| - 2-tert-butylanthraquinone |  | yellow powder | 98-100 | - |

3.2 Apparatus

3.2.1 Film blowing machine with extruder Model PE-45-AW from Siam Plastic Machinery Co., Ltd.

3.2.2 Micrometer

3.2.3 Exposure equipments, as recommended in ASTM D1435.

3.2.4 Weathering cabinet

3.2.5 Lamp - medium pressure mercury vapour lamp (Phillips 125 W) emitting a high degree of ultraviolet radiation



Figure 3.1 Medium pressure mercury vapour lamp

Table 3.3 Absolute spectrum power distribution

Absolute spectral power distribution

| Wavelength nm | 248.2 | 253.7 | 265.3 | 269.9 | 257.3 | 280.4 | 289.4 | 296.7 | 302.5 | 313.0 | 334.1 | 365.5 | 404.7/ 407.8 | 435.8 | 491.6 | 546.1 | 578.0 |
|---------------|---------|-------|-------|-------|-------|---------|-------|-------|-------|-------|---------|-------|-----------------|---------|-------|-------|-------|
| Lines W | 0.5 | 2.5 | 1.1 | 0.2 | 0.2 | 0.5 | 0.3 | 0.9 | 1.4 | 3.1 | 0.4 | 5.1 | 1.8 | 3.5 | 0.2 | 4.4 | 3.5 |
| Region nm | 240-280 | | | | | 280-315 | | | | | 315-400 | | | 400-600 | | | |
| Lines W | 4.5 | | | | | 6.2 | | | | | 5.5 | | | 13.4 | | | |
| Continuum W | 4.4 | | | | | 2.5 | | | | | 2.3 | | | 1.5 | | | |
| Total W | 8.9 | | | | | 8.7 | | | | | 7.8 | | | 14.9 | | | |

3.2.6 Tensile tester using an Instron universal testing machine Model 1123 equipped with pneumatic grips by selecting load 5 kg

3.2.7 Fourier Transform Infrared Spectroscopy : Perkin-Elmer model 1720

3.2.8 Viscosity analysis apparatus, according to ASTM D1601
- Ubbelohde viscometer, K=0.01

3.3 Sample preparation

The samples were prepared by mixing 0.5% by weight of each photosensitizers with polyethylene in a feed hopper and then blow-extruded by having temperatures at zones for LDPE and HDPE as follow:

Table 3.4 Temperatures at zones in the extruder

| PE | Feed zone (°C) | Compression zone (°C) | Metering zone (°C) | Die zone (°C) |
|------|----------------|-----------------------|--------------------|---------------|
| LDPE | 150 | 155 | 155 | 150 |
| HDPE | 180 | 200 | 200 | 210 |

The thickness of films was 0.035 ± 0.005 mm.

3.4 Sample irradiation

3.4.1 Natural exposures

Outdoor weathering of PE films was carried out, according to ASTM D1435. The natural exposures were carried out at Bangkok, Thailand which is located at latitude $13^{\circ} 44' N$ and longitude $100^{\circ} 34' E$. The exposed surfaces of samples were mounted on ASTM 45° racks, facing the equator as shown in Figure 3.2. The tests were started in September 1990 to February 1991 for 6 months. The meteorological and radiation data at the site were collected from The Monthly Report of the Climatology Division, Meteorological Department. The collected data, including averages of temperature, % relative humidity, total radiation, rainfall amount, are listed in Table 3.5 and shown

in Figure 3.4-3.5.

3.4.2 Irradiation using medium pressure mercury vapour lamp

The samples were irradiated in an UV aging cabinet equipped with a medium pressure mercury vapour lamp (HPK 125 W), as shown in Figure 3.3, and fixed on the sample holders at a distance of 15 cm around the light source. The temperature and % relative humidity were recorded for both LDPE and HDPE during irradiation, as listed in Table 3.6 and shown in Figure 3.6-3.7. When sampling, the PE-film samples were stored in the dark until testing.



Figure 3.2 Exposure equipment

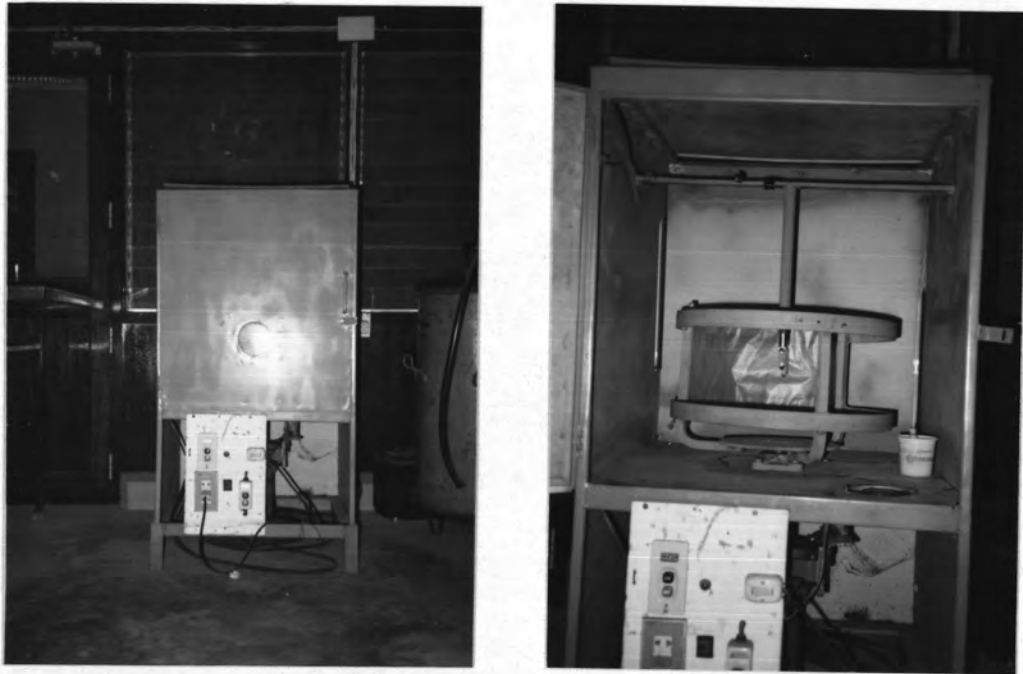


Figure 3.3 Irradiated cabinet with medium pressure mercury lamp

Table 3.5 Meteorological data

| Month | Temperature °C | % R.H. | Rainfall amount, mm | Radiation MJ/M ² |
|----------------|-------------------|--------|------------------------|--------------------------------|
| 1990 September | 28.1 | 76.9 | 257.3 | 21.62 |
| October | 27.7 | 78.4 | 402.3 | 17.06 |
| November | 27.2 | 71.7 | 22.6 | 17.12 |
| December | 26.5 | 64.6 | 0.0 | 23.48 |
| 1991 January | 28.0 | 70.5 | 3.0 | 16.67 |
| February | 28.0 | 66.2 | 7.1 | 34.73 |

Table 3.6 Temperature and % R.H. in UV aging cabinet

| Polyethylene | Time, hour | Temperature, °C | % R.H. |
|--------------|---------------|--------------------|--------|
| LDPE | 5 | 35.0 | 41 |
| | 10 | 33.5 | 46 |
| | 15 | 32.5 | 68 |
| | 20 | 34.0 | 48 |
| | 25 | 31.5 | 52 |
| | 30 | 35.0 | 41 |
| HDPE | 2 | 32.0 | 69 |
| | 4 | 34.0 | 39 |
| | 6 | 34.5 | 53 |
| | 8 | 35.5 | 45 |

Note : After exposure, the polyethylene films were stored in the dark place until testing.

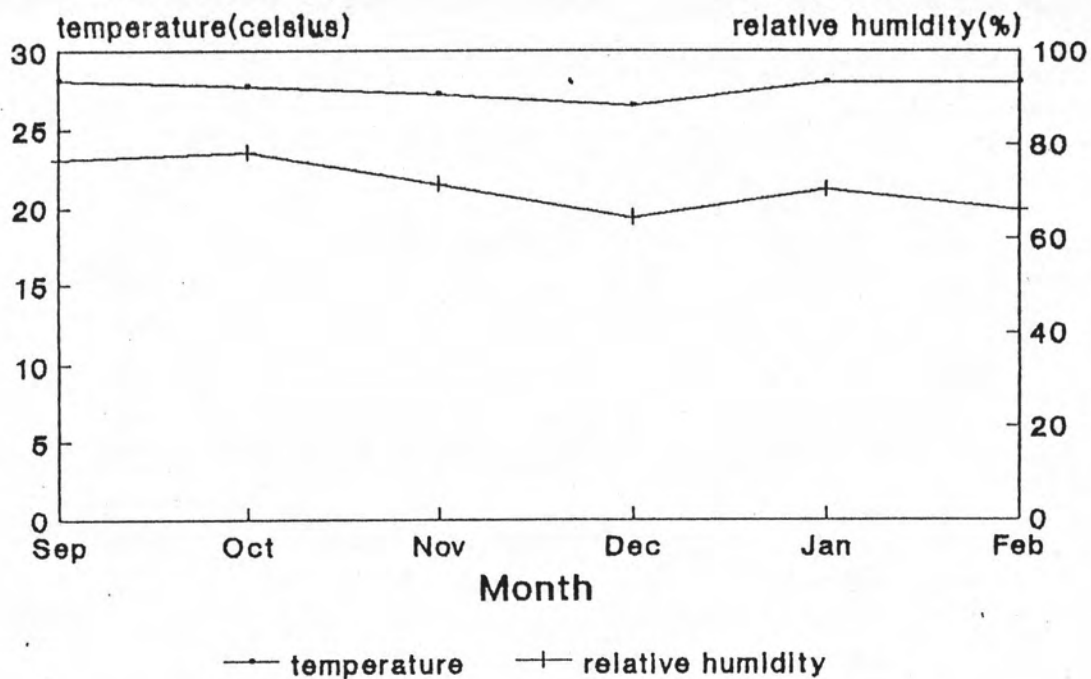


Figure 3.4 Average monthly temperature and relative humidity of Bangkok, Thailand

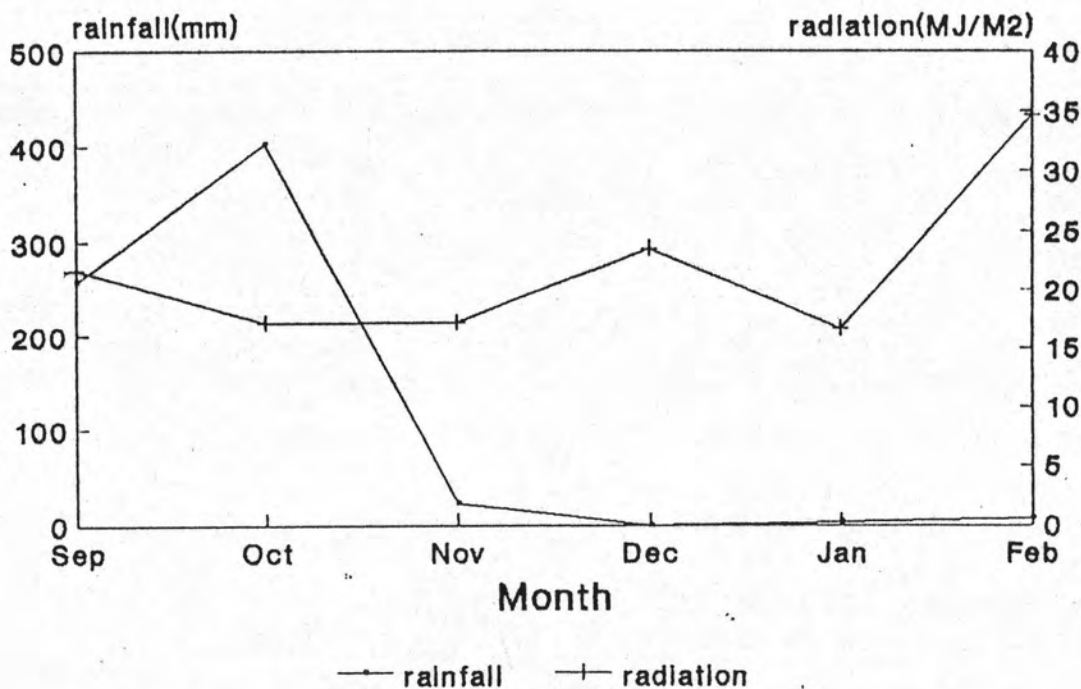


Figure 3.5 Total monthly rainfall and radiation of Bangkok, Thailand

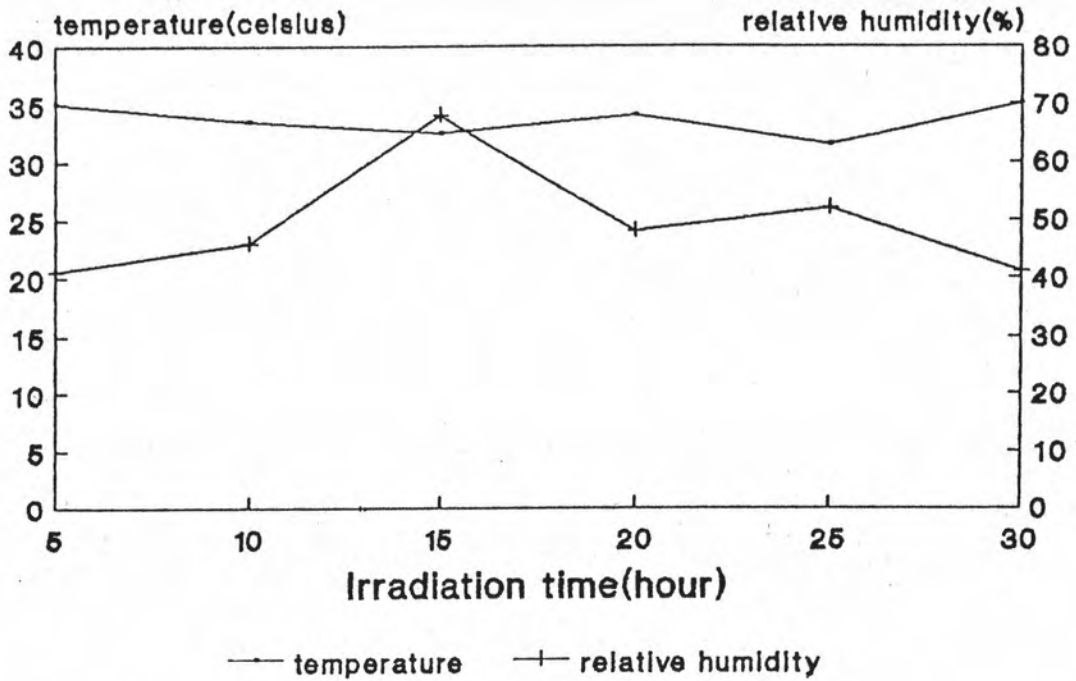


Figure 3.6 Average hourly temperature and relative humidity for LDPE during irradiation with HPK 125 W

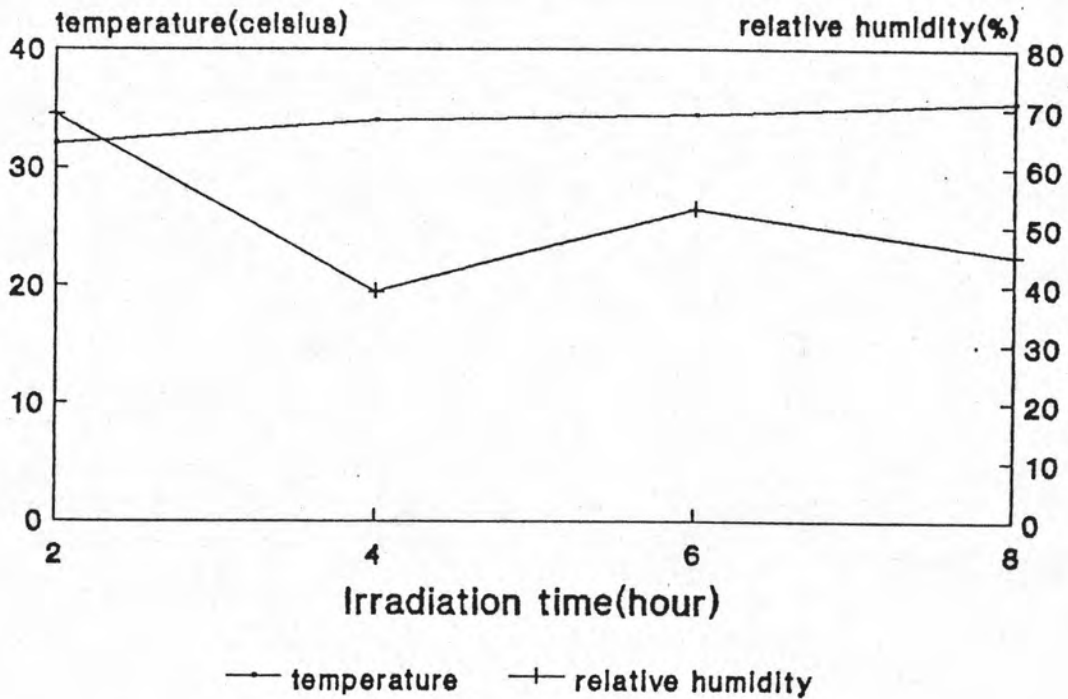


Figure 3.7 Average hourly temperature and relative humidity for HDPE during irradiation with HPK 125 W

3.5 Mechanical measurement

The samples were removed at interval period for testing. According to the ASTM D882, The specimens for tensile testing, cut out along the machine direction, were strips 25.4 mm wide with a guage length of 50 mm. A cross head speed of 100 mm/min was used in the test condition at 27 ± 2 °C and 65 ± 2 % relative humidity, and an average of five specimens was considered as representative value. The resulting stress-strain traces were then determined as an average.

3.6 FTIR measurements

FTIR adsorption spectra of the PE films were recorded on a FTIR Spectrophotometer and were used for estimating the changes in carbonyl group C=O in the chain at 1715 cm^{-1} and vinyl group $-\text{CH}_2-\text{CH}_2=\text{CH}_2$ at 909 cm^{-1} . The polyethylene band at 2019 cm^{-1} served as an internal standard to which the absorbances of the other bands were related. The results were expressed by carbonyl and vinyl index defined as

$$I_{\text{CO}} = A_{1715}/A_{2019} \quad (3.1)$$

$$I_{\text{vinyl}} = A_{909}/A_{2019} \quad (3.2)$$

where

I_{CO} = Carbonyl index

I_{vinyl} = Vinyl index

A_{909} = Absorbance of vinyl group

A_{1715} = Absorbance of carbonyl group

A_{2019} = Internal standard band in PE chain

respectively

3.7 Gel content measurements

"Gel content" measurements were used to estimate the extent of crosslinking in irradiated film samples. Samples were weighed, extracted with hot decahydronaphthalene for 1 hour, and then dried under vacuum at 65 °C. The gel fraction (%) was estimated from equation (3.2)

$$\text{Gel fraction (\%)} = (W/W_0) \times 100 \quad (3.2)$$

where W_0 = the initial weight of the polymer
 W = the weight of the insoluble polymer

3.8 Molecular weight measurements

Molecular weights of PE were determined by the viscosity method, using decahydronaphthalene solutions and calculated from the Mark-Houwink-Sakurada equation:

$$[\eta] = kM^a \quad (3.3)$$

where $[\eta]$ = intrinsic viscosity
 M = viscosity average molecular weight
 k, a = constant that can be obtained from the literature for a given polymer-solvent system [18], as listed in Table 3.6

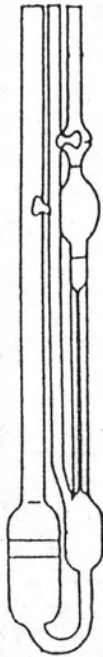
Table 3.7 Constants for viscosity molecular weight calculation [18]

| PE | Temperature, °C | $k \times 10^3$ [ml/g] | a |
|------|-----------------|------------------------|-------|
| LDPE | 70 | 38.73 | 0.738 |
| HDPE | 135 | 62.00 | 0.700 |

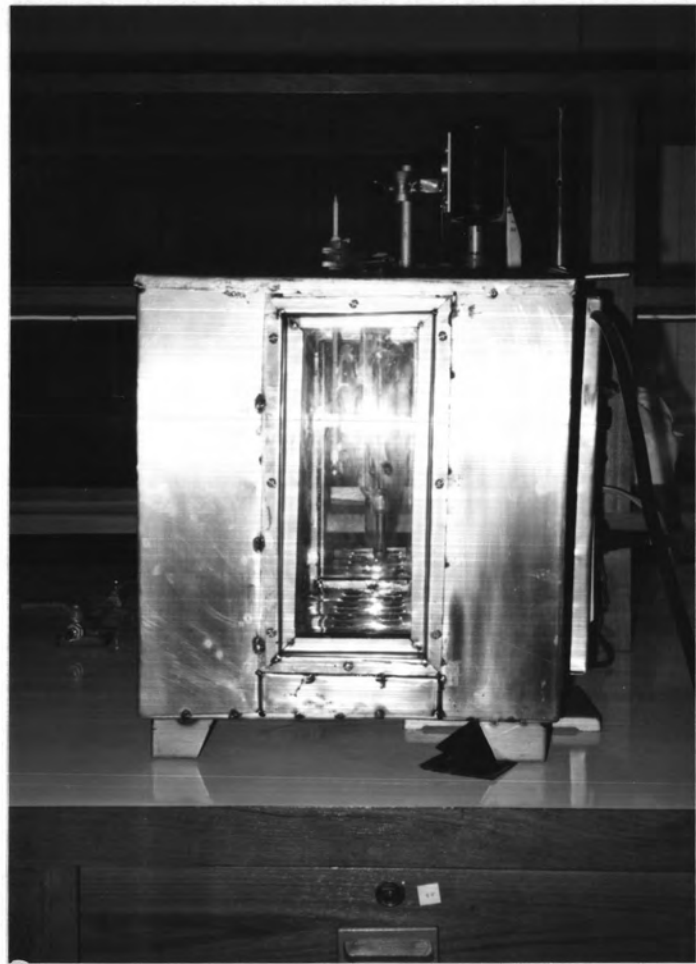
Typical procedure for viscosity determination

Approximately 15 ml of decahydronaphthalene was transferred by syringe into an Ubbelohde viscometer which is permanently positioned in the oil bath which was kept at constant given temperature until the solution attained thermal equilibrium (about 5 min.). The liquid level was brought to approximately 10 mm above the upper graduation mark in 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 (see figure 3.7). 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.

The solution from 3.7 was made up to 50 ml mark with solvent maintained at given temperature by means of a syringe and the flasks were shaken once again. In the same manner as decahydronaphthalene, three consecutive efflux times of the first PE solution in the viscometer were recorded. The first solution was then diluted by adding 15, 10, 5 ml of the first solution into the three 25 ml volumetric flasks, respectively and then all solution were made up to the 25 ml mark with the solvent maintained at given temperature. The efflux time of each times and the average efflux time of undoped HDPE sample and HDPE samples doped with one photosensitizer in a concentration of 0.5 % by weight before and after exposure to the light source were obtained.



(a) Ubbelohde
viscometer



(b) Oil bath

Figure 3.8 Viscosity measuring apparatus