

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Equipment and Apparatus

##### Sample Heating and Calcination

During the synthesis course of catalysts, the starting mixture was heated using a Memmert UM-500 oven. Heating of any solid sample at 100°C was carried out using the same oven. Calcination of the solid catalysts at elevated temperature was achieved in a Carbolite RHF 1600 muffle furnace with programmable heating rate.

##### X-Ray Diffraction

Synthesized mesoporous materials were identified for the structure using a Rigaku D/MAX-22000 X-ray diffractometer at The Petroleum and Petrochemical College, Chulalongkorn University with nickel filtered Cu K $\alpha$  radiation (30 kV, 30mA) at the angle of  $2\theta$  ranged from 5 to 50°. The scan speed was 5°/min and the scan step was 0.02°. The three slits (scattering, divergent and receiving slits) are fixed at 0.5°, 0.5° and 0.30 mm, respectively.

##### Chemical Composition

Silicon contents in the catalysts were determined using X-ray fluorescence (SISONS Instrument ARL 8410) at the Department of Scientific Service, Ministry of Science and Technology. Aluminum contents in the dealuminated mordenite samples were analyzed using either the Shimadzu AA-670 atomic absorption spectrometer with nitrous

oxide/acetylene flame, or the Perkin Elmer Plasma-1000 inductively coupled plasma-atomic emission (ICP-AE) spectrometer located at the Scientific and Technological Research Equipment Center of Chulalongkorn University.

#### **NMR Spectrometer**

Solid-state  $^{27}\text{Al}$ -MAS-NMR spectra were performed using the Bruker Advance DPX 300 MHz NMR spectrometer at National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency.

#### **Nitrogen Adsorptometer**

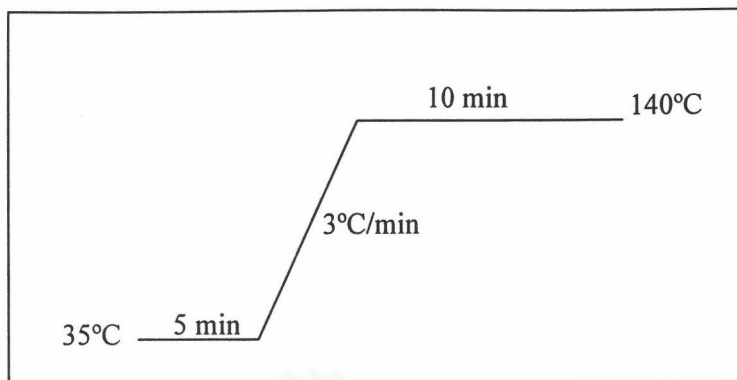
Characterization of catalyst porosity in terms of nitrogen adsorption-desorption isotherms, BET specific surface area, and pore size distribution of the catalysts was carried out using the BEL Japan BELSORP 28SA adsorptometer at Professor T. Tatsumi's Laboratory, Yokohama National University, Japan.

#### **NH<sub>3</sub>-TPD Machine**

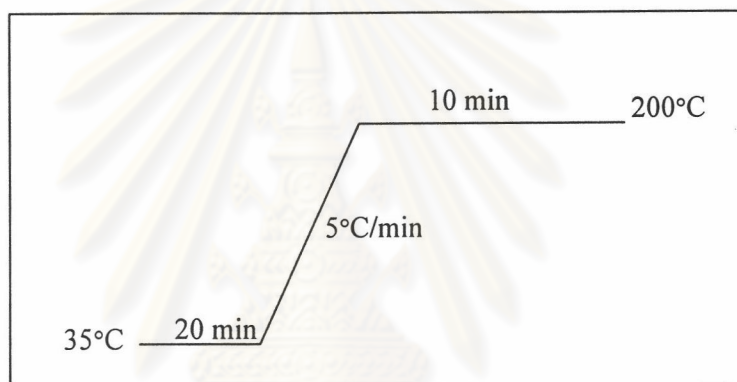
Acid strength of catalysts was determined using the BEL Japan REX-P2000 instrument equipped with the AVELVA M-QA100F quadrupolar mass spectrometer at Yokohama National University.

#### **Gas Chromatograph**

Hydrocarbon gases were analyzed using a Shimadzu GC-9A gas chromatograph equipped with a 30-m long and 0.53-mm outer diameter column of PLOT-Alumina. Liquid samples were analyzed using the Shimadzu GC-14A gas chromatograph equipped with a 30-m long and 0.25-mm outer diameter DB-1 (0.25  $\mu\text{m}$  film thickness) column. All GC detectors are flame ionization detectors (FID). The GC heating programs for 0.20-cm<sup>3</sup> gas and 0.20- $\mu\text{l}$  liquid analysis are shown in Schemes 3.1 and 3.2, respectively.



**Scheme 3.1** The GC heating program for gas analysis.



**Scheme 3.2** The GC heating program for liquid analysis.

### The Cracking Catalytic Apparatus

The catalytic apparatus for cracking of polymers assembled in our laboratory, is composed of a borosilicate tube reactor of a 3-cm wide and 22 cm long, with a side arm (as shown in Figure 3.1), our own made split tube furnace, a K-type thermocouple connected with temperature programmable controller, 2 condensers cooled with stream of ice/water. Apparatus for catalytic cracking is shown in Figure 3.1. Gaseous products were collected into a Tedlar bag. Volatile liquid products were from the reactor by vacuum evaporation to a cold trap cooled in an ice/water bath. Apparatus for collecting volatile liquid products is shown in Figure 3.2.

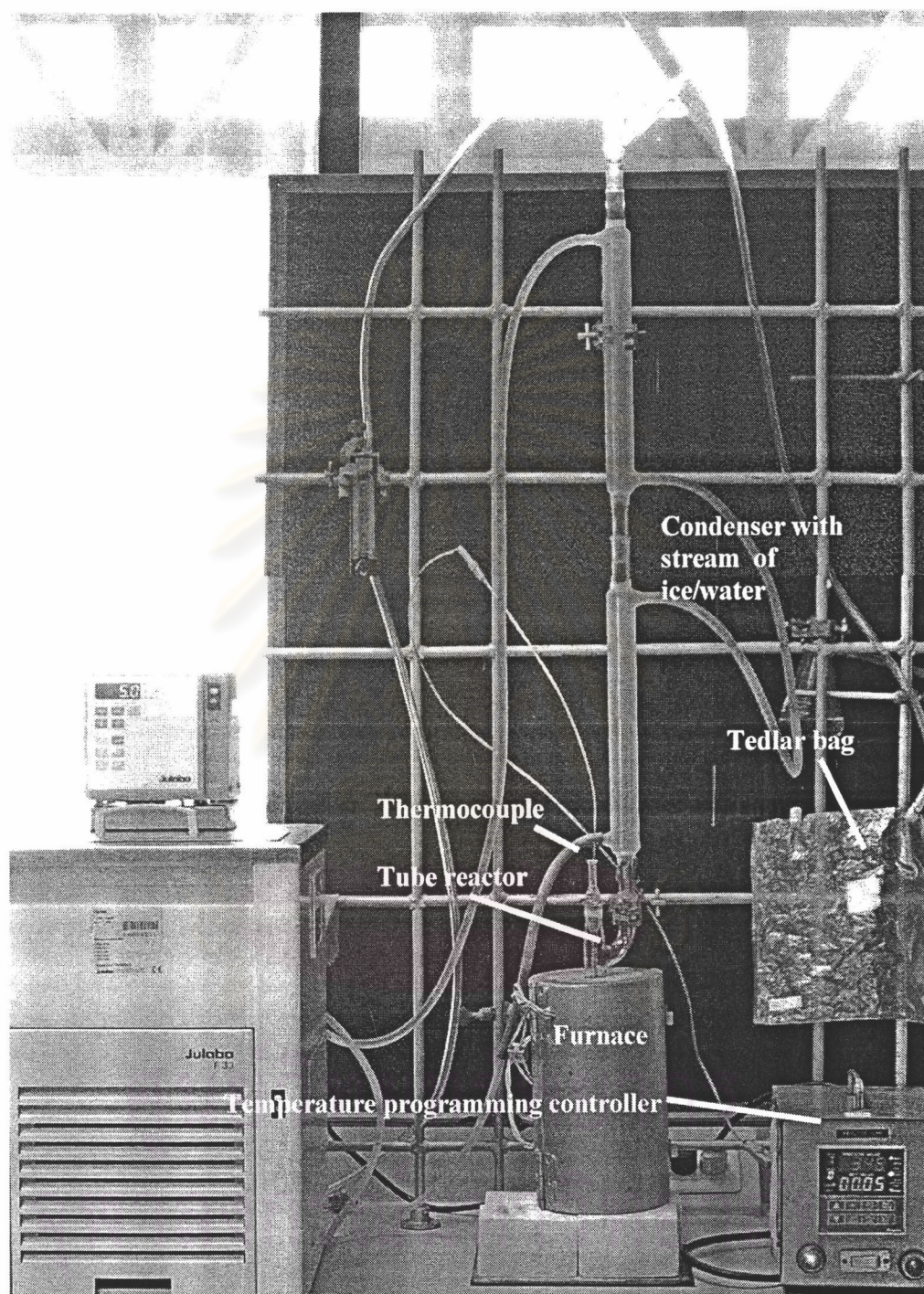
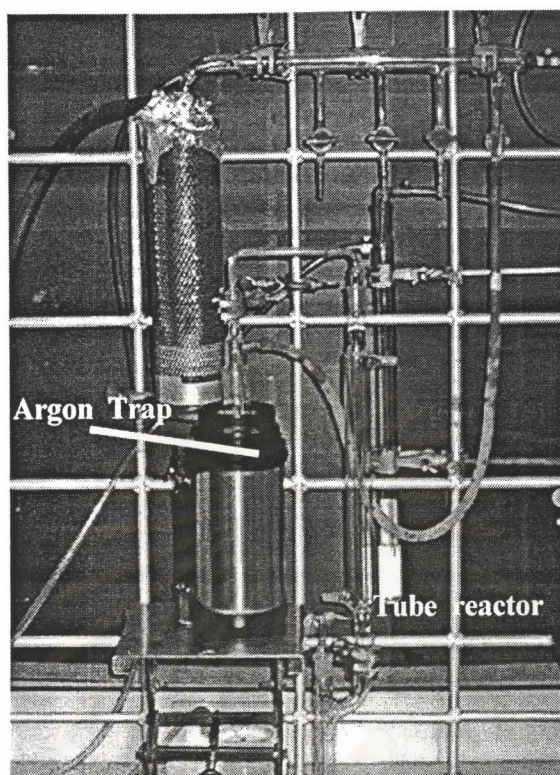


Figure 3.1 Apparatus for catalytic activity test in polymer degradation.



**Figure 3.2** Apparatus for collecting volatile liquid products from the polymer degradation.

### 3.2 Chemicals and Materials

Zeolite mordenite, Na-MOR with the Si/Al ratio of 11 and H-MOR with the Si/Al ratio of 120 were kindly provided by TOSOH Company, Japan via Professor Tatsumi at Yokohama National University. Nitrogen gas, high-purity grade was purchased from Thai Industrial Gases (TIG) and was dehydrated by passing through a 40 cm × 2.5 cm tube of molecular sieve 4A. Hydrochloric acid (HCl) solution, hydrofluoric acid solution (HF) and nitric acid solution (HNO<sub>3</sub>) from Merck were used to obtain sample for AAS and ICP-AES. Ammonium chloride that was purchased from Fluka was used in ammonium exchange. The mixture of standard hydrocarbon gases and the mixture of standard hydrocarbon liquid were kindly obtained from Thai Olefins, Rayong.

Polypropylene bottles and polyethylene disposable gloves were used as reactants for catalytic reactions.

### 3.3 Sample Preparation for AAS and ICP-AES

In a 100-cm<sup>3</sup> Teflon beaker, 0.0400 g of calcined catalyst was soaked with 10 cm<sup>3</sup> of 6 M HCl and subsequently with 10 cm<sup>3</sup> of 37% hydrofluoric acid to get rid of silica form of volatile SiF<sub>4</sub> species. The solid was heated to dryness on a hot plate. The fluoride treatment was repeated twice. An amount of 10 cm<sup>3</sup> of a mixture of 6 M HCl: 6M HNO<sub>3</sub> at a ratio 1:3 was added and further heated to dryness. An amount of 5 cm<sup>3</sup> of 6 M HCl was added to the beaker and warmed for 5 minutes to dissolve the residue. An amount of 10-cm<sup>3</sup> of deionized water was added to the beaker and warmed for 5 minutes to complete solution. The solution was transferred to a 100-cm<sup>3</sup> PP volumetric flask and made to the volume by adding deionized water. The flask was capped and shaken thoroughly. If the sample is not analyzed immediately, the solution was then transferred into a dry plastic bottle with a treaded cap lined under with a polyethylene seal.

### 3.4 Preparation of Catalyst from Na-Mordenite by Ammonium Ion Exchange

There are three methods to be studied for preparation of H-MOR from Na-MOR via the ammonium ion exchange process. The maximum level of ion exchange or the least amount of un-exchanged sodium ions, along with the unchanged structure is used as the judgement for the best method. Apparatus for ion exchange of mordenite is shown in Figure 3.3.

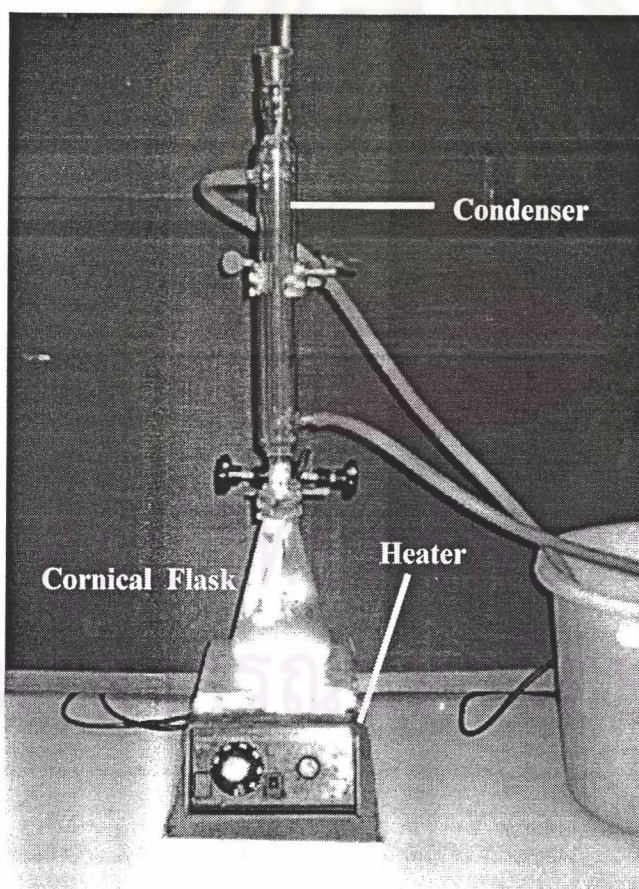
Method A: An amount of 6.0 g Na-MOR was treated with 180 cm<sup>3</sup> of 0.05 M ammonium chloride solution at boiling temperature with stirring overnight. The ammonium-form mordenite, obtained after the ion exchange, was separated from the solution by centrifugation (4000 rpm, 30 min) and washed with deionized water until no chloride. The remaining chloride would precipitate with a silver nitrate solution containing HNO<sub>3</sub>. The sample was dried at the temperature of 100°C overnight in an oven.

Method B: The treatment was performed as explained in the method A but the treatment was repeated twice more. The dried sample was eventually calcined in a muffle

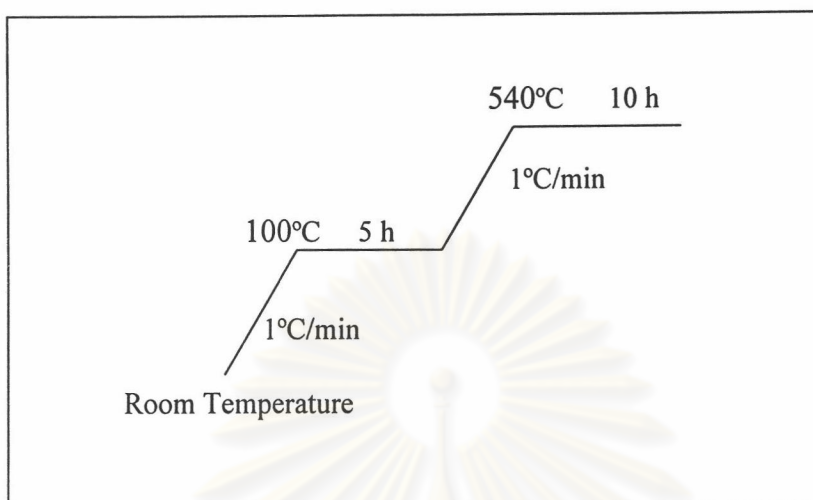
furnace at the temperature of 540°C for 10 h. Heating diagram for calcination of mordenite was shown in Scheme 3.3.

Method C: This method comprised of two-step treatment, ammonium exchange and residual sodium activation at the temperature of 540°C for 10 h, the two steps treatment was repeated twice.

The samples treated by these three different methods were analyzed for the sodium amounts left in the zeolite samples using atomic absorption spectrophotometer. The structure of the zeolite samples was investigated using XRD to ensure the remaining of the mordenite structure.



**Figure 3.3** Apparatus for the ion exchange of Na-mordenite.

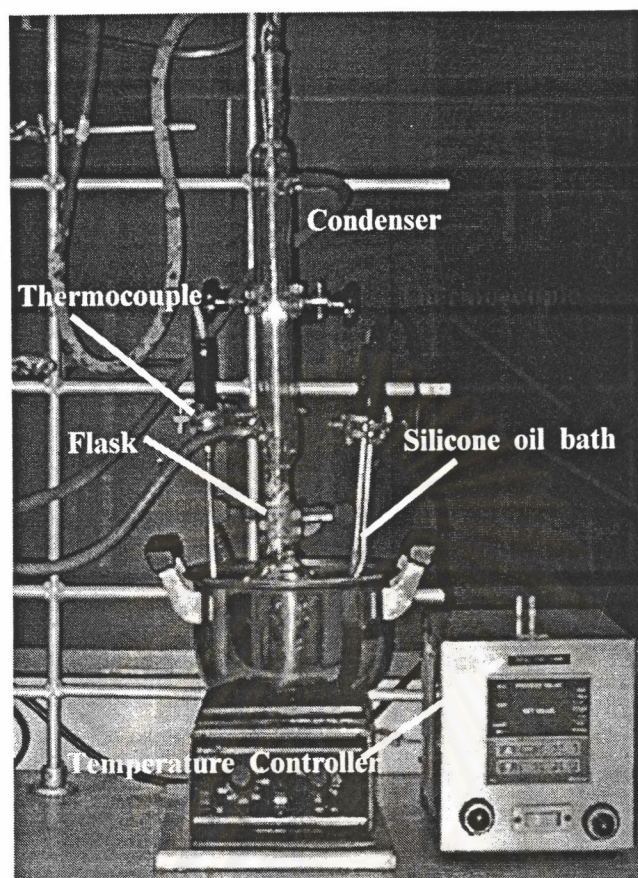


**Scheme 3.3** The heating diagram for calcination of mordenite.

### 3.5 Factors Involved in Dealumination of Mordenite

The catalysts with different Si/Al ratios were prepared by modifying the aluminum-rich sodium-form mordenite-type zeolite, so called Na-MOR with the Si/Al of 11, obtained from TOSOH, Japan. To remove a certain amount of aluminum from the zeolite, Na-MOR was converted to hydrogen-form mordenite (H-MOR), by the ion-exchange process prior to the acid treatment with hydrochloric acid at elevated temperature. To obtain the catalysts with required Si/Al ratios, those factors influencing the dealumination process via acid treatment of the hydrogen-form mordenite were studied. Apparatus for dealumination of the zeolite is shown in Figure 3.4.





**Figure 3.4** Apparatus for dealumination of H-MOR.

### 3.5.1 Effect of Temperature on Dealumination

An amount of 1.0 g H-MOR ( $\text{Si}/\text{Al} = 9.15$ ) and  $25 \text{ cm}^3$  of 1.0 M HCl solution were added into a  $50\text{-cm}^3$  round bottom flask. The reflux was conducted at a require temperature 90, 100, 110 or  $120^\circ\text{C}$ , for 3 h. The acid treated solids were separated by centrifugation (4000 rpm, 30 min) and washed several times with deionized water until no chloride. The dealuminated mordenite samples were dried in an oven at  $100^\circ\text{C}$  overnight and subsequently calcined in a muffle furnace at  $540^\circ\text{C}$  for 10 h. The calcined samples were characterized using  $\text{NH}_3$ -TPD, XRF and ICP-AES instrument.

### 3.5.2 Effect of Acid Concentration on Dealumination

The dealumination of H-MOR was carried out by reflux of 1.0 g H-MOR in 25 cm<sup>3</sup> hydrochloric acid solution of a required concentration: 0.1, 0.5, 1.0, 2.0, 4.0 or 6.0 M. The reflux was operated using an oil bath at 100°C for 3 h. The acid treated solids were separated by centrifugation (4000 rpm, 30 min) and washed several times with deionized water until no chloride. The dealuminated mordenite samples were dried in an oven at 100°C overnight and subsequently calcined in a muffle furnace at 540°C for 10 h. The calcined samples were characterized using XRD and ICP-AES instrument.

## 3.6 Preparation of Dealuminated H-MOR

### 3.6.1 H-MOR with the Si/Al Ratio of 20

A reflux of 8.0 g H-MOR in 200 cm<sup>3</sup> of 0.1 M hydrochloric acid was operated using an oil bath at the temperature of 100°C for 3 h. The acid treated solids were separated by centrifugation (4000 rpm, 30 min) and washed several times with deionized water until no chloride. The product of H-MOR (20) was dried in an oven at 100°C overnight and subsequently calcined in a muffle furnace at the temperature of 540°C for 10 h. The calcined H-MOR (20) was characterized using XRD, ICP-AES and <sup>27</sup>Al-NMR.

### 3.6.2 H-MOR with the Si/Al Ratio of 40

A reflux of 8.0 g H-MOR in 200 cm<sup>3</sup> of 2.32 M hydrochloric acid was operated using an oil bath at the temperature of 100°C for 3 h. The acid treated solids were separated by centrifugation (4000 rpm, 30 min) and washed several times with deionized water until no chloride. The product of H-MOR(40) was dried in an oven at 100°C overnight and subsequently calcined in a muffle furnace at the temperature of 540°C for 10 h. The calcined H-MOR (40) was characterized using XRD and ICP-AES.

### **3.7 Catalytic Activity Test in Polymer degradation**

#### **3.7.1 Polypropylene Degradation over H-MOR with Various Si/Al Ratios**

H-MOR catalysts with Si/AL ratio of 11, 19, 47, 90 and 127 were chosen for the catalytic activity test. An amount of 0.4 g H-MOR and 1 g polypropylene were loaded into borosilicate-tube reactor with 2 condensers that were cooled with stream of ice/water. Furthermore, the degradation was carried out under the nitrogen flow of 12 ml/min. The reactor was heated by a split-tube furnace to the reaction temperature within 15 min. The reaction temperature was 450°C that was controlled by the temperature-programming controller. After reaching 450°C, the temperature was kept constant for 30 min. The gas products were collected in a Tedlar bag, The reaction was cooled to room temperature. The volatile liquid products were evaporated to a cold trap cooled by liquid nitrogen using a vacuum pump. The products were analyzed by GC. Apparatus for catalytic degradation is shown in Figures 3.1 and 3.4.

#### **3.7.2 Polypropylene Degradation at Various Temperatures**

The catalysis was carried out at various temperatures of 350, 450 and 550°C using temperature of H-MOR with the Si/Al ratio of 127 as catalyst. The products are collected and analyzed in a similar way as described in Section 3.7.1.

#### **3.7.3 Polyethylene Degradation over H-MOR with Various Si/Al Ratios**

The catalytic test was performed similar to that described in the Section 3.7.1 but polyethylene was used instead of polypropylene.

#### **3.7.4 Polypropylene Degradation at Various Temperatures**

This experiment was carried out in a similar manner as described in Section 3.7.2 except polyethylene was replaced by polyethylene.