# CHAPTER III

# EXPERIMENTAL

## 3.1 Chemicals

### 3.1.1 2,2'-Azobis[2-methylpropanenitrile] (AIBN)

2,2'-Azobis[2-methylpropanenitrile] or 2,2'-azo(bis)isobutyronitrile (AIBN, Brighten Polytrading Co.,Ltd.) was purified twice by recrystallization from methanol. The purified moisture-free AIBN was then collected in a bottle covered with the metallized plastic film to protect the radiation from day light and stored in a refrigerator at 5°C. The melting ranges of a purified AIBN was of 107-110°C.

### 3.1.2 1-Phenylethylene (styrene)

1-Phenylethylene (styrene) monomer was cordially supplied by Thai Petrochemical Industry Public Co.,Ltd (TPI). 15-30 ppm inhibitor, 2-hydroxy-4-tertiarybutylphenol (tert-butylcatechol, TBC), was removed by using UOP alumina adsorbent type A-201 (Union Carbide Thailand Limited). The inhibitor-free styrene monomer was then added with 1g/L Copper (II) chloride ($CuCl_2$) stabilizer and was subsequently distilled under a reduced pressure less than 10 mm Hg. The distillate fraction at the temperature 60-65°C (less than 10 mm Hg) was pure styrene which was collected in a conical flask. Then it was purged with $N_2$ gas to remove the dissolved oxygen prior to storage in a refrigerator at 5°C. Normally, it was used immediately or kept not more than 3 days. In the latter case its purity was checked by GC technique prior to uses.

A gas chromatograph (GC) (Hewlett Packard model 5900 S) equipped with a flame-ionization detector and autosampler was employed. A capillary column (30 m length and 0.250 mm internal diameter) coated with 0.1 μm film thickness of 100% dimethylpolysiloxane was used. A high purity nitrogen gas (99.999%) was used as the carrier gas at a flowrate of 0.5 mL/min. The injection port and detector temperature were set at 250°C. The oven temperature was programmed initially at 60°C and raised up to 100°C with a heating rate of 5°C/min. The temperature was controlled at 100°C for 2 minutes. 0.1 μL sample was automatrically injected into GC using the autosampler device. A typical chromatogram is shown in Figure 3.1. The purity of styrene was calculated using the software supplied by Hewlett-Packard based on the normallization of the total peak area detected. In this research work, the purity of styrene used was specified to be higher than 95%.
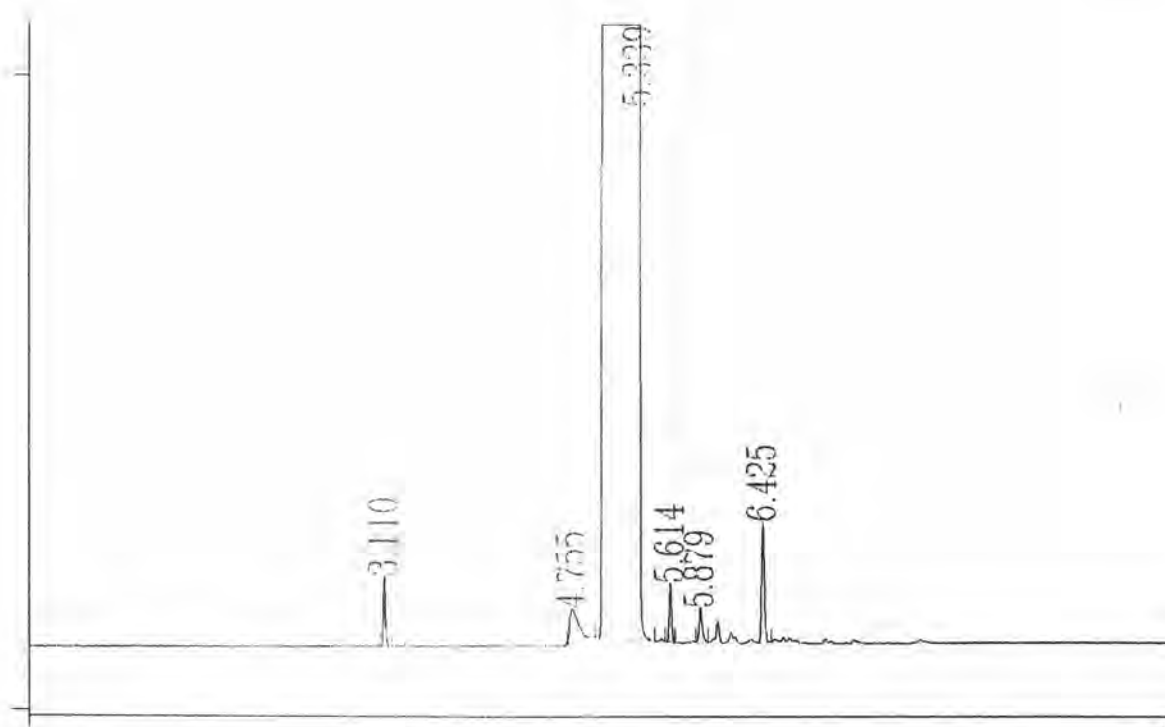


**Figure 3.1** A typical GC chromatogram of purified styrene monomer used in this study.

### 3.1.3 1-(Methoxycarbonyl)-1-(methyl)ethylene (methyl methacrylate)

1-(Methoxycarbonyl)-1-(methyl)ethylene (methyl methacrylate, MMA) was cordially supplied by Thai Polyacrylate Public Co.,Ltd. It is colourless liquid containing 30 ppm of inhibitor, 2,4-dimethyl-6-tertiarybutyl phenol which was removed by washing twice with 10% aqueous sodium hydroxide (NaOH) and subsequently twice with demineralised water until the pH of aqueous phase was neutral. After being dried over anhydrous calcium chloride, 1 g $CuCl_2$ stabilizer was added to a litre of inhibitor-free MMA. Then it was distilled under reduced pressure less than 10 mm Hg. The MMA distillate at 40-45°C was collected and the dissolved oxygen was removed by purging nitrogen gas through. It was used immediately or kept not more than 7 days in a refrigerator at 5°C prior to uses. In case of the longer storage time, the purity was measured by GC technique before uses.

The purity of distilled MMA was also determined by means of the gas chromatographic technique. The experimental conditions performed were as same as those described in Section 3.1.2 except the followings. The temperature of injection port and detector was constantly controlled at 180°C. The oven temperature was programmed to raise from 60°C to 100°C with a heating rate of 5°C/min. The temperature at 100°C was controlled to maintain for 5 minutes. Typical chromatogram is shown in Figure 3.2. The calculation method used for determination of its purity was as same as that for styrene. The specification of the purified MMA used in this study was higher than 95%.
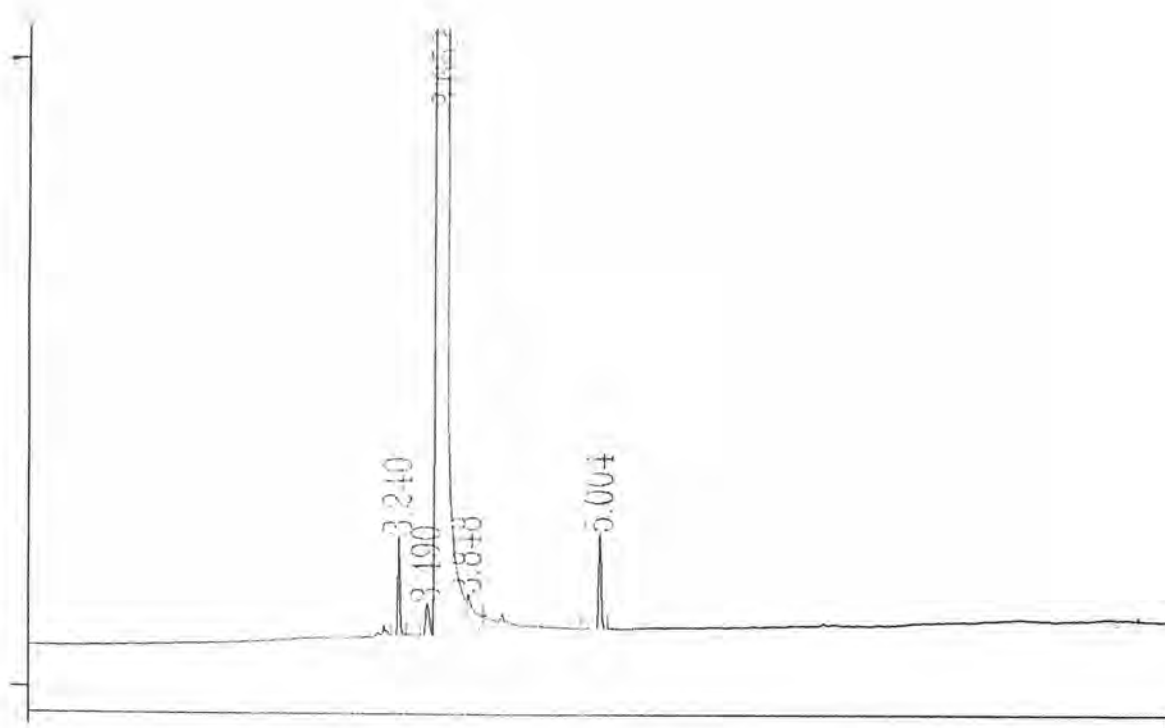
**Figure 3.2** A typical GC chromatogram of the purified methyl methacrylate used in this study.

## 3.2 Kinetics Study of the Thermal-initiated Free Radical Bulk Homopolymerization of Styrene

### 3.2.1 Preparation of the reaction mixture

All of the experimental procedures performed were carried out under the $N_2$ atmosphere. The reaction mixture was prepared by weighing an accurate quantity of the purified AIBN in a dry 1 mL volumetric flask. An accurate amount of the distilled styrene (1 mL, 8.7 mmol) was pipetted into the flask. The mixture was then shaked well until the homogeneous solution was obtained. Table 3.1 shows the quantities of initiator and monomer used in each batch of polymerization.

**Table 3.1** Quantities of AIBN and styrene used in each polymerization batch.

| Batch | Substances | Conc. (mol/L) | Weight (mg) | Volume (mL) | Initiator (%w/w) |
|---|---|---|---|---|---|
| A | AIBN | 0.0275 | 4.52 | - | 0.5 |
|   | Styrene | 8.70 | - | 1 | - |
| B | AIBN | 0.0551 | 9.05 | - | 1.0 |
|   | Styrene | 8.70 | - | 1 | - |
| C | AIBN | 0.0828 | 13.6 | - | 1.5 |
|   | Styrene | 8.70 | - | 1 | - |
| D | AIBN | 0.110 | 18.1 | - | 2.0 |
|   | Styrene | 8.70 | - | 1 | - |

### 3.2.2 Isothermal bulk homopolymerization of styrene

In the present work, the differential scanning calorimeter (Perkin-Elmer, model DSC-7) was used to follow the homopolymerization reaction according to the following procedure. 6-10 mg of the prepared mixture was weighed into a standard Perkin-Elmer aluminium pan (volatile sample-type) and then gently sealed with a sealable equipment. It was introduced into the DSC furnace controlled at 30°C. Then the temperature was programmed to raise up to the polymerization temperature at 80°C with a heating rate of 40°C/min. The heat flow data was initially recorded after the desired temperature was reached for 1 min. in order to achieve the constant initial heat flow. Isothermal polymerization was ended after exotherm peak was not observed. The polymerization was immediately stopped by quenching the sample pan in liquid nitrogen.

The total heat of isothermal polymerization was calculated from the total peak area between the DSC thermogram and the baseline established by manual extrapolation from the initial time to the time that the trace produced after completion

of polymerization. Indium standard was used as a calibrant for temperature and enthalpy.

The experiments were repeated in the same manner described above for the homopolymerization of the mixture B except the reaction temperature was at 60, 70, 75, 80, 85 °C and these were called mixture I, J, K, L and M respectively.

### 3.2.3 Determination of the residual styrene using DSC technique [9,10]

Two different methods were used to measure the residual styrene content namely DSC and GC techniques. For the former, the residual styrene content was determined by heating the quenched sample from 30°C to 180°C with a heating rate of 10°C/min.

The total heat of polymerization of the residual styrene after isothermal polymerization was calculated from the total peak area between the DSC thermogram and the baseline that no exotherm was detected. Since the polystyrene obtained from the isothermal polymerization shows the glass transition near the exothermic curve produced by the polymerization of the residual styrene, the total peak area of the exothermic curve was calculated using the baseline drawn by the extrapolation of the maximum glass transition and the temperature that no further exotherm occured.

The styrene conversion and the residual styrene content of polymerization reaction can be calculated following Equations (2.46) and (2.47), respectively.

### 3.2.4 Determination of the residual styrene using GC technique

Gas chromatography was the other alternative technique used to measure the residual monomer content. The polymerization was performed under isothermal condition using a DSC-7 furnace as described in Section 3.2.2. The quenched sample pan was then destroyed in order to dissolve the polymerized reaction mixture with the inhibitor solution which was prepared by dissolving 10 mg of TBC inhibitor in 2-butanone (methyl ethyl ketone, MEK) solvent. It was added to prevent the polymerization of the residual styrene. The sample solution was stored at the room

temperature for overnight in order to ensure that it was completely dissolved. The total volume was adjusted to 5 mL and 10 mg of n-decane was added to function as an internal standard.

A calibration curve for the residual monomer content determination was established by preparation of a set of standard styrene solution in the concentration ranges of 1.5 mg to 12 mg. A set of the fresh aluminium pans and cover used in DSC measurement was put into a 5 mL volumetric flask in order to simulate the similar matrix as that of sample. 10 mg TBC dissolved in MEK solvent was added and made up the volume to 5 mL with MEK. 10 mg internal standard was added.

The standard and sample solutions were measured using similar equipments as described in Section 3.1.2 and the following conditions. The flow rate of the carrier gas was 1.0 mL/min. The temperature of injection port and detector was set to 300°C. The oven temperature was initially set to 90°C to 290°C with a heating rate of 40 °C/min and was controlled at the final temperature for 5 minutes. 0.1 μL sample was automatrically injected into GC using the autosampler device.

The typical chromatogram of the standard solution is shown in Figure 3.3. The components at the retention time of 3.338, 4.386 and 5.692 min. were classified to be MEK solvent, styrene and n-decane, respectively.

The calibration curve was the plot of the ratio of peak areas of styrene to n-decane against the actual styrene content (see Figure 3.4).

The residual monomer content in mg was calculated referenced to the calibration curve. The total monomer conversion was obtained from Eq. (3.1) with the assumption that there was no loss of the total weight during the polymerization.

$$\text{The total monomer conversion} \quad = \quad 1 - m_r / m_i \tag{3.1}$$

where   $m_r$ is the weight of residual styrene monomer determined by GC technique, and

$m_i$ is the initial weight of styrene monomer or the reaction mixture weight that used in the DSC measurements.

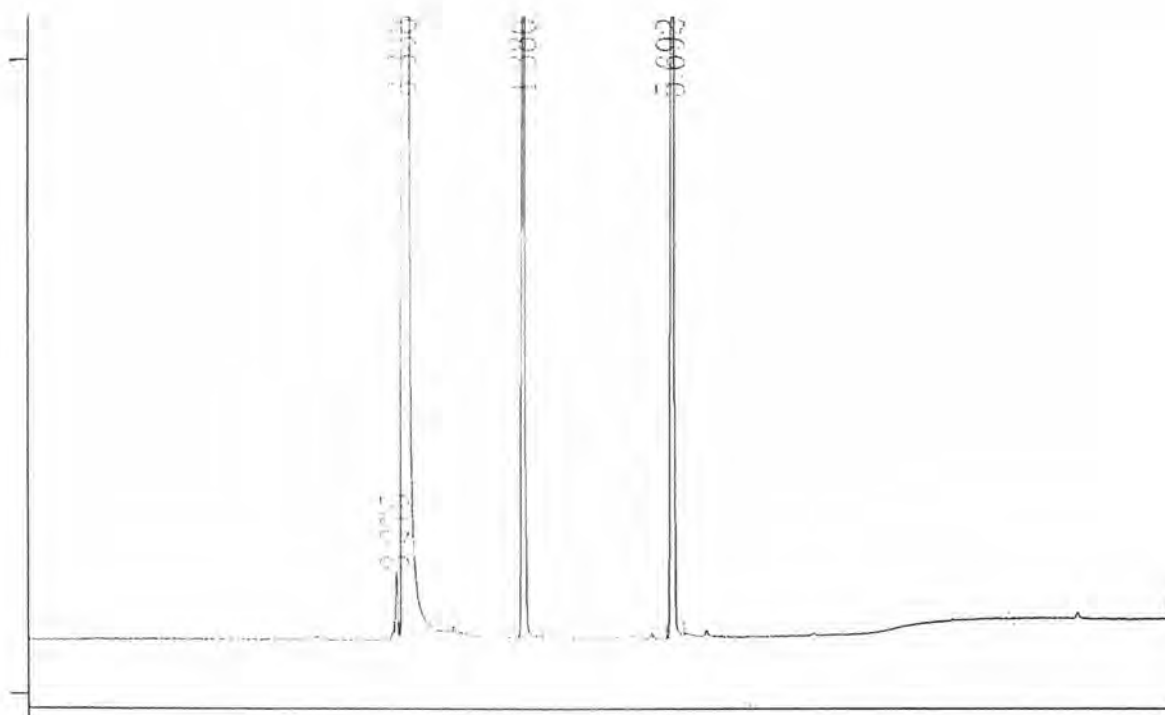All of the data cited here were the average of the two measurements.

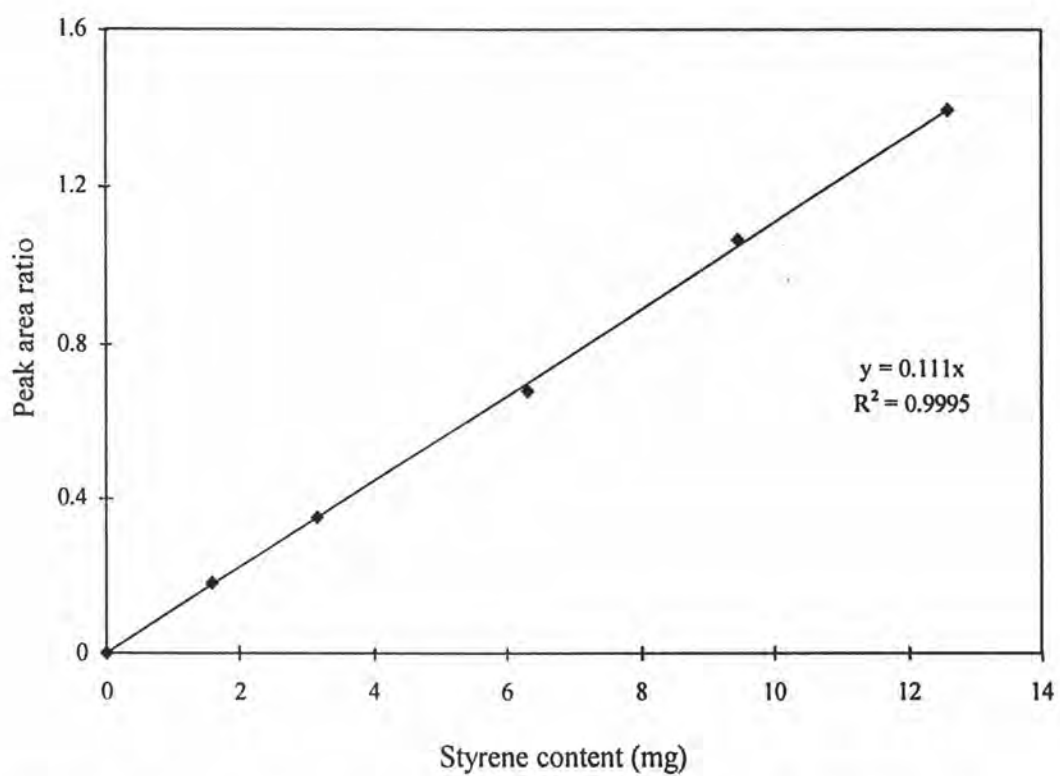**Figure 3.3** A typical GC chromatogram of the standard styrene solution.



y = 0.111x
R² = 0.9995

**Figure 3.4** The calibration curve for determination of the residual styrene.

## 3.3 Kinetics Study of the Thermal-initiated Free Radical Bulk Homopolymerization of Methyl methacrylate

### 3.3.1 Preparation of reaction mixture

The reaction mixture was prepared based on the same procedure as described in Section 3.2.1. Table 3.2 shows the quantities of initiator and monomer used in each batch of polymerization.

**Table 3.2** Quantities of AIBN and MMA used in each polymerization batch.

| Batch | Substances | Conc. (mol/L) | Weight (mg) | Volume (mL) | Initiator (%w/w) |
|-------|-----------|---------------|-------------|-------------|------------------|
| E | AIBN | 0.0286 | 4.70 | - | 0.5 |
|   | MMA | 9.40 | - | 1 | - |
| F | AIBN | 0.0572 | 9.40 | - | 1.0 |
|   | MMA | 9.40 | - | 1 | - |
| G | AIBN | 0.0859 | 14.1 | - | 1.5 |
|   | MMA | 9.40 | - | 1 | - |
| H | AIBN | 0.114 | 18.8 | - | 2.0 |
|   | MMA | 9.40 | - | 1 | - |

### 3.3.2 Isothermal bulk homopolymerization of MMA

The same experimental procedures described in Section 3.2.2 were employed to polymerize the prepared reaction mixture E-H at 80 °C. For mixture F, the reaction temperature was at 60, 70, 75, 80 and 85 °C and these mixture were coded as mixture N, O, P, Q and R, respectively.

### 3.3.3 Determination of the residual MMA using DSC technique

The residual MMA after polymerization was measured using DSC technique, following the experimental procedures described in Section 3.2.3. The total heat of polymerization of the residual MMA in the isothermal polymerized sample was calculated from the total peak area between the DSC thermogram and the baseline extrapolated from the temperature with no exotherm.

### 3.3.4 Determination of the residual MMA using GC technique

The residual MMA after the isothermal polymerization was also measured by using the gas chromatographic technique. The preparation of sample and standard solutions was similar to that for the determination of residual styrene content except for that the inhibitor solution was not added.

The gas chromatograph equipped with the same equipments as those described in Section 3.1.2 was used. The analysis conditions were employed as follows. The flow rate of carrier gas was set at 0.5 mL/min. The temperature of the injection port and the detector was controlled at 180°C. The oven temperature was initially controlled at 40°C for 5 minutes and was programmed to raise up from 40°C to 150°C with a heating rate of 40°C/min after that it was controlled at the final temperature for 5 minutes. 0.1 μL sample was automatrically injected into GC using the autosampler device.

A typical chromatogram of the standard MMA solution is shown in Figure 3.5. Three main components detected at the retention time of 2.935, 3.684 and 7.970 minutes are classified to be MEK solvent, MMA and n-decane, respectively.

The calibration curve (Figure 3.6) was established by the plot of the peak area ratio of MMA to n-decane against the actual MMA content which was used to determine the residual MMA. The total monomer conversion was calculated following Eq. (3.1).
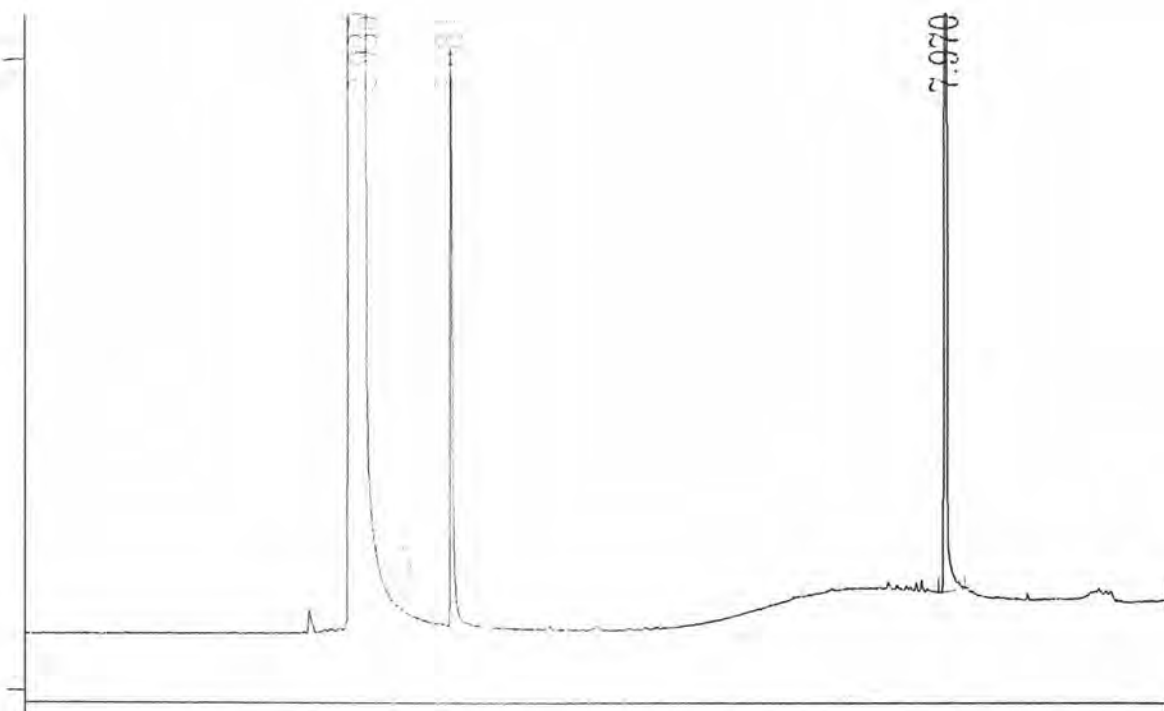
**Figure 3.5** A typical GC chromatogram of the standard MMA solution.
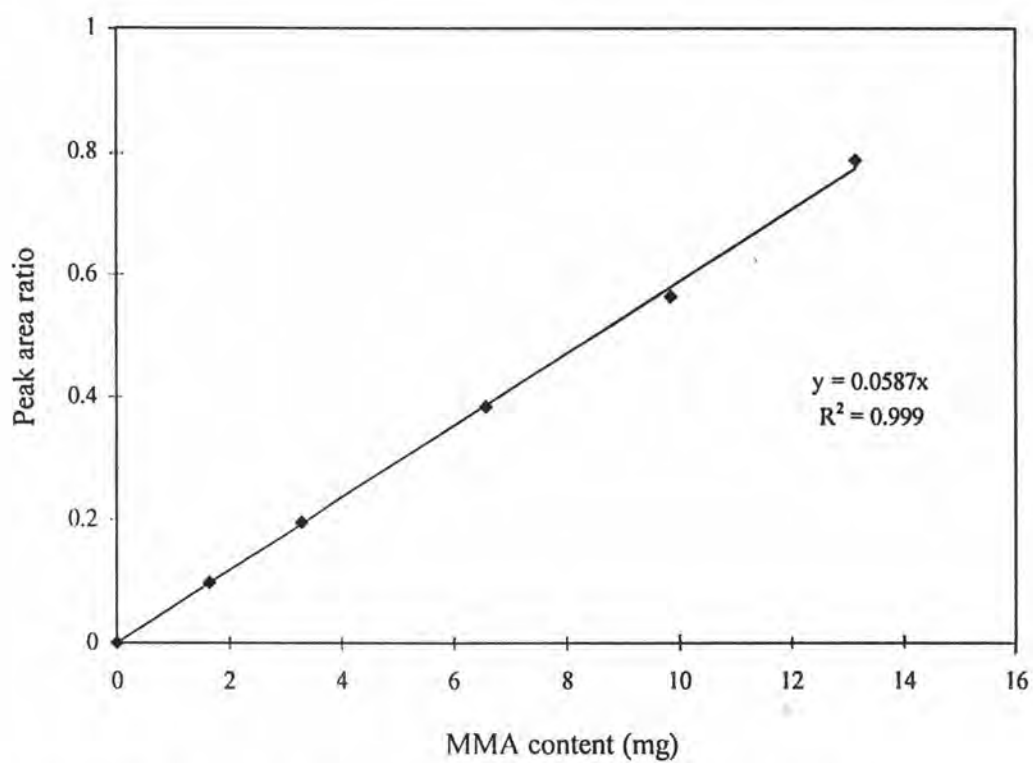


**Figure 3.6** The calibration curve for determination of residual MMA.

## 3.4 Kinetics Study of the Thermal-initiated Free Radical Bulk Copolymerization of Styrene and Methyl methacrylate

The kinetics of thermal-initiated free radical bulk copolymerization of styrene and MMA at $60^{\circ}C$ were studied by the variation of feed monomer composition at the constant initiator concentration (1.0% w/w). The experimental procedures are given subsequently in details.

### 3.4.1 Preparation of the reaction mixture

The reaction mixture was prepared by weighing an accurate amount of the purified AIBN in a dry 1 mL volumetric flask. The accurate volume of the distilled styrene and MMA was subsequently pipetted into the flask. The amount of initiator and monomers used in each batch of copolymerization is shown in Table 3.3. The mixture was gently shaked well until the initiator was completely dissolved.

**Table 3.3** Quantities of AIBN, styrene and MMA used in each batch of
copolymerization.

| Batch | Substances | Conc. (mol/L) | Weight (mg) | Volume (mL) | Initiator (%w/w) |
|-------|-----------|---------------|-------------|-------------|------------------|
| S | AIBN | 0.0568 | 9.33 | - | 1.0 |
|   | Styrene | 1.74 | - | 0.2 | - |
|   | MMA | 7.52 | - | 0.8 | |
| T | AIBN | 0.0564 | 9.26 | - | 1.0 |
|   | Styrene | 3.48 | - | 0.4 | - |
|   | MMA | 5.64 | - | 0.6 | |
| U | AIBN | 0.0560 | 9.19 | - | 1.0 |
|   | Styrene | 5.22 | - | 0.6 | - |
|   | MMA | 3.76 | - | 0.4 | |

### 3.4.2 Isothermal bulk copolymerization

6-10 mg of the reaction mixture were weighed into an aluminium pan suitable for the volatile material and subsequently sealed using a sealable equipment set. The sample pan was introduced into the DSC furnace which its temperature was previously controlled at 30°C and was programmed to raise up to the copolymerization temperature at 60°C with a heating rate of 40°C/min. The data recorded were delayed for 1 minute after the polymerization temperature was reached the set point due to the same reason as that for the homopolymerization reactions. The copolymerization reaction was stopped after no observation of further exotherm by immediate quenching the sample pan in liquid nitrogen.

Calculation of total heat of isothermal copolymerization followed the same procedures as that described in Section 3.2.3 .

### 3.4.3. Determination of the residual styrene and MMA using DSC technique

The residual styrene and MMA in each batch of the isothermal copolymerization were comparatively measured by both DSC and GC techniques. The copolymerization reactions were performed in the DSC furnace following the procedures in 3.4.2.

In case of the calorimetric measurement, the quenched sample obtained from the isothermal copolymerization was measured using the same procedures as for the homopolymerization. The calculation of the total comonomer conversion and residual styrene and MMA followed Equations (2.46) and (2.47).

### 3.4.4 Determination of the residual styrene and MMA using GC technique

The residual styrene and MMA of each batch of isothermal copolymerization were also measured by using the gas chromatograph. The quenched sample obtained from the isothermal polymerization was torn and dissolved in a 5 mL volumetric flask using MEK solvent. The sample solution was stored at the room temperature overnight. The internal standard used was n-decane solution.

The calibration curve was established by preparing a set of the mixed standard monomers having the total concentration in the ranges of 1.5 mg to 12 mg. An equal amount of styrene and MMA was weighed into a 5 mL volumetric flask. A set of the fresh aluminium pan and cover used in DSC measurement was put into the flask. 10 mg of internal standard was added after the total volume was adjusted to 5 mL.

The analysis conditions employed were as same as those for determination of the residual MMA of the homopolymerized samples.

Figure 3.7 shows the typical chromatogram of the standards solution. There are four main peaks including MEK at the retention time of 4.040, MMA of 5.081, styrene of 7.552 and n-decane of 8.919 min.

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Two separate calibration curves (Figures 3.8 and 3.9) were established by plotting the peak area ratio of MMA or styrene to n-decane against the actual monomer content. The residual monomers were calculated based on those relevant calibration curves. The total residual monomers were obtained by the addition of the residual styrene and MMA. The total monomer conversion was calculated based on Eq. 3.1.
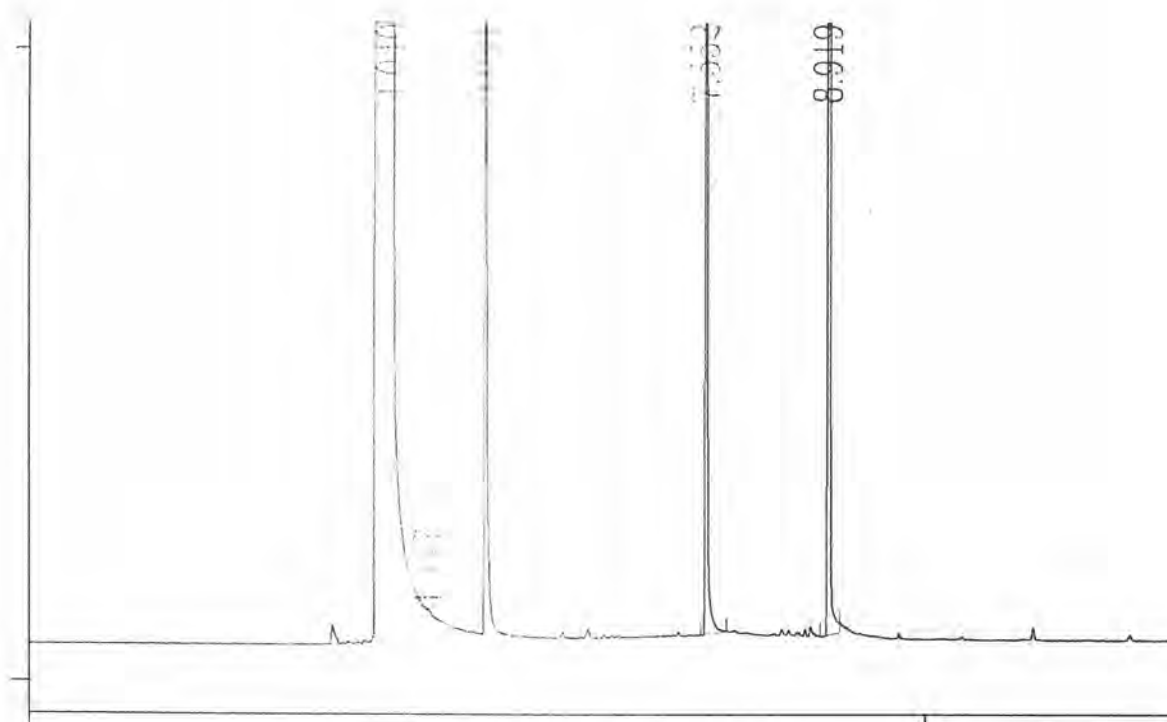


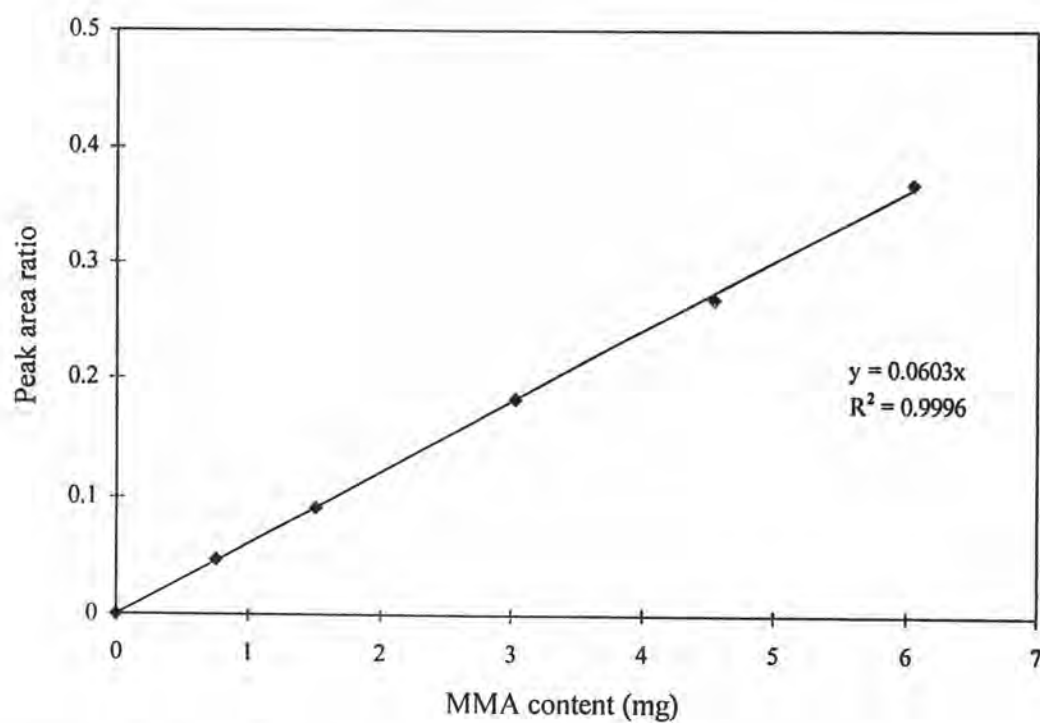**Figure 3.7** A typical GC chromatogram of the mixed standard solution of styrene and MMA.

**Figure 3.8** The calibration curve for determination of residual MMA in styrene/MMA copolymer.
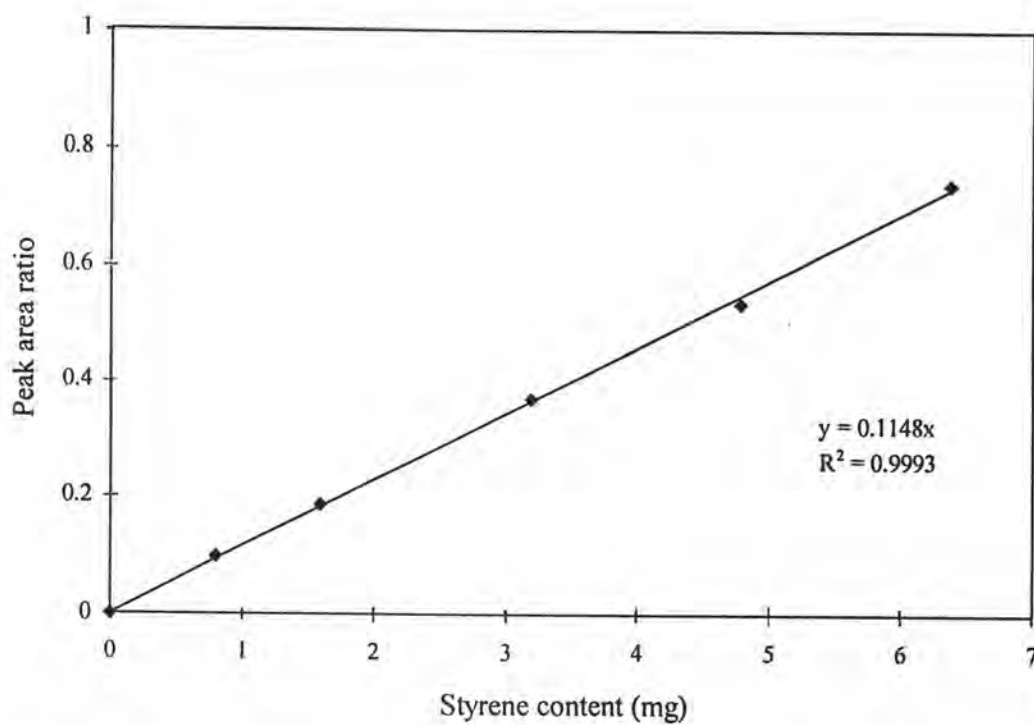


**Figure 3.9** The calibration curve for determination of residual styrene in styrene/MMA copolymer.