CHAPTER IV

EXPERIMENT

4.1 Materials

4.1.1 Polystyrene (PS)

Polystyrene used in this work was provided by Dow Chemical Company under the trade name of "STYRON 685D". It is a general-purpose polystyrene resin designed for both injection molding and extrusion applications. The average molecular weight of polystyrene is 300,000. Polystyrene in pellet form is transparent. The structure of polystyrene is shown in Figure 4-1.
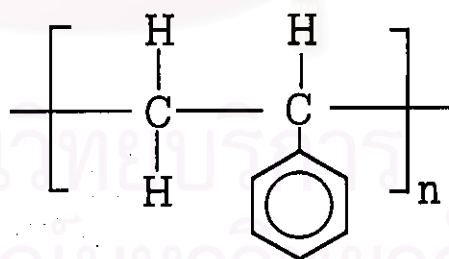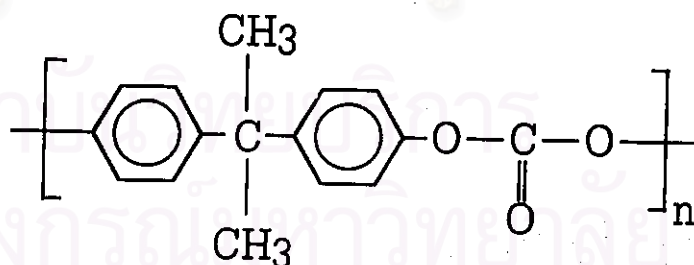

Figure 4-1 The structure of polystyrene

Normally, the glass transition temperature (T_g) of PS can be in the vicinity of 100°C (Charrier, 1991). When examined the PS as recieved from the manufacturer, the glass transition of the PS is about 107.35°C. However, the T_g of normal PS can vary depending on the method of preparation of the sample, the

thermal history of the sample and the method of measurement. This variance can be as great as 10-20°C (Kroschwitz, 1990).

In this study, the blends were prepared by solvent casting method and annealed at various temperatures. To measure the T_g of the pure PS at the experimental condition, the pure PS (Styron 685D) were prepared and annealed at various annealed temperatures in the same way as the blends. The T_g of pure PS (Styron 685D), at the experimental condition (detected by DSC), is approximately at 80°C.

4.1.2 Poly(bisphenol A carbonate) (PC)

Poly(bisphenol A carbonate) from Aldrich Chemical Company, Inc. is the other polymer used in this work. The average molecular weight of poly (bisphenol A carbonate) is 64,000. It is transparent pellet. The structure of poly (bisphenol A carbonate) is shown in Figure 4-2.

Figure 4-2 The structure of poly(bisphenol A carbonate)

The glass transition temperature (T_g) of PC is approximately at 150°C and the melting temperature (T_m) of PC is approximately at 230°C [Charrier, 1991]. The T_g of PC, used in this work, is at 150.85°C as detected by DSC. This is

sufficiently close to the T_g of PC reported above. The T_m of PC cannot be clearly detected. The pure PC, prepared in the same way as the blends, exhibits the T_g at 145°C regardless of the various annealed temperatures used (detected by DSC). The T_g detected is not much different from the above report. The T_m of pure PC, prepared by the same method as the blends, cannot be clearly detected.

4.1.3 Liquid Crystal

Low molar mass thermotropic liquid crystals were used in this work. They were manufactured by Merck under the trade name of "LICRISTAL". Two low molar mass thermotropic liquid crystals in phenyl-cyclohexylbenzoates group were chosen. Each one is used to blend with polystyrene and poly(bisphenol A carbonate), respectively.

4.1.3.1 HP35

HP35 is in the form of a white powder as recieved. Its properties are shown in Table 4-1 and its structure is shown in Figure 4-3.
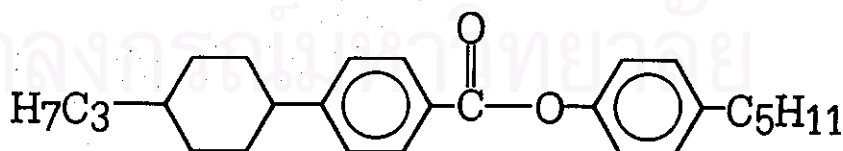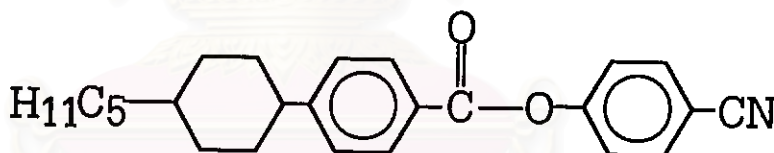

Figure 4-3 The structure of HP35

Table 4-1 Properties of HP35

Melting point	80.0 $^{\circ}$C
S $\rightarrow$ N transition temperature	87.0 $^{\circ}$C
Clearing point	176.0 $^{\circ}$C
Melting enthalpy	25.1 kJ/mol
Molecular mass	392.59 g/mol

4.1.3.2 HP5N

HP5N is in the form of a white flake as recieved. Its properties are shown in Table 4-2 and its structure is shown in Figure 4-4.

Figure 4-4 The structure of HP5N

Table 4-2 Properties of HP5N

Melting point	111.0 $^{\circ}$C
Clearing point	226.0 $^{\circ}$C
Melting enthalpy	21.4 kJ/mol
Molecular mass	375.52 g/mol

4.2 Equipment

4.2.1 Digital Hot Plate Stirrer

The Cole-Parmer hot plate/stirrer 04644 series model no. 731-2C-P which is a programmable, digital laboratory hot plate with stirrer was used for preparing the samples. All functions are settable from a digital front panel keyboard and display. Both the plate temperature and the stirrer speed are controllable.

4.2.2 Vacuum Oven & Pump

The Cole-Parmer vacuum oven model 5053-12 which has the temperature range from slightly above ambient to $220^{\circ}C$ with 0.7 cubic feet chamber was used for preparing the samples. It can be vacuummed down to -30 inch Hg.

The vacuum oven is quipped with Gast Manufacturing Corp. rotary vacuum pump model no. 0523-V4-621DX.

4.2.3 Differential Scanning Calorimeter (DSC)

The glass transition temperature (T_g) and the melting temperature (T_m) of samples were determined by using a differential scanning calorimeter (DSC).

DSC is a thermal analysis technique that measures heat flow into or out of a sample and a reference as a function of time or temperature. Figure 4-5 shows a schematic representation of DSC. A Dupont DSC model 2910 was used in this works.

In the experiment, 5-10 mg of the sample was placed in open aluminium pan. The heating rate was set at 10°C/min. The temperature reading was calibrated with indium (m.p. 156.3°C). The obtained data were collected by computer connected to the DSC for further interpretation.
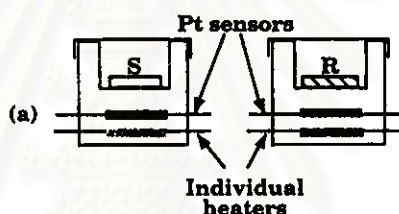
Figure 4-5 Schematic representation of DSC. S and R denote sample and reference, respectively [Gedde,1995].

4.2.4 Scanning Electron Microscope (SEM)

The morphology observed by scanning electron microscope (SEM) was used to confirm the phase behaviour of the blends determined by DSC results at some annealed temperatures and compositions.

Scanning electron microscope (SEM) uses the technique of a focus electron beam to scan the sample surface [Woodward, 1995]. The polymer specimen to be examined by SEM was first coated with a thin layer of gold to provide a conductive layer. The morphology of the blends was studied by using

a scanning electron microscope (JOEL JSM 5400). The accelerating voltage for the SEM was 15 KV.

4.3 Sample Preparation Procedure

The following four blend systems were studied:

SYSTEM I: Polystyrene & HP35.

SYSTEM II: Polystyrene & HP5N

SYSTEM III: Poly(bisphenol A carbonate) & HP35

SYSTEM IV: Poly(bisphenol A carbonate) & HP5N

Each blend was prepared as follows:

The blend components were weighed in a sample bottle in the appropriate amounts corresponding to the desired blend compositions. The amount of 3 ml of toluene for PS blends or the amount of 3 ml of methylene chloride for PC blends were added to the corresponding blend. The mixture was stirred at about 200rpm using the digital hot plate/stirrer at room temperature for about 30 minutes until the liquid crystal and polymer were dissolved completely. The resulting solution was casted into a thin film by dropping with a dropper onto a teflon sheet to be the size of DSC pan. In general, about 50 samples were made. Each sample was about 0.1 ml in volume. The solvent was allowed to evaporate in fume cupboard overnight at room temperature. After that, the samples on the teflon sheet were dried in vacuum oven at a temperature about 45°C and at -30

inch Hg for at least 3 day. These dried thin layer film samples were then used in the transition temperature measurements.

The steps involved in sample preparation were schematically shown in Figure 4-6.

4.4 Method of Measuring Transition Temperature

4.4.1 Erasure of Sample Thermal History

Polymer can remember its thermal history which can affect its transition temperature, especially the glass transition temperature (T_g). So it is necessary to erase this thermal history, or in the other word, to prepare samples that have the same thermal history before measuring its transition temperatures.

There are two methods that are usually used to erase polymer thermal history. The first method is to dissolve the blend in suitable solvent. The second method is to melt the blend at suitable time and temperature.

In this work, melting method was chosen to erase thermal history of all samples. The temperature and time used to erase polymer thermal history in this · work came from the previous experimental works [Flynn, 1974; Richardson and Savill, 1975; Peyser and Bascom, 1977; cited in Brandrup and Immergut, 1989]. Typically the melt temperature for melting should be higher than T_g of polymer. And the sample should be left at the melt temperature for sufficient time such that the sample is melted totally but without degradation of polymer. For PS

Sample Preparation Procedure

Dissolved the blend components in the solvent

⇓

Dropped onto a the teflon sheet

⇓

Allow the solvent to evaporate in fume cupboard overnight

⇓

Dry in vacuum oven

⇓

Thin layer film sample

Figure 4-6 Schematic diagram of sample preparation procedure.

blend, open DSC sample pan with sample films (5-10 mg) was put on digital hot plate/stirrer at $120^{\circ}C$ for 2 min without stirring. Then, the melted sample is quenched into solid in the beaker surrounded by dry ice (solid carbondioxide) to cool the sample down as fast as possible. For PC blend, the same procedure was followed but the temperature of the hot plate/stirrer was set at $180^{\circ}C$ for 1 min instead.

4.4.2 Sample Annealing

The samples that have already been erased thermal history (as obtained from section 4.4.1) were instantly annealed. Annealing process took place in DSC. Sample in DSC sample pan was kept in DSC cell at the prescribed annealing temperature for 6 minutes. Annealing time used in this study was deduced from the trial experiments done in this work. By comparing the transition temperatures of the samples at various annealing times, i.e. 6, 10, 15, 30 minutes, it was observed that the difference in transition temperatures was less than 1.5 % from one another. So, the annealing time of 6 minutes was used in actual experiments.

4.4.3 Sample Quenching

Quenching is the process that cools sample as fast as possible from annealing temperature down to room temperature. Quenching can preserve the sample morphology obtained at each annealing temperature. In this experiment, the process of quenching was immediately done after annealing process in DSC. The DSC cell was covered with cooling can containing dry ice until the

temperature was cooled down to about 20°C. Cooling rate was about 50 - 60 $^{\circ}$C/min.

4.4.4 Sample Scanning

Samples that have been prepared by the three steps described above were then scanned at the heating rate of 10°C/min in DSC starting from 20°C and ending at 150°C for PS blend and 230°C for PC blend. The DSC thermogram which is a plot of heat flow versus temperature was analysed by the method described in section 4.4.5.

The step involved in transition temperature measurement were shown schematically in Figure 4-7.

4.4.5 Determination of Transition Temperatures

4.4.5.1 Glass Transition Temperature (T_g)

The glass transition temperature (T_g) is an important factor in the mechanical behaviour of polymer. It is usually determined to be either the inflection point of the T_g curve or the extrapolated onset temperature [Fava, 1980], as shown in Figure 4-8. There is no general agreement on which is the correct method.

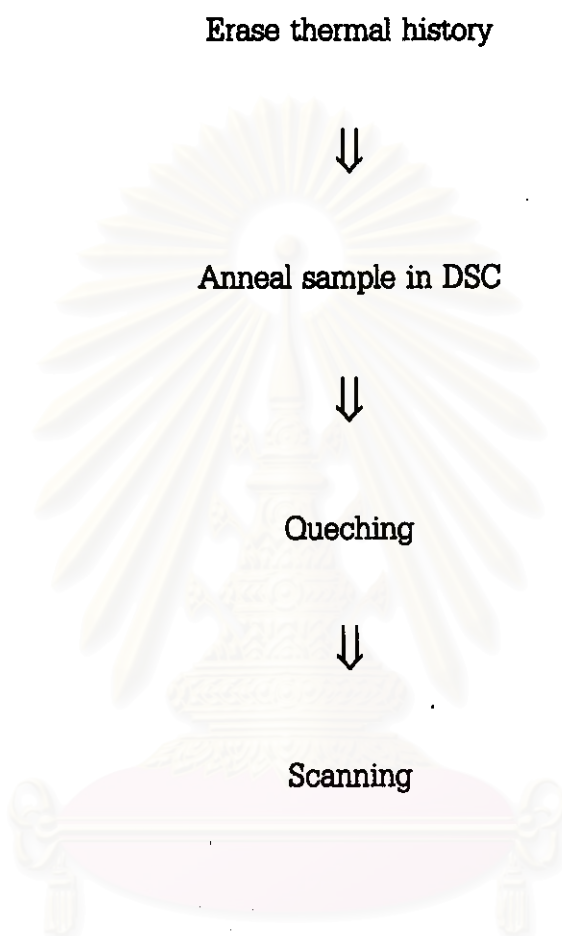**Method of Measuring Transition Temperature**

Erase thermal history

⇓

Anneal sample in DSC

⇓

Queching

⇓

Scanning

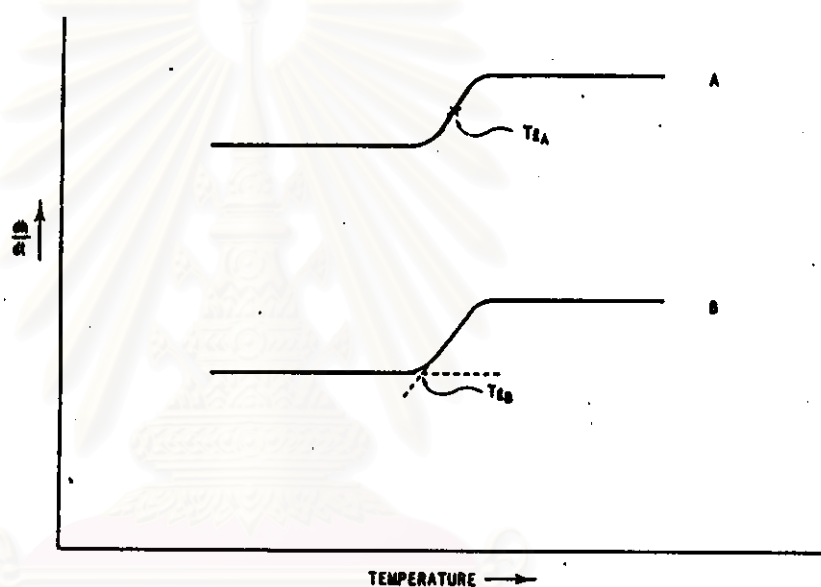**Figure 4-7** Schematic diagram of method of measuring transition temperature.

Figure 4-8 Two manners in which the glass transition temperature has been
defined. A) the glass transition temperature is taken to be the
inflection point of the curve (T_{gA}); B) T_g is chosen to be the
extrapolated onset temperature (T_{gB}) [Fava, 1980].

In this work, the glass transition temperature is taken to be the inflection point of the curve. An example of T_g determination is shown in Figure 4-9 which illustrated the DSC thermogram of PS film annealed at 80°C. The T_g of PS determined from the inflection point of the curve is 81.72°C.

4.4.5.2 Melting Temperature (T_m)

Melting temperature (T_m) is the temperature at which the polymer changes from a solid phase to a liquid phase. The melting temperature (T_m) is usually defined to be the temperature at the endothermic maximum peak in the DSC thermogram and the mesophasic transition temperatures of HP35 and HP5N are usually defined to be the temperatures at the endothermic maximum peak. An example of the mesophasic transition temperature determination at the maximum peak is shown in Figure 4-10 which illustrated the DSC thermogram of HP35 exhibits a S→N transition temperature ($T_{S\to N}$) at 86.83°C and a clearing point at 173.75°C.
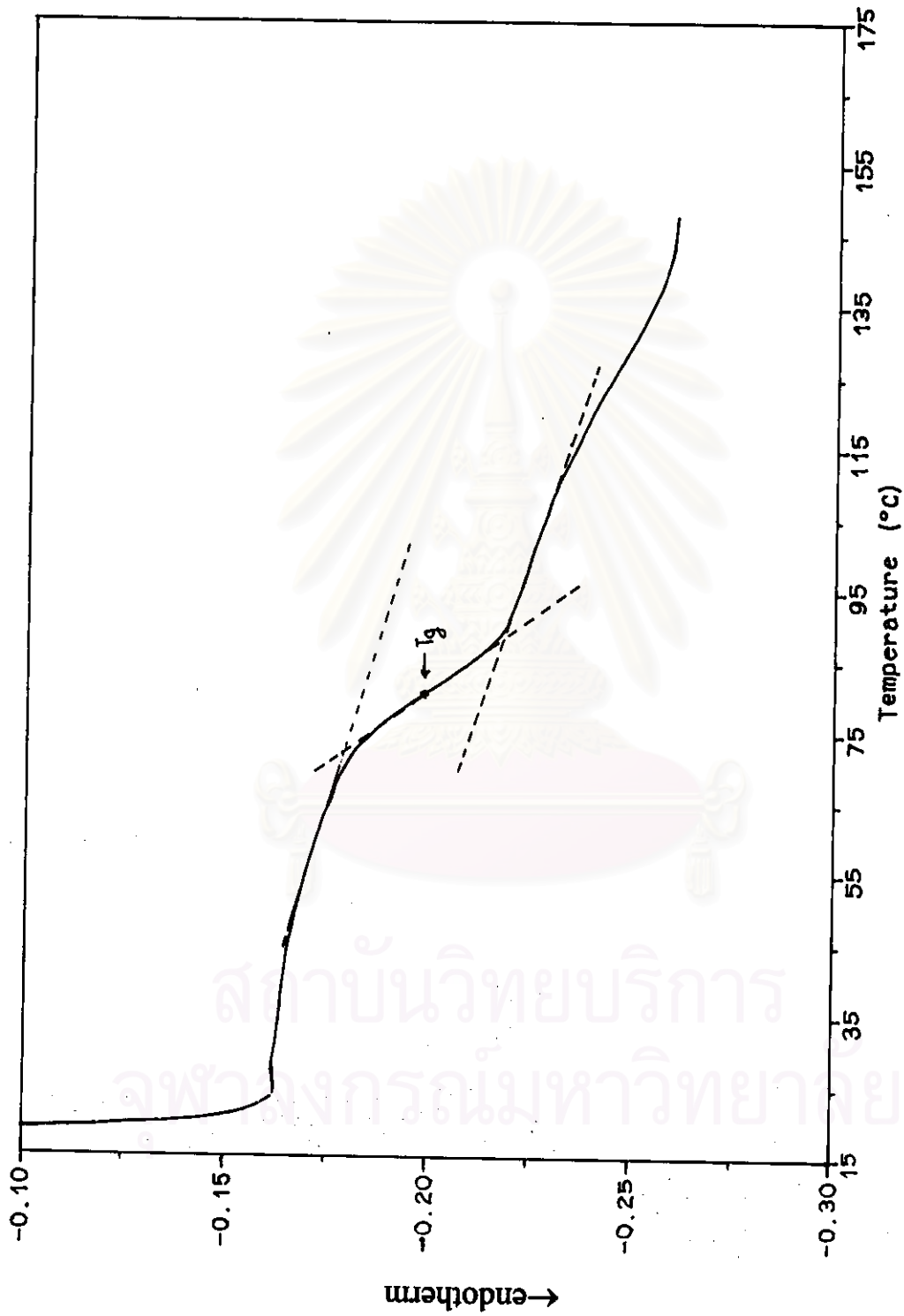
Figure 4-9 An example of the glass transition temperature of (T_g) of PS film, which annealed at 80°C, determind at inflection of the curve.
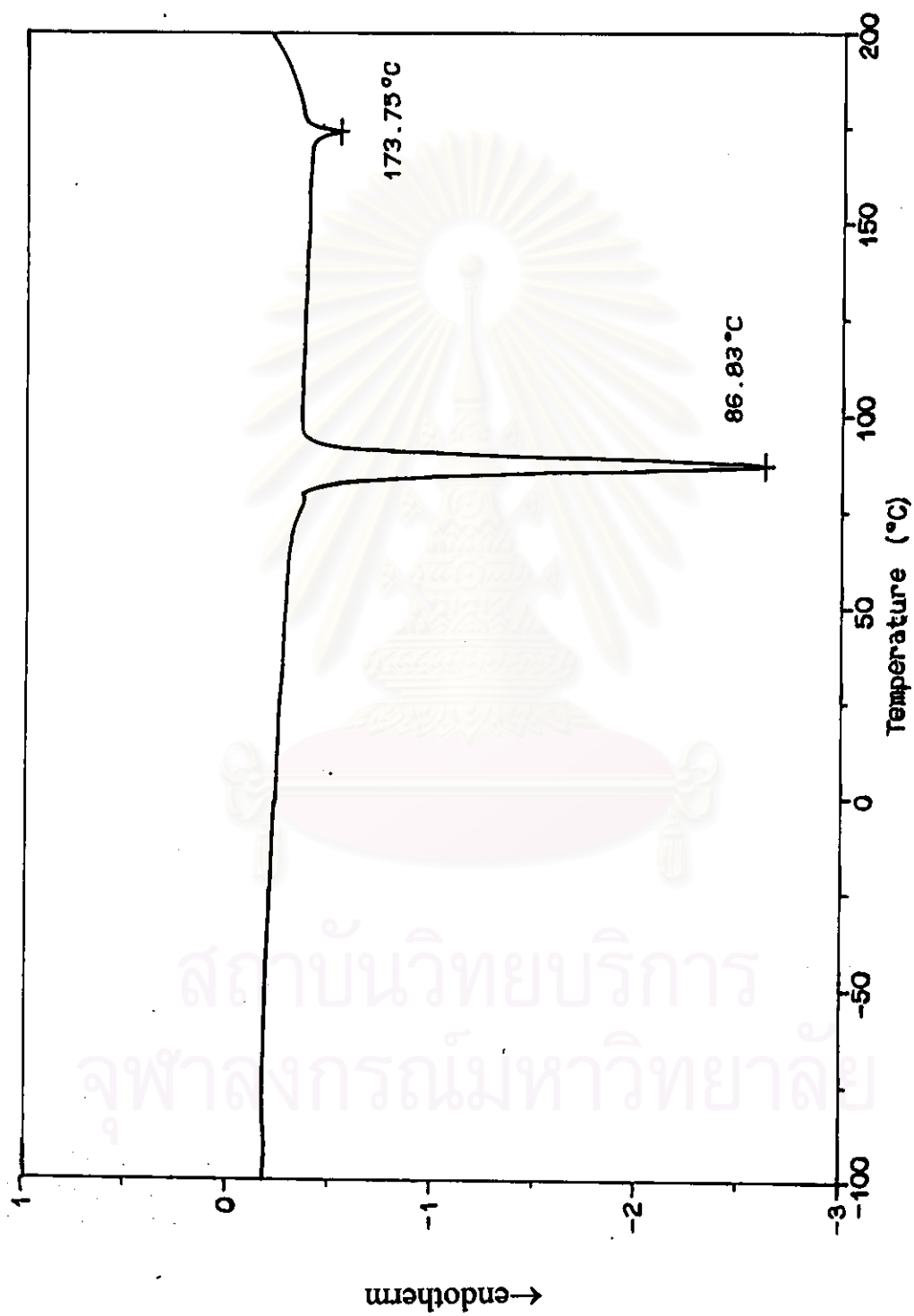
Figure 4-10 An example of the mesophasic transition temperature of HP35 determined at the maximum peak.

4.5 Method of Observation of Blend Morphology

In this study, phase behaviour determined by DSC results was confirmed by SEM technique.

The samples to be observed for blend morphology by SEM were prepared in the same way as described in sections 4.4.1-4.4.3. Firstly, the thermal history of the sample obtained from section 4.3 was erased. Then, the sample was annealed in DSC at the chosen temperature for 6 minutes. Finally, the sample was quenched with dry ice as fast as possible to preserve the morphology. After these three steps, the sample film was coated with gold prior to the observation of blend morphology by SEM.