CHAPTER V

RESULTS & DISCUSSIONS

Materials chosen in this work are two low molar mass liquid crystal in phenyl-cyclohexylbenzoates group : HP35 and HP5N, and two polymers, namely polystyrene (PS) and poly(bisphenol A carbonate) (PC). Blends of polymers with low molar mass liquid crystals can be divided into 4 systems as follows:

SYSTEM I : Polystyrene & HP35

SYSTEM II: Polystyrene & HP5N

SYSTEM III: Poly(bisphenol A carbonate) & HP35

SYSTEM IV: Poly(bisphenol A carbonate) & HP5N

The results of the four systems were presented in this chapter. DSC thermograms were carefully analysed to get transition temperatures of the blends, i.e. glass transition temperature (T_g), melting temperature (T_m), and mesophasic transition temperature. The phase diagrams of four systems were constructed by observing the changing of transition temperatures of the blends. Scanning electron microscope (SEM) pictures were used to confirm the phase behaviour in the constructed phase diagram.

5.1 Determination of Experimental Procedure

In this study, the method of solvent casting was used to prepare the film blends. Pure PS and PC were also prepared in the same way and examined at the same various annealed temperatures as studied for the blends. The T_g-s of pure PS and PC prepared from the same procedure were used to compare with the T_g-s of PS rich phase and PC rich phase in the blends.

The examples of transition temperatures as determined according to the procedure given in section 4.4.5 of the four systems: PS blended with HP35 (system I), PS blended with HP5N (system II), PC blended with HP35 (system III), PC blended with HP5N (system IV), were shown in Table 5-1,2,3,4 respectively. It can be seen from each table that data obtained for each system from different trials are reproducible and in good agreement with one another. Therefore, the experimental procedure in chapter IV is suitable for preparing the blends and measuring the transition temperatures.

Table 5.1 Transition temperatures of 25% by weight of HP35 with PS, which annealed at 87°C, at the first and the second trials.

Trial No.	T_g of PS rich phase in blends ($^\circ$C)	T_m of HP35 rich phase in blends ($^\circ$C)	Transition temp. (S→N) of HP35 rich phase in blends ($^\circ$C)
1	56.9	80.5	86.8
2	56.6	80.6	87.0

Table 5.2 Transition temperatures of 15% by weight of HP5N with PS, which annealed at 120°C, at the first and the second trials.

Trial No.	T_g of PS rich phase in blends (°C)	T_m of HP5N rich phase in blends (°C)
1	60.0	108.7
2	62.1	110.0

Table 5.3 Transition temperatures of 20% by weight of HP35 with PC, which annealed at 120°C, at the first and the second trials.

Trial No.	T_g of PC rich phase in blends(°C)	T_m of HP35 rich phase in blends (°C)	Transition temp. (S→N) of HP35 rich phase in blends (°C)	T_m of PC rich phase in blends (°C)
1	112.1	80.9	86.0	212.6
2	114.6	81.2	87.1	212.9

Table 5.4 Transition temperatures of 30% by weight of HP5N with PC, which annealed at 100°C, at the first and the second trials.

Trial No.	T_g of PC rich phase in blends (°C)	T_m of HP5N rich phase in blends (°C)	T_m of PC rich phase in blends (°C)
1	82.3	111.3	205.1
2	81.1	111.5	204.2

5.2 Phase Diagram Construction Procedure

The measuring of glass transition temperatures (T_g) of a polymer blend is the most commonly used method for determining its miscibility [Oiarzabal, 1993]. It is clear that a miscible system will show the characteristic of a single phase. Hence, a single T_g, intermediate of the components' T_g can be expected for a miscible blend. In case of partial miscibility, two transitions that shift closer to each other occur. The immiscible systems will show two separate transitions with little change from the transition temperatures of its pure components. This method, however, can be used to study polymer miscibility as long as the two T_g-s are at least $20^\circ C$ different [Oiarzabal, 1993].

Due to the fact that the glass transition temperatures (T_g) of the low molar mass liquid crystal used in this study cannot be observed even starting DSC scan at $-150^\circ C$. Only T_g of the high molecular weight polymer part in the blends can be detected. So the most commonly used method for determining polymer miscibility by measuring the two T_g-s of the blend cannot be used in this study.

From the above reasons, it is necessary to look for a suitable method for determining miscibility of the blends. There are two works that studied the miscibility of the blends of which only the T_g of the high molecular weight polymer part in the blends can be detected. The first one was done by Huh, W. and Weiss, R. A. in 1983. In this work, two pair blends of polystyrene and two low molar mass liquid crystal which are terephthal-bis-4-n-butylaniline (TBBA) and N-(p-ethoxybenzylidine)-p-n-butyl-aniline (EBBA) were studied. The second work was done by Patwardhan, A. A. and Belflore, L. A. in 1988. This work also studied two pair blends which are poly(ethylene glycol)/p-hexyloxybenzoic acid and bisphenol-A polycarbonate/p-pentyloxycinnamic acid. It was suggested in

both works that if the T_g of the high molecular weight polymer rich phase in the blend drops down from pure polymer T_g and the depression is related to weight percent of low molar mass liquid crystal, i.e. increasing weight percent of low molar mass liquid crystal lowers the T_g of the high molecular weight polymer rich phase from pure polymer T_g, hence, the blend is miscible in that concentration range.

The miscibility of the blends studied in this work can be determined by using the method of depression trend that was modified by the author from the criteria of the method described in the two mentioned works. The detail of this method are described belows:

The Method of Depression Trend:

1. Plot the graph between the T_g of polymer rich phase in the blend versus the weight percent of low molar mass liquid crytstal in the blend at each annealed temperature.

2. Divide the blend miscibility into two regions based on the following criteria:

2.1 Partially Miscible Regions (o)

If the T_g of the polymer rich phase in the blend drops when the weight percent of low molar mass liquid crystal is increased, the blend between that weight percent interval is considered to be a partially miscible region and is represented by symbol "o".

2.2 Immiscible region (*)

If the T_g of the polymer rich phase in the blend stays relatively constant or increases when the weight percent of low molar mass liquid crystal is increased, the blennd between that weight percent interval is considered to be an immiscible region and is represented by symbol "*".

Table 5-10 is the example of the different regions of the blend miscibility as determined based on the above criteria.

3. Plot the graph between the annealed temperature and the weight percent of low molar mass liquid crystal. Next, specify the region of blend miscibility as obtained from step 2 into the graph (i.e. put down symbol "o" and "*" into the graph at the appropriate annealed temperature and interval of weight percent of low molar mass liquid crytsal). Hence, the phase diagram of the blend is obtained.

The Gradient Method:

To create more detail phase diagram, the new method for constructing the phase diagram was developed by the author. The newly created criteria of four regions in phase diagram are specified as the following:

Region AP : absolutely partially miscible region (o)

Region PP : possibly partially miscible region (+)

Region PI : possibly immiscible region (-)

Region AI : absolutely immiscible region (*)

This method is called the gradient method. Based on the same criteria presented above, the miscibility determination was done by considering the decreasing of the T_g of the high molecular weight polymer rich phase in the blend. But the slope (or gradient value) of the T_g versus weight percent of liquid crystal was calculated. Then, the phase diagram can be divided into different regions from these gradient values.

The gradient method is demonstrated by using it to construct the phase diagram of system I: PS & HP35.

The steps involved are as follows:

1. List the T_g-s of the blends detected by differential scanning calorimetry in table as shown in Table 5-5.

2. The slopes (or gradient values) of T_g versus weight percent of liquid crytsal are calculated at each weight percent interval and annealed temperature. The gradient value is calculated as follow:

$$\text{gradient value} = \frac{\text{difference between } T_g \text{ of the blends at adjacent composition}}{\text{difference between \%composition at adjacent composition}}$$

example:

$$\text{gradient value (at } 48^\circ\text{C, 5.0-7.2\%composition)} = \frac{72.8 - 71.5}{5.0 - 7.2}$$
$$= -0.591$$

An example of calculated gradient values were shown in Table 5-6.

3. The gradient values obtained are then used to divide the blend miscibility into 4 different regions based on the criteria given in Table 5-7.

Table 5-8 is an example of different regions of blend miscibility (or phase behaviour) as obtained from gradient values in Table 5-6 and criteria in Table 5-7.

4. Plot the graph between the annealed temperature and the weight percent of low molar mass liquid crystal. Next, specify the region of blend miscibility as obtained from step 3 (i.e. put down symbol "o", "+", "-", "*" into the graph at the appropriate annealed tempearture and interval of weight percent of low molar mass liquid crystal). Hence, the phase diagram of the blend is obtained.

Figure 5-2 is the example of phase diagram as obtained by the gradient method.

Table 5-5 The glass transition temperatures (T_g) of PS rich phase in the blends of HP35 and PS detected by differential scanning calorimeter (DSC) at each annealed temperature and weight percent HP35 with PS.

Annealed temp.($^{\circ}$C) / Weight percent HP35	48	54	65	80	87	100	120
5.0	72.8	71.2	71.6	72.1	70.0	71.8	82.4
7.2	71.5	64.4	65.4	66.6	66.8	69.6	81.0
10.2	64.8	60.6	61.1	63.2	63.2	65.4	73.4
12.7	55.8	56.5	59.6	59.2	59.2	61.9	66.8
15.2	70.7	55.7	67.5	60.0	57.5	55.5	63.2
19.8	65.7	55.6	63.2	56.4	56.2	53.5	53.6
25.0	67.7	57.4	66.8	57.6	56.9	55.8	55.6

Table 5-6 Gradient value calculated from data in Table 5-5.

Annealed temp.($^{\circ}$C) / Weight percent HP35	48	54	65	80	87	100	120
5.0-7.2	-0.591	-3.545	-2.818	-2.500	-1.455	-1.000	-0.636
7.2-10.2	-2.233	-1.267	-1.433	-1.133	-1.200	-1.400	-2.533
10.2-12.7	-3.600	-1.640	-0.600	-1.600	-1.600	-1.400	-2.640
12.7-15.2	5.960	-0.320	3.160	0.320	-0.680	-2.560	-1.440
15.2-19.8	-1.087	-0.022	-0.935	-0.738	-0.283	-0.435	-2.087
19.8-25.0	0.385	0.346	0.692	0.231	0.135	0.442	0.385

Table 5-7 The criteria used for determining the phase behaviour of the blends from the gradient value and the symbol of each region.

Phase behaviour	Gradient value (tanθ)	θ (degree)	Represented Symbols
Absolutely partially miscible	Less than -1.000	$\theta < -45°$	O
Possibly partially miscible	Between -0.500 to -1.000	$-26.57° > \theta > -45°$	+
Possibly immiscible	More than -0.500 and less than +1.000	$45° > \theta > -26.57°$	-
Absolutely immiscible	More than +1.000	$\theta > 45°$	*

weight percent low molar mass liquid crystals
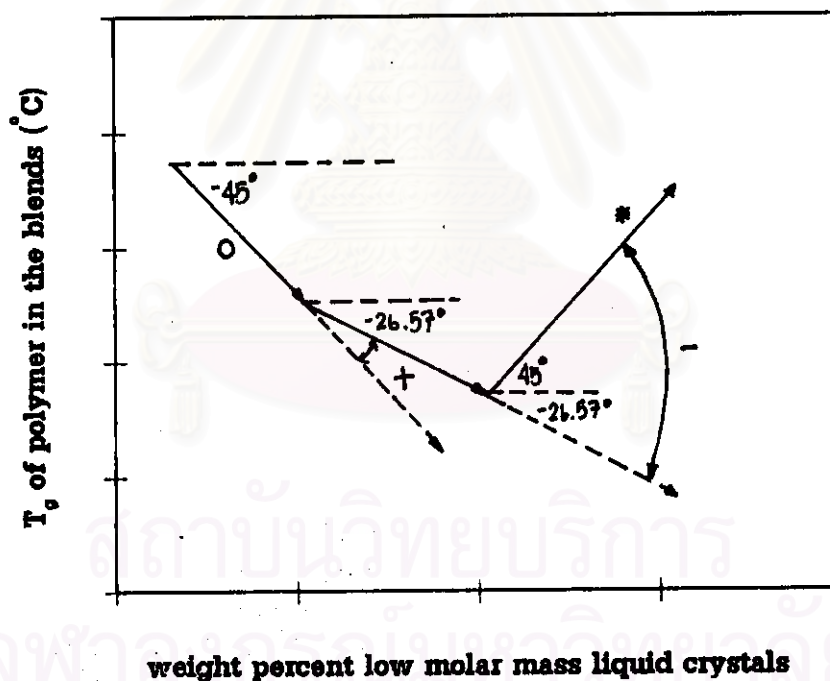
Figure 5-1 Schematic diagram that represented the angle (θ) of miscibility. O represented absolutely partially miscible region. + represented possibly partially miscible region. - represented possibly immiscible region. * represented absolutely immiscible region.

Table 5-8 Four regions divided from the gradient value of system I: PS & HP35. o represents absolutely partially misible region, + represents possibly partially misible region, - represents possibly immiscible region and * represents absolutely immiscible region.

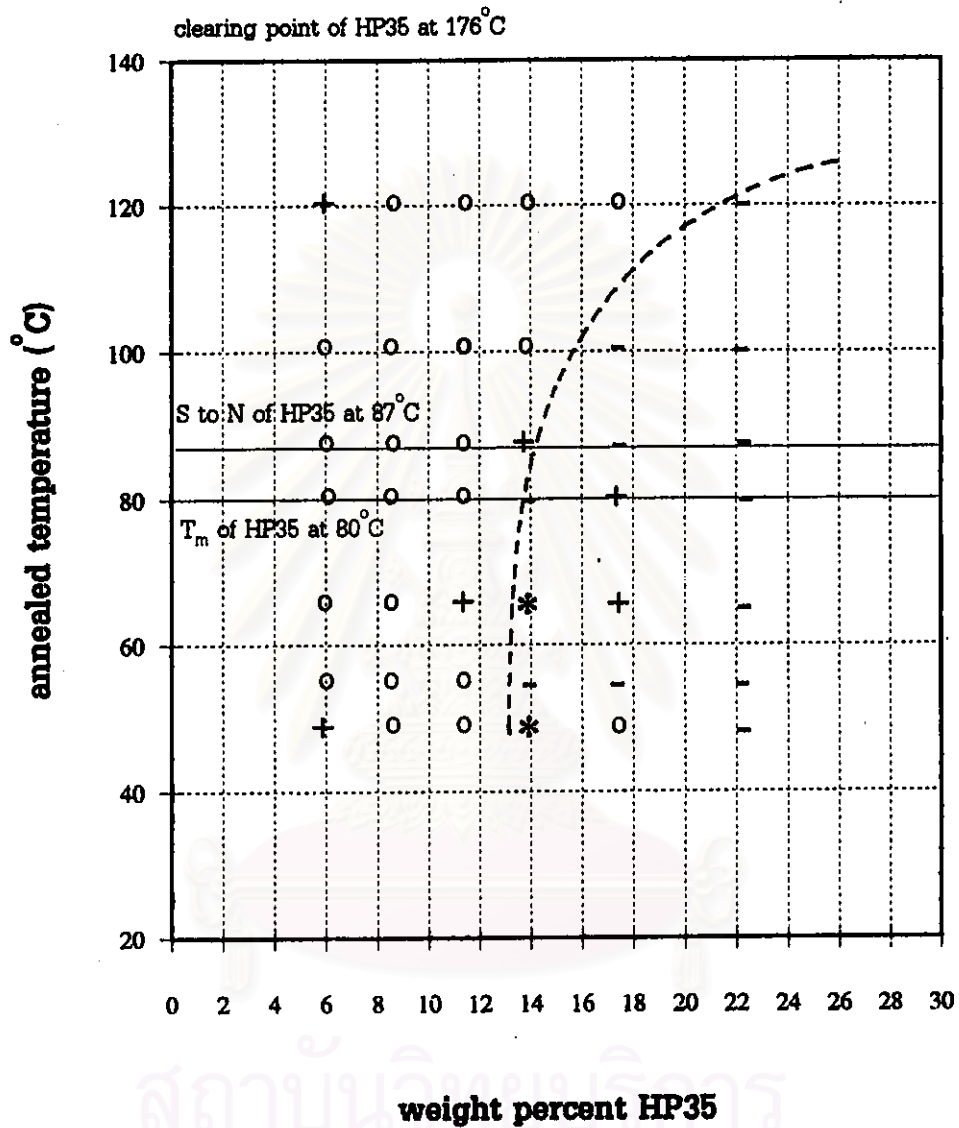| Annealed temp(°C) / Weight percent HP35	48	54	65	80	87	100	120
5.0-7.2	-0.591 +	-3.545 o	-2.818 o	-2.500 o	-1.455 o	-1.000 o	-0.636 +
7.2-10.2	-2.233 o	-1.267 o	-1.433 o	-1.133 o	-1.200 o	-1.400 o	-2.533 o
10.2-12.7	-3.600 o	-1.640 o	-0.600 +	-1.600 o	-1.600 o	-1.400 o	-2.640 o
12.7-15.2	5.960 *	-0.320 -	3.160 *	0.320 -	-0.680 +	-2.560 o	-1.440 o
15.2-19.8	-1.087 o	-0.022 -	-0.935 +	-0.783 +	-0.283 -	-0.435 -	-2.087 o
19.8-25.0	0.385 -	0.346 -	0.692 -	0.231 -	0.135 -	0.442 -	0.385 -

Figure 5-2 Phase diagram at low concentration of system I: PS and HP35 constructed
by gradient method. O represents absolutely partially miscible region. +
represents possibly partially miscible region. − represents possibly
immiscible region. * represents absolutely immiscible region and --------
represents phase separation line.

The interval of gradient value shown in Table 5-7 for each miscibility region came from carefully monitoring the gradient obtained from the experiments. Minus sign of gradient value indicates that the T_g decreases from the T_g at the adjacent lower weight percent of the low molar mass liquid crystal. From the empirical studies, it can be suggested that gradient value of less than -1.000 indicates that the T_g-s clearly drops down. Plus sign of gradient value indicates that the T_g increases from the T_g at the adjacent lower weight percent of the low molar mass liquid crystal. From the empirical studies, it can be suggested that gradient value of more than +1.000 indicates that the T_g evidently increases.

Thus, the absolutely partially miscible region (o) is designated as the region where the gradient value is less than -1.000 and the absolutely immiscible region (*) is designated as the region where the gradient value is greater than +1.000.

Based on the same general concept above, the possibly partially miscible region (+) is then designated as the region where the gradient value is between -0.500 to -1.000. This depression is less than the absolutely partially miscible region.

The possibly immiscible region (-) is then designated as the region where the gradient value is between -0.500 and +1.000.

The gradient method can provide more detail about the blend miscibility than the method of depression trend. This can be seen from two more regions obtained in the gradient method, i.e. possibly partially miscible region (+) and

possibly immiscible region (-). These two regions are classified as gray area. The gray area means that the gradient value in both regions cannot clearly separate the condition of miscibility in the blends to be either absolutely partially miscible or absolutely immiscible. These gray areas cannot be determined by the method of depression trend. Hence, this is an advantage of the gradient method. Another advantage is that the phase diagram can be constructed using mathematical method and with the utilization of computer.

However, the phase diagram constructed by the method of depression trend can be determined from the direct observation of the experimental results. No calculation is needed. Hence, the advantage of the method of depression trend is that the construction of phase diagram can be done more easily and faster than the gradient method.

Both method of depression trend and gradient method presented above were applied to construct the phase diagrams of all systems studied in this work.

5.3 SYSTEM I : Polystyrene & HP35

The phase diagram of system I: PS & HP35 was constructed only at low concentration range of HP35. The blends at 5.0, 7.2, 10.2, 12.7, 15.2, 19.8 and 25.0 percent by weight of HP35 with PS were prepared by the method described in section 4.3. The phase behaviour at various annealed temperatures, i.e. at temperatures lower than T_m of HP35: $48.0^\circ C$, $54.0^\circ C$ and $65^\circ C$, at T_m of HP35: 80 $^\circ C$, at $T_{S \rightarrow N}$ of HP35: $87^\circ C$, and at temperatures higher than T_g of pure PS: $100^\circ C$ and $120^\circ C$, was studied. Phase behaviour was studied by measuring the transition temperatures of the samples with differential scanning calorimeter (DSC).

The transition temperatures of the blends detected by differential scanning calorimeter (DSC) were shown in Table 5-9 and examples of DSC thermograms of 10 percent by weight of HP35 with PS,which annealed at $80^\circ C$, and 20 percent by weight of HP35 with PS, which annealed at $100^\circ C$, were shown in Figure 5-3.

5.3.1 Effects of HP35 on Polystyrene (PS)

From Table 5-9, it can be seen that the glass transition temperatures (T_g) of PS rich phase in the blends at each weight percent of HP35 and annealed temperature used in the experiment were depressed from the T_g of 100% PS (0 percent by weight of HP35 with PS). This phenomenon proved that HP35 can act as a plasticizer of PS.

Table 5-9 Transition temperatures detected by differential scanning calorimeter (DSC) of system I : PS & HP35.

Annealed temp. ($^\circ$C)	% by weight HP35	T_g of PS rich phase in blends ($^\circ$C)	T_m of HP35 rich phase in blends ($^\circ$C)	Transition temp. (S→N) of HP35 rich phase in blends ($^\circ$C)
48	0.0(100% PS)	81.7	-	-
	5.0	72.8	-	-
	7.2	71.5	-	-
	10.2	64.8	-	-
	12.7	55.8	82.3	86.2
	15.2	70.7	-	83.3
	19.8	65.7	-	85.5
	25.0	67.7	82.7	86.9
54	0.0(100% PS)	81.8	-	-
	5.0	71.2	-	-
	7.2	64.4	-	-
	10.2	60.6	-	-
	12.7	56.5	82.3	86.2
	15.2	55.7	81.0	86.2
	19.8	55.6	80.9	86.2
	25.0	57.4	82.0	86.6
65	0.0(100% PS)	79.0	-	-
	5.0	71.6	-	-
	7.2	65.4	-	-

Table 5-9 Transition temperatures detected by differential scanning calorimeter (DSC) of system I : PS & HP35. (continued)

Annealed temp. ($^{\circ}$C)	% by weight HP35	T_g of PS rich phase in blends ($^{\circ}$C)	T_m of HP35 rich phase in blends ($^{\circ}$C)	Transition temp. (S→N) of HP35 rich phase in blends ($^{\circ}$C)
65	10.2	61.1	-	-
	12.7	59.6	82.1	86.2
	15.2	67.5	82.5	86.3
	19.8	63.2	81.3	86.9
	25.0	66.8	81.3	86.7
80	0.0(100% PS)	81.7	-	-
	5.0	72.1	-	-
	7.2	66.6	-	-
	10.2	63.2	-	-
	12.7	59.2	-	85.8
	15.2	60.0	82.8	86.3
	19.8	56.4	82.7	86.6
	25.0	57.6	82.8	87.0
87	0.0(100% PS)	82.1	-	-
	5.0	70.0	-	-
	7.2	66.8	-	-
	10.2	63.2	-	-
	12.7	59.2	82.1	86.5
	15.2	57.5	82.7	87.3

Table 5-9 Transition temperatures detected by differential scanning calorimeter (DSC) of system I : PS & HP35. (continued)

Annealed temp. ($^{\circ}$C)	% by weight HP35	T_g of PS rich phase in blends ($^{\circ}$C)	T_m of HP35 rich phase in blends ($^{\circ}$C)	Transition temp. (S→N) of HP35 rich phase in blends ($^{\circ}$C)
87	19.8	56.2	81.0	86.7
	25.0	56.9	80.5	86.8
100	0.0(100% PS)	81.0	-	-
	5.0	71.8	-	-
	7.2	69.6	-	-
	10.2	65.4	-	-
	12.7	61.9	81.4	86.5
	15.2	55.5	80.6	86.0
	19.8	53.5	79.7	86.3
	25.0	55.8	79.2	86.2
120	0.0(100% PS)	90.0	-	-
	5.0	82.4	-	-
	7.2	81.0	-	-
	10.2	73.4	-	-
	12.7	66.8	-	-
	15.2	63.2	82.0	86.0
	19.8	53.6	81.5	86.5
	25.0	55.6	81.6	86.7
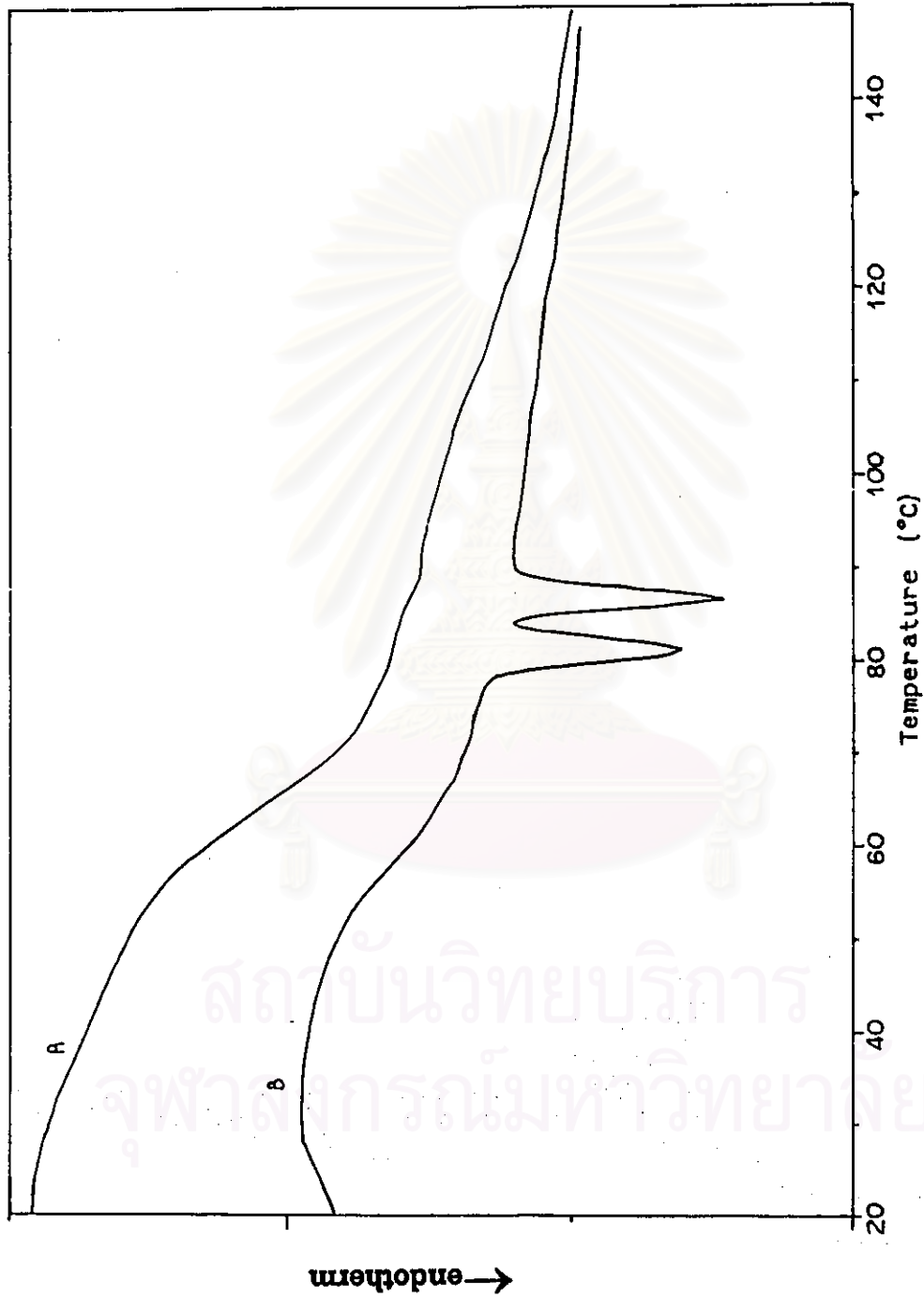
Figure 5-3 The DSC thermograms of the blends of PS and HP35. Curve A: 10% by weight of HP35, which annealed at 80°C. Curve B: 20% by weight of HP35, which annealed at 100°C.

5.3.2 The Transition Temperatures of HP35 in the Blends

From Table 5-9, it can be seen that the melting temperature (T_m) of HP35 rich phase and the transition temperature (S→N) of HP35 rich phase in the blends were not observed at the annealed temperatures of $48^\circ C$, $54^\circ C$, $65^\circ C$, $80^\circ C$, $87^\circ C$ and $100^\circ C$ for the weight percent of HP35 between 5.0-10.2. At $120^\circ C$ annealed temperature, the melting temperature (T_m) of HP35 rich phase and the transition temperature (S→N) of HP35 rich phase in the blends were not observed between 5.0-12.7 weight percent of HP35 with PS. These results should be due to the low content of HP35 in the blends that it can not be detected by differential scanning calorimeter (DSC) or HP35 in the blends were almost absolutely miscible with PS. This needs to be further proved.

However, the T_m of HP35 rich phase and the transition temperature (S →N) of HP35 rich phase in the blends that were detectable in the experiments, as shown in Table 5-9, were quite consistent with the T_m of pure HP35 ($80^\circ C$) and the transition temperature (S→N) of pure HP35 ($87^\circ C$), respectively. As predicted by Nishi-Wang equation [Olabisi, 1979], the crystalline melting temperature that does not change implies that the system has the immiscible characteristic. Hence, these results suggested that at these concentrations and annealed tempeartures the HP35 was immiscible with PS.

5.3.3 Phase Diagram Construction of System I: PS & HP35

Phase diagram constructed in this study is the phase diagram at low concentration of HP35. There are two methods used to construct phase diagrams in this study. The first method is the method of depression trend. The second method is the gradient method. The details of these two methods were already described in Section 5.2: phase diagram construction procedure.

5.3.3.1 Phase Diagram Constructed by the Method of Depression Trend of System I: PS & HP35

To clearly monitor the relation between weight percent of HP35 with PS and T_g of PS rich phase in the blends at each annealed temperature, Figure 5-4a and Figure 5-4b were made. The relation that can be drawn from these figures were shown in Table 5-10.

Phase behaviour of the blends, in which the T_g of PS rich phase is decreased when the weight percent of HP35 with PS is increased, were determined as partially miscible and represented with o symbol. For the blends that the T_g of PS rich phase are quite constant or T_g is increased, phase behaviour were determined as immiscible, and represented with * symbol. The phase diagram that was constructed by the method of depression trend was shown in Figure 5-5.
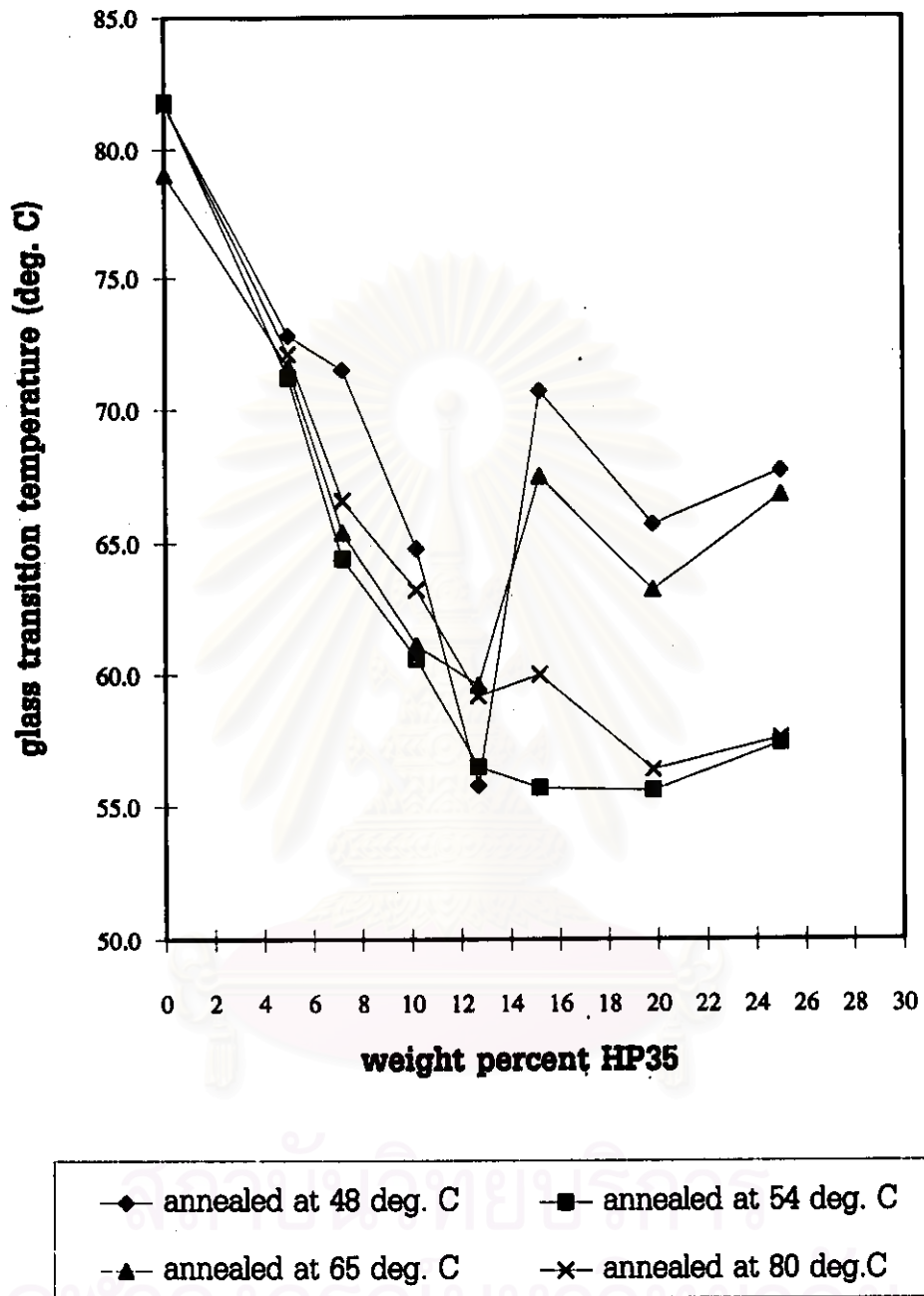
Figure 5-4a Glass transition temperatures depression in the blends of system I:

PS & HP35 annealed at 48°C, 54°C, 65°C and 80°C.
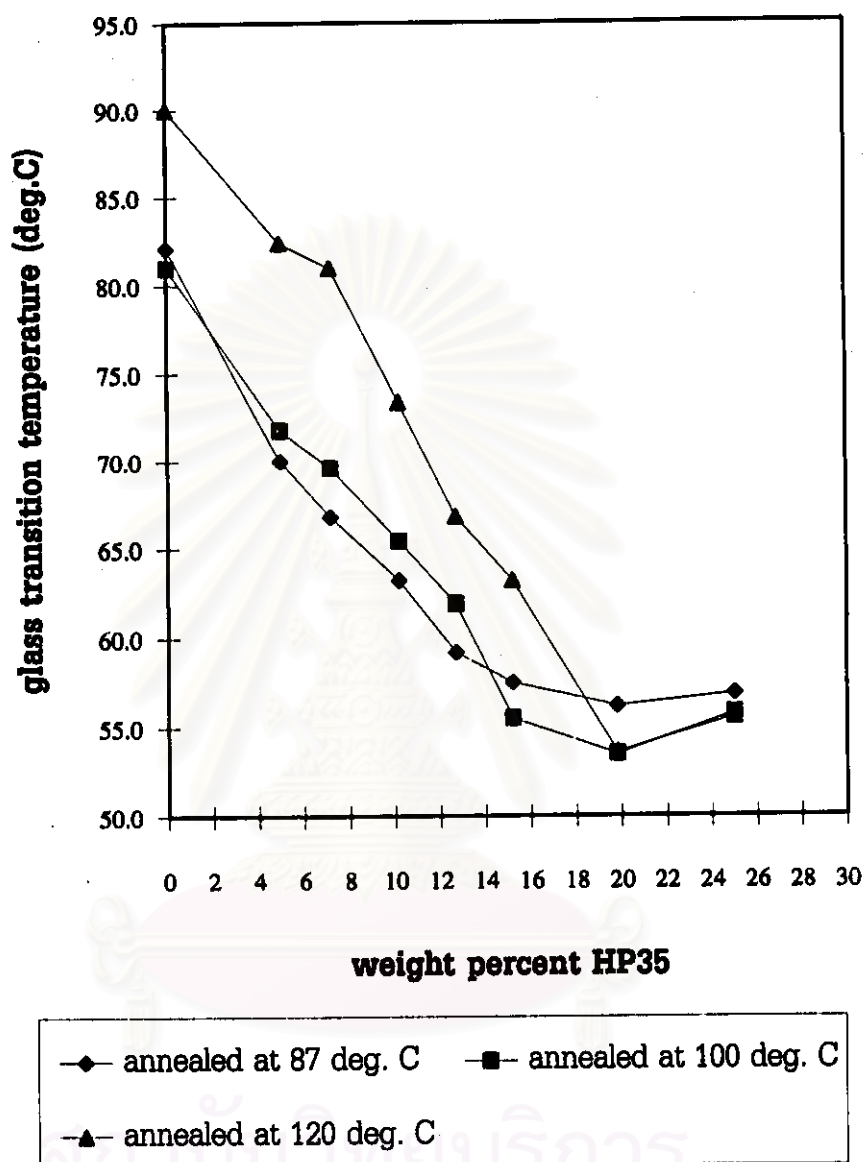
Figure 5-4b Glass transition temperatures depression in the blends of system I:
PS & HP35 annealed at 87°C, 100°C and 120°C.

Table 5-10   Relation between the T_g of the PS rich phase in the blends and weight percent HP35 with PS.

Annealed temp. ($^\circ$C)	Weight percent HP35	
	Decreasing T_g o	Increasing T_g or constant T_g *
48	5.0-12.7 15.2-19.8	12.7-15.2 19.8-25.0
54	5.0-15.2	15.2-25.0
65	5.0-12.7 15.2-19.8	12.7-15.2 19.8-25.0
80	5.0-12.7 15.2-19.8	12.7-15.2 19.8-25.0
87	5.0-15.2	15.2-25.0
100	5.0-15.2	15.2-25.0
120	5.0-19.8	19.8-25.0
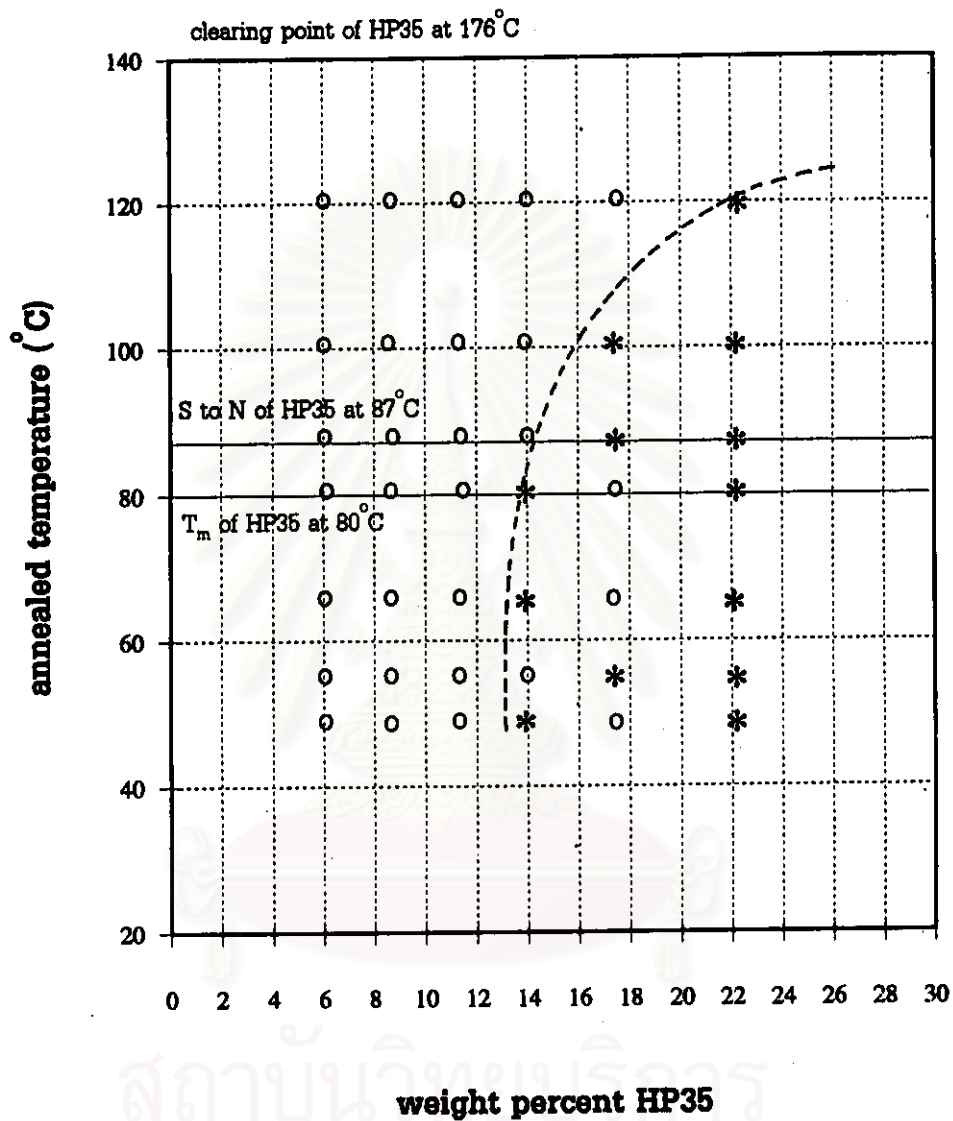
Figure 5-5 Phase diagram at low concentration of system I: PS and HP35 constructed by method of depression trend. o represents partially miscible region and * represents immiscible region. And ----- represents phase separation line.

5.3.3.2 Phase Diagram Constructed by the Gradient Method of System
I: PS & HP35

The gradient method procedure, which is used to construct phase diagram of system I : PS & HP35, was already described in Section 5.2. The phase diagram of system I: PS & HP35, shown in Figure 5-2, was constructed as an example in that section.

In this study, only the blends at low concentration of HP35 has been examined. So, the constructed phase diagram is the phase diagram of the low concentration side of HP35. Both phase diagrams of system I constructed by the method of depression trend as shown in Figure 5-5 and the gradient method as shown in Figure 5-2 seem to show the behaviour of the upper critical solution temperature (UCST) i.e. when the temperature is increased, the miscibility of the blend increases (Paul and Newman, 1978). There were different regions identified from the two methods at some points due to more details of the gradient method. The partially miscible region (o) in the method of depression trend can be divided to be the absolutely partially miscible region (o) and the possibly partially miscible region (+) in the gradient method. In the same way, the immiscible region (*) in the method of depression trend can be divided to be the absolutely immiscible region (*) and the possibly immiscible region (-) in the gradient method.

The phase boundaries in both phase diagrams represent the phase separation line but it cannot exactly divide the partially miscible region from the immiscible region. However, this boundary is the best possible

estimation and it shows that only small amount of HP35 (up to 12.7 weight percent) can be dissolved in PS.

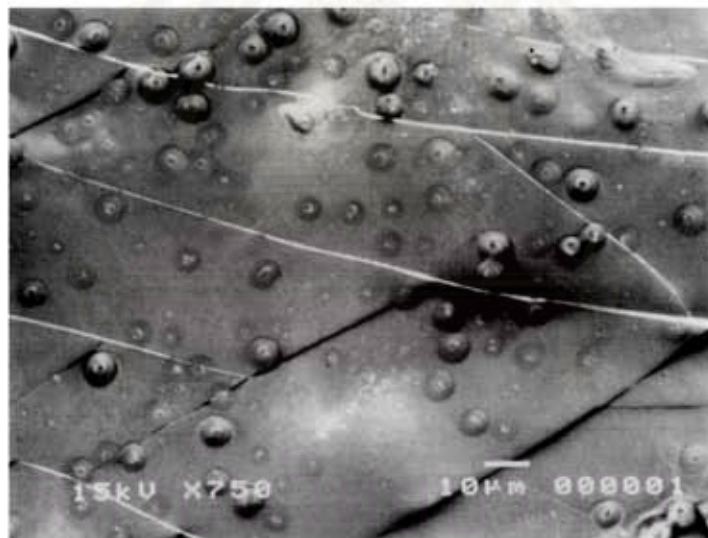### 5.3.4 Scanning Electron Microscope (SEM) of System I: PS & HP35

Scanning electron micrograph of 10 percent by weight of HP35 with PS, which annealed at 87°C, and 25 percent by weight of HP35 with PS, which annealed at 100°C, were shown in Figure 5-6 and Figure 5-7, respectively.

Sample of 10 percent by weight of HP35 with PS, which annealed at 87°C, revealed a lamella structure with the distribution of HP35 as small beads. This was considered to be the partially miscible phase behaviour of the blends which consisted of two phases. The two phases are the beads of undissolved HP35, and the amorphous of PS with dissolved HP35 as shown in Figure 5-6b. Phase separation can be seen in 25 percent by weight of HP35 with PS, which annealed at 100°C. It revealed three distinct phases as shown in Figure 5-7. The three phases were likely be to be the beads of HP35, the pure PS and the gray amorphous of PS with the dissolved HP35.

The SEM results were in agreement with the DSC results that 10 percent by weight of HP35 with PS, which annealed at 87°C, showed partially miscible blends and 25 percent by weight of HP35 with PS, which annealed at 100°C, showed immiscible blends. Hence, the scanning electron micrographs can be used to confirm the phase diagrams predicted from DSC results with the developed methods in this experiment.
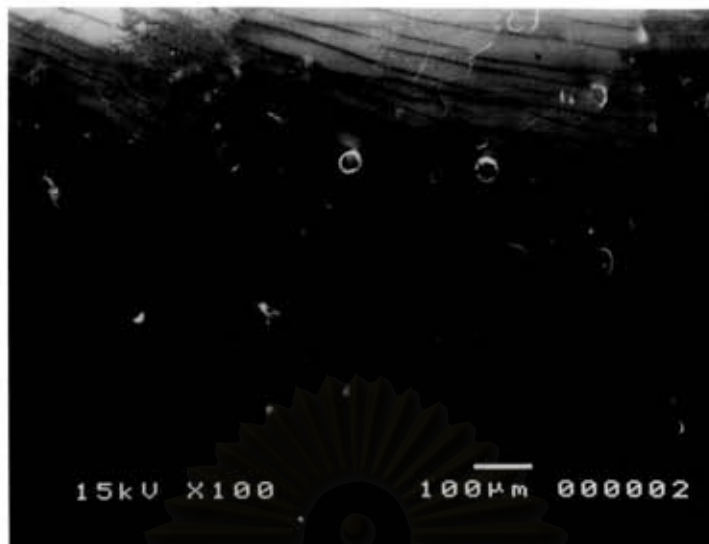
(a)

(b)

Figure 5-6 Scanning electron micrograph of 10 percent by weight of HP35 with PS, which annealed at 87°C. (a) the lower magnification (x100). (b) higher magnification (x750).
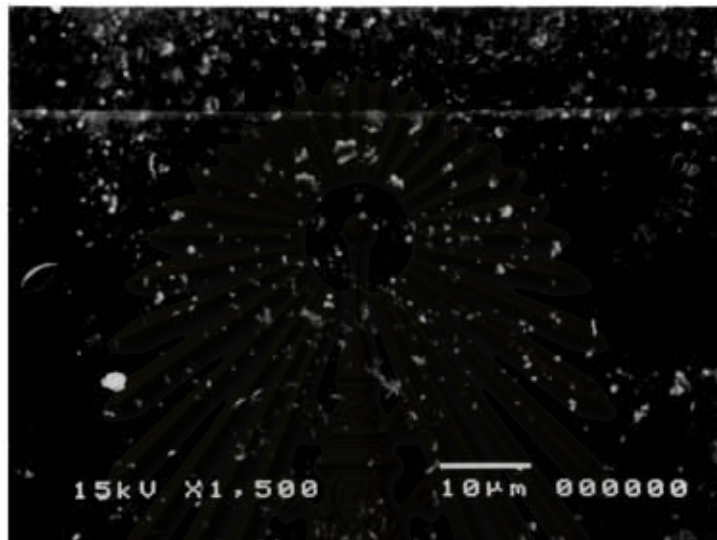
Figure 5-7 Scanning electron micrograph (x1500 magnification) of 25 percent by weight of HP35 with PS, which annealed at 100°C.

5.4 SYSTEM II: Polystyrene & HP5N

The blends at low concentration of HP5N (2.7, 5.0, 10.0, 15.0, 19.8 and 25.1 percent by weight) with PS were prepared and their phase behaviour were examined at various annealed temperatures, which are the same as in the system I: PS and HP35, i.e. at 48°C, 54°C, 65°C, 80°C, 87°C, 100°C and 120°C.

The transition temperatures of the blends detected by differential scanning calorimeter (DSC) were shown in Table 5-11 and examples of DSC thermograms of 2.7 percent by weight of HP5N with PS, which annealed at 100°C, and 10 percent by weigth of HP5N with PS, which annealed at 65°C were shown in Figure 5-8.

5.4.1 Effects of HP5N on Polystyrene (PS)

From Table 5-11, it can be seen that the glass transition temperatures (T_g) of PS rich phase in the blends at every weight percent of HP5N with PS and annealed temperatures used in the experiment were depressed from the T_g of 100% PS (0 percent by weight of HP5N with PS). This phenomenon proved that HP5N can act as a plasticizer of PS.

5.4.2 The Transition Temperatures of HP5N in the Blends

The melting temperature (T_m) of HP5N cannot be detected at 2.7 percent by weight of HP5N with PS, at any annealed temperatures, except at 120 $^{\circ}$C, the T_m of HP5N can be detected only at 15.0, 19.8 and 25.1 percent by weight

Table 5-11 Transition temperatures detected by differential scanning calorimeter
(DSC) of system II : PS & HP5N.

Annealed temp. ($^{\circ}$C)	% by weight HP5N	T_g of PS rich phase in blends ($^{\circ}$C)	T_m of HP5N rich phase in blends ($^{\circ}$C)
48	0.0(100% PS)	81.7	-
	2.7	77.3	-
	5.0	57.6	111.5
	10.0	67.9	111.4
	15.0	50.7	111.5
	19.8	50.7	108.3
	25.1	48.9	111.6
54	0.0(100% PS)	81.8	-
	2.7	77.2	-
	5.0	59.0	111.2
	10.0	64.7	111.4
	15.0	55.7	107.8
	19.8	56.5	108.1
	25.1	61.6	111.1
65	0.0(100% PS)	79.0	-
	2.7	72.0	-
	5.0	60.4	111.3
	10.0	67.9	111.1

Table 5-11 Transition temperatures detected by differential scanning calorimeter (DSC) of system II : PS & HP5N. (continued)

Annealed temp. ($^{\circ}$C)	% by weight HP5N	T_g of PS rich phase in blends ($^{\circ}$C)	T_m of HP5N rich phase in blends ($^{\circ}$C)
65	15.0	60.7	107.7
	19.8	64.1	108.3
	25.1	65.5	111.6
80	0.0(100% PS)	81.7	-
	2.7	74.8	-
	5.0	60.0	111.7
	10.0	68.1	111.4
	15.0	61.6	107.5
	19.8	64.3	108.5
	25.1	64.8	111.1
87	0.0(100% PS)	82.1	-
	2.7	75.8	-
	5.0	63.9	111.1
	10.0	67.1	111.4
	15.0	61.4	107.3
	19.8	66.4	108.5
	25.1	63.6	110.5

Table 5-11 Transition temperatures detected by differential scanning calorimeter (DSC) of system II : PS & HP5N. (continued)

Annealed temp. (^{o}C)	% by weight HP5N	T_g of PS rich phase in blends (^{o}C)	T_m of HP5N rich phase in blends (^{o}C)
100	0.0(100% PS)	81.0	-
	2.7	75.9	-
	5.0	67.3	111.2
	10.0	68.9	111.7
	15.0	62.8	108.1
	19.8	65.5	108.6
	25.1	77.7	111.9
120	0.0(100% PS)	90.0	-
	2.7	79.6	-
	5.0	68.3	-
	10.0	78.8	-
	15.0	60.0	108.7
	19.8	65.9	109.6
	25.1	65.9	111.6
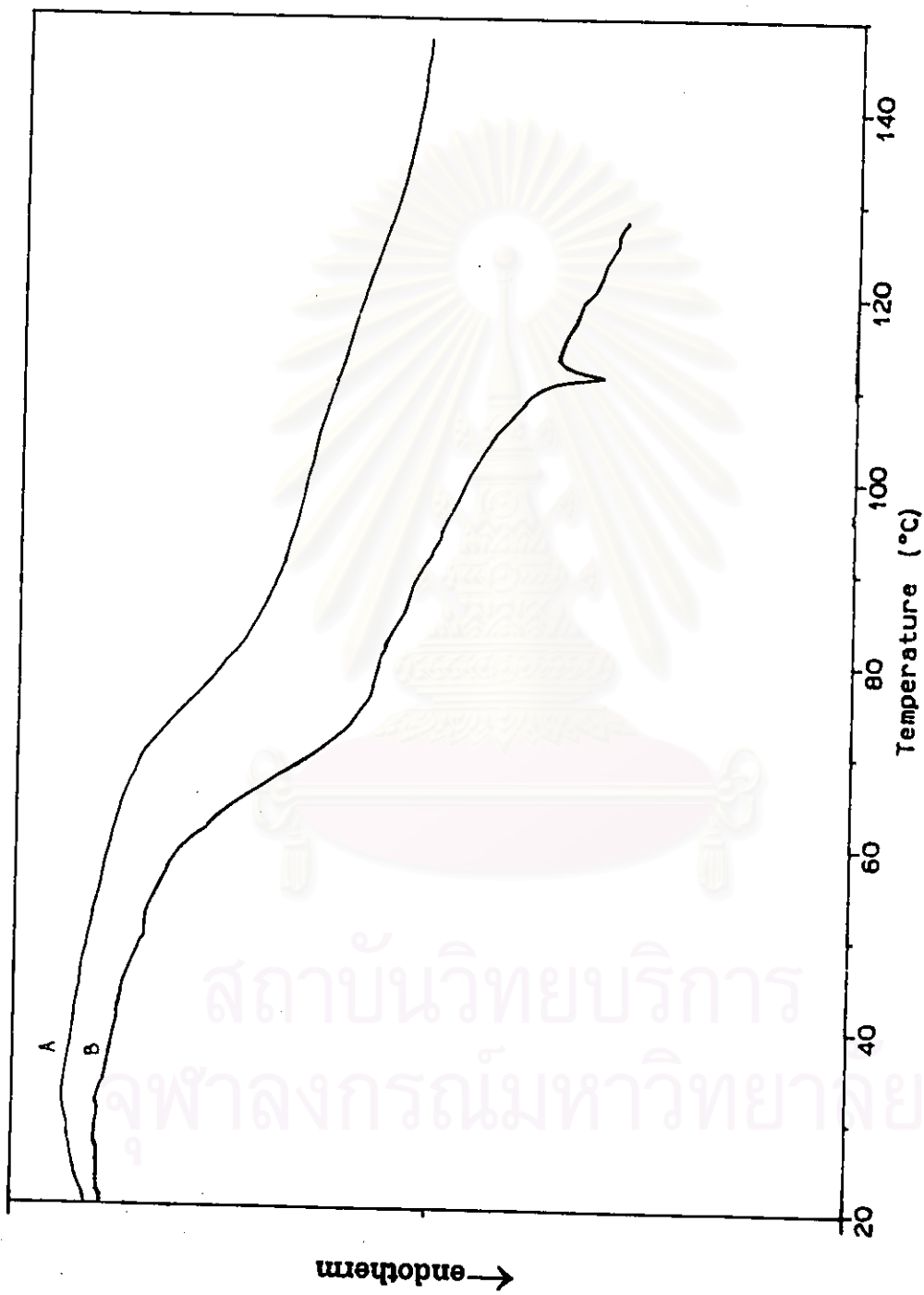
Figure 5-8 The DSC thermograms of the blends of PS and HP5N. Curve A: 2.7% by weight of HP5N, which annealed at 100°C. Curve B: 10% by weight of HP5N, which annealed at 65°C.

of HP5N with PS. This might be due to the low content of HP5N in the blends which made the T_m of HP5N rich phase not detectable by differential scanning calorimeter (DSC) or HP5N in the blends was almost absolutely miscible with PS. This needs to be further proved.

However, the T_m of HP5N rich phase in the blends that were detectable in these experiments (as shown in Table 5-11) did not vary much from $111^{\circ}C$ (T_m of pure HP5N). As predicted by Nishi-Wang equation [Olabisi, 1979], the crystalline melting temperature that did not change implies that the system has the immiscible characteristic. Hence, these results suggested that at these concentrations and annealed tempeartures the HP5N was immiscible with PS.

5.4.3 Phase Diagram Construction of System II: PS & HP5N

Phase diagrams constructed by the method of depression trend and the gradient method were presented below.

5.4.3.1 Phase Diagram Construction by the Method of Depression

Trend of System II: PS & HP5N

To clearly monitor the relation between weight percent of HP5N with PS and T_g of PS rich phase in the blends at each annealed temperature, Figure 5-9a and Figure 5-9b were made. The relation that can be drawn from these figures were shown in Table 5-12.
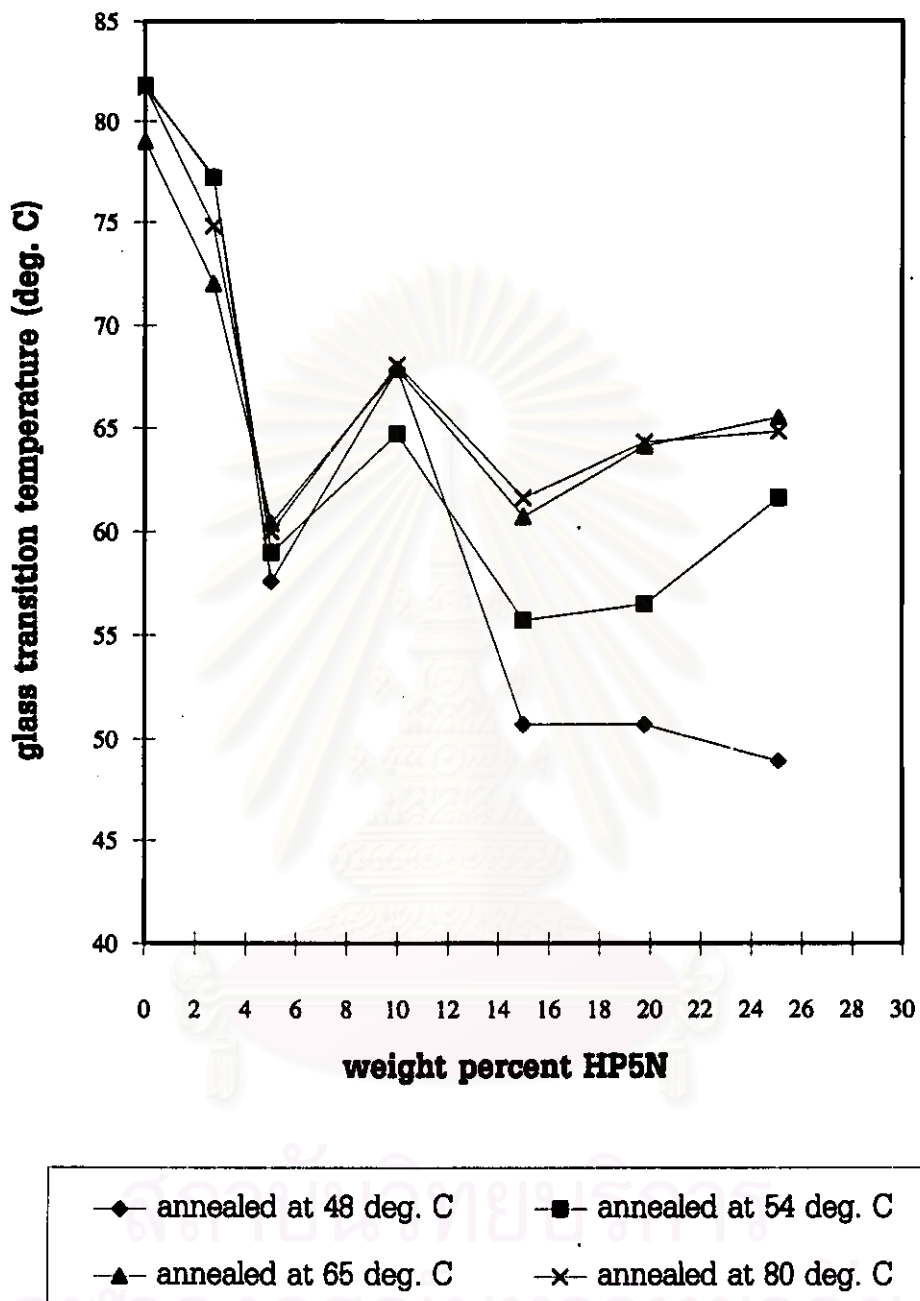
Figure 5-9a Glass transition temperatures depression in the blends of system II: PS & HP5N annealed at 48°C, 54°C, 65°C and 80°C.
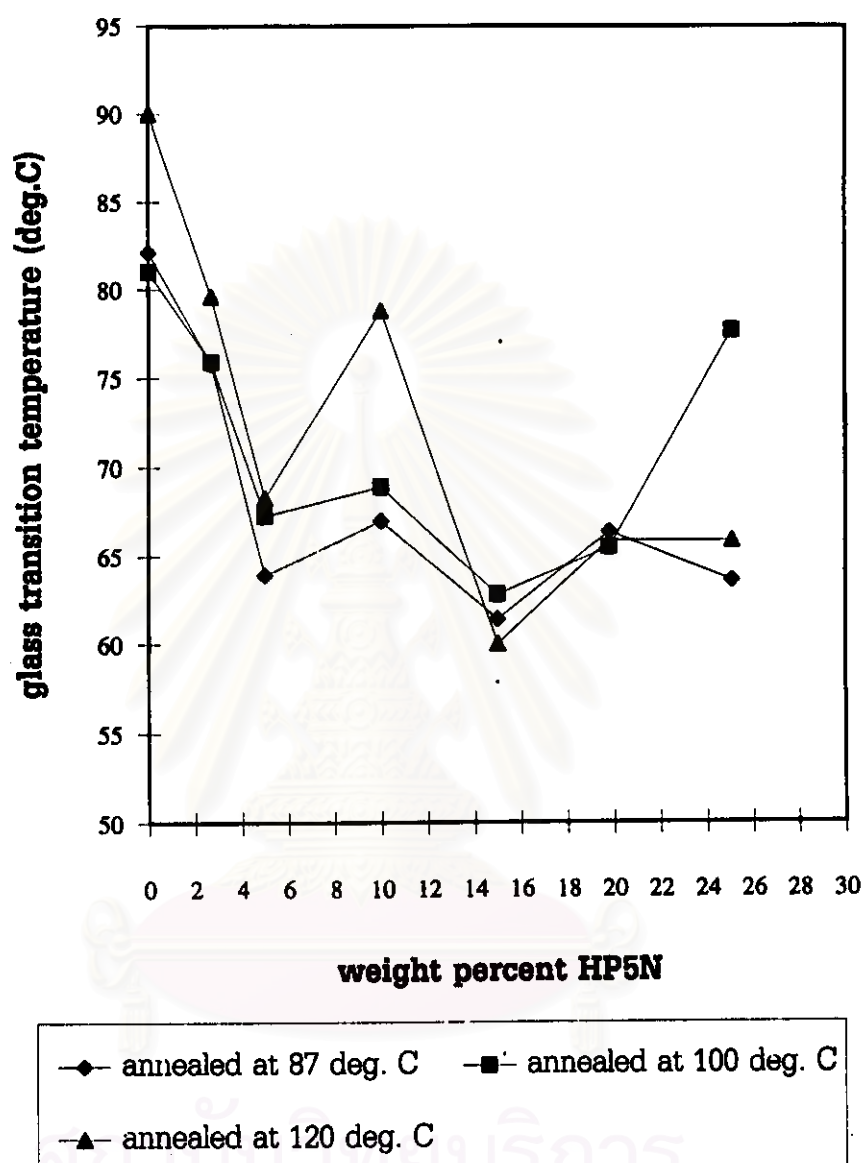
Figure 5-9b Glass transition temperatures depression in the blends of system II: PS & HP5N annealed at 87°C, 100°C and 120°C.

Table 5-12 Relation between the T_g of the PS rich phase in the blends and weight percent HP5N with PS

Annealed temp. ($^{\circ}$C)	Weight percent HP5N	
	Decreasing T_g o	Increasing T_g or constant T_g *
48	2.7-5.0; 10.0-15.0	5.0-10.0; 15.0-25.1
54	2.7-5.0; 10.0-15.0	5.0-10.0; 15.0-25.1
65	2.7-5.0; 10.0-15.0	5.0-10.0; 15.0-25.1
80	2.7-5.0; 10.0-15.0	5.0-10.0; 15.0-25.1
87	2.7-5.0; 10.0-15.0 19.8-25.1	5.0-10.0; 15.0-19.8
100	2.7-5.0; 10.0-15.0	5.0-10.0; 15.0-19.8
120	2.7-5.0; 10.0-15.0	5.0-10.0; 15.0-19.8 19.8-25.1

Phase behaviour of the blends, in which the T_g of PS is decreased when the weight percent of HP5N with PS is increased, were determined as partially miscible and represented with o symbol. For the blends that the T_g of PS are quite constant or T_g is increased, phase behaviour were determined as immiscible, and represented with * symbol. The phase diagram that was constructed by the method of depression trend was shown in Figure 5-10.

5.4.3.2 Phase Diagram Constructed by the Gradient Method of System II: PS & HP5N

The gradient method construction procedure was described previously in section 5.2 (phase diagram construction procedure). The T_g of PS rich phase in the blends were reported in Table 5-13. Then, the gradient values were calculated as shown in Table 5-14. Phase behaviour of the blends were determined from gradient values which can be divided into four regions based on the criteria in Table 5-7. In Table 5-15, symbol that represented each phase behaviour was shown. The phase diagram of system II: PS and HP5N was constructed as shown in Figure 5-11.

Both phase diagrams of system II: PS and HP5N from the method of depression trend (Figure 5-10) and the gradient method (Figure 5-11) were constructed at low concentration range of HP5N. In both phase diagrams the partially miscible region can be clearly seen at the left side (2.7-5.0 percent by weight HP5N). The phase behaviour at which the percent by weight of HP5N is more than 5.0 are immiscible. So, phase separation line should start at this
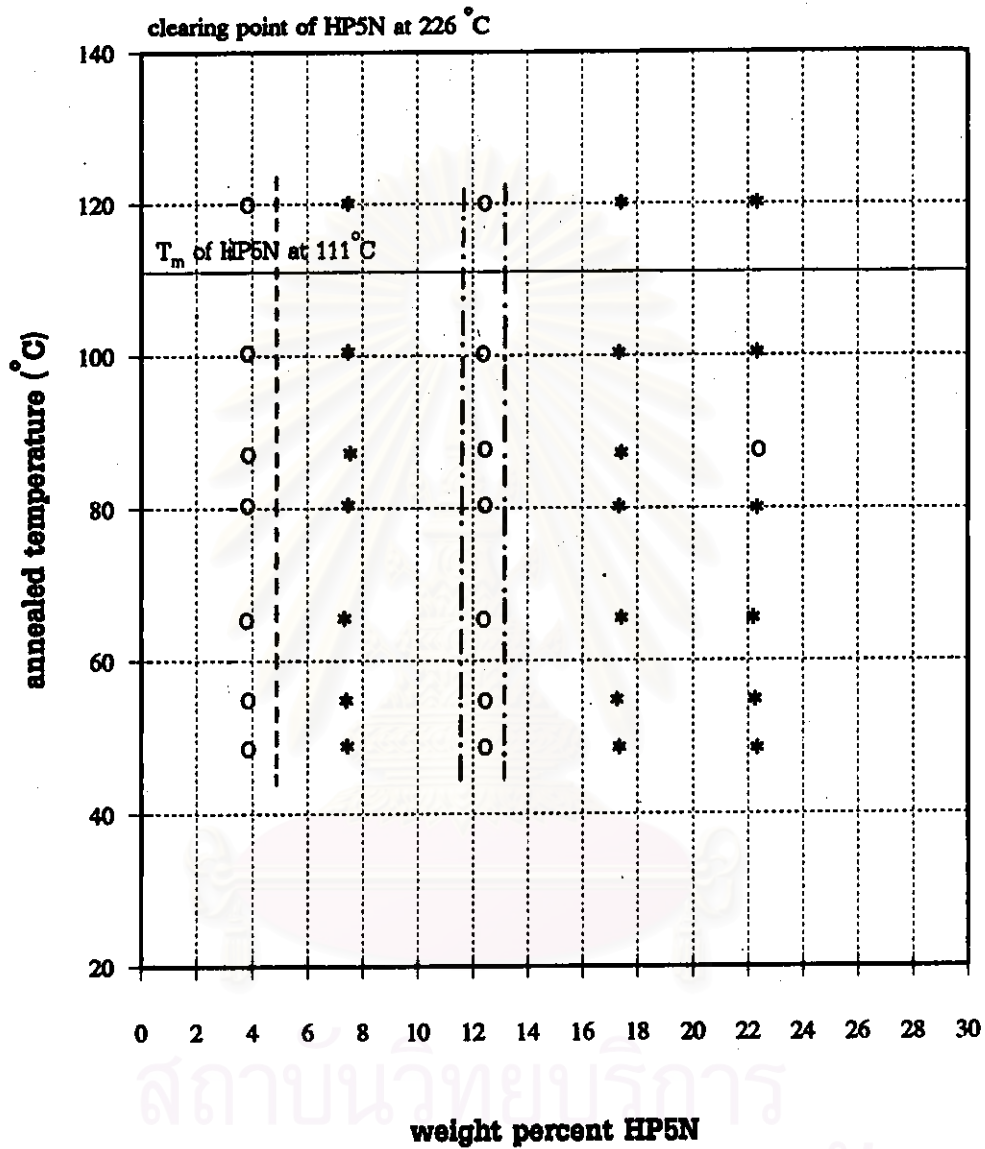
Figure 5-10 Phase diagram at low concentration of system II: PS and HP5N constructed by method of depression trend. o represents partially miscible region and * represents immiscible region. --------- represents phase separation line and —·—·— represents contour line of possibly miscible in immiscible region.

concentration. However, at 10.0-15.0 percent by weight, the partially miscible region can be clearly observed. And beyond this concentration (from 15 percent by weight upward), the immiscible region appeared again. Therefore, three phase boundary lines were drawn in this phase diagram. This behaviour of phase diagram does not follow any typical phase behaviour as shown in Figure 3-2 (with respect to the data available from this study). Hence, one plausible and simple explanation for this observed phase behaviour is that it was the nature of this blend between PS and HP5N.

There were different regions identified from the two methods at some points in diagram due to more details of the gradient method. The partially miscible region (o) in method of depression trend can be divided to be the absolutely partially miscible region (o) and the possibly partially miscible region (+) in the gradient method. In the same way, the immiscible region (*) in the method of depression trend can be divided to be the absolutely immiscible region (*) and the possibly immiscible region (-) in the gradient method.

Table 5-13 The glass transition temperatures (T_g) of PS rich phase in the blends of HP5N & PS detected by differential scanning calorimeter (DSC) at each annealed temperature and weight percent HP5N with PS.

Annealed temp.(°C) / Weight percent HP5N	48	54	65	80	87	100	120
2.7	77.3	77.2	72.0	74.8	75.8	75.9	79.6
5.0	57.6	59.0	60.4	60.0	63.9	67.3	68.3
10.0	67.9	64.7	67.9	68.1	67.0	68.9	78.8
15.0	50.7	55.7	60.7	61.6	61.4	62.8	60.0
19.8	50.7	56.5	64.1	64.3	66.4	65.5	65.9
25.1	48.9	61.6	65.5	64.8	63.6	77.7	65.9

Table 5-14 Gradient value of system II: PS & HP5N.

Annealed temp.(°C) / Weight percent HP5N	48	54	65	80	87	100	120
2.7-5.0	-8.565	-7.913	-5.043	-6.435	-5.174	-3.739	-4.913
5.0-10.0	2.060	1.140	1.500	1.620	0.620	0.320	2.100
10.0-15.0	-3.440	-1.800	-1.440	-1.300	-1.120	-1.220	-3.760
15.0-19.8	0.000	0.167	0.708	0.562	1.042	0.563	1.229
19.8-25.1	-0.340	0.962	0.264	0.094	-0.528	2.302	0.000

Table 5-15 Four regions divided from gradient value of system II: PS & HP5N. o represents absolutely partially miscible region, + represents possibly partially miscible region, - represents possibly immiscible region and * represents absolutely immiscible region.

Annealed temp(°C) / Weight percent HP5N	48	54	65	80	87	100	120
2.7-5.0	-8.565 o	-7.913 o	-5.043 o	-6.435 o	-5.174 o	-3.739 o	-4.913 o
5.0-10.0	2.060 *	1.140 *	1.500 *	1.620 *	0.620 -	0.320 -	2.100 *
10.0-15.0	-3.440 o	-1.800 o	-1.440 o	-1.300 o	-1.120 o	-1.220 o	-3.760 o
15.0-19.8	0.000 -	0.167 -	0.708 -	0.562 -	1.042 *	0.563 -	1.229 *
19.8-25.1	-0.340 -	0.962 -	0.264 -	0.094 -	-0.528 +	2.302 *	0.000 -
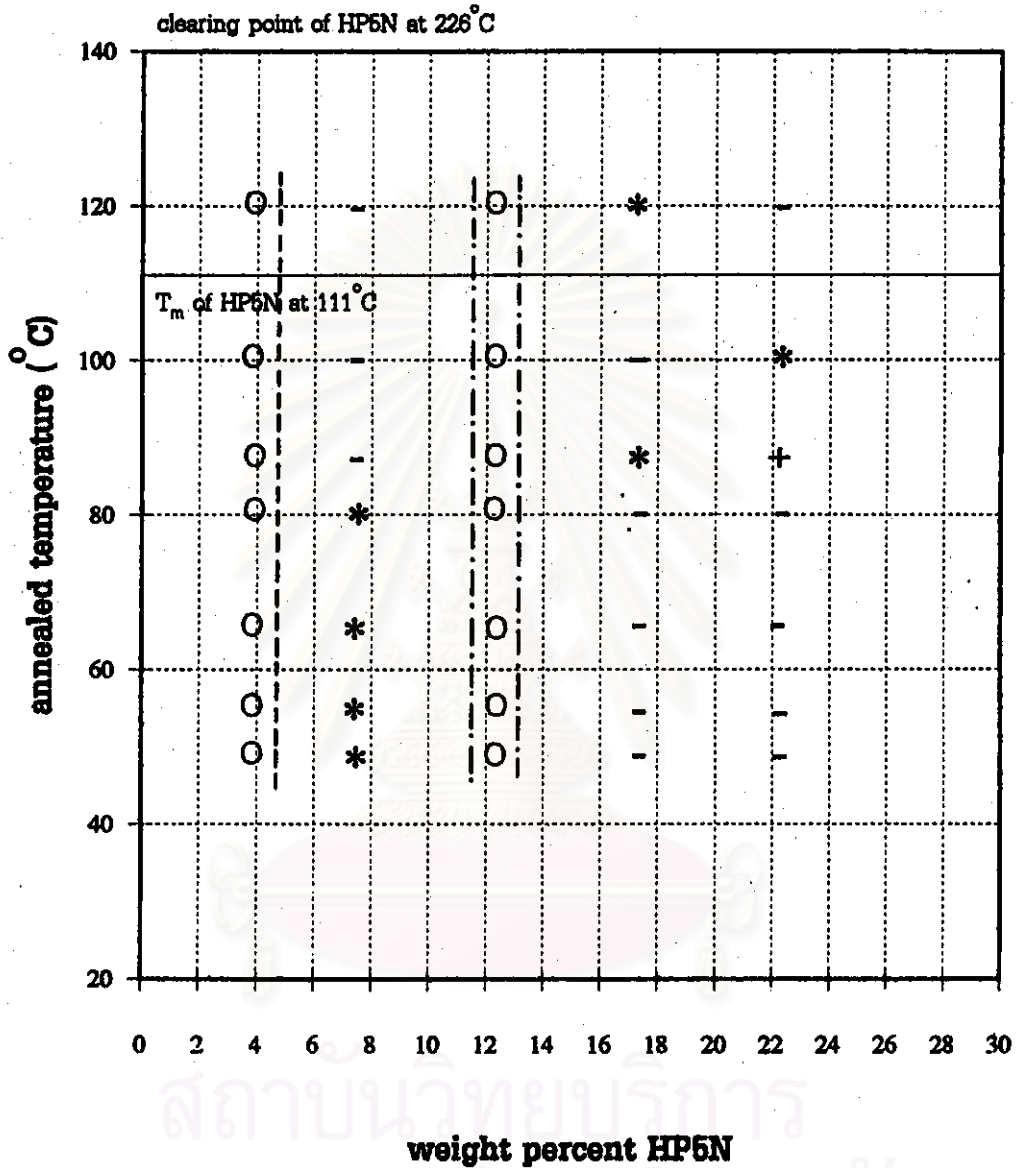
Figure 5-11 Phase diagram at low concentration of system II: PS and HP5N constructed by gradient method. O represents absolutely partially miscible region. + represents possibly partially miscible region. – represents possibly immiscible region. * represents absolutely immiscible region. ---------- represents phase separation line and —·—·—·— represents contour line of possibly miscible in immiscible region.

5.4.4 Scanning Electron Microscope (SEM) of System II: PS & HP5N

Scanning electron micrograph of 5 percent by weight of HP5N with PS, which annealed at 100°C, and 20 percent by weight of HP5N with PS, which annealed at 100°C, were shown in Figure 5-12 and Figure 5-13, respectively.

Sample of 5 percent by weight of HP5N with PS, which annealed at 100°C, revealed small particles distributed in gray area of the texture as shown in Figure 5-12. This was considered to be the partially miscible phase behaviour of the blends which consisted of two phases. The first phase was most likely to be the beads of HP5N. The second phase, which was the gray texture in the picture, was most likely to be the amorphous blend of PS and HP5N. This was in agreement with phase behaviour determined from DSC results.

Phase behaviour of the sample of 20 percent by weight of HP5N with PS determined from DSC results was immiscible. This was in agreement with the SEM results in Figure 5-13 that revealed three distinct phases. The first phase was the fine grains distributed in the texture and most likely to be the unmixed PS. The second phase was a HP5N crystal at left side of the picture and the third phase was the gray area in the texture which was most likely to be the amorphous blend of HP5N with PS.
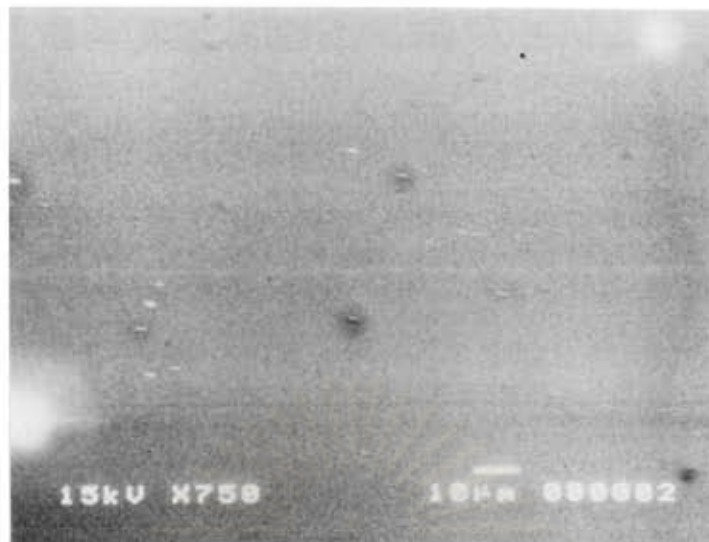
(a)

(b)

Figure 5-12 Scanning electron micrograph of 5 percent by weight of HP5N with PS, which annealed at 100°C. (a) the lower magnification (x750). (b) the higher magnification (x1500).

(a)

(b)

Figure 5-13 Scanning electron micrograph of 20 percent by weight of HP5N with PS, which annealed at 100°C. (a) the lower magnification (x750). (b) the higher magnification (x1500).

5.5 SYSTEM III: Poly(bisphenol A carbonate) & HP35

The phase diagram of system III: PC & HP35 was constructed only at low concentration part. The blends at low concentrations: 5.2, 10.0, 15.0, 20.0, 25.0 and 30.0 percent by weight of HP35 with PC, were prepared and their phase behaviour were studied at various annealed temperatures, i.e. at temperatures lower than T_g of pure PC: $60^\circ C$, $80^\circ C$, $100^\circ C$ and $120^\circ C$, at temperature nearly T_g of pure PC: $140^\circ C$, and at temperature higher than T_g of pure PC: $170^\circ C$.

The transition temperatures of the blends detected by differential scanning calorimeter (DSC) were shown in Table 5-16 and examples of DSC thermograms of 5 percent by weight of HP35 with PC, which annealed at $60^\circ C$ and 20 percent by weight HP35 with PC,which annealed at $170^\circ C$, were shown in Figure 5-14.

5.5.1 Effects of HP35 on Poly(bisphenol A carbonate) (PC)

From Table 5-16, it can be seen that the glass transition temperatures (T_g) of PC rich phase in the blends at each weight percent of HP35 and annealed temperature used in the experiment were depressed from the T_g of 100% PC (0 percent by weight of HP35). This phenomenon proved that HP35 can act as plasticizer of PC.

From 15 weight percent of HP35 with PC to other higher HP35 concentration, the melting temperature (T_m) of PC rich phase can be observed. The appearance of the melting peaks should be due to the content of HP35 in the

Table 5-16 Transition temperatures detected by differential scanning calorimeter (DSC) of system III : PC & HP35.

Annealed temp. (°C)	% by weight HP35	T_g of PC rich phase in blends (°C)	T_m of HP35 rich phase in blends (°C)	Transition temp. (S→N) of HP35 rich phase in blends (°C)	T_m of PC rich pahse in blends (°C)
60	0.0(100% PC)	144.6	-	-	-
	5.2	122.9	-	-	-
	10.0	105.5	-		-
	15.0	92.1	-	-	213.6
	20.0	112.2	81.2	86.8	212.9
	25.0	119.5	81.1	86.7	211.2
	30.0	117.7	81.5	87.1	211.5
80	0.0(100% PC)	144.9	-	-	-
	5.2	123.2	-	-	-
	10.0	102.4	-	-	-
	15.0	84.2	-	-	211.5
	20.0	78.4	-	85.9	213.6
	25.0	119.5	81.5	87.1	212.1
	30.0	115.2	81.4	86.9	209.7

Table 5-16 Transition temperatures detected by differential scanning calorimeter (DSC) of system III : PC & HP35. (continued)

Annealed temp. ($^\circ$C)	% by weight HP35	T_g of PC rich phase in blends ($^\circ$C)	T_m of HP35 rich phase in blends ($^\circ$C)	Transition temp. (S→N) of HP35 rich phase in blends ($^\circ$C)	T_m of PC rich phase in blends ($^\circ$C)
100	0.0(100% PC)	144.7	-	-	-
	5.2	121.8	-	-	-
	10.0	100.0	-	-	-
	15.0	89.6	80.9	-	213.2
	20.0	118.9	80.4	86.6	212.7
	25.0	118.3	81.9	86.9	211.4
	30.0	125.0	81.3	86.9	210.2
120	0.0(100% PC)	145.1	-	-	-
	5.2	120.7	-	-	-
	10.0	101.2	82.3	82.8	-
	15.0	89.4	81.1	-	212.3
	20.0	112.1	80.9	86.0	212.6
	25.0	111.1	81.5	87.1	212.7
	30.0	117.7	80.9	87.1	211.0

Table 5-16 Transition temperatures detected by differential scanning calorimeter (DSC) of system III : PC & HP35. (continued)

Annealed temp. ($^{\circ}$C)	% by weight HP35	T_g of PC rich phase in blends ($^{\circ}$C)	T_m of HP35 rich phase in blends ($^{\circ}$C)	Transition temp. (S$\rightarrow$N) of HP35 rich phase in blends ($^{\circ}$C)	T_m of PC rich phase in blends ($^{\circ}$C)
140	0.0(100% PC)	144.2	-	-	-
	5.2	120.5	-	-	-
	10.0	102.4	-	-	-
	15.0	87.8	81.1	-	212.3
	20.0	103.9	81.3	86.9	212.5
	25.0	110.1	81.2	86.8	210.1
	30.0	115.2	81.6	86.6	208.3
170	0.0(100% PC)	144.8	-	-	-
	5.2	121.5	-	-	-
	10.0	103.1	-	-	-
	15.0	86.2	-	-	214.1
	20.0	112.8	80.4	86.2	212.7
	25.0	112.8	81.4	87.6	213.1
	30.0	115.9	81.6	87.2	209.4
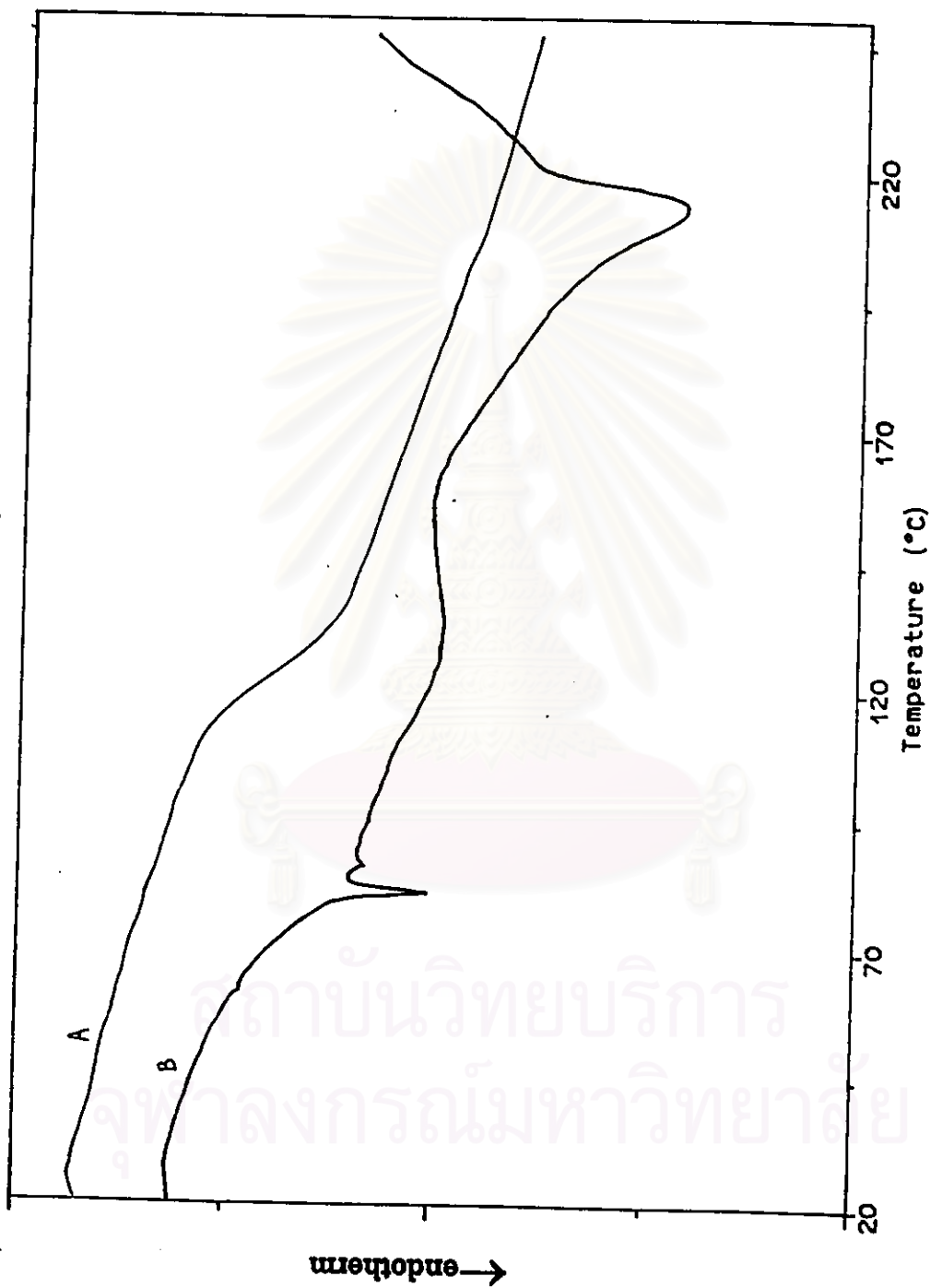
Figure 5-14 The DSC thermograms of the blends of PC and HP35. Curve A: 5% by weight of HP35, which annealed at 60°C. Curve B: 20% by weight of HP35, which annealed at 170°C.

blends. The T_m of PC rich phase did not vary much from 210°C (the T_m of pure PC). As predicted by Nishi-Wang equation [Olabisi, 1979], the crystalline melting temperature that did not change implies that the system has the immiscible characteristic. Hence, these results suggested that at these concentrations and annealed tempeartures the HP35 was immiscible with PC.

5.5.2 The Transition Temperatures of HP35 in the Blends

The melting temperature (T_m) of HP35 rich phase and the transition temperature (S→N) of HP35 rich phase in the blends cannot be observed in DSC thermograms at low weight percent HP35 with PC as shown in Table 5-16. The disappearance of transition temperatures (S→N) of HP35 rich phase in the blends should be due to low content of HP35 in the blends such that it cannot be detected by DSC or HP35 in the blends were almost absolutely miscible with PC. The T_m of HP35 rich phase and the transition temperature (S→N) of HP35 rich phase in the blends detected in the experiments were rather consistent with the T_m of pure HP35 (80°C) and the transition temperature (S→N) of HP35 (87°C), respectively. As predicted by Nishi-Wang equation [Olabisi, 1979], the crystalline melting temperature that did not change implies that the system has the immiscible characteristic. Hence, these results suggested that at these concentrations and annealed tempeartures the HP35 was immiscible with PC.

5.5.3 Phase Diagram Construction of System III: PC & HP35

Phase diagrams constructed by the method of depression trend and the gradient method were presented below.

5.5.3.1 Phase Diagram Construction by the Method of Depression Trend of System III: PC & HP35

To clearly monitor the relation between weight percent of HP35 with PC and T_g of PC rich phase in the blends at each annealed temperature, Figure 5-15a and Figure 5-15b were made. The relation that can be drawn from these figure were shown in Table 5-17.

Phase behaviour of the blends, in which the T_g of PC rich phase is decreased when the weight percent of HP35 with PC is increased, were determined as partially miscible and represented with o symbol. For the blends that the T_g of PC are quite constant or T_g is increased, phase behaviour were determined as immiscible, and represented with * symbol. The phase diagram that was constructed by the method of depression trend was shown in Figure 5-16.
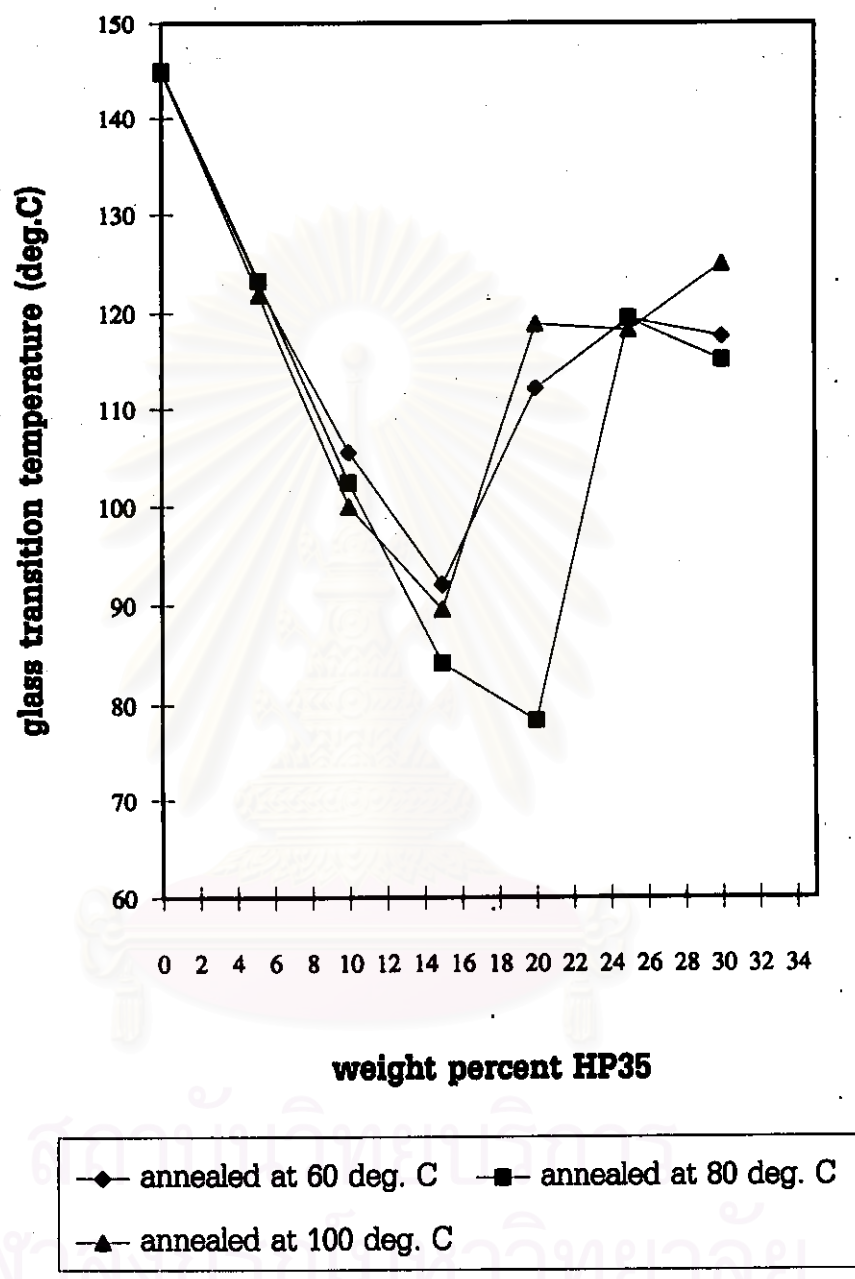
Figure 5-15a Glass transition temperatures depression in the blends of system III: PC & HP35 annealed at 60°C, 80°C and 100°C.
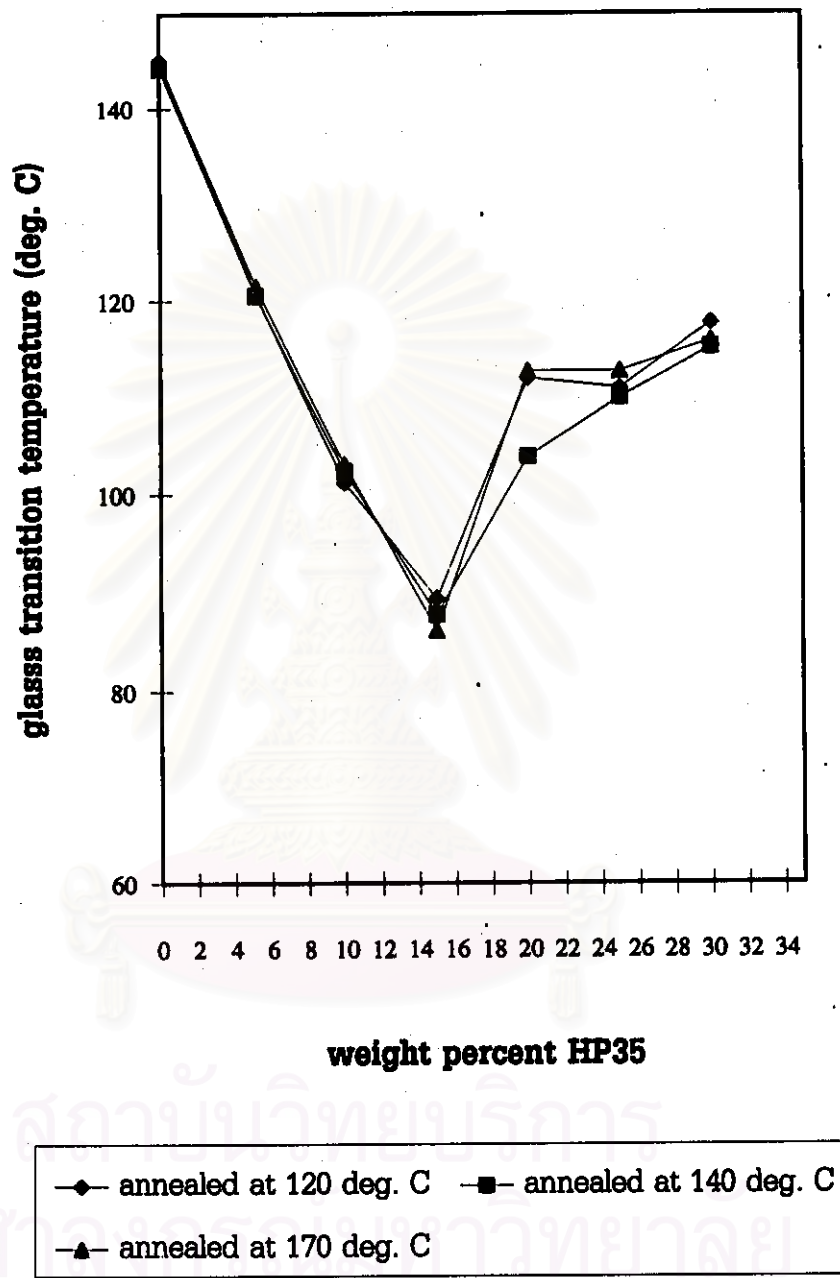
Figure 5-15b Glass transition temperatures depression in the blends of system III: PC & HP35 annealed at 120°C, 140°C and 170°C.

Table 5-17 Relation between the T_g of the PC rich phase in the blends and weight percent HP35 with PC.

Annealed temp. ($^\circ$C)	Weight percent HP35	
	Decreasing T_g o	Increasing T_g or constant T_g *
60	5.2-15.0 25.0-30.0	15.0-25.0
80	5.2-20.0 25.0-30.0	20.0-25.0
100	5.2-15.0	15.0-30.0
120	5.2-15.0	15.0-30.0
140	5.2-15.0	15.0-30.0
170	5.2-15.0	15.0-30.0
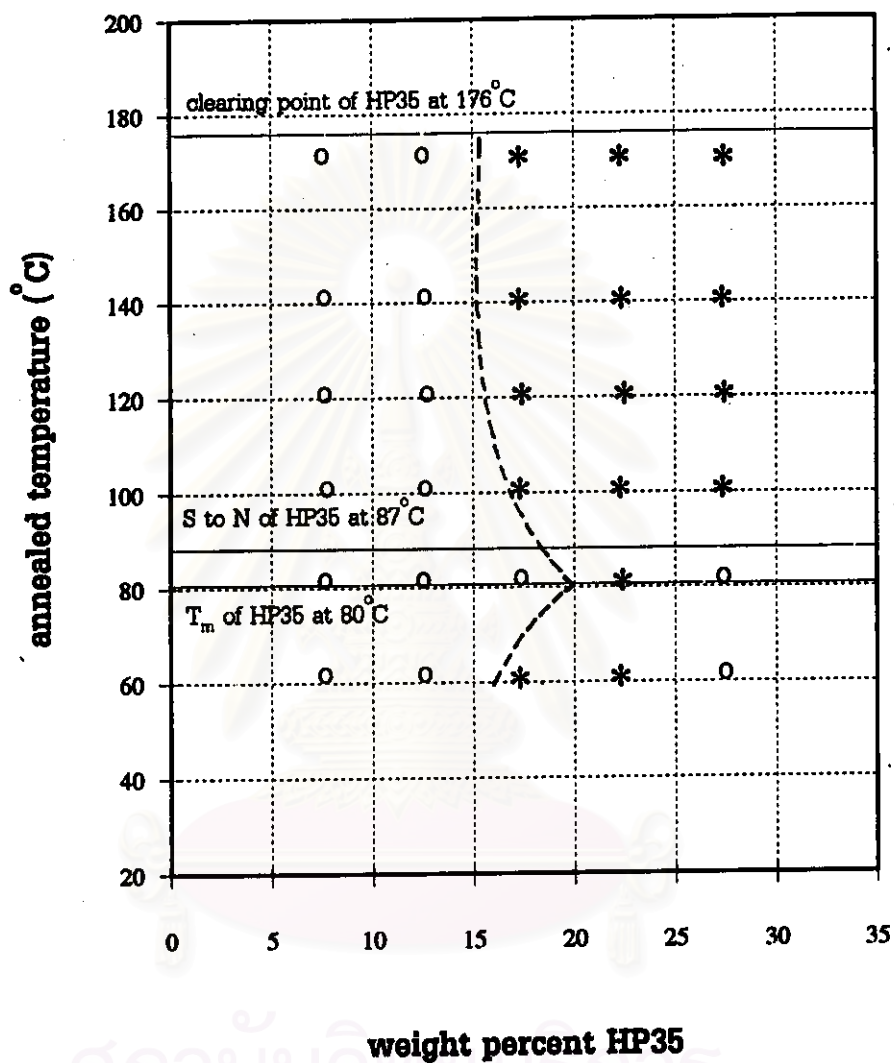
Figure 5-16 Phase diagram at low concentration of system III: PC and HP35 constructed by method of depression trend. o represents partially miscible region and * represents immiscible region. And ----- represents phase separation line.

5.5.3.2 Phase Diagram Constructed by the Gradient Method of System III: PC & HP35

The gradient method construction procedure was described previously in section 5.2 (phase diagram construction procedure). The T_g of PC rich phase in the blends were reported in Table 5-18. Then, the gradient value were calculated as shown in Table 5-19. Phase behaviour of the blends were determined from gradient value which can be divided into four regions based on criteria in Table 5-7. In Table 5-20, symbol that represented each phase behaviour are shown. The phase diagram of system III: PC and HP35 was constructed as shown in Figure 5-17.

From the estimation of phase separation line, both phase diagrams at low concentration of system III: PC and HP35, Figure 5-16 and Figure 5-17 seem to be the convergence of the upper and lower critical boudaries to form an hourglass-shaped phase boundary. Example of this type of phase diagram was shown in Figure 3-2d.

There were different regions identified from the two methods at some points in diagram due to more details of the gradient method. The partially miscible region (o) in method of depression trend can be divided to be the absolutely partially miscible region (o) and the possibly partially miscible region (+) in the gradient method. In the same way, the immiscible region (*) in the method of depression trend can be divided to be the absolutely immiscible region (*) and the possibly immiscible region (-) in the gradient method.

Table 5-18 The glass transition temperatures (T_g) of PC rich phase in the blends of HP35 and PC detected by differential scanning calorimeter (DSC) at each annealed temperature and weight percent HP35 with PC.

Annealed temp. (°C) / Weight percent HP35	60	80	100	120	140	170
5.2	122.9	123.2	121.8	120.7	120.5	121.5
10.0	105.5	102.4	100.0	101.2	102.4	103.1
15.0	92.1	84.2	89.6	89.4	87.8	86.2
20.0	112.2	78.4	118.9	112.1	103.9	112.8
25.0	119.5	119.5	118.3	111.1	110.1	112.8
30.0	117.7	115.2	125.0	117.7	115.2	115.9

Table 5-19 Gradient value of system III: PC & HP35.

Annealed temp. (°C) / Weight percent HP35	60	80	100	120	140	170
5.2-10.0	-3.625	-4.333	-4.542	-4.063	-3.771	-3.833
10.0-15.0	-2.680	-3.640	-2.080	-2.360	-2.920	-3.380
15.0-20.0	4.020	-1.160	5.860	4.540	3.220	5.320
20.0-25.0	1.460	8.220	-0.120	-0.200	1.240	0.000
25.0-30.0	-0.360	-0.860	1.340	1.320	1.020	0.620

Table 5-20 Four regions divided from gradient value of system III: PC & HP35. o
represents absolutely partially misible region, + represents possibly
partially misible region, - represents possibly immiscible region, *
represents absolutely immiscible region.

Annealed temp. (°C) / Weight percent HP35	60	80	100	120	140	170
5.2-10.0	-3.625 o	-4.333 o	-4.542 o	-4.063 o	-3.771 o	-3.833 o
10.0-15.0	-2.680 o	-3.640 o	-2.080 o	-2.360 o	-2.920 o	-3.380 o
15.0-20.0	4.020 *	-1.160 o	5.860 *	4.540 *	3.220 *	5.320 *
20.0-25.0	1.460 *	8.220 *	-0.120 -	-0.200 -	1.240 *	0.000 -
25.0-30.0	-0.360 -	-0.860 +	1.340 *	1.320 *	1.020 *	0.620 -
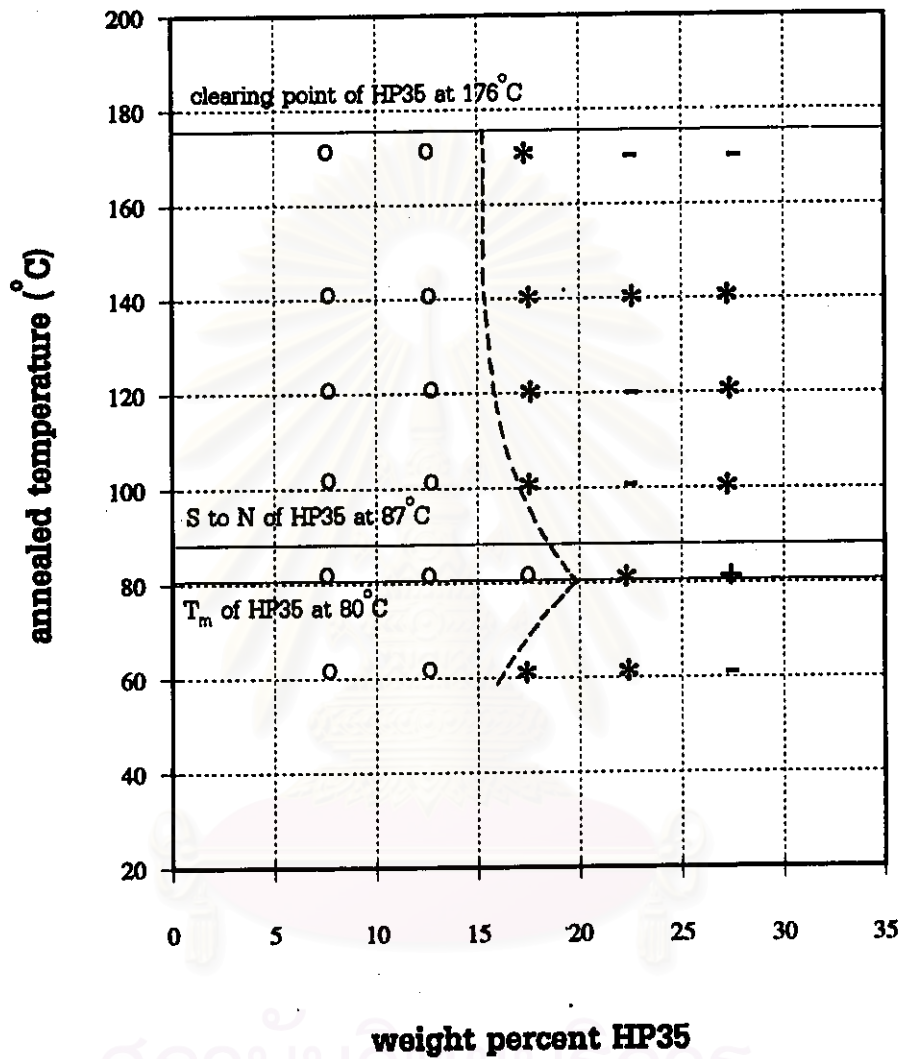
Figure 5-17 Phase diagram at low concentration of system III: PC and HP35 constructed by gradient method. o represents absolutely partially miscible region. + represents possibly partially miscible region. - represents possibly immiscible region. * represents absolutely immiscible region and ---------- represents phase separation line.

5.5.4 Scanning Electron Microscope (SEM) of System III: PC & HP35

Scanning electron micrograph of 10 percent by weight of HP35 with PC, which annealed at 140°C, and 25 percent by weight of HP35 with PC, which annealed at 120°C, were shown in Figure 5-18 and Figure 5-19, respectively.

Sample of 10 percent by weight HP35 with PC, which annealed at 140 $^{\circ}$C, revealed a HP35 particles distributed in gray area of texture as shown in Figure 5-18. This was considered to be the partially miscible phase behaviour of the blends which consisted of two phases. The first phase was most likely to be the particle of HP35. The second phase, which was the gray area of texture in the picture, was most likely to be the blend between HP35 with PC.

Sample of 25 percent by weight of HP35 with PC, which annealed at 120°C, showed phase separation of the blends. It revealed three phases as shown in Figure 5-19. The first phase was fine grains distributed in the texture and most likely to be the unmixed PC. The second phase was a group of undissolved HP35 and the third phase was the gray area in the texture which was almost likely to be the amorphous blend of HP35 with PC.

The morphology of two samples determined by SEM presented above was consistent with the phase behaviour determined from the DSC results.
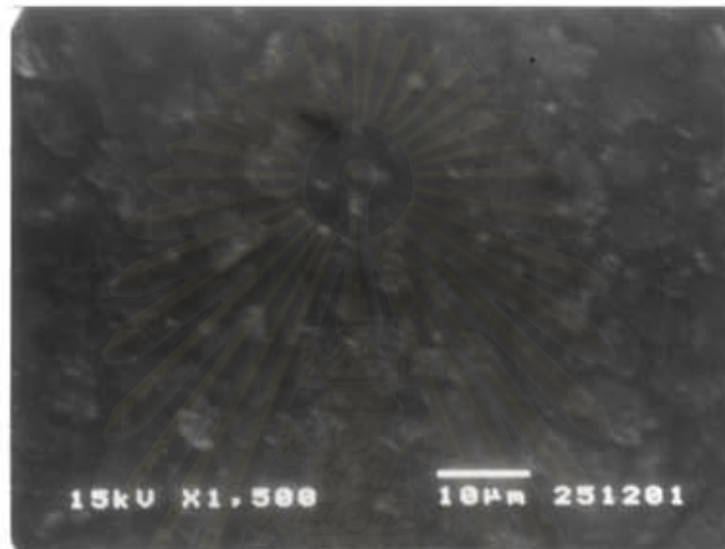
Figure 5-18 Scanning electron micrograph (x1500) of 10 percent by weight of
HP35 with PC, which annealed at 140°C.
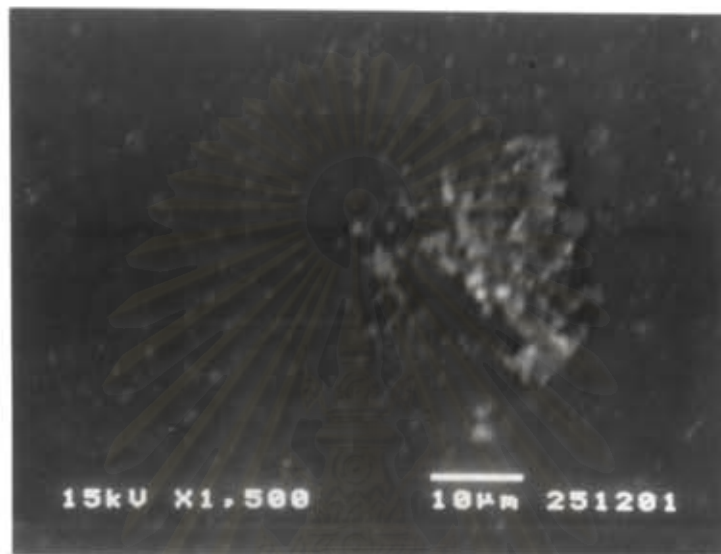
Figure 5-19 Scanning electron micrograph (x1500) of 25 percent by weight of HP35 with PC, which annealed at 120°C.

5.6 SYSTEM IV: Poly(bisphenol A carbonate) & HP5N

The blends at low concentration of HP5N (5.2, 10.1, 15.0, 19.9, 25.0 and 30.0 percent by weight) with PC were prepared and phase behaviour were studied at various annealed temperatures, which are the same as in the system III: PC and HP35, i.e. $60^{\circ}C$, $80^{\circ}C$, $100^{\circ}C$, $120^{\circ}C$, $140^{\circ}C$ and $170^{\circ}C$.

The transition temperatures of the blends detected by differential scanning calorimeter (DSC) were shown in Table 5-21 and examples of DSC thermograms of 15 percent by weight HP5N with PC, which annealed at $170^{\circ}C$, and 25 percent by weight HP5N with PC, which annealed at $170^{\circ}C$, were shown in Figure 5-20.

5.6.1 Effects of HP5N on Poly(bisphenol A carbonate) (PC)

From Table 5-21, it can be seen that the glass transition temperatures (T_g) of PC rich phase in the blends at every weight percent HP5N with PC and annealed temperatures used in the experiment were depressed from the T_g of 100% PC (0 percent by weight HP5N). This phenomenon proved that HP5N can act as plasticizer of PC.

The melting temperatures (T_m) of PC rich phase were not observed at low weight percent HP5N with PC but they were detected at higher concentrations as shown in Table 5-21. It is interesting to notice that at $60^{\circ}C$ the T_m of PC rich phase in the blends were depressed from $221.4^{\circ}C$ (10.1 percent by weight HP5N with PC) to $209.8^{\circ}C$ (19.9 percent by weight HP5N with PC). And

Table 5-21 Transition temperatures detected by differential scanning calorimeter (DSC) of system IV : PC & HP5N.

Annealed temp. (°C)	% by weight HP5N	T_g of PC rich phase in blends (°C)	T_m of HP5N rich phase in blends (°C)	T_m of PC rich phase in blends (°C)
60	0.0(100% PC)	144.6	-	-
	5.2	123.8	-	-
	10.1	108.5	-	221.4
	15.0	95.7	-	212.8
	19.9	92.0	112.7	209.8
	25.0	63.4	110.8	206.2
	30.0	61.6	110.6	204.9
80	0.0(100% PC)	144.9	-	-
	5.2	125.0	-	-
	10.1	107.9	-	-
	15.0	90.9	-	-
	19.9	77.4	110.6	-
	25.0	75.0	110.4	207.5
	30.0	74.4	109.6	205.0
100	0.0(100% PC)	144.7	-	-
	5.2	125.6	-	-
	10.1	102.4	-	-
	15.0	92.6	111.0	-
	19.9	81.1	111.2	-
	25.0	81.1	111.4	207.9
	30.0	82.3	111.3	205.1

Table 5-21 Transition temperatures detected by differential scanning calorimeter (DSC) of system IV : PC & HP5N. (continued)

Annealed temp. ($^{\circ}$C)	% by weight HP5N	T_g of PC rich phase in blends ($^{\circ}$C)	T_m of HP5N rich phase in blends ($^{\circ}$C)	T_m of PC in rich phase blends ($^{\circ}$C)
120	0.0(100% PC)	145.1	-	-
	5.2	121.9	-	-
	10.1	107.3	-	-
	15.0	93.7	-	-
	19.9	81.8	111.3	-
	25.0	77.7	111.5	206.3
	30.0	78.0	111.5	204.1
140	0.0(100% PC)	144.2	-	-
	5.2	123.7	-	-
	10.1	107.3	-	234.2
	15.0	93.3	-	208.1
	19.9	79.7	111.6	206.7
	25.0	70.0	111.6	205.9
	30.0	69.6	111.9	202.9
170	0.0(100% PC)	144.8	-	-
	5.2	123.8	-	-
	10.1	104.3	-	-
	15.0	96.7	-	-
	19.9	80.5	-	-
	25.0	70.7	111.9	207.9
	30.0	75.3	112.0	205.2
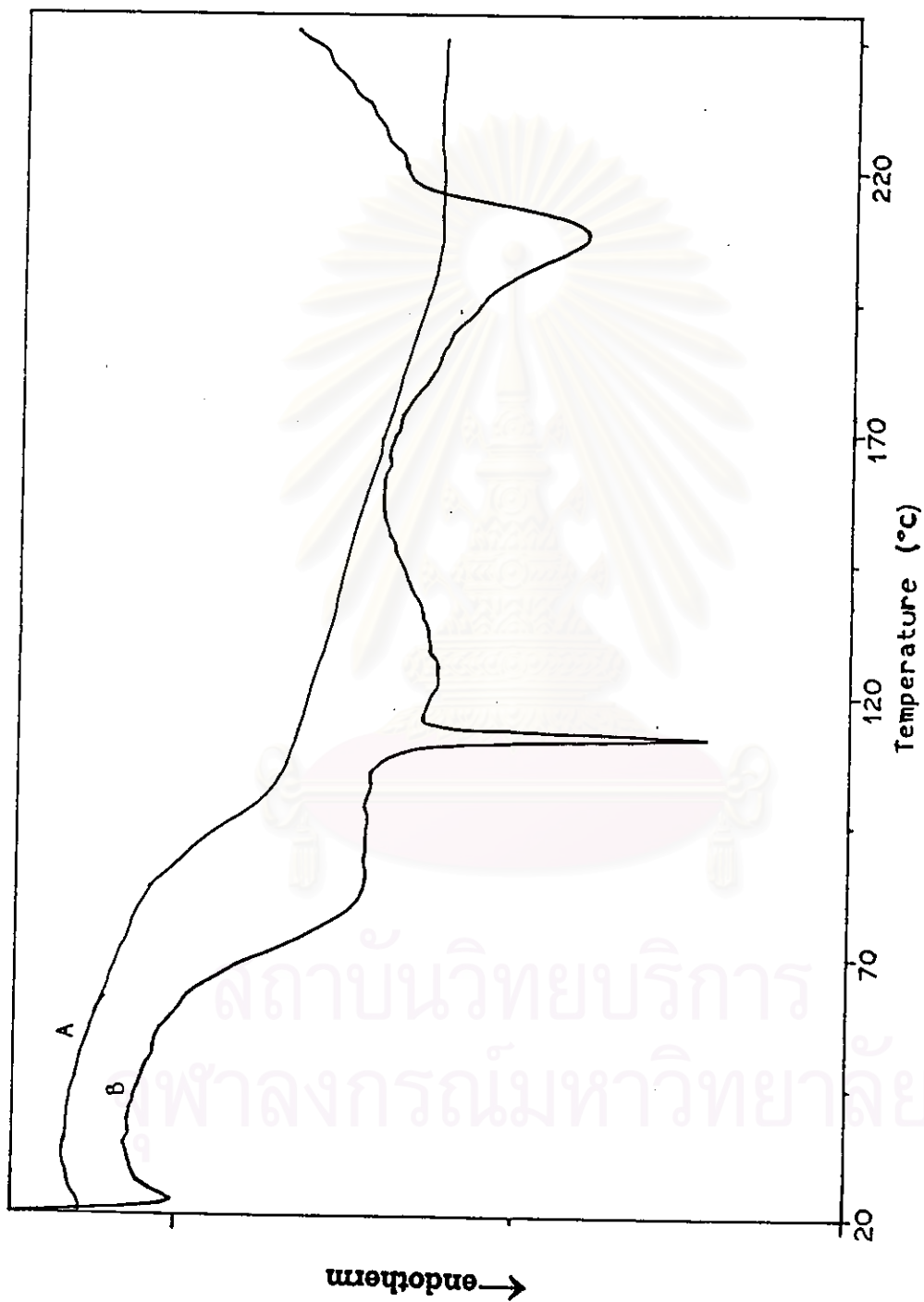
Figure 5-20 The DSC thermograms of the blends of PC and HP5N. Curve A: 15% by weight of HP5N, which annealed at 170°C. Curve B: 25% by weight of HP5N, which annealed at 170°C.

at 140°C, the T_m of PC rich phase in the blends were depressed from 234.2°C (10.1 percent by weight HP5N with PC) to 208.1°C (15.0 percent by weight HP5N with PC). This melting point depression of PC rich phase in the blends implies miscibility of the blends at these concentrations and annealed tempertures as predicted by Nishi-Wang equation [Olabisi, 1979].

5.6.2 The Transition Temperature of HP5N in the Blends

The melting temperatures (T_m) of HP5N rich phase in the blends cannot be observed in DSC thermograms at low weight percent HP5N with PC as shown in Table 5-21. The disappearance of the T_m of HP5N rich phase in the blends should be due to low content of HP5N in the blends such that it cannot be detected by DSC or HP5N in the blends were almost absolutely dissolved completely in PC.

However, at every annealed temperatures and concentration from 19.9 percent by weight of HP5N upward, the T_m of HP5N rich phase can be detected. The T_m of HP5N rich phase in the blends detected in the experiments were rather consistent with the T_m of pure HP5N (111°C). As predicted by Nishi-Wang equation [Olabisi, 1979], the crystalline melting temperature that did not change implies that the system has the immiscible characteristic. Hence, these results suggested that at these concentrations and annealed tempeartures the HP5N was immiscible with PC.

5.6.3 Phase Diagram Construction

Phase diagram constructed by the method of depression trend and the gradient method were presented below.

5.6.3.1 Phase Diagram Construction by Method of Depression Trend of System IV: PC & HP5N

To clearly monitor the relation between weight percent HP5N with PC and T_g of PC rich phase in the blends at each annealed temperature, Figure 5-21a and Figure 5-21b were made. The relation that can be drawn from these figures were shown in Table5-22.

Phase behaviour of the blends, in which the T_g of PC rich phase is decreased when the weight percent of HP5N with PC is increased, were determined as partially miscible, and represented with o symbol. For the blends that the T_g of PC rich phase are quite constant or T_g is increased from the previous T_g data, phase behaviour were determined as immiscible and represented with * symbol. The phase diagram that was constructed by the method of depression trend was shown in Figure 5-22.

5.6.3.2 Phase Diagram Constructed by the Gradient Method of System IV: PC & HP5N

The gradient method construction procedure was described previously in section 5.2 (phase diagram construction procedure). The T_g of PC rich phase in the blends were reported in Table 5-23. Then the gradient value were calculated as shown in Table 5-24. Phase behaviour of the blends were determined from gradient values which can be divided into four regions based on criteria in Table 5-7. In Table 5-25 symbol that represented each phase behaviour was shown. The phase diagram of system IV: PC and HP5N was constructed as shown in Figure 5-23.

From the estimated phase separation line, both phase diagrams at low concentration of system IV: PC and HP5N, (Figure 5-22 and Figure 5-23) seem to be the immiscible loop with upper and lower critical phase boudaries inverted. Example of this type of phase diagram was shown in Figure 3-2f.

There were different regions identified from the two methods at some points in diagram due to more details of the gradient method. The partially miscible region (o) in method of depression trend can be divided to be the absolutely partially miscible region (o) and the possibly partially miscible region (+) in the gradient method. In the same way, the immiscible region (*) in the method of depression trend can be divided to be the absolutely immiscible region (*) and the possibly immiscible region (-) in the gradient method.
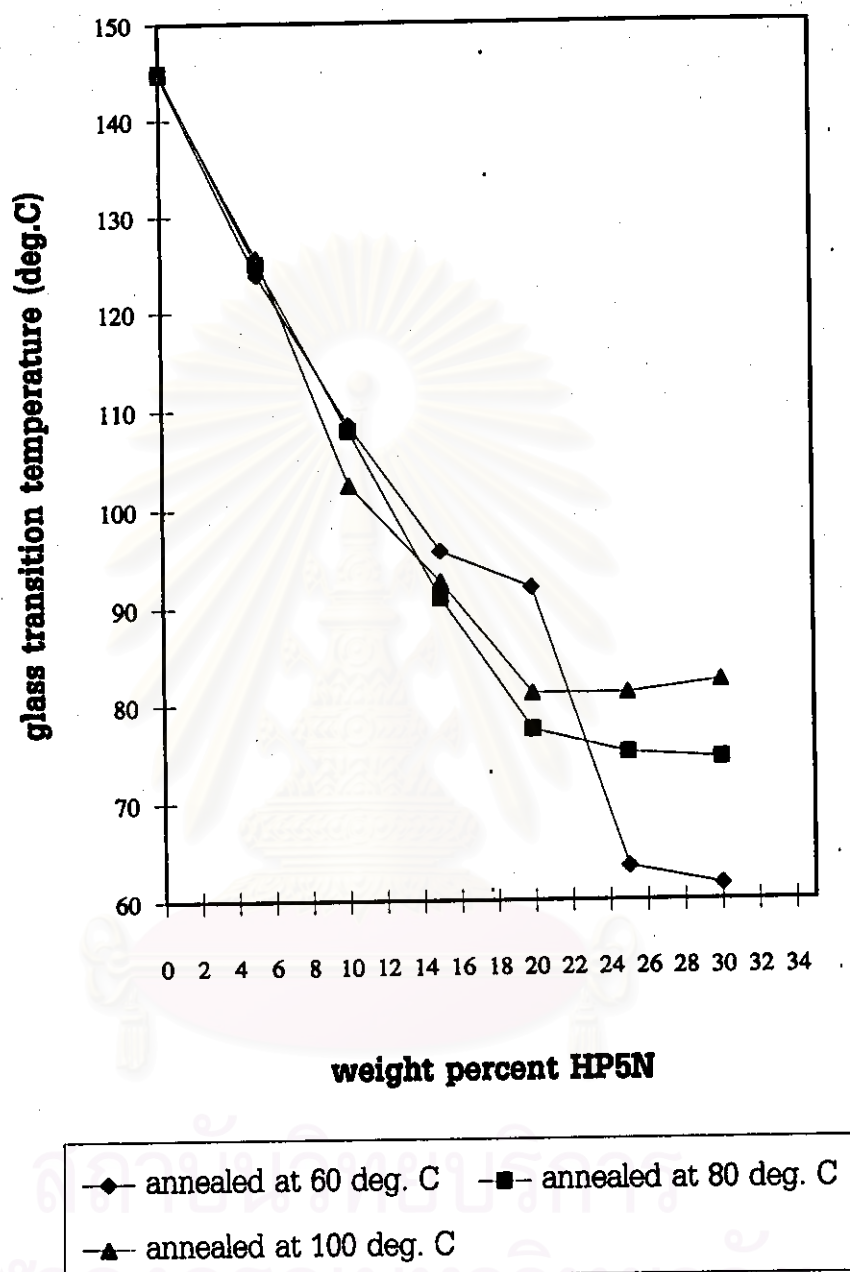
Figure 5-21a Glass transition temperatures depression in the blends of system IV: PC & HP5N annealed at 60°C, 80°C and 100°C.
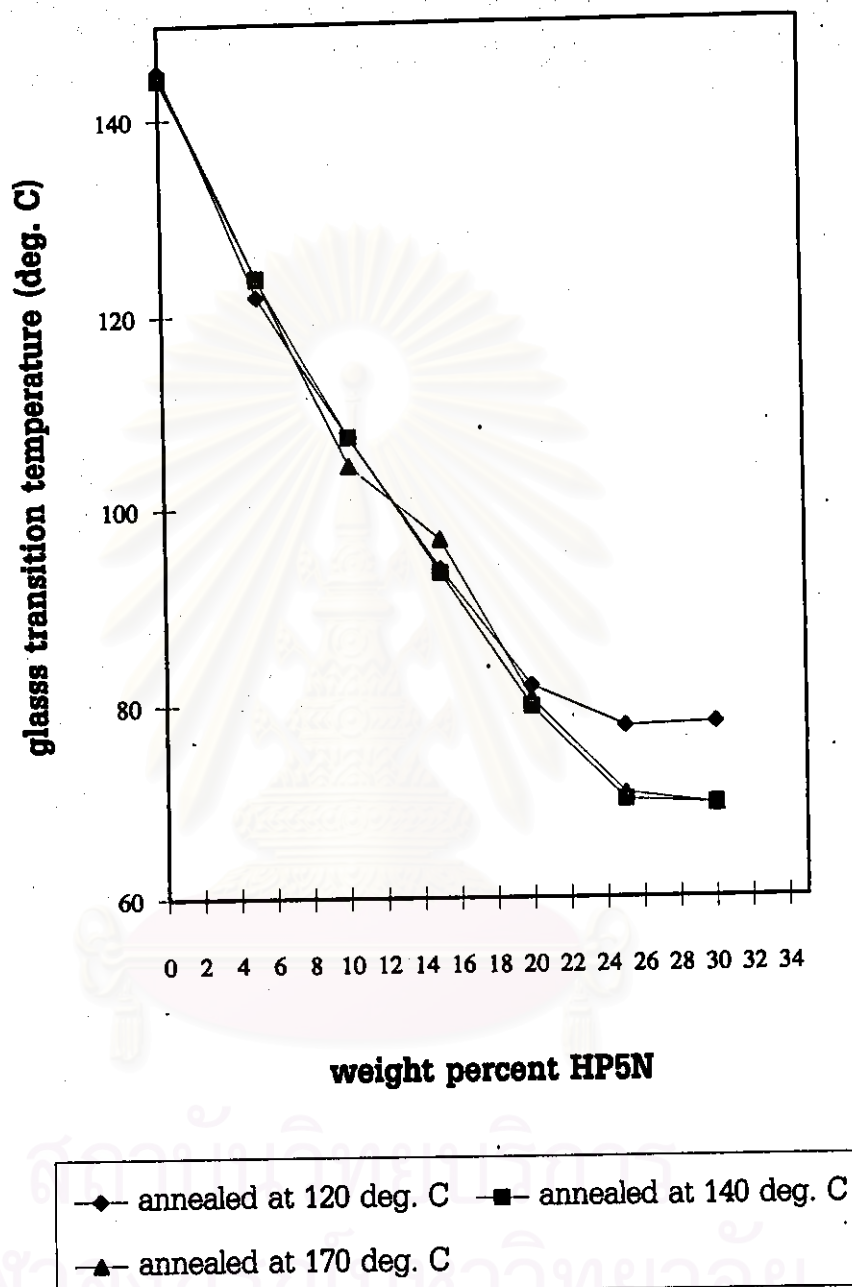
Figure 5-21b Glass transition temperatures depression in the blends of system
IV: PC & HP5N annealed at 120°C, 140°C and 170°C.

Table 5-22 Relation between the T_g of the PC rich phase in the blends and weight percent HP5N with PC.

Annealed temp. ($^{\circ}$C)	Weight percent HP5N	
	Decreasing T_g o	Increasing T_g or constant T_g *
60	5.2-25.0	25.0-30.0
80	5.2-20.0	20.0-30.0
100	5.2-20.0	20.0-30.0
120	5.2-25.0	25.0-30.0
140	5.2-25.0	25.0-30.0
170	5.2-25.0	25.0-30.0
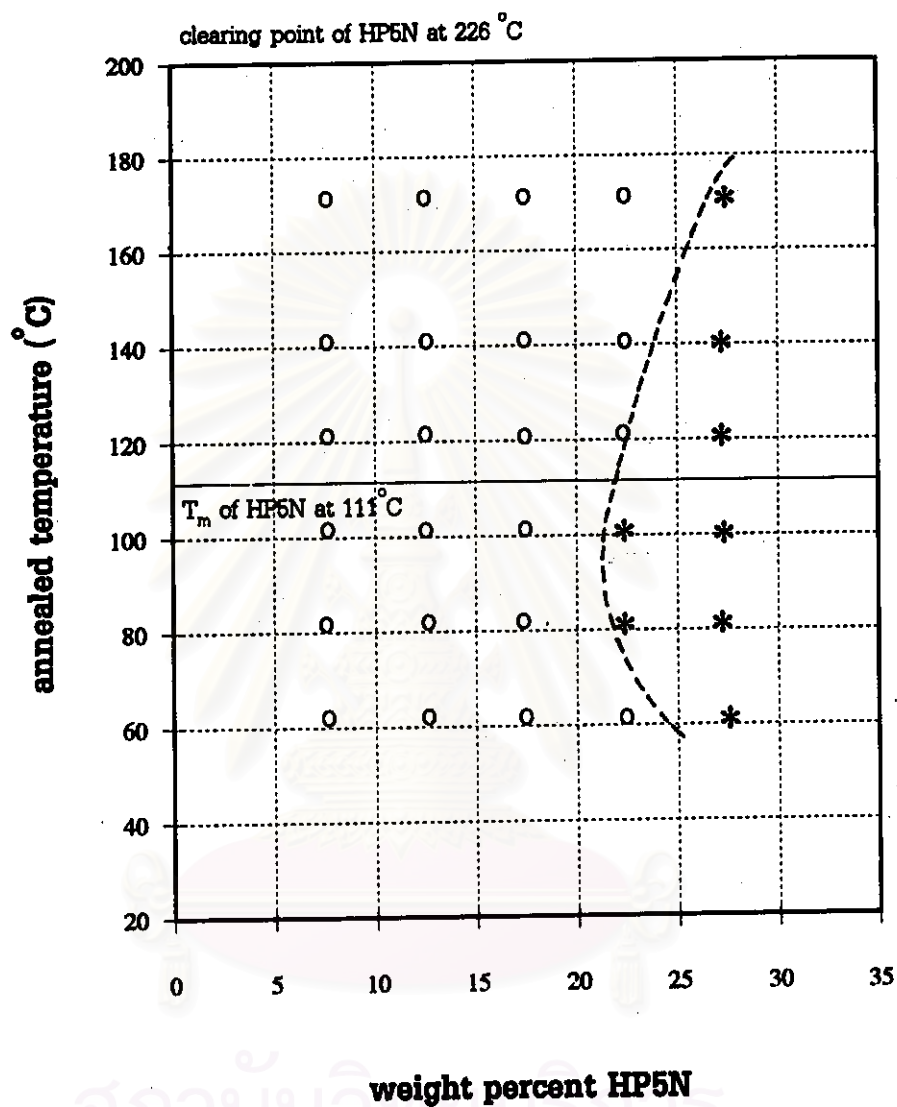
Figure 5-22 Phase diagram at low concentration of system IV: PC and HP5N constructed by method of depression trend. o represents partially miscible region and * represents immiscible region. And ----- represents phase separation line.

Table 5-23 The glass transition temperatures (T_g) of PC rich phase in the blends of HP5N and PC detected by differential scanning calorimeter (DSC) at each annealed temperature and weight percent HP5N with PC.

Annealed temp. (°C) / Weight percent HP5N	60	80	100	120	140	170
5.2	123.8	125.0	125.6	121.9	123.7	123.8
10.1	108.5	107.9	102.4	107.3	107.3	104.3
15.0	95.7	90.9	92.6	93.7	93.3	96.7
19.9	92.0	77.4	81.1	81.8	79.7	80.5
25.0	63.4	75.0	81.1	77.7	70.0	70.7
30.0	61.6	74.4	82.3	78.0	69.6	69.5

Table 5-24 Gradient value of system IV: PC & HP5N.

Annealed temp. (°C) / Weight percent HP5N	60	80	100	120	140	170
5.2-10.0	-3.122	-3.490	-4.735	-2.980	-3.347	-3.980
10.1-15.0	-2.612	-3.469	-2.000	-2.776	-2.857	-1.551
15.0-20.0	-0.755	-2.755	-2.347	-2.429	-2.776	-3.306
20.0-25.0	-5.608	-0.471	0.000	-0.804	-1.902	-1.922
25.0-30.0	-0.360	-0.120	0.240	0.060	-0.080	-0.240

Table 5-25 Four regions divided from gradient value of system IV: PC & HP5N.
o represents absolutely partially miscible region, + represents
possibly partially miscible region, - represents possibly immiscible
region and * represents absolutely immiscible region.

Annealed temp. (°C) Weight percent HP5N	60	80	100	120	140	170
5.2-10.0	-3.122 o	-3.490 o	-4.735 o	-2.980 o	-3.347 o	-3.980 o
10.1-15.0	-2.612 o	-3.469 o	-2.000 o	-2.776 o	-2.857 o	-1.551 o
15.0-20.0	-0.755 +	-2.755 o	-2.347 o	-2.429 o	-2.776 o	-3.306 o
20.0-25.0	-5.608 o	-0.471 -	0.000 -	-0.804 +	-1.902 o	-1.922 o
25.0-30.0	-0.360 -	-0.120 -	0.240 -	0.060 -	-0.080 -	-0.240 -

clearing point of HP5N at 226 $^{\circ}$C

annealed temperature ($^{\circ}$C)

T$_m$ of HP5N at 111°C

weight percent HP5N
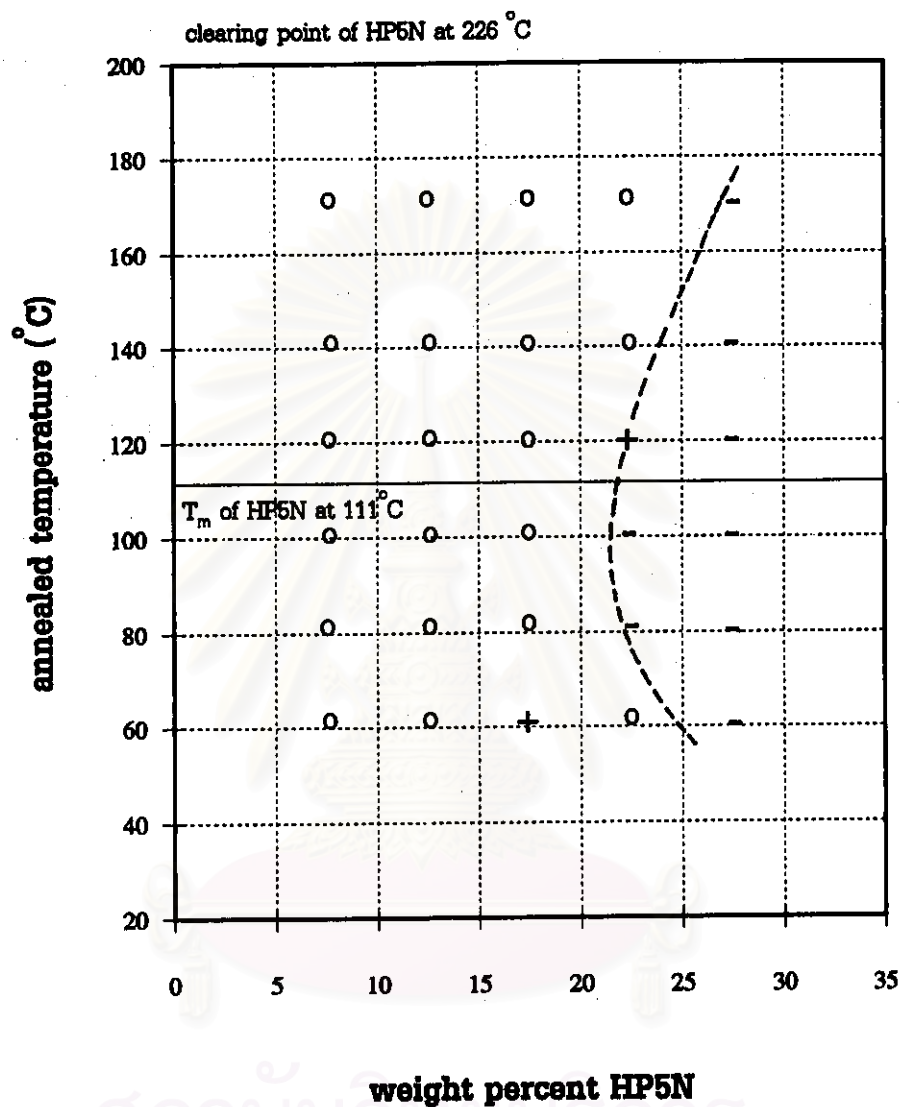
Figure 5-23 Phase diagram at low concentration of system IV: PC and HP5N constructed by gradient method. o represents absolutely partially miscible region. + represents possibly partially miscible region. − represents possibly immiscible region. * represents absolutely immiscible region and ------- represents phase separation line.

5.6.4 Scanning Electron Microscope (SEM) of System IV: PC & HP5N

Scanning electron micrograph of 20 percent by weight of HP5N with PC, which annealed at 120°C, and 30 percent by weight of HP5N with PC, which annealed at 140°C, were shown in Figure 5-24 and Figure 5-25, respectively.

Sample of 20 percent by weight of HP5N with PC, which annealed at 120°C, revealed HP5N particles distributed in gray area of texture as shown in Figure 5-24. This was considered to be the partially miscible phase behaviour of the blends which consisted of two phases. The first phase was most likely to be the particle of HP5N. The second phase, which was the gray area of texture in the picture, was most likely to be the blend between HP5N with PC.

Sample of 30 percent by weight of HP5N with PC, which annealed at 140°C, showed phase separation of the blends and revealed three distinct phases as shown in Figure 5-25. The first phase was a group of fine grains distributed in the texture and most likely to be the unmixed PC. The second phase was a HP5N crystal at the top left side of the picture and the third phase was the gray area in the texture which was most likely to be the blend between of HP5N with PC.

Phase behaviour of the two SEM samples were consistent with phase behaviour determined from DSC results.

Figure 5-24 Scanning electron micrograph (x 1000 magnification) of 20 percent
by weight of HP5N with PC, which annealed at 120°C.
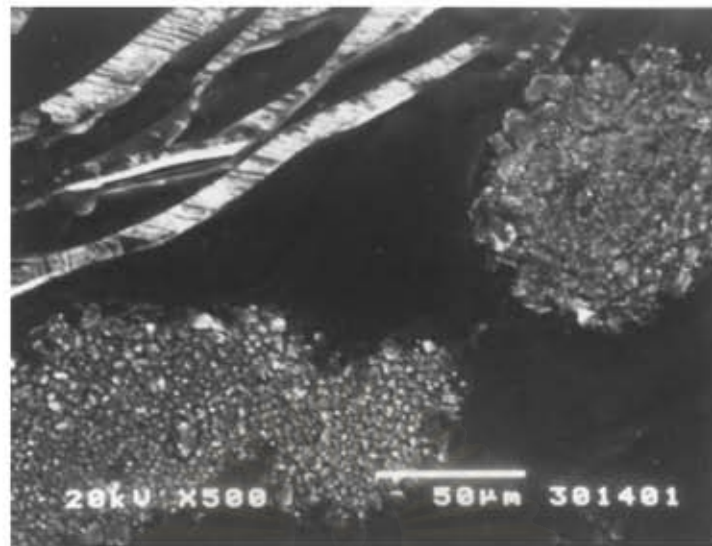
(a)
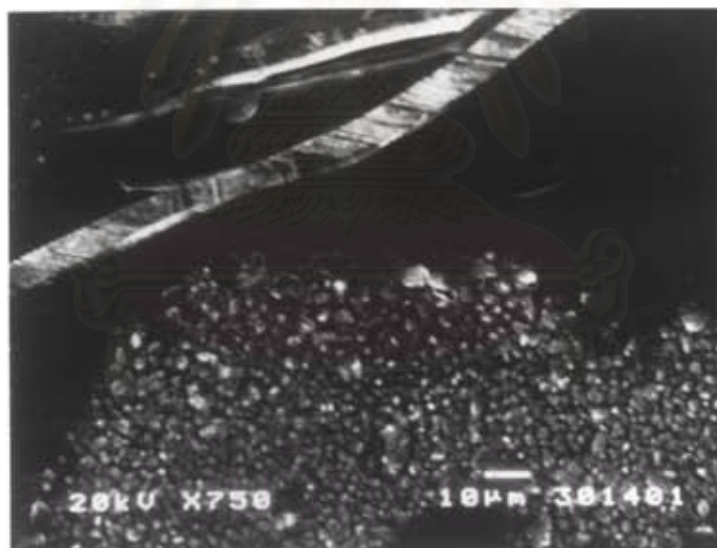
(b)

Figure 5-25 Scanning electron micrograph of 30 percent by weight of HP5N with PC, which annealed at 140°C. (a) the lower magnification (x500). (b) the higher magnification (x750).

5.7 Discussion of the Results between Systems

5.7.1 Comparison of the Effects of HP35 and HP5N on Polystyrene (PS)

Both HP35 and HP5N can act as plasticizers of PS, as discussed previously in section 5.3.1 (effects of HP35 on PS) and section 5.4.1 (effects of HP5N on PS), respectively. However, it is interesting to consider which is the better plasticizer for PS.

The question was solved by comparing the decreasing of T_g of the PS in the blends with HP35 and HP5N at the same weight percent and the same annealed temperatures. The better plasticizer is the one that can decrease the T_g of the PS in the blends more than the other. This can be clearly seen in the graphs (Figure 5-26 to Figure 5-30) between annealed temperature and the T_g of PS rich phase in the blends. The conclusion can be presented belows.

1. At 5 percent by weight, HP5N is the better plasticizer than HP35 at every annealed temperatures examined in this study, as shown in Figure 5-26.

2. At 10 percent by weight, HP35 is the better plasticizer than HP5N at every annealed temperatures examined in this study, as shown in Figure 5-27. This should be due to the limit of miscibility of HP5N with PS. The HP5N can be dissolved in PS only up to 5.0 percent by weight (see section 5.4.3.2). So, at 10 percent by weight, HP5N is not a good plasticizer of PS.
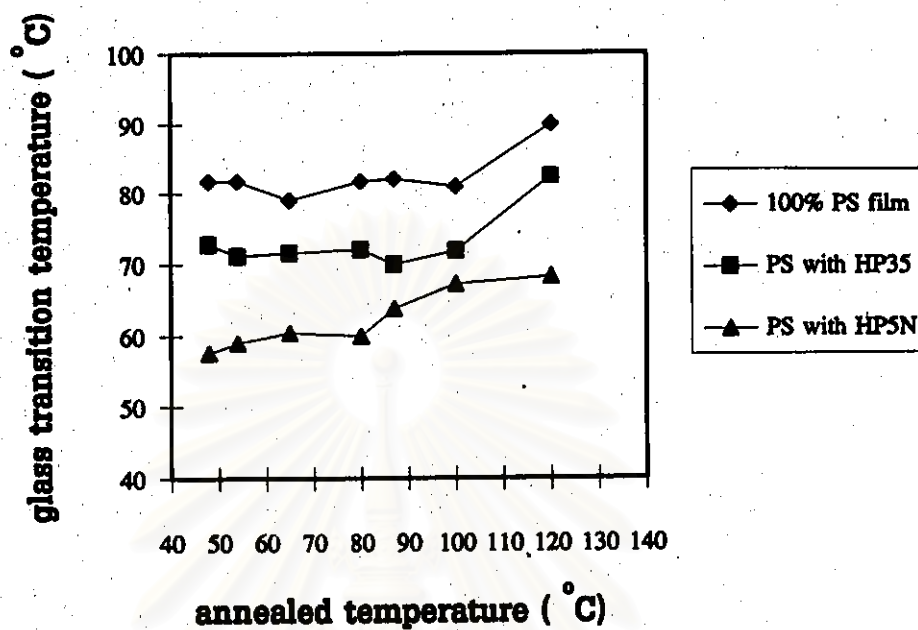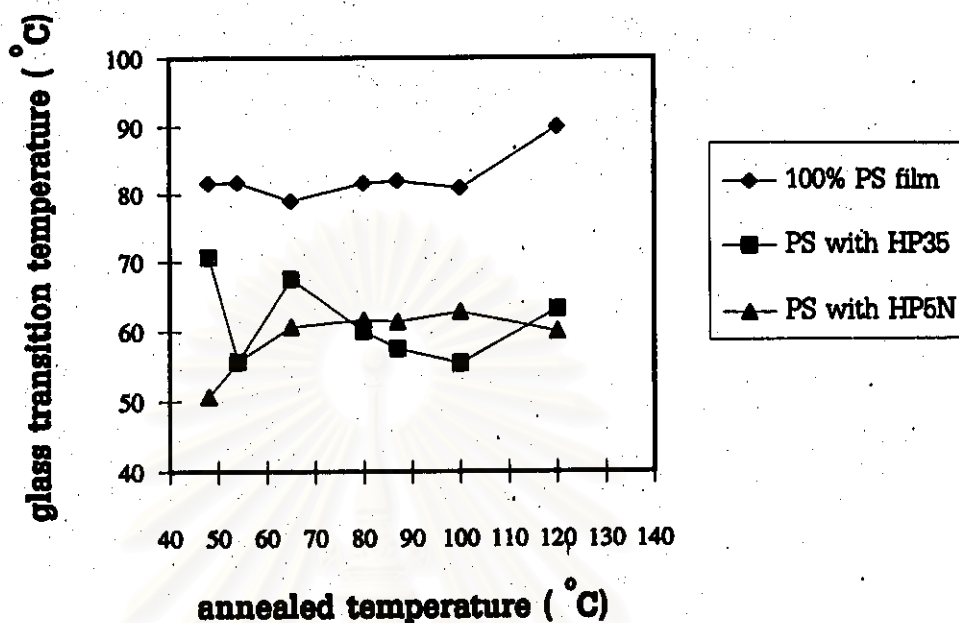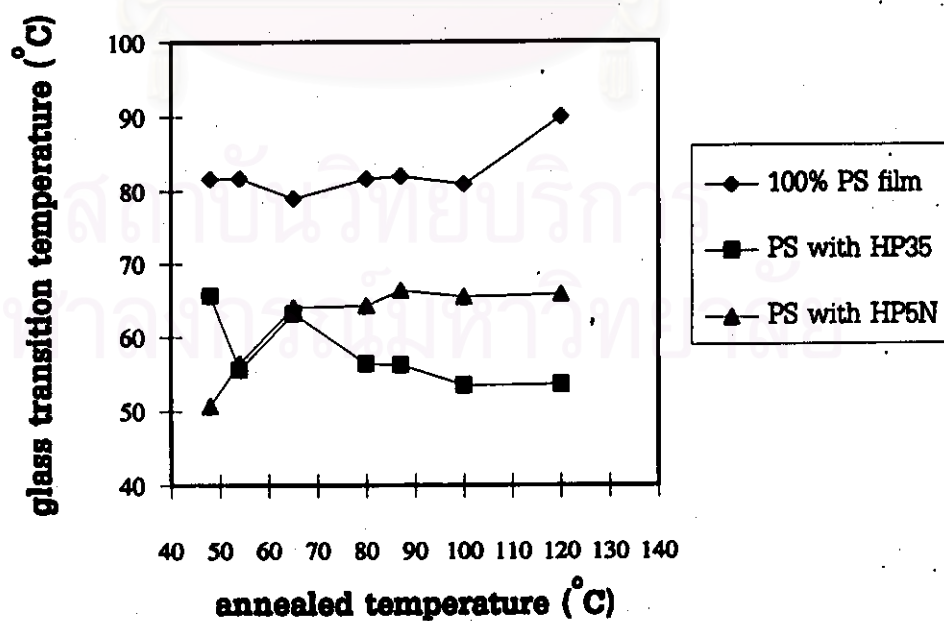
Figure 5-26 The glass transition temperatures of PS in the blends at 5 weight percent HP35 and HP5N.
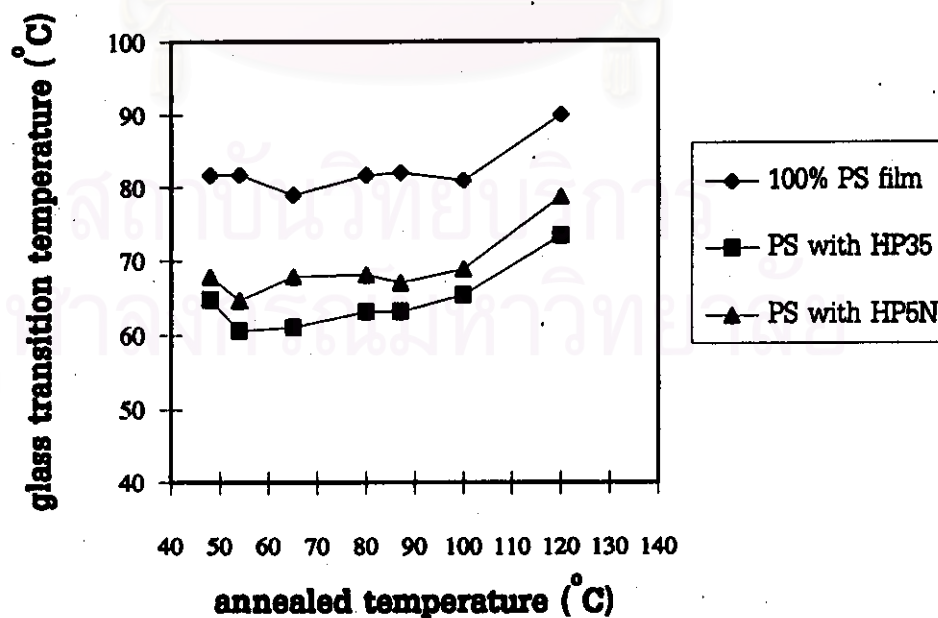
Figure 5-27 The glass transition temperatures of PS in the blends at 10 weight percent HP35 and HP5N.
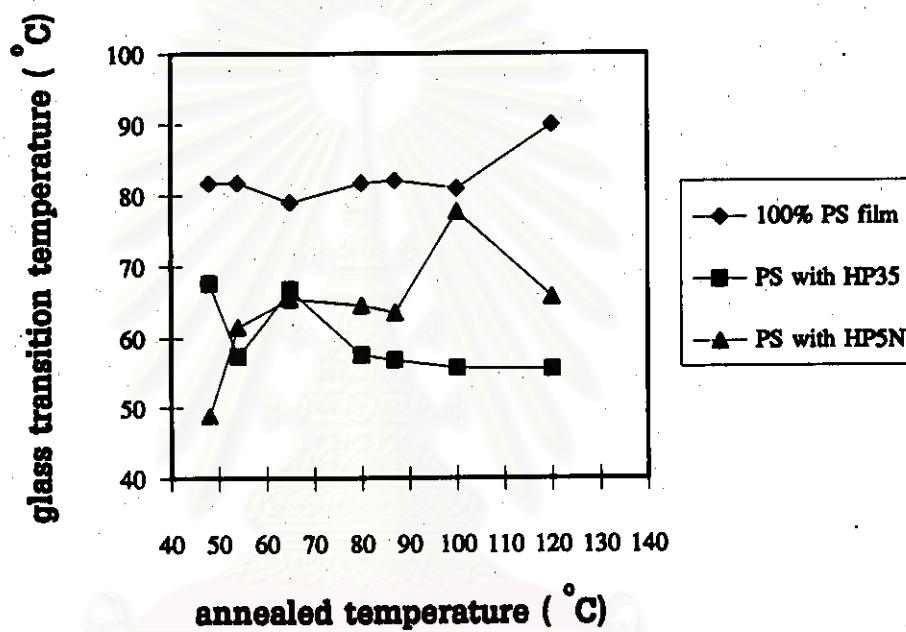
3. The plasticizer effects of HP35 and HP5N on PS in the blends at 15, 20 and 25 percent by weight can be divided into two parts:

The first part was the blends that were annealed below $80^{\circ}C$. In this part, the T_g-s data were scattered such that it cannot be determined which one is better plasticizer.

The second part was the blend that were annealed at $80^{\circ}C$ and other higher temperatures. In this part, the blends with HP35 had lower T_g than the blends with HP5N. The result showed that the HP35 was the better plasticizer for PS than the HP5N.

From the above conclusions, it can be seen that the effects of HP35 and HP5N on PS depended on the weight percent of HP35 or HP5N in PS and the annealed temperature.
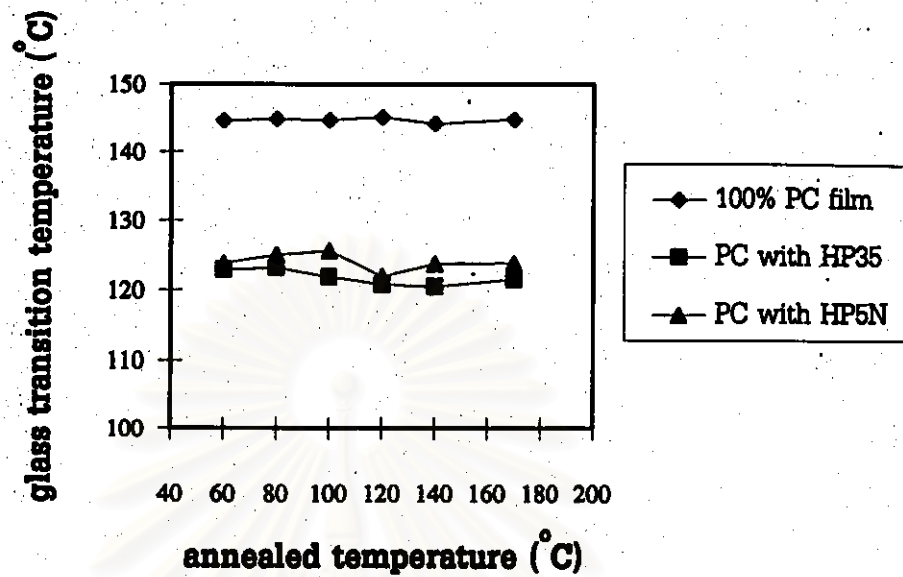
Figure 5-28 The glass transition temperatures of PS in the blends at 15 weight percent HP35 and HP5N.
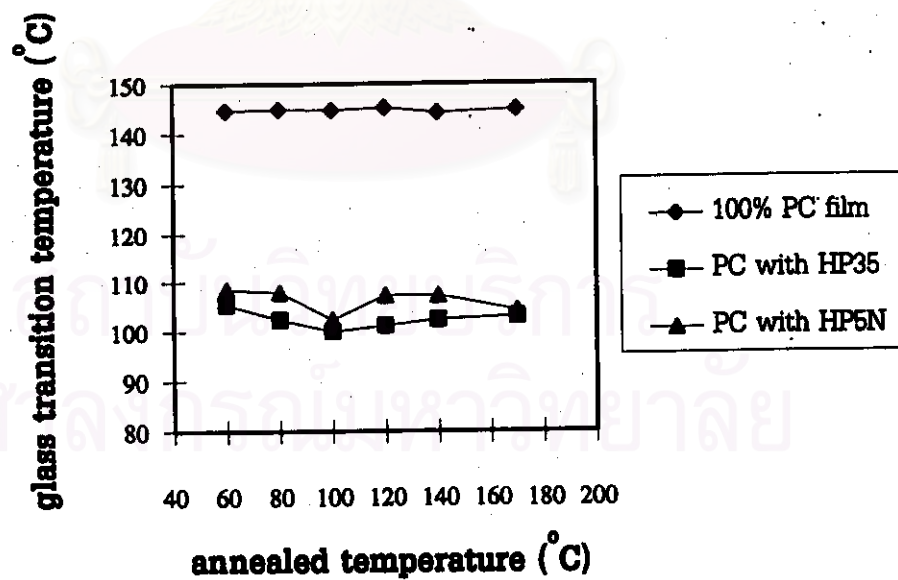

Figure 5-29 The glass transition temperatures of PS in the blends at 20 weight percent HP35 and HP5N.

Figure 5-30 The glass transition temperatures of PS in the blends at 25 weight percent HP35 and HP5N.

5.7.2 Comparison of the Effects of HP35 and HP5N on Poly(bisphenol A carbonate) (PC)

The comparison between HP35 and HP5N as the plasticizer for PC were made in the same way as for PS, that was described previously in section 5.7.1 (comparison of the effects of HP35 and HP5N on PS). The conclusions were presented below.

1. At 5, 10 and 15 percent by weight: HP35 was as good as HP5N to plasticize PC, for every annealed temperatures examined in this study, as shown in Figures 5-31,32,33, respectively.

2. At 20, 25 and 30 percent by weight: HP5N was the better plasticizer than HP35, for every annealed temperatures examined in this study, as shown in Figure, 5-34,35,36, respectively.

Figure 5-31 The glass transition temperatures of PC in the blends at 5 weight percent HP35 and HP5N.

Figure 5-32 The glass transition temperatures of PC in the blends at 10 weight percent HP35 and HP5N.
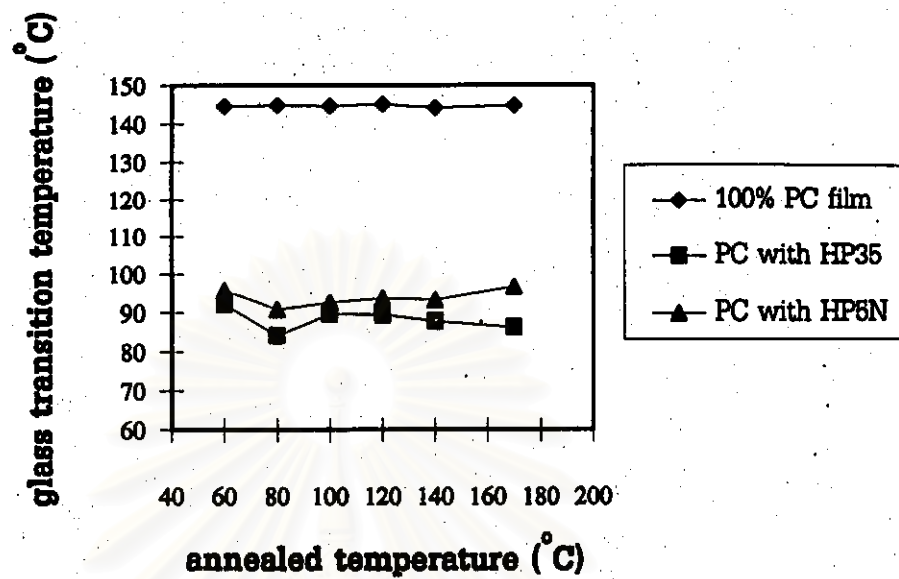
Figure 5-33 The glass transition temperatures of PC in the blends at 15 weight percent HP35 and HP5N.
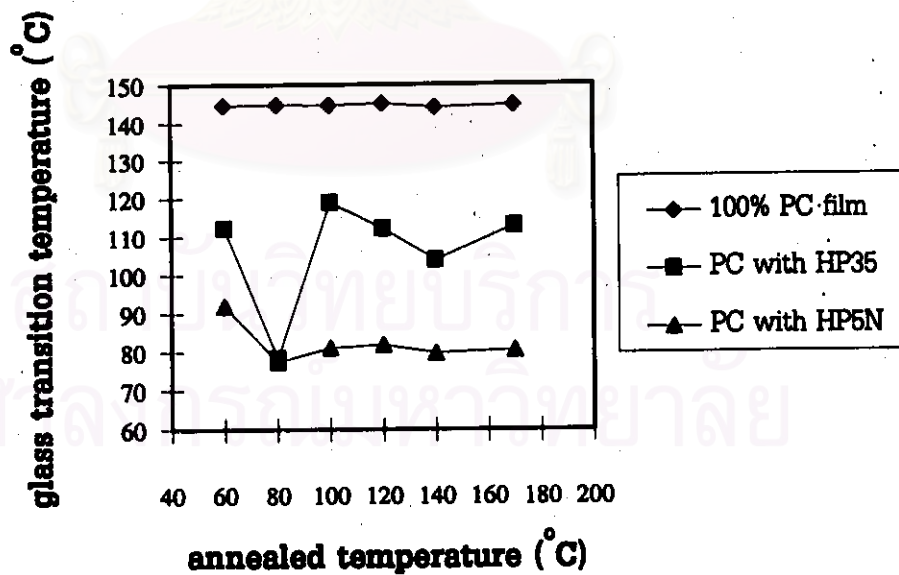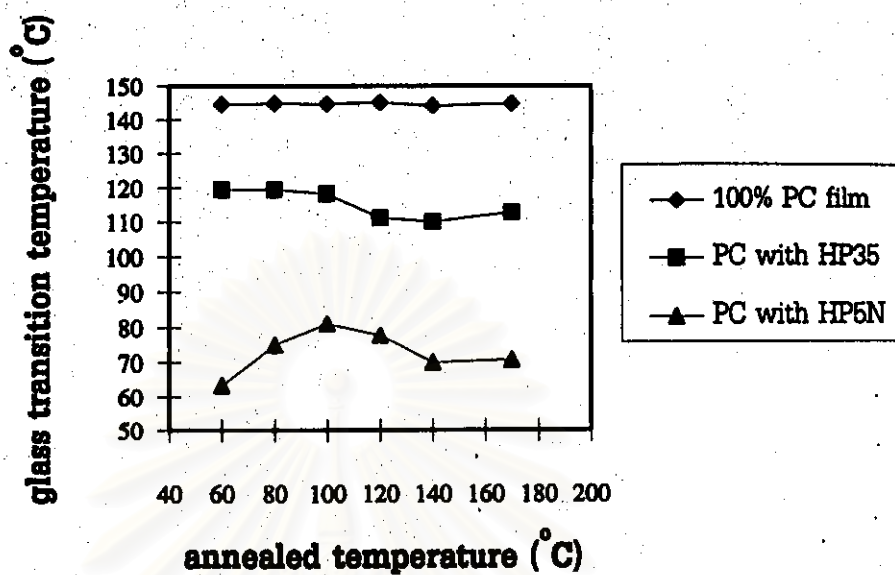

Figure 5-34 The glass transition temperatures of PC in the blends at 20 weight percent HP35 and HP5N.

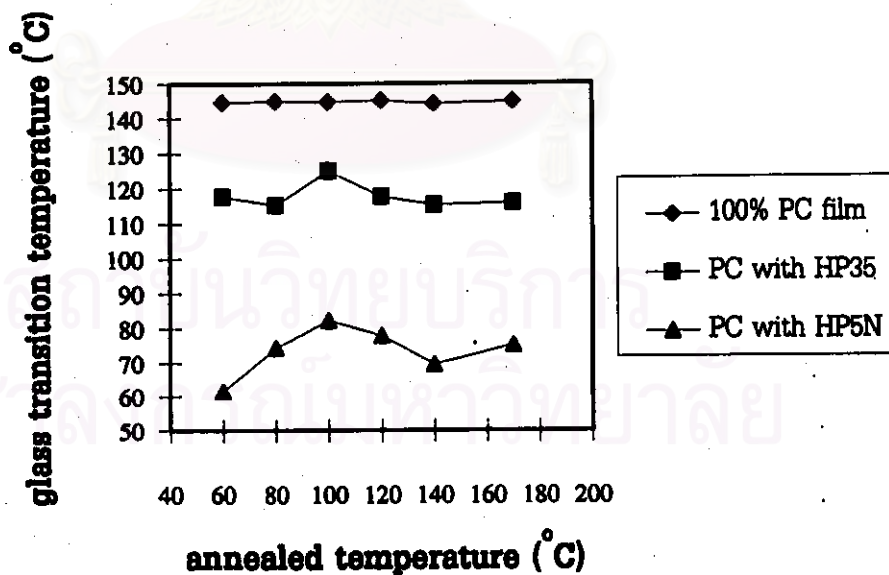**Figure 5-35** The glass transition temperatures of PC in the blends at 25 weight percent HP35 and HP5N.

Figure 5-36 The glass transition temperatures of PC in the blends at 30 weight percent HP35 and HP5N.

5.7.3 Comparison of the Effects of HP35 on PC and PS

From constructed phase diagrams of system I: PS & HP35 (Figures 5-2,5) and system III: PC & HP35 (Figures 5-16,17), it can be seen that the blends of PS and HP35 exhibited partially miscible behaviour under 12.7 percent by weight of HP35 with PS, and the blends of PC and HP35 exhibited partially miscible behaviour under 15.0 percent by weight of HP35 with PC. From above results, it can be seen that HP35 had the partially miscible region with PC in the broader range than with PS, so HP35 was more compatible with PC than PS.

5.7.4 Comparison of the effects of HP5N on PS and PC

From constructed phase diagrams of system II: PS & HP5N (Figures 5-10, 5-11) and system IV: PC & HP5N (Figures 5-22,23), it can be seen that the blends of PS and HP5N exhibited partially miscible behaviour under 5.0 percent by weight HP5N with PS, and the blends of PC and HP5N exhibited partially miscible behaviour under 20.0 percent by weight HP5N with PC. From above results, it can be seen that HP5N had the partially miscible region with PC in the broader range than with PS, so HP5N was more compatible with PC better than PS.