Chapter 9

POLYAMIDE-6,9 WITH PHENOTHIAZINE

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9.1 Introduction

Chapter 9 deals with the blending of polyamide-6,9 with phenothiazine. In this case the melting temperature of the phenothiazine is lower than that of the polyamide-6,9 rather than the situation in Chapter 5 with the carbazole having a higher melting temperature than the polyamide-6,9.

Polyamide-6,9 is different from the other polyamides studied here in that it is not a polyamide-n type and it is an even-odd rather than even-even polyamide-m,n. The length of the diamine section of the repeat unit is moderate at 6 carbons and the diacid is reasonably long at 9 carbons. This means that the amide density is lower than the industry-standard polyamide-6 and polyamide-6,6 which should give more flexibility of the chains. The even-odd status will play its part in the ability of the chains to form hydrogen bonds as they crystallise and causes this polyamide to have the lowest melting temperature of the group of polyamides being studied here. The way in which this polyamide and phenothiazine interact is not easily predictable because of the less favourable matching of amide groups to form the bonds within the crystalline structure.

The previous two chapters on polyamide-4,6 or polyamide-6 blended with phenothiazine have started to show slightly less compatibility compared to their blends with carbazole and this chapter points again to some increase in phase separation.

9.2 Thermogravimetric Analysis

TGA results of the plateau level at 300 ^{0}C for samples taken from ampoules are compared in Figure 9-1 with the expected levels for polyamide from the weights of materials used in the ampoules. In most cases the actual values are close to the expected ones. There is only one sample in this set of polyamide-6,9/phenothiazine ampoule samples where the actual concentration deviated a considerable amount from the expected.

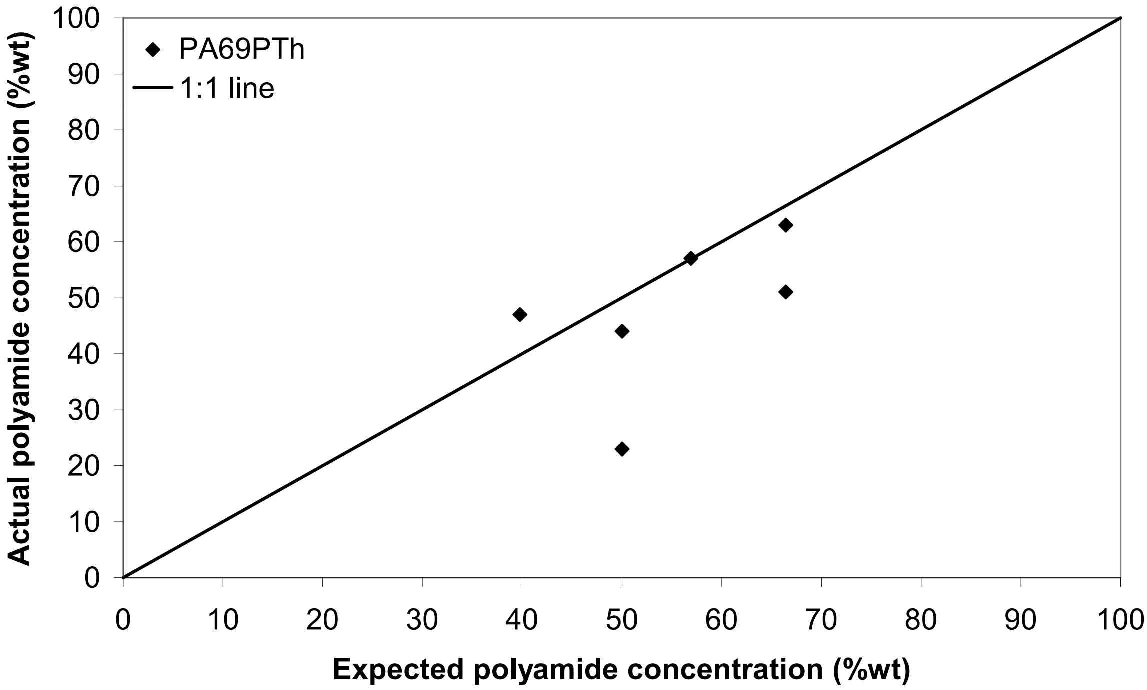

Figure 9-1 Actual vs expected weight percentage polyamide in samples from polyamide-6,9/phenothiazine ampoule samples.

That deviant data point had 27% polyamide with the "R4S4" TGA method and a separate sample from nearby in the bulk had shown 21% polyamide with the "straight" method, a reasonably consistent result. The ampoule had been one of those from just before the furnace profiles had been completely refined. This is, most likely, the reason for the deviation so far from the expected.

9.3 Differential Scanning Calorimetry

It was mentioned in Chapter 5 that polyamide-6,9 has a melting temperature close to 210 ^{0}C with crystallisation in the range 175-193 ^{0}C, depending on cooling rate.

9.3.1 Pan Melt Blending

9.3.1.1 Melting Temperatures for first heating ramp of dry powders at 5 ^{0}C/min

DSC thermograms are shown in Figure 9-2 for the first melting of powder samples of polyamide-6,9, phenothiazine and their mixtures at a heating rate of 5 ^{0}C/min. The thermograms for the first melting in DSC pans of polyamide-6,9, phenothiazine and three mixtures of the powders are shown in Figure 9-2.

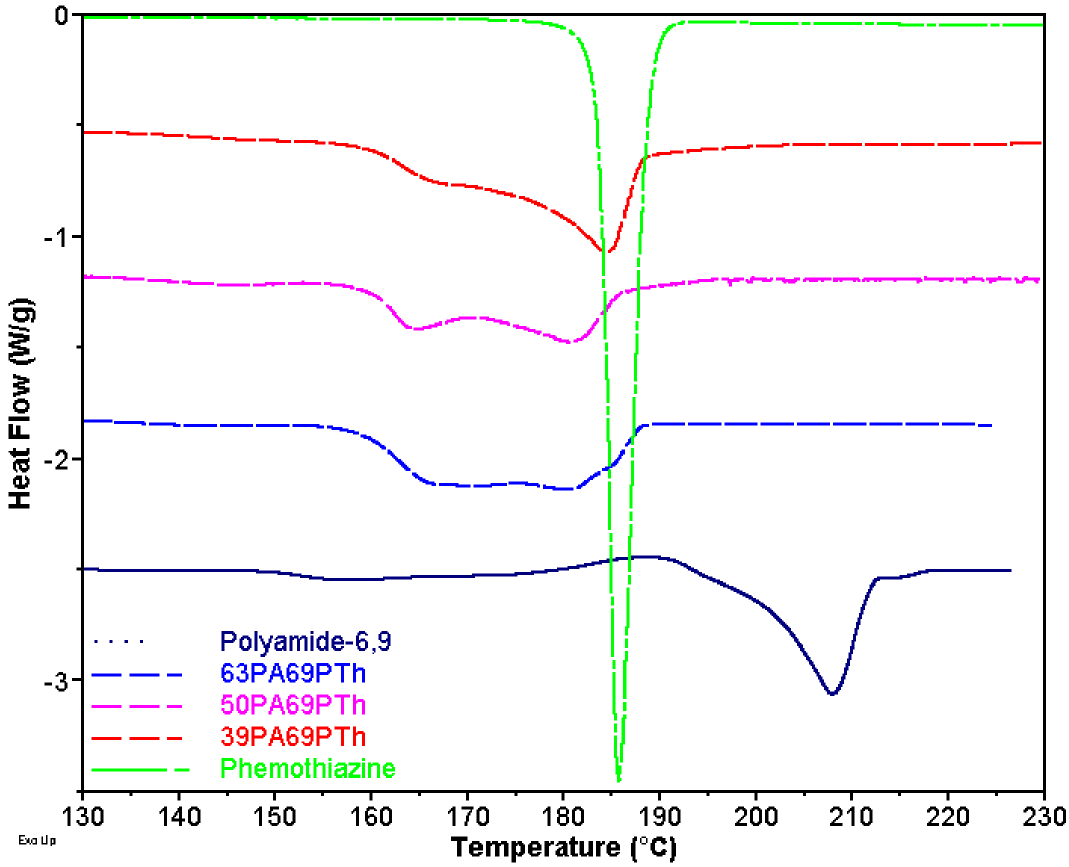

Figure 9-2 DSC thermograms during the first melting at 5 ^{0}C/min of polyamide-6,9/phenothiazine and powder mixtures blended in DSC pans.

a) The polyamide-6,9 sample has a weak endothermic peak near 160 ^{0}C for the melting of the metastable form resulting from previous thermal history. A marked exotherm for the re-crystallisation into the stable form lies prior to the main peak for the melting of the stable form. There is a minor peak above the main melting peak that is unknown in origin. Several repeat DSC runs have been made of virgin vacuum dried powder from several vacuum dryings and the peaks are to be found in all of them. They would have been found with the other polyamides if it were contamination due to the grinding and vacuum drying.

b) The 68PA69PTh thermogram has a complex, flat triple peak spreading over the range 160-190 ^{0}C with the two strongest peaks at 165 and 181 ^{0}C. One of the two materials, most likely the polyamide-6,9, is beginning to melt and dissolve the other when another process begins, leading to the second peak. A better understanding of what is happening will come from the following two samples and the remelting described in a later section. The third peak is a shoulder on the trailing edge of the combined peak and appears to be at the normal phenothiazine melting temperature. The thermogram is flat above 190 ^{0}C indicating that all polyamide-6,9 has been consumed by this stage. In addition, the complex peaks are preceded by an almost imperceptible dip centred in the range 145-150 ^{0}C. This appears to be related to the slight melting of the metastable crystalline form seen in the polyamide-6,9 thermogram. This dip is also to be seen in the following two samples.

c) The thermogram for sample 50PA69PTh is similar to that for 68PA69PTh except that the two main peaks of the composite peak are further resolved into two peaks. There are some other small differences. The small shoulder at the same temperature as the phenothiazine melting temperature is missing. There is a faint deviation from the horizontal over the range 185-195 ^{0}C that is most likely the TLS peak for dissolution of the small remaining amount of polyamide-6,9 in the sample. Noise levels in the DSC signal at temperatures above the melting peaks appear to be higher than normal. There seems to be no reason for that and the noise disappears at 160 ^{0}C as the sample temperature is lowered in cooling as can be seen in the figure immediately below. Intermittent problems had been encountered with the DSC equipment regarding noisy signals and the manufacturer's service personnel had difficulties in rectifying the problems.

d) The thermogram for 39PA69PTh is nearly the same form as the 50PA69PTh. A difference is that the relative peak heights of the main two peaks are now unequal, with the first peak smaller than the second, the second taking place a little higher at very close to the phenothiazine melting temperature. The TLS peak shoulder also extends to slightly higher temperatures. The difference in heights relate to the higher phenothiazine concentration in this sample and allows the assignment of the second peak in all three to phenothiazine rather than polyamide-6,9.

We see here the multi-stage melting/dissolution of polyamide-6,9 powder with phenothiazine in which the polyamide appears to melt/dissolve first at substantially depressed temperatures below that of phenothiazine. The phenothiazine has a limited melting temperature depression due to polyamide-6,9 interactions. Viewed over the three samples, the phenothiazine has a TLS peak as it is taken up in the saturated solution. The sample with the lowest concentration of phenothiazine has a small sub-peak on the trailing edge of the composite peak. The small shoulders on the higher temperature side of the multiple peaks are above the phenothiazine melting temperature and must be the dissolution of residual polyamide. That implies that the dissolution of polyamide grains in the eutectic solution is retarded due to kinetic effects or that the system is in a region of phase space where the formation of a solution is unfavourable.

9.3.1.2 Crystallisation for first cooling ramp of the molten blend at 25 ^{0}C/min

The DSC thermograms from the first crystallisation ramp for polyamide-6,9/phenothiazine powder mixtures taken to the melt and cooled at 25 ^{0}C/min are to be seen in Figure 9-3.

a) The crystallisation thermogram of 63PA69PTh shows a small peak for nearly pure polyamide-6,9 followed by a treble peak comprising (sequentially) the crystallisation of phenothiazine, a polyamide-6,9/phenothiazine peak on the falling side and a final peak over 10 ^{0}C lower at just under 140 ^{0}C. The first two peaks of the treble peak are almost coincident. That can be seen more clearly in an expanded view in Appendix A. The observation of the diluent beginning to crystallise and this triggering the simultaneous crystallisation of diluent with polyamide is also to be seen with some polyamide/diluent combinations in other chapters.

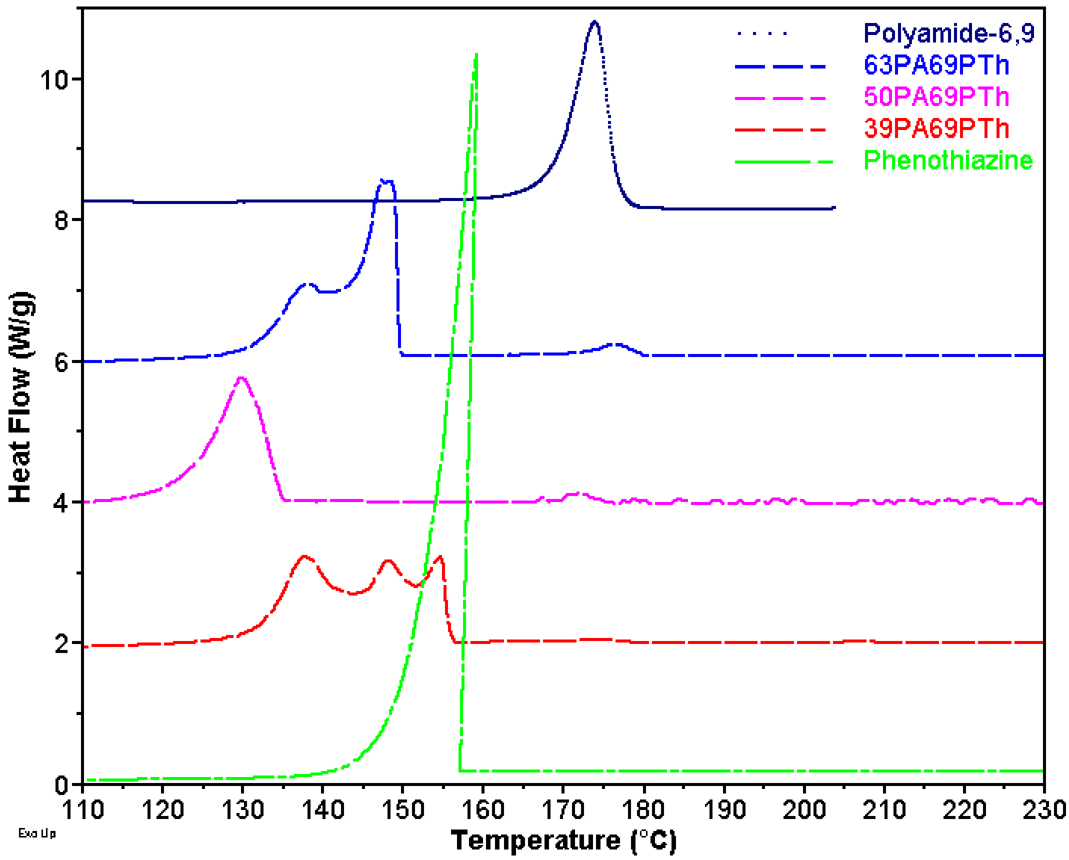

Figure 9-3 DSC thermogram for the first crystallisation of pan blended polyamide-6,9/phenothiazine blends made from powders taken to the melt and being cooled here at 25 ^{0}C/min.

b) 50PA69PTh has a small peak near the polyamide-6,9 crystallisation temperature but 4 – 5 ^{0}C lower than the equivalent one in 63PA69PTh. Unfortunately, the signal from the DSC for this cooling run was noisy which partly obscures the small peak caused by phase separation of some polyamide-6,9. The slightly lower temperature indicates a very small amount of phenothiazine is being incorporated with the polyamide at that point. There is a (double) peak starting at 135 ^{0}C which begins with phenothiazine crystallising and evolves into the concurrent crystallisation of polyamide-6,9 and phenothiazine. The double peak here is more evident when looking at the expanded curves in Appendix A.

c) The crystallisation curve for 39PA69PTh is a curious triple peak, starting with the crystallisation of nearly pure phenothiazine and followed by two subsequent crystallisations of differing proportions of polyamide-6,9 with phenothiazine. It is quite unlike other cases seen in the rest of this research work. It is interesting that, unlike many other cases where there is some phase separation, there is no crystallisation of nearly pure polyamide for the sample with the highest level of phenothiazine. There is no explanation available for the particular triple peak.

Crystallisation of a small amount of nearly pure polyamide has taken place with the two samples having higher polyamide content, apparently after some phase separation. There has been substantial crystallisation depression of those two, one of them by nearly 50 ⁰C below the polyamide-6,9 crystallisation temperature. The sample with the most phenothiazine goes through a complex triple crystallisation process but does not show evidence of phase separation.

9.3.1.3 Melting Peak Temperatures for second heating ramp at 5 ⁰C/min

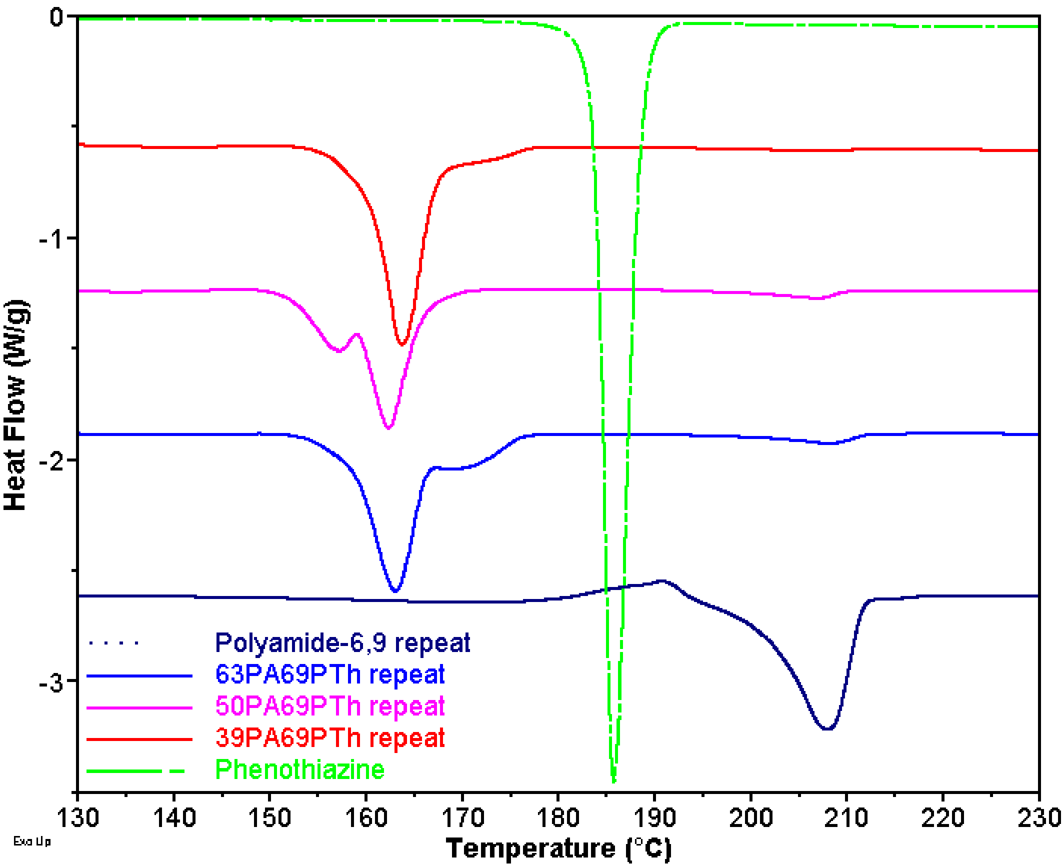

Figure 9-4 DSC thermogram at 5 ⁰C/min of second melt of materials previously blended and crystallised in DSC pans for polyamide-6,9/phenothiazine mixtures.

Figure 9-4 is the set of DSC thermograms for the reheating at 5 ⁰C/min of polyamide-6,9/phenothiazine powder mixtures melt blended in DCS pans after having been cooled previously at 25 ⁰C/min.

a) The polyamide-6,9 thermogram shows more pronounced melting and recrystallisation of metastable lamellae before the main melting peak as a result of the fast cooling in the previous crystallisation of this sample.

b) The 63PA69PTh thermogram for remelting the sample shows further resolution into separate peaks compared to that seen with the initial melting of the two powders. This sample, and the others of this group, had been crystallised at the fast cooling rate of 25 ^{0}C/min. That cooling rate leads in the case of pure polyamide-6,9 to a metastable crystalline form that changes to a more stable form as it is heated towards the polyamide-6,9 melting temperature. There is a weak exothermic peak near 150 ^{0}C that is a washed out re-crystallisation of the polyamide-6,9 lamellae into the stable form. A melting peak at higher temperatures for saturated polyamide-6,9/phenothiazine is followed by the TLS peak for the dissolution of polyamide-6,9/phenothiazine crystallised together. There is melting of some almost pure polyamide-6,9 that had been seen to crystallise near the normal polyamide-6,9 crystallisation temperature in Figure 9-3.

c) A double peak and a single peak are seen in the heating ramp for 50PA69PTh. The first endothermic peak, near 157 ^{0}C, is most likely to be melting and is followed by the exothermic re-crystallisation of polyamide-6,9 from the metastable crystalline form produced in the prior fast crystallisation. Similar effects can be seen within the thermogram for re-melting of the pan blended 63PA69Car sample in Chapter 5. The main peak is at the same temperature as the 63PA69PTh main peak in Figure 9-4 above. Alternatively, the peaks could be the melting of two different polyamide-6,9/phenothiazine compositions. There is no significant TLS peak with this sample, indicating that it is close to the eutectic composition. There is also a small peak at the polyamide-6,9 melting temperature as with 63PA69PTh, and showing the remelting of the small portion that crystallised as polyamide-6,9 in Figure 9-3.

d) The 39PA69PTh thermogram shows a main peak 2-3 ^{0}C higher than the main peaks of the other two samples. That peak is followed at higher temperatures by a TLS peak. There is no minor peak near the polyamide-6,9 melting temperature in agreement with none being present during the prior crystallisation.

We find here much more defined melting curves than during the first melt. This is similar to that seen with other material combinations. In all cases there is a main peak depressed from near 210 ⁰C to close to 163 ⁰C in eutectic melts with some evidence of phase separation in the prior crystallisation for the higher two concentrations of polyamide-6,9. The two cases with higher polyamide levels also have small polyamide-6,9 melting peaks reflecting the phase separation that took place during crystallisation.

9.3.1.4 Crystallisation Peak Temperatures for second cooling ramp at 25 ⁰C/min

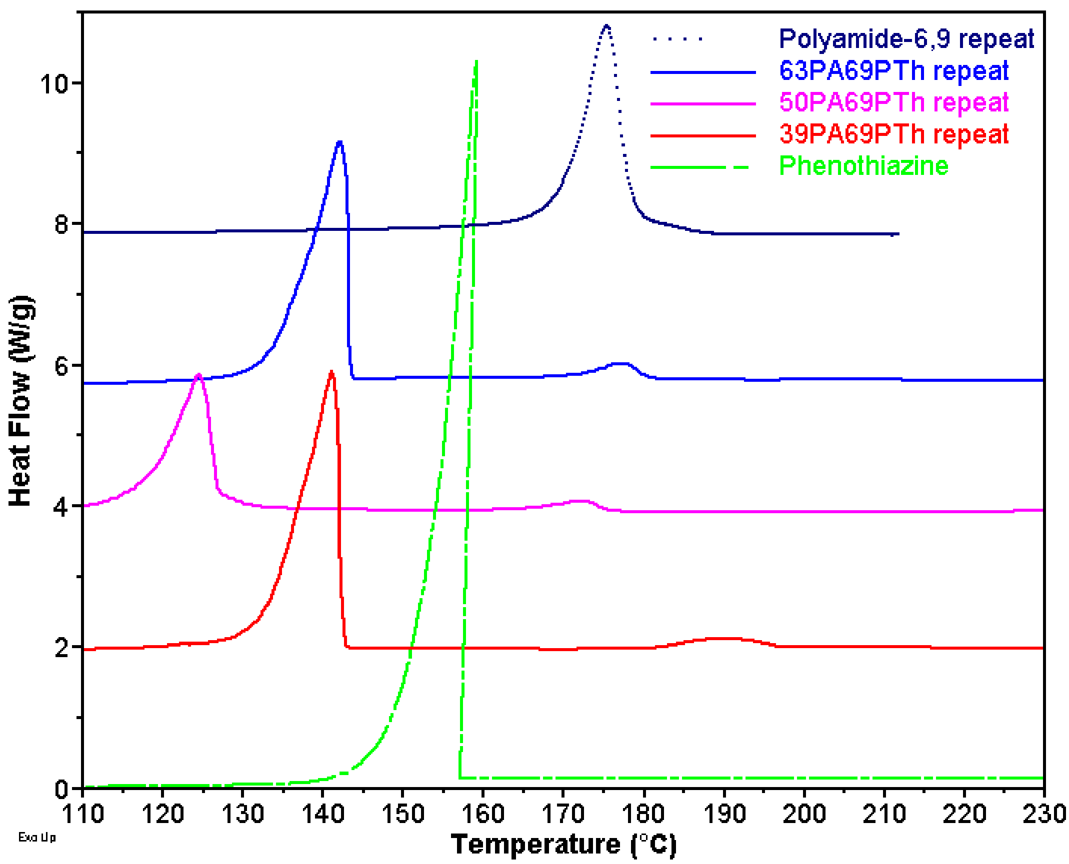

Figure 9-5 DSC thermograms of the second crystallisation at 25 ⁰C/min for pan blended polyamide-6,9/phenothiazine samples.

The thermograms In Figure 9-5 for all three mixtures of pan blended polyamide-6,9/phenothiazine show further refinement from the double peaks of the first crystallisation. This time, all had an initial small crystallisation near that of pure polyamide-6,9 and a major peak 30-45 ⁰C below the normal polyamide-6,9 crystallisation peak. The 39PA69PTh has by this time lost 33% of the phenothiazine and the sample could more accurately be termed 48PA69PTh.

The small peaks near the polyamide-6,9 melting temperature are showing, the strong tendency for polyamide-6,9 to crystallise out of the polyamide-6,9/phenothiazine solution at all concentrations. It can be seen that that peak for 39PA69PTh is slightly higher than the polyamide-6,9 melting peak. A slightly higher peak had also been seen with the 63PA69PTh sample on the first crystallisation. It is considered that this early crystallisation is due to viscosity reduction with phenothiazine enhancing the ability of the polyamide to crystallise. The peak temperature is very close to 190 ^{0}C at this fast cooling rate and it will be seen below that the crystallisation temperature for polyamide-6,9 under more ideal conditions at slower cooling rates is near 193 ^{0}C. The crystallisation here is between the temperatures for slow crystallisation and the lower temperature for the faster rate.

9.3.2 Ampoule Material

9.3.2.1 Melting Temperatures (First melt in DSC at 5 ^{0}C/min)

The DSC thermograms in Figure 9-6 are the first DSC melting at 5 ^{0}C/min of samples blended originally in ampoules.

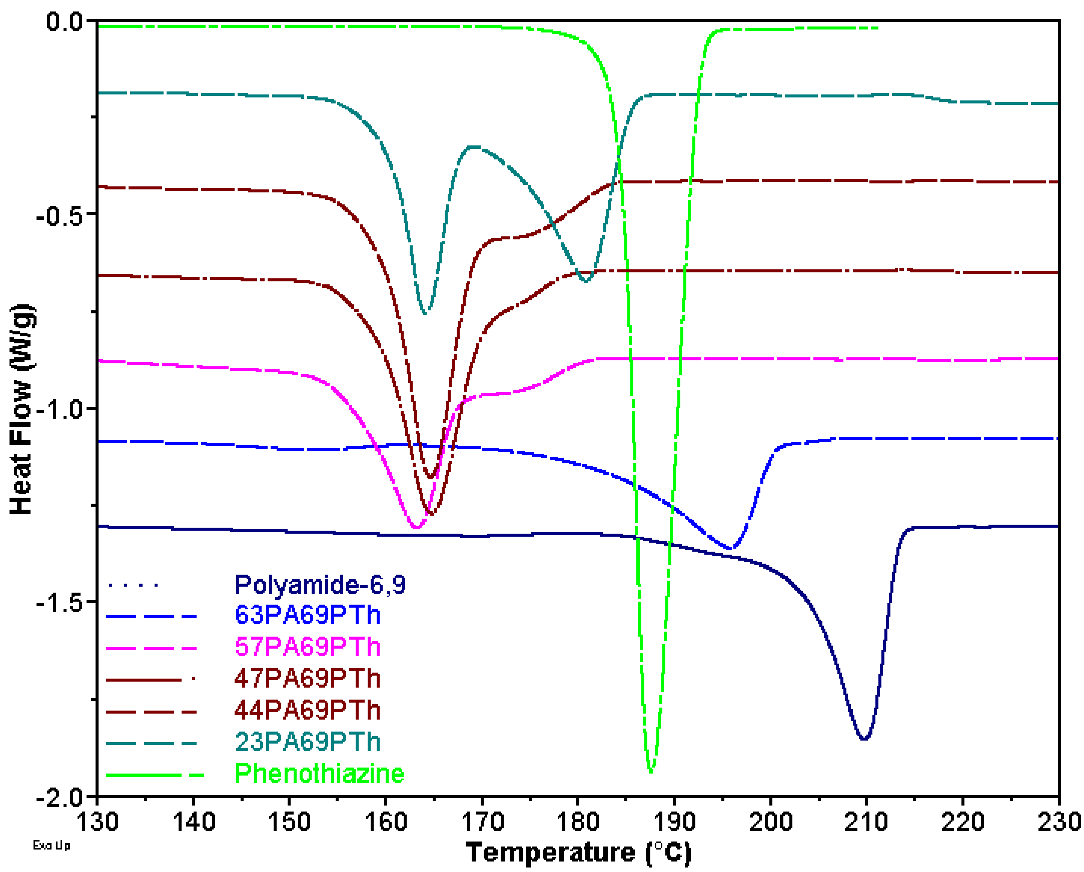

Figure 9-6 DSC thermograms of polyamide-6,9/phenothiazine blends from ampoules in their first melting in the DSC at 5 ^{0}C/min.

a) The melting thermogram of ampoule sample 63PA69PTh is similar in form to that of polyamide-6,9 but depressed by 15 ^{0}C. There appears to be a weak endotherm near 150 ^{0}C of the small amount of phenothiazine dissolving into the polyamide and this is followed by the TLS peak of polyamide-6,9 dissolving into the eutectic.

b) The 57PA69PTh sample, with a little more phenothiazine, displays the characteristics seen in earlier chapters of a depressed melting/dissolution peak for the materials giving a saturated eutectic solution. That peak is followed at higher temperatures by a TLS peak covering dissolution of the remaining polyamide. The very large change between this thermogram and the 63PA69PTh one could mean that the actual differences in percentage polyamide may well be greater than measured by the TGA samples obtained from next to the DSC samples. The 63PA69PTh may be a slightly higher percentage than 63% and/or the 57PA69PTh may be lower than 57% polyamide.

c) 44PA69PTh and 47PA69PTh appear to be minor variations of the 57PA69PTh thermogram. There are some subtleties making them different. Firstly, the main peak for both is slightly higher in temperature and has the same temperature as the first peak for 23PA69PTh described below. The size of the TLS peak is larger for the sample with higher phenothiazine and, as will be seen below, the size of the second peak for 23PA69PTh is larger again.

d) The thermogram for 23PA69PTh has a first peak at exactly the same temperature as the 47PA69PTh and 44PA69PTh samples indicating a similar situation. A second peak just below the melting temperature of phenothiazine is much larger than the TLS peaks of the other two. This shows that the composition of the 23PA69PTh sample is further away in polyamide concentration from saturation at 170 ^{0}C than the other two.

The ampoule samples here show the first melt/dissolution peak is a depressed eutectic melt, followed by residual polyamide only dissolving with a TLS peak at temperatures higher than 170 ^{0}C where polyamide concentration is more than 50%. There is a TLS peak for remaining phenothiazine dissolving in the saturated solution when the level of phenothiazine in the sample is higher than for a saturated solution. This thermal behaviour is understandable if there is a phase diagram with a eutectic composition near 50% polyamide. The further depression of the eutectic melt temperature for 57PA69PTh is typical of low eutectic temperatures near the eutectic composition has been noted with some other combinations of polyamide/diluent. The lead-in to the first major peak for these ampoule blend samples does not show the metastable form melting and recrystallising seen with some of the pan-blended samples that had been cooled at 25 ^{0}C/min.

9.3.2.2 Overall Crystallinity

The percentages of polyamide were used with the total enthalpies of the first melting heating ramp to calculate the overall crystallinity of ampoule samples in the same manner as in earlier chapters. The results are plotted below in Figure 9-7.

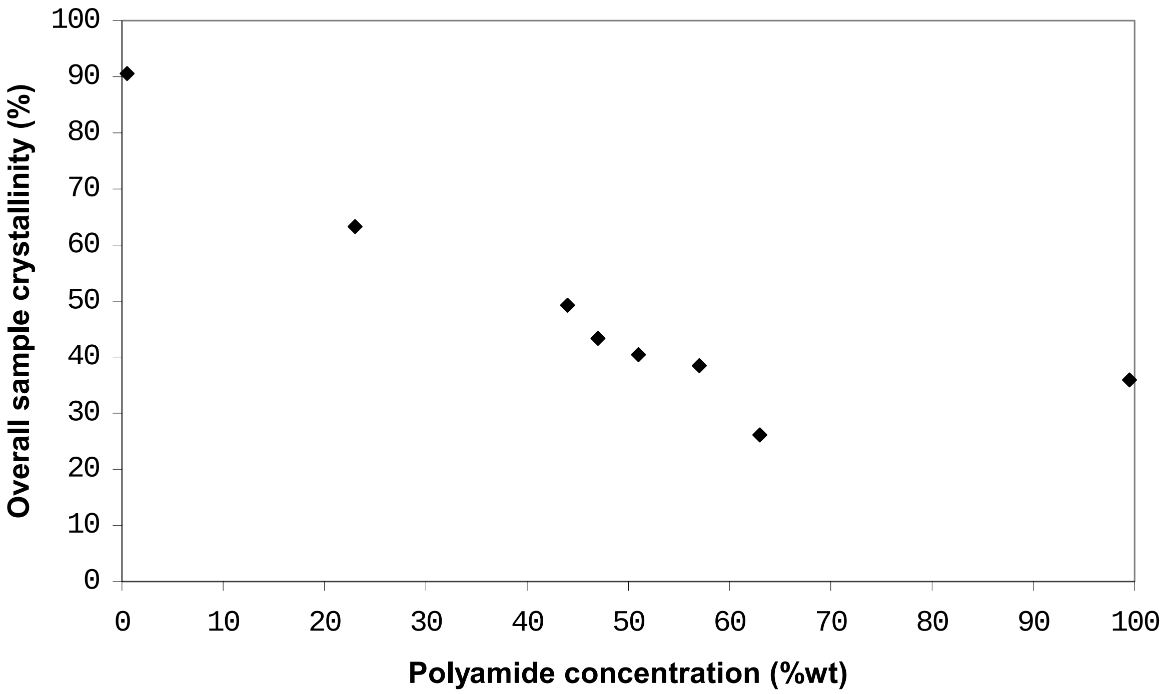

Figure 9-7 Overall crystallinity determined from TGA and total first DSC melting enthalpy of polyamide-6,9/phenothiazine.

The overall crystallinity from ampoule material samples, as seen in Figure 9-7, slowly decreases as the percentage of polyamide is increased from the high value for phenothiazine to the much lower one for polyamide-6,9. There is only one sample where the crystallinity is a little lower than for polyamide-6,9 but the series for blends are below the linear relation between the phenothiazine and polyamide-6,9. This means that the blending process is suppressing overall crystallinity to some extent.

9.3.2.3 First crystallisation in the DSC at 2 ^{0}C/min of ampoule samples

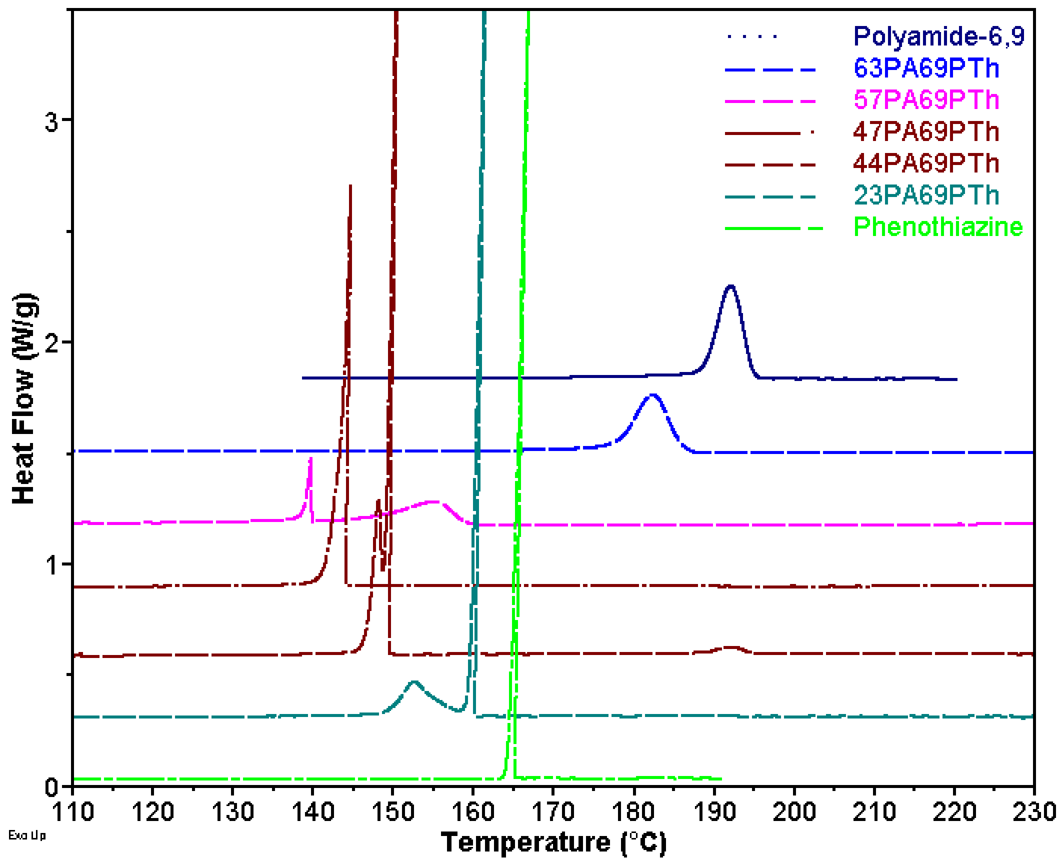

Figure 9-8 DSC thermograms of the first crystallisation in DSC at 2 ^{0}C/min of polyamide-6,9/phenothiazine ampoule material.

a) 63PA69PTh has a polyamide-6,9 crystallisation peak depressed 11 ^{0}C by the presence of phenothiazine.

b) The 57PA69PTh thermogram has a polyamide-6,9/phenothiazine peak depressed 37 ^{0}C below the polyamide-6,9 crystallisation temperature and followed by a small (depressed) phenothiazine peak depressed by 24 ^{0}C from the phenothiazine crystallisation temperature. Both of these depressions show that there are Flory-Huggins style interactions between the materials at the time of crystallisation.

c) The thermogram for sample 47PA69PTh has a single peak depressed some 50 ^{0}C below the polyamide-6,9 crystallisation temperature and nearly 20 ^{0}C below the phenothiazine crystallisation temperature. That peak actually comprises initial crystallisation of phenothiazine that goes over smoothly into the crystallisation of polyamide-6,9/phenothiazine in the latter stages. This can be seen compared to a normal phenothiazine crystallisation in a more expanded version in Appendix A.

d) The thermogram for 44PA69PTh has a small peak near the polyamide crystallisation temperature caused by some phase separation. This is followed at lower temperatures by a double peak slightly higher than for 47PA69PTh in which excess phenothiazine to the saturated solution crystallises at a temperature depressed from the phenothiazine crystallisation temperature. That peak runs into a second peak of polyamide-6,9/phenothiazine within the same peak envelope.

e) The 23PA69PTh thermogram takes matters a step further with the near complete separation of the two peaks. Those peaks are both at slightly higher temperatures than the previous samples, the first because the level of polyamide-6,9 "contaminating" the phenothiazine is less and the second because the polyamide-6,9 is having more problems in remaining in solution at those temperatures.

This set of thermograms shows a maximum depression by 50 ^{0}C of the polyamide-6,9 crystallisation peak with 47PA69PTh. This is near equal concentrations of each constituent material. The maximum depression of the phenothiazine crystallisation peak is with the 57PA69PTh sample and is by 24 ^{0}C. The phenothiazine, on the other hand, has a more well-behaved and consistent depression of the crystallisation temperature with increasing polyamide concentration in a style typical of the Flory-Huggins theory.

There is only one sample here with crystallisation at the polyamide crystallisation temperature indicating phase separation.

9.3.2.4 Crystallinity from first crystallisation in the DSC

The crystallinity of phenothiazine and polyamide as displayed in Figure 9-9 from the first cooling ramp in the DSC does have some limitations because of the evaporative loss of phenothiazine to varying degrees from the samples.

The phenothiazine enthalpy of crystallisation decreases to zero by 63% polyamide. There is a wider scatter of results in this decrease than was found with the polyamide/diluent combinations having higher polyamide than diluent melting temperature. The limited results for this combination do make it difficult to have a definitive pronouncement on this point. The crystallinity of the polyamide-6,9 is unusual in that it increases with decreasing polyamide, at least down to 23% polyamide.

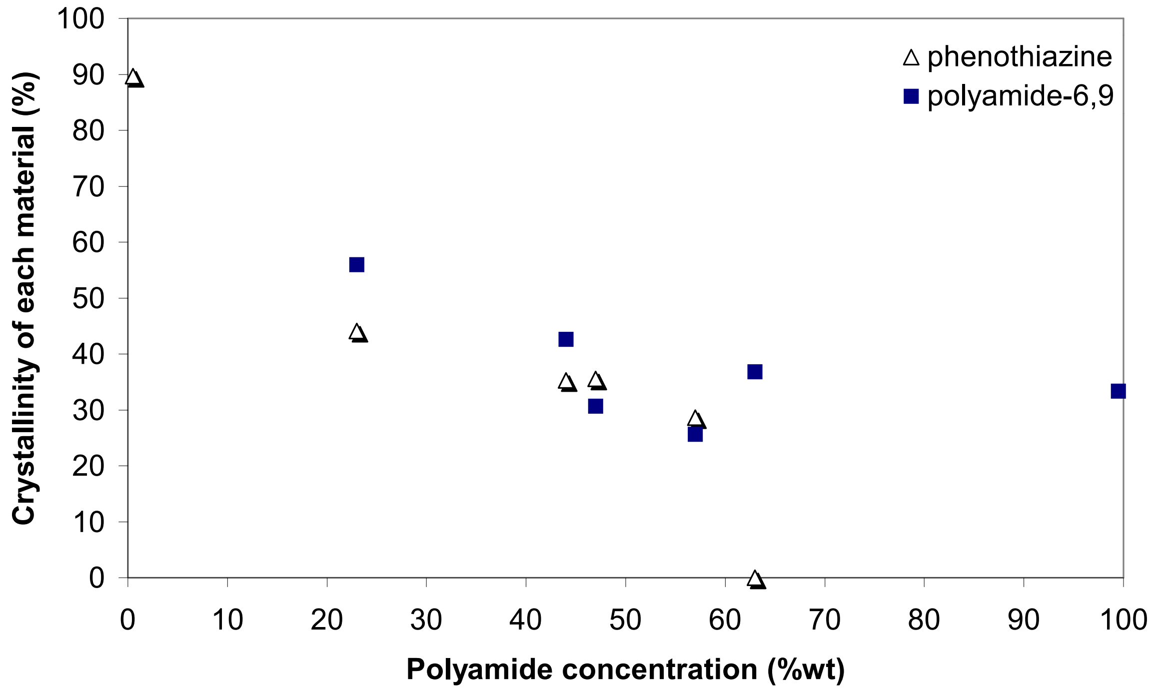

Figure 9-9 Crystallinity of Phenothiazine and Non-Phenothiazine parts determined from the first crystallisation from the melt of polyamide-6,9/phenothiazine samples that had been taken to the melt in the DSC and cooled at 2 ^{0}C/min.

9.3.2.5 Phase Diagram from first heating and cooling ampoule material in DSC

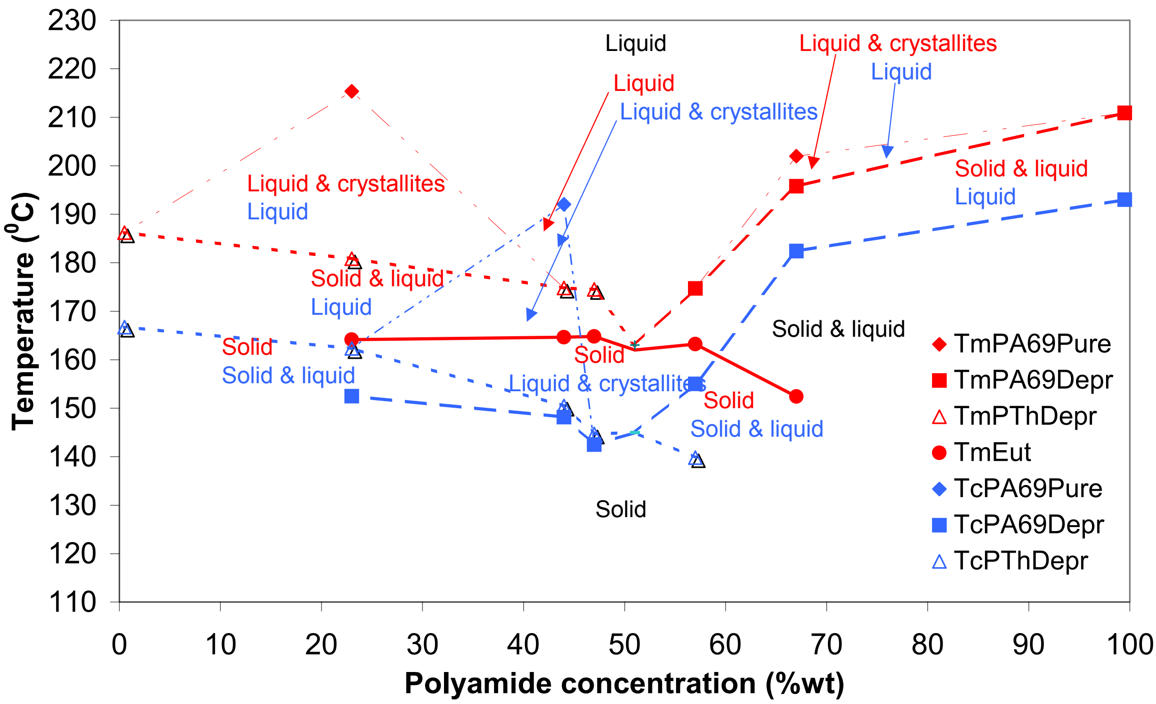

Figure 9-10 Non-equilibrium phase diagram for polyamide-6,9, phenothiazine and their blends.

Figure 9-10 shows the phase diagram characteristics seen in chapters 3, 7 and 8 of Flory-Huggins crystallisation temperature depressions, dips near the crossover concentration and crystallisation of small amounts of near-pure polyamide at or above that normal for the polyamide.

9.3.2.6 Third Melting (at 5 ^{0}C/min) of ampoule materials/Second DSC Melt

The ampoule samples in pans from the first DSC runs were passed through a repeat melt/crystallisation cycle in the DSC, as was done in earlier chapters. Figure 9-11 below shows the DSC thermograms of the melt portions of the repeat DSC runs.

Some evaporation of phenothiazine has generally taken place between the start of the first and second DSC runs of the ampoule samples. The effect will be greater than in the pan blended samples because of the protracted times spent at high temperatures due to the slower cooling ramp used with these samples. Broadly, the second melting in the DSC of the ampoule samples are similar to the first ones:

a) The small dip in 63PA69PTh near 150 ^{0}C has disappeared and there is an increase in temperature of 3 ^{0}C for the main peak, indicative of a small loss in phenothiazine through evaporation.

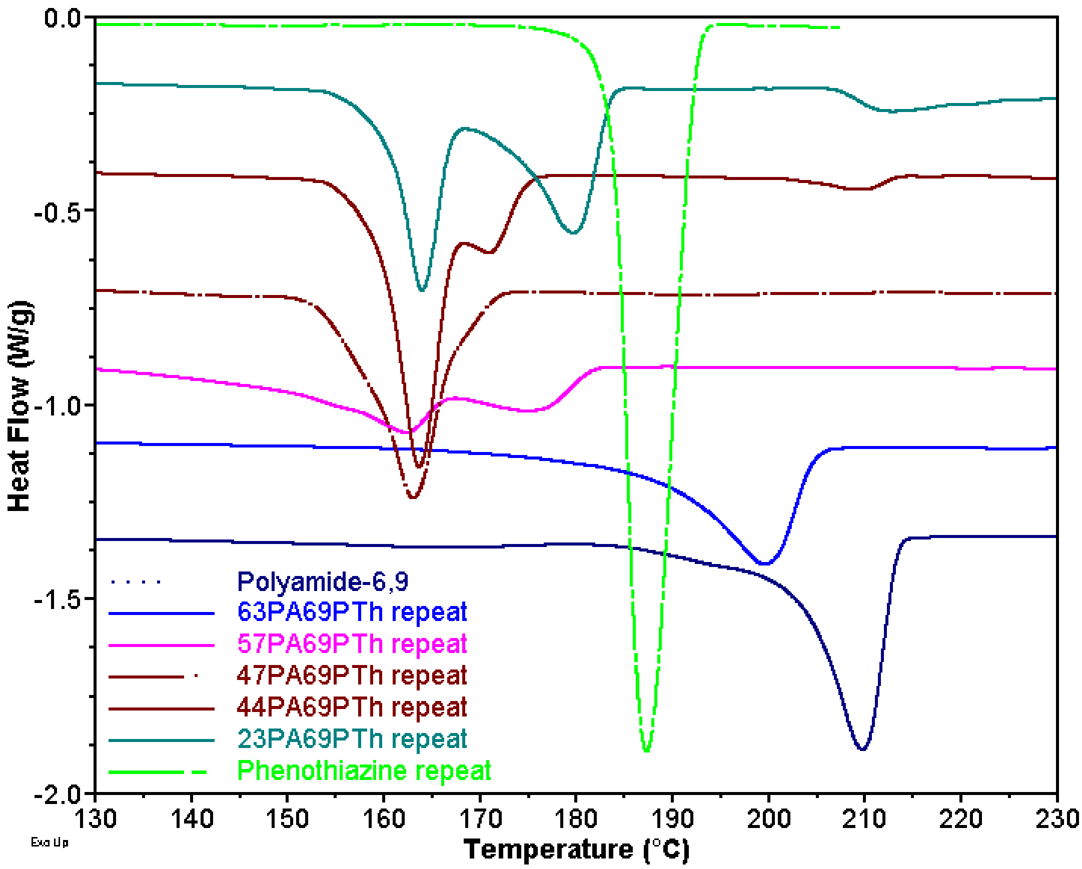

Figure 9-11 DSC thermograms of the second melt at 5 ^{0}C/min in DSC of polyamide-6,9/phenothiazine blends of ampoule material.

b) There is a reduction in the peak height, and hence crystallinity, for the main peak of 57PA69PTh. The TLS peak has become more pronounced. Both these are due to some phenothiazine evaporative loss.

c) The peak for 47PA69PTh has become slightly larger and is 2 ^{0}C higher in temperature.

d) The thermogram for 44PA69PTh, as with the 57PA69PTh, has become slightly more pronounced. There is also a small peak at the polyamide-6,9 melting temperature. These changes together perhaps indicate some phase separation having taken place, particularly when there was a small peak seen at the polyamide crystallisation temperature in the first crystallisation in the DSC.

e) The 23PA69PTh thermogram for the second DSC melt has an almost identical first peak to the first time melting in the DSC but the second peak is slightly larger and there is a small peak at the polyamide-6,9 melting temperature. These also point to slight phase separation of some regions into the polyamide-rich and diluent-rich phases.

The picture here is similar to the first melting in the DSC but modified slightly by evaporation of phenothiazine seen at lower phenothiazine levels where it is more evident and by some phase separation at higher phenothiazine levels.

9.3.2.7 Third Crystallisation of Materials/Second DSC Crystallisation

The DSC thermograms for the second cooling ramp in the DSC at 2 ^{0}C/min of polyamide-6,9/phenothiazine samples from ampoules are shown below in Figure 9-12. The small differences between the first and second DSC crystallisations are due to phenothiazine evaporation and, at higher phenothiazine concentration, of phase separation. There is a quite faint peak in the 23PA69PTh thermogram at the polyamide-6,9 crystallisation temperature consistent with the peak seen at high temperatures during remelting.

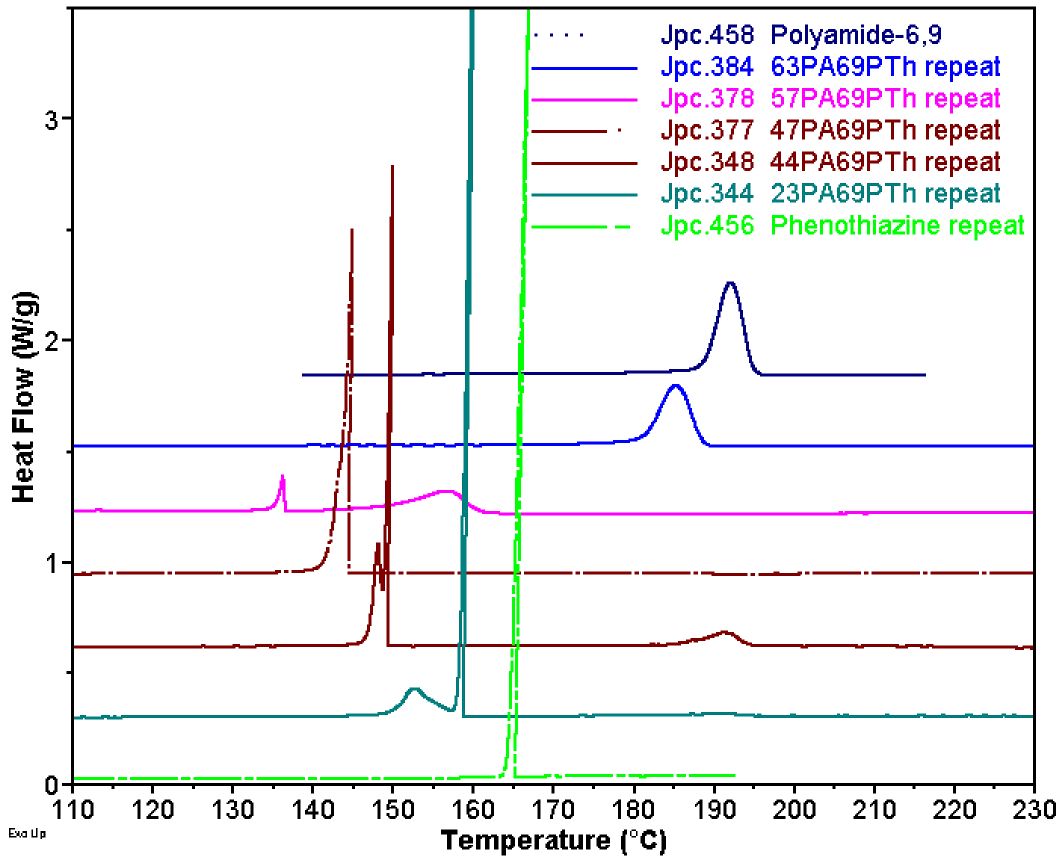

Figure 9-12 Thermograms of the second crystallisation in the DSC at 2 ⁰C/min of polyamide-6,9/phenothiazine ampoule material.

9.4 Fourier Transform Infrared Spectroscopy

Polyamide-6,9/phenothiazine samples from the ampoules were examined with FTIR in the mid range using photoacoustic techniques and in the Near Infrared using DRIFT. These showed no evidence of changes in the hydrogen bonding status of either polyamide-6,9 or phenothiazine. Spectra may be seen in Appendix D on CD.

9.5 Summary

The material combination of polyamide-6,9 and phenothiazine melt blended in pans or in ampoules displays similarities to the polyamide-4,6 and polyamide-6 combinations with phenothiazine in that there is more evidence of phase separation than in the combinations with carbazole. It is not clear at this stage whether this is related to the melting temperature of phenothiazine being lower than the polyamide or to the nature of the phenothiazine molecules.

One of the more interesting things found in these trials is that the melting of the powders together in a DSC pan leads to a melt peak depression of 45 ⁰C for the polyamide-6,9 as it initially melts and dissolves phenothiazine up to the point of saturation. There is evidence that the phenothiazine has some difficulty in dissolving easily into the solution. The temperature must be close to the phenothiazine melting temperature before the process is complete. This is confirmed to some extent by the tendency of polyamide-6,9 to crystallise as solutions are cooled at fast or slow rates. There is an optimal concentration near equal parts of both materials where the bulk of the crystallisation takes place at 45-50 ^{0}C below the polyamide crystallisation temperature, regardless of cooling rate. The faster cooling rate leads to single peaks for the crystallisation of polyamide-6,9/phenothiazine but the materials tend to crystallise separately at depressed temperatures with a slower cooling rate.

The substantial melting and crystallisation temperature depressions show that there are considerable Flory-Huggins style interaction between the two materials. The difficulties in achieving dissolution of the powders in the first instance are thus showing that there are kinetic effects at play in slowing the dissolution.

FTIR experiments in the Mid Range IR and in the Near Infrared both show that hydrogen bond interactions do not play a part in the melting and crystallisation behaviour of these two materials.