

Chapter 5

POLYAMIDE-6,9 WITH CARBAZOLE

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5.1 Introduction

This chapter extends the work done on polyamide-4,6/carbazole and polyamide-6/carbazole melt blends with further work on polyamide-6,9/carbazole melt blends.

Polyamide-6,9 differs from polyamide-4,6 in that both the diamine and diacid moieties of the repeat unit are longer and also it is an “even-odd” polyamide-m,n rather than an “even-even” polyamide. It differs from polyamide-6 in that it is a polyamide-m,n rather than a polyamide-n type. These factors influence the ways in which the polyamide can crystallise. They also affect the flexibility of the polymer chains by having a lower density of amide groups and affect other properties such as the melting temperature.

Some of the themes seen in the earlier chapters will be shown to recur here. The situation is more like that of the polyamide-6/carbazole blends in Chapter 4 because the polyamide-6,9, like the polyamide-6, melts below the carbazole melting temperature. The polyamide-6,9 also has a stronger tendency than polyamide-6 to crystallise in the high temperature stable form. The melt is a double melt as the material melts/recrystallises and melts again [48 p. 46].

5.2 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was carried out in order to determine the percentage of carbazole in ampoule samples.

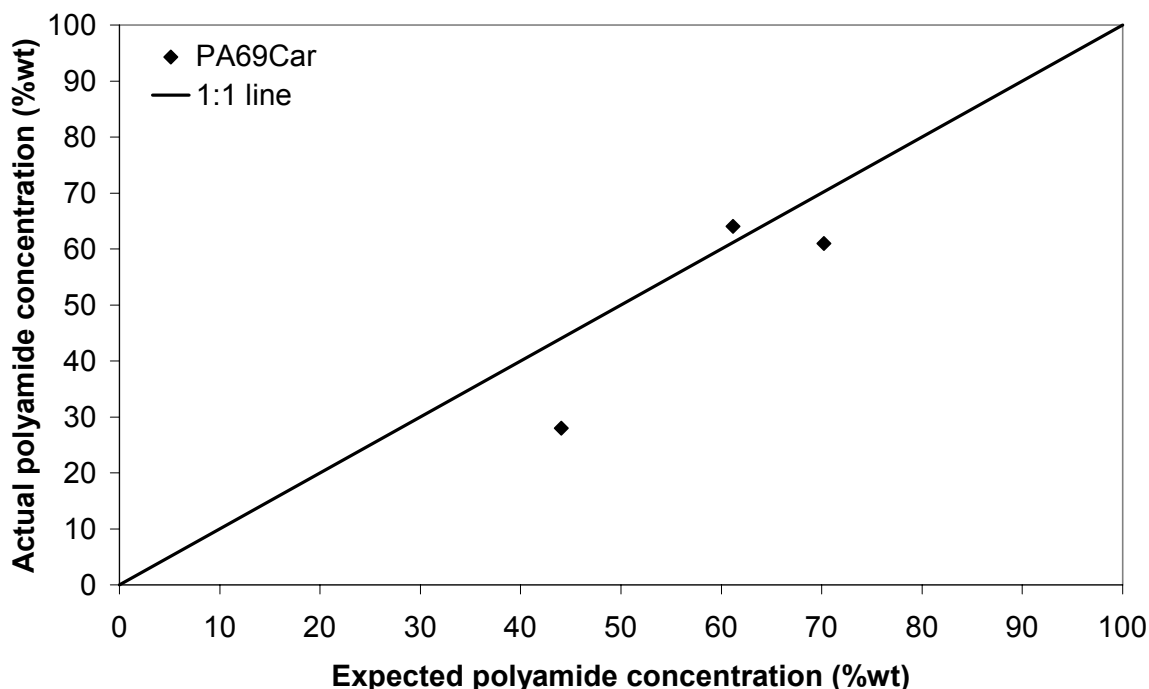


Figure 5-1 Actual versus expected weight percentage polyamide in polyamide-6,9/carbazole samples from ampoules

TGA reproducibility had been found in the polyamide-4,6/ and polyamide-6/carbazole blends to be within 5% from sample to sample. This was taken to be the expected reproducibility for these trials also.

Figure 5-1 below shows a comparison between the expected percentage of polyamide (based on the weights blended in ampoules) and the actual concentrations of polyamide in different samples taken from the ampoule material.

Some of the samples are different by more than 10% from the expected concentrations. They are well above the maximum 5% variation expected

based upon the work covered on Chapters 3 and 4. It indicates that they are real variations in material composition encountered within ampoule samples due to uneven mixing or the development of specific compositions.

5.3 Differential Scanning Calorimetry

Polyamide-6,9 has a double melting endotherm with a weak endotherm in the range 150-175 °C combined with an exotherm at 185 °C and a main endothermic peak in the range 208-211 °C. The endotherm/exotherm pair is due to the polyamide having crystallised preferentially into a metastable lamellar state. The metastable lamellae melt near 173 °C and recrystallise near 185 °C into the stable form that melts at 211 °C as the sample is heated further. The exotherm between the two endotherms is very noticeable in the case of polyamide-6,9. There is a very small thermal activity at temperatures just above the main peak. The reason for that has not been determined. The polyamide crystallises near 193 °C for a cooling rate of 2 °C/min and near 175 °C for a cooling rate of 25 °C/min.

5.3.1 Pan Melt Blending

5.3.1.1 Melting Temperatures for first heating ramp of the powders at 5 °C/min

The DSC thermograms of the melting at 5 °C/min of polyamide-6,9, carbazole and the melt blending of some mixtures of polyamide-6,9 and carbazole powders are shown Figure 5-2.

The individual thermograms will be described in more detail below:

- a) The 63PA69Car thermogram has a very weak, broad endotherm over the range 180-200 °C after a faint endotherm near 160 °C. It is most likely that this behaviour is initially the dissolution of some carbazole powder into the amorphous portion of polyamide grains that it is in contact with. There is a broad endotherm of the melt recrystallising at a temperature slightly lower than normally for polyamide-6,9 followed by a very broad and weak melting peak that finishes near the end of the normal polyamide-6,9 main melting peak. There is no separate melting endotherm for the carbazole in the powder mix indicating that all the carbazole has been taken up in the polyamide-6,9 between 160 and 210 °C. The very broad peaks are typical of those seen in Chapters 3 and 4 for the first melts of powder mixes in the DSC pans and, similarly, are at slightly lower temperatures than for the polyamide.

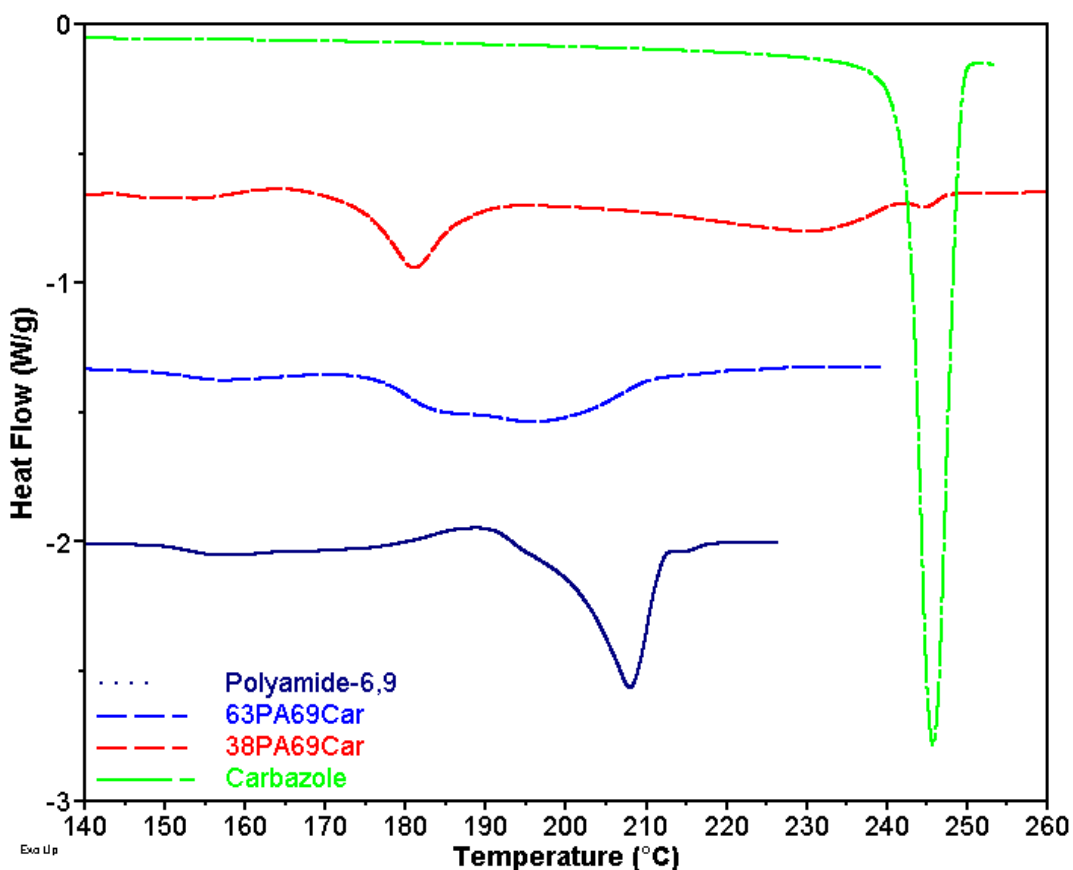


Figure 5-2 DSC thermograms during the first melting at 5 °C/min of polyamide-6,9/carbazole and powder mixtures.

- b) The 38PA69Car thermogram begins with the melting of metastable lamellae near 150 °C and is followed by the depressed melting of polyamide-6,9. Some of the available carbazole surrounding the polyamide has apparently had the opportunity by this stage to absorb/dissolve into the polyamide or the polyamide melting temperature would not have been depressed by nearly 30 °C into a eutectic melt. There is a TLS peak above that peaking near 230 °C for the consumption of excess carbazole. A minor peak exists above that at the carbazole melting temperature. This infers that by 235 °C the solubility of the carbazole has been restricted. A possible binodal near that part of the phase diagram or kinetic effects have come into play slowing the last dissolution of carbazole into the saturated solution. The pattern seen here is broadly similar overall to the 38PA6Car case in Chapter 4 and, with reverse roles of the materials, to pan-blended 83PA46Car of Chapter 3. The lower melting material dissolves as much of the higher melting material as possible until there is a saturated eutectic solution and more can only be dissolved with increasing temperature giving a TLS peak.

5.3.1.2 Crystallisation for first cooling ramp of the molten blend at 25 °C/min

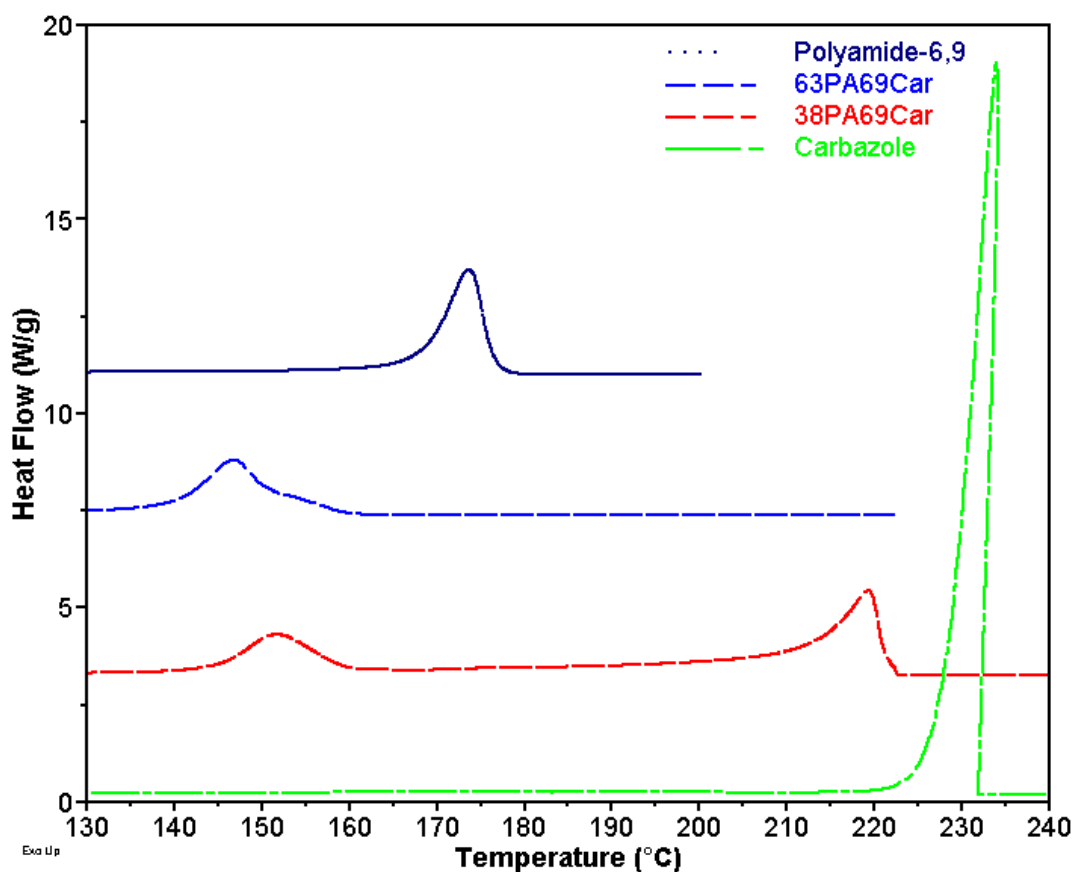


Figure 5-3 DSC thermograms for the first crystallisation of pan blended polyamide-6,9/carbazole cooled from the melt at 25 °C/min.

A set of thermograms for the first crystallisation of powders melt-blended in pans is seen in Figure 5-3. They are shown with thermograms for molten raw materials subjected to the same 25 °C/min cooling ramps.

- The 63PA69Car thermogram has no separate peaks for carbazole crystallisation and only a double peak more than 20 °C below the normal crystallisation temperature of polyamide-6,9. This means that the carbazole has not phase-separated out within the high temperature solution into carbazole domains that could crystallise near the normal temperature for carbazole. There has also been no phase separation at lower temperatures for the polyamide-6,9. The main peak is a double peak so there is a eutectic crystallisation of polyamide-6,9/carbazole after the crystallisation of a small amount of similar material with a different composition.
- The 38PA69Car thermogram has the crystallisation of a large amount of carbazole-rich material near the normal carbazole crystallisation

temperature. It also has a eutectic crystallisation peak for polyamide-6,9/carbazole.

The results seen here are consistent with those for polyamide-6/carbazole blends in Chapter 4.

5.3.1.3 Melting Peak Temperatures for second heating ramp at 5 °C/min for pan blended samples.

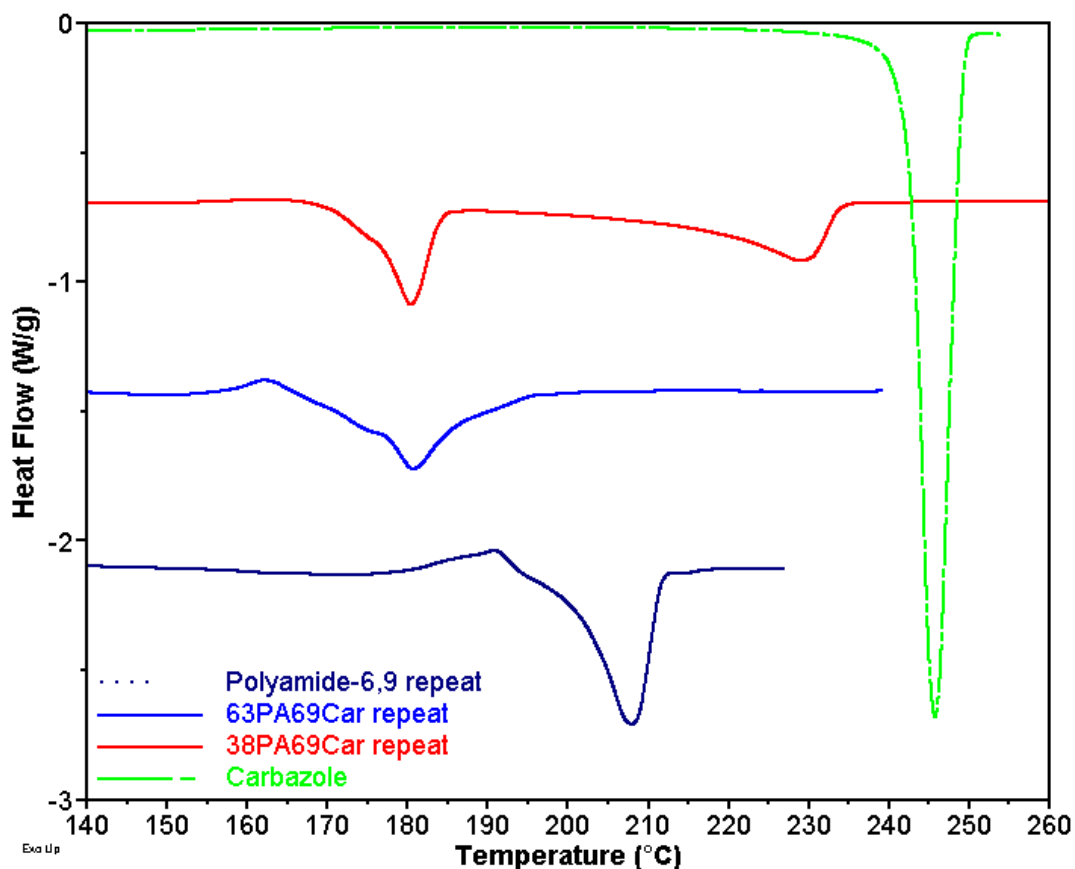


Figure 5-4 DSC thermogram at 5 °C/min of the second melting of polyamide-6,9/carbazole materials previously melt blended and crystallised in DSC pans.

The thermograms in Figure 5-4 differ slightly from the first melting of the powders in Section 5.3.1.1. This is similar to Chapters 3 and 4 where there were differences because the second melting ramp is starting from a more intimate molecular mix of the materials.

- Polyamide-6,9 displays a different thermogram for the second melting with sharp melting/re-crystallisation peaks for the metastable lamellae. This happens because of the fast cooling rate used on this sample compared with the unknown prior thermal history.
- The 63PA69Car thermogram has changed from the first time melting in that it displays sharper melting and re-crystallisation curves than

previously. Crystallisation of polyamide-6,9 had taken place at a fast rate into the metastable lamellae preferred under those conditions. The temperatures involved are 1 – 3 °C lower now, giving 30 °C depressions to both the melt/re-crystallisation and the main melting. There is some fine detail in the thermogram at the higher end of the main melting peak that is a TLS peak for polyamide-6,9 or for carbazole but it is not possible to say from that evidence which material is in excess.

- c) The 38PA69Car thermogram is also a refinement of the previous melting. There is a eutectic melt at 180 °C followed by a TLS peak for the excess carbazole. The overall form is similar to the repeat melting ramp of 38PA6Car and 63PA46Car (reversed melting relationship between the polyamide and carbazole).

The remelting of the previously melt blended pan samples shows similar changes to those from the ill-defined first melts of polyamide-4,6/ and polyamide-6/carbazole blends to the sharper melting profiles when the materials were passed through a second heating/cooling cycle. Reductions in melting temperatures with eutectic melting are also seen, as is the dissolution only at high temperatures of excess of the higher melting material into the saturated solution.

5.3.1.4 Crystallisation Peak Temperatures for second cooling ramp at 25 °C/min.

The thermograms in Figure 5-5 are very similar to those of the first crystallisation of pan blended samples in Figure 5-3, as expected, and as found in a similar situation in Chapters 3 and 4 with polyamide-4,6 or polyamide-6 and carbazole. The only change was the slightly lower crystallisation temperatures (also found in Chapters 3 and 4).

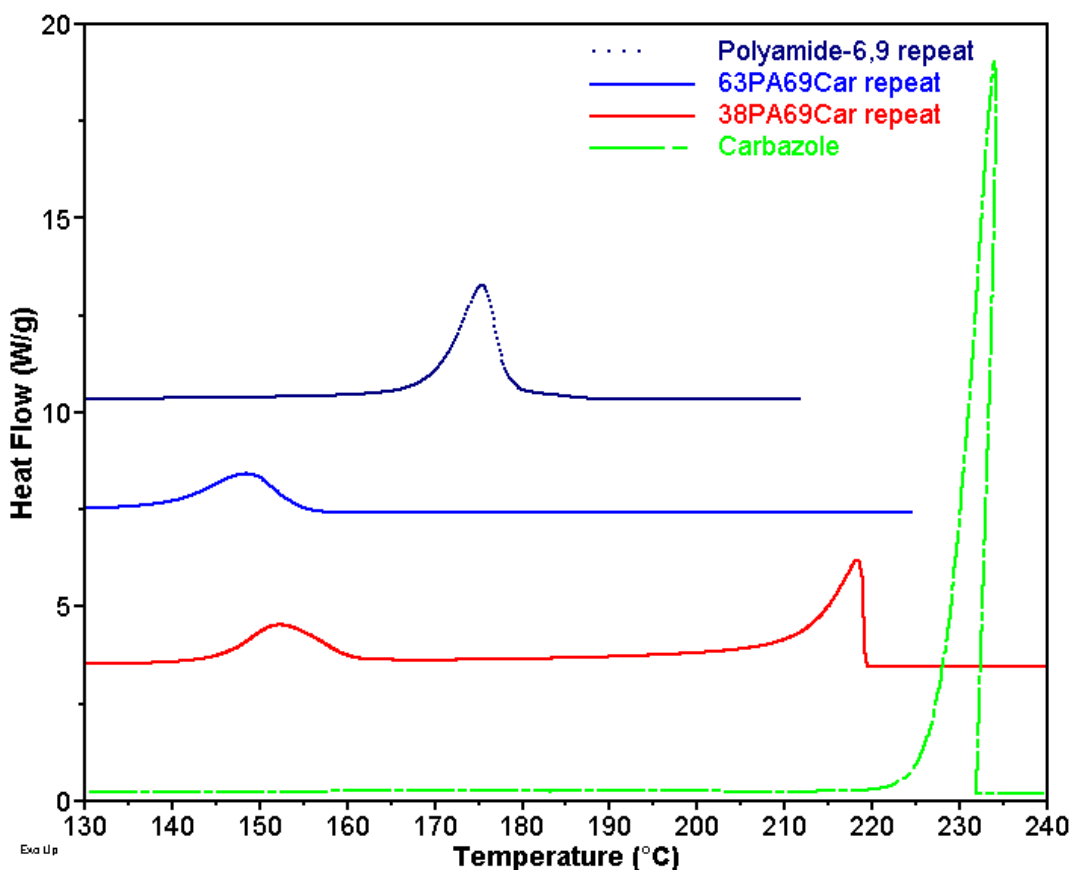


Figure 5-5 DSC thermograms of the second crystallisation of polyamide-6,9/carbazole pan blended samples at 25 °C/min.

5.3.2 Ampoule Material

5.3.2.1 Melting Temperatures (First melt in DSC) at 5 °C/min for ampoule material.

The thermograms in Figure 5-6 show the melting profiles in the first DSC heating ramp for polyamide-6,9, carbazole and their blends that had previously been formed in ampoules. They should approximate those of the second melting of the pan blended materials. There will be differences due to the 2 °C/min used to crystallise materials in ampoules rather than the pan blended samples having previously been crystallised at 25 °C/min.

- a) The polyamide-6,9 sample from the ampoule differs from the second melt of polyamide-6,9 powder in that the double peak is not so sharp in the lead up to the main peak. This is due to the differing thermal histories of the two samples. The sample from the pan blending work had previously been cooled at 25 °C/min whereas this sample had been cooled at 2 °C/min in the ampoule. The slower prior cooling here has given more time for the sample to crystallise in a more favourable manner. The situation is analogous to the polyamide-6 case.

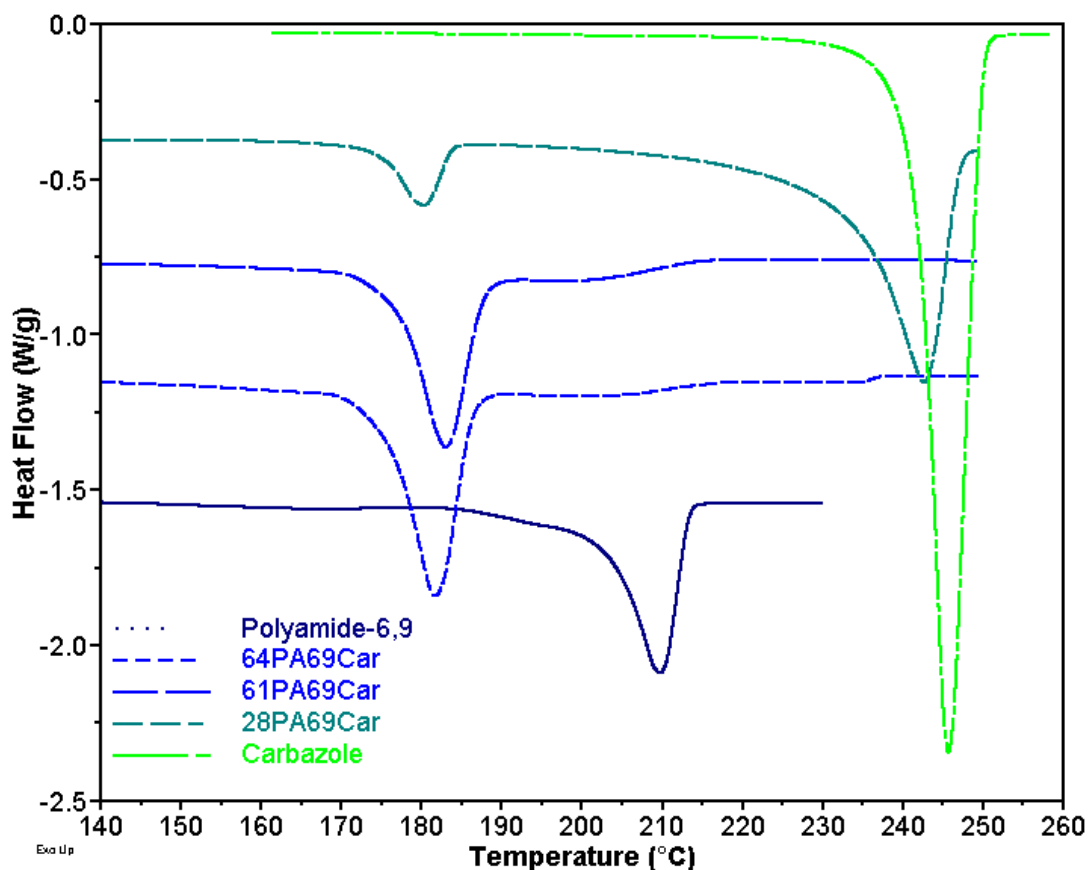


Figure 5-6 DSC thermograms of polyamide-6,9/carbazole ampoule samples during the first DSC melting at 5 °C/min.

- b) The 64PA69Car sample shows a similar thermal behaviour to the equivalent situation with 68PA6Car in Chapter 4. There are differences with the second melting of the pan blended 63PA69Car sample in the main peak not being a double peak due to the different thermal histories of the two samples (*vide infra*). The main peak has also been depressed by 30 °C compared to the polyamide-6,9 sample. This is close to the depression observed in the pan blended samples. There is another minor difference in that there is now a minor TLS peak for carbazole and a very minor melt peak just under the normal carbazole melting temperature. This last small peak shows that there is a limitation in dissolving the last carbazole into the solution. This could be either due to kinetic effects or to the high temperature part of the phase diagram including a binodal.
- c) The 61PA69Car thermogram differs little from 64PA69Car described just above. Again, there is a depression of 30 °C compared to the polyamide-6,9 melting temperature. The only difference is the absence of the very small peak just under the carbazole melting temperature. Apparently there are subtle differences between the two samples in the

way the carbazole is distributed in the sample. Little difference would be expected because of the small difference in polyamide levels between the samples.

- d) The 28PA69Car sample shows the typical behaviour seen numerous times previously with carbazole dissolving in the melting polyamide up to a saturated level followed by rapidly increasing dissolution as the temperature is increased. In this case, 72% of the material is carbazole. The end of the second peak is virtually at the carbazole melting temperature. The peak size is large because of the amount of excess material requiring that high temperature to melt. The 30 °C depression of polyamide-6,9 melt/dissolution temperature is close to that observed in the two samples immediately above and those in the second melting of pan blended samples.

The picture seen for the second melting of polyamide-6,9/carbazole incorporates a number of aspects seen in other trials described earlier in this and in other chapters. There are the more clearly defined melting peaks, the eutectic and TLS peaks, the reduced melting/re-crystallisation of metastable lamellae because of the previous slow crystallisation and some difficulties in melting all of the higher melting material.

5.3.2.2 Overall Crystallinity

The percentages of polyamide were used with the total enthalpy of the first melting heating ramp to calculate the overall crystallinity of ampoule samples in the same manner as in Chapters 3 and 4. The results are plotted below in Figure 5-7.

It can be seen that, on average, there is an overall decrease in crystallinity with decreasing carbazole in the samples. The few results show a monotonic decrease, the same as in Chapter 4 with polyamide-6/carbazole but unlike the situation in Chapter 3 with polyamide-4,6/carbazole where results were more scattered. The locus of the measured points lies below the linear relationship between the crystallinity of the pure materials and so shows that the blending process has led to some overall suppression of crystallinity of the blends.

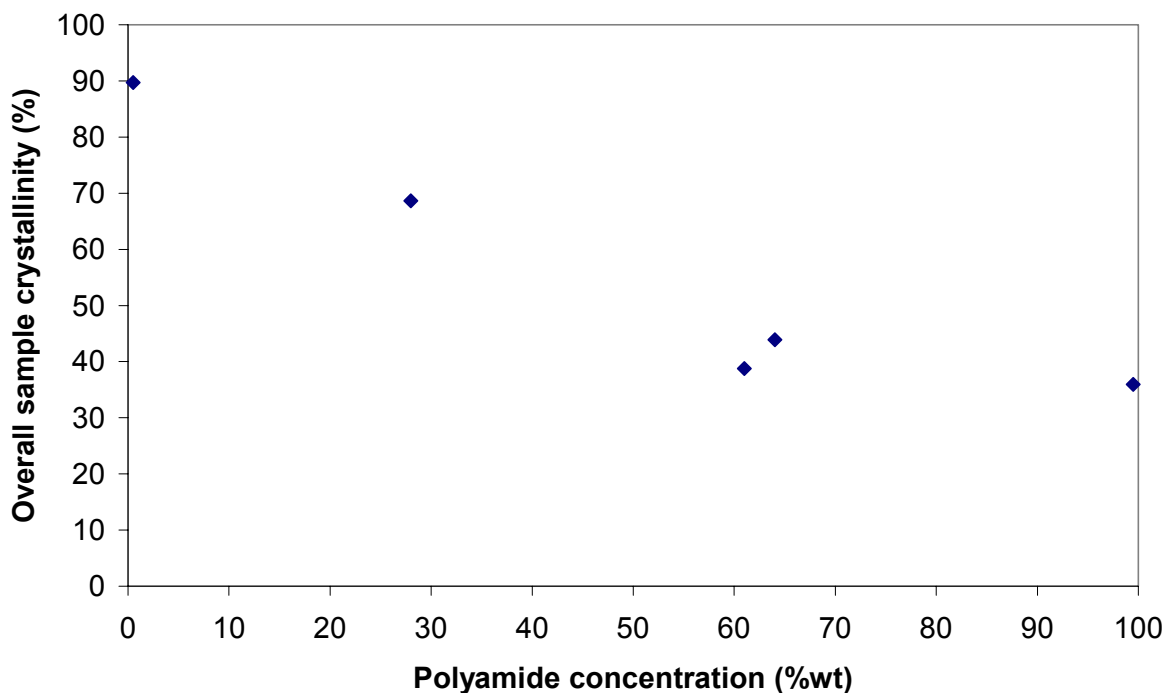


Figure 5-7 Overall percentage crystallinity of polyamide-6,9,/carbazole versus percentage polyamide determined from total first DSC melting enthalpy and TGA plateau level at 300 °C.

Thus the Gibbs free energy of mixing is non-zero. It should be noted here that the density of carbazole is close to that of a weighted average of amorphous and crystalline polyamide-6,9 and so the linear relationship on a molar volume basis will be within a few percent for a weight percentage basis. The density of phenothiazine is over 20% higher so a linear relationship on a molar volume basis will require a slight curve downwards between 0 and 100% on a weight basis to represent a colligative relationship.

5.3.2.3 DSC Crystallisation Temperatures at 2 °C/min for remelted ampoule material.

Figure 5-8 shows the thermograms of the crystallisation of material melt-blended in ampoules, taken to the melt in DSC and then crystallised at 2 °C/min.

- a) The polyamide-6,9 crystallisation curve at 2 °C/min cooling rate can be seen to be relatively sharp compared to the second crystallisation of the polyamide-6,9 powder sample and at a temperature 18 °C above that for the 25 °C/min cooling rate. The narrowness is seen here on a temperature axis rather than against time. The time taken for (90% of) the crystallisation was more than four times greater because of the slower cooling rate, allowing a more favourable development of lamellar

thickness. The increase in crystallisation temperature is typical of polymers crystallising at slower rates and requiring less temperature supercooling to crystallise.

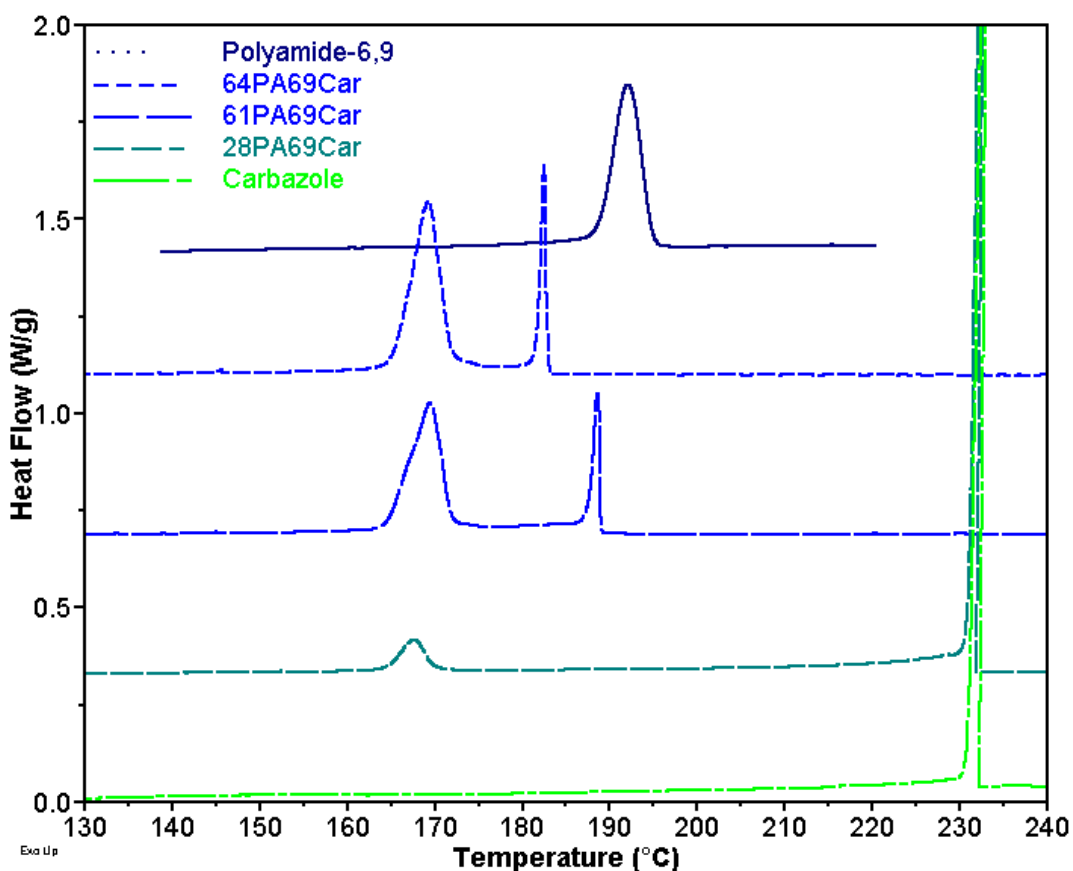


Figure 5-8 DSC thermograms of the first crystallisation of polyamide-6,9/carbazole ampoule material at 2 °C/min in the DSC.

- b) The 64PA69Car and 61PA69Car thermograms are very similar to each other in having two peaks, a “spiky” carbazole peak depressed by 40-50 °C compared to carbazole followed by a polyamide-6,9 peak depressed 25 °C below the normal polyamide-6,9 peak. The supersaturated solution has had excess carbazole crystallise first. The same situation is expected to have occurred previously in the ampoule samples although temperature control would have been poorer because of the size of the sample (1.5 g.) and the physical cooling conditions in the furnace. Some of the carbazole remains in solution and crystallises with the polyamide at lower temperatures. The ampoule sample 75PA6Car of Chapter 4, in a similar situation, had a total absence of carbazole crystallisation down to 60 °C below the normal carbazole crystallisation temperature compared to the 68PA6Car having a depression of 35 °C. The samples described in this section lie in concentrations between those

two from Chapter 4 and have carbazole crystallisation depressions broadly consistent with the polyamide-6/carbazole blends. There is another very minor difference between the two in that the 61PA69Car sample has a small peak for the crystallisation of a minuscule amount of pure polyamide just prior to the carbazole “spike”.

- c) The crystallisation of 28PA69Car takes place in a similar manner to the 25PA6Car ampoule sample of Chapter 4. Carbazole crystallises from the highly loaded solution at just under the normal crystallisation temperature for carbazole followed by the polyamide depressed to the same temperature as for the 64PA69Car and 61PA69Car samples.

In this section we have seen similar behaviour to that in the first crystallisation in the DSC of polyamide-6/carbazole blends in that there is a linear relationship between enthalpy of crystallisation and percentage polyamide. Again, the polymer/diluent system has the polyamide melting temperature lower than that of the diluent. The point where the enthalpy has fallen to zero is close to 90% polyamide.

5.3.2.4 Crystallinity from first crystallisation in the DSC

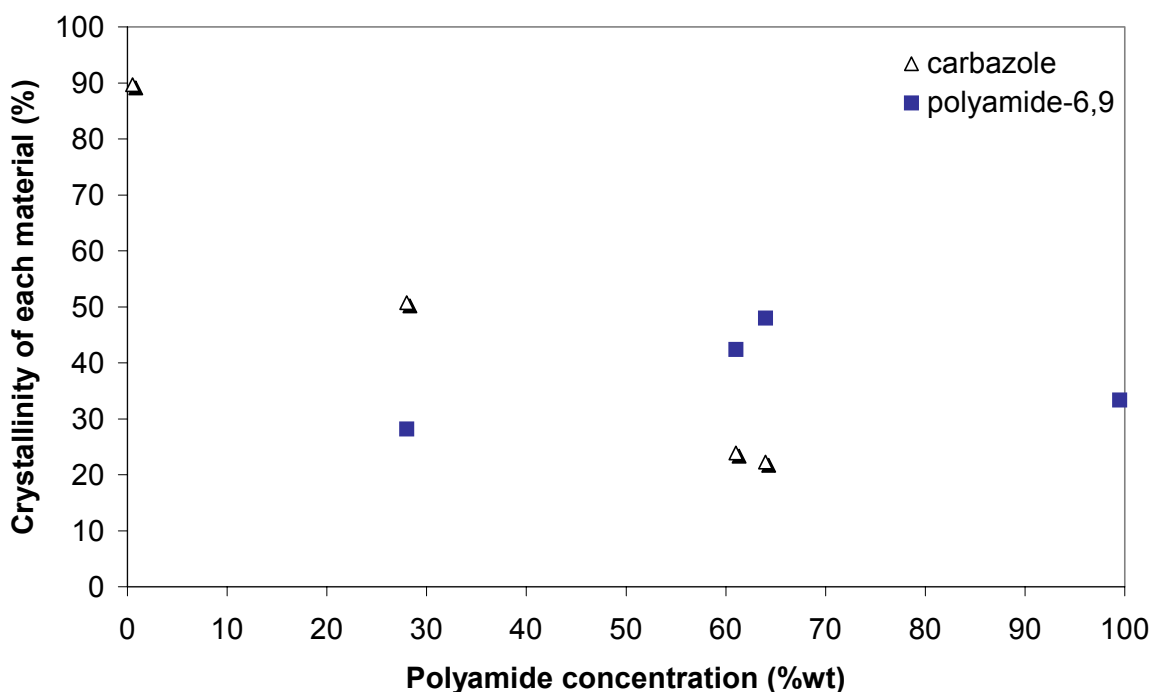


Figure 5-9 Crystallinity of Carbazole and Non-Carbazole parts from crystallisation from a polyamide-6,9/carbazole melt at 2 °C/min in the DSC.

Figure 5-9 plots the crystallinity of the phase domains that are virtually pure carbazole in the first crystallisation cooling and the crystallising peaks that

are not mainly carbazole domains. It was mentioned previously that there is no mistaking the crystallisation of phases that are almost pure carbazole (see Chapter 1, Fig. 1-20). It can be seen from Figure 5-9 that the crystallinity of the carbazole falls off towards zero with increasing polyamide content. This linear fall off without scatter is occurring in the same manner as that of polyamide-6/carbazole. The relationship appears linear but unfortunately there are few points available to make a stronger statement on this one set of data. The carbazole in these samples with high polyamide levels is being incorporated in the inter-lamellar or inter-spherulitic regions without being able to crystallise.

The crystallinity of the non-carbazole phase appears to be higher than that of the pure polyamide from the ampoule. That may be due to the mass of carbazole incorporated in the crystalline polyamide part. The results are different from those of polyamide-6/carbazole in Chapter 4. in that the level of carbazole crystallinity near 60% polyamide has not dropped to as low a value. The carbazole still has a strong inclination to phase separate and crystallise out of solution at these moderately high polyamide levels. This is consistent with the previous melting behaviour in Figure 5-6 with the same samples. There, the higher TLS peak had been seen of carbazole dissolving only at elevated temperatures. This is even more evident in Figure 5-11 below. That saturation at lower levels of carbazole is the reason the excess is crystallising here.

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

Figure 5-10 is very similar to Figure 4-13 for the phase diagrams with polyamide-6/carbazole blends in that it is a eutectic style. Heating and cooling non-equilibrium phase diagrams differ mainly in a 10 to 15 °C vertical displacement.

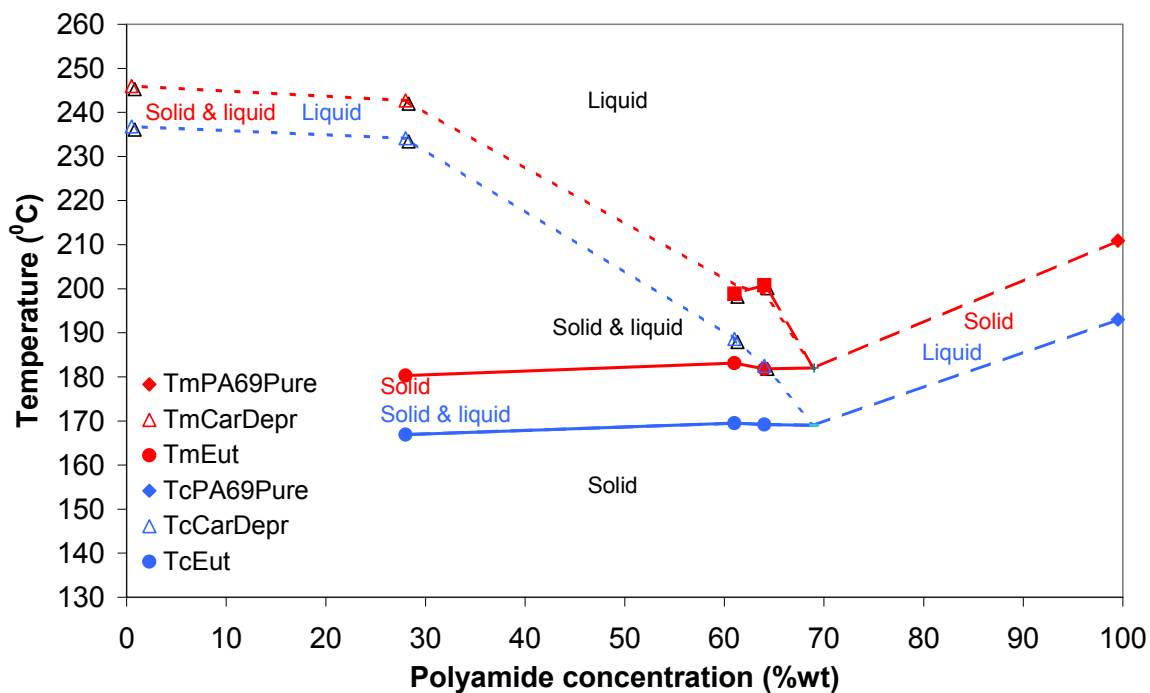


Figure 5-10 Non-equilibrium phase diagrams for polyamide-6,9, carbazole and their blends showing eutectic-like behaviour

5.3.2.6 *Third Melting of ampoule materials/Second DSC Melt at 5 °C/min.*

The ampoule samples in pans from the first DSC runs were passed through a repeat melt/crystallisation cycle in the DSC similar to chapters 3 and 4.

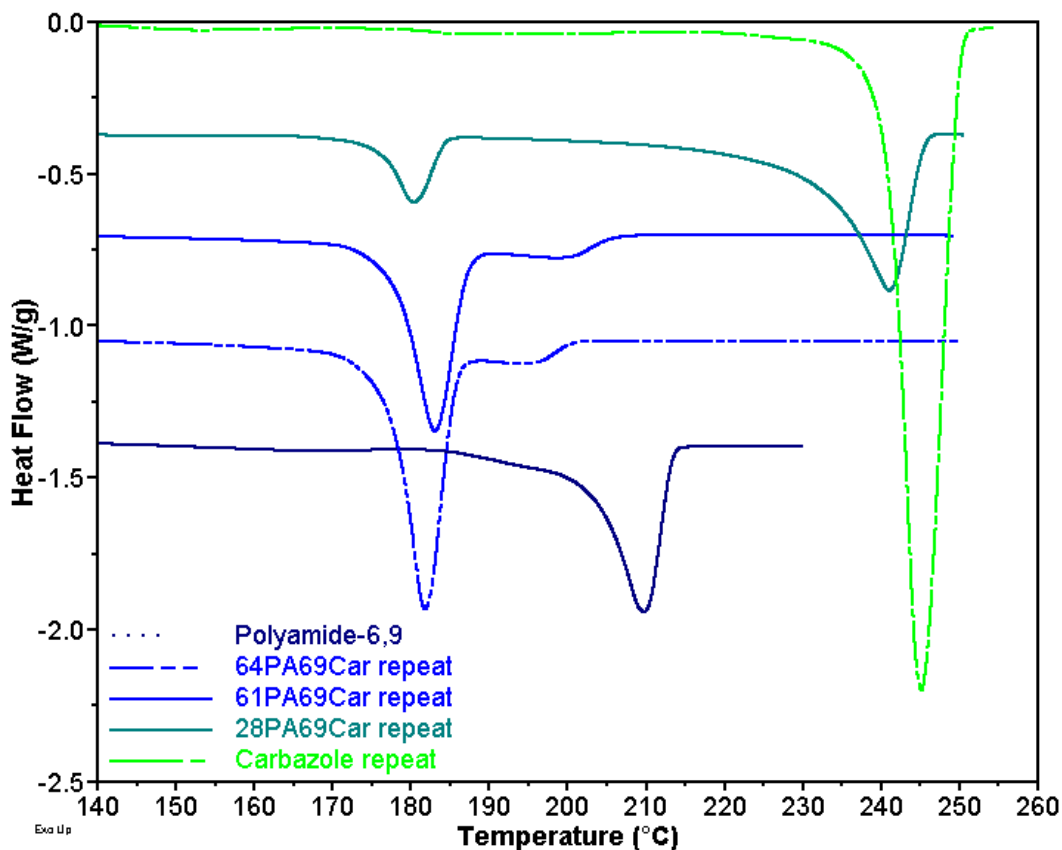


Figure 5-11 DSC thermograms of the second melt in the DSC at 5 °C/min of polyamide-6,9/carbazole ampoule material.

Figure 5-11 shows the DSC thermograms of the melt portions of the repeat DSC runs. The thermograms are very similar to those of the first melt in the DSC, as would be expected.

- a) The minor differences are that the very broad TLS peaks of 64PA69Car and 61PA69Car have become slightly sharper with the repeat run. That is due to uneven cooling in the ampoule having caused a less than ideal crystallisation that was detected in the DSC melting run afterwards. The cooling in the DSC pan was under very tightly controlled conditions and was for a small mass of material, much easier to keep all at (nearly) the same temperature. It is not obviously clear just from these thermograms whether the polyamide or the carbazole is in excess.
- b) The size of the carbazole melt/dissolution in 28PA69Car at high temperatures has reduced somewhat due to carbazole evaporation as only 45% of the original amount of was left after the second heating/cooling cycle.

5.3.2.7 Third Crystallisation of Materials/Second DSC Crystallisation at 2 °C/min.

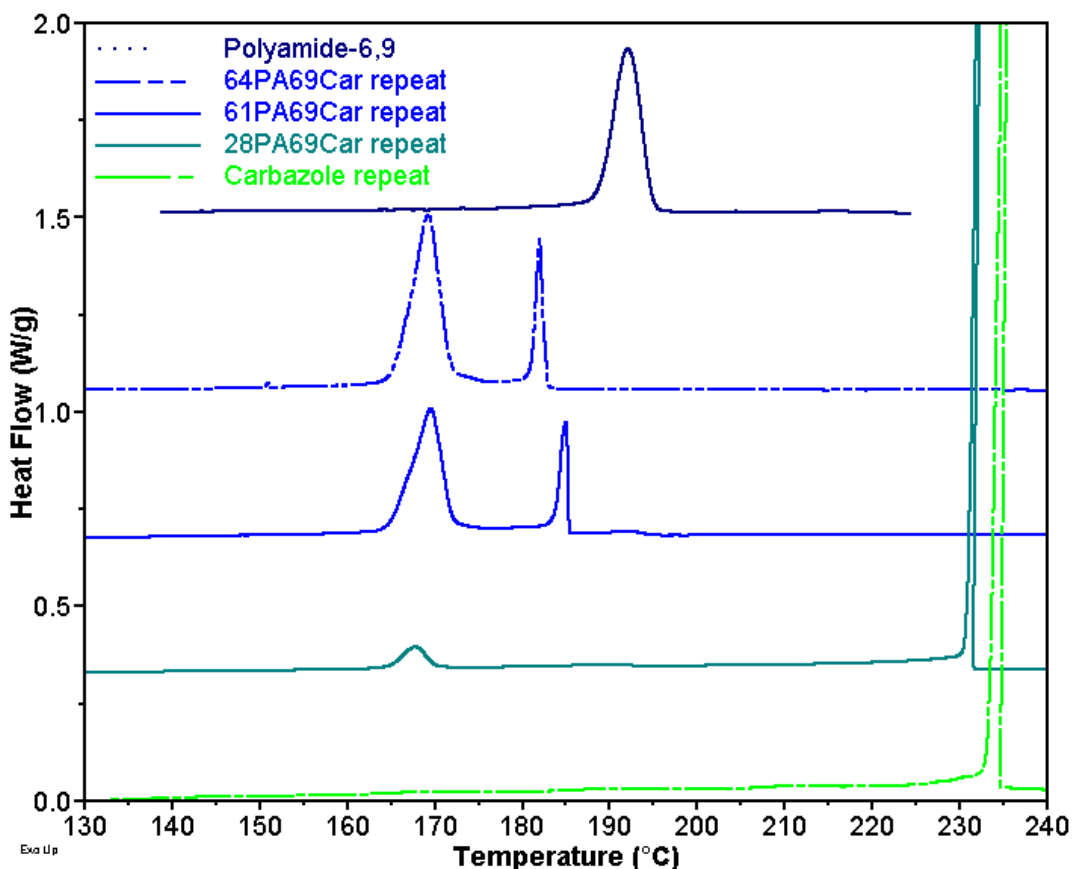


Figure 5-12 DSC thermograms of the second crystallisation at 2 °C/min in a DSC of polyamide-6,9/carbazole ampoule material.

Thermograms in Figure 5-12 of the second crystallisation in the DSC are also generally similar to the first time. The exceptions are:

- a) Evidence in 61PA69Car and perhaps in 28PA69Car for a minimal amount of nearly pure polyamide-6,9 crystallising at 190 °C. This can be seen for 28PA69Car in Appendix A.
- b) A reduction in the carbazole crystallisation temperature of 3-4 °C, probably due to loss of carbazole.

5.4 Fourier Transform Infrared Spectroscopy

Photoacoustic FTIR measurements were carried out in the Mid Infrared and DRIFT FTIR in the Near Infrared that, in all cases, resulted no evidence for hydrogen bond interactions being found between polyamide-6,9 and carbazole in polyamide-6,9/carbazole blend samples. This null result is the same as found in earlier chapters on other polyamide/carbazole blends. Detailed spectra are provided in Appendix D on CD.

5.5 Summary

As with the polyamide-6/carbazole blends, there are reasonable similarities with melt blending polyamide-4,6 with carbazole once the roles of the materials are interchanged. Again, this is because polyamide-4,6 melts at temperatures above carbazole rather than the other way around with polyamide-6/ and polyamide-6,9/carbazole blends.

The remelting of previously crystallised samples in pans from powders has led to sharper melts due to the more intimate mixing of the molecules in agreement with the other blends.

The effect on the polyamide-6,9 melting temperature is a depression of approximately 30 °C. There is approximately 25 °C depression of the polyamide-6,9 crystallisation during cooling. The depression of carbazole crystallisation in the experiments was seen to be 40-50 °C.

Polyamide-6,9 has a greater propensity than polyamide-6 to crystallise in the metastable form rather than the stable form. We have seen here similar effects to polyamide-6 in the polyamide crystallising in different forms depending upon previous thermal history.

Another similarity with both polyamide-4,6/ and polyamide-6/carbazole blends is the lower melting material starting to melt at reduced temperatures in a eutectic melt and dissolving the higher melting material to a certain limit. At that stage any excess of the higher melting material requires substantial increases in temperature to dissolve all the remainder.

We also find here that the overall crystallinity of blends from ampoules decreases with increasing polyamide level. The crystallinity of the carbazole decreases rapidly with increasing polyamide level. There is a maximum in non-carbazole crystallinity between approximately 50 and 80% polyamide.

Here again we have the experience found with polyamide-4,6/ and polyamide-6/carbazole blends that there is no evidence for hydrogen bond interactions taking place between polyamide-6,9 and carbazole when they are melt blended together in ampoules. The interactions are driven by the (limited) compatibility of the two materials and their ability to coexist sterically at a molecular level rather than due to any hydrogen bonding.

There are differences, however, compared to carbazole blends with the other two polyamides.

One difference is the carbazole not crystallising out at 63% polyamide for fast cooling but crystallising (at the same concentration range) for slow cooling. At that concentration the solution becomes saturated earlier during remelting requiring higher temperatures to dissolve the excess carbazole.

Another difference was the observation of two peaks for dissolution of excess carbazole above the melting of polyamide for both pan blended and ampoule sample monitoring in the DSC.

The crystallinity of carbazole in recrystallising ampoule samples does not drop to zero as quickly as for the other two polyamides with higher densities of amide groups.

The reasons for these differences in blend solubility/melting/crystallinity properties lie in this polyamide having longer carbon chains in the repeat unit and/or in this polyamide being an m,n type of polyamide.