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ON THE PREDICTION OF POLYMER BLEND  
MISCIBILITY

Part 2: Miscible polyketone blends

(November 1989 - June 1991)

by

A. WAKKER

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ON THE PREDICTION OF POLYMER BLEND MISCIBILITY  
PART 2.: MISCIBLE POLYKETONE BLENDS

(November 1989 - June 1991)

by

A. Wakker

Approved by : R. Reijnhart

SUMMARY

Using a practical miscibility guide developed in part 1 of this work, it is predicted and verified that Polyketone ("Carilon") is miscible with Polyacrylonitrile, and partially miscible with Nylon 4,6. It is discussed how the results can be used to produce useful Polyketone blends.

October 1991

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ON THE PREDICTION OF POLYMER BLEND MISCIBILITY  
PART 2: MISCIBLE POLYKETONE BLENDS

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## 1. INTRODUCTION

In part one of this work [1], the basic concepts governing polymer-polymer miscibility have been developed. Basically, it was shown that the molecular miscibility of two high molecular weight polymeric materials is mainly determined by the competition between unfavourable dispersive and favourable specific interactions. The upshot was that only one term in the free energy of mixing expression, namely the enthalpy of mixing due to specific interactions, is negative and hence, favourable for mixing. It was argued that this term is never very large in polymer blends, due to steric limitations. Moreover, it was shown that the entropy loss associated with the formation of specific interactions, forces the mixture towards immiscibility when temperature is increased (so called lower critical demixing). Hence, in order to establish miscibility at (high) processing temperatures, dispersive interactions, which can be predicted from the solubility parameter difference between the constituents, should not be too strong. What we found from an extensive study of available miscible blends is that the solubility parameter difference between the constituent compounds is, on the average, smaller than  $0.4 \sqrt{(\text{cal/cc})}$ . The presence of specific interactions is a necessary, but not sufficient condition to obtain miscibility.

This rule of thumb enables us to predict whether two polymeric materials are miscible or not. Although we already stated in part one that there are possibilities to quantify this novel concept in more detail, we will apply the basic concept in this part of the report to find miscible blending compounds for polyketone (Carilon).

The concept is applicable to amorphous materials only. Lots of polymers are (semi-) crystalline, and crystalline phases never mix. Thus, im(miscibility) always refers per definition to the amorphous phase of a polymer blend. However, it is known from polymer blending practice that a melt-processed semi-crystalline material has an interwoven morphology of crystalline spherulites and amorphous phase [2]. Crystallinity is never perfect and hence, on a microscopic scale, some amorphous material will always be available for molecular interactions between different polymers. Hence, our miscibility concept should also be applicable to the prediction of thermodynamic miscibility of the amorphous parts of semi-crystalline materials.

The day-to-day practice of polymer blending and mixing leads us to reflect upon an important question: Do we really want miscible polymeric materials (miscible on a molecular scale), or do we rather want to have immiscible blends in which the good properties of the constituents, by thorough mixing or by compatibilization via a surface active agent, are combined on a mesoscopic scale (typically,  $0.1-10 \mu\text{m}$  phase size) ? The answer to this question depends on the particular property envisaged. A complete list of properties of commercial polymer blends can be found in reference [3]. It will suffice here to state that anno 1991 the majority of commercial blends are immiscible. The most

encountered reason for blending immiscible materials is impact improvement (toughening). The only commercial miscible polymer blend is PS/PPO (GE's Noryl). Noryl is a typical example where blending is used to create a new material which has its glass transition temperature in between those of the constituents. Where PPO (high  $T_g$ ) is difficult to process and PS (low  $T_g$ ) is a brittle material, Noryl makes up a high impact, easy-to-process engineering thermoplastic.

In immiscible blends, good properties are only obtained when sufficient adhesion between the different materials is established, either by partial thermodynamic miscibility of the two materials, resulting in a sufficiently broad interface and hence, a low interfacial tension, or by surface active agents such as block-copolymers. Hence, thermodynamics remains the driving force behind adhesion between immiscible materials.

It is the aim of this report to test our miscibility concept by predicting miscible blending compounds for Shell's new polyketone, "Carilon". Some properties of Carilon, together with results from a WRC blending study, will be presented in chapter 2. The actual prediction of Carilon blend miscibility, together with its verification, will be presented in chapter 3. From DSC studies on solution cast blends, it will be shown that Carilon is miscible with Polyacrylonitrile, and partially miscible with Nylon 4,6. Whether these results are useful for the actual material properties of the potential blends, will be discussed in chapter 4.

## 2. POLYKETONE

### 2.1. General properties

In general, we define polyketones as copolymers of C=O with saturated olefins. In the eighties, a special kind of polyketone was developed at KSLA, namely a linear, alternating copolymer of C=O and ethene (Carilon:  $(-\text{CH}_2\text{CH}_2\text{C}=\text{O}-)_n$ ) [4]. A model presentation of this polymer is shown in figure 1. Due to its crystallinity and high melting point (220 °C for EP grade), together with its relatively cheap polymerisation route, it has become a very promising engineering thermoplastic.

However, the material has two shortcomings which do need further attention: it has an amorphous phase - approximately 50 % by volume fraction - with a glass transition temperature just around ambient. Hence, the strength of the material is expected to be quite sensitive for local changes in ambient temperature. Furthermore, the melt stability is not yet very good, which makes the material difficult to process (e.g. in an extruder). By blending Carilon with another, thermodynamically miscible polymer, which has a higher or lower  $T_g$ , a new material with a  $T_g$  in between the  $T_g$ 's of the constituents may be obtained. We expect that it is required that this polymer forms specific interactions with the Carilon carbonyl group, and that its solubility parameter matches the one of Carilon within 0.4  $\sqrt{(\text{cal}/\text{cc})}$ . In addition, if we are lucky, the formation of specific interactions could possibly contribute to an improvement of the melt stability of the material. This idea is based on the - admittedly, rather vague - assumption that after melting of the crystals, the polymer may be somewhat more "protected" against various chemical degradation reactions when part of the segments are chemically "trapped" in specific interaction channels with the blending compound.

## 2.2. WRC Carilon blend study

Previously, a considerable research effort at WRC has been devoted to the design of Carilon blends [5]. Blending was carried out in a twin screw mini-extruder, and the products were examined on, for example, melt stability, processability, phase dispersion size and phase transition temperatures. Melt stability could not be improved significantly. One truly miscible blending compound was found, namely a low molecular weight polyvinylphenol (PVP) polymer.

The PVP used in the WRC study had a molecular weight of approximately 4000, which is equivalent to a chain length of 30. This results in a critical interaction parameter  $\chi_c = 0.5(1/30) = 0.015$  (reference [1], equation 2.8). For strong hydrogen bonds, quite likely the case here, this value is, in effect, equivalent to  $\chi_c = 0$ , because no significant increase of the LCST is expected for such a small change in  $\chi_c$  (see reference [1], figure 2). This indicates that a high molecular weight PVP would probably also have been miscible. Unfortunately, these are not readily available.

Using Hoy's group contribution scheme, we calculated a solubility parameter of 8.9 for PVP [1]. Compared to  $\delta = 11.7$  for Carilon according to Small's scheme [1], the difference does not fit in our miscibility concept.

However, it should be noted that PVP is strongly associated in the liquid state: it forms hydrogen bonds with itself. In a recent publication, Coleman et al. [6] revisited the solubility parameter concept in a consistent way. Consistent means here that they used coupled group contributions for both molar cohesive energy densities and molar group volumes for the unassociated, dispersive parts of the groups. Their results are consistent with Small's scheme only (see reference [1]) and, in addition, they came up with a non-associated solubility parameter for hydroxyl containing, self associating polymers. Their result for PVP is 11.0, which brings the difference with PK close to our scheme again. However, this would bring the difference between PVP and PVA, reference 1, from 0.7 upto 1.4, which does not fit into our scheme. The only proper conclusion here must be that due to its strong self association, the dispersive solubility parameter of PVP carries too large an uncertainty to do a reasonable prediction.

The solubility parameters of many other polymers blended with Carilon at WRC can be calculated with sufficient accuracy [1] (Coleman et al. take an uncertainty of  $\pm 0.2$  in any solubility parameter of non-associated polymers). These include: Nylon 6 (Hoy: 10.7, Coleman: 10.5), polycarbonate (10.0), SAN (1/3 AN: 9.7), ANS(2/3 AN: 10.5), PCL (10.2), PPO (8.9), PVF (7.7). PETP (11.4), PBTP (11.5).

Although certainly Nylon 6 and SAN and ANS will form specific interactions with Carilon, these blends appeared not to be miscible. Clearly, the solubility parameter difference must have been too large here. Apart from PETP and PBTP, the difference with the other immiscible polymers is too large as well, but here specific interactions are not present. Hence, immiscibility can be expected a priori. Although both PETP and PBTP do have their solubility parameter within the required range, their chemical structure (similar to polycarbonate [1]) makes the formation of specific interactions with Carilon unlikely.

In conclusion, the immiscibility of Nylon (which is crystalline, but also has a substantial amorphous phase which should have been miscible), SAN and ANS (both amorphous) with Carilon fully supports our miscibility rule, in the sense that specific interactions are present, but the

solubility parameter difference is too large to establish miscibility. This is made clear in figure 2.

### 3. NEW MISCIBLE CARILON BLENDS

The basic technological challenge for finding a miscible blending compound for Carilon is to meet its relatively high solubility parameter  $\delta$  of 11.7  $\sqrt{\text{cal/cc}}$ . Basically, non-polar polymers have a solubility parameter ranging from 7 to 9, the group of moderate polar polymers (acrylics, acetates etc.) may come as high as 10, polyamides come within range, and only PAN has a higher  $\delta$  of 12.1.

PAN is a semi-crystalline polymer,  $T_m \approx 330$  °C,  $T_g \approx 70$  °C. Its thermal stability is very poor, and the material can hardly be extruded or injection moulded. The typical application found for PAN is filament winding from solution.

Since it is known that the C=O...HC-Cl interaction is responsible for negative heats of mixing in MMA/Vinylchloride mixtures [7], we expect that the C=O...HCC=N interaction is even stronger, due to the higher electronegativity of the nitril group compared to the Chlorine group. Hence, a sizable Lewis acid-base interaction [1] is expected to form in a Carilon/PAN blend.

In order to test the putative miscibility of Carilon with PAN, a 50/50 Carilon (EP grade, MD4 89/010,  $M \approx 50000$ ) / PAN (Polysciences, cat nr #18842,  $M = 25000$ ) film was solvent cast from hexafluoroisopropanol (HFIPA) at 120 °C. Indeed, by means of DSC (see appendix), one single glass transition temperature was observed in this material, in between the glass transitions of the constitutive polymers (figure 3). The material did not demix after a two minute annealing at 250 °C. Hence, lower critical demixing (see reference [1]) does at least not occur below this temperature. Single glass transitions were observed for other compositions as well. However, it was not possible to establish a clear  $T_g$  - composition relationship. Apparently, the reproducibility of the relative amount of solvent cast amorphous material is not very good. The melt stability of the Carilon/PAN material, as measured by the decrease in heat content of the melt transition due to annealing above  $T_m$  for several minutes, is even worse than that of pure Carilon.

We conclude here that our miscibility concept appears to be valid. This is illustrated in figure 2, where we have plotted the miscible blends studied in part 1 of this work, together with the miscible Carilon/PAN blend, as well as the immiscible Nylon6, SAN, and ANS blends, which do have specific interactions with Carilon.

It is quite inspiring that Nylon 6 ( $\delta = 10.5$ ) appeared to reveal the best compatibility in the WRC study, in the sense that the size of the phase separated domains (as observed by microscopy) was clearly the smallest of all blends investigated (0.2  $\mu\text{m}$ ). Moreover, melt stability was claimed to be somewhat improved.

The functional interacting group in Nylon (polyamide) is -NH-C=O-. Together with the hydrocarbon unit  $(-\text{CH}_2)_n$ , it forms Nylon-(n+1). The solubility parameter can thus be varied easily by changing n, as shown in table 1. More  $\text{CH}_2$  groups will decrease  $\delta$ , less  $\text{CH}_2$  groups will increase  $\delta$ . It can be read from table 1 that Nylon-4 should be extremely well miscible with Carilon!

The chemistry of Nylon synthesis dictates that there is a lower bound on n. Consequently, Nylon-4 is not a commercial product. Recently, DSM developed a new process for the large scale production of Nylon 4,6 (an

alternating copolymer of 3 and 5 CH<sub>2</sub> units, connected by -NH-C=O- groups). It is sold under the trade name "Stanyl", and the properties are claimed to be superior to those of Nylon 6. It is a semicrystalline material, with a melting point close to 300 °C. We expect that the solubility parameter of this material has a value somewhere in between that of Nylon-4 and Nylon-6, approximately around 11 (see table 1). Since we do not know the density of Stanyl exactly, this value should be considered with care. It is plotted in figure 2. We expect that Stanyl is just on the edge of miscibility and if we are lucky (when the solubility parameter is only a little bit larger than 11), it may even be completely miscible with Carilon.

A 50/50 blend of Carilon (EP grade, MD4 89/010, M ≈ 50000) and Stanyl (purchased from DSM, standard grade, pelletized, no molecular weight indicator) was solvent cast from HFIPA at 120 °C. In order to test the compatibility between Stanyl and Carilon, two types of DSC experiments have been performed:

1. Investigation of the glass transition of Carilon and the blend between 220 and 400 K (figures 4 and 5).
2. Investigation of both glass- and melting transitions of the blend, Carilon and Stanyl between 250 and 600 K (figures 6 to 8).

The glass transition of Carilon can be observed in figure 4. It is located around 290 K, in agreement with the result presented in figure 3. We did not carry out a similar DSC trace of the glass transition region of Stanyl. A glass transition in Nylon 6 is reported at 50 °C [8]. Inspection of figure 7, run 1 (see appendix) does not clearly reveal a glass transition for Stanyl as well.

Inspection of figure 5, in which the DSC trace of the glass transition region of the blend is shown, does not reveal a clear existence of the glass transition of either Carilon, or Stanyl. Very little structure in the DSC trace is found in this temperature region, in which we might expect a new, single glass transition temperature in case of complete miscibility (as in the PK/SAN blend), or two separate T<sub>g</sub>'s, of which the one of PK should be observable, in case of immiscibility. Most likely, this means that the blend is partially miscible, resulting in a broad glass transition temperature region, which cannot be distinguished from the background signal in the DSC experiment.

Inspection of figure 6, where the full temperature range of phase transitions of the blend is shown, reveals some noteworthy phenomena. In the solution cast blend, during first heating above the melting point of Carilon (figure 6, run 1), a quite structureless glass transition region is observed, consistent with the observation (see figure 5) discussed above. However, a new "peak" is present at 400 K, which is not present in either DSC trace of the pure components (figures 7 and 8). This peak has disappeared after a two minute annealing, at 225 K, above the melting point of Carilon (figure 6, run 2). Comparison of the decrease in heat of melting (melting peak content) and melting temperature of crystalline Carilon in the blend and in the pure polymer after annealing (see runs 2 of figures 6 and 7), reveals that the melt stabilities of Carilon in the blend and in its pure state are comparable. In any case, a significant improvement in melt stability appears not to be present. Annealing of the blend above the melting point of Stanyl completely destroys the crystallinity of Carilon (figure 6, run 3). Moreover, the

heat of melting of Stanyl in the blend has decreased more than in the pure polymer (figure 8, run 2).

#### 4. CONCLUSIONS AND OUTLOOK

We conclude that our practical guide for predicting polymer blend miscibility, namely:

1. ensure that specific interactions are present
2. keep the solubility parameter difference  $\Delta\delta$  between the constituents within  $0.4 \sqrt{(\text{cal/cc})}$ ,

can be successfully used to predict the thermodynamic miscibility of Carilon with other polymers. It was predicted and verified that the amorphous phases of Carilon and Polyacrylonitrile ( $\Delta\delta = 0.4$ ) are completely miscible. It is likely that the amorphous phases of Carilon and Nylon 4,6 ( $\Delta\delta \approx 0.7$ ) are partially miscible.

The melt stability of PK/PAN is even worse than that of pure Carilon. It is a material that probably can hardly be processed.

The melt stability of PK/Nylon 4,6 is the same as that of pure PK, if the temperature is not higher than 525 K, a typical processing temperature for pure Carilon. At this temperature, Nylon 4,6 crystalline phase is still present, so that the material cannot be processed at this temperature. If the material would be processed above the melting point of Nylon 4,6 at 600 K, Carilon will completely degradate, leading to subsequent degradation of Nylon 4,6, which is apparent from the more stronger decrease of the heat of melting of Nylon 4,6 in the blend than in the pure polymer.

Summarizing, PK/Nylon 4,6 is not an interesting blend because it cannot be processed, due to the relatively high melting point of Nylon 4,6. However, if we are looking for miscible blending compounds for Carilon, we conclude that Nylon - type materials are the best option, due to the fact that these materials do match the solubility parameter of Carilon best, and do form specific interactions with PK. Furthermore, addition of Nylon - type material does not seem to promote degradation of Carilon.

An application for Nylon - type material may be found in the lubrication of Carilon. When PK is processed in an extruder, a lot of heat is generated, leading to temperature rise and subsequent degradation of the material. The heat is generated partly by friction with the metal surfaces, partly by the high viscosity of the melt itself. The former may be overcome by adding an immiscible lubricant, the latter may be overcome by adding a thermodynamically miscible lubricant, thereby lowering the melt viscosity of the material. Since polymer lubricants need a very high boiling point, one generally uses waxes with a chain length of 10 to 20 characteristic units [9]. The value for the critical interaction parameter  $\chi_c$  [1] for a mixture of a high molecular weight polymer and a lubricant with chain length 10 is  $\chi_c = 0.05$ , already very low. Hence most lubricants are immiscible, and are used for the reduction of friction. However, some amide waxes [9] may show at least some partial mixing with PK as well, provided that their solubility parameter can be tuned into the appropriate range. In principle, the recipe for this is very simple: the non - polar parts of the amide wax should be kept as small as possible, but not so small as to keep its

melting point below that of Carilon. Whether such a material is commercially readily available, remains to be seen. Still, it may be an ideal material for Carilon lubrication: friction reduction by the wax - rich phase (which may migrate to the metal surfaces due to the very low viscosity), together with melt viscosity reduction of PK (the wax - poor phase).

Amsterdam, October 1991

TABLE I  
SOLUBILITY PARAMETERS OF POLYAMIDE [4]

<u>Polyamide</u>	<u><math>\delta</math> (/(cal/cc))</u>
Nylon 3	12.8
4	11.7
5	11.0
6	10.5
7	10.1
8	9.9
9	9.7
10	9.5
11	9.4
12	9.3

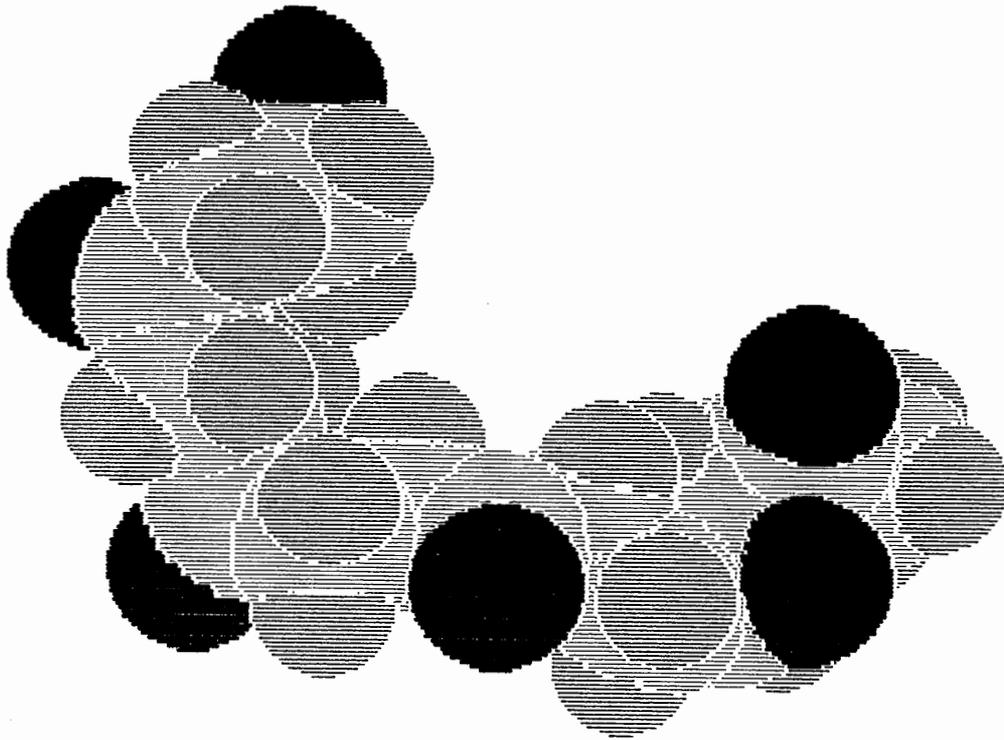
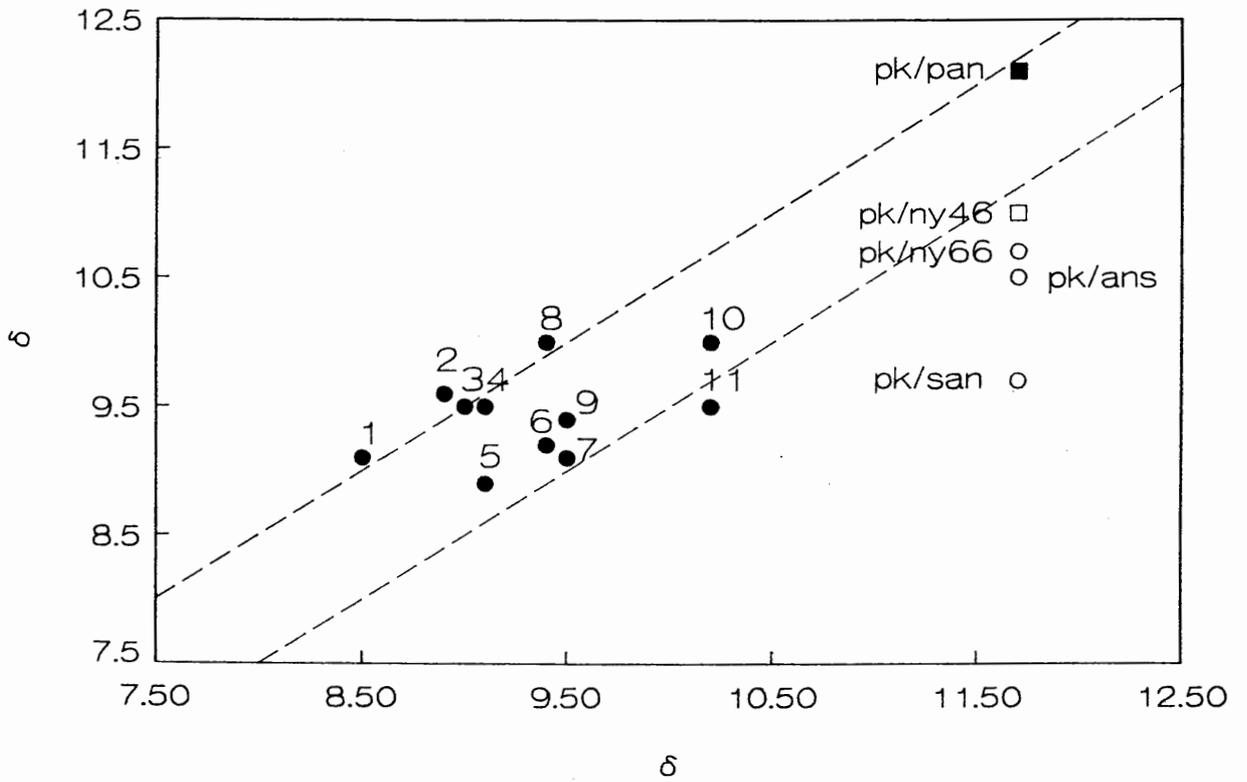


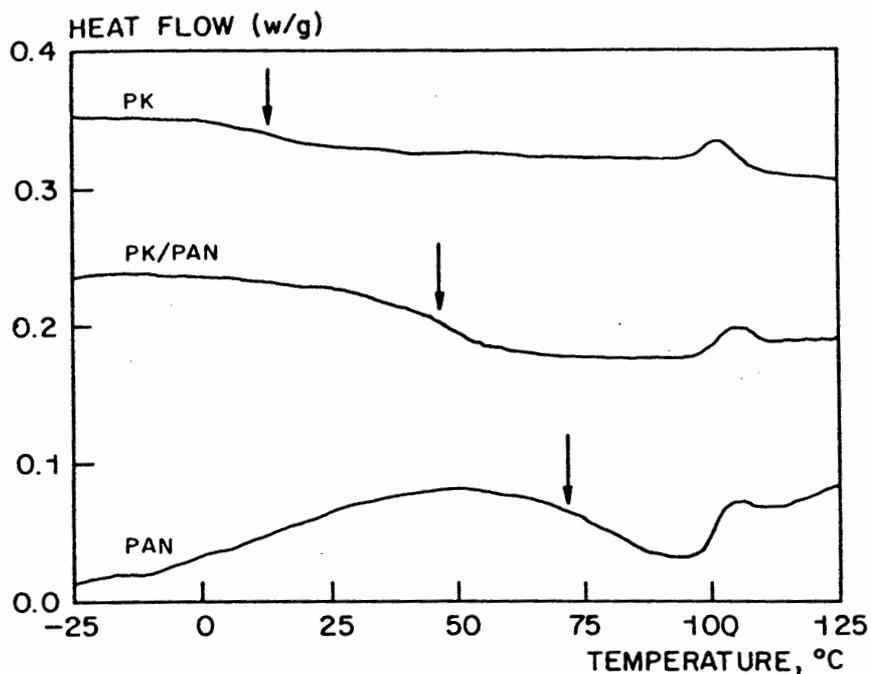
Figure 1: model presentation of a Carilon 6-mer.



● LITERATURE STUDY (1.pvme/ps, 2.pvph/pvac, 3.ppea/pvc, 4.ppra/pvc, 5.ps/ppp, 6.pmma/san, 7.pvc/pbua, 8.pmma/pc, 9.pvc/pmma, 10.pcl/pc, 11.pvc/pcl).

■ miscible  
 □ part. miscible  
 ○ immiscible

Figure 2: miscible, immiscible and partially miscible Carilon (PK) blends



DSC CURVES OF PK, PAN, AND (.55/.45) PK/PAN. ARROWS MARK THE GLASS TRANSITIONS. THE EXOTHERMIC PEAKS AT 100 °C HAVE NOTHING TO DO WITH THE POLYMERS. THEY ALWAYS APPEAR AFTER DEEP COOLING (-50 °C) AND SUBSEQUENT HEATING OF THE DSC CELL (OXIDATION REACTION ON HEATERS ?)

Figure 3: dsc traces of PK, PAN, and PK/PAN. arrows mark the glass transitions

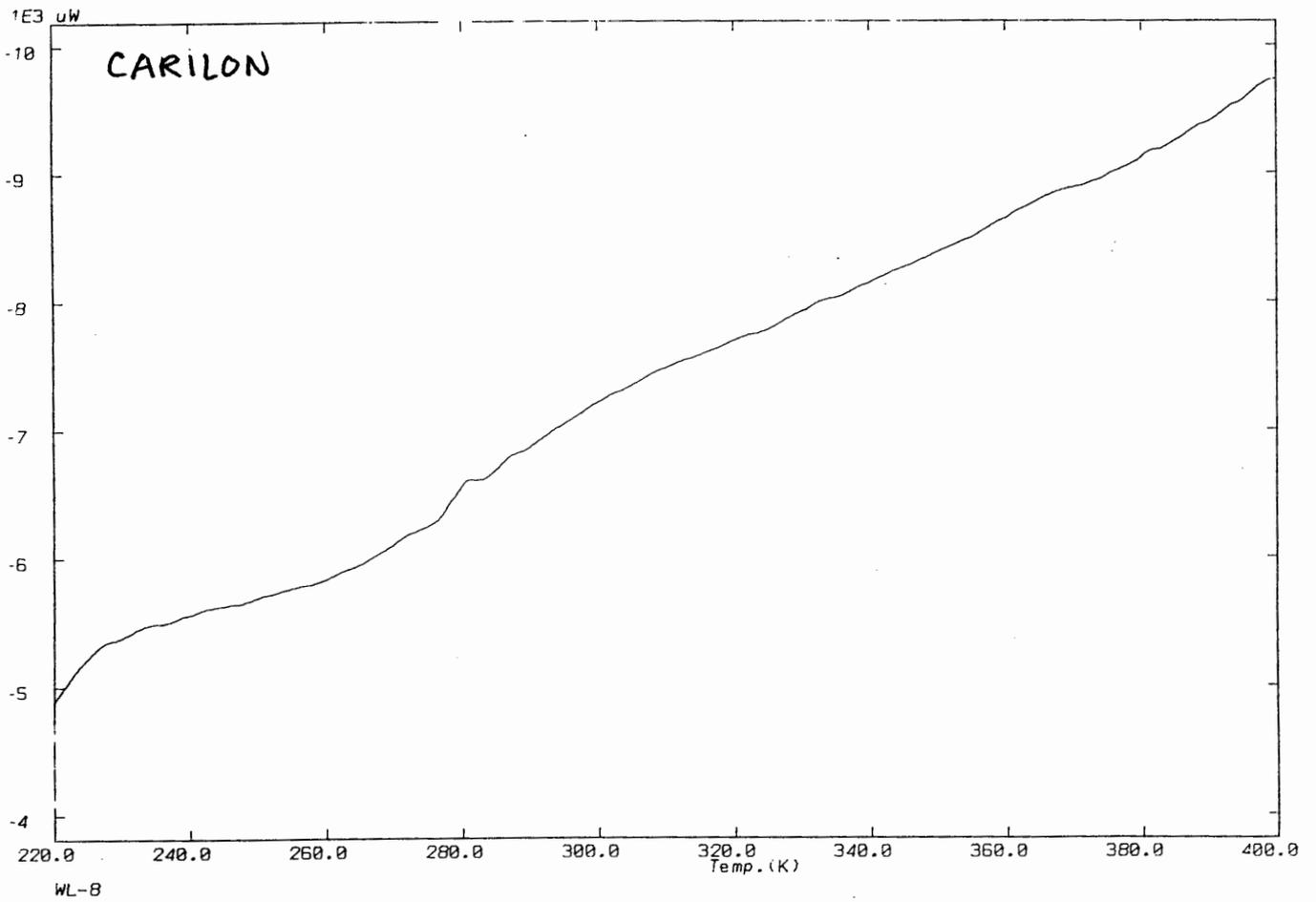


Figure 4: dsc trace of the glass transition region of PK

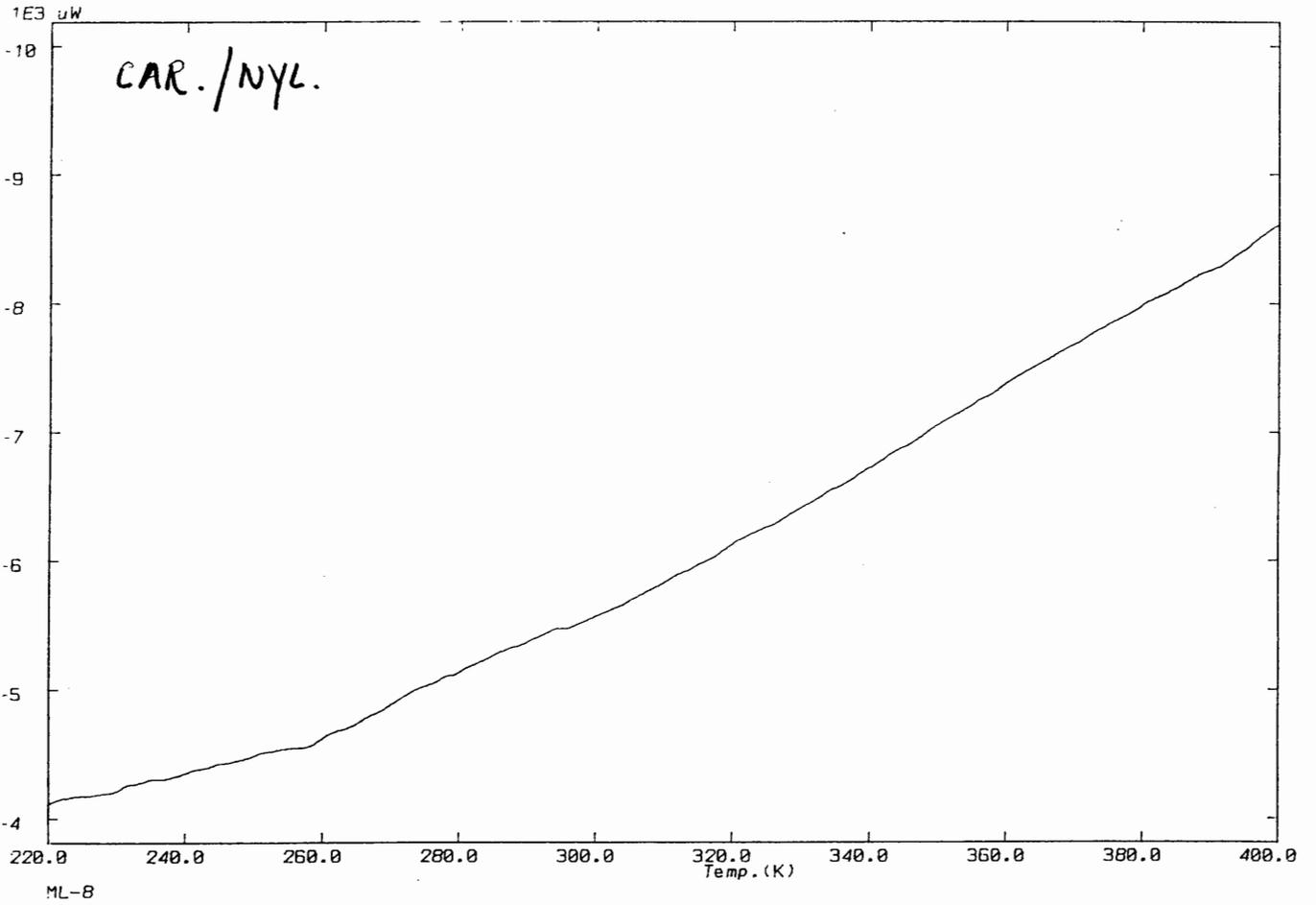


Figure 5: dsc trace of the glass transition region of PK/Nylon 4,6

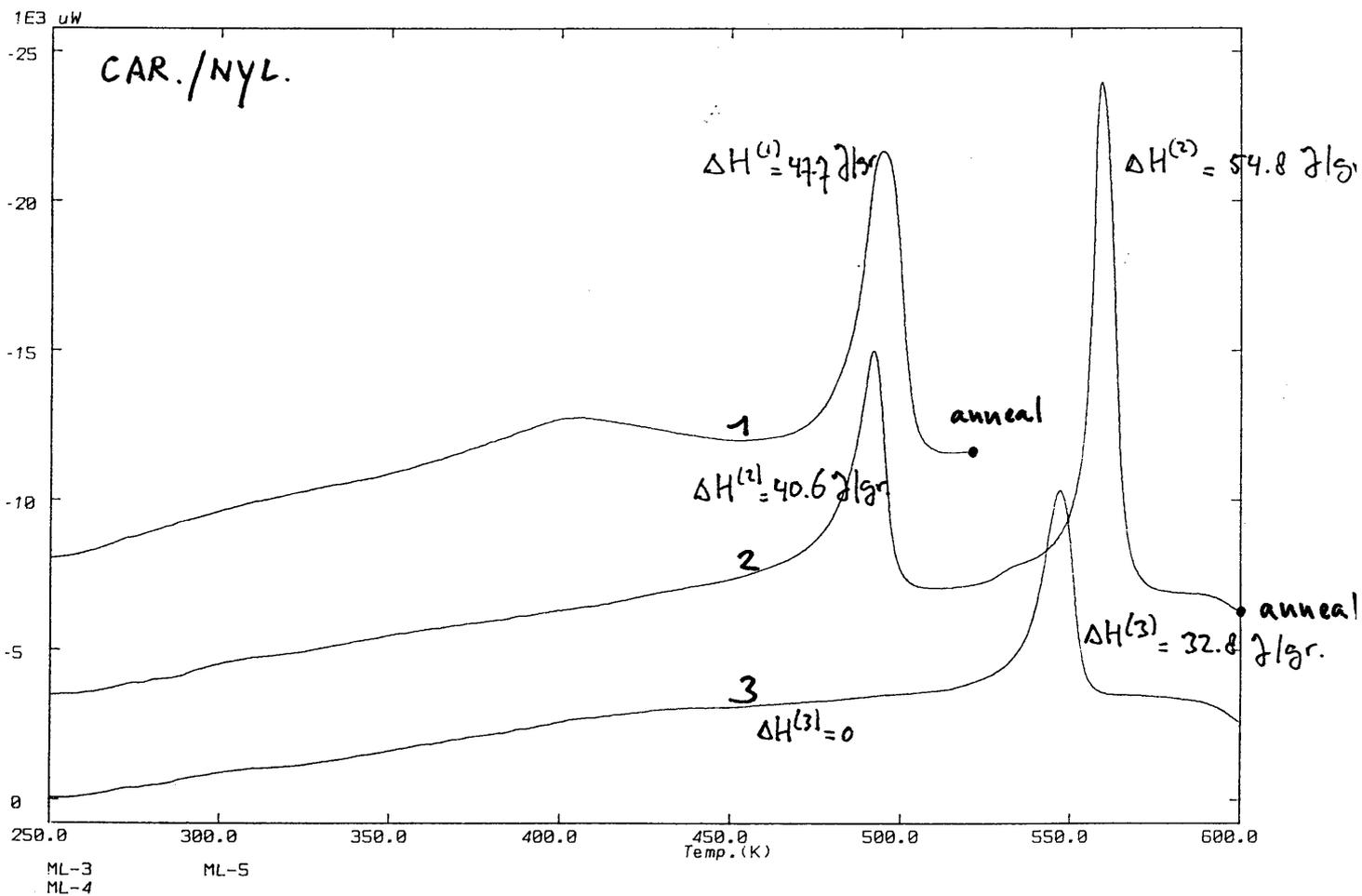


Figure 6: dsc traces of PK/Nylon 4,6, full phase transition range

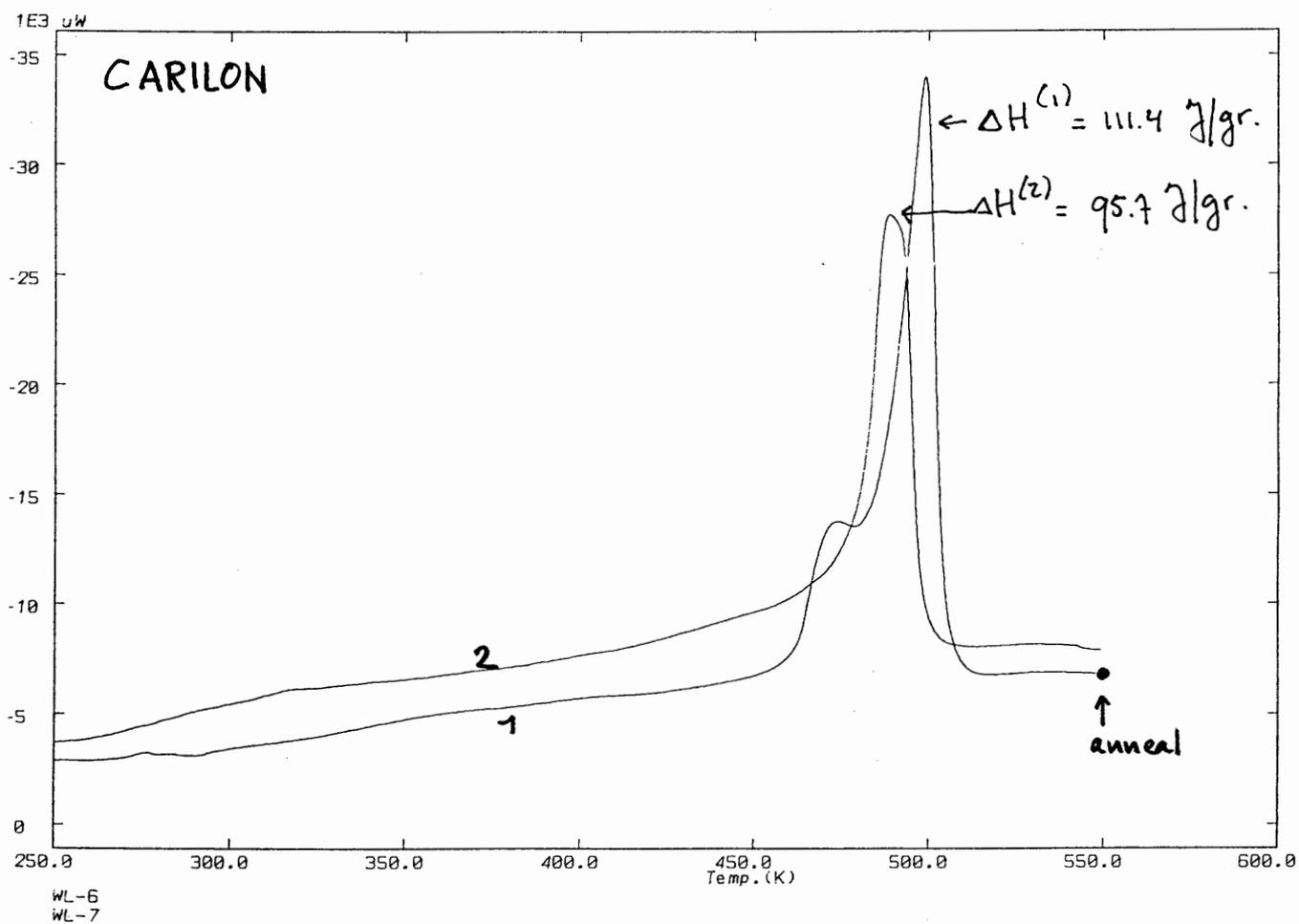


Figure 7: dsc traces of PK, full phase transition range

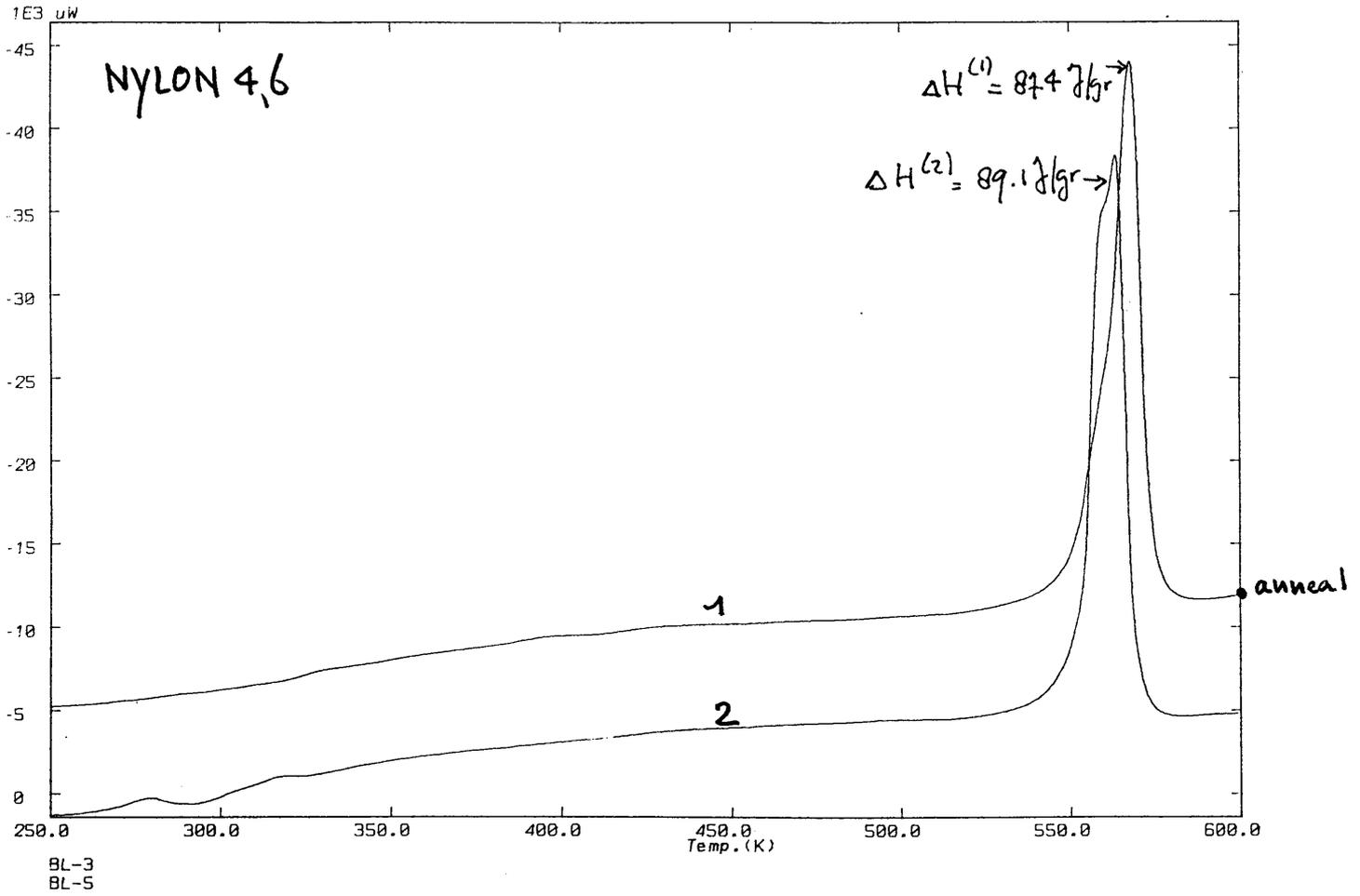


Figure 8: dsc traces of Nylon 4,6, full phase transition range

## A P P E N D I X I

## DSC Experiments

In a Differential Scanning Calorimetry experiment, one measures the difference in heat flow between a polymer - filled metal container and an empty container, necessary to keep both containers at the same temperature, while both containers are heated (or cooled) at a constant rate. This heat flow changes with temperature when the polymeric material experiences a glass or melting transition and hence, these transitions can be measured, provided that the change is large enough to be distinguished from the base heat flow. This is easy for melting transitions, but more difficult for glass transitions. For down-to-earth practical reasons, the PK/PAN materials have been investigated using apparatus 1, the PK/Nylon 4,6 materials have been investigated using apparatus 2.

Apparatus 1: A Du Pont differential calorimeter, used in the ST/1 section at KSLA. The convention is that exotherms are recorded as a positive heat flow difference. All experiments have been carried out at a heating rate of 20 K/min. During the experiments, we always found that after deep cooling (-50 °C) and heating of the samples a small exothermic peak appeared at 100 °C (see figure 3). Since the cell housing was not too well isolated, this is probably due to condensation of water at the heaters.

Apparatus 2: A Setaram DSC 111 differential calorimeter, used at the "Thermodynamisch Centrum" of the University of Utrecht. All experiments have been carried out at a heating rate of 5 K/min. All results have been corrected for the thermal behaviour of the empty container.

Two types of experiments have been carried out:

1. Investigation of the glass transition region between 220 and 400 K (figures 4 and 5).
2. Investigation of glass and melting transitions between 250 and 600 K (figures 6 to 8).

In order to inspect the structure of the glass transition region, the scale in figures 4 and 5 is enlarged compared to the scale in figures 6 to 8.

In order to test the melt stability of the PK/Nylon 4,6 blend and of its constituents, several runs with the same sample have been carried out. Each run was terminated with a two minute high temperature annealing. The consecutive runs have been numbered 1,2,.. etc. (figures 6 to 8).

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